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RHEOLOGY

Theory and Applications

Edited by
FREDERICK R. EIRICH
Polytechnic Institute of Brooklyn
Brooklyn, New York

VOLUME II



1958
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PREFACE

In this second volume, the scope of rheological fields dealt with becomes more specific and the volume contains in large measure chapters on deformational behavior in relation to the classic subjects and topics of rheology. There is considerable carry-over of material on the theory of viscoelastic and relaxation phenomena, of aspects which were not treated in the first volume, followed by applied theory and by descriptive matter concerning substances related to these phenomena. As an example of the ever-increasing ramifications of rheology, it may surprise some readers to see that geological deformations follow general principles derived from the study of less "immobile" objects. The volume is rounded out by three chapters dealing with methods and instrumentation.

The present volume benefited inevitably from the experience gained during the preparation of the first. It was not possible, however, to follow some suggestions which appeared in the generous reviews of Volume I with regard to overlap or repetitions, unequal approach or even conflicting views, and nonuniformity of nomenclature.

In the opinion of the editor, the first two of the mentioned criticisms do not do justice to the intent of this book. It is inherent in the nature of cooperative efforts that, lacking the homogeneity of one-author books, they offer, in contrast to these, the advantage of permitting the presentation of different points of view on kindred, or even the same, subjects. This may be perplexing at times, but it allows the serious student to obtain balanced information rather than be given a unified personal view.

It has further been our object to provide the reader with specific information of a rather self-contained nature without making it necessary for him to be referred continually to a number of other chapters or volumes. Obviously, there must be a compromise between this endeavor and conciseness. It has been the policy in arranging this book to err, if need be, in the direction of making the chapters more independent units rather than keeping them strictly interdependent, with the thought that it is easier to skip paragraphs than to search for them. It has been our aim to achieve this without sacrificing the unity of the book as a whole or making it unwieldy.

Concerning nomenclature, the editor has admitted defeat in the Preface to the first volume and he has not been any more successful in the present one. Today, diversity of usage is too great and the bases for uniform schemes are yet too controversial to force the issue at this juncture. It is hoped that,

by the time the third volume is ready to go to press, efforts to unify nomenclature may have reached a point where they can be applied to this book.

Brooklyn, New York

Summer, 1957

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CONTENTS

Preface	v
Contributors to Volume II	vii
 1. Viscoelasticity Phenomena in Amorphous High Polymeric Systems	
BY HERBERT LEADERMAN	1
I. Introduction.	1
II. Creep and Recovery Behavior of Amorphous Polymers ..	5
III. Stress Relaxation and Dynamic Response of Amorphous Polymers .	15
IV. Models, Spectra, and Operator Equations . ..	25
V. Superposition; Continuous Spectra	37
VI. Molecular Structure and Linear Viscoelastic Behavior	52
Nomenclature	61
 2. Stress Relaxation Studies of the Viscoelastic Properties of Polymers	
BY ARTHUR V. TOBOLSKY	63
I. Four Regions of Viscoelastic Behavior for Amorphous Behavior . .	64
II. The Time-Temperature Superposition Principle	67
III. Parameters Defined by the Relaxation Master Curves	68
IV. Stress Birefringence Ratio and the Mechanism of Viscoelastic Deformation	70
V. Distribution of Relaxation Time, Flow Viscosity, and Dynamic Modulus	72
VI. The Characteristic Relaxation Time $K(T)$ as a Function of Temperature	75
VII. Stress Relaxation of Polycrystalline Polymers	76
VIII. Chemical Stress Relaxation (Chemorheology)	79
Nomenclature	81
 3. The Relaxation Theory of Transport Phenomena	
BY TAIKYUE REE AND HENRY EYRING	83
I. Introduction	83
II. Generalized Theory of Viscosity	88
III. A Generalized Theory of Diffusion	97
IV. Applications	105
V. Nature of "Holes"	138
Nomenclature	143
 4. The Rheology of Organic Glasses	
BY ROLF BUCHDAHL	145
I. Introduction	145
II. Anelasticity and Reversible Deformations	148
III. Irreversible Deformations	152

IV. Major Experimental Techniques ..	155
V. Effect of Physical Variables on Anelasticity	158
VI. Effect of Chemical Variables on Anelasticity and Irreversible Deformations	165
Nomenclature	179
 5. The Rheology of Raw Elastomers	
By M. MOONEY	181
I. Introduction ..	181
II. Rheological Testing Equipment	184
III. Viscometric Theory ..	192
IV. Elastic Recovery ..	196
V. Surface Slip ..	197
VI. Experimental Results ..	200
VII. Theory of the Fluidity of Elastomers ..	219
VIII. Processing ..	225
Nomenclature ..	232
 6. The Rheology of Cellulose Derivatives	
By E. B. ATKINSON	233
I. The Nature of Cellulose and its Derivatives ..	233
II. Fields of Application ..	239
III. Irreversible Flow Behavior ..	242
IV. Elasticity and Toughness ..	253
Nomenclature	259
 7. The Rheology of Fibers	
By R. MEREDITH	261
I. Introduction ..	262
II. Structure ..	262
III. Creep and Relaxation ..	270
IV. Stress-Strain Relations ..	283
V. Dynamic Properties ..	293
VI. Quantitative Theoretical Interpretation ..	298
VII. Strength ..	307
Nomenclature ..	312
 8. The Rheology of Gelatin	
By A. G. WARD AND P. R. SAUNDERS	313
I. Introduction ..	314
II. Mode of Production and Composition of Gelatine ..	315
III. Rheological Properties of Gelatin ..	321
IV. Theories of Gel Formation ..	357
V. Rheological Properties in Relation to the Uses of Gelatine and Glue and to Industrial Testing Methods ..	359
Nomenclature	362

9. Rheological Properties of Asphalts

By R. N. J. SAAL AND J. W. A. LABOUT

I. Introduction	363
II. Rheological Properties of Pure Asphalts	366
III. Asphalt-Mineral Aggregate Mixtures	388
Nomenclature	400

10. Rheological Problems of the Earth's Interior

By B. GUTENBERG

I. Introduction: Structure of the Earth; Elastic Constants	401
II. Introduction to Rheological Problems in the Earth	406
III. Processes Retarding Elastic Motion in the Earth	408
IV. Flow Processes in the Earth's Outer Layers: Post-Glacial Uplift	413
V. The Coefficient of Viscosity and the Strength in the Earth	418
VI. Flow Processes in the Deeper Portion of the Earth's Mantle; Results Based on Deep-Focus Earthquakes	422
VII. Strain-Rebound Characteristics of Earthquake Series and Aftershocks	423
VIII. Rheological Phenomena in Geological and Geophysical Processes on a Small Scale	427
IX. Viscosity in the Earth's Core; Flow in the Core as Source of Terrestrial Magnetism	429
Nomenclature	430

11. Experimental Techniques for Rheological Measurements on Viscoelastic Bodies

By JOHN D. FERRY

I. Introduction	433
II. Transient Techniques	435
III. Dynamic (Sinusoidal) Techniques	440
IV. Other Time-Dependent Techniques	464
V. High-Stress Techniques	465
VI. Derived Calculations	467
Nomenclature	473

12. Fundamental Techniques: Fluids

By B. A. TOMS

I. Flow through Pipes	475
II. Flow Between Coaxial Cylinders	486
Nomenclature	500

13. Goniometry of Flow and Rupture

By A. JOBLING AND J. E. ROBERTS

I. Introduction	503
II. Goniometry of Continuous Laminar Shear	506
III. Goniometry of the Transition Region between Continuous Flow and Rupture	526
Nomenclature	535
AUTHOR INDEX	537
SUBJECT INDEX	548

CONTENTS OF VOLUME III

- Molecular Modes and the Method of Normal Coordinates in the Rheology of Polymers
BRUNO ZIMM
- The Principles for Rheological Measurements on Materials of Low Viscosity
SYOTEN OKA
- The Flow of Polyelectrolyte Solutions
A. DOBRY DUCLAUX AND BRYAN E. CONWAY
- The Deformation of Crystalline and Cross-Linked Plastics
W. O. BAKER AND J. HOPKINS
- The Rheology of Inorganic Glasses
W. A. WEYL
- The Rheology of Clay Suspensions
W. A. WEYL AND C. ORMSBY
- Concrete
M. REINER
- The Rheology of Pastes and Paints
RUTH WELTMANN
- The Rheology of Printing Inks
A. C. ZETZLEMOYER
- The Rheology of Latex
SAMUEL H. MARON AND IRVIN M. KRIEGER
- The Rheology of Lubrication and Lubricants
A. BONDI
- Viscosity and Elasticity of Surface Films
DEAN W. CRIDDLE
- The Rheology of Adhesion
J. J. BIKERMAN
- Rheology in Moulding
C. E. BEYER AND R. S. SPENCER
- The Rheology of Spinning
BRUNO R. ROBERTS
- Theory of Screw Extruders
W. L. GORE AND J. M. McKELVEY

CHAPTER 1

VISCOELASTICITY PHENOMENA IN AMORPHOUS HIGH POLYMERIC SYSTEMS

Herbert Leaderman

I. Introduction	1
II. Creep and Recovery Behavior of Amorphous Polymers	5
1. Bulk and Shear Response	5
2. Retarded Elastic Deformation in Shear: Cross-Linked Polymers	5
3. Effect of Temperature on Retarded Elasticity: Cross-Linked Polymers	8
4. Retarded Elastic Deformation in Shear: Noncross-Linked Polymers	11
III. Stress Relaxation and Dynamic Response of Amorphous Polymers	15
1. Stress Relaxation	15
2. Representation of Dynamic Response	17
3. Dynamic Behavior of Amorphous Polymers	22
IV. Models, Spectra, and Operator Equations	25
1. Three-Element Model: Cross-Linked Polymers	25
2. Five-Element Model: Cross-Linked Polymers	30
3. Six-Element Model: Noncross-Linked Polymers	33
V. Superposition; Continuous Spectra	37
1. The Superposition Principle	37
2. Relation between Creep and Relaxation	40
3. Retardation and Relaxation Spectra	42
4. Calculation of Retardation and Relaxation Spectra	45
5. Relations between Response Curves Involving Spectra	50
a. Difference Functions	50
b. Viscosity, Steady-State Compliance, and Relaxation Spectrum	51
VI. Molecular Structure and Linear Viscoelastic Behavior	52
1. Glassy State, Glass Modulus, Glass Compliance	53
2. Volume and Shear Viscoelasticity	55
3. Nonlinear Viscoelasticity	57
a. Rubberlike Region	58
b. Glasslike Behavior	58
c. Textile Fibers	59
4. Linear Viscoelastic Behavior and Constitution of Amorphous Polymeric Systems...	60
Nomenclature	61

I. Introduction

In other chapters of this and the preceding volume, certain aspects of the phenomenological theory of linear viscoelastic behavior are discussed (Chapters 2 and 11, Volume I), and also of the behavior of systems manifest-

ing linear viscoelasticity (Chapters 2 and 4, Volume II). The main purpose of this chapter is to describe some rheological phenomena manifested in high polymeric systems, more especially linear viscoelasticity in amorphous systems, and to show the qualitative and quantitative relations among the phenomena of linear viscoelasticity resulting from the phenomenological theory.

Suppose that we stretch a piece of rubber, specifically natural rubber vulcanized in the usual way without fillers. When the rubber is released, we find that it snaps back substantially to its original length. It would appear that the relationships between the applied forces and resulting deformations should be dealt with adequately by the theory of large elastic deformations, as discussed in Chapter 10 of the preceding volume. Now let us suppose that we bend a strip of polystyrene at room temperature; we find that the material undergoes only a small deformation without rupture. If such a strip is bent but not broken and then released, it will again seem to snap back to its original form. It would appear that the relations between forces and deformations in such a material should be adequately dealt with by the classical theory of elasticity, some aspects of which are discussed in Chapter 2 of the preceding volume.

However, we find in careful experiments that the rubber in the first case does not quite return immediately to its original length; there is a slight residual elongation, which gradually reduces with time, and under certain circumstances may eventually disappear completely. This effect is more marked, the greater the original elongation of the rubber and the longer the time that it was held in the stretched condition. The same type of behavior is found in the case of the polystyrene specimen; such a time-dependent elastic recovery may be thought of as a retarded elastic recovery. This time effect is manifest not only following removal of load, but also while the load is acting on the specimen. Suppose that a strictly constant transverse load is applied to the polystyrene strip, and the deformation observed from time to time; this will be found to increase very gradually, but at a decreasing rate; the same is true for measurements of the length of the vulcanized rubber stretched by a constant force. Thus the effect of a sudden application or removal of load is observed not simply as a strain which appears or disappears at the instant of load application or removal, but as a strain which appears or disappears gradually subsequent to this instant. This effect was observed over a hundred years ago in such materials as glass, metal wires, and rubber; the work was largely empirical until some phenomenological relations proposed by Boltzmann in 1874 were shown to describe these time-dependent effects.

This phenomenon was known among German scientists as "*elastische Nachwirkung*" which may be translated, *retarded elasticity*. This may be

observed in other types of experiments. Let us suppose, for example, that a constant bending deformation is applied to the strip of polystyrene. If the deformation is maintained, for example, by a transverse force, it is found that the force applied to the strip is not constant, but diminishes slightly with time, that is, *stress relaxation* takes place. If subsequently the strip is restored to its original configuration, and held clamped in that position, it is found at first that a small force is required to do this; the force decays with time and eventually disappears. Alternatively, if after stress relaxation is allowed to take place, the specimen is then simply released, there will be a gradual recovery, as in the earlier experiment described.

Again, if instead of applying a constant force or constant deformation, we apply a force or deformation which varies sinusoidally with time, then if the deformation is small enough we find that, respectively, the deformation or force also varies sinusoidally with time; in general, however, the deformation is not in phase with the force, but lags behind. The stress-strain plot under these conditions is thus an ellipse; this implies that during such cyclic deformation mechanical work is converted into heat.

While developments along these lines were taking place in the study of time effects in mechanical behavior, it was observed that similar time effects were manifested in the electrical behavior of dielectrics, and consequently very similar phenomenological theories were developed to describe time effects in elastic behavior and in dielectric behavior. The history of these developments over a hundred years up to about 1940 has been reviewed by Leaderman.¹ Furthermore, in the field of electrical engineering, specifically in linear circuit theory, the same principles were found to apply. These ideas form the basis of what may be called *linear response theory*. Some aspects of this theory, more especially as they apply to high polymeric systems, are discussed in Chapters 2 and 11 of the preceding volume.

Time effects in the elastic properties of materials such as polystyrene and vulcanized natural rubber at room temperature in simple constant-stress or constant-deformation tests as described above might be thought of as a relatively unimportant perturbation upon ideal elastic behavior. Under more general conditions, however, such time effects become more important and play a dominant role in the description of elastic behavior. Specifically, if the rubber is cooled, or if the polystyrene is heated, then these time effects become more pronounced. In fact, if the rubber is cooled to a sufficiently low temperature, say below $-70^{\circ}\text{C}.$, it will be glassy, like polystyrene at room temperature in such constant-load or constant-deformation tests. Similarly, if the polystyrene is heated to about $130^{\circ}\text{C}.$, it is found that the strip which is glassy at room temperature becomes limp and rub-

¹ H. Leaderman, "Elastic and Creep Properties of Filamentous Materials and Other High Polymers." Textile Foundation, Washington, D. C., 1943.

berlike; when stretched to a moderate extent it will snap back fairly rapidly and, after the delayed elastic recovery has ceased, it will manifest only a slight permanent deformation, which is of the nature of flow. The analogy is better if we compare the high-temperature behavior of polystyrene with the room-temperature behavior of a raw (unvulcanized) rubber. Such a material on being stretched does not return eventually to its original length but shows a permanent deformation the magnitude of which depends upon the extent and duration of the stretching, as in the case of the heated polystyrene strip.

In principle, ordinary raw or vulcanized rubber can be shown to be glass-like at *room temperature* also; this however, would require the stretching experiment to be completed in, say, a microsecond. Such an experiment would be difficult to perform. We can, however, carry out a dynamic experiment in which the force or deformation alternates with a frequency of 1 megacycle per second; as we will see, this can be thought of as equivalent to a "static" experiment in which the deformation (or force) is observed 1 microsecond after instantaneous application of force (or deformation). In such a dynamic experiment the rubber is found to exhibit the mechanical behavior of a glassy plastic. Thus, roughly speaking, a noncross-linked amorphous polymer can exhibit the behavior of a glassy plastic, or ideal rubberlike behavior, or the behavior of a viscous liquid, depending upon the temperature and time scale of the experiment. If the material is cross-linked, such as vulcanized rubber or cross-linked polystyrene, then in general it behaves under limiting conditions like an ideal glassy elastic body or an ideal rubberlike elastic body. One of the objectives of this chapter is to discuss in detail the phenomena observed under intermediate conditions, including relations between the response patterns of a given material in different types of test.

In the examples of mechanical behavior discussed above, mechanical energy is partly stored in a body undergoing deformation and partly dissipated as heat; such behavior is known as *viscoelastic behavior*. A special case is when this is *linear*; under these circumstances the behavior becomes amenable to simple mathematical treatment. Chapters 2 and 11 of the preceding volume discuss certain theoretical aspects of linear viscoelasticity; in this volume Chapters 4 and 11 deal with aspects of linear viscoelastic behavior from the experimental point of view.

In the examples previously considered, the phenomena are due to physical changes; in principle, the experiments can be repeated indefinitely. However, at sufficiently elevated temperatures it is possible for chain scission and cross-linking to take place. For example, in a cross-linked polymer subject to a constant stress at a sufficiently high temperature, chain scission will lead to a gradual increase in deformation, and cross-linking will result

in a permanent deformation subsequent to removal of stress. These time-dependent phenomena in mechanical behavior resulting from chemical changes are denoted by the term *chemorheology*. The subsequent considerations in this chapter do not refer to chemorheology, which is considered in greater detail in Chapter 2. The rheology of *crystalline* polymers is in general more complicated than that of amorphous polymers, and is not as well understood; this subject is not treated in this chapter, but is discussed in Chapter 7 of this volume.

II. Creep and Recovery Behavior of Amorphous Polymers

1. BULK AND SHEAR RESPONSE

When a body undergoes a deformation, then an originally spherical particle in general becomes deformed to an ellipsoid, and suffers a translation and a rotation as well as a change in volume. If we consider a small cubical element of the deformed material, then the stress system acting on the surfaces of this element may be resolved into normal and tangential tractions; if the orientation of the element is suitably chosen, the three pairs of normal tractions can be made to be equal. These normal tractions, which are numerically equal to the "hydrostatic stress," are responsible for the volume change, while the tangential tractions, or "shear-stress components," are responsible for the change in shape. These considerations are dealt with in Chapters 2 and 10 of the preceding volume for equilibrium elastic behavior and also in Chapter 11 for viscoelastic behavior. A material manifesting viscoelastic behavior exhibits time-dependent elasticity in the relation between the volume and the hydrostatic stress, as well as in the relation between shape and the tangential tractions, or so-called "shear stresses." If we consider, say, a piece of rubber under a simple tensile force, then there exist a hydrostatic stress as well as shear stresses. Under certain circumstances the response to shear stress dominates the response to hydrostatic stress; there is then a very simple relationship between the viscoelastic behavior in simple tension (under small elongations) and the behavior in shear. However, when the material exhibits glasslike behavior this is not true, and the response to longitudinal stress or strain is no longer simply related to shear behavior. These aspects are discussed in Section VI of this chapter. In this chapter we will deal mainly with the response to shear stress or strain.

2. RETARDED ELASTIC DEFORMATION IN SHEAR: CROSS-LINKED POLYMERS

Let us consider the viscoelastic behavior in shear of a cross-linked polymer. By way of example we will consider a specimen of vulcanized rubber, deformed in simple shear as shown in Fig. 1. When a constant force F is

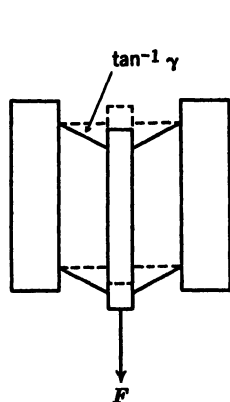


FIG. 1

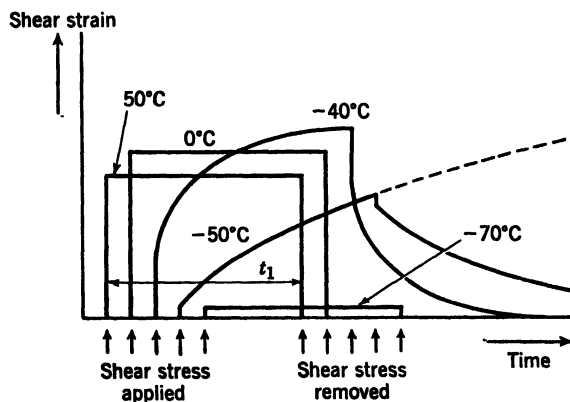


FIG. 2

FIG. 1. Simple shear creep test

FIG. 2. Shear strain as function of time and temperature, vulcanized rubber

applied as shown, the shear stress σ (or, to be correct, the shear traction) is of course equal to F divided by the total area sheared. The shear strain γ in either of the pieces of rubber is equal to the displacement divided by the thickness of either piece of rubber.

We will now discuss the response of the rubber when a constant shear stress σ_0 is applied to the specimen at zero time, and removed at some subsequent time t_1 , which may be of the order of minutes to hours. In Fig. 2 is shown a typical shear strain behavior as a function of time when the temperature covers the range from, say, 50 to -70°C . At the highest temperature there appears immediately an elastic response which stays practically constant during the time under load and disappears almost immediately following removal of load. At a somewhat lower temperature, say, 0°C ., the same is substantially true, but the deformation is greater for the same load. This is in qualitative accordance with the prediction of the statistical theory of rubberlike elasticity for such network systems, as discussed in Chapter 11 (Volume I). At a still lower temperature, for example, around -40°C . for a natural rubber gum vulcanizate, the equilibrium deformation is not reached immediately but only after some time; on removal of load the deformation does not disappear immediately but again requires the passage of time. At lower temperatures the approach to equilibrium is still slower, and the retarded elastic recovery is as indicated in Fig. 2. Finally, at a sufficiently low temperature, say, -70°C ., only a small time-independent deformation is observed, which disappears immediately on removal of the load. Under these conditions the material has the same behavior as a glassy plastic at room temperature.

Let us suppose that the experiment be repeated with a different applied load, that is, with a different shear stress. It is found generally that the de-

formation of the sample at any given temperature and time instant is *not* proportional to shear stress, but increases somewhat faster than the shear stress; hence, *in general*, the retarded elastic behavior in shear of vulcanized rubber is nonlinear.² However, if the stress is small enough, then the behavior is approximately linear. If we neglect the deviation from linearity, then, by means of the general theory of linear viscoelastic behavior discussed subsequently in this chapter and elsewhere in this treatise, we can derive relationships between the response of a material (at the same temperature) in different types of test.

With this approximation, we can specify the retarded elastic behavior of a vulcanized rubber, or any other material manifesting viscoelastic behavior, in a constant shear stress test. Let $\gamma(t)$ be the shear strain at a time t after application of a constant shear stress σ_0 . Then, at a given temperature, the ratio $\gamma(t)/\sigma_0$ is approximately independent of σ_0 if this is sufficiently small; this ratio is called the *shear creep compliance* (at time t at the specified temperature) and is denoted by $J(t)$. Let us now consider how $J(t)$ varies with temperature for some specified value of t which we will denote by t_c . From Fig. 2, we see that this behavior is given as shown by the full line in Fig. 3, in which $J(t_c)$ is plotted against temperature. At low temperatures this is substantially independent of temperature and is of the order of 10^{-10} cm.²/dyne. At high temperatures this is of the order of 10^{-6} cm.²/dyne and decreases somewhat with increase in temperature. If t_c is increased or reduced, the steeply rising portion is shifted to the left or the right in Fig. 3, as indicated by the broken lines. The reciprocal of $J(t_c)$ could be used as a measure of the "stiffness" of rubber as a function of temperature, but as seen from Fig. 3 this stiffness depends to some extent upon the arbitrary choice of t_c .

From Fig. 2 again we can draw conclusions concerning the residual deformation at a specified time subsequent to the instant of removal of stress, which time we will denote by t_r . At sufficiently high and low temperatures the residual deformation at this specified time is substantially zero; this deformation attains a maximum at some intermediate temperature, which may be around -50° C. in the rubber specimen considered above in tests of "ordinary" duration (minutes to hours). With change in t_r , the bell shaped plot of residual deformation against temperature here again shifts along the temperature scale.

If the retarded elastic behavior is linear, then it is no longer necessary to restrict the experimental method to that shown in Fig. 1. For example, the specimen could have the shape of a hollow circular cylinder, in which the inner cylindrical surface is either displaced along its axis³⁻⁵ or rotated around

² H. Leaderman, *J. Polymer Sci.* **16**, 261 (1955).

³ M. Reiner, "Twelve Lectures on Theoretical Rheology." North Holland, Amsterdam, 1949.

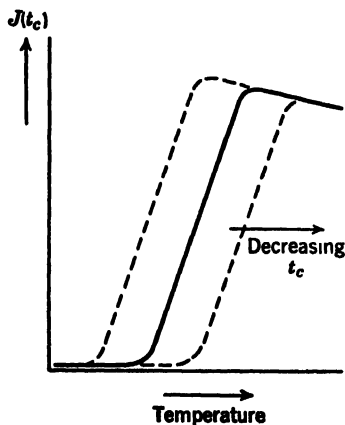


FIG. 3

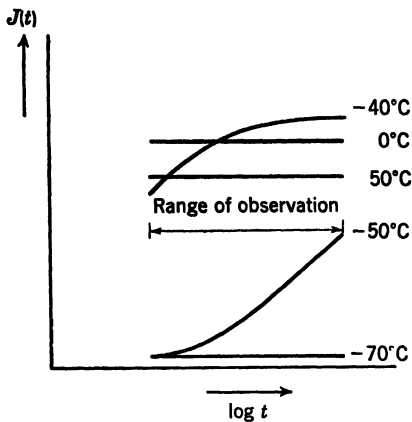


FIG. 4

FIG. 3. Creep compliance at time t_c as function of temperature

FIG. 4. Creep compliance of vulcanized rubber

its axis relative to the outer cylindrical surface,^{6, 7} as discussed in Chapter 2, Volume I, and Chapter 11, Volume II; or it could be in the form of a thin disk.^{8, 9} In fact, there are a large number of possibilities depending upon the physical properties of the test specimen at room temperature and under the test conditions; many of these methods are similar to methods used for measuring viscosity. This aspect is considered in the chapter on experimental methods (Chapter 11, Volume II) and will not be considered further here. We will assume that from the experimental observations there can be derived the response in a simple shear stress test, such as in the arrangement of Fig. 1.

3. EFFECT OF TEMPERATURE ON RETARDED ELASTICITY: CROSS-LINKED POLYMERS

It is instructive to plot the creep compliance in Fig. 2 against the logarithm of time as in Fig. 4. The effect of increase in temperature on creep compliance can be interpreted as a reduction in the equilibrium value of the creep compliance, or *equilibrium compliance*, J_e ; and a change in time scale, corresponding to a lateral shift along the logarithmic time axis. Thus by plotting for each temperature $J(t)/J_e$ as ordinate against logarithm of time, and shifting the curves horizontally on the $\log t$ axis, a single curve is

⁴ T. G. Fox, Jr., and P. J. Flory, *J. Am. Chem. Soc.* **70**, 2384 (1948).

⁵ J. D. Ferry, L. D. Grandine, and E. R. Fitzgerald, *J. Appl. Phys.* **24**, 911 (1953).

⁶ H. Leaderman, *J. Polymer Sci.* **13**, 371 (1954).

⁷ H. Leaderman, R. G. Smith, and R. W. Jones, *J. Polymer Sci.* **14**, 47 (1954).

⁸ G. J. Dienes, *J. Colloid Sci.* **2**, 131 (1947).

⁹ A. van Rossem and H. van der Meijden, *Rubber Age (N. Y.)* **23**, 438 (1928).

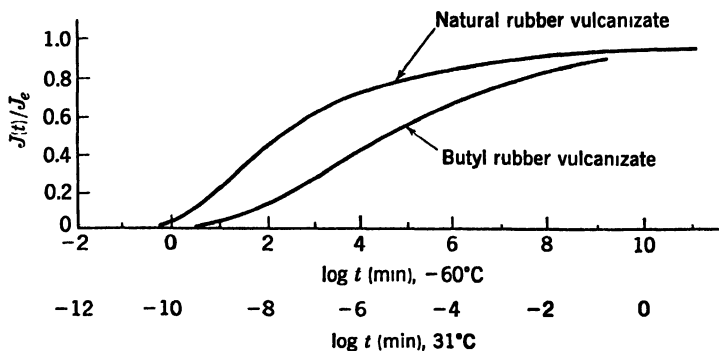


FIG. 5. Normalized creep compliance: natural rubber and butyl rubber vulcanizates.

obtained. As an example, in Fig. 5 are shown the creep compliance curves obtained in this way for two different vulcanized rubbers;¹⁰ the abscissa scales represent, respectively, the time scales for $-60^{\circ}\text{C}.$ and $31^{\circ}\text{C}.$ For the abscissa scale corresponding to temperature T , the curves in Fig. 5 represent the normalized creep compliance "reduced to temperature T ." If now the ordinate scale is multiplied by the value of J_e at the temperature T , then the curves represent the (non-normalized) creep compliance reduced to temperature T . We see, for example, from Fig. 5 that, for the particular vulcanizates represented there, 1 min. at $-60^{\circ}\text{C}.$ is equivalent to 10^{-10} min. at $31^{\circ}\text{C}.$, and 10^{-2} min. at the higher temperature is equivalent to 10^8 min. at $-60^{\circ}\text{C}.$

In Fig. 6 is represented diagrammatically the behavior of a cross-linked amorphous polymer when a constant shear stress σ_0 is applied from zero time to time t_1 , and subsequently removed; the ordinate represents values of the shear strain at time t , namely $\gamma(t)$, divided by σ_0 . The diagrams represent from top to bottom experiments carried out at successively higher temperatures. At the lowest temperature there is seen to be a substantially instantaneous deformation, which disappears immediately on removal of stress (actually a finite time is required for the propagation of a stress wave through the material). This deformation corresponds to an increase in internal energy, and is associated mainly with van der Waals' forces between polymer chains. The ratio of strain to stress, namely the compliance, is of the order of 10^{-10} cm.²/dyne; this is the order of magnitude of the compliance of organic glasses, both polymeric and nonpolymeric. It is appropriate to call this limiting value of compliance corresponding to very low temperatures (or, from Fig. 5, to very short times), the *glass compliance*; this will be denoted by J_g .

At a higher temperature it is seen from the two middle diagrams in Fig. 6

¹⁰ F. S. Conant, G. L. Hall, and W. J. Lyons, *J. Appl. Phys.* **21**, 499 (1950).

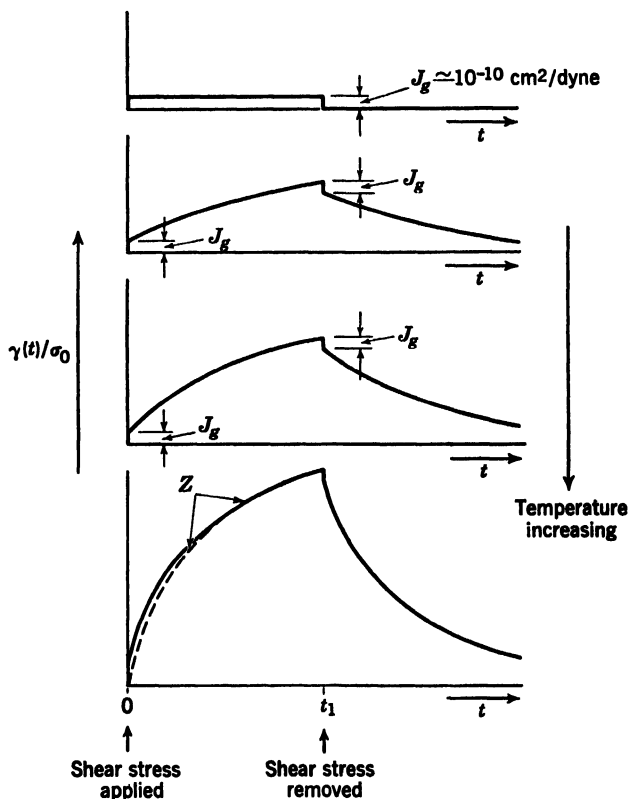


FIG. 6. Effect of temperature on retarded elasticity: cross-linked polymer

that there occurs the glassy deformation immediately upon application of stress, and then a retarded elastic deformation; on removal of stress there occurs an "immediate" elastic recovery corresponding to the glass compliance, and then the retarded elastic recovery. The retarded elasticity is due to the gradual uncurling or curling up of randomly kinked polymer chains, and this corresponds principally to a change in entropy (cf. Chapter 11, Volume I). When the temperature is further increased, as represented, for example, in the lowest diagram of Fig. 6, then the time scale of the retarded elastic deformation becomes shortened so much that it is not possible to observe the glassy deformation corresponding to J_g . Since a small but nevertheless finite time is required for the application of stress, the actual course of the deformation as a function of time may follow the curve indicated by the broken line in the lowest diagram of Fig. 6. Thus a deformation observed at an early instant after application of stress may correspond to some point such as Z in Fig. 6. Such an observation, unlike the true limiting value corresponding to J_g , has thus no scientific meaning. Under these

conditions only the creep compliance $J(t)$ is measurable; we can say that the limiting value of this quantity, namely J_e , is not experimentally accessible in such ordinary creep experiments except at a sufficiently low temperature.

4. RETARDED ELASTIC DEFORMATION IN SHEAR: NONCROSS-LINKED POLYMERS

We will now consider the response in a similar constant shear stress experiment of a noncross-linked polymer. The arrangement could be as shown, for example, in Fig. 7, where the material fills a narrow gap between two circular cylinders. One of the cylinders is fixed; a constant torque W can be applied to the other cylinder. The shear stress is proportional to the torque, and the shear strain to the angle of rotation of the "free" cylinder relative to the fixed cylinder.

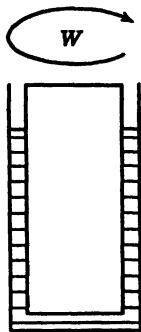


FIG. 7. Arrangement for concentric cylinder viscometer

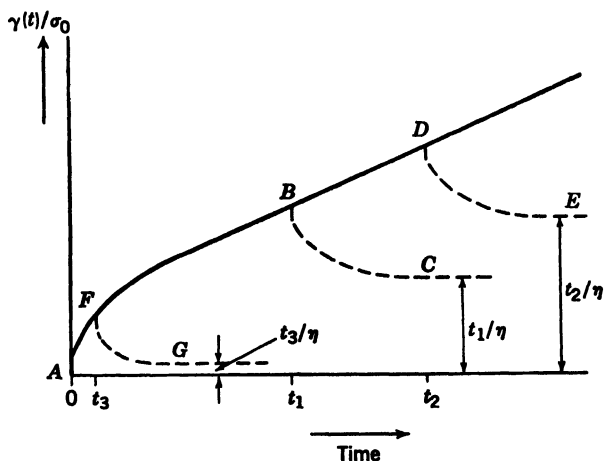


FIG. 8. Creep and recovery of noncross-linked polymer: effect of time under stress

Let us assume as before that a constant shear stress σ_0 is applied at zero time, and released at a subsequent time t_1 . The shear strain as a function of time may follow the curve ABC in Fig. 8. If the shear stress is small enough, then the shear strain at any time t is proportional to σ_0 ; the material thus manifests linear viscoelastic behavior. As before, depending upon the mechanical properties of the material at room temperature and at the test temperature, a simple shear type of apparatus,¹¹ or one of the arrangements described previously may be used; the rotational viscometer of Fig. 7 need not necessarily possess a narrow gap.^{6, 7} These considerations again come under the heading of experimental techniques, and we will again assume that from the experimental observations there can be derived the shear strain behavior during application of a constant shear stress and following removal of stress.

Returning to Fig. 8, it is seen that if the viscoelastic behavior is assumed to be linear, then we may plot as ordinate the shear strain at time t , namely $\gamma(t)$, divided by the magnitude of the shear stress σ_0 . The curve ABD which represents thus the creep compliance $J(t)$ is seen to proceed not to an equilibrium value but to a limiting slope; the reciprocal of this slope is called the *viscosity*, η . It is now assumed that the stress is removed at a time t_1 subsequent to the time at which the slope becomes constant. There is a retarded elastic recovery shown by the broken line BC , and a permanent set equal to $\sigma_0 t_1 / \eta$. If the stress is removed instead at another time t_2 , corresponding to a point D on the creep compliance curve subsequent to the time at which the slope becomes constant, then the permanent set corresponds to a compliance of t_2 / η ; the recovery curve DE is identical in shape to the recovery curve BC . The material manifests *flow* when under load (in addition to time-dependent elasticity) since the permanent set is proportional to the time under shear stress. The flow is *Newtonian* since it is proportional to the shear stress. If the stress is removed at a point F in the diagram corresponding to a time t_3 , which is previous to the attainment of the steady-flow state, then the subsequent permanent set corresponds to a compliance of t_3 / η ; the recovery curve FG is however not of the same shape as the curves BC and DE .

We will now consider the effect of temperature on the behavior of a non-cross-linked polymer in such an experiment. Let AB in Fig. 9 represent the creep compliance $J(t)$ at a temperature T_2 up to time t_1 . If the stress σ_0 is removed at this instant, then the strain $\gamma(t)$ at subsequent times decreases as shown by the curve BC' in the plot of $\gamma(t) / \sigma_0$ against time in Fig. 9. The intercept of the linear part of AB on the ordinate axis, namely AX , is equal to the compliance corresponding to the total elastic recovery. The curve ADE represents the behavior at a lower temperature T_3 . Here the

¹¹ K. E. van Holde and J. W. Williams, *J. Polymer Sci.* **11**, 243 (1953).

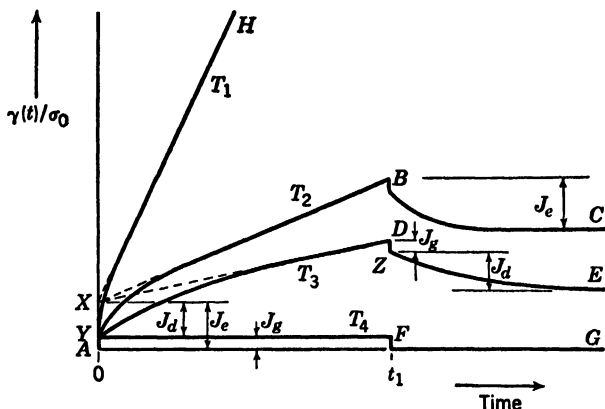


Fig. 9. Creep and recovery of noncross-linked polymer: effect of temperature

final slope is less, and the time to attain the steady state is greater than at T_2 . To a first approximation, the intercept of the straight part of AD on the ordinate axis is the same as before; the magnitude of the recovery is again approximately as at temperature T_2 , but the recovery is slower. If the temperature is low enough, there is evidence of a glassy instantaneous compliance as indicated by AY and DZ . Finally, at a sufficiently low temperature T_4 , there occurs only an instantaneous deformation corresponding to a glass compliance of the order of magnitude of 10^{-10} cm.²/dyne as represented by $AYFG$ in Fig. 9. At a higher temperature T_1 , on the other hand, the creep compliance is as shown by the curve AH .

These curves admit of a simple interpretation. The creep compliance consists of three components, a glass compliance, a time-dependent retarded-elastic compliance, and a Newtonian flow. The magnitude of the time-dependent elastic compliance is approximately independent of temperature but the rate of approach to the steady state is very temperature-dependent. At the temperature T_4 only the glass compliance is observed for the time scale of the experiment. At the higher temperature T_3 there is also observed the time-dependent elasticity and flow; at the temperature T_2 the glassy compliance can no longer be experimentally observed and at the temperature T_1 the flow dominates also the time-dependent elasticity, which is now very rapid. The compliance AY we have already called the glass compliance J_g ; the compliance AX we will call the *steady-state elastic compliance* J_e ; and XY we will call the *delayed elastic compliance* J_d . These quantities are obtainable from the recovery curves as indicated in Fig. 9.

The creep compliance curve of a noncross-linked amorphous polymer at a specified temperature has the general form as shown diagrammatically in Fig. 10, where $J(t)$ and $J(t) - t/\eta$ are plotted against $\log t$. At very small values of t there is a plateau in the curves corresponding to the glass compli-

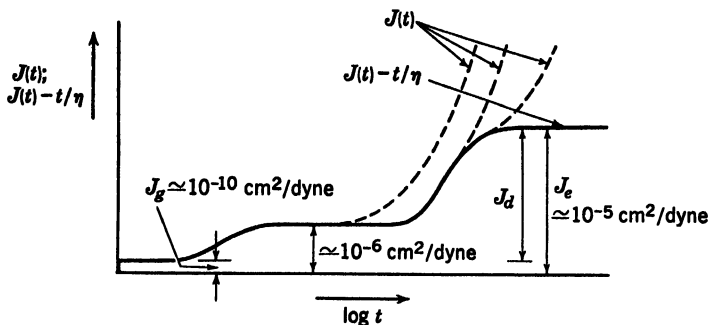


FIG. 10. Creep compliance curve of noncross-linked polymer

ance J_g of the order of $10^{-10} \text{ cm}^2/\text{dyne}$; there is a second plateau corresponding to a compliance of the order of $10^{-6} \text{ cm}^2/\text{dyne}$, as in a vulcanized rubber. Finally there occurs the steeply rising part of the $J(t)$ curve on the logarithmic time plot, as indicated by the broken curves in Fig. 10. The quantity $J(t) - t/\eta$ represents the *elastic* part of the creep compliance; as will be shown later, it represents also the recovery when the stress is removed after the steady state is reached in a constant-stress experiment. The curve of $J(t) - t/\eta$ is as represented by the continuous curve in Fig. 10. There a second retarded elastic process can be observed, leading to a plateau corresponding to a compliance of the order of $10^{-5} \text{ cm}^2/\text{dyne}$. At a given temperature, the effect of decrease of molecular weight is to move the "slow" retarded elastic process to the left, while the "fast" retarded elastic process, representing the transition from glasslike to rubberlike behavior, does not change. Change in molecular-weight distribution changes the height of the last-named plateau; the other plateaus are substantially independent of molecular weight. These factors will be considered in more detail subsequently.

The creep compliance curve for an amorphous cross-linked polymer changes significantly over some six decades of logarithmic time as can be seen from Fig. 5. For an amorphous noncross-linked polymer, the corresponding range for $J(t) - t/\eta$ is of the order of ten decades, as indicated in Fig. 25. In a creep test the practical ratio of the longest to the shortest time of observation is of the order of 10^3 to 10^4 , corresponding to three to four decades on the logarithmic time scale. Thus it is not practicable to observe the whole course of the elastic part of the creep compliance function by means of an experiment at one temperature. In order to obtain the whole curve, it is necessary to carry out experiments over a range of temperature, and it is assumed that the principal effect of change of temperature is to change the time scale of the $J(t)$ and $J(t) - t/\eta$ curves. The reduced creep compliance curve for a specified temperature is then obtained essentially

by shifting curves obtained at higher and lower temperatures along the axis of logarithmic time, until all the curves overlap to give a single continuous curve. Thus the creep compliance $J(t)$, or the elastic part of the creep compliance $J(t) - t/\eta$ which is observed at time t at a temperature T , would be observed at a time t/a_T if the experiment were carried out at the reference temperature. The temperature function a_T is called the *shifting factor*; this is less than unity for temperatures above the reference temperature, and greater than unity for temperatures below this. On theoretical grounds, this procedure should be slightly modified as discussed in Chapter 11. Generally speaking, a_T varies with temperature in the same way as the viscosity.^{7, 11} As will be shown later, a similar behavior is observed in other types of tests on noncross-linked amorphous polymers.

III. Stress Relaxation and Dynamic Response of Amorphous Polymers

1. STRESS RELAXATION

It has previously been mentioned that vulcanized rubber and polystyrene at room temperature manifest another aspect of viscoelastic behavior, namely, stress relaxation: when a given deformation is applied and held constant, the stress is not constant but decreases gradually with time. As with retarded-elasticity phenomena discussed in the previous section, stress-relaxation phenomena in vulcanized rubber and polystyrene become more marked at temperatures below and above room temperature, respectively.

Suppose that a constant shear strain be applied at zero time to an amorphous polymer. If the temperature is sufficiently low, the stress subsequently remains constant during the experiment; if the strain is small enough the stress is proportional to the strain. If the experiment is repeated at a higher temperature, it may be found that the stress, instead of remaining constant after the instant of application of strain, decreases with time. Again, if the strain is small enough, the stress $\sigma(t)$ at any time t after application of the strain γ_0 is proportional to the magnitude of the strain; hence we may consider $\sigma(t)/\gamma_0$ as a measure of the stress-relaxation behavior in shear at the particular temperature. This ratio is called the (*shear*) *relaxation modulus*, and is denoted by $G(t)$. The stress relaxation behavior of an amorphous polymer at different temperatures is represented diagrammatically in Fig. 11, in which the relaxation modulus $G(t)$ is plotted against the logarithm of the time from the instant of application of a constant shear strain. The diagram represents the behavior of a *cross-linked* polymer for a given range of values of time t . The curves labelled T_1 and T_2 represent the behavior at two different temperatures as described above. At successively higher temperatures, curves such as T_3 and T_4 may be obtained; the stress relaxes to an equilibrium value in the case of a cross-linked amorphous polymer as shown in the diagram, or to zero, in the case of a *noncross-linked*

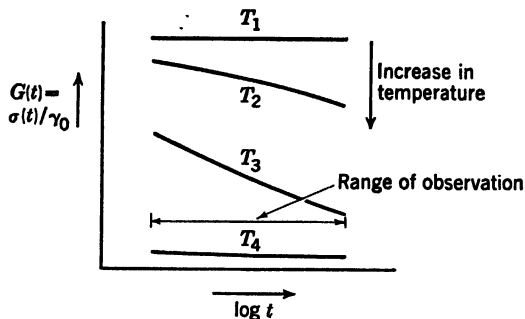


FIG. 11. Stress relaxation: effect of temperature

amorphous polymer. Here again the principal effect of change in temperature is to change the time scale of the experiment. Thus in order to obtain the stress-relaxation curve at a specified temperature, say T_3 in Fig. 11, for times longer and shorter than the practical range of observation, the observed relaxation modulus curves (or slightly modified curves as discussed in Chapter 11), obtained at higher and lower temperatures, respectively, are shifted along the axis of logarithmic time as in the case of the creep compliance curves discussed previously. This treatment of stress-relaxation data is considered in more detail in Chapter 2. For a given polymer, the same values of a_T should be obtained as from creep compliance measurements.

The relaxation modulus curve in shear for amorphous polymers reduced to a standard temperature and plotted against the logarithm of the time is as indicated diagrammatically in Fig. 12; the full curve represents the behavior of a cross-linked polymer. For large values of t the behavior of a noncross-linked polymer differs from that of a cross-linked polymer, and the behavior of the former is shown by the broken curve. The limiting value of the relaxation modulus for very small values of t is the *glass modulus* G_g ; this is the reciprocal of J_g . The value of $G(t)$ at infinite time for a cross-linked polymer is the *equilibrium modulus* G_e ; this is the reciprocal of J_e . It is convenient to denote the difference $(G_g - G_e)$ by the term *decay modulus*, G_d . The glass modulus G_g is of the order of 10^{10} dynes/cm.², while for a typical vulcanized rubber G_e is of the order of 10^6 dynes/cm.²

The relaxation modulus curve for a noncross-linked polymer is seen to possess an intermediate plateau; for longer values of time the stress decays to zero. The portion to the right of the plateau is molecular-weight dependent, and shifts to the right in Fig. 12 if the molecular weight increases.¹² This is discussed in greater detail in Chapter 2.

The relaxation modulus function $G(t)$ is seen to be approximately the

¹² A. V. Tobolsky and J. R. McLoughlin, *J. Polymer Sci.* **8**, 543 (1952).

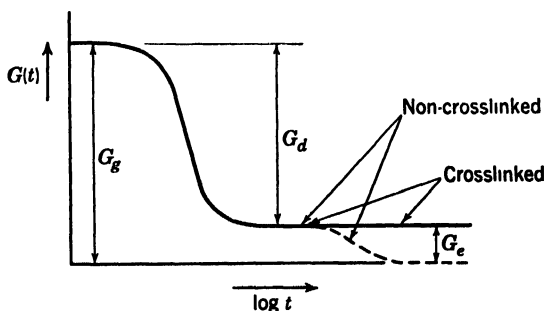


FIG. 12. Relaxation modulus curve, cross-linked and noncross-linked polymer

reciprocal of the creep compliance function $J(t)$; the exact relationship is given in Section V. In principle, the creep compliance can be computed from the relaxation modulus, and in particular two important limiting values associated with the creep compliance curve, namely the steady-state compliance J_e and the viscosity η , can be calculated from the reduced $G(t)$ curve. This is discussed in Section V of this chapter and also in Chapter 2.

A measure of the "stiffness" of a material at any temperature which is often used is the relaxation modulus at a specified time t_c after application of stress. The value of $G(t_c)$ measured as a function of temperature would be expected to fall over a small range of temperature from the order of 10^{10} dynes/cm.² to zero (for a noncross-linked polymer) or to about 10^6 dynes/cm.² (for a cross-linked polymer). The actual curve would of course depend upon the choice of t_c (compare Fig. 3). For a given value of t_c and temperature, $G(t_c)$ and $J(t_c)$ would be approximately reciprocals of each other.

As with the case of the creep test previously considered, the glass modulus is not experimentally accessible when the time scale of stress relaxation is small compared to the time of application of the strain. In the upper part of Fig. 13 is represented diagrammatically the curve of $\gamma_0 G(t)$ plotted against t , and also, by the broken curve, the values of $\sigma(t)$ which would be obtained when the strain γ_0 is applied at a finite rate, as indicated in the lower part of Fig. 13. It is seen that under these conditions an observation of stress at some instant following application of strain bears no relation to the limiting value of stress corresponding to $\gamma_0 G_0$.

2. REPRESENTATION OF DYNAMIC RESPONSE

So far we have been considering what may be called *step-function experiments*. The stress (or strain) is zero up to a given instant, and then changes discontinuously to a finite value; alternatively, the stress (or strain) may change discontinuously from one finite value to another finite value or to zero. We will now consider the response of an amorphous polymer in

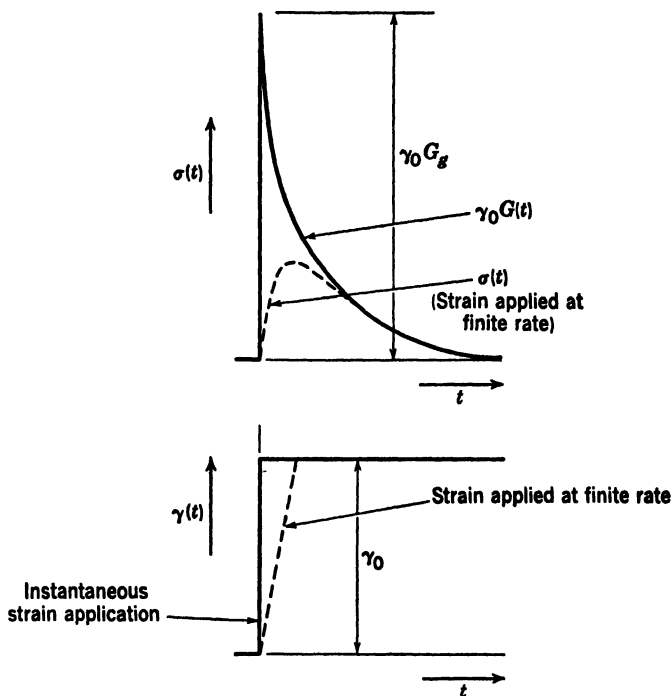


FIG. 13. Effect of finite rate of strain application

another type of test, in which the shear stress (or strain) varies *sinusoidally* with time, the so-called *dynamic response* of polymers.

If the amplitude is small enough, then the behavior can be considered as *linear*; the shear strain (or stress) is sinusoidal, and furthermore the amplitude of the strain is proportional to the amplitude of the stress. The relations between shear stress, shear strain, and time for a cross-linked amorphous polymer are represented diagrammatically in Fig. 14. At a sufficiently high frequency, as at *A* in Fig. 14, the strain is in phase with the stress, and the ratio of the amplitude of the strain to that of the stress is small. At a sufficiently low frequency, for a *cross-linked polymer* (*B* in Fig. 14) the strain is again in phase with the stress and the above ratio reaches an upper limiting value. In the case of *noncross-linked polymers*, the stress is $\pi/2$ radians or a quarter-cycle out of phase with the strain at very low frequencies, and the above ratio increases without limit as the frequency decreases. In the general case, the strain is out of phase with the stress, as shown in *C* in Fig. 14. Under these conditions we can decompose the *stress* into two components, one in phase with the strain and one *leading* the strain by $\pi/2$ radians, as in Fig. 14. Alternatively, we can decompose the *strain* into two components, one in phase with the stress and one *lagging*

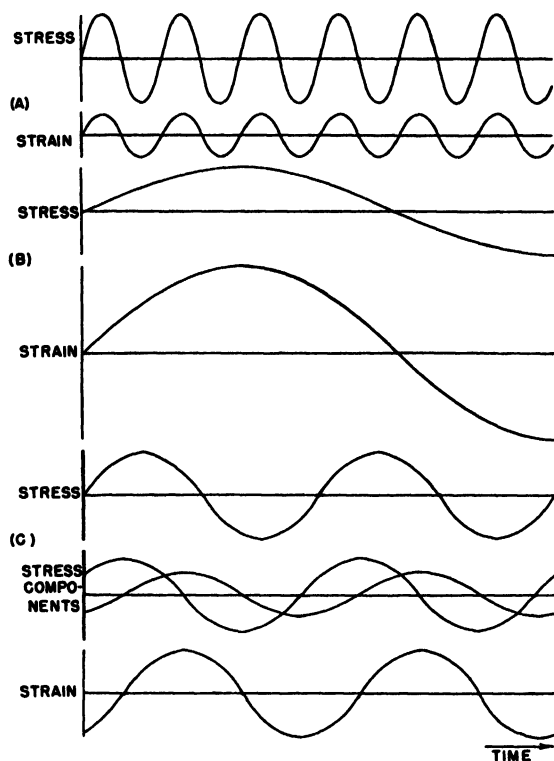


FIG. 14. Dynamic response of polymers: effect of frequency

$\pi/2$ radians behind the stress. This is brought out by the alternative rotating vector representation. In Fig. 15, OA represents the amplitude of the stress, σ_a ; OA rotates counterclockwise with a frequency equal to the frequency of the sinusoidal stress; the stress at any instant is the projection of OA on, say, a vertical axis through O . The strain is represented by a projection on the same axis of the rotating vector OB , the length of which represents the strain amplitude γ_a . The vector rotates with the same angular velocity as OA , but lags behind by an angle δ ; the tangent of this angle is called the *loss tangent*.

It is seen in Fig. 15a that OA has a component OC in phase with OB , and a component OD leading OB by one quarter of a cycle. The ratio of the former stress component to γ_a is denoted by $G'(\omega)$, and of the latter stress component by $G''(\omega)$, which may be called, respectively, the (shear) *storage modulus* and the (shear) *loss modulus*. They are, as indicated, in general functions of the circular or radian frequency ω . Alternatively, in Fig. 15b the rotating vector OB representing the strain amplitude is split up into a component OE in phase with the stress vector and a component OF lagging

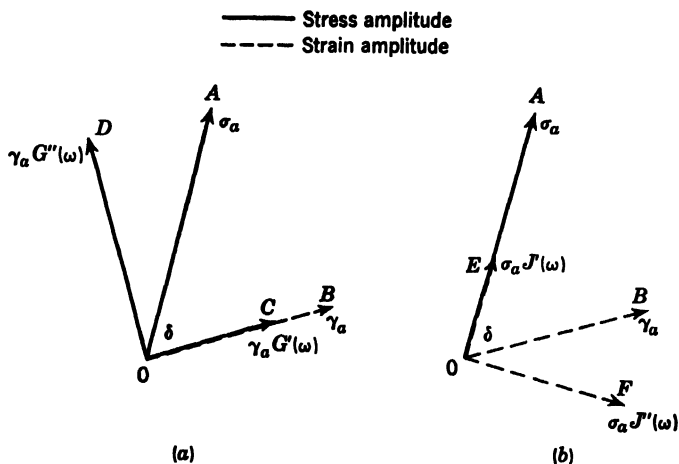


FIG. 15. Storage and loss moduli and compliances

one quarter cycle behind the stress. The ratio of the former component to the stress amplitude is denoted by $J'(\omega)$, and that of the latter component to the stress amplitude is denoted by $J''(\omega)$. These are called, respectively, the (shear) *storage compliance* and the (shear) *loss compliance*. Thus at any given frequency (at a specified temperature) the dynamic response of a polymer is specified *either* by $G'(\omega)$ and $G''(\omega)$, *or* by $J'(\omega)$ and $J''(\omega)$. Alternatively, the dynamic response is specified by the ratio of σ_a to γ_a (or the reciprocal of this ratio) and the loss tangent, $\tan \delta$. The ratio of the stress amplitude to the strain amplitude may be called the *absolute modulus*, $|G(\omega)|$, and its reciprocal the *absolute compliance*, $|J(\omega)|$. These are both again functions of frequency. It is obvious that these four methods of representation are equivalent and must be related to each other. Furthermore, since the dynamic response consists of two components differing in phase by $\pi/2$ radians, it is possible to specify the dynamic response by a single complex quantity; two such quantities are the *complex modulus* $G^*(\omega)$ and its reciprocal, the *complex compliance* $J^*(\omega)$. The relations between all these methods of specifying linear dynamic response are given in Table I.

It has been mentioned previously that in the measurement of creep compliance a maximum of three to four decades can be covered at any given temperature; thus in order to get the complete creep compliance curve, measurements over a range of temperature are necessary. This introduces some uncertainty on account of the reduction scheme; the same is true for measurements of the relaxation modulus. In the case of dynamic measurements a particular experimental arrangement covers a range of only about one-and-a-half decades. However, many methods

TABLE I
RELATIONS BETWEEN DYNAMIC RESPONSE PARAMETERS FOR LINEAR VISCOELASTIC BEHAVIOR

Quantity	in terms of G', G''	in terms of J', J''	in terms of $ G , \delta$	in terms of $ J , \delta$
J'	$G'/G'^2 + G'''^2$	J'	$\cos \delta / G $	$ J \cos \delta$
J''	$G''/(G'^2 + G'''^2)$	J''	$\sin \delta / G $	$ J \sin \delta$
G'	G'	$J'/(J'^2 + J''^2)$	$ G \cos \delta$	$\cos \delta / J $
G''	G''	$J''/(J'^2 + J''^2)$	$ G \sin \delta$	$\sin \delta / J $
$ J ^2$	$1/(G'^2 + G'''^2)$	$J'^2 + J''^2$	$1/ G ^2$	$ J ^2$
$ G ^2$	$G'^2 + G'''^2$	$1/(J'^2 + J''^2)$	$ G ^2$	$1/ J ^2$
J^*	$1/(G' + jG'')$	$J' - jJ''$	$(\cos \delta - j \sin \delta) / G $	$ J (\cos \delta - j \sin \delta)$
G^*	$G' + jG''$	$1/(J' - jJ'')$	$ G (\cos \delta + j \sin \delta)$	$(\cos \delta + j \sin \delta) / J $
$\tan \delta$	G''/G'	J''/J'	$\tan \delta$	$\tan \delta$

NOTE: In the above table, $J'(\omega)$, $J''(\omega)$, are abbreviated to J' , J'' , etc.

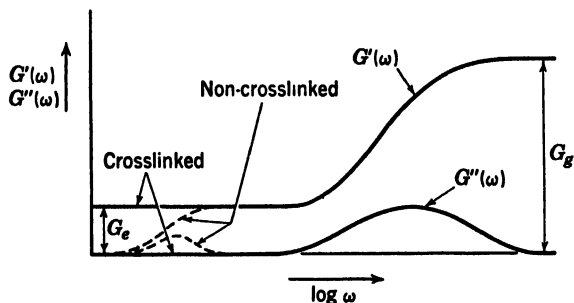


FIG. 16. Dynamic response curves: storage and loss moduli

have been developed, covering a range from less than one cycle per second to megacycle frequencies; these are discussed in more detail in Chapter 11 of this volume. Since it is possible to make measurements that involve only shear deformations, and not bulk deformations, in principle it is possible to obtain, at a given temperature, dynamic behavior in shear over a wide range of frequencies without reference to any reduction scheme.¹³

In the case of dynamic measurements, experiments carried out at different temperatures can also be "reduced" to a standard temperature, as discussed in Chapter 11. Hence, in principle, if the assumptions involved in the reduction procedure are valid, then it is possible to cover the whole frequency range of rheological interest by means of experiments over a limited frequency range but over a sufficiently wide temperature range. For a given material, the change in frequency scale with temperature as measured by a "shifting factor" a_T appears to be similar to the change in viscosity with temperature.¹⁴

3. DYNAMIC BEHAVIOR OF AMORPHOUS POLYMERS

We will consider the curves of storage and loss modulus, and also storage and loss compliance, plotted against the logarithm of the circular frequency ω . In Fig. 16 are shown curves of storage and loss modulus as a function of frequency; the continuous lines represent the behavior of a cross-linked polymer. The limiting values of $G'(\omega)$ at, respectively, very high and very low frequencies are G_g and G_e . The curve of $G''(\omega)$ is bell-shaped, with its peak somewhere near the point of inflection of the $G'(\omega)$ curve. In the case of noncross-linked amorphous polymers, the curves differ from those for the cross-linked polymers at the lower frequencies, as shown by the dashed curves. The $G'(\omega)$ curve becomes zero at zero frequency and a second peak appears in the $G''(\omega)$ curve. At a given tem-

¹³ R. S. Marvin, *Proc. 2nd Intern. Rheol. Congr., Oxford*, p. 156 (1953).

¹⁴ J. D. Ferry, E. R. Fitzgerald, M. F. Johnson, and L. D. Grandine, Jr., *J. Appl. Phys.* **22**, 717 (1951).

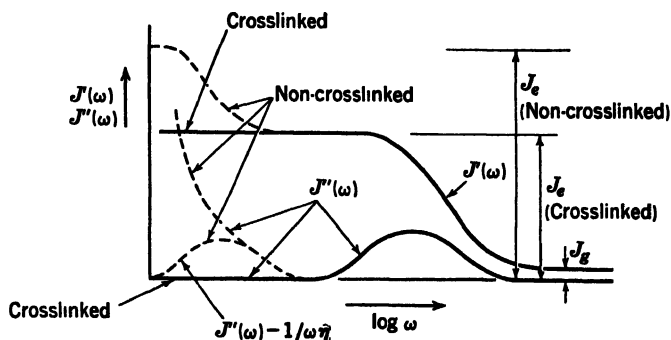


FIG. 17. Dynamic response curves: storage and loss compliances

perature, increase in molecular weight in the case of a noncross-linked polymer shifts to the left the portions of the $G'(\omega)$ and $G''(\omega)$ curves indicated by the broken lines.

In Fig. 17 are shown the curves of storage compliance and loss compliance plotted against $\log \omega$. The continuous curves represent the behavior of a cross-linked polymer; $J'(\omega)$ rises from a value equal to J_g at very high frequencies to a value equal to J_e at very low frequencies; the curve of $J''(\omega)$ consists of a single bell-shaped peak located in the region where $J'(\omega)$ is changing most rapidly with logarithm of frequency. Here again in the case of noncross-linked polymers the behavior is different at low frequencies, as shown by the broken curves. The curve of $J'(\omega)$ for noncross-linked polymers rises with decrease of frequency at low frequencies, as shown by the broken line in Fig. 17, to a limiting value equal to the steady-state compliance J_e obtained from a constant-stress experiment. The curve of $J''(\omega)$ is somewhat as shown by the broken curve at low frequencies. Its peculiar shape is due to the fact that at low frequencies the behavior of such materials approaches Newtonian flow behavior. The curve of $J''(\omega) - 1/\omega \eta$ consists simply of two bell-shaped peaks, as indicated in Fig. 17. As before, the effect of increase of molecular weight in the case of a noncross-linked polymer is to shift to the left the portions of the curves in Fig. 17 shown by the broken lines.

The curves of $G'(\omega)$, $G''(\omega)$, $J'(\omega)$, and $J''(\omega)$ are by no means independent; in fact, if the whole course of any one of these curves is known, then in principle the other three can be computed. This is a consequence of the linear viscoelastic behavior of the material, and is independent of the molecular processes responsible for the behavior. In theory any point on one curve, say the $G''(\omega)$ curve, depends not only upon the value, say, of $G'(\omega)$ for the same frequency, but the value of $G'(\omega)$ for all other frequencies. To a good approximation, as will be shown in Section V from theoretical considerations, the value of $G''(\omega)$ for a particular frequency

depends mainly upon the value of $G''(\omega)$ only for a limited range of frequencies around the specified frequency.

It is observed that there is a close resemblance between the curve of $G''(\omega)$ plotted against $\log \omega$ and the curve of $G(t)$ plotted against $\log t$ obtained in the "step-function" stress relaxation experiment; there is similarly a close resemblance between the curve of $J'(\omega)$ plotted against $\log \omega$ and the curve of $J(t) - t/\eta$ plotted against $\log t$. The last curve it will be remembered represents the *elastic* part of the creep compliance, that is, the total creep compliance from which the flow is subtracted. As will be shown in Section V, this function represents the retarded elastic recovery following removal of stress in a creep experiment after attainment of the steady state.

The curves for the step-function experiments appear in fact to be mirror images of the corresponding dynamic function curves. Let us plot the $G'(\omega)$ and $J'(\omega)$ functions against $\log (1/\omega)$. This has the effect of reflecting the curves in the axis of $\log \omega$ equal to zero. If now the corresponding step-function curves be plotted against $\log t$ to the same scale, it will be found that the storage and relaxation modulus curves nearly coincide; this is also true for the compliance curves. This is again a consequence of linear viscoelastic behavior; later on it will be shown how the dynamic curve can be computed from the corresponding step-function curve, and vice versa. By this means step-function experiments with large values of time (t greater than 1 sec.) can be combined with dynamic experiments for small values of time ($1/\omega$ less than 1 sec.), in order to obtain the response of a material over a wide range of time.^{13, 15}

Thus we see that the dynamic response at a given temperature over the significant frequency range can be obtained by three different procedures, as follows: first, by utilizing several experimental methods, the whole frequency range over which $J'(\omega)$ and $G'(\omega)$ change significantly can be covered at the specified temperature. Alternatively, for frequencies less than about 1 radian per second, the results of step-function experiments at the specified temperature can be converted into dynamic-response behavior and combined with the usual measurements of dynamic response for frequencies greater than about 1 radian per second. Thirdly, the whole significant range of the dynamic-response curve can be obtained with a single apparatus; experiments carried out over a range of temperatures can be reduced to a single temperature, as already discussed.

In conclusion, it has been shown that the linear viscoelastic behavior of a material at a given temperature may be specified in terms of the response of the material in a particular type of experiment. In practice, the most frequently used methods of specification are the four discussed above,

¹⁵ R. S. Marvin, *Phys. Rev.* **86**, 644 (1952).

namely, the step-function constant-stress (or "creep") experiment, the constant-strain ("stress relaxation") experiment, and the sinusoidal ("dynamic") experiment to measure modulus or compliance. It cannot be said that any one of the four methods of representation is more "fundamental" than the others; in principle they are equivalent to each other, and the relations between the different types of measurement (at a given temperature) are a result of the linear viscoelastic behavior and are given by phenomenological linear viscoelasticity theory. The outlines of this theory have been given rather completely in a recent monograph;¹⁶ some of the topics are discussed in the following two sections of this chapter. In practice, however, information which may be obtained easily in one type of test can be obtained only with difficulty in another type of test; these considerations will be discussed subsequently. The effect of average molecular weight, molecular weight distribution, and temperature are of course not dealt with by such a phenomenological theory but form the basis for the development of molecular theories. These aspects are considered in Chapter 2 and briefly in Section VI.

IV. Models, Spectra, and Operator Equations

Previously we have been considering the response of materials manifesting linear viscoelastic behavior in special types of experiments. We are now going to consider an elementary approach to a more general method of representation which is dealt with from another point of view in chapter 11 of the previous volume.

1. THREE-ELEMENT MODEL: CROSS-LINKED POLYMERS

We will consider first *cross-linked* amorphous polymers. It will be recalled that the response to a step-function shear stress history could be described by a glass compliance J_g , together with a delayed elastic compliance of magnitude J_d . The first component is Hookean; thus for times which are long compared to that necessary to propagate the stress through the specimen, the shear strain at any instant due to this component is merely the shear stress at that instant multiplied by J_g . The delayed elastic compliance is time-dependent; let us assume that at any instant the rate of approach of the retarded elastic component of the strain to its equilibrium value is proportional to the difference between the equilibrium strain corresponding to the stress at that instant and the actual strain at that instant. Thus if $\sigma(t)$ is the shear stress and $\gamma(t)$ the shear strain at time t , then the retarded elastic component of the strain at time t is

$$\gamma(t) - J_g\sigma(t)$$

¹⁶ B. Gross, "Mathematical Structure of the Theories of Viscoelasticity." Hermann, Paris, 1953.

The above relationship then becomes

$$\frac{d}{dt} [\gamma(t) - J_\sigma \sigma(t)] \propto (J_d + J_\sigma) \sigma(t) - \gamma(t) \quad (1a)$$

or

$$\frac{d}{dt} [\gamma(t) - J_\sigma \sigma(t)] = \frac{(J_d + J_\sigma) \sigma(t) - \gamma(t)}{\tau} \quad (1b)$$

where τ is a constant which we will call the *retardation time*. Rearranging the above equation and remembering that J_e is equal to the sum of J_d and J_σ , we get:

$$\left(\frac{d}{dt} + \frac{1}{\tau} \right) \gamma(t) = \left(J_\sigma \frac{d}{dt} + \frac{J_\sigma}{\tau} \right) \sigma(t) \quad (2)$$

The above differential equation thus relates the shear stress at time t , namely $\sigma(t)$, to the shear strain at time t , namely $\gamma(t)$, and involves three parameters; expressed in the above form, it is an *operator equation* for the shear response of the system, and the coefficients of $\gamma(t)$ and $\sigma(t)$ are the operators. The equation is thus a more general method of expressing the viscoelastic response of a system than those considered previously.

This operator equation can be represented diagrammatically by the well-known *mechanical model* convention. These mechanical models are constituted usually of linear springs and dashpots. For the springs, the force in the spring is proportional to the extension, that is, they are Hookean, while the dashpots exhibit Newtonian flow behavior, the rate of extension being proportional to the force. If we associate the over-all deformation of the model with shear strain, and the applied force with shear stress, then a model becomes a graphic way of representing an operator equation. The subject of mechanical models is discussed in Chapter 2 of the first volume, and also with a different nomenclature in Chapter 11 of that volume. In this discussion we will use the latter terminology.

Let us first consider the step-function response of a system whose behavior is given by the above operator equation. For constant stress σ_0 applied at zero time, the strain $\gamma(t)$ at time t is given by

$$J(t) = \gamma(t)/\sigma_0 = J_\sigma + J_d(1 - e^{-t/\tau}) \quad (3)$$

The creep compliance of this system is seen to increase from J_σ at zero time to $J_\sigma + J_d$ at infinite time. This result suggests immediately the equivalent mechanical model of Fig. 18, in which a spring of compliance J_d is connected in parallel with a dashpot of viscosity η_v equal to τ/J_d , and these two are connected in series with a spring of compliance J_σ . The spring together with the dashpot in parallel is usually called a *Voigt element*.

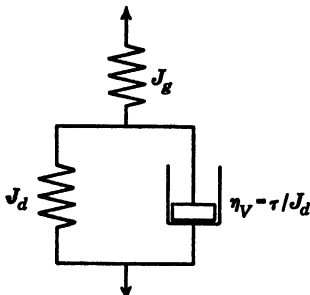


FIG. 18

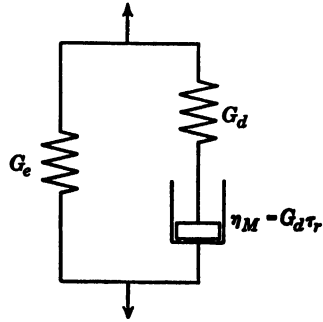


FIG. 19

FIG. 18. Three-element model with Voigt element

FIG. 19. Three-element model with Maxwell element

The relation between stress, strain, and time is given in general by equation (2).

In a similar way from the operator equation, equation (2), or from the equivalent model representation, Fig. 18, we can obtain the stress $\sigma(t)$ at a time t after application of a constant strain γ_0 . We get

$$\begin{aligned} G(t) &= \frac{\sigma(t)}{\gamma_0} \\ &= \left(\frac{1}{J_g} - \frac{1}{J_e} \right) \exp \left(- \frac{J_e t}{J_g \tau} \right) + \frac{1}{J_e} \end{aligned} \quad (3a)$$

The relaxation modulus for this system is seen to fall from $1/J_g$ at zero time to $1/J_e$ at infinite time. If we put

$$1/J_g = G_g,$$

$$1/J_e = G_e,$$

and

$$G_g - G_e = G_d$$

then equation (3a) becomes

$$G(t) = G_d e^{-t/\tau_r} + G_e \quad (3b)$$

where

$$\tau_r = G_e \tau / G_d.$$

Thus the relaxation modulus consists of a constant part and a part which decays exponentially with time, with a *relaxation time* τ_r . This result suggests an alternative model which is equivalent to the rheological behavior expressed by the operator equation, equation (2). This second model is shown in Fig. 19, where a spring of modulus G_d is connected in series with a

dashpot whose viscosity η_M is given by

$$\eta_M = \frac{\tau G_e G_d}{G_e + G_d} = G_d \tau_r$$

and this combination is connected in parallel with a spring of modulus G_e . The combination of spring in series with a dashpot is usually known as a *Maxwell element*. Thus the models of Figs. 18 and 19 are equivalent representations of the operator equation, equation (2).

This equation can be rewritten with $J_d \eta_V$ instead of τ ; it can also be rewritten with the parameters of the model of Fig. 19 instead of those of the model of Fig. 18. More generally, we can rewrite equation (2) in the form

$$\left(q_1 \frac{d}{dt} + q_0 \right) \gamma(t) = \left(\frac{d}{dt} + p_0 \right) \sigma(t) \quad (2a)$$

where the parameters q_1 , q_0 , and p_0 and the form of the above equation describe the viscoelastic response under all conditions of this hypothetical system (cf. Chapter 11, Volume I).

Finally, we will consider the dynamic response of a system whose rheological behavior is represented by equation (2a). We first wish to determine the components of the complex compliance; in order to do this, we consider the response of the model of Fig. 18 to a stress varying sinusoidally with time. If the stress is given by

$$\sigma(t) = \sigma_a \sin \omega t$$

then the strain $\gamma(t)$ is given by

$$\frac{\gamma(t)}{\sigma_a} = J_g \sin \omega t + \left(\frac{J_d}{1 + \omega^2 \tau^2} \right) (\sin \omega t - \omega \tau \cos \omega t) \quad (4)$$

Thus the storage and loss *compliances* of the system corresponding to the model are, respectively,

$$J'(\omega) = J_g + \frac{J_d}{1 + \omega^2 \tau^2} \quad (5a)$$

and

$$J''(\omega) = \frac{J_d \omega \tau}{1 + \omega^2 \tau^2} \quad (5b)$$

In order to obtain the storage and loss *moduli* corresponding to the operator equation, equation (2a), it is simpler to consider the response to a sinusoidal strain $\gamma(t)$ given by

$$\gamma(t) = \gamma_a \sin \omega t$$

for the model in Fig. 19; alternatively, these moduli may be obtained by means of the relations given in Table I from the storage and loss compliances. These moduli are found to be

$$G'(\omega) = G_e + \frac{G_d \omega^2 \tau_r^2}{1 + \omega^2 \tau_r^2} \quad (6a)$$

$$G''(\omega) = \frac{G_d \omega \tau_r}{1 + \omega^2 \tau_r^2} \quad (6b)$$

In Fig. 20 are plotted curves of $J'(\omega) - J_g$ and $J''(\omega)$ against $\ln(1/\omega\tau)$ and also a curve of $J(t) - J_g$ against $\ln(t/\tau)$. In Fig. 21 are plotted similarly curves of $G'(\omega) - G_e$, $G''(\omega)$, and $G(t) - G_e$. From these figures is

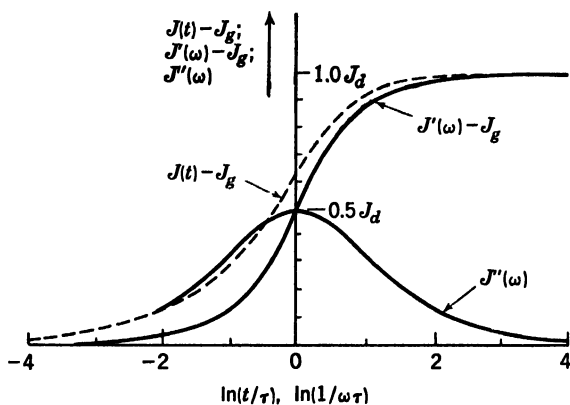


FIG. 20. Three-element model: storage, loss, and creep compliance response curves.

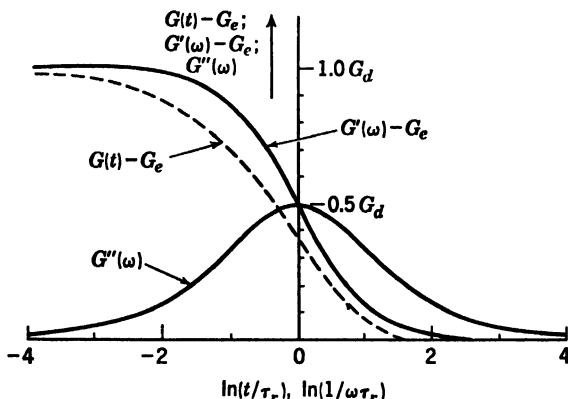


FIG. 21. Three-element model: storage, loss, and relaxation moduli response curves.

observed one characteristic of a linear system, namely that the curves of $J'(\omega)$ and $J(t)$ plotted in this way are very similar and the curve of $J(t)$ lies slightly above the $J'(\omega)$ curve. In the case of the modulus curves, the $G(t)$ curve is similar to the $G'(\omega)$ curve and lies slightly below it.¹⁸

It is noticed on comparing Fig. 20 with Fig. 5 that the experimental creep compliance curves are much more extended on the logarithmic time plot; hence the assumption made originally concerning the rate of approach to equilibrium is incorrect. The mechanical models in Figs. 18 and 19 and the operator equations, equations (2) and (2a), thus represent only to a first approximation the mechanical response of a cross-linked amorphous polymer.

2. FIVE-ELEMENT MODEL: CROSS-LINKED POLYMERS

Let us next consider the mechanical model of Fig. 22a, where the Voigt element in Fig. 18 is now replaced by *two* Voigt elements. The springs have compliances J_1 and J_2 , and the dashpots have viscosities τ_1/J_1 and τ_2/J_2 , where τ_1 and τ_2 are the retardation times of the Voigt elements. The creep compliance is given by

$$J(t) = J_g + J_1(1 - e^{-t/\tau_1}) + J_2(1 - e^{-t/\tau_2}) \quad (7)$$

The fraction of the delayed elastic compliance J_d which is attained at time t may be called the *retardation function*, which will be denoted by $\psi(t)$. In general, the creep compliance for a noncross-linked amorphous material manifesting linear viscoelastic behavior may be written

$$J(t) = J_g + J_d\psi(t) + t/\eta \quad (8)$$

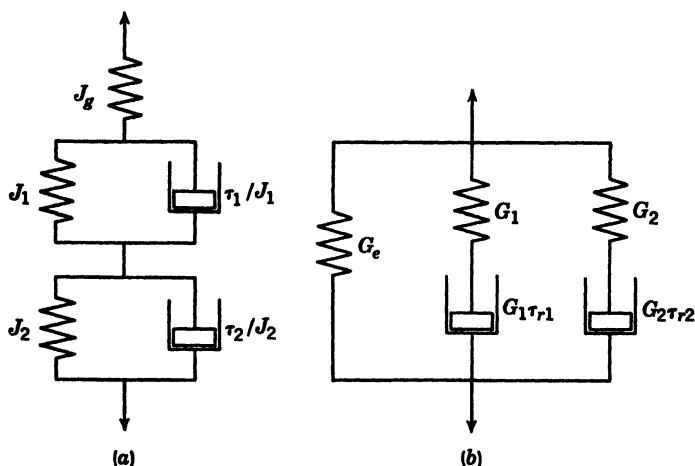


FIG. 22. Five-element model: (a) Voigt representation; (b) Maxwell representation.

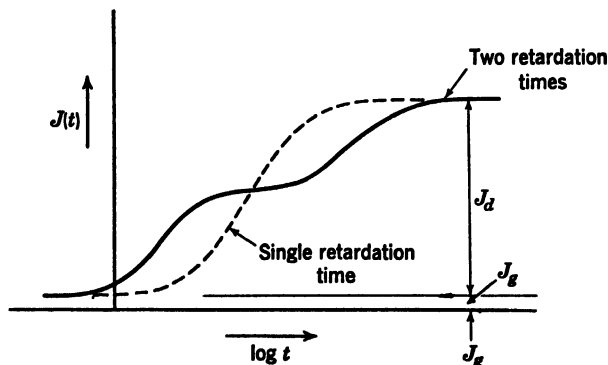


FIG. 23. Creep compliance of three-element model and of five-element model

while for a cross-linked material the last term on the right-hand side is absent. Thus, for the above model, the retardation function is given by

$$\psi(t) = \frac{J_1(1 - e^{-t/\tau_1}) + J_2(1 - e^{-t/\tau_2})}{J_1 + J_2} \quad (9)$$

The effect of adding a second Voigt element is to spread out the creep compliance curve along the logarithmic time axis, as shown in Fig. 23. It is observed that in general two points of inflection are obtained, whereas the simple model gave a curve with one point of inflection. The experimentally observed creep compliance curves (Fig. 5) also have only a single inflection.

The operator equation corresponding to this model is

$$\begin{aligned} & \left\{ \frac{d^2}{dt^2} + \left(\frac{1}{\tau_1} + \frac{1}{\tau_2} \right) \frac{d}{dt} + \frac{1}{\tau_1 \tau_2} \right\} \gamma(t) \\ &= \left\{ J_g \frac{d^2}{dt^2} + \left[\frac{J_1}{\tau_1} + \frac{J_2}{\tau_2} + \left(\frac{1}{\tau_1} + \frac{1}{\tau_2} \right) J_g \right] \frac{d}{dt} \right. \\ & \quad \left. + \frac{J_1 + J_2 + J_g}{\tau_1 \tau_2} \right\} \sigma(t) \end{aligned} \quad (10)$$

This equation can be represented alternatively by the model of Fig. 22b, in which a spring is connected in parallel with two Maxwell elements of different relaxation times. The parameters of the model of Fig. 22b can of course be calculated from those of Fig. 22a, and the operator equation, equation (10), can be expressed in terms of the parameters of the model of Fig. 22b.

We may define the *relaxation function* $\phi(t)$ as the fraction of the decay modulus which remains at time t . In terms of $\phi(t)$ the relaxation modulus

is thus given in general by

$$G(t) = G_e + G_d \phi(t) \quad (11)$$

For the models in Figs. 22a and 22b, the relaxation modulus is found to be of the form

$$G(t) = G_e + G_1 e^{-t/\tau_{r1}} + G_2 e^{-t/\tau_{r2}} \quad (11a)$$

where G_e , G_1 , G_2 are the moduli of the springs of the model in Fig. 22b, and τ_{r1} and τ_{r2} are the relaxation times associated with the springs of moduli G_1 and G_2 , respectively. For this model, the relaxation function is thus given by

$$\phi(t) = \frac{G_1 e^{-t/\tau_{r1}} + G_2 e^{-t/\tau_{r2}}}{G_1 + G_2}$$

As in the case of the retardation function, this is more spread out along the axis of logarithm of time, compared to that for the simpler model previously considered.

We can say that these models possess *discrete* retardation and relaxation spectra. The second model considered has a *retardation spectrum* consisting of compliances J_1 and J_2 with retardation times τ_1 and τ_2 ; it has also a *relaxation spectrum* consisting of moduli G_1 and G_2 with relaxation times τ_{r1} and τ_{r2} . The earlier model considered possessed a single retardation time τ of weight J_d , and a single relaxation time τ_r of weight G_d . The operator equation for the second model, equation (10), can be written in the form

$$\left(q_2 \frac{d^2}{dt^2} + q_1 \frac{d}{dt} + q_0 \right) \gamma(t) = \left(\frac{d^2}{dt^2} + p_1 \frac{d}{dt} + p_0 \right) \sigma(t) \quad (10a)$$

Comparing equation (10a) with equation (2a), it is seen that the effect of adding an additional Voigt or Maxwell element to the model corresponds to a change in the operator equation from a first-order to second-order equation; the viscoelastic behavior of the system is now characterized by *five* parameters, namely q_2 , q_1 , q_0 ; p_1 and p_0 .

The creep compliance and the relaxation modulus for the equivalent models in Fig. 22 are more spread out along the axis of logarithmic time as indicated in Fig. 23; hence in this sense, these models, or the corresponding operator equation, equation (10a), give a closer representation to the linear viscoelastic behavior of a real material than the models of Figs. 18 and 19. Let us now consider such models with a large number of Voigt or Maxwell elements. It is assumed that if the elements are arranged in order

of increasing or decreasing relaxation or retardation times, then the weights, that is, the values of spring compliances or moduli, increase or decrease smoothly. As the number of such elements is increased, the points of inflection as in Fig. 23 become less marked, and eventually disappear. Thus in principle it is possible to obtain a model which represents to any degree of approximation the linear viscoelastic behavior of a real material; it is merely necessary to select a sufficiently large number of relaxation or retardation times, and to calculate the associated moduli or compliances in order to fit at specified points the relaxation modulus or creep compliance of the model to that of the real material. If in order to get a good fit a large number of relaxation or retardation times are chosen, then the operator equation becomes unwieldy and the parameters no longer very useful for the calculation of viscoelastic response. Furthermore, there is a certain arbitrariness in this procedure, since the discrete spectrum depends upon the choice of retardation or relaxation times. A method of representing linear viscoelastic behavior which is not subject to this drawback is discussed in the next section. These ideas, which were due originally to Wiechert,^{1, 17} are also found in the literature on dielectric behavior.

It has been shown for the simple three-element model that there is a similarity between the curves of $J(t)$ and $J'(\omega)$ plotted, respectively, against $\log t$ and $\log (1/\omega)$, and also between the curves of $G(t)$ and $G'(\omega)$ when similarly plotted. The same must be true for such models containing several Voigt or Maxwell elements, such as the five-element model just considered. Since, in principle, we can fit the creep compliance of a model to that of an actual cross-linked polymer to any degree of approximation by adding enough Voigt elements, we may conclude that for a real cross-linked material manifesting linear viscoelastic behavior the relations between $J(t)$ and $J'(\omega)$, and also between $G(t)$ and $G'(\omega)$, are as indicated in Figs. 20 and 21, respectively.

3. SIX-ELEMENT MODEL: NONCROSS-LINKED POLYMERS

It has already been pointed out in Section II that the creep compliance of a noncross-linked amorphous polymer manifesting linear viscoelastic behavior possesses three components, a glass compliance, a time-dependent retarded-elastic compliance, and a compliance due to Newtonian flow; it was also pointed out that the elastic part of the creep compliance contains three plateaus. This suggests, as the simplest model to represent the viscoelastic behavior, the six-element model in Fig. 24a, where the dashpot of viscosity η is coupled in series with two Voigt elements and with a spring of compliance J_g . If J_1 and J_2 are the compliances of the springs, and τ_1 and τ_2 the retardation times of the Voigt elements, then the operator

¹⁷ E. Wiechert, *Ann. Physik* **50**, 335, 546 (1893).

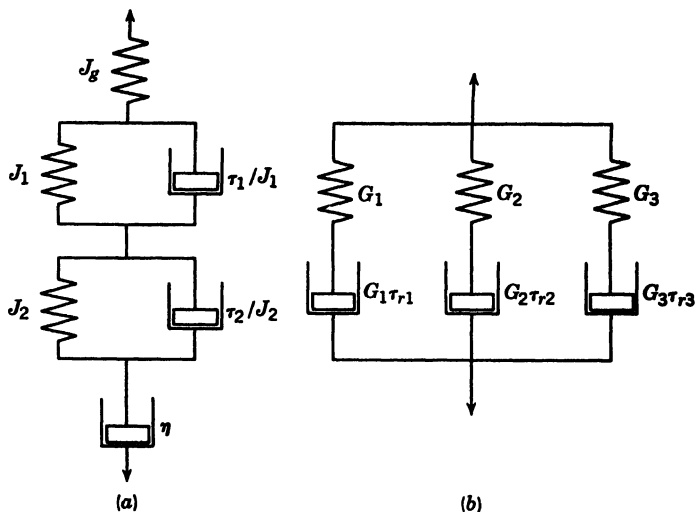


FIG. 24. Six-element model: (a) Voigt representation; (b) Maxwell representation

equation for this system is

$$\begin{aligned}
 & \left\{ \frac{d^3}{dt^3} + \left(\frac{1}{\tau_1} + \frac{1}{\tau_2} \right) \frac{d^2}{dt^2} + \left(\frac{1}{\tau_1 \tau_2} \right) \frac{d}{dt} \right\} \gamma(t) \\
 &= \left\{ J_g \frac{d^3}{dt^3} + \left[\frac{J_1}{\tau_1} + \frac{J_2}{\tau_2} + \frac{1}{\eta} + \left(\frac{1}{\tau_1} + \frac{1}{\tau_2} \right) J_g \right] \frac{d^2}{dt^2} \right. \\
 & \quad \left. + \left[\frac{J_1 + J_2 + J_g}{\tau_1 \tau_2} + \frac{1}{\tau_2 \eta} + \frac{1}{\tau_1 \eta} \right] \frac{d}{dt} + \frac{1}{\tau_1 \tau_2 \eta} \right\} \sigma(t)
 \end{aligned} \quad (12)$$

This equation is of the form

$$\left(q_3 \frac{d^3}{dt^3} + q_2 \frac{d^2}{dt^2} + q_1 \frac{d}{dt} \right) \gamma(t) = \left(\frac{d^3}{dt^3} + p_2 \frac{d^2}{dt^2} + p_1 \frac{d}{dt} + p_0 \right) \sigma(t) \quad (12a)$$

Thus the viscoelastic behavior corresponding to the model of Fig. 24a is characterized by the six parameters q_3 , q_2 , q_1 ; p_2 , p_1 , and p_0 in the above operator equation. When equation (12) is compared to equation (10) it is seen that the effect of addition of a dashpot is to introduce an additional parameter and to raise the order. An alternative model which is also equivalent to the operator equation, equation (12a), is shown in Fig. 24b, where springs of moduli G_1 , G_2 , and G_3 , respectively, are coupled in series with dashpots of viscosities $G_1 \tau_{r1}$, $G_2 \tau_{r2}$, and $G_3 \tau_{r3}$. Thus the model consists of three Maxwell elements with relaxation times τ_{r1} , τ_{r2} , and τ_{r3} arranged in parallel. The parameters of the model of Fig. 24b can of course be expressed in terms of the parameters of the model of Fig. 24a. As before, it is easier to consider the behavior of the model in Fig. 24a if we wish to

obtain the creep and storage compliances of a material whose operator equation is of the form of equation (12a). In terms of the parameters of this model, the creep and storage compliances are given, respectively, by

$$J(t) = J_0 + J_1(1 - e^{-t/\tau_1}) + J_2(1 - e^{-t/\tau_2}) + t/\eta \quad (13a)$$

$$J'(\omega) = J_0 + \frac{J_1}{1 + \omega^2\tau_1^2} + \frac{J_2}{1 + \omega^2\tau_2^2} \quad (13b)$$

In a similar way, in order to obtain the relaxation and storage moduli, it is easier to consider the behavior of the model in Fig. 24b. The relaxation and storage moduli are given, respectively, by

$$G(t) = G_1e^{-t/\tau_{r1}} + G_2e^{-t/\tau_{r2}} + G_3e^{-t/\tau_{r3}} \quad (13c)$$

$$G'(\omega) = \frac{G_1\omega^2\tau_{r1}^2}{1 + \omega^2\tau_{r1}^2} + \frac{G_2\omega^2\tau_{r2}^2}{1 + \omega^2\tau_{r2}^2} + \frac{G_3\omega^2\tau_{r3}^2}{1 + \omega^2\tau_{r3}^2} \quad (13d)$$

As before, the curve of $G(t)$ plotted against $\ln t$ resembles the curve of $G'(\omega)$ plotted against $\ln (1/\omega)$. From equations (13a) and (13b) it is seen that the curve of $J(t) - t/\eta$ plotted against $\ln t$ is similar to the curve of $J'(\omega)$ plotted against $\ln (1/\omega)$. The function $J(t) - t/\eta$ has been referred to as the *elastic* part of the creep compliance; as will be shown in the next section, this represents the recovery when the stress is removed after the steady state is reached in a constant stress experiment.

For the model of Fig. 24b we would expect from equation (13d) that the storage modulus plotted against $\ln \omega$ would be a curve with two intermediate plateaus, in addition to a plateau at very high frequencies of magnitude G_0 (equal to $G_1 + G_2 + G_3$), and a plateau with $G'(\omega)$ equal to zero for very low frequencies. We would thus expect the storage modulus of a real material to show the same behavior; actually this is not the case. In Fig. 25 are shown curves of $\log J'(\omega)$ and $\log G'(\omega)$ plotted against $\log \omega$ for a specimen of polyisobutylene of weight-average molecular weight 1.56×10^6 , the data being reduced to 25° C.¹⁸ The continuous curves represent the behavior of the polymer; the dotted curves represent the storage compliance and modulus of either six-element model, or of a material whose rheological behavior is given by equation (12a). The values of the parameters of the model in Fig. 24a were chosen so that the storage compliance of this model agreed as nearly as possible with that of the polymer; this compliance is shown by the broken curve. From these values, the values of the parameters of the equivalent model in Fig. 24b were calculated, and the storage modulus obtained from equation (13d); this modulus is represented also by a broken curve in Fig. 25. This $G'(\omega)$ curve is seen to possess only one intermediate plateau; the one corresponding to lower

¹⁸ H. Leaderman and R. S. Marvin, *J. Appl. Phys.* **24**, 812 (1953).

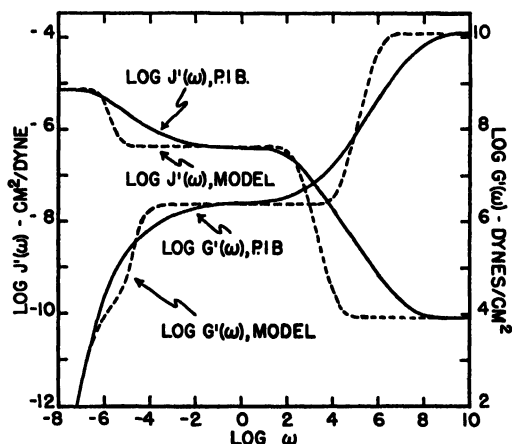


FIG 25. Storage modulus and compliance of high molecular weight polyisobutylene and of equivalent six-element model.

TABLE II
PARAMETERS OF SIX-ELEMENT MODEL

<i>Voigt representation</i>	<i>Maxwell representation</i>
$J_g = 8.3 \times 10^{-11} \text{ cm.}^2/\text{dyne}$	$G_1 = 1/J_g = 1.2 \times 10^{10} \text{ dynes/cm.}^2$
$J_1 = 4.0 \times 10^{-7} \text{ cm.}^2/\text{dyne}$	$\tau_{r1} = J_g \tau_1 / J_1 = 8.3 \times 10^7 \text{ sec.}$
$\tau_1 = 4.0 \times 10^{-3} \text{ sec.}$	$G_2 = 1/J_1 = 2.5 \times 10^6 \text{ dynes/cm.}^2$
$J_2 = 7.0 \times 10^{-8} \text{ cm.}^2/\text{dyne}$	$\tau_{r2} = J_1 \tau_2 \eta / (\eta J_2 + \tau_2) = 1.72 \times 10^4 \text{ sec.}$
$\tau_2 = 1.0 \times 10^6 \text{ sec.}$	$G_3 = \eta^2 J_2 / (\eta J_2 + \tau_2)^2 = 1.30 \times 10^4 \text{ dynes/cm.}^2$
$\eta = 6.16 \times 10^{10} \text{ poises}$	$\tau_{r3} = \eta J_2 + \tau_2 = 1.43 \times 10^6 \text{ sec.}$

frequencies has disappeared since the two shorter relaxation times of the model are close together. The values of the parameters of the two models in Fig. 24 are given in Table II, which also gives the approximate expressions for the parameters of the model of Fig. 24b in terms of those of Fig. 24a.

It is seen from Fig. 25 that the simple six-element model represents the linear viscoelastic behavior of a noncross-linked amorphous polymer only to a first approximation. As in the case previously considered, it is possible in principle to represent to any desired degree of approximation the actual linear viscoelastic behavior of a noncross-linked material, by adding more Voigt elements to the model of Fig. 24a or, what is the same thing, more Maxwell elements to the model of Fig. 24b, or more terms to the operator equation, equation (12a). Hence we can say that, for a real noncross-linked material manifesting linear viscoelastic behavior, the curve of $J(t) - t/\eta$ plotted against $\ln t$ is similar to the curve of $J'(\omega)$ plotted against $\ln (1/\omega)$

and the curve of $G(t)$ similarly resembles the curve of $G'(\omega)$. With this in mind, the relaxation modulus curves of polyisobutylene and of polymethyl methacrylate which are discussed in Chapter 2 can also be considered as approximate representations of the corresponding storage modulus curves.

Roughly speaking, we can thus describe the retarded elastic behavior of the above polyisobutylene specimen at 25° C. by a "fast" retarded elastic process of "average" retardation time 4×10^{-3} sec., representing the transition from glasslike to rubberlike behavior, and a "slow" retarded elastic process of average retardation time about 1×10^6 sec. As mentioned before, this latter retardation time is molecular-weight-dependent, and it increases with increase in molecular weight. This average retardation time is of the order of 1 sec. when the viscosity is 10^5 poises.^{7, 11} Thus this slow average retardation time varies with molecular weight at a given temperature in the same way as the variation of viscosity with molecular weight (compare Chapter 12, Volume I).

V. Superposition; Continuous Spectra

1. THE SUPERPOSITION PRINCIPLE

In this section we will consider further methods by means of which the linear viscoelastic behavior of a material can be specified, and also we will discuss the response of a material subsequent to a given stress or strain history. Let us consider first a mechanical model consisting of Voigt elements in series, together with degenerate Voigt elements (an isolated spring or dashpot). Let us suppose that a simple shear stress σ , is applied at time u , to a previously unloaded system. Then the shear strain at a subsequent time t is given by

$$\gamma(t) = \sigma J(t - u)$$

where $J(t)$ is the creep compliance as previously defined. Now suppose instead that a series of stress increments σ_i be applied at times u_i previous to time t . For such a model, it can be shown that the strain at time t is the simple sum of the shear strains which would be observed at time t if each stress increment were applied independently. Thus the strain at time t is

$$\gamma(t) = \sum_{u_i=-\infty}^{u_i=t} \sigma_i J(t - u_i) \quad (14a)$$

The summation indicates that the entire previous history is to be taken into account. Now it has been shown in the previous section that the rheological behavior of a material manifesting linear viscoelasticity can be represented to any degree of approximation by this type of model; hence equation (14a) must be valid also for such a material. This equation ex-

presses the *superposition principle* due originally to Boltzmann,^{1, 19} and relates the strain at time t to the previous stress history through the creep compliance $J(t)$. Similarly, consideration of a model consisting of Maxwell elements in parallel, with or without an isolated spring, leads to a superposition equation relating the stress to the previous strain history. If γ_i is the shear strain increment at time u_i , then the shear stress at a subsequent time t is given by

$$\sigma(t) = \sum_{u_i=-\infty}^{u_i=t} \gamma_i G(t - u_i) \quad (14b)$$

where $G(t)$ is as before the relaxation modulus.

These equations are particularly useful when the stress (or strain) varies discontinuously with time. For example, in a creep recovery experiment, let us assume that a shear stress σ_0 is applied at a time $-t_1$, and removed at zero time. If the time t_1 is sufficiently long so that the steady state has been reached, then the strain $\gamma(0)$ just before removal of the stress is given by

$$\gamma(0) = \sigma_0(J_e + J_d + t_1/\eta)$$

From equation (14a), the strain $\gamma(t)$ at a subsequent time t is that due to the original stress σ_0 applied at time $-t_1$, together with that due to a stress $-\sigma_0$ applied at zero time. Hence the strain at time t is given by

$$\gamma(t) = \sigma_0 \left[J_e + J_d + \frac{t + t_1}{\eta} - J(t) \right] \quad (15)$$

Hence the reduction in strain at time t following removal of stress is given by

$$\gamma(0) - \gamma(t) = \sigma_0 \left[J(t) - \frac{t}{\eta} \right] \quad (16)$$

Thus the reduction in strain gives the *elastic part* of the creep compliance. This result is useful under conditions where the time scale of the delayed elastic behavior is of the order of minutes, and the elastic behavior is dominated by the flow.^{6, 7} It can be seen that the reduction in strain following removal of stress at zero time is *not* given by equation (16) if the steady state has not been reached at the instant of stress removal. In Section II the recovery behavior of a noncross-linked material was described. It is now seen that this behavior is a necessary consequence of a response in a constant stress ("creep") test which is linear with stress. The superposition equations in the above form are of great use in the design of experimental

¹⁹ L. Boltzmann, *Sitzber. Kgl. Akad. Wiss. Wien* **70**, 275 (1874); *Ann. Physik.* **7**, 624 (1876).

procedures for measurement in step-function experiments of the rheological behavior of a material manifesting linear viscoelasticity.

It is now of interest to express the summations in equations (14a) and (14b) as integrals. Let the stress as a function of current time u be given by $\sigma(u)$. Then the increment of stress from time u to time $u + du$ is $\{d\sigma(u)/du\} du$ and equation (14a) becomes

$$\gamma(t) = \int_{-\infty}^t \frac{d\sigma(u)}{du} J(t - u) du \quad (17a)$$

and similarly equation (14b) becomes

$$\sigma(t) = \int_{-\infty}^t \frac{d\gamma(u)}{du} G(t - u) du \quad (17b)$$

Thus equation (17a) relates the strain at time t to the previous *stress history* through the creep compliance $J(t)$, while equation (17b) relates the stress at time t to the previous *strain history* through the relaxation modulus $G(t)$. It must be emphasized that equations (17a) and (17b), as well as the generalized operator equation as discussed in the previous section, are all equivalent to each other, and any one of the three may be used as a definition of linear viscoelastic response. If we write k equal to the elapsed time $(t - u)$, the above equations become, respectively,

$$\gamma(t) = \int_{-\infty}^0 \frac{d\sigma(t - k)}{dk} J(k) dk \quad (18a)$$

and

$$\sigma(t) = \int_{-\infty}^0 \frac{d\gamma(t - k)}{dk} G(k) dk \quad (18b)$$

If the loading history begins at zero time, then the limits of integration are zero and t . Integration of equations (18a) and (18b) by parts leads to the alternative formulations

$$\gamma(t) = J_0 \sigma(t) + \int_0^{\infty} \sigma(t - k) \frac{dJ(k)}{dk} dk \quad (19a)$$

and

$$\sigma(t) = G_0 \gamma(t) + \int_0^{\infty} \gamma(t - k) \frac{dG(k)}{dk} dk \quad (19b)$$

A simple interpretation can be given to the above equations. A stress $\sigma(u)$ applied at time u and removed at time $u + du$ results at a subsequent time t in a residual deformation given by

$$d\gamma(t) = \sigma(u) \frac{dJ(t - u)}{d(t - u)} du$$

The superposition of these residual deformations up to time t leads to the integral in equation (19a). Similarly, equation (19b) gives the stress obtained by summation of residual stresses due to application of transient strains. The foregoing considerations, together with some of the subsequent ones, are familiar concepts in linear circuit theory.²⁰

2. RELATION BETWEEN CREEP AND RELAXATION

The simultaneous existence of pairs of equations such as equations (18a) and (18b), and also equations (19a) and (19b), implies that there exists a relationship between the creep compliance $J(t)$ and the relaxation modulus $G(t)$. Without loss of generality, we set the limits of integration at zero and t . Then following Gross,^{16, 21, 22} this relationship may be obtained by taking Laplace transforms of both sides of equations (18a) and (18b). Making use of Borel's theorem to obtain the Laplace transform of the convolution integrals in these equations,²⁰ we obtain

$$\mathcal{L}\{\gamma(t)\} = p\mathcal{L}\{\sigma(t)\}\mathcal{L}\{J(t)\} \quad (20a)$$

and

$$\mathcal{L}\{\sigma(t)\} = p\mathcal{L}\{\gamma(t)\}\mathcal{L}\{G(t)\} \quad (20b)$$

where

$$\mathcal{L}\{f(t)\} = \int_0^\infty e^{-pt}f(t) dt$$

The desired relationship is thus

$$p\mathcal{L}\{J(t)\} = \frac{1}{p\mathcal{L}\{G(t)\}} \quad (21)$$

It is observed that while in classical elasticity theory the shear modulus G_0 and shear compliance J_0 are reciprocals of each other, the corresponding reciprocal quantities in viscoelasticity theory are the complex quantities $G^*(\omega)$ and $J^*(\omega)$ (compare Table I) and the quantities $p\mathcal{L}\{G(t)\}$ and $p\mathcal{L}\{J(t)\}$. By making use of the theorem giving the Laplace transform of the differential of a function, and by means of other methods of representing $J(t)$ and $G(t)$ as in equations (8) and (11), equation (21) can be put into alternative forms.

In principle, equation (21) implies that if $J(t)$ is known over the whole range of time, either in analytical form or graphically, then $G(t)$ can be

²⁰ See, for example, S. Goldman, "Transformation Calculus and Electrical Transients." Prentice-Hall, New York, 1949.

²¹ B. Gross, *J. Appl. Phys.* **18**, 212 (1947).

²² B. Gross, and H. Pelzer, *J. Appl. Phys.* **22**, 1035 (1951).

calculated, and vice versa. This requires the inversion of a Laplace transform to obtain, for example, $G(t)$ from $J(t)$; this may not always be possible if $\mathcal{L}\{G(t)\}$ is expressed in analytical form, while the numerical inversion of a Laplace transform is generally an approximate procedure. Furthermore, $J(t)$ or $G(t)$ may be known only over a limited range of time. For example, the relaxation modulus of certain materials over a limited range of values of time may be of the form²³

$$G(t) = a \left(\frac{t}{b} \right)^{-m} \quad (22a)$$

where b is a suitable unit of time, say 1 min., and a and m are experimentally determined constants; m may be of the order of 0.1. From equation (21) the creep compliance is found to be

$$J(t) = \frac{\sin m\pi}{am\pi} \left(\frac{t}{b} \right)^m \quad (22b)$$

It is observed that at zero time the relaxation modulus and creep compliance are, respectively, infinity and zero, hence these relations cannot hold for very small values of time. However, it seems justifiable to use equation (21) to obtain the creep compliance from measurements of the relaxation modulus; the significant range of time t for the derived data must be somewhat less than the range of time for the observed data. It is seen that when m is small, then $G(t)$ and $J(t)$ in equations (22a) and (22b) are approximately reciprocals of each other.

Under certain circumstances, the "average" retardation time for the fast viscoelastic process as discussed in the previous section is very long compared to the times involved in an experiment. Under these conditions the viscoelasticity in an amorphous polymer manifests itself as a perturbation on glasslike behavior, as for example in polystyrene at room temperature as discussed in the introductory section of this chapter. It is then convenient to define a *non-normalized* retardation function $\psi(t)$ given by

$$J(t) = J_0[1 + \psi(t)] \quad (23a)$$

where $\psi(t)$ has now a meaning different from that in equation (8). Similarly, it is convenient to define a *non-normalized* relaxation function $\phi(t)$ given by

$$G(t) = G_0[1 - \phi(t)] \quad (23b)$$

From equation (21) we now obtain^{21, 22}

$$\left[1 + \mathcal{L} \left\{ \frac{d\psi(t)}{dt} \right\} \right] \left[1 - \mathcal{L} \left\{ \frac{d\phi(t)}{dt} \right\} \right] = 1 \quad (24)$$

and three other similar relationships.

²³ A. A. MacLeod, *Ind. Eng. Chem.* **47**, 1319 (1955).

3. RETARDATION AND RELAXATION SPECTRA

It has been pointed out in the previous section that the creep compliance of a real material could be approximated by a model containing several Voigt elements. Hence from equation (13a), if the selected retardation times be denoted in general by τ_i , and the corresponding compliances by J_i , then

$$J(t) = J_0 + \sum_i J_i (1 - e^{-t/\tau_i}) + \frac{t}{\eta} \quad (25a)$$

This leads to the introduction of a new auxiliary function to represent the delayed elastic component of the creep compliance. We may write

$$J(t) = J_0 + \int_0^\infty f_1(\tau) (1 - e^{-t/\tau}) d\tau + \frac{t}{\eta} \quad (25b)$$

With the substitution

$$\tau f_1(\tau) = L(\tau)$$

We obtain finally

$$J(t) = J_0 + \frac{t}{\eta} + \int_{-\infty}^\infty L(\tau) (1 - e^{-t/\tau}) d \ln \tau \quad (25c)$$

The function $L(t)$ is usually called the *retardation spectrum*. Since the delayed elastic component of the creep compliance increases monotonically from zero at zero time to a limiting value J_0 at infinite time, this component of the deformation can always be represented by an integral of the form given in equations (25b) and (25c).

Similarly, the relaxation modulus of a generalized Maxwell model is from equation (11a):

$$G(t) = \sum_i G_i e^{-t/\tau_i} + G_e \quad (26a)$$

This suggests a second auxiliary function to represent the decay modulus component of the relaxation modulus. From equation (26a) we may write

$$G(t) - G_e = \int_0^\infty f_2(\tau) e^{-t/\tau} d\tau \quad (26b)$$

and with the substitution

$$\tau f_2(\tau) = H(\tau)$$

we obtain finally

$$G(t) - G_e = \int_{-\infty}^\infty H(\tau) e^{-t/\tau} d \ln \tau \quad (26c)$$

Since $G(t)$ decreases monotonically with time from G_0 at zero time to G_∞ at infinite time, we can always write an equation of the form of equation (26c). We may call the function $H(t)$ the *relaxation spectrum*. Thus the retardation and relaxation spectra $L(t)$ and $H(t)$ are two alternative, related ways of specifying the viscoelastic behavior of a material. In principle, if $J(t)$ is known over the whole significant range to t , then $L(t)$ can be calculated, and similarly $H(t)$ can be calculated from $G(t)$. In practice, if the experimental results are given in graphical or numerical form, this can be done only by approximate procedures; these will be considered subsequently.

We will now consider the relationship between the $G'(\omega)$ and also the $G''(\omega)$ response functions and the relaxation spectrum, as well as the relationship between the $J'(\omega)$ and $J''(\omega)$ functions and the retardation spectrum. Returning to the superposition equation, equation (17a), we put

$$\sigma(t) = \sigma_a \sin \omega t$$

as before, and for $J(t)$ we write the expression given in equation (25c). We obtain for the steady-state response an equation of the form

$$\gamma(t) = \sigma_a J'(\omega) \sin \omega t - \sigma_a J''(\omega) \cos \omega t$$

where $J'(\omega)$ and $J''(\omega)$ are the storage and loss compliances as defined and discussed in Section III of this chapter. These functions are given, respectively, by

$$J'(\omega) - J_0 = \int_{-\infty}^{\infty} \frac{L(\tau)}{1 + \omega^2 \tau^2} d \ln \tau \quad (28a)$$

and

$$J''(\omega) - \frac{1}{\omega \eta} = \int_{-\infty}^{\infty} \frac{L(\tau) \omega \tau}{1 + \omega^2 \tau^2} d \ln \tau \quad (28b)$$

Either of these equations may alternatively be used to define the retardation spectrum.

Similarly, with a strain given by

$$\gamma(t) = \gamma_a \sin \omega t$$

then by making use of equations (17b) and (26c) we obtain

$$\sigma(t) = \gamma_a G'(\omega) \sin \omega t + \gamma_a G''(\omega) \cos \omega t \quad (29)$$

where the storage and loss moduli $G'(\omega)$ and $G''(\omega)$ are given by

$$G'(\omega) - G_0 = \int_{-\infty}^{\infty} \frac{H(\tau) \omega^2 \tau^2}{1 + \omega^2 \tau^2} d \ln \tau \quad (30a)$$

and

$$G''(\omega) = \int_{-\infty}^{\infty} \frac{H(\tau)\omega\tau}{1 + \omega^2\tau^2} d \ln \tau \quad (30b)$$

The quantity $G''(\omega)/\omega$ has the dimensions of viscosity, and it is sometimes called the *dynamic viscosity*, $\eta'(\omega)$.

As before, either equation (30a) or (30b) may be used to define $H(t)$. In principle, $H(t)$ may be obtained from experimental data of either $G'(\omega)$ or $G''(\omega)$, and similarly $L(t)$ may be obtained from experimental data of $J'(\omega)$ or $J''(\omega)$. Here again, if the data are given in graphical or numerical form, then the calculation of $L(t)$ or $H(t)$ can be carried out only by approximation methods.

We now have three equations defining $H(t)$, and also three equations defining $L(t)$, in terms of, respectively, $G(t)$, $G'(\omega)$, and $G''(\omega)$; and $J(t)$, $J'(\omega)$, and $J''(\omega)$. Thus in principle if, for example, $G(t)$ is known at a given temperature over the whole range of t for which it differs significantly from its limiting values, then $H(t)$ can be calculated for this temperature and hence $G'(\omega)$ and $G''(\omega)$ can be obtained for the same temperature. In principle also the value of, say, $G'(\omega)$ at a given frequency depends not only upon the value of $G''(\omega)$ at the same frequency, but upon the values over the whole range of frequencies. However, it will be shown subsequently that to compute the values of $L(t)$ or $H(t)$ for a given value of t , the response curve need be known only in the vicinity of time t (in step-function experiments) or of frequency $1/t$ (in dynamic experiments). Hence in the above example the value of $G'(\omega)$ at any given frequency (and temperature) depends in practice on the value of the $G''(\omega)$ function only in the vicinity of the frequency.

In the general presentation of Sections II and III certain limiting values were introduced. The values reappeared in the discussion of mechanical models in Section IV, in which section the coefficients in the operator equations were also found to contain these limiting values. Finally, in the relationships in this section arising from the superposition equations, the same limiting values have appeared. They are, namely, the glass modulus G_g and glass compliance J_g ; and the equilibrium modulus G_e and equilibrium compliance J_e for cross-linked amorphous polymers. For noncross-linked polymers we have the steady-state elastic compliance J_e and the viscosity η . From equations (25c), (26c), (28), and (30) these may now formally be defined as follows:

$$J_g = \lim_{t \rightarrow 0} J(t) = \lim_{\omega \rightarrow \infty} J'(\omega) \quad (31a)$$

$$G_g = \lim_{t \rightarrow 0} G(t) = \lim_{\omega \rightarrow \infty} G'(\omega) \quad (31b)$$

$$\frac{1}{\eta} = \lim_{t \rightarrow \infty} \frac{dJ(t)}{dt} = \lim_{\omega \rightarrow 0} \omega J''(\omega) \quad (31c)$$

$$\eta = \lim_{\omega \rightarrow 0} \eta'(\omega) \quad (31d)$$

$$J_e = \lim_{t \rightarrow \infty} \left[J(t) - \frac{t}{\eta} \right] = \lim_{\omega \rightarrow 0} J'(\omega) \quad (31e)$$

For cross-linked polymers we have

$$J_e = \lim_{t \rightarrow \infty} J(t) = \lim_{\omega \rightarrow 0} J'(\omega) \quad (31f)$$

$$G_e = \lim_{t \rightarrow \infty} G(t) = \lim_{\omega \rightarrow 0} G'(\omega) \quad (31g)$$

It has been mentioned that the idealized linear system is strictly speaking only an approximation to real behavior. In the same way the idealized frequency-independent or time-independent glass modulus and glass compliance do not always represent the actual behavior. This is discussed further in Section VI of this chapter and in Chapter 4.

4. CALCULATION OF RETARDATION AND RELAXATION SPECTRA

We see that the $H(t)$ and $L(t)$ functions are of importance, first because they represent the viscoelastic behavior of a material (at a specified temperature) in a somewhat more general way than the functions such as $J(t)$ and $G'(\omega)$, which represent the response of a material in a specific type of test; and secondly because the former functions are of use in calculating two of the previously considered response functions from data on another response function. The important problem arises, how the $H(t)$ and $L(t)$ functions are to be calculated from experimental data presented in graphical or tabular form.

One method is to *assume* a given form for the $H(t)$ or $L(t)$ function. For example we may assume a "box" type of function,^{12, 24-26} that is, $H(t)$ or $L(t)$ is constant between specified values of $\ln t$, and zero outside this range (cf. Chapter 2). The appropriate response function, for example $G(t)$, is then calculated, in this case from equation (26c). If the observed $G(t)$ function is of the same shape as the calculated function, then the three parameters defining the height and range of the "box" can be determined, and thus the $H(t)$ or $L(t)$ function is specified. A "wedge" type function for $H(t)$ has also been considered, in which $\ln H(t)$ varies linearly with $\ln t$

²⁴ R. D. Andrews, N. Hofman-Bang, and A. V. Tobolsky, *J. Polymer Sci.* **3**, 669 (1948).

²⁵ A. V. Tobolsky, *J. Am. Chem. Soc.* **74**, 3786 (1952).

²⁶ E. Catsiff and A. V. Tobolsky, *J. Appl. Phys.* **25**, 145 (1954).

between specified limits, and is zero beyond these limits.^{25, 26} By means of such considerations, a wedge together with a box has been proposed²⁵ for the relaxation spectrum of the high molecular weight polyisobutylene for which the storage and loss moduli are shown in Fig. 25. However, spectra calculated in this way turn out to be poor approximations, and response curves calculated therefrom do not always agree very well with observed curves.⁵

We will now consider two approximation methods, which utilize respectively an analytical and a quasi-empirical approach. The former originated in a method proposed by Alfrey,²⁷ and has been developed by Schwarzl and others.²⁸⁻³⁵ The latter has been developed by Ferry and associates,³⁶⁻³⁸ and applications of this procedure are given in Chapter 11 of this volume. The former method depends upon the existence of approximations to step functions or to delta functions in integrals containing $L(\tau)$ or $H(\tau)$, as in equations (25c), (26c), (28), and (30) above.

Following Alfrey, let us consider as an example the calculation of $L(t)$ from equation (25c). Using the nomenclature in equation (8), we have for the delayed elastic component of the creep compliance

$$J_d\psi(t) = \int_{-\infty}^{\infty} L(\tau)(1 - e^{-t/\tau}) d \ln \tau \quad (32a)$$

With the substitution

$$\tau = e^z; \quad t = e^n$$

this becomes

$$J_d\psi(n) = \int_{-\infty}^{\infty} L(z)(1 - \exp[-e^{n-z}]) dz \quad (32b)$$

Now for values of n less than z , the coefficient of $L(z)$ in the integrand is approximately zero; it then rises steeply to a value approximately unity

²⁷ T. Alfrey and P. Doty, *J. Appl. Phys.* **16**, 700 (1945); T. Alfrey, "Mechanical Behavior of High Polymers," p. 551. Interscience, New York, 1948.

²⁸ F. Schwarzl, *Physica* **17**, 830, 923 (1951).

²⁹ F. Schwarzl and A. J. Staverman, *Physica* **18**, 791 (1952).

³⁰ F. Schwarzl and A. J. Staverman, *Appl. Sci. Research* **A4**, 127 (1953).

³¹ F. Schwarzl, *Proc. 2nd Intern. Rheol. Congr., Oxford*, p. 197 (1953).

³² R. D. Andrews, *Ind. Eng. Chem.* **44**, 707 (1952).

³³ D. G. Ivey, B. A. Mrowca, and E. Guth, *J. Appl. Phys.* **20**, 486 (1949).

³⁴ H. Leaderman, *J. Appl. Phys.* **25**, 294 (1954).

³⁵ H. Fujita, *Buseiron-Kenkyu* No. **63**, 48 (1953).

³⁶ J. D. Ferry, E. R. Fitzgerald, L. D. Grandine, Jr., and M. L. Williams, *Ind. Eng. Chem.* **44**, 703 (1952).

³⁷ J. D. Ferry and M. L. Williams, *J. Colloid Sci.* **7**, 347 (1952).

³⁸ M. L. Williams and J. D. Ferry, *J. Polymer Sci.* **11**, 169 (1953).

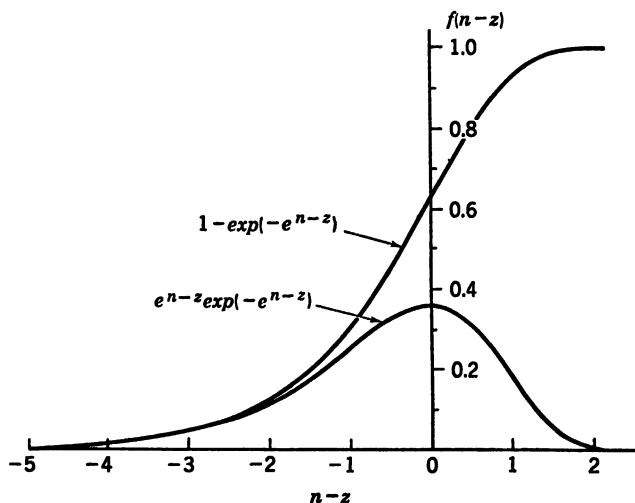


FIG. 26. Step and delta function approximations

for values of n greater than z . The function $1 - \exp(-e^{n-z})$ is shown in Fig. 26. Hence the integral in equation (32b) can be approximated as follows:

$$J_a \psi(n) \simeq \int_{-\infty}^n L(z) dz \quad (33a)$$

Differentiating this equation with respect to n , we obtain

$$\left(\frac{d}{dn}\right) J_a \psi(n) \simeq L(n) \quad (33b)$$

From equation (33b) we can deduce Alfrey's rule.²⁷ The elastic component of the creep compliance, namely $J(t) - t/\eta$, is plotted against $\ln t$. The slope of this plot gives an approximation to the value of $L(t)$ for any particular value of $\ln t$.

The same result is obtained by differentiating equation (32b) with respect to n . We then obtain

$$\left(\frac{d}{dn}\right) J_a \psi(n) = \int_{-\infty}^{\infty} e^{n-z} \exp(-e^{n-z}) L(z) dz \quad (32c)$$

In this case the coefficient of $L(z)$ in the integrand is zero except over a small range of values around n equal to z . If $L(z)$ does not vary very much over this range, then we may assume that it is constant and approximately equal to $L(n)$. Thus equation (32c) becomes

$$\left(\frac{d}{dn}\right) J_a \psi(n) \simeq L(n) \int_{-\infty}^{\infty} e^{n-z} \exp(-e^{n-z}) dz \quad (32d)$$

The value of the integral is unity, and so equation (33b) is again obtained. The function in the integrand of equation (32d) is also shown in Fig. 26. In a similar way the function $\exp(-t/\tau)$ occurring in equation (26c) can be considered as an approximation to a step function, and hence an approximation to $H(t)$ is obtained by differentiating $G(t)$ with respect to $-\ln t$.

If we make the substitution

$$\omega = e^{-n}$$

it can be seen that the functions $1/(1 + \omega^2 \tau^2)$ and $\omega^2 \tau^2/(1 + \omega^2 \tau^2)$ in equations (28a) and (30a) are approximations to a step function when plotted against $\ln \omega$. Since this approximation is better than the one considered above, the approximations for $L(1/\omega)$ and $H(1/\omega)$, obtained by differentiating, respectively, $J'(\omega)$ and $-G'(\omega)$ with respect to $\ln(1/\omega)$, are better than the approximations obtained from the slopes of curves of $J(t) - t/n$ and $G(t)$ plotted against $\ln t$.³² The function $\omega \tau/(1 + \omega^2 \tau^2)$ when plotted against $\ln \omega \tau$ gives a very crude approximation to a delta function, and hence $G''(\omega)$ and $J''(\omega) - 1/\omega \eta$ may be considered as very roughly proportional to $H(1/\omega)$ and $L(1/\omega)$, respectively.

Schwarzl^{29, 30} has obtained relations involving higher differential coefficients of the observable response functions $J(t)$, $G(t)$, $J'(\omega)$, $J''(\omega)$, $G'(\omega)$, and $G''(\omega)$. These relations correspond to integrals in which the integrands contain functions which are better approximations to either step functions or delta functions, and hence better approximations are obtained for the $L(t)$ and $H(t)$ functions. There is a practical limit to the use of such expressions containing higher derivatives of observed response curves, since the second and higher derivatives are very sensitive to small experimental variations in the response curve.

In Table III are given (in our notation) some of the approximations derived by Schwarzl, from the creep compliance, relaxation modulus, and storage and loss moduli and compliances. In this table, $L_1'(1/\omega)$ represents the first approximation to $L(1/\omega)$ obtained from $J'(\omega)$, and so on. It is observed that approximations of the same order are not necessarily equivalent; for example, $L_1'(1/\omega)$ is nearly as good as $L_2(t)$. It is also observed that approximations such as $L_1''(1/\omega)$ do not exist.^{30, 32} Some of the first-order approximations in Table III are also given (with a different nomenclature) in Chapter 11.

The approximations considered above are obtained by successive differentiation of the response curves with respect to either $\ln t$ or $\ln \omega$. In many cases where a wide range of values of the response function is covered, as in the curves of Fig. 25, it is preferable to plot, for example, $\ln J'(\omega)$ instead of $J'(\omega)$, since this quantity may range from about 10^{-10} cm.²/dyne to 10^{-5}

TABLE III
APPROXIMATIONS FOR RETARDATION AND RELAXATION SPECTRA

Type of test	Order of approximation	Approximation for $L(t)$, $L(1/\omega)$, $H(t)$, $H(1/\omega)$
Creep	1	$L_1(t) = (d/d \ln t)[J(t) - t/\eta]$
	2	$L_2(t/2) = [d/d \ln t - d^2/d(\ln t)^2] A(t)$
	0	$L_0''(1/\omega) = (2/\pi)[J''(\omega) - 1/\omega\eta]$
Dynamic	1	$L_1'(1/\omega) = -(d/d \ln \omega)J'(\omega)$
	2	$L_2''(1/\omega) = (2/\pi)[1 - d^2/d(\ln \omega)^2]B(\omega)$
	3	$L_3'(1/\omega) = -[d/d \ln \omega - (1/4)d^2/d(\ln \omega)^2]J'(\omega)$
Stress Relaxation	1	$H_1(t) = -(d/d \ln t)G(t)$
	2	$H_2(t/2) = -[d/d \ln t - d^2/d(\ln t)^2]G(t)$
	0	$H_0''(1/\omega) = (2/\pi)G''(\omega)$
Dynamic	1	$H_1'(1/\omega) = (d/d \ln \omega)G'(\omega)$
	2	$H_2''(1/\omega) = (2/\pi)[1 - d^2/d(\ln \omega)^2]G''(\omega)$
	3	$H_3'(1/\omega) = [d/d \ln \omega - (1/4)d^2/d(\ln \omega)^2]G'(\omega)$

NOTE: $A(t) = J(t)$ or $J(t) - t/\eta$.

$B(\omega) = J''(\omega)$ or $J''(\omega) - 1/\omega\eta$.

cm.²/dyne. In this case the first approximation to $L(1/\omega)$ is obtained by multiplying the slope of the double logarithmic plot by $J'(\omega)$ since

$$\begin{aligned}
 L_1' \left(\frac{1}{\omega} \right) &= - \frac{d J'(\omega)}{d \ln \omega} \\
 &= - J'(\omega) \frac{d \log J'(\omega)}{d \log \omega}
 \end{aligned} \tag{34}$$

The other approximations in Table III can similarly be put into this form. Some of these (with a different nomenclature) are given in Chapter 11.

The second higher approximation method, due to Ferry and Williams,^{37, 38} assumes that the $L(t)$ or $H(t)$ function can be represented by a power function of t ; for example, let

$$H(t) = At^m$$

If a response function such as $G'(\omega)$ is calculated from the appropriate relation given previously, and the first approximation to the spectrum calculated by differentiation as already described, it is found that this approximation differs from the assumed power law spectrum only by a factor which is a function of m . The second approximation to the spectrum is thus obtained from the first approximation by multiplying by an appropriate factor. This procedure is discussed further in Chapter 11. Of course, in practice both A and m in the above equation are functions of t , and hence the correction factor is a function of t (or $1/\omega$). The method can be justified

because we are dealing as before with integrands which can be considered as approximations to step or delta functions.

In this section recent developments in approximation methods for the calculation of retardation and relaxation spectra from observed response curves have been discussed. In conclusion, we can say that an approximation method is satisfactory if the original response curve can be regained with satisfactory accuracy from the calculated $H(t)$ or $L(t)$ function; the spectrum can then be used with confidence for the calculation of other response curves.

5. RELATIONS BETWEEN RESPONSE CURVES INVOLVING SPECTRA

a. Difference Functions

We have seen previously by considering generalized models that there is a close connection between the elastic part of the creep compliance plotted against $\ln t$ and the storage compliance $J'(\omega)$ plotted against $-\ln \omega$; there is similarly a close connection between the relaxation modulus $G(t)$ and the storage modulus $G'(\omega)$. This can be demonstrated, for example, by writing $\omega = 1/t$ in equation (30a). Then it becomes

$$G' \left(\frac{1}{t} \right) - G_e = \int_{-\infty}^{\infty} H(\tau) \left[\frac{\tau^2}{t^2 + \tau^2} \right] d \ln \tau \quad (35)$$

The expression in brackets on the right-hand side of equation (35) is very similar to $\exp(-t/\tau)$ in equation (26c), hence $G(t)$ and $G'(1/t)$ should be very nearly the same. Furthermore,

$$G' \left(\frac{1}{t} \right) - G(t) = \int_{-\infty}^{\infty} H(\tau) f \left(\frac{t}{\tau} \right) d \ln \tau \quad (36)$$

where the function $f(t/\tau)$ is of course obtained from equations (26c) and (35). In equation (36), $f(t/\tau)$ is always positive, hence the storage modulus curve lies above the relaxation modulus curve when plotted according to the procedure discussed in Sections III and IV.^{13, 15} Similarly, it can be shown that the storage compliance curve lies close to the curve of the elastic part of the creep compliance when plotted in this way. In the latter case the storage compliance curve lies below the creep compliance curve.³⁹

By means of equation (36) an approximation for $G(t)$ can be obtained if $G'(\omega)$ is known, and vice versa. From the known response curve a first approximation is calculated for $H(t)$ by the Alfrey differentiation procedure as discussed in the previous section. Using this approximation in equation (36), the difference function is evaluated by numerical integration. As indicated above, a better approximation is obtained in going from $G'(\omega)$ to $G(t)$ than in the reverse direction, since we obtain a better approximation

³⁹ H. Leaderman, *Proc. 2nd Intern. Rheol. Congr., Oxford*, p. 203 (1953).

to $H(t)$ in the former case. Since we are calculating by this means only the relatively small difference between $G(t)$ and $G'(\omega)$, we obtain a value for the computed response function which is better than that obtained using the first approximation to $H(t)$, and either equation (26c) or (30a).¹⁵ Similar considerations apply to the calculation of $J'(\omega)$ from $J(t)$ and of $J(t)$ from $J'(\omega)$.³⁹ By means of such calculations it is possible to combine, for example, measurements of $G'(\omega)$ with stress relaxation measurements in order to extend the $G'(\omega)$ curve to regions of very low frequency,¹³ as mentioned in Section III.

b. Viscosity, Steady-State Compliance, and Relaxation Spectrum

We have seen, in the discussion of limiting values, that the limiting values associated with $G'(\omega)$ or $G(t)$ for a *cross-linked* amorphous polymer are the reciprocals of the limiting values associated with $J'(\omega)$ or $J(t)$ for the same material. In the case of the *noncross-linked* polymer, there are *three* limiting values associated with $J'(\omega)$ and $J(t)$, the additional one being the viscosity η , while there is associated with $G(t)$ and $G'(\omega)$ only one non-zero limiting value, namely G_g . Since the stress relaxation behavior of a noncross-linked polymer must depend upon the viscosity and also the steady-state elastic compliance J_e , it follows that these two quantities must be calculable from the relaxation spectrum.

The required relationships can be derived most easily by considering a generalized model consisting of many Maxwell elements in parallel. If G_i is the "modulus" of a particular spring and τ_i the relaxation time of the Maxwell element of which it is a part, then the viscosity of the dashpot of the same element is $G_i\tau_i$. The viscosity of the whole model is the sum of the elementary viscosities, thus:

$$\eta = \sum_i G_i\tau_i$$

On going from a discrete model to a continuous spectrum, we get

$$\eta = \int_0^\infty \tau f_2(\tau) d\tau = \int_{-\infty}^\infty \tau H(\tau) d \ln \tau \quad (37a)$$

In the same way, the steady-state elastic compliance is found to be

$$J_e = \frac{\int_{-\infty}^\infty \tau^2 H(\tau) d \ln \tau}{\eta^2} \quad (37b)$$

These equations have been used to calculate viscosity and steady-state compliance from stress relaxation measurements.^{40, 41} Here as before the

⁴⁰ R. D. Andrews and A. V. Tobolsky, *J. Polymer Sci.* **7**, 221 (1951).

⁴¹ F. W. Schrepf, J. D. Ferry, and W. W. Evans, *J. Appl. Phys.* **22**, 711 (1951).

relevant integrals extend to infinity in both directions, and the integrands are bell-shaped functions. In order to obtain either of these functions over the significant range of values of τ , it is necessary in dynamic tests to go to very low frequencies, where the material behaves practically in a Newtonian manner and where the elasticity is a very small perturbation upon ideal flow behavior. In stress relaxation tests it is necessary to go to very small values of stress. Thus while equations (37a) and (37b) may be interesting tests of linear viscoelasticity theory, their practical use may be somewhat limited.

We have seen in the previous section that a response curve of a real material can be represented to any degree of accuracy by an equivalent model consisting of a series assembly of Voigt elements or a parallel assembly of Maxwell elements. The retardation or relaxation times of the elements are spread over the range of values of time (or reciprocal frequency) for which the response curve differs appreciably from its significant limiting values. If there are only a few such Voigt or Maxwell elements, then we would expect from Fig. 23 that the response curve for the model would show points of inflection; these would be expected to disappear as the number of retardation or relaxation times is increased. The discrete retardation or relaxation spectrum that is thus obtained is however not unique, since it depends upon the somewhat arbitrary choice of retardation or relaxation times. The alternative procedure assumes on the other hand that the observed response function is related to a continuous spectrum; the continuous spectrum as defined and calculated in this section is thus unique.

Recent molecular theories of the viscoelastic behavior of polymers lead to the existence of a discrete relaxation or retardation spectrum with somewhat closely spaced relaxation or retardation times for monodisperse materials. If the Schwarzl procedure is followed to obtain higher approximations to the spectrum from an observed response curve, then peaks should appear in the computed spectrum corresponding to the discrete retardation or relaxation times.²⁹ Since these discrete times are closely spaced, this would require a very high order of experimental precision to obtain a sufficiently high order of approximation to the true spectrum; hence it is not possible in practice to distinguish from experimental data between a continuous spectrum and a closely spaced discrete spectrum. Thus the representation of the linear viscoelastic behavior of a material by means of a continuous spectrum yields a unique and useful function; this representation does not preclude the existence of a discrete spectrum.

VI. Molecular Structure and Linear Viscoelastic Behavior

The discussion up to now has been concerned principally with the phenomenological theory of linear viscoelastic behavior. If we define this in

one of several equivalent ways, then the whole theory can be constructed without reference to the behavior of real materials and regardless of considerations of constitution. The major importance of the theory is to demonstrate the relationship between mechanical response patterns observed under different test conditions, and to derive methods for the specification of linear viscoelastic behavior.¹⁶ The objective of this section is to review aspects of viscoelastic behavior which are related to the molecular constitution of amorphous polymers.

1. GLASSY STATE, GLASS MODULUS, GLASS COMPLIANCE

It is well known that certain physical properties of polymers possess a discontinuity in the derivative with respect to temperature; such properties are, for example, specific volume and enthalpy. One effect of change in temperature in an amorphous polymer (or in the amorphous region of a crystalline polymer) is to change the degree of local order; decrease of temperature corresponds to an increase in local order, and thus the amorphous structure becomes more crystal-like. If the change in order with temperature is associated with a potential barrier, then the change in properties associated with degree of packing does not in general occur instantaneously with instantaneous change in temperature, but requires the passage of time. At high temperatures, this characteristic time would be expected to be very small. As the temperature is reduced, then the time scale for these rearrangements increases; in some temperature region this would be expected to be of the order of the time scale of the experimental measurement, that is, minutes to hours. Finally, if the temperature is reduced still further, this time scale is increased so much that no further change in order is observed over practical time scales. Thus a discontinuity is observed in the derivative of certain thermodynamic properties with respect to temperature, at a temperature which depends somewhat upon the time scale of the measurement. The temperature at which this transition is observed is often called the *glass transition* temperature, and is denoted by T_g . Measurements of T_g from thermal expansion of polystyrene over widely different time scales correspond to a very high activation energy;⁴² this is of the same order of magnitude as the (temperature-dependent) activation energy for viscous flow extrapolated to the glass transition temperature.

Let us suppose now that we are making dynamic measurements in shear on an amorphous polymer at a temperature above T_g . At low frequencies, the deformation is due principally to orientation of polymer chains, as discussed later in this section. If the frequency is increased sufficiently, then there is no time for this ordering to take place under stress, and the deformation is associated principally with the van der Waals' forces be-

⁴² T. G. Fox, Jr., and P. J. Flory, *J. Appl. Phys.* **21**, 581 (1950).

tween the polymer chains. Thus the material exhibits glasslike elasticity, even though it is at a temperature above T_g . Now in such a test if the frequency be increased from a very small value to a very large value, then $G'(\omega)$ increases from about 10^6 dynes/cm.² in the case of a cross-linked amorphous polymer (and from zero in the case of a noncross-linked polymer) to about 10^{10} dynes/cm.². With the cross-linked polymer $G''(\omega)$ necessarily exhibits a maximum value at some intermediate frequency, and as we have seen, the noncross-linked polymer possesses a second maximum in $G''(\omega)$ at a lower frequency; it will be recalled that the $G''(\omega)$ function is a rough representation of the relaxation spectrum. Since, with increase in frequency, the dynamic behavior becomes glasslike, it is sometimes said that the polymer possesses a glass transition at the temperature of the experiment, for the frequency of the peak in the $G''(\omega)$ response curve. However, it seems better to restrict the definition of glass transition to the small temperature range associated with thermodynamic measurements of fairly long time scale. In such a dynamic experiment carried out above the glass transition as defined in this way, we would expect the limiting dynamic modulus G_g to be quite temperature dependent, since the degree of order will be very dependent upon temperature. Strictly speaking, this limiting modulus in tests carried out above the glass transition temperature should be called the "liquid modulus," since it is associated with the elasticity of liquids.

It has been assumed previously in this chapter that if the frequency in dynamic tests is sufficiently high, or if the time in step-function tests is sufficiently small, then the limiting modulus or compliance is independent of time or frequency. Actually, it appears that there are relaxation or retardation phenomena in this region of glasslike behavior. Whereas the relaxation or retardation phenomena we have been discussing up to now appear to be related to ordering of chain molecules, the viscoelasticity phenomena in the region of glasslike behavior appear to be associated with local movements of groups attached to the main chain. If this movement is associated with a potential barrier, then the motion will become evident in rheological tests at a temperature which depends upon the time scale of the experiment. It will be manifested, for example, as a plateau in the creep compliance curve,⁴³ or as a peak in the curve of $\tan \delta$ or $G''(\omega)$ plotted against frequency or temperature.⁴⁴⁻⁴⁶ Such glass relaxation phenomena appear to be due to the detailed chemical constitution of the polymer

⁴³ W. Lethersich, *Brit. J. Appl. Phys.* **1**, 294 (1950).

⁴⁴ J. Heyboer, P. Dekking, and A. J. Staverman, *Proc. 2nd Intern. Rheol. Congr.*, Oxford, p. 123 (1953).

⁴⁵ K. Deutsch, E. A. W. Hoff, and W. Reddish, *J. Polymer Sci.* **13**, 565 (1954).

⁴⁶ R. Buchdahl and L. E. Nielsen, *J. Polymer Sci.* **15**, 1 (1955).

chain; they do not obey the same time-temperature relationships which are apparently obeyed by viscoelasticity phenomena associated with ordering of polymer chains. Accordingly, the whole viscoelastic behavior of amorphous polymers cannot now be simply represented by a spectrum, the shape of which is independent of temperature, or by a related "reduced" response function as discussed in the previous section.

2. VOLUME AND SHEAR VISCOELASTICITY

Up to now we have been considering the response to shear stress or strain of materials manifesting linear viscoelastic behavior; in tensor language, we have been considering the deviator components of the stress and strain tensors. It has been demonstrated, however, that materials also exhibit viscoelastic behavior under hydrostatic stress or strain; this has been done by dynamic tests.⁴⁷ There has also been an indirect demonstration by considering the response of a material which was subjected to a sinusoidal stress which was partly shear and partly hydrostatic.⁴⁸ Whereas the viscoelastic response in shear is due to ordering of polymer chains, the response under hydrostatic stress must be associated with the loss of free volume and the increase in order of the atoms in the polymer chains; the effect of increase in hydrostatic stress is presumably similar to the effect of decrease in temperature.

It appears reasonable to represent the viscoelastic behavior of any amorphous material under hydrostatic stress in a manner analogous to that used to represent the behavior in shear of a cross-linked amorphous polymer. Let B_g be the limiting compliance for very small values of time (or infinite frequency) and B_e the value for infinite time or zero frequency. The corresponding moduli may be denoted by K_g and K_e . Now, whereas for vulcanized rubbers (and other cross-linked amorphous polymers) the ratio G_g/G_e or the ratio J_e/J_g has a value of the order of 10^4 , it appears that the corresponding ratio for volume viscoelasticity, namely K_g/K_e or B_e/B_g , is of the order of ten.⁴⁸ Since K_g and K_e are of the same order of magnitude as G_g , it would be expected that the response would depend upon volume viscoelasticity as well as upon shear viscoelasticity, in tests when the stress has a hydrostatic component, and when the shear response is approximately glasslike. Under other conditions, that is, when $G'(\omega)$ or $G(t)$ is much less than G_g , then the response to shear dominates the response to hydrostatic stress, and the latter can be neglected.

We now have to consider the viscoelastic response of a body when it is subjected to both hydrostatic and shear stress or strain. Suppose that a unit hydrostatic stress is suddenly applied at zero time; that is, for negative

⁴⁷ W. Philippoff and J. Brodnyan, *J. Appl. Phys.* **26**, 846 (1955).

⁴⁸ R. S. Marvin, R. Aldrich, and H. S. Sack, *J. Appl. Phys.* **25**, 1213 (1954).

values of time the stress is zero, and the stress is unity for positive values of t . Let the *bulk creep compliance* at time t be denoted by $B(t)$. Similarly, for unit hydrostatic strain applied at zero time, let the hydrostatic stress at a subsequent time t be $K(t)$ the *bulk relaxation modulus*. It is assumed that the material manifests linear viscoelastic behavior. Then, as with shear response, equation (21), we have

$$p\mathcal{L}\{B(t)\} = \frac{1}{p\mathcal{L}\{K(t)\}} \quad (38)$$

Now let us consider the case of simple tension. It can be shown that if the material manifests linear viscoelastic behavior in shear and in volume stress and strain, then it must do so also when a specimen of the material is subjected to longitudinal stress or strain; it is assumed that there is no lateral stress on the specimen and that the longitudinal strain is small. Assume that a constant tensile traction σ_0 is applied at zero time, to a previously unloaded specimen. Then the longitudinal strain $\epsilon(t)$ at time t is equal to $\sigma_0 D(t)$, where $D(t)$ is the *longitudinal creep compliance*. This is related to $B(t)$ and $J(t)$ according to the equation

$$D(t) = \frac{J(t)}{3} + \frac{B(t)}{9} \quad (39)$$

We will secondly consider the case where a small longitudinal strain ϵ_0 is applied at zero time to a previously unloaded body. Then the stress at time t is equal to $\epsilon_0 E(t)$, where $E(t)$ is the *longitudinal relaxation modulus*. The relation between $E(t)$, $K(t)$, and $G(t)$ is found to be

$$p\mathcal{L}\{E(t)\} = \frac{9p\mathcal{L}\{K(t)\}p\mathcal{L}\{G(t)\}}{3p\mathcal{L}\{K(t)\} + p\mathcal{L}\{G(t)\}} \quad (40)$$

Now, using the relation between $K(t)$ and $B(t)$ in equation (38), and the relation between $G(t)$ and $J(t)$ in equation (21), we obtain finally

$$p\mathcal{L}\{E(t)\} = \frac{1}{p\mathcal{L}\{D(t)\}} \quad (41)$$

Thus the relationship between creep and stress relaxation for small longitudinal deformations is the same as that for shear or volume deformations.

We can extend the relationships given in equations (39) and (40). The well-known relations between Hookean moduli and compliances in the theory of elasticity^{49, 49a} can be generalized for linear viscoelastic behavior,

⁴⁹ See, for example, T. Alfrey, "Mechanical Behavior of High Polymers," p. 15. Interscience, New York, 1948.

^{49a} A. J. Staverman and F. Schwarzl, in "Die Physik der Hochpolymeren" (H. A. Stuart, ed.), Vol. IV, Chapter I. Springer, Berlin, 1956.

if we replace a modulus m by the function of the corresponding relaxation modulus given by $p\mathcal{L}\{m(t)\}$; a compliance c is similarly replaced by $p\mathcal{L}\{c(t)\}$.^{49b, 49c} These rules apply to the interpretation and analysis of step-function experiments. In the case of dynamic experiments,^{48, 49a} the corresponding quantities are the complex compliances $c^*(\omega)$ and complex moduli $m^*(\omega)$. These results may be obtained from general considerations as in Chapter 11 of the first volume.

In elasticity theory, there are two further moduli and their reciprocal compliances associated with, respectively, the transverse stress and the longitudinal stress resulting from a longitudinal deformation without lateral deformation. We could thus define, if necessary, further time-dependent relaxation moduli and creep compliances. From the above relations, equations (21), (38), and (41), we see that the viscoelastic behavior of a given material may be specified completely either by any two creep compliances, or by any two relaxation moduli. Thus, while on molecular considerations there appear to be two different types of viscoelastic response, the phenomenological theory cannot tell us which two of the types of response are the basic ones.

If the time scale of a longitudinal experiment is such that a material does not exhibit glasslike behavior, then, from equation (40) and the discussion given previously, we see that $G(t)$ is much less than $K(t)$. Under these conditions equation (40) reduces to

$$E(t) = 3G(t) \quad (42a)$$

and similarly equation (39) reduces to

$$D(t) = \frac{J(t)}{3} \quad (42b)$$

Thus with these important relationships the shear creep compliance and relaxation modulus can be obtained from longitudinal creep and stress relaxation tests under small deformations.

An application of the relationship in equation (41) is to the stress relaxation behavior of certain plastics in tension at room temperature.²³ The longitudinal relaxation modulus was found to follow the law given in equation (22a), over a certain range of values of t . Then, for a somewhat more limited range of values of t , the longitudinal creep compliance is given by an equation of the form of equation (22b).

3. NONLINEAR VISCOELASTICITY

It has been pointed out in Section II of this chapter that the viscoelastic behavior of amorphous high polymers is not in fact linear; however, as we

^{49b} J. Mandel, *Compt. rend.* **241**, 910 (1955).

^{49c} H. Leaderman, *Trans. Soc. Rheol.* **1**, 213 (1957).

have seen, the behavior under certain circumstances can be approximated to linear viscoelastic behavior, and the linear theory can be used to interpret experimental data. We will now discuss briefly in what way the viscoelastic behavior of amorphous and certain other polymers departs from linearity.

a. Rubberlike Region

We will consider in the first place the viscoelasticity of vulcanized rubber. The equilibrium behavior of certain materials of this type is discussed in Chapter 10 of the preceding volume. The shear stress as a function of shear strain is given by equation (44) while the nature of the observed strain energy function is given in Section IX of that chapter. From these results we conclude that vulcanized natural rubber without fillers does *not* obey Hooke's law in shear, and furthermore, that increase of shear stress produces a more-than-proportionate increase in shear strain. Accordingly, we would not expect such a material to manifest *linear* viscoelastic behavior in simple shear. From the nature of the strain energy function we would expect in general that the shear stress or shear strain at which nonlinear effects are observable would be dependent upon the sensitivity of the measuring apparatus. In creep tests under constant shear stress nonlinear behavior is easily observable at shear strains of the order of 0.5,² while in precise dynamic tests they are observable at much smaller shear strains.⁵⁰ In creep tests under constant shear stress for such materials $\gamma(t)/\sigma_0$ is no longer independent of σ_0 but increases with σ_0 . This nonlinearity implies that the relation as discussed in the preceding section between the deformation behavior in such a creep test and the retarded elastic recovery, following removal of stress, is no longer valid. For example, we may take as a rough representation of the mechanical behavior of these materials a three-element model, in which the "stiffness" of the spring in the Voigt element decreases with increase in elongation. We find that the recovery is more rapid than would be expected for the linear model, and this, in fact, is how the actual vulcanizate behaves. In the case of noncross-linked polymers, nonlinear behavior is also observed at large enough strains in the "slow" retarded elastic process discussed in Section II.²

b. Glasslike Behavior

Nonlinear viscoelasticity is also observed in amorphous polymers in the region of the time scale in which the behavior is glasslike.⁴³ In this case nonlinear behavior appears at very small strains, above which the recovery seems to be very slow, and may not become complete, at least on the first loading of the specimen. It also appears that with such materials there may

⁵⁰ R. S. Marvin, personal communication.

be an elastic hysteresis of the Coulomb type; that is, there may exist a stress-strain loop which is dependent only on the stress amplitude in a dynamic test, but which is independent of frequency.⁵¹ This could lead to both $G'(\omega)$ and a non-zero $G''(\omega)$ being independent of frequency. Such a behavior would of course not be expected from a linear response mechanism such as has been discussed in the two preceding sections. We have seen that for a material manifesting linear viscoelastic behavior the dynamic response is completely determined from a knowledge of the creep or stress relaxation behavior. For a material possessing such a Coulomb type hysteresis loop such would not be the case.⁵¹

c. Textile Fibers

Finally, the nonlinear behavior of two groups of materials which are *not* amorphous will be referred to. It is well known that the retarded elastic behavior of synthetic textile fibers, such as acetate rayon, viscose rayon, and nylon, is very nonlinear.¹ Recently, however, it has been shown that *unoriented* cellulose acetate films show linear viscoelastic behavior;⁵² the nonlinear behavior of the filamentous materials must therefore be due to their oriented structure.

Wool and other keratin fibers show a marked nonlinear viscoelastic behavior which cannot be described satisfactorily by arrangements of linear springs and nonlinear dashpots. However, the behavior of such fibers has been described phenomenologically by a "thermodynamic" model.⁵³ Segments of chain in a folded configuration are assumed to pass over an energy barrier into a stretched configuration. Burte and Halsey have calculated the parameters for a particular fiber from analysis of load-elongation loops. From these parameters it is possible to calculate the creep and recovery behavior of this fiber under the same conditions from the model referred to above. The creep under constant load is as shown in Fig. 27; it is observed that the equilibrium length is independent of load for large loads, and that the retardation time is a function of load. The theory indicates that the recovery is rapid and is given by a single retardation time which is independent of previous history. The creep and recovery behavior of keratin fibers appears to follow this pattern.⁵⁴ This model thus describes qualitatively the rheological behavior of keratin fibers; however, a molecular interpretation is open to question, since unlike the other materials that have been considered so far, keratin fibers consist of several microscopically distinguishable components.

⁵¹ H. Leaderman, *Trans. Am. Soc. Mech. Engrs.* **61**, A-79 (1939).

⁵² D. L. Swanson and J. W. Williams, *J. Appl. Phys.* **26**, 810 (1955).

⁵³ H. Burte and G. Halsey, *Textile Research J.* **17**, 465 (1947).

⁵⁴ H. Leaderman, unpublished experiments.

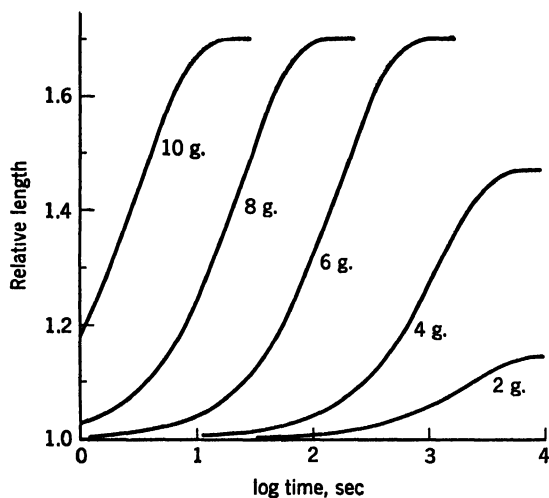


FIG. 27. Computed retarded elastic behavior, wool fiber

4. LINEAR VISCOELASTIC BEHAVIOR AND CONSTITUTION OF AMORPHOUS POLYMERIC SYSTEMS

In this chapter we have dealt with aspects of the phenomenological theory of linear viscoelasticity, and with the applications of this theory to the study of the rheology of amorphous noncross-linked and cross-linked polymers. It is now apparent that this theory provides a firm basis for the experimental investigation of rheological behavior under conditions where the assumptions are valid. The theory of course gives no information concerning the detailed nature of the spectra, nor of their dependence on molecular weight or molecular weight distribution; nor does it give information concerning the relationship between temperature and time scale.

Research along these lines will lead to information by means of which molecular theories of viscoelasticity and of flow can be tested. The present situation in the experimental study of various amorphous polymers and of polymer solutions has been reviewed by Ferry.⁵⁵ During the past few years there have appeared several important contributions to the development of molecular theories; these have also been reviewed by Ferry.⁵⁶

The contribution of mechanics to the study of the rheology of amorphous polymers is twofold. In the first place we are enabled to design experimental test procedures in order to obtain basic response data, such as $J(t)$, $G'(\omega)$, and so on; and secondly, we are enabled by the theory of

⁵⁵ J. D. Ferry, in "Die Physik der Hochpolymeren" (H. A. Stuart, ed.), Vol. IV, Chapter VI. Springer, Berlin, 1956.

⁵⁶ J. D. Ferry, in "Die Physik der Hochpolymeren" (H. A. Stuart, ed.), Vol. IV, Chapter I, p. 96. Springer, Berlin, 1956.

linear viscoelasticity to relate these quantities to each other through the derived functions $H(t)$ and $L(t)$. This leads to the development of molecular theories which account for the experimental results, especially for the aspects mentioned above which are not specified by mechanics. Finally, such theories should lead eventually to quantitative relationships which cannot always be predicted by mechanics, between linear viscoelastic behavior and other rheological phenomena such as non-Newtonian flow and normal stress effects.

Nomenclature

$\sigma(t)$	Shear stress	G_e	Shear equilibrium modulus
σ_0	Shear stress (in step-function experiment)	G_d	Shear decay modulus
σ_a	Shear stress amplitude (in dynamic experiment)	$G'(\omega)$	Shear storage modulus
$\gamma(t)$	Shear strain	$G''(\omega)$	Shear loss modulus
γ_0	Shear strain (in step-function experiment)	$ G(\omega) $	Absolute shear modulus
γ_a	Shear strain amplitude (in dynamic experiment)	$G^*(\omega)$	Complex shear modulus
$J(t)$	Shear creep compliance	$\eta'(\omega)$	Dynamic shear viscosity
J_e	Shear equilibrium compliance; shear steady-state elastic compliance	$\tan \delta$	Shear loss tangent
J_g	Shear glass compliance	$J'(\omega)$	Shear storage compliance
J_d	Delayed elastic shear compliance	$J''(\omega)$	Shear loss compliance
η	Shear viscosity	$ J(\omega) $	Absolute shear compliance
$J(t) - t/\eta$	Elastic part of shear creep compliance	$J^*(\omega)$	Complex shear compliance
$G(t)$	Shear relaxation modulus	$\psi(t)$	Retardation function
G_g	Shear glass modulus	$\phi(t)$	Relaxation function
		$L(t)$	Retardation spectrum
		$H(t)$	Relaxation spectrum
		$B(t)$	Bulk creep compliance
		$K(t)$	Bulk relaxation modulus
		$D(t)$	Longitudinal creep compliance
		$E(t)$	Longitudinal relaxation modulus

NOTE: where in the text the type of deformation is not specified, it is understood that the quantity refers to *shear* deformation. A complete system of nomenclature for linear viscoelastic behavior is given in reference 49c.

CHAPTER 2

STRESS RELAXATION STUDIES OF THE VISCOELASTIC PROPERTIES OF POLYMERS

Arthur V. Tobolsky

I. Four Regions of Viscoelastic Behavior for Amorphous Behavior	64
II. The Time-Temperature Superposition Principle	67
III. Parameters Defined by the Relaxation Master Curves	68
IV. Stress Birefringence Ratio and the Mechanism of Viscoelastic Deformation	70
V. Distribution of Relaxation Time, Flow Viscosity, and Dynamic Modulus	72
VI. The Characteristic Relaxation Time $K(T)$ as a Function of Temperature..	75
VII. Stress Relaxation of Polycrystalline Polymers	76
1. Decay of Stress of Constant Extension Resulting from the Growth of Oriented Crystallites	78
VIII. Chemical Stress Relaxation (Chemorheology)	79
Nomenclature	81

An ideally elastic substance subjected to simple tension obeys Hooke's law in the region of small strains:

$$\text{Stress} = E \times \text{Strain}$$

The quantity E is a constant known as the Young's modulus. It is a very important property of the material in question, being a measure of stiffness or resistance to deformation. For many metallic substances the value of E is of the order of 10^{11} dynes/cm.². For soft vulcanized rubbers the value of E is of the order of 10^7 dynes/cm.². The Young's modulus of a substance generally varies with the temperature.

The concept of modulus can be generalized to nonideally elastic substances by recognizing that the modulus is a function of time and also to some extent a function of the method of measurement. For example, experiments may be conducted in which the substance is subjected to a fixed extension, and the stress is measured as a function of time. The stress per unit strain necessary to maintain the sample at constant extension will be defined as the stress relaxation modulus $E_r(t)$. Similarly, the substance may be subjected to a constant tensile load, and the extension measured as a function of time—a so-called creep experiment. The stress per unit strain measured by this kind of experiment will be denoted by $E_c(t)$, the creep modulus. Furthermore vibrational experiments may be carried out

in which the substance is subjected to vibrations of angular frequency ω . From these experiments a complex dynamic modulus $E'(\omega) + iE''(\omega)$ may be determined. (In actual fact the vibrations used are generally shear vibrations so that the quantity really determined is $G'(\omega) + iG''(\omega)$, where the symbol G denotes shear modulus).

In most cases the moduli $E_r(t)$, $E_e(t)$ and $E'(1/\omega)$ —where ω corresponds to $1/t$ —are approximately equal. For substances which obey the laws of classical linear viscoelasticity, a determination of any one of these quantities over the entire time scale can be used to calculate the other two time-dependent moduli, or indeed can be used in principle to predict the results of any viscoelastic experiment.

During the past several years extensive data have been accumulated in our laboratory concerning the stress relaxation modulus $E_r(t)$ of a wide variety of polymers over a wide temperature range. The practical experimental methods for measuring stress at constant extension vary with the magnitude of the stiffness modulus and are described in the original papers. The following pages present a brief summary and generalization of some of the experimental and theoretical findings arising from this work.

Polymers divide very sharply into two categories so far as their physical properties are concerned: on one hand there are the amorphous polymers whose X-ray scattering is very similar to the scattering of liquids; on the other hand there are the polycrystalline polymers. The viscoelastic properties of amorphous polymers are relatively simpler than those of polycrystalline polymers. In the first place amorphous polymers obey the classical laws of linear viscoelasticity (at small deformations) whereas crystalline polymers frequently do not. Secondly amorphous polymers obey a time-temperature superposition principle which permits the use of data obtained at different temperatures to extend the time scale at any temperature. This is not generally true for crystalline polymers. Finally, the amorphous polymers show many features of similarity to one another in their viscoelastic behavior. For these reasons I shall discuss them first.

1. Four Regions of Viscoelastic Behavior for Amorphous Polymers

The first complete viscoelastic data for any polymers were obtained by stress-relaxation studies on polymethylmethacrylate of two different molecular weights.^{1, 2} The stress relaxation data at various temperatures are plotted in the form $\log E_r(t)$ vs $\log t$ for the entire temperature range in Fig. 1. In Fig. 2 are shown similar results for polyisobutylene of molecular weight 1.35×10^6 for average viscosity. The pattern of behavior for these polymers as shown in these figures is very much the same, and this is also

¹ J. R. McLoughlin and A. V. Tobolsky, *J. Colloid Sci.* **7**, 555 (1952).

² A. V. Tobolsky and J. R. McLoughlin, *J. Polymer Sci.* **8**, 543 (1952).

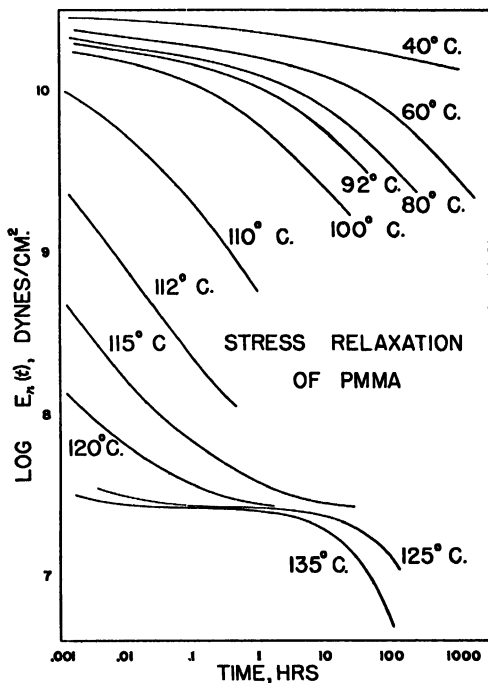


FIG. 1. $\log E_r(t)$ vs. $\log(t)$ for polymethylmethacrylate¹

true of other amorphous polymers. As was first pointed out by Tobolsky and McLoughlin² and as can be clearly seen from the figures, there are four well-defined regions of viscoelastic behavior:

1. A low-temperature *glassy region* in which the modulus $E_r(t)$ is of the order of magnitude of $10^{10 \times 6}$ dynes/cm.². The time effects are not very pronounced in this region so that we may speak of a quasi-static glassy modulus E_1 . $E_r(t)$ is fairly independent of molecular weight in this region but depends very markedly on the rate at which the sample is annealed.³

2. A *transition region* of viscoelastic behavior in which $E_r(t)$ changes very rapidly with time and temperature, the values of $E_r(t)$ ranging between 10^{10} dynes/cm.² and 10^7 dynes/cm.². The polymers feel "leathery" to the touch in this region. The values of $E_r(t)$ are independent of molecular weight in this region for polymers of sufficiently high molecular weights.⁴ The time effects in the transition region are produced by short-range motions of relatively small segments of the polymer molecules.

3. A quasi-static "rubbery plateau" region in which the modulus $E_r(t)$ is of the order of magnitude of 10^7 dynes/cm.² and changes quite slowly with

³ J. R. McLoughlin and A. V. Tobolsky, *J. Polymer Sci.* **7**, 658 (1951).

⁴ G. M. Brown and A. V. Tobolsky, *J. Polymer Sci.* **6**, 165 (1951).

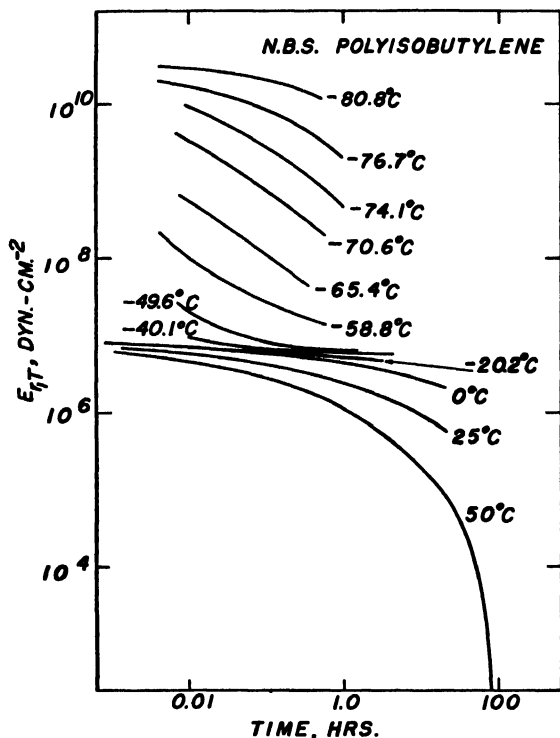


FIG. 2. $\log E_r(t)$ vs. $\log(t)$ for polyisobutylene of molecular weight $\bar{M}_v = 1.35 \times 10^5$.^{25, 26}

time. The stress in this region appears to be maintained by "entanglements" between the long chain molecules as was first pointed out in these researches.⁵ From the rubbery plateau region a quasi-static rubbery modulus E_2 can be defined, and the molecular weight between "entanglements" can be calculated.⁵ The presence of chemical cross-links will of course increase the value of the rubbery modulus E_2 .

4. A flow region in which $E_r(t)$ changes very rapidly with time from values of 10^7 dynes/cm.² to values of zero. The $E_r(t)$ curves in this region are very markedly dependent on the molecular weight and the molecular-weight distribution. For samples of the same molecular-weight distribution but different average molecular weight $\bar{M}_v$, the $E_r(t)$ curves appear to be shifted horizontally along the log-time axis, the shifting factor being $3.3 \log \bar{M}_v$.⁶ For samples of different molecular-weight distribution, but

⁵ H. Mark and A. V. Tobolsky, "Physical Chemistry of High Polymeric Systems," Chapter X, p. 344. Interscience New York, 1950.

⁶ R. D. Andrews, N. Hofman Bang, and A. V. Tobolsky, *J. Polymer Sci.* **3**, 669 (1948).

the same value of $\bar{M}_v$, the shape of the $E_r(t)$ curve vs. $\log t$ curve appears to change, but the relative position along the log-time axis remains the same.^{5, 7}

The time effects in the rubbery flow region are due to motions of the molecules as a whole or to very large molecular segments.

When the chemical cross-linking between the linear chains is sufficient to form a continuous three-dimensional structure, the flow region is completely suppressed, to be replaced at higher temperatures by a region of chemical flow produced by the breaking of primary valence bonds by oxygen, by ionic interchanges, or by other means.

In the original publication,² the rubbery plateau region and the flow region were considered together as the "rubbery flow" region. It seems desirable to separate these into two regions for purposes of greater clarity.

II. The Time-Temperature Superposition Principle

The time-temperature superposition principle whereby viscoelastic data at one temperature are transformed to another temperature by a simple multiplicative transformation of the time scale^{6, 8, 9, 10} was independently proposed by Tobolsky and Andrews⁸ and by Leaderman.⁹ In its simplest form this principle means that curves of $E_r(t)$ or $\log E_r(t)$ vs. $\log t$ that are obtained at different temperatures can be superimposed by means of a horizontal shift along the $\log t$ axis. Refinements on this procedure are treated elsewhere.¹¹

By means of this principle it is possible to extend the values of $E_r(t)$ obtained at any temperature to both shorter and longer times than can be obtained experimentally. Master curves of $\log E_r(t)$ vs. $\log t$ can be constructed that are applicable for all temperatures and all times. Figure 3 shows a somewhat schematized master curve for unfractionated polyisobutylene of three different average molecular weights. The graph as it stands is valid for 25° C. because the log time origin ($\log t = 0$) is directly under the indicated mark for 25° C. The master curve for any temperature shown on the graph can easily be obtained by sliding the log time axis to the new indicated origin. The number of decades of time comprised in this master curve is truly staggering. The validity of the time-temperature

⁷ R. D. Andrews, F. H. Holmes, and A. V. Tobolsky, unpublished results.

⁸ A. V. Tobolsky and R. D. Andrews, *J. Chem. Phys.* **11**, 125 (1943); *J. Polymer Sci.* **3**, 669 (1948).

⁹ H. Leaderman, "Elastic and Creep Properties of Filamentous Materials." Textile Foundation, Washington D. C. 1943.

¹⁰ J. D. Ferry, *J. Am. Chem. Soc.* **72**, 3746 (1950).

¹¹ J. D. Ferry and E. R. Fitzgerald, *J. Colloid Sci.* **8**, 224 (1953); see also E. Catsiff and A. V. Tobolsky, *J. Colloid Sci.* **10**, 375 (1955).

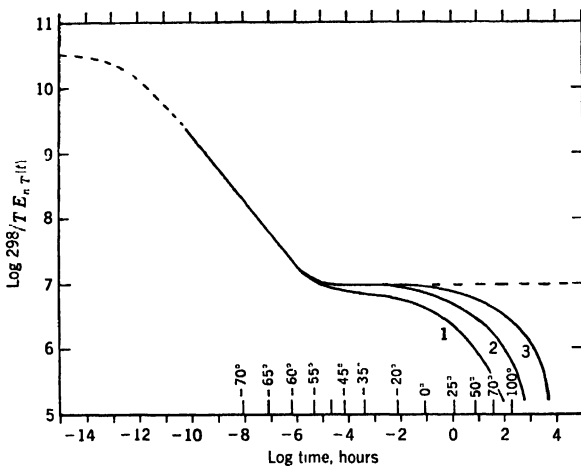


FIG. 3. Idealized master relaxation curve $\log E_r(t)$ vs. $\log t$ for polyisobutylene of three different average molecular weights (1) $\bar{M}_n = 1.36 \times 10^5$; (2) $\bar{M}_n = 2.80 \times 10^5$; (3) $\bar{M}_n = 6.60 \times 10^5$.¹

superposition principle will be proved later when relaxation modulus and dynamic modulus are compared.

III. Parameters Defined by the Relaxation Master Curves

Stress-relaxation data, such as are embodied in Figs. 1, 2, and 3 can be used to define certain parameters that are characteristic of the polymers being studied.¹² In the first place we have E_1 and E_2 , the quasi-static glassy modulus and the quasi-static rubbery modulus. At any temperature T the time required for the logarithm $E_r(t)$ to reach the value $(\log E_1 + \log E_2)/2$ was called the characteristic relaxation time K .¹² K is obviously a function of temperature $K(T)$. An attempt was also made to define a distinctive temperature T_d from the $E_r(t)$ curves alone which would correspond in some way to the glass transition temperature T_g obtained from volume-temperature curves. As is well known, evidence exists which indicates that the T_g value obtained from V - T curves depends on the rate at which specimen is cooled (or heated). It was hoped that the $\log E_r(t)$ vs. $\log t$ curves would provide a value of T_d that did not depend upon time effects. T_d was defined as the temperature at which $K(T)$ had a maximum value of apparent activation energy. The apparent activation energy is defined as $Rd \ln K/d(1/T)$. A difficulty that arises with this definition is that the time-temperature superposition principle very probably becomes only partially valid at temperatures close to T_g and lower. The horizontal shifts along the log time scale which produce superposition of the $\log E_r(t)$ curves

¹² J. Bischoff, E. Catsiff, and A. V. Tobolsky, *J. Am. Chem. Soc.* **74**, 3378 (1952).

for temperatures below T_g may well be valid only for the time scale of the relaxation experiments. Nevertheless, the values of T_d obtained by the method described above seems to be very close to the T_g values obtained from V - T curves, at least for the polymers we have studied thus far. The determination of T_d appears to have experimental-operational validity.

The value of T_g or T_d is perhaps the most important characteristic of the polymer. Should our experimental-operational definition of T_d fail for certain polymers, our discussion of these polymers could be couched in terms of T_g rather than of T_d .

The characteristic relaxation time K at the temperature T_d is denoted by K_d .

Another important parameter which characterizes the master relaxation curves is the quantity n , which is the negative slope of the master curve $\log E_r(t)$ vs. $\log t$ at the point at which $\log E_r(t) = (\log E_1 + \log E_2)/2$. Another characteristic parameter is the quantity h , related to n , whose quantitative definition will be discussed subsequently.

Table I contains a compilation of the parameters E_1 , E_2 , h , n , T_d , and K_d for the polymers whose viscoelastic properties have been studied by stress relaxation.

It is, of course, of great interest to inquire how these parameters depend on the molecular structure of the polymers. Among the polymers studied there does not appear to be a tremendous variation in the values of E_1 and E_2 . The glassy modulus E_1 may well depend upon the strength of the secondary valence forces between atomic groups and upon the amount of "free volume" in the glass. Nevertheless the value of E_1 obtained thus far for various polymers appears to lie in the range 10^{10} to $10^{10 \times 5}$ dynes/cm.². E_2 will depend on the chain stiffness in the case of linear polymers and upon

TABLE I
PARAMETERS CHARACTERIZING STRESS RELAXATION OF AMORPHOUS POLYMERS

<i>Polymer</i>	T_d , °K	$\log E_1$	$\log E_2$	n	h	$\log K_d$
Polymethyl meth- acrylate	384	10.35	7.35	0.52 ₆	0.31	-1.5
Paracril 26	241.0	10.10	7.40	0.63	0.41 ₆	-1.54
GR-S	220	10.24	7.44	0.71	0.45	-1.50
60/40 buta/sty	237.1	10.27	8.03	0.50 ₆	0.40	-1.94
50/50 buta/sty	250.8	10.212	7.558	0.545	0.364	-1.12
30/70 buta/sty	285.1	9.955	7.255	0.55	0.36	-1.13
Polyisobutylene	197.0	10.48	6.88	0.745	0.367	+1.04
(Dynamic)	—	10.52	6.88	0.723	0.352	—

the amount of cross linkage in the case of cross-linked polymers. The quantity n and the related quantity h may depend upon such factors as chain configuration and the heterogeneity of composition along the chain. Thus far the variation in these quantities as between different polymers has not proved to be very great, although larger variations have been found in the case of other polymers now under study.

The parameter which is of greatest importance in determining the properties of amorphous polymers is T_d (or T_g). To a very crude approximation one can state that the viscoelastic properties of most amorphous polymers are roughly similar for the same values of T/T_d^{13} or $T - T_d$. The qualitative validity of this principle may be verified by inspecting Figs. 1 and 2. The value of T_d (or T_g) for any given polymer is determined by the cohesive energy density of the polymer (measured by swelling or solubility) and the stiffness of the chains (which can be measured by light scattering in polymer solutions). The higher the cohesive energy density, the higher is the value of T_d ; the stiffer the chain, the higher the value of T_d . The latter point is nicely demonstrated by the fact that polyacenaphthalene has a much higher T_g value than polystyrene.

Although all amorphous homopolymers and homogeneous copolymers studied thus far show the qualitative features of viscoelastic behavior described above, polymer alloys or polyblends, which are finely dispersed mechanical mixtures of two polymers just barely on the borderline of compatibility, show a splitting of the transition region into two discrete parts,¹⁴ as if the polyblend had preserved the two T_d values of each individual component.

IV. Stress Birefringence Ratio and the Mechanism of Viscoelastic Deformation

For an ideal cross-linked rubber (in the rubbery plateau region of viscoelastic behavior), the stress at constant extension is proportional to the absolute temperature. This means that the entropy of the rubber sample is decreased when the rubber is stretched isothermally, and the stress in the stretched rubber sample actually arises from this decrease in entropy.

The decrease in entropy occurring when a rubber sample is stretched is, in turn, due to a decrease in the long-range configurational possibilities of the chain molecules. Since birefringence is also a measure of the long-range chain configurations, it is not surprising that the following relation can be derived.¹⁵

$$\frac{\text{Stress}}{\text{Temperature} \times \text{Birefringence}} = \text{constant}$$

¹³ A. V. Tobolsky and E. Catsiff, *J. Am. Chem. Soc.* **76**, 4204 (1954).

¹⁴ R. Buchdahl and L. E. Nielsen, *J. Polymer Sci.* **15**, 1 (1955).

The value of the constant in the above equation can be used to determine the size of the "freely rotating segment" of the polymer chains.^{15, 16}

It was further shown that the quantity stress/(temperature $\times$ birefringence) is a constant independent of temperature and time during stress-relaxation experiments, provided that the experiments were carried out in the rubbery flow region, the rubbery plateau region, or the low modulus portion of the transition region.^{17, 18} This indicates that in these regions of viscoelastic behavior even during a stress-relaxation experiment, where stress is changing rapidly with time, the stress must be considered as an "entropy stress," arising from long-range configurational changes. On the other hand, as one enters the high modulus portion of the transition region and the glassy region, the ratio stress/(temperature $\times$ birefringence) changes its magnitude and often changes its sign.^{17, 19} This indicates that the molecular mechanism of stretching in the glassy region must be different from that operating in the rubbery region. Very probably the stress in the glassy region arises from internal energy changes corresponding to distortion of van der Waals' bonds and bending of valence angles, rather than from configurational entropy changes.

This fundamental change in the mechanism giving rise to stress should be taken as an indication that the time-temperature superposition principle may become invalid (or only partially valid) at temperatures close to and below the glass transition temperature.

1. MATHEMATICAL FUNCTIONS DESCRIBING $E_r(t)$

The function $E_r(t)$ has been fitted quite well by empirical functions in both the transition region and the rubbery flow region. In the transition region the following empirical function holds very well:^{12, 20}

$$\log E_r(t/K) = \frac{\log E_1 + \log E_2}{2} - \left(\frac{\log E_1 - \log E_2}{2} \right) \operatorname{erf} [h \log (t/K)]$$

where

$$\operatorname{erf} x = 2\pi^{-1/2} \int_0^x e^{-u^2} du.$$

Erf is an abbreviation of the term error function, and h is the adjustable parameter of the Gauss error curve). The quantity h , related to n , has

¹⁵ W. Kuhn and F. Grun, *Kolloid-Z.* **101**, 248 (1942); L. R. G. Treloar, *Trans. Faraday Soc.* **43**, 277, 289 (1947).

¹⁶ R. S. Stein and A. V. Tobolsky, *J. Polymer Sci.* **11**, 285 (1953).

¹⁷ R. S. Stein, S. Krimm, and A. V. Tobolsky, *Textile Research J.* **19**, 8 (1949).

¹⁸ R. S. Stein and A. V. Tobolsky, *J. Polymer Sci.* **14**, 443 (1954).

¹⁹ J. R. McLoughlin, Ph.D. thesis, Princeton University (1950).

²⁰ E. Catsiff and A. V. Tobolsky, *J. Appl. Phys.* **25**, 1092 (1954).

already been considered as one of the characteristic parameters of the master relaxation curve $E_r(t)$.

In the region of rubbery flow the relaxation curve $E_r(t)$ for polyisobutylene at 298° K. is fitted quite well by the following empirical function:^{6, 21, 22} $E_r(t) = E_0[E_1(-t/\tau_3) - E_1(-t/\tau_m)]$ where $E_1(-x)$ is the exponential integral function, τ_3 and τ_m are parameters that depend on the 3.3 power of the average molecular weight and E_0 is a parameter that appears to depend upon the molecular-weight distribution (see ref. 5, p. 343).

For a class of amorphous polymers, notably the butadiene-styrene copolymers, the empirical relation $hT_d = 100$ appears to be valid. When this is true, expressions for $E_r(t)$, which are essentially universal functions of T/T_d , can be derived.¹³ This reduced equation of state for viscoelastic behavior is not valid for polymers like polyisobutylene where $hT_d \neq 100$.

V. Distribution of Relaxation Times, Flow Viscosity, and Dynamic Modulus

A distribution function of relaxation times $H(\log \tau)$ can be defined in terms of $E_r(t)$ by means of the following integral equation:

$$E_r(t) = \int_{-\infty}^{\infty} H(\log \tau) e^{-t/\tau} d(\log \tau)$$

The distribution function $H(\log \tau)$ is very useful since other viscoelastic properties such as the flow viscosity and the real and imaginary components of the dynamic modulus can be calculated therefrom.

$$\eta = \int_{-\infty}^{\infty} \tau H(\log \tau) d(\log \tau)$$

$$E' = \int_{-\infty}^{\infty} \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} H(\log \tau) d(\log \tau)$$

$$E'' = \int_{-\infty}^{\infty} \frac{\omega \tau}{1 + \omega^2 \tau^2} H(\log \tau) d(\log \tau)$$

Formulas relating E' and E'' to the distribution of relaxation times were first presented by Tobolsky and Eyring.^{22, 23} All of these formulas presuppose the validity of the laws of linear viscoelastic behavior. Then laws have been proved valid for amorphous polymers but are invalid for crystalline polymers under certain conditions.

An idealized distribution of relaxation times at 298° K. had previously been presented (in ref. 22) which had the simple graphical aspects of a "box" for the rubbery flow region and a "wedge" for the transition region.

²¹ R. D. Andrews and A. V. Tobolsky, *J. Polymer Sci.* **6**, 221 (1951).

²² A. V. Tobolsky, *J. Am. Chem. Soc.* **74**, 3786 (1952).

²³ A. V. Tobolsky and H. Eyring, *J. Chem. Phys.* **11**, 125 (1943).

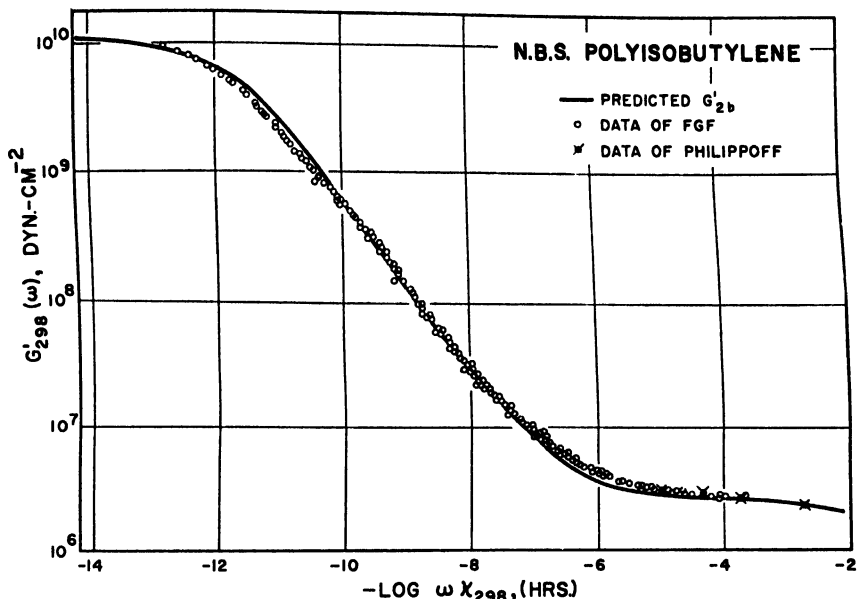


FIG. 4. Dynamic shear modulus G' vs. negative log frequency for polyisobutylene at 25° C. Comparison of experimental points with solid curve predicted from stress relaxation results.^{25, 26}

The "wedge" is unaffected by the molecular weight of the sample (for sufficiently high molecular weights), whereas the "box" is shifted along the log time axis with a shift factor $3.3 \log \bar{M}_v$. Although this idealized function is only an approximation of the true values of H ($\log \tau$), it has the virtue that exact mathematical expressions for $E_r(t)$ and for E' and E'' can be derived from it, so that no mathematical approximations are necessary for converting relaxation modulus to dynamic modulus in this case.

A very accurate determination of H ($\log \tau$) can be obtained from the experimental value of $E_r(t)$ by the use of first- and second-order approximations.^{24, 25, 26} The values of H ($\log \tau$) at 298° K. as a function of $\log \tau$ are tabulated in ref. 26.

From the distribution function H ($\log \tau$), obtained entirely from stress-relaxation data and the stress-relaxation data master curve $E_r(t)$, one can compute and predict the values of $E'(\omega)$ and $E''(\omega)$. Such computations (and tabulations) have been made in refs. 25 and 26. Figures 4 and 5 show the comparison between predicted values and the experimental values

²⁴ J. D. Ferry, E. R. Fitzgerald, L. D. Grandine, Jr., and M. L. Williams, *Ind. Eng. Chem.* **44**, 703 (1952).

²⁵ E. Catsiff and A. V. Tobolsky, *J. Colloid Sci.* **10**, 375 (1955). See also *J. Appl. Phys.* **25**, 145 (1954).

²⁶ A. V. Tobolsky and E. Catsiff, *J. Polymer Sci.* **19**, 111 (1956).

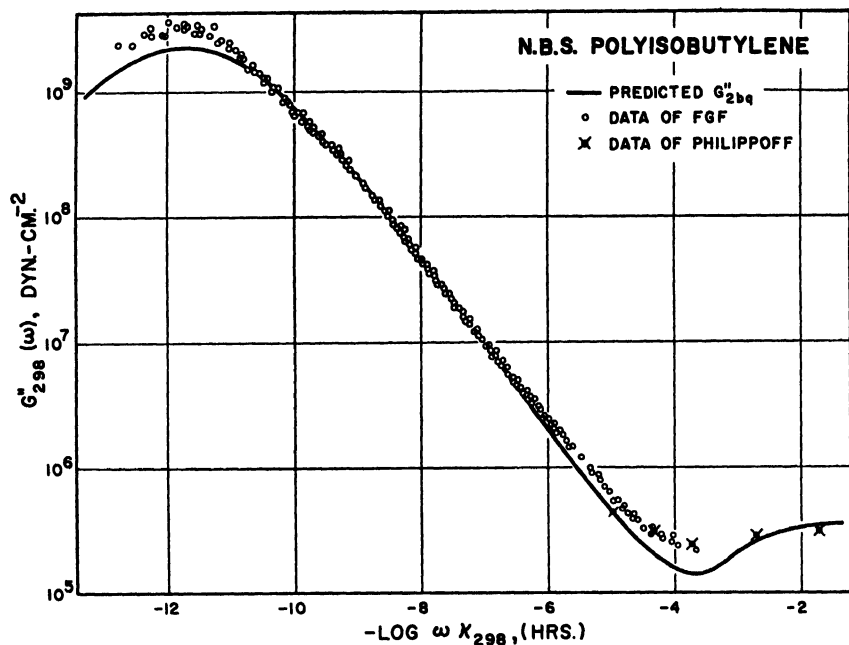


FIG. 5. Complex dynamic shear modulus G'' vs. negative log frequency for polyisobutylene at 25° C. Comparison of experimental points with solid curve predicted from stress relaxation results.^{25, 26}

obtained elsewhere.²⁷ The extremely good agreement provides another verification of the validity of the theory of linear viscoelastic behavior in the case of polyisobutylene. It also provides a verification of the time-temperature superposition principle, because stress-relaxation data and dynamic-modulus data are obtained in very different time intervals. Figure 6 shows stress-relaxation data and dynamic data for polyisobutylene obtained at -44° C. The solid curve represents the master curve $E_r(t)$ obtained from stress-relaxation data at various temperatures by the time-temperature superposition principle. The agreement between the two types of data is striking.

The relaxation curves of polyisobutylene in the rubbery flow region have been used to predict the bulk viscosity, using the "box" distribution as the approximation for the relaxation time distribution in that region.²⁸ Very satisfactory agreement was obtained between predicted values and experimental values of viscosity.

²⁷ J. D. Ferry, L. D. Grandine, Jr., and E. R. Fitzgerald, *J. Appl. Phys.* **24**, 911 (1953).

²⁸ R. D. Andrews and A. V. Tobolsky, *J. Polymer Sci.* **7**, 221 (1951).

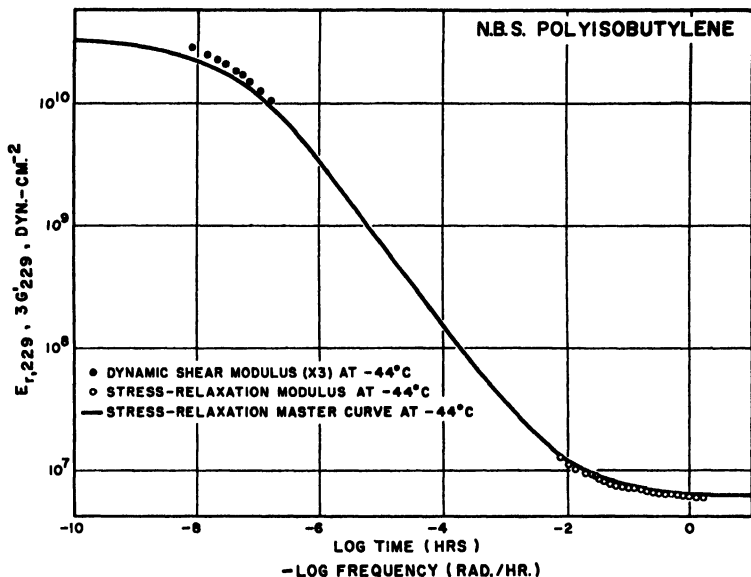


Fig. 6. Dynamic shear modulus (times three) vs. negative log frequency and stress relaxation modulus vs. log time for polyisobutylene at 44°C . Solid curve represents the stress relaxation master curve. Shear modulus G' multiplied by three to convert to a tension modulus.

VI. The Characteristic Relaxation Time $K(T)$ as a Function of Temperature

It is clearly very desirable to express the temperature variation of $K(T)$ in a manner that would be applicable to all linear polymers. Catsiff and Tobolsky had suggested that $\log K(T)/K_a$ vs. T/T_a should be the same for all amorphous polymers.^{13, 12} Recently Williams²⁹ has proposed that $\log A_T$ vs. $T - T_s$ is a universal function for all polymers, where T_s is a reference temperature selected for each polymer. The function A_T is linearly proportional to $K(T)$. The two theories discussed above are in agreement over the limited temperature interval over which they were commonly tested. Williams, Landel, and Ferry have ascribed a functional form for the variation of $\log A_T$ with $T - T_s$.³⁰ Expressed in terms of the notation and the parameters used in this article this new theory has the following form:

$$\log \frac{K(T)}{K_a} = -16.14 \frac{T - T_a}{56 + T - T_a}$$

All of our values for $K(T)$ for the polymers studied by stress relaxation fit this formula very well.^{25, 26} The agreement obtained with this formula and the experimental data is shown in Fig. 7.

²⁹ M. L. Williams, *J. Phys. Chem.* **59**, 95 (1955).

³⁰ M. L. Williams, R. F. Landel, and J. D. Ferry, *J. Am. Chem. Soc.* **77**, 3701 (1955).

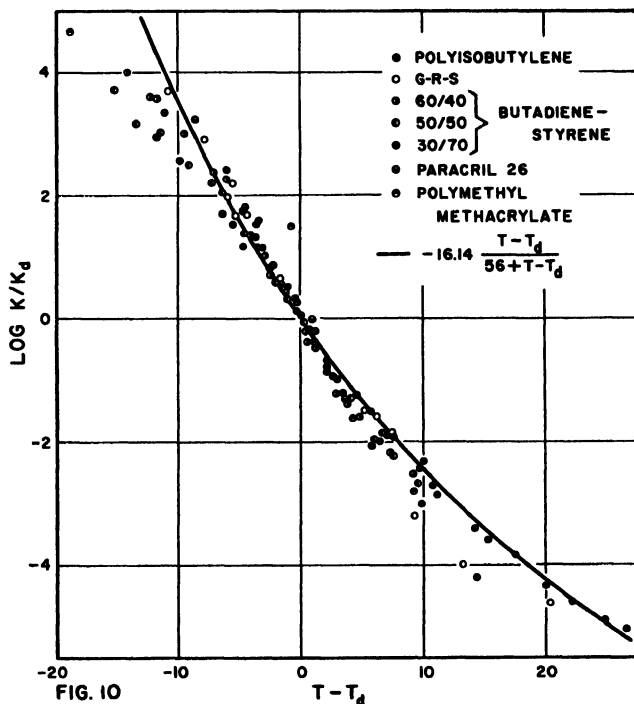


FIG. 7. $\log K(T)/K_d$ vs. $T - T_d$ for several polymers^{25, 26}

VII. Stress Relaxation of Polycrystalline Polymers

In the previous discussion of the viscoelastic properties of linear amorphous polymers it was shown that certain features are common to the behavior of all of these polymers. In particular it was shown that there are four characteristic regions of viscoelastic behavior: a glassy region, a transition region, a rubbery plateau region, and a rubbery flow region. In Fig. 2 which presents $\log E_r(t)$ vs. $\log t$ for polyisobutylene the behavior in the transition region is to be especially noticed. In the time scale of the relaxation experiments (.01 to 10 hr.) the transition region occurs in the temperature interval between -80°C. and -40°C. , a matter of 40 degrees. In this interval the modulus changes very rapidly with time and temperature between values of 10^{10} dynes/cm.² and 10^7 dynes/cm.² The behavior of partially crystalline polymers is rather different and shall be discussed, using polytrifluorochloroethylene as a well studied example.

Polytrifluorochloroethylene

Polytrifluorochloroethylene is a polycrystalline polymer whose melting temperature T_m is 215°C. Its glass transition temperature has not been

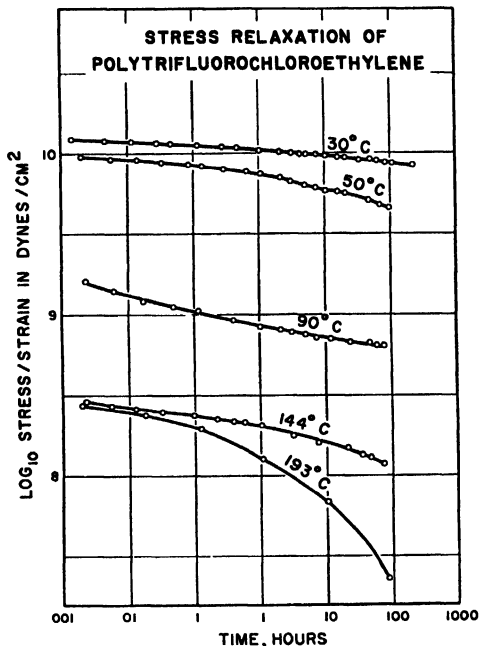


FIG. 8. $\log E_r(t)$ vs. $\log t$ for polytrifluorochloroethylene³¹

accurately determined but should be somewhere in the neighborhood of room temperature if the approximate relation $T_g = \frac{2}{3} T_m$ is valid. Figure 8 shows stress relaxation data³¹ for polytrifluorochloroethylene in the temperature range between 30 and 193° C. In this interval the modulus varies from $10^{10.1}$ to $10^{7.2}$ dynes/cm.² It is particularly interesting to contrast Figs. 2 and 8. In Fig. 8 the $\log E_r(t)$ vs. $\log t$ curves between 30° and 144° C. are relatively flat, i.e., the modulus change with time in the "transition region" polymer is much smaller for the polycrystalline polymer as compared to the amorphous polymers. Also in Fig. 8 the value of $\log E_r(t)$ at $t = 0.01$ hr. changes from a value of $10^{10.1}$ dynes/cm.² at 30° to a value of $10^{8.35}$ at 144° C., a very gradual change. The transition region, if such it can be called, for a polycrystalline polymer extends over a much wider temperature range than for an amorphous polymer. The "transition region" blends into a high-modulus "rubbery region" at high temperatures, crystallites playing the same role in the polycrystalline polymer that entanglements or cross links do in the amorphous polymers.

Because there are changes with temperature in the microcrystalline structure and in the stress-bearing mechanisms, it is certain that the simple time-temperature superposition that is valid for amorphous polymers in the tran-

³¹ A. V. Tobolsky and J. R. McLoughlin, *J. Chem. Phys.* **59**, 989 (1955).

sition region is not valid for polycrystalline polymers. There is not only a horizontal displacement along the log-time axis due to changing rate of molecular motions with temperature, but also an even more important vertical shift along the log $E_r(t)$ axis resulting from the changing structure and other factors.

It is interesting to note that the polycrystallinity of plasticized polyvinyl chloride was first discovered by Tobolsky and Stein from an examination of the $E_r(t)$ curves.³² These rubbery samples behaved like cross-linked rubbers in that $E_r(t)$ was relatively independent of time. At progressively higher temperatures the values of $E_r(t)$ became smaller, although the time dependence of $E_r(t)$ always was slight. It was inferred that crystallites were acting as temperature-sensitive but not time-sensitive cross links. The presence of crystallites was also proved by X-ray, birefringence, and other techniques.³²

1. DECAY OF STRESS AT CONSTANT EXTENSION RESULTING FROM THE GROWTH OF ORIENTED CRYSTALLITES

The first observations on the decay of stress at constant extension due to the growth of oriented crystalline material was made in this laboratory in 1946.^{33, 34, 35} It was found that vulcanized Neoprene showed very little relaxation of stress after 100 hr. at 35° C. and 50 % extension. However, a complete decay of stress at zero stress was observed after only 50 hr. at 0° C. and 50 % extension—a rude shock to any simple-minded belief that rate of stress relaxation should follow the Arrhenius law in all cases. Actually the Neoprene sample, after decaying to zero stress, began to increase in length beyond the original 50 % stretched value, a phenomenon known as spontaneous elongation. This phenomenon was attributed by us to crystallization of the Neoprene. Observations of spontaneous elongation, but no stress decay measurements, were previously reported for natural rubber and for ether polysulfide rubber.^{36, 37}

An extensive study was made^{34, 35} on the effect of temperature and elongation on the stress decay curves of unvulcanized natural rubber (cast latex sheet) in the temperature region of crystallization. In Fig. 9 stress decay curves are shown for samples maintained at 50 % elongation at temperatures of 0, -10, -20, -25, -30, -40, and -50° C. Taking the time required to attain zero stress as an index of the rate of crystallization, it is clear that the results of Figure 9 are in accord with the results of Bekkedahl, who

³² R. S. Stein and A. V. Tobolsky, *Textile Research J.* **18**, 302 (1948).

³³ R. D. Andrews, Ph.D. thesis, Princeton University (1948).

³⁴ G. M. Brown, Ph.D. thesis, Princeton University (1948).

³⁵ A. V. Tobolsky and G. M. Brown, *J. Polymer Sci.* **17**, 547 (1955).

³⁶ C. Park, *Rubber Chem. Technol.* **12**, 778 (1939).

³⁷ W. H. Smith and C. P. Saylor, *Rubber Chem. Technol.* **12**, 18 (1939).

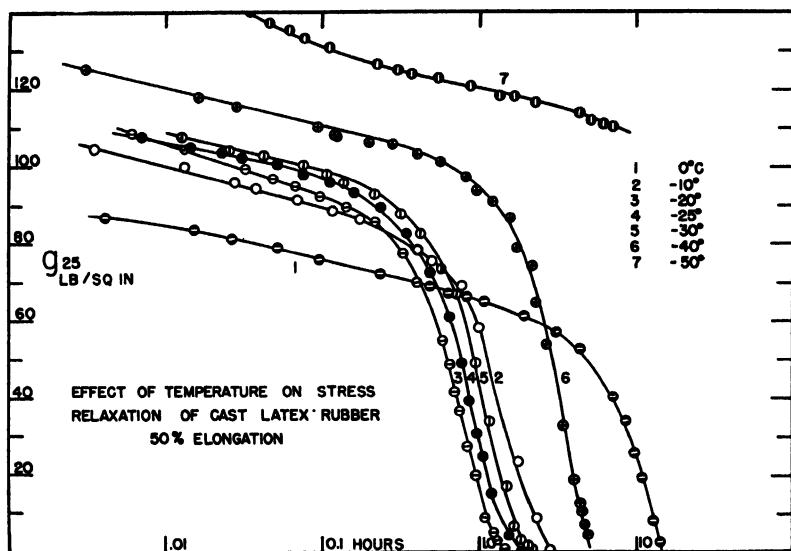


Fig. 9. Effect of temperature on stress relaxation of unvulcanized natural rubber in the crystallizing region.³⁵

studied the rates of crystallization in unvulcanized natural rubber by a dilatometric procedure.³⁸ The stress-relaxation data show a maximum rate of stress decay at -20°C . At -50°C the rate of crystallization is very slow.

In many crystalline polymers for which no phenomenon of spontaneous elongation was observed, the decay of stress was nevertheless accompanied by an increase of birefringence, indicating that even in these cases stress decay may be caused in the part by a growth of oriented crystalline material, probably around pre-existing crystal nuclei.³⁹

VIII. Chemical Stress Relaxation (Chemorheology)

It might be expected that for chemically cross-linked rubbers, in the region of the rubbery plateau, the stress-relaxation curves $E_r(t)$ should remain constant with time, inasmuch as thermoplastic flow is suppressed by the cross links. In actual fact it was discovered that all rubbers show $E_r(t)$ curves that decay to zero stress at sufficiently high temperatures, and we attributed this stress decay to chemical reactions such as chain scission by oxidative cleavage or reorganization of the network structure by ionic interchanges.^{40, 41}

³⁸ N. Bekkedahl, *J. Research Natl. Bur. Standards* **13**, 411 (1934).

³⁹ R. S. Stein and A. V. Tobolsky, *Textile Research J.* **18**, 201, 302 (1948).

⁴⁰ A. V. Tobolsky, I. B. Prettyman, and J. H. Dillon, *J. Appl. Phys.* **15**, 309 (1944).

⁴¹ M. D. Stern and A. V. Tobolsky, *J. Chem. Phys.* **14**, 93 (1946).

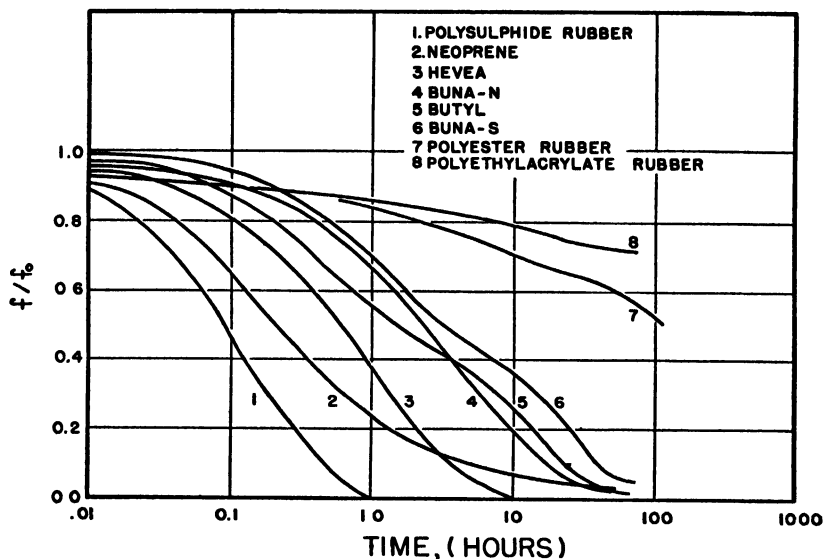


FIG. 10. Chemical stress relaxation for various vulcanized rubbers at 130° C⁴²

In many cases the decay curves produced by chemical stress relaxation follow the decay law $\exp(-k^1 t)$ where k^1 is a rate constant that obeys the Arrhenius law for temperature dependence. The number of chain scissions per gram of rubber occurring per unit time can be calculated from the stress relaxation curves.⁴²

In many of the hydrocarbon rubbers (natural rubber, GR-S, Butyl, and so on) the chemical stress relaxation is brought about by a cleavage induced by molecular oxygen. At the same time there are simultaneously occurring cross-linking reactions. Fortunately these two reactions can be both examined by physical techniques. Decay of stress at constant extension measures the scission reaction alone, even though cross linking is occurring simultaneously. On the other hand, if the sample is kept in a relaxed condition at the elevated temperature and the modulus measured "intermittently," the net effect of cross linking and scission is measured. In rubbers for which cross linking predominates over scission, the "intermittent" modulus increases with time, in rubbers in which scission predominates the intermittent modulus decreases with time.^{8, 40} The concept of simultaneous scission and cross-linking originally introduced in these studies to explain the physical changes produced by high temperatures and oxygen now plays a vital role in the interpretation of the changes produced in polymers by high energy radiation.

Thin samples of rubber maintained in a stretched condition at elevated

⁴² A. V. Tobolsky, D. Metz, and R. B. Mesrobian, *J. Am. Chem. Soc.* **72**, 1942 (1950).

temperatures develop an irrecoverable permanent set because of the simultaneous cross linking and scission reactions. The permanent set can be predicted from the "continuous" relaxation curves and the "intermittent" measurements of the modulus.⁴³

The polysulfide- or Thiokol-type rubbers show a chemical stress relaxation resulting from catalyzed interchanges involving the disulfide linkage.^{41, 44} In this case the "intermittently" measured modulus shows no change with time, inasmuch as the interchanges leave the over-all structure of the network unaffected. Various types of ionic reagents catalyze the interchange.⁴⁴ In 1947 our studies on the stress relaxation of vulcanized silicone rubbers convinced us that the relaxation process was due to an ionic interchange of S; O linkages catalyzed by some unknown reagent.³⁴ In 1950 we prepared cross-linked silicone rubbers in a special way which unavoidably contained traces of H_2SO_4 as a residual catalyst.^{19, 45} These rubbers showed complete decay to zero stress at room temperature in a matter of several minutes unless the residual catalyst was stabilized by water or pyridine. Once stabilized, these specially prepared silicone rubbers showed practically no stress decay even at elevated temperatures.

A recent paper has identified the trace catalysts that cause stress relaxation in commercially prepared silicones.⁴⁶

In Fig. 10 chemical stress relaxation is shown for a number of synthetic crossed linked rubbers at 130° C. The data is plotted in the form stress/initial stress vs. log time. The tremendous variation that can be obtained in the rate of chemical stress relaxation as between several different synthetic rubbers is clearly seen from the graph. Although the stability to reactions at high temperatures is partly inherent in the structure of the polymers, very great variations in stability can be achieved—and have been achieved—by suitable purification, incorporation of stabilizers anti-oxidants etc.

Nomenclature

$E_r(t)$	Relaxation modulus; modulus measured with sample at constant extension	E'	Real part of complex dynamic modulus
$E_c(t)$	Creep modulus; modulus measured with sample under constant stress	E''	Imaginary part of complex dynamic modulus
		ω	Angular frequency of vibration

⁴³ R. D. Andrews, A. V. Tobolsky, and E. E. Hanson, *J. Appl Phys* **17**, 352 (1946).

⁴⁴ M. Mochulsky and A. V. Tobolsky, *Ind. Eng. Chem.* **40**, 2155 (1948).

⁴⁵ D. H. Johnson, J. R. McLoughlin, and A. V. Tobolsky, *J. Phys Chem.* **58**, 1073 (1954).

⁴⁶ R. C. Osthoff, A. M. Bueche, and W. T. Grubb, *J. Am. Chem. Soc.* **76**, 4659 (1954).

CHAPTER 3

THE RELAXATION THEORY OF TRANSPORT PHENOMENA

Taikyue Ree and Henry Eyring

I. Introduction	83
II. Generalized Theory of Viscosity	88
1. Heterogeneity of Flow Units	88
2. Incomplete Equilibration of the Activated Complex	89
3. The Equation of State for Flow Units Using the Virial Theorem	90
4. Generalized Viscosity Formula	91
5. Deformable Flow Units	92
a. Entanglement-Disentanglement Transition	92
b. α - β Transition	94
c. Primary Creep	96
III. A Generalized Theory of Diffusion	97
1. The Relation between Viscosity and Diffusion	97
2. Free Diffusion	99
3. Stokes-Einstein Equation	100
4. Membrane Diffusion	101
IV. Applications	105
1. Solid Plastic System	105
a. Determination of the Parameters	106
b. Results	107
c. Discussions	111
2. Solution System of High Polymers	114
a. Viscosity Formulas for Solution Systems	114
b. Results	115
c. Discussions	128
3. Deformable Systems	131
a. Classification of Flow Curves	131
b. Ostwald Curve	132
4. Metals	134
5. Diffusion in Solution	136
V. Nature of "Holes"	138
1. Structure of Liquids	138
2. Melting of Solids	141
3. The Volume Providing an Additional Equilibrium Site	142
Nomenclature	142

I. Introduction

We treat in this chapter the transport phenomena in condensed systems from the viewpoint of rate processes. The molecules (atoms, ions, molecular segments) in a condensed phase occupy positions of equilibrium, and

may be considered as vibrating about the minimum of a free energy well. The structure of all condensed systems may be thought of as possessing a more or less regular lattice arrangement. The regularity of the lattice is different from substance to substance. There are many substances which have well-defined regular lattice structures; solid crystals belong to this category. On the other hand, the lattices of liquids are less regular, i.e., there are many empty equilibrium places in the lattices; such lattices are readily deformable. Even in solid crystals, however, the lattices are incomplete because of dislocations and crystal imperfections.

The effect of a stress on a body is to cause displacements from equilibrium along the various planes separating molecular layers. If the body is perfectly *elastic*, the stored potential energy is immediately and completely released when the stress is released. The result is the immediate and complete return of the molecular patches to their original minimum positions in the energy wells. Thus, the elasticity modulus, shear modulus, bulk modulus, and hardness are all functions of the steepness of the energy wells. Hooke's law describes the relation between the stress and the displacement in this case when these quantities are relatively small.

If a relatively large stress acts constantly on a body, however, molecular patches on the two sides of a shear plane jump with respect to each other over the energy barrier, and take up the neighboring new equilibrium position. In this way the energy stored up in stress is released as thermal energy. This statistical displacement of patches by jumping along shear planes continues as long as the stress acts, i.e., the substance *flows* in a direction to release the stress. In this way permanent deformation occurs. This relative displacement to new equilibrium positions along shear planes we call the *relaxation theory* of transport phenomena. As we shall see later, diffusion is to be thought of as a multiple shear process.

Before presenting the recent achievement of the relaxation theory in this field, it would be advisable to depict the fundamental results reported in papers, reviews and monographs. Consider that shear occurs along sets of parallel shear layers. The distance between these layers is represented by the symbol λ_1 . The stress (shear force per unit area) is indicated by f . Let λ be the distance of two equilibrium positions for patches in the direction of shear, the distance between neighboring patches in the same direction being λ_2 ; the latter is not necessarily equal to λ . Finally, the mean distance between two adjacent flowing patches in the moving layer in a direction at right angles to the shear is λ_3 . Eyring^{1, 1a} represented the shear

¹ H. Eyring, *J. Chem. Phys.* **4**, 283 (1936).

^{1a} S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," pp. 477-551. McGraw-Hill, New York, 1941.

rate $\dot{s}$ in this case by

$$\dot{s} = \frac{\lambda}{\lambda_1} 2k' \sinh \frac{\lambda\lambda_2\lambda_3 f}{2kT} \quad (1a)$$

where a symmetrical potential barrier was assumed for the flow process. In equation (1a) k' is a rate constant for the jumping patches when no stress is acting, that is

$$k' = \kappa \frac{kT}{h} \exp(-\Delta F^\ddagger) \quad (1b)$$

where $\Delta F^\ddagger$ is the activation free energy for the flow process. According to the definition of viscosity, η , the latter is given as the ratio of stress to strain rate. Thus, from equation (1a), we obtain

$$\eta = \frac{\beta}{\alpha} \frac{\sinh^{-1} \beta \dot{s}}{\beta \dot{s}} \quad (2)$$

where,

$$\alpha = \frac{\lambda\lambda_2\lambda_3}{2kT} \quad (3)$$

and

$$\beta = \left(\frac{\lambda}{\lambda_1} 2k' \right)^{-1} \quad (4)$$

The properties of the function $\sinh^{-1}(\beta \dot{s})/(\beta \dot{s})$ are as follows:

$$\lim_{\beta \dot{s} \rightarrow 0} \frac{\sinh^{-1} \beta \dot{s}}{\beta \dot{s}} = 1 \quad (5)$$

$$\lim_{\beta \dot{s} \rightarrow \infty} \frac{\sinh^{-1} \beta \dot{s}}{\beta \dot{s}} = 0 \quad (6)$$

Thus, at low stress and low shear rate, viscosity is given according to equations (2) and (5) by

$$\eta \simeq \beta/\alpha = \frac{kT}{\lambda^2 k'} \frac{\lambda_1}{\lambda_2 \lambda_3} \quad (7)$$

while at high values of f and $\dot{s}$, the viscosity approaches zero. The viscosity expressed by equation (7) is called Newtonian viscosity, i.e., the viscosity is independent of stress and shear rate. Non-Newtonian viscosity is expressed by equation (2), i.e., the viscosity decreases with stress and shear rate.

We represent Newtonian viscosity by η_s , the subscript s indicating the conditions of *small* values of stress and shear rate. Introducing the expression for k' into β , one obtains from equation (7) the following formula:

$$\eta_s = \frac{hN}{V} e^{(\Delta F^\ddagger)/RT} \quad (8)$$

Here the approximations $\lambda \simeq \lambda_1 \simeq \lambda_2 \simeq \lambda_3$ and $\lambda^3 \simeq V/N$ were made, where V and N are the volume of one mole of flow patches and the Avogadro number, respectively. Powell, Rosevear, and Eyring² found the relation

$$\Delta E_{\text{vap}}/\Delta F^\ddagger = 2.45 \quad (9)$$

where ΔE_{vap} is the vaporization heat of a liquid. Equation (9) holds for nearly 100 substances, excluding metals but including associated liquids. Thus, the Newtonian viscosities of many liquids at atmospheric pressures are calculated with good results, using the values of V and ΔE_{vap} . Plotting the activation heat for viscous flows E_{vis} , against vaporization heats, the same authors² found the relation

$$E_{\text{vis}} = \frac{\Delta E_{\text{vap}}}{n} \quad (10)$$

where $n \simeq 3$ for nonassociated liquids, while $n \simeq 4$ for associated liquids. For metals, the value of n changes from 8 to 25 or more. This is due to the fact that the unit in the vaporization of metals is the neutral atom, while the unit for viscous flow is the much smaller metal ion.^{1b, 2}

We must still discuss the effect of pressure on viscosity. Generally, viscosity increases with the pressure at constant temperature. This fact indicates that activation free energy for flow processes increases with the pressure, p . From well-known basic considerations the dependence is given by the following equation:

$$\Delta F^\ddagger = \Delta F_1^\ddagger + \int_{p=1}^p \bar{\Delta V}^\ddagger dp \simeq \Delta F_1^\ddagger + p\bar{\Delta V}^\ddagger \quad (11)$$

where, $\bar{\Delta V}^\ddagger$ is the mean volume increase accompanying the activation, and $\Delta F_1^\ddagger$ is the activation free energy at $p = 1$. Using the viscosity data at high pressures obtained by Bridgman³ Ewell and Eyring,⁴ and Frish *et al.*⁵ determined the activation free energy, $\Delta F^\ddagger$. Plotting $\Delta F^\ddagger$ against p , these authors determined $\bar{\Delta V}^\ddagger$ from the slope of the straight line of the

² R. E. Powell, E. Rosevear, and H. Eyring, *Ind. Eng. Chem.* **33**, 430 (1941).

³ P. W. Bridgman, "The Physics of High Pressures." Macmillan, New York, 1931.

⁴ R. H. Ewell and H. Eyring, *J. Chem. Phys.* **5**, 726 (1937).

⁵ D. Frish, H. Eyring, and J. F. Kincaid, *J. Appl. Phys.* **11**, 75 (1940).

diagram [cf. equation (11)]. They found the following relation:

$$\overline{\Delta V}^\ddagger = \frac{V}{n'} \quad (12)$$

where $n' \simeq 7$ for nonassociated liquids, and $n' \simeq 21$ for liquid metals.

The physical significance of these results is interesting. As previously mentioned, the relaxation theory assumes the presence of empty sites, or "holes," in condensed systems. If there are no holes available, flow does not occur. The energy needed for the formation of the hole is a function of the bond strength between molecules. The activation heat for viscous flow is used mostly for the formation of the new hole. The change of volume, $\overline{\Delta V}^\ddagger$, in equation (11) is associated with the formation of the new hole. According to equation (12), the size of the new hole is considered as $1/7$ normal molecular volume for nonassociated liquids, while as $1/21$ the normal volume for metals. The very small hole volume for metals is probably due to the fact that in metals the flow units are ions which are $1/3$ the normal neutral atoms in size.

The energy required to make a hole of molecular size in a liquid is equal to the vaporization heat, ΔE_{vap} .¹ If we assume that (1) the energy required to make the new hole which is needed for viscous flow is proportional to the size of the hole, and that (2) all of the activation energy is spent to make the new hole, then equation (10) would indicate that the size of the new hole is about $1/3$ the normal molecular volume for nonassociated liquids. This result must be reconciled with the value found from equation (12), i.e., the size of the new hole is $1/7$ the normal molecular volume. This seeming contradiction arises from our first assumption, which is not true. Rather one must assume that the energy required to make the hole of size $V/7$ is $\Delta E_{\text{vap}}/3$, instead of $\Delta E_{\text{vap}}/7$. Actually, these holes, a fraction of molecular size, are more expensive per unit volume because neighbors presumably bond more poorly with each other than in a perfect lattice as a result of poorer fit as well as because of the absence of bonding to a lacuna.

Walter and Eyring⁶ calculated the potential energy of a condensed system, E , as a function of the numbers of moles of holes, ζ , per mole of molecules. When ζ is very small, the result was

$$E = E_s(1 - \zeta) \quad (13)$$

while it turns out to be

$$E = E_s \left[\frac{v_s}{v} - \frac{1}{2n'} \left(\frac{v_s}{v} \right)^3 \right] \quad (14)$$

⁶ J. Walter and H. Eyring, *J. Chem. Phys.* **9**, 393 (1941).

under the condition that $2\zeta \gg 1/(n' - 1)$, which is nearly true in the normal liquid range. In equations (13) and (14) E_s is the potential energy per mole of the solid of the condensed system (the gaseous phase being taken as reference), v and v_s are the volumes per molecule in the liquid and solid, respectively, n' is a constant which is numerically equal to 8.35. Thus, according to equation (13), the first holes to be introduced into a solid cost the amount of energy required to vaporize a molecule from the solid. The volume difference, $v - v_s$, is considered proportional to the number of holes in the liquid. Thus, equation (14) shows that the energy of vaporization of a liquid does not decrease linearly with the number of holes. Consequently, it is wrong to assume that the energy required to make a hole is proportional to the size of the hole.

The nature of the holes is very important in the relaxation theory of transport phenomena. We will return to this problem later.

II. Generalized Theory of Viscosity

The fundamental equations in the relaxation theory, (1a), (1b), (2), and (8), were derived under the following assumptions: Firstly, the flow system is homogeneous, being composed of only one kind of flow unit. Secondly, the activated complex for flow is in complete equilibration with ambient temperature. This situation, however, is rather a special one, there being many cases where the system has heterogeneous flow units. We must, therefore, generalize the old theory of relaxation.

1. HETEROGENEITY OF FLOW UNITS

Consider, for example, a shear plane in a sheet of rubber. The flow patches may consist of segments of a molecule, whole molecules, or several molecules shifting as a unit. One may see then that there are many kinds of flow units which differ in the degree of entanglement, which a flow patch has with the patches on the opposite side of the shear plane. Some flow units will not have any bonds except van der Waals' bonds acting across the shear plane, while others have such bonds. The two kinds of flow units will be referred to as *nonentangled* and *entangled* units, respectively. Heavily entangled units will resist the shear more strongly than lightly entangled ones. The relaxation time of a flow unit is defined as the reciprocal of the rate constant for the flow of the unit, i.e., $1/k'$. The heavily entangled units have large relaxation times while the converse is true for the lightly entangled units. All flow patches involve the quantity $\beta = \left(\frac{\lambda_1}{2\lambda}\right)/k'$, which is the relaxation time multiplied by a dimensionless factor. Since this unknown factor is probably near unity, it will be convenient to speak of β itself as the relaxation time.

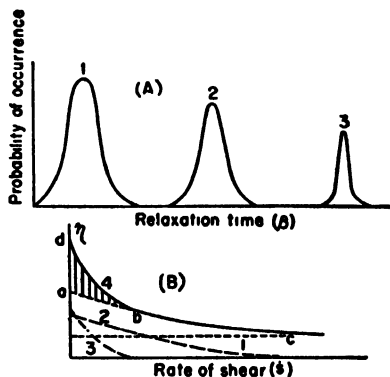


FIG. 1A. Probability of the occurrence of flow units vs. relaxation time.

FIG. 1B. Viscosity vs. shear rate. Actual viscosity is composed of the contribution from three groups of flow units. Curve 1: $\eta = x_1\beta_1/\alpha_1$. Curve 2: $\eta = (x_2\beta_2/\alpha_2) \sinh^{-1} \beta_2\dot{\gamma}/(\beta_2\dot{\gamma})$. Curve 3: $\eta = (x_3\beta_3/\alpha_3) \sinh^{-1} \beta_3\dot{\gamma}/(\beta_3\dot{\gamma})$. Curve 4: Superposition of Curves 1, 2, and 3.

We consider that a flow system is composed of several groups of flow units. Each group is characterized by an average relaxation time, β_n . We frequently find marked variations such as $\beta_1 \ll \beta_2 \ll \beta_3$. Each β_n is an average for a closely related set of relaxations. The relaxation time spectrum is as shown in Fig. 1A, where a near-Gaussian-type distribution probably exists in each group. We assume that through the whole range of $\dot{\gamma}$ in an actual experiment, the following conditions are satisfied:

$$\beta_1\dot{\gamma} \ll 1 \quad (15)$$

$$\beta_2\dot{\gamma} \geq 1 \quad (16)$$

$$\beta_3\dot{\gamma} \gg 1 \quad (17)$$

$$\beta_n\dot{\gamma} > > > 1 \quad (18)$$

$$(\text{for } n \geq 4)$$

2. INCOMPLETE EQUILIBRATION OF THE ACTIVATED COMPLEX

The activated complex, lying at the top of the potential barrier, involves many degrees of freedom. These degrees of freedom are in equilibrium with a large number of neighboring oscillators. If the latter behave classically, the mean available energy is kT for each. However, various kinds of incomplete equilibration of activated complex degrees of freedom with ambient temperature are observed in plastic flow. For example, in the annealing of a lump of glass, the inside flow units are in equilibrium with the local temperature. Thus, the rate constant for flow is given by⁷

⁷ H. Eyring and T. Ree, *Proc. Natl. Acad. Sci. U. S.* **41**, 118 (1955).

$$k' = \kappa \frac{\gamma_0}{h} \exp - \sum_{i=1}^n (\Delta F_i^\ddagger) / \gamma_i \quad (19)$$

Here, γ_0 is the mean available energy of those oscillators equilibrating with the translational degree of freedom corresponding to crossing the potential barrier, and γ_i is the same mean available energy of those oscillators equilibrating with the i th group of activated complex degrees of freedom requiring the activation free energy, $\Delta F_i^\ddagger$. If there are classical degrees of freedom equilibrating with all the degrees of freedom of the activated complex, each γ can be replaced by kT . In this case, equation (19) reduces to the familiar equation (1b).

As far as the available evidence indicates, it is usually satisfactory to write $\gamma_0 = kT$. However, to the approximation that γ_0 can be identified with the average energy of an oscillator, we have

$$\frac{\gamma_0}{h} = \frac{1}{h} \left(\frac{1}{2} h\nu + \frac{h\nu}{e^{h\nu/kT} - 1} \right) \quad (20)$$

$$= \nu \left(\frac{1}{2} + \frac{1}{e^{h\nu/kT} - 1} \right) \quad (21)$$

At low temperatures this has the value $\nu/2$, and at high temperatures the usual value kT/h . The essentially frictionless flow of HeII seems at least in qualitative accord with the low temperature form of equation (21), since there is no evidence that the process ceases at absolute zero in the way indicated by kT/h . Because of quantum effects at low temperatures, the transmission coefficient, κ , including barrier leakage will be important, and $\kappa\gamma_0/h$ will be best treated as a unit.

3. THE EQUATION OF STATE FOR FLOW UNITS USING THE VIRIAL THEOREM⁷

Flow units vibrate about their equilibrium positions. The equation of state for the flow units may be obtained by applying the virial theorem

$$\overline{Xx} = -\overline{m\dot{x}^2} \quad (22)$$

where X , x , and $\dot{x}$ are the force, displacement, and velocity of the flow unit in the x -direction (the direction of relative displacement), m is the mass of the unit, and the bars represent the average over a very long time. Let f_0 be the local microstress on the flow unit resulting from its surroundings. The microstress is to be distinguished from the over-all macrostress f . Then, the following identifications can be made:

$$X = \lambda_2 \lambda_3 f_0 \quad (23)$$

and

$$x = g\lambda \quad (24)$$

where g is the ratio of the length of free vibration, x , of the flow unit whose area is $\lambda_2\lambda_3$ to the distance jumped, λ . Thus, $1/g$ should approximate the ratio of sound velocity in the solid to that in the gas—a value in the neighborhood of 7. Further,

$$\overline{m\dot{x}^2} = \gamma_s \quad (25)$$

From equations (22) to (25), we obtain

$$\lambda\lambda_2\lambda_3 f_0 g = \gamma_s \quad (26)$$

This is the equation of state of the flow unit.

4. GENERALIZED VISCOSITY FORMULA

The generalized equation of the rate of shear is obtained by the substitutions of equations (19) and (26) into (1a), the results being

$$\dot{s} = \frac{1}{\beta} \sinh \alpha f \quad (27)$$

$$\dot{s} = \frac{1}{\beta} \sinh \frac{f}{2gf_0} \quad (28)$$

where

$$\beta = \left(\frac{\lambda}{\lambda_1} 2\kappa \frac{\gamma_0}{h} \right)^{-1} \exp \left(\frac{\Delta F_s^\ddagger}{\gamma_s} + \sum_{i=1}^{n-1} \frac{\Delta F_i^\ddagger}{\gamma_i} \right) \quad (29)$$

and

$$\alpha = \frac{\lambda\lambda_2\lambda_3}{2\gamma_s} \quad (30)$$

Here, the quantities with the subscript s indicate the corresponding quantities in the shear coordinate.

When there are several groups of flow units, each characterized by different relaxation times, β , the total shear stress f is given as follows

$$f = \sum_{n=1}^r x_n f_n \quad (31)$$

Here, x_n is the fractional area on a shear surface occupied by the n th group of units and f_n is the force per unit area acting on the n th group. The shear rates of all kinds of units are equal, otherwise the slowly moving units would be left behind. In the latter circumstance, a structural change occurs in the flowing substance. Such changes are not generally observed. Thus, all the different groups of units are obliged to move with the same shear rate, $\dot{s}$, with differing appropriate stresses on each group. The longer the natural relaxation time β , the higher the stress, and vice versa. From

equation (27), the relation between the stress f_n and the relaxation time β_n for the n th group is given by the formula

$$f_n = \frac{1}{\alpha_n} \sinh^{-1} (\beta_n \dot{s}) \quad (32)$$

The substitution of equation (32) into (31) yields

$$f = \sum_{n=1}^r \frac{x_n}{\alpha_n} \sinh^{-1} (\beta_n \dot{s}) \quad (33)$$

Dividing both sides of equation (33) by $\dot{s}$, one obtains the viscosity formula

$$\eta = \sum_{n=1}^r \frac{x_n \beta_n}{\alpha_n} \frac{\sinh^{-1} (\beta_n \dot{s})}{\beta_n \dot{s}} \quad (34)$$

Equation (34) is the *generalized viscosity* formula derived by Ree and Eyring,⁸ and it has been applied to a wide variety of cases with good results. The properties of the function, $\sinh^{-1} (\beta \dot{s}) / (\beta \dot{s})$, have been mentioned before [cf., equations (5) and (6)]. Because of these properties, equation (34) gives Newtonian viscosity when $\dot{s}$ is very small, while it gives non-Newtonian viscosity when $\dot{s}$ is very large.

5. DEFORMABLE FLOW UNITS

Thus far we have assumed that the structure of flow systems is not a function of time and stress. That is, the structure is the same at any time under any stress. It is, however, a common experience for cases to arise where structural change occurs with time and with stress. The fracture of a system by a force is an example of structure change. We omit treatment of such time-dependent changes here, but we consider steady-state stress-dependent flow phenomena. Such systems show thixotropy, birefringence, etc. Here we extend our generalized flow-rate equation (33) to systems undergoing structural change.

a. Entanglement-Disentanglement Transition

We have mentioned that intermolecular entanglement determines the relaxation times of flow units. The state of entanglement will not be changed by low stresses. High stresses, on the contrary, tend to break bonds which may not immediately form again.

We consider the case where entangled and disentangled units are in kinetic equilibrium, and the system shifts toward disentanglement with increasing stress. The free-energy curve for the transition is represented by Fig. 2, where E and D indicate the entangled and disentangled units, respectively. The transition, $E \rightarrow D$, is promoted by the elastic energy stored up on the flow unit. Such a flow unit is formally represented as a Maxwell

* T. Ree and H. Eyring, *J. Appl. Phys.* **26**, 793, 800 (1955).

unit—a spring in series with a dashpot. The elastic energy, w , stored up during the relaxation time, τ , is given by

$$w = \int_0^{s_1} f \, ds = \frac{G(\tau \dot{s})^2}{2} = c \dot{s}^2 \quad (35)$$

Here, G is the spring constant of the unit, and the relations, $f = Gs$, and $s_1 = \tau \dot{s}$, were used. Here s_1 is the strain at the time of relaxation.

Let C_e and C_d be the mole fractions of the entangled and disentangled units at time t , respectively. Then the net rate of transition, $E \rightarrow D$, is given by

$$-\frac{dC_e}{dt} = C_e k'_f e^{\mu c \dot{s}^2 / kT} - C_d k'_b e^{-(1-\mu) c \dot{s}^2 / kT} \quad (36)$$

For an unsymmetrical barrier μ will differ from one-half. k'_f and k'_b are the rate constants for the forward and backward reactions at zero stress, respectively. The condition of *steady flow* is that the left side of equation (36) is zero. Thus, we obtain

$$C_e = \frac{1}{1 + K e^{c \dot{s}^2 / kT}} \quad (37)$$

and

$$C_d = \frac{K e^{c \dot{s}^2 / kT}}{1 + K e^{c \dot{s}^2 / kT}} \quad (38)$$

where the following relations were introduced:

$$K = k'_f / k'_b \quad (39)$$

$$-\Delta C_e = \Delta C_d \text{ or } C_e + C_d = 1 \quad (40)$$

In equation (39) K is the equilibrium constant at zero stress, and the quantities ΔC in (40) are the changes of the concentrations of the entangled and disentangled units. The substitutions of equations (37) and

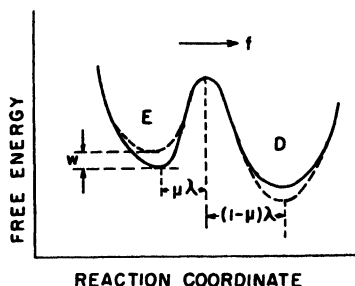


FIG. 2. Free energy curve for entanglement-disentanglement transition.

(38) into (33) yield

$$f = \frac{1}{1 + Ke^{c^2/kT}} \left[\frac{a_1 \beta_1 \dot{s}}{\alpha_1} Ke^{c^2/kT} + \frac{a_2}{\alpha_2} \sinh^{-1} (\beta_2 \dot{s}) \right] + \sum_{n=3}^{\nu} \frac{x_n}{\alpha_n} \sinh^{-1} (\beta_n \dot{s}) \quad (41)$$

Here, the disentangled units are treated as Newtonian units, and the relation

$$x_n = (Ca)_n \quad (42)$$

is introduced, where a is the area occupied by one unit. If one substitutes the condition, $c = 0$ [i.e., $G = 0$ from equation (35)], into equation (41), the latter reduces to (33). Thus, equation (41) is more general than (33).

In the above, we considered the case where the equilibrium between entangled and disentangled units shift to the side of the disentangled units. Thus, the viscosity decreases more rapidly with increasing stress than in the ordinary case. As will be shown later, we meet this case frequently in polymeric solutions. Any thixotropic substance exemplifies this case. On the other hand, there is the opposite case where the equilibrium shifts to the side of entangled units with increasing stress increasing viscosity. Systems showing this effect are said to show dilatancy. Equation (41) thus covers both the thixotropic and dilatant cases.

b. α - β Transition

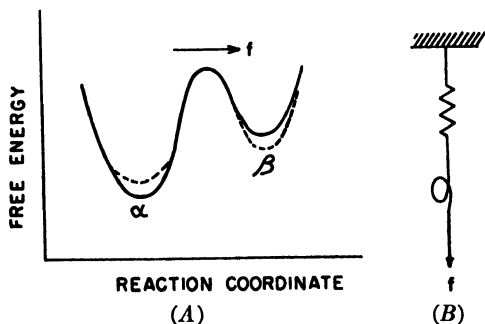
In some cases a phase transition is brought about by a stress. The α - β transition in keratin fibers is a famous example. Keratin fibers consist of polymeric chains cross-linked by disulfide bonds. These polymeric chains are polypeptides produced by the condensation of α -aminocarboxylic acids. According to Astbury and Street⁹ and Astbury and Woods,¹⁰ natural and stretched wool present different X-ray diffraction patterns. The crystalline structure of natural wool (hair) is called α -keratin, while the stretched form is called β -keratin. X-ray patterns show also that there is a large amount of unoriented material. The presence of amorphous regions in wool is shown by the infrared studies of Elliott¹¹ and by the studies of Steel¹² on the change in the tensile properties of wool with changing concentrations of LiBr. The exact structure of the α and β crystalline forms is still not agreed upon. However, there is near agreement on the 1.5 Å. distance per amino acid along the helical axis in α -keratin, and the 3.3 Å. distance per amino acid in β -keratin. Two types of bonds, the hydrogen bond and di-

⁹ W. T. Astbury and A. Street, *Phil. Trans. Roy. Soc.* **A230**, 75 (1932).

¹⁰ W. T. Astbury and H. J. Woods, *Phil. Trans. Roy. Soc.* **A232**, 333 (1934).

¹¹ A. Elliott, *Textile Research J.* **22**, 783 (1952).

¹² R. Steel, *J. Soc. Cosmetic Chem.* **3**, 99 (1952).

FIG. 3A. Free energy curve for α - β transition.FIG. 3B. Mechanical model for a flow unit suffering α - β transition.

sulfide cross-link, play important roles in the structure of keratin fibers. Pauling and Corey¹³ showed that hydrogen bonds are responsible for the formation of the helix in the simple α -keratins.

Burte and Halsey,^{14a} Burte *et al.*^{14b} and Speakman and Peters¹⁵ introduced the idea of the α - β transition to explain the mechanical properties of keratin fibers. In a recent paper, Ruoff and Eyring¹⁶ considered this idea in explaining their experimental results for hair in water, formic acid, and dimethyl formamide $[N(CH_3)_2CHO]$. The free energy curve for the α - β transition is shown in Fig. 3A. The conditions of the first set of the experiments carried out by Ruoff and Eyring were that the fibers were stretched in water at 15 to 35° C. at a uniform rate to an extension of 30 %, in about 5 minutes. In these conditions, the plastic flow was so slow that it could be neglected compared to the *aperiodic elongation* resulting from the α - β transition. Thus, the flow unit was represented by a spring in series with an *aperiodic element* as shown in Fig. 3B, the latter being responsible for the α - β transition. The rate of the α - β transition under stress f is given by

$$-\frac{dC_\alpha}{dt} = C'_\alpha k'_f e^{\mu(\lambda_2\lambda_3)_a f/kT} - C'_\beta k'_b e^{-(1-\mu)(\lambda_2\lambda_3)_a f/kT} \quad (43)$$

where C_α and C_β are the concentrations of the α and β forms, respectively, $(\lambda_2\lambda_3)_a$ indicates the flow-unit parameters belonging to the aperiodic unit, and μ has the same significance as in equation (36). The total strain, s , is the sum of the aperiodic strain, s' , and the spring strain, s'' . Since the aperiodic strain depends on the number of the transformed β -forms, the

¹³ L. Pauling and R. B. Corey, *Proc. Roy. Soc. (London)* **B141**, 21 (1953).

^{14a} H. Burte and G. Halsey, *Textile Research J.* **17**, 465 (1947).

^{14b} H. Burte, G. Halsey, and J. H. Dillon, *Textile Research J.* **18**, 449 (1948).

¹⁵ L. Peters and J. B. Speakman, *Textile Research J.* **18**, 511 (1948).

¹⁶ A. L. Ruoff and H. Eyring, *Proceedings of International Wool Conference*, Volume D, p. 9, Australia (1955).

following relations hold:

$$C_{\beta} = \frac{s'}{s'_{\infty}} \quad (44)$$

$$C_{\alpha} = \frac{s'_{\infty} - s'}{s'_{\infty}} \quad (45)$$

$$\rho = \dot{s}' + \dot{s}'' \quad (46)$$

where ρ is the strain rate of the fiber which was kept constant in these experiments, and s'_{∞} is the strain where the $\alpha \rightarrow \beta$ transition is completed. Substituting equations (44) to (46) into (43), one obtains

$$\rho - \dot{s}'' = (s'_{\infty} - s')Kk'_be^{2\mu\alpha_a f} - s'k'_be^{-2(1-\mu)\alpha_a f} \quad (47)$$

where $K = k'_f/k'_b$ and $\alpha_a \equiv (\lambda\lambda_2\lambda_3)_a/2kT$. According to Hooke's law, the equation

$$f = G(s)s'' \quad (48)$$

holds for the spring, where for the general case the spring constant, G , was considered to change with strain. From equation (48), one obtains

$$\dot{s}'' = \frac{\rho}{G} \frac{df}{ds} \quad (49)$$

The substitution of equation (49) into (47) yields the result

$$\rho \left(1 - \frac{1}{G} \frac{df}{ds} \right) = (s'_{\infty} - s')Kk'_be^{2\mu\alpha_a f} - s'k'_be^{2(\mu-1)\alpha_a f} \quad (50)$$

which is the general differential equation for extension of wool fibers at a rapid rate. Using equation (50) Ruoff and Eyring analyzed their experimental curves, and showed that under the experimental conditions previously mentioned the $\alpha \rightarrow \beta$ transition is the principal factor for flow in the elongation of keratin fibers.^{16, 17}

c. Primary Creep

The creep curves of solid materials under a constant stress follow usually the form shown in Fig. 4. The curve is composed of three parts—I, II, and III. In part I, the strain rate, $\dot{s}$, decreases with time; in II, $\dot{s}$ is about constant; and in III, $\dot{s}$ increases rapidly with time, and eventually breakage occurs. The parts I, II, and III are called the *primary*, *secondary*, and *tertiary* creep, respectively.

It is considered that during primary creep a structural change is brought about by the stress. By this change, the material becomes more resistant to flow, or work-hardens. Work-hardening is very important in engineering;

¹⁷ A. L. Ruoff, dissertation, University of Utah, Department of Chemistry (1955).

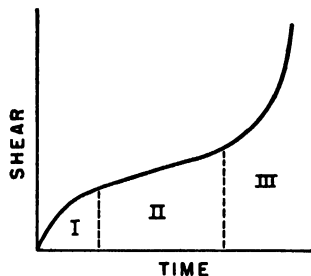


FIG. 4. Creep curve under a constant load; shear vs. time.

however, it is still not fully understood, and will not be treated further here. The secondary creep occurs during steady flow, while primary and tertiary creeps are *transient phenomena*.

III. A Generalized Theory of Diffusion

1. THE RELATION BETWEEN VISCOSITY AND DIFFUSION

Diffusion results from a suitable succession of shear displacement promoted by free-energy (chemical potential) gradient. We assume that at the initial position the diffusing molecules have a concentration, C , an activity coefficient, γ , and a rate constant of jumping forward to the next equilibrium position, k'_f , which is given by^{1, 2}

$$k'_f = k' \frac{\gamma}{\gamma^\ddagger} = k' - \frac{\gamma}{\gamma + \frac{d\gamma}{dx} \frac{\lambda}{2}} \quad (51a)$$

$$\simeq k' \left(1 - \frac{\lambda}{2} \frac{d \ln \gamma}{dx} \right) \quad (51b)$$

Here, k' is the rate constant in an ideal system, $\gamma^\ddagger$ is the activity coefficient of the activated complex lying half-way between two equilibrium positions; the distance between the two is λ , and the direction of the diffusion is x . For the backward direction over the same barrier, these quantities are

$C + \frac{dC}{dx} \lambda$, $\gamma + \frac{d\gamma}{dx} \lambda$, and k'_b , which is given by

$$k'_b = k' \frac{\gamma + \frac{d\gamma}{dx} \lambda}{\gamma + \frac{d\gamma}{dx} \frac{\lambda}{2}} \quad (52a)$$

$$\simeq k' \left(1 + \frac{\lambda}{2} \frac{d \ln \gamma}{dx} \right) \quad (52b)$$

The net rate of diffusion, v , is obtained by subtracting the backward rate, v_b , from the forward rate, v_f . Thus, we obtain

$$v = v_f - v_b = C\lambda k'_f - \left(C + \lambda \frac{dC}{dx}\right) \lambda k'_b \quad (53a)$$

$$= -\lambda^2 k' \frac{dC}{dx} \left(C \frac{d \ln \gamma}{dC} + 1\right) \quad (53b)$$

where equations (51b) and (52b) were substituted into the second equality of equation (53a), and the term involving λ^3 was neglected. By definition,

$$v = -D \frac{dC}{dx} \quad (54)$$

Hence, for the diffusion coefficient, one obtains

$$D = \lambda^2 k' \frac{d \ln a}{d \ln C} \quad (55)$$

where a is the activity defined by γC .

We next relate the lattice distance λ and the frequency of relaxation k' for diffusion to the corresponding quantities for viscous flow. In a hexagonal close-packed system, a central molecule is surrounded by the six nearest neighbors in the same plane. As a result of the central molecule shearing separately past each of the six nearest neighbors by one lattice distance, it achieves an advance of one lattice distance with respect to all neighbors. In general, if ξ is the number of nearest neighbors lying in the same plane, which can independently shear past the central molecule, we have

$$\lambda = \lambda_\eta / \xi \quad (56)$$

$$k' = \xi k'_\eta \quad (57)$$

Here, the quantities λ and k' with the subscript η indicate the corresponding quantities for viscous flow while those with no subscript indicate the quantities for diffusion. Thus, we obtain

$$D = \frac{\lambda_\eta^2 k'_\eta}{\xi} \frac{d \ln a}{d \ln C} \quad (58)$$

Combining equations (58) and (7) yields^{18, 19}

$$D\eta = \frac{kT}{\lambda\xi} \frac{k'_\eta}{k''} \frac{d \ln a}{d \ln C} \quad (59)$$

where all the λ parameters are assumed to be approximately equal, and

¹⁸ T. Ree and H. Eyring, Proceedings of International Wool Conference, Volume D, p. 162, Australia (1955).

¹⁹ H. Eyring, F. W. Cagle, and C. J. Christensen, to be published.

the k' for viscous flow in a pure system is indicated by k'' . Since diffusion occurs in a mixed system, the k' generally will not be exactly equal to k'' . Equation (59) yields several cases.

2. FREE DIFFUSION

The diffusion of D_2O into H_2O is an example of self-diffusion, which is a special case of free diffusion. In self-diffusion

$$\frac{d \ln a}{d \ln C} \simeq 1 \quad (60)$$

$$k'_\eta \simeq k'' \quad (61)$$

$$\lambda \simeq \left(\frac{V}{N} \right)^{1/3} \quad (62)$$

where V is the molecular volume of the system and N is the Avogadro number. Substituting equations (60) to (62) into equations (59), we obtain

$$D\eta = \frac{kT}{\xi} \frac{1}{\lambda} \quad (63)$$

$$D\eta = \frac{kT}{\xi} \left(\frac{N}{V} \right)^{1/3} \quad (64)$$

Hoffman²⁰ showed that in the self-diffusion of mercury (tracer, Hg^{204}) the λ value calculated from equation (63)—if ξ is taken equal to unity—is five times larger than the value obtained from an X-ray study. The data of Watts *et al.*²¹ for the self-diffusion of carbon tetrachloride (tracer, CCl_3Cl^{36}) indicates that the ξ value from equation (63), using X-ray data for λ , again has the value 5. Li and Chang²² found that in various cases of self-diffusion in liquids the quantity ξ in equation (64) is about 6. As will be shown later, we have found that the value of ξ for a wide variety of dilute solutions is also about 6, except for solvents showing a great tendency of forming hydrogen bonds.¹⁸ The structure of simple liquids seems to be quasi-hexagonal close-packed.

Often, the activation energy for diffusion of the solute in a solution is approximately equal to the activation energy for viscous flow and of self-diffusion of the solvents.^{1b, 20} This fact is confirmed by the data of Haycock *et al.*²³ and of Watts *et al.*²¹ That is, the activation energy for the diffusion of iodine in carbon tetrachloride²³ is identical with that for the self-diffusion of carbon tetrachloride.²¹ All these facts require that for these cases $k'_\eta =$

²⁰ R. E. Hoffman, *J. Chem. Phys.* **20**, 1567 (1952).

²¹ H. Watts, B. J. Alder, and J. H. Hildebrand, *J. Chem. Phys.* **23**, 659 (1955).

²² J. C. M. Li and P. Chang, *J. Chem. Phys.* **23**, 518 (1955).

²³ E. W. Haycock, B. J. Alder, and J. H. Hildebrand, *J. Chem. Phys.* **21**, 1601 (1953).

k'' . However, the above model requires amplification for heterogeneous systems. Thus, Na^+ ions diffuse through the silica network present in a soft glass with an activation energy much lower than the activation energy for viscous flow of the glass. This is not surprising since viscous flow requires the breaking of silicon-oxygen bonds. On the other hand, in a heterogeneous system, flow may proceed with different facility along certain of the sides of the planar polygon (lying normal to the diffusing direction) which separates a molecule from its neighbors. In such a case, viscous flow will proceed mainly by slip along the easy planes, whereas diffusion will require, in addition, that there be slip along the difficult plane. In such a case the measured activation energy for diffusion will exceed the value measured for viscous flow. The diffusion of bismuth through lead belongs to this category.

3. STOKES-EINSTEIN EQUATION

Using hydrodynamic theory, Stokes showed that the force, F , required to pull a sphere of radius, r , at a velocity, u , through a continuum of viscosity, η , is

$$F = 6\pi\eta ru \quad (65)$$

As previously mentioned, diffusion is caused by a force which is due to a chemical potential gradient in the system, i.e.,

$$F = - \frac{\partial \mu}{\partial x} \quad (66)$$

Here, μ is the chemical potential, and it is given by

$$\mu = kT \ln a + \mu_0 \quad (67)$$

where a is the thermodynamic activity (effective concentration) of the spheres, and μ_0 is the chemical potential at unit activity. If the friction force given by (65) equals the force arising from the potential gradient given by (66), we have a steady-state diffusion. Thus, from equations (65), (66), and (67), we obtain

$$\begin{aligned} 6\pi\eta ru &= -kT \frac{\partial \ln a}{\partial \ln C} \frac{\partial \ln C}{\partial x} \\ &- \frac{kT}{6\pi r \eta} \frac{\partial \ln a}{\partial \ln C} \frac{dC}{dx} = uC \end{aligned} \quad (68)$$

Since $v = uC = -D \frac{dC}{dx}$ by equation (54), the following results:

$$D\eta = \frac{kT}{6\pi r} \frac{\partial \ln a}{\partial \ln C} \quad (69)$$

If $\partial \ln a / \partial \ln C = 1$, equation (69) is identical with the so-called Stokes-Einstein formula, which was derived by Einstein.²⁴ The Stokes-Einstein formula holds for spheres diffusing in a continuum. Obviously, it requires modification for self-diffusion, for nonspherical molecules, and for any molecules whose size is comparable to the size of solvent molecules.

Comparing equations (63) and (69), we obtain the relation

$$\xi = 3\pi \left(\frac{2r}{\lambda} \right) \quad (70)$$

where activity is assumed to be equal to concentration. Thus, one may see that if the ratio $2r/\lambda$ approaches infinity, the value of ξ is represented by (70) while ξ is around 6 if the ratio approaches unity. The problem of the simple type of diffusion which occurs by relaxation of the solvent is thus reduced to the problem of evaluating ξ . The latter is the number of solvent relaxations of the kind important for viscous flow required to advance the diffusing molecule one lattice distance. Clearly, ξ will depend on the shapes of diffusing solute and solvent as well as on their relative size.

4. MEMBRANE DIFFUSION

One of the basic physical phenomena for sustaining the growth and development of plants and organisms is that of diffusion through membranes. The latter plays an important role also in many other biological phenomena like nerve action, metabolism, and so on. Filtration is membrane diffusion, and consequently it is of great significance in chemical engineering too. Thus, recently many elaborate studies of membrane diffusion have been published to clarify established concepts and to provide a fresh approach to the existing problems—especially in the field of biological diffusion problems. Because of the light it throws on viscous relaxation, it will be useful to describe briefly the recent developments in this field.

We consider the molecular jumping of a diffusing substance in a membrane. The point-to-point jumps continue from one side of the membrane to the other where the diffusing molecule passes out of the membrane. The driving force in this case is the free-energy difference on the two sides. The succession of potential barriers over which the molecule passes is shown in Fig. 5.²⁵⁻²⁸ Since an actual molecular lattice is three-dimensional, we should think of the λ s as indicating the projection along the direction

²⁴ A. Einstein, *Ann. Physik* [4] **17**, 549 (1905); **19**, 371 (1906).

²⁵ B. J. Zwolinski, H. Eyring, and C. E. Reese, *J. Phys. Chem.* **53**, 1426 (1949).

²⁶ H. Eyring, R. Lumry, and J. W. Woodbury, *Record Chem. Progr.* **10**, 100 (1949).

²⁷ F. H. Johnson, H. Eyring, and M. Polissar, "The Kinetic Basis of Molecular Biology." Wiley, New York, 1954.

²⁸ R. B. Parlin and H. Eyring, in "Ion Transport Across Membranes (H. T. Clarke, ed.), p. 103. Academic Press, New York, 1954.

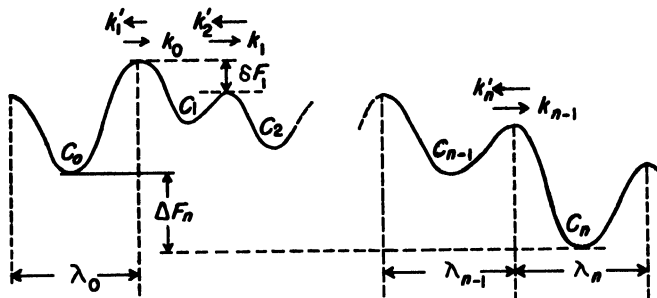


FIG. 5. Free energy diagram representing diffusion in the liquid or solid state.

of the gradient of the appropriate mean jump distance for the molecule. If C_0 is the concentration of molecules per cubic centimeter at the zeroth position, then $\lambda_0 C_0$ is the number of molecules which are candidates to jump across the barrier in a square centimeter of an area normal to the direction of diffusion. The specific rate constant in the forward direction from the i th position is written as k_i , and in the backward direction as k'_i . For the steady state we may indicate by Q the number of molecules passing over each successive square centimeter of barriers, and write for the successive barriers the following set of equations:

$$\begin{aligned} Q &= \lambda_0 C_0 k_0 - \lambda_1 C_1 k'_1 \\ Q &= \lambda_1 C_1 k_1 - \lambda_2 C_2 k'_2 \\ Q &= \lambda_2 C_2 k_2 - \lambda_3 C_3 k'_3 \\ &\dots\dots\dots \\ Q &= \lambda_{n-1} C_{n-1} k_{n-1} - \lambda_n C_n k'_n \end{aligned} \quad (71)$$

If we multiply the second equation above by k'_1/k_1 , the third by $k'_1 k'_2/(k_1 k_2)$, and the last equation by $k'_1 k'_2 \dots k'_{n-1}/(k_1 k_2 \dots k_{n-1})$ and add, we obtain

$$Q = \frac{\lambda_0 k_0 \left(C_0 - \frac{\lambda_n}{\lambda_0} \frac{k'_1 k'_2 \dots k'_{n-1} k'_n}{k_0 k_1 \dots k_{n-1}} C_n \right)}{1 + \frac{k'_1}{k_1} + \frac{k'_1 k'_2}{k_1 k_2} + \dots + \frac{k'_1 k'_2 \dots k'_{n-1}}{k_1 k_2 \dots k_{n-1}}} \quad (72)$$

Remembering that the rate constants are expressed by equation (1b), equation (72) becomes, assuming for κ a value of unity,

$$Q = \frac{\lambda_0 k_0 \left(C_0 - \frac{\lambda_n}{\lambda_0} e^{\Delta F_n/RT} C_n \right)}{1 + e^{\delta F_1/RT} + \dots + e^{\delta F_{n-1}/RT}} \quad (73)$$

Here ΔF_n is the free energy of molecules in the n th minimum minus that of those in the zeroth, and $\delta F_i^\ddagger$ is the free energy at the top of the barrier to the right of the i th minimum minus that at the top of the barrier to the right of the zeroth minimum.

A variety of special cases follows from equation (73), and each leads to commonly accepted formulations of practical interest.

Case I. Suppose all barriers are of equal height; then the denominator of (73) becomes n , the total number of intervening barriers, and

$$\begin{aligned} Q &= \frac{\lambda_0 k_0}{n} \left(C_0 - \frac{\lambda_n}{\lambda_0} e^{\Delta F_n / RT} C_n \right) \\ &= \frac{\lambda_0^2 k_0}{\gamma_0 \delta} \left(\gamma_0 C_0 - \gamma_0 \frac{\lambda_n}{\lambda_0} e^{\Delta F_n / RT} C_n \right) \\ &= \frac{D_0^0}{\delta} (a_0 - a_n) = P_0^0 (a_0 - a_n) \end{aligned} \quad (74)$$

Here, we have written δ for $n\lambda_0$, the membrane thickness, and γ_0 as the activity coefficient at concentration C_0 . D_0^0 indicates $\lambda_0^2 k_0 / \gamma_0$, and it may be called the standard diffusion coefficient. The quantities, a_0 and a_n are the activities at the zeroth and n th minima, respectively. The standard permeability P_0^0 is defined by

$$P_0^0 = D_0^0 / \delta \quad (75)$$

Case II. We consider now a membrane which consists of n barriers of equal heights. If charges of unlike sign lie on the two sides of the membrane with negligible net charge between, this will give rise to a potential difference of ϵ volts between the zeroth and the n th minimum. Thus, we have the following relations:

$$\Delta F_n = z\mathfrak{F}\epsilon \quad (76)$$

$$\delta F_i^\ddagger = (i/n)z\mathfrak{F}\epsilon \quad (77)$$

$$k_0 = k_0^0 \exp \left(- \frac{z\mathfrak{F}\epsilon}{2nRT} \right) \quad (78)$$

where z is the valence number of the ion, $\mathfrak{F} = 23,063$, the faraday in units of cal/volt, and k_0^0 is the specific rate constant over the first barrier in the absence of the electric field. We write also

$$x = e^{z\mathfrak{F}\epsilon / nRT} \quad (79)$$

With these substitutions, equation (73) becomes

$$\begin{aligned} Q &= \frac{\lambda_0 k_0^0 x^{-1/2} \left(C_0 - \frac{\lambda_n}{\lambda_0} x^n C_n \right)}{1 + x + x^2 + \dots + x^{n-1}} \\ &= \lambda_0 k_0^0 \frac{x^{-1/2} - x^{1/2}}{x^{-n/2} - x^{n/2}} \left(C_0 x^{-n/2} - \frac{\lambda_n}{\lambda_0} C_n x^{n/2} \right) \end{aligned} \quad (80)$$

Expanding the exponentials, we find that

$$\frac{g}{n} \equiv \frac{x^{-1/2} - x^{1/2}}{x^{-n/2} - x^{n/2}} \simeq \frac{1}{n} \quad (81)$$

provided that the total electrical work, $z\mathfrak{F}\epsilon$ is somewhat smaller than RT . In this case,

$$\lambda_0 k_0^0 g/n \simeq \lambda_0 k_0^0/n \equiv P \quad (83)$$

and

$$Q = P \left(C_0 e^{-z\mathfrak{F}\epsilon/2RT} - \frac{\lambda_n}{\lambda_0} C_n e^{-z\mathfrak{F}\epsilon/2RT} \right)$$

Thus, the transport of matter, Q , is proportional to a permeability, $P = \lambda_0 k_0^0/n$. If the exponentials in equation (83) are expanded and only the first terms retained as is, of course, consistent with the approximation (81), we obtain

$$Q = P \left[\left(C_0 - \frac{\lambda_n}{\lambda_0} C_n \right) - \frac{1}{2} \left(C_0 + \frac{\lambda_n}{\lambda_0} C_n \right) \frac{z\mathfrak{F}\epsilon}{RT} \right] \quad (84)$$

Thus, the total transport is the sum of a diffusion term and an electrical transport term.

In nerve membranes where ϵ is around 80 millivolts, the expansion (81) is not always justified, and the assumption ordinarily made of an effective permeability, which is independent of voltage, should be corrected accordingly. In view of the popularity of expressions of the forms (83), (84), and others involving equivalent assumptions, it may be worthy of note to point out just how much in error such approximations may be.

We have assumed in the above discussions that negligible net charge accumulates within the membrane, and also that the barriers are homogeneous. We will consider the properties of these assumptions. Let us assume that at any instant there is an excess charge in a particular "pocket." Then, this charge in itself would cause the potential gradient to decrease automatically the driving force for transport in one direction and increase it in the reverse direction until the potential gradient as a whole is again essentially constant. We may term this phenomenon the "incompressibility of ions" in a membrane. In a similar way, one may argue that if the membrane is such that there exists *a priori* a barrier which is much higher than those on either side, the piling up of charge at this barrier will reduce its effective height, and bring about the situation in which the sequence of barriers is very nearly a uniform one. Thus, in either case, there will be an effectively uniform succession of barriers in agreement with our assumptions.

Using equation (80) Parlin and Eyring²⁸ explained the establishment of the resting potential across a nerve membrane and the decay law of nerve impulse.

It may also be pointed out that through the use of equation (80) one can also derive the expression for the liquid junction potential in accordance with those obtained by Planck,²⁹ Henderson,³⁰ and others³¹ by classical treatments.

IV. Applications

In this section we give some examples showing the applications of the equations derived in the above sections. Because of the limited space for this chapter only typical examples are given. For additional examples the readers are referred to the original papers cited.

We treat only the cases of complete equilibration of activated complexes with ambient temperature.

1. SOLID PLASTIC SYSTEM

Because of the conditions given by equations (15) to (18), the generalized viscosity equation (34) is written as

$$\eta = \frac{x_1\beta_1}{\alpha_1} + \frac{x_2\beta_2}{\alpha_2} \frac{\sinh^{-1}(\beta_2\dot{s})}{\beta_2\dot{s}} + \frac{x_3\beta_3}{\alpha_3} \frac{\sinh^{-1}(\beta_3\dot{s})}{\beta_3\dot{s}} \quad (85)$$

In equation (85), the relations given by (5) and (6) were introduced. Group 1, for which the condition of equation (15) holds, behaves as Newtonian units while other groups are non-Newtonian. Group 2 for the condition of equation (16) behaves differently from other non-Newtonian groups. It acts as Newtonian in the low range of shear rate, $\dot{s}$, while it acts as non-Newtonian in the high range. In solid plastic systems, frequently Group 1 becomes non-Newtonian just as Group 2, but at higher values of $\dot{s}$. Thus in plastics, condition (15) usually does not hold.

The viscosities for plastics are thus given by the following formula:

$$\eta = \frac{x_1\beta_1}{\alpha_1} \frac{\sinh^{-1}(\beta_1\dot{s})}{\beta_1\dot{s}} + \frac{x_2\beta_2}{\alpha_2} \frac{\sinh^{-1}(\beta_2\dot{s})}{\beta_2\dot{s}} + \frac{x_3\beta_3}{\alpha_3} \frac{\sinh^{-1}(\beta_3\dot{s})}{\beta_3\dot{s}} \quad (86)$$

Generally, equation (85) holds for solution and for finely milled rubber, while (86) usually holds for solid systems.

Equation (85) shows that the total viscosity η is represented by a superposition of three curves in a plot of η vs. $\dot{s}$, as is schematically shown in Fig. 1B.

In applying equations (85) and (86), it is necessary to determine the parameters in these equations. We consequently mention next the procedures for determining these parameters.

²⁹ M. Planck, *Ann. Physik* **39**, 161 (1890); **40**, 561 (1890).

³⁰ P. Henderson, *Z. Physik. Chem.*, **59**, 118 (1907); **63**, 325 (1908).

³¹ G. N. Lewis and L. W. Sargent, *J. Am. Chem. Soc.* **31**, 363 (1909); D. A. MacInnes, "Principle of Electrochemistry," p. 231. Reinhold, New York, 1939.

a. Determination of the Parameters

We can resolve an experimental curve of η vs. $\dot{s}$ into its component curves using equations (85) and (86). We mention below the procedures for this resolution in the various cases.

(1) *Complete Newtonian system.* The case where the plot of η vs. $\dot{s}$ gives a straight line which is parallel to the $\dot{s}$ -axis is the simplest case; i.e., the system behaves as a completely Newtonian system. In this case, $\eta = x_1\beta_1/\alpha_1$.

(2) *Non-Newtonian system without units of Group 3.* In a non-Newtonian case, we first need to determine the Newtonian term, $x_1\beta_1/\alpha_1$, by extrapolating the curve of η vs. $1/\dot{s}$ to a zero value of $1/\dot{s}$; for this reason, the Newtonian term is often represented by η_∞ in our papers, the ∞ indicating the infinite shear rate.

Using the equation

$$\eta - \eta_\infty = \frac{x_2\beta_2}{\alpha_2} \frac{\sinh^{-1} \beta_2\dot{s}}{\beta_2\dot{s}} \quad (87)$$

which is derived from equation (85) for the case, $x_3 = 0$, we can determine β_2 . The value of $x_2\beta_2/\alpha_2$ is the value which the quantity $(\eta - \eta_\infty)$ takes at $\dot{s} = 0$. If the parameters, η_∞ , β_2 , and $x_2\beta_2/\alpha_2$, thus determined reproduce the original experimental curve in good agreement, it is concluded that the system does not have units belonging to Group 3.

(3) *Non-Newtonian system with Groups 2 and 3 in addition to Group 1.* In this case, an experimental curve of η vs. $\dot{s}$ rises sharply in the low range of $\dot{s}$. There are several ways to obtain curves 2 and 3 corresponding to Groups 2 and 3, respectively, from the experimental data. The simplest procedure is as follows: The part of the experimental curve which would depend purely on Groups 1 and 2 is extrapolated to the zero value of $\dot{s}$; this is shown in Fig. 1B by the dotted line ab extrapolating curve 4 for large $\dot{s}$ back to $\dot{s} = 0$.

The curve abc , so obtained, is due to the units 1 and 2. From this curve, the values of β_2 and $x_2\beta_2/\alpha_2$ are obtained by the same procedure as in Case (2). The contribution of Group 3 to the total viscosity is represented in Fig. 1B by the shaded area. Thus, the length of the vertical line between curves ab and db is the contribution of the flow unit of Group 3 at the value of $\dot{s}$. Consequently, we have

$$\eta - \eta_\infty - \left(\frac{x_2\beta_2}{\alpha_2} \frac{\sinh^{-1} \beta_2\dot{s}}{\beta_2\dot{s}} \right)_{\text{calc}} = \frac{x_3\beta_3}{\alpha_3} \frac{\sinh^{-1} \beta_3\dot{s}}{\beta_3\dot{s}} \quad (88)$$

the values of $x_3\beta_3/\alpha_3$ and β_3 are calculated as before, since the values of all terms on the left side of equation (10) are known, and the value of $x_3\beta_3/\alpha_3$ is obtained from the value of the left side at $\dot{s} = 0$.

(4) *Non-Newtonian system without Newtonian Group.* In some cases, the

extrapolation of the curve η vs. $1/\dot{s}$ to the zero of $1/\dot{s}$ gives an extremely small value. This is the evidence for the absence of the Group 1, Newtonian units. Even in this case, the experimental curve in the lower range of $\dot{s}$ is well fitted by equation (87) for Case (2), a system composed of Newtonian units and non-Newtonian units of Group 2. This illustrates the fact that the Newtonian units became non-Newtonian in the higher range of $\dot{s}$.

Assuming there is no Group 3, the viscosity formula in this case is derived from equation (86) as follows:

$$\eta = \frac{x_1\beta_1}{\alpha_1} \frac{\sinh^{-1} \beta_1\dot{s}}{\beta_1\dot{s}} + \frac{x_2\beta_2}{\alpha_2} \frac{\sinh^{-1} \beta_2\dot{s}}{\beta_2\dot{s}} \quad (89)$$

From equation (89) one obtains the equation

$$f = \frac{x_1\beta_1}{\alpha_1} \dot{s} + \frac{x_2}{\alpha_2} \ln 2\dot{s} + \frac{x_2}{\alpha_2} \ln \beta_2 \quad (90)$$

where equation (5) and the relation

$$\sinh^{-1} \beta_2\dot{s} \simeq \ln 2\beta_2\dot{s} \quad (91)$$

are introduced into equation (89). Equation (91) holds only for large values of $\dot{s}$, while equation (5) holds for small values of $\dot{s}$. That is, the two paradoxical relations are introduced into the same equation, equation (86). Although equation (90) thus may seem illogical, it is in fact very useful in determining the approximate values for the parameters, $x_1\beta_1/\alpha_1$, x_2/α_2 , and β_2 in equation (89). These approximate values are then introduced in equation (87) to make it fit the experimental curve in the low range of $\dot{s}$. Using the best values for the parameters, the viscosity η' is calculated from equation (87) for the whole range of $\dot{s}$. The value of η' deviates in the high range of $\dot{s}$ from the experimental η which fits equation (89). From equations (87) and (89), the deviation $\eta' - \eta$ may be written

$$\eta' - \eta = \frac{x_1\beta_1}{\alpha_1} \left(1 - \frac{\sinh^{-1} \beta_1\dot{s}}{\beta_1\dot{s}} \right) \quad (92)$$

The value of β_1 can now be calculated, since $x_1\beta_1/\alpha_1$ is already known.

Applying the principles previously outlined, one can determine the parameters in the case where three non-Newtonian units are present [see equation (86)]. The details will not be given here.

b. Results

(1) *Natural rubber*. Saunders and Treloar³² obtained $\dot{s}$ vs. f curves for

³² D. W. Saunders and L. R. G. Treloar, *Trans. Inst. Rubber Ind.* **24**, 92 (1948); L. R. G. Treloar, "The Physics of Rubber Elasticity," p. 198. Oxford Univ. Press, New York, 1949.

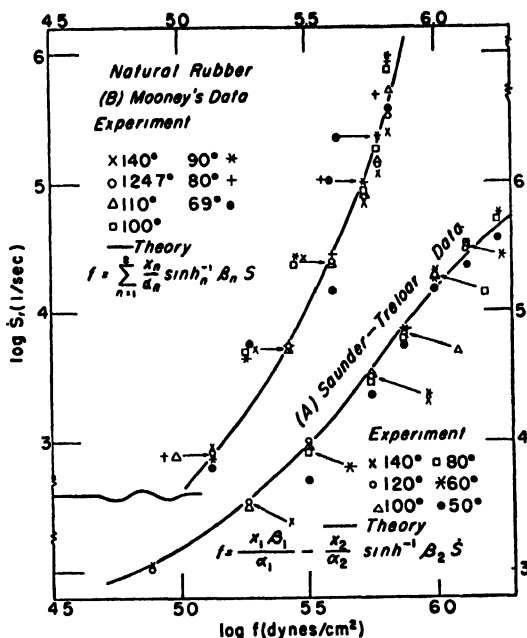


Fig. 6. Logarithm of reduced shear rate vs. logarithm of shear stress for masticated rubber. The data of Saunder and Treloar (see ref. 32) are referred to the right and bottom coordinates while Mooney's data (see ref. 33) are referred to the left and upper coordinates. To avoid the complexity caused by the superposition of many data around the same point, the following procedure was adopted in this figure: Those data which could not be plotted in their real position, because of the superposition, were put outside the points, and arrows were used to show where the data belonged.

masticated rubber at temperatures from 50 to 140° C. They found that the so-called Ostwald-de Waele equation, $\dot{s} = kf^n$ (k and n are constant), does not adequately represent their curves. They found also that the activation heat for the flow process was 8.1 kcal./mole. We calculate a reduced shear rate, $\dot{s} \exp(\Delta H^\ddagger/RT)$, from their curves using their activation heat; the logarithms of the reduced shear rates $\dot{s}_r$ are plotted against $\log f$ in Fig. 6A. We see that the reduced rates calculated from the data at various temperatures agree very well except at 50° C. The deviation of the data at 50° C. may be due to some second-order transition which takes place around this temperature.^{32a} The full curve was obtained by calculation from equation (87), using the values of the parameters in Table I, where the parameters for other samples are also summarized. We see that the

^{32a} If this is true, this transition is different from that which takes place at -73° C. See H. Mark and A. V. Tobolsky, "Physical Chemistry of High Polymeric Systems," p. 346. Interscience, New York, 1950.

agreement between theory and experiment are satisfactory, except for the data at 50° C.

Mooney³³ measured flow rates of lightly milled crepe at temperatures from 69 to 140° C. The heat of activation was found to be 7.9 kcal. by Saunder and Treloar^{32a} from Mooney's data. This value agrees very closely with 8.1 kcal., which was obtained by them from their own data. Using this value, 7.9 kcal., we calculate $\dot{s} \exp (\Delta H^\ddagger/RT)$, and the results are shown in Fig. 6. *B* One sees that the value of 7.9 kcal. gives good reduced shear rates except for the rates at shear stresses higher than 5.5×10^5 dynes/cm.², where some irregularity appears. The theoretical curve for the Mooney data is obtained from equation (89), using the values of the parameters in Table I.

The main difference of the Mooney data from that of Saunders-Treloar is the following: (i) The latter shows distinctly the presence of Newtonian flow units, while the former shows that the Newtonian units which act as such at low stresses become non-Newtonian at high stresses. (ii) The Mooney data yields values of β_2 and $x_1\beta_1/\alpha_1$ which are larger by a factor of 10 and 4, respectively, than the values from the Saunder-Treloar data. It is interesting that in spite of these differences the heats of activation and the values of x_2/α_2 are the same for the two sets of experiments. The differences mentioned are due to differences in the samples used by Mooney and by Saunder and Treloar. The latter authors claim that the Mooney sample was less severely broken down^{32a} and therefore had a higher molecular weight than did their sample. The agreement in the $\Delta H^\ddagger$ values in the two series of experiments indicates that the flow process is performed by independent segmental motions under their coordination. On the other hand, the discrepancies in the β values illustrate the fact that the larger the size of the flow molecules (i.e., the higher the degree of polymerization), the more difficult the coordination of the segmental motions; this, in turn, produces a large negative activation entropy. The relatively large value of β_1 in Mooney's sample leads Newtonian units to non-Newtonian behavior at high stresses.

(2) *Polystyrene*. Spencer and Dillon³⁴ measured flow rates of polystyrene using capillary viscometers at temperatures from 165 to 250° C. The experimental points in Fig. 7, were taken from their results for a polymer of molecular weight 3.60×10^5 . As reduced shear rates, they used $\eta_s \dot{s}$, where η_s is the viscosity at small $\dot{s}$. The theoretical curve was obtained using Eq. (89). Namely, the system is composed of flow units of two non-Newtonian groups. The parameters are tabulated in Table I. The agreement between

³³ M. Mooney, *Physics* **7**, 413 (1936).

³⁴ R. S. Spencer and R. E. Dillon, *J. Colloid Sci.* **3**, 163 (1948); **4**, 241 (1949).

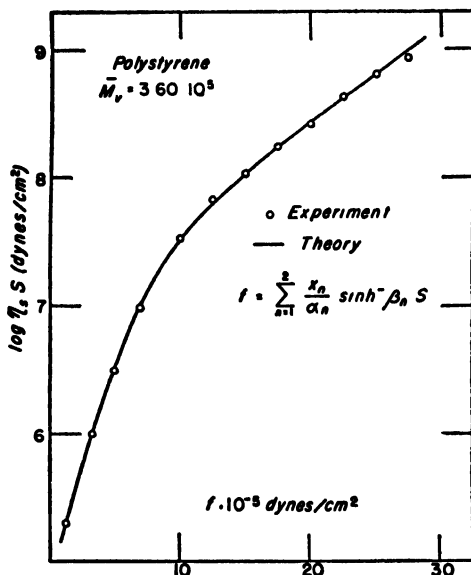


FIG. 7. Logarithm of reduced shear rate vs. shear stress for polystyrene of viscosity-averaged molecular weight of 3.60×10^5 .

theory and experiment is surprisingly good except at extremely high shear rates, where the experimental data are not accurate. Spencer³⁵ explained this flow curve from a different viewpoint.

(3) *X-672 GR-S and X-518 GR-S rubber*. The symbol X 672 GR-S rubber indicates a copolymer 21 % styrene and 79 % butadiene. Its viscosity-average molecular weight $\bar{M}_v$ is about 2×10^5 . The rubber X-518 GR-S is a copolymer containing 24 % styrene and 76 % butadiene. Its $\bar{M}_v$ is about 2×10^5 . Bestul and Belcher³⁶ measured flow rates of these systems at various temperatures ranging from 37.8 to 93.3° C.

We calculate reduced shear rate [$\dot{s}_r = \dot{s} \exp (\Delta H^\ddagger / RT)$] from their data using the activation heats which they reported (8.85 kcal. for X-672, 12.5 kcal. for X-518 GR-S rubber). The experimental points in Fig. 8 (see curve A and B) are calculated from their flow curves. The same formula as in polystyrene is applicable to both X-672 and X-518 GR-S rubber. Curve A and B in Fig. 8 are the calculated results for the polymers, respectively.

(4) *Vistanex LM-S polyisobutylene*. The molecular weight $\bar{M}_v$ of this substance is about 7×10^4 . Bestul and Belcher³⁶ measured the flow rates at 38, 93 and 149° C. The experimental points for curve C in Fig. 8 were obtained for their data. In the calculation of $\dot{s}_r$, the activation heat 11.7 kcal

³⁵ R. S. Spencer, *J. Polymer Sci.* **5**, 591 (1950).

³⁶ A. B. Bestul and H. V. Belcher, *J. Appl. Phys.* **24**, 696 (1953); A. B. Bestul, H. V. Belcher, F. A. Quinn, and C. B. Brayant, *J. Phys. Chem.* **56**, 432 (1952).

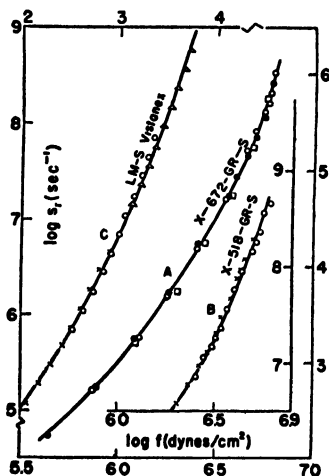


FIG. 8. Logarithm of reduced shear rate vs. logarithm of shear stress. Full curves were theoretically calculated. Curve *A* is referred to the right and bottom axes. Sample: X-672 GR-S rubber with viscosity averaged molecular weight of 2×10^5 ; solid circles, open circles, and squares are the data at 93.3, 65.6, and 37.8° C., respectively. Curve *B* is referred to the inlet axes. Sample: X-518 GR-S rubber with viscosity-averaged molecular weight of 2×10^5 ; crosses and circles are the data at 50 and 40° C., respectively. Curve *C* is referred to the left and upper axes. Sample: LM-S polyisobutylene with viscosity-averaged molecular weight of 7.00×10^4 ; crosses, circles, and triangles are the data at 149, 93, and 38° C., respectively.

was used, which was the authors' reported value. This case is described by equation (86) with the parameters in Table I. That is, this system is composed of flow units of three non-Newtonian groups. We see that the agreement between theory and experiment is exceedingly good. Before reaching this good agreement, we tried fewer parameters, but failed to obtain good agreement.

c. Discussions

(1) *Segmental motion.* The fact that a reduced viscosity equation for temperature is found in many cases even where the viscosity involving more than one relaxation time shows that the slower relaxation times are due to greater negative entropies rather than to increased activation heats. This is what one would expect for long molecules progressing by segmental motion. Thus a segment in the shear surface may be supposed to require no bigger hole to move into than do the molecules. On the other hand, a flow segment will frequently be prevented from flowing by attached segments, thus giving rise to a larger negative entropy of activation in the large molecules. This, in turn, leads to a larger relaxation time.

(2) *Temperature independence of α .* The parameter α is $\lambda\lambda_2\lambda_3/(2kT)$ as previously mentioned, where $\lambda\lambda_2\lambda_3$ is a parameter belonging to a flow unit.

TABLE I
VALUES OF THE PARAMETERS IN THE VISCOSITY FORMULA FOR SOLID PLASTIC SYSTEMS*

Sample	Temperature °C.	$(r_1/\alpha_1)\beta_1$ sec- dynes/ cm. ²	r_1/α_1 dynes/cm. ²	x_2/α_2 dynes/cm. ²	x_3/α_3 dynes/ cm. ²	β_1 sec.	β_2 sec.	β_3 sec.	$\Delta H^\dagger$ kcal./ mole
Natural rubber (Treloar data)	140, 120, 100, 80, 60, 50	2.25		1.31×10^5	0		0.500×10^{-3}	...	8.1
Natural rubber (Mooney data)	140, 124, 110, 100, 90, 80, 69	..	1.50×10^5	1.80×10^5	0	6.01×10^{-5}	0.680×10^{-2}	...	7.9
Polystyrene Molecular wt. = 3.60×10^5	253 to 165	...	4.30×10^5	1.23×10^5	0	1.77×10^{-3}	0.800×10^{-5}	.	
X-672 GR-S† Molecular wt. = 2.00×10^5	93.3, 65.6, 37.8	...	6.17×10^5	3.10×10^5	0	1.51×10^{-4}	0.957×10^{-2}	...	8.85
X-518 GR-S‡ Molecular wt. = 2.00×10^5	50, 40	...	2.71×10^5	5.68×10^5	0	0.927×10^{-7}	0.405×10^{-5}	...	12.5
LM-S polyiso- butylene Molecular wt. = 7.00×10^4	149, 83, 38	...	1.59×10^3	4.50×10^3	73.7	0.264×10^{-8}	0.250×10^{-6}	1.51×10^{-5}	11.7

* The β 's in this table are the reduced quantities for temperature, $\beta \exp(-\Delta H^\dagger/RT)$. The reduced β 's for polystyrene are β/η , where η is the viscosity at small δ .

† A copolymer of 21% styrene and 79% of butadiene.

‡ A copolymer of 24% styrene and 76% of butadiene.

Kauzmann³⁷ analyzed the creep data of tin, lead, zinc, steel, and alloys at various temperatures using Eyring's hyperbolic sine function [equation (1a)], and found that the factor, $\lambda\lambda_2\lambda_3$, increased linearly with temperature, i.e., that α is independent of temperature. Sherby and Dorn³⁸ analyzed their creep data for aluminum and its alloys in the light of the hyperbolic sine function. They found that their curves of the reduced shear rates ($\dot{\epsilon} \exp \Delta H^\ddagger/RT$) vs. f at different temperatures were brought together into one curve, and that α was independent of temperature. We also found the same result.³⁹ From Tobolsky and Andrews's stress relaxation curves for polyisobutylene,⁴⁰ we calculated the factor $\lambda\lambda_2\lambda_3$ and found it increased linearly with temperature. In the present paper, we have shown that reduced curves are obtained when reduced shear rates are plotted against stresses. This fact is due to the constancy of α with temperature. Thus, the constancy of the factor α for temperature is a well-founded experimental fact. We will refer to this fact later.

(3) *Other problems concerning the hyperbolic sine function.* There are several criticisms of the simple hyperbolic sine function besides those mentioned above. Most of the criticisms, however, have neglected the distribution factor, i.e., their main difficulty has originated from this point. Eley and Pepper⁴¹ found that in their experiment on the flow properties of plasticized cellulose derivatives, the flow-rate has an exponential dependence of f at moderate stresses just as the simple relaxation theory, equation (1a), predicts, but that at higher stresses the flow rate approaches linearity with stress. This linearity at high stress caused them to reject the hyperbolic sine theory. As Powell and Eyring⁴² pointed out, the difficulty arose from neglect of the Newtonian units in their system. Spencer and Dillon³⁴ pointed out that their observed behavior of polystyrene was not in agreement with Eyring's equation. Spencer³⁵ claimed that the hyperbolic sine function did not give a satisfactory fit of Saunders and Treloar's data on the flow of masticated rubber.³² As mentioned above, our generalized flow equation gives excellent agreement with the experimental data in both cases. It has often been pointed out that any existing theories of non-Newtonian flow were not applicable to flow of high polymer solutions.^{35, 43} The reason is as follows: Most of the investigators observed that as the shear stress is raised early

³⁷ W. Kauzmann, *Trans. Am. Inst. Mining Met. Engrs.* **143**, 57 (1941).

³⁸ O. D. Sherby and J. E. Dorn, *J. Metals* **4**, 959 (1952); **5**, 324 (1953).

³⁹ T. Ree and H. Eyring, University of Utah Technical Report XXXVIII, 1952.

⁴⁰ R. D. Andrews, N. Hofman-Bang, and A. V. Tobolsky, *J. Polymer Sci.* **5**, 669 (1948); R. D. Andrews and A. V. Tobolsky, *J. Polymer Sci.* **7**, 221 (1951), and the allied papers.

⁴¹ D. D. Eley and D. C. Pepper, *Nature* **154**, 52 (1944); **154**, 428 (1944).

⁴² R. E. Powell and H. Eyring, *Nature* **154**, 427 (1944).

⁴³ T. G. Fox, Jr., J. C. Fox, and P. J. Flory, *J. Am. Chem. Soc.* **73**, 1901 (1951).

deviations from Newtonian flow come about through a term which contained the first power of the shear stress. The expansion of the hyperbolic sine function in a power series shows that these early deviations should be caused by a term containing the square of f ; this difficulty is also resolved by introducing a distribution function (cf. below).

The shear volume, $\lambda\lambda_2\lambda_3$, decreases with increasing percentage of stretch for solid materials as was noted very early by Kistler⁴⁴ for the stress relaxation in polyvinyl acetate and for the creep of latex. This fact has been noted also by Tobolsky and Eyring⁴⁵ for the stress relaxation in steel and raw rubber, by Tobolsky and Andrews⁴⁶ for the stress relaxation in GR-S rubber and Hevea gum, and by Ree and Eyring³⁹ for the stress relaxation in polyisobutylenes. The change of the shear volume with the per cent stretch has been held to be a defect of the simple hyperbolic sine function theory.³⁵

Applying the virial theorem⁷ as previously mentioned, we derive equation (26), i.e.,

$$\int_0 g \lambda \lambda_2 \lambda_3 = \gamma_s$$

When the flow units are equilibrating with the ambient temperature, $\gamma_s = kT$. Thus we obtain

$$\lambda \lambda_2 \lambda_3 = \frac{kT}{gf_0} \quad (93)$$

According to equation (93), the shear volume, $\lambda \lambda_2 \lambda_3$, is proportional to temperature T and is inversely proportional to the microstress f_0 , which is frequently found proportional to the initial stress in relaxation experiments.^{39, 45, 46} Thus the constancy of the factor α with temperature, and the decrease of the shear volume with the per cent stretch, are a natural consequence of equation (93).

2. SOLUTION SYSTEM OF HIGH POLYMERS

Here solvent molecules are designated as the zeroth group of flow units. They generally flow more easily than do the high polymer patches; thus the solvent molecules behave as Newtonian units. We treat the solution viscosities being used in the literature in terms of our theory.

a. Viscosity Formulas for Solution Systems

The relative viscosity, η_r , which is equal to η/η_0 , is found from equation (85) to be

$$\eta_r = \sum_{n=1}^3 \frac{x_n \beta_n}{\alpha_n \eta_0} \frac{\sinh^{-1}(\beta_n \dot{\epsilon})}{\beta_n \dot{\epsilon}} + x_0 \quad (94)$$

⁴⁴ S. S. Kistler, *J. Appl. Phys.* **11**, 769 (1940).

⁴⁵ A. V. Tobolsky and H. Eyring, *J. Chem. Phys.* **11**, 125 (1943).

⁴⁶ A. V. Tobolsky and R. D. Andrews, *J. Chem. Phys.* **13**, 3 (1945).

where the relation $\eta_0 = \beta_0/\alpha_0$ has been introduced. If the relation $x_0 = 1 - x_1 - x_2 - x_3$ is substituted into equation (94), one obtains for the *specific viscosity* η_{sp} , which is $\eta_\gamma - 1$, the formula

$$\eta_{sp} = \sum_{n=1}^3 x_n \left(\frac{\beta_n}{\alpha_n \eta_0} \frac{\sinh^{-1}(\beta_n \dot{s})}{\beta_n \dot{s}} - 1 \right) \quad (95)$$

The *intrinsic viscosity* η_i is defined as η_{sp}/C , where C is concentration. Thus, we have

$$\eta_i = \sum_{n=1}^3 \frac{x_n}{C} \left(\frac{\beta_n}{\alpha_n \eta_0} \frac{\sinh^{-1}(\beta_n \dot{s})}{\beta_n \dot{s}} - 1 \right) \quad (96)$$

If the concentration is very low, i.e., $x_0 \simeq 1$, then the following equation results from equation (94):

$$\eta_i \simeq \sum_{n=1}^3 \frac{x_n}{C} \frac{\beta_n}{\alpha_n \eta_0} \frac{\sinh^{-1}(\beta_n \dot{s})}{\beta_n \dot{s}} \quad (97)$$

From the definition of the *limiting intrinsic viscosity* $[\eta]$ the following is given:

$$[\eta] = \lim_{c \rightarrow 0} \sum_{n=1}^3 \frac{x_n}{C} \frac{\beta_n}{\alpha_n \eta_0} \frac{\sinh^{-1}(\beta_n \dot{s})}{\beta_n \dot{s}} \quad (98)$$

Inherent viscosity, η_{inh} , is defined as $(\ln \eta)/C$. Therefore, the limiting inherent viscosity as the concentration approaches zero is equal to $[\eta]$. Frequently, data are presented in term of inherent viscosities. The formula for the latter is obtained from equation (94) as follows:

$$\frac{\ln \eta_r}{C} = \frac{1}{C} \ln \left[x_0 + \frac{x_1 \beta_1}{\alpha_1 \eta_0} + \sum_{n=2}^3 \frac{x_n \beta_n}{\alpha_n \eta_0} \frac{\sinh^{-1}(\beta_n \dot{s})}{\beta_n \dot{s}} \right] \quad (99)$$

b. Results

(1) *Polystyrene solutions*. Sherman *et al.*⁴⁷ measured the viscosities of the solutions of polystyrene fractions by a capillary viscometer specially designed for their investigation. We analyze their data by the method described in Section 1a of Applications, and represent the results in Figs. (9–14).

(a) *The Effect of Molecular Weight*. In Fig. 9 the results for the benzene solutions of polystyrene fractions at 25° C. are represented. The theoretical curves are obtained from equation (99), using the values of the parameters in Table II. In our work the necessary viscosities of solvents are obtained from Timmermans' tables.⁴⁸ From Fig. 9 one sees that the theoretical curves

⁴⁷ L. J. Sherman, R. H. Sones, and L. H. Cragg, *J. Appl. Phys.* **24**, 703 (1953).

⁴⁸ J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds." Elsevier, New York, 1950.

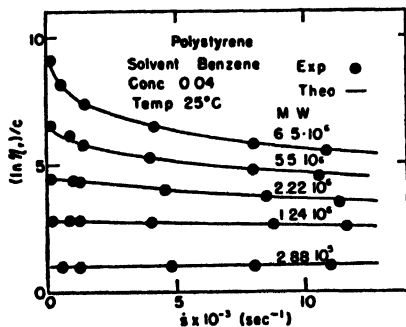


FIG. 9. Effects of molecular weight on inherent viscosity vs. shear-rate curves. Solute, polystyrene fractions with various molecular weights; solvent, benzene; concentration, 0.04 g./100 cc.; temperature, 25° C. The theoretical curves are calculated from equation (99) using the parameters in Table II.

accord well with experiment. Table II shows that more types of flow units are involved as the molecular weight increases. Thus, in the solution of polystyrene with molecular weight 0.228×10^6 , only the Newtonian group is present; in the solution of polystyrene with molecular weights 1.24×10^6 and 2.22×10^6 two types of flow units are present. Finally in the case of the fractions with $\bar{M}$, 5.5×10^6 and 6.5×10^6 , all three types of flow units are acting. We also observe the following facts: in the first case, the curve of $(\ln \eta_r)/C$ vs. $\dot{s}$ is a straight line parallel to the $\dot{s}$ axis; in the second case, the curve is nearly a straight line with negative slope whose absolute value is a function of β and which increases with increasing molecular weight; in the third case, this straight line makes a curve at the low values of $\dot{s}$, and the curvature of this curve increases with increasing molecular weight.

The data of Sherman, *et al.*⁴⁷ for polystyrene fractions at 65 and 35° C. dissolved in cyclohexane exhibit the changes of the slopes of inherent vis-

TABLE II

THE EFFECTS OF MOLECULAR WEIGHT. SOLUTION SYSTEM: SOLUTE, VARIOUS POLYSTYRENE FRACTIONS; SOLVENT, BENZENE; CONCENTRATION, 0.04 g/100 cc.; TEMPERATURE, 25° C.; $\eta_0 = 6.01 \times 10^{-3}$ POISE

Molecular weight $\bar{M}, \times 10^{-6}$	$x_0 + \frac{x_1\beta_1}{\alpha_{1\eta_0}}$	$\frac{x_2/\alpha_2}{\text{dynes}} \frac{\text{cm.}^2}{\text{cm.}^2}$	$\frac{x_3/\alpha_3}{\text{dynes}} \frac{\text{cm.}^2}{\text{cm.}^2}$	β_2/η_0	β_3/η_0	$\frac{(x_0 + \frac{x_1\beta_1}{\alpha_{1\eta_0}} - 1)}{C} \frac{\text{cm.}^3/\text{g.}}{\text{cm.}^3/\text{g.}}$	$\frac{(\frac{x_2}{\alpha_2})}{C} \frac{\text{dyne-cm.}}{\text{g.}}$	$\frac{(\frac{x_3}{\alpha_3})}{C} \frac{\text{dyne-cm.}}{\text{g.}}$
6.5	1.168	20.1	0.0129	0.0795	1.57	4.20	503	0.323
5.5	1.138	1.81	0.00421	0.0669	2.01	3.45	45.3	0.105
2.22	1.094	1.94	0.0	0.0521	..	2.35	48.5	0.0
1.24	1.092	0.601	0.0	0.0466	..	2.30	15.0	0.0
0.288	1.043	0.0	0.0	...	.	1.08	0.0	0.0

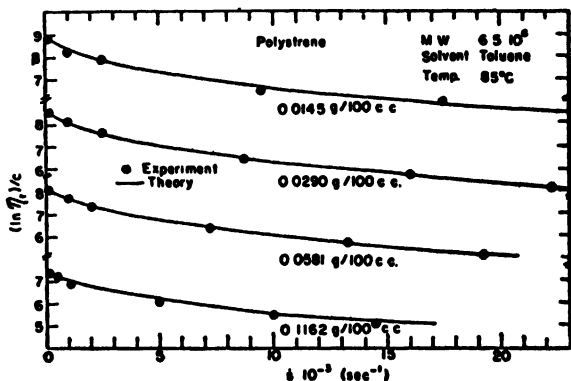


FIG. 10. Effects of concentration on inherent viscosity vs. shear-rate curves. Solute, polystyrene fraction with $\bar{M}_v = 6.5 \times 10^5$; solvent, toluene; temperature, 85° C. The theoretical curves are calculated from equation (99) using the parameters in Table IV.

cosity vs. shear-rate curves in a like manner to the case of polystyrene fractions dissolved in benzene. The parameters are tabulated in Table III. Using these values, the experimental curves are fitted as well as in Fig. 9 (cf. ref. 18).

(b) The Effect of Concentration. The viscosities of the toluene solutions

TABLE III

THE EFFECTS OF MOLECULAR WEIGHT. SOLUTION SYSTEM: SOLUTE, VARIOUS POLYSTYRENE FRACTIONS; SOLVENT, CYCLOHEXANE; CONCENTRATION, 0.06 g./100 cc.; TEMPERATURE, 65° AND 35° C.

Molecular weight $\bar{M}_v \times 10^{-5}$	$x_0 + \frac{x_1\beta_1}{\alpha_1\eta_0}$	$\frac{x_2/\alpha_2}{\text{dynes/cm}^2}$	$\frac{x_3/\alpha_3}{\text{dynes/cm}^2}$	β_2/η_0	β_3/η_0	$\frac{1}{c} \left(x_0 + \frac{x_1\beta_1}{\alpha_1\eta_0} - 1 \right)$ cm. ³ /g.	$\frac{\frac{x_2/\alpha_2}{C}}{\text{g.}}$	$\frac{\frac{x_3/\alpha_3}{C}}{\text{g.}}$
65° C. $\eta_0 = 5.00 \times 10^{-3}$ poise								
9.2	1.158	2.25	0.101	0.0590	0.506	2.63	37.5	1.68
5.2	1.132	2.07	0.0149	0.0454	0.872	2.20	34.5	0.248
2.4	1.114	0.777	0.0	0.0386	...	1.90	13.0	0.0
1.5	1.094	0.0	0.0	...	...	1.57	0.0	0.0
0.70	1.066	0.0	0.0	...	...	1.10	0.0	0.0
0.30	1.041	0.0	0.0	...	...	0.683	0.0	0.0
35° C. $\eta_0 = 7.52 \times 10^{-3}$ poise								
9.2	1.120	0.384	~0	0.0834	...	2.00	6.40	~0
5.2	1.111	0.150	0	<0.0665	...	1.85	2.50	0
2.4	1.080	0.0	0	...	...	1.33	0.0	0
1.5	1.060	0.0	0	...	...	1.00	0.0	0
0.70	1.044	0.0	0	...	...	0.733	0.0	0
0.30	1.029	0.0	0	...	...	0.483	0.0	0

TABLE IV

THE EFFECTS OF CONCENTRATION. SOLUTION SYSTEM: SOLUTE, POLYSTYRENE
FRACTION WITH $\bar{M}_v = 6.5 \times 10^6$; SOLVENT, TOLUENE; CONCENTRATION,
VARIED; TEMPERATURE, 85° AND 15° C.

Concentration $\frac{g.}{100 \text{ cc.}}$	$x_0 + \frac{x_1\beta_1}{\alpha_1\eta_0}$	$\frac{x_2/\alpha_2}{\text{dynes}} \frac{\text{cm.}^2}{\text{cm.}^2}$	$\frac{x_3/\alpha_3}{\text{dynes}} \frac{\text{cm.}^2}{\text{cm.}^2}$	β_2/η_0	β_3/η_0	$\frac{1}{c} \left(x_0 + \frac{x_1\beta_1}{\alpha_1\eta_0} - 1 \right) \frac{\text{cm.}^3/\text{g.}}{\text{cm.}^3/\text{g.}}$	$\frac{(x_2/\alpha_2)}{c} \frac{\text{cm.}}{\text{g.}} \frac{\text{dyne-cm.}}{\text{g.}}$	$\frac{(x_3/\alpha_3)}{c} \frac{\text{cm.}}{\text{g.}} \frac{\text{dyne-cm.}}{\text{g.}}$
85° C. $\eta_0 = 2.99 \times 10^{-3}$ poise								
0.0145	1.051	0.952	0.0151	0.0679	1.39	3.52	67.0	1.04
0.0290	1.087	2.28	0.0338	0.0679	1.39	3.00	78.6	1.17
0.0581	1.162	5.18	0.0726	0.0679	1.39	2.79	89.2	1.25
0.1162	1.353	11.7	0.186	0.0679	1.39	3.04	100.7	1.60
15° C. $\eta = 6.23 \times 10^{-3}$ poise								
0.0157	1.056	1.09	0.0226	0.0562	1.86	3.57	69.4	1.44
0.0314	1.118	2.23	0.0516	0.0562	1.86	3.76	71.0	1.64
0.0628	1.230	5.25	0.106	0.0562	1.86	3.66	83.6	1.69
0.1257	1.372	13.8	0.279	0.0562	1.86	2.96	109.8	2.22

of the polystyrene fraction with $\bar{M}_v = 6.5 \times 10^6$ in various concentrations were measured at 85 and 15° C. by Sherman *et al.*⁴⁷ The experimental data of $(\ln \eta_r)/C$ at 85° C. are plotted against s in Fig. 10. The theoretical curves are obtained from equation (99) using the parameters in Table IV. The agreement between theory and experiment is satisfactory. The same degree of agreement was also obtained for the data at 15°, using the parameters in Table IV. Sherman, Sones, and Cragg measured the flow rates of the cyclohexane solutions of the polystyrene fraction with $\bar{M}_v = 9.2 \times 10^6$ at 50° C. in various concentrations. The determined parameters are tabulated in Table V. In this case also, the agreement between theory and experiment was as good as in Fig. 10. The figures of the two cases are not shown

TABLE V

THE EFFECTS OF CONCENTRATION. SOLUTION SYSTEM: SOLUTE, POLYSTYRENE
FRACTION WITH $\bar{M}_v = 9.2 \times 10^6$; Solvent, Cyclohexane; Concentration,
VARIED; TEMPERATURE, 50° C.; $\eta_0 = 6.11 \times 10^{-3}$ POISE

Concentration $\frac{g.}{100 \text{ cc.}}$	$x_0 + \frac{x_1\beta_1}{\alpha_1\eta_0}$	$\frac{x_2/\alpha_2}{\text{dynes}} \frac{\text{cm.}^2}{\text{cm.}^2}$	$\frac{x_3/\alpha_3}{\text{dynes}} \frac{\text{cm.}^2}{\text{cm.}^2}$	β_2/η_0	β_3/η_0	$\left(x_0 + \frac{x_1\beta_1}{\alpha_1\eta_0} - 1 \right) \frac{\text{cm.}^3/\text{g.}}{\text{cm.}^3/\text{g.}}$	$\frac{(x_2/\alpha_2)}{c} \frac{\text{cm.}}{\text{g.}} \frac{\text{dyne-cm.}}{\text{g.}}$	$\frac{(x_3/\alpha_3)}{c} \frac{\text{cm.}}{\text{g.}} \frac{\text{dyne-cm.}}{\text{g.}}$
0.029	1.079	0.516	0.0160	0.0678	0.712	2.72	17.8	0.583
0.057	1.161	1.02	0.0309	0.0678	0.712	2.82	17.9	0.542
0.115	1.324	2.63	0.0941	0.0678	0.712	2.82	22.9	0.818
0.153	1.427	4.02	0.171	0.0678	0.712	2.79	26.3	1.12
0.230	1.64	7.28	0.416	0.0678	0.712	2.78	31.7	1.81

here, because the trends of the curves of $(\ln \eta_r)/C$ vs. $\dot{\gamma}$ at different concentrations are the same as those in Fig. 10 (cf. ref. 18).

As one can see from Fig. 10, the slopes of the curves are constant, irrespective of the concentrations. In Tables IV and V, the values of β_2/η_0 and β_3/η_0 are independent of concentration. The first fact is a natural consequence of the second because, according to our theory, the slopes of the curves of $(\ln \eta_r)/C$ vs. $\dot{\gamma}$ are solely determined by the β 's. The values of x_n/α_n increase with increasing concentration. As the values of $(x_n/\alpha_n)/C$ in Table IV and V indicate, the increase is more than linear. The values of $[x_0 + (x_1\beta_1/\alpha_1\eta_0) - 1]/C$ show an apparent constancy for concentration. At low concentrations, the latter values are nearly equal to $(x_1/C\alpha_1)(\beta_1/\eta_0)$, since $x_0 \simeq 1$. For Group 1, the separation of the two factors x_1/α_1 and β_1/η_0 is impossible. However, we may assume that β_1/η_0 is independent of concentration as in Groups 2 and 3. Thus, the value of $x_1/C\alpha_1$ for Group 1 does not increase with concentration, while the values for the Groups 2 and 3 increase rapidly.

(c) The Effect of Solvents. It is a well-known fact that the viscosities of the solutions of a high polymer in good solvents are higher than those in poor solvents. This is true for polystyrene solutions as Fig. 11 shows, where the inherent viscosities of the solutions of the polystyrene fraction with $\bar{M}_v = 2.22 \times 10^6$ in benzene, toluene, and butanone are plotted against $\dot{\gamma}$.⁴⁷ Both benzene and toluene are good solvents for polystyrene, while butanone is a poor one. The theoretical curves are calculated from equation (99) using the values of the parameters in Table VI. The values of β_2/η_0

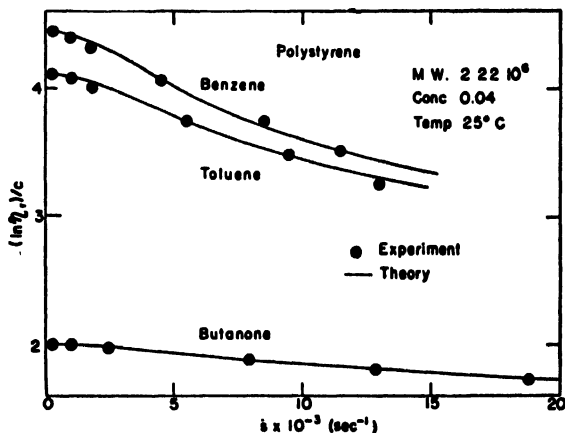


FIG. 11. Effects of solvent on inherent viscosity vs. shear-rate curves. Solute, polystyrene fraction with $\bar{M}_v = 2.22 \times 10^6$; concentration, 0.04 g./100 cc.; temperature, 25°C. The theoretical curves are calculated from equation (99) using the parameters in Table VI.

TABLE VI

THE EFFECTS OF SOLVENTS. SOLUTION SYSTEM: SOLUTE, POLYSTYRENE FRACTION WITH $\bar{M}_v = 2.22 \times 10^6$; SOLVENT, VARIED; CONCENTRATION, 0.04 g./100 cc.; TEMPERATURE 25° C.

Solvent	$\eta_0 \times 10^4$ poises	$x_0 + \frac{x_1\beta_1}{\alpha_1\eta_0}$	$\frac{x_2/\alpha_2}{\text{dynes}} \frac{\text{cm.}^2}{\text{cm.}^2}$	$\frac{x_3/\alpha_3}{\text{dynes}} \frac{\text{cm.}^2}{\text{cm.}^2}$	β_2/η_0	β_3/η_0	$\left(x_0 + \frac{x_1\beta_1}{\alpha_1\eta_0} - 1\right) \frac{c}{\text{cm.}^3/\text{g.}}$	$\frac{(x_2/\alpha_2)/c}{\text{dyne-cm. g.}}$	$\frac{(x_3/\alpha_3)/c}{\text{dyne-cm. g.}}$
Benzene	6.01	1.094	1.94	0	0.0521	...	2.35	48.5	0
Toluene	5.52	1.090	1.83	0	0.0487	..	2.25	45.8	0
Butanone*	3.93*	1.050	0.518	0	0.0501	..	1.25	13.0	0

* Methyl-ethyl ketone. N. Friend and W. D. Hargreaves, Phil. Mag. **34**, 643 (1943).

are about the same for these three solvents, while the values of x_2/α_2 for the first two are higher by a factor of 3.7 than the value for butanone. Thus, the difference in a good and poor solvent is in the factors, x_n/α_n , rather than in the factors β_n/η_0 .

The experimental curves⁴⁷ of $(\ln \eta_r)/C$ vs. s for the toluene and butanone solutions of the polystyrene fractions with $\bar{M}_v = 5.5 \times 10^6$ and 5.2×10^6 were compared with the theoretical curves which were calculated from equation (99), using the values for the parameters in Table VII. The agreement was satisfactory.¹⁸ One sees from this table that the aforementioned conclusion is also true for this case. That is, the β_2/η_0 values for the two solvents are approximately equal, while the x_2/α_2 value for toluene is larger by a factor of 8.2 than the value of butanone. The most striking thing is that the value of x_3/α_3 for toluene is 0.851, while for butanone it is nearly zero. We will discuss the effect of solvents in detail later.

(d) The Effect of Temperature. In Fig. 12, the experimental data⁴⁷ of $(\ln \eta_r)/C$ and at various temperatures for the benzene and toluene solutions of the polystyrene fractions with $\bar{M}_v = 2.22 \times 10^6$ and $\bar{M}_v = 9.2 \times 10^6$

TABLE VII

THE EFFECTS OF SOLVENTS. SOLUTION SYSTEM: SOLUTE, POLYSTYRENE FRACTIONS WITH $\bar{M}_v = 5.5 \times 10^6$ AND 5.2×10^6 ; SOLVENT, VARIED; CONCENTRATION, 0.03 g./100 cc.; TEMPERATURE, 65° C.

Solvent	$\eta_0 \times 10^4$ poises	$x_0 + \frac{x_1\beta_1}{\alpha_1\eta_0}$	$\frac{x_2/\alpha_2}{\text{dynes}} \frac{\text{cm.}^2}{\text{cm.}^2}$	$\frac{x_3/\alpha_3}{\text{dynes}} \frac{\text{cm.}^2}{\text{cm.}^2}$	β_2/η_0	β_3/η_0	$\left(x_0 + \frac{x_1\beta_1}{\alpha_1\eta_0} - 1\right) \frac{c}{\text{cm.}^3/\text{g.}}$	$\frac{(x_2/\alpha_2)/c}{\text{dyne-cm. g.}}$	$\frac{(x_3/\alpha_3)/c}{\text{dyne-cm. g.}}$
Toluene*	3.57	1.075	2.19	0.851	0.0552	4.12	2.50	73.0	28.4
Butanone*	2.74	1.079	0.268	~0	0.127	..	2.63	8.93	...

* The solutes of the toluene and butanone solutions are the polystyrene fractions with $\bar{M}_v = 5.5 \times 10^6$, and $\bar{M}_v = 5.2 \times 10^6$, respectively.

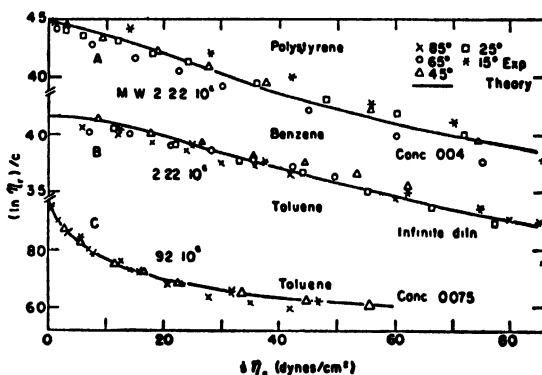


FIG. 12. Effects of temperature on inherent viscosity vs. reduced shear-rate curves for the polystyrene solution in "good" solvents. Curve A: solute, polystyrene fraction with $\bar{M}_n = 2.22 \times 10^6$; solvent, benzene; concentration, 0.04 g./100 cc. Curve B: solute, polystyrene fraction with $\bar{M}_n = 2.22 \times 10^6$; solvent, toluene; concentration, infinite dilution. Curve C: solute, polystyrene fraction with $\bar{M}_n = 9.2 \times 10^6$; solvent, toluene; concentration, 0.075 g./100. Theoretical curves are calculated from equation (99) using the parameters in Table VIII.

TABLE VIII
THE EFFECTS OF TEMPERATURE.

Experi- mental temper- atures ° C.	$\eta_0 \times 10^3$ poises	$x_0 + \frac{x_1\beta_1}{\alpha_1\eta_0}$	$\frac{x_2/\alpha_2}{\text{dynes}} \frac{\text{cm.}^2}{\text{cm.}^2}$	$\frac{x_3/\alpha_3}{\text{dynes}} \frac{\text{cm.}^2}{\text{cm.}^2}$	β_2/η_0	β_3/η_0	$\frac{1}{c} \left(x_0 + \frac{x_1\beta_1}{\alpha_1\eta_0} - 1 \right) \frac{(x_2/\alpha_2)}{c} \frac{(x_3/\alpha_3)}{c}$ $\frac{\text{cm.}^3}{\text{g.}} \frac{\text{dyne-cm.}}{\text{g.}} \frac{\text{dyne-cm.}}{\text{g.}}$		
Solution system: solute, polystyrene fraction with $\bar{M}_n = 2.22 \times 10^6$; solvent, benzene; concentration, 0.04 g./100 cc.; the parameters are reduced for temperatures.									
65, 45,	3.76, 4.65,	1.094	1.94	0	0.0521	.	2.35	48.5	0
25, 15	6.01, 7.00								
Solution system: solute, polystyrene fraction with $\bar{M}_n = 2.22 \times 10^6$; solvent, toluene; concentration, infinite dilution; the parameters are reduced for temperatures.									
							Limit value at $c \rightarrow 0$	Limit value at $c \rightarrow 0$	Limit value at $c \rightarrow 0$
85, 65,	2.98, 3.57,		.		0.0367		1.88	2.28	0
45,	4.45,								
25, 15	5.52, 6.23								
Solution system: solute, polystyrene fraction with $\bar{M}_n = 9.2 \times 10^6$; solvent, toluene; concentration, 0.075 g./100 cc.; the parameters are reduced for temperatures.									
85, 45,	2.98, 4.45,	1.43	2.44	0.243	0.129	1.34	5.73	32.5	3.24
15	6.23								

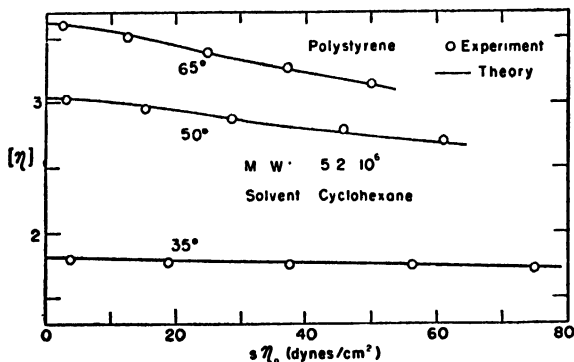


FIG. 13. Effects of temperature on inherent viscosity vs. reduced shear-rate curves for the polystyrene solutions in a "poor" solvent. Solute, polystyrene fraction with $\bar{M}_v = 5.2 \times 10^5$; solvent, cyclohexane; concentration, infinite dilution. The theoretical curves are calculated from equation (99) using the parameters in Table IX.

are plotted against reduced shear rates, $\eta_0 \dot{s}$. One sees that reduced curves for temperature are obtainable. That is, the parameters $x_0 + (x_1 \beta_1 / \alpha_1 \eta_0)$, x_n / α_n , and β_n / η_0 are independent of temperature. The theoretical curves are obtained from equation (99) using the values of the parameters in Table VIII. The agreement between theory and experiment is well within experimental error.

The experimental values⁴⁷ of $[\eta]$ at 65, 50, and 35° C. for the cyclohexane solution of the polystyrene fraction with $\bar{M}_v = 5.2 \times 10^5$ are plotted against $\eta_0 \dot{s}$ in Fig. 13. One sees that in this case a reduced curve for temperature such as in Fig. 12 is not obtainable. In the whole range of reduced shear rates, the higher the temperature the larger is the limiting intrinsic viscosity. The theoretical curves in Fig. 13 are obtained from equation (99) using the values of the parameters in Table IX. One sees from this table the fact that x_2 / α_2 increases with increasing temperature. This is in sharp contrast with the good solvent solutions like benzene and toluene solutions of poly-

TABLE IX

THE EFFECTS OF TEMPERATURE. SOLUTION SYSTEM. SOLUTE, POLYSTYRENE FRACTION WITH $\bar{M}_v = 5.2 \times 10^5$; SOLVENT, CYCLOHEXANE; CONCENTRATION, INFINITE DILUTION; TEMPERATURE, VARIED

Temperature ° C.	$\eta_0 \times 10^3$	$x_0 + \frac{x_1 \beta_1}{\alpha_1 \eta_1}$	$\frac{x_2 / \alpha_2}{\text{dynes}} \frac{\text{cm.}^3}{\text{cm.}^3}$	$\frac{x_3 / \alpha_3}{\text{dynes}} \frac{\text{cm.}^3}{\text{cm.}^3}$	β_2 / η_0	β_1 / η_0	$\frac{1}{c} \left(x_0 + \frac{x_1 \beta_1}{\alpha_1 \eta_0} - 1 \right) \frac{\text{cm.}^3}{\text{g.}}$	$\frac{(x_2 / \alpha_2)}{c} \frac{\text{cm.}}{\text{g.}}$	$\frac{(x_3 / \alpha_3)}{c} \frac{\text{cm.}}{\text{g.}}$
65	5.00	..	...	...	0.0600	...	2.43	1.98	~0
50	6.11	.	..	.	0.0524	.	2.17	1.68	0
35	7.52	..	.	.	0.0385	.	1.60	0.527	0

TABLE X

THE EFFECTS OF CONCENTRATION. SOLUTION SYSTEM: SOLUTE, POLYISOBUTYLENE FRACTION WITH $\bar{M}_v = 1.46 \times 10^6$; SOLVENT, CYCLOHEXANE; CONCENTRATION, VARIED; TEMPERATURE, 40° C. $\eta_0 = 7.01 \times 10^{-3}$

Concentration g./100 cc.	$x_0 + \frac{x_1\beta_1}{\alpha_1\eta_0}$	$\frac{x_2/\alpha_2}{\text{dynes}} \frac{\text{cm.}^3}{\text{cm.}^3}$	$\frac{x_3/\alpha_3}{\text{dynes}} \frac{\text{cm.}^3}{\text{cm.}^3}$	β_2/η_0	β_3/η_0	$\left(x_0 + \frac{x_1\beta_1}{\alpha_1\eta_0} - 1\right)$	$\frac{(x_2/\alpha_2)}{c}$	$\frac{(x_3/\alpha_3)}{c}$
						$\frac{c}{\text{cm.}^3}$ g.	$\frac{c}{\text{dyne-cm.}}$ g.	$\frac{c}{\text{dyne-cm.}}$ g.
0.05	1.274	0.119	0	0.264	.	5.48	2.38	0
0.06	1.339	0.143	0	0.264	.	5.65	2.38	0
0.08	1.428	0.170	0	0.264	.	5.35	2.12	0
0.13	1.732	0.291	0	0.264	..	5.63	2.24	0

styrene, where the values of x_n/α_n are independent of temperature, as mentioned in the beginning of this section. We will discuss the effect of temperature later.

(2) *Polyisobutylene solutions.* The non-Newtonian behavior of polyisobutylene solutions was observed by Fox *et al.*⁴³ We analyzed the experimental data of these authors using the equation

$$\log \eta_{sp} = \log \left(x_0 + \frac{x_1\beta_1}{\alpha_1\eta_0} - 1 + \sum_{n=2}^3 \frac{x_n\beta_n}{\alpha_n\eta_0} \frac{\sinh^{-1} \beta_n \dot{\gamma}}{\beta_n \dot{\gamma}} \right) \quad (100)$$

Equation (100) is obtained from equation (99) if the relation $\eta_{sp} = \eta_r - 1$ is introduced. The values of the parameters obtained from the data of Fox *et al.*⁴³ for the cyclohexane solutions of the polyisobutylene fraction with $\bar{M}_v = 1.46 \times 10^6$ in various concentrations are tabulated in Table X. In Fig. 14 the theoretical curves are reproduced from equation (100) using the parameters in Table X. One sees that the agreement between theory and experiment is satisfactory. As in the case of the polystyrene solutions in Fig. 10 and Table IV, the value of β_2 is independent of concentration; consequently, the slope of the theoretical curves is also independent of concentration. The experimental points approximate straight lines with a constant slope over the experimental range of shear rates. In fact, however, the theoretical curves are not straight lines, as one sees from Fig. 14, although they describe the experiments very well. Ferry^{49a} found non-Newtonian flow in the system, polystyrene-xylene, in the concentrations of 15.4 to 52.3% polymer, and noticed the linearity between the viscosities and shear stresses. The approximate linearity has often been mentioned as evidence against the simple hyperbolic sine function theory of viscosity, because according to the latter, the early deviation from Newtonian flow should result from a term containing the square of shear rate or shear

^{49a} J. D. Ferry, *J. Am. Chem. Soc.* **64**, 1330 (1942).

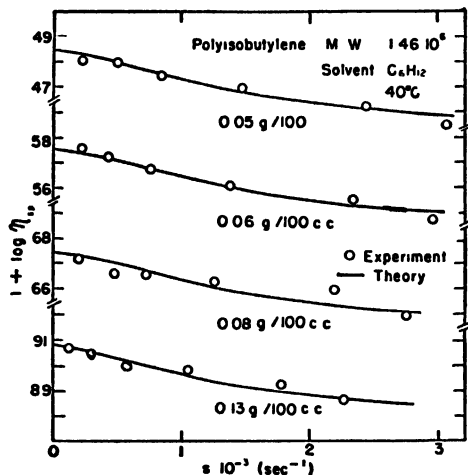


FIG. 14. Effects of concentration on the curve for $\log \eta_{sp}$ vs. shear rate. Solute, polyisobutylene fraction with $\bar{M}_v = 1.46 \times 10^6$; solvent, cyclohexane; temperature, 40°C . Theoretical curves are calculated from equation (100), using the parameters in Table X.

stress.^{35, 43} The so-called linearity is, however, of an approximate nature as already mentioned, and is explained very well from our theory.

Fox *et al.*⁴³ studied the solvent dependence of $\log \eta_{sp}$ of the solutions of the polyisobutylene fraction with $\bar{M}_v = 1.46 \times 10^6$. The theoretical curves which are not shown here were calculated from equation (100), using the values of the parameters in Table XI. The agreement between theory and experiment is good also in this case.¹⁸ The solvent power of the solvents in Table XI for polyisobutylene is in the following order: carbon tetrachloride, diisobutylene, toluene, benzene. From Table XI one sees that the values of β_2/η_0 are approximately constant for the four solutions while the values of

TABLE XI

THE EFFECTS OF SOLVENT. SOLUTION SYSTEM: SOLUTE, POLYISOBUTYLENE FRACTION WITH $\bar{M}_v = 1.46 \times 10^6$; SOLVENT, VARIED; CONCENTRATION, 0.08 ~ 0.12 g./100 cc.; TEMPERATURE, 40°C .

Solvent	$\eta_0 \times 10^3$ poises	Conc. g./ 100 cc.	$x_0 + \frac{x_1\beta_1}{\alpha_1\eta_0}$	$\frac{x_2/\alpha_2}{\text{dynes}} \text{ cm.}^2$	$\frac{x_3/\alpha_3}{\text{dynes}} \text{ cm.}^2$	β_2/η_0	β_3/η_0	$\left(x_0 + \frac{x_1\beta_1}{\alpha_1\eta_0} - 1\right) \frac{(x_2/\alpha_2)}{c} \frac{(x_3/\alpha_3)}{c}$ cm. ³ /g.	$\frac{c}{\text{dyne-cm.}}$	$\frac{(x_3/\alpha_3)}{c} \frac{(x_2/\alpha_2)}{c}$ g.
CCl_4	7.39	0.10	1.453	0.687	0	0.135		4.53	6.87	0
$\text{C}_6\text{H}_5\text{CH}_3$	4.67	0.12	1.377	0.0673	0	0.248	..	3.14	0.561	0
DIB*	4.22*	0.09	1.301	0.0936	0	0.236	.	3.34	1.04	0
C_6H_6	4.94	0.08	1.163	0.0221	0	0.217	..	2.04	0.276	0

* Diisobutylene. E. B. Evans, J. Inst. Petroleum Technol. **24**, 321 (1938).

TABLE XII

THE EFFECTS OF SOLVENT. SOLUTION SYSTEM: SOLUTE, POLYISOBUTYLENE FRACTION WITH $\bar{M}_v = 15 \times 10^5$; SOLVENT, VARIED; TEMPERATURE, 40° C.

<i>Solvent</i>	$\eta_0 \times 10^3$ poises	$x_0 + \frac{x_1\beta_1}{\alpha_1\eta_0}$	$\frac{x_2/\alpha_2}{\text{dynes}} \text{ cm.}^2$	$\frac{x_1/\alpha_1}{\text{dynes}} \text{ cm.}^2$	β_2/η_0	β_1/η_0
C ₆ H ₁₂	7.01	1.292	0.755	0.0478	0.220	2.51
C ₆ H ₅ CH ₃	4.67	1.207	0.381	0.0271	0.244	2.29

$(x_2/\alpha_2)/C$ are in the order of the solvent power. We have already observed this same fact in the solutions of the polystyrene fractions in benzene, toluene, and butanone (see Tables VI and VII).

Another example of the solvent effect is found in the literature.⁴³ The solute is the polyisobutylene fraction with $\bar{M}_v = 15 \times 10^5$, and the solvents are cyclohexane and toluene. The values of the parameters for the theoretical curves which are not shown here are tabulated in Table XII. Again the difference between a better (C₆H₁₂) and a poorer solvent (C₆H₅·CH₃) does not appear in the values of β_n/η_0 , but only in those for x_n/α_n (cf. ref. 18).

(3) *X-518 GR-S rubber solutions*. Bestul and Belcher³⁶ measured the flow rates of the solutions of X-518 GR-S rubber (24 % styrene and 76 % butadiene copolymer) in alpha-methylnaphthalene. We calculate the reduced shear rates $\dot{\gamma}$, by multiplying their shear rates by $\exp(\Delta H^\ddagger/RT)$. The activation heat $\Delta H^\ddagger$ is 3.9 and 9.75 kcal. for the 10 % and 50 % polymer solution, respectively. The experimental data of $\log \dot{\gamma}$, are plotted against the values of $\log f$; reduced curves for temperature were obtained for the 50 % and for the 10 % polymer solutions. Using the values of the parameters in Table XIII, these two curves were exactly reproduced (Fig. 15) from the

TABLE XIII

THE VALUES OF THE PARAMETERS.* SOLUTION SYSTEM: SOLUTE, X-518 GR-S RUBBER WITH $\bar{M}_v = 2 \times 10^5$; SOLVENT; ALPHA-METHYLNAPHTHALENE; TEMPERATURE, VARIED

Con- centration %	Experimental temperatures ° C.	$(\frac{x_1}{\alpha_1}) \beta_1$ poises	$(\frac{x_1}{\alpha_1}) 10^{-3}$ $\frac{\text{dyne}}{\text{cm.}^2}$	$(\frac{x_2}{\alpha_2}) 10^{-3}$ $\frac{\text{dyne}}{\text{cm.}^2}$	$(\frac{x_3}{\alpha_3}) 10^{-3}$ $\frac{\text{dyn}}{\text{cm.}^2}$	$\beta_{1(r)} \cdot 10^7 \text{ sec.}$	$\beta_{2(r)} \cdot 10^5 \text{ sec.}$	$\beta_{3(r)} \cdot 10^3 \text{ sec.}$	$\frac{\Delta H^\ddagger}{\text{kcal. mol.}}$
10	50, 40, 30	0.535	.	0.0745	2.29	.	13.7	2.97	3.9
50	50, 40	...	1.44	1.09	0.0	4.23	2.45	...	9.75
100	50, 40		2.71	5.68	0.0	0.927	0.405	...	12.5

* The parameters $\beta_{n(r)}$ in this table are reduced for temperature by dividing the ordinary β , which is equal to $1/(2\lambda k'/\lambda_1)_n$, by $\exp(\Delta H^\ddagger/RT)$. The activation heat, 3.9 kcal. for the 10% solution, is approximately equal to the activation heat for the viscous flow of alpha-methylnaphthalene.

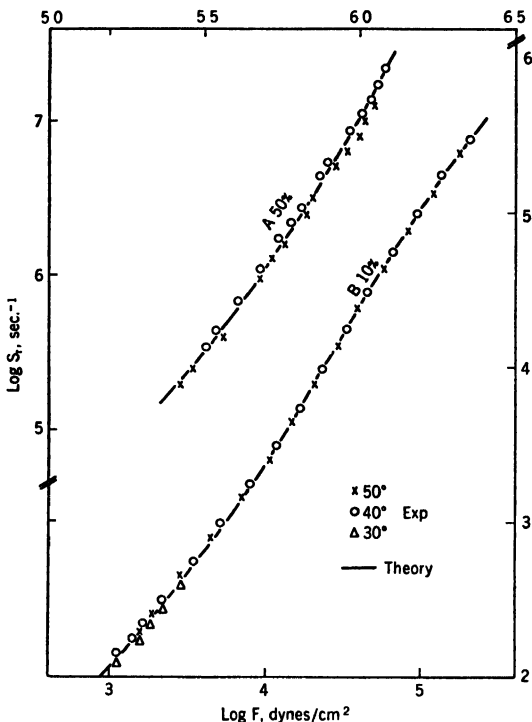


FIG. 15. Logarithm of reduced shear-rate vs. logarithm of shear-stress for solutions of X-518 GR-S rubber with $\bar{M}_v = 2 \times 10^5$ in alpha-methylnaphthlene. Curve A is for the 50% solution, and is referred to the left and top scales. Curve B is for the 10% solution of GR-S rubber, and is referred to the right and bottom scales.

following two equations, respectively:

$$f = \frac{x_2}{\alpha_2} \sinh^{-1} \beta_2 \dot{s} + \frac{x_1}{\alpha_1} \sinh^{-1} \beta_1 \dot{s} \quad (101)$$

$$f = \frac{x_3}{\alpha_3} \sinh^{-1} \beta_3 \dot{s} + \frac{x_2}{\alpha_2} \sinh^{-1} \beta_2 \dot{s} + \frac{x_1 \beta_1 \dot{s}}{\alpha_1} \quad (102)$$

Equations (101) and (102) are derived from equations (89) and (85), respectively. In Table XIII, the data for the pure X-518 GR-S, which was reported in Section 1b(3) of Applications, are included for the comparison with the solution data. The 10% solution has the Newtonian group, while the 50% solution and the pure polymer do not have this group. Thus the concentrated solution behaves like the solid plastic, while the dilute solution behaves similar to the solutions of polystyrene fractions with the three groups of flow units. From Table XIII, we see also the following facts: (i) the factors, x_1/α_1 and x_2/α_2 , increase with concentration. (ii) The activa-

tion heats increase with concentration. (iii) The reduced values of the β_1 and β_2 factors decrease with concentration.^{49b} If we assume that the factors, α_1 and α_2 , do not change with concentration, the increase of the parameters, x_1/α_1 and x_2/α_2 , with concentration is natural. The number of bonds between a flow unit and its neighbors increases with concentration. Consequently, the heat of activation increases with concentration. The $\beta_{n(r)}$ parameter, which is the quantity reduced for temperature, is given as follows:

$$\beta_{n(r)} = \frac{\exp(-\Delta S_n^\ddagger/R)}{2(kT/h)(\lambda/\lambda_1)_n}$$

The decrease of β_n with increasing concentration indicates that $\Delta S_n^\ddagger$ increases with concentration. This fact indicates that, in activated states, the higher the concentration the more bonds are broken. This will be natural if one considers that the activation heat increases with concentration, and that this increase is due to the increase of the bonds between a flow unit and its neighbors with increasing concentration.

(4) *Lime-base grease*. Blott and Samuel⁵⁰ measured the flow rates of the lime-base greases, which are a kind of colloidal solution of calcium soap in oil. Their results are well explained by one Newtonian and one non-Newtonian group of flow units, as shown in Fig. 16. The experimental curves are exactly calculable using the parameters in Table XIV from the formula

$$f = \frac{x_1\beta_1}{\alpha_1} \dot{s} + \frac{x_2}{\alpha_2} \sinh^{-1} \beta_2 \dot{s} \quad (103)$$

which is a special case of equation (101). They used four different kinds of grease, A, B, C, and D; the composition of the greases is shown in Table XIV. The viscosities of the four greases are in the order $C > D > B > A$, in the range of $\dot{s}$ covered by these experiments. Among the factors in Table XIV only the values of x_2/α_2 accord with this order, while the factor β bears no relation to this order. We reached the same conclusion as this before regarding the effect of solvents on the viscosities of the solutions of styrene and polyisobutylene [see Sections 2b(1)(c) and 2b(2) of Applications].

Stevens⁵¹ measured flow rates of 15 % Napalm in kerosene, 3 % sodium carboxymethyl cellulose in water, and 33 % hydrated lime in water, and ex-

^{49b} The facts, (ii) and (iii), are contrasted with the case in dilute solutions (0.01 ~ 0.13 per cent) of polystyrene and polyisobutylene, where the values of $\Delta H^\ddagger$ and β are independent of concentration. See Secs. 2b(1)(b) and 2b(2) of Applications.

⁵⁰ J. F. T. Blott and D. L. Samuel, *Ind. Eng. Chem.* **32**, 68 (1940).

⁵¹ W. E. Stevens, dissertation, University of Utah (1953); W. E. Stevens, E. B. Christiansen, and E. W. Ryan, *Am. Inst. Chem. Engrs. J.* **1**, 544 (1955).

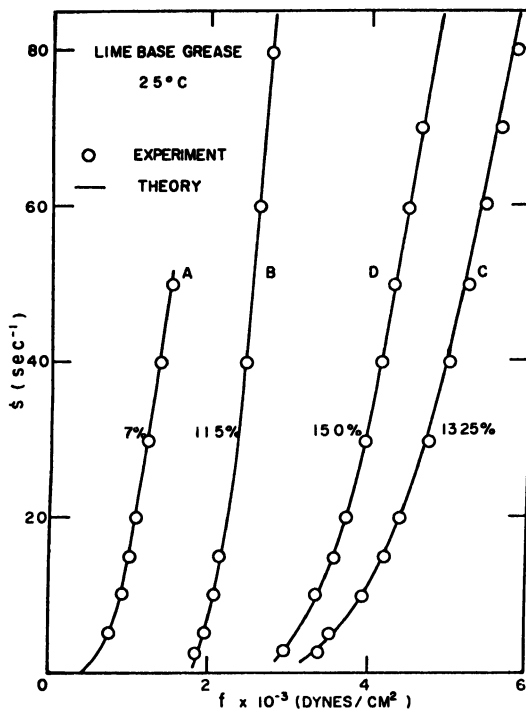


Fig. 16. Shear-rate vs. shear stress for lime base grease. The percentages of lime in greases A, B, C, and D are 7, 11.5, 13.25, and 15.0, respectively.

plained his flow curves by the Powell-Eyring equation,⁴² which is a special case of equation (103).

c. Discussion

(1) *Viscosity equation reduced for temperature.* The viscosities of high polymeric systems dissolved in good solvents are generally reduced for temperature by dividing them by the viscosities of solvents. Three examples for this are shown in Fig. 12. The reducibility indicates that the activation heat for the flow process of polymeric flow units is the same as that for the

TABLE XIV
THE PARAMETERS FOR THE LIME-BASE GREASES AT 25° C

Kind of grease	Percentage of lime	η_{oil} at 25° poises	$(x_1/a_1)\beta_1$ poises	$\frac{x_1/a_2}{\text{dynes}} \text{ cm}^2$	$\beta_2 \times 10^{-3} \text{ sec.}$
A	7	2.74	9.94	115	0.0456
B	11.5	0.29	4.80	140	86.6
C	13.25	1.52	12.6	475	0.152
D	15.0	0.29	11.34	297	2.68

solvent. That is, the rate-determining step for the solute unit involves the jump of the solvent molecule. The solvent molecule must move in the opposite direction, while the flow unit moves forward to fill out the space vacated by the solvent molecule. The same phenomenon occurs in the diffusion of a large molecule in a solvent of small molecules.^{1b} This will be likewise true in poor solvents for polystyrene such as cyclohexane. The nonreducibility in this case (see Fig. 13) is due to the structure change accompanying the unfolding of polystyrene molecules with increasing temperature.

The reducibility of relative viscosities, η/η_0 , is limited to low concentrations. Thus we found that the $\dot{s}$ data for the 10% solution of the X-518 GR-S rubber with $\bar{M}_v = 2 \times 10^5$ in alpha-methylnaphthalene are reduced⁵² by $\dot{s}\eta_0$, while the $\dot{s}$ data for the 50% solution of the polymer are not reduced by $\dot{s}\eta_0$, but are reduced by $\dot{s} \exp(\Delta H^\ddagger/RT)$, where $\Delta H^\ddagger$ is the activation heat for the flow of the solutions, but not of the solvent (see Table XIII). The irreducibility of the quantity, η/η_0 , for temperature in concentrated solutions and the increase of the activation heat for the flow of the solutions with concentration shows that the solvent molecules trapped between the polymer molecules flow with difficulty. In highly concentrated solutions, the solvent molecules will move together with the polymer flow units. Thus the 50% solution behaves like the pure solid of X-518 GR-S rubber.

(2) *Changes in the types of flow units with conditions.* We have already seen examples in which the distribution over types of flow units changes with conditions. Thus, the number of types in a flow process is a function of the molecular weights of polymer molecules, solvents, temperature, and concentration. We have pointed out the fact that molecules of low molecular weights behave as Newtonian flow units while those of high molecular weights show in addition the non-Newtonian behavior of Groups 2 and 3 (see Fig. 9 and Tables II and III). We postulated that Group 1 units are bonded loosely with their neighbors, Group 2 units are bonded firmly, and Group 3 units are still more firmly bonded. One may readily see that the larger the molecule, the more are the bonds formed with the neighbors. Thus, the probability for having all three types of flow units is larger for the molecules with high molecular weights than those with low molecular weights. In other words, the probability for the appearance of Groups 2 and 3 decreases with decreasing molecular weight.

We have seen that in a good solvent a polymer molecule has larger x_n/α_n values than in a poor solvent (see Fig. 11 and Tables VI, VII, XI, and XII). We assume that the factor α_n is about constant irrespective of the solvents,

⁵² The viscosities, η_0 , of alpha-methylnaphthalene at 50°, 40°, and 30° C are 1.74×10^{-2} , 2.11×10^{-2} , and 2.61×10^{-2} poise, respectively [E. B. Evans, *J. Inst. Petroleum Technol.* **24**, 573 (1938)].

i.e., that the cross-sectional area, $\lambda_2\lambda_3$, of a flow unit and the jumping distance, λ , are about constant in different solvents. Then, the factor x_n/α_n is proportional to the surface concentration of the n th type of flow unit. Thus, the increase of the x_n/α_n value in a good solvent implies the increase of the flow units. This is only possible if a nonbonded (folded) flow unit unfolds, and if it makes bonds with its neighbors. Thus, a polymer molecule extends more in a good solvent than in a poor one. Consequently, the polymer molecule in a good solvent has more probability of making firm bonds with the neighbors. We saw in Table VII that in toluene the polystyrene fraction with about $\bar{M}_v = 5.4 \times 10^6$ shows the non-Newtonian behavior of flow units of Group 3 as well as Groups 1 and 2, while in butanone it shows only the behaviors of Groups 1 and 2. This will be a natural phenomena from the foregoing viewpoint.

We have seen that the x_n/α_n value for a polymer solution in a poor solvent increased with temperature, while they remained constant in a good solvent. We assume that, as is so true in solid plastic systems,⁸ the α_n factor does not change with temperature. (This is also theoretically true as mentioned in Section 1c(2) of Applications.) Then, the x_n/α_n value is proportional to the surface concentration of the n th type of flow unit. Thus, the increase of the x_n/α_n value with temperature indicates that in a poor solvent the polymer molecules unfold at high temperatures, while they fold with decreasing temperatures. Thus, one may expect that at sufficiently high temperatures a polymer molecule in a poor solvent will behave quite differently than at low temperatures. In an extreme case, the polymer molecule will show non-Newtonian nature at high temperatures. This is clearly seen from Table III, that is, comparison of the flow data of solutions of the polystyrene fraction with $\bar{M}_v = 2.4 \times 10^6$ in cyclohexane at 35 and 65° C. shows that at the lower temperature the solution is a Newtonian fluid while at the higher temperature it is non-Newtonian. The data for the fraction of $\bar{M}_v = 5.2 \times 10^6$ at 35 and 65° C. show that the solution at 35° shows a slightly non-Newtonian nature resulting from Group 2 while it exhibits pronounced non-Newtonian nature caused by both Group 2 and Group 3 at 65° C. The same conclusion is obtained from a comparison of the two data for the fraction with $\bar{M}_v = 9.2 \times 10^6$.

We have known that the values of x_2/α_2 and x_3/α_3 increase at a rate more than proportional to the concentration of the polymer. Consequently, one may predict that the number of types of flow units will change with polymer concentration. The comparison of the flow data for the fraction with $\bar{M}_v = 5.2 \times 10^6$ at 65° in Table III and the corresponding data in Table IX indicates that this is true. One sees that the former, which are the data at the concentrations of 0.06 g./100 cc., are due to the presence of Groups 1, 2, and 3, while the latter, which are the data at infinite dilution, involve only Groups 1 and 2.

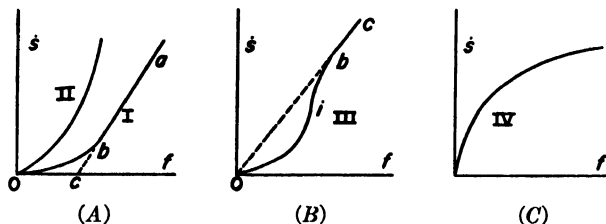


FIG. 17. Four types of flow curves: (A) flow curves of a system without structural change; (B) flow curves of a system with structural change; (C) flow curves of a dilatant system.

Bueche⁵³ treats the flow properties of high polymeric systems from a different point of view. Readers are referred to his papers.⁵³

3. DEFORMABLE SYSTEM

a. Classification of Flow Curves

There are several types of non-Newtonian curves for which the flow rate, $\dot{s}$, is plotted against stress, f . Curve I in Fig. 17A shows *nearly* Newtonian behavior at high stresses and high rates of flow, while it shows non-Newtonian behavior at low values of f and $\dot{s}$. Point c is the crossing of the Newtonian line of Curve I, ab , with the f -axis. A Bingham body has the flow curve, $ocba$. Curve II does not show Newtonian behavior even at high stresses and high rates of flow. Curve III in Fig. 17B has an inflection point, i ; the upper branch above the latter, bc , is a straight line, whose extension passes through the origin as shown in Fig. 17B. This figure also shows that a non-Newtonian system at low stresses and rates of flow changes over completely to a Newtonian one at high values of f and s . In this respect, Curve III is different from Curve I where the straight line, ab , is due to Newtonian units with a negligible non-Newtonian contribution to the viscosity because of the vanishing of the factor $\sinh^{-1}(\beta\dot{s})/(\beta\dot{s})$ at high $\dot{s}$ [cf. equation (6)]. This effect should not be confused with the notion that non-Newtonian units become Newtonian at high rates of flow. There is another type of behavior, dilatancy, in Curve IV of Fig. 17C, where the viscosity increases with increasing f and $\dot{s}$. Dilatancy will not be considered further at this time.

If we plot flow data on a double logarithmic scale, the two types of flow curve V and VI in Fig. 18 are obtained, where V has an inflection while VI has no inflection. It is of interest to note that curves of the type I and III plotted on a double logarithmic scale are both of the type V in Fig. 18, while type II transforms to the type VI. Among the flow curves previously mentioned, those involving Newtonian units belong to the type I while those involving only non-Newtonian units belong to type II. So far, we have not treated the flow curves belonging to our type III and IV. The fact that

⁵³ F. Bueche, *J. Chem. Phys.* **22**, 603 (1954); **22**, 1570 (1954).

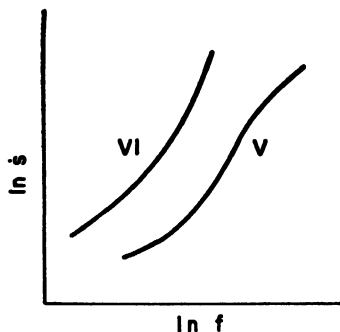


FIG. 18. Two types of flow curves represented by logarithm of shear rate versus logarithm of stresses.

the flow curves of type I transform to type V in a double logarithmic plot is exemplified by curve A in Fig. 6 (Saunders-Treloar's data for masticated natural rubber) and Curve B in Fig. 15 (10% solution of GR-S in α -methyl naphthalene). It is noteworthy that the S-shaped curve in a double logarithmic plot is obtained only where one deals with concentrated solutions and in a wide range of $\dot{\gamma}$. When the concentrations of solutions are too small, the S-shaped curve is hardly recognizable. There are many examples of type I flow curves in the literature.⁵⁴⁻⁵⁶

The thixotropic behavior of type III systems illustrated in Fig. 17B obviously differs from nonthixotropic substance illustrated as type I in Fig. 17A. Type I behavior has frequently been erroneously interpreted as thixotropy because in the double logarithmic plots there is a similar appearance. The term *Ostwald curve* will be used only for type III behavior, since it alone exhibits W. Ostwald's postulated structural change.

b. Ostwald Curve

Reiner and Schoenfeld-Reiner,⁵⁷ and Reiner^{58, 59} studied solutions of natural rubber dissolved in toluene, and obtained the Ostwald curves. Figure 19 exemplifies their results, where the reduced shear rates $\dot{\gamma}_r (= \eta_0 \dot{\gamma})$ at 20° C. for the 1.69 volume percent natural rubber solution is plotted against stress, f . Reiner studied the effect of concentration on the shape of the flow curves, and found that at a low concentration such as 0.08% (volume) the inflection point disappeared. Philippoff^{54, 60} reinvestigated the solution system, and presented his results on a double logarithmic scale. By plotting his re-

⁵⁴ W. Philippoff, "Viscosität der Kolloide." Dresden, 1942.

⁵⁵ H. Umstätter, "Strukturmechanik." Steinkopff, Dresden, 1948.

⁵⁶ K. Edelman, *Proc. 2nd Intern. Rheol. Congr., Oxford*, p. 107 (1954).

⁵⁷ M. Reiner and R. Schoenfeld-Reiner, *Kolloid-Z* **65**, 44 (1933).

⁵⁸ M. Reiner, *Physics* **5**, 342 (1934).

⁵⁹ M. Reiner, "Deformation and Flow." Lewis, London, 1949.

⁶⁰ W. Philippoff, *Kautschuk* **12**, 124 (1936).

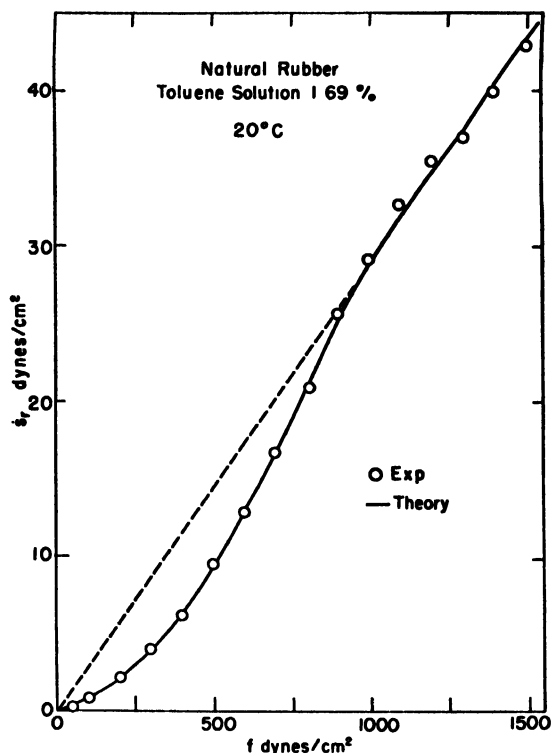


FIG. 19. Flow curve for natural rubber dissolved in toluene.

sults on a linear scale, one finds that Philippoff confirmed Reiner's results. Ostwald curves are also obtained from the data of Edelmann⁵⁶ for nitrated American raw cotton dissolved in butyl acetate, and from Philippoff's data^{54, 55} for Oppanol dissolved in decalin.

We analyze Fig. 19 using equations (41) with only two types of flow units. The following values of the parameters occurring in (41) are obtained:⁶¹

$$K = 9.00$$

$$c = G\tau^2/2 = 2.00 \times 10^{-3}$$

$$a_1\beta_1/\alpha_1 = 34.5$$

$$a_2/\alpha_2 = 0.5556 \times 10^3$$

$$\beta_2 = 2.57$$

The theoretical curve in Fig. 19 is obtained by calculations substituting

⁶¹ T. Ree, S. J. Hahn, and H. Eyring, to be published.

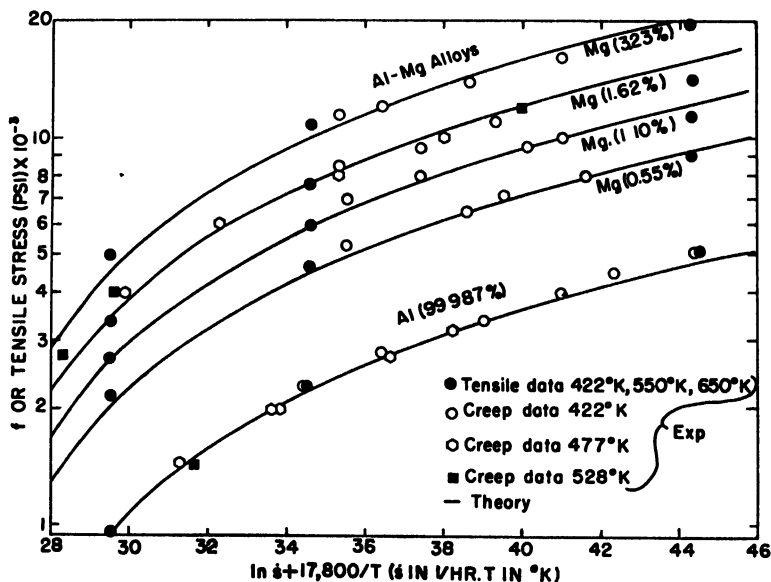


FIG. 20. Creep curves for pure aluminum and for aluminum-magnesium alloys.

the above values into equation (41). The agreement between theory and experiment is satisfactory. From the above parametric values, we can calculate for the shear modulus of rubber $G \approx 10^6$. This value is reasonable for rubber.⁶¹

4. METALS

The relation between stresses vs. the rates of secondary creep of metals are described by equation (33). A few examples will be given below.

In Fig. 20 the creep data of Sherby and Dorn³⁸ for pure aluminum (99.987%) and Al-Mg alloys (atomic percentage of Mg being 0.55, 1.10, 1.62, and 3.23) are reproduced. They found that the activation heat for the secondary creep of these metals is 35.8 kcal., irrespective of the composition. Thus the shear rates are reduced by multiplying by $\exp(35,800/RT)$. In Fig. 20 values of $\log f$ are plotted against $\ln \dot{\epsilon}$, the ultimate tensile stresses in the ordinate referring to the tensile data. We analyzed the data, and found that both pure aluminum and Al-Mg alloys are represented by one type of flow units, i.e.,

$$f = \frac{x_2}{\alpha_2} \sinh^{-1}(\beta_2 \dot{\epsilon})$$

where $x_2 = 1$ and $x_1 = 0$. The values of x_2/α_2 and β_2 are summarized in Table XV. From the latter one sees that for Al-Mg alloys the x_2/α_2 value

TABLE XV
PARAMETERS FOR ALUMINUM AND ITS ALLOYS

Sample	Temperature* °K	$\frac{x_2}{\alpha_2} \times 10^{-2}$	$\beta_2 \times 10^3$	$\frac{x_1}{\alpha_1} \times 10^{-2}$	$\beta_1 \times 10^{10}$
Al (99.987%)	C. 422, 477, 528	2.57	3.97	0	—
	T. 422, 550, 650				
Al-Mg (0.55%)	C. 422	4.86	5.15	0	—
	T. 422, 550, 650				
Al-Mg (1.10%)	C. 422	6.40	5.15	0	—
	T. 422, 550, 650				
Al-Mg (1.62%)	C. 422, 477, 528	8.30	5.15	0	—
	T. 422, 550, 650				
Al-Mg (3.23%)	C. 422	10.80	5.15	0	—
	T. 422, 550, 650				
Al-Cu (0.10%)	C. 422, 477, 528	2.45	17.7	2.53	2.64
	T. 422, 550, 650				
Al-Zn (1.62%)	C. 422, 477, 528	2.04	19.9	1.11	1.83
	T. 422, 550, 650				
Al (25-0)†	C. 408, 450, 491, 533	2.25	881	1.08	3.51
Al (99.995%)§	C. 477, 533, 644, 755, 866	0.614	548	2.70	7820
Al (2S-H18)	C. 533, 644, 755, 866	0.873	0.524	2.70	0.02

* Under this heading, the temperatures are shown under which creep and tensile tests (abbreviated by C. and T. in this table, respectively) were conducted.

† Annealed at 650° F. for 1 hour.

§ With various grain sizes.

|| Annealed at 1000° F. for 3 hours.

increases about linearly with Mg content, while the β_2 value remains constant.

In Fig. 21 the data³⁸ for Al-Cu alloy (Cu: 0.10 atomic percent) and Al-Zn alloy (Zn: 1.62 atomic percent) are reproduced. In these cases, two types of flow units are needed. The parametric values for x_1/α_1 , β_1 , x_2/α_2 , and β_2 are listed in Table XV. The theoretical curves are calculated from equation (33) for two types of units using the parametric values in Table XV. The same analysis was conducted for 2S-O Aluminum wire,^{38, 62} high purity aluminum (99.995 %) with various grain sizes,^{38, 63} and 2S-H18 Aluminum^{38, 63} (annealed at 1000° F. for three hours, $\Delta H^\dagger$ for this material was 57.4 kcal.). All of these materials are described by equation (33) with two types of flow units. The parametric values are summarized in Table XV.

At present, we are not in a position to draw definite conclusions from the data in Table XV. We believe, however, that this kind of data is very important for understanding mechanical properties of metals.

⁶² D. I. Sinizer and C. W. MacGregor, Technical Report, Massachusetts Institute of Technology, ONR, Contract N5-ori-78, T. O. XIII, NR 031-126 (1951).

⁶³ I. S. Servi and N. J. Grant, *J. Metals* **3**, 909 (1951).

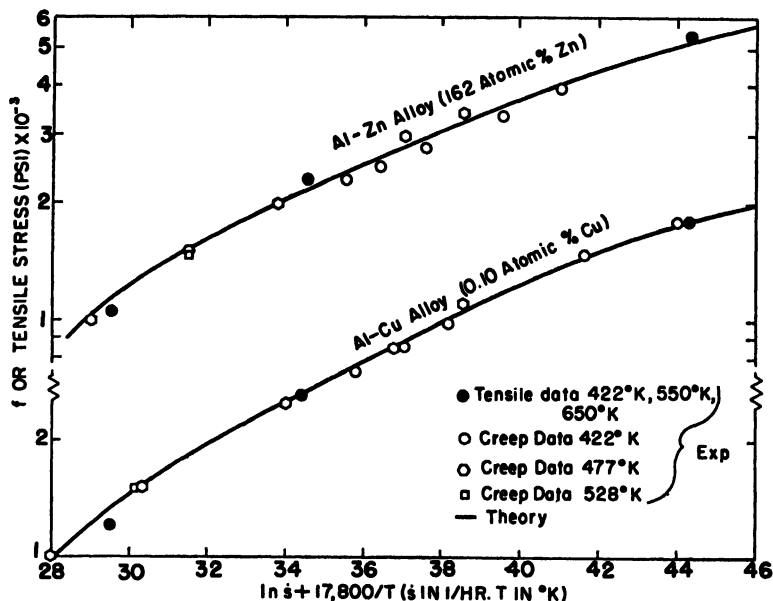


FIG. 21. Creep curves for the alloys of aluminum-zinc and of aluminum-copper.

Creep of metals is caused by many factors—for example, movement of dislocations and diffusion through grain boundaries. We interpret our results as the movement of dislocations, the high activation heat being an evidence for this idea. There are two types of dislocations—*edge* and *screw* dislocations.⁶⁴⁻⁶⁶ There are considerable variations even in dislocations of the same kind. Thus we may assume the same general sort of distribution of flow units (dislocations) in metals as in plastics. At present we are not sure whether the two types of flow units discussed above belong to the same kind of dislocations with varying degrees of imperfections or whether they belong to different kinds, namely, edge dislocations and screw dislocations.

5. DIFFUSION IN SOLUTION

We calculate the ξ values from equation (64). The results on the diffusion of iodine in various solvents⁶⁷ are summarized in Table XVI. One sees that ξ , the average number of viscous relaxations required for one diffusion relaxation, is 6.3. The diffusion data of bromoform in various solvents⁶⁸ are

⁶⁴ W. T. Read, Jr., "Dislocations in Crystals." McGraw Hill, New York, 1953.

⁶⁵ A. H. Cottrell, "Dislocations and Plastic Flow in Crystals." Oxford Univ. Press, New York, 1953.

⁶⁶ F. B. Cuff, Jr., and L. McD. Schetky, *Sci. American* **193**, No. 1, 80 (1955).

⁶⁷ C. C. Miller, *Proc. Roy. Soc. (London)* **A106**, 724 (1924).

⁶⁸ H. S. Taylor, *J. Chem. Phys.* **6**, 331 (1938).

TABLE XVI*
DIFFUSION OF IODINE IN VARIOUS SOLVENTS AT 19.9° C.

<i>Solvent</i>	<i>V (c.c.)</i>	<i>D</i> × 10 ⁵	<i>η</i> × 10 ⁵	<i>ξ</i>
CHBr=CHBr	87	0.8319	1714	5.40
CBr ₂ =CBr ₂	117	0.1823	9797	3.91
CHCl ₃	81	2.118	580	6.42
CCl ₄	97	1.362	958	5.69
CCl ₄	97	1.336†	958	5.80
Ethyl acetate	98	2.151	457	7.53
isomamyl acetate	149	1.239	872	5.96
C ₆ H ₅ OC ₂ H ₅	126	0.9754	1318	5.72
C ₆ H ₅ OCH ₃	109	1.130	1080	5.85
C ₆ H ₅ Br	105	1.201	1133	5.32
m-CH ₃ C ₆ H ₄ CH ₃	123	1.682	643	6.35
CH ₃ OH	40	1.819	611	8.99
Benzene	89	1.932	642	6.16
Toluene	106	1.951	582	6.35
Heptane	140	2.761	481	4.95
CS ₂	60	3.120	376	7.43
Acetic acid	57	1.026	1253	6.90

* All the data for *V* (molecular volume), *D*, and *η* are taken from reference 67. It is known that the aromatic compounds complex with iodine.

† See ref. 23.

TABLE XVII*
DIFFUSION OF BROMOFORM IN VARIOUS SOLVENTS 20° C.

<i>Solvent</i>	<i>V (c.c.)</i>	<i>D</i> × 10 ⁵	<i>η</i> × 10 ⁵	<i>ξ</i>
Ether	103.9	3.391	234.5	9.13
Acetone	73.47	2.685	324	9.38
Methyl alcohol	40.48	1.933	582	8.84
Benzene	88.86	1.690	649	6.98
Ethyl alcohol	58.36	0.9664	1187	7.67
Propyl alcohol	72.28	0.7697	1920	5.57
Amyl alcohol	107.7	0.5162	3990	3.48

* See ref. 68.

summarized in Table XVII. The average *ξ* value is 7.3 in this case. Table XVIII represents the diffusion of various solutes in benzene.^{1b, 69} The mean value of *ξ* is 6.4. The diffusion data of various solutes in water⁶⁹ in Table XIX give 15.5 for the average *ξ* value. This is exceedingly large compared to the ordinary value of 6. This large value of *ξ* suggests that the Einstein treatment of a large solvated sphere moving in a continuum is probably be-

⁶⁹ A. E. Stearn, E. M. Irish, and H. Eyring, *J. Chem. Phys.* **44**, 981 (1940).

TABLE XVIII
DIFFUSION OF VARIOUS SOLUTES IN BENZENE AT 7.5° C.

<i>Solute</i>	<i>V (c.c.)</i> †	<i>D</i> × 10 ⁸ *	$\eta \times 10^3$ †	ξ
CCl ₄	87.5	1.51	790	6.17
Iodoform	87.5	1.12	790	8.32
Methyl iodide	87.5	2.06	790	4.53
<i>n</i> -Amyl iodide	87.5	1.41	790	6.61
Ethylene chloride	87.5	1.77	790	5.27
Bromobenzene	87.5	1.45	790	6.43
1:2:4-Trichlorobenzene	87.5	1.34	790	6.95
Naphthalene	87.5	1.19	790	7.83

* See ref. 69 and 1b.

† See ref. 48.

coming appropriate. Hydrogen bonding, as might be expected, has no special effect on ξ . Thus Li and Chang²² find the ξ values for the process of self-diffusion in water, methyl alcohol, ethyl alcohol, *n*-propyl alcohol, isopropyl alcohol, *n*-butyl alcohol and *t*-butyl alcohol are around 6. ξ , of course, represents the number of neighbors surrounding the central molecule which relax independently.

V. Nature of "Holes"

We now reconsider the nature of "holes." A brief discussion has already been given in the introduction. We will begin with the structure of liquids.

1. STRUCTURE OF LIQUIDS

The liquid state is considered as an intermediate state between a solid and a gas. Thus a liquid has some of the properties of a solid, and some of

TABLE XIX
DIFFUSION OF VARIOUS SOLUTES IN WATER

<i>Solute</i>	<i>Temperature</i> °C.	<i>D</i> × 10 ⁸ *	$\eta \times 10^3$ †	ξ
Methyl alcohol	18	1.37	1060	8.88
Amyl alcohol	18	0.88	1060	13.8
Phenol	18	0.80	1060	15.2
Glycerol	20	0.83	1009	15.6
Pyrogallol	18	0.61	1060	20.0
Urea	20	1.18	1009	10.9
Caffein	20	0.57	1009	22.6
Urethane	18	0.87	1060	14.0
Glucose	18	0.57	1060	21.3
Sucrose	20	0.57	1009	22.6

* See ref. 69 and 1b.

† Lange, Handbook of Chemistry, Handbook Publishers, Sandusky, Ohio, 1954.

the properties of gas. The resemblance between a liquid and a solid is seen both in having a free surface while a gas will always completely fill any container. The most prominent resemblance between a liquid and a gas is their lack of shear rigidity; hence neither a liquid nor a gas possesses a shape of its own, but always takes the shape of its container.

The theory of liquids proposed by Walter and Eyring⁶ assumes that the molecule of a liquid is distributed at random among solidlike and gaslike equilibrium positions. Let N and n_h be the number of each equilibrium position, respectively. The volume of the gaslike equilibrium positions (or the hole volume per mole) is assumed to be V_s/n' , where V_s is the volume per mole in the solid, and n' is a numerical factor. Thus, n_h is given by

$$n_h = \frac{n'N(V - V_s)}{V_s} \equiv \zeta N \quad (104)$$

where V is the volume per mole in the liquid, and $\zeta \equiv n'(V - V_s)/V_s$. For a molecule in one of the solid-type equilibrium positions, we use the standard harmonic oscillator partition function

$$f_s \exp \frac{E_s}{RT} = \left(\frac{e^{-\theta/2T}}{1 - e^{-\theta/T}} \right)^3 \exp \frac{E_s}{RT}$$

where $\theta = (3/4)\theta_{\text{Debye}}$ and E_s is the potential energy of the solid. For a molecule in one of the gaslike equilibrium positions, we use the partition function for a molecule in a free volume, V_s/n' , which is

$$f_g \exp \frac{-\delta E_s}{RT} = \frac{(2\pi mkT)^{3/2}}{h^3} \frac{V_s}{n'} e^{-\delta E_s/RT}$$

where δ is a function of volume to be discussed later.

If the N molecules are distributed at random among the $N + n_h$ positions, there will be a combinative term in the complete partition function equal to $(N + n_h)!/(N!n_h!)$. This assumption of random distribution of the molecules over the equilibrium positions leads to the correct partition function for the two limiting cases of solid and gas.

We have assumed that the most stable configuration will be the one in which the molecules are distributed among the two kinds of equilibrium positions in a ratio equal to the volume fractions of the two kinds, i.e., a fraction V_s/V in the solid type and a fraction $(V - V_s)/V$ in the gaseous type. Using this assumption, the complete partition function becomes

$$f = \left[(f_s e^{E_s/RT})^{V_s/V} (f_g e^{-\delta E_s/RT})^{(V-V_s)/V} \right]^N \frac{(N + n_h)!}{N!n_h!} \quad (105)$$

If we introduce the parameter ζ , defined by the second equality of equa-

tion (104), we can write the Helmholtz free energy, A , in the simple form:

$$A = -RT \left[\frac{n'}{n' + \zeta} \left(\ln f_s + \frac{E_s}{RT} \right) + \frac{\zeta}{n' + \zeta} \left(\ln f_g - \frac{\delta E_s}{RT} \right) + \ln(1 + \zeta) + \zeta \ln \left(\frac{1 + \zeta}{\zeta} \right) \right] \quad (106)$$

From equation (106), we see that for $\zeta = 0$ the free energy for the solid is obtained, while the free energy for a perfect gas comes out when $\zeta \rightarrow \infty$ and $\delta \rightarrow 0$. The various thermodynamic functions are given explicitly in terms of A ; thus we have the following equations:

$$p = \frac{RT}{V_s} \left\{ n' \ln \left(\frac{1 + \zeta}{\zeta} \right) + \frac{V_s^2 (\ln f_g - \ln f_s)}{V^2} - \frac{E_s}{RT} \left[\left(\frac{V_s}{V} \right)^2 - \frac{3}{2n'} \left(\frac{V_s}{V} \right)^4 \right] \right\} \quad (107)$$

$$C_v = (3R/2)(1 + V_s/V) \quad (108)$$

$$\begin{aligned} C_p &= C_v + T \left(\frac{\partial p}{\partial T} \right)_v \left(\frac{\partial V}{\partial T} \right)_p \\ &= C_v + \frac{\alpha^2 TV}{\beta} \end{aligned} \quad (109)$$

In the derivation of equation (108) it was assumed that the specific heat of the solid is classical.

Walter and Eyring⁶ applied the above formulas for the liquids of Ar, N₂, and benzene, assuming for δ the empirical formula

$$\delta = \left(\frac{V_s}{V} \right)^2 \left(2\zeta + \frac{1}{n' - 1} \right)^{-1} \quad (110)$$

and for n' the value of 8.35. Using the θ values in the literature, the data of E_s were calculated from the vapor pressures of the solids at the melting points. Substituting the E_s values thus obtained and the values of V_s in the literature into equations (106) to (109), the liquid volumes and vapor pressures at various temperatures, the melting point constants, the critical constants, the specific heats, and the second virial coefficients were calculated with good results. Eyring, Walter, and Stearn⁷⁰ extended the application to the liquids of neon, krypton, and xenon for the calculations of the thermodynamical data. Also, in these cases, the agreement with experiment was satisfactory. Thus, the assumption that the extra volume required to

⁷⁰ H. Eyring, J. Walter, and A. E. Stearn, in "Surface Chemistry," No. 21, p. 88. American Association for the Advancement of Science, Washington, D. C., 1953.

provide a new equilibrium position is $1/8.35$ times the volume of the solid atom accords in an interesting way with the value $1/7$ found from viscosity.

The work of Lennard-Jones and Devonshier⁷¹ is especially illuminating with respect to the nature of liquids. Hirschfelder *et al.*⁷² and Green⁷³ have given the whole matter effective detailed consideration.

2. MELTING OF SOLIDS

The most conspicuous feature associated with the solid to liquid transition is the sudden facilitation of all transport properties. Most solids except metals expand approximately 10 % on melting. We find that from the pressure effect on viscosity the volume increase of the activated complex for viscous flow is $1/7$ the normal volume [cf., equation (12)]. If we insert the relations $n' \simeq 7$ and $(V - V_*)/V_* \simeq 0.1$ into the first equality of equation (104), we obtain $n_h/N \simeq 0.7$. Thus, the 10 % expansion on melting introduces a substantial number of empty equilibrium sites.

In the fusion of metals, the volume increase is about 3 % of the normal volume. And the volume increase of the activated complex for viscous flow is only $1/21$ the normal volume. Thus also in the case of metals one calculates that about 0.7 moles of equilibrium sites per metallic atom are introduced on melting. The small expansion on melting, and the small volume increase accompanying the activated complex for viscous flow are understandable if the atomic kernel moves independently of the valence electrons, so that the flow unit is only about one-third as large as the neutral atom; thus the volume required per additional equilibrium site provided by the melting process and by the activation are proportionately smaller than for the neutral atom.

As previously mentioned, a nonassociated liquid is considered as a random mixture of empty and filled equilibrium sites. Let n_h and N be the number of empty and full sites, respectively. Then, the entropy of mixing is given by

$$\begin{aligned}\Delta S &= k \ln \frac{(N + n_h)!}{N!n_h!} \\ &= -Nk \ln \frac{N}{N + n_h} - n_h k \ln \frac{n_h}{N + n_h}\end{aligned}\tag{114}$$

where Stirling's approximation is applied, both N and n_h being a large number. Fusion is thus thought of essentially as a kind of a random mix-

⁷¹ J. E. Lennard-Jones and A. F. Devonshier, *Proc. Roy. Soc. (London)* **A169**, 317 (1939); **A170**, 464 (1939); J. E. Lennard-Jones, *Proc. Phys. Soc. (London)* **52**, 38 (1940).

⁷² J. O. Hirschfelder, C. F. Curtis, and B. G. Bird, "Molecular Theory of Gases and Liquids." Wiley, New York, 1954.

⁷³ H. S. Green, "The Molecular Theory of Fluids." Interscience, New York, 1952.

ing. Thus, the entropy of fusion is roughly calculated by equation (114). Introducing the value 0.7 for n_h/N into (114), one obtains two entropy units, in rough agreement with the experimental data obtained for monatomic solids, and also of some systems of a complex nature which rotate equally in the liquid and solid states.^{1b, 72}

3. THE VOLUME PROVIDING AN ADDITIONAL EQUILIBRIUM SITE

We summarize our knowledge of the volume of an empty equilibrium site. From the pressure dependency of viscosity, we obtained an estimate for the size of the hole which is $1/7$ the normal volume; we call this size the pressure-viscosity estimate of the hole volume. From the thermodynamic properties, the hole size was obtained as $1/8.35$ the volume of the solid atom; this size is called the thermodynamic estimate of the hole volume.

By applying the virial theorem⁷ to the relaxation theory, we have obtained equation (26), where g is the ratio of the mean free length of the vibrating atom, $\bar{x}$, to its distance of advance in plastic flow, λ , i.e., $\bar{x} = g\lambda$. Using equation (26) we obtained the value 6.32, for the $1/g$ factor from Tobolsky-Eyring's analysis⁴⁶ of Trumpler's data⁷⁴ for stress relaxation of steel. That means that the free length is $1/6.32$ the lattice distance. If we assume that the empty and filled sites have the same cross section normal to the shear direction, the volume of the empty site is estimated as $1/6.32$ of the solid atom. This size may be called the virial estimate of the hole volume. All the three estimates for the volume of an empty equilibrium site are approximately equal.

We conclude our consideration by noting that the relaxation theory of transport phenomena needs much refinement but that there are no serious inconsistencies apparent.

ACKNOWLEDGMENT

We wish to express our appreciation to the *Journal of Applied Physics* for permission to use graphs and tables from our published papers. We also wish to thank the Office of Naval Research for their continuing support of our investigations of viscous and plastic flow.

Nomenclature

a	Activity	C	Concentration
a_n	Area occupied by one of the flow units belonging to the n th group. $n = 0, 1, 2, \dots, \nu$	C_p	Specific heat at constant pressure
A	Helmholtz free energy	C_v	Specific heat at constant volume
c	Constant defined by $c \equiv Gr^2/2$	D	Diffusion coefficient
		E	Potential energy of a condensed system per mole

⁷⁴ W. E. Trumpler, Jr., *J. Appl. Phys.* **12**, 248 (1941).

E_{vis}	Experimental activation heat for viscous flow	k''	Specific rate constant for viscous flow in a pure system
E_{vap}	Vaporization heat	K	Equilibrium constant
f	Stress (shear force per unit area)	m	Mass of a particle
f	Partition function for a molecule	$\bar{M}_v$	Viscosity averaged molecular weight
f_0	Local micro-stress	n	Number
f_g	Partition function for a molecule of gas	n	Ratio of vaporization heat, E_{vap} , to the activation energy for viscous flow, E_{vis} , i.e., $n = E_{vap}/E_{vis}$
f_s	Partition function for a molecule of solid	n'	Ratio of molar volume of flow units, V , to the average molar volume increase accompanying the activation for flow, $\Delta V^\ddagger$, i.e., $n' = V/\Delta V^\ddagger$
F	Force	n_h	Number of holes, i.e., the number of empty equilibrium sites
$\mathcal{F}$	Faraday	N	Number of solidlike molecules in a liquid
ΔF	Change of free energy per mole	N	Avogadro number
$\Delta F^\ddagger$	Activation free energy for flow	p	Pressure
$\Delta F_s^\ddagger$	Activation free energy for the degree of freedom involving the shear coordinate of an activated complex for flow	P	Permeability
δF_i	Free energy of diffusing units at the i th potential barrier minus that of those at the zeroth barrier of a succession of potential barriers which exists in a membrane. $i = 0, 1, 2, 3, \dots, n$	Q	Number of molecules passing through a barrier in a square centimeter of an area normal to the direction of diffusion
g	Ratio of the length of free vibration, x , of a flow unit to the distance jumped, λ , i.e., $g = x/\lambda$	s	Strain
g	Λ function defined by equation (81)	s'	Strain due to an aperiodic element
G	Spring constant	s''	Strain of a spring element
$\Delta H^\ddagger$	Activation heat	$\dot{s}$	Rate of shear
h	Planck constant	$\dot{s}_r$	Reduced rate of shear for temperature
k	Boltzmann constant	ΔS	Change of entropy
k'	Specific rate constant	$\Delta S^\ddagger$	Activation entropy for flow
k_0^0	Specific rate constant over the zeroth barrier in the absence of an electrical field	t	Time
k_η'	Specific rate constant for viscous flow in a solution system	T	Absolute temperature
		u	Velocity of a particle
		v	Flow velocity
		v	Volume of a liquid per molecule
		v_s	Volume of a solid per molecule
		V	Volume per mole of a liquid

- w Work
 x Displacement of flow units along the x -direction
 $\dot{x}$ Rate of displacement along the x -direction
 X Force acting along the x -direction
 z Ionic Charge

 α Expansion coefficient
 α Ratio of shear volume $\lambda_2\lambda_3$ to twice average kinetic energy $2kT$.
 β Compressibility
 β Relaxation time, defined by $\beta = \left(\frac{\lambda}{\lambda_1} 2k'\right)^{-1}$
 γ Activity coefficient
 γ_0 Mean available energy of those oscillators equilibrating with the translational degree of freedom corresponding to crossing a potential barrier
 γ_i Mean available energy of those oscillators equilibrating with the i th group of activated complex degrees of freedom
 γ_s Mean available energy of those oscillators equilibrating with the activated complex degree of freedom in the shear coordinate
 δ Depth (thickness) of a membrane
 λ Distance of two equilibrium positions for flow units in the direction of shear
 $\lambda_2\lambda_3$ Shear volume

 ϵ Electric potential across a membrane
 ζ Number of moles of holes
 κ Transmission coefficient
 η Viscosity
 η' Viscosity due to Newtonian flow units and non-Newtonian units of group 2
 $[\eta]$ Limiting (intrinsic) viscosity number,
 η_i Intrinsic viscosity, i.e., $\eta_i = \eta_{sp}/C$
 η_{inh} Inherent viscosity, i.e., $\eta_{inh} = (1/\eta_r)/C$
 η_r Relative (or reduced) viscosity, i.e., $\eta_r = \eta/\eta_0$
 η_s Viscosity at small rates of shear
 η_{sp} Specific viscosity, i.e., $\eta_{sp} = \eta_r - 1 = (\eta - \eta_0)/\eta_0$
 η_∞ Viscosity at infinite rate of shear
 η_0 Viscosity of solvent
 μ A fractional number. $\mu\lambda$ is the distance between an initial and the activated state in the reaction coordinate.
 μ Chemical potential
 μ_0 Chemical potential at unit activity
 ν Frequency of vibration
 ν Number of groups of flow units
 ξ Number of solvent relaxations required to advance a diffusing unit one lattice distance
 ρ Rate of elongation of a fiber
 τ Relaxation time (approximately equal to β)

CHAPTER 4

THE RHEOLOGY OF ORGANIC GLASSES

Rolf Buchdahl

I. Introduction	145
II. Anelasticity and Reversible Deformations	148
III. Irreversible Deformations	152
1. Viscous Flow	152
2. Stress-Strain and Ultimate-Strength Properties	153
IV. Major Experimental Techniques	155
V. Effect of Physical Variables on Anelasticity	158
1. Temperature and Frequency	158
2. Pressure, Stress, and Orientation	162
VI. Effect of Chemical Variables on Anelasticity and Irreversible Deformations	165
1. Molecular Weight and Molecular Weight Distribution	165
2. Monomer Units	167
3. Plasticization, Copolymerization, and Polymer Mixtures	175
Nomenclature	179

I. Introduction

From a mechano-rheological point of view, organic glasses can be defined as a group of materials exhibiting (a) a high shear modulus G' of the order of 10^{10} dynes/cm.², (b) a considerable amount of mechanical damping δ as compared to other materials of similar rigidity, and (c) a very high resistance η to purely viscous deformation. In the glassy state G' , δ , and η are slowly varying functions of the temperature. As the material reaches the glass transformation region the mechanical properties undergo significant changes: The shear modulus and the (steady-state) viscosity decrease very rapidly, whereas the mechanical damping increases as more and more of the energy of deformation is transformed into heat. Above the glass transformation region the organic glasses are either viscous liquids or rubberlike materials. A rubber has a low shear modulus ($G' \approx 10^7$ dynes/cm.²) and a low mechanical damping coefficient and, as a result, the damping goes through a maximum in the glass transformation region. Viscous liquids, on the other hand, have a zero shear modulus and the mechanical damping is very large or infinite. In addition, G' and δ are also functions of the time or the frequency, whereas η is by definition independent of time. The dependence of these quantities on frequency and temperature is shown best in a

the glass transformation arises from a structural change in the system. The fact that time (or frequency) has a marked effect not only on the temperature region at which the glass transformation occurs, but also on the magnitude of the "discontinuity" has led many investigators to conclude that the glass transformation is a diffusion-controlled relaxation mechanism^{6, 7} (for work prior to 1948 see ref. 4). However, this interpretation ignores and leaves unanswered certain facts which lend support to the equilibrium-mechanism interpretation:⁸ (a) For organic glasses it has not been possible to remove completely the discontinuities in the specific volume-temperature curve.⁹ (b) The relaxation mechanism is unable to explain why, in a certain temperature range, the viscosity (or the relaxation times) suddenly increases and, as a result, it has been found necessary to introduce a structural concept—an undefined "degree of order"—to represent the changing configurational state of the system.¹⁰ (c) In the study of the glass transformation by x-ray diffraction² and nuclear magnetic resonance¹¹ changes are observed which are essentially independent of time and the correlation of the intensity of the diffraction pattern (as a function of temperature) with specific volume-temperature curves¹²—in the case of polystyrene—is of particular significance. It appears that the complete elucidation of the nature of the glass transition will have to take into account both mechanisms mentioned above.^{12a}

Many organic glasses undergo spontaneous crystallization in a time interval comparable to or shorter than the time of the desired experiment. However, the mechano-rheological properties of organic glasses have, with very few exceptions, been studied on systems where spontaneous crystallization is essentially nonexistent. The majority of materials falling in this category are substances of very high molecular weight (polymers), such as polystyrene and polymethylmethacrylate; these polymeric organic glasses are characterized by the fact that the intermolecular forces are relatively weak.¹³

⁶ E. Jenckel, *Kolloid-Z.* **120**, 160 (1951); J. J. Benbow, *Proc. Phys. Soc. (London)* **B67**, 120 (1954).

⁷ R. O. Davies and G. O. Jones, *Proc. Roy. Soc. (London)* **A217**, 26 (1953).

⁸ R. Buchdahl and L. E. Nielsen, *J. Appl. Phys.* **21**, 482 (1950).

⁹ R. S. Spencer and R. F. Boyer, *J. Appl. Phys.* **17**, 398 (1946).

¹⁰ J. Frenkel, "Kinetic Theory of Liquids." Oxford Univ. Press, London, 1946.

¹¹ L. V. Holroyd, R. S. Codrington, B. A. Mrowca, and E. Guth, *J. Appl. Phys.* **22**, 696 (1951); H. S. Gutowsky and L. H. Meyers, *J. Chem. Phys.* **21**, 2122 (1953).

¹² T. G. Fox, Jr., and P. J. Flory, *J. Appl. Phys.* **21**, 581 (1950).

^{12a} J. H. Gibbs, *J. Chem. Phys.* **25**, 185 (1956).

¹³ H. Mark and A. V. Tobolsky, "Physical Chemistry of High Polymeric Systems," p. 146. Interscience, New York, 1950.

II. Anelasticity and Reversible Deformations

For an ideal or perfectly elastic body the various moduli of elasticity completely specify the mechanical behavior at a given temperature. However, organic glasses are not ideal elastic bodies, so that a modulus of rigidity G' —which is of particular interest from the rheological point of view—does not suffice to describe the behavior, and it is necessary to introduce the concept of a complex modulus $\bar{G}$ defined by the well-known expression¹⁴

$$\bar{G} = G' + iG'' \quad (1)$$

where G'' is the “imaginary” out-of-phase-part of the rigidity modulus and measures the damping, or energy dissipated into heat, within the material. The description of the mechanical behavior of anelastic bodies^{14, 14a} in terms of complex variables has the advantage that no reference need be made as to the mechanism of damping, or to a particular experimental method. Anelasticity has often been expressed in terms of a “viscosity” or internal friction; such terms imply a certain mechanism for the dissipation of energy. On the other hand, anelasticity is frequently described by such terms as logarithmic decrement, attenuation factor, half-width of the resonance peak, and resilience. These terms imply a certain type of experimental technique. It can easily be shown that all of the above ways of expressing anelasticity can be expressed formally in terms of G' and G'' , or the ratio G''/G' .¹⁵

In the following, a brief derivation will be given of the terms most frequently used during this discussion. These terms are a matter of choice and others could have been selected. For details, see Vol. II, Chapter 1.

The equation of motion of a vibrating system can be derived by considering the forces acting on the system. For a mechanical system these forces may be (a) inertial force, $F_1 = -M d^2y/dt^2$ where M is the mass of the vibrating system, y is the amplitude of the deformation at any time, t ; (b) restoring force, $F_2 = -G'y$,¹⁶ where G' is the spring constant; (c) fric-

¹⁴ C. M. Zener, “Elasticity and Anelasticity of Metals.” Univ. of Chicago Press, Chicago, 1948; J. D. Ferry, W. M. Sawyer, and J. N. Ashworth, *J. Polymer Sci.* **2**, 593 (1944).

^{14a} J. D. Ferry, “Rheology: Theory and Applications,” Vol. II, Chapter 11. Academic Press, New York, 1957.

¹⁵ The author is indebted to Dr. L. E. Nielsen for this treatment of anelasticity in terms of a complex modulus; the subsequent equations are given for one coordinate only, but can easily be extended to more complicated cases.

¹⁶ This definition assumes the validity of Hooke’s law and is justified for small deformations; for an extension to “large” deformations see reference 17. The spring constant can be represented by various kinds of moduli, and might also contain different shape factors.

tional forces leading to damping, $F_3 = -i G''y$; (d) external forces $F_4 = -F(t)$. For free vibrations ($F_4(t) = 0$) and using equation (1) the general equation of motion¹⁸ becomes

$$M \frac{d^2 y}{dt^2} + \bar{G}y = 0 \quad (2)$$

The solution is of the form

$$y = y_0 e^{-\alpha t} e^{i w t} = y_0 e^{(i w - \alpha) t} \quad (3)$$

where α is the attenuation factor and w is the frequency of vibration. Separating this equation into real and imaginary parts results in

$$\begin{aligned} G' &= M(w^2 - \alpha^2) \\ G'' &= 2w\alpha M \end{aligned} \quad (4)$$

The attenuation of a free vibration can be expressed in terms of the logarithmic decrement δ defined as the natural logarithm of the ratio of two successive maxima Y_1 and Y_2 which occur at a time interval P equal to the period of vibration,

$$\delta = \ln(Y_1/Y_2) = \alpha P \quad (5)$$

where

$$P = \frac{2\pi}{w} \quad (6)$$

Substitution of (5) and (6) into (4) gives G' and G'' in terms of experimentally observable quantities

$$G' = Mw^2 - \frac{G''^2}{4Mw^2} \quad (7a)$$

¹⁷ T. Alfrey, "Mechanical Behavior of High Polymers," Interscience, New York, 1948.

¹⁸ These equations are valid whenever the frequency of deformation is sufficiently low to minimize inertial effects ($\sim d^2 y/dx^2$). When the period of vibration becomes short enough to approach the time required for the propagation of a wave through the solid, an equation of the following form must be used, in place of the above given equation of motion:

$$\rho \frac{d^2 y}{dt^2} = G \frac{d^2 y}{dx^2}$$

where ρ is the density of the material and x is the direction in which the wave is traveling. Again it can be shown that this equation can be solved in a general way for inelastic bodies if one replaces the real modulus by a complex modulus. (Kolsky^{18a} has given an excellent review of the propagation of waves through such solids.)

^{18a} H. Kolsky, "Stress Waves in Solids." Oxford Univ. Press, London, 1953.

$$G'' = \frac{4\pi M\delta}{P^2}; \quad \delta = \frac{G''P^2}{4\pi M} \quad (7b)$$

It is often more desirable to express results in terms of the total modulus ($G = \sqrt{G'^2 + G''^2}$) and the ratio of the imaginary to the real part of the modulus, G''/G' ; the latter quantity is frequently referred to as the mechanical dissipation factor. From previous equations it is easily shown that

$$G = \frac{M}{P^2} (4\pi^2 + \delta^2) = Mw^2 + \frac{G''^2}{4Mw^2} \quad (8a)$$

$$\frac{G''}{G'} = \frac{4\pi\delta}{4\pi^2 - \delta^2} \quad (8b)$$

For small damping ($\delta < 1.0$) the second term in (8a) can be neglected and the dissipation factor is given to a good approximation by

$$\frac{G''}{G'} = \frac{\delta}{\pi} \quad (8c)$$

For forced vibrations [$F_4(t) = F_0 e^{i\omega t}$] G' and G''/G' are given by the following expressions:

$G' \simeq w_r^2 M$, where w_r is the resonance frequency

$\frac{G''}{G'} = \frac{1}{2\sqrt{3}} \frac{w_2^2 - w_1^2}{w_r^2}$, where $\frac{w_2 - w_1}{w_r}$ is the half width of the resonance peak.

The fact that it is necessary to introduce a complex modulus (or a complex compliance = 1/modulus) to describe the mechanical behavior of organic glasses means, as stated above, that their properties depend on time and not only on temperature. As a relaxation process,¹⁴ anelasticity is thus defined as a measure of the dissipation of stored energy into heat by whatever mechanism. Anelasticity, creep, and stress relaxation are therefore manifestations of the same process (or processes) which occur during the deformation of most solid bodies. Although this was recognized in a qualitative way many years ago,^{19, 20} it has only been quite recently that the interrelationship of these quantities has been clearly formulated in the most general manner.^{21, 22} For example, the relationship between the

¹⁹ W. Voigt, *Ann. Physik* **47**, 671 (1892).

²⁰ E. Wiechert, *Wied. Ann. Phys. Lp.* **5**, 335 (1893); *Ann. Physik* **40**, 817 (1913); H. Leaderman, "Elastic and Creep Properties of Filamentous Materials and Other High Polymers," The Textile Foundation, Washington, D. C., 1943.

²¹ B. Gross, *J. Appl. Phys.* **18**, 212 (1947); **19**, 257 (1948).

²² F. Schwarzl, *Physica* **17**, 830, 923 (1951).

complex shear modulus and the "creep spectrum" $\phi(\tau)$ is of the following form.

$$\bar{G}(w) = G' \left[1 - \int_0^\infty e^{-i w \tau} \phi(\tau) d\tau \right]$$

where $w = 1/t$ and τ is a relaxation time which is a property of the material. Equations of this type, however, cannot be applied directly to the experimental data and it has been found necessary to introduce approximations using Laplace or Fourier transforms,²³ or mechanical models consisting of springs and dashpots.¹⁷ Based on such approximations which can be carried to various degrees of refinement,²⁴ the following interrelationships between measurable quantities have been obtained. (a) The product of the creep $\phi(t)$ and "relaxation function" $\psi(t)$ is approximately unity,

$$G^{-1} [1 + \phi(t) \times G[1 - \psi(t)]] \simeq 1.$$

(b) At equal times, $t = 1/w$, the real part of the complex modulus is approximately identical with the relaxation curve, $G' (1/t) \simeq G [1 - \psi(t)]$.

(c) $\frac{G''}{G'} \approx \frac{\pi}{2} \left[\frac{d \ln \psi(t)}{d \ln t} \right]_{t=\pi/8\bar{w}}$. Other expressions similar to (c) have been given by Zener.¹⁴

Intimately associated with the phenomenon of anelasticity is the theoretical concept of a retardation, or a relaxation time, τ . The quantities, not to be confused with the experimentally obtainable relaxation times t , are characteristic constants of the materials determining stress τ_1 or strain τ_2 decay in a material. It was soon recognized²⁰ that single or even multiple values of τ were insufficient to describe the behavior of anelastic bodies, and it became necessary to introduce two continuous distribution functions, $F(\tau_1)$ and $\bar{F}(\tau_2)$ for stress and strain relaxation, respectively. These functions, or spectra as they are sometimes called, are one more way of specifying the properties of viscoelastic bodies and, until it is possible to derive them with the aid of a molecular theory, their usefulness is rather limited. Some rather interesting attempts have been made recently to derive relaxation spectra for dilute polymer solutions^{25, 26} but for solids, including organic glasses, no satisfactory solution to this difficult problem is apparent.^{26a}

²³ B. Gross, "Mathematical Structure of the Theories of Viscoelasticity." Hermann, Paris, 1953.

²⁴ J. D. Ferry and N. L. Williams, *J. Colloid Sci.* **7**, 347 (1952).

F. Schwarzl and A. J. Staverman, *Physica* **18**, 791 (1952).

²⁵ J. G. Kirkwood, *Rec. trav. chim.* **68**, 649 (1949).

²⁶ P. E. Rouse, Jr., *J. Chem. Phys.* **21**, 1272 (1953).

^{26a} Attempts to extend consideration following Rouse to rubber-like solids have been quite successful. [See J. D. Ferry, R. F. Landel and M. L. Williams, *J. appl. Phys.* **28**, 250 (1955)]

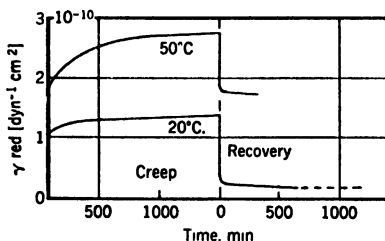


FIG. 2. Creep and recovery of an organic glass (polystyrene) at two temperatures. [From E. Klein and E. Jenckel, *Z. Naturforsch.* **7a**, 800 (1952).]

In order to obtain the functions $F(\tau_1)$ and $\bar{F}(\tau_2)$ from the experimental data, it is necessary to make use of certain approximations^{21, 22} as indicated above, and the error introduced by these approximations depends on the true relaxation spectrum (which is unknown) and can therefore be estimated only with difficulty, using progressively higher orders of approximation; in general, the approximations are more reliable when the spectrum is broad. Within the limits of these approximations the following equations, relating these functions to measurable quantities, are valid:

$$F(\tau) \approx - \frac{d}{dt} G'(w)$$

$$tF(\tau) \approx \frac{d}{dt} [tG''(w)]$$

Similar expression can also be given for $\bar{F}(\tau)$.

III. Irreversible Deformations

1. VISCOUS FLOW

It is usually assumed that a certain fraction of a creep deformation below the glass transformation temperature is due to viscous flow. To establish the validity of this assumption, it is necessary to follow the creep deformation by a recovery experiment (at the same or slightly higher temperature) as shown in Fig. 2. Only that fraction of the deformation which does not recover is of a purely viscous nature. Quite frequently it is suggested that the linear portion of a creep curve is due to viscous flow. This argument assumes, however, that the viscosity coefficient itself is independent of time and also that the linear term can readily be separated from the remaining portion of the creep curve by graphical or algebraic methods.

Among organic glasses the viscosity of glucose⁷ has been studied more extensively than any other material. It is found that within, and slightly below, the glass transformation region the viscosity is very high (10^{12} to 10^{14} poises) and independent of shear stress; furthermore, within a narrow

temperature range (34 to 28° C.) the viscosity varies exponentially with temperature and has an activation energy of about 125 kcal./mole. Similar, but not as extensive, data for other low-molecular-weight organic glasses have been summarized by Jenckel.⁶ During the last few years several investigators^{27a,b,c} have studied the long-time creep behavior of high-molecular-weight organic glasses, without specifying the viscosity coefficient in any detail. Actually our knowledge of this field is extremely limited. All that is known with reasonable certainty is that organic glasses can deform by purely viscous flow and that the coefficient of viscosity is at least 10^{10} poises or higher. Whether or not the viscosity coefficient is a function of time; whether or not it is always independent of stress, and if not, what the functional relationship is; what the temperature, dependence of the viscosity is below the glass transformation and to what extent the viscosity depends on the chemical composition—all these questions have yet to be answered.

2. STRESS-STRAIN AND ULTIMATE-STRENGTH PROPERTIES

It is clear from the foregoing that the stress-strain behavior of an inelastic body at a given rate of strain must be a function of this rate. Indeed, the phenomenon is observed every time the stress-strain relationship of organic glasses is investigated as a function of the rate of strain and a typical example is shown in Fig. 3. To the extent that such deformations are reversible and conform to the Boltzmann superposition principle, it should be possible to predict the shape of such curves from the relaxation function of the stress decay at equivalent times.¹⁷ A rather satisfactory agreement can be obtained between calculated and measured stress-strain data of organic glasses, as shown by Knowles and Dietz²⁸ in the case of plasticized and unplasticized polymethylmethacrylate. The extension of this kind of analysis of stress-strain data to higher frequencies (or shorter times) is of particular value in clarifying the as yet poorly understood behavior of organic glasses under impactlike deformation. The problems connected with accurate stress-strain measurements at high frequencies and amplitudes are quite formidable,²⁹ but in recent years some of these techniques have been applied to polymers and organic glasses with promising results.^{30, 30a}

As the stress (or strain) increases, one begins to approach the region where the material will break and the interpretation of experimental data

^{27a} J. A. Sauer, J. Marin, and C. C. Hsiao, *J. Appl. Phys.* **20**, 507 (1949).

^{27b} W. N. Findley, *J. Appl. Phys.* **21**, 258 (1950).

^{27c} F. Marin, Yoh-Han Pao, and G. Cuff, *Trans. ASME* **73**, 705 (1951).

²⁸ J. K. Knowles and A. G. H. Dietz, *Trans. ASME* **77**, 177 (1955).

²⁹ G. I. Taylor, *J. Inst. Civil. Engrs.* **26**, 486 (1946).

³⁰ H. Kolsky, *Proc. Phys. Soc. (London)* **B62**, 676 (1949).

^{30a} J. C. Smith, *J. Research* **57**, 83 (1956).

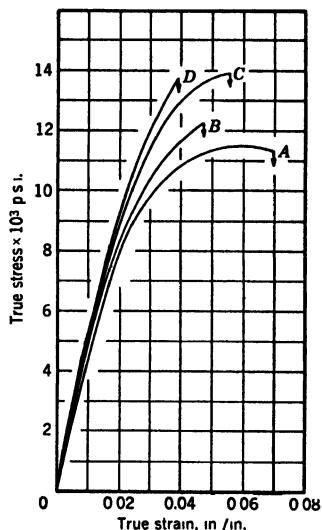


FIG. 3. Effect of rate of strain on the ultimate strength properties of an organic glass (polymethylmethacrylate $M_w = 3.2 \times 10^6$).

	Crosshead rate, in./in.
A	0.02
B	0.08
C	0.32
D	1.28

[From F. K. Knowles and A. G. H. Dietz, *Trans. ASME* **77**, 177 (1955).]

becomes increasingly difficult. In the first place, the superposition principle will no longer be applicable. Secondly, organic glasses frequently develop small but visible crack marks, a phenomenon known as "crazing";³¹⁻³³ these small fracture surfaces or flaws not only grow in size under an applied stress but also produce very large stress concentrations which, in turn, lead to brittle fracture³⁴ and low ultimate-strength properties.³⁵ However, the same material—polystyrene, for example—which exhibits brittle fracture under tension will behave as a ductile material under compression.³⁶ Ductil-

³¹ B. Maxwell and L. F. Rahm, *Ind. Eng. Chem.* **41**, 1988 (1949).

³² C. C. Hsiao and J. A. Sauer, *J. Appl. Phys.* **21**, 1071 (1950); **24**, 957 (1953).

³³ M. A. Sherman and B. M. Axilrod, *ASTM Bull. No.* 191, 65 (1953).

³⁴ P. W. Bridgman [*J. Appl. Phys.* **18**, 246 (1947)] has pointed out that fractures are always brittle, but that the essential differences occur prior to actual rupturing of the material.

³⁵ R. N. Haward, "The Strength of Plastics and Glass." Interscience, New York, 1948.

³⁶ T. S. Carswell and H. K. Nason, "Symposium on Plastics." Am. Soc. Testing Materials, Philadelphia, 1944; see also H. Kolsky [*Nature* **166**, 235 (1950)] for the dependence of birefringence on strain in the glassy state.

ity—and the related phenomena of yielding and “cold flow”—is generally associated with the flow of a solid under applied stress and is therefore of particular interest from a rheological point of view. For crystalline bodies clear evidence about the nature of the process of plastic deformation—resulting from slip along certain crystal planes—has been provided by experiments on single crystals.³⁷ Slip takes place along a given slip plane and direction when the shear stress acting along them reaches a critical value. Because it is believed that slip spreads consecutively and not simultaneously over a slip plane, there is usually not enough energy available to produce a change (such as melting³⁸) in a slip plane. It appears unlikely, although not altogether impossible, that this same mechanism is responsible for the ductility in amorphous glasses. Müller and Jäkel^{39, 39a} have suggested that “cold flow” of organic glasses can be interpreted as a successive melting or softening process and recently demonstrated experimentally a significant temperature rise in the draw zone during a stress-strain experiment.⁴⁰ These experiments lend strong support to the assumption that the ultimate-strength properties of organic glasses are intimately connected with the temperature dependence of the elastic and inelastic properties at small deformations or amplitudes. It is also interesting to note that the temperature dependence of the ultimate-strength properties⁴¹ show many similarities to the temperature dependence of G' and G''/G' , and Boyer⁴² has drawn attention to the relationship between tensile strength and the glass transformation temperature.^{39a}

IV. Major Experimental Techniques

The experimental techniques which have been used to study the rheological behavior of organic glasses are not unique to this class of materials. In fact, almost all of them have been employed, at some time or another, to study the mechanical behavior of metals, glasses, and other solid bodies. The various methods can be subdivided into certain groups, (a) transient techniques which include stress relaxation, creep, free (damped) vibrations, and what is commonly described as “stress-strain measurements”;⁴³ (b) forced vibration techniques which include measurements at resonance frequencies, direct measurements of stress and strain, wave propagation (of

³⁷ A. H. Cottrell, “Dislocations and Plastic Flow in Crystals,” Oxford Univ. Press, London, 1953.

³⁸ R. Fürth, *Proc. Roy. Soc. (London)* **A177**, 217 (1941).

³⁹ F. H. Müller and K. Jäkel, *Kolloid-Z.* **129**, 145 (1952); **137**, 130 (1954).

^{39a} I. J. Gruntfest, *J. Polymer Sci.* **20**, 491 (1956).

⁴⁰ F. H. Müller and P. Brauer, *Kolloid-Z.* **135**, 1 (1954).

⁴¹ H. K. Nason, T. S. Carswell, and C. H. Adams, *ASTM Spec. Tech. Publ. No. 78* (1949).

⁴² R. F. Boyer, *J. Appl. Phys.* **22**, 723 (1951).

⁴³ A.S.T.M. Standards on Plastics, Part 6 (1952).

low and high amplitudes) and transducer measurements of shear to strain ratio. A critical review of many of these methods can be found in another chapter of this book⁴⁴ and in ref. 18, whereas a description of the more conventional engineering-type techniques is given in ref. 43 and discussed by Freudenthal.⁴⁵

For organic glasses the majority of the experimental work has been done using the following techniques: creep, stress relaxation, free vibration, resonance vibration, and conventional stress-strain measurements; some of the other techniques, referred to above, have been used in isolated cases. In order to obtain accurate creep (or recovery) data of rigid materials it is necessary to measure small deformations very precisely and, if possible, continuously; these requirements can be met either by optical or electrical methods using strain gages, differential transformers, transducer tubes, etc.⁴⁶ The nonrecoverable or purely viscous deformation is usually obtained from a measurement of the rate of creep in tension and the calculation of the viscosity coefficient assumes the validity of Trouton's rule, a relationship which, as Davies and Jones⁷ point out, has never been verified experimentally. In stress-relaxation measurements the continuous recording of the stress decay is equally desirable and can be achieved by various means (see, for example, Stein and Tobolsky).⁴⁷ For transparent substances creep and stress-relaxation measurements in tension can readily be combined with birefringence measurements to follow changes in configurational or bond orientation.

There exist numerous ways to start free vibrations in a specimen and to record their decay, but it appears that the method of the torsion pendulum is the preferred one; it was first applied to organic polymers by Kuhn and Künzle⁴⁸ and the design of Nielsen⁴⁹ using electronic means to measure and to record the vibration has greatly extended the range and precision of this method. In the vibrating-reed method one end of the specimen is attached to a "drive," of variable frequency, and the resonance frequency and half-width of the resonance peak is measured directly or recorded photographically; this method has been used by Sack *et al.*,⁵⁰ Nielsen,⁵¹ Hiorio and

⁴⁴ J. D. Ferry, "Rheology: Theory and Applications," Vol. II, Chapter 3. Academic Press, New York, 1957.

⁴⁵ A. M. Freudenthal, "The Inelastic Behavior of Engineering Material and Structures." Wiley, New York, 1950.

⁴⁶ D. Telfair, T. S. Carswell, and H. K. Nason, *Modern Plastics*, February (1944); R. Stein and H. Schaevitz, *Rev. Sci. Instr.* **19**, 835 (1948); E. Baker, *Rev. Sci. Instr.* **22**, 373 (1951).

⁴⁷ R. S. Stein and A. V. Tobolsky, *Textile Research J.* **18**, 302 (1948).

⁴⁸ W. Kuhn and O. Künzle, *Helv. Chim. Acta* **30**, 839 (1947).

⁴⁹ L. E. Nielsen, *Rev. Sci. Instr.* **22**, 690 (1951).

⁵⁰ H. S. Sack, J. Motz, H. L. Raub, and R. N. Work, *J. Appl. Phys.* **18**, 450 (1947).

⁵¹ L. E. Nielsen, *ASTM Bull.* **165**, 48 (1950).

Onogi,⁵² and Ballou and Smith.⁵³ Two methods based on the forced oscillations have been used primarily to study the stress dependence of the internal friction: in the method first introduced by Kimball⁵⁴ the specimen is in the form of a cylindrical rod which is being rotated by a suitable device; at the free end of the rod different loads can be applied which deflect the rod vertically. The magnitude of the horizontal deflection during rotation is a measure of the phase lag between stress and strain. In another method, first developed by Lazan⁵⁵ and employed by other investigators,⁵⁶ the specimen, in the form of a solid cylinder, is rigidly attached to two large masses which are supported on frictionless steel rollers. A mechanical oscillator, driven by a synchronous motor, is attached to one of the masses and can generate alternate cycles of tension and compression in the specimen. The large masses are varied until the system is operating at resonance and the damping capacity is obtained from the measured value of the displacement vector from the oscillator force. (Reference has already been made to methods which extend the conventional stress-strain measurements⁴³ to very much higher rates of loading.^{29, 30})

Which method should be employed in a study of the rheological behavior of organic glasses depends, to a very large extent, on the particular functional relationship one wishes to obtain between dependent and independent variables. This is particularly true for dynamic measurements (forced or free vibration and wave propagation), whereas the choice is very limited for creep, stress-relaxation, and viscosity measurements. If one desires to study the anelastic properties (G' , G'' , or G''/G') primarily as a function of the frequency it is usual to combine several different methods in order to cover a sufficiently large frequency range, as was done, for example, by Nolle⁵⁷ who employed altogether five different methods to cover a frequency range of 10^6 decades. Even then such a procedure contains certain inherent difficulties: (a) The frequency dependence usually is measured in selected regions because most methods perform satisfactorily only within a rather narrow frequency range (one and one-half to two decades). (b) The various methods should be checked against each other to eliminate systematic errors (this can become an experimental problem of considerable magnitude). (c) The moduli obtained do not always refer to the same deformation process, hence their interrelation requires a knowledge of Poisson's ratio, which is frequently assumed rather than determined for the specific experi-

⁵² M. Horio and S. Onogi, *J. Appl. Phys.* **22**, 977 (1951).

⁵³ J. W. Ballou and J. C. Smith, *J. Appl. Phys.* **20**, 493 (1949).

⁵⁴ A. L. Kimball, *J. Appl. Mechanics* **8**, A37 and A135 (1949).

⁵⁵ B. J. Lazan, *Trans. ASME* **65**, 87 (1943).

⁵⁶ F. M. Robertson and A. Yorgiadis, *Trans. ASME* **68**, A173 (1946); J. A. Sauer and W. F. Oliphant, *Am. Soc. Testing Materials, Proc.* **49**, 1119 (1949).

⁵⁷ A. W. Nolle, *J. Appl. Phys.* **19**, 753 (1948).

mental conditions. It is therefore not surprising to find that various efforts have been made to obtain the frequency dependence by other procedures. The theoretical approach is based on the assumption of equivalence, under certain conditions, of temperature and frequency. To the extent that this procedure is valid, which is discussed in the following section, it is possible to study the frequency dependence over an extremely wide range (up to 14 or 15 decades) by making measurements at various temperatures. The preferred experimental approach consists in studying the mechanical properties over as wide a frequency as possible with a single instrument; using a method based on the measurement of the hysteresis loop, Philippoff⁵⁸ has been able to cover six decades of frequencies below 10 c.p.s.

Although in principle, any instrument can be put at the desired temperature, certain methods are much to be preferred over others for various experimental reasons, such as the size of temperature bath, effect of temperature on supports and measuring devices. Creep, stress relaxation, the torsion-pendulum, free-vibration and reed resonance instruments are particularly well suited to make measurements over a wide temperature range, because the specimen size can be quite small and the measuring devices can be readily separated from the specimen itself. In creep and stress-relaxation measurements one obtains only one quantity (the modulus or compliance), whereas the torsion pendulum and the vibrating-reed give modulus and the logarithmic decrement or loss factor. It is obvious that creep or stress relaxation measurements can cover a very large frequency range provided one is patient enough, but in actual practice the range seldom extends beyond 10^3 to 10^4 decades, from 1 c.p.s. ($t = 1/w$) downward. For the torsion pendulum and the vibrating-reed instrument the frequency range is more restricted, between one and two decades extending from about 0.05 to 3 c.p.s. and 10 to 500 c.p.s., respectively. The vibrating-reed instrument can give more precise measurements of the modulus and the loss factor at small losses, whereas the torsion pendulum does not possess quite the same precision but can cover a much wider range of anelastic properties.

V. Effect of Physical Variables on Anelasticity

1. TEMPERATURE AND FREQUENCY

Before reviewing the experimental material it seems appropriate to discuss briefly the interdependence of these two variables in their effect on the anelastic properties. If anelasticity is essentially a relaxation phenomenon, it is immediately obvious—as has been already pointed out in Section I—that these properties must be both time and temperature dependent. Furthermore, as relaxation times generally decrease with increasing temperature

⁵⁸ W. Philippoff, *J. Appl. Phys.* **24**, 685 (1953).

one should expect a certain correlation between measurements conducted at increasing frequencies and decreasing temperatures, and vice versa, and indeed this has been observed many times. The question then arises whether or not it is possible to obtain a quantitative relationship which combines the effect of both variables on the mechanical behavior. It is obvious that a fundamentally valid relationship of this kind would be of great usefulness from a theoretical and experimental point of view. Alfrey¹⁷ was probably the first one to suggest a quantitative relationship, namely, that a change in temperature from T_2 to T_1 ($T_2 < T_1$) shifts the distribution function $F(\ln \tau)$ on a logarithmic time scale by an amount

$$E_a/R \times \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

without changing the shape of the distribution function, where E_a is an activation energy and R is the gas constant. This idea has been extended and further developed by Ferry⁵⁹ and Tobolsky and Andrews⁶⁰ and has led to the development of the "method of reduced variables," which is based on the following assumptions: (a) The moduli G_i defined by the equation $G'(w) = \Sigma G_i w^2 \tau_i^2 / (1 + w^2 \tau_i^2)$ are proportional to the absolute temperature T , and to the density, ρ , of the material. (b) All the relaxation times, τ_i , have the same temperature dependence, that is, when the temperature is changed from a reference temperature, T_0 , to another temperature, T , every τ_i is multiplied by the same factor a_t . (c) The multiplication factor, a_t , can be determined independently from the temperature dependence of the steady-state viscosity, η . Schwarzl and Staverman,⁶¹ investigating the conditions a material must fulfill in order to justify the procedure of replacing any change of temperature by a shift on the logarithmic time scale [which is identical with assumption (b)], conclude that the functions describing the temperature dependence of the various processes must be the same, or that the apparent activation energies of all molecular rate processes must be identical. The fact that for a few polymeric systems—and particularly for polyisobutylene⁶²—good agreement has been obtained between a_t values determined from steady-state viscosity and dynamic mechanical measurements lends strong support to the assumptions underlying the method of reduced variables. Nevertheless, the validity and the usefulness of this procedure, when extended to the glass state, is still rather questionable for the following reasons: (a) Extensive steady-state or non-

⁵⁹ J. D. Ferry, *J. Am. Chem. Soc.* **72**, 3746 (1950).

⁶⁰ A. V. Tobolsky and R. D. Andrews, *J. Chem. Phys.* **13**, 3 (1945).

⁶¹ F. Schwarzl and A. J. Staverman, *J. Appl. Phys.* **23**, 838 (1952).

⁶² E. R. Fitzgerald, I. D. Grandine, Jr., and J. D. Ferry, *J. Appl. Phys.* **24**, 650 (1953).

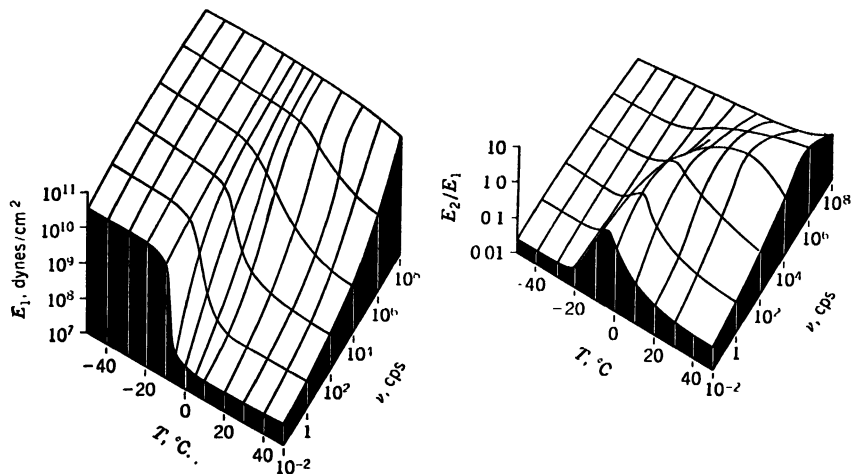


FIG. 4. Approximate frequency and temperature dependence of E' and E''/E' . [From A. W. Nolle, *J. Polymer Sci.* **5**, 1 (1950).]

recoverable viscosity data at the low temperature side of the glass transition and in the glassy region itself are practically nonexistent, which makes it impossible to check the validity of the theory and—under these circumstances—reduces the method to a curve-fitting procedure. (b) It is doubtful whether the first assumption is valid for the glassy state as it is based on the kinetic theory of rubber elasticity. (c) Direct⁶³ and indirect⁶⁴ evidence has been accumulated which shows that assumption 2 is not always applicable in the glassy state: the relaxation processes do not necessarily have the same temperature dependence. It would appear, therefore, to be more desirable to represent the dependence of such data in a three-dimensional diagram (as shown, for example, in Fig. 1) in order to bring out clearly the detailed mechanical behavior of the glass state.

Because of the difficulties associated with measurements covering a very broad frequency range at a fixed temperature, relatively few detailed investigations have been carried out up to now and Nolle's work⁶⁵ on several amorphous copolymers (isobutylene–isoprene, butadiene–acrylonitrile, styrene–butadiene) is still one of the most comprehensive studies in this field. His data show (Fig. 4) that G' and G''/G' are only very slightly dependent on frequency for sufficiently high G' values and low internal friction; recent work on unvulcanized *GR-S* rubber⁶⁶ (a copolymer of styrene–

⁶³ S. Iwayanagi and T. Hideshima, *J. Phys. Soc. Japan* **8**, 368 (1953); A. B. Thompson and D. W. Woods, *Trans. Faraday Soc.* **52**, 1383 (1956).

⁶⁴ R. M. Fuoss, *J. A. C. S.* **63**, 378 (1941); A. Dyson, *J. Polymer Sci.* **7**, 133 (1951).

⁶⁵ A. W. Nolle, *J. Polymer Sci.* **5**, 1 (1949); see also Maxwell.⁷²

⁶⁶ L. J. Zapas, S. L. Shufler, and T. W. DeWitt, *Rubber Age* **72**, 763 (1953).

butadiene) confirms the essential frequency independence of G' and G''/G' at low temperatures over four frequency decades. In order to establish experimentally the existence of a frequency dispersion (at constant temperature) it would be necessary to extend a creep or stress-relaxation measurement to time values which are, for all intents and purposes, impossible to reach. Under these circumstances various investigators continue the experimental investigations at a higher temperature and, using the previously referred to procedure of curve fitting, obtain the well-known dispersion curves as a function of the reduced frequency. The inherent insensitivity of this method to detect the fine structure⁶⁷ of anelasticity in the glassy state can easily lead to an oversimplification of the experimental facts as has been shown in the case of polymethylmethacrylate; combining stress-relaxation data obtained at various temperatures, Tobolsky and Loughlin⁶⁸ obtained a reduced stress-relaxation function which is decreasing in a monotone fashion toward the dispersion region whereas several other investigators^{63, 69-72} using different techniques have shown that, within the same temperature region, the behavior is more complex (see Fig. 1).

The study of G' and G''/G' as a function of temperature, at essentially constant frequency, is easier from an experimental point of view. Both quantities appear to reach a constant value as the temperature decreases although there exist no experimental data for organic glasses below -200°C . As the temperature is increased, the shear modulus and the internal friction will decrease and increase, respectively. The material under investigation may exhibit only a single dispersion region (see Fig. 4) or it might possess multiple (or secondary) dispersion regions, as shown in Fig. 1. It appears that measurements of the internal friction as a function of temperature—preferably at a few frequencies—are best suited to detect this fine structure of the anelastic properties whose existence has only been recognized during the last few years (for example, Alfrey's book¹⁷ does not discuss it at all) and which seems to be a much more common phenomenon than had been at first anticipated. As the material approaches the dispersion region which is due to the transition from the glassy to the rubbery or liquid state, the general features of the frequency and temperature dependence of G' and G''/G' are always the same: The shear modulus decreases by two to three decades and the internal friction goes through a maximum. However, the width of this dispersion region varies significantly among different high

⁶⁷ F. Schwarzl and A. J. Staverman, *Appl. Sci. Research* **A4**, 127 (1953).

⁶⁸ A. V. Tobolsky and F. R. Laughlin, *J. Polymer Sci.* **8**, 543 (1952).

⁶⁹ K. Schmieder and K. Wolf, *Kolloid-Z.* **127**, 65 (1952).

⁷⁰ J. Heyboer, *Kolloid-Z.* **148**, 36 (1956).

⁷¹ E. A. W. Hoff, K. Deutsch, and W. Reddish, *J. Polymer Sci.* **13**, 565 (1954); E. A. W. Hoff, D. W. Robinson, and A. H. Willbourn, **18**, 161 (1955).

⁷² B. Maxwell, *J. Polymer Sci.* **20**, 551 (1956).

polymeric organic glasses. These variations appear to be a function of the molecular and colloidal structure of the system (see Section VI).

2. PRESSURE, STRESS, AND ORIENTATION

It is well known that pressure has a significant effect on the irreversible viscous deformation⁷³ and it would therefore be of interest to investigate to what extent this quantity affects the anelastic properties of an organic glass. Hughes *et al.*⁷⁴ are apparently the only ones who have studied this problem experimentally. It is found that, for polystyrene, the rigidity modulus increases by approximately 6% for an increase in pressure of 15,000 p.s.i. whereas the bulk modulus increases over the same range by about 30%. Corresponding to this rise in bulk modulus Poisson's ratio increases uniformly. For polymethylmethacrylate the changes with pressure are more complex.

The behavior of organic glasses at large stresses (or strains) has been touched upon in a previous section in connection with a discussion of the ultimate-strength properties. For many engineering applications the energy dissipation during cyclic stress application (at various stress values) is of considerable importance. Although there exist some questions^{27b} whether or not the data which have been obtained so far are completely free of systematic errors, the major conclusions arrived at by several investigators^{27a, 75, 76} are as follows: (a) The damping capacity increases approximately with the second or third power of the applied stress. (b) The damping capacity is—within the investigated range— independent of frequency, this being in general agreement with the fact that, at the temperatures where these measurements are usually made, one would have to go to extremely low frequency to find the dispersion region. (c) The dependence of the damping capacity on stress and strain amplitude appears to undergo a significant change as the fatigue strength value⁷⁷ of the material is approached.

Until now the effect of molecular orientation has not been taken into account, and it was assumed the configuration of the polymer molecules was completely random. However, it is well known that chain segments of organic glasses can be aligned or orientated preferentially along a given direc-

⁷³ S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill, New York, 1941.

⁷⁴ D. S. Hughes, E. B. Blankenship, and R. Mims, *J. Appl. Phys.* **21**, 294 (1950).

⁷⁵ F. M. Robertson and A. Yorgiadis, *Trans. ASME* **68**, A173 (1946); A. Yorgiadis, *Product Eng.* **25**, No. 11, 164 (1954).

⁷⁶ A. L. Kimball and D. E. Lowell, *Phys. Rev.* **30**, (1927); B. F. Lazan and A. Yorgiadis, A.S.T.M. Symposium on Plastics p. 66 (1944).

⁷⁷ B. J. Lazan, F. Podnieks, and R. Johnson, Society of Rheology Meeting, New York, November, 1953.

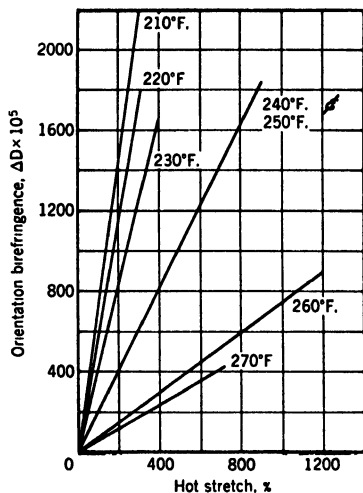


Fig. 5. Effect of amount of elongation, at various temperatures in the rubbery state, on the birefringence orientation below the glass transformation temperature [From K. J. Cleereman, H. J. Karam, and J. L. Williams, *Modern Plastics*, **30**, No. 9, 119 (1953).]

tion and this partial ordering can readily be detected by birefringence measurements, provided the polarizabilities of the backbone chain and side groups of the polymer are sufficiently different. (For a detailed discussion of the relationship between orientation and birefringence, see Treloar.⁷⁸) By stretching a polymer in the rubbery state, followed by rapid quenching below the glass transformation temperature, it is possible to incorporate into the material various amounts of orientation. The extent of orientation depends essentially on the relative magnitude of the viscoelastic to the purely viscous responses of the polymer which, in turn, are a function of temperature, amount and rate deformation (or stretch), rate of quenching, and molecular weight;^{79, 80} Figure 5 shows, as a specific example, the dependence of birefringence orientation as a function of amount of stretch at several temperatures. As a result of this partial ordering the anelasticity of the glass is changed: the damping and modulus both increase and the transition region shifts to lower temperatures (see Fig. 6 and Table I). The shift in the glass transformation region to lower temperatures is interpreted to be the result of a more unstable configuration in the glass state which requires less thermal energy to destroy, but the causes for the in-

⁷⁸ L.R.G. Treloar, "Physics of Rubber Elasticity," Oxford Univ. Press, London, 1949.

⁷⁹ L. E. Nielsen and R. Buchdahl, *J. Colloid Sci.* **5**, 282 (1950).

⁸⁰ K. J. Cleereman, H. J. Karam, and J. L. Williams, *Modern Plastics*, **30**, No. 9, 119 (1953).

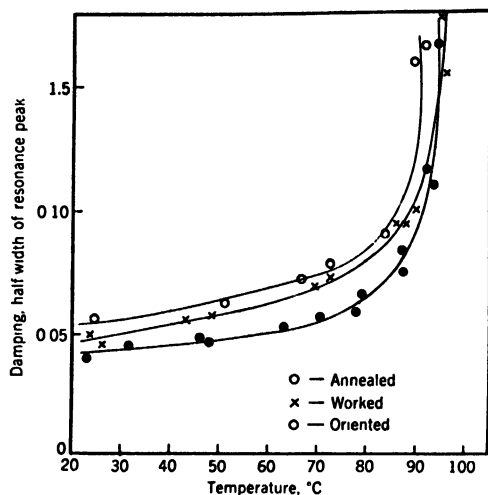


FIG. 6. Effect of orientation on damping. [From J. E. Nielsen and R. Buchdahl, *J. Appl. Phys.* **21**, 488 (1950).]

TABLE I
EFFECT OF ORIENTATION ON THE MODULUS AND DAMPING OF
POLYSTYRENE IN THE GLASSY STATE⁸¹

Birefringence, Δ /mil.	Dynamic Young's Modulus, dynes/cm. ²	Half Width of Resonance Peak
0 (annealed)	3.24×10^{10}	0.046
0 (worked)	3.18×10^{10}	0.049
1580	3.46×10^{10}	0.050
2090	3.39×10^{10}	0.051
4500	4.04×10^{10}	0.054

crease in the damping at a temperature considerably below the glass transformation region are not as readily understood at this time.⁸¹ As a uniaxially oriented glass strives to reach a more stable configuration, it will contract in the direction of stretch. The rate of this internal stress relaxation or annealing process^{80, 82, 83} is a function of time and temperature (Fig. 7) in the same way as the external stress relaxation is dependent on these

⁸¹ It should be pointed out that the anelasticity can be changed by "working"⁷⁹ the glass above the transition region without leaving residual strains in the material as shown in Fig. 6; similar observations were made by Tobolsky and McLaughlin for polymethyl methacrylate.⁸²

⁸² J. R. McLoughlin and A. V. Tobolsky, *J. Polymer Sci.* **7**, 658 (1951).

⁸³ F. H. Muller, *Kolloid-Z.* **95**, 138, 306 (1941); E. F. Gurnee, L. T. Patterson, and R. D. Andrews, Jr., *J. Appl. Phys.* **26**, 1106 (1955).

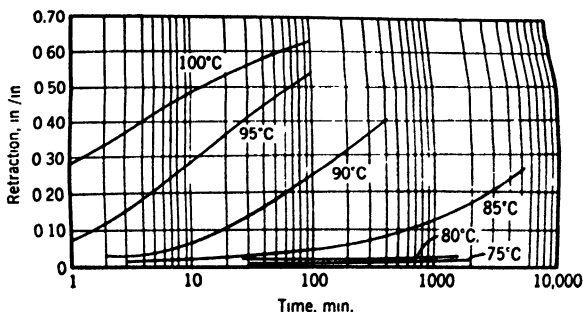


FIG. 7. Retractions of an oriented organic glass as a function of time and temperature. (Temperature at which retraction is measured is indicated on graph.) [From K. J. Cleereman, H. J. Karam, and J. L. Williams, *Modern Plastics*, **30**, No. 9, 119 (1953).]

variables. Calculations of an apparent activation energy for the process by the method of curve-shifting along the logarithmic time scale leads to values of the order of 100 to 200 kcal./mole, characteristic of deformation processes occurring in the transition range. Orientation has also a very marked effect on the stress-strain and ultimate-strength properties,^{80, 84, 85} which is of importance in the technology of fibers and thin films. A significant fact is the development of a yield point and "cold flow" leading to materials of higher strength.

VI. Effect of Chemical Variables on Anelasticity and Nonrecoverable Deformations

1. MOLECULAR WEIGHT AND MOLECULAR-WEIGHT DISTRIBUTION

Investigations of Merz *et al.*⁸⁶ showed that Young's modulus and the dissipation factor of polystyrene in the glassy state are independent of molecular weight (or chain length) above a certain minimum molecular-weight value, as shown in Fig. 8. On the basis of mechanical investigations it is impossible to establish this minimum molecular-weight value because below a certain molecular weight ($\sim 130,000$ for polystyrene) the specimen breaks into small fragments. However, it is possible to obtain some information on this point from dilatometric studies of the glass transition temperature and the specific volume as a function of molecular weight. Fox and Flory¹² showed that (a) the transition temperature for polystyrene is practically independent of molecular weight above 25,000 and (b) the molecular weight dependence of the specific volume and of the glass transition temperature are closely related. They interpreted the linear increase of the specific volume with $1/M_n$ as being the result of changes in the

⁸⁴ F. Bailey, *India Rubber World* **118**, 25 (1948).

⁸⁵ L. E. Nielsen and R. Buchdahl, *J. Appl. Phys.* **21**, 488 (1950).

⁸⁶ F. H. Merz, L. E. Nielsen, and R. Buchdahl, *Ind. Eng. Chem.* **43**, 1396 (1951).

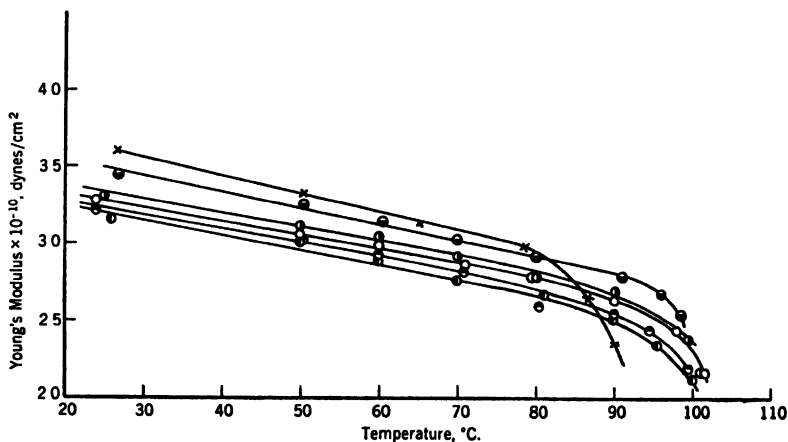


FIG. 8a

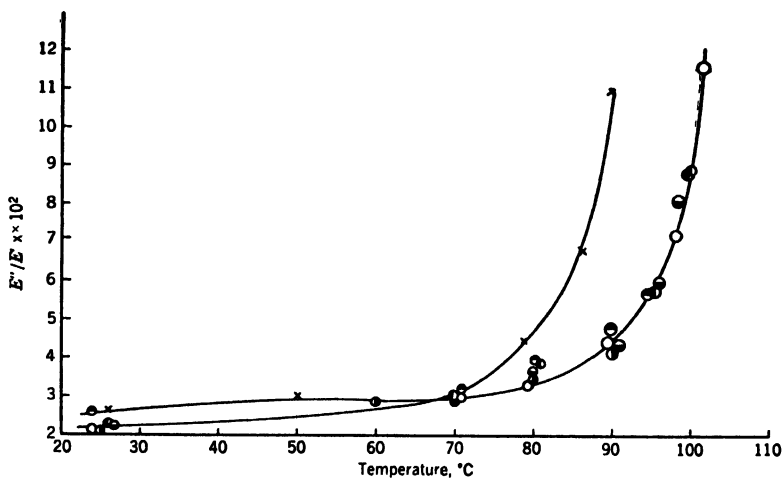


FIG. 8b

FIG. 8. Modulus (8a) and dissipation factor (8b) of polystyrene in the glass state as a function of molecular weight. Molecular weight (M_n) of fractions: ○ = 1.36×10^6 ; ● = 9.92×10^5 ; ◐ = 7.65×10^5 ; ◑ = 2.31×10^5 ; ⊗ = 1.46×10^5 ; × = Mixture with low molecular weight polystyrene: $M_n = 5.12 \times 10^3$. [From E. H. Merz, L. E. Nielsen, and R. Buchdahl, *Ind. Eng. Chem.* **43**, 1953 (1951).]

average density of packing with the concentration of end groups; Altenburg⁸⁷ has expanded this idea along more quantitative lines and obtained reasonably good agreement between the measured⁸⁸ and calculated specific volume expansion coefficients for polystyrene of different molecular weight.

⁸⁷ K. Altenburg, *Z. physik. Chem.* **201**, 75 (1952).

⁸⁸ K. Überreiter and K. Kanig, *Z. Naturforsch.* **6a**, 551 (1951).

Applying these considerations to the mechanical behavior, the following conclusions can be reached: (a) Because the dilatometric glass transition temperature and the mechanical glass transformation are different measurements of the same phenomenon, the dependence on molecular weight should be the same and experiments on mixtures (using a very low-molecular-weight polystyrene with a high-molecular-weight fraction (see Fig. 8) lend strong support to this conclusion.^{88a} (b) To what extent different end groups affect the modulus and damping below the transition region has not been too clearly established, although Buchdahl and Nielsen⁸⁹ have interpreted certain secondary maxima in polyvinylchloride as being due to the effect of specific end groups. The stress-relaxation function of polyisobutylene fractions also is independent of molecular weight (between 300,000 and 800,000) in the glassy state and the transition region, as was shown by Andrews and Tobolsky.⁹⁰

It appears justified, on the basis of the results which have been obtained for polystyrene and polyisobutylene, to generalize that the mechanical behavior of organic glasses (at small stresses or strains) is independent of molecular weight and that the apparent molecular-weight dependence, at low molecular weights, is not due to the molecular weight itself, but is the result of the introduction of different chemical units in the form of end groups. (The ultimate-strength properties are affected in the same manner by changes in molecular weight.^{86, 91}) Extending these conclusions to systems containing a distribution of molecular weights (whole or unfractionated polymers) should not introduce any new effects in the mechanical behavior; and, indeed, stress-relaxation⁸⁸ and torsion-pendulum⁹² measurements on unfractionated polyisobutylene of different average molecular weight confirm this conclusion⁹³ (Figs. 9 and 10). It is important to note that in the rubbery region—long relaxation times—molecular weight has a marked effect on the rheological properties.

2. MONOMER UNITS

A discussion of the effects of the building block on the mechanical behavior can conveniently be separated into two aspects, (a) the properties below the glass transformation region (secondary dispersion regions), and (b) the effect of the monomer unit on the value of the glass transformation temperature.

^{88a} T. G. Fox, Jr., and S. Loshaek, *J. Polymer Sci.* **15**, 371, 391 (1955).

⁸⁹ R. Buchdahl and L. E. Nielsen, *J. Polymer Sci.* **15**, 1 (1954).

⁹⁰ R. D. Andrews and A. V. Tobolsky, *J. Polymer Sci.* **7**, 221 (1951).

⁹¹ A. G. H. Dietz, PMMA Reports, Mass. Inst. of Technol., 1952.

⁹² K. Schmieder and K. Wolf, *Kolloid-Z.* **134**, 149 (1954).

⁹³ The very limited facts known concerning the effect of chain branching on the mechanical behavior of organic glasses⁸⁹ would indicate that moderate amounts of branching leave these properties unchanged.

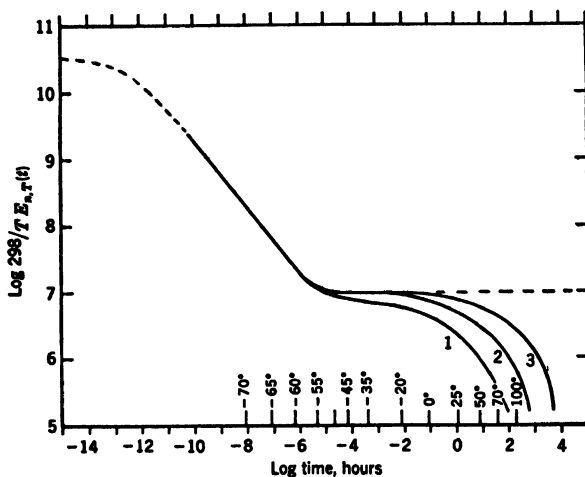


FIG. 9. Stress-relaxation function of polyisobutylenes of different molecular weights in the glass and transition region. Viscosity average molecular weights: 1- 1.36×10^6 ; 2- 2.80×10^6 ; 3- 6.60×10^6 . [From A. V. Tobolsky and J. R. McLoughlin, *J. Polymer Sci.* **8**, 543 (1952).]

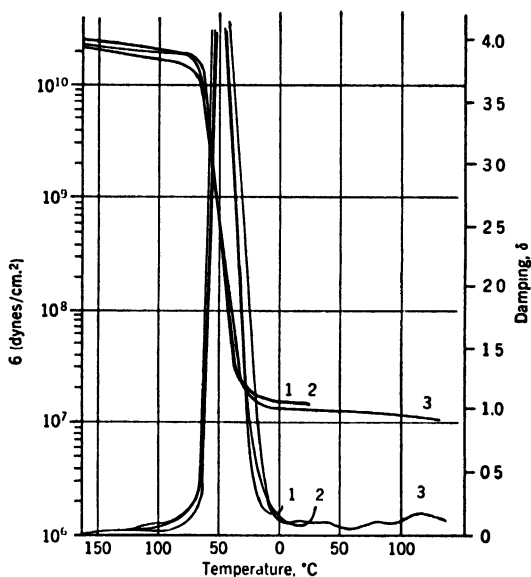


FIG. 10. Shear moduli and damping of polyisobutylenes of different molecular weights as a function of temperature. Molecular weights: I-50,000; II-100,000; III-200,000. [From K. Schmieder and K. Wolf, *Kolloid-Z.* **134**, 149 (1954).]

Until a few years ago it was generally assumed that G' and G''/G' (or E' and E''/E'), in the glassy state, were always monotone functions of temperature and frequency, as indicated in Fig. 8, and that the absolute value of these quantities in the glassy state was very little influenced by the specific nature of the repeat unit. This reasoning is based on the argument that once the configurations are effectively "frozen in," no further relaxation processes (or transitions) will occur and that the van der Waal's forces, which act between the various chain segments, are roughly of the same order of magnitude for various organic glasses. Although this is the true state of affairs for a good many organic glasses—such as polystyrene, polyvinylcarbazole, styrene-butadiene copolymers—it is now quite obvious that many polymers exhibit a more complex mechanical behavior in the glassy state; a typical example—polymethylmethacrylate—is shown in Fig. 1.⁶⁹ Based on a comparison of the temperature dependence of mechanical and electrical⁹⁴ relaxation processes, Iwayanagi and Hideshima⁶³ suggested that the secondary mechanical dispersion and the electrical dispersion are due to the motion of polar COCH_3 side groups. Further support of this interpretation was recently obtained by Heyboer *et al.*⁷⁰ and by Hoff *et al.*,⁷¹ who investigated the effect of chemically different side groups on the mechanical behavior of acrylate polymers. Heyboer obtained chemical modification by copolymerization, whereas Hoff studied differently substituted homopolymers. Both groups of investigators reach the conclusion that the position and the height of the secondary maximum is influenced by the nature of the side group; in addition, it appears that the flexibility of the backbone chain has also a marked effect, as can be seen from Table II. Secondary maxima have also been observed for other amorphous polymers—various polyvinylethers,⁹² polyvinylchloride,⁹² and polyisobutylene.⁹⁵ However, no satisfactory explanation for their occurrence in these materials has been advanced so far. In this connection, attention might be drawn to the very interesting work of Baker and co-workers⁹⁶ on the mechanical properties of polymer molecules in solution, during which it was established that the shear stiffness of an essentially isolated polyisobutylene molecule also exhibits multiple relaxation regions.

The second point mentioned above—namely, the dependence of the glass transition temperature T_g on the chemical nature of the monomer unit—is actually not particularly relevant to the subject under discussion. However, in conjunction with a study of the mechanical behavior of organic glasses,

⁹⁴ D. J. Mead and R. M. Fuoss, *J. Am. Chem. Soc.* **64**, 2389 (1942).

⁹⁵ J. D. Ferry, L. D. Grandine, Jr., and E. R. Fitzgerald, *J. Appl. Phys.* **24**, 911 (1953).

⁹⁶ W. O. Baker and J. H. Heiss, *Bell System Tech. J.* **31**, 306 (1952).

TABLE II
EFFECT OF MOLECULAR FINE STRUCTURE ON
SECONDARY DISPERSION REGIONS⁷⁰

<i>Name and Amount of Comonomers</i>	<i>Formula of Comonomer</i>	<i>Feature of Comonomer</i>	<i>Effect on Secondary Dispersion Region</i>
Methyl methacrylate	$ \begin{array}{c} \text{CH}_3 \\ \\ \text{H}_2\text{C}=\text{C} \\ \\ \text{COOCH}_3 \end{array} $	—	—
Glycol dimethacrylate, 20%	$ \begin{array}{c} \text{CH}_3 \\ \\ \text{H}_2\text{C}=\text{C} \\ \\ \text{COOCH}_2 \\ \\ \text{COOCH}_2 \\ \\ \text{H}_2\text{C}=\text{C} \\ \\ \text{CH}_3 \end{array} $	Crosslinking	Somewhat depressed; slightly shifted to lower frequency
N-Methyl methacrylamide, 30%	$ \begin{array}{c} \text{CH}_3 \\ \\ \text{H}_2\text{C}=\text{C} \\ \\ \text{CONHCH}_3 \end{array} $	Polarity	Depressed; shifted to lower frequency
Cyclohexyl methacrylate, 60%	$ \begin{array}{c} \text{CH}_3 \\ \\ \text{H}_2\text{C}=\text{C} \\ \\ \text{COOC}_6\text{H}_{11} \end{array} $	Bulkiness of side group	Depressed; stays at same frequency
Methyl acrylate; 20, 40, 60 and 80%	$ \begin{array}{c} \text{H} \\ \\ \text{H}_2\text{C}=\text{C} \\ \\ \text{COOCH}_3 \end{array} $	Flexibility backbone chain	Strongly depressed; shifted to higher frequency
Acrylic acid, 60%	$ \begin{array}{c} \text{H} \\ \\ \text{H}_2\text{C}=\text{C} \\ \\ \text{COOH} \end{array} $	Flexibility backbone chain and polarity	Strongly depressed; shifted to higher frequency

many investigators have given some consideration to the problem because of its great theoretical and technical importance. The theoretical aspects are closely akin to the problem of the relationship between chemical structure and melting or other order-disorder transitions, a much discussed but still poorly understood subject except for the very simplest molecules. From the technical point of view, the glass transition region is important because it determines whether or not an organic polymeric material of high molecular weight is, at normal temperatures, a glass (plastomer) or a rubber (elastomer). As a result of this interest, collected data of the transition temperatures of chemically different polymers are found quite frequently in recent literature.^{3, 6, 92, 97, 98} In trying to evaluate these data, several factors should be kept in mind: (A) As all glass transition temperatures are functions of time,⁹⁹ fairly wide discrepancies can and have been reported for the same substance. (B) The accuracy and precision of the different methods used to determine T_g (by mechanical or dielectric dispersion, by linear- or volume-expansion coefficient, by refractive index change with temperature) can differ considerably and are not always clearly expressed. (C) Molecular weight and soluble additives (plasticizers) have a significant effect on the glass transition and can lead to incorrect conclusions concerning the effect of molecular structure on this property. A precise and detailed analysis of such data, therefore, seems hardly warranted at this time. All that can be done is to recognize the major structure factors governing the transition from a glass to a rubber or a liquid. The value of the glass transformation temperature¹⁰⁰ is determined by the interplay of intermolecular forces and (chain) molecular flexibility.¹³ Because in organic glasses the intermolecular forces are, on the whole, rather weak and of the same order of magnitude, segment flexibility, resulting from differences in monomer structure, can bring about large variations of the glass transformation temperature, as illustrated in Table III^{101, 102}. The introduction of molecular groups which increase the intermolecular forces, because of dipole interac-

⁹⁷ R. H. Wiley and G. M. Breuer, *J. Polymer Sci.* **3**, 455, 647, 704 (1948).

⁹⁸ F. Wurstlin, *Kolloid-Z.* **120**, 84 (1951).

⁹⁹ If a comparison of T_g values of different polymers is restricted to the low-frequency portion of the dispersion, errors caused by time effects are usually quite small.

¹⁰⁰ In terms of the reduced-variable method T_g is equivalent to the temperature of maximum activation energy of the relaxation process.

¹⁰¹ The verification of the qualitative relationships between structure and T_g is primarily due to the extensive mechanical and electrical investigations of Wolf and his collaborators.⁹²

¹⁰² This same effect has also been observed for amorphous silicone polymers¹⁰³ where the chains ($-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}-$) appear to be very flexible and exhibit little intermolecular cohesion.

¹⁰³ C. E. Weir, W. H. Leser, and L. A. Wood, *J. Research Natl. Bur. Standards* **44**, 367 (1950).

TABLE III
EFFECT OF CHAIN BULKINESS ON THE GLASS TRANSFORMATION
TEMPERATURE OF VINYL-TYPE POLYMERS^a

<i>Name of Polymer</i>	<i>Chemical Structure of Polymer</i>	<i>Glass Transformation Temp^a</i>
Polyethylene	$ \begin{array}{ccccccc} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \\ & & & & & & \\ - & \text{C} & - \text{C} & - \text{C} & - \text{C} & - \text{C} & - \\ & & & & & & \\ & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \end{array} $	Between -40 and -20°C.
Polyisobutylene	$ \begin{array}{ccccccc} & \text{H} & \text{CH}_3 & & \text{H} & \text{CH}_3 & \text{H} \\ & & & & & & \\ - & \text{C} & - \text{C} & - & \text{C} & - \text{C} & - \text{C} - \\ & & & & & & \\ & \text{H} & \text{CH}_3 & & \text{H} & \text{CH}_3 & \text{H} \end{array} $	-48°C.
Polystyrene	$ \begin{array}{ccccccc} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \\ & & & & & & \\ - & \text{C} & - \text{C} & - \text{C} & - \text{C} & - \text{C} & - \\ & & & & & & \\ & \text{H} & \text{C}_6\text{H}_5 & \text{H} & \text{C}_6\text{H}_5 & \text{H} & \end{array} $	$+105^{\circ} \text{C.}$
Polyvinylcarbazole	$ \begin{array}{ccccccc} & \text{H} & & \text{H} & & \text{H} & \\ & & & & & & \\ - & \text{C} & - & \text{C} & - & \text{C} & - \\ & & & & & & \\ & \text{H} & & \text{N} & & \text{H} & \\ & & \text{C}_6\text{H}_4 & & & \text{C}_6\text{H}_4 & \end{array} $	$+210^{\circ} \text{C.}$

^a Based on dynamic mechanical measurements at frequencies between 1 and 10 c.p.s.

tion and hydrogen bonding between chain segments of separate chain molecules, contribute in some degree to a rise in T_g , although the effectiveness of such interactions can quite readily be overcome by (a) shielding the specific group, or (b) a simultaneous increase in the chain stiffness, as shown in Table IV. Even when the dipole moment is considerably increased—as in polyvinylfluoride, polyvinylchloride, and polyacrylonitrile—the significant influence of the accompanying changes in chain mobility (or stiffness) are still readily apparent (Table IV).

TABLE IV
EFFECT OF CHAIN INTERACTION AND DIPOLE MOMENT ON THE GLASS
TRANSFORMATION TEMPERATURE OF VINYL-TYPE POLYMERS⁹²

<i>Name of Polymer</i>	<i>Chemical Structure of Polymer</i>	<i>Glass Trans-formation temp.^a</i>
Polyisobutylene	$ \begin{array}{ccccccccc} & \text{H} & & \text{CH}_3 & & \text{H} & & \text{CH}_3 & & \text{H} \\ & & & & & & & & & \\ - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - \\ & & & & & & & & & \\ & \text{H} & & \text{CH}_3 & & \text{H} & & \text{CH}_3 & & \text{H} \end{array} $	-48° C.
Polyvinylmethylether	$ \begin{array}{ccccccccc} & \text{H} & & \text{H} & & \text{H} & & \text{H} & & \text{H} \\ & & & & & & & & & \\ - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - \\ & & & & & & & & & \\ & \text{H} & & \text{O} & & \text{H} & & \text{O} & & \text{H} \\ & & & & & & & & & \\ & & & \text{CH}_3 & & & & \text{CH}_3 & & \end{array} $	-10° C.
Polyvinylethylether	$ \begin{array}{ccccccccc} & \text{H} & & \text{H} & & \text{H} & & \text{H} & & \text{H} \\ & & & & & & & & & \\ - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - \\ & & & & & & & & & \\ & \text{H} & & \text{O} & & \text{H} & & \text{O} & & \text{H} \\ & & & & & & & & & \\ & & & \text{CH}_2 & & & & \text{CH}_2 & & \\ & & & & & & & & & \\ & & & \text{CH}_3 & & & & \text{CH}_3 & & \end{array} $	-25° C.
Polyvinyl- <i>n</i> -butylether	$ \begin{array}{ccccccccc} & \text{H} & & \text{H} & & \text{H} & & \text{H} & & \text{H} \\ & & & & & & & & & \\ - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - \\ & & & & & & & & & \\ & \text{H} & & \text{O} & & \text{H} & & \text{O} & & \text{H} \\ & & & & & & & & & \\ & & & \text{CH}_2 & & & & \text{CH}_2 & & \\ & & & & & & & & & \\ & & & \text{CH}_2 & & & & \text{CH}_2 & & \\ & & & & & & & & & \\ & & & \text{CH}_3 & & & & \text{CH}_3 & & \end{array} $	-52° C.
Polyvinylisobutylether	$ \begin{array}{ccccccccc} & \text{H} & & \text{H} & & \text{H} & & \text{H} & & & \\ & & & & & & & & & & \\ - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - \\ & & & & & & & & & & \\ & \text{H} & & \text{O} & & \text{H} & & \text{O} & & & \\ & & & & & & & & & & \\ & & & \text{CH}_2 & & & & \text{CH}_2 & & & \\ & & & & & & & & & & \\ & & & \text{CH}_3 - \text{C} - \text{CH}_3 & & & & \text{CH}_3 - \text{C} - \text{CH}_3 & & & \\ & & & & & & & & & & \\ & & & \text{H} & & & & \text{H} & & & \end{array} $	-5° C.

TABLE IV—CONTINUED

<i>Name of Polymer</i>	<i>Chemical Structure of Polymer</i>	<i>Class Transformation temp.^a</i>
Polyvinyltertiary-butyl-ether	$ \begin{array}{ccccccccc} & \text{H} & & \text{H} & & \text{H} & & \text{H} & & \text{H} \\ & & & & & & & & & \\ - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - \\ & & & & & & & & & \\ & \text{H} & & \text{O} & & \text{H} & & \text{O} & & \text{H} \\ & & & & & & & & & \\ & & & \text{CH}_3 - \text{C} - \text{CH}_3 & & & & \text{CH}_3 - \text{C} - \text{CH}_3 & & \\ & & & & & & & & & \\ & & & \text{CH}_3 & & & & \text{CH}_3 & & \end{array} $	+88° C.
Polymethylacrylate	$ \begin{array}{ccccccccc} & \text{H} & & \text{H} & & \text{H} & & \text{H} & & \text{H} \\ & & & & & & & & & \\ - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - \\ & & & & & & & & & \\ & \text{H} & & \text{C}=\text{O} & & \text{H} & & \text{C}=\text{O} & & \text{H} \\ & & & & & & & & & \\ & & & \text{O} & & & & \text{O} & & \\ & & & & & & & & & \\ & & & \text{CH}_3 & & & & \text{CH}_3 & & \end{array} $	+16° C.
Polymethylmethacrylate	$ \begin{array}{ccccccccc} & \text{H} & & \text{CH}_3 & & \text{H} & & \text{CH}_3 & & \text{H} \\ & & & & & & & & & \\ - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - \\ & & & & & & & & & \\ & \text{H} & & \text{C}=\text{O} & & \text{H} & & \text{C}=\text{O} & & \text{H} \\ & & & & & & & & & \\ & & & \text{O} & & & & \text{O} & & \\ & & & & & & & & & \\ & & & \text{CH}_3 & & & & \text{CH}_3 & & \end{array} $	+120° C.
Polyvinylfluoride	$ \begin{array}{ccccccccc} & \text{H} & & \text{H} & & \text{H} & & \text{H} & & \text{H} \\ & & & & & & & & & \\ - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - \\ & & & & & & & & & \\ & \text{H} & & \text{F} & & \text{H} & & \text{F} & & \text{H} \end{array} $	+50° C.
Polyvinylchloride	$ \begin{array}{ccccccccc} & \text{H} & & \text{H} & & \text{H} & & \text{H} & & \text{H} \\ & & & & & & & & & \\ - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - \\ & & & & & & & & & \\ & \text{H} & & \text{Cl} & & \text{H} & & \text{Cl} & & \text{H} \end{array} $	+90° C.
Polyacrylonitrile	$ \begin{array}{ccccccccc} & \text{H} & & \text{H} & & \text{H} & & \text{H} & & \text{H} \\ & & & & & & & & & \\ - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - \\ & & & & & & & & & \\ & \text{H} & & \text{C} & & \text{H} & & \text{C} & & \text{H} \\ & & & & & & & & & \\ & & & \text{N} & & & & \text{N} & & \end{array} $	+105° C.

^a Based on dynamic mechanical measurements at frequencies between 1 and 10 c.p.s.

The crystallinity of polyethylene shows that for molecules of very high chain flexibility, the relatively weak dispersion forces are sufficient to effect a partial three-dimensional ordering. For segment units of reduced flexibility crystallization will occur spontaneously¹⁰⁴ in the presence of sufficiently strong intermolecular forces (high heat of fusion), in as the case of many polyamides, or by a very marked reduction in the entropy of fusion, as in the case of certain *p*-phenylene copolymers.¹⁰⁵ In this connection attention should be drawn to the empirical relationships which have been established between the melting point and the glass transformation temperature.^{106, 107} However, the constant ratio of T_f/T_g can only be considered a very crude approximation, in view of the different functional dependence of the two quantities in copolymers and plasticized systems.

3. PLASTICIZATION, COPOLYMERIZATION, AND POLYMER MIXTURES

Within the framework of this review, it is impossible to discuss in all its aspects the broad and very complex subjects of plasticization, copolymerization, and polymer mixtures. It will be necessary to restrict our considerations to the effect which these variables have on the following rheological properties of organic glasses: glass transformation temperature T_g , width of the glass transformation region, the appearance of secondary and multiple dispersion regions, and ultimate-strength properties in the glassy state.

T_g values of such systems can vary between the limits of the T_g value of the components or can remain essentially unaffected by the presence of another component (or components), in which case the system will exhibit multiple transition regions. Both cases can be realized experimentally, as shown in Fig. 11a and b. The appearance of discrete damping maxima or dispersion regions means that there exist volumes of sufficient size in which the concentrations of the components are distinctly different. From a mechanical point of view, one can say that a phase separation has taken place and electron microscope observations on certain plasticized systems¹⁰⁸ and polymer mixtures⁸⁹ give a direct proof of this interpretation, which was first suggested by Würstlin¹⁰⁹ on the basis of dielectric measurements of plasticized compositions covering the complete concentration range. Würstlin also pointed out that the multiple dispersion regions are not

¹⁰⁴ Polyvinylchloride and polyacrylonitrile are typical examples of a large group of polymers which do not crystallize spontaneously, but can be brought to various degrees of crystallinity by the application of external forces.

¹⁰⁵ O. B. Edgar and R. Hill, *J. Polymer Sci.* **8**, 1 (1952).

¹⁰⁶ E. Jenckel, *Kolloid-Z.* **130**, 64 (1953).

¹⁰⁷ R. G. Beaman, *J. Polymer Sci.* **9**, 470 (1952); R. F. Boyer, *J. Appl. Phys.* **25**, 825 (1954).

¹⁰⁸ W. R. Richard and P. A. S. Smith, *J. Chem. Phys.* **18**, 230 (1950).

¹⁰⁹ F. Würstlin, *Kolloid-Z.* **113**, 18 (1949); **120**, 84 (1951).

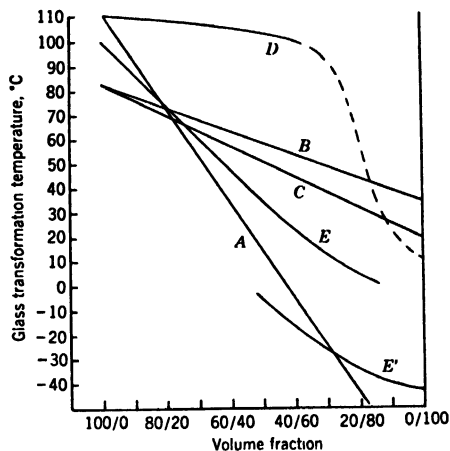


FIG. 11a. Glass transition temperatures as a function of concentration of components.

Curve A: Styrene—*isobutylene* copolymers (mech).¹²

Curve B: Vinylchloride-vinylacetate copolymers (mech).¹¹²

Curve C: Vinylchloride-methylacrylate copolymers (mech).¹¹²

Curve D: Polystyrene-styrene-butadiene copolymer mixture (mech).⁸

Curve E, E': Polyvinylbenzoate plasticized with benzylbenzoate.¹⁰⁹

necessarily characteristic of volumes consisting of a single component only. These types of multiple dispersion regions—in contrast to those discussed above—are closely related to polymer-polymer and polymer-plasticizer compatibility or solubility, quantities which can also be studied by solution

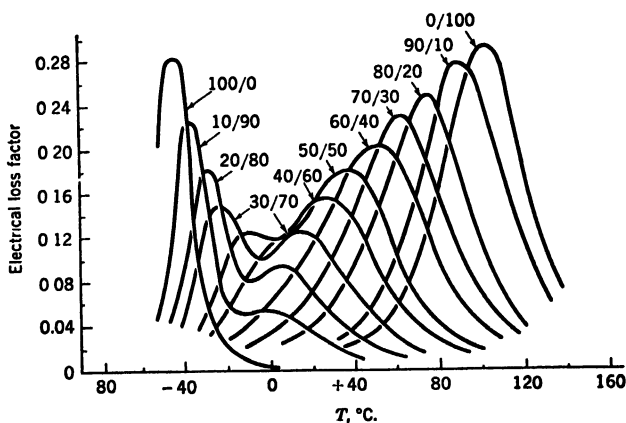


FIG. 11b. Multiple dispersion regions and broadening of the transition region in a plasticized polymer (polyvinylbenzoate plasticized with benzylbenzoate). [From F. Wüstlin, *Kolloid-Z.* **120**, 84 (1951).]

measurements of single or multicomponent systems.^{110, 111} If compatibility between two components extends over the investigated concentration range, the transition temperature T_g^{AB} is a linear fraction of the volume fraction, n , and the slope is determined by the glass transformation temperature of the components: $T_g^{AB} = nT_g^A + (1 - n)T_g^B$. This relationship has been verified for homogeneous copolymer systems^{112, 92} on the basis of mechanical studies (Fig. 11a); for plasticized compositions, where mechanical measurements over the whole concentration range are difficult to carry out, the relationship has been verified by electrical dispersion measurements.^{109, 113} Deviations from this simple relationship occur in plasticized systems with the onset of incompatibility^{108, 114} or partial phase separation, resulting in multiple dispersions and nonlinear dependence of the transition temperatures on volume fraction (Fig. 11b). Earlier attempts to explain the glass transformation temperature of plasticized compositions on the basis of the plasticizer viscosity¹¹⁵ (and viscosity-temperature coefficient), by the assumption of T_g^{AB} as an isoviscous state¹¹⁶ and on the basis of solvent-polymer interaction as measured by the μ value¹¹⁶ were shown to be incorrect.¹¹⁴ Whereas the melting point varies with the mole fraction of the diluent¹¹⁷ the glass transformation temperature depends on the volume fraction—in agreement with Fox and Flory's conclusion that this temperature represents a state of "iso free-volume" and not an "isoviscous" state.

Aside from changes in T_g , plasticization and copolymerization also lead to a broadening of the transition region^{117a} (see, for example, Fig. 11b). In copolymers, heterogeneity on a molecular scale broadens the transition range noticeably, as was shown by Nielsen¹¹⁸ (Fig. 12a). In plasticized compositions, the width of the transition first increases with plasticizer concentration, goes through a maximum, and then decreases again;^{114, 119} for a given volume fraction this appears to be primarily a function of the size of the various plasticizers, as can be seen from Fig. 12b. Although an adequate explanation of this phenomenon has not yet been given, it appears likely

¹¹⁰ P. J. Flory, *J. Chem. Phys.* **10**, 51 (1942).

¹¹¹ R. L. Scott, *J. Chem. Phys.* **17**, 279 (1949).

¹¹² L. E. Nielsen, R. Pollard, and E. McIntyre, *J. Polymer Sci.* **6**, 661 (1951).

¹¹³ A. J. Warner, *ASTM Bull. TP79*, April, 1950; M. L. Dannis, *J. Appl. Phys.* **21**, 505, 510 (1950).

¹¹⁴ L. E. Nielsen, R. Buchdahl, and R. Leverault, *J. Appl. Phys.* **21**, 607 (1950).

¹¹⁵ H. Jones, *J. Soc. Chem. Ind. (London)*, **67**, 415 (1948).

¹¹⁶ R. F. Boyer and R. S. Spencer, *J. Polymer Sci.* **2**, 157 (1947).

¹¹⁷ P. J. Flory, *J. Chem. Phys.* **17**, 223 (1949).

^{117a} H. Thurn and K. Wolf, *Kolloid-Z.* **148**, 16 (1956).

¹¹⁸ L. E. Nielsen, *J. Am. Chem. Soc.* **75**, 1435 (1953).

¹¹⁹ K. Wolf, *Kunststoffe* **41**, 89 (1951).

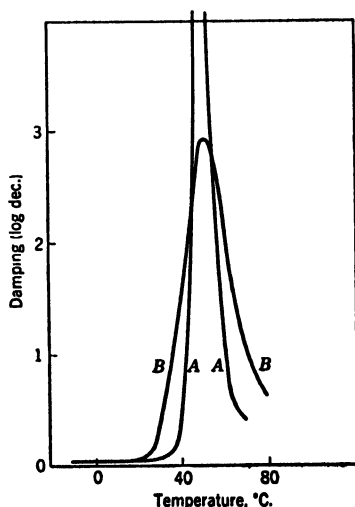


FIG. 12a. Broadening of transition region in copolymers.

Curve A: Homogeneous copolymer of vinylchloride-methacrylate

Curve B: Heterogeneous copolymer of vinylchloride-methacrylate

[From L. E. Nielsen, *J. Am. Chem. Soc.* **75**, 1435 (1953).]

that in copolymers and plasticized polymers, the broadening is the result of the existence of a large number of closely spaced and unresolved dispersion regions which can be due to slight differences in the nearest neighbor configurations; such fluctuations are likely to increase with the size of the molecules and it is worth while to point out that the width of the electrical dispersion region is always considerably broader than the mechanical dispersion region.

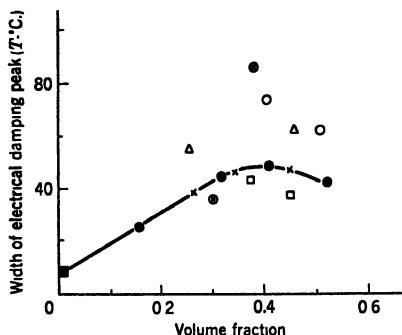


FIG. 12b. Half-width of electrical damping of peak of plasticized polyvinylchloride as a function of kind and amount of plasticizer. ■—unplasticized polyvinylchloride; ○—dimethylphthalate; ×—diethyl phthalate; ●—dibutylphthalate ○—dioctylphthalate ⊗—dilauryl phthalate; △—dibutylsebecate; □—tricresylphosphate. [From L. E. Nielsen, R. Buchdahl and R. Leverault, *J. appl. Phys.* **21**, 607 (1950)]

Creep¹²⁰ and stress-relaxation⁴⁷ measurements on plasticized systems do not yield any additional information which cannot be obtained from a study of the anelasticity as a function of temperature and frequency. Furthermore, the general features of the ultimate-strength properties are very similar to those of systems containing only one component, provided plasticization and copolymerization lead to a single dispersion region. For systems exhibiting multiple dispersion regions, ultimate-strength properties can be significantly modified.¹²¹

Nomenclature

G'	Real part of shear modulus	G''	Imaginary part of shear modulus
δ	Logarithmic decrement or damping, a measure of internal friction $\delta = \ln Y_1/Y_2$ (see page 149) for $\delta \leq 1.0$: $G''/G' = \delta/\pi$	w	Frequency of vibration
η	Newtonian viscosity	τ	Relaxation time
$\bar{G}$	Complex shear modulus $\bar{G} = G' + iG''$	$F(\tau)$ and $\bar{F}(\tau)$	Stress and strain relaxation functions
		T_g	Glass transformation temperature or "apparent" second order transition temperature

¹²⁰ F. S. Conant and J. W. Liska, *J. Appl. Phys.* **15**, 767 (1944); W. H. Aiken, T. Alfrey, A. Janssen, and H. Mark, *J. Polymer Sci.* **2**, 178 (1947); A. Dyson, *J. Polymer Sci.* **7**, 147 (1951).

¹²¹ L. E. Nielsen and R. Buchdahl, *SPE Journal* **9**, No. 5 (1953).

CHAPTER 5

THE RHEOLOGY OF RAW ELASTOMERS

M. Mooney

I. Introduction	181
II. Rheological Testing Equipment	184
1. Rotational Instruments	184
2. Extrusion Instruments	189
3. Compression Instruments	190
III. Viscometric Theory	192
1. Rotational Instruments	192
2. Extrusion Instruments	194
3. Compression Instruments	195
IV. Elastic Recovery	196
V. Surface Slip	197
VI. Experimental Results	200
1. The Fluidity or Flow Curve	200
2. Temperature Effects	211
3. Comparison of Different Plastometers	212
4. Thixotropy	213
5. Elastic Recovery	214
6. Surface Slip	217
7. Rheological Flow Units	218
VII. Theory of the Fluidity of Elastomers	219
VIII. Processing	225
1. General Remarks	225
2. Breakdown and Mixing	226
3. Forming Operations	227
Nomenclature	232

I. Introduction

Raw elastomers, or rubbers, both natural and synthetic, consist basically of long, chainlike polymer molecules having hundreds of monomer units in a chain. At room temperature the elastomers are essentially viscoelastic solids.¹ They are capable of large elastic deformation and capable also of slow continuous deformation under moderate stress, though the continuous deformation may be so slow as to be unobservable by ordinary means. At a sufficiently high stress the material breaks or tears. At higher temperatures,

¹ If the second-order transition temperature, T_s , of a high polymer is above room temperature, the polymer is generally classed as an elastomer, not a plastomer, even if it exhibits typical elastomeric properties at temperatures above T_s .

such as 50° C. or more, elastomers are capable of continuous shear at any imposed rate without rupture; or, if rupture occurs, the material is sufficiently tacky that it will form a single coherent mass when the ruptured pieces are pressed firmly together.

In order to prevent the flow or permanent deformation of commercial rubber articles it is necessary to cure the raw elastomer. Curing consists of forming chemical bonds, usually of sulfur, between the chain molecules at occasional points, thus forming a three-dimensional tangled network. In preparation for the curing operation the curative agents, together with powdered fillers and other compounding ingredients, must first be thoroughly mixed with the raw rubber. The raw mixed stock is then put through a forming operation, perhaps built into a composite structure such as a tire or a shoe, and then cured by heating in a mold or, in some cases, in an autoclave.

In the mixing and forming operations the rheological properties of the raw elastomer are of primary importance and must be held within established limits for successful processing. As suggested by the opening paragraph, the processing temperature must be considerably above room temperature; but even so, the viscosity of the raw rubber usually must be reduced by reducing its molecular weight, or by "breaking the rubber down." This is accomplished by mechanical mastication, usually assisted by a limited amount of oxidation. The mastication may be carried out in a Plasticator, which operates on the principle of a meat grinder; or in a Banbury, which consists of a pair of heavy curved knives rotating in a closed chamber; or on a rubber mill, which consists of a pair of rotating parallel steel rolls with a small clearance, or nip, through which the rubber is passed repeatedly.

After sufficient breakdown, mixing is begun, usually in a Banbury. The sulfur is often omitted in the first mixing step, in order to avoid premature curing at the high temperatures attained in the Banbury. The practice with regard to subsequent mixing operations varies. Remilling one or more times, with further reduction in viscosity, may be necessary to obtain satisfactory results in the later forming operation. The rheological properties are profoundly affected also by the kind and amount of compounding ingredients that are used in the stock—carbon blacks of different kinds, plasticizers, rubber-soluble oils, oxidizing chemicals, pigments, and dozens of different powdered fillers.

Forming operations are usually carried out with a screw extruder or with a calender. The screw extruder, like the Plasticator, operates like a meat grinder except that a forming die is substituted for the chopper. The product is extruded as a continuous rod with a cross section corresponding to the shape of the die. A calender, consisting of three or more parallel steel rolls,

passes the stock in a continuous sheet on successive rolls to the final nip, whence it is delivered as a formed sheet or pressed into a fabric which is fed continuously with the rubber into the last nip. In both extruder and calender the stock is subjected to severe mechanical working before the final forming action occurs. The stock is thereby warmed up, its thixotropic structure is broken down, and it is therefore reduced temporarily to a more plastic condition conducive to precise forming. Even so, allowance must always be made for some longitudinal shrinkage and lateral expansion resulting from the elastic recovery of the stock.

The injection processing method, which is coming into some use at the present time for solid rubber articles, succeeds in by-passing the forming operation by injecting under high pressure directly into a closed mold.

It is obviously a difficult problem to maintain adequate processing controls when dealing with materials that are highly thixotropic, non-Newtonian and elastic, undergo changes during processing, and are likely to cure in the processing equipment if the temperature, increased by the mechanical work of processing, gets out of control. As aids in this control work, a large number of rheological tests for raw elastomers have been developed.

Rheological testing equipment, like the processing equipment, is operated at elevated temperatures, usually within the range from 70 to 100° C. Nevertheless, the viscosity is so high that gravitational forces can produce but little flow, and either mechanical force or air pressure must be employed. In rheological instruments of the rotational type the sample must be confined in order to keep it from climbing out of the instrument under the secondary forces that develop within the sample.

The marked thixotropy of elastomers requires consideration in the design and interpretation of rheological tests. As will later be shown, the initial viscosity when deformation begins may be ten times greater than the later, steady-state viscosity. Such thixotropic behavior makes it impossible to interpret reliably any test in which the deformation is limited. On the other hand there is a certain difficulty that arises when any attempt is made to attain in a rotational viscometer a state of true thixotropic equilibrium. This difficulty is that, in addition to the rapid breakdown of recoverable thixotropic structure, there is usually a slow, permanent softening of the elastomer if the test method involves extensive and continuous deformation. Consequently, a strictly steady state of viscosity may not be attainable; and if a single figure is to be reported as "the viscosity," an arbitrary criterion must be adopted as to when the viscosity is changing slowly enough to be considered essentially steady.

Elastomers always exhibit considerable elasticity, even when raw, hot, and reduced to a state of minimum thixotropic structure. When released

from an imposed deformation, they snap back and then slowly creep further toward their last previous form. This elastic recovery makes precise forming of elastomers impossible and often causes difficulty in holding even to the liberal tolerances which the rubber technologist allows himself. Measurement of elastic recovery is therefore of practical importance and must be included with a viscosity measurement for the best processing control.

In a screw extruder there must be some slippage of the raw mixed stock over the smooth metal surfaces of the barrel, screw, throat, and die. If this were not the case the nonmoving stock in contact with the metal would, at the existing temperatures, sooner or later cure and would then interfere with the smooth operation of the extruder. On the other hand, the slippage, while important, is normally quite slow; so slow, in fact, that it has proved difficult to obtain direct evidence of slippage or any measurement of it. A few rough measurements of this kind have been published only recently.

In the following sections the principal types of rheological testing instruments for raw elastomers will be described and the related rheometric equations will be stated; various rheological test results will be reviewed; a new theory of the viscosity of an elastomer will be briefly presented; and the chapter will close with a discussion of the applications of rheological tests in processing control.

II. Rheological Testing Equipment

1. ROTATIONAL INSTRUMENTS

In rheological instruments of the rotational type a sample can be maintained indefinitely in a state of continuous shear until a steady or quasi-steady state is attained. The earliest such instrument suitable for rubbers was the rubber rheometer, developed by Mooney.²

Essential details of the apparatus are shown in Figs. 1 and 2. The outer cylinder, or stator, 1 and 2, is in the form of a split block, which opens up for easy insertion of the sample. The inner cylinder, or rotor, 7, is mounted on a hollow shaft, 8, which is driven by weights (not shown) connecting by steel cables with the sheave, 23. Both inner and outer cylinder surfaces are covered with fine, longitudinal V-grooves to prevent slippage of the sample.

Besides the sample proper, located in the narrow space between the two cylinders, additional sample material is placed in the annular channels, 16 and 17. The pressure rings, 14 and 15, faced with cured rubber, are brought to bear against this reserve sample in the channels; and the weights, 12 and 13, operating on the pressure rings, maintain the sample under pressure and keep it from working out of the test space. Temperature is maintained by means of hot oil which flows under gravity through the hollow shaft and under pressure through cavities (not shown) in the outer cylinder blocks.

² M. Mooney, *Physics* 7, 413 (1936).

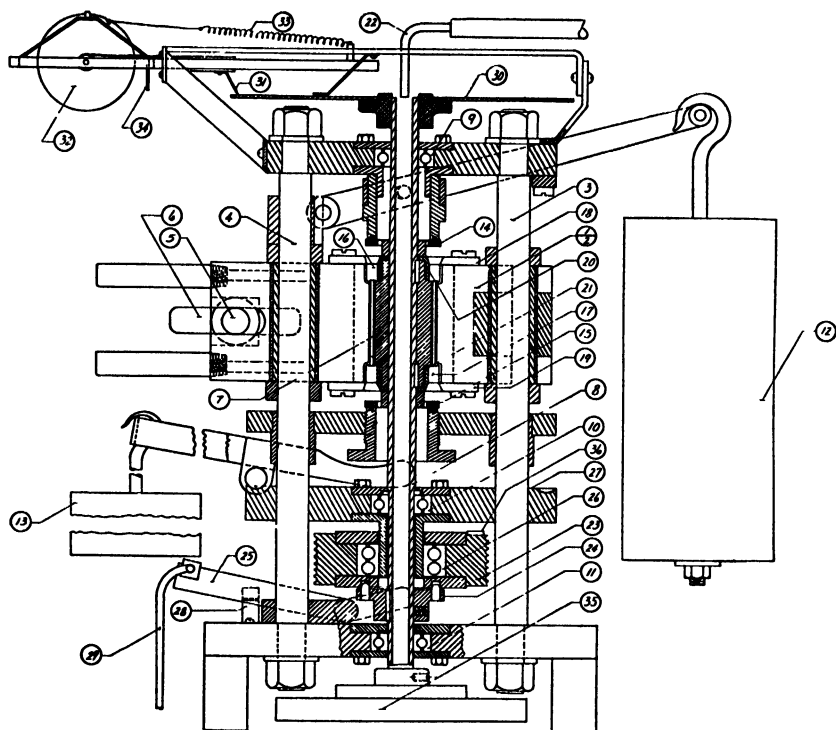


FIG. 1. The rubber rheometer of Mooney, vertical section. [From M. Mooney, *Physics* 7, 413 (1936).]

The angular velocity of the rotor is measured with a stop watch at slow and moderate speeds. At high speeds a spark record is obtained on a sensitive chart on the circular table, 30, mounted on the rotor shaft. The driving weight in this instrument turns the rotor $2\frac{1}{4}$ revolutions before it hits the floor, after which the weight must be lifted and adjusted for the next driving period. In this rest period the sample always recovers thixotropic structure, which must be broken down again during the next driving period. The initial rotor velocity during any driving period is therefore always low. The rotor velocity of significance for a steady-state rheological flow curve is the constant velocity observed during the latter part of a driving period. If a constant velocity is not attained the terminal velocity lacks significance.

For making elastic recovery measurements the sheave, 23 can be thrown free of the clutch plate, 24, while the rotor is still moving under the torque of the driving weight. The subsequent movement of the rotor under the elastic restoring force of the sample can be recorded by means of the stylus, 31, which is pulled radially across the chart at the right moment and at an

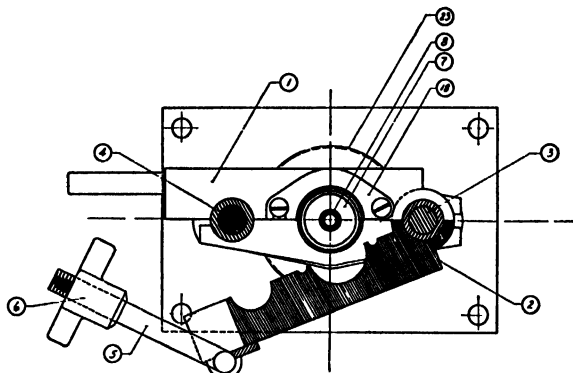


FIG. 2. The rubber rheometer of Mooney, horizontal section. [From M. Mooney, *Physics* 7, 413 (1936).]

appropriate speed. The mechanical gadgets on the instrument also include an arrangement for stopping the rotor suddenly and then releasing it after a short time lapse.

The rubber rheometer, though useful as a research tool, is too slow in operation to be satisfactory for routine control tests. For this purpose there was developed another rotational instrument,³ in which the rotor is a flat disk and the stator a shallow cup enclosing the disk.⁴ As shown in Fig. 3, the stator of this instrument is split along a central plane parallel to the face of the disk; and the hand-closing mechanism, involving a double lever system, is sufficiently powerful that it can cut and shape the sample without appreciable delay, except with very tough, cold samples.

The rotor has a split shaft which engages with the key, 10, in the spindle, 9, which is driven by a synchronous motor through the worm, 12, and worm gear, 13. The worm shaft floats in its bearings and is forced by the reaction of the sample to press against the spring, 15. The deflection of the spring, measured on the gage, 17, thus indicates the viscous force developed in the sample under the imposed continuous shear. Temperature is usually maintained by electric heaters. The plungers, 5 and 6, backed by the steel springs, 7 and 8, are forced up by the sample as the instrument is closed. They later come back down to some extent, keeping the sample under pressure in spite of slight leakage of rubber and trapped air from the chamber.

³ M. Mooney, *Ind. Eng. Chem. Anal. Ed.* 6, 147 (1934).

⁴ As many in the rubber industry know, this rotating disk viscometer is now generally referred to as the "Mooney viscometer." The present writer decries the use of proper names instead of descriptive names to identify a test apparatus or method. In the present instance he argued for retention of the name "disk viscometer;" but it was a losing battle.

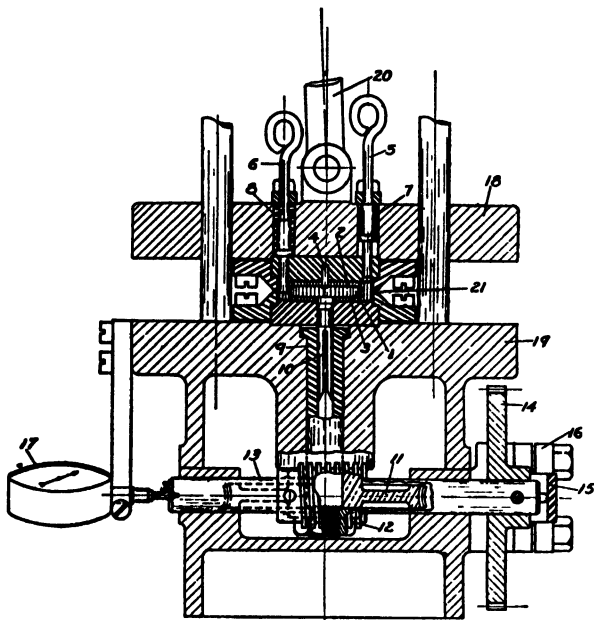


FIG. 3. The shearing disc, or Mooney, viscometer. [From M. Mooney, *Ind. Eng. Chem. Anal. Ed.* **6**, 147 (1934).]

A few Mooney viscometers have been made in which the worm gear engages the spindle through a clutch which, when disengaged, permits the rotor to reverse and show the elastic recovery of the sample. The reverse rotation registers on a dial at the side of the instrument case.

The usual operating temperature of the viscometer is 100° C. When operated at somewhat higher temperatures it can be used to measure scorch,^{5, 6} or incipient cure of a compounded stock. Scorching is indicated by a steep rise in the viscosity-time curve observed during the viscosity test. A rotor of less than standard diameter is usually employed in the scorch test, in order to avoid overloading the driving mechanism.

An interesting variation of the disk viscometer has been introduced by Piper and Scott,⁷ who substituted a biconical rotor for the flat disk. The biconical form, shown in Figs. 4 and 5, has the advantage that the rate of shear in the sample is uniform over the face of the rotor, which is not the case with the disk rotor. Hence, the biconical rotor permits theoretically a calculation of the true viscosity at a known, single rate of shear, except for edge effects; while the flat disk rotor gives only an average viscosity over a

⁵ J. V. Weaver, *Rubber Age N. Y.* **43**, 89 (1940).

⁶ R. W. Whorlow, *India Rubber J.* **125**, 214 (1953).

⁷ G. H. Piper and J. R. Scott, *J. Sci. Instr.* **22**, 206 (1945).

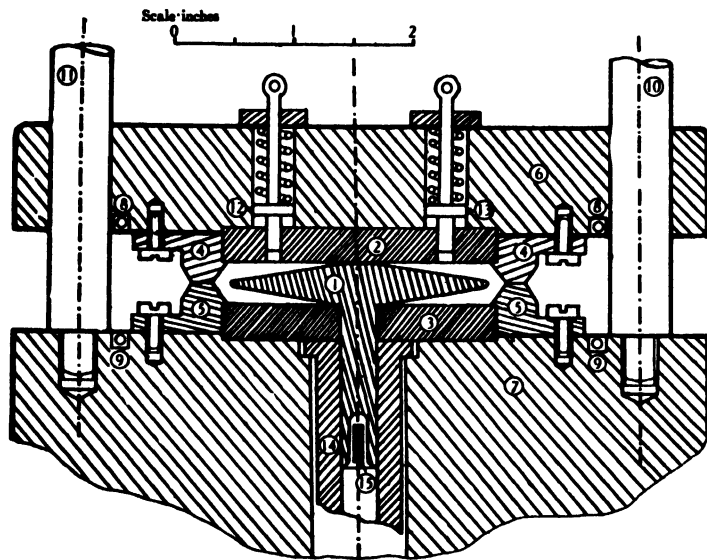


FIG. 4. The shearing-cone plastimeter of Piper and Scott; vertical section. [From G. H. Piper and J. R. Scott, *J. Sci. Instr.* **22**, 206 (1945).]

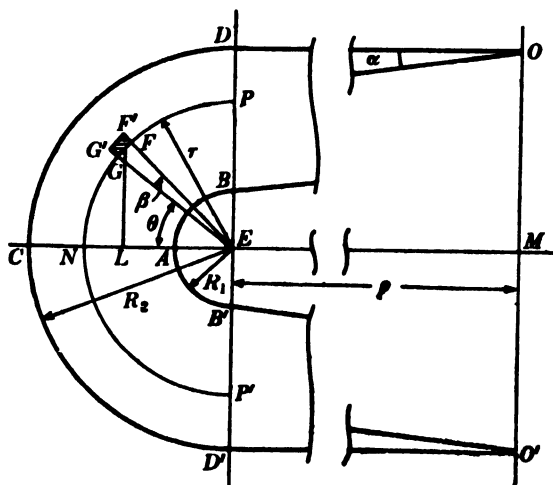


FIG. 5. The shearing-cone plastimeter of Piper and Scott; horizontal section through center of rotor. [From G. H. Piper and J. R. Scott, *J. Sci. Instr.* **22**, 206 (1945).]

range in rate of shear. On the other hand, if the rheological curve is desired, then the advantage of the biconical rotor is not so great; for such a curve can be obtained with either rotor from data covering a range in rotor speeds. This point, and also the question of edge effects, will be discussed later.

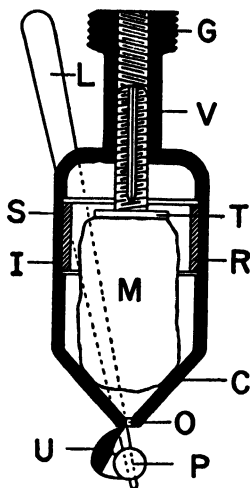


FIG. 6. The extrusion plastometer of Marzetti. [From B. Marzetti, *India Rubber World* **68**, 776 (1923).]

Other rotational instruments of cylindrical form have been used by Hamm⁸ and by Eccher.⁹ Hamm's viscometer was of the same form essentially as Mooney's except that the pressure rings were omitted. This omission reduced friction but limited the rotational speeds at which measurements could be made. Eccher employed two independent rotors of different lengths in a common stator. End effects were thus eliminated by taking the difference between the torques of the two rotors at the same speed. Instead of pressure rings to keep the instrument filled, Eccher employed a forced continuous feed into the space between the rotors.

2. EXTRUSION INSTRUMENTS

The extrusion type of viscometer is of historical interest, because this was the type used by Marzetti,¹⁰ the pioneer in rheological testing in the field of rubber technology. His instrument, shown in Fig. 6, consisted of a cylinder with a conical bottom terminating in a hole through which the sample was extruded by compressed air. A loose fitting piston on top of the sample prevents the air from channeling through to the delivery hole. The required heating period of one-half hour is a disadvantage of this type of viscometer.

The extrusion rates employed by Marzetti were quite slow; and the conical shape of the exit makes accurate computation of true viscosity impossible. Nevertheless, the instrument served to obtain a considerable body

⁸ G. G. Hamm, Thesis, Naamloze Vennootschap, W. D. Meinema, Delft (1946).

⁹ S. Eccher, *Ind. Eng. Chem.* **43**, 479 (1951).

¹⁰ B. Marzetti, *India Rubber World* **68**, 776 (1923).

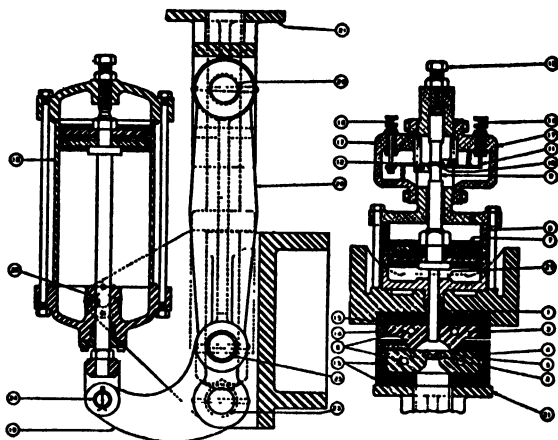


FIG. 7. The extrusion plastometer of Dillon. [From J. H. Dillon, *Physics* **7**, 73 (1936); *Rubber Chem. and Technol.* **9**, 496 (1936).]

of relative quantitative data on the viscosity of various raw rubbers and mixes in various stages of processing.

A number of other extrusion viscometers have been used by other investigators.¹¹⁻¹⁴

The most elaborate, and at the same time the most practical plastometer in many ways is the Dillon¹⁴ extrusion plastometer, shown in Fig. 7. All mechanical movements are powered with compressed air, including the operation of charging the hemispherical extrusion chamber with the sample. Electric switches on the extrusion ram automatically record the time of extrusion of a fixed volume.

The McKee Worker viscometer¹⁵ has the advantage that, unlike other extrusion instruments, it can bring the sample essentially to a state of thixotropic breakdown. This is accomplished by pushing the sample back and fourth any number of times through one or several holes in a plate dividing the extrusion cylinder into two halves. The pistons, one in each half of the cylinder, are mechanically driven at a controlled speed, the required force being observed.

3. COMPRESSION INSTRUMENTS

In the viscometers of the compression type, a sample, initially in the form of a small pellet, is pressed between flat plates under a given load. The

¹¹ R. W. Griffiths, *Trans. Inst. Rubber Ind.* **1**, 308 (1926).

¹² J. Behre, *Kautschuk* **8**, 2, 167 (1932); *Rubber Chem. and Technol.* **6**, 244 (1933).

¹³ J. H. Dillon and N. Johnston, *Physics* **4**, 225 (1933); *Rubber Chem. and Technol.* **7**, 248 (1934).

¹⁴ J. H. Dillon, *Physics* **7**, 73 (1936); *Rubber Chem. and Technol.* **9**, 496 (1936).

¹⁵ S. A. McKee and H. S. White, *J. Research Natl. Bureau Standards* **46**, 18 (1951).

thickness of the sample after a given compression time is generally taken as a measure of its plasticity.

The Williams plastometer¹⁶ was the first instrument of this type to be used extensively. It consists essentially of a flat base plate and a 5-kg. weight mounted on guides to hold it straight. The standard procedure adopted by Williams was to use a 2-cm. sample which was preheated and then pressed for 5 min. at 100° C. In order to keep the sample from sticking to the plastometer plates the sample is usually placed between sheets of rice paper or other thin sheet material. Garner¹⁷ has reported slight slippage in some cases when the sample was in direct contact with the plates.

Elastic recovery is measured by the height of the sample a minute or more after removal from the plastometer. A test is not considered satisfactory if the compressed height and the recovered height are not both considerably less than the initial sample height.

Many minor variations of the Williams plastometer have been developed,¹⁸⁻²¹ and there is another series of compression instruments²²⁻²⁵ in which a small table or a pair of small plates is used with a sample of initial diameter equal to or greater than the table or plate diameter. In these designs the deforming pressure remains constant during the test. DeVries²⁶ reports difficulties with this test because of variability in the behavior and effects of the ring of extruded sample around the edge of the table.

Two investigators^{25, 26} have described compression plastometers with accessories which permit converting into various forms at will.

A variation in testing procedure, the Defo method, much used in Germany involves two or more tests with different compressing loads which permit interpolation to that load required to compress the sample to the standard compressed thickness in the standard time. The details, as given by Baader²⁵ are: Sample form, circular cylinder 1 cm. in diameter and 1 cm. in height; compressed to 0.4 cm. in height in 30 sec. at 80° C. Preheating period 20 min. Recovery height measured at 30 sec. after release. A more

¹⁶ I. Williams, *Ind. Eng. Chem.* **16**, 362 (1924).

¹⁷ T. L. Garner, *India-Rubber J.* **78**, 20 (1929).

¹⁸ J. Hoekstra, *Physics* **4**, 285 (1933); *Rubber Chem. and Technol.* **7**, 136 (1934).

¹⁹ R. Houwink and P. N. Heinze, *Ind. Eng. Chem. Anal. Ed.* **10**, 689 (1938).

²⁰ H. Hagen, *Kautschuk* **14**, 203 (1938).

²¹ W. N. Keen, *India Rubber World* **110**, 174 (1944).

²² W. de Visser, "The Calender Effect and the Shrinkage of Unvulcanized Rubber." Crosby Lockwood & Son, London, 1926.

²³ A van Rossem and H. van der Meijden, *Kautschuk* **3**, 369 (1927); *Rubber Chem. and Technol.* **1**, 393 (1928).

²⁴ E. Karrer, J. M. Davies, and E. O. Dieterich, *Ind. Eng. Chem. Anal. Ed.* **2**, 96 (1930); *Rubber Chem. and Technol.* **3**, 295 (1930).

²⁵ T. Baader, *Kautschuk* **14**, 223 (1938).

²⁶ O. de Vries, *India-Rubber J.* **75**, 429 (1928).

detailed description and critical analysis of the Defo plastometer has been published by Whorlow.²⁷

III. Viscometric Theory

The problem considered here is that of computing viscosities from the raw data of observation given by the three types of testing instruments described in the previous section.

1. ROTATIONAL INSTRUMENTS

For a coaxial rotating cylinder viscometer of small intercylinder clearance, the well-known formulas are:

$$g = \Omega \frac{R_2^2 + R_1^2}{R_2^2 - R_1^2}$$

$$\tau = \frac{C}{4\pi L} \left(\frac{1}{R_1^2} + \frac{1}{R_2^2} \right) \quad (1)$$

where g is the rate of shear, τ the shearing stress, R_1 and R_2 the radii of the inner and outer cylinder, respectively, L their length, Ω the angular rotor velocity, and C the driving torque. The viscosity is

$$\eta = \tau/g = \frac{C}{4\pi L\Omega} \left(\frac{1}{R_1^2} - \frac{1}{R_2^2} \right) \quad (2)$$

The rubber rheometer lends itself also to another rheological measurement. The autographic traces of the elastic recovery show at the beginning a few rapidly damped oscillations superimposed on the recovery curve. From the frequency and damping rate it is possible to calculate the dynamic shear modulus and viscosity for the observed frequency and amplitude. The reader is referred to the published article² for the theoretical formulas for dynamic viscosity and modulus.²⁸

²⁷ R. W. Whorlow, *J. Rubber Research* **18**, 51 (1949).

²⁸ Dillon and Cooper²⁹ have criticized the use of these equations in this application on the grounds that the equations assume constant viscosity although the sample shows large variations in viscosity with rate of shear. In reply to this criticism it can be said that the viscosity variation is established for continuous, unidirectional shear; but whether the viscosity of Hevea rubber varies under shear oscillations of small amplitude is not known. Data reported by Marvin³⁰ on polyisobutylene show constant viscosity in oscillation in the frequency range 0.0016 to 16 c.p.s. at 25° C. The frequency in the author's oscillation test was approximately 100 c.p.s. On the basis of our present limited knowledge, the assumption of constant viscosity of Hevea in shear oscillations at the frequency concerned is probably as good as any that can be suggested.

²⁹ J. H. Dillon and L. V. Cooper, *Rubber Age N. Y.* **41**, 306 (1937).

³⁰ R. S. Marvin, National Bureau of Standards, Interim Report on the Cooperative Program on Dynamic Testing (1951).

The viscometric theory of the disk and the biconical rotor viscometer is complicated by the geometry of the boundary conditions. As a practical procedure it is convenient to assume the Porter-Rao power law of fluidity,

$$g = f\tau^n \quad (3)$$

where g is the steady rate of shear, τ the shearing stress, and f and n are material constants. On this basis Piper and Scott⁷ have analyzed the biconical viscometer, their results being expressible in the form

$$C = \frac{4\pi\rho^3}{3} \left(\frac{\Omega}{\alpha f} \right)^{1/n} + 2\pi^2 \rho^2 R_1 \left(\frac{\rho\Omega(n-1)}{fR_1(1-\lambda^n)} \right)^{1/n} \quad (4)$$

where C is the driving torque, Ω the rotor angular velocity, λ is R_1/R_2 and α , ρ , R_1 and R_2 are as indicated in Fig. 5.

If it is found experimentally that C is proportional to $\Omega^{1/n}$ the above equation then serves to determine f and n . However, if the logarithmic plot of C vs. Ω is not strictly linear, a more elaborate computation procedure is required to obtain the true $g - \tau$ relationship.

If we identify g as Ω/α , then the above equation is equivalent to

$$g = \frac{\Omega}{\alpha}$$

$$\tau = \frac{C}{\frac{4\pi\rho^3}{3} + 2\pi^2 \rho^2 R_1 \left(\frac{n-1}{1-\lambda^{n-1}} \right)^{1/n}} \quad (5)$$

Now for any chosen value of Ω the local value of n can be determined graphically from the logarithmic $C - \Omega$ plot. The corresponding stress, τ , can then be computed from equation (5), and a point on the rheological curve is thereby determined. The computation can be repeated for other values of Ω , and the complete experimental $g - \tau$ curve is thus obtained.

An analysis of the disk viscometer by the method of Piper and Scott leads to the torque equation

$$C = \left[\frac{4\pi R_1^3}{3 + \frac{1}{n}} + \frac{4\pi n b R_1 h}{1 - \lambda^{2n}} \right] \tau^n \quad (6)$$

where R_1 is the rotor radius, R_2 the stator radius, λ is R_1/R_2 , b is the rotor thickness, and h is the clearance, top or bottom, between rotor and stator,

Corresponding to equations (5) we have in this case

$$g = \frac{R_1 \Omega}{h}$$

$$\tau = \frac{C'}{\frac{4\pi R_1^3}{3 + \frac{1}{n}} + \frac{4\pi n b R_1 h}{1 - \lambda^{2n}}} \quad (7)$$

Computation of the $g - \tau$ curve would proceed in the manner described in connection with equations (5).

With regard to the fluidity power law stated by equation (3), the point is sometimes made that the law is probably not valid in the limit as the stress approaches zero. No doubt, this criticism is correct. However, from a practical point of view it is not important; for the absolute error in the postulated fluidity at low stress is small and has a very small or negligible effect in the computations outlined above.

2. EXTRUSION INSTRUMENTS

Several extrusion plastometers have been used with dies which were of conical form or were short in comparison with their diameters. The viscometric theory of such instruments will not be attempted, the theory which follows being limited to dies or delivery tubes of uniform circular section and of considerable length.

The published data on the extrusion of rubbers usually cover variations in pressure, sometimes variations in temperature, but only rarely do they cover variations in tube diameter and length. This is regrettable, because measurements that have been made with two or more tube lengths show that the entrance pressure drop in the extrusion of rubbers is very high, sometimes as much as half the total extrusion pressure. Consequently, the pressure drop within the extrusion tube remains unknown when only a single tube length is used; and viscosities cannot be accurately computed from such limited data. In particular it may be noted that if a pressure-efflux curve has a positive intercept on the pressure axis, it cannot be concluded that the flowing material within the extrusion tube has a yield point. It is more likely that the rubber is thixotropic and has a yield point for initial flow within the extrusion chamber.

For the flow in the lower section of an extrusion tube within which there is no further thixotropic or elastic change, the viscometric equation can be obtained for any liquid, Newtonian or non-Newtonian. The equation, first published by Rabinowitsch³¹, can be written in the form

$$g = E \left(3 + \frac{d \log E}{d \log \tau} \right) \quad (8)$$

³¹ R. Rabinowitsch, *Z. physik. Chem.* **A145**, 1 (1929).

where g is the rate of shear at the tube wall, τ is the shear stress at the tube wall, E is the reduced efflux, $Q/\pi a^3$, Q being the volume of flow per unit time, and a the tube radius. τ is given by the well-known expression $aP/2L$, P being the pressure drop in the tube and L the tube length.

3. COMPRESSION PLASTOMETERS

In all the published theories of the compression plastometer, in either the plate or table form, thixotropy is neglected; it is assumed that at all points in the sample at all times the stress-rate of strain relationship is that corresponding to a steady state of continuous deformation at the instantaneous local rate. This is a highly questionable assumption when the deformation is so limited and is so variable in time and space. Other, more acceptable, assumptions are, first, that there is no slip of the sample on the compressing surfaces and, second, that the vertical component of the velocity can be neglected except insofar as it requires and determines the net radial flow as a function of the radius.

For a Newtonian liquid in a plate plastometer Stefan³² deduced the formula

$$\frac{1}{h^4} - \frac{1}{h_0^4} = \frac{8\pi Mgt}{3\eta V^2} \quad (9)$$

where h_0 is the initial height of the sample, h its height at time t , M is the compressing weight, g the acceleration of gravity, η the viscosity, and V the sample volume.

In application to the table form of compression plastometer with a constant sample area, Martin³³ quotes a formula for a Newtonian liquid derived by Taylor.³⁴

$$\frac{1}{h^2} - \frac{1}{h_0^2} = \frac{4Mgt}{3\pi a^4 \eta} \quad (10)$$

where a is the diameter of the table.

In more recent analyses Peek³⁵ and Scott³⁶ have derived equations based on the assumed flow law

$$g = \left(\frac{\tau - Y}{\eta_0} \right)^n \quad (11)$$

where Y , n , and η_0 are material constants. The equations are complicated and have not been frequently used. For the case $Y = 0$ Scott³⁶ has more

³² M. J. Stefan, *Sitzber. Akad. Wiss. Wien. Math. Naturw. Kl. Abt. II* **69**, 713 (1869).

³³ G. Martin, *Trans. Inst. Rubber Ind.* **6**, 298 (1930).

³⁴ G. S. Taylor, *Proc. Roy. Soc. (London)* **108**, 12 (1925).

³⁵ R. L. Peek, Jr., *J. Rheol.* **3**, 345 (1932).

³⁶ J. R. Scott, *Trans. Inst. Rubber Ind.* **10**, 481 (1935); *Rubber Chem. and Technol.* **8**, 587 (1935).

recently published the theoretical results in a simplified form and has included curves of some parametric functions required in computations.

All these theoretical equations are usually ignored by those who use compression plastometers, their results normally being reported simply as the sample height or as certain height ratios after a given compression time.

IV. Elastic Recovery

Most rheological testing devices used for elastomers permit some kind of measurement of elastic recovery after the sample is released, but the rubber rheometer is the only one that yields a figure representing the degree of recovery in a simple, homogeneous recovery deformation. The figure is the simple shear recovery

$$\gamma_r = \theta_r \frac{R_2^2 + R_1^2}{R_2^2 - R_1^2} \quad (12)$$

where θ_r is the observed reverse rotation of the rotor, and R_1 and R_2 are as defined for equation (1).

The Piper and Scott⁷ biconical viscometer, if used in recovery tests, would give an approximate value for simple shear recovery. There is some error arising from two facts. First, the edge effect, represented by the last term in equation (4) is not small, and, second, the rate of shear in the edge region is not uniform.

A measurement closely related to elastic recovery has been used by Blow and Schofield³⁷ with the Mooney viscometer. After completing a viscosity test and stopping the motor, they leave the sample in the instrument and observed the decay of stress in the sample as indicated by the falling of the dial reading. The figure which they use as significant is the ratio V/R , where V is the standard viscosity reading and R is the decayed reading at 60 sec. after stopping the motor. This ratio is inversely related to elastic recovery as directly measured.

Elastic recovery in an extrusion test, or extrusion swell, is measured by the diameter of the extruded worm relative to the diameter of the delivery tube. Extrusion swell has been analyzed by Spencer and Dillon,³⁸ but the type of shearing deformation they assume to exist in the sample at exit could only lead to a telescopic elastic deformation after exit, not to longitudinal contraction and diametric swell. Their agreement with experimental results must be fortuitous or, more likely, result from relationships among some factors in the extrusion test that are not yet understood.

³⁷ C. M. Blow and J. R. Schofield, *Rubber Chem. and Technol.* **23**, 601 (1950); "Principles of Rheological Measurement," published for the British Rheologists Club, Nelson, London.

³⁸ R. S. Spencer and R. E. Dillon, *J. Colloid Sci.* **3**, 163 (1948).

Those who use compression plastometers use different methods for expressing the elastic recovery in terms of the data of observation. Since the recovery, like the deformation, is nonuniform, any compression recovery figure is an average value.

V. Surface Slip

In the Introduction it was indicated that slippage of raw stocks on hot metal surfaces is known to occur but is slow and difficult to measure. Two different experimental approaches to this problem have recently given positive results. One approach involves such a series of test conditions as to apparatus dimensions that it becomes possible to distinguish between the effects of the shearing deformation and the surface slip on the total observed movement. The other approach involves paired measurements with the same apparatus dimensions but with smooth and roughened surfaces, respectively, in contact with the test material.

An application of the first method, involving extrusion measurements with dies of different lengths and diameters, was mentioned in the paper by Mooney and Black.³⁹ The theory of the slip calculations has been published by Mooney.⁴⁰

As an example of the second method of measuring slip, recent data by Decker and Roth⁴¹ may be cited. Measurements were made with a standard serrated rotor and with a smooth rotor in the Mooney viscometer. Lower torque readings with the smooth rotor when observed can be attributed to surface slip.

The computation of absolute slip velocity requires experimental data over a range of rotor speeds. The theory has been developed by the present writer, but not yet published. Here, however, the results will be stated. The theory assumes that the slip velocity obeys a power law similar to equation (3); thus

$$v = s\tau^p$$

where v is the slip velocity, τ is the surface shearing stress, and s and p are material constants characteristic of the elastomer and the surface on which it is slipping.

The complex geometry makes a solution in closed form impossible. Two different power series solutions are developed, to the first approximation only, one value for small slip and the other for large slip. For the intermediate range, where the slip velocity is of the order of the displacement velocity associated with shear, no solution of satisfactory precision has been obtained. The solutions for the two extreme cases are:

³⁹ M. Mooney and S. A. Black, *J. Colloid Sci.* **7**, 204 (1952).

⁴⁰ M. Mooney, *J. Rheol.* **2**, 210 (1931).

⁴¹ G. E. Decker and F. L. Roth, *India Rubber World* **128**, 339 (1953).

(i) for small slip velocity,

$$v = \frac{nR_1\Omega(C_0 - C)F_1}{C_0} \quad (14)$$

$$\tau = \frac{3C_0F_2}{4\pi R_1^3}$$

$$F_1 = \frac{(2n + p + 1) \left[1 + \frac{(3n + 1)bA^{1/n}}{2nR_1} \right]}{(3n + 1) \left[1 + \frac{(2n + p + 1)bA^{(p+1)/n}}{2nR_1} \right]}$$

$$F_2 = \frac{3n + 1}{3n \left[1 + \frac{(3n + 1)bA^{1/n}}{2nR_1} \right]} \quad (15)$$

$$A = \frac{2nh}{(1 - \lambda^{2n})R_1}$$

$$\lambda = \frac{R_1}{R_2}$$

R_1 , R_2 , b , h and Ω are as defined for equations (1). C and C_0 are the observed torques at rotor velocity Ω with and without slip, respectively; that is, with the smooth and the serrated rotors, respectively.

(ii) for large slip velocity

$$v = R_1\Omega \left(1 - \frac{\Omega_0}{\Omega} F_3 \right) \quad (16)$$

$$\tau = \frac{3CF_4}{4\pi R_1^3}$$

$$F_3 = \frac{\frac{3p + 1}{3p + n + 1} \left(\frac{1 + \frac{1}{3p}}{1 + \frac{1}{3n}} \right)^n}{1 + \frac{(3p + 1)b}{2pR_1}} \times \quad (17)$$

$$\left[1 + \frac{(2p + n + 1)(1 - \lambda^{2n})b}{4pnh} \right] \left[1 + \frac{(3n + 1)bA^{1/n}}{2nR_1} \right]^n$$

$$F_4 = \frac{1 + \frac{1}{3p}}{1 + \frac{(3p + 1)b}{2pR_1}}$$

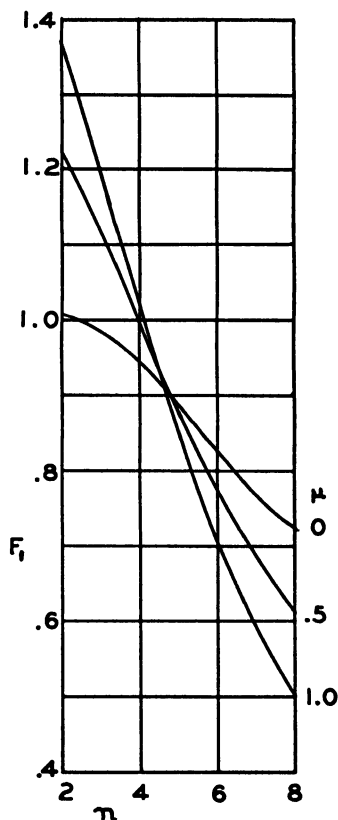


FIG. 8. The slip velocity computation factor F_1 of equations (14.1) and (15.1) for small slip velocity. $\mu = p/n - 1$. p and n are the exponents in the slip velocity and the fluidity power laws, respectively.

Ω and Ω_0 are the rotor velocities at torque C' with and without slip, respectively.

The values of n and p can be determined from logarithmic plots of observable data. Thus, according to equations not included in this summary,

$$\begin{aligned}
 &\text{for no slip} && C' = \text{const} \times \Omega^{1/n} \\
 &\text{for small slip} && C_0 - C' = \text{const} \times \Omega^{(p+1)/n} \\
 &\text{for large slip} && C' = \text{const} \times \Omega^{1/p}
 \end{aligned} \tag{18}$$

For convenience in computing slip, Figs. 8 to 11 give in graphical form the values of the F -factors in equations (15) and (17) for a limited range of the parameters n and p and for the instrument dimensions of the standard Mooney viscometer.

An analysis similar to the one summarized here can be made also for the

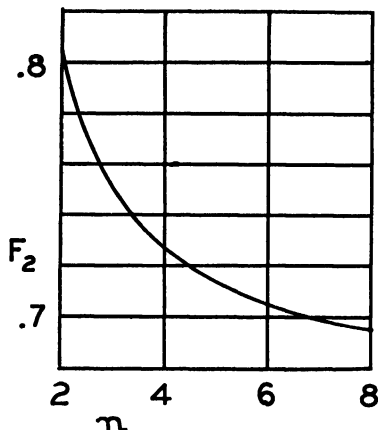


FIG. 9. The shear stress computation factor F_2 of equations (14.2) and (15.2) for small slip velocity. n is the exponent in the fluidity power law.

bioconical rotor of Piper and Scott, but in slip measurements the biconical form loses its advantage relative to the disk form.

VI. Experimental Results

1. THE FLUIDITY OR FLOW CURVE

Many rheological measurements on rubbers have been reported which consist of single observations under arbitrarily chosen test conditions. Such measurements are inadequate for determining the viscosity function of a non-Newtonian liquid.

The first published data giving rheological curves for elastomer are those obtained by Mooney² in measurements on Hevea rubbers in the rubber rheometer. As was explained above in Section III, 1, there is thixotropic recovery during the rest periods in this weight-driven instrument; and the initial rotor velocity within a driving period is low. Figure 12 shows a curve of velocity vs. angle of rotation after the driving weight starts falling. It is seen that in this case the initial velocity is only $1/10$ of the final, constant velocity.

Figure 13 shows in curve A, the rheological curve of the steady-state rate of shear vs. shearing stress for a sample of slightly milled Hevea Pale Crepe tested at 100° C.⁴² In addition to this curve obtained by Mooney, several other curves are shown which were obtained by Hamm,⁸ Scott and Whorlow,⁴³ Saunders and Treloar,⁴⁴ and Eccher.⁹ All of these investigators used rotational instruments which yielded absolute flow data.

⁴² A slight revision has been made here to correct a scale error in Mooney's original curve.

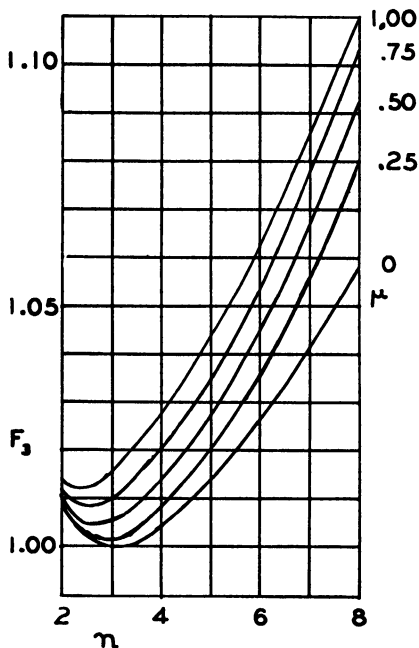


Fig. 10. The slip velocity computation factor F_s of equations (16.1) and (17.1) for large slip velocity. $\mu = p/n - 1$. p and n are the exponents in the slip velocity and the fluidity power laws, respectively.

These various curves are in fair agreement as to general form except at stresses below 10^4 dynes/cm.² where the slopes of the two curves extending so far are quite different. Mooney's limiting slope is roughly 2, while Scott and Whorlow's⁴³ is roughly 1. Scott and Whorlow attribute this difference to the friction of the pressure collars in Mooney's apparatus; but this is an incorrect conclusion. It apparently results from Mooney's failure to state clearly that when using the smaller driving weights the pressure collars 14 and 15 (Fig. 1) were removed from contact with the rotor. The bearing frictions that remained are too small to explain the discrepancy between the curves in Fig. 13. In view of the different milling treatments of the two samples concerned, it is probable that the samples are truly different in their rheological curves.

It is necessary to refute also another criticism of Mooney's results offered by Scott and Whorlow,⁴³ based on their computation of the temperature rise caused by energy dissipation by viscosity in the sample. Their computation is for the steady-state temperature rise after constant rotation for an

⁴³ J. R. Scott and R. W. Whorlow, *Proc. 2nd Rubber Technol. Conf., London* p. 244 (1948); *Rubber Chem. and Technol.* **23**, 683 (1950).

⁴⁴ D. W. Saunders and I. R. G. Treloar, *Trans. Inst. Rubber Ind.* **24**, 92 (1948).

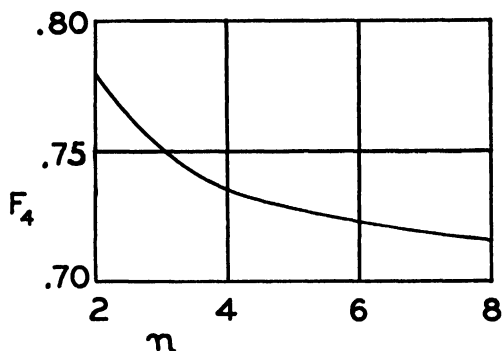


FIG. 11. The shear stress computation factor F_4 of equations (16.2) and (17.2) for large slip velocity. n is the exponent in the fluidity power law.

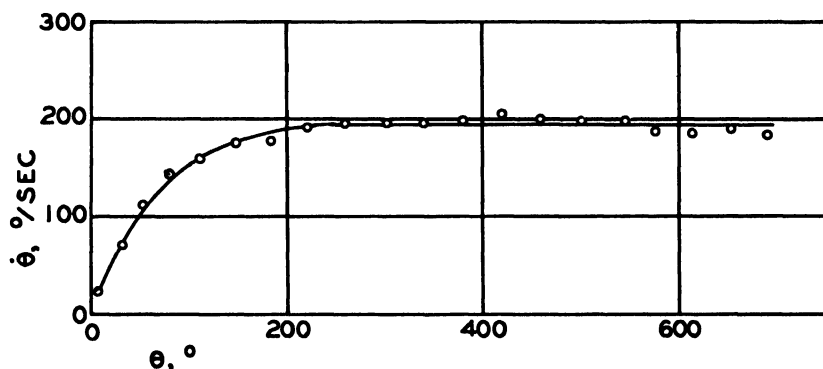


FIG. 12. Angular rotor velocity, $\dot{\theta}$, versus angle of rotation, θ , in the rubber rheometer. Hevea Pale Crepe, milled 5 min., tested at 100°C . Shear = $.162\theta^{\circ}$.

indefinite period. However, in Mooney's measurements at the higher rates of shear the driving weight hits the flow long before a steady temperature could be reached. If we assume that there is temperature equilibrium when the driving weight begins to fall, and none of the heat generated is lost by conduction, then the computed temperature rise under 100 lb. driving load is 6°C . after one rotor revolution by which time the rotor velocity has become constant. In view of the relatively low temperature coefficient of viscosity and the low experimental precision under the conditions considered here, this temperature rise does not require any significant correction to the published data.

The continuously increasing slope of the rate of shear curves at high stresses in Fig. 13 suggests the possibility of an upper limit to the stress that can be sustained by the test material. A weight-driven instrument is not so well suited to test this point as is an instrument with controlled, imposed speed and a measured stress.

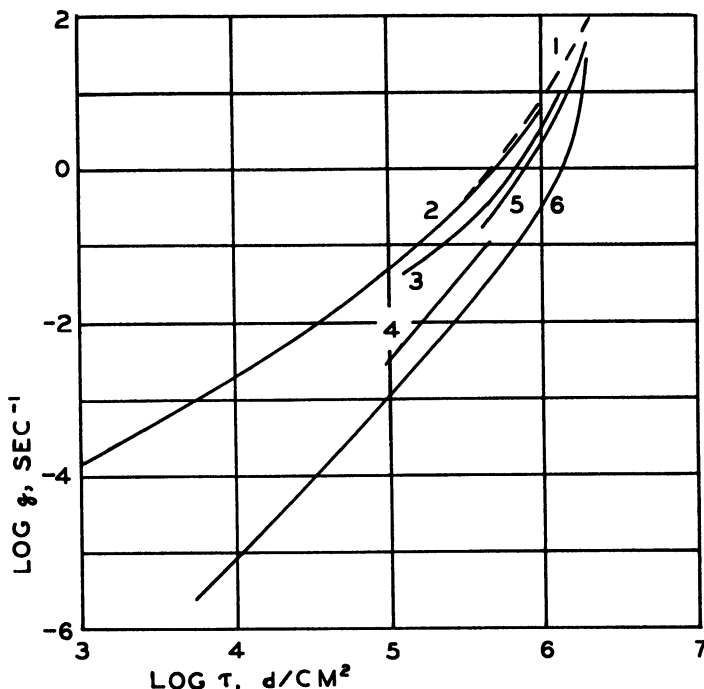


FIG. 13. Logarithmic steady state flow curves, rate of shear, g , sec^{-1} , vs. shear stress, τ , dynes/cm.².

1. Smoked sheet passed 60 times through tight mill, tested at 80°C. (Echer)
2. Smoked sheet milled 60 min. 100°C. (Piper and Scott)
3. Smoked sheet milled, 100°C. (Saunders and Treloar)
4. Pale crepe milled 12 min. 90°C. (Hamm)
5. Pale crepe milled 30 min. 140°C. (Mooney)
6. Pale crepe milled 5 min. 100°C. (Mooney)

These requirements are met by a Mooney viscometer with a multispeed drive, as used by Decker and Roth.⁴¹ The curves obtained with Hevea, GR-S and GR-I rubbers of various viscosities are reproduced in Figs. 14 and 15. Four of these curves, No. 1 GR-I and Nos. 1, 2, and 3 Hevea, have apparently reached an upper limit of Mooney torque reading at a rotor speed of 1 r.p.m.

It is true that the Mooney reading represents an average viscosity or average shear stress; but even so, the leveling of these curves still proves that in the samples referred to there is an upper limit to the shearing stress that the sample can develop under any rate of shear. It is to be noted, on the other hand, that other curves in Figs. 14 and 15 fail to reach a maximum within the range of the measurements; and if stress maxima exist for these other samples they must lie at higher stresses and rates of shear.

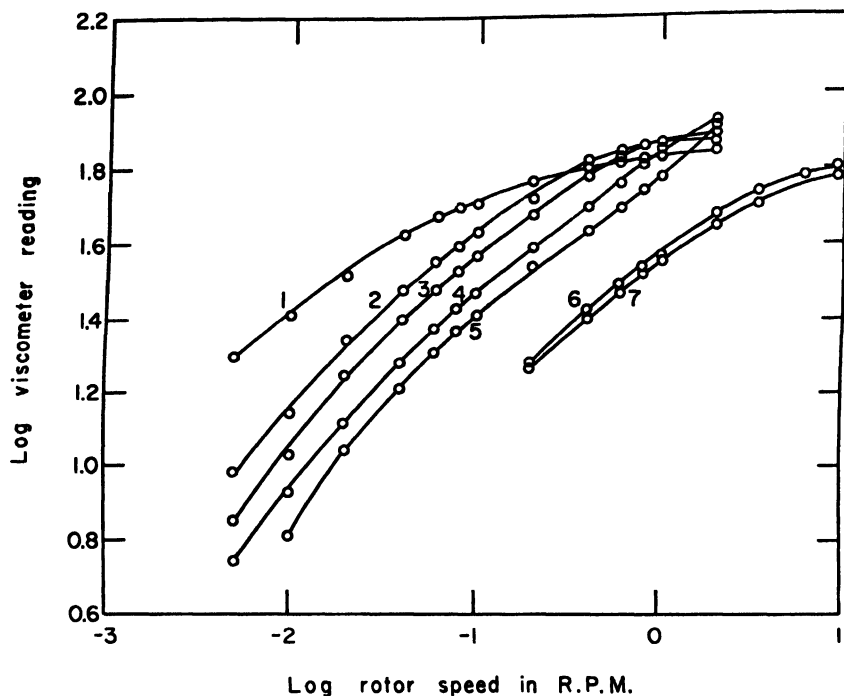


FIG. 14. Mooney viscosity reading vs. rotor r.p.m., 100°C. Curves 1 to 5 are for samples of GR-I having high molecular weight; 6 and 7 are for Y-103 and Y-108 GR-I, respectively. [From G. E. Decker and F. L. Roth, *India Rubber World* **128**, 339 (1953).]

For a Mooney reading of 100, the mean shear stress on the rotor surface is 2 megadynes-cm.². The upper limit of the shear stress for the samples in Fig. 14 is therefore in good agreement with the upper limit indicated by Mooney's curve in Fig. 13.

A question might be raised regarding heat dissipation and temperature rise in the sample at the higher rotor speeds in the Mooney viscometer. Decker and Roth⁴¹ do not discuss this point; but similar curves have been obtained in the writer's laboratory by a procedure in which the viscosity at high speeds is read as quickly as possible, before the sample has had time to heat up appreciably. Thus, at the highest speed of about 40 r.p.m. the reading can be made in 2 to 3 sec. Presumably, some such procedure was used by Decker and Roth.

Some recent rheological curves for Hevea published by Whorlow⁴⁵ show minor differences in the form of the curves, depending on the previous treatment of the sample. Cold-milled rubbers showed smaller slopes of log stress

⁴⁵ R. W. Whorlow, *Research Assoc. Brit. Rubber Mfrs. Research Rept.* No. 68, (1952); *Rubber Chem. and Technol.* **27**, 20 (1954).

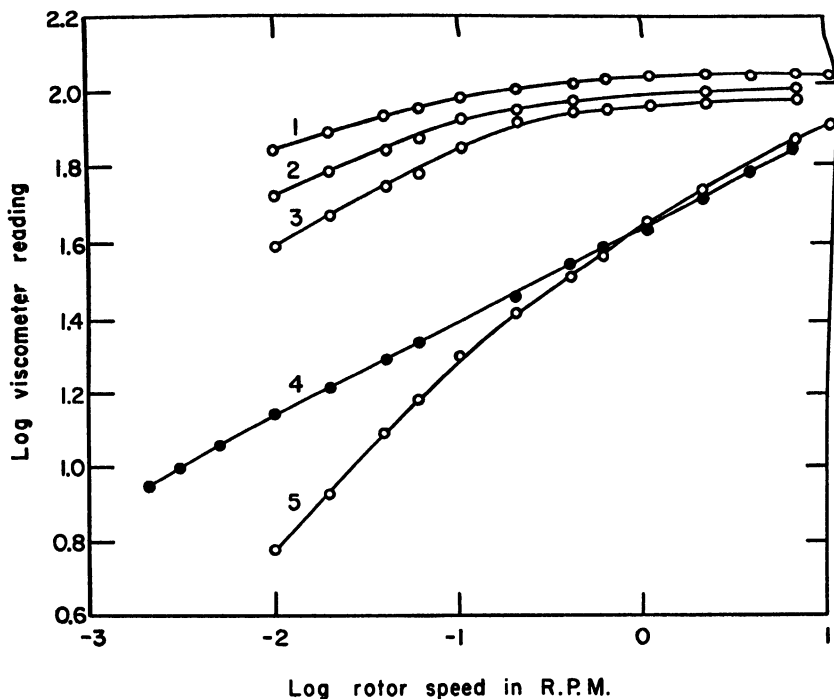


FIG. 15. Mooney viscosity reading vs. rotor r.p.m., 100°C. Curves 1 and 2 are for pale crepe and smoked sheet as taken from the bale; 3 is for slightly masticated smoked sheet; 4 is for x-603 GR-S mill-massed according to the procedure given in the "Specifications for Government Synthetic Rubbers;" and 5 is for well masticated pale crepe. [From G. E. Decker and F. L. Roth, *India Rubber World* **128**, 339 (1953).]

vs. log strain rate, with numerous crossovers when such curves were plotted on the same graph with curves for hot-milled rubbers.

The effect of temperature on the fluidity of Hevea is shown in the family of curves in Fig. 16, obtained by Mooney.² The irregularities and slight maxima in some of the curves might seem to be the spurious results of experimental error, but they have been observed with other rubbers also, particularly with rubbers of high viscosity and low tack. It appears that such rubber exhibit a phenomenon at given stress and temperature which might well be described as partial failure by internal tearing. The phenomenon disappears at a higher temperature because of the resulting increase in tack. This view is supported by experimental results in tack testing. Beckwith *et al.*,⁴⁶ and Beaven *et al.*⁴⁷ have found that the maximum ad-

⁴⁶ R. K. Beckwith, L. M. Welch, J. F. Nelson, A. L. Chaney, and E. A. McCracken, *Ind. Eng. Chem.* **41**, 2247 (1949).

⁴⁷ E. W. Beaver, P. Q. Croft-White, P. J. Garner, and G. Rooney, *Proc. 2nd Rubber Technol. Conf. London*, p. 224 (1948); *Rubber Chem. and Technol.* **23**, 719 (1950).

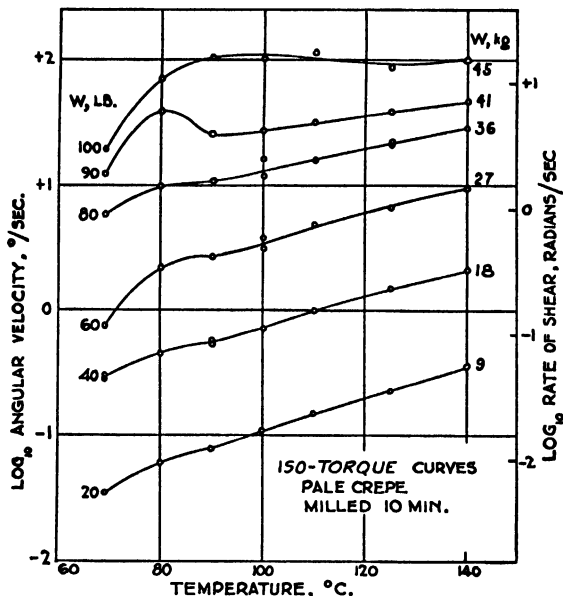


FIG. 16. Iso-stress curves, rate of shear *vs.* temperature. The shear stress in dynes/cm.² is $4.67 \times 10^4 \times W$ in kg. [From M. Mooney, *Physics* 7, 413 (1936)]

hesion of a tacky surface does not develop immediately on contact but requires a measurable time.

Smallwood⁴⁸ has analyzed the data of Fig. 16 in terms of Eyring's non-linear theory of viscosity. The energy of flow activation is found to be 10.2 kcal./mol. Other features of Smallwood's theoretical work will be discussed in a later section.

Rheological curves have been published for relatively few of the many synthetic elastomers now in commercial use. A number of unpublished curves obtained in the author's laboratory have the same general shape as the curves for Hevea; and some of them show similar irregularities in the variations with temperature and stress. GR-S, however, gives at least in some cases a curve of a different character in that the logarithmic plot of the flow data within the experimental range yield a straight line. Thus these curves agree with the fluidity power law of equation (3). This was found by Treloar,⁴⁹ whose results are shown in Fig. 17 for a range of temperature and rate of shear. The value of n for all temperatures is approximately 4.0. The heat of activation is 10.0 to 10.5 kcal., showing a slight variation with the applied shear stress. Similarly in Fig. 15, the GR-S data

⁴⁸ H. M. Smallwood, *J. Appl. Phys.* **8**, 505 (1937).

⁴⁹ L. R. G. Treloar, *Trans. Inst-Rubber Ind.* **25**, 167 (1949); *Rubber Chem. and Technol.* **23**, 347 (1950).

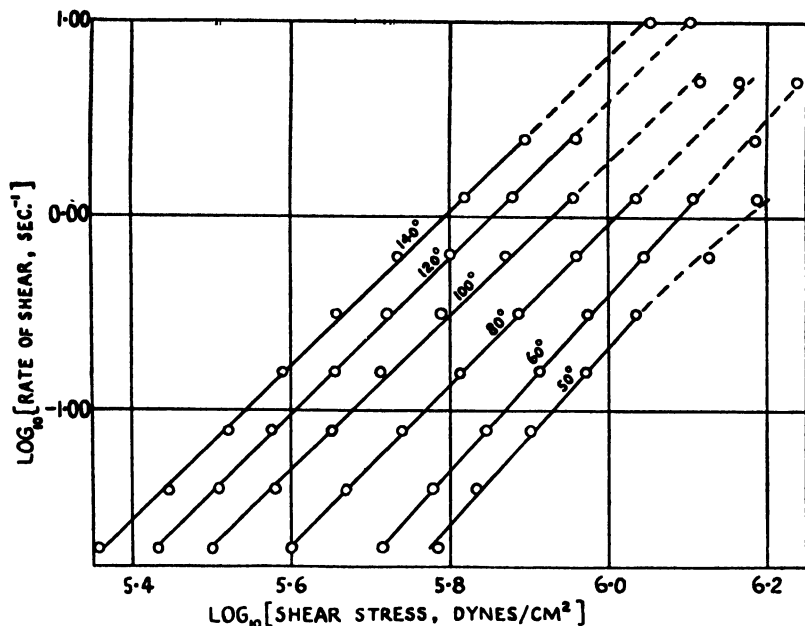


FIG. 17. Logarithmic flow curves for GR-S. [From L. R. G. Treolar, *Trans. Inst. Rubber Ind.* **25**, 167 (1949); *Rubber Chem. and Technol.* **23**, 347 (1950).]

give a straight line, the value of n being 3.8 in this case. The curves in Fig. 15 are not true rheological curves; but if a graph is straight in this Figure the corresponding rheogram also must be straight.

It must be added, however, that some unpublished data by the present author on GR-S shows curvature at higher rates of shear, in conformity with other elastomers. Furthermore, data on GR-S obtained by Bestul *et al.*⁵⁰ show a slight but continuous curvature. The fact that their data are plotted as viscosity instead of shear rate against shear stress cannot account for the curvature. We must conclude that while some GR-S samples follow the fluidity power law within a limited range in the test conditions, this law cannot be considered valid for all GR-S samples or for all test conditions.

Of the many published flow curves obtained with extrusion viscometers, only those published by Mooney and Black³⁹ make allowance for the entrance pressure drop ahead of the delivery tube and give the true stress within the tube. Two sets of curves for Hevea and GR-S from this report are shown in Figs. 18 and 19. The materials tested were Hevea smoked sheet, broken down to Mooney viscosities 48 and 18; GR-S of Mooney viscosity 40 at 250° F., and a group of GR-S mixes with four different fillers.

⁵⁰ A. B. Bestul, G. E. Decker, and H. S. White, *J. Research Natl. Bur. Standards* **46**, 283 (1951).

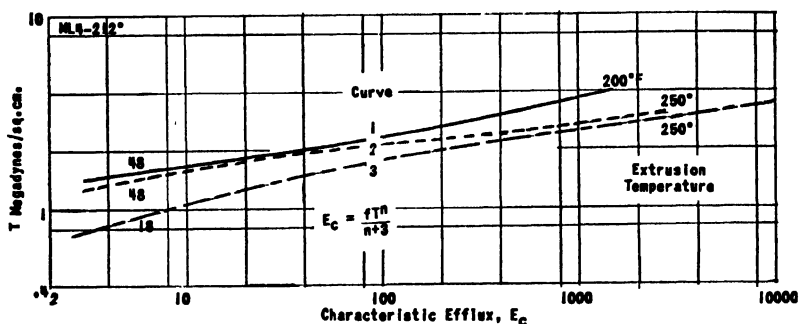


FIG. 18. Shear stress, τ , in megadynes/cm.², vs. characteristic efflux, $f\tau^n/(n + 3)$ for smoked sheet. [From M. Mooney and S. A. Black, *J. Colloid Sci.* **7**, 204 (1952).]

E	Curve 1		Curve 2		Curve 3	
	n	f	n	f	n	f
3	6.7	1.3×10^{-40}	4.4	3.2×10^{-26}	3.2	2.2×10^{-17}
30	7.2	2.6×10^{-43}	7.7	2.2×10^{-46}	4.9	1.9×10^{-28}
300	5.0	7.9×10^{-30}	8.8	3.9×10^{-52}	6.2	2.7×10^{-36}
3000	—	—	—	—	6.9	8.3×10^{-40}

The shearing stress at the wall is in the range from 1 to 7 megadynes/cm.². It thus overlaps and extends beyond the stresses developed in the rotational viscometer measurements presented above. The rates of shear at the wall are considerably higher, reaching values above 10^4 rad./sec. The rate of shear itself is not shown by the graphs; but it can be computed from the indicated characteristic efflux by means of equation (8).

It is clear that the data give in most cases roughly straight lines; but as the authors point out, n generally increases slightly with increasing efflux. The Hevea curves of Fig. 18 are in rough agreement in the region of overlap with those of Figs. 13 and 16. The over-all value of n for GR-S with no filler, 4.2, is in agreement with the values found by Treloar⁴⁰ and by Decker and Roth.⁴¹ The absolute shear rates, on the other hand, are not in good agreement, the rate at 1 megadyne/cm.² for curve 1 of Fig. 15 being 3 times the corresponding rate in Fig. 13.

Two investigations, those of Eccher⁹ and Bestul *et al.*⁵⁰ have established agreement between the extrusion method and the rotation method, in spite of failure to allow for the entrance pressure drop in extrusion; but in both cases the rubber shortly before extrusion had been subjected to large, fairly rapid deformations. The agreement obtained in these two investigations supports the view that the large entrance pressure drop found by Mooney and Black³⁹ was largely due to thixotropy.

Nearly all published data on rubbers obtained with compression plastometers consist of single-point measurements of compressed thickness and recovered thickness after a single standardized procedure. The viscosity can

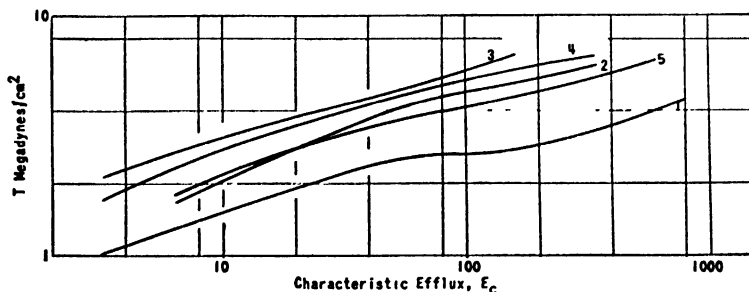


FIG. 19. Shear stress, τ , in megadynes/cm.², vs. characteristic efflux, $f\tau^n/(n + 3)$, for GR-S with various fillers. [From M. Mooney and S. A. Black, *J. Colloid Sci.* **7**, 204 (1952).]

Curve	Feature	ML-4 250°	n	f
1	No Filler	40	4.2	4.0×10^{-26}
2	Kosmos 40 Black	44	3.5	2.5×10^{-22}
3	Shawinigan Black	49	6.4	5.1×10^{-22}
4	Celite 322	50	3.5	2.8×10^{-22}
5	Gilder's Whiting	36	3.6	1.1×10^{-22}

be computed from such data only if the test material is Newtonian. However, a few investigations have been reported in which the compression-time curves were obtained. Notable among such investigations are those reported by Martin,³³ Scott,⁵¹ and the Research Association of British Rubber Manufacturers.⁵² Martin, using data obtained by Van Rossem, showed that a particular sample of Hevea at 70° C. followed closely Taylor's equation (10), based on Newtonian viscosity. Scott, using the plate plastometer, found that much of his data required a more general equation, based on the plasticity power law of equation (11). However, the existence of a positive yield value, Y , is later questioned, at least for unmixed rubbers, in the general discussion of plasticity measurements by Scott and Whorlow.⁴³ It seems that thixotropic effects, discussed above in Section III, 3, were more important in Scott's measurements than was realized at the time. In the anonymous report for the Research Association of British Rubber Manufacturers⁵² data are reported which, when plotted, agree well in most cases with equation (11) with $Y = 0$, that is, with equation (3). Test temperature was 100° C. The values of the exponent n vary from 1.1 and 1.2, for masticated Hevea of Mooney viscosities 8.5 and 3₀, respectively, up to 7.2 for a GR-S carbon black mix. The low values indicate almost Newtonian behavior.

Among the samples here referred to is a sample of Hevea "masticated 15

⁵¹ J. R. Scott, *Trans. Inst. Rubber Ind.* **7**, 169 (1931).

⁵² Research Assoc. Brit. Rubber Mfrs. Rept. No. 216 (1944); *Rubber Chem. and Technol.* **18**, 877 (1945).

min." of Mooney viscosity 54. In order to compare the rheological data on this sample with the curves of Fig. 13, the values of Y and n in the fluidity power law were computed by Peek's theory.³⁴ The corresponding linear graph is shown by the dotted line in Fig. 13. The agreement with the curve by Scott and Whorlow⁴³ is good; but the agreement is perhaps fortuitous, since it is doubtful that the two samples concerned were closely alike, the milling treatments being considerably different.

Two different studies have been reported on the viscosity of polyisobutylene at very low shear stresses as a function of mean molecular weight. Fox and Flory⁵³ used a coaxial falling-cylinder viscometer, while Van Holde and Williams⁵⁴ used a sandwich shearing viscometer. In either of these instruments the extent of deformation is extremely limited. After allowing for elastic deformation, the observed flow was found to be Newtonian for low molecular weight and high temperature, and non-Newtonian for high molecular weight and low temperature; but in the latter case the viscosity data extrapolated easily to a limiting finite viscosity at zero shear stress.

Results obtained in the two investigations were in good agreement, as is shown by Fig. 20, taken from the Van Holde and Williams report. The viscosity data are best fitted by an equation proposed by Leaderman *et al.*⁵⁵

$$\log \eta = -14.44 + 3.14 \log M_w + .504 \times 10^6/T^2 \quad (19)$$

where M_w is the weight average molecular weight and T is the temperature. The range in M_w is from 10^5 to 10^6 .

The many results that have been reviewed here on the form of the flow curves for raw elastomers can be summarized in the following statements:

- (1) Elastomers are non-Newtonian when examined over a wide range in rate of shear.
- (2) GR-S obeys the fluidity power law, with $n \sim 4$, for shear stresses from 0.3 to 1.5 megadynes/cm.² but shows an increase in n at higher stresses.
- (3) The chosen samples of Hevea show a nearly constant slope, or n , in the stress range from 3×10^3 to 3×10^5 dynes/cm.², but a slope that increases more and more rapidly with stress at higher stresses.
- (4) There are indications that Hevea of moderate or high Mooney viscosity has an infinite slope at a finite shear stress; and an upper limit to the shear stress it can support.
- (5) The heat of activation of viscous flow for Hevea or GR-S is approximately 10 kcal./mol.

⁵³ T. G. Fox, Jr., and P. J. Flory, *J. Am. Chem. Soc.* **70**, 2384 (1948).

⁵⁴ K. E. Van Holde and J. W. Williams, *J. Polymer Sci.* **11**, 243 (1953); *Rubber Chem. and Technol.* **27**, 393 (1954).

⁵⁵ H. Leaderman, R. G. Smith, and R. W. Jones, *Natl. Bur. Standards Rept.* **1317**, *Tech. Rept.* No. 7 to Office of Naval Research Rheology of Polyisobutylene (1951).

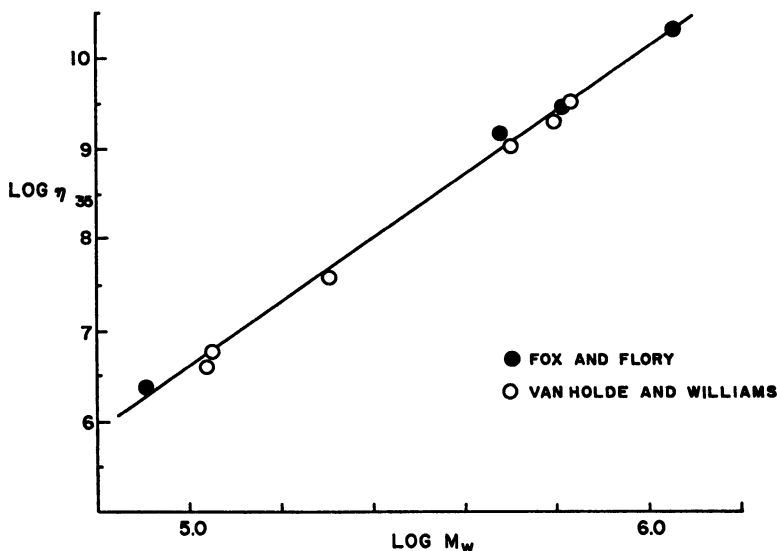


FIG. 20. Viscosity, η , vs. weight average molecular weight, M_w , of polyisobutylene, 35°C. [From K. E. Van Holde and J. W. Williams, *J. Polymer Sci.* **11**, 243 (1953); *Rubber Chem. and Technol.* **27**, 393 (1954).]

- (6) The results of different investigators with Hevea at low stresses are not in good agreement and seem to depend considerably on the degree of previous milling of the samples.
- (7) Polyisobutylene of molecular weight of the order of 10^5 shows Newtonian viscosity at low ratio of shear. The log of the viscosity varies as $1/T^2$.

2. TEMPERATURE EFFECTS

The effect of temperature on the fluidity of one sample of Hevea and of GR-S has already been shown in Figures 13, 16, and 17. The Mooney viscosity of several elastomers measured by Ganzhorn and Ebers⁵⁶ is shown in Fig. 21, and the viscosity of Hevea smoked sheet, measured by the same investigators at three stages of breakdown is shown in Fig. 22. In the latter figure a maximum in the viscosity curve for unbroken Smoked Sheet again is observed. The irregular forms of all the Hevea curves and some of the other curves in these two figures show clearly that the viscous flow of an elastomer is a complicated phenomenon in which the thermal activation of a molecular rearrangement or slippage process cannot always be the only important factor.

⁵⁶ G. H. Ganzhorn and E. S. Ebers, private communication.

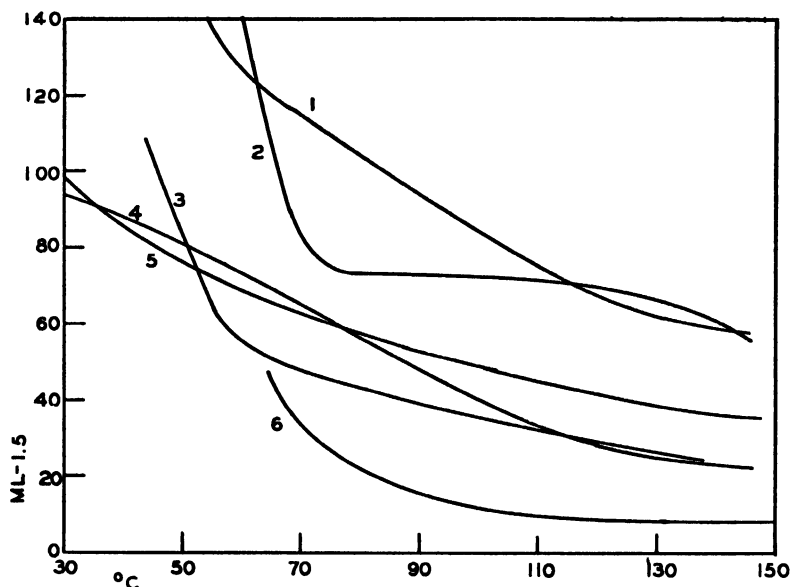


Fig. 21. Mooney viscosity at 1.5 min. shearing time, ML-1.5, vs. temperature. (Ganzhorn and Ebers)

- | | |
|-----------------|-----------|
| 1. Perbunan | 4. GR-I |
| 2. Smoked sheet | 5. GR-S |
| 3. Neoprene GN | 6. Balata |

3. COMPARISON OF DIFFERENT PLASTOMETERS

If two plastometers are true viscometers and yield absolute rheological data, they can be compared by testing identical samples in each and comparing the resulting flow rates or fluidities in the overlap of the experimental ranges. Such comparisons by Eccher⁹ and by Bestul *et al.*⁵⁰ have been discussed in Section VI, 1.

Another kind of comparison is one in which a series of different stocks is measured by a standard procedure in each of two different plastometers. Thus the Williams or the Defo compression plastometers, the Dillon extrusion plastometers, and the Mooney or the Scott rotation plastometers can all be compared. Many such comparisons have been carried out; but it turns out that there is no close correlation between any two instruments of different classes. It is only when the stocks tested are similar in character, differing only in extent of milling or some other single variable, that there exists a close correlation and a conversion factor or conversion curve from one instrument reading to another. For each different type of stock, a different curve is obtained.^{13, 33, 43, 51, 52, 57-59}

⁵⁷ J. H. Dillon, *Ind. Eng. Chem.* **26**, 345 (1934).

⁵⁸ R. W. Whorlow, *India-Rubber J.* **120**, 658 (1951).

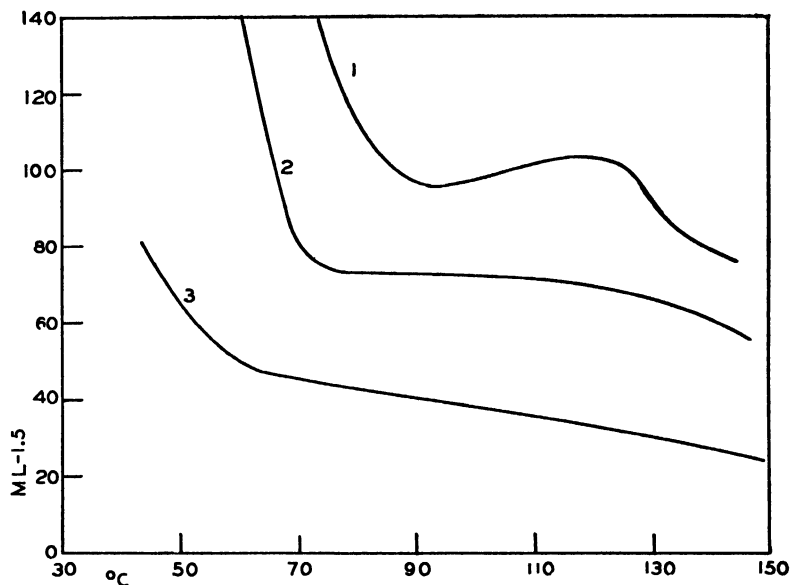


Fig. 22. Mooney viscosity at 1.5 min. shearing time, MI-1.5, vs. temperature. (Ganzhorn and Ebers)

1. Unbroken smoked sheet
2. Short plastication
3. Long plastication

This is not surprising, in view of the complex rheological nature of elastomers and the radically different rheologic treatment of the sample in the different tests. The Research Association Report 216⁵² shows that the correlation between the Williams and Mooney plastometers is improved if the Williams compression test is carried out at a higher speed.

Several of these comparison studies examine critically the relative discriminating power of the different test instruments. The broadest study of this kind is that by Whorlow.⁵⁹

4. THIXOTROPY

The thixotropy of elastomers has been discussed to some extent in the Introduction; an example of thixotropic behavior in Hevea was shown in Fig. 6; and the importance of thixotropy in the extrusion and the compression plastometer was stressed in Sections III, 2 and III, 3.

The earliest extensive and systematic published study of thixotropy in elastomers is that by Dillon and Cooper.²⁹ Using a Mooney viscometer, these investigators showed that a brief rest period leads always to an initial

⁵⁹ R. W. Whorlow, *India-Rubber J.* **125**, 174 (1953); *Rubber Chem. and Technol.* **27**, 248 (1954).

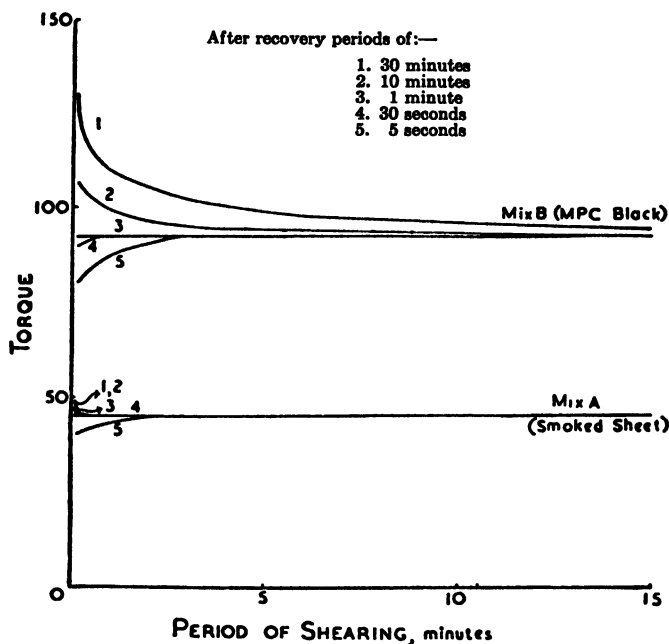


FIG. 23. Increment of peak or initial stress reading, after a rest period, above the steady reading; Piper and Scott shearing cone viscometer, shear rate 1 sec.^{-1} . [From R. W. Whorlow, *India-Rubber J.* **125**, 252 (1953); *Rubber Chem. and Technol.* **27**, 16 (1954).]

high viscosity reading when the driving motor is turned on again. Whorlow⁴⁵, using a Piper and Scott biconical rotor, investigated the effect of the duration of the rest period on the initial shear-stress increment over the previous steady reading. His curves for a masticated smoked sheet sample at three different temperatures are shown in Fig. 23.

Carbon black in a rubber mix leads to greatly increased thixotropy. Furthermore the reversible viscosity changes are often complicated by some permanent changes resulting from chemical surface reactions between the carbon black and the elastomer which may occur during storage, especially at high temperatures. A few curves on thixotropic recovery in carbon black mixes have been reported by Mullins⁶⁰ and by Whorlow.⁶¹

5. ELASTIC RECOVERY

Elastic recovery in radians of simple shear was measured by Mooney² as a function of recovery time and with various annealing times, t_a , during

⁶⁰ L. Mullins, *J. Phys. & Colloid Chem.* **54**, 239 (1950).

⁶¹ R. W. Whorlow, *India-Rubber J.* **125**, 252 (1953); *Rubber Chem. and Technol.* **27**, 16 (1954).

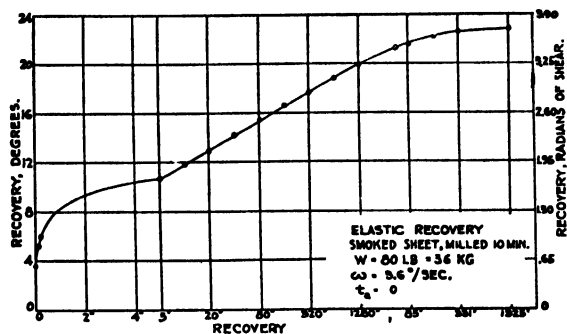


FIG. 24. Elastic recovery in the rubber rheometer *vs.* recovery time, following shear at stress 1.7 megadynes/cm.² and at rate .58 sec.⁻¹. Logarithmic time scale after 5 sec. [From M. Mooney, *Physics* 7, 413 (1936).]

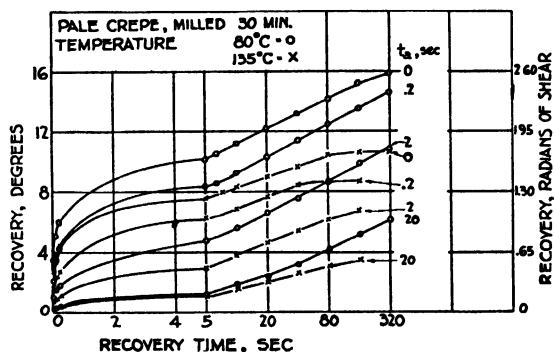


FIG. 25. Elastic recovery in the rubber rheometer *vs.* recovery time. At the two temperatures, 80° and 135°C., the previous shear stresses and rates of shear were, respectively, 1.05×10^6 and $.74 \times 10^6$ dynes/cm.², and 1.6 and 1.9 sec.⁻¹. The annealing time, t_a , is the time between stopping the rotor and releasing it. [From M. Mooney, *Physics* 7, 413 (1936).]

which the deformation was held constant before release. Results with Hevea are shown in Figs. 24 and 25. The first figure shows that approximate complete recovery at 100° requires a day or longer. The second figure shows that the time required for complete recovery is less at a higher temperature. If the logarithm of the recovery at 320 sec. in Fig. 25 is plotted against t_a , the resulting curve is far from linear. Hence decay of recovery by stress relaxation during annealing is not exponential. The initial rate of decay is high in comparison with the later rate. This is not surprising, since stress relaxation in cured elastomers is far from exponential in form.

Since stress relaxation is taking place continuously during any continuous deformation, it is to be expected that subsequent elastic recovery like the, deforming stress during deformation, will increase with the rate of deformation. This has been shown by Dillon and Johnston,¹³ who measured the

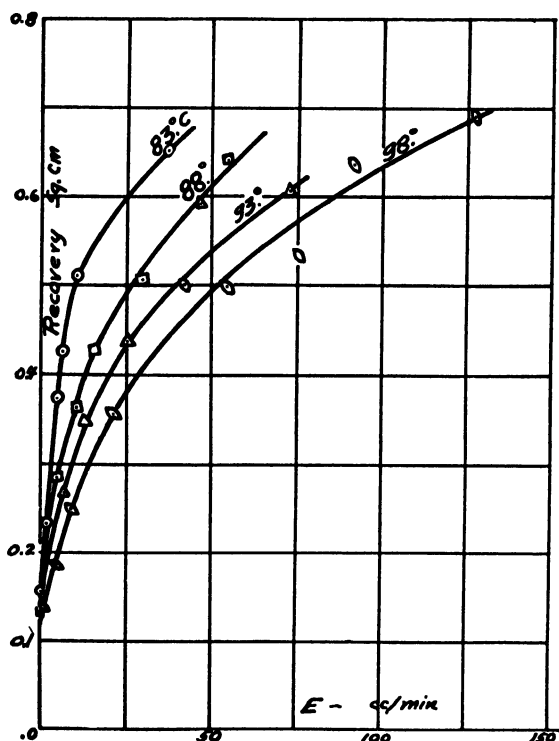


FIG. 26. Elastic recovery vs. efflux rate, E , crude rubber, mill massed. The recovery is measured as the cross-section of the extrudate. Area of the extrusion die was .079 cm.². [From J. H. Dillon and N. Johnson, *Physics* 4, 225 (1933); *Rubber Chem. and Technol.* 7, 248 (1934).]

elastic recovery of an extruded rod as a function of rate of extrusion. Some of their results are shown in Fig. 26.

A number of curves of elastic recovery vs. previous shearing torque in the Mooney viscometer have been obtained in the author's laboratory. In many cases the recovery at 1 min. is initially approximately proportional to the previous shearing torque; but at high torques the points fall away from the linear low toward lower recovery values. However, this degree of simplicity is not the universal rule. Many curves are nonlinear and show various irregularities. This work has not reached a stage suitable for a detailed report.

While the problem of computing absolute viscosity from disk viscometer data has been solved, as in Section III, 1, the corresponding problem for elastic recovery in the disk viscometer has not been solved; and a satisfactory analysis of the recovery irregularities just mentioned is at present impossible.

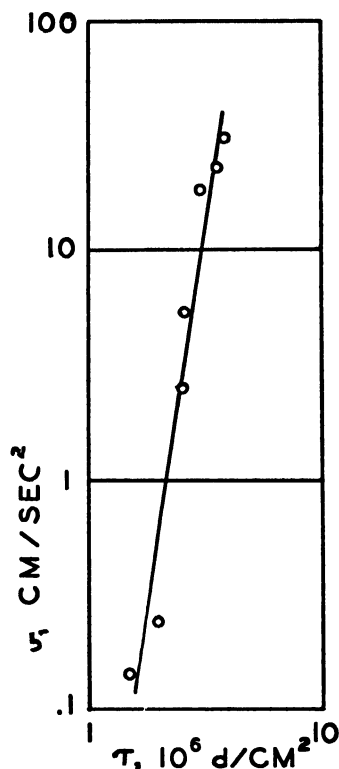


FIG. 27. Slip velocity, v_s , at the wall of a capillary extrusion viscometer *vs.* shear stress at the wall. 100°C. (Parshall and Black)

Many elastic recovery measurements with various instruments under arbitrary standard conditions have been made for processing control purposes. They will be discussed later in Section IX.

6. SURFACE SLIP

In the paper on laws of extrusion by Mooney and Black³⁹ it was mentioned that some experimental data had been obtained which gave consistent evidence of surface slip of raw Hevea on smooth steel at 100° C. The data referred to, obtained by C. M. Parshall and analysed by S. A. Black, are shown in Fig. 27. The test instrument used was an extrusion viscometer, and the method of analysis was that depending on the effect of capillary diameter on efflux as developed by Mooney.²⁹ The points shown in Fig. 27 represent slip velocities computed from smoothed extrusion curves.

The slip data are not very precise, but two facts seem to be definitely indicated. One is that there is measurable slip. The other is that the velocity increases rapidly with shear stress, but not at an infinite rate. If slip veloc-

TABLE I
SLIP VELOCITIES, AT 100° C.*

<i>Elastomer</i>	<i>Mooney Viscosity, M</i>	<i>Metal Surface†</i>		
		<i>Steel</i>	<i>Chromium</i>	<i>Cadmium</i>
		<i>Slip Velocity, cm./sec.</i>		
Y108 GR-I	48	0.006	0.016	0.022
Gr-I-18	83	0.004	0.008	0.007
Hevea	107	—	0.005	0.26
X-672 GR-S	47	0.020	0.082	0.002
X-603 GR-S	53	0.014	—	0.72
GR-S 1700	126	0.008	0.014	0.17
GR-S (A)	124	0.22	0.33	0.47
GR-S (B)	152	0.20	0.52	0.87
GR-S (C)	166	0.20	0.22	0.22

* Blank spaces correspond to indicated negative velocities. A velocity less than 0.01 cm./sec. is of doubtful significance.

† The surface shearing stress is roughly $2.3 \times 10^4 M$ dynes/cm.², M being the viscosity in Mooney units.

ity, v , is represented by the power law of equation (13), the slope in Fig. 27 shows that $p = 7$.

The implication is that slip may be similar in its mechanism to viscous flow; and, like viscous flow, may be a thermally activated process.

Some data obtained with a smooth and a standard serrated rotor in the Mooney viscometer, published by Decker and Roth,⁴¹ show in certain instances a lower Mooney torque reading with the smooth rotor. The difference can only be attributed to slippage on the smooth rotor. The computation of absolute slip velocities by equations (14) or (16) requires measurements with both rotors over a range of rotor speeds. Since the published data are limited to a single speed (2 r.p.m.) the computations in this case cannot be carried out exactly; but it is possible to compute approximately single slip values if we assume values for n and p . With $n = p = 4$, equations (14) give the slip velocities and shear stresses shown in Table I.

The dependence of slip velocity on the chemical nature of the surface indicates that slip is dependent to some extent on how well the rubber wets the surface.

7. RHEOLOGICAL FLOW UNITS

When a material containing a continuous, three-dimensional thixotropic structure is subjected to continuous deformation, the structure must be broken up. At first, the broken units may be very large in comparison with molecular dimensions and contain many molecules still held together by

forces of appreciable strength. If the shear strength of such units is greater than the shear stresses that develop between the units as they roll and slide over each other, the units may persist indefinitely while the material is continuously being sheared. There are reasons for thinking that such units exist and persist in raw elastomers subjected to continuous deformation.

In order to test this hypothesis a new test procedure with the Mooney viscometer was developed by Mooney and Wolstenholme.⁶² A smooth rotor was coated with a thin, dried film of raw elastomer containing a rubber-soluble dye in high concentration. A preformed elastomer sample was then placed around the rotor and, after warm-up, was subjected to shear in the viscometer.

If the theory is correct, the thixotropic units, or "rheological units," will roll continuously and will transfer the dye across the shear planes as inking rollers on a printing-press transfer ink. The velocity of the color front is proportional to the radial distance from the rotor axis; and, α , the angle of the resulting conical color front is

$$\alpha = \frac{DN}{h} \quad (20)$$

where D is the mean diameter of the rheological units, N is the number of rotor revolutions, and h is the rotor-stator clearance.

After an appropriate shearing time the sample is removed, chilled, and sectioned. There are disturbing factors in the test and valid results are not always obtained; but usually the expected conical color front is observed. Some mean diameters of rheological units as found by this method are given in Table II. These measurements are rough, as is the theory of the measurement; but presumably the data are correct in order of magnitude. In its present form the method is applicable only to transparent or white samples.

VII. Theory of the Fluidity of Elastomers

The various experimental results reviewed in the preceding section reveal a number of effects which could be the subject of theoretical analysis: the dependence of viscosity on temperature, shear stress and nature of the test material; the magnitude of the elastic recovery and the details of the recovery-time curve; the rate and extent of breakdown and build-up of thixotropic structure. However, only two of these effects have so far been successfully treated theoretically. These are the effects of temperature and of shear stress on rate of shear or the viscosity.

It was mentioned above that Mooney's² measurements on Pale Crepe shown in Fig. 12 have been interpreted by Smallwood⁴⁸ in terms of the

⁶² M. Mooney and W. E. Wolstenholme, *J. Appl. Phys.* **25**, 1098 (1955).

TABLE II
SIZE OF RHEOLOGICAL UNITS IN ELASTOMERS*

<i>Polymer</i>	<i>Mooney Viscosity ML4</i>	<i>Average Diameter of Rheological Unit</i>
Pale crepe	20	3.1×10^{-4} cm.
Pale crepe	34	5.0
Pale crepe	35	8.3
Pale crepe	54	14
Pale crepe	76	26
Butyl, GR-I 15	48	2.5
Butyl, GR-I 17	69	2.5
Hot GR-S	26	5.7
Cold GR-S (X-101)	29	20
Paracril B	46	13
Paracril AJ	44	23.0
Paracril C	52	36

* Test conditions: 100° C.; rotor speed, 2 r.p.m.

Eyring theory of flow as an activated process. Spencer,⁶³ in a modification of the Eyring theory, has taken into account the entropy of the elastic deformation of the sheared elastomer and improved the fit obtained with the experimental data published by several different authors.

These theories treat the shearing material as being homogeneous and undergoing uniform shear. However, the rheological units indicated by the work described in Section VI, 6 are large compared with elastomer molecule and large also compared with the moving rheological unit computed by Smallwood.⁴⁸ Consequently it appears that, so far as rubbers are concerned, a viscosity theory assuming homogeneity of the material is unrealistic. In a recent publication⁶⁴ the present writer undertook to revise the Eyring theory to bring it into harmony with the large size of the rheological units in elastomers.

In the revised theory the macroscopic viscosity is assumed to result from the friction of the rheological units as they slide over each other. The frictional force is treated as a consequence of temporary molecular attachments across the boundaries of the units. From the moment of attachment until release by thermal activation, the stress on the attachment builds up at a rate which is proportional to the relative sliding velocity of the two rheological units and to the dynamic elastic modulus of the units and is inversely proportional to the unit diameter and to the number of cross-attachments per unit area. The explicit introduction of the elasticity is something added

⁶³ R. S. Spencer, *J. Polymer Sci.* **5**, 591 (1950).

⁶⁴ M. Mooney, *J. Appl. Phys.* **27**, 691 (1956).

to the Eyring theory of activated flow; but it is in accordance with the Maxwell picture of flow as a continuous process of relaxation of continuously renewed elastic stress.

The basic quantitative postulate of the theory deals with the rate of breakage of the cross-surface attachments as the stress on the attachments increases from zero stress at the time they are formed. The assumed law, suggested by Mooney *et al.*⁶⁵ is:

$$\frac{dn}{dt} = -n \frac{kTR}{h} e^{-E/kT} \cosh \frac{\lambda f}{kT} \quad (21)$$

where n is the number of attachments left unbroken out of a group which formed at time $t = 0$, k is Boltzmann's constant, T is temperature, h is Planck's constant, E is the activation energy, f is the force on the attachment, and λ is the distance of molecular force. R is a rate factor, usually expressed in terms of an entropy of activation. It is the probability that rupture will actually occur when the necessary thermal energy is supplied at the attachment.

Before we undertake to integrate the above equation we must take cognizance of the fact that the force on a given attachment varies with time, being zero at the moment the attachment is formed and increasing linearly with time thereafter. The rate of increase is derived from a bit of theory in which the molecular group involved in a local cross-surface attachment is treated as two hemispheres, each lying within its respective rheological unit. Due to the sliding relative movement of the two units, each hemisphere is undergoing a continuously increasing elastic displacement with respect to its unit. By analogy with Stoke's law⁶⁶ for the force on a continuously moving sphere in a viscous medium, the force, f on a hemisphere displaced momentarily a distance δ in an elastic medium is $3\pi aG\delta$, where a is the hemisphere radius, and G is the elastic modulus of the medium, the rheological unit. By classical hydrodynamics the rotational velocity of a rheological unit is $g/2$.⁶⁷ From these facts it can be shown that, at an interface parallel to the shear planes, the disruptive force on an attachment grows according to the equation

$$f = 3\pi agDGt/4, \quad (22)$$

where D is the diameter of the rheological units.

With f substituted into equation (21), integration is possible; and an

⁶⁵ M. Mooney, W. E. Wolstenholme, and D. S. Villars, *J. Appl. Phys.* **15**, 324 (1944).

⁶⁶ H. Lamb, "Hydrodynamics," 6th ed., p. 598. Dover Publications, New York, 1945.

⁶⁷ H. Lamb, "Hydrodynamics," 6th ed., p. 31. Dover Publications, New York, 1945.

explicit law of rate of attachment rupture is obtained. If it is assumed that N , the number of attachments per unit area of interface, is constant in a state of constant rate of shear, then it is possible to obtain expressions for the mean life of an attachment and for the mean shear stress on an interface. The equations are

$$\begin{aligned}\tau &= NkT_p/\lambda, \\ t_a &= 4kTI_1/3\pi\lambda agDG \\ I_1 &= \int_0^\infty \exp\left(-\frac{\sinh y}{\alpha}\right) dy, \\ I_2 &= \int_0^\infty y \exp\left(-\frac{\sinh y}{\alpha}\right) dy \\ \rho &= I_2/I_1 \\ \alpha &= \frac{3\pi a h \lambda DG}{8k^2 T^2 R} e^{k/k\tau} g\end{aligned}\tag{23}$$

where τ is the shear stress and t_a is the mean life of an attachment.

The theoretical law of flow is the relationship between g and τ expressed implicitly by these equations through the parameter α . The equations show that g is proportional to α , and τ is proportional to ρ which is a function of α . Hence a logarithmic plot of experimental data for g versus τ should have the same form as α plotted against ρ on the same logarithmic coordinates. If the agreement in form is satisfactory, any chosen pair of values for g and τ determine a corresponding pair of values of α and ρ .

In Fig. 28 the solid lines show the fit obtained in applying this theory to Mooney's² data on Pale Crepe Hevea rubber. The dotted lines give the best fit obtainable with Eyring's non-linear equation as used by Smallwood.⁴⁸

These two theories have been tested also with the data on Hevea obtained by Saunders and Treloar,⁴⁴ the results being similar to those shown in Fig. 28. Spencer⁶³ shows no fitted curves; but he claims improvement over the Smallwood equation. Presumably, therefore, his fit with experiment is as good as is obtained in Fig. 28 by means of the equation (23).

It appears from the results referred to that in the experimental range covered by the data of Fig. 28 or by the data of Saunders and Treloar, it is possible to obtain good agreement with the experimental data if the Eyring non-linear theory is slightly modified in form, one or two additional adjustable parameters being introduced into the equation. The choice between Spencer's theory and the theory presented here therefore seems to depend for the present on the existence or non-existence of densely packed rheological units.

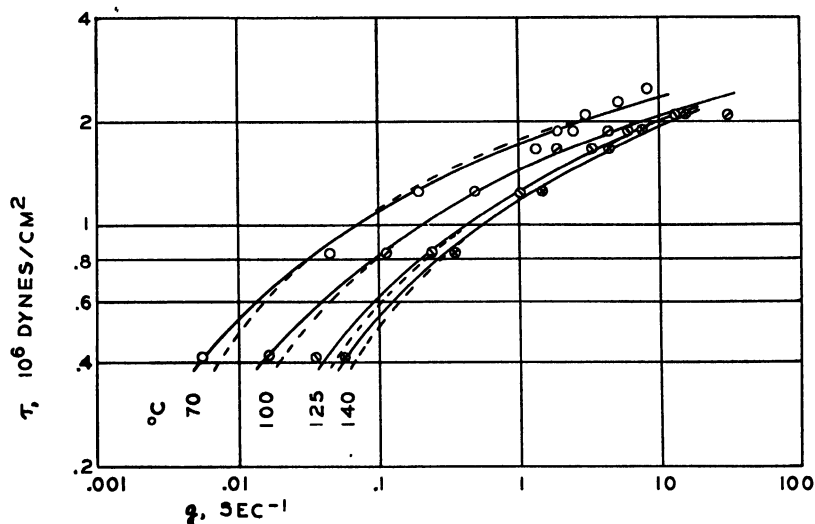


FIG. 28. Theoretical curves for shear stress, τ , vs. rate of shear, g , fitted to experimental data by Mooney on pale crepe milled 5 min. Full curves, Mooney-Eyring theory. Dashed curves, Smallwood-Eyring theory.

For purposes of interpreting the experimental data in terms of the present theory, the values of a , λ , D and G must be assumed or estimated from measurements of low precision or of uncertain applicability. The values estimated for a and λ are $a = 5 \times 10^{-18}$ cm and $\lambda = 10^{-18}$ cm. On the basis of work of Mooney, and Wolstenholme,⁶² values of D were assumed to be 19μ for Mooney's Hevea sample and 10μ for Saunders and Treloar's sample. The value assumed for G , the same for both rubbers, is Mooney's value computed from the frequency of free oscillation in the rubber rheometer.²

The results of the analysis of the flow curves are given in Table III. These data show that a major difference between the two samples of rubber is in the values of E , the activation energy, the softer sample of Saunders and Treloar having the smaller value. The values of t_a , the mean life of an attachment, are also appreciably different; but this difference might be anticipated from the difference in E -values. The values of N , the number of attachments per unit area, show that only a very small fraction of the isoprene chain segments in an interface are involved in a cross-surface attachment at any one time.

The values of R are very small and indicate a large entropy term in the release process. Conceivably there is a caging effect, such that two locked chain segments, after temporary separation by local volume expansion, may return to their same locked position if, while they are separated, the local chain molecules are too slow in their response to the displacing

TABLE III
VALUES OF RHEOLOGICAL PARAMETERS

<i>Material*</i>	<i>Pale Crepe (Mooney)</i>	<i>Smoked Sheet (Saunders & Treloar)</i>
Milling time, min.,	5	30
Estimated Mooney Viscosity at 100°C.	80	45
Assumed Parameters		
$\lambda \times 10^8$, cm.	1	1
$a \times 10^8$, cm.	5	5
D , μ	19	10
$G \times 10^{-8}$, dynes/cm. ²	3	3
Computed Parameters		
E , kcal./mol.	10.1	7.5
$N \times 10^{11}$, cm. ⁻² at 100°C.	1.2	1.0 to 1.4
t_a , sec., at 100°C., $g = .2$ sec. ⁻¹	.012	.007
$R \times 10^8$, at 100°C.	8.1	14.5

* λ is the range of molecular force, a the equivalent radius of a group of two or more chain segments constituting an interfacial attachment, D is the mean diameter of the rheological units, G their modulus of rigidity, E the activation energy of flow, N the number of attachments per unit interfacial area, t_a the mean life of an attachment, R the rate constant.

mechanical stress. According to this view R will be smaller, the larger the polymer molecular weight and the more complex the polymer structure.

The theory presented above has been found to fit quite well a large number of flow curves of elastomers, and also of plastics above their second order transition temperature; but quite often the experimental curves differ in shape and fail to agree with the theory at either high or low rates of shear, or both. As shown in Fig. 17, GR-S follows the fluidity power law over a wide range in shear rate and hence does not conform at all well with the theory.

The systems analyzed in this theory are very complex, and it is not difficult to think of many factors, not included in the theory, which could influence considerably the flow behavior. The direction of the effect can be predicted in most cases with little doubt. When the breakup of thixotropic structure begins, the broken pieces, besides being large, are presumably quite irregular in shape. The assumption that the number of cross-surface attachments per unit area is constant is an obvious oversimplification. In a raw carbon black stock the effective dynamic modulus of the rheological units probably decreases temporarily with working, as does the dynamic modulus of a curved carbon black stock. The dynamic viscosity of the rheological units varies with the polymer, mean molecular weight, molecular weight distribution, and with impurities of low molecular weight. The viscosity of the units probably affects the value of the rate constant, R , in the manner which has been suggested in the discussion of the caging effect.

The nonlinear Eyring theory in all of its published variations, including the present theory, expresses the stress effect as an exponential function of which the argument is linear in the stress. Higher order terms should be included to describe the flow response of rubbers to stresses sufficiently high to cause rupture or tearing at room temperature. Such terms will surely be required to explain, for example, an upper stress limit in continuous shear at 100° C.

If the rate of shear is progressively lowered, cross-surface diffusion and entanglement will become more and more important; and in the limit the boundary surfaces of the rheological units will disappear and the material will become homogeneous, with high thixotropic structure. Newtonian flow at a high viscosity could conceivably result, as described in the linear Eyring theory and as exemplified in Fox and Flory's⁵³ and Van Helde and Williams⁵⁴ samples of polyisobutylene, and as exemplified approximately in some of the low viscosity Hevea samples tested with the Williams plastometer.⁵² The situation in Hevea is complicated by the possibility of chemical cross-linking by free radicals, as pointed out by Pike and Watson⁶⁸ and by Whorlow.⁴⁵

The various factors that have been discussed here are probably adequate to explain most of the peculiarities in the rheological curves that have been presented above; but the reduction of these factors to quantitative expression for comparison with the data remains a formidable task.

VIII. Processing

1. GENERAL REMARKS

The principle operations required in processing raw rubbers were briefly referred to in Section I. Most of the processing difficulties that are encountered and require control tests result from too high a molecular weight of the elastomer. By breakdown methods which have been alluded to, the mean molecular weight can be reduced to any desired value; but there are limitations on the acceptable degree of breakdown. Breakdown is a costly operation, and excessive breakdown injures the physical properties of the cured stock. It would seem logical to polymerize the elastomer to a lower molecular weight to begin with; but this method also results in an inferior cured stock. Polymerization to a high molecular weight followed by mechanical plastication gives better quality, probably because it produces a more favorable molecular weight distribution.

An alternative method of softening an elastomer is to add a suitable oil. This method has advantages and is used; but here also quality requirements impose limitations on the amount of oil that can be employed.

As a consequence of the conflicting needs for a high and for a low molecu-

⁶⁸ M. Pike and W. F. Watson, *J. Polymer Sci.* **9**, 229 (1952).

lar weight, there must be a compromise, and this means that most processing is carried out under conditions which are on the verge of being impossible; and this means, in turn, that processing controls are required in a rubber factory and are coming into more and more general use as more and better control tests are developed.

The following are the principal difficulties encountered in processing. The first three result from excessively high viscosity of the crude elastomer or mixed stock.

- (1) Excessive power consumption, overloading the power supply;
- (2) Excessive stresses in the processing machinery, possible breakage;
- (3) Excessive temperature rise in the stock because of viscous conversion of mechanical energy into heat, possible scorching of the stock.
- (4) Low extrusion rate at a given screw speed.
- (5) Longitudinal shrinkage of calendered or extruded stock.
- (6) Roughness and distortion of calendered or extruded stock.
- (7) Torn edges of extruded stock of sharp angular section.
- (8) Low tack, adhesion failure in building operations.

Processing behavior in a number of respects can be fairly well predicted by certain laboratory tests. Viscosity and elastic recovery are the tests most frequently used, for they seem to have the greatest predictive value.

2. BREAKDOWN AND MIXING

Experimental work by Cotton⁶⁹ and Busse⁷⁰ on the breakdown of Hevea led to the belief that the reduction in molecular weight and the softening of the rubber was initially and primarily due to oxidation. However, later work, beginning with Staudinger and Heuer⁷¹ showed that chain molecules in flowing systems could be ruptured by mechanical stress, free radicals being produced in the process. Subsequent chemical action might include more or less oxidation, depending on the temperature and the availability of oxygen; or, failing oxidation, the free radicals could react with other polymer chains and thus maintain the mean molecular weight unchanged. The illuminating study by Pike and Watson⁶⁸ showed that conditions during mastication variously affected the molecular weight distribution, chain branching and cross-linking; and furthermore that these properties of the masticated rubber affected, in turn, the measured relationship between Mooney viscosity and the intrinsic viscosity in solution. The increase in the viscosity of GR-S by gel formation can take place under the action of heat alone, according to Hagen;⁷² and some additional chemical mechanism therefore seems to be involved in this case.

⁶⁹ F. H. Cotton, *Trans. Inst. Rubber Ind.* **6**, 487 (1931).

⁷⁰ W. F. Busse, *Ind. Eng. Chem.* **20**, 140 (1932).

⁷¹ H. Staudinger and W. Heuer, *Ber.* **67**, 1159 (1934).

⁷² H. Hagen, *Kautschuk* **14**, 203 (1938); *India Rubber World* **108**, 45 (1943).

Knowledge of the effects of fillers and of plasticizers or softeners on the rheology of elastomers is largely empirical. The relative effectiveness of many plasticizers has been examined by Burbridge⁷³ and Jacobs.⁷⁴ The viscosity increase and other rheological effects produced by various fillers have been studied by van Rossem and Hoekstra,⁷⁵ Mullins and Whorlow,⁷⁶ and Drogin *et al.*⁷⁷ The range in the viscosity effects of different fillers is enormous. Maximum viscosity increase, accompanied always by high thixotropy, is produced by some of the carbon blacks of smaller particle size. According to Kruse,⁷⁸ the carbon black is not uniformly distributed but is concentrated in clouds of individually separated particles. Such non-uniform distribution may be explained as the result of the exclusion of the carbon black from the stronger and more persistent of the rheological units of the gum rubber.

Some fillers, ZnO for example, cause a viscosity decrease. In such cases the filler accelerates the rate of breakdown of the rubber during mixing, apparently by increasing the rate of oxidation.

3. FORMING OPERATIONS

After a raw stock has been completely mixed by a suitable sequence of Banbury and open-mill operations, there follows the forming operation, usually the most critical of the processing steps.

The tendency of a stock to scorch at operating temperatures can be measured by suitable heat treatment combined with a viscosity test, since in the early stage of scorching the viscosity rises steeply.⁷⁹⁻⁸¹

Machine stresses and stock temperature rise should both be proportional to the effective mean viscosity of the stock; but experimental data to test these expected relationships are lacking. Data on power consumption, on the other hand, as related to viscosity have been reported by Vila.⁸² His results are expressible by the equation

$$P = A + BS + CSM \quad (24)$$

where P is the power consumption in an extruder, S is the screw speed, M is the Mooney viscosity, and A , B , and C are constants for a given extruder.

⁷³ W. N. Burbridge, *Trans. Inst. Rubber Ind.* **1**, 129 (1926).

⁷⁴ F. Jacobs, *Rev. gen caout chouc.* **7**, 15 (1930).

⁷⁵ A. van Rossem and J. Hoekstra, *Trans. Inst. Rubber Ind.* **25**, 43 and 56 (1949).

⁷⁶ L. Mullins and R. W. Whorlow, *Trans. Inst. Rubber Ind.* **27**, 55 (1951).

⁷⁷ I. Drogin, H. R. Bishop, and P. Wiseman, *Rubber Age N. Y.* **74**, 707 (1954).

⁷⁸ J. Kruse, *Kolloid-Z.* **136**, 152 (1954).

⁷⁹ E. O. Dieterich and J. M. Davies, *Ind. Eng. Chem. Anal. Ed.* **3**, 297 (1934).

⁸⁰ J. V. Weaver, *Rubber Age N. Y.* **48**, 89 (1940).

⁸¹ R. W. Whorlow, *India-Rubber J.* **125**, 214 (1953); *Rubber Chem. and Technol.* **27**, 242 (1954).

⁸² G. R. Vila, *Ind. Eng. Chem.* **36**, 1113 (1944).

If A in this equation is interpreted as mechanical and electrical power loss the next two terms indicate a viscous resisting force which is proportional to $B + CM$ but is independent of the rate of shear within the mean rates covered by the experiments. Such viscous properties are unusual; but they should not be considered impossible for rubber if we recall the apparent limiting viscous resistance indicated by Figs. 13, 14, and 15.

The rate of flow through an extruder at a given screw speed varies with the stock; but it is general processing experience that the viscosity of the stock is not the deciding factor. That this is the case can be understood on the basis of a rough analysis of the rheology of an extruding operation.

The threads on the rotating screw push the stock forward with a force which, to a first approximation, is proportional to the viscosity of the stock; but the stock flows through the die with a resistance which, to a first approximation, is likewise proportional to the viscosity of the stock. Consequently, the rate of extrusion should, to a first approximation, be independent of the viscosity. The rate must therefore be dependent on secondary factors, such as variations in viscosity with rate of shear and possibly surface slip. Mooney⁸³ has demonstrated, as shown in Fig. 23, that the rate of extrusion increases with the relative increase in flow resistance of the stock when tested in the Mooney viscometer at 2 and 8 r.p.m. This relationship would be expected if the effective mean rate of shear in the barrel of the extruder is greater than in the throat and die.

Elastic recovery after a forming operation is a complex phenomenon. This is proved by the fact, found by Drogin *et al.*,⁷⁷ that the correlation between mill shrinkage and extruder shrinkage is not close. It follows from this that no laboratory elastic recovery test under a single set of test conditions can accurately predict longitudinal shrinkage in all forming operations. Nevertheless, good correlation between a laboratory elastic recovery test and calender or extruder shrinkage has been established in a number of cases, notably by Zapp and Gessler,⁸⁴ Mooney,⁸³ van Rossem and Hoekstra,⁷⁵ and Drogin, Bishop, and Wiseman.⁷⁷ Figure 29 shows Mooney's experimental results.

A rather simple testing device, called the rugosimeter, has been developed by Mooney⁸⁵ for measuring the surface roughness or rugosity of a calendered sheet. An earlier form of the same instrument was used in a study of the rheological properties of a stock that determined its rugosity.⁸³ The quantity experimentally observed in the earlier test is a measured air pressure, P_s , which is empirically related to the surface roughness through the equation,

⁸³ M. Mooney, *J. Colloid Sci.* **2**, 69 (1947).

⁸⁴ R. L. Zapp and A. M. Gessler, *Rubber Chem. and Technol.* **17**, 882 (1944).

⁸⁵ M. Mooney, *Ind. Eng. Chem. Anal. Ed.* **17**, 514 (1945).

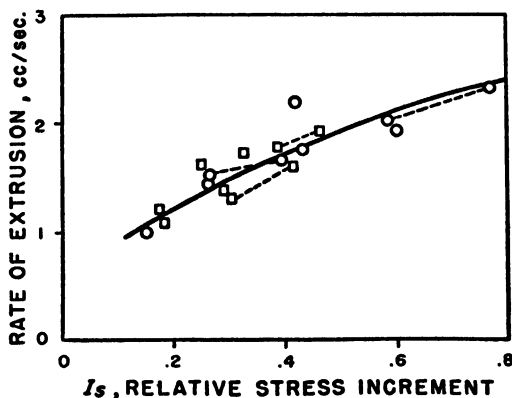


FIG. 29. Rate of extrusion *vs.* Relative stress increment $(M_s - M_2)/M_2$, where M_x is the Mooney viscosity reading at x r.p.m. [From M. Mooney, *J. Colloid Sci.* **2**, 69 (1947).]

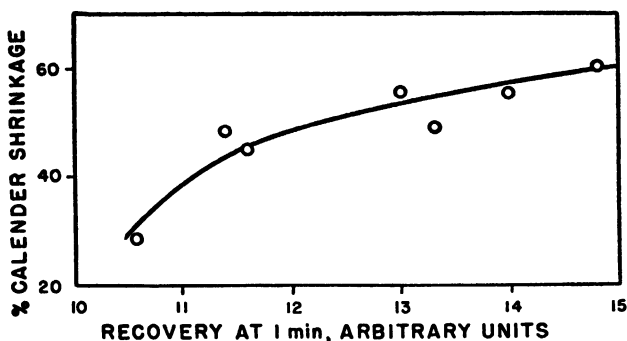


FIG. 30. Longitudinal elastic shrinkage of calendered sheet *vs.* elastic recovery measured in a Mooney viscometer. (From M. Mooney, *J. Colloid Sci.* **2**, 69 (1947).)

$$P_s = P_0 \frac{R_s}{R_0 + R_s} \quad (25)$$

where P_0 is a fixed air pressure, R_0 a fixed air flow resistance, and R_s is the air-flow resistance of the channels between the calendered sheet and a smooth annular metal plate resting on the sheet. Since R_s increases with the smoothness of the sheet, this equation shows that P_s is a direct measure of smoothness and an inverse measure of roughness.

The rheological properties used in this study of calendering quality were the calender length shrinkage, and relative increase in torque in the Mooney viscometer with rotor velocity increase from 2 to 8 r.p.m. Figure 30 shows the correlation obtained between observed P_s and the value computed by the empirical equation indicated in the figure.

More recent correlation attempts similar to the above were much less suc-

cessful. Probably an important factor in the situation not yet included in the rheological tests is rheological inhomogeneity of the stock as it goes through the nip of a calender or the forming die of an extruder. No amount of shrinkage can produce roughness unless the shrinkage is nonuniform; and such nonuniformity can be caused only by corresponding nonuniformity in the rheological properties of the stock, the viscosity, thixotropic structure and state of elastic stress of the stock within the calender nip or extruder die. White *et al.*⁸⁶ seem to be the first to have given explicit recognition to the existence and importance of rheological inhomogeneity. A laboratory test for measuring it is clearly needed. The rheological units measured by the cross-current color diffusion test described in Section VI, 6, are much smaller than the macroscopic regions of viscosity variation under discussion here; and furthermore the color diffusion test cannot be used with black stocks.

During the development of the synthetic butadiene-styrene copolymer, GR-S, there was considerable research of a purely practical type in which attempts were made to establish a measure of the processability of an elastomer. In addition to some of the measurements already described—viscosity at various processing stages, and rugosity of a sheeted sample—a number of new measurements were developed which made use of laboratory-size processing machines. These machines included the Banbury, screw extruder, and the two-roll rubber mill.

Among the various measurements employed was the time on the laboratory rubber mill required to soften a batch to the point where it would form a continuous band on one of the rolls, and, likewise, the time to form a band with no holes in it. With the extruder observations were made on the shape, surface roughness, torn edges, and longitudinal shrinkage of the extruded stock. These measurements and ratings, it may be noted, depend greatly on the operators' judgment.

A figure of processing quality was computed in the form of an arbitrarily weighted average of two or more of the above measurements, each group of investigators adopting its own selection of measurements and averaging formula.

The criterion of validity of these laboratory ratings consisted of factory-scale experiments in which two or more elastomers were compared under controlled processing conditions. The factory ratings, like some of the laboratory measurements, depended to a large extent on visual inspection and subjective judgments. In spite of these handicaps considerable correlation was found between the laboratory and factory ratings. On the other hand, all comparisons showed some badly scattered points, and it seems fair to say that none of the laboratory rating methods can be accepted as quite

⁸⁶ L. M. White, E. S. Ebers, and G. E. Shriver, *Ind. Eng. Chem.* **37**, 767 (1945).

satisfactory. A recent summarizing report of the work in this field has been published by Taylor *et al.*⁸⁷

It is this writer's opinion that these over-all rating methods have little possibility of much improvement; for they are based on an incorrect concept of the problem. Processability is not a single property. On the contrary, there are as many processabilities as there are processing defects; and as has been pointed out by White *et al.*,⁸⁸ while the various qualities in a series of stocks may sometimes be positively correlated, they are also sometimes antithetical, or independent.

A scientific approach to the problem of rating stocks in their processing qualities would be to seek, for each processing defect, a laboratory or a group of laboratory tests which, by means of a mathematical formula, would predict reliably the degree of that defect as measured in the actual processing operation. By such an approach it may eventually be possible to interpret processing qualities in terms of polymer molecular structure, if the measurable rheological properties can themselves some day be so interpreted.

The rheological theory of processing machines is relatively undeveloped. There are no theoretical formulas, for example, for the pressure in a calendar nip, the efflux from an extruder, the shrinkage or the rugosity of a calendered sheet or an extruded form. Thixotropy, non-Newtonian viscosity, and complex, nonlinear elasticity and relaxation all combine to make rigorous solutions mathematically impossible and attainable approximate solutions unrealistic.

However, certain published theoretical analyses are interesting and may have limited usefulness for rubber processings. Gatecombe⁸⁹ has discussed the flow of a pressure-sensitive Newtonian liquid between two rotating cylinders. Strub⁸⁹ has treated the flow of Newtonian materials in a screw extruder. The flow of non-Newtonian materials through channels of different sections has been treated by Beyer and Towsley,⁹⁰ and Mooney and Black,³⁹ by quite different mathematical methods. In both treatments thixotropy is ignored. A theory of elastic recovery in extrusion, proposed by Spencer and Dillon,³⁸ was discussed above in Section IV.

A word must be said about the current theory of viscoelasticity which has successfully explained and related so many transitory phenomena in terms of a postulated distribution of relaxation times characterizing a series of elementary relaxation mechanisms. A major defect of this theory, as

⁸⁷ R. H. Taylor, J. H. Fielding, and M. Mooney, *Rubber Age N. Y.* **61**, 567 (1947).

⁸⁸ E. K. Gatecombe, *Trans. Am. Soc. Mech. Engrs.* **67**, 177 (1945).

⁸⁹ R. A. Strub, *Proc. 2nd Midwestern Conf. Fluid Mechanics* p. 481 (1952); *Ohio State Univ. Eng. Expt. Sta. Bull. No. 149*, (1952).

⁹⁰ A. E. Beyer and F. E. Towsley, *J. Colloid Sci.* **7**, 204 (1952).

applied to the flow of elastomers, is that it predicts Newtonian flow.⁹¹⁻⁹² The Eyring concept of a thermally activated stress-sensitive flow mechanism is therefore a better theoretical approach to raw elastomers in continuous deformation.

Nomenclature

a	radius of extrusion die	M	Mooney viscosity
a	radius of a molecular group constituting an interfacial attachment between rheological units	N	number of rotor revolutions
b	thickness of disc rotor	N	number of interfacial attachments per unit area
f	fluidity factor	P	power consumption in extrusion
g	rate of shear	P	air pressure in rugosity test
g	gravitational acceleration	Q	efflux
h	rotor-stator clearance in disk viscometer	R	radius
h	plate separation in compression plastometer	R	rate factor in rupture of interfacial attachments
h	Planck's constant	R	resistance to air flow in the rugosity test
k	Boltzmann's constant	S	speed of extruder screw
n	exponent in fluidity power law	T	temperature, °K
n	number of interfacial attachments remaining at time t after formation	V	sample volume in a compression plastometer
p	exponent in slip power law	Y	yield value
s	slip factor	α	cone angle of biconical rotor
t	time	α	angle of color front in rheological unit test parameter (equation 23)
v	slip velocity	γ	shear elastic recovery
A, B, C, F	constants	η	viscosity, (viscosity factor, equation 11)
C	driving torque	θ	rotation angle in the cylindrical viscometer
D	diameter of rheological unit	λ	instrument constant
E	reduced efflux	λ	range of molecular force
E	activation energy for bond release	ρ	rotor dimension, biconical rotor
G	rigidity modulus	ρ	parameter (equation 23)
L	cylinder length	τ	shear stress
M	weight in the compression plastometer	Ω	rotor velocity
M	molecular weight		

⁹¹ J. D. Ferry and M. L. Williams, *J. Colloid Sci.* **7**, 347 (1952).

⁹² W. Kuhn, O. Kunzle, and A. Preissmann, *Helv. Chim. Acta* **30**, 307, 464 (1947); *Rubber Chem. and Technol.* **37**, 36 (1954).

CHAPTER 6

THE RHEOLOGY OF CELLULOSE DERIVATIVES

E. B. Atkinson

I. The Nature of Cellulose and its Derivatives	233
1. Chemical	233
2. Physical	235
3. Plasticization and Solubility	237
II. Fields of Application	239
1. Plastics	239
2. Solutions and Melts	241
III. Irreversible Flow Behavior	242
1. Solutions	242
2. Melts	244
3. Plastics	247
IV. Elasticity and Toughness	253
1. Modes of Response	253
2. Stress-Strain Curves	255
3. Creep	256
4. Toughness	257
Nomenclature	259

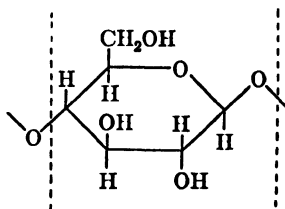
The rheological properties of cellulose derivatives are best studied against the background of their structure, as revealed by physical and chemical methods. As yet no complete synthesis of the flow properties of any thermo-plastic can be made, given the chemical structure and molecular-weight distribution of the component polymer molecules, but a knowledge of the underlying structure of a plastic throws some light on the observed rheological behavior, and often suggests ways in which this behavior can be altered by changes in the structural details.

I. The Nature of Cellulose and its derivatives¹

1. CHEMICAL

Cellulose occurs naturally as the main constituent of jute, cotton, flax and other plant fibres. It is a polysaccharide based on the glucose ring, the cellulose molecule,

¹ For fuller details of the chemistry, physics, and technology of cellulose and its derivatives, readers are referred to Emil Ott, "Cellulose and Cellulose Derivatives," Interscience, New York, 1942.



consisting of a large number of such units (i.e., over 1000) joined end to end in a long flexible molecule. Starch is a chemically similar polysaccharide, but differs from cellulose in the details of its chain structure. Whereas the cellulose chain has the oxygen linkages alternating between positions above and below the planes of the glucoside rings (β -glucoside linkage) in starch the oxygen linkages occur on the same side of each ring (α -glucoside linkage). The effect of this difference of structure on the physical properties of starch and cellulose is discussed by Schoch.²

Cellulose may be dissolved in certain solvents (cuprammonium and xanthate solutions) and reprecipitated in acid media to give "regenerated cellulose" in the form of films or fibers, (cellophane, viscose rayon) processes which form the basis of very large industries. Here we shall be mainly concerned with chemical derivatives of cellulose which find application as thermoplastic molding materials such as

nitrocellulose or cellulose nitrate	}	esters
cellulose acetate and triacetate		
cellulose tripropionate	}	"mixed ester"
cellulose aceto-butyrate		
ethyl cellulose	}	"ethers"
benzyl cellulose		

Other derivatives such as methyl cellulose and carboxymethyl cellulose are made as water-soluble thickening and suspending agents for foodstuffs, pharmaceutical products, detergents, etc.

Each glucoside ring in the cellulose chain has three hydroxyl groups—one "primary" and two "secondary" which may be esterified by various organic and mineral acids or may also be "etherified" (ethyl and benzyl cellulose). The degree to which the hydroxyl groups are substituted has a considerable effect upon the physical properties of the derivative, and a large part of the chemical technology of the production of cellulosic plastics is concerned with controlling the degree of substitution. In nitrocellulose the degree of substitution may be controlled by the strength of the acids used, but in the case of cellulose acetate substitution must be allowed to proceed to completion, i.e., to cellulose triacetate, if a homogeneous product

² T. J. Schoch, *J. Chem. Educ.* **25**, 626 (1948).

is to be obtained. The cellulose triacetate is then hydrolyzed ("back hydrolysis") to reduce the acetyl content to the required value, producing "secondary" cellulose acetate. Ethyl cellulose is formed by the reaction of ethyl chloride with soda cellulose (made by treating cellulose with caustic soda solutions) and the degree of substitution may be varied by a suitable choice of reaction conditions.

The degree of substitution of a cellulose derivative determines its degree of crystallinity, melting point, and solubility characteristics, and also such properties as chemical stability and water absorption. In native cellulose highly ordered regions occur known as "crystallites" or crystalline micelles, within which the molecular chains run parallel. X-ray diffraction patterns indicate that the same three-dimensional order which occurs in ordinary crystals, prevails within the crystalline micelles, although there may be transition regions between micelles which have a more random, less ordered structure ("fringe" or amorphous regions). Cellulose crystallites are held together by strong "hydrogen bond" forces between hydroxyl groups on neighboring chains—a feature which explains the insolubility of cellulose in common solvents, as well as its high "melting point." As more and more of these hydroxyl groups are substituted by less strongly interacting chemical groups, (i.e., ordinary "polar" groups such as acetyl radicles or nonpolar ethyl groups) the cohesion between the chains is reduced. If the substituting groups are also bulky (butyrate or propionate) the cellulose chains cannot approach each other closely, and so the interaction forces are still further reduced. Since substitution usually takes place at random along the chains, the resultant irregularity of the chain makes crystallization more difficult, and solvent attack easier. Thus chemical substitution of cellulose lowers the melting point, reduces crystallinity, and produces a material which can be dissolved in common organic solvents. When the degree of substitution is increased to such a degree that nearly all the available hydroxyl groups are substituted, the chain becomes regular again, the ease of crystallization and the melting point increases, and the solubility in organic solvents decreases. Thus for use as plastics and for applications as solutions, intermediate degrees of substitution are preferred, i.e., average number of hydroxyl groups substituted per glucoside residue

cellulose nitrate...	2-2.26
ethyl cellulose...	2.29-2.58
cellulose acetate...	2.2-2.62

2. PHYSICAL

X-ray diffraction studies of cellulosic plastics and other evidence point to a structure in which cellulose or substituted chains pass through both ordered (or crystalline) regions and "amorphous" regions within which no

long-range order occurs. There is probably no sharp dividing line between the crystalline and amorphous regions, but one may merge imperceptibly into the other. It is assumed that an equilibrium may be established between the two regions, equivalent to a solid in equilibrium with its solution or melt. At high temperatures the amorphous regions will grow at the expense of the crystalline regions, but the nature of the equilibrium between the two "phases" is such that the progressive melting of crystallites will occur over a range of temperature. By analogy with other polymers it is to be expected that the degree of crystallinity, the size and morphology of the crystalline regions and their subsequent melting points would be determined by the thermal history of the sample. At low temperatures, especially below the 'second-order transition temperature' of the derivative, the amorphous regions become extremely "viscous," the mobility of the chain segments passing through them, and especially their rotational mobility almost disappears. This shows itself as a loss of flexibility and toughness in the thermoplastic. Moreover the equilibrium between the amorphous and crystalline regions will be "frozen," and only extremely slow changes in the crystalline-amorphous ratio are to be expected. In general the great length of polymer molecules makes their response to changing conditions slow, since any considerable change in the relative positions of the molecule involves the statistical cooperation of a large number of chain segments in random Brownian movement, and when more chain segments are involved in any change, motions favorable to the change occur less frequently. Thus equilibrium in the thermodynamic sense is probably the exception rather than the rule in solid thermoplastics.

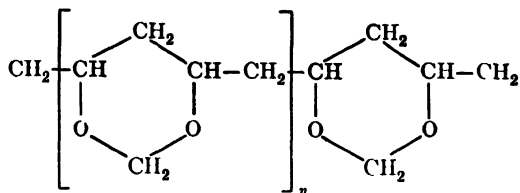
The crystalline regions of a thermoplastic are mainly responsible for its cohesion, since they act as "cross links" between chemically unconnected chains and prevent large-scale relative movements. The amorphous regions, however, are more readily deformed by stress, especially above the transition temperature, and largely determine the elastic modulus, resilience, and brittleness of the thermoplastic, whereas the crystalline regions contribute strength. Solvents and plasticizers are generally confined to the amorphous regions and lower the transition temperature by conferring greater mobility to the disordered parts (there are exceptions to this in the case of some cellulose nitrate—terpene systems in which the "plasticizer" seems to form a "mixed crystal" with the cellulosic crystallites).³ By "swelling" the amorphous regions the plasticizer also upsets the equilibrium between the two regions and lowers the melting range of the crystallites.

At high temperatures, when all crystallites have melted, cellulose and other high polymers behave as very viscous and elastic liquids when sub-

³ K. H. Meyer, "Natural and Synthetic High Polymers," p. 310. Interscience, New York, 1942.

jected to small stresses. Under these conditions, and in solution, the viscous and elastic properties are greatly affected by the chain length and by the distribution of chain lengths in the bulk polymer. In order that cellulose derivatives with useful flow and solution properties may be made it is usual to "degrade" the cellulose to a controlled degree in order to reduce the molecular weight. Further degradation may occur during substitution reactions with the result that the final material has a considerably shorter chain length than the original cellulose and a very broad molecular weight distribution.

Cellulosic chains differ from those of rubbers and vinyl polymers in respect of their greater rigidity and linearity, caused by the lack of free rotation about the chain linkages. Rotation through a limited arc is possible and thus gives the chain a slight flexibility. Nevertheless the average configuration of a cellulose molecule in solution would be that of a rod bent at random or a very open coil compared with the more tightly coiled configurations possible with materials having relatively free rotation about chain linkages. This restriction of free rotation and the rigidity of the chain as a whole resulting from the "rigid" glucoside rings is probably responsible for the greater tendency of celluloses to crystallize, and for the higher melting points of their crystallites than those of vinyl polymers with similar inter-chain cohesion. In the solid state, too, the greater degree of mutual interpenetration possible with chains of a more extended configuration may give rise to greater toughness and strength—a familiar feature of cellulosic plastics when compared with ordinary rigid vinyl materials. It is interesting to note that the toughest vinyl-based polymer, polyvinyl formal, has a structure which is



also likely to have its freedom of rotation about chain linkages restricted and to have a more rigid chain structure.

3. PLASTICIZATION AND SOLUBILITY

The mechanical properties and processing characteristics of cellulose derivations may be modified by the addition of various softening agents, i.e., solvents, plasticizers, "plasticizer extenders," and lubricants. Although large "entropy" effects play an important part in the thermodynamics of the solution of polymers, the factors which influence the solubility are

mainly those which operate in systems of low molecular weight. Compatibility or mutual solubility between a polymer and a solvent or plasticizer is encouraged by (a) similarity of chemical nature (i.e., similar type and strength of Van der Waals' forces between neighboring molecules, which means the same "cohesive energy density"; (b) specific interaction or complex formation between the plasticizer or solvent and the polymer. This helps to keep the chains separated and, by shrouding the chain with less strongly interacting groups, prevents aggregation and precipitation.

Cellulose nitrate is readily soluble in ketones and organic esters but is insoluble in hydrocarbons and alcohols. However, mixtures of alcohols with esters or ketones have a high solvent power, as also has the mixture of ethyl alcohol and ether used to make dopes for film casting. Camphor (which is a ketone) makes an excellent plasticizer whereas isoborneol (isomerically related to camphor but an alcohol) is a poor plasticizer and of limited compatibility. The specific effect of small structural changes can be appreciated when the plasticizing effect of camphor and its isomer isofenchone (also a ketone) are compared.⁴ The "activation" of nonsolvents by ketones and esters is probably due to complex formation between the carbonyl group containing molecules and cellulose nitrate, the resulting "complex" being soluble in alcohol. The properties of mixed solvent systems are of great interest in nitrocellulose or cellulose acetate lacquer technology.

Cellulose acetate has not the wide range of solvents available for cellulose nitrate. Both solvents and plasticizers need to be of a strongly polar nature (i.e., a high ratio of strongly polar groups to nonpolar groups such as the methylene or methyl group). Thus the only common solvents are such materials as acetone, ethyl acetate, and methyl "Cellosolve," and the common plasticizers used are the methyl and ethyl esters of phthalic and phosphoric acid. Mixed solvents of alcohols and nitroparaffins, analogous to the alcohol-ester of ketone systems for nitrocellulose have high solvent power for cellulose acetate. Cellulose triacetate is only soluble in chlorinated hydrocarbons or mixtures of these with alcohols. Ethyl cellulose is soluble in aromatic hydrocarbons and in their mixtures with alcohols (i.e., 80-20 toluene-ethyl alcohol mixtures).

Minor proportions of plasticizers are used with rigid ethyl cellulose and cellulose aceto-butyrate plastics to modify the mechanical properties and promote easy extrusion. Lubricants, which are materials of limited solubility, are often added to promote easy extrusion or injection molding. Waxes, stearic acid, etc., are generally used to exude or bloom to the surface of the material to form a lubricating film and prevent adhesion to the hot metal of extrusion dies. (It should be noted that the term "internal lubricant" is occasionally used as a synonym for a plasticizer. True plasticizers

⁴ G. Swann, *Ind. Chemist* **25**, 3 (1950).

act by virtue of their solvent action, i.e., dispersing the polymer chains on a molecular scale, "lubricants" by lowering the frictional forces between the plastic and metal surfaces.)

II. Fields of Application

To appreciate the variety of rheological problems which arise during the manufacture of cellulose derivatives it is necessary to consider the main fields in which they are used and the processes used during manufacture.

1. PLASTICS

Nitrocellulose plastics (Celluloid, xylonite, pyroxylin):

The first synthetic thermoplastic material is still one of the main cellulosic plastics, and is manufactured in the form of rod, sheet, tube, and cast film. The other important cellulosic plastics—cellulose acetate, cellulose aceto-butyrate and ethyl cellulose—as well as being made in these forms are used extensively as injection-molding powders. (Cellulose nitrate is not used as an injection-molding powder because of its limited stability at high temperatures.)

Nitrocellulose plastics are compounded and fabricated by a "solvent" process, i.e., up to the final "stoving" of the half-finished sheets, tubes, etc., the plastic contains more than 10% of volatile materials (water and alcohol), which enables the mixing and forming operations to be carried out at temperatures below 100° C. Alcohol-wet nitrocotton is mixed with camphor, alcohol, and coloring matter in an enclosed mixer to form a stiff dough. The dough is filtered under high pressure to remove dirt, and is milled on hot rolls to remove excess solvent. At approximately 10% solvent content it is rolled into "hides." These are pressed at moderate temperatures into thick blocks from which sheets are cut by "slicing." Sliced sheet can be cut in thicknesses between 10/1000" and 1/2". The sliced sheets are dried of their residual solvent by hanging in heated chambers or "stoves" and are polished by hot pressing between polished metal plates in an hydraulic press. The block process of pressing and slicing lends itself readily to the production of configured patterns in the sheet, and artificial horn, ivory, and tortoiseshell effects can be produced. Rods and tubes are produced by extrusion from chipped-up rough sheet in screw extrusion machines, or from cylinders of rolled-up sheets (dollies) in hydraulic extruders. The material used contains 8 to 10% of alcohol enabling extrusion to be carried out at temperatures below 90° C. Higher temperatures are generally ruled out because of the danger of decomposition and fire. Rods and tubes produced thus are "stoved" or seasoned in the same way as the sheet material to remove residual solvent. The manufacture of the explosive cordite, consisting of a high nitrogen content (13%) nitrocellulose plasticized with

TABLE I

Plastic	Type	Grade	Flow Temp.	Impact Strength	
				25° C.	-40° C
Cellulose Nitrate (sheet)	General Purpose				
	Transparent		—	3.0	0.75
	Improved Toughness				
	Transparent		—	4.0	1.0
Ethyl Cellulose (Molding powder)	General Purpose	2	143° C.	3.5	0.5
	Low temperature resistant	6	143° C.	5.0	1.0
Cellulose Aceto-Butyrate (Molding powder)	General Purpose	3	149° C.	1.0	0.4
	Impact resistant	8	127° C.	3.1	1.0
Cellulose Acetate (Molding powder)	General Purpose	1	156° C.	0.8	0.3
	Impact resistant	8	149° C.	1.7	0.4

nitroglycerin, is carried out by similar processes. Cellulose acetate injection-molding chips or powders are made by two processes, the solvent or "wet" process and the dry process. The "wet" process is fundamentally that described above for the production of nitrocellulose plastic extrusion chips. Cellulose acetate molding powder, for instance, may be made by the wet process using acetone/alcohol or methyl ethyl ketone/alcohol mixtures as solvents. Plasticizers are added to the initial mixture, and the chipped-up sheet is dried to remove residual solvent before use as an injection material. Sliced sheet may be produced from cellulose acetate by the wet process as in the case of nitrocellulose.

The dry process consists of mixing the cellulose acetate powder or "flake" with colorants, plasticizers, stabilizers, etc., in a Banbury mixer at high temperatures to form a uniformly gelled mass which may be rolled into sheet and cut into chips. A variation on this process uses screw extrusion machines to homogenize the flake, plasticizer and color. The mixed material issues from the forming die of the extruder as a number of small diameter rods which may be broken up by a rotary cutter into injection-molding granules of uniform size and shape.

All the cellulosic plastics with the exception of nitrocellulose are used to make large numbers of articles by means of the injection-molding process. For the technology of this process readers are referred to the chapter "The Rheology of Molding" by C. E. Boyer and R. S. Spencer, in Volume III. Cold molding granules are forced by means of a hydraulic or pneumatically operated ram into a heated cylinder, usually with some form of torpedo or spreader at the hot end. As the granules move with successive strokes of the

plunger into the hot zone they become softened and, in turn, issue from a nozzle at the end of the cylinder into a cold metal mold.

After allowing sufficient time for the material to "set" in the mold by cooling below the softening point, the mold is opened and the molded piece ejected. The mold then closes and the cycle is repeated. Cellulose acetate injection-molding powders are supplied in a number of flow grades, i.e., soft, medium, medium hard, or hard, according to the temperature required to render them sufficiently plastic to be injection molded. Flow tests such as the "Rossi-Peake"⁵ test are sometimes used to characterize a temperature at which the material will have standard flow properties. The "Rossi-Peake" temperature of cellulose acetate molding powders may vary from 130 to 170° C. according to the flow grade. The flow grade may be varied by changing the degree of acetylation and viscosity of the original "flake" or the plasticizer content. Absorbed moisture in the injection powder has a considerable effect on the flow properties, in effect acting as a plasticizer, and also gives rise to steam bubbles in the moldings. Thus it is of great importance both in injection-molding practice and in experimental rheological work on cellulose derivatives to dry the molding powder carefully before use.

Cellulosic films, i.e., sheet below 10/1000 in. in thickness are manufactured by spreading or casting a concentrated solution or "dope" onto a moving metal wheel or band. The surface of the band is usually coated with a layer of gelatin to provide a smooth uniform surface from which the film may be stripped, and moves inside a large heated box. The conditions are arranged so that the film has lost most of its solvent by evaporation by the time it has reached the point at which it will be stripped off as a continuous sheet. By passing through further heated cabinets, the remaining solvent is removed and the film wound up in a roll. The technology of this process is complex, since, in addition to the rheological problems of mixing, filtering and conveying the dope to the spreader, the effect of solvent composition on the properties of the film must be taken into account. The solvents used are recovered from the vapor-laden air from the casting box and seasoning cabinets, and efficient recovery is a prime necessity in the economic success of the process. Similar principles apply to the "dry spinning" of acetate rayon.

2. SOLUTIONS AND MELTS

Solutions of cellulose derivatives are used very extensively as adhesives, paints, and other protective coatings. Cellulosic enamels are used extensively for motor vehicles, and for other metal articles. Nitro-cellulose solutions are used for coating textile materials (synthetic leathercloth) and for applying decorative finishes to leather, paper, etc. Both cellulose acetate

⁵ F. E. Piech and W. E. Gloor, *Am. Soc. Testing Materials Bull.* **151**, 70-75 (1948).

and cellulose nitrate solutions are used as adhesives. The main technological problem in formulating cellulosic paints is to reconcile the various requirements, i.e., high solids content, short drying time, freedom from "blushing," or other drying defects and good brushing or spraying characteristics.

Ethyl cellulose plasticized with an excess of a high-boiling-point mineral oil is used as a "hot dip" protective coating for metal parts, i.e., cutting tools, ball races, etc. The part to be protected is quickly dipped in the molten composition at 160 to 180° C. A chilled layer of the material forms a tough elastic skin around the article, which is impervious to water and moisture. This coating may be readily peeled off when the article is required for use.

III. Irreversible Behavior Flow

1. SOLUTIONS

From early in their history, the viscosity of their solutions at a fixed concentration has been regarded as one of the most important properties of cellulose derivatives. While it was clear that the solution viscosity was of importance in relation to the rheological properties of adhesives, dopes, and enamels, it was soon recognized that the viscosity of, say, a 12% solution could be used as an index of many other properties of a particular batch of a cellulose ester or ether, such as its toughness, solubility characteristics, and extrusion and molding behavior. The work of Staudinger made it evident that the viscosity of dilute solutions of linear polymers was related to their average chain length, upon which most of the useful properties of the bulk polymer depend. Measurement of the viscosity of dilute solutions, as a means of determining the molecular weight of polymers is a routine practice in all branches of the plastics industry and has a very extensive literature. Only a brief outline of the main facts in relation to cellulose derivatives will be attempted here.

When the viscosity of a cellulose derivative is measured at several concentrations in the range 0 to 2% the results can be expressed in the following form:

$$\eta = \eta_0[1 + (\eta)C + BC^2] \quad (1)$$

Other equations have been proposed by various workers. The constant (η) which determines the fractional viscosity increase of the solution at low concentrations resulting from the addition of polymer molecules is termed the "intrinsic viscosity." The intrinsic viscosity is found to be related to the weight average molecular weight in the following manner:

$$(\eta) = KM^a \quad (2)$$

The appropriate values of K for cellulose derivatives are discussed elsewhere.⁶

⁶ Molecular Weights of Cellulose, a Symposium, *Ind. Eng. Chem.* **45**, 2483 (1953).

Theory relates the exponent α to the type of configuration of the polymer chain in solution—whether a rigid rod, tight or loose coil, etc. It is almost certain that the same value of α would not apply for any polymer throughout the whole molecular-weight range. For most cellulose derivatives α is very nearly equal to 1. The constant B is commonly regarded as an index of the degree of interaction between solute molecules. For discussion of the significance of the slope of specific viscosity-concentration plots see Huggins,⁷ and Eirich and Riseman.⁸

At high concentrations and even at low concentrations when the molecular weight of the solute is high, deviations from Newtonian behavior occur, further complicating the measurements. Viscometers have been constructed to give varying rates of shear in order that the measured viscosity should be extrapolated to its value at very low shear rates (see ref. 6, p. 2489). As the concentration is increased non-Newtonian behavior and elastic effects become more apparent. Eizenschitz⁹ has measured the relation between shear stress, τ , and rate of shear, g , in this region and found that the results may be fitted to the following type of formula

$$g = A\tau + B\tau^3 \quad (3)$$

At low shear stresses (τ being small) the second term becomes negligible and the solution behaves as a Newtonian fluid. At high shear stresses the apparent viscosity decreases with increasing shear stress. The quantity $\sqrt{A/B}$ has the dimensions of an elastic modulus, and a theory of Hencky¹⁰ relates this to the "evanescent" elasticity of the solution. Certainly at these concentrations and shear stresses orientation and elastic effects become evident, and give rise to flow birefringence, "elastic recoil," and the set of phenomena variously described as "secondary flow," "cross elasticity," and the "Weissenberg effect." In cellulose derivative solutions these may be associated with the partial alignment of the molecules in the flow field together with some elastic distortion of the average chain segment distribution. The Weissenberg effect, i.e., the appearance of normal surface tractions in liquids subjected to a simple shearing action, has been suggested to be also an expression of evanescent elasticity. Weissenberg¹¹ has suggested the following relation between the tension acting along the stream lines p_{xx} and the shear stress τ

⁷ M. L. Huggins, *J. Am. Chem. Soc.* **64**, 2716 (1942).

⁸ F. Eirich and J. Riseman, *J. Polymer Sci.* **4**, 417 (1949).

⁹ R. Eizenschitz, *Kolloid-Z.* **64**, 184 (1933); see also W. Philippoff and K. Hess, *Z. physik. Chem.* **B31**, 237 (1936); K. Edelman, *Proc. 2nd Intern. Rheol. Congr., Oxford* pp. 107-115 (1953).

¹⁰ H. Hencky, *Ann. Physik.* [5] **2**, 617 (1929).

¹¹ K. Weissenberg, *Rept. General Conf. Brit. Rheologists' Club* p. 36 (1946).

$$p_{xx} = \frac{\tau^2}{G} \quad (4)$$

where G is the "evanescent" shear modulus of the liquid. Some experiments made by the author showed that solutions of nitrocellulose in cyclohexanone obeyed this relation (4) within experimental error. The apparatus used was a simple shearing disk viscometer with a device for measuring the excess hydrostatic pressure at the centre of the disk due to the "strangling" tendency of the circular streamlines, as well as the total shearing forces acting on the disk surface. Thus the variation of the magnitude of the secondary forces and of the viscosity of the material could be measured simultaneously. The solutions obeyed relations (3) and (4) within experimental error, and the magnitude of G in (4) was close in value to $\sqrt{A/B}$ derived from (3). This suggests a connection between anomalous viscosity effects, elasticity, and the Weissenberg effect which could be profitably investigated further.

2. MELTS

The rheological properties of ethyl cellulose "hot dip" compositions described earlier are essentially those of concentrated solutions when they are in the molten state (120 to 180° C.), i.e., they are liquids, but with anomalous viscosity. With decreasing temperature, however, a rapid increase in viscosity occurs over a narrow temperature range and the material forms a soft elastic gel. This gel becomes more rigid with decreasing temperature to become a tough flexible compound at room temperatures. The formation of gels with a virtual "yield stress" below a fairly well-defined temperature is characteristic of solutions of crystallizable polymers such as cellulosics, polyvinyl chloride, polyethylene, etc., as distinct from polystyrene, polyvinyl acetate and other amorphous polymers which show less marked gelling properties in solution. The rheological properties of highly plasticized ethyl cellulose compositions in the gel range are also of interest since these have been used as "cements" or "binders" for cork-based flooring compositions, as a replacement for "bodied" (i.e., partially polymerized) linseed oil.

The rheological properties of interest are as follows:

a. Melt Viscosity and Its Variation with Temperature

The melt viscosity determines to a large extent the thickness of the film adhering to the article when dipped in the melt and allowed to drain. The viscosity increases with the intrinsic viscosity (i.e., molecular weight) of the ethyl cellulose used, and decreases with increase in temperature or plasticizer content. A convenient method of measuring the viscosity is to use an Umstatter or other type of rotational viscometer, electrically heated. The compound may be melted directly in the viscometer and the viscosity

determined over a range of temperatures. The empirical method of dipping a metal plate into the mixture, draining, and measuring the thickness of the adherent film has also been used.

b. Softening Point or Melting Point

Various methods have been used to determine a temperature at which the material will flow continuously under small sustained stresses. The ring and ball softening point test as used for bitumens can be used for this purpose. The specimen used is a small disk fitting into a metal ring. A steel ball, smaller than the internal diameter of the ring rests on the disk, and the whole assembly is heated at a constant rate in a liquid heating path. The temperature is found at which the ball penetrates the disk and falls through the ring. This temperature will clearly be related to the viscosity-temperature curve of the hot-dip compound and the rate of heating.

In Fig. 1 the viscosity-temperature curves of three ethyl cellulose hot-dip compositions obtained using an Umstatter viscometer. The corresponding ring-and-ball softening points T_R will be seen to correspond to viscosities of approximately 7×10^3 poises.

As a test of the maximum storage temperature for articles with a hot-dip coating, the deformation of cylinders of the composition compressed in a parallel-plate plastometer has been used. In one case the test consists of

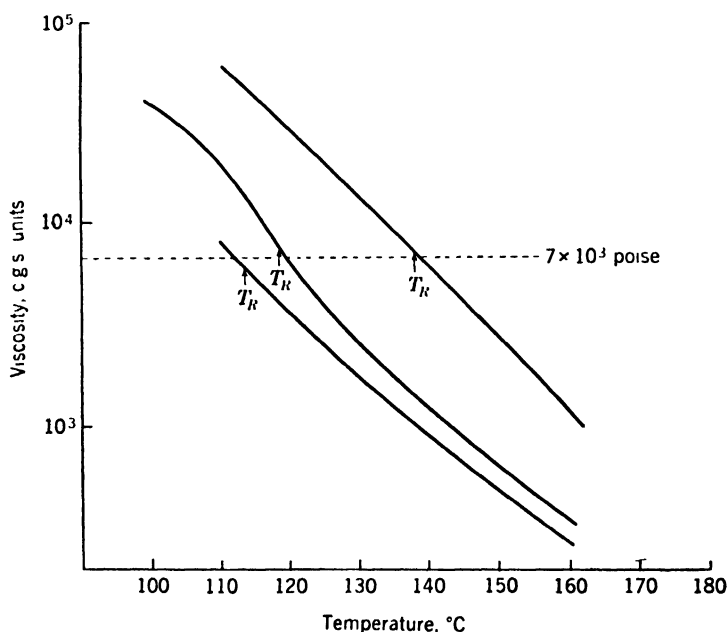


FIG. 1. Viscosity-temperature curves of 3 ethyl cellulose hot-dip compositions.

loading a cylinder of the composition 0.5 in. in diameter and 0.5 in. high with a load of 5 kg. applied between parallel plates 3 in. in diameter, at a temperature of 71° C. A maximum deformation of 0.35 in. is allowed after 5 min. under load, corresponding to a 'viscosity' of approximately 10^8 poises.

c. "Creep" or "Cold Flow" at Room Temperatures

Apart from such tests as for tensile strength, it is of importance to measure the deformation of the dip coating gels described above under small stresses applied for long periods of time, since in many applications—e.g., in cork-filled floor coverings—the material may be subjected to indentation stresses from furniture, and so on. A simple method of measuring the cold-flow properties of these materials is to hang a small weight at one end of a "dumbbell" tensile-test specimen and measure, at intervals, the length between two gage marks on the parallel portion of the specimen. The creep curves of Fig. 2 were obtained in this way.

The rheological behavior over the whole range of temperature involved in the use and manufacture of ethyl cellulose melt compositions may be controlled by the molecular weight and degree of substitution of the ethyl cellulose, by the proportion and aromatic content of the mineral oil used, and by the addition of cross-linking agents and fillers. These different agencies do not have identical effects at all temperatures, and so the possibility occurs of judiciously blending their effects to obtain the best all-round results.

The action of calcium in the form of slaked lime on the flow properties of ethyl cellulose hot-dip compositions is peculiar and is illustrated in

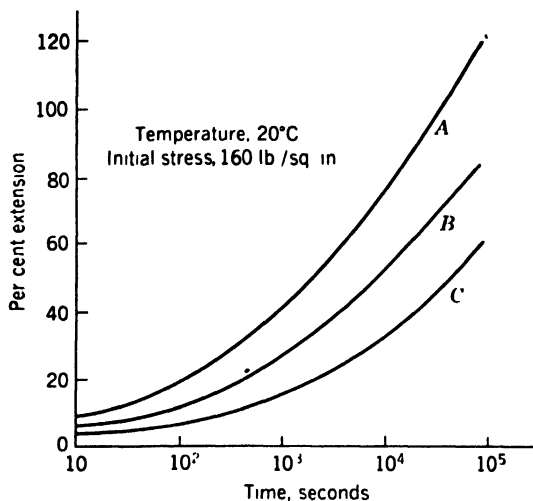


FIG. 2. Creep curves for three Ethyl cellulose 'hot dip' compositions. A, B, and C contain progressively smaller proportions of mineral oil plasticiser.

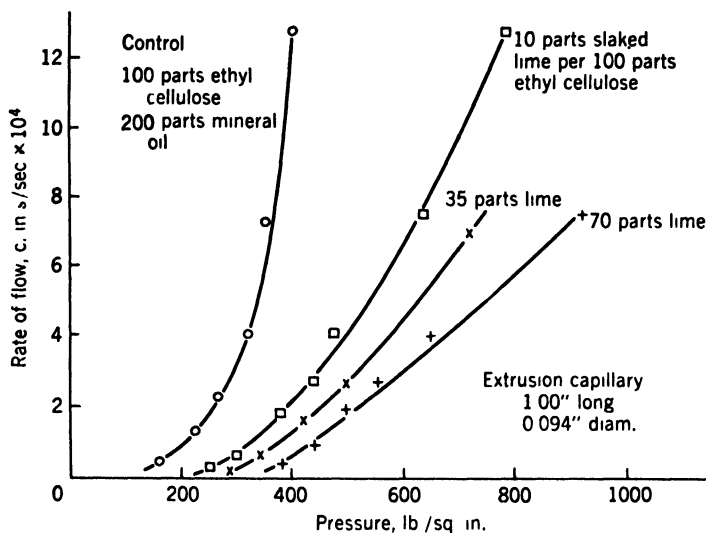


FIG. 3. Action of slaked lime on the flow properties of ethyl cellulose hot-dip compositions.

Fig. 3. The flow curves (extrusion pressure rate of flow curves for an extrusion plastometer)^{11a} were obtained at 90° C. i.e., in the "plastic" range and below the "ring-and-ball" softening point. The large increase in flow pressure obtained by the addition of 10% by weight of lime suggests that the calcium hydroxide has a specific chemical effect on the ethyl cellulose, such as cross-linking residual OH groups between neighboring chains. Finely divided calcium carbonate had little effect on the flow curves beyond that expected from an inert filler.

3. PLASTICS

Studies of the flow behavior of plastics in the range of temperature used in the fabrication of forms and articles (extrusion, calendering, and injection and compression molding) are of obvious technical value. They lead to a fuller understanding of the mechanics of the process concerned, and they suggest how the process may be modified to accommodate less tractable thermoplastics or how the plastic must be altered to suit the process concerned. The exact behavior of polymers in the plastic range under even simple stresses is very complicated¹² and a study of the exact details of the flow of a plastic in the general case would not be practical for technical purposes. Fortunately sufficient information can be derived from relatively

^{11a} E. B. Atkinson and H. A. Nancarrow, *Proc. 1st Intern. Rheol. Congr., Scheveningen* Part II, pp. 103-107 (1949).

¹² W. F. O. Pollett, *Proc. 2nd Intern. Rheol. Congr., Oxford* pp. 85-90 (1953).

simple flow tests to determine the approximate behavior of a polymer during extrusion and calendering operations.

Plasticity measurements have been used for very many years in the rubber industry as tests of extrusion of sheet calendering behavior, and the three main types of plastometer used in the rubber industry have been adapted for thermoplastic flow testing, i.e., the parallel-plate plastometer of Williams has been used;^{13, 14, 15} rotational viscometers (Mooney) by Buchdahl, Nielsen, and Merz;¹⁶ extrusion plastometers by Nason,¹⁷ Spencer and Dillon,¹⁸ Atkinson and Nancarrow.^{11a} These plastometers are all capable of giving information concerning the relation between the shear stress and the shear rate in the plastic compound. It is also desirable for them to simulate the conditions of the process they are used to study or control. Each type has its advantages for the study of different aspects of a plastic's rheological behavior. For instance, the parallel-plate plastometer is ideally suited for measuring flow properties at very low rates of shear and for measuring elastic recovery. Very high rates of shear comparable to those in technical extrusion and calendering may be obtained with the extrusion plastometer, while the rotational plastometer can be used to follow progressive changes in properties under a continued shearing action such as may occur in internal mixers, mills, and in extrusion screws.

The flow grades of cellulose acetate injection-molding powders are often specified by the Rossi-Peake Flow temperature⁵ (A.S.T.M. D 569-43), this being the temperature at which the plastic will flow 1 in. in 2 min. into a $\frac{1}{8}$ in. tube under a pressure of 1500 lb./sq. in. The Rossi-Peake temperatures of cellulose acetate molding powders vary from 130° C. for "soft" grades to 180° C. for hard, heat-resistant grades. This test gives some indication to the molder of the temperature required in the cylinder of the injection machine—usually 20° C. higher than the Rossi-Peake temperature.

Practical experience of the injection process has shown that no simple flow test will give complete picture of the behavior of the plastic in an injection-molding machine. This is possibly due to the fact that the temperature of the material undergoes large changes during the molding cycle. In the injection cylinder the plastic undergoes progressive heating and softening until it reaches the nozzle at which it is of the consistency of a thick treacle. During the injection stroke this material is forced into a cold or cool mold in a matter of a few seconds. As the hot plastic travels through the mold passages progressive cooling will occur and the situation will be

¹³ W. M. Gearhart and W. D. Kennedy, *Ind. Eng. Chem.* **41**, 695 (1949).

¹⁴ G. J. Dienes and H. F. Klemm, *J. Appl. Phys.* **17**, No. 6, 458 (1946).

¹⁵ R. Buchdahl, *Proc. 2nd Intern. Rheol. Congr., Oxford* pp. 116-122 (1953).

¹⁶ R. Buchdahl, L. E. Nielsen, and E. H. Merz, *J. Polymer Sci.* **6**, No. 4, 403 (1951).

¹⁷ H. K. Nason, *J. Appl. Phys.* **16**, 338 (1945).

¹⁸ R. S. Spencer and R. E. Dillon, *J. Colloid Sci.* **4**, 241 (1949).

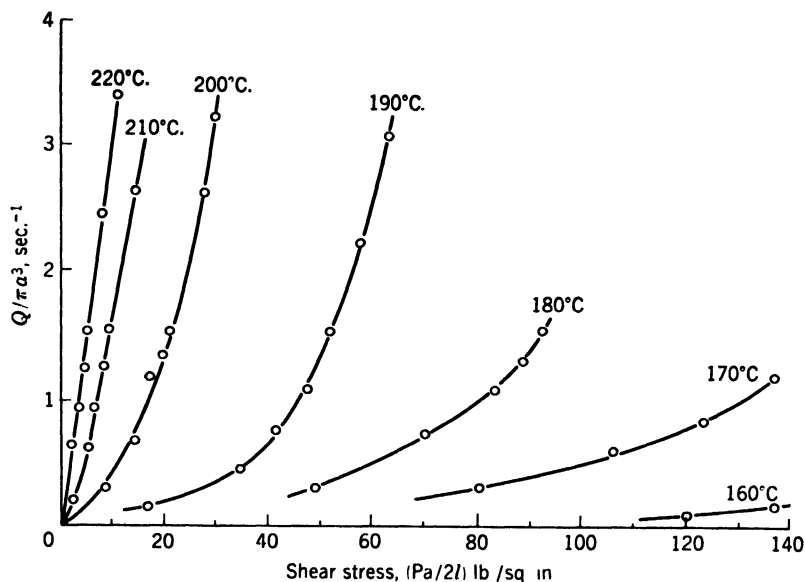


FIG. 4. Relation between shear stress and rate of shear for cellulose acetate "hard" grade injection molding powder.

complicated by the freezing of a cold skin of plastic on the metal surfaces. Molecular orientation resulting from the flow stresses occurs and the finished molding will exhibit the effects of this as a variation of strength properties in different directions in the molding.

By measuring the flow properties of plastics over a relatively wide temperature range it is possible to obtain a clearer picture of their injection behavior. A convenient method is to measure the pressure required to extrude the material through a capillary of standard dimensions at a number of different speeds, corresponding to the shear rates obtained in the cylinders, molds, and runners of injection molding machines. The pressure-rate of discharge data may be analyzed to give the relation between shear stress or "apparent viscosity" and rate of shear for the plastic at any temperature.¹⁹ Data of this kind for a cellulose acetate molding powder is shown in Fig. 4 and its behavior may be taken as typical of many thermoplastics.

At high temperatures or low shear stresses the "flow curve" relating shear stress and rate of shear is almost linear, whereas at lower temperatures and high shear stresses markedly non-Newtonian flow curves are obtained. It is thus impossible to specify a viscosity at any temperature unless the shear stress or rate of shear is known (except perhaps at very low stresses). When it is required to illustrate the temperature-dependence of

¹⁹ E. N. da C. Andrade, "Viscosity and Plasticity," p. 56. Heffer, Cambridge, 1947; see also A. G. Ward and E. L. E. Westbrook, *J. Soc. Chem. Ind.* **67**, 389 (1948).

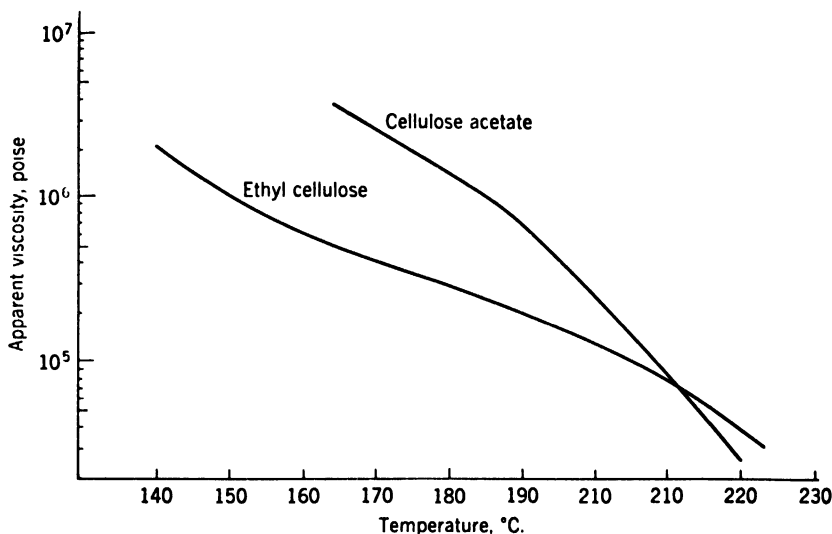


Fig. 5. Temperature variation in the flow properties of cellulose acetate and ethyl cellulose molding powders. Average shear rate = 10 sec.⁻¹.

the plastic flow properties of the system, a choice must be made between two methods of presentation—whether to plot the “viscosity” measured at a fixed rate of shear or at a fixed shear stress against temperature. On theoretical grounds the latter method is a more sound method, but practical considerations make the former desirable. The shear rates at the same position in an injection-molding machine, extruder, or plastics calender are generally fixed by the mechanics of the machine, while the shear stresses induced by shearing the plastic vary with temperature. Thus the shear stress or apparent viscosity measured at fixed shear rates are the more useful quantities to examine for temperature-dependence. Figure 5 illustrates the temperature variation in the flow properties of cellulose acetate and ethyl cellulose molding powders. The lower viscosity temperature coefficient of ethyl cellulose compared with cellulose acetate is very evident, and argues a lower activation energy for the flow process in the former. Since the ethyl and acetyl groups are of comparable sizes it may be assumed that the higher activation energy of flow in cellulose acetate is due to the stronger secondary bonds formed by interaction between the polar carbonyl groups in neighboring chains.

Addition of plasticizers or solvents lowers the apparent viscosity of cellulosic compositions. Figure 6 shows the effect of progressive plasticizer additions on the flow properties of cellulose acetate compositions.²⁰

²⁰ For other data on effect of plasticization on the flow properties of Cellulose acetate see V. Stannett and R. Whitfield, *Plastics (London)* **13**, 15 (1949).

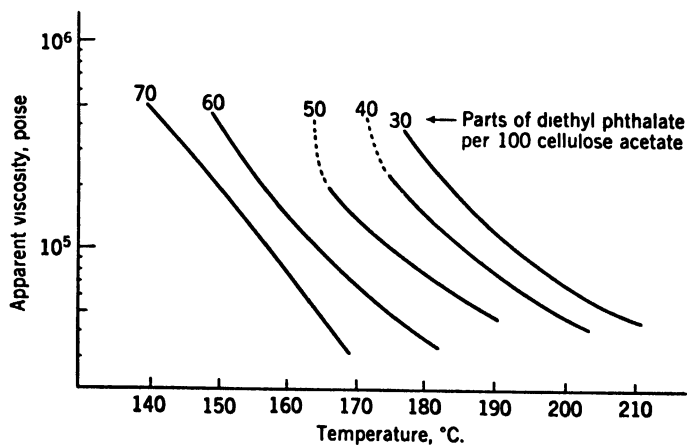


FIG. 6. Effect of progressive plasticizer additions on the flow properties of cellulose acetate compositions. Average shear rate = 10 sec^{-1} .

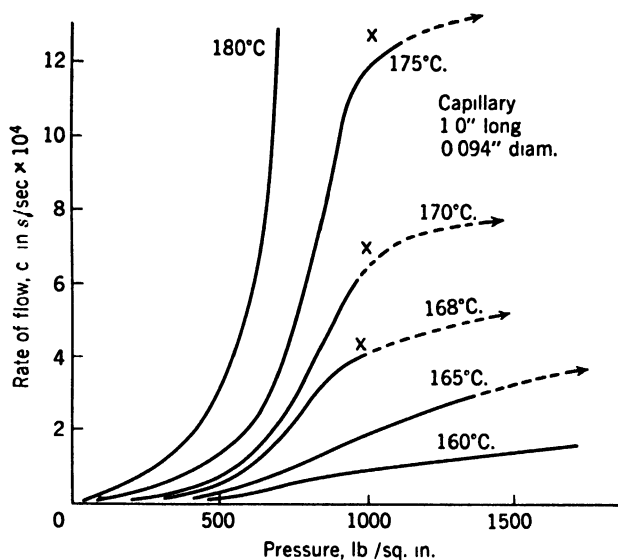


FIG. 7. Pressure rate of flow for a cellulose aceto-butyrate molding compound.

Cellulose aceto-butyrate exhibits a curious phenomenon when its flow properties are investigated by extrusion methods. Figure 7 shows pressure-rate of flow curves for a cellulose aceto-butyrate molding compound. As the extrusion speed is increased, the pressure drop through the capillary increases progressively at each temperature to the point X. Beyond X a slight increase in speed causes a sharp and catastrophic rise in flow pressure, as though the plastic had suddenly "frozen" in the capillary. The appear-

ance of the extruded rods also shows an abrupt change at X , changing from smooth and shiny to a dull, rough, and highly swollen extrusion. Cellulose aceto-butyrate has a relatively sharp softening range almost akin to a "melting point" compared with cellulose acetate, and this phenomenon may be likened to a "freezing" of the molten plastic under the influence of orientation induced by flow through the capillary. A similar phenomenon might occur if the viscosity of the plastic increased rapidly with the mean hydrostatic pressure, but the experimental results favor the "orientation" theory.

Because of their thermal instability and inflammability, nitrocellulose plastics are not injection-molded and are only rolled, calendered, and extruded, as "wet" or solvent-containing mixes at temperatures below 100°C . (usually 80 to 90°C .). A typical nitrocellulose extrusion material would contain 100 parts of nitrocellulose, 40 parts of camphor (as plasticizer) 10 parts of ethyl alcohol, and 2 parts of water (from "industrial" alcohol introduced at earlier stages), and would be extruded from a screw extruder having a die temperature of approximately 80°C . Figure 8 gives typical "flow curves" of a nitrocellulose mix in this temperature range, and nearly approximate to a "Bingham body" with a yield point. This yield point, however, is only apparent, since permanent flow will occur at much smaller stresses. Elastic effects are very marked and can give rise to ripple-like markings and gross distortion of extruded rods and tubes. The temperature and extrusion speed range within which smooth uniform extrusions can be produced is restricted compared with other plastics.

The flow curve alters with changes in the solution viscosity and nitrogen content of the nitrocellulose and proportions of alcohol, camphor, and water in the mixture.

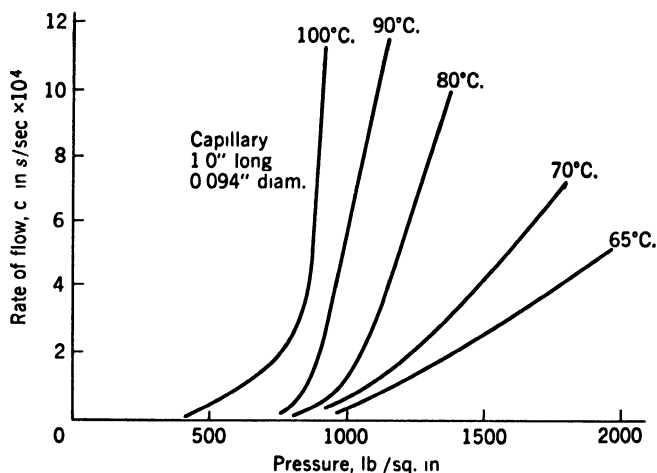


FIG. 8. Flow of a nitrocellulose mix (extrusion compound).

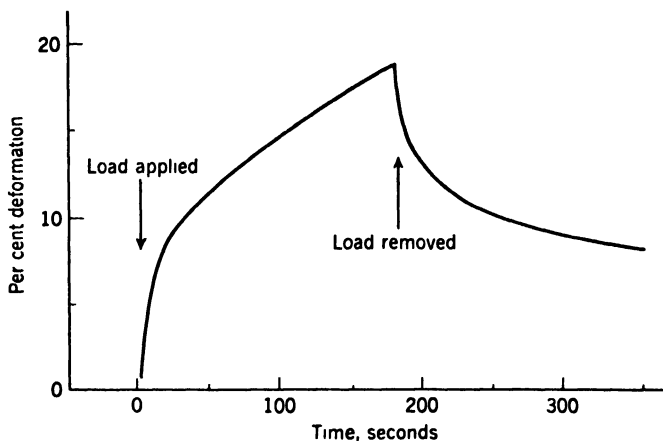


FIG. 9. Deformation and recovery of a nitrocellulose extrusion compound. Compression and recovery at 90°C.

The elastic properties of nitrocellulose compositions may also be studied by means of the parallel plate or "recovery" plastometer or by the extension of strips. Eley and Pepper²¹ have studied the viscoelastic properties of cordite in a similar way. Figure 9 shows deformation and recovery curves of a nitrocellulose extrusion compound in the form of an axially loaded cylinder, at 90° C. It will be observed that a considerable proportion of the deformation is recoverable on removal of the applied load, and that delayed rubber-like elastic effects as well as viscous flow are present.

IV. Elasticity and Toughness

1. MODES OF RESPONSE

In this final section a brief survey will be made of the mechanical properties of cellulosic plastics at ordinary temperatures.

The response of solid high polymer materials to stress is complex, and as yet no completely satisfactory molecular explanation of all the observed features has been made, but for convenience the following classification of the modes of response can be made.

Ordinary Elastic Straining

An "ordinary" elastic deformation is always assumed to be superimposed on other deformations resulting from stress. This "ordinary" elasticity caused by the bending of valency bond angles, straining of interchain van der Waals' "bonds," etc., is attained very rapidly, is linear with stress and completely recoverable. At very low temperatures when configurational changes in the polymer chains cannot take place this mechanism is assumed

²¹ D. D. Eley and D. C. Pepper, *Trans. Faraday Soc.* **43**, 559 (1947).

to account for all the elastic deformation. The value of the elastic modulus of this process would lie between 10^{11} and 10^{12} dynes/sq. cms.

Configurational Elasticity

The elastic behavior of rubber and other polymers that are capable of large reversible extensions is ascribed to the possibility of large deformations in a network of randomly coiled high polymer chains when the chains can easily alter their configurations under thermal Brownian movement by free rotation about single C—C bonds. The same process can occur in rigid or semirigid plastics, but at a much slower rate. A rigid plastic is rigid (as is rubber at, say, -180° C.) by virtue of the fact that configurational changes are greatly restricted by interchain attractions, energy barriers restricting free rotation about the carbon-carbon bonds of the polymer chain "backbone," and crystallization. An increase in temperature above the "second-order transition temperature" increases enormously the rate at which configurational changes can occur, and all linear polymers under these conditions display configurational elasticity.

At room temperatures the slow and progressive configurational changes under load give rise to a time-dependent deformation or "creep." Some configurational changes can occur rapidly and so give rise to an elastic deformation which may be mistaken for "ordinary elasticity." The orientation times of the molecular processes involved cover many decades, i.e., the elastic process has a distribution of orientation times. At low stresses the configurational elastic deformations are reversible, i.e., on removal of the load the specimen slowly recovers its original shape. An increase in temperature accelerates both creep and recovery.

At higher stresses the rate of configurational deformation increases very rapidly with increase of stress, a phenomenon which gives rise to "plastic yielding" and "necking" in tensile-test specimens. This presumably occurs when the applied stress is sufficient to overcome the restraints which hinder configurational changes, e.g., rotational barriers, and van der Waals' forces of crystallites. Above the "yield-point" strains of 100 to 1000 % are possible in polymers because of this mechanism. Nearly all of this deformation is recoverable by heating above the second-order transition temperature.

Fracture

Total failure of the specimen subjected to a tensile stress may occur by the propagation of a crack or tear across it. There is evidence that fracture is the culmination of progressive changes in the specimen brought about by the applied stress. Similar changes, no doubt, occur in specimens subjected to alternating stresses or repeated blows, which ultimately fail by cracking.

When mechanical tests such as tensile-strength, fatigue, creep, and im-

pact tests are applied to a plastic test specimen, the various modes of response listed above will be involved in varying degrees, depending upon the stresses, rates of stressing, and the temperature. The "ordinary" elastic deformation is not in general a large component of the deformation and is not affected by stress or the rate of stress application, so that the type of behavior exhibited by a plastic in any test is determined by the interrelation of the other factors: configurational elasticity, structural changes, and fracture. The shape and extent of a stress-strain curve in a tensile test is determined by these three factors in competition. Toughness and high impact strength in a plastic is dependent upon an ability to absorb energy at high strain rates without fracture, and Haward²² has indicated how this is dependent upon the relation between the stress rate of creep curves and the stress-fracture time curves of a plastic.

The main factors which influence the tensile and yield strength of cellulose plastic compositions are molecular weight, degree and type of substitution, temperature, plasticizer content and relative humidity (since absorbed water has plasticizing properties). Of particular interest is the effect of the chain length of the substituent groups, the tensile strength of triesters falling rapidly with increasing aliphatic chain length.²³ Substituent groups and plasticizers both have the effect of increasing the distance between the chains and so reducing the interchain forces and the tendency to crystallize. Both factors lead to a reduction in strength.

2. STRESS-STRAIN CURVES

Stress-strain curves of cellulose derivatives have been published by Lawton *et al.*²⁴ This paper also gives a considerable amount of information on the variation of mechanical properties with temperature, humidity, rate of strain, etc. Another paper by Carswell and Nason²⁵ gives useful comparative data on the variation of the properties of several plastics (including vinyls, thermosetting materials, and cellulose derivatives) with temperature, humidity, weathering, and so on. Stress-strain curves in shear for cellulose acetate have been determined by Findley²⁶ and shear strengths have been reported by Schwartz and Dugger.²⁷

The stress-strain curves and other mechanical properties described in the above papers fit into the general scheme of response described above. The stress-strain curves of cellulose acetate, cellulose nitrate and ethyl cellulose

²² R. N. Haward, "Strength of Plastics and Glass," pp. 179-185. Interscience, New York, 1949.

²³ S. E. Sheppard and P. T. Newsome, *J. Phys. Chem.* **39**, 143 (1935).

²⁴ T. S. Lawton, T. S. Carswell, and H. K. Nason, *Modern Plastics* **22**, 145 (1944).

²⁵ T. S. Carswell and H. K. Nason, *Modern Plastics* **21**, 125 (1944).

²⁶ W. N. Findley, *Modern Plastics* **20**, 99 (1943).

²⁷ R. T. Schwartz and E. Dugger, *Modern Plastics* **21**, 117 (1944).

plastic materials show an initial recoverable elastic response at low stresses, with noticeable departures from linearity at stresses approaching the "yield stress."

The "yield stress" is not a sharply defined quantity when applied to organic thermoplastics and (unlike, for instance, tough metals) varies considerably with the rate of strain imposed during the tensile test. In fact the "yield stress" may be taken as the stress at which the rate of creep of the specimen becomes equal to the linear speed of the cross-head of the tensile testing machine. Yielding is often accompanied by "necking" of the specimen because of the inevitable increase in stress caused by a local reduction in area, and occasionally "slip bands" will appear similar to those found on metal specimens stressed beyond their yield point. However, such slip bands are found to lie at angles greater than 45 deg. to the direction of the tensile stress, which suggests that the yield stress in shear is reduced by a hydrostatic tension.

Beyond the yield point a cellulosic plastic can be "cold drawn" (often with necking) by an extension of up to 50 %. Haward²⁸ has suggested that the high elastic extensibility of cellulose derivatives may be limited by the comparative straightness of the cellulose chains which does not allow much extension by "uncoiling." Extensibility, especially two-dimensional extensibility at ordinary and elevated temperatures is of considerable technical importance, as it is essential for such forming operations as bending and punching, at room temperatures and vacuum and "blow" molding, at elevated temperatures. The elongation at break as measured by tensile tests on cellulosic plastic sheet materials increases in a general way with increase in temperature, until values of 100 to 150 % are obtained in the blow-molding temperature range (110 to 130° C.) for cellulose acetate and nitrate sheets. Ethyl cellulose sheet has a higher elongation in this temperature range (150 to 300 %) but generally suffers from other difficulties resulting from its tendency to stick to hot metals.

3. CREEP

When subjected to fixed loads, cellulose plastics, like many other thermoplastics, "creep," that is, they extend progressively with time. As has already been indicated, the rate of creep increases rapidly when the stresses approach the yield stress. Other investigations of the creep behavior of cellulosic plastics^{28a} have been made by Burns,²⁹ Chasman,³⁰ Haward,²² and

²⁸ R. N. Haward, *Trans. Faraday Soc.* **38**, 394 (1942).

^{28a} For an excellent introduction to the nature and origin of creep in organic materials (including viscose and acetate rayon) and to its scientific study the reader is referred to "The Elastic and Creep Properties of Filamentous Materials and Other High Polymers" by Herbert Leaderman (Textile Foundation, Washington).

Ward and Marriott.³¹ An interesting feature of much of this work is that the creep curves obtained can very often be fitted to an equation which is very similar to Andrade's equation for the creep of metals:

$$\text{Creep strain} = at^{1/3} + bt$$

Under a constant load a thermoplastic material may eventually fail by fracture. The time required for fracture to take place varies with the stress applied, becoming short at stresses approaching the breaking stress as measured in an ordinary tensile-strength test. The relation between applied stress and time to rupture for cellulose derivatives has been discussed by Haward,²² Findley,³² and Chasman.³⁰ There is evidence that progressive irreversible changes take place under a constant stress which finally result in fracture, in a similar manner to the fatigue damage caused by alternating stresses. There seems to be a need for clarifying the connection between the effect of sustained and alternating stresses on fatigue, crazing, creep, dynamic loss, and so on.

4. TOUGHNESS

Toughness and resistance to shock in plastic materials are usually assessed by impact-strength tests. There is a variety of these based on test specimens in the form of notched or plain bars which may be clamped at one end and struck at the other end (Izod test) or supported at each end and struck in the middle (Charpy test). In these tests the striker may be a heavy pendulum or a falling weight. Another type of test used consists of dropping a weighted carriage or a steel ball on to a plate or disk of plastic material which may be clamped around its edge. The "impact strength" is expressed either as (a) the minimum energy required to fracture the specimen, or as (b) the energy absorbed from the striker in breaking the specimen, a quantity which is not necessarily the same as (a). Opinions differ over the relative usefulness of these two methods of testing and indeed over the relevance of "impact strengths" as a guide to the toughness of a thermoplastic, since two kinds of impact test will often grade a series of thermoplastic materials in a different order of merit.

The nature of toughness and the meaning of impact-test results have been discussed by Haward,³³ Coker and Filon,³⁴ and others. The impact strength

²⁹ R. Burns, *Modern Plastics* **21**, 111 (1943).

³⁰ B. Chasman, *Modern Plastics* **21**, 145 (1944).

³¹ A. G. Ward and R. R. Marriott, *J. Sci. Instr.* **25**, No. 5, 147 (1948).

³² W. N. Findley, *Modern Plastics* **18**, 83 (1941).

³³ R. N. Haward, "Strength of Plastics and Glass," p. 146. Cleaver-Hume Press, London, Interscience, New York, 1949).

³⁴ E. G. Coker and L. N. G. Filon, "A Treatise on Photoelasticity," p. 595. Cambridge Univ. Press., London, and New York, 1931.

of cellulose nitrate, cellulose acetate, cellulose aceto-butyrate or ethyl cellulose compositions decreases at lower temperatures. Ordinary grades of cellulose acetate sheet generally become quite brittle at temperatures of about -15°C . whereas ethyl cellulose, cellulose nitrate and some grades of cellulose aceto-butyrate plastics retain a certain degree of toughness at a temperature of -50°C .

Some idea of the relative order of toughness of the principle types of cellulose derivatives can be derived from the table on p. 240 of required values (A.S.T.M. D 706-44T) for impact strength of molding powder and sheet plastics (Izod impact strengths in foot-pounds per inch of notch).

These properties can be varied widely by change of plasticizer content etc. While increase in plasticizer content increases impact strength at ordinary temperatures it also reduces yield strength, heat distortion temperature, and the flow temperature.

It is difficult to account fully for the differences in impact strength between the various cellulose derivatives, and a comprehensive theory would need to take into account the strength of the interchain forces, the relative degree of "free rotation" between glucoside residues, and the "internal viscosity" associated with the motion of small chain segments. It is essential that rapid deformations should be able to occur without producing stresses higher than that required to start and propagate a crack, in order that a material should have a high impact strength. It is possible that for high impact strengths a reasonable degree of crystallization and a certain amount of mobility in the disordered regions would give the required combination of strength and compliance to rapidly applied stresses.

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Nomenclature

C	Concentration (e.g. grams/ 100 c.c.)	p_{xx}	Normal stress component in x direction
η	Solution viscosity	P	Pressure
η_0	Solvent viscosity	a	Diameter of capillary
(η)	Intrinsic viscosity	l	Length of capillary
M	Molecular weight	$P\alpha/2l$	Shear stress at wall of capillary
g	Rate of shear (reciprocal seconds)	Q	Volume rate of discharge
G	Elastic shear modulus	$Q/\pi\alpha^3$	Quantity with dimensions of rate of shear in capil- lary flow experiments
τ	Shear stress		
t	Time (seconds)		

THE RHEOLOGY OF FIBERS

R. Meredith

CHAPTER 7

I. Introduction	262
II. Structure	262
1. Molecular Structure	263
2. Crystalline and Amorphous Regions	266
3. Fine Structure	268
4. Moisture Absorption	269
III. Creep and Relaxation	270
1. Introduction	270
2. Creep and Creep Recovery	272
a. Small Stresses	272
b. Larger Stresses	273
3. Relaxation	276
a. Constant Extension	276
b. Constant Twist	279
4. Influence of Humidity and Temperature	279
a. Creep	279
b. Relaxation	282
IV. Stress-Strain Relations	283
1. Load-Extension Curves under Standard Conditions	283
a. Effect of Rate of Extension	286
b. Influence of Humidity and Temperature	286
2. Recovery from Strain	289
a. Resilience	290
b. Crease Resistance	291
3. Flexural Rigidity	292
V. Dynamic Properties	293
1. Elastic Modulus and Internal Friction	293
2. Influence of Static Strain and Dynamic Strain Amplitude	293
3. Effect of Frequency and Humidity	295
4. Flexural Rigidity	295
5. Torsional Rigidity	296
VI. Quantitative Theoretical Interpretation	298
1. Thermodynamical Approach	298
2. Reaction-Rate Theory	300
a. Three-Element Model	300
b. Two-State Theory	303
3. Distributions of Relaxation Times	305
VII. Strength	307
1. Tensile Strength	307

2. Shear Strength	311
3. Resistance to Repeated Bending	311
Nomenclature	312

I. Introduction

Since some knowledge of fiber structure is essential to an understanding of the rheological behavior of fibers, the first section describes the general features of fiber structure, with some detailed description of particular fibers where this is of special interest. The section on creep and relaxation emphasizes the important part played by time. This is followed by a section on stress-strain relations with a controlled time factor. In the section on dynamic properties the response to sinusoidally varying stress or strain has been recorded. A short section on quantitative theoretical interpretation gives references for further reading and, finally, rupture properties are discussed.

This survey is necessarily brief and touches only lightly on certain aspects. A much more complete account is to be found in a monograph by the present author.¹

II. Structure

Fibers may be divided into three main classes: (i) cellulose fibers, (ii) protein fibers, and (iii) synthetic fibers. The natural cellulose fibers comprise flax, cotton, jute, hemp, ramie, and other minor vegetable fibers such as kapok and coir fiber. Viscose rayon and cuprammonium rayon are man-made regenerated cellulose fibers, while cellulose acetate rayon is a cellulose ester fiber. Wool, silk, and the many varieties of hair fiber are natural protein fibers; regenerated protein fibers that have been used commercially may be made from the casein in milk (Aralac), from the vegetable proteins in peanuts (Ardil), or zein (Vicara). Synthetic fibers are made by the polymerization of monomers to form such materials as the polyamides, polyesters, polyvinyls, or polyethylene. Glass and asbestos can be produced in the form of filaments or fibers, but they will be mentioned in this chapter only incidentally since their rheological properties do not have the interesting characteristics possessed by the organic fibers which consist of linear macromolecules.

It is proposed to discuss briefly those features of fiber structure which have a bearing on the interpretation of the rheological behavior of fibers. Further information on the structure of fibers will be found in books by Astbury,^{1a} Meyer,² Ott,³ Mauersberger,⁴ Hermans,⁵ R. D. Preston,⁶ J. M. Preston,⁷ Hill,⁸ Urquhart and Howitt,⁹ and Woods.^{9a}

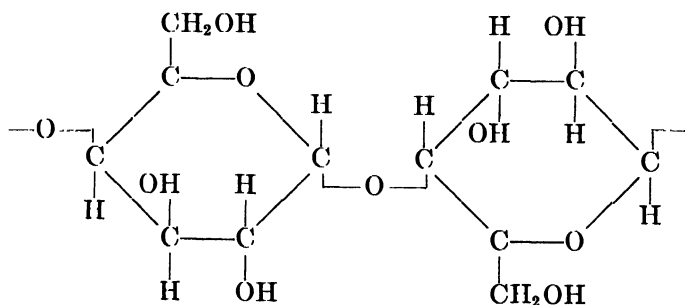
¹ R. Meredith, ed., "Mechanical Properties of Textile Fibers." North-Holland Publishing, Amsterdam, 1956.

^{1a} W. T. Astbury, "Fundamentals of Fibre Structure." Oxford Univ. Press, New York, 1933.

1. MOLECULAR STRUCTURE

Fibers consist essentially of long chain molecules in which comparatively simple groups of atoms are joined together by a condensation or addition polymerization reaction to form a long chain of atoms joined by primary valency linkages. Rotation about single bonds allows the chain molecule to be a very strong but flexible unit, and this fundamental property is reflected in the macroscopic rheological behavior of a fiber. Of course, the degree to which the individual molecules can bend and coil is restricted by the mutual interaction of active groups along the molecule, and from this point of view the chemical constitution of the different fibers is important. Close packing is hindered by bulky side groups which may even form electrovalent or covalent primary linkages (as in wool), but in most cases the intermolecular forces are in the nature of secondary bonds such as hydrogen bonds or van der Waals' forces.

The fundamental building unit in cellulose fibers is the glucose residue linked as in cellobiose and expressed by the formula



Adjacent glucose residues are identical except that each one is turned through 180 deg. about the chain axis with respect to the next one. The chain molecules in cellulose are extremely long compared with their diame-

² K. H. Meyer, "Natural and Synthetic High Polymers." Interscience, New York, 1942.

³ E. Ott, ed., "Cellulose and Cellulose Derivatives." Interscience, New York, 1943.

⁴ H. R. Mauersberger, "Mathews' Textile Fibres." Wiley, New York, 1947.

⁵ P. H. Hermans, "Physics and Chemistry of Cellulose Fibres." Elsevier, Amsterdam, 1949.

⁶ R. D. Preston, "Molecular Architecture of Plant Cell Walls." Chapman & Hall, London, 1952.

⁷ J. M. Preston, ed., "Fibre Science." Textile Institute, Manchester, 1953.

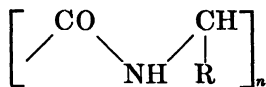
⁸ R. Hill, ed., "Fibres from Synthetic Polymers." Elsevier, Amsterdam, 1953.

⁹ A. R. Urquhart, and F. O. Howitt, ed., "The Structure of Textile Fibres." Textile Institute, Manchester, 1953.

¹⁰ H. J. Woods, "Physics of Fibres." Institute of Physics, London, 1955.

ter; a convenient way of expressing this length is by using the term degree of polymerization (D.P.) which represents in this case the average number of glucose residues in the chain molecule. The D.P. of ordinary viscose rayon is about 350 and that of native cellulose fibers such as cotton and ramie is at least 10,000. The ratio of the length to the diameter of the chain molecules is thus very high and the D.P. of undegraded native cellulose is much higher than that of regenerated cellulose. This has an influence on the relative mechanical properties of native and regenerated cellulose, as will be seen later.

Wool and all mammalian hair fibers are composed mainly of the protein called keratin; silk filaments consist of the protein called fibroin. These proteins are polypeptides which have the basic structure



where the amino-acid residue, R , is different for successive units of structure in the polypeptide chain. As many as 18 different amino acids have been identified from wool keratin and silk fibroin contains about 15 different amino acid residues. Thus the protein chain molecules are far more complex than those of cellulose. A striking feature of the polypeptide chain is its richness in peptide bonds and the CO— and NH— groups may give rise, under suitable conditions, to hydrogen bonds between these groups in neighboring chain molecules. The proteins may therefore be expected to show intensive interchain secondary bonding but the possibilities are considerably restricted by the side chains, consisting of amino-acid residues, which occur so frequently along the main chain and which must separate the main chains sufficiently to allow for their accommodation. The polypeptide chains can interact by means of their side chains to form "salt linkages" (ionic in nature) or covalent linkages via the cystine groups. These more stable covalent linkages confer on keratin a network structure and they are responsible for many of its peculiar elastic properties. The regenerated protein fibers are made from "globular" proteins in which the polypeptide chains are folded in specific ways to give relatively compact molecules. Destruction of this specific configuration by "denaturation" allows the molecules to be drawn into alignment when spun into fibers.

The synthetic fibers have much simpler structures than any of the natural fibers and the ideas involved in explaining their rheological properties are simpler. Polythene, i.e., polymerized ethylene, has the chemical formula $(\text{CH}_2)_n$. It is the simplest type of linear macromolecule and behaves to some extent like frozen rubber. Fibers of polythene may be quite highly crystalline, caused by the lack of side groups on the chain molecules, which allows close approach of the chain molecules over extended

lengths: the molecules are held together side by side by van der Waals' forces.

A number of synthetic fibers are based on vinylchloride ($\text{CH}_2\text{:CHCl}$) polymerized with vinyl acetate ($\text{CH}_3\text{COOCH:CH}_2$) to form Vinyon (90 % vinyl chloride and 10 % vinyl acetate) or with acrylonitrile ($\text{CH}_2\text{:CHCN}$), to form the fibers known as Vinyon N and Dynel (60 % vinyl chloride and 40 % acrylonitrile). This copolymer has a higher softening point than Vinyon which it has superseded. If these fibers are heated, a considerable thermal contraction occurs and they show long-range rubberlike elasticity from the shortened length. The X-ray photograph indicates poor crystallinity. Acrylonitrile itself can be polymerized and formed into fibers (e.g., Orlon, Acrilan, and Creslan) which are poorly crystalline. The long chain molecules interact by virtue of the polar CN groups to form hydrogen bonds.

Another fiber-forming material is vinylidene chloride ($\text{CH}_2\text{:CHCl}_2$) which can be copolymerized with vinyl chloride to form filaments, manufactured under the trade names Saran and Velon; they contain about 85 % vinylidene chloride and 15 % vinyl chloride. Vinyl alcohol ($\text{CH}_2\text{:CH(OH)}$) forms the basis of yet another synthetic fiber in the vinyl family. When polymerized it is highly crystalline and can be produced with a high degree of orientation. Fibers such as Vinyon and Kuralon are based on polyvinylalcohol which has been treated with formaldehyde to form cross linkages between the chain molecules in the noncrystalline regions and so render the fiber insoluble in water.

The best known synthetic fiber is nylon, a polyamide formed by the condensation polymerization of dicarboxylic acids and diamines. The commonest type is nylon 66, made from adipic acid and hexamethylene diamine: it has the formula $[\text{—NH(CH}_2)_6\text{NH—CO(CH}_2)_4\text{CO—}]_n$. The outstanding characteristic of the nylon chain molecule is the occurrence at intervals along it of the peptide linkage —CO—NH— , with the possibility of hydrogen bonding between the CO and NH groups of neighboring molecules. Nylon is spun from the molten polymer and crystallizes on cooling even before it is cold-drawn by some 300 or 400 % to orientate the chain molecules and so strengthen the fiber. In the noncrystalline regions the chain molecules have considerable freedom to kink and fold owing to the relatively large distance between the CO—NH groups in the main chains, which are the only points where there is an appreciable degree of interaction between adjacent chains. The low elastic modulus and considerable elasticity are no doubt dependent on this lack of interaction over an appreciable fraction of the length of the chain molecule.

By introducing bulky side chains at not too frequent intervals along the main chain, thus preventing their close approach and introducing a very

pronounced tendency for the chains to fold, a highly extensible "elastic nylon" can be produced. For example, by replacing the hydrogen atom on every other nitrogen atom in nylon 66 by the group $-(CH_2)_3-CH_3$, fibers with striking long-range reversible elasticity at ordinary temperatures are obtained. This material has a crystalline component with moderate orientation.

Dacron polyester fiber (Terylene in England) is a relatively new synthetic fiber made by polymerizing ethylene glycol and terephthalic acid. The chemical constitution of the chain molecule of polyethylene terephthalate may be written $(-O \cdot CH_2 \cdot CH_2 \cdot O - CO - \text{ - CO -)_n$. The chain repeat distance of 10.75 Å. is only slightly less than that required for a fully extended chain containing one chemical unit to the geometrical repeating unit with successive ester groups in the *trans* configuration to each other. The degree of crystallinity is about 55 to 75% and the length of the crystallites has been estimated to be 60 to 80 Å.

2. CRYSTALLINE AND AMORPHOUS REGIONS

At this stage it is appropriate to consider the structure resulting from the interaction of the long chain molecules.

During the formation of a fiber there is a tendency for the chain molecules to orientate themselves preferentially in the direction of the fiber axis, either as the result of the growth process in natural fibers or of the drawing which takes place during the spinning of regenerated or synthetic fibers. Consider, for example, a material spun into a filamentary form: the molecules will be arranged in a rather haphazard way, being entangled and crimped or folded in some of the many possible configurations made possible by their flexibility. The later stages of the spinning process in which the filaments are stretched tend to align the molecules in the direction of the fiber axis. As they are drawn into parallelism some of the chain molecules will find themselves in positions favorable to strong interaction with neighbors and will produce crystalline regions or smaller bundles of chains if the regularly arranged material is not large enough to be described as crystalline. In other regions the chain molecules will not be so favorably placed and may remain in a partially orientated state. Thus in the fiber there will be a continuous gradation of degrees of orderliness of arrangement, ranging from crystalline areas to patches with only traces of alignment. It is convenient to describe the regions of perfect order as crystalline and those of complete disorder as amorphous: all those regions which do not show perfect order may be called noncrystalline.

From the breadth of the interferences in X-ray photographs of fibers, the dimensions of the crystalline regions or "crystallites" have been esti-

mated. For example, in ramie the cellulose crystallite has been estimated to have a length of at least 600 Å. and a breadth of 50 to 60 Å. Filaments of viscose rayon give smaller values, about 300 Å. in the direction of the fiber axis and about 40 Å. across. It is generally assumed that in fibers the average length of the individual chain molecules is much greater than that of the crystallites so that the concept of a network structure arises. The junctions of the network are crystallites or chain bundles in the noncrystalline regions and the links are chain molecules which may pass through several junction points.

With these ideas of long chain molecules, crystalline regions, and network structure in mind we may next consider the structure of particular fibers in a little more detail.

X-ray examination shows that the alignment of the chain molecules with the fiber axis varies considerably in different fibers, at least in the crystalline regions. Optical methods using polarized light, which give the average orientation of both crystalline and noncrystalline parts of the fiber, show similar ranges of orientation. Flax, ramie, hemp, and jute are highly orientated, cotton shows an intermediate orientation while viscose rayon may have medium or high orientation depending on the amount of stretch applied during its formation.

Silk is perhaps the simplest protein fiber, consisting of fibroin in which nearly half the amino-acid residues are from glycine and one quarter from alanine. It is believed that the crystalline parts consist mainly of these compact amino acids. Other more complex amino acids such as serine and tyrosine occur with moderate frequency and fall in the noncrystalline regions. There is no cystine to form disulfide bridges between the polypeptide chains so that, on the whole, the interaction between the chains is predominately of the weaker type, with hydrogen bonding likely to be important.

Wool and hair fibers consist of keratin, which contains a wide range of amino-acid residues of which none forms more than 16% by weight. Approximately half of the total number of side chains are either basic, acidic, or cystine: side-chain interactions may thus be expected to be far more important in keratin than in fibroin. Keratin is not highly crystalline but such X-ray reflections that occur indicate good crystalline orientation in the direction of the fiber axis. In the unstretched form the X-ray photograph shows a repeat distance along the fiber axis of 5.1 Å. compared with about 7 Å. for the fully extended polypeptide chains in fibroin: the unstretched keratin is said to be in the α -form and it is inferred that the chain molecules are folded in some way. This is significant rheologically, for keratin fibers immersed in water show perfect long-range elasticity of form, e.g., at ordinary temperatures the range of elastic extension is as much as

70%. As extension proceeds, the X-ray pattern corresponding to the α -form becomes progressively weaker and is replaced by a different one, corresponding to the β -form, and similar to that of fibroin. In other words, stretched keratin contains fully extended chain molecules which are produced from the regularly folded α -keratin. This transformation is reversible and the perfect elasticity of keratin appears to be related to this reversible transformation between folded and straightened chains. The nature of the α -fold is still under discussion.¹⁰

There are two points of view with regard to the explanation of the long-range elasticity of keratin. On the one hand, the fact that the crystallites have specifically folded chains suggests that folding of this type may be expected to occur in the noncrystalline regions also. The long-range elasticity of keratin might then be explained in terms of the α - β transformation. On the other hand, it may be argued that the heterogeneity of the degree of order in the packing of the polypeptide chains in the fiber as a whole suggests that the extensibility of the fiber has its origin in the noncrystalline parts and that the elasticity of keratin is of a rubberlike type, governed by entropy considerations.¹¹ The rheological properties of keratin fibers shed some light on this subject and, on balance, appear to favor the first point of view.

3. FINE STRUCTURE

The rheological properties of fibers will depend to some extent on the way in which the fundamental building units of the fiber are assembled: this is especially the case with natural fibers of biological origin such as cotton, flax, and wool. For details reference may be made to the books already mentioned; in what follows, a brief sketch of some of the outstanding structural features of the various fibers will be given.

An essential feature of all native cellulose fibers is the existence of fibrils which range in size from 50 A. diameter (and possibly less) up to the order of a few microns. In highly swollen fibers some of these fibrils become visible under the optical microscope and they can be separated and examined under the electron microscope. A spiral structure is frequently observed which may vary from a left-hand to a right-hand screw texture in successive layers. The angle between the direction of the fibrils in the cell wall and the fiber axis is small in flax, ramie, and hemp fibers (<6 deg) but in cotton the spiral angle near the surface is about 30 deg. and coir fiber has a spiral angle of 45 deg. Cotton fibers have a thin outer primary cell wall with a criss-cross fibrillar structure of about 70 deg. spiral angle, inside of which there is a secondary cell wall, which forms the major part of the fiber, with

¹⁰ A. Elliott, *Textile Research J.* **22**, 783 (1952).

¹¹ K. H. Meyer, A. J. A. van der Wyk, W. Gonon, and C. Haselbach, *Trans. Faraday Soc.* **48**, 669 (1952).

a 30-deg. spiral angle that alternates many times along the length of the fiber from a left-hand to a right-hand spiral. These reversals in the spiral structure are peculiar to cotton and occur about 20 times in a centimeter length. When the fiber first dries out, the tubular wall collapses and the spiral structure causes the fiber to convolute or twist. The average number of convolutions or 180 deg. twists ranges from 40 to 80 per centimeter, depending on the variety and maturity of the cotton, and these convolutions reverse their direction of rotation about the fiber axis at those places where the underlying spiral structure reverses.

The regenerated cellulose fibers are simpler to deal with, for the "cellulose" from which they are made is purified during the processes of manufacture and they have a simpler fine structure. However, many commercially produced viscose rayons do have a skin and a core differing in molecular orientation and density with a fairly sharply defined boundary between them: the orientation usually decreases as the core is approached. When rayon fibers are ground in a ball mill, splitting takes place in the direction of the fiber axis owing to the anisotropic structure but the fibrillae are observed to be not so well formed as with native cellulose fibers.

Wool fibers are made up of several distinct parts. The main body of the fiber is the cortex composed of long spindle-shaped cells; within this is a medulla, or central channel, composed of a network of cells enclosing air spaces. Covering the cortex is the cuticle composed of a layer of scales rather like those of a fish and outside this is a very thin continuous membrane called the epicuticle, which is only visible under the electron microscope. The elastic properties are controlled by the behavior of the cortex: recently this part of the fiber has been found to consist of two different halves called the paracortex and orthocortex, which differ in their cystine content and on that account may be expected to have different mechanical properties, for the behavior of wool keratin has been shown to depend closely on the sulfur linkages between the chain molecules and the number of these linkages is proportional to the cystine content.

Raw silk is a twin filament consisting of two filaments of fibroin embedded in a matrix of silk gum. This silk gum is mainly sericin and is removed by the chemical process of degumming to leave isolated filaments of degummed silk. Since these filaments are spun rapidly from solution by the silk worm and are not the product of a slow growth process, they have a simpler fine structure than wool fibers in much the same way that regenerated cellulose fibers are simpler than native cellulose fibers.

4. MOISTURE ABSORPTION

The amount of water held within a fiber can have a considerable influence on the rheological behavior. The weight of absorbed water expressed as a fraction of the bone-dry weight of the fibers is called the moisture regain: a

TABLE I
MOISTURE REGAIN OF VARIOUS FIBERS AT 25° C.

<i>Fiber</i>	<i>Moisture regain (%) at relative humidity of</i>	
	<i>65%</i>	<i>95%</i>
Cotton	7.0	15.0
Viscose	13.3	27.5
Acetate	6.0	13.8
Wool	14.7	27.7
Silk	10.0	23.8
Nylon	4.2	7.7
Dacron	0.5	0.9
Orlon	2.0	2.5

few examples of the moisture regains of fibers at 65 and 95% relative humidity are given in Table I. It will be seen that wool, silk, and viscose rayon have high regains, cotton, acetate rayon, and nylon show intermediate values whilst Dacron and Orlon have very low regains.

At any given relative humidity, a fiber has a greater capacity for holding water if brought into equilibrium with this humidity from a higher relative humidity than is the case when brought from a lower relative humidity; this fact must be considered when conditioning fibers for rheological tests. The data in Table I refer to fibers which have been conditioned from dryness to the stated relative humidity, i.e., they have been brought along the absorption isotherm as distinct from the desorption isotherm, which would be followed in conditioning them from the wet state.

Since the mechanical properties depend on the moisture regain of the fiber, it is usual to measure these properties in a standard atmosphere which has been defined as $65 \pm 2\%$ r.h. at 20° C.; of course, this is not necessary for some of the synthetic fibers like Polythene, Vinyon, or Saran which have negligible moisture regain at relative humidities normally encountered.

III. Creep and Relaxation

1. INTRODUCTION

This section is concerned with the simpler time-dependent phenomena of creep, or slow deformation under constant stress, and relaxation, or decay of stress at constant deformation.

When a fiber is stretched under constant load, the extension is found to increase rapidly at first and more slowly later: when the load is removed, the fiber contracts, initially at a fast rate, which decreases almost to zero after a sufficiently long time. In some fibers, under the proper conditions, the recovery after stretching proceeds until the initial length is attained

while in others, or the same fibers under different conditions, there remains a residual extension or 'set' even after prolonged times of retraction. Alternatively, if a fiber is rapidly stretched and held stretched, the tension developed decreases rapidly and may reach an equilibrium value: when the fiber is released and allowed to recover freely, the tension on restretching to the same extension as before will exceed the equilibrium value and may equal the tension originally developed on first stretching, showing that a "tension recovery" takes place rather similar to the creep recovery which occurs after a creep test.

Studies of creep in filaments of silk were made as early as 1835 by Weber and a detailed review of early work on the subject of creep in filamentous materials is to be found in a book by Leaderman.¹² Creep tests on fibers have generally been made under constant load rather than under constant stress, because of the greater experimental simplicity. Although the distinction between experiments made under constant load and constant stress is hardly significant from the point of view of theoretical interpretation when the strain is small, this is not generally true for the strains which are commonly encountered with fibers and more satisfactory data for theoretical interpretation are obtained from relaxation tests in which the geometrical form of the fiber remains constant during the experiment.

Stretching a fiber may involve two main processes which may be called bond stretching and chain straightening. The bonds with which we are concerned are not the primary covalent linkages in the chain molecules themselves but rather those linking the molecules together to form a network structure. Before a bond can contribute effectively to the extension of a fiber it must be orientated in the direction of the fiber axis and the shorter "chains of bonds" will orientate first. The breaking of one bond may allow the stress to pass to another one in parallel with it: thus a broken bond may remain in a condition where reformation is possible when the fiber is released. Set will arise if the degree of breakdown of the bond network is sufficiently drastic or if new bonds are formed which are sufficiently stable. If they are not, the residual unbroken bonds in the network will tend to pull the system back toward the unstrained state but this will be resisted by the action of the new bonds. Creep recovery arises from the gradual breakdown of these bonds as they become stressed in resisting contraction. The rate of creep recovery will therefore depend on the degree of bond breakdown, the number of new bonds, and the stability of these with respect to the strength of the unbroken bonds. The breaking and building of bonds involves internal energy changes but these will be almost inextricably mixed up with con-

¹² H. Leaderman, "Elastic and Creep Properties of Filamentous Materials and other High Polymers." Textile Foundation, Washington, 1943.

figurational changes caused by chain straightening and these configuration changes will add an entropy term to the elastic force within the fiber.

2. CREEP AND CREEP RECOVERY

a. Small Stresses

A detailed investigation of the creep and creep recovery of single filaments of viscose rayon, acetate rayon, silk, and nylon under small stresses has been made by Leaderman.¹² The specimens he used were "mechanically conditioned" by allowing the specimen to creep for 24 hr. under load, then removing the load and allowing 24 hr. recovery: in any subsequent 24-hr. test the constant applied load did not exceed the conditioning load. By this technique, the specimens were brought into an elastic state in which recovery of strain was perfect so that the same filament could be used for many experiments.

He attempted to see how far the superposition principle of Boltzmann¹³ could be used to describe the observed creep behavior. This principle states, in effect, that, at any instant, the deformation in a body showing delayed elasticity does not result only from the load acting at that instant but also from the entire previous loading history. For the superposition principle to apply, the magnitude of the delayed component of extension at any time must be proportional to the load and the total extension caused by a complex loading history must be equal to the sum of the extensions produced by the separate loading effects, removal of load being equivalent to the application of a negative load.

Creep tests of 24-hr. duration and 24-hr. creep-recovery tests made by Leaderman show by their coincidence when suitably plotted that this principle is obeyed by viscose rayon, acetate rayon, and silk up to "loads" of 3, 3.5, and 6×10^8 dynes/cm.², respectively. Beyond these loads the first assumption with respect to proportionality of the delayed elastic extension and load breaks down but the second assumption concerning the summation of separate loading effects holds, at least up to twice the loads quoted above. Nylon obeys a modified form of the superposition principle for small strains up to about 2% extension. All the above results are for tests made in the standard atmosphere of $65 \pm 2\%$ r.h. and 20° C.

The validity of the principle may be tested by applying more complex loading procedures. Suppose that a long-duration creep and recovery test is first carried out on a mechanically conditioned specimen. Next a sequence of short-duration tests is made in which the load is applied for 10 min. followed by 10 min. free recovery and this loading cycle is repeated. From the superposition principle, if the extensions at times t , $(10 + t)$, $(20 + t)$,

¹³ L. Boltzmann, *Pogg. Ann. Phys.* 7, 624 (1876).

TABLE II
CONSTANT LOAD OF 3×10^8 DYNES/CM² FOR 20 HR. AT 65% R.H.

Fiber	Total extension, %	Instantaneous extension	Delayed extension
		% of total extension	
Viscose I	0.57	51	49
Viscose II	0.30	71	29
Acetate	0.76	70	30
Silk	0.34	69	31
Nylon	2.16	40	60
Nylon II	1.26	50	50

($30 + t$), etc., are a, b, c, d , etc., then the extensions at these times in a continuous creep test without recovery will be $a, (a + b), (b + c), (c + d)$, etc. Good agreement between calculated and observed extensions was found in experiments made on viscose rayon.

Some typical data showing the relative amounts of instantaneous and delayed extension for mechanically conditioned specimens under a constant "load" of 3×10^8 dynes/cm.⁶ for 20 hr. at 65% r.h. (from Leaderman's curves) are recorded in Table II. Under these conditions, ordinary viscose rayon I has a delayed extension equal to about half the total extension, the same as for nylon II. Stretching viscose rayon I in the swollen state to produce viscose II has the effect of increasing the amount of instantaneous extension to 70% of the total extension. Its creep behavior is then similar to that of silk and acetate rayon. The nylon II sample is less extensible than nylon I and its percentage of instantaneous extension is higher.

b. Larger Stresses

At higher stresses than those which have just been considered, the instantaneous and delayed extensions are no longer proportional to the stress. Typical behavior of an ordinary viscose rayon is shown in Fig. 1, which is based on data by O'Shaughnessy¹⁴ for specimens which had received no mechanical conditioning. To emphasize the nature of the creep curves, the ratio of strain to stress has been plotted against the logarithm of the time for a series of constant loads corresponding to stresses from 2.6 to 13.3×10^8 dynes/cm.².

It will be seen that at low stresses the creep curve is convex to the log time axis: at high stresses it is concave to the log time axis. At intermediate stresses, the creep curve is sigmoid in shape. This is a general description of the creep curves observed with fibers over a time range from 10 to 10^5 sec.

¹⁴ M. T. O'Shaughnessy, *Textile Research J.* **18**, 263 (1948).

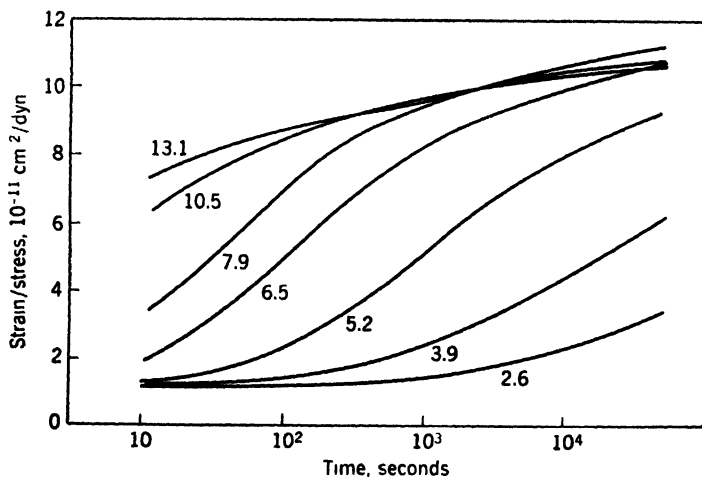


FIG. 1. Creep of viscose rayon at 60% r.h. and 21° C. (O'Shaughnessy.¹⁴) The numbers on the curves give the constant loads in 10^8 dynes/cm.².

The curves suggest that each is part of a common sigmoidal curve which may be called the creep function. At low stresses the relaxation mechanisms responsible for the high rate of creep at intermediate stresses have not been invoked in the experimental time interval, at high stresses the relaxation produced by these mechanisms has already taken place before observations have been started. It appears that increase of stress is equivalent to a shift in the time scale.

Recently the creep curves observed for nylon over a range of stresses have been generalized by Catsiff, Alfrey, and O'Shaughnessy¹⁵ to give a "master creep curve," which represents the data as a single sigmoidal curve by the application to the individual curves of scale factors and shifts along the log time axis. A typical result of this process is shown in Fig. 2. To reconstruct the creep curve at any particular stress one proceeds as follows: First the master curve is translated along the log time axis until its inflexion point falls at the characteristic retardation time for the given stress, next the ordinates of the curve are multiplied by a scale factor, and finally the instantaneous extension for the given stress is added. Thus, to describe the creep behavior of a particular fiber one requires a master creep curve, and plots or tables of characteristic retardation time, scale factor, and instantaneous extension for a range of stresses. Data for the creep and recovery of nylon obtained by Abbott¹⁶ show the general features indicated by the master creep curve.

¹⁵ E. Catsiff, T. Alfrey, and M. T. O'Shaughnessy, *Textile Research J.* **23**, 808 (1953).

¹⁶ N. J. Abbott, *Textile Research J.* **21**, 227 (1951).

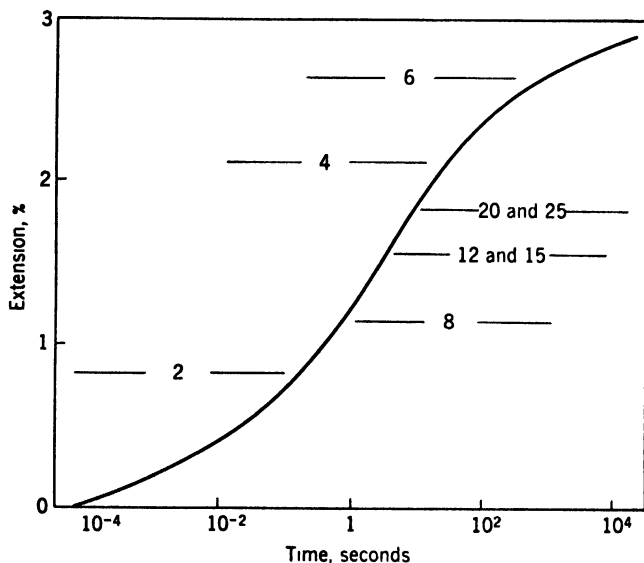


FIG. 2. Master creep curve for nylon at 30% r.h. and 36°C., showing its synthesis by fitting together individual creep curves shifted vertically and laterally and multiplied in ordinate. The numbers refer to constant loads in units of 10^8 dynes/cm.². (Catsiff *et al.*¹⁵)

An attempt to analyze the creep curves of viscose¹⁷ and acetate rayon has been made by Mark and Press.¹⁸ For the particular viscose-rayon creep curve chosen by these authors, the following equation was deduced from the experimental data:

$$e(\%) = 0.6 + 1.9 + 1.0(1 - e^{-t/50}) + 0.9 \log_{10}(t + 1)$$

Dynamic modulus measurements of very short duration gave a value for the instantaneous extension of 0.6%. Between 0.01 and 1 sec. a very slightly retarded elastic extension of 1.9% with retardation time less than 1 sec. was postulated. Beyond $t = 120$ sec. the creep was mainly logarithmic and is represented by the last term of the above equation. The remaining term on the right-hand side represents delayed creep with a retardation time of $\lambda = 50$ sec. This term assumes that the delayed extension follows an exponential law based on the rheological equation $p = Ee + \eta \dot{e}$ and that the retardation time $\lambda = \eta/E$.

The molecular interpretation of the terms in the above equation is that the first term represents the stretching of strong intermolecular bonds. Immediately afterward, the material responds with a fast elastic mechanism,

¹⁷ J. J. Press, *J. Appl. Phys.* **14**, 224 (1943).

¹⁸ H. Mark and J. J. Press, *Rayon Textile Monthly* **24**, 297, 339, 405 (1943).

probably associated with the straightening of kinked chain molecules. Following this comes a considerably retarded elasticity with a retardation time of 50 sec. which represents the displacement of larger units such as clusters of entangled chain molecules. Superimposed on these processes is a logarithmic creep which represents both the molecular mechanisms with longer retardation times and a certain amount of crystallization.

Wegener¹⁹ has represented his data on creep and creep recovery of viscose, cuprammonium, and cellulose acetate rayon over a wide range of stresses at 55 % r.h. and 18° C. by a power law represented by $\log e = A \pm B \log t$ over the time range from 30 to 3000 sec. A formula of this type is obviously applicable to only a limited time range.

The creep of wool fibers under constant stress has been investigated by Speakman,²⁰ who found that up to 150 min. the creep curves could be described by the formula $l = l_0 (1 + \beta t^{1/3})$, where the parameter β indicates the rate of creep. A minimum value of β was observed for a stress of 9×10^8 dynes/cm.²: for Cotswold wool, β was 0.022, 0.008, and 0.013 at constant stresses of 6, 9 and 15×10^8 dynes/cm.², respectively. The above creep formula has been found to hold for soft metal wires when multiplied by a term of the form e^{kt} to allow for the plastic flow which occurs in these metals. Ripa and Speakman²¹ have studied the creep of wool fibers under a load of 7×10^8 dynes/cm.² and found an exponential approach to a limiting extension ($e_{lim.}$) of about 75 %. The rate constant found from their linear plot of $\log (e_{lim.} - e)$ against time varied widely from fiber to fiber of Lincoln wool or of human hair. By separating the fibers into groups according to their creep rates they showed that the rate constants were inversely proportional to the sulfur content of the fibers, which emphasizes the importance of the disulfide cross links in the rheology of keratin fibers. From creep at different temperatures, they deduced a value of 26 kcal./mole for the activation energy, which is of the same order of magnitude as the 20 kcal./mole obtained by the hydrolysis of cystine with dilute hydrochloric acid.

3. RELAXATION

a. Constant Extension

The phenomenon of relaxation is closely related to that of creep and methods of expressing creep behavior might be expected to be satisfactory for describing relaxation of stress. This is perhaps best demonstrated by taking the data obtained by Meredith²² for viscose and acetate rayon at 65 % r.h. and 25° C. for a number of constant extensions and replotting them

¹⁹ W. Wegener, *Zellwolle, Kunstseide, Seide* **46**, 298, 342 (1941).

²⁰ J. B. Speakman, *J. Textile Inst.* **17**, T472 (1926).

²¹ O. Ripa and J. B. Speakman, *Textile Research J.* **21**, 215 (1951).

²² R. Meredith, *J. Textile Inst.* **45**, T438 (1954).

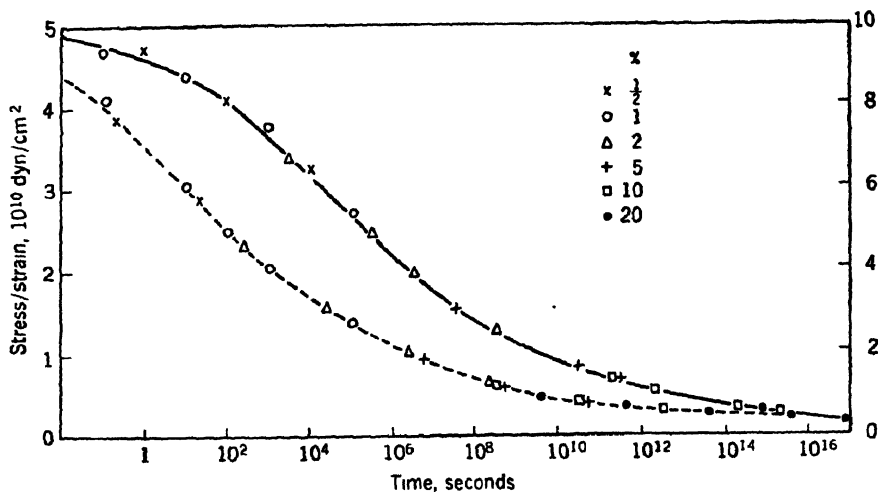


FIG. 3. Composite curves for relaxation of tension at 65% r.h. and 25° C. under constant extensions shown in the key. Continuous curve and left-hand scale refer to acetate rayon; dashed curve and right-hand scale refer to viscose rayon.

as stress divided by strain against the logarithm of the time. When this was done it was observed that the slopes of the curves were the same for different constant extensions at any given value of stress over strain, i.e., the family of curves obtained at different constant extensions appeared to be part of a common curve which shifted to lower values of $\log t$ as the extension was increased. A composite or master relaxation curve was therefore made by translating each individual curve along the log time axis until a fit of the overlapping ends was obtained. The result is shown in Fig. 3 for viscose rayon and cellulose acetate rayon. Sigmoid curves are obtained which are rather similar to the master creep curve of Fig. 2. The composite creep curve gives the correct relation between stress over strain and log time for a constant extension of 1%: to obtain the curves corresponding to higher constant extensions, a relation between extension and the amount of shift ($\Delta \log t$) is required. For acetate rayon the relation was found to be approximately $\Delta \log_{10} t \simeq 12 \log_{10} e$ and for viscose rayon

$$\Delta \log_{10} t \simeq 26 \sqrt[3]{\log_{10} (1 + e)},$$

where e is expressed as a percentage and t is in seconds. It is clear from Fig. 3 that at low and high extensions the relative rate of decay of stress is small, whereas at intermediate extensions of 5 to 10% the rate of stress decay is appreciably higher.

Wegener²³ has made a detailed study of the decay of tension with time

²³ W. Wegener, *Melliand Textilber.* **30**, 90, 138, 184, 229, 282, 388, 443, 501, 558 (1949).

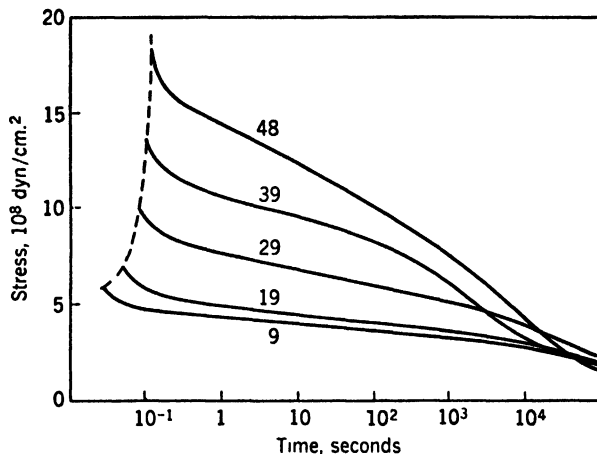


FIG. 4. Relaxation of wool in water at 25° C. The numbers on the curves give extensions per cent. (Wood.²⁴)

for viscose rayon, cuprammonium rayon, and cellulose acetate rayon when extended by various amounts at 65% r.h. and 20° C. The tension decay was observed over a rather restricted time range from 1 sec. to 5 min. but his results agree with those already given in Fig. 3 as far as the shape of the relaxation curve and the rate of decay of stress are concerned. He represented his data by the formula $p/p_0 = [(t + a)/a]^{-n}$ where p_0 is the stress at time $t = 0$ and a and n are constants. This formula reduces to the form $\log e = A + B \log p$ when $t \gg a$, as is the case for $t > 10$ sec. A power law of this latter type can also be used to describe the tension decay in cotton and flax yarns²² over a time range of $1/10$ to 10^5 sec.

The relaxation behavior of wool and hair fibers is rather more complicated than that of the cellulosic fibers in that there is a possibility, under suitable conditions, of the breakdown of the disulfide cross linkages between adjacent chain molecules. The relaxation of tension in wool fibers^{23a, 24} extended by different amounts in water at 25° C. is shown in Fig. 4. There is a rapid initial decay of stress within the first second, followed by a slower decay, and later by a further slow decay which accounts for most of the tension decay at the higher extensions. The influence of pH throws some light on this slow relaxation process.²⁵ In acid the slow relaxation is inhibited or deferred whereas in alkali it is hastened. The bonds whose breakdown leads to the slow relaxation are thus stable at low pH and unstable at high pH, which is consistent with the idea that these bonds may be

^{23a} B. J. Rigby, *Australian J. Sci. Research* **A8**, 176 (1955).

²⁴ G. C. Wood, *J. Textile Inst.* **45**, T462 (1954).

²⁵ J. B. Speakman, and S. Y. Shah, *J. Soc. Dyers Colourists* **57**, 108 (1941).

disulfide linkages between the polypeptide chains, their hydrolysis being catalyzed by hydroxyl ions. Some further evidence favoring this hypothesis is provided by the experiments of Reese and Eyring²⁶ who studied the influence of reducing agents on this slow relaxation.

Lasater, Nimer, and Eyring²⁷ are using the change in the rate of relaxation of wet cotton fibers to study the reaction of cotton to acids and alkalis.

b. Constant Twist

Some measurements of the decay of torque in twisted bundles of fibers and yarns made from cotton were made by Peirce²⁸ who found that the results could be described empirically over a time range from several seconds to a day by the equation

$$T = c + a \exp. (-\beta t^{1/3})$$

where T is the torque, c is the elastic couple which persists for the duration of the experiment and a is a couple which decays with time at a rate controlled by β . The same law was found to hold for many materials, e.g., silk, wool, tin foil, aluminium foil, and glass. Peirce²⁹ also expressed this torsional relaxation in terms of a spectrum of relaxation times which he translated into activation energies and with which he attempted to explain the values so found in physical terms (see Section VI-3).

The relaxation of torque in a twisted nylon monofilament was found by Hammerle and Montgomery³⁰ to be approximately linear with log time from 20 to 20,000 sec. and this was interpreted in terms of a distribution of relaxation times such that the contribution to the torque from a mechanism with a given relaxation time is inversely proportional to the magnitude of the relaxation time (see Section VI-3).

4. THE INFLUENCE OF HUMIDITY AND TEMPERATURE

One would expect the rates of creep and of relaxation to increase with increasing humidity or temperature, and this is found to be the case.

a. Creep

Steinberger³¹ made a series of measurements on the creep of single filaments of cellulose acetate rayon and cuprammonium rayon covering a range of relative humidities from 0 to 100% at a constant load equivalent to a nominal stress of about 6.5×10^8 dynes/cm.² The effect of increasing the relative humidity in steps of about 10% can be seen for cellulose acetate

²⁶ C. E. Reese and H. Eyring, *Textile Research J.* **20**, 743 (1950).

²⁷ J. A. Lasater, E. L. Nimer, and H. Eyring, *Textile Research J.* **23**, 237, 481 (1953).

²⁸ F. T. Peirce, *J. Textile Inst.* **14**, T390 (1923).

²⁹ F. T. Peirce, in "Essays in Rheology," p. 47. Pitman, London, 1946.

³⁰ W. G. Hammerle and D. J. Montgomery, *Textile Research J.* **23**, 595 (1953).

³¹ R. L. Steinberger, *Textile Research* **6**, 191, 267 (1936).

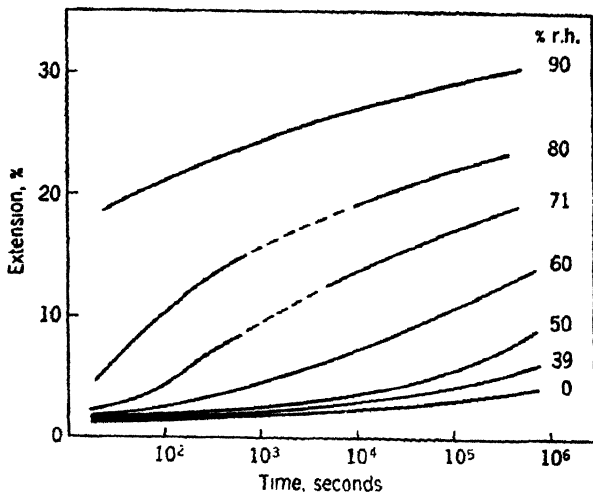


Fig. 5. Influence of humidity on the creep of acetate rayon at 6.5×10^8 dynes/cm.² and 28° C. (Steinberger.²¹)

rayon from Fig. 5. From 0 to 40 % r.h. the amount of creep is small, but above this relative humidity it rises rapidly. It will be noticed that each curve appears to be part of a common sigmoidal curve that is shifted along the log time axis to shorter times as the relative humidity is raised, thus resembling the family of creep curves obtained for viscose rayon at constant relative humidity and various loads. Nylon¹² under a constant "load" of 1.8×10^8 dynes/cm.² gives a similar family of creep curves for relative humidities of 0, 62, and 100 % r.h. The creep of viscose and acetate rayon under constant loads from 1.2 to 9.4×10^8 dynes/cm.² at 30 to 65 % r.h. has also been studied by Pinte and Henno.²² By wetting and reconditioning fibers to remove internal strain set up by creep, it is possible to show how much of the strain produced by creep is elastic and how much represents permanent change in the fiber. Press¹⁷ found that up to 12% extension, the recovery of ordinary viscose rayon could be divided roughly into three ranges. Extensions up to $\frac{3}{4}$ % are retarded and completely elastic, representing the maximum movement of molecular segments before weaker secondary bonds in the noncrystalline regions begin to break. From $\frac{3}{4}$ to 4%, extension is not completely recoverable until the sample is swollen in water: swelling reduces the steric hindrance and allows the weakened restoring forces to bring chain segments back to their original state of order. Above 4% of the extensions are not completely recoverable because of molecular segments having been moved to new equilibrium positions.

²² C. Pinte and M. Henno, *Bull. inst. textile France* **6**, 35 (1948).

The effect of temperature on the amount of creep of dry viscose rayon may be quite large. Thus, although the general form of the creep curve remained unchanged, Smith and Eisenschitz³³ found that the amount of creep at any time was seven times as great at 114° C. compared with that at 20° C.: lowering the temperature to -180° C. reduced the amount of creep to one-sixth of that at 20° C. If all the relaxation times of the mechanisms responsible for creep are similarly affected by a change of temperature, the shape of the creep curve should be unaltered for moderate temperature changes, i.e., a change of temperature should merely displace the creep curves on the logarithmic time plot along the time axis. This kind of effect was found for cellulose acetate rayon and nylon by Leaderman.¹² Under a stress of 3.7×10^8 dynes/cm.² in the temperature range from 51 to 75° C., a decrease in temperature of 10° C. corresponded to a multiplication of the time scale by nine for dry cellulose acetate rayon: for nylon, a decrease in temperature of 10° C. corresponded to a multiplication of the time scale by six. The rate of creep of wool has been shown by Speakman²⁰ to increase with increasing temperature.

Keratin fibers show perfect elasticity of form when stretched quickly by 30% or less in water at room temperature. If the time under strain, or the temperature or the strain is increased, the recovery is incomplete and the material acquires a "set." To be able to retain a set in fibers has important technological advantages and the conditions required to produce a set have been much studied.³⁴ Two possible effects in the bond network can lead to set, namely, irreversible bond breakdown and bond rebuilding. The set may be recovered if the conditions under which it was produced are altered and it is necessary to distinguish between "cohesive" set (produced by dehydration with the formation of hydrogen bonds which are easily broken when the fiber is placed in water), "temporary" set (which requires hot water or steam for its removal and is associated with the formation of more stable bonds than the hydrogen bond), and "permanent" set (which resists the action of prolonged steaming). Although keratin fibers can be permanently set by relaxation at high temperatures, this can only occur in the presence of water since strained fibers heated at 100° C. in dry air do not acquire even temporary set. Steam is quite effective but aqueous solutions which are alkaline or which contain a setting agent such as sodium bisulfite are more effective. When treated fibers are placed in boiling water, for example, there is a slow creep recovery and the amount of truly permanent set is only a fraction of the setting extension. It is believed that the disulfide bonds play a primary part in the setting of keratin. For example, the basis

³³ H. de Witt Smith and R. Eisenschitz, *J. Textile Inst.* **22**, T170 (1931).

³⁴ L. Peters and H. J. Woods, in "Mechanical Properties of Textile Fibres" (R. Meredith, ed.), Chapter 11, North-Holland Publishing, Amsterdam, 1956.

of cold permanent-waving systems is the reduction of the disulfide bond followed by its reoxidation in the strained state.

Before leaving this subject of set, the phenomenon of supercontraction in keratin fibers should be mentioned. Steaming stretched fibers for 2 min. at high tensions is followed by a contraction in steam or boiling water which, after a long time, reduces the length of the fiber to as much as 30 % less than its initial unstrained length. This treatment hydrolyzes some of the disulfide bonds but does not allow sufficient time for appreciable bond rebuilding to take place.

b. Relaxation

The decay of tension in viscose rayon over a period of 5 min. has been studied by Wegener and Luyken³⁶ at relative humidities of 45, 65, 85, and 100 % r.h. with constant extensions from 2 to 18 % reached at a constant rate of extension of 0.66 % per sec. The curves are of the form given by $p/p_0 = [(t + a)/a]^{-n}$, where a and n are disposable constants. The rate of relaxation is higher at 65 to 85 % r.h. than it is at 45 and 100 % r.h. It is possible that the apparently low rate of relaxation at 100 % r.h. is a result of the relatively slow extension up to the desired constant extension which allows the mechanisms with short relaxation times to relax while the specimen is being extended.

Speakman³⁶ measured the decay of tension in wool fibers stretched about 30 % at 25, 50, 75, and 100 % r.h. The decay of stress remained linear with log time up to 75 % r.h. but the slope of the relaxation curve increased at the longer times at 100 % r.h., giving a curve of the same shape as that for 30 % extension shown in Fig. 4. It appears then that the relaxation of disulfide bonds is inhibited at relative humidities of 75 % r.h. and less.

As the temperature is increased,²⁴ the relaxation curve of wet wool changes in shape and from 65 to 95° C. it becomes convex to the log time axis over the whole of its observed course (from 30 sec. to 100 min.): the rate of relaxation is higher than at room temperature and is characteristic of a single rate process: this is probably so because of the first rapid relaxation taking place before observations could be made.

At room temperature the relaxation curve of nylon at 15 % extension shows an almost linear relation between stress and log time at all humidities. However, the relaxation curve changes considerably with increase in temperature³⁷ as shown in Fig. 6, which refers to nylon in water. The shape of the curves for temperatures greater than 53° C. is rather similar to that for wool²⁴ in water or in alkali at room temperature.

³⁶ W. Wegener and E. Luyken, *Melliand Textilber.* **33**, 37 (1952).

³⁶ J. B. Speakman, *Proc. Roy. Soc.* **B103**, 377 (1928).

³⁷ J. B. Speakman and A. K. Saville, *J. Textile Inst.* **37**, P271 (1946).

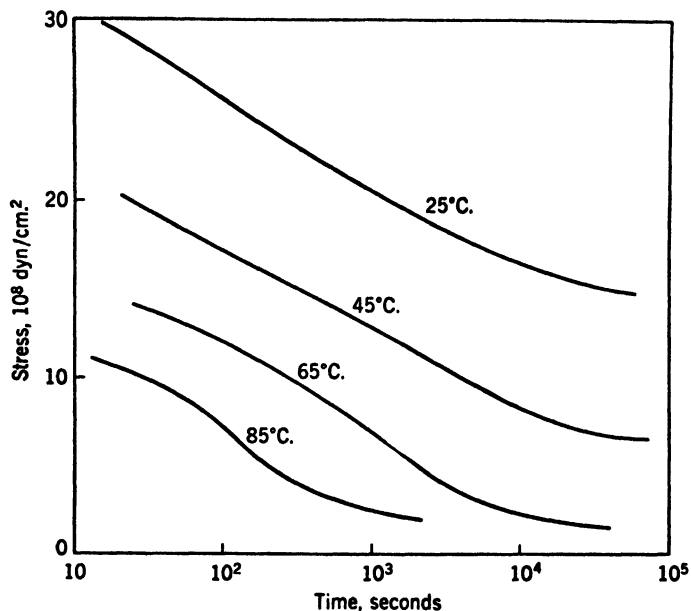


FIG. 6. Influence of temperature on the relaxation of nylon in water at 15% extension. (Speakman and Saville.⁵⁷)

IV. Stress-strain Relations

1. LOAD-EXTENSION CURVES UNDER STANDARD CONDITIONS

The stress-strain curve of a fiber is a good illustration of the resistance to stretching or twisting; it shows graphically the influence of humidity and temperature on the elastic properties and enables us to assess the effect of physical and chemical treatments. Since the stress corresponding to a given strain depends quite appreciably on the time factor, it is necessary to control either the rate of extension or the rate of loading. To simplify quantitative theoretical interpretation, it is desirable to use a constant rate of extension but for practical purposes a constant rate of loading may be easier to achieve and equally satisfactory. The load-extension curves obtained in a standard atmosphere of 65 % r.h. and 20° C. will be considered first, and later the influence of the rate of extension, humidity, and temperature will be considered.

Typical stress-strain curves for various cellulose fibers are shown in Fig. 7. The high Young's modulus and high strength of flax is characteristic of the bast fibers in general, all of which have a high degree of crystallinity and a highly orientated molecular structure. The two stress-strain curves for cotton illustrate two points: firstly, that different varieties of cotton have curves of typical shape but different elastic moduli and, secondly, that the

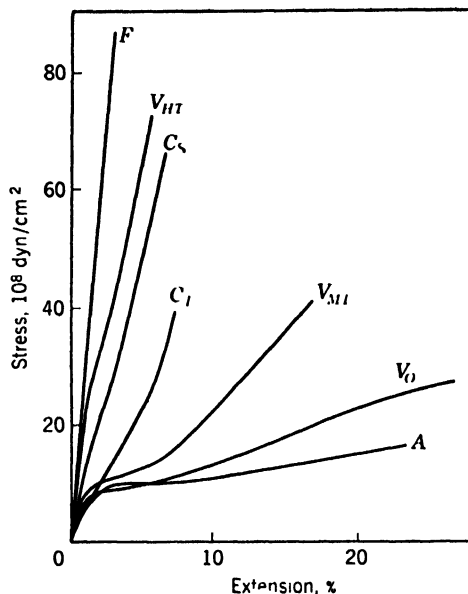


FIG. 7. Stress-strain curves of cellulose fibers at 65% r.h. and 20° C. Key: F = flax; C_s = Sea Island cotton; C_T = Texas cotton; A = acetate rayon; V_{HT} = high-tenacity viscose rayon; V_{MT} = medium-tenacity viscose rayon; V_O = ordinary viscose rayon.

extensibility of cotton is appreciably greater than that of the bast fibers, because of the spiralling of the fibrils about the fiber axis. Ordinary viscose rayon has an initial Young's modulus similar to that of cotton but the fiber yields at an extension of about 2% and beyond this point it shows a much greater extension per unit increase in stress and reaches a higher extension at rupture than any of the natural cellulose fibers. The three curves for viscose rayon illustrate a general feature of man-made fibers, namely, that increasing the molecular orientation by stretching the fibers during manufacture increases the modulus of elasticity and the strength, and lowers the breaking extension. This general principle is followed by synthetic fibers such as nylon, Dacron, Orlon,³⁸ etc. The stress-strain curves for these materials shown in Fig. 8 correspond to the 'regular' types in current production for textile purposes; higher resistance to extension with higher strength and correspondingly lower breaking extension can easily be obtained for special applications such as use in tire cords. One striking feature of nylon is its low initial modulus compared with Dacron and Orlon (continuous filament). The wool fiber has a characteristic stress-strain curve consisting

³⁸ G. H. Fremon, in "Fibres from Synthetic Polymers" (R. Hill, ed.), p. 461. Elsevier, Amsterdam, 1953.

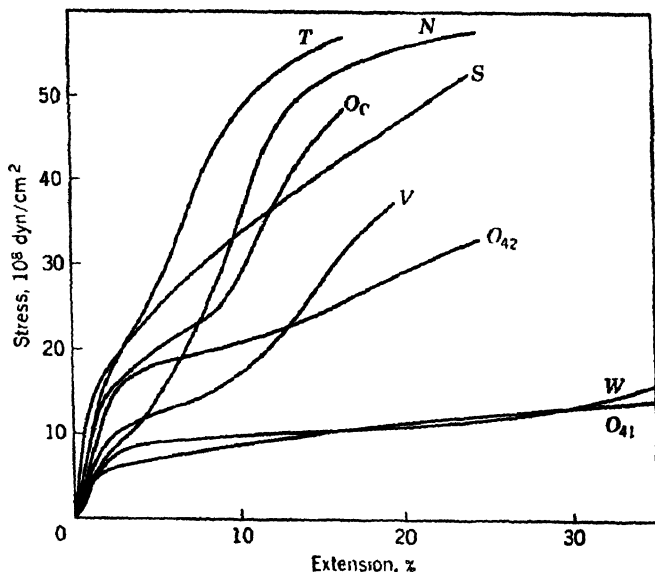


FIG. 8 Stress-strain curves of protein and synthetic fibers at 65% r.h. and 20° C. Key: *T* = Terylene; *N* = nylon 66; *S* = silk; *W* = wool; *O_c* = Orlon (continuous filament); *O₄₁*, *O₄₂* = Orlon (staple fiber); *V* = Vinyon N.

of three regions: up to 2% extension the resistance to extension is fairly high and is caused by straining the bond network; next the hydrogen bonds yield and the polypeptide chains in the noncrystalline regions start to unfold. At extensions of 20 to 30% the resistance to extension increases and at this stage the transformation of the crystalline phase from the α - to the β -form begins, as shown by X-rays. Silk has a much higher initial modulus than wool, as may be expected since the polypeptide chain molecules are already in the fully extended β -form in the unstressed state of the fiber. For further information, reference can be made to Meredith,³⁹ Hermans,⁵ Speakman,⁴⁰ Susich and Backer,⁴¹ Farrow^{41a}, Lucas *et al.*^{41b}

The manner in which the torque in a filament develops as twist is inserted has been studied by Morton and Permanyer,⁴² using viscose rayon, acetate rayon, and nylon. The shapes of the torque-twist curves are similar to the corresponding tensile load-extension curves. There is an initial linear part up to twists of about 3 turns per cm., followed by a yielding of the fiber so

³⁹ R. Meredith, *J. Textile Inst.* **36**, T107 (1945).

⁴⁰ J. B. Speakman, *J. Textile Inst.* **18**, T431 (1927).

⁴¹ G. Susich and S. Backer, *Textile Research J.* **21**, 482 (1951).

^{41a} B. Farrow, *J. Textile Inst.* **47**, T58 (1956).

^{41b} F. Lucas, J. T. B. Shaw, and S. G. Smith, *J. Textile Inst.* **46**, T440 (1955).

⁴² W. E. Morton and F. Permanyer, *J. Textile Inst.* **40**, T371 (1949).

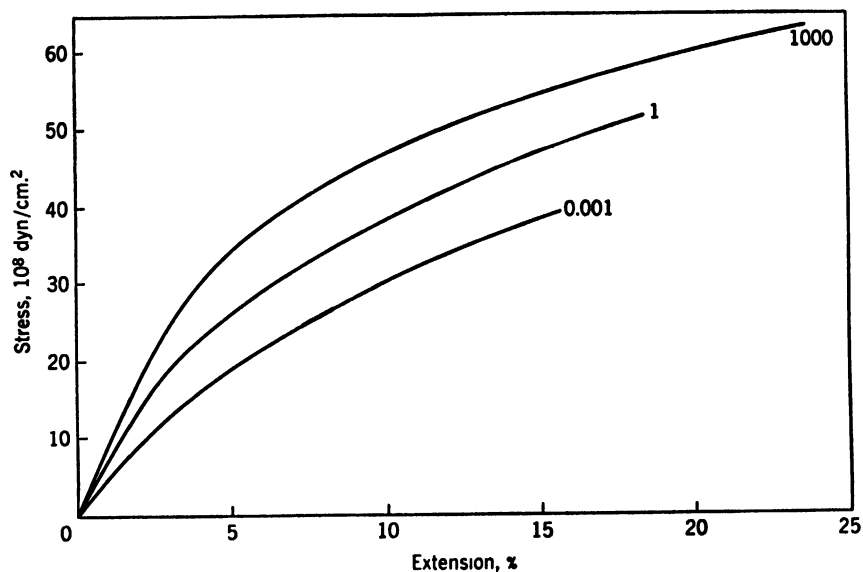


FIG. 9. Effect of rate of extension on the stress-strain curve of silk at 65% r.h. and 20° C. The numbers give the rates of extension in per cent per second. (Meredith.⁴³)

that the rate of increase of torque per unit increase in twist decreases, and finally the curves bend toward the stress axis as rupture is approached.

a. Effect of Rate of Extension

The higher the rate of extension, the greater is the stress developed for a given strain. The magnitude of the effect is illustrated by the curves for silk shown in Fig. 9, where the lowest curve corresponds to a time to rupture of about 3 hr. and the highest curve to a time to rupture of about $\frac{1}{50}$ sec. Similar results are obtained for viscose rayon, acetate rayon, nylon,⁴³ and wool.⁴⁰ In all cases, the initial Young's modulus and the stress corresponding to a given strain increase approximately linearly with the logarithm of the rate of extension. Schiefer *et al.*^{43a} have succeeded in determining the load-extension curve of nylon with an initial rate of extension as high as 30 meters per sec. (attaining 12% extension in 3 milliseconds).

b. Influence of Humidity and Temperature

The stress-strain curves of most fibers are considerably modified by changes in the relative humidity and temperature of the surrounding air, the exceptions being those synthetic fibers such as Dacron, Orlon, Saran, Vinyon N, etc., which have very low or negligible moisture regains and are consequently unaffected by changes in relative humidity. Data for cotton

⁴³ R. Meredith, *J. Textile Inst.* **45**, T30 (1954).

^{43a} W. K. Stone, H. F. Schiefer, and G. Fox *Textile Research J.* **25**, 520 (1955).

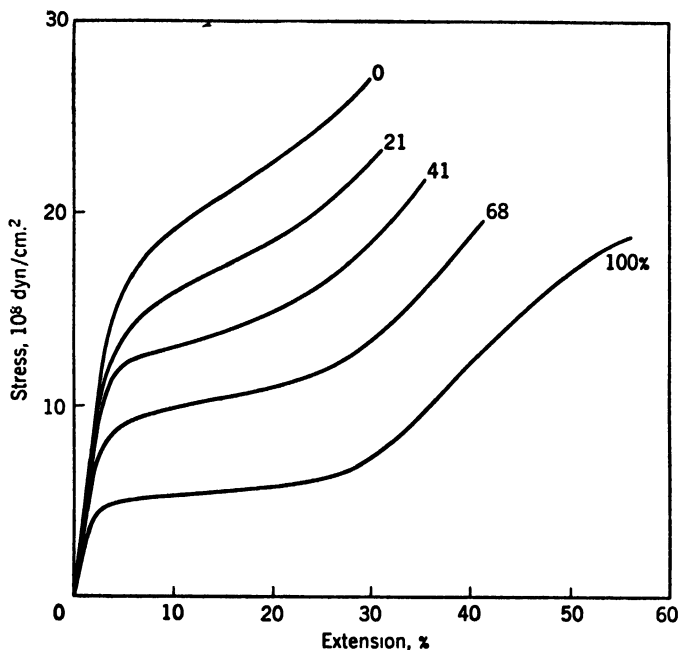


FIG. 10. Effect of humidity on the stress-strain curve of wool at 25° C. The numbers on the curves give relative humidities. (Speakman.⁴⁰)

and rayons are given by Brown, Mann and Peirce,⁴⁴ Hindman and Fox,⁴⁵ Andersen,⁴⁶ for wool by Speakman,⁴⁰ for silk by Denham and Lonsdale,⁴⁷ and for nylon by Speakman and Saville.³⁷ In general, increase of humidity reduces the resistance to extension by reducing the cohesive forces between the chain molecules. An example showing the effect of humidity on the stress-strain curve of wool at 25° C. is given in Fig. 10. Wool, cotton, acetate rayon, silk, and nylon require somewhat less than half the force to extend the wet fiber by a given amount compared with the dry fiber; this contrasts sharply with the behavior of viscose rayon and casein fiber which, in the wet state, require only one-twentieth of the force to extend the fiber by 2% compared with the bone-dry material. Regenerated cellulose fibers show no inflexion in their stress-strain curves in the dry state, then a definite yield region appears as the humidity is increased, occurring at lower and lower stresses until in the wet state it has almost disappeared. To a first approximation, the stress-strain curve of ordinary viscose rayon when wet

⁴⁴ K. C. Brown, J. C. Mann, and F. T. Peirce, *J. Textile Inst.* **21**, T186 (1930).

⁴⁵ H. Hindman and K. R. Fox, *Rayon Textile Monthly* **24**, 235 (1943).

⁴⁶ F. Andersen, *Trans. Danish Acad. Tech. Sci.*, Part 3, (1950).

⁴⁷ W. S. Denham and T. Lonsdale, *Trans. Faraday Soc.* **29**, 305 (1933).

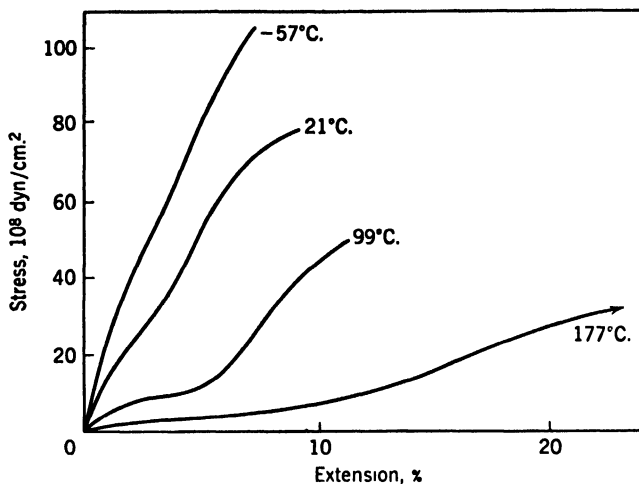


FIG. 11. Effect of temperature on the stress-strain curve of Dacron. (Coplan.⁴⁹)

is a straight line. Rose and Griffiths⁴⁸ have shown that the logarithm of the slope of this line increases linearly with the birefringence of the fiber.

The tensile behavior of cotton, regenerated cellulose rayon, silk, nylon, Dacron, Orlon, and Vinyon over a wide range of temperature (-57 to $177^{\circ}\text{C}.$) has been investigated by Coplan.⁴⁹ A typical example of the behavior of a synthetic fiber is shown in Fig. 11. All extensions are given as the elongation of the fiber expressed as a percentage of the original length at $21^{\circ}\text{C}.$ Thus, the extension will include removal of shrinkage which occurs at the higher temperatures. Since Dacron is relatively inert to moisture, the four curves may be taken as showing the effect of temperature alone, even though the fiber was in a saturated atmosphere at $-57^{\circ}\text{C}.$ and in a dry atmosphere at 99 to $177^{\circ}\text{C}.$ At the lowest temperature the yield stress is high and prerupture flow is not apparent. At room temperature the initial Young's modulus and yield stress have been almost halved and prerupture flow is present. A further increase of $78^{\circ}\text{C}.$ produces a further reduction in initial modulus and a marked increase in extension after the initial linear part of the stress-strain curve. At $177^{\circ}\text{C}.$ there is only a relatively small resistance to extension up to 10% extension but thereafter the fiber stiffens until at 20% extension the structure begins to break down irreversibly and the fiber breaks at about 30% extension. At this highest temperature, Dacron shrinks by about 19% of its length at room temperature so that a large part of its breaking extension consists of the extension required to restore the fiber to its original length at room temperature, leaving a net

⁴⁸ L. Rose and J. D. Griffiths, *J. Textile Inst.* **39**, P265 (1948).

⁴⁹ M. J. Coplan, *WADC Tech. Rept. No. 53-21*. (1953)

TABLE III
EFFECT OF TEMPERATURE ON THE INITIAL YOUNG'S MODULUS

Fiber	Initial Young's Modulus (10^{10} dynes/cm. ²) at temperatures (°C.) of			
	-57	21	99	177
Dacron	20	14	3.7	0.8
Orlon	14	7.5	0.8	0.4
Nylon dry	—	8.0	2.5	1.2
Nylon wet	11	1.8	0.9	—
Tenasco dry	—	16.5	11.9	5.3
Tenasco wet	17	1.0	—	—
Wool wet	—	2.0	1.0	—

extension beyond this length of 11 %, which is not much greater than the 9 % extension at room temperature. Orlon and nylon⁵⁰ are affected by temperature in a similar manner to Dacron.

Table III shows that the initial modulus decreases considerably with increase in temperature. The influence of temperature on the tensile behavior of hydrophilic fibers like Tenasco, cotton, silk, and wool is often masked at ordinary relative humidities by the effect of dehydration caused by the lowering of relative humidity with increased temperature. Investigation of the effect of temperature on fibers in water avoids this complication. For nylon³⁷ and wool⁴⁰ in water the effect of temperature increase is quite similar to the effect of increasing the relative humidity at room temperature.

2. RECOVERY FROM STRAIN

Elasticity, or the ability of a fiber to recover its size and shape after deformation, is a highly desirable property. The recovery behavior can be assessed by carrying out repeated loading and unloading cycles at constant rate of loading or extension. One difficulty is that the recovery of a fiber that has been strained takes a considerable time so that to obtain the necessary information in a reasonable time an arbitrary limit has to be set to the time allowed for recovery. Various loading or extension cycles have been used by different authors^{41, 41a, 51, 52, 52a} but in spite of this the values for strain recovery, defined as the ratio of the recovered extension to the total imposed extension, are remarkably consistent in ranking the various fibers.⁵³ The

⁵⁰ E. R. Kaswell, *Am. Dyestuff Repr.* **38**, P127 (1949).

⁵¹ R. Meredith, *J. Textile Inst.* **36**, T147 (1945).

⁵² G. Susich, *Textile Research J.* **23**, 545 (1953).

^{52a} G. Susich and W. Zagieboylo, *Textile Research J.* **23**, 405 (1953).

⁵³ E. R. Kaswell, "Textile Fibres, Yarns and Fabrics," Chapter 2. Reinhold, New York, 1953.

work recovery defined as the ratio of the amount of work recovered to the total work imposed on the fiber is perhaps a better over-all measure of recovery and this quantity has been used by Beste and Hoffman⁵⁴ in their studies on fiber resilience.

As defined above, the strain recovery gives the ratio of the combined immediate and delayed elastic components to the total strain (including any permanent set). Susich and Backer⁴¹ have separated the immediate and delayed elastic components by taking the elastic extension to be equal to the difference between the extension reached in any given cyclic extension test and the point on the extension axis where a line drawn tangential to the initial part of the unloading curve cuts the extension axis. Their results agree quite well with those of Hamburger,⁵⁵ who obtained the elastic component of strain by measuring the dynamic modulus by a pulse propagation technique, calculating the elastic strain as the integral of $(1/E) dp$, where E is the dynamic modulus and p the stress. With respect to both strain recovery and work recovery nylon, silk and wool are distinctly superior to any of the cellulosic fibers such as cotton, viscose rayon, or cellulose acetate.

Wool fibers show perfect elasticity of form when extended in water at room temperature and this fact has been used by Speakman⁵⁶ to assess changes which take place on treatment with chemical reagents. Such treatments are of special interest in the case of keratin, for they help to elucidate the part played by the different types of bond linking the polypeptide chains. The best index of modification appears to be the difference in the amount of work required to extend a fiber by 30 % in water at room temperature, before and after treatment.

Brown^{56a} has studied the effect of temperature on the recovery from 1 % extension of thermoplastic synthetic fibers and found that the strain recovery shows a minimum at their second-order transition temperatures. The higher the noncrystalline phase content of the polymer, the greater is the magnitude of the effect. The fact that the recovery of Dacron remains at relatively low values for a relatively long temperature interval above its second-order transition temperature is interpreted to mean that the distribution of relaxation times is broader in Dacron than in nylon, for example.

a. Resilience

A resilient fiber⁵⁷ is such that an irregular bunch of fibers (i) offers moderate resistance to compression and (ii) springs back vigorously on release,

⁵⁴ L. F. Beste and R. M. Hoffman, *Textile Research J.* **20**, 441 (1950).

⁵⁵ W. J. Hamburger, *Textile Research J.* **18**, 705 (1948).

⁵⁶ J. B. Speakman, *J. Textile Inst.* **38**, T102 (1947).

^{56a} A. Brown, *Textile Research J.* **25**, 891 (1955).

⁵⁷ H. Mark, *Textile Research J.* **16**, 361 (1946).

even after being in compression for a considerable time. A distinction should be made between resilience and resiliency. Resiliency refers to a property of a substance and resilience to the behavior of an entity, such as a whole fiber, or a mass of fibers. Thus, between a solid block and a fibrous mass of glass there is a difference in resilience but not in resiliency. Resiliency has two aspects⁵⁸—type and extent. The type of resiliency can be separated into two factors, one the modulus of elasticity and the other the change in modulus with extension and time. The extent of resiliency or the ability of a body to recovery from strain may be measured by either the work recovery or the strain recovery, which depend on the time allowed for recovery from strain.

To describe the type of resiliency the modulus is preferably the dynamic modulus (Section V) and the time effect may be assessed by the slope of the strain recovery curve when a fiber has been subjected to a given stretch or load. In practice, it is convenient to assess resiliency from a single experiment,⁵⁴ for example, from a stress-strain curve at constant rate of extension. The modulus may be taken as the slope of the linear part of the curve and the change in modulus with extension and time as the compliance ratio calculated as $(10/p_{10} - 5/p_5)/5$ where p_x is the stress at $x\%$ extension. Measurements of this kind show that the resiliency of protein fibers and nylon is superior to that of cellulose fibers and this superiority increases with increase in relative humidity. These results are supported by resilience measurements^{59, 59a} on a randomly arranged mass of fibers.

b. Crease Resistance

“Crease resistance” is the property of a fiber that enables it to recover from folding deformations and is closely related to resiliency. The speed and completeness of recovery are a measure of this property. When a fiber is folded sharply the part of the fiber that is on the outside of the bend is stretched while the part on the inside of the bend is compressed. It would appear that good recovery from creasing depends essentially on the ability to recover from fairly large deformations. Tendency to creasing rises with increasing crystallinity and with increasing degree of orientation: it increases in the series wool, silk, cellulose acetate rayon, viscose rayon, cotton, and bast fibers.

The chain molecules in wool normally exist in a folded form which can unfold when the fiber is stretched, without breaking primary cross linkages between them so that complete recovery from larger strains is possible. By contrast, the molecules of cellulose are rigid and relatively inextensible so

⁵⁸ R. M. Hoffman, *Textile Research J.* **18**, 141 (1948).

⁵⁹ W. H. Rees, *J. Textile Inst.* **39**, T131 (1948).

^{59a} H. J. Kolb, H. E. Stanley, W. F. Busse, and F. W. Billmeyer, *Textile Research J.* **23**, 84 (1953).

that they slip over each other when the strain is large, and permanent strain results. The freedom of the chain molecules to move elastically depends in part on their closeness of packing in the fiber. In wool and silk close packing is prevented by the presence of bulky side groups but in cellulose fibers the chain molecules readily crystallize. Improved mobility is obtained by inserting bulky acetyl groups which resist molecular close packing.⁶⁰

By introducing a synthetic resin within cellulose fibers their resistance to creasing can be greatly improved. It appears essential that the resin used should be capable of forming a three-dimensional network within the fiber.⁶¹

3. FLEXURAL RIGIDITY

When a fiber is bent the elastic modulus called into play is the same Young's modulus that is involved in stretching, provided the fiber is uniform in its properties across a diameter. However, this is not so with most fibers because the structure of the outer layers differs from that of the inner layers, and therefore the bending modulus (E_b) may differ from Young's modulus. Defining the flexural rigidity (Y) as the couple required to produce unit curvature, we have $Y = Ak^2E_b$ where k is the radius of gyration of the cross section, A , about a line through the neutral axis and perpendicular to the plane of bending.

The flexural rigidity of jute⁶² fibers has been determined by measuring the force required to bend a fringe of fibers arranged as a cantilever, giving a bending modulus at 76 % r.h. of about 11×10^{10} dynes/cm.² Khayatt and Chamberlain⁶³ also used a cantilever method with wool fibers and found a value of E_b lower than the Young's modulus for the linear part of the stress-strain, which is not surprising in view of the pronounced low modulus toe in the stress-strain curve of wool (Fig. 8) and of the fact that the largest strains involved in the bending experiments were quite small. Descaling the fibers reduced both E_b and the extension modulus to the same extent. A simpler method experimentally consists in bending a length of fiber through 360 deg. to form a ring and measuring the distortion of the ring caused by a small weight hung from the ring. Carlene⁶⁴ found by this method that the flexural rigidity of viscose filaments was proportional to their mass per unit length raised to the power 1.8 (which is less than 2, the value for the bending of an isotropic beam). The classical relation for the stability of a loaded pillar has also been used to measure the bending modu-

⁶⁰ G. S. Buck and F. A. McCord, *Textile Research J.* **19**, 216 (1949).

⁶¹ W. G. Cameron and T. H. Morton, *Am. Dyestuff Repr.* **38**, 575 (1949).

⁶² M. K. Sen, *J. Textile Inst.* **39**, T339 (1948).

⁶³ R. M. Khayatt and N. H. Chamberlain, *J. Textile Inst.* **39**, T185 (1948).

⁶⁴ P. W. Carlene, *J. Textile Inst.* **41**, T159 (1950).

lus, a number of rayons tested in yarn form giving a mean effective bending modulus of 8.5×10^{10} dynes/cm.²

V. Dynamic Properties

1. ELASTIC MODULUS AND INTERNAL FRICTION

The two quantities that are usually measured in order to characterize the dynamical mechanical behavior of materials are elastic modulus and internal friction. The elastic modulus may be either the Young's modulus obtained from stretching and bending experiments or the rigidity modulus from experiments in which the fiber is twisted by a pure torque. Dynamic modulus will generally be taken to refer to a modulus measured with stress and strain varying sinusoidally with time. The deformations involved in such measurements are usually sufficiently small that the effects of nonlinear terms are not detectable. If viscous losses accompany the deformation, the complex modulus can be used to express both the ordinary dynamic elastic modulus and the internal friction as a complex number. Thus the complex Young's modulus $E^* = E + j\eta\omega$, where ω is the radian frequency, η is a viscosity coefficient, and the product $\eta\omega$ is the dynamic internal friction. The ratio $\eta\omega/E = \tan \delta$, where δ is the angle of phase lag between the impressed force and the resulting deformation, and is called the loss tangent.

There are several ways of expressing the loss tangent in terms of directly measured quantities,⁶⁵ provided it is not too large. If the amplitude of vibration is observed under conditions of forced oscillation, it will be a maximum when the impressed frequency equals a critical resonant frequency (ν_0) of the specimen. Let $\Delta\nu$ be the change in impressed frequency between the two points on the resonance curve where the amplitude is $1/\sqrt{2}$ of its maximum value, then the loss tangent $\tan \delta = \Delta\nu/\nu_0$. The specific damping capacity ($\Delta W/W$) is the energy dissipated per cycle of vibration divided by the strain energy when the strain is a maximum and for small values of $\tan \delta$ we have $\Delta W/W = 2\pi \tan \delta$. The gradual decay of amplitude of vibration during free oscillation provides a third method of measuring the loss tangent: the natural logarithm of the ratio of successive amplitudes is called the logarithmic decrement and equals $\pi \tan \delta$.

2. INFLUENCE OF STATIC STRAIN AND DYNAMIC STRAIN AMPLITUDE

Results obtained by various authors^{46, 55, 66, 67, 68} using different frequencies show that in general the dynamic Young's modulus increases with

⁶⁵ C. M. Zener, "Elasticity and Anelasticity of Metals," p. 60. Univ. of Chicago Press, Chicago, 1948.

⁶⁶ H. de Vries, thesis, Delft, 1953.

⁶⁷ T. Ree, M. C. Chen, and H. Eyring, *Textile Research J.* **21**, 789 (1951).

⁶⁸ H. Tipton, *J. Textile Inst.* **46**, T322 (1955).

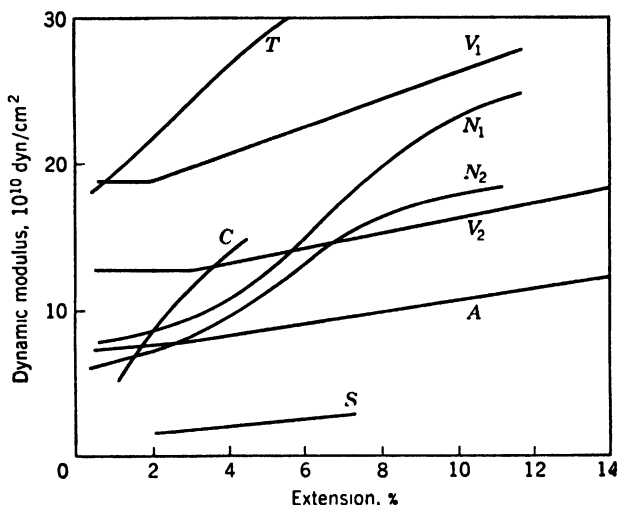


Fig. 12. Dynamic modulus versus static strain at 65% r.h. and 20° C. Key: *A* = acetate rayon *N*₁ = nylon 66— $\nu \sim 20$ kc.p.s.; *V*₁ and *V*₂ = viscose rayon— $\nu \sim 9$ kc.p.s.; *T* = Terylene *N*₂ = nylon 66— $\nu \sim 50$ c.p.s.; *C* = cotton— $\nu \sim 30$ c.p.s.; *S* = Saran— $\nu \sim 2$ –30 c.p.s.

static strain or tension, as shown by the selected examples in Fig. 12. The two curves for nylon have similar shapes, although the upper curve was obtained at a high frequency using a pulse propagation technique, whereas the lower curve refers to a different sample measured by a resonance method⁶⁹ at a frequency lying between 30 and 60 c.p.s. The behavior of viscose rayon⁶⁶ is especially interesting in that the shape of the dynamic modulus-static strain curve is characteristic of all viscose rayons of widely different degree of molecular orientation: there is an initial part where the dynamic modulus is independent of static strain up to a critical value e_c , and beyond this the modulus increases linearly with static strain, the slope being given by $dE/de = b E_c^2$ where E_c is the dynamic Young's modulus at low strains and b is the same for all ordinary viscose rayons. Since $E_c e_c^{2/3}$ is a constant⁶⁶ for a wide range of viscose rayons, a single determination of E_c for a given sample determines the whole of the dynamic modulus-static strain relation. Cellulose acetate rayon behaves in a similar way to viscose rayon.

In most dynamic measurements the strain amplitude is very small but, using resonance methods, quite large strain amplitudes can be obtained.⁶⁸ Up to a dynamic strain amplitude of 0.1 to 0.3 % depending on the fiber, the dynamic properties are constant but at higher amplitudes the dynamic modulus usually decreases slightly and the internal friction increases.

⁶⁹ B. A. Dunell and J. H. Dillon, *Textile Research J.* **21**, 393 (1951).

3. EFFECT OF FREQUENCY AND HUMIDITY.

Dunell and Dillon⁶⁹ have measured the dynamic properties of filaments of viscose rayon, acetate rayon, nylon, silk, and Polythene in the frequency range 1 to 100 c.p.s. at 65 % r.h. and found the dynamic Young's modulus and internal friction ($\eta\omega$) to be approximately independent of frequency. The slope of the plot $\log \eta$ vs. $\log \omega$ should be -1 if $\eta\omega = \text{constant}$; for viscose rayon, acetate rayon, nylon, and Polythene the slope was about 0.9 so that internal friction actually increases slightly with frequency. A similar result was found for Saran.⁶⁷ There appeared to be a slight increase in modulus with frequency for Polythene filaments, which is supported by other work.⁷⁰

Fujino *et al.*^{70a} have measured the dynamic Young's modulus and internal friction of viscose and cuprammonium rayons, acetate, nylon 6, and silk at frequencies from 2×10^{-1} to 2×10^5 c.p.s., using four experimental methods to cover this wide range. The dynamic Young's modulus was found to be almost independent of frequency except for a slight increase in the supersonic range. On the other hand, the loss tangent seemed to increase at both ends of the frequency range except for degummed silk for which the loss tangent showed no definite trend with frequency. The relaxation spectrum of these fibers was found to be flat over the range from 10^{-6} to 1 sec. which is quite different from the spectra of rubberlike materials over the same relaxation-time range.

The effect of humidity on the dynamic Young's modulus of textile fibers is much less than on the quasi-static Young's modulus measured at low rates of straining. Thus, Chaikin and Chamberlain^{70b} found that, as the relative humidity increased from 25 % to 65 %, the dynamic modulus of human hair decreased by about 10 % compared with a decrease of 26 % for wool at a low rate of straining.^{70c} Andersen⁴⁶ found that, from 37 % to 70 % r.h., the dynamic modulus of viscose rayon decreased by 16 % compared with a decrease in static modulus of about 45 %.

4. FLEXURAL RIGIDITY

Static methods of determining flexural rigidity have already been referred to. From the lateral vibration of fibers, either loaded or free, the dynamic bending modulus and internal friction can be calculated. Searle's double pendulum has been used to measure the flexural rigidity of a fringe of cotton fibers and bending moduli of 27×10^{10} dynes/cm.² for dry soda-boiled

⁷⁰ K. W. Hillier, *Brit. J. Appl. Phys.* **2**, 167 (1951).

^{70a} K. Fujino, H. Kawai, and T. Horino, *Textile Research J.* **25**, 722 (1955).

^{70b} M. Chaikin and N. H. Chamberlain, *J. Textile Inst.* **46**, T25, T44 (1955).

^{70c} H. J. Woods, *Proc. Leeds Phil. Lit. Soc.* **3**, 577 (1940).

Texas cotton⁷¹ and 14×10^{10} dynes/cm.² for the same material at 65 % r.h. were found. Using fibers as vibrating cantilevers, Lincoln⁷² measured the bending modulus and internal friction of wool fibers over a range of moisture regains and found that the bending modulus decreased with increasing regain to a greater extent than the longitudinal Young's modulus; internal friction increased with moisture regain. The effect of moisture regain on both modulus and internal friction was greater for wool fibers carbonized by treatment with sulfuric acid solution than for untreated fibers or carbonized fibers which had been neutralized with sodium carbonate solution.

Lochner⁷³ found that the dynamic bending modulus of cellulose acetate fibers was independent of frequency from 45 to 1100 c.p.s. Similarly, Horio *et al.*^{73a} showed that, from 20 to 100 c.p.s., the dynamic bending modulus of a low orientation viscose monofil was independent of frequency but that of a high orientation monofil increased slightly. As the double refraction increased from 0.0043 to 0.03, the dynamic bending modulus increased linearly from 6 to about 18×10^{10} dynes/cm.². When the draw ratio of nylon 66 and Dacron was increased from 1 to 6 the dynamic bending modulus increased by a factor of 3.5 and 5.8 respectively.^{73b}

5. TORSIONAL RIGIDITY

The resistance of fibers to twisting is most conveniently measured by suspending a bar or disk by means of the fiber and timing the low-frequency oscillations of the system, which forms a torsion pendulum. A selection of values of rigidity moduli for various fibers^{74, 74a} are recorded in Table IV together with approximate shape factors which express the ratio of the torsional rigidity of a fiber to that which it would have if its cross-sectional shape were circular; thus, Kapok fibers are very thin-walled fibers and this makes the couple required to twist the fiber very high compared with other fibers. Observations with highly orientated viscose rayon fibers gave the same modulus of rigidity as for the less well-orientated ordinary viscose rayon. This lack of dependence of modulus of rigidity on orientation was also found by Wakelin *et al.*^{73b} for nylon and Dacron filaments with draw

⁷¹ F. H. Clayton and F. T. Peirce, *J. Textile Inst.* **20**, T315 (1929).

⁷² B. Lincoln, *J. Textile Inst.* **43**, T158 (1952).

⁷³ J. P. A. Lochner, *J. Textile Inst.* **40**, T220 (1949).

^{73a} M. Horio, S. Onogi, C. Nakayama, and K. Yamamoto, *J. Appl. Phys.* **22**, 966 (1951).

^{73b} J. H. Wakelin, E. T. L. Voong, D. J. Montgomery, and J. H. Dusenbury, *J. Appl. Phys.* **26**, 786 (1955).

⁷⁴ R. Meredith, *J. Textile Inst.* **45**, T489 (1954).

^{74a} J. C. Guthrie, T. H. Morton, and P. H. Oliver, *J. Textile Inst.* **45**, T912 (1954).

TABLE IV
TORSIONAL RIGIDITY MODULUS AT 65% R.H. AND 20° C.

<i>Fiber</i>	ϵ	G	<i>Fiber</i>	ϵ	G
Flax	0.96	1.4	Wool	1	1.1
Cotton	0.7	2.5	Silk	0.84	2.2
Kapok	5	3.1	Ardil	1	1.3
Viscose	0.95	1.1	Nylon	1	0.5
Cuprammonium	1	1.5	Dacron	1	0.9
Acetate	0.7	0.8	Orlon	0.6	1.2

ϵ = approximate shape factor.

G = modulus of rigidity (10^{10} dynes/cm²).

ratios ranging from 1 to 6. Cuprammonium rayon has a higher modulus than viscose rayon, indicating a difference in internal structure.⁷⁵

Clayton and Peirce⁷¹ showed that the rigidity of cotton fibers is halved by the addition of 10% moisture, the ratio of torsional rigidity at regain M (%) to that of the dry fiber being $\exp. (-0.07 M)$. Assuming the shape factor to remain constant and correcting for the change in area of cross section with regain, the ratio of the modulus of rigidity at regain M to that of the dry fiber is $G/G_0 = \exp. (-0.09 M)$. Now according to Peirce's two-phase theory of moisture absorption⁷⁶ in cellulose fibers, the number of molecules of water per glucose residue that are bound by hydroxyl bonds, and which may therefore be expected to influence the elastic properties, is given by $C_a = 1 - e^{-0.09M}$ so that we arrive at the simple relation $G/G_0 = 1 - C_a$. An expression involving C_a was also deduced for the temperature coefficient of rigidity. Jancke⁷⁷ observed the effect of temperature on the torsional rigidity of dry viscose rayon: at temperatures of 110, 20, -65, and -185° C. the modulus of rigidity was 0.70, 1.22, 17.3, and 60.3×10^{10} dynes/cm², respectively.

Speakman⁷⁸ has analyzed the variation of rigidity with regain for wool on the basis of Peirce's two-phase theory of moisture absorption and found a simple relation between the rigidity modulus and the fraction of moisture which is bound to the peptide groups.

The relation between moisture regain and rigidity modulus, bending modulus or Young's modulus of wool⁷⁹ has a similar form so that the influence of moisture on all three moduli might find a simple explanation in terms of the theory of moisture absorption.

⁷⁵ N. H. Chamberlain and M. P. Khara, *J. Textile Inst.* **43**, T123 (1952).

⁷⁶ F. T. Peirce, *J. Textile Inst.* **20**, T133 (1929).

⁷⁷ W. Jancke, *Melliand Textilber.* **11**, 359 (1930).

⁷⁸ J. B. Speakman, *Trans. Faraday Soc.* **28**, 92 (1929).

⁷⁹ C. M. van Wyk, *S. African J. Sci.* **47**, 127 (1951).

VI. Quantitative Theoretical Interpretation

1. THERMODYNAMICAL APPROACH

In the previous sections the results of experiments to measure the stress-strain-time behavior of fibers have been discussed with some reference to qualitative interpretation in terms of molecular structure. Thermodynamics provides us with a general approach to the quantitative relations between the variables but gives no specific relations with molecular structure and is restricted to reversible processes. However, some useful information can be obtained: for example, the degree to which the restoring forces arising from strain depend on internal energy changes and entropy changes.

The tension P in a fiber is related to these changes by the equation

$$P = \left(\frac{\partial U}{\partial l} \right)_T - T \left(\frac{\partial S}{\partial l} \right)_T \quad (1)$$

where U is the internal energy, S is the entropy, l is the length and T is the absolute temperature. It can readily be shown that

$$\left(\frac{\partial S}{\partial l} \right)_T = - \left(\frac{\partial P}{\partial T} \right)_l \quad (2)$$

so that the change in entropy can be calculated from a plot of force against absolute temperature for constant extension and hence the change in internal energy from equation (1). The change in internal energy arises from the straining of intermolecular bonds, whereas the change in entropy represents the change in mean statistical configuration of the molecules.

Some fibers show considerable recovery from large deformations, especially in the wet state. This suggests a network structure which remains coherent even when the fiber is highly swollen. Since the elastic deformation that can be attributed to primary and secondary bonds is limited to a few percent, one is forced to conclude that the molecules responsible for the observed large deformations must be coiled or kinked. Hermanne⁸⁰ postulates that extension of cellulose fibers beyond 5% is associated with the entropy of the orientation of the links in the cellulose chain molecule. If the recovery from strain depends only on entropy, then $(\partial P / \partial T)_l$ should be positive. Such an effect has been observed with rubber and nylon but, with the possible exception of cellulose acetate, the stress in cellulose fibers increases with temperature decrease.⁴⁶ Also, cellulose fibers have a positive coefficient of thermal expansion whereas materials showing entropy elasticity have negative coefficients. The observations suggest that recovery

⁸⁰ L. Hermanne, *Textile Research J.* **19**, 61 (1949).

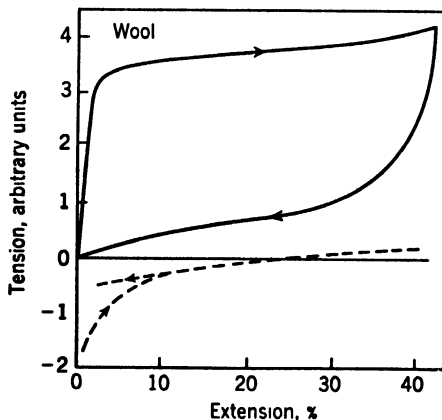


FIG. 13. Wool in water at 20 to 40° C. Continuous line gives total tension; dashed line gives entropy contribution to tension. (Woods.⁸¹)

from large strains in cellulose fibers may involve an entropy effect but that this is usually overshadowed by internal energy changes^{80a, 80b}.

It is contended by some authors¹¹ that the long range elasticity of keratin (wool) fibers is entropic in nature but an analysis of the stress-strain curve for fibers stretched in water does not support this. Figure 13 shows how much of the tension in wet wool fibers⁸¹ arises from change in entropy. At low extensions, the entropy contribution to the tension is negative and even at high extensions, when it becomes positive, its value is so small in comparison with the total tension that it must be concluded that internal energy is the dominant factor.⁸² The negative sign of the entropy contribution to the tension up to extensions of 20% may be interpreted as a disordering of the noncrystalline fraction as the chain molecules begin to unfold; when the polypeptide chain molecules straighten in the later stages of extension, the entropy contribution becomes positive.

Reduction of the disulfide linkages by thioglycollic acid and the resultant swelling leaves the polypeptide chains much freer and rubberlike behavior might be expected; however, keratin swollen in formic acid is not rubberlike and this must be ascribed to the still-intact disulphide linkages, emphasizing their important role in determining the characteristic rheological behavior of keratin.

It is interesting to compare keratin and casein fiber, which is shown by

^{80a} G. M. Bryant and H. Wakeham, *Textile Research J.* **25**, 224 (1955).

^{80b} W. E. Roseveare and L. Poore, *J. Polymer Sci.* **14**, 341 (1954); *Textile Research J.* **25**, 709 (1955).

⁸¹ H. J. Woods, *J. Colloid Sci.* **1**, 407 (1946).

⁸² J. Bull, *J. Am. Chem. Soc.* **67**, 533 (1945).

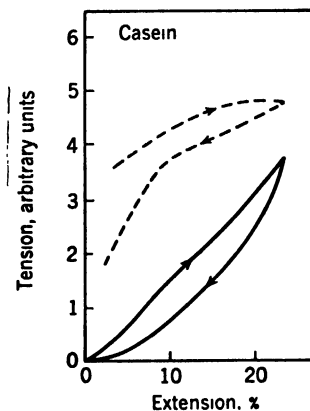


FIG. 14. Casein in water at 20 to 40° C. Continuous line gives total tension; dashed line gives entropy contribution to tension. (Woods.⁸¹)

X-rays to be poorly crystalline with the chain molecules folded in a highly irregular manner. The results given in Fig. 14 for casein fiber⁸¹ in water show a large positive entropy force (also found for acetylated casein⁸³), necessitating a negative contribution to the force from internal energy which must be produced by something in the nature of an internal compression developed by the strongly contractile effect of the entropy. The same phenomenon of a negative internal energy force appears with nylon^{81, 84} stretched in water up to 4 to 10%; for higher extensions ($\partial U/\partial l$)_T becomes positive. When the temperature is raised, synthetic fibers such as nylon, Vinyon, and Vinyon N contract in length: with Vinyon and Vinyon N the contraction is considerable and rubberlike elasticity might be expected. Clark and Preston⁸⁵ have measured the contributions to the force from entropy and internal energy for the contracted fibers in dry air and found essentially the same behavior as that shown in Fig. 14 for casein fiber in water, i.e., a large positive contribution to the tension from entropy and a smaller but still large negative contribution from internal energy.

2. REACTION-RATE THEORY

a. Three-Element Model

A system consisting of a Hookean spring in series with a Newtonian dashpot (Maxwell unit), linked in parallel with another spring (Fig. 15) is capable of representing the creep, relaxation, and stress-strain behavior of a fiber up to extensions of 5% or so, at least qualitatively, when secondary creep or permanent set is absent. Such a linear model has a single relaxation

⁸³ S. R. Hoover, E. L. Kokes, and R. F. Petersen, *Textile Research J.* **18**, 423 (1948).

⁸⁴ G. M. Bryant, *Textile Research J.* **23**, 788 (1953).

⁸⁵ J. F. Clark and J. M. Preston, *J. Textile Inst.* **44**, T596 (1953).

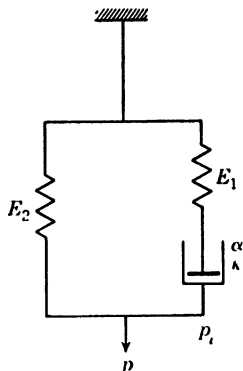


FIG. 15. Three-element model.

time and when the number of Maxwell units is increased to give a distribution of relaxation times, the time scales of the relaxation and creep functions can be extended to ranges which approach those observed experimentally. However, the more complicated linear system is difficult to handle^{85a}, particularly when used to explain stress-strain data. A three-element system with Hookean springs and Eyring-type viscous element accomplishes the extension of the time scale for relaxation and creep and also accounts for the observed relation between stress and time when the rate of extension is changed. For an excellent account of the theory of nonlinear elasticity, reference should be made to Halsey⁸⁶ who summarizes the application of Eyring's theory of rate processes^{86a, 87, 88} to explain the rheological behavior of fibers.

The rate of strain of the viscous element in Fig. 15 may be written

$$\dot{e} = K \sinh \alpha p \quad (3)$$

where K is a function of molecular parameters including the activation energy for the flow process ($\Delta F^\ddagger$), $\alpha = \lambda/2NkT$ (λ being the distance that a flow unit—e.g., segment of a chain molecule—jumps), and N is the number of flow units per unit area of cross section. Assuming Hookean springs it can be shown that the differential equation governing the model is

$$\frac{d}{dt} [(E_1 + E_2)e - p] = E_1 K \sinh \alpha (p - eE_2) \quad (4)$$

^{85a} T. Alfrey, "Mechanical Properties of High Polymers." Interscience, New York, 1948.

⁸⁶ G. Halsey, *J. Appl. Phys.* **18**, 1072 (1947).

^{86a} S. Glasstone, K. J. Laidler, and H. Eyring, "Theory of Rate Processes." McGraw-Hill, New York, 1941.

⁸⁷ G. Halsey, H. J. White, and H. Eyring, *Textile Research J.* **15**, 295 (1945).

⁸⁸ A. V. Tobolsky and H. Eyring, *J. Chem. Phys.* **11**, 125 (1943).

For stress relaxation, e is a constant, say e_c so that

$$\alpha p = \alpha p_\infty + \ln \coth \frac{1}{2}(At + B) \quad (5)$$

where $A = \alpha K(p_0 - p_\infty)/e_c$ and $B = \ln \coth \frac{1}{2}\alpha(p_0 - p_\infty)$: p_0 is the external stress at $t = 0$, p_∞ is the external stress at $t = \infty$. Equation (5) can be reduced to

$$\alpha p \simeq \alpha p_\infty + \ln (2/A) - \ln t \quad (6)$$

for stresses which are not too near p_0 or p_∞ , in which case the stress p varies linearly with the logarithm of the time. An equation similar to equation (5) has been used to evaluate the energy of activation and the number of flow units per unit area by Burleigh and Wakeham,⁸⁹ for viscose rayon and cotton cords; by Halsey, White and Eyring⁸⁷ for viscose rayon and by Andersen⁴⁶ for cotton and viscose rayon fibers. The main difficulty is to fix values of p_0 and p_∞ , since the initial stress depends on the rate of extension; the final stress is indeterminate owing to relaxation proceeding for times beyond those for which observations can conveniently be made. The values of $\Delta F^\ddagger$ evaluated by Burleigh and Wakeham⁸⁹ are probably too high, since p_∞ was assumed by them to be zero.

For creep under constant stress (p_c) we have $\dot{p} = 0$ and equation (4) can be integrated to give

$$e = e_\infty [1 - (1/\alpha p_c) \ln \coth \frac{1}{2}(A't + B')] \quad (7)$$

where $A' = \alpha K p_c (1 - e_0/e_\infty)/e_\infty$ and $B' = \ln \coth \frac{1}{2}\alpha p_c (1 - e_0/e_\infty)$. Equation (7) is similar in form to the equation for stress relaxation and for small stresses and times not exceeding 10^5 sec. we have

$$e \simeq e_0 + (e_\infty/\alpha p_c) \ln [1 + (A'/B')t] \quad (8)$$

which has been successfully fitted⁸⁷ to some of Leaderman's data on the creep of viscose rayon, acetate rayon, and silk. Steinberger's data on the creep of cellulose acetate filaments have been analyzed by Reichardt, Halsey, and Eyring⁹⁰ on the basis of a similar three-element model to that shown in Fig. 15 but consisting of a spring in series with a Voigt unit (spring and dashpot in parallel): under constant stress the series spring remains constant in length and the mathematics are easier but it should be borne in mind that for these two models to be equivalent in their external effect, the viscous element in each model must have different values of α and different values of K . This means that the values of K as determined by Reichardt *et al.*⁹⁰ from their creep experiments do not correspond to the values K determined from their relaxation experiments.

⁸⁹ E. G. Burleigh and H. Wakeham, *Textile Research J.* **17**, 245 (1947).

⁹⁰ C. H. Reichardt, G. Halsey, and H. Eyring, *Textile Research J.* **16**, 382 (1946).

For constant rate of extension, $\dot{\epsilon}$ is constant. Let $\dot{\epsilon}/K = \beta$ and $S^2 = 1 + \beta^2$ then equation (4) can be integrated to give

$$p = E_2 e + (1/\alpha) \ln \{ \beta + S \tanh [\frac{1}{2} \alpha \beta S E_1 e + \tanh^{-1} (1 - \beta)/S] \} \quad (9)$$

which gives the relation between stress and strain in terms of α , K , E_1 , E_2 , and $\dot{\epsilon}$. Using reduced variables to express $p - E_2 e$ as a function of β and t only, this equation has been used by Reichardt and Eyring⁹¹ to calculate K and hence $\Delta F^\ddagger$ for cellulose acetate from its stress-strain curve. Using a single value of K a reasonable fit of calculated and observed extension and retraction curves was obtained up to 5 % extension.

Sometimes the stress on re-extending a specimen rises temporarily above the curve obtained on straining continuously to rupture. Dunell and Halsey⁹² have attempted to explain this thixotropic behavior by supposing that a relatively high potential barrier must be surmounted before shear flow occurs but the theoretical rate of fall of excess stress was not fast enough to give good agreement with observation.

The three-element model with sinh law dashpot has been applied with some success to the stress-strain curves of fibers such as viscose and acetate rayon up to, say, 5 % extension. However, this approach fails when attempts are made to explain the sigmoid curves of wool and nylon, for it would be necessary to postulate non-Hookean springs.

b. Two-State Theory

The unfolding of the polypeptide chains in wool when stretched suggests that a theory of viscoelasticity might be based on this process. Burte and Halsey⁹³ and Peters and Speakman⁹⁴ developed such a theory almost concurrently. It is assumed that a potential barrier of the type shown in Fig. 16 separates the folded α -state and the unfolded β -state, and the extension is proportional to the fraction of the segment of a molecule that is in the β -state, except for a small elastic extension which is neglected for the present. If l_∞ is the extension when all of a molecular segment is in the β -state and b is the proportion in that state at extension l , then $b = l/l_\infty$. If the specific rate of folding at zero force and unit concentration is $K = (kT/h) \exp. (-\Delta F/RT)$, then at zero applied stress the rate of folding is bK and the rate of unfolding is $(1 - b)KD$ where $D = \exp. (-\Delta F^*/RT)$. Applied stress p affects the rate of reaction (K) by $\exp. (\alpha p)$ so that the net rate of reaction can be written

$$\dot{l}/l_\infty = \dot{b} = (1 - b)KDe^{\alpha p} - bKe^{-\alpha p} \quad (10)$$

which is the basic differential equation of the two-state model.

⁹¹ C. H. Reichardt and H. Eyring, *Textile Research J.* **16**, 635 (1946).

⁹² B. A. Dunell and G. Halsey, *Textile Research J.* **18**, 178 (1948).

⁹³ H. Burte and G. Halsey, *Textile Research J.* **17**, 456 (1947).

⁹⁴ L. Peters and J. B. Speakman, *J. Textile Inst.* **39**, P253 (1948).

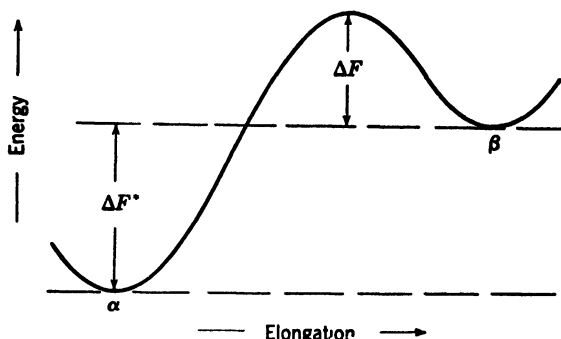


FIG. 16. Energy barrier for two-state system.

For constant stress, equation (10) may easily be integrated to give

$$(b_{\infty} - b)/(b_{\infty} - b_0) = e^{-At} \quad (11)$$

where b_0 , b_{∞} are the values of b at $t = 0$ and $t = \infty$ and A is a constant. Equation (11) predicts creep with the extension approaching a limiting value exponentially, exactly as found experimentally by Feughelman^{94a} and by Ripa and Speakman²¹. Actually, a single exponential is inadequate to account for the complete creep behavior of keratin: two phases acting in series are required, one with a much quicker response than the other. For constant rate of extension (l_c) let $\beta = l_c/Kl_{\infty}$, then for large β equation (10) yields for extension

$$\alpha p_{\text{out}} = \ln(\beta/D) - \ln(1 - b) \quad (12)$$

and for retraction

$$\alpha p_{\text{in}} = \ln b - \ln \beta \quad (13)$$

For a very slow rate of extension, the locus of points of no relaxation (the spring line) is

$$2\alpha p_0 = \ln b - \ln(1 - b) - \ln D \quad (14)$$

Thus, for the two-state model with symmetrical potential barrier, the spring line lies half way between the extension and retraction curves. The two-state theory reproduces the upward inflection of the stress-strain curve which had not previously been accounted for: it predicts the displacement of the curve to higher stress for more rapid extension, the stress at the mid-point being proportional to the logarithm of the rate of extension. There is some arbitrariness in choosing l_{∞} to be 30%: beyond this extension, another, more slowly extending, model in series with the rapidly extensible

^{94a} M. Feughelman, *J. Textile Inst.* **45**, T630 (1954).

model is needed. According to equation (10), putting $\beta =$ zero for relaxation of stress at constant extension gives equation (14) gives a constant equilibrium tension independent of time. Actually, to account for the relaxation of keratin in water (Fig. 4) requires two mechanisms in series: rapid extension leading to overstretching of one phase followed by slow creep of the other: evidence in favor of this hypothesis is the observation of the α - β transformation taking place at constant extension in appropriate circumstances. Some of the more complex phenomena, including thixotropy, can be explained by postulating a three-state theory.⁹³

3. DISTRIBUTIONS OF RELAXATION TIMES

From the creep and relaxation curves already described it will be clear that a distribution of relaxation times is necessary to account for the observed behavior. If a discrete distribution of relaxation times is assumed in a linear system, then the number of relaxation times required to describe creep or relaxation is proportional to the logarithm of the time range of observations. Thus, a single relaxation time, λ_1 , gives a linear relation between stress at constant strain and log time over a range of times from $\lambda_1/5$ to $2\lambda_1$; for two relaxation times suitably chosen, say $\lambda_2 = 10\lambda_1$, the linearity of the stress-log time plot is extended to cover a 100-fold range of times; for three relaxation times, say, $\lambda_3 = 10\lambda_2 = 100\lambda_1$, the linear range covers a 1000-fold range of times, and so on. Deviation from linearity of stress and log time can be allowed for by assuming unequal numbers of elements with the various relaxation times.

A discrete distribution of the type just described has been used by Peirce²⁹ to account for the observed relaxation of torque at constant twist in a number of fibers. For a uniform population of cohesive bonds, the number of bonds breaking per unit time was assumed to be proportional to the number of bonds remaining unbroken at any time leading to a shear stress at time t equal to $\tau_t = \tau_0 e^{-t/\lambda}$ where λ is the mean relaxation time of a bond. For a disperse population of bonds, the shear stress may be written $\tau_t = \tau_0 \int_0^\infty \phi(\lambda) e^{-t/\lambda} d\lambda$. To determine $\phi(\lambda)$ he assumed a geometrical progression of the relaxation times, so that the torque at time t would be

$$T_t = c + \sum_{r=0}^{\infty} a_r \exp\left(\frac{-t}{10^r}\right)$$

where c is a constant. Assuming a_r is proportional to the slope of the torque-log time curve at the time $t = 10^r$, a differential curve was obtained which approximately represents the frequency distribution of the terms a_r . By assuming that $\lambda = 1/K$ where $K = (kT/h) \exp. (-\Delta F^\ddagger/RT)$ the relaxation times can be translated into activation energies thus

$$\Delta F^\ddagger = RT[\ln \lambda + \ln (kT/h)]$$

so that, for example, when $T = 293^\circ \text{K}$. a relaxation time of 1 sec. corresponds to $\Delta F^\ddagger = 17.1 \text{ kcal./mole}$ and $\lambda = 10^5$ corresponds to $\Delta F^\ddagger = 23.8 \text{ kcal./mole}$.

If the strains are small, the relaxation of stress is frequently a linear function of log time over a considerable time range and this behavior can be described by a continuous distribution of the type⁹⁵ in which the contribution to the stress from mechanisms with a given relaxation time is inversely proportional to the relaxation time, so that in the general equation

$$p_t = e_0 \int_0^\infty E(\lambda) e^{-t/\lambda} d\lambda$$

we write $E(\lambda) = E_0/\lambda$ for $\lambda_{\min.} < \lambda < \lambda_{\max.}$ and $E(\lambda) = 0$ for $\lambda \leq \lambda_{\min.}$, $\lambda \geq \lambda_{\max.}$ where $\lambda_{\min.} \ll \lambda_{\max.}$, leading to $p_t = e_0 (\ln \lambda_{\max.} - \lambda - \ln t)$ γ being Euler's constant ($= 0.57722$). Differentiating with respect to $\ln t$ gives $-\frac{d(p_t/e_0)}{d \ln t} = E_0$, i.e., the negative slope of the relaxation curve gives the constant E_0 .

When the distribution of relaxation times takes the simple form just described, the dynamic modulus and internal friction can be predicted from stress relaxation data for frequencies lying between $1/\lambda_{\min.}$ and $1/\lambda_{\max.}$. Thus, the dynamic modulus

$$E(\omega) = \int_0^\infty \frac{\omega^2 \lambda^2 E(\lambda)}{1 + \omega^2 \lambda^2} \cdot d\lambda \simeq E_0 \ln \omega \lambda_{\max.}$$

and is almost constant over a range of frequencies for which $\omega \gg 1/\lambda_{\max.}$. For the internal friction,

$$\omega \eta(\omega) = \int_0^\infty \frac{\omega \lambda E(\lambda)}{1 + \omega^2 \lambda^2} \cdot d\lambda \simeq \frac{\pi E_0}{2}$$

so that $\omega \eta = (\pi/4.606)$ (negative slope of the relaxation curve) when the relaxation curve is plotted as p/e_0 against log time. Tobolsky, Dunell, and Andrews⁹⁶ have analyzed the results obtained by Dunell and Dillon⁶⁹ on this basis and have found an order of magnitude agreement between observed and calculated values of $\eta \omega$ for viscose rayon, acetate rayon, silk, nylon, and Polythene fibers. They pointed out that better agreement might be found by using relaxation data covering the same time region as that in which the dynamic measurements are made and this has been confirmed for viscose rayon.²² The same type of analysis has been made by Hammerle and Montgomery³⁰ for relaxation of torque in nylon at constant twist and

⁹⁵ W. Kuhn, O. Künzle, and A. Preissmann, *Helv. Chim. Acta* **30**, 307 (1947).

⁹⁶ A. V. Tobolsky, B. A. Dunell, and R. D. Andrews, *Textile Research J.*, **21**, 404 (1951).

they found that the dynamic rigidity modulus could be predicted to within about 3% and the internal friction to within about 13%.

Saran⁶⁷ monofilaments have been subjected to longitudinal free vibrations by displacing a suspended weight from its equilibrium position: the frequency was varied from 1.75 to 31.5 c.p.s. by changing the length of filament using four different weights. The logarithmic decrement was found to increase slightly with frequency at constant static strain and this was explained in terms of two relaxation times, the contribution to the damping from elements with the shorter relaxation time being the larger one. When nylon⁹⁷ was subjected to forced longitudinal vibrations over a frequency range from 0.6 to 6 c.p.s. the energy loss per cycle per unit volume was found to be independent of frequency and again two relaxation times were assumed, each associated with a maximum energy loss at a frequency of $\omega_1 = 1/\lambda_1$ or $\omega_2 = 1/\lambda_2$. It was indicated earlier in this section that equal contributions to the stress at constant strain from mechanisms with relaxation times separated by a factor of 10 will give an approximately linear stress-log time plot: similarly equal contributions to the internal friction from mechanisms with relaxation times separated by a factor of 10 will give value of internal friction approximately independent of frequency.

VII. Strength

A certain minimum strength is necessary for any fiber to be of practical use. Two main groups of factors determine fiber strength: (i) constitution, fine structure, and morphology; and (ii) test conditions such as relative humidity and temperature, rate or duration of loading, and test length. Since fibers are extremely long compared with their diameter, they are usually stressed in tension and tensile strength has been more thoroughly studied than, say, shear strength or resistance to twisting.

1. TENSILE STRENGTH

It is difficult to compare the strengths of different kinds of fiber because for each type there frequently exists a whole range of strengths depending on the source of the natural fibers or the method of manufacture of rayons and synthetic fibers. In general, however, the strength of a given kind of fiber increases as the molecular orientation increases: the extension at break shows a corresponding decrease.^{39, 98} Among the cellulose fibers, the highest

⁹⁷ H. Eyring, M. G. Alder, S. A. Rossmassler, and C. J. Christensen, *Textile Research J.* **22**, 223 (1952).

⁹⁸ E. R. Kauswell, "Textile Fibres, Yarns and Fabrics," Chapter 1. Reinhold, New York, 1953.

strengths are given by flax, hemp, jute, ramie,^{98a, 98b} and regenerated cellulose rayons that have been greatly stretched during manufacture. The relation between orientation and strength of cotton fibers has been studied by means of X-rays^{99, 100} and by polarized light.¹⁰¹ Hermans⁵ and de Vries⁶⁶ have shown that the strength of rayon is highly dependent on the optical orientation factor.

The degree of polymerization (D.P.)¹⁰² is related to the strength of native cellulose fibers: the strength of acid-treated cotton increases with D.P. from 200 to 700, then increases only slightly with further increases in D.P. from 700 to 1000 and is practically unaffected by a further increase in D.P. from 1000 to 3000. In preparing solutions of viscose suitable for spinning, the D.P. is reduced to, say, 500 and the question arises, why is the strength of rayon frequently so much higher than that which the original cellulose would have at the same D.P. and the same orientation. This can be explained if the chemical attack occurs preferably at certain parts of the fiber, such as the noncrystalline regions, and produces a number of weak spots. When such degraded material is dissolved and reprecipitated the chain molecules will have a more random distribution in a lengthwise direction so that the weak spots caused by chemical attack are no longer present.

Silk has a moderately high tensile strength but other protein fibers such as wool, hair, and regenerated fibers have relatively low strength, which is compensated for by their high extension at break that gives them the characteristic of toughness or high work of rupture. The synthetic fibers can be varied in strength over a wide range but if one takes the strength at a given breaking extension as a criterion, then nylon and Terylene or Dacron are comparatively strong, followed in decreasing order by Kuralon, Vinyon N, Orlon, Vinyon, and Polythene.

The strength of a fiber is sensitive to the time taken in loading to rupture. With all fibers, the strength decreases as the time to break increases and over limited ranges of time the sensitivity to time may be expressed by the relation

$$\Delta f = cf_{10} \Delta(\log t)$$

where f_{10} is the strength for a breaking time (t) of 10 sec. and c is a 'strength-time' coefficient. A tenfold increase in breaking time causes the strength to decrease by about 6% for acetate rayon,⁴³ 8% for nylon⁴³ and silk,⁴³ 8½%

^{98a} H. P. Stout and J. A. Jenkins, *Congr. Intern. Res. Sci. Appl. l'Ind. Text., Bruxelles* (1955).

^{98b} E. R. Kaswell and M. M. Platt, *Textile Research J.* **21**, 263 (1951).

⁹⁹ E. E. Berkley and H. D. Barker, *U.S.D.A. Tech. Bull.*, **949**, 21 (1948).

¹⁰⁰ R. Meredith, *J. Textile Inst.* **42**, T291 (1951).

¹⁰¹ R. Meredith, *J. Textile Inst.* **37**, T205 (1946).

¹⁰² H. Staudinger and J. Jurisch, *Melliand Textilber.* **20**, 693 (1939).

for viscose rayon⁴³ and 9% for cotton. The breaking extension is less affected by time than the strength: for viscose rayon and silk it increases with breaking time, for acetate rayon it is unaffected and for cotton and nylon it has a maximum value for breaking times of about 10 sec.

A theoretical treatment has been given^{102a} of the longitudinal impact of a yarn and it leads to a formula for a limiting breaking velocity that is a characteristic property of the material and is independent of the dimensions of the specimen. A specimen impacted at a velocity greater than its limiting breaking velocity will always be broken. The values for cotton, nylon, and undrawn nylon yarns were found to be 130, 228, and 550 meters per sec., respectively.

Native cellulose fibers such as flax, ramie, and cotton are the only fibers which show an increase in strength with increase in relative humidity; regenerated cellulose rayons, protein fibers, nylon, and Kuralon decrease in strength while hydrophobic fibers such as Terylene, Orlon, and Vinyon N are unaffected. All hygroscopic fibers show an increase in breaking extension on absorption of moisture, those which absorb most moisture being most affected. The increase in strength of native cellulose fibers as moisture is absorbed^{103, 104, 105} is due essentially to the release of internal stress acting on the extremely long chain molecules; native cellulose fibers in which the chain length has been reduced by acid attack show the same decrease in strength with increase in humidity as rayons of the same D.P.

Increase in temperature^{37, 40, 49} reduces the strength of all fibers by a considerable amount as shown in Fig. 17. The materials were either bone-dry or tested in water, as indicated in the figure. The relative rate of change of strength based on the strength at 20° C. is about the same for nylon and Dacron but higher for Orlon. Wet Tenasco is at least as sensitive as these synthetic fibers but the dry fiber is less sensitive, having about the same sensitivity as dry silk.

Fibers may vary along their length in both area of cross section and regularity of internal structure and since the strength of a fiber is no greater than that of its weakest part, the strength will depend on the length of specimen used in its determination¹⁰⁶ and on the magnitude of the variation in strength from point to point along the fiber. If the standard deviation of strength of short lengths within a fiber is σ_1 and the strength values form a normal Gaussian distribution, then the mean strength of a length r times

^{102a} F. L. McCrackin, H. F. Schiefer, J. C. Smith, and W. K. Stone, *Textile Research J.* **25**, 529, 701 (1955).

¹⁰³ H. Hoffman, *Zellwolle u. Kunstseide* **2**, 45 (1944).

¹⁰⁴ Z. A. Rogovin and R. S. Nieman, *J. Appl. Chem. (U.S.S.R.)* **18**, 208 (1945).

¹⁰⁵ R. Meredith, in "Fibre Science" (J. M. Preston, ed.), Chapter 13. Textile Institute, Manchester, 1953.

¹⁰⁶ F. T. Peirce, *J. Textile Inst.* **17**, T355 (1926); **18**, T475 (1927).

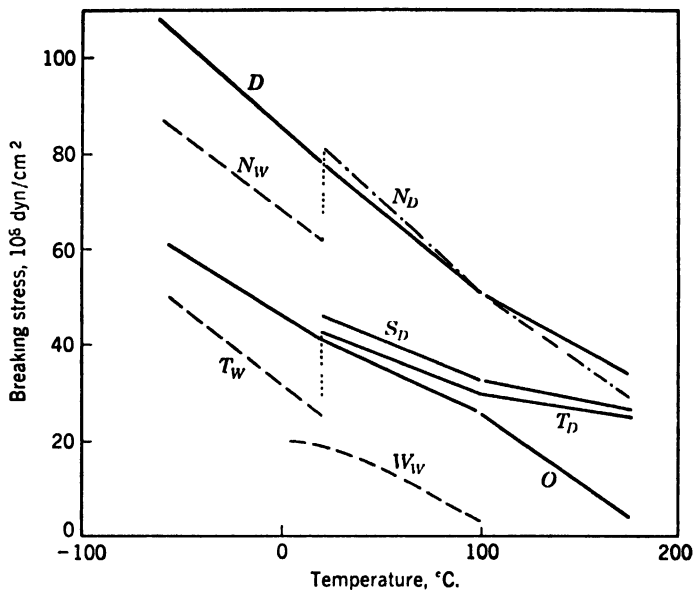


FIG. 17. Effect of temperature on strength. Key: D = Dacron; O = Orlon; S_D = silk (dry); W_W = wool (wet); N_D = nylon 66 (dry); N_W = nylon 66 (wet); T_D = Tenasco (dry); T_W = Tenasco (wet).

the short length is given approximately by

$$f_r = f_1 - v_r \sigma_1$$

where f_1 is the mean strength of the short lengths and v_r is approximately $4.2(1 - r^{-1/5})$. For a sample of highly orientated cellulose acetate rayon the distribution of the strengths of 1-mm. lengths was observed to be normal and the mean strength of 1-cm. lengths could be predicted with fair accuracy from the mean strength of the 1-mm. lengths and the standard deviation for variation within filaments. If the fibers vary slowly in area of cross section along their length, a correlation between the strength of contiguous short lengths will exist and the equation given above will not be directly applicable.

It is evident that the tensile strength of fibers at room temperature depends to a large extent on at least three factors: rate of loading, moisture regain, and test length. An estimate of the maximum observable tensile strength of cellulose, for example, can be obtained by considering a flax fiber broken in $\frac{1}{100}$ sec. in water with test length of 0.2 mm. Such a fiber would have a tensile strength of at least 290×10^8 dynes/cm.². Mark¹⁰⁷

¹⁰⁷ H. Mark, in "Cellulose and Cellulose Derivatives" (E. Ott, ed.), p. 999. Interscience, New York, 1943.

and de Boer¹⁰⁸ have estimated the theoretical strength of a perfectly orientated crystalline cellulose as about 1700×10^8 dynes/cm.² if all the chain molecules broke simultaneously. This value is much higher than any observed value, as would be expected, since highly crystalline fibers such as flax contain only about 60 to 70 % crystalline cellulose and have many imperfections of structure that act to reduce the strength. Since the observed strength falls short of the theoretical value, it has sometimes been argued that the chain molecules slip rather than break. However, there are facts which suggest considerable chain breakage; the increase in strength with absorbed moisture, the shape of the stress-strain curve near rupture, and the unchanged breaking load of carefully nitrated or acetylated ramie.¹⁰⁹

2. SHEAR STRENGTH

Finlayson¹¹⁰ has measured the force required to shear a bundle of fibers by passing the fiber bundle through a hole in three adjacent metal plates and withdrawing the center plate to shear the fibers. Compared with the tensile strengths of short lengths of fiber, the shear strengths were only fractional. The range of shear strengths was smaller than the range of tensile strengths, the more highly orientated fibers having the higher ratios of tensile strength to shear strength. The wet strength expressed as a fraction of the air-dry strength was much the same in shear as in tension except for the native cellulose fibers which show increased wet tensile strength but decreased wet shear strength.

Another measure of resistance to shear is the breaking twist angle, α , as measured by Koch¹¹¹ and defined by $\tan \alpha = l/\pi d \tau_B$ where l is the length of fiber of diameter d and τ_B is the number of twists to rupture. The breaking twist angle is independent of diameter and those fibers with high elastic moduli and low breaking extension gave high breaking twist angles, e.g., 42° for nylon, 50° for wool, 57° for viscose rayon, 60° for raw flax, 67° for highly orientated viscose rayon and 86° for glass fiber. Some information on the effect of moisture, temperature, test length, and rate of twisting for staple fiber rayons is given by Breuer.¹¹²

3. RESISTANCE TO REPEATED BENDING

All textile fibers are extremely flexible but repeated bending^{73, 113, 114} causes first cracking and, ultimately, rupture. Instruments for measuring

¹⁰⁸ J. H. de Boer, *Trans. Faraday Soc.* **32**, 10 (1936).

¹⁰⁹ I. Sakurada, *Papierfabr.* **36**, 252 (1938).

¹¹⁰ D. Finlayson, *J. Textile Inst.* **38**, T50 (1947).

¹¹¹ P. A. Koch, *Textil Rundschau* **4**, 199 (1949); **6**, 111, 281 (1951).

¹¹² K. Breuer, *Kunstseide u. Zellwolle* **21**, 324 (1939).

¹¹³ E. Franz and H. J. Henning, *Melliand Textilber.* **17**, 121 (1936).

¹¹⁴ R. H. K. Thompson and D. Traill, *J. Textile Inst.* **38**, T43 (1947).

this resistance usually consist of a set of grips, each holding one fiber supporting a small weight, the grips being rocked to and fro so that the point where the fiber emerges from the grip is at the center of rotation. There is a large variation in the number of oscillations required to rupture and the distribution is log normal so that the geometric mean is preferable to the arithmetic mean. Type of grip, static tension, and angle of bend all affect the result. For a static stress of 1.5×10^8 dynes/cm.², angle of bend 180 deg., and 200 oscillations per minute, the numbers of oscillations to rupture were⁵ nylon, 250,000; wool, 150,000; silk, 76,000; cotton, 64,000; and staple fiber rayon, 6,800. The superiority of nylon and wool over the cellulose fibers and the outstanding resistance of cotton compared with regenerated cellulose rayon are confirmed by the results of other workers.¹¹⁶ The resistance to repeated bending of cotton and ramie fibers depends on D.P. in a similar way to the tensile strength: thus for D.P. less than 1500, the logarithm of the number of oscillations to rupture (or the tensile strength) decreases linearly with increase in reciprocal D.P. Wool⁷² which has been carbonized by treatment with 4% sulfuric acid shows lowered resistance to repeated bending but when carbonized and neutralized with alkali, the original resistance to repeated bending is restored.

Nomenclature

e	longitudinal strain	S	entropy
E	Young's modulus; E_b bending modulus	T	torque; absolute temperature
f	tensile strength	U	internal energy
$\Delta F^\ddagger$	free energy of activation; also ΔF^* , ΔF	W	strain energy
G	modulus of rigidity	Y	flexural rigidity
h	Planck's constant (6.556×10^{-27} erg. sec.)	α	a parameter = $\lambda/2NkT$; breaking twist angle
j	$\sqrt{-1}$	β	a parameter; rate of creep; rate of decay of torque
k	radius of gyration; Boltzmann's constant (1.379×10^{-16} erg./deg.)	δ	angle of phase lag
K	a parameter = $2(\lambda/\lambda_1) \cdot (kT/h) \exp(-\Delta F^\ddagger/RT)$	ϵ	shape factor
l	length	η	viscosity coefficient
M	moisture regain (%)	λ	distance of jump of molecular segment; relaxation time
N	number of flow units per unit area of cross section	λ_1	distance between points of flow in the direction of flow
p	tensile stress	ν	frequency
P	tension	σ	standard deviation
R	universal gas constant	ω	angular frequency

¹¹⁶ H. Staudinger, M. Sorkin, and E. Franz, *Melliand Textilber.* **18**, 681 (1937).

CHAPTER 8

THE RHEOLOGY OF GELATIN

A. G. Ward and P. R. Saunders

I. Introduction	314
II. Mode of Production and Composition of Gelatine	315
1. The Manufacture of Gelatine	315
2. The Composition of Gelatine	318
III. Rheological Properties of Gelatin	321
1. Viscosity of Gelatin Solutions Outside the Anomalous Region	323
a. Rate of Shear	323
b. Hydrolysis	323
c. Dilute-Solution Viscosity	324
(1) Effect of pH and Added Electrolyte	325
(2) Relation of Reduced Viscosity to Temperature	326
(3) Relation of Reduced Viscosity to Molecular Weight	327
d. Concentrated Solution Viscosity	327
(1) Concentration Dependence	328
(2) pH Dependence	328
(3) Effect of Added Electrolyte	329
(4) Temperature Dependence	329
(5) Action of Ultrasonics	330
(6) Effect of Added Substances	331
2. Rheological Properties of Gelatin Gels	331
a. The Elastic Moduli	332
(1) Strain Dependence	332
(2) Methods of Measurement	334
(3) Effect of Ageing	336
(4) Temperature Dependence	337
(5) Concentration Dependence	339
(6) Swollen Gel.....	342
(7) pH Dependence	343
(8) Effect of Added Substances.	344
(9) Molecular-Weight Dependence.....	346
b. Stress Relaxation and Plastic Flow.. . . .	350
c. Mechanical Properties of Sheet Gelatin.....	351
3. Rheological Properties in the Gelation Region....	353
a. Melting Point and Setting Point	353
(1) Method of Measurement	354
(2) Factors Affecting the Melting Point	354
b. Changes in Viscosity and Rigidity at the Melting Point.....	355

c. Anomalous Viscosity.	356
(1) Rate of Shear	356
IV. Theories of Gel Formation	357
V. Rheological Properties in Relation to the Uses of Gelatine and Glue and to Industrial Testing Methods	359
Nomenclature . . .	362

I. Introduction

The simplicity of forming either a viscous solution or a gel from air-dry gelatin¹ has tempted many investigators to study the rheological properties of the gelatin-water system. Unfortunately the value of the results obtained, and also often of the theories advanced to explain them, has been severely restricted in many of the investigations by a failure to recognize that "gelatin" is a family name, covering a wide range of related materials. The properties of different members of the family can show very large divergences, so that the particular gelatin used in any research work requires most careful specification. Otherwise it may not be possible to relate the work to existing knowledge, nor will it be possible to repeat it using a similar gelatin.² A short account of the manufacture of gelatine is included in Section II to make clear how the different types of gelatin arise, and also to indicate what range of properties may be encountered.

A further difficulty, which occurs especially in measurements on the gel forms, arises from the influence of thermal history on the elastic and related rheological properties. Thermal history is also of importance for the sol forms which exist in the region of the melting and setting temperatures. This is emphasized by the difference between these two temperatures as usually measured for a single gelatin gel.

Precautions must also be taken in order to avoid hydrolysis of the gelatin molecule in aqueous solutions or gels during experiments. This will become increasingly significant, under neutral pH conditions, either as the temperature is raised above 40° C. or as the concentration of proteolytic enzymes (in the solution or as intracellular bacterial enzymes) is increased. The thermal hydrolytic reactions are catalyzed by hydrogen and hydroxyl ions so that the rate of breakdown is increased sharply at acid and alkaline pH's. In these conditions, however, bacteria do not multiply and most enzymes have little action. The extent to which hydrolysis has occurred can normally be assessed by subsequent measurement of some suitable property such as the reduced viscosity, but this is complicated by the simultaneous occurrence of at least two and possibly more different types of hydrolytic reaction (p. 323), which affect different properties in varying degrees.

¹ The term "gelatine" is used for the commercial or laboratory product including inorganic salts and any other impurities. "Gelatin" refers to the derived protein only.

² A. G. Ward, *Brit. J. Appl. Phys.* **5**, 85 (1954).

The main section of this chapter (Section III) is a presentation of the more important experimental facts concerning the behavior of gelatin, whether in the form of a gel, a concentrated or dilute solution, or a dry solid material. Although the results quoted, in most instances, have quantitative validity only for the actual gelatins used, other gelatins would show qualitatively similar behavior.

There have been numerous theories concerning the structure and behavior of gelatin gels, but the complexity of the problem is at present too great for any satisfactory quantitative theory to be developed. In Section IV the more important theoretical views are briefly discussed but no attempt has been made to include speculative theories for which there is little direct evidence.

In Section V a brief review of industrial gelatine testing will be given relating it to the requirements of the many industries which use gelatin, either under the commercial name "gelatine" or as the main constituent of hide and bone glues. In virtue of the small value of most of the early papers, the bibliography has not been made exhaustive but the more reliable papers have in general been included.

II. The Mode of Production and Composition of Gelatine

1. THE MANUFACTURE OF GELATINE

Gelatin is a derived protein, the precursor for all commercially manufactured gelatine being mammalian collagen. Collagen is widely distributed throughout the body in the connective tissues; it occurs in skin, bone, and sinew associated with only minor quantities of other organic substances. Skin and bone are the main commercial sources of collagen for conversion to gelatin, but sinew is also used to a limited extent. Bone is demineralized with hydrochloric acid to give "ossein," which can be handled by the same processes as skin. The same or similar raw materials are used in the manufacture of hide and bone glue, although the process is somewhat different in the latter instance.

If the collagen of any tissue is heated with water at a neutral pH a slow conversion to gelatin takes place, the gelatin being found in solution. The temperature and duration of heating needed are, however, so prolonged that extensive hydrolysis of the gelatin takes place, leaving a product with impaired gel-forming power and lowered viscosity in solution. The essence of the commercial gelatine-manufacturing process lies in treating the collagenous raw material so that a product as little degraded as possible is obtained. This involves increasing the rate at which collagen can be converted to gelatin, at a sufficiently low extraction temperature (e.g., 60° C.) without at the same time impairing the gel-forming power by the treatment used or by effecting too radical a reduction of the viscosity of the product.

Two processes are used commercially:^{3, 4} the alkaline process, in which the collagen receives a lengthy low-temperature pretreatment with mild alkali before being extracted with warm water at a pH near neutrality, and the acid process, in which little or no pretreatment is used other than that necessary to give the raw material an acid pH (pH = 3.5 to 4.0) in some instances), and the extraction with warm water takes place at this pH. The gelatins obtained by these two processes differ in properties in important respects. This emphasizes the need for care in selecting gelatins to use for rheological work.

In the alkaline process, a lime suspension is normally used, to pretreat the raw material, which is placed in large concrete pits or tanks either at ambient temperatures or at a controlled temperature in the region of 15 to 20° C. A period of two to three months is quite usual for the duration of the pretreatment. The full extent of the modifications to the raw material caused by the alkali is only imperfectly understood. Certain impurities are removed, of which some (mucopolysaccharides, other proteins) may well have a cementing action on the collagen. The collagen chain is ruptured at certain points giving fragments more readily dissolved during extraction, and an over-all loss of cohesion is shown by the increased swelling which occurs. In addition the amide (—CONH_2) groups present in the side chains of glutamine and asparagine residues become converted into carboxyl (—COOH) groups. This changes the charge balance in collagen, and in the gelatin derived from it, by increasing the number of acidic groups (negatively charged when ionized). As a result the isoionic (and isoelectric) point, pI, is reduced from the region of pH = 9 to pH = 4.8 to 5.0. The value of the isoionic point of gelatin is usually very similar to that of the pretreated collagen from which it is derived. The position on the pH scale of the isoionic point has a marked influence on the pH dependence of various gelatin properties, especially the viscosity (p. 325).

After completion of the alkaline pretreatment, the collagenous material is washed in various types of drum and paddle washers and brought to a pH near neutrality (pH = 5 to 8 according to individual requirements). Water is added and extraction is carried out in stainless steel or aluminium tanks at 60 to 65° C. After a few hours the first "liquor" or gelatine solution is run off, filtered, evaporated, set, and dried. Water is again added and the extraction continued at a rather higher temperature. In this way, a number of liquors are obtained at higher and higher temperatures, usually ending near 100° C. for the last liquor. The gel-forming power drops uniformly through the extraction, but the solution viscosity (measured under standard conditions) may be a maximum in the second, third, or fourth extraction.

³ W. M. Ames, *J. Sci. Food Agr.* **3**, 454 (1953).

⁴ A. G. Ward, *Chemistry & Industry* p. 502 (1954).

TABLE I
TYPICAL FIGURES FOR THE PROPERTIES OF EXTRACTED GELATINES⁵

Raw material, hide. Lime pretreatment, 10 weeks at 20° C.

Extraction, pH = 6. Gelatine isoionic points, c. pH = 5.

	<i>Extraction</i>				
	<i>1st</i>	<i>2nd</i>	<i>3rd</i>	<i>4th</i>	<i>5th</i>
Temperature of extraction	60° C.	70° C.	80° C.	90° C.	100° C.
Bloom jelly strength (at 6½% concn.)	230 g.	189 g.	125 g.	98 g.	70 g.
Viscosity. Cp. (40° C. 6½% concn.) . .	5.9	7.4	7.7	7.1	5.1

In Table I figures are given to show how the "jelly strength" (p. 361) and solution viscosity change with the successive extractions.

Commercial products are often blends of two or more extractions from different batches of material. This makes fractionation of commercial samples into portions of differing molecular weight of little value unless the history of the sample is known.

In the acid process, the raw material is steeped in dilute acid for a sufficiently long period for a reasonably uniform pH to be established throughout the thickness, and extraction then proceeds as for the alkali-pretreated material. The increased rate of hydrolysis during extraction at the acid pH appears to affect the viscosity more sharply than the jelly strength, at least for the earlier extractions. In contrast to the example of Table I, the viscosity falls throughout extraction. The amide groups are largely intact after the acid process, so that isoionic points near pH = 9 are usual.

Hide glue is made by the same processes as gelatine but often the raw material, or the extent of pretreatment, is such that extraction must be carried on at higher temperatures to give reasonable extraction rates. This reduces the values of the jelly strength and viscosity.

In bone-glue manufacture, degreased bones are treated successively with live steam (pressure 5 to 30 p.s.i.) and hot water, the glue being extracted in the hot water. The mineral present in the bone lessens the effectiveness of the pretreatment of the collagen and also reduces the extraction rate by rendering contact between liquor and collagen difficult. As a consequence, although gelatin is the main constituent of bone glue, it has a reduced gel-forming power and also a lower solution viscosity. This, however, increases the range of properties from which to select a material for a particular use.

⁵ D. Fysh, private information.

TABLE II
TYPICAL PROPERTIES OF GELATINES, BONE AND HIDE GLUES

Sample	Raw Material	Process	Rigidity	Viscosity	pH	pI
			5.65% ¹ 10° C. dynes/sq. ²	5.65% ¹ 40° C. c.p.		
A	Ossein	Alkaline ⁶	100,000	7.1	6.1	4.9
B	Ossein	Alkaline ⁶	62,500	22.8	6.2	5.1
C	Hide	Alkaline	70,000	7.4	7.5	4.9
D	Hide	Alkaline	39,300	9.1	7.2	5.0
E	Hide	Acid	72,000	6.2	4.2	9.1
F	Ossein	Acid	74,600	4.2	4.5	8.6
G	Hide	Alkaline	29,600	6.2	7.0	5.0
H	Hide	Alkaline	15,000	3.5	6.0	5.0
I	Bone	Bone glue	9,000	2.8	5.5	5.3
J	Bone	Bone glue	3,400	2.1	5.5	5.3
K	Bone	Bone glue	650	1.9	5.3	5.1
Viscosity of water 40°C.				0.656		

In Table II, typical figures are given for the properties of a number of gelatines and glues, illustrating the very great quantitative differences in properties encountered.

2. THE COMPOSITION OF GELATINE

Commercial gelatines consist—apart from 1 to 3% of inorganic salts—almost entirely of the derived protein gelatin. The salts present depend to a considerable extent on the process used, but are usually made up of sodium, potassium, and calcium chlorides and sulphates, with small amounts of many other metals, phosphate, etc. It is possible to remove these salts either by dialysis—using the method of Loeb—or more simply by de-ionization using a mixed bed of anion and cation exchange resins. In Table III the most recent amino acid analysis of two hide alkali-process gelatins is given. The technique used was that of Moore and Stein,⁸ and the results are of a high order of accuracy. This is illustrated by the agreement between the figures for the two gelatins, which were first and third extractions of the same raw material.

The figures are in good agreement with other recent published figures. The discrepancy between the recoveries by weight and by nitrogen is probably due to small quantities of nonnitrogenous impurities, some possibly linked to the gelatin molecule.

⁶ Laboratory samples prepared by the authors.

⁷ This concentration W/W is that used in industrial testing (7.5 g. gelatine or glue at 15% moisture content with 105 ml. water). For practical reasons many glues are tested at twice this concentration. The rigidity is after 17 hr. maturing at 10° C.

⁸ S. Moore and W. H. Stein, *J. Biol. Chem.* **192**, 663 (1951).

TABLE III
AMINO ACID COMPOSITION OF FIRST AND THIRD EXTRACTION
LIMED HIDE GELATINS (EASTOE⁹)

	Grams Amino Acid per 100 g. of Dry, Ashfree Gelatin		Residues per 100,000 Molecular Weight	
	1st Extn.	3rd Extn.	1st Extn.	3rd Extn.
Total N ^a	18.19	18.15		
Alanine	11.0	10.8	123	121
Glycine	27.6	27.49	368	366
Valine	2.57	2.49	22.0	21.2
Leucine	3.41	3.23	26.0	24.6
Isoleucine	1.72	1.73	13.1	13.3
Proline	16.5	16.32	143.3	141.6
Phenylalanine	2.29	2.17	13.8	13.2
Tyrosine	0.27	0.32	1.5	1.7
Tryptophan	—	—	—	—
Serine	4.08	4.29	38.9	41.2
Threonine	2.20	2.22	18.5	18.6
Cystine/2	0.00	0.00	0.0	0.0
Methionine	0.86	0.98	5.8	6.7
Arginine	8.7	8.8	50.2	50.5
Histidine	0.82	0.80	5.2	5.1
Lysine	4.26	4.38	29.0	30.0
Aspartic acid	6.6	6.93	49.7	52.1
Glutamic acid	11.6	11.42	79.4	77.7
Amide N ^a	0.12	0.11	8.5	8.1
Hydroxyproline	13.4	13.9	102.3	106.0
Hydroxylysine	0.91	0.95	5.6	5.8
	118.0	119.2	1098.1	1098.2
Mean residue weight (by wt.)	90.4	90.7		
Mean residue weight (by N)				
% recovery (by wt.)	99.1	99.4		
% recovery (by N)	100.2	100.6		

^a Not included in totals.

In acid process gelatins 36% of the total aspartic and glutamic acid residues are present as amide groups.

Neuman^{10, 11} has shown that there is little significant difference in amino acid composition between gelatins or between their parent collagens, within the mammalian class. Fish collagens and gelatins, however, show

⁹ J. E. Eastoe, *Biochem. J.* **61**, 589 (1955).

¹⁰ R. E. Neuman, *Arch. Biochem.* **24**, 289 (1949).

¹¹ R. E. Neuman and M. A. Logan, *J. Biol. Chem.* **154**, 314 (1950).

TABLE IV
N-TERMINAL RESIDUES OF GELATIN
Residues per 100,000 M.W.

	Alkali Processed Hide Gelatin	Acid Process Pigskin Gelatin
Glycine	0.83	0.74
Serine	0.19	0.10
Threonine	0.11	0.08
Alanine	0.11	0.24
Aspartic acid	0.11	0.13
Glutamic acid	0.10	0.07
Others	0.12	0.19
Total	1.57	1.55
M_n	64,000	65,000

appreciable differences which may well be related to the inferior gel-forming power of certain of the fish "gelatins" or of fish glue.

The amino end groups of gelatin have been determined by Courts,¹²⁻¹⁴ using the Sanger fluoro dinitrobenzene technique. Some typical results are given in Table IV.

The values of the number average chain weight C_n are similar to those given by Pouradier from osmometry^{15, 16}. Results with fractions, for C_n using fluoro dinitrobenzene, and for M_w by light scattering suggest that it is unlikely that gelatin molecules have each single polypeptide chains.

The active groups in gelatin are listed in Table V. The important ionizing groups behave in the expected manner when titrated with acid or alkali. Figure 1¹⁷ shows a typical titration curve for an alkali-process gelatin. From the curve, analytical figures for the ionizable groups may be found, in fairly good agreement with the figures of Table III.

All gelatin samples are very heterodisperse^{15, 16} with a range of molecular weights which may extend up to 400,000. Gelatins made from alkali-processed precursors at low extraction temperatures probably contain little low-molecular-weight material. Short fragments produced in the pretreatment dissolve in the alkaline pretreatment liquor, and the extraction causes little further breakdown. Acid-process gelatins will be likely to contain a

¹² A. Courts, reported in A. G. Ward, *Nature* **171**, 1099 (1953).

¹³ A. Courts, *Biochem. J.* **58**, 70 (1954).

¹⁴ A. Courts, *Biochem. J.* **58**, 74 (1954); **59**, 382 (1955).

¹⁵ J. Pouradier and A. M. Venet, *J. chim. phys.* **47**, 11 (1950).

¹⁶ J. Pouradier and A. M. Venet, *J. chim. phys.* **49**, 85 (1952).

¹⁷ A. W. Kenchington and A. G. Ward, *Biochem. J.* in press.

TABLE V
ACTIVE GROUPS IN GELATIN

	<i>No. of Active Groups per 60,000 M.W.</i>	<i>pK (40° C.)</i>	<i>Sign of Charge</i>
α -amino	1	c. 7	Positive
Imidazole	3	7	Positive
ϵ -amino	20	9-10	Positive
Guanidino	30	>12	Positive
Carboxyl (alkali processed gelatin)	78*	3.5-5	Negative
Carboxyl (acid processed gelatin)	50*	3.5-5	Negative
Hydroxyl	105	—	None
Peptide bonds	657	—	None

* Difference due to amide groups in acid-process gelatin.

proportion of low-molecular-weight material produced during extraction. Lower grade material, including bone glue, in which considerable breakdown occurs during extraction, will contain a low-molecular-weight portion.

Summarizing, the only fully verified major chemical differences between gelatins are in the proportion of carboxyl groups remaining in the amide form, and in the number of end groups, the latter corresponding to variations in chain length. Physically, both the various mean molecular weights (M_n , M_w , etc.), and the distribution of molecular weights vary from sample to sample. The existence of ionizable groups on the gelatin molecule causes certain properties to be pH dependent, the behavior varying according to the isoionic point of the gelatin being studied.

It is not yet possible to analyze all the rheological data in terms of structure but it will be seen (p. 349) that the structural description of the previous paragraph is inadequate to account for all properties even qualitatively. This is also evident from a comparison of the properties of the pairs of gelatines in Table II, A, B, and C, D.

III. The Rheological Properties of Gelatin

Gelatin is a powerful gel-forming agent, the lower limit of concentration to form a detectable gel in water at 2° C. being 0.5 g./100 ml. for the highest grades of gelatine. The ability of gelatin gels of a given concentration to support a shearing stress is dependent on the temperature. If the temperature is raised slowly the elastic deformation for a given shearing stress increases rapidly, and plastic components become significant. At a fairly well-defined temperature, the gel melts to a solution devoid of yield value, even at short loading times. The viscosity of the resulting solution decreases

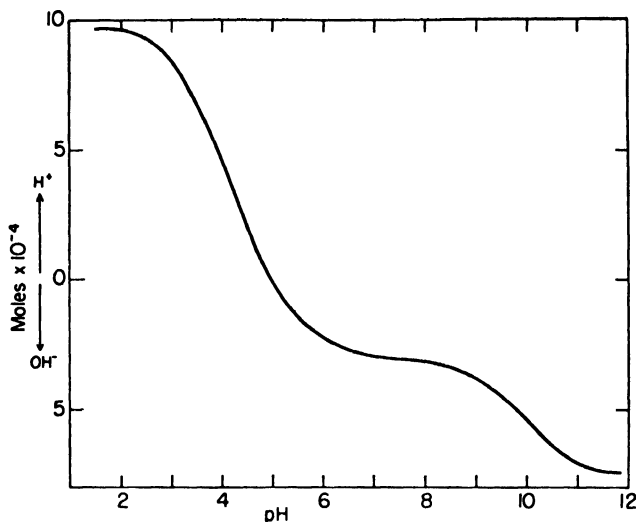


FIG. 1. Titration curve of an alkali-processed gelatin $pI = 4.92$, $40^{\circ}C$.¹⁷

as the temperature is increased. The gel-sol transition temperature or melting point is not a constant of the gelatin but depends also on the concentration, although the change in melting point for a substantial change in concentration is not large. The viscosity of gelatin solutions in the region of the melting point changes with time, decreasing if the solution was obtained by warming a gel (or a solution) originally at a lower temperature, and increasing if obtained by cooling a solution that originally was at a higher temperature. This anomalous behavior is attributed to the formation of aggregates of the gelatin particles which, in the limit, leads to gel formation. Above a temperature in the region of 35 to $40^{\circ}C$. there is no sign of aggregation effects, and changes in solution viscosity only result from degradation.

Lower quality gelatines and the majority of glues, which contain a substantial proportion of the products of hydrolytic breakdown, are not able to form gels at the lower concentrations. The gels which are formed melt more readily than those of high-grade gelatines and give solutions, the viscosities of which indicate the reduced size of the dissolved molecules. It is convenient to classify the rheological properties of aqueous solutions and gels of gelatin in three main groups, corresponding to the simple picture of the molecular processes given above.

1. Properties of the solutions outside the anomalous region.
2. Properties of the gels.
3. Properties in the transition range between gels and sols.

1. VISCOSITY OF GELATIN SOLUTIONS OUTSIDE THE ANOMALOUS REGION

The viscosity of gelatin solutions has been the subject of many studies. The results given below are selected to illustrate the more important aspects. There are two ranges of concentration into which the experiments can be divided: (i) Below 1%. In this range interference, even of purely hydrodynamic character, between the molecules is small. (ii) Above 1%, where normal viscometry is reasonably applicable. At the highest concentrations, the material is only appreciably fluid at temperatures near 100° C., and few data are available concerning this region.

Although in many instances the origin and characteristics of the gelatins which have been used in these investigations are unknown, the viscous behavior of gelatins shows much greater regularity from sample to sample than for many other properties in spite of wide numerical differences. It will be seen, however, that the distinction between acid-process and alkali-process gelatins is a factor of some importance. Before describing the main results, the effect of rate of shear is considered as this indicates the validity of using a viscosity coefficient where nonuniform rates of shear are used (e.g., Ostwald viscometers). The effect of hydrolysis will be briefly noted as this also affects all measurements.

a. Rate of Shear.

The dependence of the viscosity of gelatin solutions, above the gelation temperature, on the rate of shear has been investigated by Bungenburg de Jong and co-workers.¹⁸ They used an Ostwald-type viscometer and varied the rate of shear by applying different air pressures to one limb of the viscometer. Measurements made over the range of concentration from 1.93 to 16.6 g. gelatine per 100 ml., for pH values from 3.4 to 6.6 and at temperatures from 42.10 to 50.79° C. showed that under these conditions the viscosities were independent of the rate of shear. A slight dependence is, however, shown at low concentrations.

b. Hydrolysis.

The viscosity of gelatin solutions decreases irreversibly with time when they are heated, the effect becoming more marked at higher temperatures or at higher acidities or alkalinities. Many observers^{19, 20} have followed the degradation of gelatin in solutions, under various conditions of temperature and pH. Sheppard and Houck^{21, 22} investigated the thermal deg-

¹⁸ H. G. Bundenberg de Jong, H. R. Kruyt, and J. Sens, *Kolloid Beihefte* **36**, 429 (1932).

¹⁹ W. M. Ames, *J. Soc. Chem. Ind.* **66**, 279 (1947).

²⁰ C. E. Davis, E. T. Oakes, and H. H. Browne, *J. Am. Chem. Soc.* **43**, 1526 (1921).

²¹ S. E. Sheppard and R. C. Houck, *J. Phys. Chem.* **34**, 273 (1930).

²² S. E. Sheppard and R. C. Houck, *J. Phys. Chem.* **36**, 2319 (1932).

radation of gelatin solutions at 40, 50, 60, 70, and 85° C. and at several values of pH. By plotting graphs of rate of change of fluidity against pH, and by comparing these with the curves of Northrop²³ for the variation of the velocity constant of hydrolysis with pH determined by the rate of release of amino groups, they concluded that the decrease in viscosity was the result of the hydrolytic rupture of the molecular chains of gelatin. This result has been largely confirmed by the recent studies of Courts¹²⁻¹⁴ on end groups. It would appear that 40° C. is, in most conditions, a temperature at which both aggregation and degradation of molecules are small and it is therefore a useful temperature of measurement whenever these effects should be avoided. The kinetics of gelatin degradation have recently been considered by Pouradier and Venet,²⁴ the assumption being made that the rate of chain breaking depends on the molecular weight by means of the relation $K_x = kM_x$, where K_x is the rate of bond breaking in the molecular species x of molecular weight M_x and k is a constant. Although the exact relation is probably in error, the general treatment appears likely to be a useful contribution.

c. Dilute-Solution Viscosity

For many materials it is possible to define an intrinsic viscosity by extrapolating the reduced viscosity-concentration graph to zero concentration. This technique is valid so long as the environment of the solute molecules does not change as the concentration changes except for the substitution of solvent for solute molecules. For gelatin, this latter condition cannot be fulfilled owing to difficulties in maintaining both pH and ionic strength constant during dilution. Even using deionized gelatin, which gives a solution at a pH virtually identical with the isoionic point for concentrations greater than 1%, the low concentrations cannot be achieved by simple dilution with conductivity water since the pH would then rise toward neutrality as the gelatin concentration approaches zero. Even small pH variations produce marked changes in dilute-solution viscosity for deionized gelatins.

A more satisfactory approach is the use of values of pH and ionic strength such that small variations in these quantities do not affect the viscosity. Stainsby²⁵ has shown that in the presence of 1M NaCl in the pH range 7 to 10 the reduced viscosity $1/C \log_e \eta_{rel.}$, which to a first order is mathematically equivalent to $\eta_{sp.}/C$, is nearly independent of gelatin concentration up to 1% concentration, and consequently it is sufficient to measure the reduced viscosity at one gelatin concentration with these conditions, say 0.2 g. (100 ml.), in order to characterize a gelatin. This is also found in

²³ J. H. Northrop, *J. Gen. Physiol.* **3**, 715 (1921).

²⁴ J. Pouradier and A. M. Venet, *J. chim. phys.* **49**, 238 (1952).

²⁵ G. Stainsby, private information.

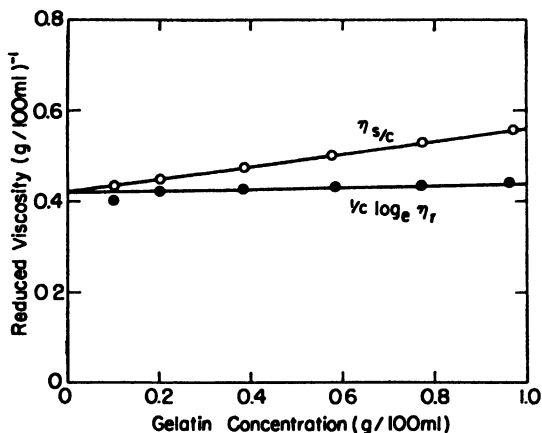


Fig. 2. η_{sp}/C and $1/C \log_e \eta_r$ as a function of concentration for an ashfree alkali-processed gelatin at its isoelectric point (pH = 5.08) in pure water. Temperature 35° C.²⁵

practice for deionized gelatin at the isoionic point, although the pH of each solution requires adjustment. Figure 2 illustrates the variation of η_{sp}/c and $1/C \log_e \eta_{rel}$ with concentration for a deionized alkali-treated calfskin gelatin at its isoionic point (pH = 5.08) and at a temperature of 35° C. Pouradier and co-workers have used the $\lim_{C \rightarrow 0} \eta_{sp}/C$ at the isoionic point to determine the relation between this limit and the molecular weight.

(1) *The effect of pH and added electrolyte.* The effect of pH and electrolyte on the reduced viscosity of a deionized alkali-treated calfskin gelatin (pI = 5.08) is illustrated in Figure 3. The reduced viscosity is a minimum at the isoionic point and rises to maxima at pH = 3.1 and pH = 10.7. This behavior is similar to that found for aqueous solutions of polyelectrolytes by Katchalsky.²⁶ The reduced viscosity of co-polymers of methacrylic acid and vinylpyridine was a minimum at the isoionic point and increased to maxima in both the acid and alkaline ranges. The addition of electrolyte decreases the dependence of reduced viscosity on pH, and in 1.0M NaCl, the reduced viscosity is independent of pH in the pH range 7 to 10 (see curve 3 of Fig. 3). These conditions of pH and electrolyte content are very convenient in use, because small discrepancies in pH or salt concentration have a negligible effect on the reduced viscosity. Stainsby²⁷ has accounted for his results theoretically on the assumption that the presence of a net charge distributed along the gelatin molecule gives rise to repulsive forces which are a maximum at zero ionic strength. At the isoionic point there is no net charge, and the numerically equal positive and negative charges

²⁶ A. Katchalsky, *J. Polymer Sci.* **7**, 393 (1951).

²⁷ G. Stainsby, *Nature* **169**, 662 (1952).

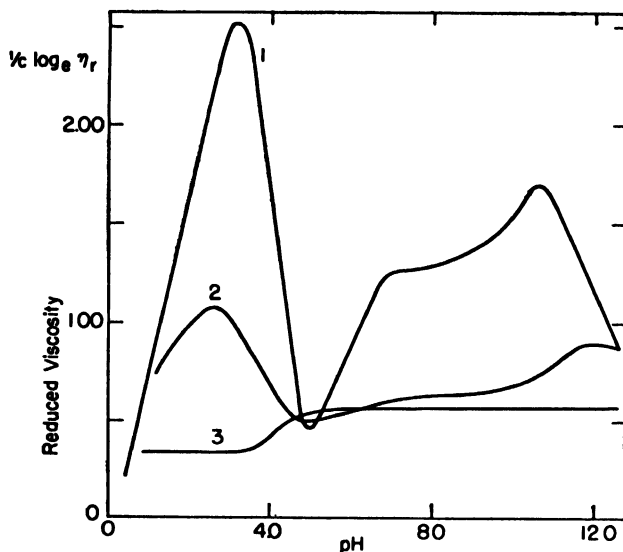


FIG. 3. Reduced viscosity of gelatin in dilute solutions as a function of pH and salt content. Alkali-treated precursor, $pI = 5.08$. Curve 1, 0.2% ashfree gelatin in pure water; curve 2, 0.2% ashfree gelatin in 0.017 M salt; curve 3, 0.2% ashfree gelatin in 1.00 M salt.²³

along the chains cause the maximum folding. As the pH is raised or lowered, the net charge increases, and the chains unfold. However, in order to raise or lower the pH, acid or alkali requires to be added. At a certain stage the counter ions resulting from these additions are sufficiently numerous to reduce the forces between the charges. Hence beyond certain pH's the unfolding is reduced again. Electrolyte addition similarly reduces the forces for a given net charge. The pH dependence of the reduced viscosity of an acid-processed pigskin gelatine²⁵ is very different, as would be expected from the different relation of net charge to pH; in particular when deionized material is used to which acid and alkali have been added, there is a broad minimum stretching from pH 6 to 10. This illustrates that each type of gelatin should be studied individually and great care is necessary when applying the known properties of one gelatine to another.

(2) *Relation of reduced viscosity to temperature.* Stainsby²⁵ has measured the reduced viscosity of 0.2% solutions of an alkali processed calfskin gelatin ($pI = 5.08$) at temperatures of 10, 25, 35, and 40° C., in the presence of 1.0M NaCl and in the pH range 7 to 10. While the reduced viscosity is independent of temperature in the range 35 to 60° C., it is higher, and increases with time, at 25 and 10° C., presumably because of molecular ag-

²³ J. Pouradier and A. M. Venet, *J. chim. phys.* **47**, 391 (1950).

gregation. At 0.1 % concentration, the figure at 25° C. agrees with that at 35° C. if measured a short time after cooling.

(3) *Relation of reduced viscosity to molecular weight.* Pouradier and Venet²⁸ fractionated an alkali-processed gelatin (pI = 4.75) and investigated the osmotic pressure and reduced viscosity of solutions of the fractions at several concentrations. Values for the number average molecular weight, M_n , of the fractions were calculated from the limiting value of osmotic pressure at zero concentration and these were compared with the values of reduced viscosity extrapolated to zero concentration. The osmotic-pressure measurements were made at 38.5° C., the pH being maintained at the isoionic point by means of acetic acid buffer. The reduced viscosities were also measured at the isoionic point at 35° C. The limiting value of the reduced viscosity was related to the number average molecular weight according to the equation

$$\lim_{C \rightarrow 0} \eta_{\text{red.}} = 1.66 \times 10^{-5} M_n^{0.885}$$

It is doubtful whether Pouradier's results justify quoting three significant figures for the index. Without serious error the results could be interpreted as a direct proportionality between the limiting value of reduced viscosity and M_n , or alternatively a lower figure for the index.

Scatchard *et al.*²⁹ measured the reduced viscosity and osmotic pressure of degraded ossein gelatin solutions. They determined the limiting value of the reduced viscosity $1/C \log_e \eta_{\text{rel}}$ at pH 7.0 in the presence of 0.15M NaCl, at a temperature of 55° C. Values of M_n from the osmotic pressure measurements were shown to be approximately proportional to $\lim_{C \rightarrow 0} 1/C \log_e \eta_{\text{rel}}$.

for values of M_n from 45,700 to 15,000.

d. Concentrated Solution Viscosity.

One might expect the nature of the gelatin solution to change as the concentration is increased, quite apart from the increased hydrodynamic interaction between the gelatin molecules. However, no fundamental change has been detected from viscosity measurements at concentrations as high as 50 g./100 ml.

The viscosity of solutions of an alkali-processed gelatine (Davis Co., Australia) of pI = 5.0 and in the concentration range 15 to 48 g./100 ml. was measured by Cumper and Alexander,³⁰ using a concentric-cylinder apparatus at 40° C. They found that the limiting value of $\eta_{\text{sp.}}/C$ as $C \rightarrow 0$ was in excellent agreement with the value of the reduced viscosity obtained from dilute-solution measurements. The authors with Stainsby³¹ investi-

²⁹ G. Scatchard, J. L. Oncley, J. W. Williams, and A. Brown, *J. Am. Chem. Soc.* **66**, 1980 (1944).

³⁰ C. W. N. Cumper and A. E. Alexander, *Australian J. Sci. Research* **A5**, 146 (1952).

³¹ G. Stainsby, P. R. Saunders, and A. G. Ward, *J. Polymer Sci.* **12**, 325 (1954).

gated the concentrated-solution viscosity (at a concentration of 5.5 g./100 ml.) and the dilute-solution viscosity (at 0.2 g./100 ml.) of fractions of several types of gelatin, including acid- and alkali-processed hide and ossein gelatines. The temperatures used were 40° C. for the concentrated-solution measurements and 35° C. for the dilute-solution measurements. The pH of the solutions used was approximately 7.0. It was found that there was no significant departure from a unique connection between the two measurements for all fractions of all types of gelatine, and it was concluded that the concentrated-solution viscosity could be used as a measure of the average size and shape of gelatin molecules under given ionic conditions.

(1) *Concentration dependence.* The concentration dependence of the viscosity of concentrated gelation solutions has been investigated by many observers.^{18, 32-34} Although neither the gelatin samples nor the conditions of measurement of the viscosities were identical, all the results indicated that the viscosity of a given gelatine solution is approximately an exponential function of the concentration, at least over a limited concentration range. Davis and Oakes,³³ using a hide gelatine, found that the logarithm of the relative viscosity of solutions measured at pH = 8.0 and at a temperature of 40° C. was directly proportional to the gelatin concentration, in the concentration range of 1 to 5 g./100 ml. The authors' work has shown that this is only an approximation, the divergence in the concentration range 1 to 6% being quite marked. At much higher concentrations, Cumper and Alexander³⁰ found that the viscosity of solutions of a demineralized alkali-processed gelatine (Davis Co., Australia) in the concentration range of 15 to 48 g./100 ml. could be represented by the equation

$$\log \frac{\eta_{sp.}}{C} = -1.5 + 4.3 \times 10^{-3}C + 3.5 \times 10^{-6}C^2$$

(2) *pH dependence.* Several workers^{32, 33} have investigated the manner in which the viscosity of concentrated gelatin solutions depends on pH. The pH effect is similar to that for dilute solutions, in that the viscosity is a minimum at the isoionic point and there are maxima in the acid and alkali ranges. Stainsby²⁵ found that the viscosity of solutions of the same alkali-processed calfskin gelatine already studied in dilute solution (p. 325) gave, at a concentration of 5.5 g./100 ml., a minimum at the isoelectric point and maxima at pH = 3 and pH = 11. Under the conditions used, it was confirmed experimentally that hydrolysis was negligible. Using a de-ashed Eastman gelatine (presumably alkali-processed), Sheppard and Houck²¹

³² R. H. Bogue, *J. Am. Chem. Soc.* **43**, 764 (1921).

³³ C. E. Davis and E. T. Oakes, *J. Am. Chem. Soc.* **44**, 464 (1922).

³⁴ J. H. Northrop and M. Kunitz, *J. Phys. Chem.* **35**, 162 (1931).

investigated the viscosity of solutions of concentration of 7 g./100 ml. at 40° C., at many values of pH between 1.9 and 12.0. Their results followed the behavior indicated above, but they found that the shape of the viscosity-pH curve changed with the age of the solutions, and that the viscosities at the extreme values of pH decreased rapidly, particularly on the acid side, as the result of hydrolysis. For solutions of age 14 hr., there was no maximum on the acid side of the viscosity-pH curve.

(3) *Effect of added electrolyte.* The viscosity of concentrated solutions of gelatin is in general decreased by the addition of electrolyte. Cumper and Alexander²⁰ found that the viscosity of solutions of the alkali-processed gelatin they were using, at 40° C. in the concentration range 27 to 45 g./100 ml., was decreased by adding NaCl up to an ionic strength of 1.5, when it began to increase again, possibly because of salting-out effects. Stainsby²⁵ has investigated the effect of sodium chloride on the viscosity of solutions of the alkali-processed calfskin gelatine (pI = 5.08 and concentration 5.6 g./100 ml.) at 35° C. as a function of pH. His results are illustrated in Fig. 4. The relative viscosity is reduced by the presence of salt at all values of pH. It should be noted that the viscosity difference between the maxima, and the minimum at the isoelectric point, is much smaller than for the dilute solutions. This is to be expected because the ionic strengths are very much higher at a given pH for the solutions to which salt has not been added, owing to the buffering power of the gelatin molecules. There may be some secondary effects resulting from the presence of other gelatin molecules.

(4) *Temperature dependence.* The decrease in the viscosity of concentrated solutions of gelatin with increasing temperature is roughly exponential for temperatures above the gelation region. If measurements are continued into

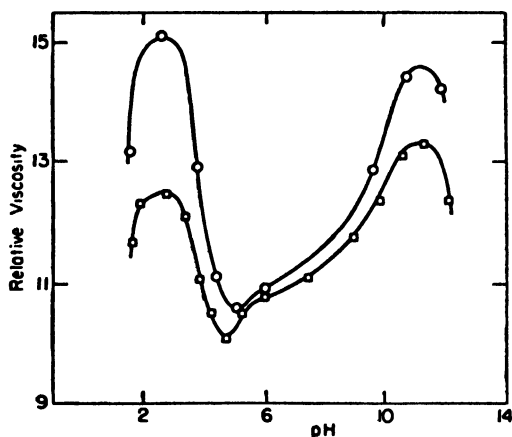


FIG. 4. The relative viscosity for 5.6% solutions of an alkali-processed calfskin gelatin at 35° C. Upper curve—no salts. Lower curve—0.03 M NaCl.²⁵

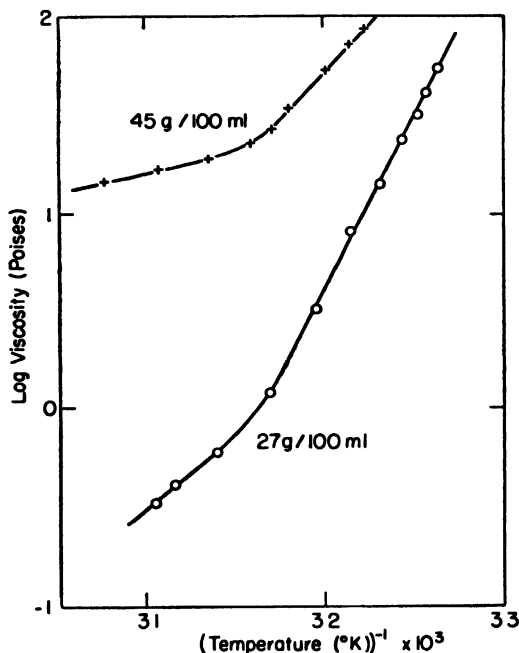


Fig. 5. Viscosity as a function of temperature for two concentrations of an alkali processed gelatine.³⁰

the gelation region then the viscosity rises rapidly, e.g., Davis and Oakes³³ found that the slope of the viscosity-temperature curve changed discontinuously at 38° C. for a 1 % solution of a hide gelatin (pH = 8.0). Cumper and Alexander³⁰ treated their results in a different way. They plotted the logarithm of the viscosity against the reciprocal of the absolute temperature (Fig. 5). They used deionized alkali-processed gelatine (Davis Co., Australia) at concentrations of 27 and 45 g./100 ml. The slopes of the graphs changed abruptly at a temperature of 43° C., indicating that the viscosity increases more rapidly with temperature below 43° C. It appears from this that the minimum temperature of measurement for the viscosity of gelatin solutions, in order to be uninfluenced by gelation effects, must rise above 40° C. for the higher gelatin concentrations.

(5) *Action of ultrasonics.* The irradiation of a solution of gelatin by ultrasonics reduces the viscosity of the solution. This is presumably due to breakdown of the gelatin molecules. It has been confirmed by Morel and Grabar,³⁵ who found that the number average molecular weight, deduced by osmotic pressure measurements, was reduced. When the gelatin solutions were subjected to prolonged irradiation, the viscosity decreased until finally it became almost steady. It would appear that the molecules are not broken

³⁵ J. Morel and P. Grabar, *J. chim. phys.* **48**, 632 (1951).

down further once a limiting size has been reached ($M_n = 20,000$). These solutions failed to gel when cooled.

(6) *Effect of added substances.* Organic Liquids. The viscosity of aqueous solutions of gelatin is modified by the addition of organic liquids miscible with water. These liquids may be classified in two groups: (1) those which precipitate gelatin, such as ethyl alcohol and acetone, and (2) liquids such as acetic acid and formamide, for which gelatin is soluble in the pure liquid. The absolute viscosity of solutions of gelatin in mixtures of water and ethyl alcohol increases with increasing percentage composition of ethyl alcohol, until at sufficiently high concentrations the gelatin is precipitated. However, the relative viscosity of these solutions decreases with increasing alcohol concentration, which parallels the effect of precipitants with nonpolar polymers. Mardles³⁶ studied the viscosities of solutions of best quality Coignet and Nelson gelatines in solutions of water mixed with acetic acid or formamide. He found that the curve relating viscosity and composition of the solvent was similar in shape to that for the pure liquids but greatly exaggerated, i.e., the viscosity of the gelatin solutions increases to a maximum and then decreases as the composition of the solvent changes from one extreme to the other.

Chrome Alum. Hardening substances such as chrome alum form bonds with certain groups on the gelatin molecule, and consequently the viscosity of chrome alum gelatin solutions changes with time. Pouradier,³⁷ using a de-ashed Eastman-Kodak limed calfskin gelatine showed that at a gelatin concentration of 0.85 g./100 ml. and chrome alum concentrations between 2.5 at 10.0 %, at pH = 4.75, the specific viscosity decreased and that at a gelatin concentration of 1.7 g./100 ml. and similar conditions of chrome alum and pH the specific viscosity increased as the time increased. This can be explained by assuming a preponderance of intramolecular bonding in dilute gelatin solutions, which becomes negligible in comparison with intermolecular bonding as the gelatin concentration increases.

Formaldehyde. Bogue³⁸ states that formaldehyde reacts with gelatin to form an insoluble condensation product. He studied the viscosity temperature curves of formaldehyde-glue solutions and found that below 40° C. there was in the initial stages a reduction in viscosity, whereas above 50° C. a rapid reaction occurred with increasing viscosity and finally gelation.

2. RHEOLOGICAL PROPERTIES OF GELATIN GELS

The temperature range of existence of gelatin gels is small—from the point at which the gel melts to a solution (which depends on the grade of

³⁶ E. W. J. Mardles, *Biochem. J.* **18**, 215 (1924).

³⁷ J. Pouradier, *Discussions Faraday Soc.* **16**, 180 (1954).

³⁸ R. H. Bogue, "The Chemistry and Technology of Gelatin and Glue," p. 190. McGraw-Hill, New York, 1922.

gelatin and on its concentration) to the ice point (below which ice crystallizes out). The properties of gelatin gels are continually changing with time, e.g., the rigidity of a gelatin gel maintained at constant temperature increases with time and shows no sign of becoming constant. For precise work, it is essential to maintain accurate temperature control because the mechanical properties of the gels are sensitive, not only to the temperature of measurement, but also to the thermal history of the gel. It is clear from the foregoing that measurements of the mechanical properties of gelatin gels require special apparatus and techniques.

It is convenient to express the results of experiments where a shearing stress is applied to gelatin gels in terms of a modulus of elasticity, the rigidity modulus. Such a modulus can always be defined for vanishingly small deformations but it will be seen that within reasonable limits of accuracy the modulus can be used for a variety of measurements where the strain is not sufficiently large to require the use of finite strain theory. When a gel is maintained at constant strain, the stress gradually decreases with time, and the gel exhibits stress relaxation. Experiments where small stresses are applied for short times indicate that although time-dependent effects are present (elastic aftereffects), the strain is recoverable when the stress is removed. However, when the stress is applied for a time of the order of an hour, the strain does not return to zero on removal of stress, corresponding to the occurrence of plastic flow. When a shearing stress is applied to a gelatin gel for a short time, of the order of 30 sec., creep is very small and, provided a certain limiting strain is not exceeded, Hooke's law is obeyed. Under these conditions, assuming Poisson's ratio to be 0.5, and that the conditions of setting produced no preferred orientations, it is possible to calculate Young's modulus of elasticity from the modulus of rigidity by means of the relation $Y = 2G(1 + \sigma) = 3G$. It will be seen that at higher values of strain, Hooke's law does not apply and the interpretation of these results requires the use of finite strain theory. No serious attempt has yet been made to apply to gelatin gels an approach similar to that used so successfully for rubber, and other elastomeric high polymers.

a. The Elastic Moduli

(1) *Dependence of the modulus of elasticity of gelatin gels on strain.* Sheppard and Sweet³⁹ using a torsion apparatus, investigated the validity of Hooke's law for gels of a typical "hard gelatin" at concentrations ranging from 8.5 to 34 g./100 ml. Hooke's law was obeyed almost to the breaking point and there was no evidence of a yield point. However, Poole⁴⁰ found that Young's modulus of gels of Nelson's No. 1 photographic gelatin was a function of extension for values of $\Delta e/e_0$ between zero and 0.4 (Fig. 6). This variation

³⁹ S. E. Sheppard and S. S. Sweet, *J. Am. Chem. Soc.* **43**, 539 (1921).

⁴⁰ H. J. Poole, *Trans. Faraday Soc.* **21**, 114 (1925).

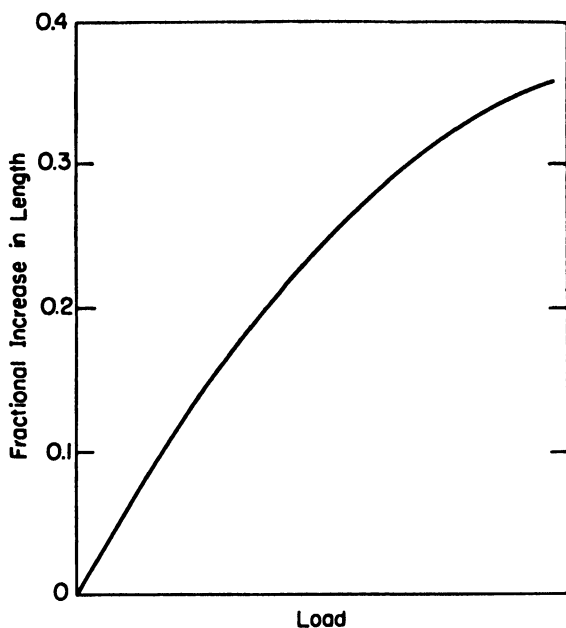
FIG. 6. Load-strain curve for a gelatin gel in extension.⁴⁰

TABLE VI

DEPENDENCE OF MODULUS OF RIGIDITY ON SHEAR STRAIN⁴¹

Modulus of rigidity $\times 10^{-4}$ (dynes/cm. ²)	6.56	6.58	6.61	6.64	6.66	6.69	6.75	6.80	6.84
Average shear strain	0.044	0.056	0.069	0.081	0.108	0.121	0.135	0.147	0.161

has recently been confirmed by the authors' results in shear⁴¹ for an alkali-processed calfskin gelatin ($pI = 5.08$). Table VI gives results for a gel of concentration 5.5 g./100 ml. after maturing for 17 hours at 10°C. and measuring at 10° C. (p. 336 for method). These results show clearly that when values of rigidity are quoted, it is necessary to quote the strain region in which they were measured. The authors have found that the apparent rigidity increases rapidly with increasing strains of the order of 0.5 to 1.0 and also that the rigidity of different grades of gelatin depends on the strain in different manners. Consequently any methods of measuring the rigidity or related properties of gelatin gels, which depend on high local strains, such as many industrial methods of measuring "jelly strength"

⁴¹ P. R. Saunders and A. G. Ward, *Proc. 2nd Intern. Congr. Rheol., Oxford* p. 284 (1954).

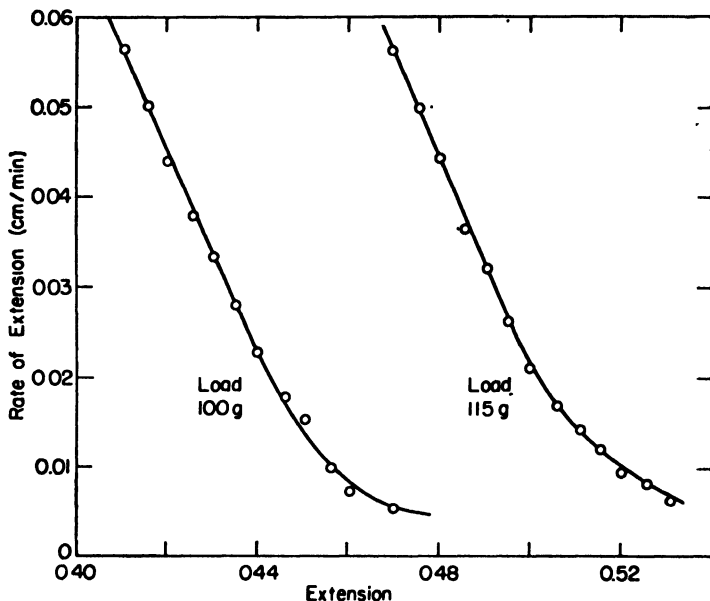


FIG. 7. Rate of extension-extension curves for a 16.7% gelatin jelly at 15° C.⁴⁰

are suitable only for comparisons of the rigidity of gels of similar gelatins. Hatschek⁴² confirmed Poole's results for increase of Young's modulus with increasing strain in extension, but found that Young's modulus for 10% gels of a hard gelatine at 17° C. decreased with increasing strain in compression.

(2) *Methods of measuring the elasticity modulus of gelatin gels.* Longitudinal Extension of Gel Specimens. Young's modulus of gelatin gels may be determined by methods normally applicable to solids, e.g., the bending or stretching of strips of known dimensions.⁴³ Poole⁴⁰ investigated the behavior in tension of gels of Nelson's No. 1. gelatine with concentrations ranging from 3.2 to 32.0 g./100 ml. and at temperatures from 5.7 to 27° C. He extended cylinders of gel of known dimensions by hanging weights on the end. Gels which were so weak that they might distort under their own weight were supported by buoyancy in an immiscible liquid and the stress was applied by means of one arm of a gravimetric balance. He also investigated the extension of the gels at constant load as a function of time of loading and found that plots of rate of extension vs. extension were linear up to a certain extension, and then became curvilinear (Fig. 7). The slope of the linear part was independent of load and the final portion of the curve corresponded to an irreversible flow, since for extensions greater

⁴² E. Hatschek, *J. Phys. Chem.* **36**, 2994 (1932); *Trans. Faraday Soc.* **29**, 1108 (1933).

⁴³ A. Leick, *Ann. Physik* **14**, 139 (1904).

TABLE VII
EXTENSION OF GELATIN GELS (POOLE⁴⁰)

Nature and Condition		Load	Permitted Extension	Extension at Transition Point	Difference	Observed Permanent Extension
33.3%	19° C.	100 g.	0.172 cm.	0.154 cm.	0.018 cm.	0.023 cm.
33.3%	19° C.	150	0.244	0.222	0.020	0.020
33.3%	19° C.	200	0.308	0.292	0.016	0.018
33.3%	19° C.	308	0.482	0.452	0.030	0.039
15%	5.7° C.	60	0.189	0.179	0.010	0.009
21%	5.7° C.	100	0.179	0.170	0.012	0.009
40%	5.7° C.	300	0.158	0.152	0.006	0.006
20%	18.7° C.	30	0.129	0.124	0.005	0.005

than the critical value the jelly acquired a permanent extension. The irreversible extensions probably involved the same mechanism as Ferry's stress relaxation (see p. 350). Some of Poole's results are shown in Table VII.

Longitudinal Compression Method. One serious difficulty encountered in extension methods is the gripping of the gel specimens without damage. This difficulty is removed if the gels are compressed instead of extended. Hatschek⁴² measured Young's modulus by compressing cylinders of gelatin gel in a simple press. The cylinders were cast in wax-coated metal tubes and by setting the gels above paraffin wax and below paraffin oil the ends of the cylinders were flat. The ratio of length to diameter of cylinder was never greater than 1.4. This method, however, introduces serious difficulties in connection with friction at the surfaces at which the compression loads are applied.

Torsion of Cylinders of Gel. The modulus of rigidity of a gel may be determined by subjecting cylinders of gel to torsion, in the same way that the static rigidity of a metal wire or rod is measured. Sheppard *et al.*⁴⁴ modified the technique by rotating one end of the cylinder of gel at a constant speed while the other end was free to rotate against a restoring torque, which increased in proportion to the rotation. He was able to measure the modulus of rigidity right up to the point at which the gel ruptured. This method, like all methods which involve the use of gel test pieces, has the disadvantage that the dimensions of the specimens must be known accurately and that the specimens are fragile and easily damaged. These difficulties are overcome in the following methods.

Concentric-Cylinder Apparatus. Many workers have used a concentric cylinder apparatus to measure the modulus of rigidity of gelatin gels⁴⁵⁻⁴⁸.

⁴⁴ S. E. Sheppard, S. S. Sweet, and J. W. Scott, *Ind. Eng. Chem.* **12**, 1007 (1920).

⁴⁵ E. Hatschek and R. S. Jane, *Kolloid-Z.* **39**, 300 (1926).

This method has the advantage of involving a nearly constant shearing stress. The gel is set in the annular space between the concentric cylinders and a known torque is applied to one of the cylinders, while the other cylinder is allowed to rotate against the known restoring force of a wire suspension. Kinkel and Sauer⁴⁶ used this type of apparatus to investigate the creep curve of gelatin gels, at constant shearing stress. They found that the angular increase $\Delta\theta$ after time t was given by the empirical equation $\Delta\theta = k \log t + C$. However, the duration of the observations was only of the order of minutes and it is not clear whether the equation would hold for longer times. It is also not clear what proportion of the deformation must be regarded as irreversible. The relation they give cannot be reconciled with Poole's equation for creep.

Longitudinal Shearing of Gels Set in a Glass Tube. Kinkel and Sauer⁴⁶ measured the rigidity of gelatin gels by observing the distortion of the gel meniscus when air pressure was applied to a gel set in a glass tube. Adhesion of the gel to the wall was sufficient to prevent slip. The shearing stress varied from a maximum at the tube wall to zero along the axis of the tube. Recently the authors⁴¹ have modified this method by measuring the volume displacement of the gel instead of its longitudinal displacement. By allowing this volume change to displace mercury along a capillary tube it was possible to measure the volume displacement accurately. The method is now probably the most convenient for a rapid measurement of the rigidity modulus in the small-strain region.

Transverse Wave Propagation. Ferry⁴⁹ has described a method for measuring the modulus of rigidity of gelatin gels, which makes possible an investigation into any dispersion of the dynamic rigidity with frequency. The wavelengths of transverse vibrations Λ in a gelatin gel of density ρ are measured at various frequencies ν by observing the strain double refraction stroboscopically. The modulus of rigidity $G = \rho\Lambda^2\nu^2$. This method could be used to investigate the damping characteristics of a gelatin gel by observing the decay in the amplitude of vibration as a function of the distance from the source of vibration.

(3) *Change of rigidity with time at constant temperature.* When a gelatin solution gels, it does not assume a constant value of rigidity, even though its temperature is constant; on the contrary, the rigidity increases rapidly with time for several hours before settling down to a slow increase. It has never been observed to attain a constant value. The rigidity, as measured by Ferry's method of transverse vibrations, at three concentrations of com-

⁴⁶ E. Kinkel and E. Sauer, *Z. angew. Chem.* **38**, 413 (1925).

⁴⁷ F. W. Schremp, J. D. Ferry, and W. W. Evans, *J. Appl. Phys.* **22**, 711 (1951).

⁴⁸ C. W. N. Cumper and A. E. Alexander, *Australian J. Sci. Research A5*, 153 (1952).

⁴⁹ J. D. Ferry, *Rev. Sci. Instr.* **12**, 79 (1941).

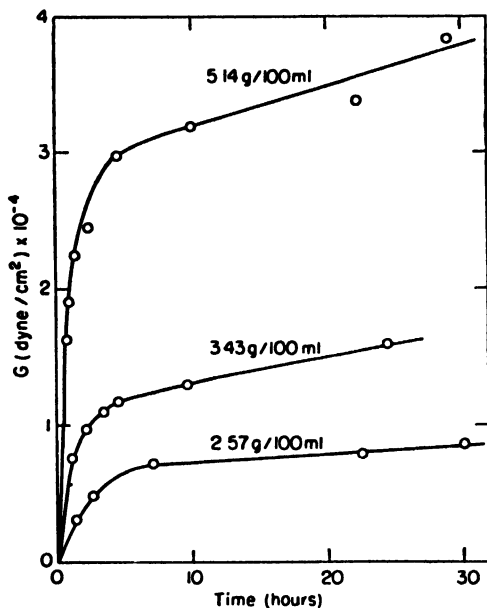


FIG. 8. Increase of rigidity of gelatin gels with time⁵⁰

mercial calfskin gelatine,⁵⁰ is shown in Fig. 8 as a function of time of maturing the gel. It is clear from these results that a gelatin gel cannot possess a unique value of the modulus of rigidity, and that for comparative work it is essential to specify the age as well as the aging temperature of the gel. However, Ferry⁵¹ has found that by precooling the gel at a low temperature of, say, 0° C. for 24 hours and then raising the temperature to the temperature of measurement, the rigidity changes rapidly at first, but reaches an approximately constant value within about five hours. This is illustrated in Fig. 9 for an Eastman-Kodak calfskin gelatine $M_n = 37,000$, gel concentration 2.74 g./100 ml., aging conditions 0° C. for 24 hours, and measuring temperature 15° C. It is likely that slow further maturing would occur, but the method is a useful practical device.

(4) *Rigidity as a function of temperature.* It has long been recognized that the rigidity of gelatin gels is markedly dependent on the temperature of measurement, varying from relatively large values at 0° C. to zero at the melting point. Ferry⁵¹ has measured the rigidities of gels of a degraded ossein gelatine ($M_n = 45,000$) at several different concentrations ranging from 2.3 to 5.75 g./100 ml. and at several temperatures, and has plotted his results as G/C^2 vs. temperature (Fig. 10). These results were obtained by

⁵⁰ J. D. Ferry, *Advances in Protein Chem.* **4**, 21 (1948).

⁵¹ J. D. Ferry, *J. Am. Chem. Soc.* **70**, 2244 (1948).

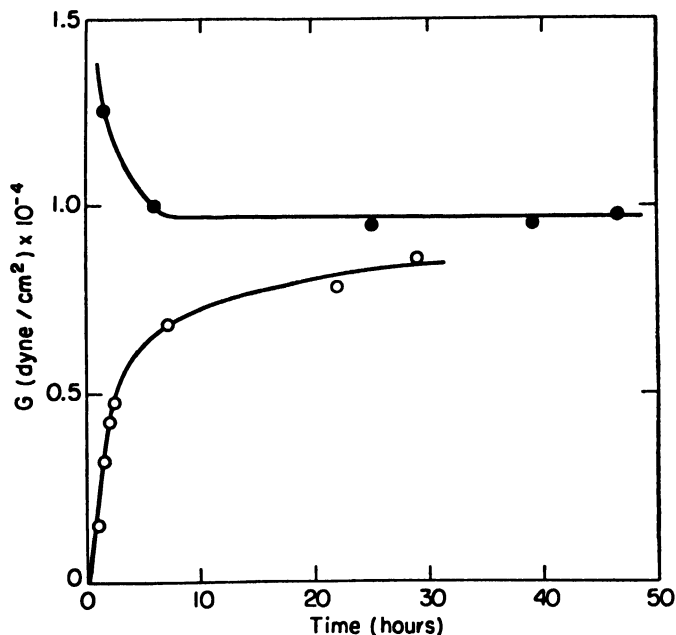


Fig. 9. Change of rigidity with time at 15° C., gelatin $M_n = 37,000$, concentration = 2.74 g./100 ml., pH = 5.4, ● after warming from 0° C.; ○ after cooling from 37° C.⁵¹

precooling, and aging at 0° C., then bringing the gel to the temperature of measurement as described earlier. Since the points representing several different concentrations of the same gelatin fell on the same curve, the rigidity for this gelatin is seen to be proportional to the square of the gelatin concentration (see p. 339). The points in the neighborhood of 0° C. clearly do not represent equilibrium values, because the gels have only been matured for 24 hours without precooling. Consequently the point of inflection in the curve may be regarded as an artefact. Higher values of the rigidity at 0° C. would be obtained if it were possible to precool below 0° C. There is a spread of values of G/C^2 , at temperatures near the melting point, but this is to be expected because the melting point of a gelatin gel is a function both of the concentration and of the time at a given temperature. Several other gelatines were investigated, including calfskin and pigskin gelatines supplied by the Atlantic Gelatin Company, and the general shapes of the curves were similar. However, a degraded ossein gelatin ($M_n = 34,000$) gave a separate curve for each concentration, indicating that the square law of concentration dependence did not apply. Ferry and Eldridge⁵² investigated the temperature dependence of the rigidity of a gel of a degraded

⁵² J. D. Ferry and J. E. Eldridge, *J. Phys. & Colloid Chem.* **53**, 184 (1949).

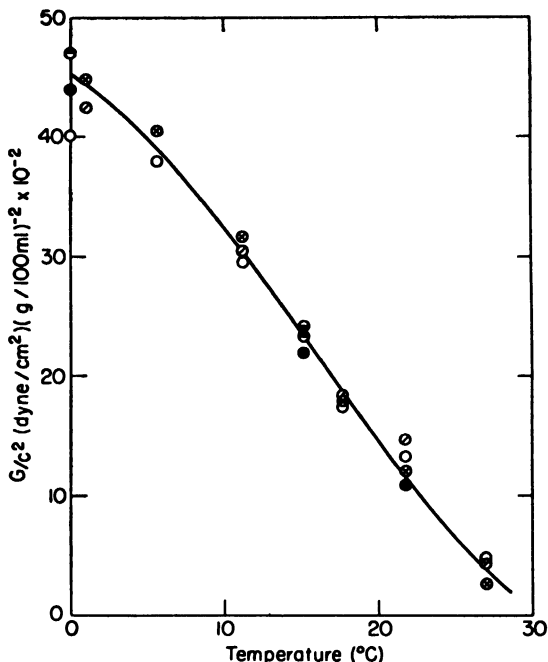


FIG. 10. G/C^2 plotted against temperature for a gelatin, $M_n = 45,000$. Concentrations in grams per 100 ml. $\circ$ 5.75; $\bullet$ 4.6; $\odot$ 4.0; $\ominus$ 3.45; $\otimes$ 2.5; $\ominus$ 2.3.⁵¹

ossein gelatin ($M_n = 44,440$), at 4.17 g./100 ml. concentration, which had been precooled at 15° C. for 24 hours, instead of at 0° C., the temperature then being raised before measuring the modulus. The results, together with those for a gel aged at 0° C., are shown in Fig. 11. In both cases, the values of rigidity are identical, except for temperatures in the immediate vicinity of 15° C.

(5) *Dependence of rigidity of gelatin gels on concentration.* The investigations of Leick⁴³ indicated that the rigidity of a gelatin gel was proportional to the square of the gelatin concentration. In the light of their own work on a typical "hard gelatin," Sheppard and Sweet³⁹ concluded that Leick's results applied to a special limiting case and that the rigidity was proportional to the n^{th} power of the gelatin concentration, where $n \leq 2$. However, Kinkel and Sauer⁴⁶ investigated several types of gelatin, including some which had been thermally degraded, and found that the square law was true for unspecified commercial gelatines but that the more general law of Sheppard and Sweet applied to degraded gelatins, with n being greater than 2; e.g., a gelatin which had been degraded at 100° C. for 3½ hours, gave $n = 2.745$, while the undegraded gelatin gave $n = 2.0$. Poole⁴⁰ working with Nelson's No. 1 gelatine in the concentration range 3.23 to 32.0 g./100

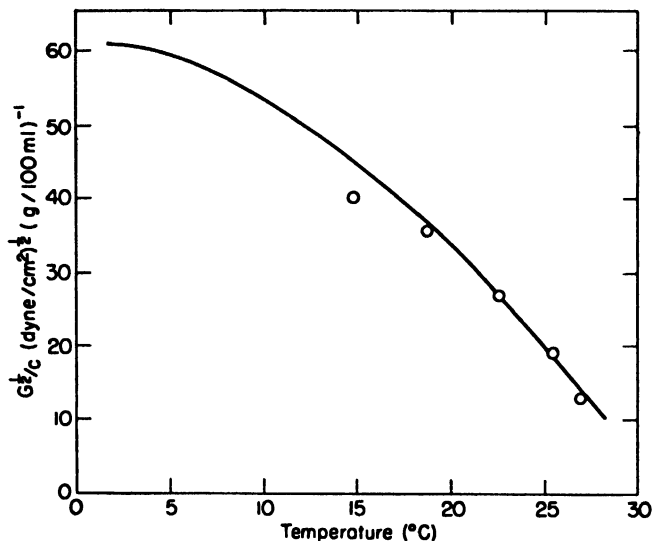


FIG. 11. Comparison of rigidity after chilling at 0° C. and at 15° C. — chilled at 0° C. ○ chilled at 15° C.⁵²

ml., found that the square law was approximately correct at 5.7° C., 11.5° C., 18.0° C., and 27.0° C. More recently Ferry,⁵¹ using the method of transverse vibrations, found that the rigidity of a degraded ossein gelatin ($M_n = 45,000$) at pH 7.0 in the presence of 0.15M NaCl, was closely proportional to the square of the gelatin concentration, up to a concentration of 5 g./100 ml., the relation being confirmed at several temperatures. However, at higher concentrations there was a slight departure from the square law. The rigidity of another degraded ossein gelatin ($M_n = 29,000$) did not obey the square law at any concentration. The authors⁴¹ have investigated the concentration dependence of the rigidity of an alkaline-treated calfskin gelatin (pI = 5.08) both deionized and as supplied. The results are illustrated in Fig. 12, where the rigidity, measured at $10 \pm 0.02^\circ$ C. after ageing for 17 hours at 10° C., is plotted against the square of the gelatin concentration. Some of the gelatin was deionized using a mixed resin bed,⁵³ giving an ash content of 0.05 %. No part of either the demineralized or natural curves is linear and the gradient of the curves decreases steadily with increasing concentration. This is illustrated by Table VIII, which contains values of n , from the general equation $G = k(c - \alpha)^n$ for various ranges of concentration. α is the minimum concentration for gelling. These values were obtained from a graph of $\log G$ vs. $\log (c - \alpha)$.

⁵³ J. W. Janus, A. W. Kenchington, and A. G. Ward, *Research (London)* **4**, 247 (1951).

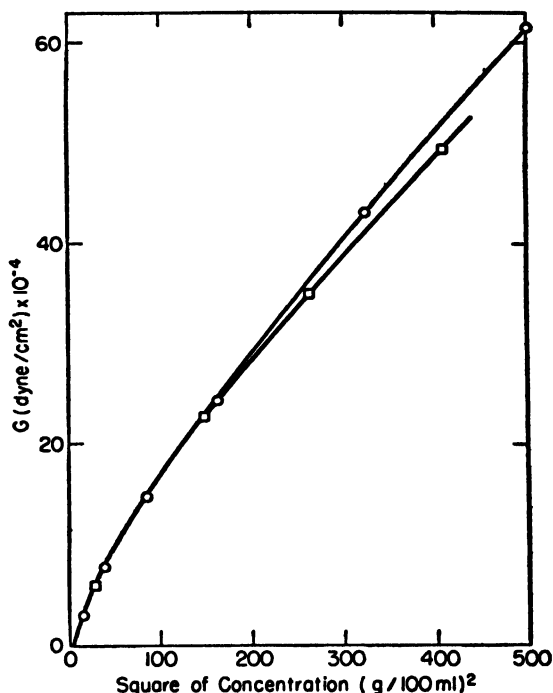


FIG. 12. Dependence of rigidity on gelatin concentration for demineralized gelatin and gelatin as supplied. Upper curve—demineralized gelatin. Lower curve—gelatin as supplied.⁴¹

Although the rigidity of demineralized gelatin is higher than that of the gelatin as supplied, at concentrations above 10 g./100 ml., the reverse is true below this concentration. For instance, at 20 g./100 ml. the rigidity of demineralized gelatin is 6% higher than the gelatin as supplied, while at 1.6 g./100 ml. it is 30% less. Differences in rigidity between deionized gelatin and normal gelatin containing a small amount of inorganic ash might be expected, because of the different ionic strengths (see p. 345). It was found experimentally, by adding NaCl to the demineralized gelatin, that the rigidity difference at 20% concentration could be completely accounted for by differences of ionic strength, and also the larger percentage differences at very low concentrations could be partly accounted for. Very similar results were obtained for an acid-processed pigskin gelatin.

Cumper and Alexander⁴⁸ have recently investigated the concentration dependence of the rigidity of gels of a gelatine (Davis Co., Australia) (pI = 5.0 at 25° C.) over the concentration range 5.0 to 52 g/100 ml. They found that the square law was approximately valid up to a concentration of about 20 g./100 ml., but that above this concentration the rigidity began to in-

TABLE VIII
MEAN VALUES OF n FOR VARIOUS RANGES OF CONCENTRATION

Demineralized gelatin					
Concentration range (g./100 ml.)	1.5-2.0	2.0-5.0	5.0-8.0	8.0-20.0	
n	2.44	2.13	1.64	1.55	
Natural gelatin					
Concentration range (g./100 ml.)	1.2-1.5	1.5-2.0	2.0-5.0	5.0-8.0	8.0-20.0
n	2.18	1.98	1.87	1.62	1.49

crease more rapidly than predicted by the square law. This result is unique in that the results of other observers for many different gelatines indicate that as the concentration rises toward 20 g./100 ml., the rigidity tends to be less than the value predicted from square law. This could mean that there is a point of inflection in the graph of rigidity against the square of concentration, and it is clear from the elasticity of sheet gelatin that the rigidity must increase more rapidly than predicted by the square law at some stage in the high-concentration region.

From the considerable amount of work on the concentration dependence of the rigidity of gelatin gels, it is unlikely that there is a simple relation between concentration and rigidity which would apply to all gelatines. Furthermore, a general relation of the type suggested by Sheppard and Sweet does not hold over the whole concentration range for any one gelatin, but it could be of use over short ranges of concentration. A fact which must not be overlooked, in assessing the work of the many contributors in this field, is that not all of them have investigated the same property, since the pretreatments which the gels have received are very different.

The Rigidity of a Mixture of Gelatins. Ferry⁵⁹ has investigated the rigidity of the gels of a mixture of two degraded ossein gelatines ($M_n = 45,000$ and 22,000) as a function of temperature. Assuming the validity of the square law of the concentration dependence of rigidity, the rigidity of a mixture of equal parts of each gelatin is given by $\sqrt{G_{mix.}} = (\sqrt{G_1} + \sqrt{G_2})/2$. The experimental results are illustrated in Fig. 13, together with the calculated mean values $(\sqrt{G_1} + \sqrt{G_2})^2/2$ and $(G_1 + G_2)/2$. The gelatin concentration was 5.75 g./100 ml. The equation based on the square law is completely verified and the arithmetic mean values are in considerable error. Although the same agreement for mixtures would not be expected for all gelatins, the square law forms a satisfactory basis for industrial blending where a particular rigidity or jelly strength is required.

(6) *The elasticity of a swollen gel.* Northrop and Kunitz⁵⁴ investigated the

⁵⁴ J. H. Northrop and M. Kunitz, *J. Gen. Physiol.* **8**, 317 (1926).

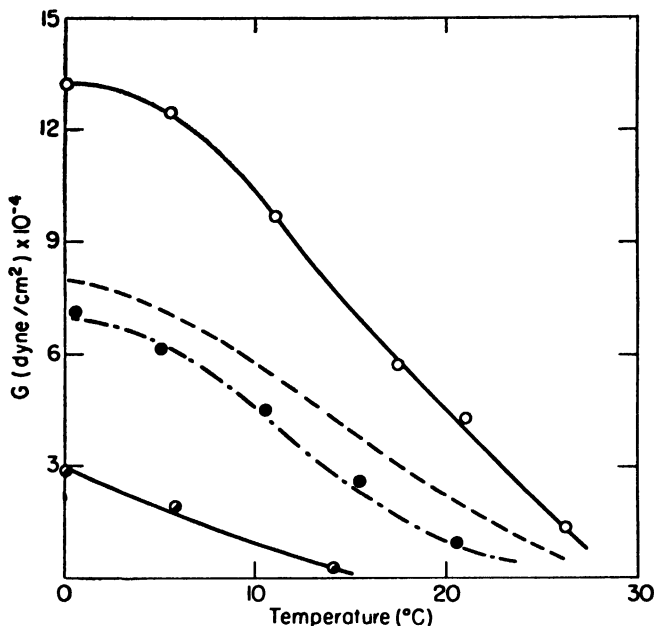


FIG. 13. Comparison of rigidities of a mixed sample and its components at a concentration of 5.75 g./100 ml.: O gelatin 1, $M_n = 45,000$; ● gelatin 2, $M_n = 22,000$; ● mixture of equal parts by weight; — $\frac{G_1 + G_2}{2}$ (calculated);

----- $\left(\frac{\sqrt{G_1} + \sqrt{G_2}}{2}\right)^2$ (calculated).⁵¹

elasticity of a gelatin gel as a function of the concentration, which was changed by allowing the gel to swell in water. Contrary to the results for the elasticity of gels prepared in the normal way by allowing solutions to gel, they found that the modulus of elasticity was nearly proportional to the gelatin concentration itself. They interpreted these results as indicating that the elasticity of the gelatin chains remains constant independently of the amount of water held in the gel.

(7) *Rigidity as a function of pH.* Gerngross⁵⁵ found that the rigidity of gelatin gels, measured in arbitrary units by means of a penetration instrument, was independent of pH, over the pH range 4.4 to 9.0, at 10% concentration, and from pH 4.3 to 6.7 at 1.5% concentration. Cumper and Alexander⁴⁸ (1954) have investigated the rigidity of gels of a gelatine pI = 5.0 (Davis Co., Australia), concentration 27 g./100 ml. gelatin, at a constant ionic strength of 0.15, at a temperature of 25° C., over the pH range 0 to 13

⁵⁵ O. Gerngross, *Kolloid-Z.* **40**, 279 (1926).

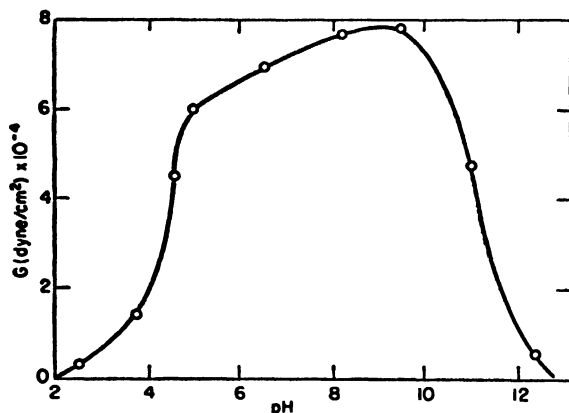


FIG. 14. The rigidity of an alkali-processed gelatin $pI = 5.0$, at a concentration of 27 g./100 ml., as a function of pH.⁴⁸

(Fig. 14). The rigidity is slightly dependent of pH , in the range 6 to 9, and it is interesting that it is a maximum at $pH = 9$ and not at the isoelectric point. However, there is a change of slope near the isoelectric point, and the rigidity drops rapidly as the pH decreases below 5. Similarly the rigidity drops rapidly as the pH is increased above 10. Since there is no indication of whether the reduced viscosity of the solutions formed on melting the gels was measured after the rigidity measurements, it is not clear whether the decrease in rigidity observed at extreme values of pH was due at least in part to degradation. Work in progress at the British Gelatine and Glue Research Association has, however, confirmed that even in the absence of chain degradation, the rigidity of gels is lower at pH 's outside the region 5 to 8. A particularly sharp fall is shown by acid-process gelatins at acid pH 's, especially at temperatures above $15^{\circ}C$.

(8) *Dependence of rigidity on added substances.* It has already been seen that the presence of the small amount of inorganic ash normally found in commercial gelatine is sufficient to change the rigidity of gelatin gels. In the past, several investigations into the effect of electrolytes on the rigidity of gelatin gels have been made but they were mainly of a semiquantitative nature. However, it was known that rigidity was usually reduced by the presence of electrolyte.⁵⁴ Bundenburg de Jong and Henneman⁵⁶ showed that the modulus of elasticity of a 14 % isoelectric gelatin gel ($pI = 4.8$) in the presence of increasing concentrations of potassium fluoride passed through a minimum at about $0.5 M$ and then increased. The elasticity decreased steadily with increasing concentration of potassium chloride, nitrate, and iodide, and the relative magnitude of the effect increased in the order given. $0.75 M$ potassium iodide decreased the elasticity to 36 % of

⁵⁶ H. G. Bundenburg de Jong and J. P. Henneman, *Kolloid-Z.* **36**, 123 (1932).

photoelastic pattern can also be followed by high-speed photography.⁸² An alternative method for following shear wave propagation, which has been suggested⁷ but not utilized, is the observation of small particles immersed in a transparent liquid or soft solid. From photographs with and without synchronization of stroboscopic illumination, the wave parameters could be determined. The effects of the container walls have been investigated theoretically,⁷⁸ but are usually not taken into account.

Longitudinal waves have been followed in fibers and strips by electromagnetic or piezoelectric pickup devices.^{83, 84, 85, 85-87} The disturbance is set up at one end, usually by an electromagnetic drive, and the pickup is moved at a constant rate along the sample. Automatic recording devices may provide graphs from which λ and x_0 can be obtained,⁸⁵ as indicated schematically in Fig. 14. Reflectance from the pickup must be avoided; reflectance from the far end of the sample may be taken into account,⁸⁸ though usually it is not.⁸⁹ The effect of superimposed static strain or even of a constant rate of strain can be investigated.

Flexural waves may also be employed. In a method devised by Oberst,^{89a} a material too soft or with too much damping for direct measurement is layered on a thin metal sheet; from the velocity and damping of flexural waves in the compound system and the properties of the metal, the components of $\mathbf{E}^*$ for the applied layer can be obtained.

The modulus $\mathbf{E}^*$, measured by longitudinal wave propagation along a thin sample as in Fig. 14, may be thought of as representing a combination of shear and bulk compression properties, since $\mathbf{E}^* = 3\mathbf{G}^*/(1 + \mathbf{G}^*/3\mathbf{K}^*)$, where $\mathbf{K}^*$ is the bulk modulus (whose real part is the reciprocal of the compressibility). For soft solids at low frequencies, $G' \ll K'$, and the shear properties of course dominate the behavior. However, when longitudinal waves are propagated into a wide sample (bulk waves), their velocity and attenuation depend on a different combination of $\mathbf{G}^*$ and $\mathbf{K}^*$; equations (8), or their equivalent, provide the real and imaginary parts of a complex modulus $\mathbf{K}^* + (4/3)\mathbf{G}^*$. In this case, the bulk modulus dominates the behavior, at least as far as the real part is concerned; for soft solids, again, $K' \gg G'$. However, usually K'' is much less than G'' and may be zero within experimental error, so the energy loss is still dominated by the shear proper-

⁸² D. G. Christie, *Trans. Soc. Glass Tech.* **36**, 74 (1952).

⁸³ J. W. Ballou and S. Silverman, *Textile Research* **14**, 282 (1944).

⁸⁴ J. W. Ballou and S. Silverman, *J. Acoust. Soc. Amer.* **16**, 113 (1944).

⁸⁵ R. S. Witte, B. A. Mrowca, and E. Guth, *J. Appl. Phys.* **20**, 481 (1949).

⁸⁶ J. W. Ballou and J. C. Smith, *J. Appl. Phys.* **20**, 493 (1949).

⁸⁷ K. W. Hillier and H. Kolsky, *Proc. Phys. Soc. (London)* **62**, 111 (1949).

⁸⁸ K. W. Hillier, H. Kolsky, and J. P. Lewis, *J. Appl. Phys.* **20**, 227 (1949).

⁸⁹ A. W. Nolle, *J. Appl. Phys.* **20**, 227 (1949).

^{89a} H. Oberst, *Acustica* **4**, Beiheft 1, 433 (1954).

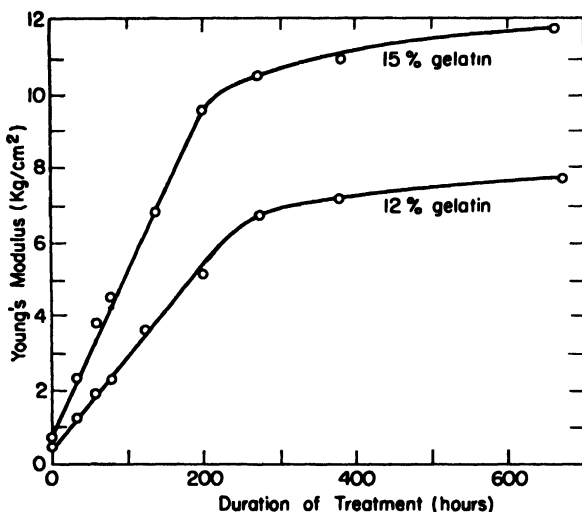


Fig. 16. Young's modulus of elasticity of 12 and 15% gelatin gels, measured at 9.2° C. after immersion in 2% formaldehyde for various durations.⁴²

21° C. The modulus increased with increasing content of cane sugar or glycerine, but there was no simple relation between the increase and the composition. The modulus for gels containing glycerine increased continuously for two months.

When gelatin gels are immersed in formaldehyde or exposed to formaldehyde vapor the modulus of elasticity of the gels increases very markedly. This increase is irreversible and Hatschek⁴² suggested that it is the result of the formation of condensation products. Hatschek investigated Young's modulus by compression of cylinders of hard gelatine gels which had been immersed in 2% formaldehyde for times up to 600 hr. His results for two gelatin concentrations are shown in Fig. 16 (temperature of measurement 9.2° C.). The elasticity increased rapidly for the first 200 hours and then became almost constant. The maximum values of Young's modulus attained by the hardened gels expressed as a ratio of the values for the unhardened gels were 17.4 and 16.7 for the 12 and 15% gels, respectively.

It is clear that substances such as urea and phenol, which depress the melting point and which in large concentrations prevent gel formation, will, at lower concentrations, cause a decrease in the rigidity.

(9) *Rigidity as a function of molecular weight.* When a solution of gelatin is subjected to high temperatures, say 50 to 100° C., the rigidity of the gels formed from this solution decreases irreversibly.^{19, 57} The more severe the conditions, the larger the decrease in rigidity, until in the limit the gelling properties of the solution are completely destroyed. Scatchard *et al.*²⁹ pre-

⁵⁷ R. J. Croome, *J. Appl. Chem.* **3**, 280 (1953).

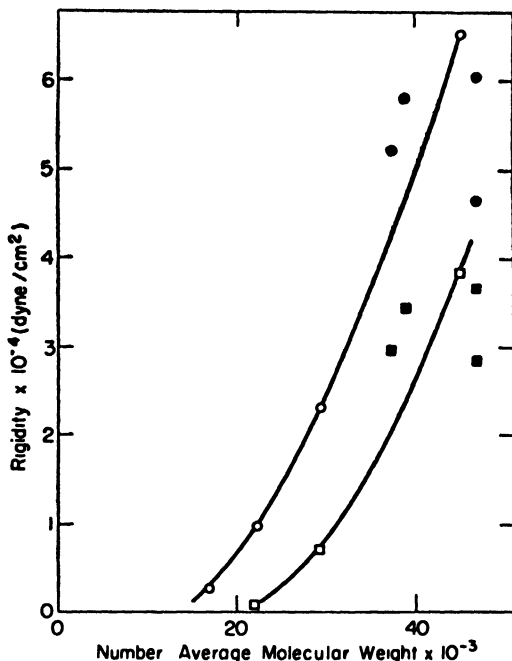


FIG. 17. Rigidity plotted against number average molecular weight, at 5° C., O, at 15° C. □: open points, degraded series; closed points, additional samples.⁵¹

pared several samples of gelatin of differing average molecular weight, measured viscometrically and osmotically, by deliberately degrading an ossein gelatin. The rigidity at 5 and 15° C. of these samples was investigated by Ferry⁵¹ by the method of transverse wave propagation, and his results are illustrated in Fig. 17, where rigidity is plotted against number average molecular weight. The points for the degraded series fall on a smooth curve but some additional points representing undegraded gelatins are scattered about the curves. These results indicate that the details of the gelatine preparation are of importance in determining the rigidity of a gelatin gel. Using a further set of degraded samples, Ferry⁵² measured the rigidity of their 4% gels at 5, 10, 15, and 25° C. He plotted the results as $\sqrt{G}/C$ vs. weight average molecular weight (Fig. 18). He also recalculated his earlier results on this basis and found that all the results fell on straight lines, characteristic of the temperature of measurement, and that the slopes of all the lines were identical. The intercepts on the molecular-weight axis were a function of $e^{-B/RT}$ and the results could be expressed by the empirical equation

$$\frac{G^{1/2}}{C} = 1.22 \times 10^{-4} (M_w - 3.1 \times 10^{10} e^{-7900/R T})$$

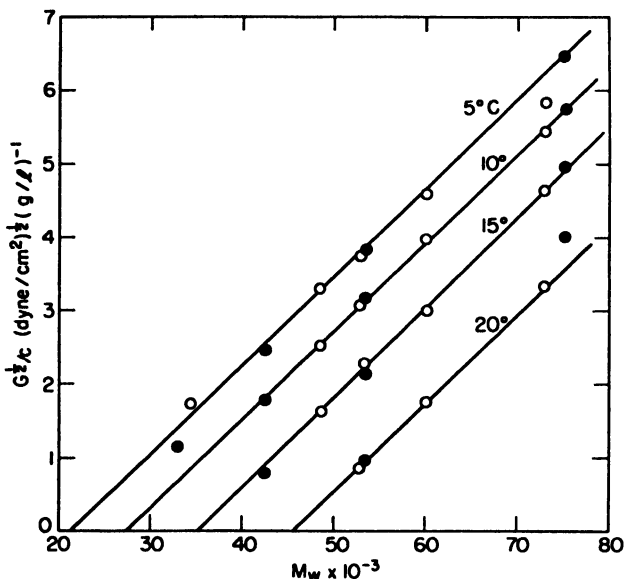


FIG. 18. $G^{1/2}/C$ plotted against weight average molecular weight at four different temperatures. ○ data of reference 52, ● data of reference 51.

In a footnote Ferry mentions that the rigidity of the fractions of a calf-skin gelatin, fractionated by Sheppard, with number average molecular weight varying from 80,000 to 120,000, was almost independent of molecular weight. He pointed out that these results were difficult to reconcile with those for the degraded samples.

Recently, the authors³¹ have investigated the mechanical properties of the fractions of several different types of gelatine, including acid- and alkaline-processed hide and ossein gelatines. The fractions were prepared by two different methods⁵⁸ but the main results were independent of the method of fractionation. The molecular weights of the gelatin fractions have not yet been determined, but the reduced viscosities of the fractions, which (c.f. Pouradier²⁴) are approximately proportional to the weight average molecular weight, were determined and used to indicate relative molecular weights. The reduced viscosity of the five fractions of a typical lime-processed hide gelatin were 0.37, 0.56, 0.79, 1.02, and 1.05. The rigidities were measured at 0° C., after ageing for 17 hrs. at 0° C.; then the temperature was raised and the rigidities were measured, after sufficient time had elapsed for the rigidity to become reasonably steady at the new temperature. Using this procedure, the rigidity was measured at progressively increasing temperatures of 10, 17.5, and 25° C., which almost cover the whole of the temperature range of existence of a gelatin gel. At 0 and 10° C., the rigidity of the

⁵⁸ G. Stainsby, *Discussions Faraday Soc.* **18**, 288 (1954).

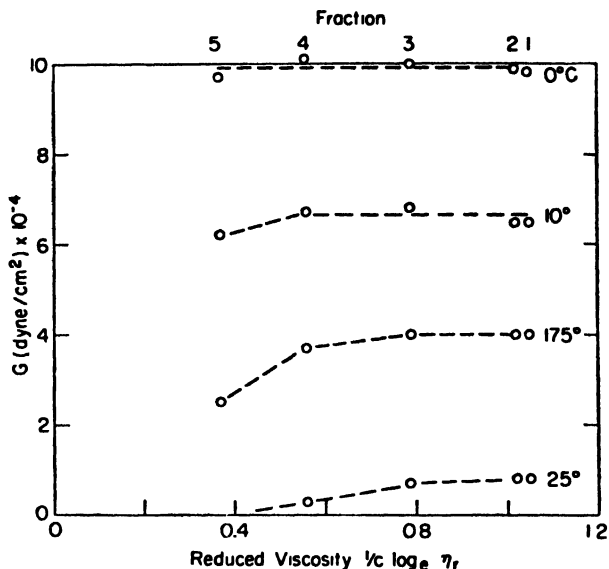


FIG. 19. Rigidity of 5.5% gels of the fractions of an alkali-processed gelatin, at four temperatures as a function of reduced viscosity.³¹

fractions of all gelatins of the same isoionic point not only failed to give a common relationship to the reduced viscosity (and hence molecular weight), but were found to be effectively constant for all fractions of any one gelatin and identical with the value of the unfractionated gelatin (Fig. 19). It is, of course, evident that below a certain limiting molecular weight, the rigidity will be dependent on the molecular weight, but it appears that only the last fraction of any of the high-grade gelatins examined contains even a small percentage of such material. It is also clear that at higher temperatures and lower gelatin concentrations, the rigidity will be influenced by the molecular weight, and this has in fact been observed experimentally. At 17.5° C., the molecular weight appeared to influence the rigidity, and this tendency became more pronounced at 25° C. As might be expected from this, all fractions of a single gelatin did not have the same melting point, the range being up to 7° C. The rigidity of 2% gels of the fractions depend on the molecular weight at all temperatures, including 0° C., and again the effect is more pronounced at higher temperatures. The rigidities of 11% gels of the fractions behave in a manner similar to the 5.5% gels. Although the rigidities of the 2% gels show a dependence on molecular weight at all temperatures, there is no unique relation between rigidity and reduced viscosity at any temperature. Table IX gives the results for a lime-processed hide gelatin ($pI = 4.95$) and an acid-processed pigskin gelatine ($pI = 9.2$) at 5.65 g./100 ml. concentration.

TABLE IX
 RIGIDITIES OF FRACTIONATED GELATINS

	Reduced Viscosity ^a	Rigidity (dynes/cm. ²) ^b			
		0° C.	10° C.	17.5° C.	25° C.
Alkali Process					
Unfractionated	0.56	109,000	72,000	43,000	6,000
Fraction 1	0.80	107,000	69,000	43,000	9,000
Fraction 2	0.68	111,000	73,000	44,000	8,000
Fraction 3	0.54	105,000	71,000	43,000	5,000
Fraction 4	0.45	112,000	76,000	43,000	3,000
Fraction 5	0.30	101,000	62,000	19,000	0
Acid Process Pigskin					
Unfractionated	0.47	117,000	73,000	41,000	8,500
Fraction 1	0.77	118,000	72,000	43,000	12,000
Fraction 2	0.52	111,000	72,000	40,000	8,000
Fraction 3	0.38	110,000	68,000	36,000	3,200
Fraction 4	0.24	99,000	55,000	18,000	50

^a $1/C \log \eta_{rel}$, Gelatin conc. = 0.2 g./100 ml. 1 M NaCl, pH = 7.35° C.

^b Gelatin conc. 5.65 g/100 ml.

Since the rigidity of the gels of different gelatin samples show considerable differences, and since the rigidities of the fractions of any one of these gelatins are independent of molecular weight at 0 and 10° C., it is necessary that some other structural feature, at present unidentified, will be present in varying degree in different gelatins and that this structural feature must be associated with the mechanism of gel formation. A necessary consequence of these experiments is that the relation between rigidity and weight average molecular weight, obtained by Ferry for degraded gelatins, is almost certainly fortuitous, although the degradation will produce some low molecular weight material which will not take part in gel formation. The thermal degradation of gelatin may perhaps be a process which changes the structural feature postulated above as well as reducing the average molecular weight.

b. Stress Relaxation and Plastic Flow

Ferry and co-workers⁵⁹ have used a concentric-cylinder apparatus to investigate stress relaxation in gelatin gels and its dependence on temperature and thermal history. They used an ossein gelatin $M_n = 34,000$ which had been deliberately degraded by Scatchard *et al.*²⁹ The gelatine concentration was 5.92 g./100 ml. The outer cylinder of the apparatus was rotated through

⁵⁹ M. Miller, J. D. Ferry, F. W. Schremp, and J. E. Eldridge, *J. Phys. & Colloid Chem.* **55**, 1387 (1951).

a known angle and the inner cylinder, which was restrained by a very stiff suspension, responded with a small rotation. Stress relaxation was followed by observing the change in the rotation of the inner cylinder with time. The static rigidity modulus was identical with the values of the dynamic rigidity modulus as determined by the method of transverse wave propagation, which showed that there are no elastic mechanisms with relaxation times between 10^{-3} and 10^2 sec. contributing to the rigidity. It is possible that the creep observed by Poole in times of the order of 10^2 sec. is too small to give significant results under Ferry's conditions. The stress-relaxation data indicate a distribution of viscoelastic mechanisms with relaxation times between 10^3 and 10^6 sec. This distribution is shifted to shorter times by increasing the temperature and to longer times by increasing the time of ageing before application of stress. The short-time rigidity was unchanged during stress relaxation and, consequently, the relaxation was attributed to dissociation of linkages which join again to form unstrained configurations similar to those originally present.

c. Mechanical Properties of Sheet Gelatine

It is convenient to consider the mechanical properties of sheet gelatine in this section, since sheet gelatine, which contains something like 10 to 20 % moisture, may be regarded as a gel of extremely high concentration. Poole⁴⁰ measured Young's modulus for sheets of Nelson's No. 1 gelatine and another unspecified gelatine, which had been dried to constant weight at 135° C. The results were the same for both gelatines, within experimental error (i.e., 3.1×10^{10} dynes/cm.²), and corresponded to zero moisture content. Bradbury and Martin⁶⁰ have investigated the elasticity, tensile strength, and extension at break of gelatin films, as a function of the temperature of drying the film and also of the relative humidity during measurement. They prepared gelatin films in two ways:

(i) The normal industrial method of allowing a 5 % solution to gel and then drying it initially with cool and then with warm air. Bradbury and Martin used air at 20° C. and 70 % R.H. which was satisfactory for the thin films.

(ii) Preventing the solution from gelling by drying at 56 to 60° C. and at a relative humidity of 70 %. The nearest industrial approximation to this is drum drying.

Specimens, 5 by 6 cm. were cut from the sheets and were conditioned in atmospheres of controlled humidity and temperature, before being submitted to tensile test, using a loading rate of 25 kg./cm.²/sec. The results are shown in Fig. 20 and 21.

At all humidities, the low-temperature preparation had a greater tensile strength than the high temperature preparation and also up to 65 % rela-

⁶⁰ E. Bradbury and C. Martin, *Proc. Roy. Soc. (London)* **214**, 183 (1952).

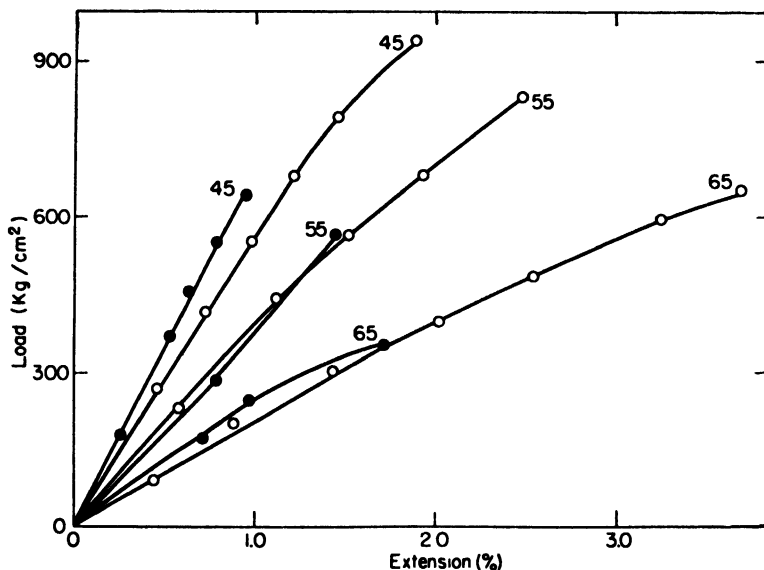


Fig. 20 Load-extension curves at relative humidities from 45 to 65% indicated on the curves: O film dried at 20° C.; ● film dried at 56 to 60° C.⁶⁰

tive humidity it had a greater extension at break, although above 65% relative humidity, the reverse was true. Up to 65% relative humidity, the load extension curves show no obvious yield point, but at 75 and 85% relative humidity, the curves show an apparent yield point, beyond which the extension per unit load is greater than in the initial part of the curve. At these high humidities, the extension is of a different order of magnitude and increases extremely rapidly with increasing humidity. It is of interest that even when the hot film had been extended by 130% of its length, it returned to within a small percentage of its original length on the removal of load. There was probably little plastic flow during the extension of the film owing to the high rate of loading. The different properties of the hot- and cold-dried films might possibly have been due to two other factors, namely, the rate of drying and the moisture content of the film when equilibrium was attained with the moist atmosphere. However, subsidiary experiments showed that these two factors had a negligible effect on the mechanical properties of the film. Films were also prepared at temperatures of 60 to 90° C. and 80 to 100° C., but the properties of these films were very similar to those prepared at 56 to 60° C. It was demonstrated that degradation was absent, by redissolving the hot-dried film and redrying at 20° C., when the properties of the film were the same as the cold-dried films. It was concluded that the difference in properties of the films was caused by a difference in structure.

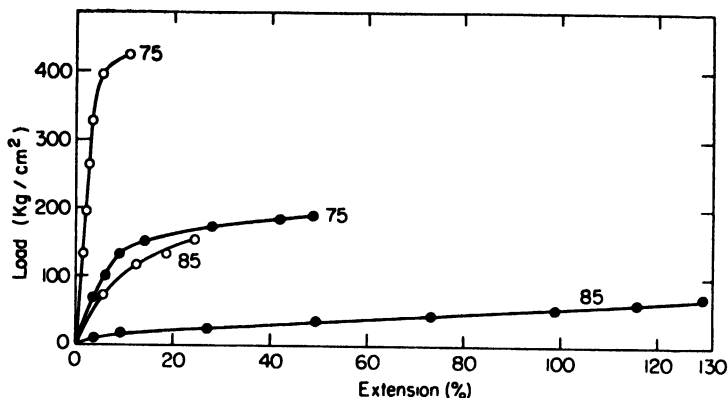


FIG. 21. Load-extension curves at relative humidities of 75 and 85%. ○ and as in Fig. 20.

Bradbury and Martin suggest that the proportion of "crystalline" regions differs in the two instances, being higher for the cold-dried films. This would be expected to affect the physical properties. An alternative explanation would suggest a molecular rearrangement during gel formation involving intermolecular hydrogen bonds in place of the intramolecular bonds at higher temperatures. It is possible that both these explanations are true in part, and that also the effects of varying degrees of orientation produced in different drying processes requires careful consideration.

3. RHEOLOGICAL PROPERTIES IN THE GELATION REGION

The boundary between gelatin solutions and gels is in no way as definite as that between solid and liquid for a crystalline type of material. Rather, there is a boundary region, where the properties of solutions of gelatin depend on the thermal and mechanical history. Thus, by rapid cooling of a gelatin solution it is possible for the solution to be liquid at temperatures where it would normally be a gel, although gelation cannot be long delayed. It becomes impossible to obtain conditions where the measured properties remain even approximately constant as a function of time. The formulation of methods of measuring physical quantities, such as melting point and apparent viscosity, requires care even if the objective is only reproducible results.

a. The Melting and Setting Points of Gelatin-Water Systems

Although many of the methods of measuring the melting and setting points of gelatin gels and sols, at present in existence, are satisfactory for relative results, none of them can be considered suitable for measuring what might be termed absolute melting and setting points. The main difficulty appears to be one of definition. The absolute melting point of a gelatin gel

would be the temperature at which the gel ceases to support a finite shearing stress, when the temperature is increased at an infinitesimal rate. All practical methods must of necessity involve a finite rate of change of temperature, and usually appreciable stresses. An extrapolation procedure, although possible, is extremely tedious for a measurement mainly of industrial interest. The melting and setting points, as determined by related methods, never coincide, the former always occurring at the higher temperature. The slower the rates of change of temperature, in any experiment, the smaller the discrepancy between the two temperatures. The mechanical history of a solution of gelatin also has a pronounced effect on the melting point; e.g., Richardson⁶¹ found that by vibrating a dipper in the surface of a gelatin solution, he was able to depress the setting point by 8° C., i.e., from 18 to 10° C.

(1) *Empirical Methods of Measuring the Melting and Setting Points of Gelatin.* Many empirical methods have been devised for measuring the melting and setting points of gelatin gels and sols, and have been described in detail elsewhere.⁶² However, the operating principles of a few of the better known methods are described below. Cambon's method, which is specified in British Standard Nos. .757/1944 and .847/1945, measures the temperature at which a brass cup falls away from a plug of jelly, after heating at a constant rate of 0.25° C. per minute. The temperature of collapse of a gel set in an inverted test tube has been used as a measure of the melting point by several workers, including Gordon and Ferry.⁶³ Sheppard and Sweet⁶⁴ described a method which depends on the penetration of a weight into the gel when the latter melts. These two workers also devised a method which can be used for determining both the setting and the melting points. The method measures the temperature at which air bubbles, from a constant pressure reservoir, stop flowing (setting point) or start flowing (melting point) through the solution of gelatin, the temperature of which is lowered (setting point) or raised (melting point) at a known rate.

(2) *Factors Affecting the Melting Point.* The melting point of gelatin gels increases rapidly with gelatin concentration up to a concentration of about 5 g./100 ml. and then more slowly (Sheppard and Sweet⁶⁴). Using an ossein gelatine ($M_n = 45,000$) Ferry⁶⁵ found that the plot of $\log_e$ (conc.) against $1/T$ (melting), was linear above a concentration of 2 g./100 ml. The linear part could be represented by an equation of the form $\log_e C = (a - b)/RT$.

⁶¹ E. G. Richardson, *Trans. Faraday Soc.* **29**, 494 (1933).

⁶² R. H. Bogue, "The Chemistry and Technology of Gelatin and Glue," p. 404. McGraw-Hill, New York, 1922.

⁶³ R. S. Gordon and J. D. Ferry, *Federation Proc.* **5**, 136 (1946).

⁶⁴ S. E. Sheppard and S. S. Sweet, *Ind. Eng. Chem.* **13**, 423 (1921).

⁶⁵ J. D. Ferry, *Advances in Protein Chem.* **4**, 23 (1948).

For another ossein gelatin ($M_n = 29,000$) this general equation held, but both the constants a and b had different values.

Pleass⁶⁶ investigated the effect of pH on the gelation of solutions of purified Coignet's "Gold Label" leaf gelatin (ash content approximately 0.02 %). The results were presented as isothermal contours, plotting the concentration of gelatin necessary for gelation, against the pH. At 0, 12, and 18° C., the concentration required for setting was constant at about 0.5 % in the pH range 4 to 8, but outside this range the concentration required for setting increased rapidly. The presence of electrolyte of the order of 1M either reduces the melting point of gelatin gels, as with NaCl and KSCN, or increases the melting point as, for example, with Na₂SO₄. However, these effects are usually of the order of only 1 or 2° C., a notable exception being KSCN. Ferry⁶⁷ found that the 1.1 % gels of an ossein gelatin ($M_n = 45,000$) which usually set at 26° C., were prevented from setting even at 0° C., by the presence of 1M KSCN.

Pouradier and Venet,²⁸ and subsequently the authors,³¹ have investigated the melting points of the fractions of several gelatins, and find that for any one gelatin there is a unique relation between melting point and reduced viscosity (and therefore molecular weight). However, for all gelatins, including both alkali- and acid-process types, there was no unique relation between melting point and reduced viscosity. This may result from the same unknown factor which determines the rigidity of gelatin gels, since the melting point may be considered as the temperature at which the rigidity becomes zero.

b. Changes in Viscosity and Rigidity at the Melting Point

It would be reasonable to predict a discontinuous change in viscosity and rigidity at the melting point. However, Richardson⁶¹ has shown that while this prediction is correct for the rigidity, it is quite erroneous for viscosity. Measurements of damped torsional oscillations of a disc suspended in a 1 % solution of an unspecified gelatin, cooled at a rate of about 3° C. per hour, provided values of both the viscosity (or internal friction for the gel) and the rigidity. Figure 22 illustrates the results. Curve *A* is a quantity inversely proportional to the rigidity, while curve *C* is a quantity inversely proportional to the viscosity. Curve *B* gives the fall of temperature with time. The initial part of curve *A* is related to the rigidity of the torsion suspension, and the discontinuous change illustrates the sudden appearance of elastic properties in the gelatin solution. The viscosity increased gradually as the solution cooled, with no discontinuity at the moment of gelation. Richardson concluded from these results that the increase of viscosity is not the dominant factor in determining gelation.

⁶⁶ W. B. Pleass, *Proc. Roy. Soc. (London)* **A126**, 406 (1930).

⁶⁷ Reported in J. D. Ferry, *Advances in Protein Chem.* **4**, 20, 26 (1948).

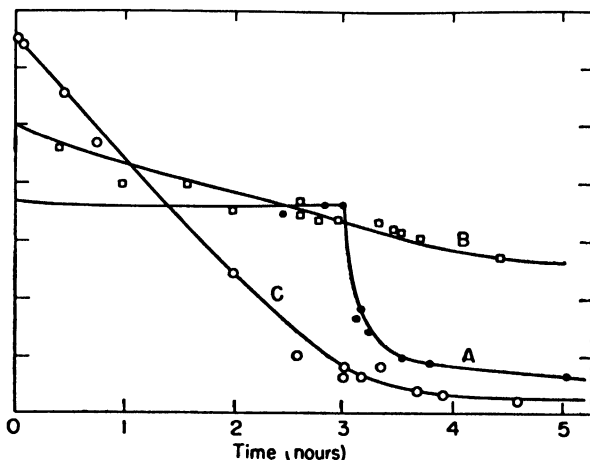


FIG. 22. Changes in viscosity and elasticity during gelation of a 1% gelatin solution. For explanation of curves, see text.⁶¹

c. Anomalous Viscosity

The viscosity of gelatin solutions in the neighborhood of the melting point changes with time and also is dependent on the rate of shear. Consequently, it is regarded that the solutions show anomalous viscosity. Davis and Oakes³³ found that there was a temperature (38.0° C.) at which the viscosity of the 4% solutions of a high-grade commercial hide gelatin was independent of time. Below this temperature the viscosity increased with time and above it there was a decrease with time. It was shown by Bogue,⁶⁸ and independently by Sheppard and co-workers⁶⁹ that the temperature at which anomalous viscosity effects disappeared depended on the concentration. They concluded that there was no critical transition temperature from gel form to sol form but rather a zone of transition temperatures. Sheppard and Houck²¹ studied the viscosity of solutions of a commercial calfskin gelatin and two lots of Eastman "de-ashed" gelatin. They found no evidence of a transition temperature, but found that there was an intermediate temperature at which the viscosity at first increased because of gelation effects and then decreased as the result of hydrolysis. It appears that the solutions of all gelatins exhibit anomalous viscosity under certain conditions of temperature and pH. Also it seems probable that factors, such as extremes of pH or the presence of substances such as KSCN or urea which prevent gelatin solutions from gelling even at 0° C., will depress the temperature at which anomalous viscosity effects are observed.

(1) *Rate of Shear*. The direct effect of shear has been observed by Ostwald

⁶⁸ R. H. Bogue, *J. Am. Chem. Soc.* **44**, 1343 (1922).

⁶⁹ S. E. Sheppard, F. A. Elliott, and S. S. Sweet, *Trans. Faraday Soc.* **19**, 261 (1923).

and Stuart⁷⁰ in the concentration range of 0.8 to 1.4 g./100 ml. The fall in apparent viscosity with shear was sufficient to be apparent even when measurements were made at successively smaller rates of shear. There would appear to be a time thixotropic effect, together with other anomalous effects from the orientation of the large aggregated particles.

IV. Theories of Gel Formation

A full review of theories of gel formation in relation to protein gels has been given by Ferry,⁷¹ and it is not proposed to duplicate this discussion. Ferry's concludes (p. 46 in ref. 71): "Many of the properties of gelatin gels can be at least qualitatively explained on the basis of a network structure formed by the junction of these elongated molecules here and there, caused by secondary bonds at widely separated loci of attraction. The bonds are evidently dissociated by increasing temperature and result probably from van der Waals forces. The details of the association equilibrium and chemical nature of the groups involved are still uncertain." Elsewhere (ref. 71, p. 43) Ferry suggests that only some five to six such loci may be necessary per gelatin molecule.

None of the more recently reported work is seriously in conflict with the point of view Ferry has put forward, which was based in part on the earlier work of Hermann and Gerngross.⁷² Unfortunately recent work has added comparatively little to make the theory more definite and quantitative. Only three aspects need further consideration: the recent work on the rigidity of fractionated gelatins,^{31, 58, 73} the new interpretation by Robinson and Bott⁷⁴ of the muta-rotation effect, and recent studies by Boedtker and Doty using light scattering.⁷⁵

It appears likely that, at a molecular weight corresponding to a reduced viscosity of about 0.2,⁵⁸ the power of gelatin molecules to take part in gel formation is lost, certainly at normal concentrations (5 to 10 %). This stage may be regarded as corresponding to only two loci per molecule or perhaps less. The corresponding molecular weight is in the region of 15,000, which means that in a gelatin molecule of molecular weight 60,000 there would be some eight loci. This agrees well in order of magnitude with Ferry's estimate. In gel formation at low temperatures it is clear from the experimental results that, provided the molecular weight exceeds the minimum, it matters little whether there are two molecules of, say, 30,000 M.W. (molecular weight) or one of 60,000. This is understandable if effectively all loci are

⁷⁰ W. Ostwald and W. W. Stuart, *Kolloid-Z.* **78**, 324 (1937).

⁷¹ J. D. Ferry, *Advances in Protein Chem.* **4** (1948).

⁷² K. Hermann and O. Gerngross, *Kautschuk* **8**, 181 (1932).

⁷³ G. Stainsby, *Adhesives and Resins* **1**, 222 (1953).

⁷⁴ C. Robinson and M. J. Bott, *Nature* **168**, 325 (1951).

⁷⁵ H. Boedtker and P. Doty, *J. Phys. Chem.* **58**, 968 (1954).

used in either instance. It is true that the gels continue ageing, indicating either more bonds or firmer structures, but under the conditions usually used in measuring gelatin rigidities, most bonds have already been formed in 18 hr., the rate of increase of rigidity modulus being then rather small.

The problem of deciding the precise structural form of the loci and of the bonds formed between them has been greatly complicated by recent work^{31, 58} since it is now clear that the structural feature constituting each locus must be capable of being broken down and blocked in certain circumstances. The breakdown clearly occurs during the making of gelatin from collagen, and probably also occurs in gelatin solutions, at least under some conditions of degradation.

Robinson and Bott⁷⁴ have utilized the known configurations of polypeptide chains, in relation to their optical rotation, to suggest that the marked muta-rotation effect (change of optical rotation in the sol-gel transition) for gelatin may result from a change in chain folding. They suggest a change from intrachain hydrogen bonding in the gelatin sol to interchain hydrogen bonding in the gel. In virtue of the magnitude of the muta-rotation effect, it is a little difficult to reconcile this view with Ferry's suggestion that there are only rare loci of attractive centers which form the interchain links.

Boedtker and Doty⁷⁵ have studied the light scattering from gelatin solutions at temperatures above the transition region, from dilute solutions at temperatures below the normal region of setting, and also from dilute gels. Their results confirm the complete dispersion of gelatin molecules in solution at 40° C. The ossein gelatin used (P111-20, alkali-pretreated, extracted pH = 4.5, of the Charles B. Knox Gelatine Co.), was precipitated with alcohol to give the staring material, which gave a value of M_w of 90,000. This is rather high in relation to values of M_n of 60,000 to 70,000 previously obtained for high-grade ossein gelatins, but may well be explained by the distribution of molecular weights present.

By taking very dilute gelatin solutions (0.09 to 0.9 g./100 ml.), cooling them to 4° C. for 24 hr. and then returning to the region of 18° C., reproducible light-scattering results were obtained. Most measurements were made at the isoionic point (pH = 5.1) with 0.15M NaCl. In these conditions stable aggregates were formed, the size of which was a function of the initial concentration but not of subsequent dilution. This suggests that the aggregation forces affect a number of groups and act co-operatively as in crystallization so that, once formed, the aggregates have stability. The particle weight of the aggregates increased from 208,000 for $C = 0.087$ g./100 ml. to 5,900,000 for $C = 0.539$ g./100 ml. Analysis of the results showed a particle shape corresponding to a Gaussian distribution of the mass about the center of gravity, rather than to rigid spheres or rods. In the absence of salt, at the isoelectric point, very large aggregates

(40,000,000 M.W.) are formed, presumably because of electrostatic interaction. These aggregates give rise to the isoelectric opalescence which has previously been so extensively studied.

In the gel state the light-scattering results were explained by the assumption that stable aggregates are formed, which are then linked together by molecular fringes or elongated particles, essentially as suggested by Hermann and Gerngross.⁷² The aggregates are of the same order of size as the largest particle formed in nongelling solutions in the same conditions of temperature.

One of the outstanding properties of collagen is the highly ordered bonded structure revealed by low-angle X-ray scattering by the electron microscope.⁷⁶ The forces bringing about this order are powerful enough so that when certain types of collagen are induced to pass into solution or pseudo-solution (without heating), the same ordered patterns may be recreated by precipitation.

It is interesting to speculate that the structural features of the collagen molecule causing the ordering may be carried by the irregular fragments of the collagen chain present as gelatin in gelatin solutions. Although no longer able to restore a fibrillar order as in collagen, they may still cause bonds which give a firm and stable gel. This view has been put forward also by Boedtker and Doty⁷⁵ on the basis of their light-scattering results. Some slight increase in probability is given to the hypothesis by the parallel effects observed with fibrin⁷⁷ where also long spacings have been detected.

V. Rheological Properties in Relation to the Uses of Gelatine and Glue, and to Industrial Testing Methods

Gelatine and glue find uses in the majority of industries, although certain industries—food, paper, textiles, photography, abrasives, gummed paper, distemper, joinery, and furniture—may be of greater quantitative importance than the others. In many of these industries, the rheological properties are either essential in the product, or exert their influence during the manufacturing process itself.

Table jellies, when prepared by the housewife from tablets or crystals, must set in a reasonably short time to a gel which melts in the mouth. In addition, the viscosity of the gelatine-sugar-acid mixture used has a marked effect on the manufacturing process, which involves mixing, eliminating air bubbles, and pouring onto glass or into moulds.

In most adhesive uses of glue, the solution viscosity influences the thickness of the film of adhesive which is applied, and the strength of the final dry glue is a contributory factor in the strength of the bond formed. In

⁷⁶ Reviewed by R. S. Bear, *Advances in Protein Chem.* **7**, 1 (1951).

⁷⁷ C. Z. Hawn and K. R. Porter, *J. Exptl. Med.* **86**, 285 (1947).

addition, the "tack" at the stage at which two surfaces are to be joined when the glue is on the point of setting, is an essential feature of animal glues. The rapid formation of a gel, after the joint is made, is of key importance in assembly work or in packaging, since the gel strength obtained is often sufficient to secure the joint until drying out occurs.

The viscosity plays a most important part also in the various sizing operations (textiles, paper, carpets, house walls), since here again it determines the amount of the glue solution (size) which is transferred to the surface to be sized. The dry-film properties then modify the behavior of the sized materials, and will themselves be dependent on the method of drying.

There are, of course, other properties which influence the uses of gelatine and glue such as surface activity, color, photographic sensitivity, taste, smell, content of heavy metals or of calcium salts, but there are very few instances in which a gelatine or glue can be specified for a particular use without referring either to its power of gel forming or to the viscosity or some characteristic (melting point, setting point, setting time) of the melting process.

On the basis of existing knowledge of gelatin structure and properties, a gelatin (or animal glue) must be specified by means of its isoionic point, its molecular weight distribution, and a suitable measure of the gel-forming power, such as the rigidity of a carefully matured gel of known concentration at 10° C. However, such a program is not commercially practicable, even if adequate for the purpose.

The value of pI may in most instances be deduced from the process used in manufacture, all alkaline-process gelatins giving pI's from 4.8 to 5.2, while acid-process gelatins (where no alkali has been used) giving a pI of about 9. The direct measurement of pI by the mixed-bed-resin technique of Janus, Kenchington, and Ward⁷⁸ is, however, very simple, and may be applied to materials of unknown origin.

An idea of the mean molecular weight can be obtained from the viscosity measurement. Alternatively, the viscosity determination under standard conditions (B.S.757) may be regarded as a direct guide to the viscous behavior in use. There is considerable evidence that this is a reliable procedure, since changes of temperature or concentration do not normally change the order for a set of samples as far as viscosity is concerned. It is necessary to bear in mind the different pH dependences of the viscosity for gelatins of different pI's (p. 326).

This leaves the assessment of the gel-forming power to be considered. This is the least satisfactory measurement. The Standard Instrument (B.S. 757, A.O.A.C.,⁷⁸ etc.), now widely used in America, the British Com-

⁷⁸ Official Methods of Analysis of the Association of Official Agricultural Chemists p. 339 (1950).

monwealth, and in Europe, called the Bloom Gelometer,^{79, 80} is itself difficult to maintain at high accuracy. In the test, a gel is set in a wide-necked bottle at 10° C. for 17 hr. A plunger, 0.5 in. in diameter, is then forced 4 mm. into the gel by loading at 40 g./sec., the load necessary being recorded as the Bloom jelly strength. The measurement is essentially concerned with elastic strains. Recent improvements,^{81, 82} including means of checking the instrument using a spring steel strip called the Dummy Bloom,⁸² and the issue of the British Gelatine and Glue Research Association Jelly Strength Standard Gelatines and Glues, have made the test commercially satisfactory.

There is no certainty that the order of a series of gelatins as indicated by the Bloom test will be the same when the modulus of elasticity, or any other mechanical property, is measured at other temperatures, and especially at different pH values. The results are also affected by the presence of salts, sugars, glycols, glycerols, polyvalent ions, etc., in different ways. As a result many user industries have empirical tests in which the gelatine is tested under conditions simulating those of use. The Bloom test is especially valuable in securing uniform supplies from a single manufacturer using a consistent process, or from a group of manufacturers using similar processes.

No attempt is made here to review the innumerable mechanical tests for gelatin gels which have been devised.⁸³ At one stage almost every firm in every country had its own variant. Although some are still retained for internal use, their results are now translated with varying degrees of reliability into figures on the Bloom scales. Some of the early tests measured a fracture property rather than an empirical modulus. Such tests give figures quite unrelated to Bloom grading figures, but so little is yet known concerning rupture of gelatin gels that there is no point in discussing these methods.

As soon as the main problems of relating structure and properties have been solved, it will be possible to devise tests to ensure that all significant gelatin and glue properties are controlled. Although this stage can be clearly envisaged, it is still some years from realization.

Acknowledgments

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⁷⁹ U. S. Patent 1,540,979 (June 9, 1925).

⁸⁰ W. D. Richardson, *Chem. & Met. Eng.* **28**, 551 (1923).

⁸¹ D. Fysh and A. G. Ward, *Food* **22**, 111 (1953).

⁸² Developed by B.G.G.R.A. Available through Griffin & Tatlock, Ltd.

⁸³ R. H. Bogue, "The Chemistry and Technology of Gelatin and Glue," p. 366. McGraw-Hill, New York, 1922.

Nomenclature

C	Concentration g./100 ml. solution	pK	Dissociation Constant (logarithmic)
Cn	Number average chain length	R	Gas constant
G	Shear modulus	T	Absolute temperature
I	Ionic strength	Y	Young's modulus
M_n	Number Average Molecular Weight	η_{red}	Reduced viscosity ($1/C \log_e \eta_{rel.}$)
M_w	Weight Average Molecular Weight	η_{rel}	Relative viscosity
pI	Isoionic point	η_{sp}	Specific viscosity (number)
		σ	Poisson's ratio

CHAPTER 9

RHEOLOGICAL PROPERTIES OF ASPHALTS

R. N. J. Saal and J. W. A. Labout

I. Introduction	363
II. Rheological Properties of Pure Asphalts	366
1. Description of Rheological Properties	366
2. Rheological Properties of Asphalts	369
<i>a.</i> Influence of Type on Time Dependence of Stiffness	369
<i>b.</i> Deviations from Linearity; Constitution	371
<i>c.</i> Mechanical Model System of Various Types of Asphalts	374
<i>d.</i> Influence of Hardness on Time Dependence of Stiffness	377
<i>e.</i> Influence of Temperature on Stiffness	377
<i>f.</i> Influence of Pressure on Rheological Properties	380
<i>g.</i> Breaking Strength	381
3. Routine Analyses	382
<i>a.</i> Penetration	382
<i>b.</i> Softening Point Ring and Ball	386
III. Asphalt-Mineral Aggregate Mixtures	388
1. Introduction	388
<i>a.</i> Methods	389
2. Rheological Properties of Asphalt-Mineral Aggregate Mixtures	391
<i>a.</i> Influence of the Mineral Aggregate Concentration	391
(1) Dynamic Investigation at Short Loading Times	391
(2) Static Investigation at Long Loading Times	393
<i>b.</i> Relation between the Rheological Properties of the Mixture and Those of the Asphalt Component	397
<i>c.</i> Breaking Strength	399
Nomenclature	400

I. Introduction

Asphalt is the highly viscous residue of certain kinds of petroleum obtained by merely removing most of their volatile components. This process is sometimes combined with a chemical treatment to obtain a larger quantity of highly viscous residue or to produce asphalts with special rheological properties. In other cases the viscosity of the natural product is already so high that it need not be artificially increased (native asphalts).

Asphalts are mainly used as a binding material and in protective coatings, taking both forms of application in a very general sense. Their suitability for these uses is largely dependent on their mechanical properties, in particular on those relating to rheology. For a correct judgment of this

suitability, therefore, a thorough knowledge of these properties is indispensable.

The composition of petroleum varies widely with its origin. In fact, not all types are suitable base materials for asphalt, and those which are still differ so much from one another that only by choosing the right processing conditions can the asphalts produced from them be made to meet the same quality requirements. Research into the manufacture of asphalts also comprises rheological studies, which aim at gaining more knowledge on the structure of the material.

These two aspects of rheological work, viz., applicational and manufacturing research, require a different approach.

In the numerous applications of asphalt the mechanical conditions, such as magnitude of stresses and time of loading, cannot be given with a high degree of precision. Hence knowledge of the rheological properties of the asphalt need not be so very accurate either, but may be restricted to the primary effects, and the relation between stress and deformation may be considered linear.

In the study of the structure of asphalts the understanding of any effect may contribute toward a deepening of insight. Hence, in this case more exact knowledge is necessary and the study also comprises secondary effects, such as small deviations from linearity, thixotropy, etc.

The various types of application of asphalt may be divided into those using the asphalt in the pure state or mixed with only small quantities of fillers, and those employing the asphalt in mixtures with other materials in a comparatively low concentration. In the latter case, the rheological behavior of the asphalt composition will be largely determined by that of the other components. Therefore, a discussion of the rheology of asphalt has to be divided into two parts, one dealing with the pure asphalt (Part I), the other with mixtures poor in asphalt (Part II).

Most asphalts are colloidal systems; they contain high-molecular components ("asphaltenes"), which may be precipitated as a solid by diluting the asphalt with low-boiling saturated hydrocarbons. The remaining part is a highly viscous oil of the Newtonian type ("maltenes"). It has been found that at not too high temperatures the disperse-colloidal phase of the asphalt system consists of the asphaltenes together with a proportion of the maltenes varying with the temperature. The continuous phase is a Newtonian oil of lower viscosity than the maltenes.

The rheological characterization of asphalts is, as a rule, based on two properties: penetration and softening point Ring and Ball. The penetration indicates the distance, in tenths of a millimeter, a needle will penetrate into the asphalt under standardized conditions of loading and time. The softening point Ring and Ball (temp. R & B) is the temperature at which

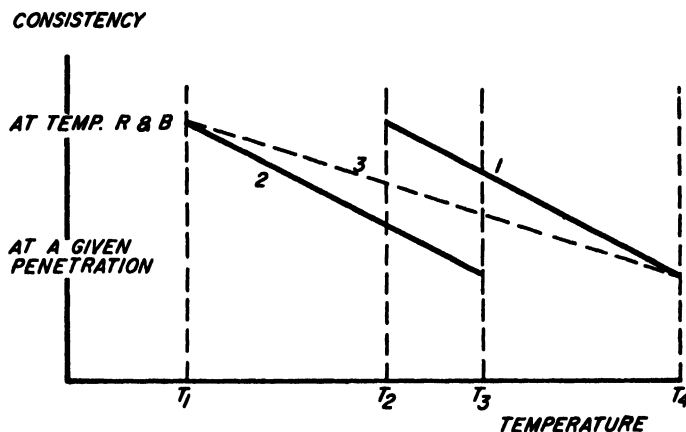


FIG. 1. Hardness and type of asphalts. (a) 1 and 2: Equal type but different hardness ($T_4 - T_2 = T_3 - T_1$). (b) 1 and 3: Different type.

the consistency of the asphalt is such that a steel ball placed on a disk of asphalt in a brass ring will cause a certain deformation of the disk, also under accurately specified conditions.

In accordance with these analytical methods asphalts have been classified according to "hardness" and to "type." Asphalts differ in type when the distance between their temp. R & B and the temperature corresponding with a certain penetration is different. They are said to differ in hardness when at equal type the temp. R & B differs (Fig. 1).

When expressed in this way the differences in hardness between the asphalts used in actual practice may be as high as about 100°C . Types may vary so widely that the distance between temp. R & B and the temperature corresponding with a given penetration may vary by a factor of 4.

Various systems have been developed to describe the type of an asphalt. In the following, use will be made of the "penetration index" (P.I.); it represents the above-mentioned distance between the temp. R & B and the temperature at a given penetration in the form of an index number. In this system a P.I. of -2.5 applies to asphalts with a small difference and a P.I. of about 6 to asphalts with a large difference between these two temperatures. The majority of asphalts have penetration indexes lying between these two values.

It has been found that the penetration index is closely related to the extent to which various asphalts, on deformation, show deviations from Newton's law. In static measurements at not too short loading times asphalts with a low index number (-2 or lower) obey Newton's law. A higher index (> -2) goes with visco-elastic properties, the latter being more pronounced

according as the index is higher, and at a penetration index higher than ca. +2 thixotropic phenomena may be observed.

For a more detailed description of this subject matter reference may be made to "The Properties of Asphaltic Bitumen" by J. P. Pfeiffer.¹

II. Rheological Properties of Pure Asphalts

1. DESCRIPTION OF RHEOLOGICAL PROPERTIES

The object of an investigation into the rheological behavior of asphalts is to find the relation between deformation, stress, time of loading and temperature.

On deformation most asphalts display visco-elastic properties. For a given asphalt the ratio of the elastic to the permanent part of the deformation depends on stress, time of loading, and temperature. At slight deformations and short times of loading the deformation is predominantly elastic; at considerable deformations and long loading times viscous deformation dominates. In most cases elastic deformation consists of an ideally elastic part and a part showing retarded elasticity.

At small deformations the relation between deformation and stress is linear; at considerable deformations and long loading times deviations from linearity may occur in certain cases. They are secondary effects and will be left out of consideration for the time being.

The resistance to deformation of materials which obey Hooke's or Newton's law can be described by means of two primary quantities, viz.:

(a) the modulus of elasticity, E , which is defined as the ratio of the tensile stress, σ , to the strain, ϵ :

$$E = \frac{\sigma}{\epsilon} \quad (1)$$

(b) the viscosity, η , which is defined as the ratio of the shearing stress, τ , to the rate of shear, $\frac{d\gamma}{dt}$:

$$\eta = \frac{\tau}{\frac{d\gamma}{dt}} \quad (2)$$

The modulus of elasticity, E , is usually determined at small deformations, the viscosity η , at deformations which are generally considerable. The latter quantity can, however, be expressed in terms of tensile stress and strain according to

$$\eta = \frac{\tau}{\dot{\gamma}} t = \frac{1}{2\left(1 + \frac{1}{m}\right)} \cdot \frac{\sigma}{\epsilon} \cdot t \quad (3)$$

¹ J. P. Pfeiffer, "The Properties of Asphaltic Bitumen with Special Reference to Its Technical Application." Elsevier, Houston, Tex., 1950.

where m is Poisson's constant. For asphalts this constant is about 2, from which it follows that

$$3\eta = \frac{\sigma}{\epsilon} \cdot t \quad (4)$$

Van der Poel,² in describing the resistance to deformation of viscoelastic materials, which include asphalt, uses the ratio σ/ϵ as a function of the time of loading, t , and temperature, T . This ratio σ/ϵ is called "stiffness," S , and will also be used here to describe the rheological behavior of asphalts. Only in those cases where measurements based on direct shear are difficult to express in terms of elongation will the rheological behavior be given in terms of viscosity.

In general, the relation between stiffness and time at a given temperature is, for viscoelastic materials, represented by a curve of the shape illustrated in Fig. 2.

The left-hand (horizontal) part of the curve refers to loading times which are so short that the deformation is mainly elastic; the stiffness is then identical with Young's modulus. The right-hand part of the curve, which makes an angle of 45 deg. with the time axis, refers to long loading times, at which the deformation has a predominantly viscous character and hence is proportional to time. At intermediate times the deformation slowly increases and from elastic gradually becomes viscous.

In measuring the stiffness as a function of time two methods of loading can be distinguished, viz., static and dynamic.

In the static method a constant load is applied to the material and the deformation is measured as a function of time. Below the temp. R & B use is made of strain and bending tests on asphalt specimens and of rotational viscometers of the type described by Couette.³ Above temp. R & B capillary viscometers are commonly used; the stiffness can then be calculated from the viscosity according to equation (4). These methods are suitable for deformation times longer than 1 sec.

The dynamic method applies an alternating load to a rod of the material under test, which is suspended freely or is held fixed on one end. The load varies sinusoidally with time; the stress at any moment can be expressed by

$$\sigma = \hat{\sigma} \sin \omega t \quad (5)$$

The amplitude of the deformation also varies sinusoidally with the same frequency and can, at any moment, be represented by

$$\epsilon = \hat{\epsilon} \sin (\omega t - \varphi) \quad (6)$$

² C. Van der Poel, *Proc. 2nd Intern. Rheol. Congr., Oxford* p. 331 (1953); *J. Appl. Chem. (London)* **4**, 221 (1954).

³ M. Couette, *Ann. chim. et phys.* [6] **21**, 433 (1890); *J. phys.* [2] **9**, 566 (1890).

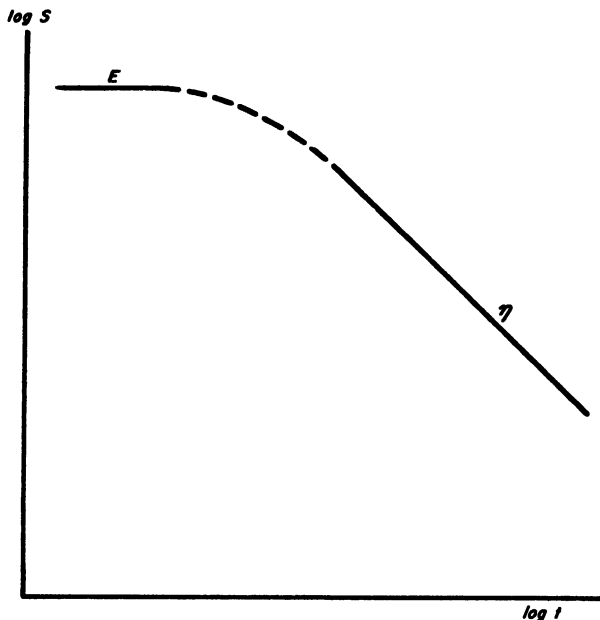


FIG. 2. General picture of the relation between stiffness and time at constant temperature for viscoelastic materials.

where ω = angular frequency and φ = the difference in phase between stress and deformation.

The stiffness is calculated from the resonance frequency as related to the dimensions of the specimen.

The dynamic method is used for measurements at not too high temperatures and short loading times (< 1 sec.).

For a graphic representation of the relation between stiffness and time Van der Poel² uses the same time scale for the two types of loading; for the static method $\log$ time and for the dynamic method $\log (1/\omega)$ is plotted on the abscissa, using the same scale.

The correctness of this method of plotting has been tested by means of a mechanical model consisting of an elastic and a viscous element.

For the Maxwell element of Fig. 3, σ/ϵ determined by the static method can be calculated from the equation

$$\left(\frac{\sigma}{\epsilon}\right)_s = \frac{E}{1 + \frac{t}{\lambda}} \quad (7)$$

σ/ϵ determined by the dynamic method follows from:

$$\left(\frac{\hat{\sigma}}{\hat{\epsilon}}\right)_d = \frac{E}{\sqrt{1 + \frac{1}{\omega^2 \lambda^2}}} \quad (8)$$

In these equations the symbol $\lambda = Q/E =$ relaxation time, and $Q =$ coefficient of viscous traction (according to Trouton).

In Fig. 4 $\log (\sigma/\epsilon)_s$ and $\log (\dot{\sigma}/\dot{\epsilon})_d$ have been plotted in one diagram against the same time scale.

It will be seen that the two curves practically coincide except in a small area of transition. For a first approximation, however, the two ways of representation may be used side by side without making a distinction between dynamic and static method.

2. RHEOLOGICAL PROPERTIES OF ASPHALTS

a. Influence of Type on Time Dependence of Stiffness

The relation between stiffness and time of loading at constant temperature ($25^\circ \text{C}.$) is represented in Fig. 5 for different types of asphalt. It will be seen that the differences in rheological character show up as differences in time dependence of the stiffness.

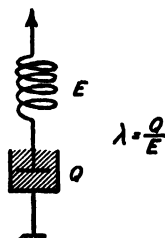


FIG. 3. Maxwell model

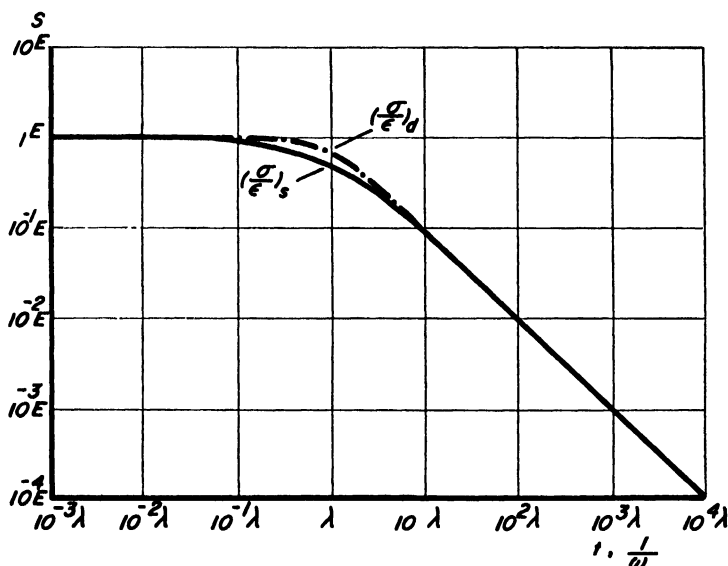


FIG. 4. Comparison of static and dynamic stiffness moduli for Maxwell model

ASPHALT	a	b	c
PEN / 25 °C	3	15	13
TEMP R & B, °C	66	67	120
P. I.	-2.4	-0.2	+5.5
ASPHALTENES, %	3	20	34

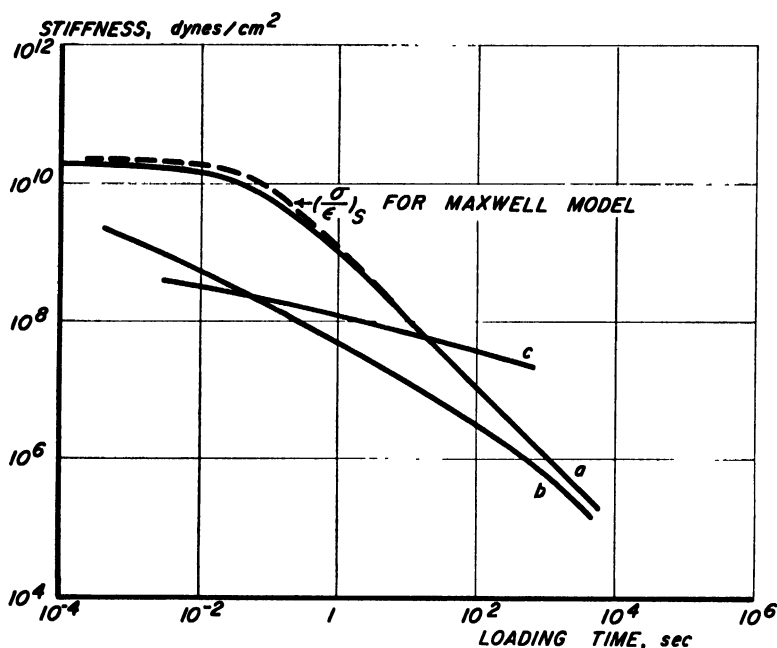


Fig. 5. Stiffness as a function of loading time for different types of asphalt at 25° C.

Asphalt *a* is a material with a very low asphaltene content, which has been prepared from a Borneo base material by distillation (P.I. = -2.4). At short loading times the asphalt displays an almost purely elastic, at long loading times a purely viscous behavior. This asphalt shows hardly any effects of retarded elasticity and hence no partial recovery after removal of the load. The transition from the elastic to the viscous part of the curve is fairly sharp.

A similar behavior can sometimes be observed with asphalts having a higher content of asphaltenes; in this case these asphalts also have a low penetration index (-2 or lower).

Asphalt *b* has been prepared from Venezuelan base material by distillation. It displays retarded elasticity and shows partial recovery after longer loading times when the load is removed. The transition from the elastic to

the viscous part of the curve is not so sharp as that of asphalt *a*. Asphalts with a similar behavior are characterized by a penetration index of from -2 to ca. $+2$; according as the P.I. is higher the transition area is larger.

Asphalt *c* has been prepared from Venezuelan base material by blowing (i.e., oxidation by air). This asphalt shows strongly retarded elasticity; its stiffness is little influenced by the time of loading. In static measurements with short loading times the recovery after removal of the load is practically complete. At considerable deformations and long loading times thixotropy is observed and the relation between deformation and stress is no longer linear. This type of asphalts is characterized by a penetration index higher than $+2$, usually from $+4$ to $+6$.

b. Deviations from Linearity; Constitution

The differences between various asphalts in the stiffness-time relation are linked up with differences in colloid-chemical structure.

As has been said in the Introduction, on deformation the continuous phase of the colloidal system behaves as a Newtonian liquid. The elastic effects shown by most asphalts must therefore be attributed to the disperse phase, which, as has also been stated, consists of the asphaltenes and part of the maltenes. Asphalts which contain hardly any asphaltenes have a noncolloidal structure and consequently these asphalts behave as Newtonian liquids. An example of this is asphalt *a* of Fig. 5. On deformation for not too short times this asphalt shows a purely viscous flow; only at very short times can ideally elastic effects be observed.

Some asphalts of high asphaltene content show a similar behavior, e.g., asphalts prepared from cracked base materials (i.e., base materials which by exposure to high temperatures have thoroughly changed their composition). The disperse phase of these asphalts must then consist of particles which, at the stresses prevailing during the measurements, do not show elastic deformation.

Most asphalts containing asphaltenes display retarded elasticity. Two types can be distinguished, of which asphalts *b* and *c* in Fig. 5 are representatives. The differences found can be derived from Figs. 6 and 7, which contain more detailed data of two corresponding asphalts *b'* and *c'*.

Figure 6 refers to asphalt *b'*; the stiffness derived from the total deformation (S_t) and that calculated from the elastic part of the deformation (S_e) have been plotted against the time of loading. The two curves do not coincide; the difference is caused by the resulting permanent deformation. For this asphalt the relation between deformation and stress is practically linear also at long times of loading, which appears from the fact that the values of S_t determined at different loads are equal.

For asphalt *c'* (Fig. 7) the values of S_t and S_e coincide at loading times up to about 10^2 sec. Below this limit there is practically no permanent deforma-

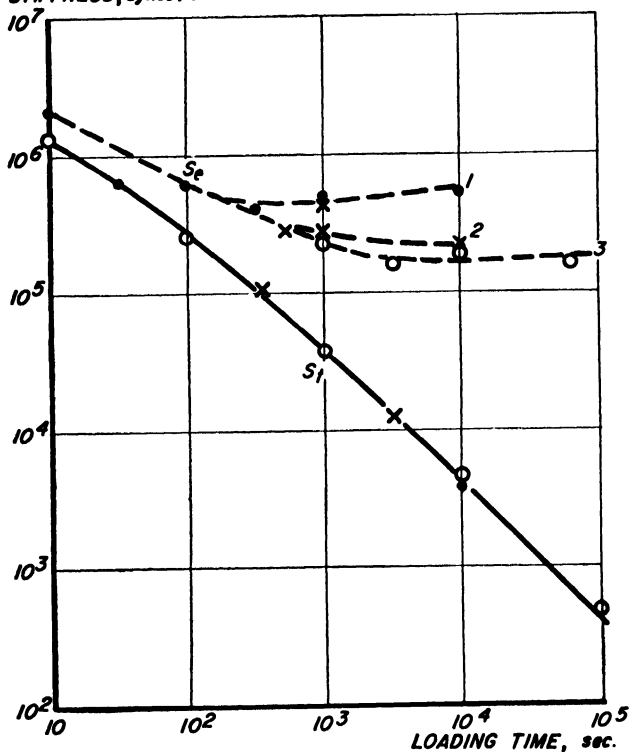
PROPERTIES OF ASPHALT

PEN / 25°C = 17

TEMP. R & B = 63°C

P.I. = -07

ASPHALTENES = 25.3 % w

1 • $\sigma = 13.3 \cdot 10^4$ dynes/cm²2 x $\sigma = 6.60 \cdot 10^4$ "3 o $\sigma = 1.63 \cdot 10^4$ "STIFFNESS, dynes/cm²FIG. 6. Stiffness as a function of loading time and stress for asphalt *b'* at 35° C.

tion; a certain yield stress may be assumed. At longer loading times there is permanent deformation; moreover, the relation between total deformation and stress is no longer linear, which appears from a spread of the curves for various loads. The fact that thixotropy occurs at higher loads can be derived from the slope of the log *S_l* curve in respect of the log time axis. At long times the curve makes an angle greater than 45 deg. with the axis, which means that the deformation increase with time is more than proportional. The rheological behavior of this type of asphalt points to its having a coherent structure which, at slight deformations for short times, is capable of complete elastic deformation and which, if the deformation is continued,

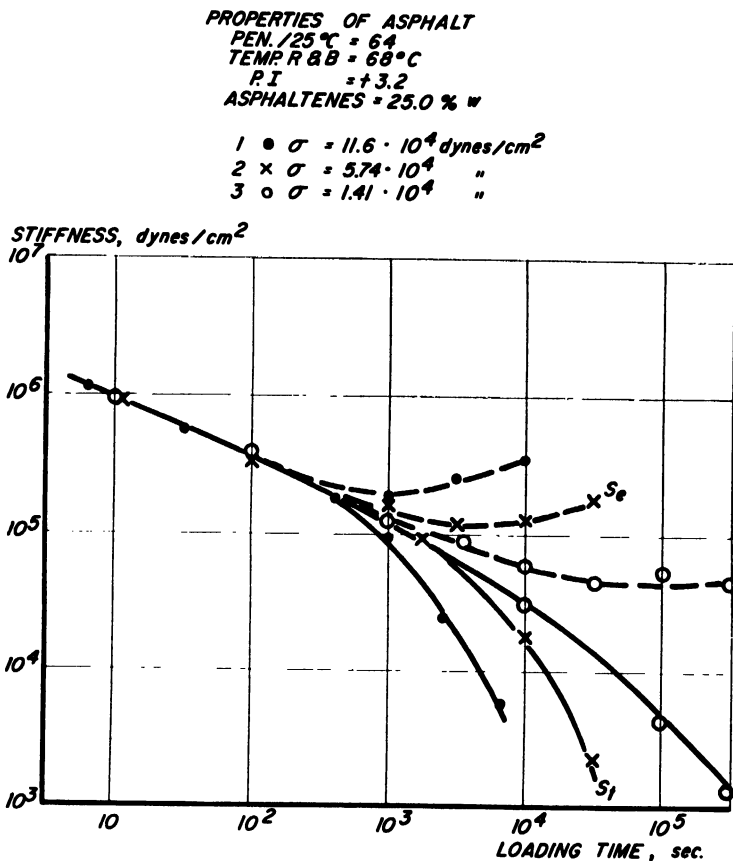


FIG. 7. Stiffness as a function of loading time and stress for asphalt c' at 35°C.

collapses. The colloidal character of this type of asphalt is, therefore, that of a gel. The coherent structure is formed as a result of mutual attraction of the disperse particles; this idea is confirmed by other investigations, in which, e.g., synecrisis is observed.

Unlike asphalt c' , asphalt b' must have such a structure that its disperse phase consists of free-moving elastic particles, and hence it has a sol character.

The differences discussed are extremes; in general, intermediate forms also occur.

The extent to which a coherent structure is formed in asphalts and the measure of elasticity of the disperse particles depend on the chemical composition of the disperse and continuous phases.

As will be seen from Figs. 6 and 7, the elastic deformation of either type of asphalt on deformation at long loading times does not proceed linearly

with time and stress; the recovery, ϵ_e , reaches a maximum and decreases again. This decrease is greater for a gel type than for a sol type. The relation between this maximum and the load for a sol-type asphalt is represented in Fig. 8. It can be described by the following equation:

$$\frac{1}{\text{maximum values for } \epsilon_e} = \frac{1}{\epsilon_m} + \left(\frac{b}{\sigma}\right)^k \quad (9)$$

where b and k are constants (for sol-type asphalts $k = 1$); ϵ_m represents the maximum elastic deformation at infinite time and stress (Fig. 8).

c. Mechanical Model System of Various Types of Asphalts

A mechanical model designed to represent the rheological properties of asphalts at short loading times may consist of combinations of linear elements, viz., an ideally elastic and a purely viscous element and one showing retarded elasticity. A simple representation of such a model is given in Fig. 9, which is a combination of a Maxwell and a Voigt element. For this

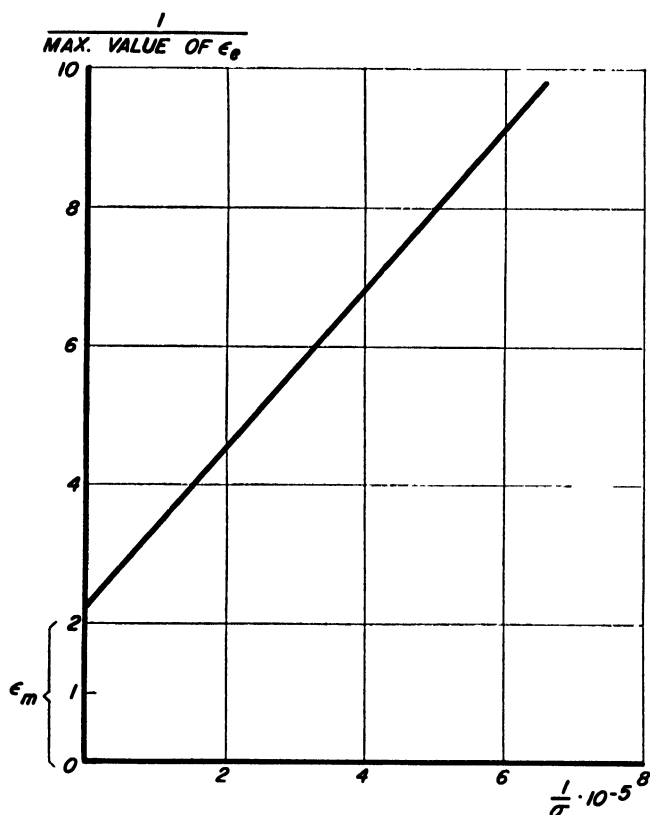


FIG. 8. Relation between maximum recovery and stress for asphalt b'

model the following equation obtains for deformation at constant stress:

$$\epsilon = \frac{\sigma}{E_1} + \frac{\sigma}{Q_1} \cdot t + \frac{\sigma}{E_2} (1 - e^{-t/\lambda_r}) \quad (10)$$

where $\lambda_r = \frac{Q_2}{E_2}$ = retardation time.

Differences in rheological properties between asphalts can be represented in the model by different values for the parameters.

For asphalts of type *a* in Fig. 5, which have practically no retarded elasticity, the parameters E_2 and Q_2 are almost insignificant. Figure 5 shows that the rheological behavior of this type of asphalt can almost completely be described by E_1 and Q_1 (Maxwell model).

Asphalts of the elastic sol type (*b* in Fig. 5), which show ideal and retarded elasticity as well as viscous flow, can be described by the four elements of the model.

The rheological behavior of gel-type asphalts (*c* in Fig. 5), which at not too high shearing stresses and at slight deformations do not show permanent deformation, can be described by means of the model, omitting the viscous element Q_1 .

Figure 9 gives, in its simplest form, the rheological character of different asphalts. Since, however, asphalts consist of a large number of components differing in chemical character, molecular weight, and size of disperse particles, their rheological properties will in general not allow of exact repre-

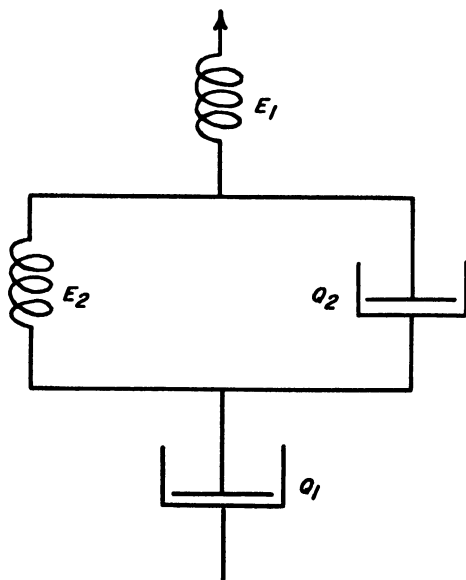


FIG. 9. Simple model illustrating rheological behavior of asphalts

N ^o	PEN/25°C	TEMP. R & B, °C	P. I.
1	4	82	0
2	16	67	0
3	64	57.5	0

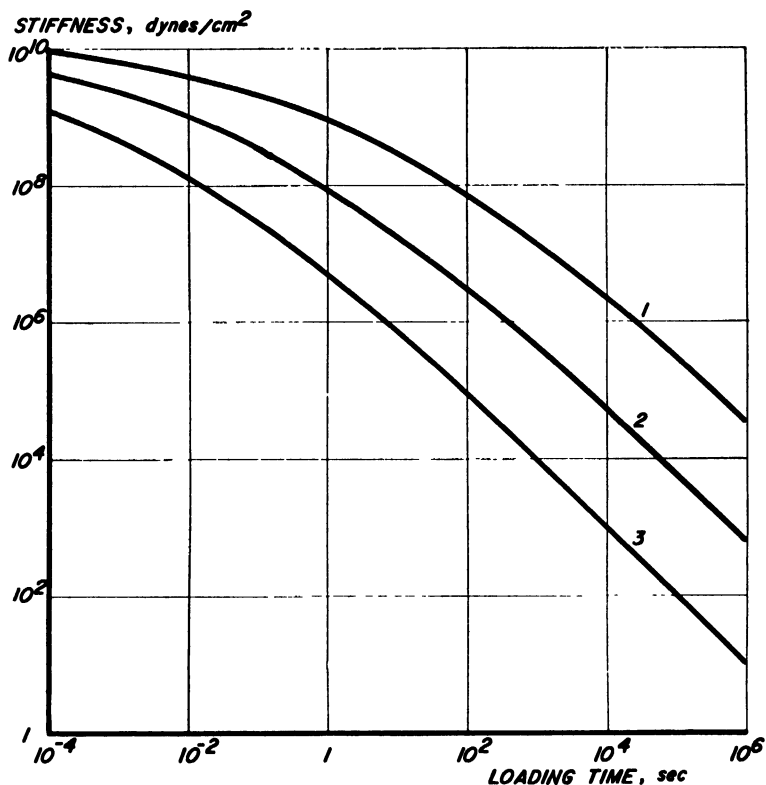


Fig. 10. Stiffness as a function of loading time for asphalts of different hardness but of equal P.I.

sensation by a simple model. A suitable model will have to contain a series of elements and the most adequate representation is by an infinite series of Voigt elements with a continuous spectrum of retardation times from $\lambda_r = 0$ to $+\infty$.

The nonlinear functions at considerable deformations and long loading times are not described by the model of Fig. 9. The representation of the maximum in the elastic recovery requires a nonlinear elastic model (as suggested by Saal⁴); still more complicated models are necessary to represent

⁴ R. N. J. Saal, in "The Properties of Asphaltic Bitumen with Special Reference to Its Technical Application" (J. P. Pfeiffer, ed.), p. 52. Elsevier, Houston, Tex., 1950.

thixotropy of gel-type asphalts, as the structure of the material changes during deformation. This matter will not be discussed here.

d. Influence of Hardness on Time Dependence of Stiffness

The relation between stiffness and time of loading at a given temperature is, for asphalts of the same rheological type, dependent on the hardness of the asphalt, as can be derived from measurements on asphalts with different penetrations at 25° C. and equal penetration indexes. The results of these measurements are represented in Fig. 10 for sol-type asphalts with penetrations at 25° C. of 4, 16, and 64 and a P.I. = 0.

This figure shows that for asphalts of the same rheological type but of different hardness the log stiffness—log time curves have approximately the same shape. Hence, differences in hardness can manifest themselves in the curve being shifted along the log time axis. If the ratios between the hardnesses (penetrations) are equal, the curves are shifted over equal distances.

e. Influence of Temperature on Stiffness

Asphalts are thermoplastic materials; their stiffness decreases considerably as the temperature is raised.

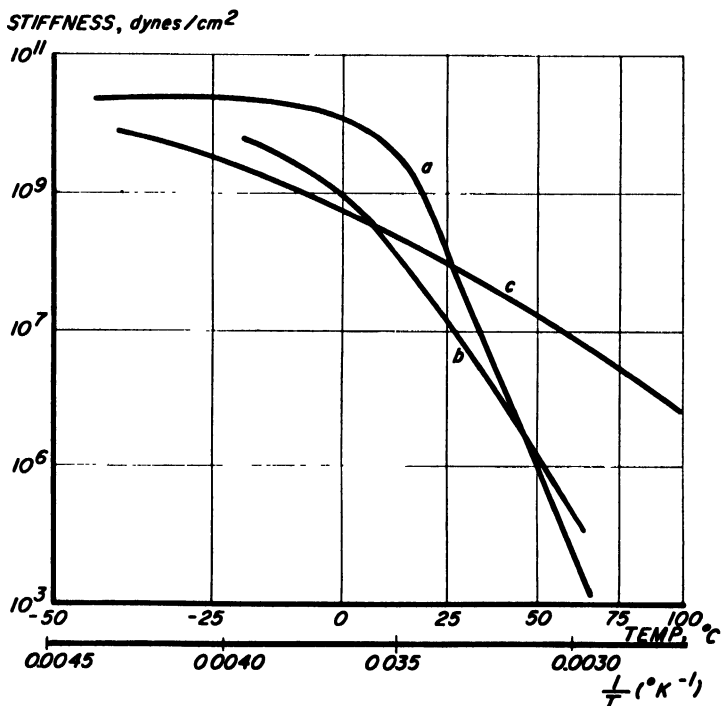


FIG. 11. Relation between stiffness and temperature for asphalts a, b, and c (Fig. 5) at loading times of 10 sec.

The relation between stiffness and temperature of the three above-mentioned asphalts *a*, *b*, and *c* at a constant loading time of 10 sec. is represented in Fig. 11.

At low temperatures the deformation is predominantly elastic; at high temperatures it is mainly the viscous properties which determine the character of the deformation. When asphalts are arranged according to temperature dependence of the stiffness at equal times they are in the same order as when arranged according to the time dependence at equal temperatures, as shown in Fig. 5. The dependence of the stiffness on temperature grows with its dependence on time.

A change in temperature implies shifting of the $\log S - \log t$ curves. Curves which have been determined at different temperatures can be made to coincide by shifting along the $\log t$ axis (Fig. 12); $\log S - (1/T)$ curves which have been determined at different loading times can be made to coincide by shifting along the $(1/T)$ axis (Fig. 13). For a limited temperature

PROPERTIES OF ASPHALT
 PEN / 25°C = 50
 TEMP R & B = 55°C
 P.I. = 0

- 1 TEMP = 0 °C
 2 " = 25 °C
 3 " = 50 °C

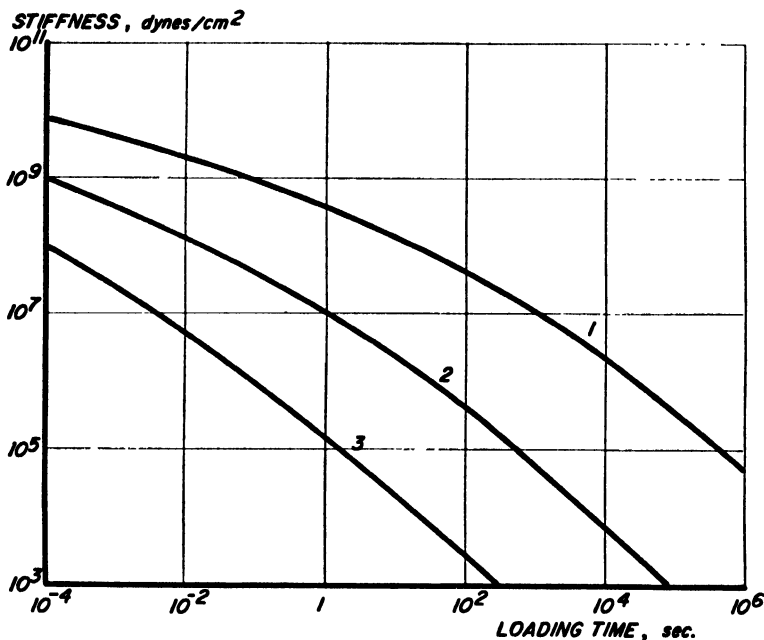


FIG. 12. Influence of temperature on the relation between stiffness and loading time

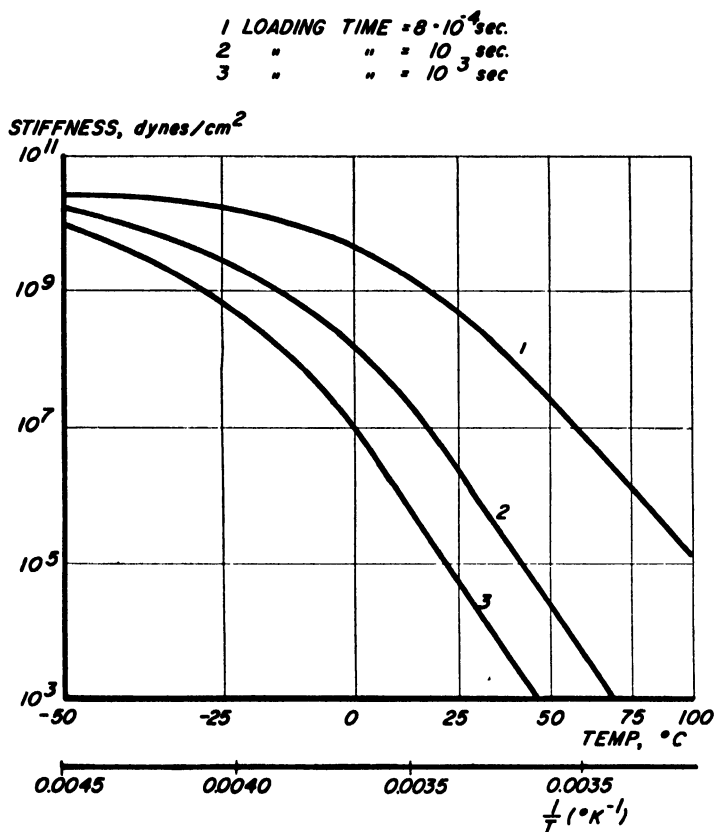


FIG. 13. Relation between stiffness and temperature at different loading times for the asphalt of Fig. 12.

range (below the temp. R & B) this general principle can be approximately expressed by the equation

$$S = f \left(\ln \frac{t}{t_0} - \frac{F}{RT} \right) \quad (11)$$

where R is the gas constant, F an activation energy, and t_0 a constant.⁵ This relation can be introduced into the mechanical model by assigning to all the viscous elements the same value of F .

The shift of the $\log S - \log t$ curve on the temperature being increased from T_1 to T_2 can, in the above-mentioned temperature range, be represented by

$$0.43 \frac{F}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

⁵ C. Van der Poel, in "The Rheology of Building and Road Making Materials" (M. Reiner, ed.), Chapter IX. North Holland Publ. Co., Amsterdam, 1950.

From this and from the experimental values, F' can be calculated, which for most asphalts is of the order of about 50 kcal./mole.

On the whole, the $\log S - \log t$ curves of an asphalt determined at different temperatures below the temp. R & B have approximately the same shape; at higher temperatures there may be deviations owing to a change in the rheological character of the asphalt. For instance, in gel-type asphalts the gel structure is changed at high temperatures to become a sol structure. It will be clear that this influences the relation between $\log S$ and $\log t$, so that in this case curves determined at different temperatures cannot be made to coincide.

At low temperatures and short loading times all asphalts show an ideal elastic behavior. The stiffness is then identical with Young's modulus E and has a value of ca. $2.5-3 \times 10^{10}$ dynes/cm.², which holds for all asphalts.

As already said the deformation at high temperatures is predominantly viscous. The ideal elastic effects will certainly still exist, but they are largely or entirely obscured by the much more pronounced viscous effects. In this connection it is of interest to point to the relation with the compressibility of asphalts. For a number of asphalts with penetrations at 25° C. between 40 and 60 Nederbragt⁶ finds practically the same value for the compressibility at temperatures between 25 and 90° C. This value is of the order of 40×10^{-12} cm.²/dyne, which corresponds to a bulk modulus K of 2.5×10^{10} dynes/cm.² As the relation between K and E is given by the equation

$$K = \frac{m}{3(m-2)} \times E \quad (12)$$

and, in this case, m may be put ca. 3, there is a satisfactory agreement between the value of E calculated from the compressibility at high temperatures and the maximum value found for the stiffness at lower temperatures.

f. Influence of Pressure on Rheological Properties

The viscosity of liquids and hence their stiffness increases at increasing external pressure. The effect of a pressure increase on the stiffness of asphalts, particularly of those with a low asphaltene content, may be very considerable as is seen in Table I (which gives the ratios between the stiffnesses at zero and at higher pressures for equal loading times and various asphalts at different temperatures).

The increase in stiffness produced by a pressure increase is linked up with a decrease of the "free volume" between the molecules. It has been said in Section 2c that the compressibilities of different asphalts are about

⁶ G. W. Nederbragt, in "The Properties of Asphaltic Bitumen with Special Reference to Its Technical Application" (J. P. Pfeiffer, ed.), p. 93. Elsevier, Houston, Tex., 1950.

TABLE I

INFLUENCE OF PRESSURE ON THE STIFFNESS OF DIFFERENT ASPHALTS
AT TEMPERATURES BETWEEN 20 AND 60° C.

Asphalt						Me- asur- ing temp., °C	Pressure P , kg/cm ²					
Origin	Type	Pen./ 25° C.	Temp. R & B, °C	P.I.	As- phal- tenes, % wt.		0	100	200	300	400	500
							Ratio $\frac{\text{stiffness at pressure } P}{\text{stiffness at pressure } P = 0}$					
Borneo	Newton- ian type sol type	47	47	-2.2	1.2	25.0 40.0 49.0	14.0 1 — 12.2	13 — 5.8	45 20 15	167 59 37	597 170 90	
California	sol type	54	48	-1.8	5.1	20.0 40.0 49.4	12.5 12.1 11.8	6.6 4.5 3.7	17 9.2 7.1	44 19 14	115 40 27	
Venezuela	sol type	44	55	-0.3	15.5	20.9 30.0 40.0	12.2 12.0 11.9	4.9 4.2 3.6	11 8.5 7.0	24 18 14	54 36 26	
Venezuela (blown)	gel type	35	86.5	+1.4	28.9	50.0 60.0	11.8 11.7	3.1 3.0	5.5 5.2	10 9.1	19 16	

the same, which means that for these materials the decrease of the "free volume" caused by pressure increase is about equal. The "free volume" of high-molecular products is smaller than that of low-molecular substances, so that at equal compressibility the decrease of this volume caused by pressure is relatively greater in the former case. Consequently, the increase in stiffness of asphalts owing to increase of pressure is greater as the molecular weight of the constituents of these asphalts increases.

The increase in stiffness of asphalts owing to pressure must, in the first place, be attributed to an increase in viscosity of the continuous phase. At equal stiffnesses of the asphalts the viscosity of the continuous phase of asphalts with a low asphaltene content, i.e., with a low concentration of disperse particles, is higher than that of asphalts with a high asphaltene content. Consequently, the change in stiffness under increased pressure is greater for the first-mentioned type of asphalts.

As the "free volume" increases at rising temperature the effect of the higher pressure on the stiffness is smaller as the temperature rises. This is also illustrated by Table I.

g. Breaking Strength

Strictly speaking, breaking strength is not a rheological property. Never-

theless, in the rheology of asphalts it is a very important quantity for their practical application as it sets a limit to the permissible stresses. Since in most applications the asphalt undergoes a certain deformation the resulting stress is determined by the stiffness at the time of loading and the temperature in that particular case.

The breaking strength of asphalts is not a constant value but depends on the time of loading and on the temperature, although to a much smaller extent than does the stiffness. At low temperatures and short times of loading the maximum value for the breaking strength of various asphalts is about 3×10^7 dynes/cm.²; this value decreases at longer loading times.² As the maximum value of the stiffness is 3×10^{10} dynes/cm.², there is no risk of rupture at strains smaller than $\epsilon = 10^{-3}$, i.e., 0.1 %. At greater strains rupture does not necessarily occur, but may do so depending on the stiffness and therefore also on the time of loading and the temperature.

3. ROUTINE ANALYSES

a. Penetration

In actual practice asphalts are classified according to hardness on the strength of routine analyses, among which the determination of the penetration⁷ is one of the most frequently used.

As a rule, the penetration is determined by applying a load of 100 gm. to a standardized needle for a time of 5 sec.; the distance of penetration is recorded in tenths of a millimeter.

If the asphalt adheres to the needle shear occurs in the material. Hence, a given penetration represents a certain deformation under a certain load or, in other words, a certain stiffness during a certain time.

For asphalts which do not display retarded elasticity and which, in static measurements at not too short loading times, behave as Newtonian liquids, the relation between penetration and stiffness can be derived theoretically.

For this case the rate of penetration of the needle $\frac{d \text{ pen.}}{dt}$ is proportional to the load P and inversely proportional to the viscosity, hence to $S \cdot t$ and, approximately, to the penetration already reached, so that

$$\frac{d \text{ pen.}}{dt} = C \frac{P}{Q \times \text{pen.}} \quad \text{or} \quad Q = 2C \frac{Pt}{\text{pen.}^2}$$

or

$$S = 2C \frac{P}{\text{pen.}^2} \tag{13}$$

the stiffness and the penetration being taken at the same time.

⁷ *Am. Soc. Testing Materials Standards* D 5-25; I P 49/46.

Thus, for the above-mentioned asphalts the stiffness at the loading time in the penetration test is approximately inversely proportional to pen.² (Any influence of the point of the needle has here been neglected.)

The relation between penetration and stiffness of asphalts is complicated by the fact that the penetration determination is carried out at decreasing stress, whereas the stiffness is defined at constant (or sinusoidally alternating) stress. Consequently, the greater part of the deformation in the penetration test takes place in the very beginning, so that the time at which the stiffness must be computed for comparison with penetration (the "equivalent" loading time) is likely to be shorter than the actual penetration time.

It is very difficult to derive this equivalent loading time theoretically; therefore an empirical approach has been used. It appears that if, for asphalts of a different rheological character but with equal penetrations at 5 sec., $\log S$ is plotted against $\log t$, the resulting curves intersect, on an average, at a time of about 0.4 sec. (see Fig. 14). This means that different asphalts with equal penetrations at 5 sec. show the same stiffness determined under constant stress at a loading time of 0.4 sec. This time is used to derive a general relation between stiffness and penetration. Figure 15 shows this relation between stiffness at $t = 0.4$ sec. and penetration at $t = 5$ sec. for different asphalts with P.I. between -2 and $+6$. At high penetrations, hence, at considerable deformations, the quadratic relation between stiffness and penetration is approximated; however, at low penetrations, hence, at small deformations, the maximum value for the stiffness, as dealt with on page 380, cannot be exceeded.

The same ratio between equivalent and actual loading time exists, if other penetration times are taken. This follows from the fact that also the slopes of the $\log \text{pen.}$ - $\log t$ and the $\log \text{stiffness}$ - $\log t$ curves are closely related. This is shown by Table II, in which $\frac{d \log \text{pen.}}{d \log t} = B$ and $\frac{d \log S}{d \log t} = B'$ are given for a number of different asphalts and also the ratio B'/B which always is approximately -2 , the value which according to formula (13) must apply to asphalts without retarded elastic effects.

The above relationships imply that the influence of temperature upon penetration and stiffness are also closely related.

According to the empirical relation⁸

$$\log \text{pen.} = B \log t + AT + C \quad (14)$$

⁸ M. C. Siegmann, in "The Properties of Asphaltic Bitumen with Special Reference to Its Technical Application" (J. P. Pfeiffer, ed.), pp. 160-66. Elsevier, Houston, Tex., 1950.

No	PEN/25°C	P. I.
1	30	-2
2	30	0
3	30	+2
4	30	+4
5	30	+6
6	250	-2
7	250	0
8	250	+2

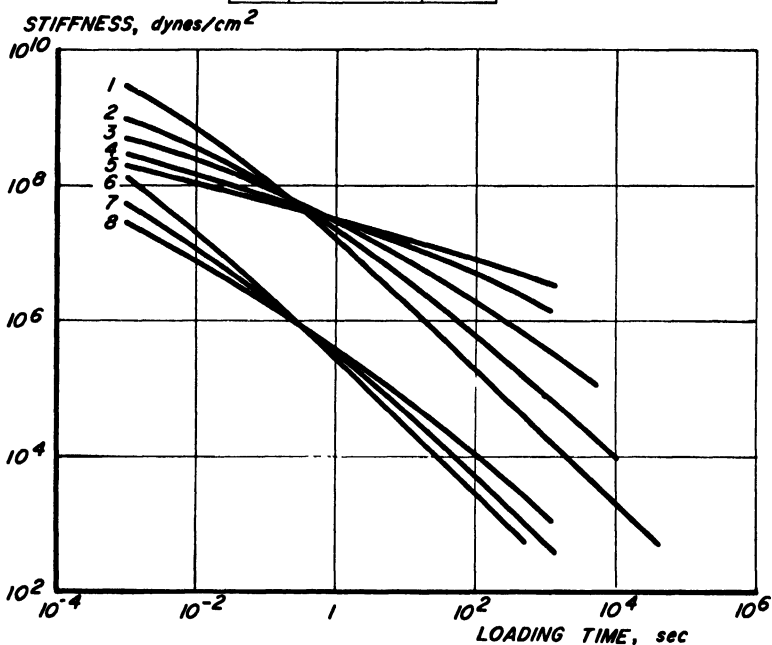


FIG. 14. Stiffness as a function of loading time at 25° C. for asphalts with penetrations at 25° C. of 30 and 250 and different P.I.

equal penetrations are obtained at constant $B \log t + AT$, hence at

$$\frac{1}{t} \frac{dt}{dT} = -2.3 \frac{A}{B}$$

According to equation (11) equal stiffnesses are obtained at constant $\ln \frac{t}{t_0} - \frac{F}{RT}$, i.e. at

$$\frac{1}{t} \frac{dt}{dT} = -\frac{F}{RT^2}$$

From this it follows that

$$\frac{A}{B} = 0.43 \frac{F}{RT^2} = 0.12 \quad \text{at} \quad 25^\circ\text{C.}$$

which value is in satisfactory agreement with experimental data (Table II).

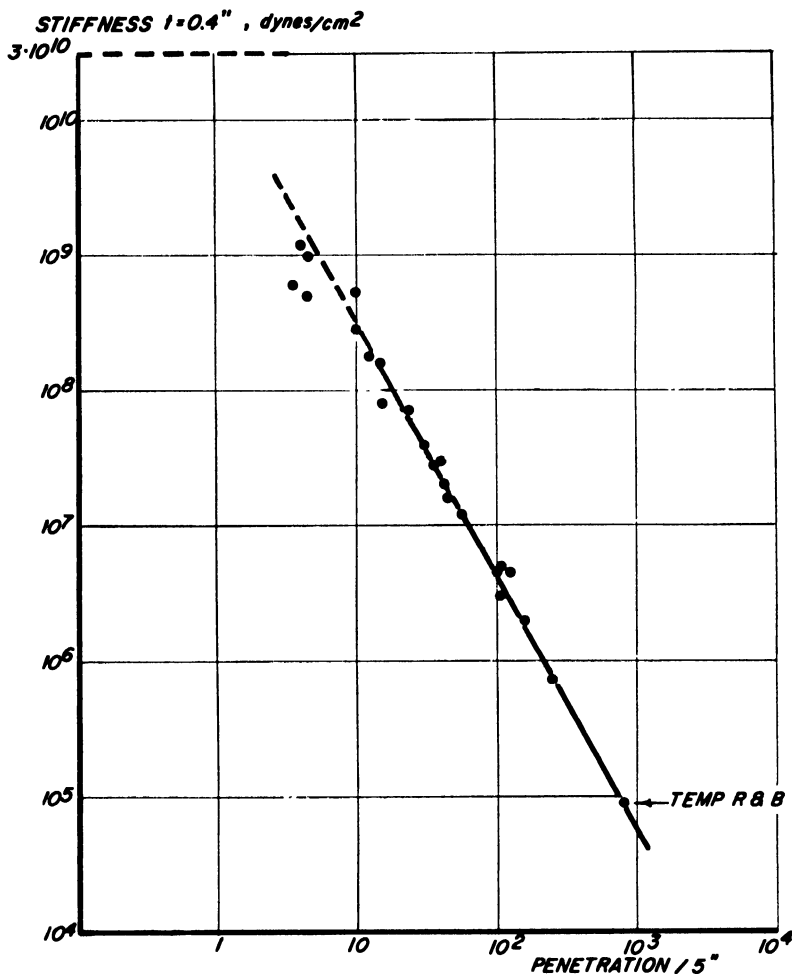


FIG. 15. Relation between stiffness at $t = 0.4$ sec. and penetration at $t = 5$ sec. for different asphalts with P.I. between -2 and $+6$.

In the technical applications of asphalts it is usual to express the temperature dependence of the penetration as the change of log pen. with temperature at a constant time. This change depends upon the slope of the log pen.-log time curve, i.e., upon the value of B . According as B has a lower value for a given change in temperature a smaller change of log pen. is found. The description of the temperature dependence of log pen. at a constant time is thus, in fact, mainly a representation of the rheological character of the asphalt, as expressed by B . Since the ratio A/B is practically constant (Table II), the rheological character of the asphalt is expressed to the same extent in the constant A . Now the latter has been

TABLE II
VALUES OF SOME CONSTANTS FOR DIFFERENT ASPHALTS REFERRING
TO STIFFNESS AND PENETRATION

<i>Pen./5" at 25° C. P.I.</i>		<i>B'</i>	<i>B</i>	<i>B'/B</i>	<i>A</i>	<i>A/B</i>
30	-2 0	-1.00	0.50	-2.0	0.055	0.11
	0.0	-0.70	0.37	-1.9	0.040	0.11
	+2 0	-0.53	0.26	-2.0	0.030	0.11
	+4 0	-0.38	0.19	-2.0	0.023	0.12
	+6.0	-0.29	0.15	-1.9	0.018	0.12
17	+0.1	-0.60	0.30	-2.0	0.039	0.13
96	+0.1	-0.77	0.39	-2.0	0.039	0.10
207	+0.6	-0.80	0.37	-2.2	0.037	0.10

taken as the basis of the penetration index:⁹

$$A = \frac{20 - \text{P.I.}}{10 + \text{P.I.}} \cdot \frac{1}{50} \quad (15)$$

Hence, the penetration index strongly reflects the rheological character of the asphalt. It will now be clear that the relation between stiffness and time, which is governed by the rheological character of the asphalt, may be related to the penetration index.

b. Softening Point Ring and Ball

Asphalt cannot be said to have a precise melting point in the strict sense of the term; on heating its stiffness gradually decreases. The softening point refers to an arbitrary point on the stiffness-temperature curve of the asphalt. This point is entirely dependent on the conditions of determination.

In the Ring and Ball method¹⁰ a "disk" of asphalt in a copper ring is loaded with a steel ball of 3.5 gm. The assembly is heated in a water bath at a rate of 4–5° C. per min. until the asphalt, under the weight of the ball, has sunk through a distance of 1 in. The temperature at which this takes place is the softening point Ring and Ball (temp. R & B).

The softening point R & B can be conceived as a point on the $\log S - 1/T$ curve at a given time of loading. This time must be very much shorter than the total time in which the R & B determination is carried out as the greatest deformation takes place in a short time immediately preceding the moment at which the recorded temperature is reached.

For an approximation of the "equivalent" loading time in the R & B test, use can be made of a theoretical deduction showing that for a material satisfying the equation

$$S = f(t \cdot e^{A'T})$$

⁹ J. P. Pfeiffer and P. M. van Doormaal, *J. Inst. Petroleum Technol.* **22**, 414 (1936).

¹⁰ *Am. Soc. Testing Materials Standards* D 36-26; E 28-42; I P 58/46.

under isothermal conditions, an analogous equation

$$S = f(t' \cdot e^{A'T}) \quad (16)$$

holds, if $t' = 1/pA'$ and the material has been subjected to a constant temperature rise of $p^\circ \text{C.}$ per second over a sufficiently long time; T being in this case the final temperature.¹¹

At the temp. R & B, A' appears to amount to about 0.2 reciprocal degree for all asphalts, whereas in the test a value of $p = 5^\circ/60 \text{ sec.}$ is prescribed, so that $1/pA' = 60 \text{ sec.}$ This value has to be corrected, because in the R & B test the temperature of the asphalt is somewhat lower than that of the liquid bath. This temperature difference can be deduced from R & B determinations at various rates of heating.

Differences in the rate of heating give rise to different final temperatures for the same deformation under the same load according to

$$\frac{e^{A'T_1}}{A'p_1} = \frac{e^{A'T_2}}{A'p_2} \quad (17)$$

so that an increase in the rate of heating by a factor 2 results in an increase in temp. R & B of 3°C. Actually, differences in temp. R & B are found as given in Table III.⁸

It is evident that a large part of the differences in temp. R & B can be directly explained by the influence of the rate of heating. The remainder is related to heat transfer from bath to bitumen, which requires a temperature difference proportional to the rate of heating. This difference, as calculated from the experimental data, is given in the last column of the table.

Under the condition of the R & B test (rate of heating 5°C./min.) the difference between the average temperature of the asphalt and that of the bath is about 3°C. Therefore, the time of 60 sec. calculated above obtains for a temperature 3°C. below the temp. R & B. This time has to be corrected by a factor of $e^{-3A'} \equiv 0.5$, so that theoretically the "equivalent" loading time in the R & B test amounts to about 30 seconds. For asphalts with a P. I. not exceeding +2 the stiffness is found to be on an average $1.5 \cdot 10^3 \text{ dynes/cm.}^2$ at this time.²

At the temp. R & B the penetration in 5 sec. of asphalts is of the order of 800. As in the penetration text the "equivalent" loading time has been deduced to be 0.4 sec., asphalts with a P. I. lower than +2 should also show equal stiffnesses at the temp. R & B and a time of 0.4 sec. This is actually the case, as appears from Fig. 15, which also includes the stiffness at the temp. R & B., viz. $9 \cdot 10^4 \text{ dynes/cm.}^2$ at 0.4 sec. This figure is in agreement with direct viscosity measurements on various asphalts at the temp. R & B. carried out earlier¹² giving a value of $\eta = 1.2 \cdot 10^4 P$. From the relation $S = 3\eta/t$ a stiffness of the same value as given above is calculated.

¹¹ R. N. J. Saal, *Proc. 4th World Petroleum Congr., Rome Sect. VI/A*, p. 29 (1955).

¹² R. N. J. Saal, *Proc. 2nd World Petroleum Congr., London* p. 515 (1933).

TABLE III
TEMP. R & B AT DIFFERENT RATES OF HEATING

Rate of heating °C./min.	Temp R & B °C.		Difference minus 3°C.		Temp. diff. between bath and asphalt
	Javanese asphalt	Mexican asphalt	Javanese asphalt	Mexican asphalt	
2.5	53	51	1.5 2	2 2.5	1.3
5	57.5	56			2.7
10	62.5	61.5			5.3

The fact that for asphalts with different values of the P. I. below +2 at the temp. R & B equal stiffnesses are found at a time of 30 sec. ($S = 1.5 \cdot 10^3$ dynes/cm.²) as well as at a time of 0.4 sec. ($S = 9 \cdot 10^4$ dynes/cm.²) explains why penetrations at the temp. R & B generally do not show appreciable differences for asphalts of different P. I. This is in agreement with the conclusion given at the end of section 3a, that P. I. figures based on one penetration and the temp. R & B. may describe the visco-elastic nature of an asphalt just as well as figures based on two penetrations at different times and the same temperature.

III. Asphalt-Mineral Aggregate Mixtures

1. INTRODUCTION

In many technical applications use is made of mixtures of asphalt and mineral aggregate. Dependent on the nature of the application the ratio between the quantities of asphalt and mineral aggregate and the nature of the mineral used may vary considerably. So-called protective coatings usually contain mixtures with a content of mineral material varying between 0 and 20% volume. In mastics this quantity varies between 45 and 70% volume; in so-called dense road carpets, such as sandsheet and asphaltic concrete, between 70 and 85% volume. In open graded mixtures even larger quantities may occur. The two first-mentioned mixtures have no voids, dense road carpet mixtures a low percentage of voids and open graded mixtures a voidage up to, say, 20%. The mineral aggregate used may vary from filler to coarse stones. In mastic and sandsheet mixtures filler and sand are used, asphaltic concrete also contains coarser material. The aggregate is mostly applied in the form of a graded mixture.

This chapter will not deal with all the types of mixtures enumerated above, but will be confined to mastics and dense road carpet mixtures. As blown-type asphalts are not used in road carpets they have not been dealt with either.

In applying these compositions it is the rheological properties of the mixture that count, which, naturally, are closely linked up with those of the

asphalt, but on which the mineral aggregate exerts a strong influence. The asphalt imparts visco-elastic properties to the asphalt-mineral aggregate mixtures. At small deformations and short loading times the relation between deformation and stress is a linear one. Again, the rheological behavior of the composition in this area can be completely described by means of the ratio σ/ϵ , i.e., by the stiffness, which, like that of pure asphalts, depends on the time of loading and the temperature.

If long loading times and considerable deformations are applied the relation between shearing stress and shear is no longer linear. This is stated by Lee and Markwich,¹³ among others. According to Nijboer¹⁴ a yield stress is found to exist under these conditions.

a. Methods

For the examination of asphalt-mineral aggregate mixtures at small deformations and short loading times dynamic methods have been applied. Van der Poel⁵ uses the torsional vibration test to determine stiffness. In this test a vertical cylindrical rod of composition is fixed on one end, carrying a cylindrical mass, which is many times that of the rod, at the top. A small electric motor with eccentric weights on its shaft and fixed to the mass on top of the rod sets up torsional vibrations in the system around the longitudinal axis of the rod. From the resonance frequency of the system the shear modulus τ/γ is calculated and also the stiffness, according to $\sigma/\epsilon = \text{about } 3 \tau/\gamma$. In this method stresses up to 10^7 dynes/cm.² can be applied.

For the study of rheological properties at considerable deformation and long loading times Nijboer¹⁴ uses the triaxial test, particularly on dense road carpet mixtures. A cylindrical test piece of the asphalt composition is placed in a water-impermeable elastic jacket surrounded by a liquid (water) in a closed space. The test piece is axially loaded with a constant load so that a constant stress σ_1 is developed. Owing to the deformation caused in the test piece a stress develops in the surrounding liquid, which reaches a constant value σ_3 and acts on the cylinder in a horizontal direction. Under these two stresses the test piece is in a state of equilibrium. By repeating this procedure at various stresses σ_1 a combination of different values for σ_1 and σ_3 is obtained. If these data are represented in the form of a Mohr stress diagram, the relation between the normal stress σ and the shearing stress τ can be derived. An example of this is given in Fig. 16. The tangent to the Mohr stress circles cuts off part of the ordinate. This value of τ is considered as the yield stress of the material at zero pressure and is called the initial resistance τ_e .

¹³ A. R. Lee and A. H. D. Markwich, *J. Soc. Chem. Ind. (London)* **56**, 146 (1937).

¹⁴ L. W. Nijboer, "Plasticity as a Factor in the Design of Dense Bituminous Road Carpets." Elsevier, Houston, Tex., 1948.

In the plane of shear, however, there is not only a shearing stress but also a normal stress. At plastic deformation of the material this normal stress causes a frictional resistance between the aggregate particles. The boundary condition for plastic flow can be derived and may be described as follows:

$$\frac{\sigma_1 - \sigma_3}{2} = \left(\frac{\sigma_1 + \sigma_3}{2} \tan \varphi + \tau_e \right) \cos \varphi \quad (18)$$

where φ is related to the coefficient of friction f between the particles according to $\varphi = \arctan f$, and is equal to the slope of the tangent to the Mohr stress circles in Fig. 16.

The two factors τ_e and φ refer to the material in a state of equilibrium; no allowance is made for elastic effects.

To determine the resistance at flow Nijboer withdraws, at a constant rate, a small quantity of the surrounding liquid. Consequently, the stress σ_3 is reduced and flow occurs in the material at a constant rate of shear. It appears that the stress σ_3 also remains constant at a lower level. By repeating this procedure, each time at higher loads, and by analyzing the results in a Mohr stress diagram, the resistance of the mixture at flow in relation to the stress applied can be derived with the aid of the formula

$$\eta_m \cdot \frac{d\epsilon_1}{dt} = \frac{2}{3 - \sin \varphi} \left[\frac{\sigma_1 - \sigma_3}{2} - \left(\frac{\sigma_1 + \sigma_3}{2} \tan \varphi + \tau_e \right) \cos \varphi \right] \quad (19)$$

where η_m is a differential viscosity of the mixture.

The constants τ_e , φ , and η_m , which are used for the description of the

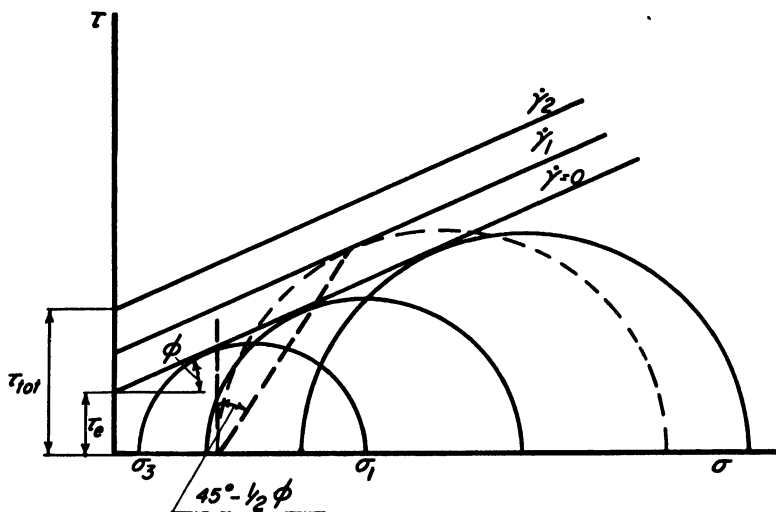


FIG. 16. Mohr's diagram of stresses in triaxial shear test

rheological behavior of the asphalt compositions at plastic deformation, have been derived by Nijboer at stresses $\sigma_1 > 5 \times 10^6$ dynes/cm.²

In this system the material is considered to be a Bingham material with a yield stress dependent upon stress conditions. This naturally implies a certain idealization, so that the values of τ_e and η_m are somewhat dependent upon experimental conditions. As with many other materials, the introduction of a yield stress, however, is a very convenient form of description of the properties of the material, so that the method can be considered suitable for engineering purposes and for obtaining a fundamental idea of the behavior of asphalt compositions at plastic deformations.

2. RHEOLOGICAL PROPERTIES OF ASPHALT-MINERAL AGGREGATE MIXTURES

a. Influence of the Mineral Aggregate Concentration

(1) *Dynamic Investigation at Short Loading Times.* The stiffness of asphalt-mineral aggregate mixtures depends on the stiffness of the asphalt and the volume ratio of asphalt to aggregate. When considering mixtures in which the asphalts have the same stiffness, the influence of the volume concentration of the aggregate can be derived from Fig. 17.

In this figure the stiffness of various mastics has been plotted as a function of the concentration by volume C_v of mineral aggregate. These mastics have been prepared using two different asphalts and the measurements have been carried out at such a temperature and time of loading that the two asphalts show the same stiffness, viz., 2×10^{10} dynes/cm.². The mineral aggregate consists of filler (particle size $< 74 \mu$) and sand (particle size from 74μ to 2 mm.). It will be seen that the ratio by volume of asphalt to mineral aggregate is the only important factor. In these compositions the nature and the particle size of the mineral have no influence on the stiffness of the mixture; in spite of the variations in particle size and grading of the mineral (filler, sand, and mixtures of these) all the points practically lie on a single curve. Only at high aggregate concentrations (ca. 80 % volume and higher) is some influence of the grading of the aggregate mixture and the corresponding variations in voidage observed. The stiffnesses may differ here by a factor of 2.

For mineral aggregate concentrations up to about 25 % volume the relation between stiffness and concentration may be expressed by means of an empirical equation developed by Eilers and Van Dijk:¹⁵

$$\frac{S_m}{S_a} = \left(1 + \frac{1.25C_v}{1 - 1.128C_v} \right)^2 \quad (20)$$

where m and a refer to mixture and asphalt, respectively.

¹⁵ H. Eilers, *Kolloid-Z.* **97**, 313 (1941).

	MINERAL AGGREGATE	ASPHALT		
		PEN/25°C	TEMP R & B °C	P. I.
▲ ▼ ○ □	QUARTZ FILLER LIMESTONE FILLER SAND QUARTZ FILLER + SAND	3	66	-2.3
● ■	SAND QUARTZ FILLER + SAND	13	54	-2.6

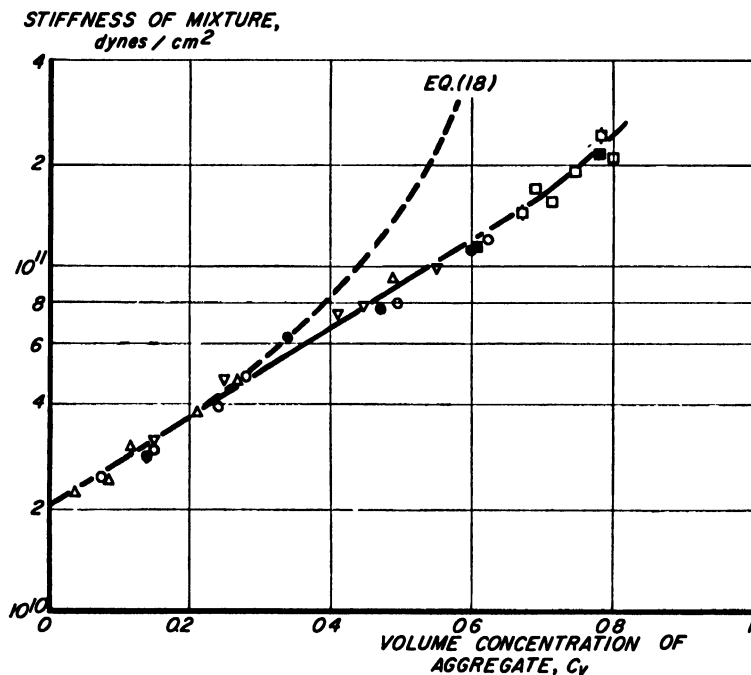


Fig. 17. Relation between stiffness of mixture and volume concentration of mineral aggregate.⁵

For very low concentrations this equation changes into Einstein's formula as follows:

$$\frac{\eta_m}{\eta_a} = 1 + 2.5C_v \quad (21)$$

At high concentrations the stiffness of the mixture is limited by the Young's modulus of the stone, which is of the order of 2×10^{12} dynes/cm.².

The influence of the temperature on the stiffness has been ascertained for dense sandsheet mixtures at a frequency of 60 c.p.s. This is illustrated by Fig. 18. These sandsheet mixtures contain either asphalts of the elastic

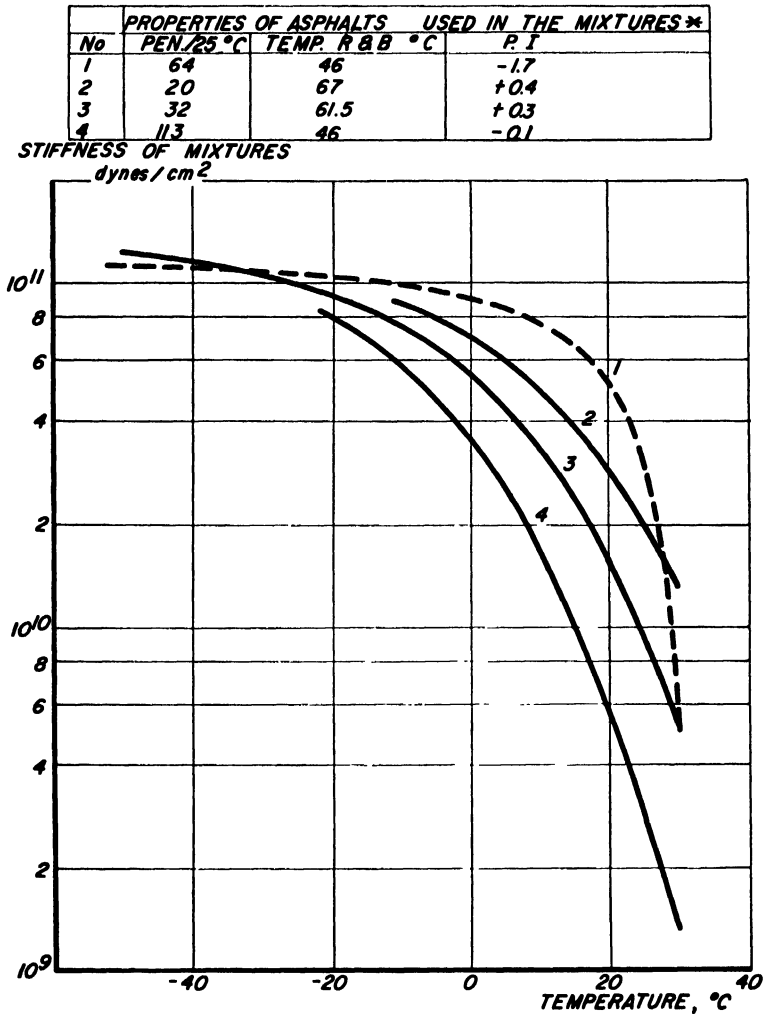


Fig. 18. Influence of temperature on stiffness at 60 c.p.s. of sandsheet mixtures containing different asphalts.⁵

sol type or an asphalt without visco-elastic effects. The composition of the mixtures under test is: 78 % weight of sand ($> 74 \mu$ –2 mm.), 13 % weight of limestone filler ($< 74 \mu$), 9 % weight of asphalt.

(2) *Static Investigation at Long Loading Times.* Asphalt-mineral aggregate mixtures also containing coarse particles have been examined with the aid of the triaxial test. Using this type of mixtures it is found that under the conditions of the test the concentration as well as the nature of the aggregate have an influence on the properties of the compositions. As in this test,

TABLE IV
INFLUENCE OF THE COMPOSITION ON THE PROPERTIES OF SANDSHEET
AND ASPHALTIC CONCRETE IN THE TRIAXIAL TEST

Composition of mineral aggregate, parts by wt.	Composition of mixture, % wt.			Triaxial test		
	Mineral agg., % wt.	Asphalt, % wt.	Voidage, % vol.	τ_e , 10 ⁸ dynes/ cm. ²	φ , degrees	η_m , 10 ⁹ poises
Sandsheet						
Sand, 80 pts. by wt.	92.16	7.84	9.0	1.2	27	84
	91.30	8.70	7.5	1.1	26	82
Filler, 20 pts. by wt.	90.50	9.50	3.8	1.0	27	83
	89.70	10.30	2.6	0.5	28-22	76
	88.90	11.10	1.1	0.0	19	28
Asphaltic concrete						
Chippings 10/30, 50.1 pts. by wt.	95.24	4.76	3.3	1.9	30	136
	94.34	5.66	2.5	1.5	30	130
Do. 5/12, 7.8 pts. by wt.	93.45	6.55	0.7	0.6	30-19	95
Do. 3/6, 2.9 pts. by wt.						
Sand, 32.0 pts. by wt.						
Filler, 8.0 pts. by wt.						

in which the mixtures are subjected to considerable deformations during long loading times, the relation between deformation and stress is not linear the behavior of the mixtures has been expressed by the quantities τ_e , φ , and η_m .

Table IV gives a survey of these quantities derived for sandsheets and asphaltic concrete mixtures of different compositions at stresses above 5×10^6 dynes/cm.². The asphalt used is of the elastic sol type with a penetration at 25° C. between 50 and 60.¹⁶

The initial resistance τ_e of the sandsheet gradually decreased with increasing asphalt content in the mixture up to ca. 9.5 % weight; at higher asphalt concentrations the decrease is very considerable. The same is observed for the viscosity of the mixture η_m ; the decrease of the angle of internal friction φ is more gradual.

A similar behavior is shown by asphaltic concrete, but the considerable decrease in resistance to deformation sets in at a lower asphalt content (5.66 %) owing to the lower voidage of the aggregate. In both asphalt compositions the resistance decreases considerably when the voidage has dropped to below 3 % volume.

¹⁶ L. W. Nijboer, "Plasticity as a Factor in the Design of Dense Bituminous Road Carpets," p. 46. Elsevier, Houston, Tex., 1948.

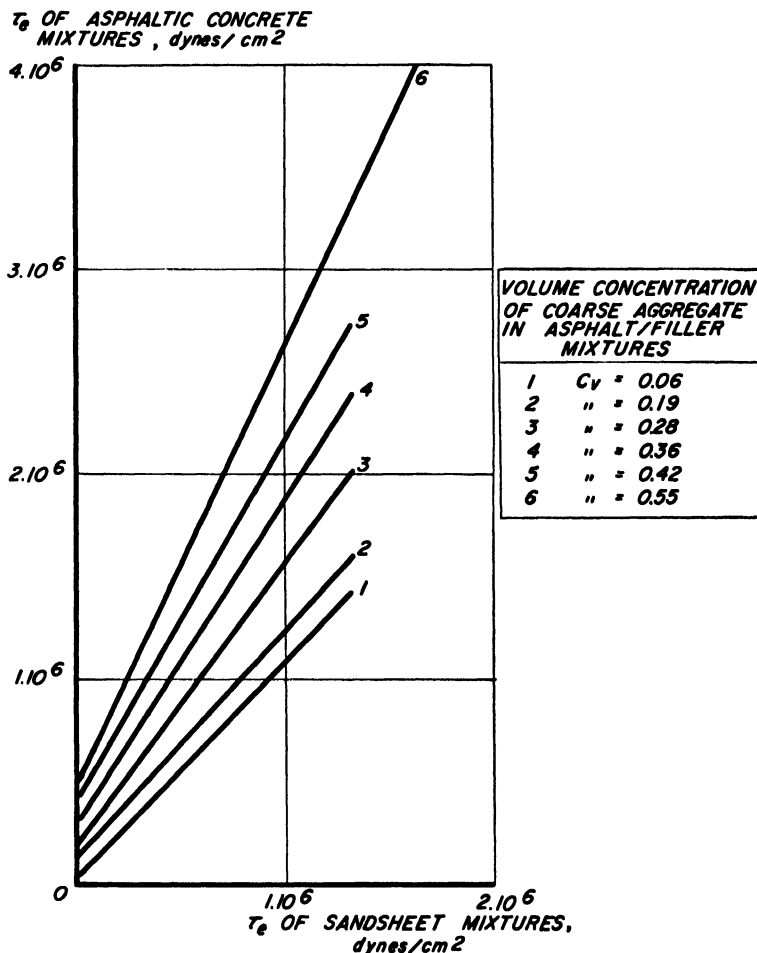


FIG 19. Relation between initial resistance of asphaltic concrete mixtures and that of sandsheet mixtures for different concentrations of coarse aggregate.

The significance of the above-mentioned boundary values for the practical application of these compositions in road constructions is that they are a limit for the asphalt concentration and the voidage in relation to the bearing capacity of the construction.

The initial resistance τ_0 is strongly influenced by the composition of the mineral aggregate in respect of filler content (particle size $< 74 \mu$) and coarser material content (> 2 mm.). According to Nijboer¹⁷ the initial resistance of a composition increases with the square of the ratio concen-

¹⁷ I. W. Nijboer, "Plasticity as a Factor in the Design of Dense Bituminous Road Carpets," p. 83. Elsevier, Houston, Tex., 1948.

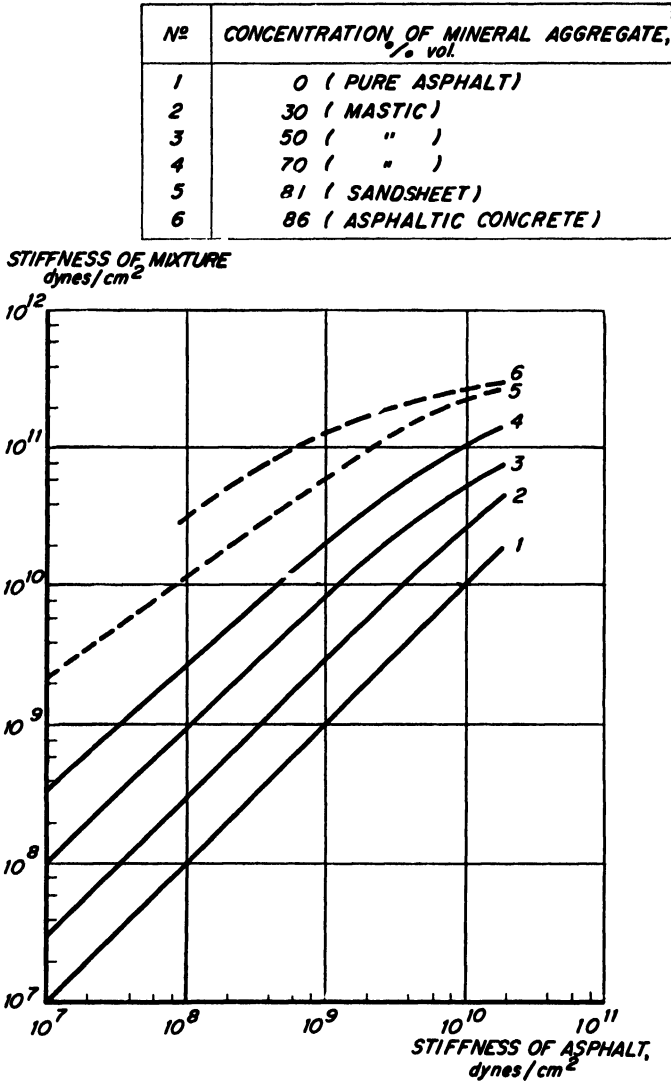


FIG. 20. Relation between stiffness of mixtures and that of pure asphalts at equal frequencies for different concentrations of mineral aggregate in the mixture.

tration by volume filler to asphalt (the $(F/B)_v$ ratio). The influence of coarser particles (>2 mm.), which moreover depart widely from the spherical shape, is illustrated by Fig. 18. Here τ_e of the coarse mixture (asphaltic concrete) has been plotted against the initial resistance of corresponding mixtures without coarse material (sandsheets) for various values of C_v of the coarse material.

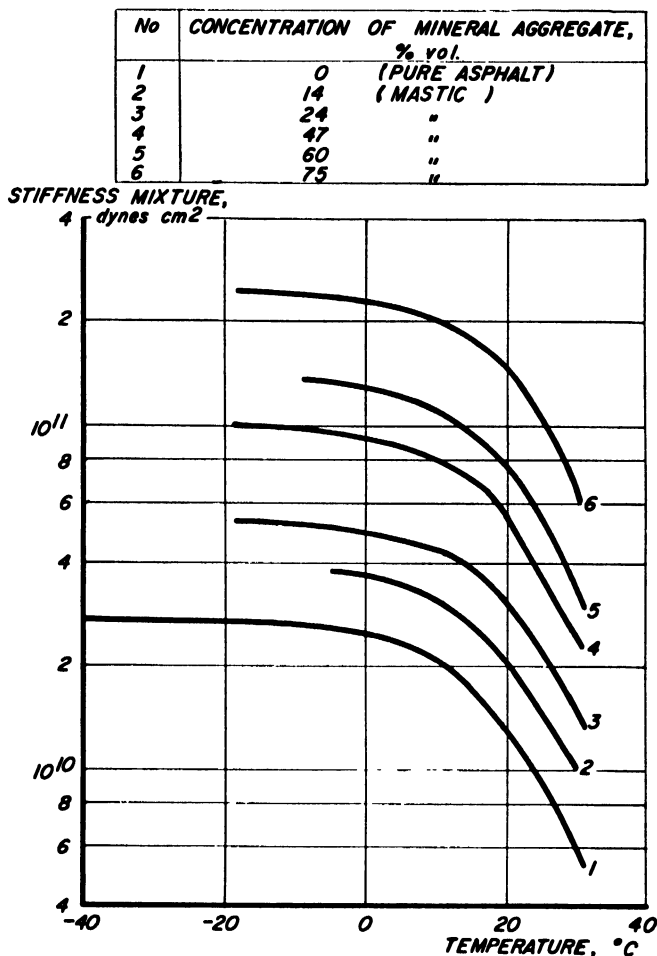


FIG. 21. Stiffness of mastics with different concentrations of mineral aggregate as a function of temperature at a frequency of 200 c.p.s.

The influence of temperature on initial resistance is considerable. According to Nijboer¹⁸ τ_e of sandsheet compositions decreases by a factor of about 1.7 on the temperature being raised 10° C.

In conclusion, it may be said that the factors governing the initial resistance τ_e of an asphalt composition exert similar influences on the viscosity of the mixture η_m .

b. Relation between the Rheological Properties of the Mixture and Those of the Asphalt Component

¹⁸ L. W. Nijboer, "Plasticity as a Factor in the Design of Dense Bituminous Road Carpets," p. 117. Elsevier, Houston, Tex., 1948.

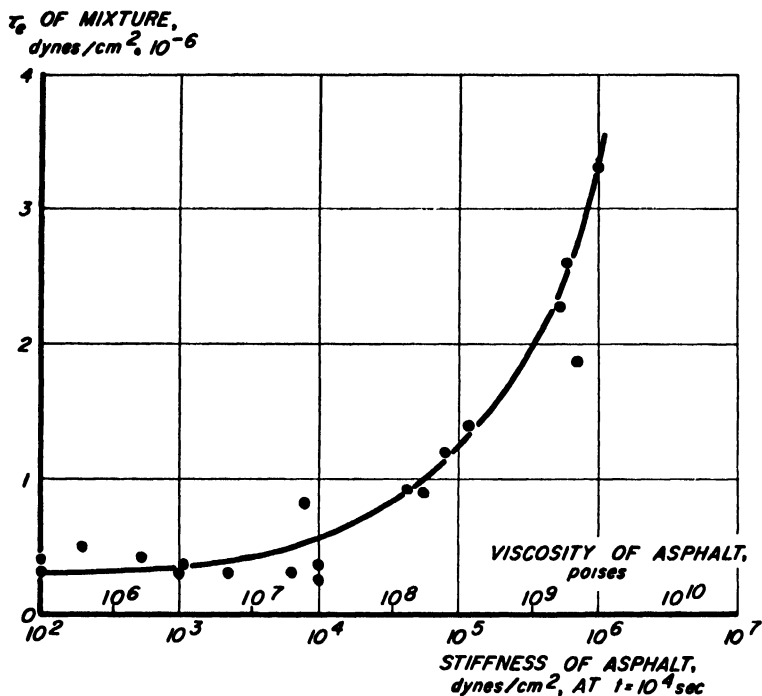


FIG. 22. Relation between τ_s of sandsheet mixtures and stiffness of asphalt at test temperature.

The rheological properties of asphalt-mineral aggregate mixtures are closely linked up with those of the asphalt used.

If mastics are subjected to dynamic tests applying short loading times and slight deformations, the relation between the stiffness of the composition and that of the asphalt can be derived from Fig. 20, where the stiffness of the composition has been plotted against that of the asphalt at equal loading times for different concentrations of mineral material. For every concentration of mineral aggregate the stiffness of the asphalt determines the stiffness of the composition. This is also illustrated by Fig. 21 which shows that the relation between the stiffness of the mixture and the temperature is analogous to the relation between the stiffness of the asphalt and the temperature. On closer study of the relation between the stiffness of asphalt and mixture it appears that the ratio of the stiffness of the mixture to that of the asphalt increases slightly as the stiffness of the asphalt decreases.

In the static measurements, in which large deformations and long loading times are applied at stresses greater than 5×10^6 dynes/cm.² (triaxial test), the values of τ_s and η_m of the composition are also determined by the stiffness (viscosity) of the asphalt.

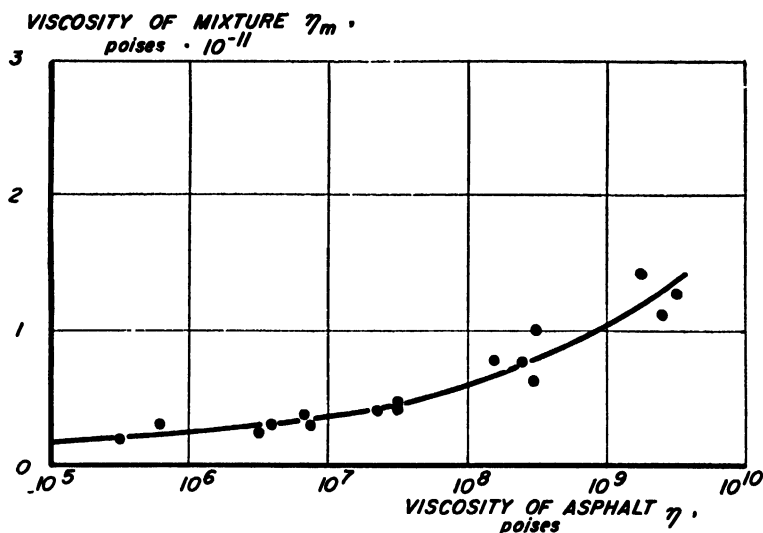


Fig. 23. Relation between viscosity of sandsheet mixtures and viscosity of pure asphalt at test temperature.

Figure 22 gives the relation between τ_e of the composition and the stiffness of the asphalt at a loading time of 10^4 sec., which more or less corresponds to the loading time used in the triaxial test (for comparison with Fig. 23 the viscosity of the asphalt is also given). The figures refer to sandsheet mixtures containing different asphalts, the measurements having been carried out at various temperatures between 5 and 40° C. (for the composition of the mineral aggregate see Table IV). The initial resistance τ_e increases with increasing stiffness of the asphalt under the conditions of the determination.

The viscosity of the mixture η_m in relation to the viscosity of the pure asphalt is given in Fig. 23. Here the viscosity of the asphalt is taken instead of its stiffness, because an exact comparable figure for the loading time is difficult to give. In the triaxial test the loading time during which the viscosity η_m is measured, is only part of the total loading time of the sample.

The value of the angle of internal friction φ of the mixture is only little influenced by the stiffness of the asphalt. At the variations in stiffness of the asphalts from 10^2 to 10^6 dynes/cm.² (as shown in Fig. 22) the value of φ for sandsheets changes from about 30° to about 25° .

For asphaltic concrete mixtures similar relations are found between τ_e , η_m , and the stiffness (viscosity) of the asphalt as in the case of sandsheet mixtures. The values of τ_e and η_m for asphaltic concrete are, however, twice as high as those for sandsheet.

c. Breaking Strength

The stresses on asphalt constructions permissible in actual practice are

limited by the breaking strength of the material. Under different conditions Van der Poel⁵ finds for sandsheets and asphalt-filler mixtures a maximum value of about $4 \text{ to } 5 \times 10^7$ dynes/cm.², which decreases at longer loading times. The maximum value may increase to about 1×10^8 dynes/cm.² at a high filler-asphalt ratio.¹⁹

The maximum value of the breaking strength of the compositions is of the same order of magnitude as that measured on pure asphalts. Hence, the breaking strength of the composition is predominantly determined by that of the asphalt; the mineral aggregate component has only little influence.

Nomenclature

E	Modulus of elasticity	S	Stiffness = $\frac{\sigma}{\epsilon}$
σ	Tensile stress	S_e	Stiffness = $\frac{\sigma}{\epsilon_e}$
σ_1, σ_3	Compressive stress in tri-axial test	m	Poisson's constant
ϵ	Strain	λ	Relaxation time
ϵ_e	Elastic strain	λ_r	Retardation time
ϵ_m	Maximum elastic strain	φ	Phase angle between alternating stress and strain
$\hat{\epsilon}$	Amplitude of alternating strain	φ	Arc tan f if f = coefficient of internal friction in triaxial test
$\hat{\sigma}$	Amplitude of alternating stress	ω	Angular frequency
τ	Shearing stress	F	Activation energy
τ_e	Initial resistance in tri-axial test	R	Gas constant
γ	Shear	K	Bulk modulus
η	Viscosity	P	Load
η_m	Viscosity of mixture	p	Rate of heating
Q	Coefficient of viscous traction = 3η	$A, A', B, B',$ C, b, k, t_0	= Constants
t	Time		
T	Temperature		

¹⁹ R. Eriksson, *Medd. Statens Vaginstitut.* **82**, 31 (1951).

CHAPTER 10

RHEOLOGICAL PROBLEMS OF THE EARTH'S INTERIOR

B. Gutenberg

I. Introduction: Structure of the Earth; Elastic Constants . . .	401
II. Introduction to Rheological Problems in the Earth	406
III. Processes Retarding Elastic Motion in the Earth	408
IV. Flow Processes in the Earth's Outer Layers: Post-Glacial Uplift . . .	413
V. The Coefficient of Viscosity and the Strength in the Earth	418
VI. Flow Processes in the Deeper Portion of the Earth's Mantle; Results Based on Deep-Focus Earthquakes	422
VII. Strain-Rebound Characteristics of Earthquake Series and Aftershocks . .	423
VIII. Rheological Phenomena in Geological and Geophysical Processes on a Small Scale	427
IX. Viscosity in the Earth's Core; Flow in the Core as Source of Terrestrial Magnetism	429
Nomenclature	430

I. Introduction: Structure of the Earth; Elastic Constants

About four to five billion years ago the earth began to develop as an individual body. Until about 1940 it was widely believed that it condensed from a hot cloud. However, most specialists now prefer the hypothesis that the earth has developed from accretion of cold particles. It is assumed on both hypotheses that heavier material, especially iron and metals associated with it, settled in the central portion of the earth and formed the core there, which was first suspected from the fact that the mean density of the earth—5.52—is considerably greater than that of the materials found in the upper layers. In 1912 the radius of the core—3450 km.—was determined from travel times of waves refracted through it, and later the observed times of waves reflected at its surface, either at the outside or at its inside, confirmed the result. A further complication was introduced when a relatively large increase in the velocity of longitudinal waves was established at a distance of about 1300 km. from the earth's center (Fig. 1, insert). The question is still unsolved whether the two boundaries, at depths of 2900 and at about 5000 km., are a consequence of a change in state, phase, or of material.

Observations of the tides of the earth's body and of the free movements of the earth's axis (a period of $420 \pm$ days instead of 305 days calculated for an absolutely rigid earth) leave no doubt that the average rigidity of

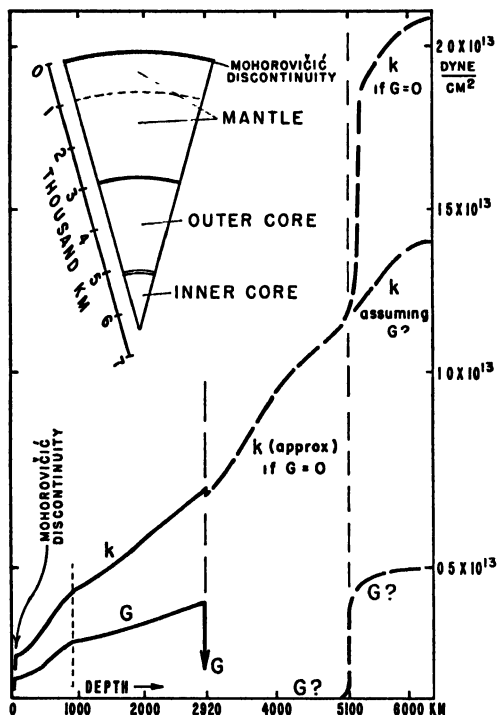


FIG. 1. Rigidity G and bulk modulus k as function of depth in the earth. Insert: Cross section through the earth. (Drafted by Mr. John M. Nordquist.)

the earth's core must be appreciably lower than that of the mantle. Since no transverse waves have been observed passing through the core (Fig. 1), it is generally believed that at least its outer portion is liquid. Thus far we have no indication of waves which have traversed the inner core as transverse waves, but this may be due to the difficulty of observing such waves which are expected to carry only relatively little energy since a large fraction of the already small percentage entering the inner core would be reflected back into the inner core when the waves reach its boundary on their way out.

Combination of the various hypotheses has led to an ever-increasing number of conclusions^{1, 2} concerning the properties of the core. Apparently, the assumption is still preferred that the whole core consists mainly of iron, which is liquid at least in the outer part. Other scientists prefer the combination of a liquid outer core consisting of rock with an inner core of solid

¹ B. Gutenberg, ed., in "Internal Constitution of the Earth," p. 183. Dover Publications, New York, 1951.

² H. Jeffreys, "The Earth," 3rd ed., p. 295. Macmillan, New York, 1952.

iron. Other hypotheses (summaries in refs. 1, 2) suppose that the whole core consists of rock and that the boundary of the inner core is a result of a change in phase of the material forming the whole core, or that the pressure which increases from about $1\frac{1}{2}$ million atmospheres at its outer boundary to about $3\frac{1}{2}$ million in its center has rendered difficult or even prevented an exchange of material in the deeper parts of the earth, so that even hydrogen remaining from the (solar) origin of the earth may play an appreciable role in the core.

In the mantle, a well-marked change occurs at a depth of between 900 and 1000 km. Above this depth the wave velocities and elastic constants (Fig. 1) increase more rapidly with depth than below. It is not certain whether or not the rapid increase between depths of about 200 and 1000 km. can be explained without the assumption of a (gradual) change in material or phase. The fact that earthquakes rather suddenly terminate at a depth of about 720 km. is probably not related to this change occurring at least 200 km. deeper, but may be caused by a decrease in stresses with depth, or by a decrease in viscosity resulting in flow rapid enough to prevent the reaching of the breaking strength.^{2a}

A layer with relatively low wave velocity (minimum a few per cent smaller than the velocities above and below) extends from a depth of about 50 km. roughly 100 km. downward and is probably a result of greater effect of the increase in temperature than that of the increase in pressure on the elastic constants in the depth range where the temperature is relatively close to the melting point. At greater depth the effect of the continued relatively rapid increase in pressure prevails again over that of the relatively small increase in temperature.^{2b}

A sharp discontinuity marked by a sudden increase in wave velocities and elastic constants at depths of 10 to 15 km. below sea level under the deeper parts of the oceans and at about 30 km. (lowlands) to 50 km. (mountains) in the continents is called "Mohorovičić discontinuity" after its discoverer. There are several types of evidence³ that starting at a depth of about 10 km. wave velocities and elastic constants decrease by small amounts downward in each of the crustal layers. Whereas the elastic constants (Table I) in the layers above the discontinuity differ regionally (e.g., ref. 4) with probably basaltic material (gabbro, olivine gabbro) forming their deeper portion, there is good evidence that at a given depth below the discontinuity the physical constants are everywhere the same within the

^{2a} B. Gutenberg, *Quart. J. Geol. Soc. London* **112**, 1, (1956).

^{2b} B. Gutenberg, *Bull. Geol. Soc. Amer.* **66**, 1203 (1955).

³ B. Gutenberg, *Geophysics* **20**, 283 (1955).

⁴ L. H. Adams, in "Internal Constitution of the Earth" (Gutenberg, ed.), p. 50. Dover Publications, New York, 1951; see also B. Gutenberg, *ibid.*, p. 364.

TABLE 1

SELECTED CHARACTERISTIC VALUES OF THE COEFFICIENT G OF RIGIDITY AND THE BULK MODULUS k IN THE EARTH'S CRUST; UNIT: 10^{11} DYNES/CM².

	G	k
Alluvium near the surface in continents ..	0.1	0.2
Alluvium at depth of 1 km. in continents .	1	2
Tertiary sandstone at 2 km. in continents	2	3
Granite at depth of 2 km. in continents	3	5
Continental layers at depth of $20 \pm$ km.	4	7
$5 \pm$ km. below oceanic bottoms (excluding shelf)	5	10
Depth of $80 \pm$ km. everywhere	$6\frac{1}{2}$	12

limits of observation. There is no agreement about the types of rock which form the mantle below the Mohorovičić discontinuity. Olivine, dunite, and others are being considered as representative. The suggestion by Lees^{4a} that the discontinuity may be produced by a change in phase and not in material has some merits^{4b} but it needs support by more results of laboratory research of the type now undertaken by Kennedy^{4c} and by MacDonald^{4d}.

It is still undecided whether at present the earth is cooling or getting hotter. It is believed that more heat is developed inside the continental layers of the earth by radioactive processes than in the ocean bottoms. On the other hand, recent observations indicate that the heat flow through the earth's surface is of the same order of magnitude (about $1\frac{1}{2} \times 10^{-6}$ cal./cm.² sec.) regardless of the location of the point of observation in continents or ocean bottoms. However, reliable data are still very scanty.

An additional difficulty in the investigation of the temperature in the earth's interior results from the fact that the change of thermal conductivity with depth is not known. It has been found that the electric conductivity increases 1000 fold or more in the upper 200 km. of the earth, and that its deeper parts are good electric conductors. If also in these layers an appreciable increase in the thermal conductivity takes place (a good correlation of the two coefficients under surface conditions is known only for metals), all deeper portions of the earth must have practically the same temperature. The highest and lowest scientifically supported values at a depth of 100 km. are about 1600 and 600° C., respectively. For the temperature in the core, values between about 1500 and many thousand degrees C.

^{4a} M. Lees, *Quart. J. Geol. Soc. London* **109**, 217 (1953).

^{4b} B. Gutenberg, *Stille-Festschrift*, p. 411. Enke, Stuttgart, 1956.

^{4c} G. Kennedy, Oral communication.

^{4d} G. MacDonald, Discussion during Conference on Theoretical Geophysics, Washington, 1956.

are being considered possible, with a current preference for values between 2000 and 4000°. This uncertainty as well as the unknown melting points of rocks at pressures of the order of one million atmospheres render very doubtful all estimates of the depth where the melting point of a given material can be expected. In addition, the amount of heat which is being developed at the various depths is still in doubt. Appreciably more heat must have been developed during the earth's earlier history when more short-lived radioactive elements existed. Another poorly known source of heat has been furnished by the hypothetical sinking of heavier material and rising of corresponding amounts of lighter material (see also Urey, ref. 4e, p. 13).

The first numerical values⁵ of the elastic constants in the earth as a function of depth have been obtained in 1923 after the velocity of earthquake waves throughout the earth had been calculated and the density in the earth as a function of depth had been obtained to a first approximation. In a purely elastic material and under conditions which permit the neglect of second-order terms the coefficient G of rigidity (in seismological papers usually indicated by μ) and the bulk modulus k may be found from the density ρ and the velocities V of longitudinal and v of transverse waves from the following equations:

$$G = \rho v^2 \quad (1)$$

$$k = \rho \left(V^2 - \frac{4}{3} v^2 \right) \quad (2)$$

These equations have been used generally to calculate the elastic constants in the earth (Table I, Fig. 1). However, on the basis of experiments with an organic glass⁶ and theoretical considerations,⁷ Kuhn and Vielhauer believe that the observed velocities of elastic waves are smaller by increasing amounts than those calculated from the elastic constants by use of equations (1) and (2) when the viscosity coefficient decreases below about 10^4 poises. Consequently, if for a material with such low viscosity the bulk modulus k is calculated from observed wave velocities by use of equation (2), the resulting value may be appreciably smaller than the bulk modulus for very rapid motion.

The accuracy of the values for G and k resulting from equations (1) and (2) decreases in general with depth as a consequence of the decreasing accuracy with which the density ρ is known in the deeper parts of the earth. In addition, for the earth's core the coefficient of rigidity G is not known.

^{4e} Symposium "Le noyau terrestre," *Ann. géophys.* **11**, 49 (1955).

⁵ B. Gutenberg, *Physik. Z.* **24**, 296 (1923); "Der Aufbau der Erde," p. 78. Borntraeger, Berlin, 1925.

⁶ W. Kuhn and S. Vielhauer, *Geochim. et Cosmochim. Acta* **3**, 160 (1953).

⁷ W. Kuhn and S. Vielhauer, *Z. physik. Chem.* **202**, 124, 161 (1953).

In the outer part of the core (Fig. 1, insert) ν and G are at least several powers of 10 smaller than in the mantle. The assumption that in the core $G = 0$ does not lead to discrepancies between any calculated and observed quantities such as tides of the earth's body or movements of the earth's axis.⁸ In the inner core G is possibly greater than in the outer core and may even be of the same order of magnitude as in the mantle. The possible effect of a corresponding small viscosity in the core on the observed wave velocities is an additional source of uncertainty in the calculation of k in the core. Kuhn and Vielhauer⁶ estimate that in the core of the earth the actual value of k may be 40 % greater than the value calculated from equation (2).

In the calculations of the bulk modulus k for Fig. 1 it has been assumed that ν and G are negligible in the outer core between depths of 2900 and 5100 km.; for the inner core two curves are given, one supposing $\nu = G = 0$, and a second on the hypothesis of Bullen^{9, 10} that, under high pressure, k depends on the pressure only and not on the material. The hypothetical effect of the low viscosity in the core on the wave velocity has not been considered in the calculation of k for Fig. 1. However, if Bullen's hypothesis is correct, the low viscosity would rather affect the calculation of the density than that of k .

II. Introduction to Rheological Problems in the Earth

In most early theoretical studies of geophysical phenomena it is assumed that mechanical processes on a large scale can be treated as purely elastic. Jeffreys¹¹ was one of the first to consider nonelastic processes. Originally, he represented delayed elastic processes (elastic afterworking, firmoviscosity, internal friction) following Sir J. Larmor, and time-dependent flow processes ("elastico-viscosity") following Maxwell by introducing the following convenient (but frequently very rough) approximation for a shear strain γ produced by a tangential stress S :

$$\gamma = \frac{S}{G} - \lambda_r \frac{d\gamma}{dt} + \frac{1}{\eta} \int S dt \quad (3)$$

where

$$\eta = G\lambda \quad \text{and} \quad \nu = G\lambda_r \quad (4)$$

G = rigidity, η = "coefficient of viscosity," λ = time of relaxation in vis-

⁸ P. J. Melchior, "Les Marées Terrestres," Monograph 4, Observatoire Royal de Belgique, 1954.

⁹ K. E. Bullen, *Monthly Notices Roy. Astron. Soc., Geophys. Suppl.* **6**, 50 (1950).

¹⁰ K. E. Bullen, *Ann. geofis. (Rome)* **6**, 1 (1953).

¹¹ H. Jeffreys, *Monthly Notices Roy. Astron. Soc.* **77**, 449 (1917).

cous flow; ν is designated the "coefficient of retarded elastic motion" or "coefficient of internal friction," and λ_r is the "time of retardation" in elastic processes (firmoviscosity, internal friction), that is, the time in which in such processes the strain falls to $1/e$ of its value, if the stress is removed. In the present section, η and ν are expressed in poises ($= \text{g./cm. sec.}$), G in g./cm. sec.^2 ($= \text{dynes/cm.}^2 = \text{baryes}$), λ and λ_r in seconds.

The first part of equation (3), $\gamma = S/G$, corresponds to Hooke's law; the following term is important only for short-period stresses ($d\gamma/dt$ not too small), and the last term only for stresses lasting for intervals of at least a noticeable fraction of the time $\lambda = \eta/G$. Consequently, in most equations for elastic processes at least one of these additional terms is insignificant. Jeffreys¹² suggests that to account for viscous flow (elastico-viscosity) in basic equations for elastic processes concerning the earth, the rigidity G should be replaced by $G/[1 + (\Omega/\lambda)]$ where Ω is the operator of definite integration defined generally by

$$\Omega f(t) = \int_{-\infty}^t f(u) du \quad (5)$$

For harmonic motion proportional to $e^{i\omega t}$, (5) can be evaluated, and it follows that G is to be replaced by

$$Giq\lambda/(1 + iq\lambda) \quad (6)$$

In equations representing first-order approximations of processes in which the effect of retarded elastic response (firmoviscosity, internal friction) is significant, the product $G f(t)$ of the rigidity G and any time-dependent function $f(t)$ should be replaced in the fundamental equations by

$$G f(t) + \nu \partial f(t)/\partial t \quad (7)$$

Terms containing only the bulk modulus k remain unchanged.¹³ Equation (18) is an example of the use of substitution (7). Even these rough approximations which in several respects lead to inconsistencies result in very complicated equations for which frequently no general solution can be given.

It is sometimes overlooked that firmoviscosity (retarded elastic response) in solids corresponds to viscosity in true liquids. In case of a suddenly starting constant stress, both result in a displacement which is always smaller than that given by Hooke's law, but approaches it asymptotically, whereas viscous flow in solids results in a displacement which starts with the value given by Hooke's law but continues to increase [compare also equations (10) and (11)]. Applications of substitution (5) or of the last term in equation (3) to equations for true liquids, or of equations containing

¹² H. Jeffreys, "The Earth," 3rd ed., pp. 8 and 242. Macmillan, New York, 1952.

¹³ B. Gutenberg and H. Schlechtweg, *Physik. Z.* **31**, 745 (1930).

ν or λ_r to equations for viscous flow of solids, lead to erroneous results. The following tabulation illustrates results obtained from equation (3) in special cases (t = time).

<i>Assumed Condition</i>	<i>Viscous Response in Solids</i>	<i>Retarded Elastic Response</i>
Short-period motion ($t \sim \lambda_r$)	Effect usually negligible	$\gamma = \frac{S}{G} - \lambda_r \frac{\partial \gamma}{\partial t} \quad (8)$
Long-period motion ($t \sim \lambda$)	$\gamma = \frac{S}{G} + \frac{1}{\eta} \int S \, dt$	} Effect usually negligible
Long-period motion ($t \gg \lambda$)	S approaches $\eta(\partial\gamma/\partial t)$	
$G = 0$ and $\nu > 0$ (viscous fluid)	—	$S = \nu(\partial\gamma/\partial t) \quad (11)$

It should be emphasized again that equation (3) and all equations derived from it describe at best very crude approximations to the processes involved since they have to fulfill the requirement of leading to expressions which can be solved without too great difficulties. Equation (3) can be applied to a delaying process (second term on right side) as well as to a viscous-type process (last term), but the representation of details is limited by the form of these terms and may not correspond to the details of the process in nature. Frequently, quantities assumed to be constant in the equations actually change with time, frequency of vibrations involved, and the amount of stress or strain. For further discussion, see Hardtwig.¹⁴ Equations (31) and (32) in Section VII are examples of equations based on observed nonelastic processes.

Numerical values of quantities related to nonelastic processes at selected depths in the interior of the earth are summarized in Table II; a few corresponding data found in laboratory experiments and from processes at the earth's surface are added. Except for the uppermost layers, even the order of magnitude of most of these quantities is doubtful, and it also should be considered that they depend on the assumptions made in their determination, on the duration or period of the process, on the history of the material and other variables.^{14a}

III. Processes Retarding Elastic Motion in the Earth

Various phenomena, such as internal friction, creep, elastic afterworking, may be considered to be "delayed elastic processes" to a first approxima-

¹⁴ E. Hardtwig, *Ann. geofis. (Rome)* **7**, 143 (1954).

^{14a} H. Mattice and P. Lieber, *Trans. Am. Geophys. Union* **35**, 613 (1954).

TABLE II
ORDER OF MAGNITUDE OF NONELASTIC CONSTANTS (A) IN SOME
MATERIALS AT THE SURFACE OF THE EARTH, AND (B) AT
SELECTED DEPTHS IN THE INTERIOR OF THE EARTH

(A) Material	$\log \text{Str.}^*$	$\log \eta$	$\log \lambda$		$\log \nu$	$\log \lambda_r$
			(a)	(b)		
Solenhofen lime-stone	$9\frac{1}{2} \pm$	$22 \pm$	$10\frac{1}{2} \pm$	$3 \pm$	$9 \pm$	$-2\frac{1}{2} \pm$
Gabbro	?	?	?	?	$9\frac{1}{4} \pm$	$-2\frac{1}{2} \pm$
Glacier ice	?	13 to 14	$3 \pm$	$-4 \pm$	?	?
Flowing lava	?	$\leq 5 \pm$	?	?	?	?
Flowing mud	?	$\leq 4 \pm$	?	?	?	?
(B) Depth						
10 km. (continent)	$9 \pm$	22 to 23	11	$4 \pm$	$9 \pm$	-2 to -3
100	$7?$	$22 \pm$	10	$2 \pm$	$9 \pm$	-2 to -3?
700	$< 7?$	$20 \pm?$	$8?$	$1?$	9 to $10?$	$-3 \pm?$
800 to 2900	$< 7?$	$< 20?$	$\leq 7?$	$\leq 0?$	$10?$	$-3?$
> 2900	$\ll 7?$	$5??$	?	?	?	?

* Str. = strength resisting viscous flow, in poises; η = coefficient of viscosity, in poises; λ = corresponding time of relaxation, (a) in seconds, (b) in years; ν = coefficient of retarded elastic response for elastic waves with periods of 0.1 to $20 \pm$ seconds, in poises; λ_r = corresponding time of retardation, in seconds.

tion. The only type of this group for which numerical data are available on the basis of geophysical observations is usually called "internal friction." It has a time of retardation λ_r of a small fraction of a second. Most large-scale geophysical phenomena, such as movements of the earth's axis or the tides of the earth's body, proceed too slowly to be delayed noticeably by internal friction. In these processes, $d\gamma/dt$ is very small in equation (3) in addition to the small value of λ_r . On the other hand, earthquake waves through the interior of the earth usually consist mainly of waves having periods of the order of 1 to 20 sec. Consequently, $d\gamma/dt$ may become large enough to result in a noticeable decrease in the amplitudes of waves traveling over distances of the order of magnitude of 1000 km. Jeffreys^{15, 16} finds that, to a first approximation, the distance Δ^* to which these waves have to travel before their amplitude a is reduced to $1/e$ as a consequence of retarded elastic motion alone is given by

$$\Delta^* = \frac{2V}{q^2\lambda_r} \quad (12)$$

¹⁵ H. Jeffreys, "The Earth," 3rd ed., p. 242. Macmillan, New York, 1952.

¹⁶ H. Jeffreys, *Monthly Notices Roy. Astron. Soc., Geophys. Suppl.* 1, 412 (1926).

where $q = 2\pi/T$. λ_r is defined by equation (4), V is the wave velocity and T is the period of the waves. The decrease in amplitudes of seismic waves by absorption (after corrections have been made for the expansion or contraction of the wave front) is usually expressed by

$$a = e^{-\kappa\Delta} a_0 \quad \text{or} \quad K = 1/\Delta^* \quad (13)$$

where a is the amplitude of the wave at the distance Δ , a_0 its amplitude at $\Delta = 0$, and K is designated the "coefficient of absorption."

For longitudinal waves through the interior of the earth (excluding the layers very close to the surface) the average value¹⁷ of K is about 0.12 per 1000 km. This corresponds to $\Delta^* = 8000 \pm$ km. for the distance along which the amplitude decreases by absorption to $1/e$. Since q is approximately unity, and V is of the order of 10 km./sec., it follows from equation (12) that λ_r is of the order of 0.003 sec. Combining this value with an average coefficient of rigidity of 2×10^{12} dynes/cm.² for the earth's mantle, equation (4) indicates that at depths of between about 20 and 2900 km. ν is of the order of 10^9 to 10^{10} poises. For the earth's core the absorption coefficient K is of the same order of magnitude as for the mantle.¹⁷ However, no corresponding values can be given for λ_r and ν on account of the unknown rigidity and viscosity in the core.

The coefficient of absorption of seismic surface waves with wavelengths of about 100 km. is of the order of 0.1 to 0.2 per 1000 km., that is, about the same as that for longitudinal waves through the earth's interior. It decreases noticeably with increasing wavelength. For about 1000 km. long surface waves of the Rayleigh wave type with periods of 230 sec. Ewing and Press¹⁸ have found that K is 0.018 per 1000 km. In this connection they have used the dimensionless quantity $1/Q$ to indicate the internal friction. It is defined by

$$1/Q = dE/2\pi E = \delta/\pi \quad (14)$$

where dE is the loss of energy per cycle in a vibrating body, E the total energy and δ the logarithmic decrement of free vibrations. For the $1000 \pm$ km. long surface waves, Ewing and Press find $1/Q = 590 \times 10^{-5}$. For elastic waves spreading spherically in a homogenous medium the absorption coefficient K is related to $1/Q$ approximately (ref. 19, p. 88) by

$$K = q/2QV \quad (15)$$

where again $q = 2\pi/T$, T = wave period, V = wave velocity. Combining

¹⁷ B. Gutenberg, *Bull. Seismol. Soc. Amer.* **35**, 57 (1945).

¹⁸ M. Ewing and F. Press, *Bull. Geol. Soc. Amer.* **63**, 1248 (1952).

¹⁹ F. Birch, J. F. Schairer, and H. C. Spicer, *Geol. Soc. Amer. Spec. Paper* **36**, 88-92 (1942).

equations (12), (13), and (15) we find that for elastic waves with a period T , approximately

$$\lambda_r = 1/qQ = T/2\pi Q \quad (16)$$

For seismic waves with periods of a few seconds, λ_r in seconds should be of the same order of magnitude as the dimensionless quantity $1/Q$. For a number of rock types, $1/Q$ has been determined from longitudinal as well as torsional vibrations of bars in laboratory experiments (ref. 19, p. 92); most values are between 10^{-2} and 2×10^{-3} , in agreement with the value of 3×10^{-3} found from longitudinal waves through the earth's interior. The laboratory experiments also indicate that $1/Q$ depends on a variety of factors, among them the period T . If T increases from 0.0001 to 1 sec., $1/Q$ for steel seems to increase by a factor $5 \pm$.

Sezawa²⁰ has introduced two friction terms into the equations for purely elastic waves, one for compressional and one for shear motion. For example, the equation for N_1 , the normal stress in the direction of the x -axis, is given on the assumption of Hooke's law by

$$N_1 = L\Theta + 2G \frac{\partial u}{\partial x} \quad (17)$$

where $L = k - (2/3)G$. L is one of Lamé's constants; it is usually indicated by λ in geophysical publications. Θ is the change in volume per unit volume, u is the displacement component in the direction of the x -axis. On Sezawa's assumptions for delayed elastic motion, equation (17) is replaced by

$$N_1 = L\Theta + 2G \frac{\partial u}{\partial x} + L' \frac{\partial \Theta}{\partial t} + 2\nu \frac{\partial^2 u}{\partial x \partial t} \quad (18)$$

where L' and ν are constants for the delayed elastic motion; ν , for delayed shearing motion, is given by (4); L' is a similar constant for delayed compressional motion. The equations for the tangential stresses T_1 , T_2 , T_3 in a purely elastic medium have to be treated similarly. For example, if v and w are the displacements in the direction of the y - and z -axis, respectively, we find for a medium with retarded elastic motion

$$T_1 = G \left(\frac{\partial w}{\partial y} + \frac{\partial v}{\partial z} \right) + \nu \frac{\partial}{\partial t} \left(\frac{\partial w}{\partial y} + \frac{\partial v}{\partial z} \right) \quad (19)$$

The resulting equations for the change Θ in volume per unit volume, and the shear ω are

$$\frac{\partial^2 \Theta}{\partial t^2} = \frac{k + \frac{4}{3}G}{\rho} \nabla^2 \Theta + \frac{L' + 2\nu}{\rho} \frac{\partial \nabla^2 \Theta}{\partial t} \quad (20)$$

²⁰ K. Sezawa, *Earthquake Research Inst. Tokyo Bull.* **3**, 43 (1927).

$$\frac{\partial^2 \omega}{\partial t^2} = \frac{G}{\rho} \nabla^2 \omega + \frac{\nu}{\rho} \frac{\partial \nabla^2 \omega}{\partial t} \quad (21)$$

where ρ = density. They cannot be solved without introduction of specific wave forms. On the basis of his findings for a number of such forms, Sezawa came to the conclusion that, as a consequence of internal friction, seismic waves are gradually getting longer and flatter in traveling. The velocity of the beginning of the disturbance remains unchanged.

Gutenberg and Schlechtweg¹³ have pointed out that the effect of friction in compressional motion is negligible relative to its effect in shear motion and have modified Sezawa's equations correspondingly. Especially, the constant L' is then given by

$$L' = -\frac{2\nu}{3} \quad (22)$$

Gutenberg²¹ has studied the resulting changes in wave form. Since Sezawa's method cannot be applied to sinusoidal waves, Gutenberg defines the wave period T for the various wave forms used by Sezawa, e.g.,

$$y = Bb^{-2}xe^{-x^2b^{-2}} \quad (23)$$

as twice the time between successive crossings of the rest line in opposite directions, and finds that for seismic waves the so defined original wave period T_0 increases with distance Δ to the value T_Δ given approximately by

$$T_\Delta^2 = T_0^2 + \frac{5\nu\Delta}{\rho V^3} \quad (24)$$

where ρ is the density and V the wave velocity. Equation (24) permits the calculation of ν and λ_r [equation (4)] from the observed increase in the periods of seismic waves with distance. The resulting values of ν and λ_r depend on the wavelength. If this increases from 100 m. to 100 km., ν increases from about 10^7 poises to about 5×10^9 poises, and λ_r increases approximately from 10^{-4} to 10^{-3} sec.²²⁻²⁵ These values are of the same order of magnitude as those mentioned above which result from the absorption coefficient K and from torsional vibrations of bars in laboratory experiments. However, other phenomena are involved in the observed increase

²¹ B. Gutenberg, ed., "Handbuch der Geophysik," Vol. 4, p. 22, 1932; Vol. 2, p. 553, Borntraeger, Berlin 1933.

²² B. Gutenberg, ed., in "Internal Constitution of the Earth," p. 385. Dover Publications, New York, 1951.

²³ B. Gutenberg, *U. S. Coast and Geodetic Survey, Spec. Publ. No. 201*, 163 (1936).

²⁴ B. Gutenberg, *Beitr. angew. Geophys.* **6**, 125 (1936).

²⁵ O. Meisser, *Veröffentl. Reichsanstalt Erdbebenforsch. Jena*, **9**, 70 (1929).

in prevailing wave periods with distance or time, such as decrease of absorption with increasing wavelength,²⁶ scattering,²⁷ and phenomena related to group velocity.^{28, 29} Since the actual process is very complicated it is usually assumed that only one type of mechanism is responsible for the combined effect of several.^{14, 14a, 30} Mathematically the various approaches are different types of approximations to fit a given functional relationship between the change in period of the waves on one hand and their distance from the source or their travel time on the other.

IV. Flow Processes in the Earth's Outer Layers. Postglacial Uplift

In practically all "classical" investigations of flow inside the earth it is assumed that the flow is Newtonian, i.e., that the ratio of the stress to the shear rate D does not depend on D . This is a rather special assumption, but frequently it can be used as a first approximation since usually the available observations are scanty, and the processes are too complicated to permit the finding of precise quantities. It should be noted that in most geophysical and geological publications the expression "viscous" is used to indicate Newtonian flow, the expression "plastic" for more general types of flow.

The only phenomenon which thus far has provided sufficient data for the qualitative investigation of subcrustal flow is the "postglacial uplift." In portions of Fennoscandia (Fig. 2), as well as in the Great Lakes-Hudson Bay region, the land is rising at a rate which has its maximum of the order of 1 m./century at present in the center of the respective formerly glaciated area, decreases toward zero near the boundary of the former ice sheet, and becomes slightly negative beyond.

In nearly all of the extensive literature concerning Fennoscandia^{31, 32, 33} it is assumed that the contemporary uplift is mainly a consequence of the removal of the ice sheet. According to Daly^{33a} this had a maximum thick-

²⁶ N. Ricker, *Geophysics* **18**, 10 (1953).

²⁷ H. Jeffreys, "The Earth," 3rd ed., p. 40. Macmillan, New York, 1952.

²⁸ H. Jeffreys, *Monthly Notices Roy. Astron. Soc., Geophys. Suppl.* **1**, 286 (1925); see also "Operational Methods in Mathematical Physics," Cambridge Univ. Press, London and New York, 1927.

²⁹ F. Press and M. Ewing, *Trans. Am. Geophys. Union* **29**, 163 (1948); see also M. Ewing and F. Press, *Bull. Seismol. Soc. Amer.* **42**, 315 (1952).

³⁰ H. Menzel, *Geophys. Prospecting* **2**, 139 (1954).

³¹ B. Gutenberg, *Bull. Geol. Soc. Amer.* **52**, 721 (1941).

^{31a} Data for Oslo, Stavanger, Bergen, and Narvik to 1952 furnished by H. S. Jellstrup, Norges Geografiske Oppmåling, Geodet. Afdeling, Oslo.

³² H. Renquist, in "Suomi, A General Handbook of the Geography of Finland," 40. 1952.

³³ A. Siren, *Fennia* **75**, 1 (1951); *Fennia* **72**; M. Sauramo, *Ann. Acad. Sci. Fennicae, Ser. A. III.* **44** (1955)

^{33a} R. Daly, "Our Mobile Earth," p. 189. Scribner, New York, 1926.

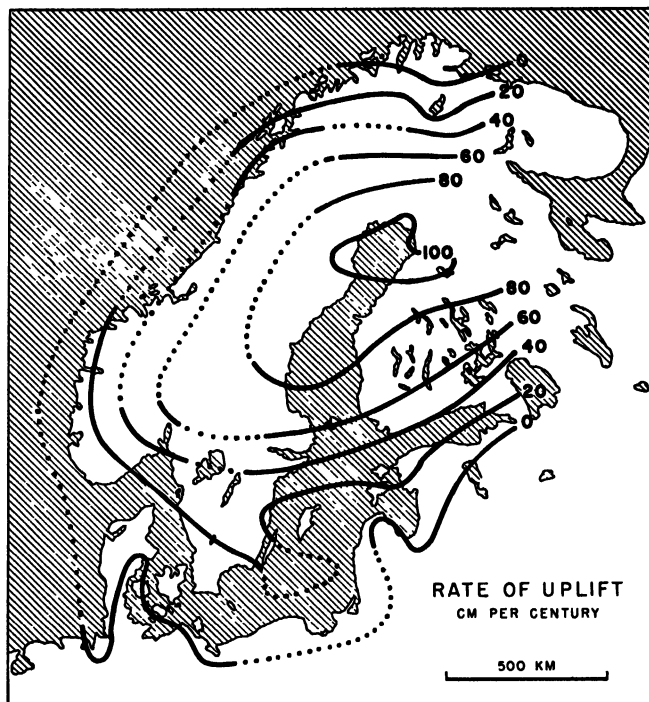


FIG. 2. Present uplift in Fennoscandia in centimeters per century based on records of tide gages (Gutenberg³¹ and recent data from Norway^{31a}) and on lake water levels in Finland (Siren³²). (Drafted by Mr. John M. Nordquist.)

ness of at least 2000 m. over the northern Baltic; other estimates are as high as 3000 m. The ice sheet began to melt, slowly at the beginning, about 40,000 years ago. About 9000 years ago, when the ice was reduced to patches northwest of the Baltic, the land near the former center of glaciation had risen between 250 and 300 m. An uplift of about 260 m. has been added there since. Figure 3 indicates that for the past 8000 years the flow was Newtonian with a fair approximation. Calculations assuming a viscous process lead to the conclusion that the center of the area is still about 200 m. below its equilibrium position. Negative gravity anomalies increase to about -40 mgal. as the center of the uplift is approached.³⁵⁻³⁸ However, effects of tectonic disturbances which are superposed upon those produced by the postglacial mass deficit result in irregularities in the distribution of

³⁴ F. Nansen, *Avhandl. Norske Videnskaps-Acad. Oslo*, Kl. 1, No. 12 (1928).

³⁵ W. Heiskanen, *Trans. Am. Geophys. Union* **32**, 524 (1951).

³⁶ E. Niskanen, *Ann. Acad. Sci. Fennicae, Ser. A* **53**, No. 10 (1939).

³⁷ R. A. Hirvonen, *Veröff. Finn. Geodät. Inst. No. 24* (1937).

³⁸ F. Model, *Mitt. geogr. Ges. Hamburg* **49**, 92 (1950).

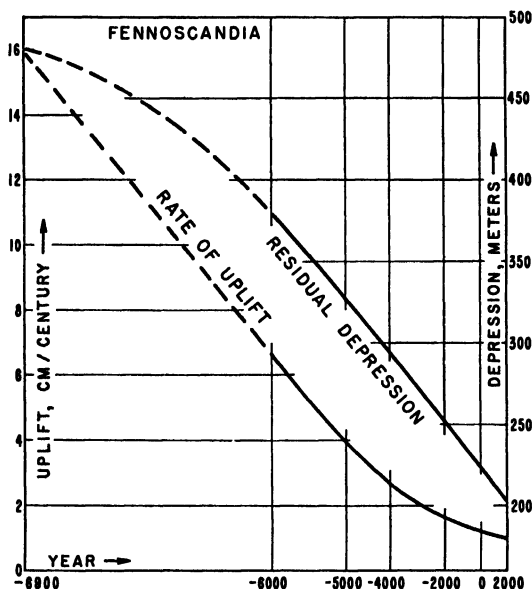


FIG. 3. Depression of the center of glaciation in Fennoscandia since 6900 B.C. and rate of uplift, based on data given by Nansen.³⁴ (Drafted by Mr. John M. Nordquist.)

gravity anomalies. It is therefore not possible to decide on the basis of the gravity anomalies how much of the present mass deficit of about 300 or even 400 m. indicated by the gravity data for the center of uplift³⁹ is a remainder of that mass deficit, caused by the melting of the ice.

The phenomena related to the uplift in northern North America correspond to those observed in Fennoscandia. However, all data are less plentiful and do not provide results of the same accuracy as those found for Fennoscandia. The maximum thickness of the North American icecap is estimated to have been between 2 and 3 km. Stanley⁴⁰ points out that along the east coast of Hudson Bay "south of latitude 55°50' North neither the islands nor the highest hills of the coastal zone are high enough to have recorded the marine limits, and abandoned beaches may be found up to their summit." The center of the uplift is probably in the southern part of Hudson Bay, and its maximum amount seems to exceed 300 meters. The most reliable findings for the present uplift in northern North America are based on records of tide gages in the Great Lakes. In Fig. 4 selected relative changes in sea level at pairs of tide gage stations are reproduced. They are calculated from differences in five-year means of the observed water

³⁹ W. Heiskanen, in "Handbuch der Geophysik" (Gutenberg, ed.), Vol. 1, p. 938. Borntraeger Berlin, 1936.

⁴⁰ G. M. Stanley, *Bull. Geol. Soc. Amer.* 50, 1936 (1939).

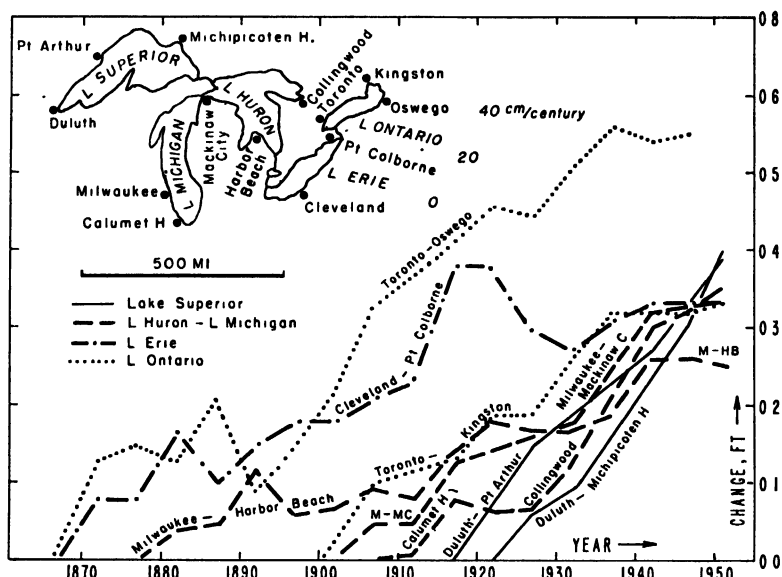


Fig. 4. Relative change in level (in feet) at pairs of gages in the Great Lakes.^{31, 41} Insert: Location of these gages and lines of equal uplift in centimeters per century, after Gutenberg.³¹ (Drafted by Mr. John M. Nordquist.)

level at pairs of gages. For each gage the measurements refer to an individual arbitrary reference point and for each pair the difference in the first five-year period is taken as zero.

Unfortunately, there is only one tide gage in the Hudson Bay with records covering a time interval long enough for use in calculations of sea-level changes. It is at Churchill, Manitoba, and even there data exist for only 24 years. Moreover, adverse meteorological conditions during a large part of the year, as well as ice which piles up during the winter and does not disappear until late in May or during June, make it advisable to use tide-gage data for Churchill for the months July to September only. Application of the method of least squares to the yearly sea level averages for the months July to September 1928 to 1951 gives an average rate of 1.05 ± 0.18 m./century for the uplift at Churchill.⁴¹ Six-year averages for the sea level at Churchill during July to September give the following values relative to an arbitrary zero point:

1928/33	1934/39	1940/45	1946/51	
+5 $\pm$ 4	-8 $\pm$ 5	-11 $\pm$ 4	-15 $\pm$ 6	cm.

The change from year to year is rather irregular, but this is true also for the changes of sea level in Fennoscandia. A part of the irregularities results

⁴¹ B. Gutenberg, *Arch. Meteorol. Geophys. u. Bioklimatol.* 7, 243 (1954).

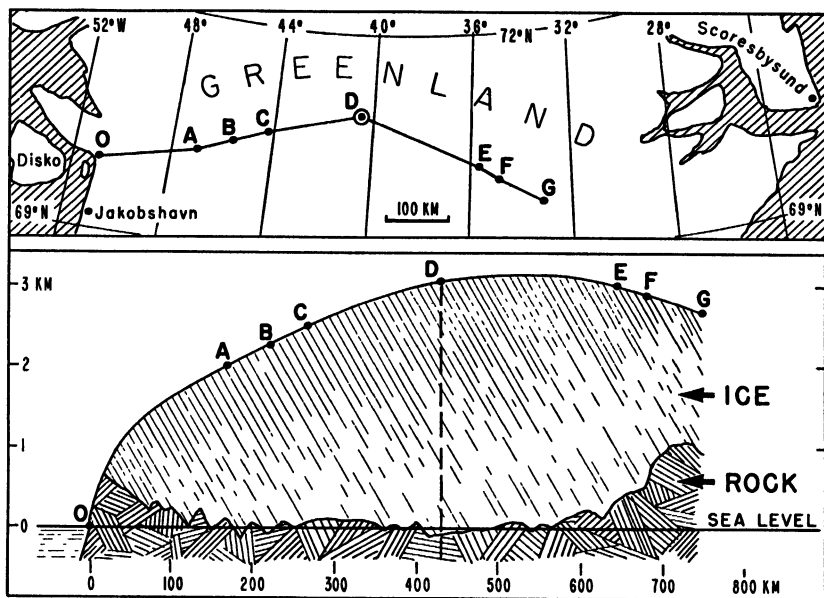


FIG. 5. Profile through Greenland showing rock surface after Joset⁴¹ on the basis of seismic exploration. (Drafted by Mr. John M. Nordquist.)

from the fact that the sea level (or lake level) at a given coast depends rather strongly on meteorological conditions, especially precipitation and winds during a given year. In addition, the process called "postglacial uplift" does not only include uplift in the formerly glaciated area but also subcrustal flow from the surrounding regions which correspondingly show a sinking. Temporary blocking of the subcrustal currents which control the process must be expected to slow down or stop the uplift in portions of the affected area from time to time. Earthquakes³² prove the existence of occasional increase in strain in and about areas of postglacial uplift.

From all evidence it follows that the uplift in North America proceeds in time and space similarly to that in Fennoscandia and that in these two areas the physical constants involved in the process are of the same order of magnitude. There seems to be no justification⁴¹ for the belief which has been expressed repeatedly that the present uplift in northern North America is no longer related to a mass deficit as a consequence of the past glaciation, but has mainly a tectonic cause.

As soon as the uplift in Fennoscandia was found to be a result of the decrease in the ice load, it was pointed out that regions which at present are heavily loaded by ice, e.g., Antarctica and Greenland, should show a corresponding depression of the rock surface. Nansen expected the thickness of the ice in central Greenland to be of the order of 2 km. Alfred Wegener

considered the measurement of the ice thickness in Greenland by seismic methods (recording of echoes from explosions) one of the most important tasks for his expeditions to Greenland, which ended with his death there. The measurements indicated a rapid increase in ice thickness with increasing distance from the coast. About 40 km. inland at points roughly 200 km. northeast of Disco (Fig. 5, left top) with the ice surface about 1570 m. above sea level, an ice thickness of 1200 m. was found. However, the further result that in the central part of Greenland the rock surface is not far from sea level,⁴² was considered to be doubtful⁴³ until it was definitely confirmed by the French expedition, Missions Paul-Émile Victor⁴⁴ (Fig. 5). The fact that the rock surface in central Greenland forms a basin under the ice load furnishes a strong support for the theory of post-glacial uplift. This uplift is probably the viscous process for which observations cover the longest time interval and the widest area.

V. The Coefficient of Viscosity and the Strength in the Earth

The coefficient of viscosity η in the earth's upper few hundred kilometers has been calculated on various assumptions. Usually it is supposed that η does not change with depth in the layers involved. Haskell⁴⁵ has given a formal solution for the motion of a highly viscous fluid when a symmetrical pressure is applied at the surface. He starts with the problem of the motion of a semi-infinite, incompressible, viscous fluid (viscosity η , density ρ) under the action of a radially symmetrical load of radius r applied at the time $t = 0$ upon the free surface. He neglects the curvature of the earth as well as inertial terms in the equations of motion in comparison with those arising from viscosity. The equations of motion (rate V , stress p) in a gravitational field g are

$$\eta \nabla^2 V = \text{grad } p - (0, 0, \rho g) \quad \text{and} \quad \text{div } V = 0 \quad (25)$$

with the positive z -axis directed downward. In cylindrical coordinates (r, z, Φ) , setting $\bar{p} = p - \rho g z$, the components of stress in which we are interested are

$$p_{zz} = -(\bar{p} + \rho g z) + 2\eta \frac{\partial V_z}{\partial z} \quad \text{and} \quad p_{rz} = \eta \left(\frac{\partial V_r}{\partial z} + \frac{\partial V_z}{\partial r} \right) \quad (26)$$

At the free surface, $p_{rz} = 0$, and p_{zz} equals the applied stress; at infinity,

⁴² B. Brockamp, F. Sorge, and K. Wölcken, "Wissenschaftliche Ergebnisse der Deutschen Grönlandexpedition Alfred Wegener, 1929 und 1930/31," Vol. 2. Brockhaus, Leipzig, 1933.

⁴³ B. Brockamp, *Z. Gletscherkunde* **23**, 277 (1935).

⁴⁴ A. Joset, "Expéd. Polaires Françaises P. E. Victor," *Ser. Sci.* **15**, (repp. prelim.) 43 (1952); A. Joset and J. J. Holtzschner, *Ann. géophys.* **10**, 351 (1954).

⁴⁵ N. W. Haskell, *Physics* **6**, 265 (1935); **7**, 56 (1936).

stresses and velocities are zero. If the equation of the actual free surface is $z = \zeta(r, t)$, and if the plane $z = 0$ is taken at the undisturbed surface, the values of the quantities in equation (26), except for $\rho g z$, may be replaced by their values at $z = 0$. If the applied pressure is $-\sigma(r, t)$, the boundary conditions become

$$\bar{p}(r, 0, t) + \rho g \zeta(r, t) - 2\eta \left(\frac{\partial V_z}{\partial z} \right)_{(r, 0, t)} = \sigma(r, t) \quad (27)$$

$$\left(\frac{\partial V_r}{\partial z} + \frac{\partial V_z}{\partial r} \right)_{z=0} = 0 \quad \text{and} \quad \frac{\partial \zeta}{\partial t} = V_z(r, 0, t) \quad (28)$$

Introduction of functions for V_r , V_z , and $\bar{p}$ leads to Bessel equations which are solved by Haskell. He has applied the resulting formal equations to the subsidence of a cylindric body. In this case $\sigma(r, t)$ is zero for all values of $r > r_0$ and all times $t \leq 0$, and constant otherwise. He has then calculated the change in form of the viscous half space under the load of a cylindric body as well as under the load of an infinite long strip with parallel sides. Haskell also has applied his results to the viscous recoil of the earth after the disappearance of the Pleistocene ice on Fennoscandia. His results indicate that as a consequence of the melting of the ice load appreciable flow processes must affect most of the earth's mantle. At a depth equal to the radius of the original (cylindrical) ice load (order of magnitude 500 km.), the vertical displacement should scarcely decrease under Haskell's assumptions, and at twice this depth it is about half that at the surface (many hundred meters).

On the basis of Nansen's³⁴ results for the uplift in Fennoscandia Haskell finds, on the assumption that the coefficient of viscosity η is constant throughout the mantle, the following values for η

Starting year	5000 B.C.	4000 B.C.	3000 B.C.	2000 B.C.	
η	2.6×10^{21}	3.2×10^{21}	3.0×10^{21}	2.9×10^{21}	poises

Attempts to consider the decrease of viscosity with depth⁴⁶ or the effect of the strength in the upper $50 \pm$ miles of the earth, as well as use of more recent data concerning the uplift^{31, 47} have resulted in values between 10^{22} and 10^{23} poises for the coefficient of viscosity at depths roughly between 50 and 200 miles. The corresponding value of the time of relaxation [λ , equation (4)] is of the order of 8000 years.

There are other methods to get information about the value of η inside the earth. On the basis of the well-established and repeatedly confirmed fact that there is no phase displacement between the tidal forces and the

⁴⁶ F. A. Vening Meinesz, *Proc. Koninkl. Akad. Wetenschap. Amsterdam*, **40**, 654 (1937).

⁴⁷ E. Niskanen, *Isostatic Inst. Helsinki I. A. G. Publ. No. 20* (1948).

observed tides of the earth's body in excess of the errors of observation ($5 \pm$ min.), Schweydar⁴⁸ in 1912 has concluded that there can be no layer in the mantle of a thickness of even 100 km. with a viscosity η of 10^9 poises (more than that for pitch at normal temperature) nor a layer with a thickness of 600 km. and a viscosity of 10^{13} poises (about as viscous as ice). Data on the Chandler movement of the poles (variation of latitude) have been discussed by Prey.⁴⁹ The earth's axis rotates to a first approximation along the surface of a cone with variable vertex angle. This causes deviation of the poles from their average position by a maximum amount of 10 m., and a corresponding variation of latitude, which depends on the earth's viscosity. If this were zero, the earth's figure would change immediately to fit the position of the earth's axis. The greater the viscosity the smaller would be the damping effect. However, no accurate result for the earth's viscosity can be found from these observations. On one hand, the change of viscosity with depth is not known; on the other hand, in the case of the body tides as well as that of the polar movement, the period of the motion (order of magnitude one day and about 420 days, respectively) is small compared with the time of relaxation (probably $\lambda \geq 100 \pm$ years) connected with the viscous process, so that observations of these phenomena can furnish at best a lower limit for the time of relaxation λ and the coefficient of viscosity η . In addition, the interference of a yearly period (forced vibration) in the variation of latitude (related to meteorological phenomena) with the free period of the gyroscopic motion of the earth's axis of about 420 days results in a periodic (7-year $\pm$) increase and decrease of the amplitudes.⁵⁰ This renders very difficult⁵¹ the finding of the decay in amplitudes and the determination of λ , and may result in mistaking a decrease in amplitude from interference of these two major periods for a decay as a consequence of viscosity. Finally, effects produced by a redistribution of angular momentum on or within the earth have to be considered.⁵² (For further discussion of these problems, see refs. 52a (which does not consider some of the difficulties discussed above), 52b, 52c, and 52d.)

Most data for the body tides (for details, see ref. 8) are based on pendulum observations. Already in 1919 Schweydar has pointed out that on a viscous earth the pendulum motion should precede the corresponding theo-

⁴⁸ W. Schweydar, *Veroeffentl. preuss. geodät. Institut* [N. F.] **54** (1912).

⁴⁹ A. Prey, *Gerlands. Beitr. Geophys.* **56**, 155 (1942).

⁵⁰ W. Schweydar, *Sitzber. preuss. Akad. Wiss. Physik. Math. Kl.* **20**, 357 (1919).

⁵¹ H. Jeffreys, "The Earth," 3rd ed., p. 214. Macmillan, New York, 1952.

⁵² T. Gold, *Nature* **175**, 526 (1955).

^{52a} P. Rudnick, *Trans. Am. Geophys. Union* **37**, 137 (1956).

^{52b} A. M. Walker and A. Young, *Monthly Notices Roy. Astron. Soc.* **115**, 443 (1955).

^{52c} B. Gutenberg, *Nature* **177**, 887 (1956).

^{52d} P. J. Melchior, *Atti accad. nazl. Lincei, Rend.* [8] **19**, 137 (1955).

retical motion calculated for a purely elastic earth by an amount α which, for the semi-daily tide, is given by

$$\cot \alpha = \frac{19n\eta}{2gr_0\rho_m} \quad (29)$$

where n = rotational velocity of the earth, η = viscosity, g = gravity, r_0 = radius of the earth, and ρ_m = its mean density. From the fact already mentioned that the phase difference α is zero within the errors of observation of a few degrees it follows that the coefficient of viscosity in the outer part of the earth is greater than 10^{17} poises.

In instances of viscous motion of the earth as a whole or of relatively large portions of it, it is frequently accurate enough to estimate the time of relaxation λ for the respective process. Calculations may appear to give a higher accuracy, but usually other processes than that under consideration produce effects greater than that resulting from errors in the estimated value of λ . However, details related to the order of magnitude of displacements during the flow and of changes with depth can be estimated only on a theoretical basis.

There are other processes which require the assumption of viscous flow without permitting at present an estimate of the time of relaxation or of the coefficient of viscosity. An indication for the existence of viscous flow in the earth's crust is given by "isostasy." This is an expression for the fact that gravity anomalies at the earth's surface are relatively small except for narrow belts where earthquakes or other evidence indicate active tectonic processes. Findings of Ewing⁵³ and his group for the Puerto Rico Deep and of Revelle and his collaborators for the Tonga Deep⁵⁴ by means of exploration with elastic waves from artificial explosions indicate downwarping of lighter material to relatively great depth (order of $30 \pm$ km.), which could result in negative gravity anomalies of the observed order of magnitude—100 to more than 200 mgal.—over such deep trenches.

Unfortunately, various errors are introduced in the reduction of gravity observed at the earth's surface to values which would exist at sea level; there is neither agreement on the best method of reduction nor on some quantities involved in the calculations, especially the change in density with depth. However, the fact of relatively small resulting gravity anomalies (usually less than $30 \pm$ milligals) in recently undisturbed areas, regardless of whether the measurements are taken in mountain areas or over the ocean, requires the assumption of viscous flow at a depth of the order of 100 km. or even less under stresses as small as 10^7 or 10^6 dynes/cm.² The resisting strength which must be surpassed to permit viscous flow at these depths,

⁵³ M. Ewing and F. Press, *Handbuch Physik* **27**, 256 (1956).

⁵⁴ W. Raitt, R. Fisher, and R. Mason, *Geol. Soc. Amer. Spec. Paper* **62**, 237 (1955).

therefore, cannot exceed 10^7 dynes/cm.²; it may be much smaller. It is not known at what depth in approaching the surface the strength increases to the order of 10^9 dynes/cm.² which is found from the fact that up to 10-km. high mountains have not shown an observable decrease in height by viscous flow during history. The transition can be expected below a depth of about 10 km. where the velocities of elastic waves and the elastic constants begin to decrease.⁴ Jeffreys⁵⁵ estimates that the strength for mountain support should exist at least down to a depth of 20 or 30 km. On the other hand, experiments of Griggs indicate that under stresses continuing for years—and still more for geological periods—any amorphous or polycrystalline substance may flow even if the stresses are smaller than the strength. With other words, for the material investigated by Griggs strength is dependent upon the time during which a stress acts. More such experimental or theoretical data are needed for drawing of conclusions concerning the earth's interior,⁵⁶ especially since there are no data for the crystalline rocks forming the outer layers of the earth's crust.

VI. Flow Processes in the Deeper Portions of the Earth's Mantle; Results Based on Deep-Focus Earthquakes

As we go deeper into the earth the investigation of rheological problems must be based on an increasing number of assumptions. Effects of deep-seated processes on observations made at the earth's surface are scarce, and the physical conditions at depth are not well known, as has been pointed out in Section I on the structure of the earth. Doubt about the possibility of viscous flow across the whole mantle is expressed by Birch.⁵⁷ He points out that the observed, rather rapid increase in seismic wave velocities at depths between about 200 and 800 or 900 km. below the surface may indicate a zone of transition to a high-pressure form of the material and possibly also changes in chemical composition. Verhoogen⁵⁸ disagrees with some of these conclusions. If Birch is correct, circulation between 200 and 900 km. "might be limited by the requirement of an exchange of latent heat, possible irreversibility of phase changes and intrinsic differences of density. It is not clear at present how serious any of these effects may be, but to assume unimpeded circulation in this region is to ignore its definitely transitional nature."⁵⁹

Viscous flow, especially in convection currents, plays an important role in many tectonic theories, but, as mentioned, all basic data are very un-

⁵⁵ H. Jeffreys, "The Earth," 3rd ed., p. 192. Macmillan, New York, 1952.

⁵⁶ D. T. Griggs, *Trans. Am. Geophys. Union* **32**, 505 ff. (1951).

⁵⁷ F. Birch, *J. Geophys. Research* **57**, 227 (1952).

⁵⁸ J. Verhoogen, *Geophys. Research* **58**, 337-346 (1953).

⁵⁹ F. Birch, *Trans. Am. Geophys. Union* **32**, 533 (1951).

certain and incomplete (see, e.g., Adams *et al.*,⁶⁰ Gutenberg,⁶¹ Meinesz,⁶² Nadai,⁶³ Scheidegger,⁶⁴ all with many additional references). Heat developed in physical-chemical (especially radioactive) processes is usually considered to be the source of energy.

A few geophysicists believe that viscous flow in the mantle of the earth is impossible since otherwise earthquakes caused by rupture along fault surfaces down to a depth of about 700 km. could not exist. However, the time of relaxation for viscous flow is of a higher order of magnitude than the time needed in active earthquake regions for accumulation of strain to the breaking point. In most active belts relatively large shocks follow each other at intervals of the order of one hundred or even ten years. Consequently, the strain which, in such belts, accumulates from tectonic processes should not be reduced appreciably by viscous flow in the outer portion of the earth's mantle with a time of relaxation of the order of thousands of years during the relatively short time intervals between successive deep shocks.

The fact that no deep-focus earthquakes have been observed below a depth of about 700 km. since instrumental records make it possible to fix their depth—that is, since about 1905—may either result from a rather rapid decrease in the effects of disturbing processes near this depth or from an increase in speed of flow there, great enough to prevent an accumulation of strain. In the latter case, λ would be of smaller order of magnitude than 10^8 sec. (about 30 years) below 700 km., and, correspondingly, η would decrease below an order of magnitude of 10^{20} poises at a depth of about 700 km. On the other hand, the existence of earthquakes in the upper 700 km. of the mantle indicates that above a depth of $700 \pm$ km. η probably exceeds 10^{20} poises.^{2a}

VII. Strain-Rebound Characteristics of Earthquake Series and Aftershocks

In recent years Benioff⁶⁵⁻⁶⁸ has devised a procedure for determining the relative size of elastic strain-rebound increments from earthquake magnitudes and has applied it to series of aftershocks of earthquakes, as well as

⁶⁰ Colloquium., *Trans. Am. Geophys. Union* **32**, 499 (1951).

⁶¹ B. Gutenberg, ed., in "Internal Constitution of the Earth (Gutenberg, ed.)," p. 186. Dover Publications, New York, 1951.

⁶² F. A. Vening-Meinesz, *Proc. Koninkl. Akad. Wetenschap. Amsterdam* **B55**, 527 (1952).

⁶³ A. Nadai, *Trans. Am. Geophys. Union* **33**, 274 (1952).

⁶⁴ A. E. Scheidegger, *Bull. Geol. Soc. Amer.* **64**, 127 (1953).

⁶⁵ H. Benioff, *Bull. Geol. Soc. Amer.* **60**, 1837 (1949).

⁶⁶ H. Benioff, *Bull. Seismol. Soc. Amer.* **41**, 31 (1951).

⁶⁷ H. Benioff, *Trans. Am. Geophys. Union* **32**, 508 (1951).

⁶⁸ H. Benioff, in "Internal Constitution of the Earth" (Gutenberg, ed.), p. 391. Dover Publications, New York, 1951.

to series of earthquakes in certain regions and at certain depth ranges. He assumes that an earthquake is generated by the elastic rebound of a volume of rock having an average rigidity G and an average elastic strain γ preceding the rupture. The energy stored in a unit volume of the rock is $G\gamma^2/2$. Benioff assumes that the conversion efficiency of strain energy into seismic waves is unity, and that consequently γ is the strain rebound. The square root of the energy J is then proportional to γ . For a sequence of shocks occurring on a given fault, a graph of the accumulated sum of the increments $J^{0.5}$ plotted against time represents the elastic strain-rebound characteristic (times the constant factor C) of the sequence. For a first approximation, values for $J^{0.5}$ may be derived from Richter's instrumental earthquake magnitude M by means of the tentative equation⁶⁹

$$\log J^{0.5} = a + bM. \quad (30)$$

Originally Gutenberg and Richter used $a = 6$, $b = 0.9$, but later they preferred $a = 4.5$, $b = 0.9$; recently^{69a, 69b} they have revised the equation. The resulting value of $\log J^{0.5}$ may well be incorrect by one unit in large shocks, but this does not seriously affect the following conclusions of Benioff.

Most strain-rebound characteristics of aftershock sequences show for certain time intervals either a form as given by

$$S_1 = l + m \log t \quad (31)$$

or as given by

$$S_2 = O - Ne^{-P\sqrt{t}} \quad (32)$$

where l , m , O , N , P are constants of the process. S_1 is the strain-rebound given by Griggs⁷⁰ for rocks and by others for other materials under compressional elastic or recoverable creep strain. S_2 is of a form derived empirically by Michelson⁷¹ for shearing creep recovery. However, this form has not been verified by subsequent experimenters. Unpublished creep tests in shear by C. Lomnitz under Dr. Benioff's supervision have yielded only the form (31). Consequently the occurrence of form (32) in aftershock sequences remains unexplained. In the aftershock sequences of the form of equation (31), activity followed for intervals varying from 100 days minimum to 600 days maximum. On the other hand, sequences having the dual form came to early definite terminations in intervals varying from 1 to 500 days. For example, the aftershock series (Fig. 6) of the Kern County,

⁶⁹ B. Gutenberg and C. F. Richter, *Bull. Seismol. Soc. Amer.* **32**, 163 (1942).

^{69a} B. Gutenberg and C. F. Richter, *Bull. Seismol. Soc. Amer.* **46**, 105 (1956).

^{69b} B. Gutenberg and C. F. Richter, *Ann. geofis. (Rome)* **9**, 1, (1956).

⁷⁰ D. T. Griggs, *J. Geol.* **47**, 225 (1939).

⁷¹ A. A. Michelson, *J. Geol.* **25**, 405 (1917); **28**, 18 (1920).

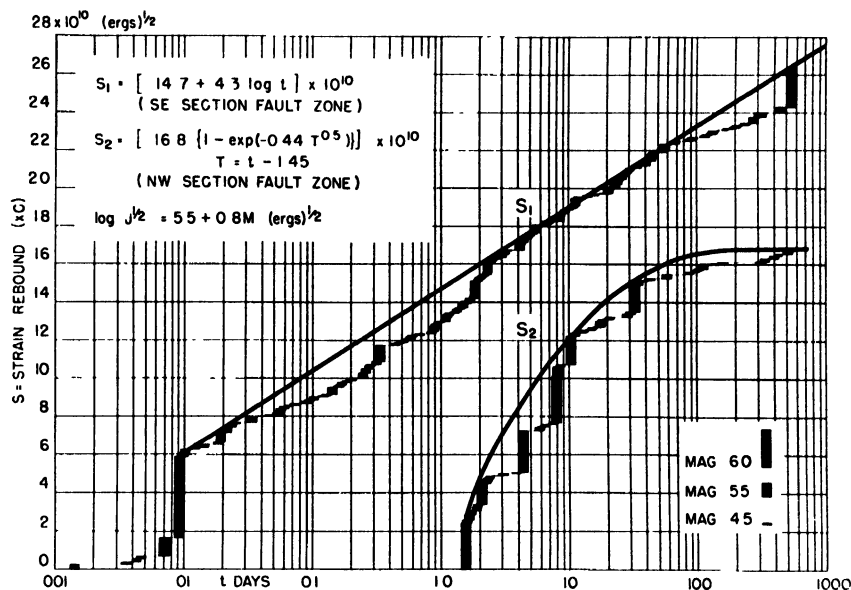


FIG. 6. Strain-rebound characteristics of the aftershock sequence of the Kern County, California, earthquake of July 21, 1953 after Benioff.⁷² t = time after main shock. (Drafted by Mr. Ralph Gilman.)

California, earthquakes starting on July 21, 1952, exhibit⁷² one series of the form S_1 , corresponding to shocks southeast of the fault and a second of the form S_2 for aftershocks northwest of the fault; the first known shock of the second series occurred 37 hours after the main shock. Studies of such aftershock series can be expected to yield valuable information on the tectonic background of the processes on one hand and on the nonelastic behavior of rock bodies of the size of crustal blocks over many years on the other hand.

Benioff^{67, 72} has applied the same method to series of earthquakes in certain areas, and has found strain-rebound characteristics of forms similar to those discussed above. Figure 7 is a graph of the strain-rebound characteristic of the sequence of all earthquakes of the world having magnitudes equal to or greater than 8.0, which have occurred since 1904. It has an approximately saw-tooth shape with amplitudes and periods decreasing linearly with time. In Fig. 7 the initial points A , B , C , and D of the active intervals mark the times when the accumulated world strain was maximum. The end points a , b , c , d , e , and f mark the times at which the accumulated world strain passed through minima. The upper dashed line drawn through the points of minimum strain should therefore represent the total secular

⁷² H. Benioff, *Bull. Geol. Soc. Amer. Spec. Paper* **62**, 61 (1955).

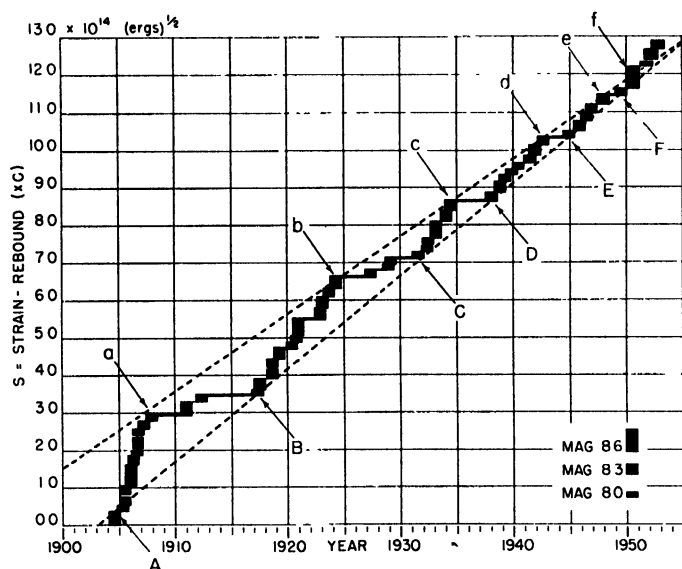


FIG. 7. Elastic strain-rebound characteristic; sequence of all shallow earthquakes of magnitude ≥ 8 since 1904, after H. Benioff. (Drafted by Mr. Ralph Gilman.)

strain-generation (times a constant of the system). The small spread of points on this line indicates that the rate of strain-generation has been very constant since 1907. Since during the active intervals the average strain-release segment is very nearly linear, it may be concluded that earthquakes in this magnitude range are not independent events, because release of strain by one shock affects the time and presumably the amount of strain release of subsequent shocks. In order to explain the alternating intervals of activity and quiescence it is necessary to assume that there exists a worldwide mechanism which locks all faults simultaneously—possibly through variations in the normal stress on the fault surfaces. Thus, although global strain is being generated at a constant rate given by the slope of the upper dotted line in Fig. 7, it is released only during intervals when the fault-locking is reduced.

A similar plot of the strain-rebound characteristic on all great deep earthquakes (focal depth 300 to 680 km.) is reproduced in Fig. 8. Contrasting with the energy release in great shallow shocks, the rate of strain release in deep-focus earthquakes has been decreasing as $1/t$, at least from 1905 to 1950. The fact that the observed points fit a logarithmic curve so well may be interpreted as evidence that all great deep earthquakes also are related to a single stress system in which a compressional elastic creep strain has been accumulating or relaxing. There are indications in both curves that the year 1950 may mark the beginning of a new cycle.

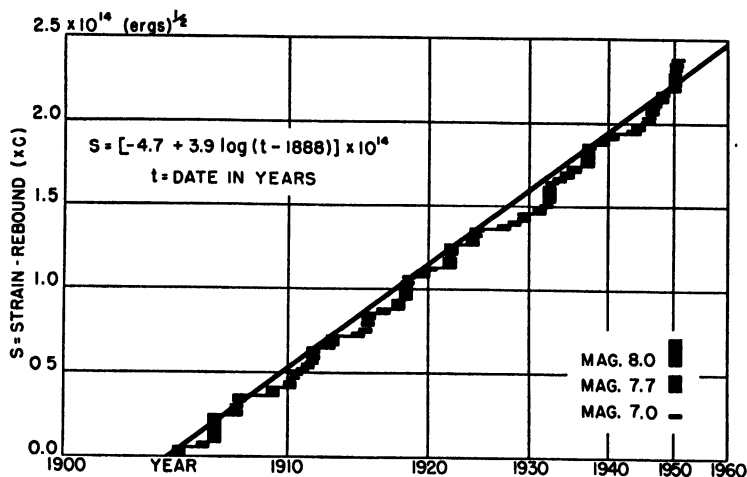


FIG. 8. Elastic strain-rebound characteristic; sequence of all known earthquakes with focal depths > 300 km. and magnitude ≥ 7 since 1905 (probably incomplete for magnitudes 7 to $7\frac{1}{2}$ for the years 1905 to 1917), after H. Benioff. (Drafted by Mr. Ralph Gilman.)

VIII. Rheological Phenomena in Geological and Geophysical Processes on a Small Scale

Flow phenomena on a small scale are fairly common in those portions of the earth which are accessible to direct observation. However, in most instances the physical constants involved change appreciably within the material and with its temperature. Few conclusive results have been published. Ice flow in glaciers is an example. A short summary has been given by Sharp⁷³ who, in a detailed review,⁷⁴ discusses the following mechanisms of glacier movement: slippage on the floor of the glacier, slippage along discrete shear planes within the glacier, transfer of material associated with changes of state, intergranular shifting including fragmentation and healing, and intergranular yielding. Demorest⁷⁵ considers four processes involved in flow of glacier ice: (1) regelation, (2) idiomolecular transfer, (3) basal plane slip, (4) instantaneous crystallization. Newtonian flow of glacier ice (coefficient of viscosity of the order of 10^{13} or 10^{14} poises) seems to be limited to portions in the interior of glaciers.⁷⁶ Basic theoretical data and experiments showing, e.g., velocity distributions along vertical lines through glaciers, have been summarized by Perutz.⁷⁷

⁷³ R. P. Sharp, *Bull. Geol. Soc. Amer.* **64**, 97 (1953).

⁷⁴ R. P. Sharp, "Glacier Flow," *Bull. Geol. Soc. Amer.* **65**, 821 (1954).

⁷⁵ M. H. Demorest, *J. Glaciol.* **2**, 201 (1953).

⁷⁶ R. Streiff-Becker, *J. Glaciol.* **2**, 181 (1953).

⁷⁷ M. F. Perutz, *Nature* **172**, 929 (1953); see also J. F. Nye, *Proc. Roy. Soc. (London)* **A219**, 477 (1953).

The study of lava flows offers other difficulties, especially the evaluation of effects of the considerable change in temperature with space and time and the irregularities in the flow. Measurements of the viscosity coefficient of lava indicate values of the order of 10^4 to 10^5 poises at a temperature of 1100° , decreasing to the order of 200 poises if the temperature increases to 1400° (ref. 19, pp. 133–136; 77a).

Mudflows form another group of phenomena belonging to this group. An instance in Southern California has been investigated by Sharp and Nobles.⁷⁸ On the assumption of Newtonian flow, they found a viscosity coefficient of the order of 10^3 to 10^4 poises.

Various types of rheological problems are encountered in the study of tectonic processes. There is little agreement about the processes by which folds are formed. At some time in the past the rocks have been subjected to conditions which have resulted in flow. But neither the temperatures and pressures involved nor the possible influence of solution, recrystallization, or chemical actions are known well enough to draw conclusions.⁷⁹

Certain features of geological “grabens” and of folded mountains have been studied theoretically by Kuessner.⁸⁰ He represents the earth’s crust by a homogeneous elastic plate floating on a highly viscous fluid of infinite thickness. On the assumption of relatively small movements, equations of motion can be linearized. In addition, he restricts the discussion to instances which can be treated by use of special operators, and he assumes special load patterns.

Data for movements in the earth’s crust along faults are scanty. The best information concerns the San Andreas fault in California. Stream offsets indicate that in the geological Recent period the southwestern block of the fault has moved northwestward relative to the continental side. A part of this displacement has occurred in earthquakes but, in addition, a continuous viscous distortion of the fault zone is indicated by geodetic measurements.⁸¹ Hill and Dibblee⁸² believe that “tens of miles of lateral movement have probably occurred on these faults with the possibility of a cumulative movement on the San Andreas of hundreds of miles since Jurassic time.” Results of special triangulations by the U. S. Coast and Geodetic Survey indicate that the motion continues at an average (but irregular) differential displacement rate of about 5 m./century. Whitten⁸³ estimates that the

^{77a} C. K. Wentworth, *J. Geol.* **62**, 425 (1954).

⁷⁸ R. P. Sharp and L. N. Nobles, *Bull. Geol. Soc. Amer.* **64**, 547 (1953).

⁷⁹ D. T. Griggs, *Bull. Geol. Soc. Amer.* **51**, 1001 (1940).

⁸⁰ H. O. Kuessner, *Inst. Fluid Dynamics and Appl. Math., University of Maryland, Lecture Series No. 22*, 20 pp., 1953.

⁸¹ C. A. Whitten, *Trans. Am. Geophys. Union* **29**, 318 (1948).

⁸² M. L. Hill and T. W. Dibblee, Jr., *Bull. Geol. Soc. Amer.* **64**, 443 (1953).

⁸³ C. A. Whitten, *J. Jour. Coast and Geodetic Survey No. 2*, 84 (1949).

width of the area involved in the distortion varies from 30 to 40 miles. Movements on a similar scale are known from other parts of the disturbed belt surrounding the Pacific Ocean, especially from Japan,⁸⁴ the Philippines, and from New Zealand.⁸⁵

Nonelastic movements on a smaller scale may result in faulting. In the Buena Vista Hills oil field, Kern County, California, relatively large continuous movements, about 4 cm./year, have been observed⁸⁶ for many years without any known earthquake in the affected area, though pipes in oil wells have been sheared off and other pipes crossing the fault horizontally at the surface have been bent. Apparently the stress normal to the fault is insufficient for locking.

Non-elastic tilt due to meteorological conditions has been discussed by Tomascheck.^{86a}

IX. Viscosity in the Earth's Core; Flow in the Core As Source of Terrestrial Magnetism

Little is known about the viscosity in the earth's core. From the damping of longitudinal waves with periods of 1 sec. passing through the earth's core Jeffreys⁵¹ concludes that about 10^8 poises is the upper limit for the coefficient of viscosity in the core, but he believes that "it is improbable that the true value is anywhere near as large as 10^8 poises." On the other hand, on the basis of his assumed decay of the movement of the earth's axis with a period of about 14 months, which was discussed in Section VI, Jeffreys finds⁸⁷ that this could be due to viscosity of the core of the order of 10^5 poises. However, his assumed value of $\lambda = 15 \pm$ years is probably of too small an order of magnitude, and the damping of the "variation in latitude" is also affected by tidal friction in seas and by imperfections of elasticity in the mantle.⁵¹

Kuhn and Rittman⁸⁸ believe that the transition from the earth's mantle to the core is a consequence of a rapid decrease of the coefficient of viscosity at depths near 2900 km. Kuhn and Vielhauer⁶ consider it likely that η decreases from about 10^{20} poises at a depth of 2000 km. to about 10^{12} at 2900 km. where the time of relaxation λ would be about 1 sec. In the critical region near the "core boundary" this could imply a decrease in λ by a factor 10 over a depth interval of 50 km. They point out that this would enable reflection of 50-km. long waves. However, waves reflected in the mantle at the core boundary with wavelengths of only 20 km. or even less are observed

⁸⁴ Many papers in *Earthquake Research Inst. Tokyo, Bull.*

⁸⁵ H. W. Wellmann, *New Zealand J. Sci. Technol.* **B33**, 409 (1952).

⁸⁶ T. W. Roch, *Am. Assoc. Petroleum Geol. Bull.* **17**, 694 (1933).

^{86a} R. Tomascheck, *Geofis. pura e appl.* **25**, 17 (1953).

⁸⁷ H. Jeffreys, "The Earth," 3rd ed., p. 247. Macmillan, New York, 1952.

⁸⁸ W. Kuhn and A. Rittman, *Geol. Rundschau* **32**, 215 (1941).

not infrequently, and waves reflected inside the core at the boundary are found occasionally to have wavelengths as short as 10 km. On the other hand, wavelengths of 50 km. or more are rarely observed in waves reflected at the core boundary. Thus, there is some doubt that the transition from the mantle to the core is as gradual as it is assumed by Kuhn, Rittmann, and Vielhauer. No explanation has been given thus far for the lack of longer waves passing through the core.

Recent hypotheses concerning the earth's magnetic field assume viscous flow in the earth's core. When all attempts to explain the earth's magnetism (which is known to have its source in the interior of the earth) failed on the assumption of a magnetic iron core, it was pointed out by Elsasser that convection currents in the core may be responsible: "We may assume that in the core there exist simultaneously fluid motions and electric currents. The two interact with each other, producing a number of rather complex phenomena."⁸⁹

Bullard^{90, 91} has extended Elsasser's investigations. He concludes⁹¹ that it cannot "be said that the known properties of the earth positively require convection to take place in the core. There is no difficulty on the other hand in choosing admissible constants that will give convection." Experiments to illustrate the hypothetical convection currents in the earth have been carried out by Hide⁹² under supervision of Runcorn.⁹³ However, their results give more information concerning convection currents than concerning the behavior of the core. Too little is known about the structure of the core and the physical or chemical difference between its outer and inner part. On the other hand, the pressure of over three million atmospheres is believed to produce physical properties required by the Elsasser-Bullard hypothesis, especially high electric conductivity, in almost any material which can reasonably be expected to form the core.

Nomenclature

G	coefficient of rigidity	η	coefficient of viscosity
k	bulk modulus	λ	time of relaxation
ρ	density	λ_r	time of retardation
ρ_m	mean density of earth	ν	coefficient of retarded elastic motion
V	velocity of longitudinal waves	t	time
v	velocity of transverse waves	Δ	distance along surface of earth
γ	shearing strain	Δ^*	distance at which amplitude is reduced to $1/e$
S	tangential stress		

⁸⁹ W. M. Elsasser, *Revs. Mod. Phys.* **22**, 1 (1950).

⁹⁰ E. C. Bullard, *Proc. Roy. Soc. (London)* **A197**, 433 (1949).

⁹¹ E. C. Bullard, *Monthly Notices Roy. Astron. Soc., Geophys. Suppl.* **6**, 36 (1950).

⁹² R. Hide, *Ann. geophys.* **8**, 128 (1952).

⁹³ S. K. Runcorn, *Trans. Am. Geophys. Union* **34**, 329 (1953).

r	distance along radius	S_1, S_2	elastic strain recovery
a	amplitude of waves	u, v, w	components of displacements
a_0	amplitude at origin	L	one of Lamé's constants
T	period of waves	L'	corresponding constant in delayed elastic motion
$q = 2\pi/T$		Θ	change in volume per unit volume
K	coefficient of absorption	ω	shear
J or E	energy	p	stress
δ	logarithmic decrement of vibrations	g	gravity acceleration
$Q = \pi/\delta$		σ	pressure
N_1, N_2, N_3	components of normal stress	M	magnitude of earthquakes, Richter scale
T_1, T_2, T_3	components of tangential stress		

CHAPTER 11

EXPERIMENTAL TECHNIQUES FOR RHEOLOGICAL MEASUREMENTS ON VISCOELASTIC BODIES

John D. Ferry

I. Introduction	433
II. Transient Techniques	435
1. Stress Relaxation	435
2. Creep	437
III. Dynamic (Sinusoidal) Techniques	440
1. Direct Measurements of Stress and Strain	443
2. Resonance Devices with Added Inertia	445
3. Transducer Measurements of Stress-Strain Ratios	449
4. Wave Propagation	453
5. Characteristic Impedance Measurements	458
6. Resonance Vibrations	461
7. Comparisons of Dynamic Techniques	462
IV. Other Time-Dependent Techniques	464
1. Monotonic Changes of Stress or Strain with Time	464
2. Impulse Measurements	464
3. Nonsinusoidal Periodic Changes	465
V. High-Stress Techniques	465
1. Dynamic Stress Superimposed on High Static Stress	465
2. High Dynamic Stress	466
VI. Derived Calculations	467
1. Distribution Functions of Relaxation and Retardation Times	467
2. Reduced Variables for Describing Effects of Temperature and Concentration	470
Nomenclature	473

I. Introduction

In the rheology of viscoelastic bodies, interest centers primarily on anomalies which depend upon time rather than upon stress. Indeed, the great majority of such studies deal with systems which approach linear viscoelastic behavior-- i.e., in which the stress-strain ratio, though a function of time, is independent of stress, at least for the low stresses to which these studies are restricted. The basic aim of rheological experiments on viscoelastic bodies is, therefore, the measurement of stress-strain ratios under some kind of time-dependent loading pattern.

In principle, for a linear viscoelastic body, the same information can be derived from any time-dependent loading pattern--transient experiments

such as stress relaxation or creep; dynamic experiments in which stress and strain vary sinusoidally with time, at different frequencies; or more complicated experiments in which either stress or strain is increased linearly with time, or a nonsinusoidal periodic stress is imposed. Equations are available for translating the results of one type of experiment into those of another,¹⁻⁵ though some of the transformations are so complicated as to be scarcely practical. In practice, transient and sinusoidal methods are the most useful.

In studying stress relaxation, a strain is suddenly imposed and then held constant, while the stress required to maintain it is measured as a function of time. In studying creep, a constant stress is applied and the strain is measured as a function of time. These transient methods are obviously most appropriate for the long end of the time scale, and they also have the advantages of much simpler apparatus and greater ease of obtaining a wide *range* of time scale. They are treated in Section II.

In studying dynamic properties, a stress which varies sinusoidally with time is imposed, and the resulting strain, which also varies sinusoidally but in general is out of phase with the stress, is measured as a function of frequency. In some cases the stress-strain ratios are measured directly without knowledge of the individual magnitude of either. Dynamic methods provide twice as much direct experimental information as transients because at each frequency two independent measurements can and should be made. These are usually expressed by the ratio of the stress component in phase with strain to the strain and the corresponding out-of-phase ratio (the real and imaginary parts of a complex modulus), as explained in more detail subsequently. Dynamic measurements are obviously most appropriate for the short end of the time scale. They are treated in Section III.

The results from other types of loading patterns, which are briefly described in Section IV, are more difficult to analyze, especially if there is any departure from linear viscoelastic behavior. Measurements under nonlinear conditions are mentioned in Section V. Certain derived calculations from measurements of viscoelastic properties are described in Section VI.

Of the various transient and dynamic techniques which are described below, some are adapted to the study of "solids" and others to "liquids." Strictly, such a classification is meaningless, since viscoelastic bodies are neither solid nor liquid; but for the purposes of this discussion a viscoelastic solid is considered to be one which supports its own weight without signifi-

¹ T. Alfrey and P. Doty, *J. Appl. Phys.* **16**, 700 (1945).

² B. Gross, *J. Appl. Phys.* **18**, 212 (1947).

³ B. Gross, *J. Appl. Phys.* **19**, 257 (1948).

⁴ B. Gross and H. Pelzer, *J. Appl. Phys.* **22**, 1035 (1951).

⁵ R. Sips, *J. Polymer Sci.* **5**, 69 (1950).

cant distortion under the experimental conditions, while a viscoelastic liquid flows and must be confined. The magnitudes of the shear stress-strain ratios measured in those bodies called solid may range from 10^4 to 10^{11} dyne/cm.²; in those called liquid, from 5 to 10^{10} dyne/cm.². These enormous ranges naturally require a wide variety of experimental methods. Some aspects of experimental techniques for rheology of viscoelastic bodies have been treated in several other review articles.⁶⁻¹⁰

II. Transient Techniques

1. STRESS RELAXATION

In a stress relaxation experiment, the stress is determined as a function of time either after sudden imposition of strain or (much less commonly) after cessation of steady-state flow, while holding the strain constant. The stress may decay either to an equilibrium value or to zero, depending on the structure of the material. The stress is ordinarily measured by some element of the apparatus which is strained in series with the sample under investigation. If, per unit force, the deformation of the stress-measuring element is much smaller than that of the sample (as with a strain gage¹¹), the relaxation will occur to a close approximation at constant strain if the over-all deformation is simply maintained constant. Otherwise, and for more accurate measurements, the stress must be continuously adjusted either manually or automatically to maintain constant strain of the sample.

Solid samples, in the great majority of cases, are studied in extension, by stretching strips, fibers, or rings; less often, in unilateral compression.^{11, 12} Liquid samples have been studied in shear between coaxial cylinders.^{13, 14} Results from extension (or unilateral compression) are readily interconvertible with those of shear when the bulk modulus far exceeds the shear modulus, as is the case for liquids and soft solids. Thus, for a perfect elastic solid, the ratio of stress to strain is denoted by Young's modulus E in extension and by the shear modulus (modulus of rigidity) G in shear; these moduli are related by the equation $E/G = 3/(1 + G/3K)$, where K is the bulk modulus. When $G \ll K$, the stress-strain ratios differ simply by a

⁶ F. R. Eirich, *Proc. 1st Intern. Rheol. Congr., Scheveningen* p. IV-3. (1949).

⁷ J. D. Ferry, W. M. Sawyer, and J. N. Ashworth, *J. Polymer Sci.* **2**, 593 (1947).

⁸ R. S. Marvin, *Ind. Eng. Chem.* **44**, 696 (1952).

⁹ J. H. Dillon and S. D. Gehman, *India Rubber World* **115**, 61-8, 76, 217-22 (1946).

¹⁰ A. J. Staverman and F. Schwarzl, in "Die Physik der Hochpolymeren," (H. A. Stuart, ed.) Vol. IV, pp. 80-95. Springer, Berlin, 1956.

¹¹ W. S. MacDonald and A. Ushakoff, *J. Colloid Sci.* **3**, 135 (1948).

¹² S. L. Dart and E. Guth, *J. Appl. Phys.* **17**, 314 (1946).

¹³ G. Stainsby and A. G. Ward, *Proc. 1st. Intern. Rheol. Congr., Scheveningen* p. II-108 (1949).

¹⁴ F. W. Schremp, J. D. Ferry, and W. W. Evans, *J. Appl. Phys.* **22**, 711 (1951).

factor of 3, and this is true even for viscoelastic bodies under conditions of stress relaxation where the stresses are changing with time. Systems which comply with this condition are sometimes (though inaccurately) called incompressible. However, when G and K are of the same order of magnitude, as in hard solids, stress relaxation in shear cannot be related to that in extension without knowledge of the bulk modulus and the relaxation, if any, of bulk stresses within the experimental time scale.

In any experimental arrangement, the direct measurements of load and deformation must be converted to stress and strain by consideration of sample geometry. As a first approximation, this is a simple calculation; but end effects, distortions and restraints due to clamping, and other complications must be taken into account to obtain accurate absolute values. Often absolute accuracy is limited by the analysis of sample geometry.^{6, 15}

Measurement of the load may be accomplished by a balance, either modified from an ordinary analytical balance¹⁶ or specially constructed;^{17, 18} by deflection of light from a mirror mounted on a torsion wire, which is twisted either directly by the torsion of the sample¹⁴ or by another element of low compliance deformed in series with the sample;¹⁹ by a strain gage mounted on a low compliance element;^{11, 20-22} or by a differential transformer which measures the deformation of a low-compliance element such as a stiff ring²³ or a pair of bowed strips.²⁴ For automatic recording, the torsion mirror deflection can be photographed, and the output from a strain gage or a differential transformer can be transcribed by a recording potentiometer. Usually the time scale covered is from a few seconds to several hours or days. For a time scale of a few milliseconds to a few seconds, which requires a much more elaborate apparatus design,²⁰ oscillographic recording has been employed.

Measurement of the deformation is simple if it is imposed by extension to a fixed stop at a predetermined position. A dial gage has been used when the strain is rather small.²⁴ In the case of stress relaxation after cessation of steady-state flow, studied with a coaxial cylinder apparatus,¹⁴ it is not the strain but the rate of strain before relaxation that must be obtained; this can be done by conventional tachometry.

¹⁵ W. T. Read, *J. Appl. Mech.* **17**, 349 (1950).

¹⁶ A. M. Sookne and M. Harris, *J. Research Natl. Bur. Standards* **19**, 535 (1937).

¹⁷ R. S. Stein and A. V. Tobolsky, *Textile Research J.* **18**, 302 (1948).

¹⁸ R. D. Andrews and A. V. Tobolsky, *J. Polymer Sci.* **7**, 221 (1951).

¹⁹ H. P. Lundgren, A. M. Stein, V. M. Koorn, and R. A. O'Connell, *J. Phys. & Colloid Chem.* **52**, 180 (1948).

²⁰ M. T. Watson, W. D. Kennedy, and G. M. Armstrong, *Phys. Rev.* **82**, 301 (1951).

²¹ W. J. Thorsen, *Textile Research J.* **24**, 407, 899 (1954).

²² H. Hindman and G. S. Burr, *Trans. Am. Soc. Mech. Engrs.* **71**, 789 (1949).

²³ R. S. Stein and H. Schaevitz, *Rev. Sci. Instr.* **19**, 835 (1948).

²⁴ J. R. McLoughlin, *Rev. Sci. Instr.* **23**, 459 (1952).

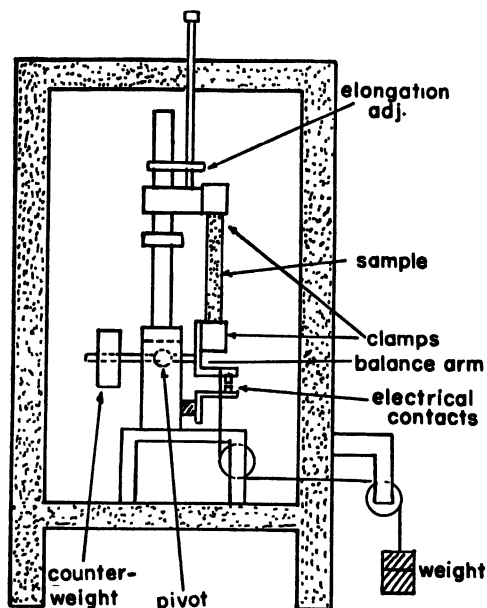


FIG. 1. Apparatus for stress relaxation measurements (from reference 17). The sample is kept at constant strain by adjusting the weight to maintain the balance arm in equilibrium, as indicated by electrical contacts.

Temperature control is important because in some ranges of temperature and time scale the rate of stress relaxation is exceedingly temperature-sensitive. With complicated equipment it is impractical to control the temperature of the entire apparatus;^{14, 22} but in this case thermal leakage is unavoidable unless insulating segments are placed in the mechanical system, and it may be impossible to maintain the sample at temperatures that are very different from room temperature. Most often the entire equipment is surrounded by an air thermostat.^{17, 23} Liquid thermostats are used for fibers which must be immersed in a liquid of fixed composition to specify their mechanical behavior.^{16, 19}

An example of stress relaxation equipment for use with soft solids, described by Tobolsky and collaborators, is shown in Fig. 1. An example of stress relaxation data is shown in Fig. 2, taken from the work of Andrews and Tobolsky¹⁸ on polyisobutylene. The time scale extends over five powers of ten, and, as is customary, is plotted logarithmically.

2. CREEP

In a creep experiment, the strain is determined as a function of time after sudden imposition of stress, or (in creep recovery) after removal of stress. The strain may continue increasing indefinitely or may approach a

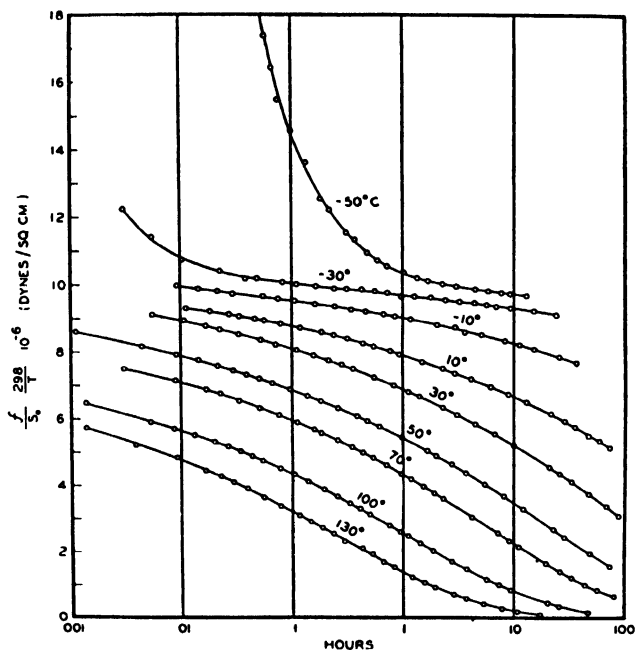


FIG. 2. Stress relaxation of polyisobutylene at various temperatures as indicated (viscosity-average molecular weight 6,600,000). The ordinate is stress divided by strain (multiplied by a reduction factor $298/T$, where T is the absolute temperature; this does not affect the general course of the relaxation). (From reference 18.)

constant value, depending on the structure of the material. The principles of such experiments have been discussed at length in a treatise by Leaderman.²⁵ They have been widely applied to the study of metals, and methods for applying large stresses, determining very small strains, and operating over wide ranges of temperature have been described in several monographs.^{26, 27, 28}

As in stress relaxation, solid samples are usually studied in extension, though occasionally in simple shear,²⁹ torsion (of cylinders or, preferably, tubes³⁰), or compression.³¹⁻³³ Liquid samples are usually studied in shear

²⁵ H. Leaderman, "Elastic and Creep Properties of Filamentous Materials and Other High Polymers," Textile Foundation, Washington, 1943.

²⁶ H. J. Tapsell, "Creep of Metals," Oxford Univ. Press, New York, 1931.

²⁷ A. H. Sully, "Metallic Creep and Creep Resistant Alloys," Butterworths, London, 1949.

²⁸ E. G. Stanford, "The Creep of Metals and Alloys," Temple Press, London, 1949.

²⁹ K. E. Van Holde and J. W. Williams, *J. Polymer Sci.* **11**, 243 (1953).

³⁰ W. Lethersich, *J. Sci. Instr.* **24**, 66 (1947).

³¹ D. T. Griggs, *J. Geol.* **47**, 225 (1939).

³² G. J. Dienes and H. F. Klemm, *J. Appl. Phys.* **6**, 458 (1946).

³³ G. J. Dienes, *J. Colloid Sci.* **2**, 131 (1947).

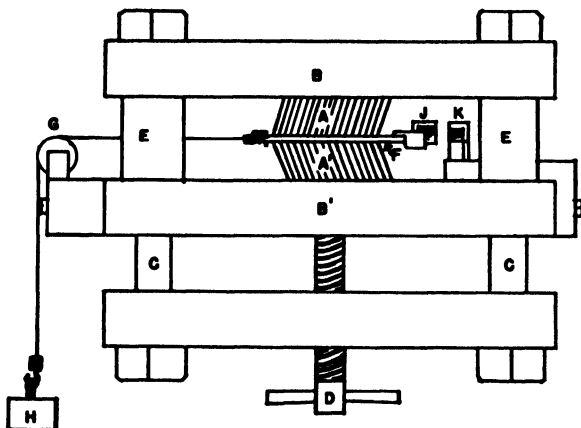


FIG. 3. Apparatus for measurements of creep in shear, for soft high polymers (from reference 29). The samples, A and A' , are clamped by blocks B and B' , their thickness being controlled by spacers E . A horizontal force is applied by the weight H to a thin plate F between the samples, and their shear deformation is determined by measuring the displacement of scale J relative to a fixed scale K .

between rotating coaxial cylinders or a rotating cone and plate.^{34-36, 36a} The same problems of sample geometry arise in converting load and deformation to stress and strain. The case of compression is particularly complicated^{32, 33, 6} because of changes in shape as the deformation proceeds.

Constant load is usually applied by weights, acting either directly,³⁷ over pulleys,³⁴ or on a balance beam.²⁵ Friction must be taken into account.³⁴ For small deformations, or in shear even for larger deformations, constant load assures constant stress. For larger deformations in extension, however, the cross-section area changes with time and the load must be continually adjusted to maintain constant stress. Such adjustments can be achieved automatically by mechanical devices³⁸⁻⁴⁰ or, more simply, by allowing the loading weight, suitably shaped, to be lowered into water with increasing deformation.^{41, 42}

³⁴ J. D. Ferry and G. S. Parks, *Physics* **6**, 356 (1935).

³⁵ H. Leaderman, R. G. Smith, and R. W. Jones, *J. Polymer Sci.* **14**, 47 (1954).

³⁶ L. J. Hastewell and F. J. U. Ritson, *J. Sci. Instr.* **29**, 20 (1952).

^{36a} H. Markovitz, L. J. Elyash, F. J. Padden, Jr., and T. W. DeWitt, *J. Colloid Sci.* **10**, 165 (1955).

³⁷ W. Aiken, T. Alfrey, A. Janssen, and H. Mark, *J. Polymer Sci.* **2**, 178 (1947).

³⁸ E. N. daC. Andrade and B. Chalmers, *Proc. Roy. Soc. (London)* **A138**, 348 (1932).

³⁹ R. L. Peek, Jr., *J. Rheol.* **3**, 345 (1932).

⁴⁰ W. L. Holt, E. O. Knox, and F. L. Roth, *J. Research Natl. Bur. Standards* **41**, 95 (1948).

⁴¹ E. N. daC. Andrade, *Proc. Roy. Soc. (London)* **A84**, 1 (1910); **A90**, 339 (1914).

⁴² C. A. Dahlquist, J. O. Hendricks, and N. W. Taylor, *Ind. Eng. Chem.* **43**, 1404 (1951).

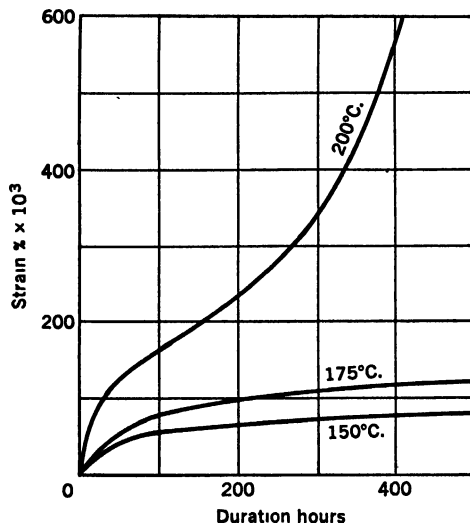


FIG. 4. Creep of a duralumin-type alloy at three temperatures (from reference 28). The applied stress is 7 tons per sq. in.

The deformation may be measured simply by a scale or cathetometer telescope,³⁷ by a dial gage,³² or, in torsional types of apparatus, by deflection of a beam of light by a mirror.³⁵ It may be recorded by perforating sparks,⁴² by a pen recorder,³⁵ or by successive photographs of a scale. The methods of temperature control are similar to those used in stress relaxation experiments.

Analysis of creep data is more complicated than that of stress relaxation data because of the necessity of separating the elastic and viscous responses, as discussed in Chapter 1 of this volume.

An example of apparatus for measurements of creep of soft solids in shear, described by Van Holde and Williams,²⁹ is shown in Fig. 3. Some results on creep of a hard solid—a metallic alloy, at high temperatures—are shown in Fig. 4.

III. Dynamic (Sinusoidal) Techniques

When a linear viscoelastic body is subjected to a stress varying sinusoidally with time, its mechanical behavior at a single frequency must be specified by two independent quantities. These may be chosen in various ways. For example, the stress, which is generally not in phase with the strain (Fig. 5A), may be separated into two components, one in phase and the other 90 deg. out of phase, as illustrated in the figure. For deformation in shear, the component in phase divided by the strain is the real part of a complex modulus of rigidity, G' ; the out-of-phase stress component divided

by the strain is the imaginary part G'' . The moduli G' and G'' may be added vectorially on a complex plane (Fig. 5B) to give $G^* = G' + iG''$. The absolute modulus is $|G^*| = \sqrt{G'^2 + G''^2}$; this is the ratio of *peak* stress to *peak* strain. The phase angle between strain and stress is ψ (Fig. 5B). The two independent quantities used to specify the dynamic behavior may be chosen as $|G^*|$ and ψ instead of G' and G'' . For a single cycle of deformation at a given amplitude, the energy stored and recovered is proportional to G' , and the energy dissipated is proportional to G'' . In extension, the corresponding quantities are E' and E'' , the real and imaginary parts (in-phase and out-of-phase components) of a complex Young's modulus E^* .

Alternatively, the strain may be separated into two components, one in phase with and the other 90 deg. out of phase with the stress. These components, each divided by the stress, give (in shear) the real and imaginary parts of a complex compliance $J^* = J' - iJ''$, which is also symbolized vectorially in Fig. 5B. It should be emphasized that J' , the in-phase strain/stress, is not simply the reciprocal of G' , the in-phase stress/strain; actually, $J' = G'/(G'^2 + G''^2)$, and $J'' = G''/(G'^2 + G''^2)$. The phase angle ψ is the same in either case, and $\Delta t = \psi/\omega = (\tan^{-1} G''/G')/\omega$.

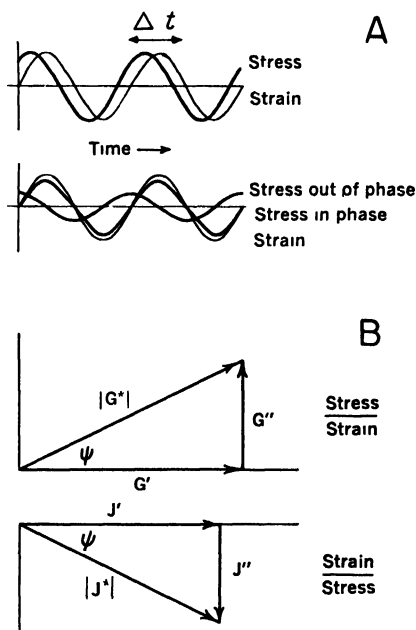


FIG. 5. Sinusoidally varying stress and strain and their in-phase and out-of-phase ratios. A, stress and strain plotted against time; the lower graph shows the stress separated into two components, one in phase and one 90 deg. out of phase with the strain. B, real and imaginary components of stress/strain and strain/stress.

Still another alternative, often used for liquids, is to separate the stress into two components, one in phase with and the other 90 deg. out of phase with the *rate* of strain (the latter being, for sinusoidal deformations, 90 deg. out of phase with the strain itself). These stress components, each divided by the rate of strain, give the real and imaginary parts of a complex viscosity $\eta^* = \eta' - i\eta''$. All these quantities are interrelated by the following equations:

$$\begin{aligned} G'' &= \omega\eta'; & G' &= \omega\eta''; \\ |G^*| &= 1/|J^*| = \omega|\eta^*|; \\ \tan\psi &= G''/G' = J''/J' = \eta'/\eta'', \end{aligned}$$

where ω is the circular frequency ($2\pi\nu$, if ν is the ordinary frequency).

If G' and η' are chosen as the two independent quantities for characterization, they may be visualized in terms of a mechanical model, representing a spring and dashpot in parallel (Voigt element) whose mechanical constants *change with frequency*. Similarly, a choice of J' and $\omega J''$ may be visualized as the reciprocals of a spring stiffness and dashpot viscosity in a series arrangement (Maxwell element), both of which *change with frequency*. These visualizations should not be confused, however, with the common use of mechanical models whose constants are supposed to be independent of frequency.

In some dynamic experimental methods, the two quantities measured are less obviously related to the mechanical properties of the material; for example, the velocity and attenuation of a sound wave, or a resonance vibration frequency and the width of the associated response peak. In all cases, however, there are two independent measurements. Moreover, in all cases the data can be converted to the complex moduli G' and G'' (or G' and η' , or J' and J'') in shear or E' and E'' in extension; so it has become customary to use the complex moduli as a basis for comparing data from diverse sources.

A basic classification of dynamic techniques⁷ is based on comparing the size of the sample (for extension, length in direction of stretch; for shear, thickness perpendicular to direction of slide) with the wavelength of elastic waves propagated at the frequency of measurement. Sections 1 to 3 below treat techniques in which the critical dimension, l , is small compared with the wave-length; i.e., $l \ll (G'/\rho)^{1/2}/\nu$ in shear or $l \ll (E'/\rho)^{1/2}/\nu$ in extension, where ν is the frequency. Under these circumstances the inertia of the sample can be disregarded, though inertia of moving parts of the apparatus must usually be taken into account. Sections 4 and 5 treat techniques in which the critical dimension, l , is large compared with the wavelength. Under these circumstances, viscoelastic waves are propagated. Finally, Section 6 treats

techniques in which l is of the same order of magnitude as the wavelength. Here resonance vibrations of various modes are excited in the sample.

In many types of apparatus it is necessary to impose an additional static stress, which may or may not be in the same direction as the dynamic stresses, to attach the sample. Even if this stress does not relax, it can usually be kept small enough to avoid influencing the dynamic response. Under high static stresses, however, the time-dependent mechanical properties may be considerably altered, as mentioned in Section V.

1. DIRECT MEASUREMENTS OF STRESS AND STRAIN

When the sample size, consistency, and frequency are such that inertia can be neglected, following the criterion given above, the simplest way to determine the in-phase and out-of-phase elastic responses is to measure both stress and strain as functions of time in sinusoidal deformations (Fig. 5A). Such measurements can be made by direct mechanical means if the sample is strained in series with a stress-sensing element—a spring of some kind. If the spring is stiff compared with the sample, a prescribed sinusoidally varying strain can be applied to the pair, which will be practically equal to the strain of the sample; the spring deflections are then proportional to the stress. Alternatively, if the sample is stiff compared with the spring, a prescribed sinusoidally varying strain applied to the pair is almost equal to the strain of the spring and is therefore proportional to the stress on the sample; the strain of the sample can be measured separately.

A straightforward example of the recording of two sine graphs of stress and strain against time is that of the apparatus of Lethersich,⁴³ in which a tube of a moderately hard solid is subjected to oscillating torsional deformation through a small angle and the stress and strain are proportional to deflections of two light beams from mirrors. In the so-called autographic devices, the imposed strain and spring displacement trace graphical records, often at right angles to form a stress-strain ellipse, usually for deformation of soft solids in compression.^{44, 45} In the popular apparatus of Roelig,⁴⁶ which also deforms in compression, the ellipse is traced by a beam of light reflected from mirrors which are rotated at right angles. In the elegant apparatus of Philippoff for deformation of soft solids in shear,⁴⁷ the two displacements proportional to stress and strain are recorded by differential transformers whose outputs, suitably amplified, are applied to the horizontal and vertical plates of a cathode-ray oscilloscope; again an ellipse is

⁴³ W. Lethersich, *J. Sci. Instr.* **27**, 303 (1950).

⁴⁴ D. M. Davies, *Brit. J. Appl. Phys.* **3**, 285 (1952).

⁴⁵ L. Mullins, *Trans. Inst. Rubber Ind.* **26**, 27 (1950).

⁴⁶ H. Roelig, *Proc. Rubber Technol. Conf.* pp. 821–829 (1938).

⁴⁷ W. J. Philippoff, *J. Appl. Phys.* **24**, 685 (1953); **25**, 1102 (1954).

traced, and may be photographed. This device provides a very wide range of frequencies, from 10^{-5} to 10 c.p.s. In any of these methods, the two components of the complex elastic modulus can be calculated from the ellipse geometry. It should be remarked that ellipse geometry, never highly precise, becomes quite inadequate for phase angles near 0 deg. or near 90 deg., and under such conditions some artificial phase shift must be introduced.

In an ingenious device^{47a, 47b} for hard solids, one end of a horizontal rod is clamped and rotated while a weight on the other end produces a flexural deformation. The weighted end undergoes both a vertical and a horizontal displacement which are related to the in-phase and out-of-phase elastic responses.

In other types of apparatus, a prescribed strain is imposed by a mechanical drive and the stress is recorded by indirect means such as deflection of a beam of light, as in the device of Müller⁴⁸ which deforms a strip in flexure. In the shear apparatus used by Blizard,⁴⁹ the stress is prescribed by an electromagnetic drive and the strain is measured by displacement of one plate of an electrical condenser.

It is easier, of course, to measure only the peak stress and strain, instead of following their periodic changes in detail; this can be accomplished by noting the width of a spot of light produced by oscillatory motion of a narrow beam,⁵⁰ or the peak voltage generated by a coil moving in a magnetic field. The ratio of the two maxima gives the absolute value of the elastic modulus—in the case of shear, $|\mathbf{G}^*| = (G'^2 + G''^2)^{1/2}$ —and some devices provide only this absolute modulus.^{50, 51} The individual components G' and G'' , representing energy storage and energy loss, can be determined only if the phase angle, ψ , between the two maxima is also known. In this case, as illustrated in Fig. 55,

$$G' = |\mathbf{G}^*| \cos \psi; \quad G'' = |\mathbf{G}^*| \sin \psi \quad (1)$$

An example of a method in which a phase angle is measured is the elaborate apparatus of Markovitz, DeWitt, and associates,^{52, 53} in which a liquid sample is sheared between two coaxial cylinders. The outer cylinder is rotated

^{47a} B. J. Lazan, *Trans. Am. Soc. Metals* **4**, 499 (1950).

^{47b} B. Maxwell, *J. Polymer Sci.* **20**, 551 (1956).

⁴⁸ F. H. Muller, *Z. Elektrochem.* **54**, 204 (1950).

⁴⁹ R. B. Blizard, *J. Appl. Phys.* **22**, 730 (1951).

⁵⁰ A. P. Aleksandrov and Y. S. Lazurkin, *J. Tech. Phys. (USSR)* **9**, 1249–60, 1261–66, 1267–79 (1939).

⁵¹ It has sometimes been erroneously stated that observation of such maxima provides G' .

⁵² H. Markovitz, P. M. Yavorsky, R. C. Harper, Jr., L. J. Zapas, and T. W. DeWitt, *Rev. Sci. Instr.* **23**, 430 (1952).

⁵³ H. Markovitz, *J. Appl. Phys.* **23**, 1070 (1952).

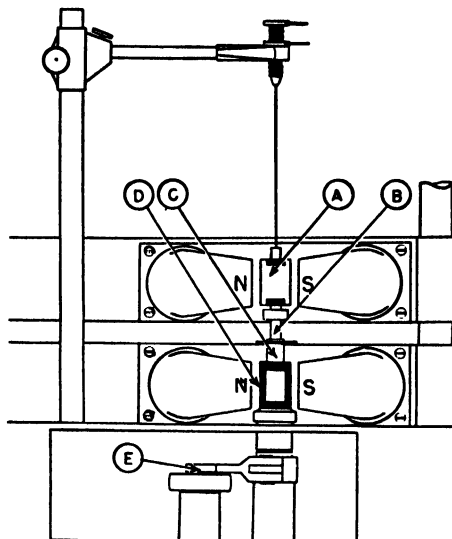


FIG. 6. Apparatus for measuring sinusoidally varying stress and strain in viscoelastic liquids (from reference 52). The liquid is sheared between the two cylinders *B* and *C*. The angular oscillations of the cylinders are measured by alternating currents generated in coils *A* and *D*.

through a small angle varying sinusoidally with time, and the coaxial inner cylinder is freely suspended from a torsion wire (Fig. 6). From the ratio of the peak amplitudes of rotation of the two cylinders and the phase angle between them, determined from voltages generated by attached coils located in magnetic fields, the individual components G' and G'' can be calculated. It is necessary also to know the moment of inertia of the inner cylinder and the torsional stiffness of the wire; the details of the calculations are too complicated to be given here.

2. RESONANCE DEVICES WITH ADDED INERTIA

When the applied sinusoidally varying force not only deforms the sample under investigation but also simultaneously oscillates a mass M , whose inertia is deliberately chosen to be large compared with that of the sample itself, there are simple relations at the frequency of mechanical resonance from which the dynamic mechanical properties can be calculated. This type of experiment usually involves less complicated apparatus than those of the preceding section, but at the sacrifice of a continuously variable frequency range; the measurement can be made only at the resonant frequency, whatever it happens to be, and this can be altered only by adjusting the added inertia or, to a limited extent, the sample geometry. An example of such an apparatus for deformation in shear is shown in Fig. 7.

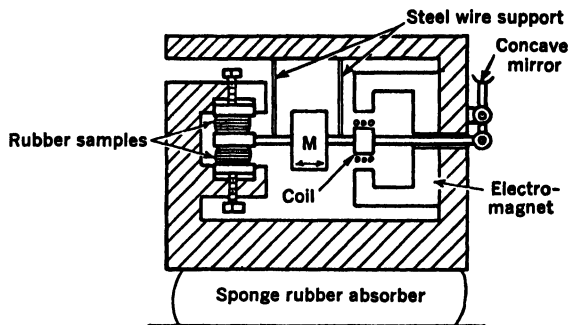


FIG. 7. Apparatus for measuring complex shear modulus at a resonance frequency determined by apparatus inertia (from reference 9).

If the oscillating motion is linear (the sample being strained in compression, shear, flexure, etc.) the driving force may be represented as complex ($\mathbf{f}$), with a real part in phase with the rate of displacement (v) and an imaginary part in quadrature; it is convenient to define a mechanical impedance,

$$\mathbf{Z}_M = \frac{\mathbf{f}}{v} = R_M + iX_M = \frac{aG''}{\omega} + i\left(\omega M - \frac{S_M^\circ}{\omega} - \frac{aG'}{\omega}\right) \quad (2)$$

where R_M and X_M are the mechanical resistance and reactance, M is the moving mass, and S_M° is the elastance, if any, associated with the apparatus independently of the sample. (The mechanical resistance and reactance are the in-phase and out-of-phase ratios, respectively, of driving force to velocity, while the elastance of a spring is the ratio of force to elastic displacement). The constant a , which has the dimensions of length, depends on sample geometry. It should be remarked that the geometry may involve unexpected complications, especially if there is bulging as shown in Fig. 7; cf. Section 1 above. The coefficients G' and G'' are the moduli which would be measured in shear, as in Fig. 7; in compression, extension, or flexure they would be replaced by E' and E'' . If the oscillating motion is angular rather than linear, an equation similar to (2) can be written with $\mathbf{f}$, v , and M replaced by torque, angular velocity, and moment of inertia, respectively.

At constant peak force, $|f|$, either M or ω is adjusted until either maximum velocity, $|v|$, or amplitude, $|x|$, is observed; the difference between these two maxima will be small if $R_M \ll \omega M$, as is usually the case. Subject to the latter restriction, at the observed resonance,

$$G' = \frac{\omega^2 M}{a} - \frac{S_M^\circ}{a} \quad \text{and} \quad G'' = \frac{|f|}{a|x|} \quad (3)$$

so the resonance frequency specifies the in-phase and the absolute magnitude of the peak response specifies the out-of-phase modulus. An alternative

way of obtaining G'' is to measure the response $|x|$ at various frequencies near resonance and note the half width, $\Delta\omega$, of the response curve corresponding to the difference between the frequencies at which the response is half its maximum value. Then, if the curve is fairly sharp,

$$G'' = \frac{G'\Delta\omega}{\omega\sqrt{3}} \quad (4)$$

In this case neither $|f|$ nor $|x|$ requires an absolute calibration, but the measurements are more laborious because a response curve must be constructed at each frequency.

The frequency can be specified by a mechanical drive,⁵⁴ measured by tachometry (in the case of a rotating cam drive), or, when the drive is electrical, read from an oscillator setting. In the popular electromagnetic type of drive⁵⁵⁻⁵⁸ the peak force $|f|$ is measured by the current drawn. The peak displacement $|x|$ may be measured directly with a traveling microscope taken from the width of a spot of light reflected by a mirror, or determined by contact of the moving system with an adjustable micrometer screw.⁵⁵ This type of resonance method has been applied to soft solids in the low audio frequency region, strained in alternate extension and compression^{54, 56, 57} or in shear.^{58, 59} It was also used for liquids in the classical apparatus of Philippoff,⁵⁶ where the sample was strained in shear (with rather complicated hydrodynamics). Usually⁵⁶⁻⁵⁹ the moving parts are lightly hung from wires or leaf springs so that S_M° is small compared with aG' and the elastic stiffness is dominated by the sample. Otherwise⁵⁵ it may be impossible to calculate G' , and only the out-of-phase modulus can be obtained.

Liquid samples may also be studied by shear between coaxial cylinders;^{60, 61} the physical arrangements are similar to those of the apparatus of Markovitz and DeWitt,⁵² but measurements are restricted to the resonance frequency of torsional oscillations. From the resonance frequency, the peak angular displacements of the two cylinders, and the torsional stiffness of the suspension of the inner cylinder, the two components G' and G'' can be calculated. In one modification⁶¹ the inner cylinder is suspended with negligible torsional stiffness.

⁵⁴ C. W. Kosten and C. Zwicker, *Physica* **4**, 221 (1937).

⁵⁵ W. Philippoff, *Physik. Z.* **35**, 884 (1934).

⁵⁶ W. J. S. Naunton and J. R. S. Waring, *Trans. Inst. Rubber Ind.* **14**, 340 (1939).

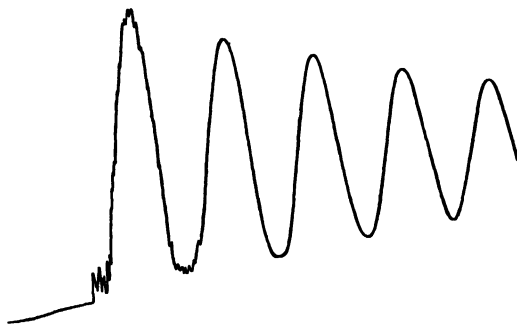
⁵⁷ S. D. Gehman, D. E. Woodford, and R. B. Stambaugh, *Ind. Eng. Chem.* **33**, 1032 (1941).

⁵⁸ J. H. Dillon, I. B. Prettyman, and G. L. Hall, *J. Appl. Phys.* **15**, 309 (1944).

⁵⁹ R. S. Enabnit and S. D. Gehman, *Ind. Eng. Chem.* **43**, 346 (1951).

⁶⁰ H. Goldberg and O. Sandvik, *Ind. Eng. Chem. Anal. Ed.* **19**, 123 (1947).

⁶¹ J. R. Van Wazer and H. Goldberg, *J. Appl. Phys.* **18**, 207 (1947).



8. Exponentially damped sinusoidal free torsional vibration, traced against time (from reference 43).

When the elastic stiffness of the moving system is dominated by the sample, resonance appears only if the loss tangent G''/G' (or E''/E') is moderately small, and this imposes a restriction on the types of materials that can be studied. Alternatively, the elastic stiffness can be deliberately dominated by the apparatus itself. In this case, G' is derived not from the absolute resonance frequency but from the difference between resonance frequencies with and without attachment of the sample. Examples of this type of resonance method are the tuning fork apparatus of Rorden and Grieco⁶² for soft solids in shear at audio frequencies, also modified by Hopkins^{63, 64} for liquids of fairly high viscosity, and the magnetostrictive rod device of Nolle⁶⁵ for solids in compression in the high kilocycle frequency range. A piezoelectric device has also been described for the high kilocycle range.⁶⁶

All of the above resonance methods are "forced" in the sense that a continuous oscillating force is applied during the measurements. Closely related are the "free" resonance vibration methods in which the moving system is displaced from equilibrium and then allowed to oscillate freely. For the same schematic arrangement as in Fig. 7, with a small initial displacement, the amplitude is an exponentially damped sinusoidal function of the time. From a trace of this function, or simply from observation of successive peak displacements, the logarithmic decrement Δ is obtained as the natural logarithm of the ratio of two successive displacements. Such a trace for free torsional vibrations is illustrated in Fig. 8. The in-phase modulus G' (or E') is related to the resonance frequency to a close approximation as in equations (3), and the out-of-phase modulus is calculated

⁶² H. C. Rorden and A. Grieco, *J. Appl. Phys.* **22**, 842 (1951).

⁶³ I. L. Hopkins, *Trans. Am. Soc. Mech. Engrs.* **73**, 195 (1951).

⁶⁴ I. L. Hopkins, *J. Appl. Phys.* **24**, 1300 (1953).

⁶⁵ A. W. Nolle, *J. Appl. Phys.* **19**, 753 (1948).

⁶⁶ M. O. Kornfeld, *J. Exptl. Theoret. Phys. (USSR)* **13**, 116 (1943).

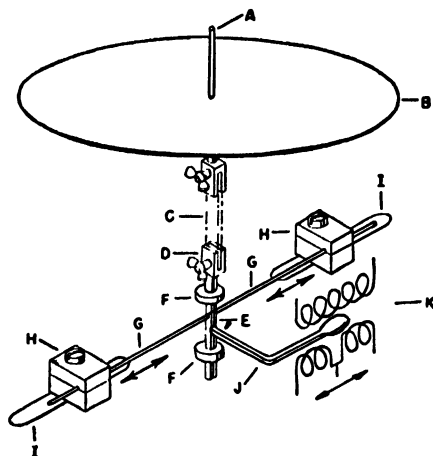


FIG. 9. Apparatus for measuring damped free torsional vibrations (from reference 70). The sample *C* is subjected to torsional oscillations when the moment of inertia disc *B* is turned through a small angle and released. The periodic torques exerted on the lower sample clamp *D* are recorded by the differential transformer *K*, whose core *J* moves through a very small amplitude constrained by the spring rods *G*.

from the relation

$$G''/G' \text{ (or } E''/E') = \Delta/\pi \quad (5)$$

For a given experimental arrangement it may be simpler to calibrate by substituting a spring for the sample than to attempt to determine the effective mass *M* from geometry.

In the free vibration devices of Yerzley⁶⁷ and Nolle,⁶⁵ soft solids are deformed in extension. There are many examples of oscillating torsion balances for deformation of cylindrical or prismatic samples in torsion (shear);^{68-70a, 43} one is shown in Fig. 9. Here moment of inertia and angular displacement are involved rather than mass and linear displacement. The motion may be followed by a direct trace,⁶⁷ microscopic observation,⁶⁵ a differential transformer,⁷⁰ or displacement of a reflected beam of light. The general frequency range of such devices is from 0.1 to 10 c.p.s.

3. TRANSDUCER MEASUREMENTS OF STRESS-STRAIN RATIOS

An electromechanical transducer is a device for converting electrical into mechanical energy or vice versa, and in this sense some of the methods de-

⁶⁷ F. L. Yerzley, *Ind. Eng. Chem. Anal. Ed.* **9**, 392 (1937).

⁶⁸ M. Mooney and R. H. Gerke, *India Rubber World* **103**, No. 4, 29 (1941).

⁶⁹ W. Kuhn and O. Kunzle, *Helv. Chim. Acta* **30**, 839 (1947).

⁷⁰ L. E. Nielsen, *Rev. Sci. Instr.* **22**, 690 (1951).

^{70a} J. Koppelman, *Kolloid-Z.* **144**, 12 (1955).

scribed above with electromagnetic drives⁵⁶ or electromagnetic⁵² or electrostatic⁶⁵ pickups for detection of amplitude possess transducer elements. However, electromechanical converters can be utilized in a far more powerful way so that ratios of electrical voltage to current are measured in place of mechanical ratios of stress to strain. Thus the actual measurements are of electrical resistance and capacity, which can easily be made with high precision. It is this type of apparatus which will be designated as a transducer, in a more restricted sense, in the present discussion. It has the advantage, shared by none of the other methods, that neither stress nor strain need be measured directly, and displacements can be kept exceedingly small; it also has the advantage, shared by the direct stress-strain devices of Section 1, that the frequency can be continuously varied. In the methods described in this section, as in both the preceding sections, the sample deformed is thin compared with the wavelength of elastic waves, and the effect of its inertia can be neglected, or at least reduced to a small correction.

The experimental arrangement shown in Fig. 7 could be used as an electromagnetic transducer, preferably without the added mass. A current i passed through the coil will cause a force f to be exerted on the moving system, given by $f = Bli$, where B is the magnetic flux density and l the length of wire in the coil. The system will oscillate with a velocity $v = f/Z_M$, where, as in equation (2), v is taken in phase with the real part of f and therefore written as real. The moving coil will generate a back e.m.f. given by $e = Blv$. The applied e.m.f. is $Z_0 i$ where Z_0 is the electrical impedance of the coil at rest; the total e.m.f. is $Z_0 i + e = Zi$, where Z is the electrical impedance of the coil while in motion. Thus

$$(Z - Z_0)i = Blv = (Bl)^2 i / Z_M \quad (6)$$

This is the fundamental equation of an electromagnetic transducer,⁷¹ which makes it possible to calculate a mechanical impedance from the difference between two electrical impedances. Separation into real and imaginary parts gives the following expressions for mechanical resistance and reactance:

$$R_M = \frac{(Bl)^2(R - R_0)}{[(R - R_0)^2 + (X - X_0)^2]} \quad (7a)$$

$$X_M = \frac{-(Bl)^2(X - X_0)}{[(R - R_0)^2 + (X - X_0)^2]} \quad (7b)$$

Here R and R_0 are the electrical resistances of the coil in motion and at rest, and X and X_0 are the corresponding electrical reactances. If the coil is

⁷¹ W. P. Mason, "Electromechanical Transducers and Wave Filters," Van Nostrand, New York, 1942.

placed in one arm of an impedance bridge,⁷² these electrical quantities can be measured with high precision. The moduli G' and G'' can then be obtained from R_M and X_M as indicated in equation (2).

The characteristic feature of this type of method is that complex stress-strain ratios are measured in terms of complex voltage-current ratios, and neither stress, strain, voltage, nor current need be measured directly. If the deformations are small enough so that linear viscoelastic behavior holds, the electrical impedance is found to be independent of the driving current. Strains as small as 10^{-6} may be employed.

The electrical measurements of R_0 and X_0 must be made with the moving system tightly clamped to prevent the current from evoking motion. In practice, it may be difficult or impossible to make such clamping absolute. There are, therefore, modifications of the transducer method in which two or more sets of electrical measurements are repeated at the same frequency in such a way that R_0 and X_0 cancel out or can be determined by solving simultaneous equations. For example, the mechanical impedance can be modified by attaching added masses; it is unnecessary to know their magnitude if three or more different values are used.⁷²

In the twin^{73, 74} and double⁷⁵ transducers, two coils oscillate in separate magnetic fields, both rigidly attached to the moving system which deforms the material investigated. One coil may be used as a driver and the other as a detector,⁷³ in which case potentiometer measurements can be used to find the relations between driving current and generated voltage with respect to amplitude and phase. Determination of the phase requires some tedious adjustments, however. Alternatively, driving current can be sent through both coils and the impedance of one coil measured for two different ratios of the two driving currents.⁷⁵ This permits rapid and accurate determination of Z_M without knowledge of Z_0 ; the calculations are more complicated than equation (6) but are based on the same relationships.

The transducer methods have been applied to liquids in a limited frequency and temperature range⁷² and to solids in the range from soft gels to rather hard glasses.⁷⁵ In the apparatus of Fitzgerald and Ferry,⁷⁵ shown in Fig. 10, a pair of disc-shaped samples is sheared between a tube carrying the driving coils and a freely suspended heavy mass. The slight motion of the latter must be taken into account in calculating Z_M for the samples. The frequency range is from 20 to 5000 c.p.s. and the temperature can be accurately controlled from -50 to $+150^\circ$ C. An example of results⁷⁶ ob-

⁷² T. L. Smith, J. D. Ferry, and F. W. Schrepf, *J. Appl. Phys.* **20**, 144 (1949).

⁷³ R. S. Marvin, E. R. Fitzgerald, and J. D. Ferry, *J. Appl. Phys.* **21**, 197 (1950).

⁷⁴ R. S. Marvin and F. Weiss, unpublished experiments.

⁷⁵ E. R. Fitzgerald and J. D. Ferry, *J. Colloid Sci.* **8**, 1 (1953).

⁷⁶ E. R. Fitzgerald, L. D. Grandine, Jr., and J. D. Ferry, *J. Appl. Phys.* **24**, 650 (1953).

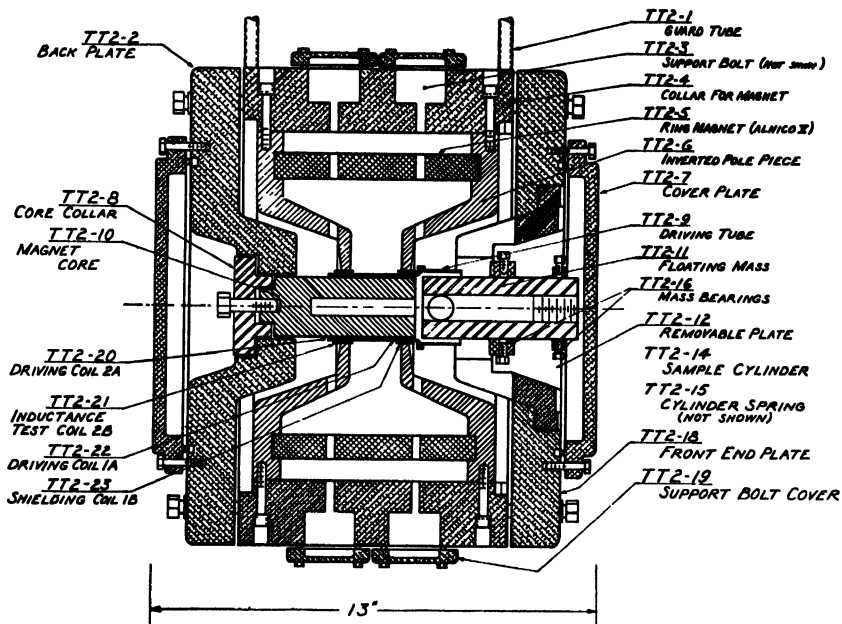


FIG. 10. Double transducer for measuring complex shear modulus at audio frequencies. Two disc-shaped samples are sheared between flat areas on the thin driving tube (TT2-9) and the flat ends of cylinders mounted in the floating mass (TT2-11). Both moving parts are suspended from fine wires and essentially isolated from the body of the apparatus. The driving tube is oscillated with a very small amplitude along its axis by passing alternating currents through the driving coils (TT2-20, 22). Electrical impedance measurements are made on coil TT2-20, after balancing out mutual inductance with coils TT2-21, 23. The entire apparatus is sealed for immersion in a liquid thermostat. (From reference 75.)

tained with this transducer is shown in Fig. 11, where the real part of the complex compliance is plotted against the frequency (with logarithmic scales) at numerous temperatures, for a sample of polyisobutylene.

Transducer methods may also be applied^{76a, 76b} to measurements of the complex bulk modulus K^* , whose real part is the reciprocal of the compressibility.

The inertia of the sample is almost always neglected in the methods described in Sections 1 to 3 above. When it is large enough to influence the mechanical impedance slightly—when the sample thickness is of the order of a tenth of the wavelength of elastic waves—it may be taken into account in an approximate correction.⁷³

^{76a} W. Philippoff and J. Brodnyan, *J. Appl. Phys.* **26**, 846 (1955).

^{76b} J. E. McKinney, S. Edelman, and R. S. Marvin, *J. Appl. Phys.* **27**, 425 (1956).

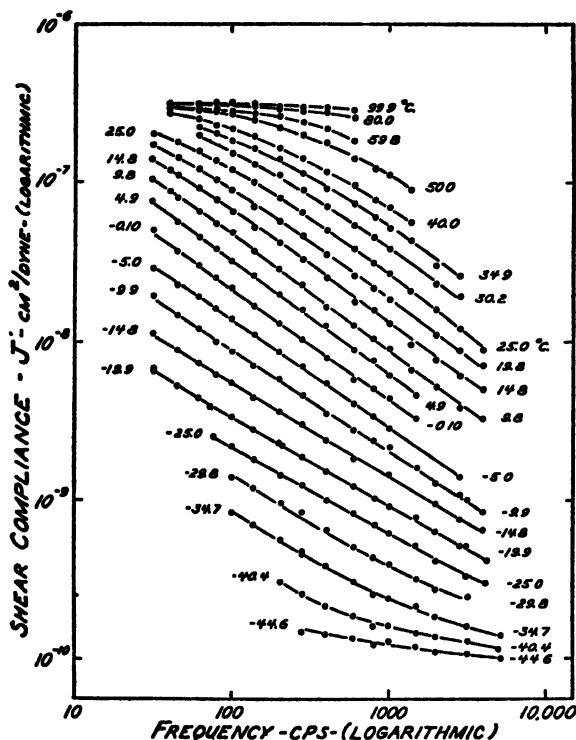


FIG. 11. Real part of complex shear compliance of polyisobutylene ($J' = G' / (G'^2 + G''^2)$) measured by double transducer at 22 temperatures. (Viscosity-average molecular weight 1,350,000; from reference 76.)

4. WAVE PROPAGATION

When the critical dimension of the sample is large compared with the wavelength of elastic waves propagated at the frequency of measurement, the inertia of the sample itself cannot be neglected, and because of the presence of elastic waves there is no simple relation between applied load and observed displacement such as described in the preceding three sections. However, the mechanical characteristics of the sample can be derived from observations of these waves—from their velocity and attenuation. The velocity of waves of distortion depends on the shear modulus alone, but the velocity of waves of dilatation depends on both shear and bulk moduli and also on the geometry of the sample,⁷⁷ as discussed below.

Often conditions are chosen so that the wave approximates a one-dimensional disturbance and the attenuation prevents perceptible reflection

⁷⁷ H. Kolsky, "Stress Waves in Solids," Oxford Univ. Press, New York, 1953.

from the far side of the sample opposite the source. In this case the wave is exponentially damped and may be characterized by its wavelength, λ , and the critical damping distance, x_0 , within which its amplitude falls off by a factor of $1/e$ (Fig. 12).^{78, 79} The dimensionless ratio λ/x_0 is a convenient index of the severity of damping.⁷⁸

For a shear wave (pure distortion), the components of the complex modulus G' and G'' are related to the wavelength and attenuation as follows:

$$G' = \frac{\omega^2 \lambda^2 \rho [4\pi^2 - (\lambda/x_0)^2]}{[4\pi^2 + (\lambda/x_0)^2]^2} \quad (8a)$$

$$G'' = \frac{4\pi\omega^2 \lambda^2 \rho (\lambda/x_0)}{[4\pi^2 + (\lambda/x_0)^2]^2} \quad (8b)$$

Here ρ is the density of the medium.

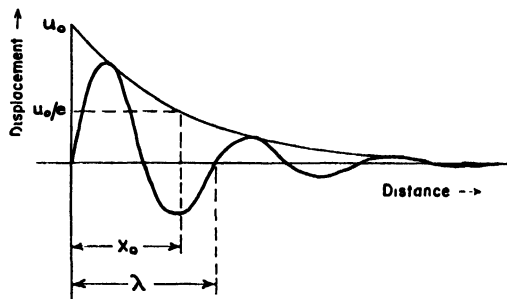


FIG. 12. Exponentially damped shear wave with definitions of characteristic parameters (from reference 78).

For a longitudinal wave in a sample of cross-section small compared with the wavelength, i.e., a fiber or thin strip, equations (8) yield the moduli E' and E'' rather than G' and G'' . For a bulk wave, a longitudinal wave in a sample large compared with the wavelength in all dimensions, the measurements are not related simply to either G^* or E^* .

Shear wave measurements have been applied primarily to liquids and very soft solids,^{78, 80, 81} the disturbance being created by a plate oscillating in its own plane. The values of λ and x_0 are most conveniently measured by taking advantage of the strain double refraction produced by deformation of many viscoelastic systems. If the system is transparent and shows strain double refraction, stroboscopic illumination between crossed pola-

⁷⁸ F. T. Adler, W. M. Sawyer, and J. D. Ferry, *J. Appl. Phys.* **20**, 1036 (1949).

⁷⁹ R. Sips, *J. Polymer Sci.* **6**, 285 (1951).

⁸⁰ J. D. Ferry, *Rev. Sci. Instr.* **12**, 79 (1941).

⁸¹ J. N. Ashworth and J. D. Ferry, *J. Am. Chem. Soc.* **71**, 622 (1949).

rizers (at the frequency of the wave propagation) shows a pattern of alternate dark and light bands. The axes of the polarizers must be parallel and perpendicular to the direction of wave propagation. The transmitted intensity is proportional to $\sin^2 \varphi/2$, where φ , the double refraction (phase difference), is in turn proportional to strain amplitude. From the periodic variations of intensity with distance in the direction of wave propagation, therefore, λ and x_0 can be obtained. More usually, a double quartz wedge is inserted in the optical path, with its axis inclined at a small angle to the direction of wave propagation; the resulting pattern is a damped wave whose geometry is related to the shear wave itself, and λ and x_0 can be determined from direct observation or photography of the pattern. An example of such a photograph is shown in Fig. 13. The propagation of a

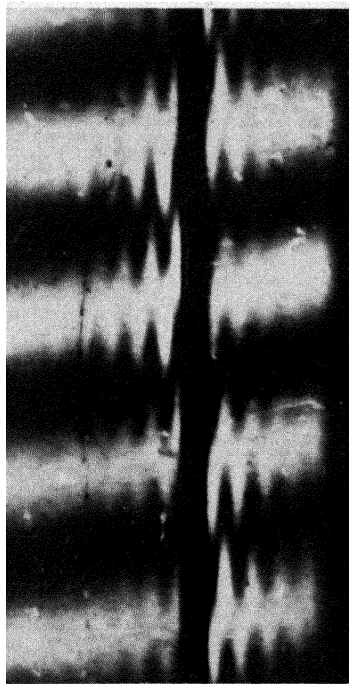


FIG. 13. Photograph of wave of shear-strain double refraction in a 26% solution of cellulose tributyrat in 1,2,3-trichloropropane at 40° C., frequency 5000 c.p.s. (data of R. F. Landel). The driving plate, seen in the center, is oscillated vertically in its own plane. Shear waves propagated in both directions horizontally produce patterns of strain double refraction; the vertical displacements, photographed here stroboscopically, are proportional to the arctangents of the relative retardation (phase difference) in the components of polarized light passing through the strained medium. The relative retardation is assumed to be proportional in turn to the shear strain.

photoelastic pattern can also be followed by high-speed photography.⁸² An alternative method for following shear wave propagation, which has been suggested⁷ but not utilized, is the observation of small particles immersed in a transparent liquid or soft solid. From photographs with and without synchronization of stroboscopic illumination, the wave parameters could be determined. The effects of the container walls have been investigated theoretically,⁷⁸ but are usually not taken into account.

Longitudinal waves have been followed in fibers and strips by electromagnetic or piezoelectric pickup devices.^{81, 81, 65, 85-87} The disturbance is set up at one end, usually by an electromagnetic drive, and the pickup is moved at a constant rate along the sample. Automatic recording devices may provide graphs from which λ and x_0 can be obtained,⁶⁰ as indicated schematically in Fig. 14. Reflectance from the pickup must be avoided; reflectance from the far end of the sample may be taken into account,⁸⁸ though usually it is not.⁸⁹ The effect of superimposed static strain or even of a constant rate of strain can be investigated.

Flexural waves may also be employed. In a method devised by Oberst,^{89a} a material too soft or with too much damping for direct measurement is layered on a thin metal sheet; from the velocity and damping of flexural waves in the compound system and the properties of the metal, the components of $\mathbf{E}^*$ for the applied layer can be obtained.

The modulus $\mathbf{E}^*$, measured by longitudinal wave propagation along a thin sample as in Fig. 14, may be thought of as representing a combination of shear and bulk compression properties, since $\mathbf{E}^* = 3\mathbf{G}^* (1 + \mathbf{G}^*/3\mathbf{K}^*)$, where $\mathbf{K}^*$ is the bulk modulus (whose real part is the reciprocal of the compressibility). For soft solids at low frequencies, $G' \ll K'$, and the shear properties of course dominate the behavior. However, when longitudinal waves are propagated into a wide sample (bulk waves), their velocity and attenuation depend on a different combination of $\mathbf{G}^*$ and $\mathbf{K}^*$; equations (8), or their equivalent, provide the real and imaginary parts of a complex modulus $\mathbf{K}^* + (4/3)\mathbf{G}^*$. In this case, the bulk modulus dominates the behavior, at least as far as the real part is concerned; for soft solids, again, $K' \gg G'$. However, usually K'' is much less than G'' and may be zero within experimental error, so the energy loss is still dominated by the shear proper-

⁸² D. G. Christie, *Trans. Soc. Glass Tech.* **36**, 71 (1952).

⁸³ J. W. Ballou and S. Silverman, *Textile Research* **14**, 282 (1944).

⁸¹ J. W. Ballou and S. Silverman, *J. Acoust. Soc. Amer.* **16**, 113 (1944).

⁸⁵ R. S. Witte, B. A. Mrowca, and E. Guth, *J. Appl. Phys.* **20**, 481 (1949).

⁸⁶ J. W. Ballou and J. C. Smith, *J. Appl. Phys.* **20**, 493 (1949).

⁸⁷ K. W. Hillier and H. Kolsky, *Proc. Phys. Soc. (London)* **62**, 111 (1949).

⁸⁸ K. W. Hillier, H. Kolsky, and J. P. Lewis, *J. Appl. Phys.* **20**, 227 (1949).

⁸⁹ A. W. Nolle, *J. Appl. Phys.* **20**, 227 (1949).

^{89a} H. Oberst, *Acustica* **4**, Beiheft 1, 433 (1954).

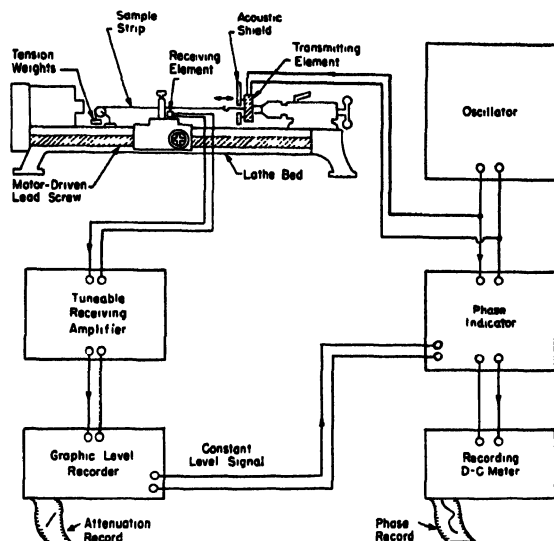


FIG. 14. Schematic arrangement for measuring propagation of longitudinal waves in thin strips of soft viscoelastic solids (from reference 65). The waves are propagated to the left from the transmitting element and detected by the receiving element. The amplitudes and phases at these two points are compared electronically. The wavelength and critical damping distance are obtained from the phase record and attenuation record respectively.

ties. The propagation of such bulk waves in a solid can be studied by interposing a disc- or plate-shaped sample between two columns of another medium (either liquid^{90, 91} or solid⁹²) in which K^* is known, and sending longitudinal wave pulses across. The source and pickup are usually both piezoelectric crystals, and the transit time and attenuation are measured with a cathode-ray oscilloscope. For a viscoelastic liquid, a transmitting and a receiving crystal can be immersed in the sample; the change in phase and amplitude of a longitudinal wave pulse crossing the gap are measured by a suitable electrical circuit,⁹³ such as illustrated in the block diagram of Fig. 15.

In a transparent medium with low loss, high-frequency standing waves can be set up with resulting periodic differences in density and refractive index which serve as an optical grating for diffraction of visible light.⁹⁴

⁹⁰ A. W. Nolle and S. C. Mowry, *J. Acoust. Soc. Amer.* **20**, 432 (1948).

⁹¹ D. G. Ivey, B. A. Mrowca, and E. Guth, *J. Appl. Phys.* **20**, 486 (1949).

⁹² A. W. Nolle and P. W. Sieck, *J. Appl. Phys.* **23**, 888 (1952).

⁹³ W. P. Mason, W. O. Baker, H. J. McSkimin, and J. H. Heins, *Phys. Rev.* **73**, 1074 (1948); **74**, 1873 (1949).

⁹⁴ L. Bergmann, "Der Ultraschall und seine Anwendung in Wissenschaft und Technik," S. Herzel Verlag, Leipzig, 1949.

which have been given (in different form) by Mason.⁹⁵ Equations (9) can be rearranged to provide G' and G'' in terms of $\Re_M$ and $\Im_M$.

The resistance and reactance per unit area, $\Re_M$ and $\Im_M$, could in principle be measured in various ways, but in practice they have thus far been obtained mostly from transducer measurements, usually by generation of the waves at the surfaces of piezoelectric crystals following the techniques of Mason.⁹⁶ At high frequencies and with high attenuation it is easy to ensure that the wave train vanishes before it can be reflected from the oppo-

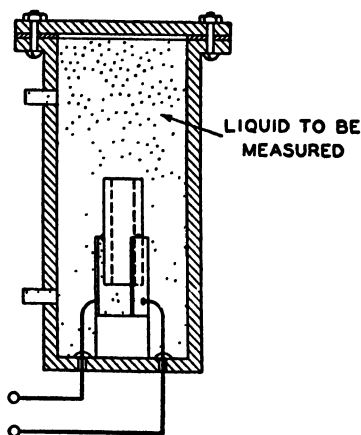


FIG. 16. Torsional piezoelectric crystal for measuring characteristic impedance of a surface propagating shear waves in viscoelastic liquid (from reference 95). The hollow cylindrical crystal, completely immersed in the liquid, is excited in torsional vibrations around its vertical axis by applying an alternating potential to electrodes plated on its inner and outer surfaces. At the same time, its electrical resistance and reactance are measured, and from these the mechanical impedance per unit area of surface is calculated.

site surface of the sample; indeed, in the megacycle range, a thin smear of a liquid sample on the surface of the crystal provides adequate thickness.⁹⁶

In the frequency range from 10^4 to 10^5 c.p.s., torsionally oscillating piezoelectric crystals can be used to generate shear waves in liquid samples.^{95, 97, 98} The entire crystal may be immersed in the liquid (Fig. 16); then from measurements of its electrical resistance and reactance near the resonance frequency, or electrical resistance and change in the resonant frequency, $\Re_M$ and $\Im_M$ can be calculated by relations which are somewhat

⁹⁵ W. P. Mason, *Trans. Am. Soc. Mech. Engrs.* **69**, 359 (1947).

⁹⁶ W. P. Mason, W. O. Baker, H. J. McSkimin, and J. H. Heiss, *Phys. Rev.* **75**, 936 (1949).

⁹⁷ H. J. McSkimin, *J. Acoust. Soc. Amer.* **24**, 355 (1952).

⁹⁸ P. E. Rouse, Jr., and K. Sittel, *J. Appl. Phys.* **24**, 690 (1953)

analogous to the electromagnetic transducer relations given in equations (7) but are too complicated to reproduce here.⁹⁶ Alternatively, a rod of metal or glass may be immersed in the liquid and torsional pulses sent down it from a piezoelectric crystal attached to the top.⁹⁷ In this case, $\Re_M$ and $\Im_M$ are obtained from measurements of phase shift and attenuation of the reflected pulses as they return from the bottom of the rod to the crystal driver.

In the neighborhood of 10^7 c.p.s., shear waves may be propagated in a liquid or solid by placing the sample in contact with a surface of fused quartz and reflecting a shear wave within the quartz from the surface at a low angle of incidence.⁹⁹ The wave is excited and, after reflection, detected by piezoelectric crystals. By comparing the change in amplitude and phase upon reflection with and without presence of the sample, the resistance and reactance per square centimeter, $\Re_M$ and $\Im_M$, can again be obtained.

A quite different means of measuring impedance at a propagating surface is the hollow torsion pendulum of Rouse,¹⁰⁰ in which rotational waves are set up at the inner surface of a disc filled with a liquid sample. The experimentally measured quantities are the resonance frequency of free torsional oscillation and the logarithmic decrement, just as in the torsion pendulums described in Section 2 above, but the deformation of the sample corresponds to the conditions prescribed for an attenuated wave and the behavior is therefore determined by $\Re_M$ and $\Im_M$, from which G' and G'' can in turn be calculated. This torsion pendulum bears the same relation to those described in Section 2 that the transducers of Mason and collaborators bear to the transducers described in Section 3.

Still another method for measuring the resistive part of the characteristic impedance is utilized in a commercial instrument,¹⁰¹ consisting of a blade through which longitudinal waves are propagated by a magnetostrictive oscillator at a frequency of about 30 kc. If the blade is immersed in a viscoelastic liquid, transverse waves are propagated in the latter; from observations of the damping of the waves within the blade, the mechanical resistance at the surface, $\Re_M$, can be calculated. Although according to equation (9a) it is impossible to obtain either G' or G'' from this single measurement, in practice the contribution of G' is often small and G'' can be calculated as $2\Re_M^2/\rho$.

These characteristic impedance devices suffer from a restricted choice of frequencies, since the propagating element operates only at its own resonance frequency and even by interchanging elements the choice is usually

⁹⁹ W. P. Mason, W. O. Baker, H. J. McSkimin, and J. H. Heiss, *Phys. Rev.* **75**, 936 (1949).

¹⁰⁰ K. Sittel, P. E. Rouse, Jr., and E. D. Bailey, *J. Appl. Phys.* **24**, 1312 (1955).

¹⁰¹ W. Roth and S. R. Rich, *J. Appl. Phys.* **24**, 940 (1953).

limited to three or four discrete values. However, they are capable of high precision, and are applicable in a range of frequencies and sample consistencies which cannot be covered by any other method. In particular, unlike the methods for directly observing wave propagation, they can be used for systems in which damping is extremely high.

6. RESONANCE VIBRATIONS

When the critical dimension of the sample is neither small compared with the wavelength of elastic waves (as in Sections 1 to 3) nor large compared with that wavelength (as in Sections 4 and 5), resonance vibrations can be excited in the sample. In this case the inertia necessary for resonance is provided by the sample itself instead of by part of the apparatus as in the methods described in Section 2.

The calculations resemble those of Section 2 in that the resonance frequency of a particular vibrational mode determines the real part of the associated elastic modulus, while the imaginary part is obtained by observing (a) the absolute magnitude $|x|$ of maximum response, or (b) the half-width of a response curve against frequency, or (c) the logarithmic decrement in free vibrations. The relations for the loss tangent G''/G' or E''/E' given in equations (4) and (5) hold generally for such resonance vibrations, but the relation between the resonance frequency and G' or E' is more complicated than equation (3) and depends on detailed sample shape as well as the vibrational mode.

A commonly used arrangement for this purpose is the vibrating reed, strained either in extension¹⁰² or in flexure,^{65, 70a} as illustrated in Fig. 17. The vibration is usually excited electromagnetically; the displacement can be measured by visual observation with a microscope⁶⁵ or by an oscilloscope trace from a phototube activated by a beam of light interrupted by the moving sample.¹⁰² All three methods mentioned above for determining the mechanical loss have been employed.

Both longitudinal and torsional vibrations in hard solids have been measured by similar techniques,^{103-108, 108a} providing the components of $\mathbf{E}^*$ and $\mathbf{G}^*$, respectively. By exciting the fundamental resonant frequency and several overtones, measurements may be made at several discrete frequencies on a single sample. For soft materials, however, often only the funda-

¹⁰² H. S. Sack, J. Motz, H. L. Raub, and R. N. Work, *J. Appl. Phys.* **18**, 450 (1947).

¹⁰³ R. L. Wegel and H. Walther, *Physics* **6**, 141 (1935).

¹⁰⁴ F. Birch, *J. Appl. Phys.* **8**, 129 (1937).

¹⁰⁵ F. Birch and D. Bancroft, *J. Geol.* **46**, 59, 113 (1938).

¹⁰⁶ A. Gemant, *J. Appl. Phys.* **14**, 204 (1943).

¹⁰⁷ T. S. Ke, *Phys. Rev.* **71**, 533 (1947); **72**, 41 (1947).

¹⁰⁸ C. A. Wert, *J. Appl. Phys.* **20**, 29 (1949).

^{108a} J. J. Benbow, *J. Sci. Instr.* **30**, 412 (1953).

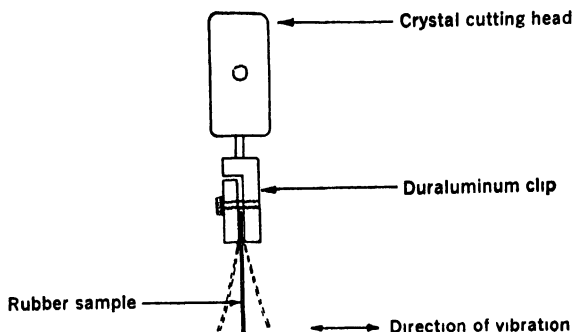


FIG. 17. Vibrating reed for measurement of complex Young's modulus at a resonance frequency determined by sample geometry and viscoelastic properties (from reference 65).

mental resonance possesses sufficient amplitude for measurement. Nevertheless, flexural resonance vibrations for compound systems,^{108b} in which a soft material is layered over a hard bar with known properties, can serve to determine the components of E^* even when the damping in the soft material is severe.

Resonance vibration measurements may also be made in viscoelastic liquids. Torsional vibrations have been excited within such a liquid by an oscillating disc or cylinder,¹⁰⁹ with use of a hot wire anemometer probe to measure the amplitude. Alternatively, the frequency and decay of free vibrations has been followed simply by observing the oscillatory motions of small bubbles in various modes¹¹⁰ (rotational, meridional, and quadrantal in a spherical vessel). The equations of motion are quite complicated in both cases.¹¹¹

In general, the resonance vibration techniques are more severely restricted with respect to frequency choice than any other, and their precision is limited. They are, however, the easiest means for obtaining measurements on systems of high rigidity and low loss, and for this reason have been widely used for metals, crystals, and glasses.

7. COMPARISONS OF DYNAMIC TECHNIQUES

Because of the wide variety of dynamic techniques, a comparative summary is desirable to show their respective limitations and advantages. Be-

^{108b} W. P. Van Oort, *Microtecnic* **7**, 246 (1952).

¹⁰⁹ F. G. Richardson, *Phil. Mag.* [7] **36**, 490 (1945).

¹¹⁰ H. G. Bungenberg de Jong and H. J. van den Berg, *Koninkl. Ned. Akad. Wetenschap. Proc.* **51**, 1197 (1948).

¹¹¹ J. M. Burgers, *Koninkl. Ned. Akad. Wetenschap. Proc.* **51**, 1211 (1948).

TABLE I
COMPARISONS OF DYNAMIC (SINUSOIDAL) TECHNIQUES

<i>Class</i>	l/λ	G''/G'	<i>Frequency, c.p.s.</i>
1. Direct measurements of stress and strain	Small	Not limiting	Continuous 10^{-6} to 10^2
2. Resonance devices with added inertia	Small	Small (except in compound systems)	Discrete 10^{-2} to 10^5
3. Transducer measurements of stress-strain ratios	Small	Not limiting	Continuous 10 to 10^4
4. Wave propagation	Large	Small	Continuous 10^2 to 4×10^4 (Bulk waves to 10^7)
5. Characteristic impedance measurements	Large	Not limiting but usually large	Discrete 10^3 to 10^7
6. Resonance vibrations	Order of unity	Small	Discrete 1 to 10^4

sides the importance of the ratio of sample size to elastic wavelength, l/λ , on which the above classification is based, the applicability of the different methods depends on the magnitude of the loss tangent G''/G' (or E''/E'). These relationships, together with approximate ranges of frequency, are summarized in Table I. The frequency ranges represent those which have usually been covered and are not absolute limitations. The variety of techniques within each class provides a wide range of material consistencies which can be handled. Similar comparisons with more limited assortments of methods have been given elsewhere.^{7, 68}

The choice of methods for specific problems may be illustrated by three cases—a slightly viscoelastic liquid, a rubbery polymer, and a hard solid such as a metal or plastic. For a liquid whose deformation is almost entirely viscous, such as a partially polymerized liquid resin or a dilute polymer solution, the ratio G''/G' will be large, at once eliminating many methods. At extremely low frequencies, even though G' may be quite small, λ will be large enough to allow a small l/λ ratio with reasonable sample dimensions, and direct measurements of stress and strain can be made. At high frequencies, λ will be small and a method suited for a large l/λ ratio must be employed—*viz.*, characteristic impedance measurements. For a rubbery plastic with low loss, G''/G' is small and generally imposes no limitations. At low frequencies, any of the first three classes of measurements can be used; with increasing frequency, as the ratio l/λ for reasonable sample dimensions increases, these are abandoned first in favor of class 6 and then

of classes 4 and 5. For a hard solid, the same sequence is followed with increasing frequency except that the modulus (at low frequencies, at least) is now higher by about 10^4 ; from equation (8a) it can be seen that the frequencies which limit applicability of the respective classes are higher by about 10^2 . An additional complication for a hard solid is that the members of the apparatus will have moduli of similar magnitude and must therefore be carefully designed to avoid spurious frequency-dependent effects associated with deformation of the apparatus. There is danger of such spurious effects in all dynamic measurements, but especially in those on materials of high modulus.

IV. Other Time-Dependent Techniques

1. MONOTONIC CHANGES OF STRESS OR STRAIN WITH TIME

There are many devices for obtaining stress as a function of strain either when the strain is increased at a constant rate (as in conventional Scott testers) or, less commonly, when the stress is increased at a constant rate. Some are designed for fundamental measurements^{16, 22} and others for routine testing. For a *linear* viscoelastic material, this type of experiment yields the same information as the other time-dependent methods described above.

Specifically, the stress developed at constant rate of strain is related to the integral under the stress relaxation function, so the latter can be derived from differentiation of a stress-strain curve obtained in this way.⁵ Similarly, the strain produced by a constant rate of increase of stress is related to the integral under the creep function, and the latter can be derived from differentiation of a stress-strain curve at constant rate of loading.

Methods for such analysis have been discussed¹¹² and applied very successfully^{112a} to stress-strain measurements on a soft viscoelastic polymer. It must be remembered, however, that such measurements often involve large strains with the possibility of deviation from linear viscoelastic behavior. It may then be difficult to separate the time-dependent effects from the deviations from Hookean elasticity and Newtonian flow.

2. IMPULSE MEASUREMENTS

Another type of time-dependent loading pattern involves a single brief application of stress, followed by observation of strain. Such impulse methods have been used for compression of soft solids¹¹³⁻¹¹⁵ between a bar swung as a ballistic pendulum and a freely swinging bar, using photographic re-

¹¹² G. Halsey, *J. Appl. Phys.* **18**, 1072 (1947).

^{112a} T. L. Smith, *J. Polymer Sci.* **20**, 89 (1956).

¹¹³ G. I. Taylor, *J. Inst. Civil Engrs.* **26**, 486 (1946).

¹¹⁴ E. Volterra, *Nuovo cimento* **4**, 1 (1948).

¹¹⁵ H. Kolsky, *Proc. Phys. Soc. (London)* **62B**, 676 (1949).

cording. The impulse from a detonation has been used to produce a transient compressive stress of duration about 20 $\mu\text{sec.}$ in solid samples, the strain being followed by a condenser pickup with oscillographic recording.^{115, 116, 116a}

Liquid samples have been similarly studied in shear between coaxial cylinders, with impulsive torque applied by a pulse through a coil in a magnetic field,¹¹⁷ the response being followed by photographic recording. The rebound tests used in the rubber industry are also of this type. These measure the amount of energy dissipated when a solid sample is struck by a ball^{118, 118a} or pendulum.¹¹⁹ The results of these various measurements are not related in a simple manner to those of the more direct methods of sinusoidal deformations, stress relaxation, and creep, but for a linear viscoelastic body all such measurements are in principle interconvertible.

3. NONSINUSOIDAL PERIODIC CHANGES

The application of periodic stresses whose time dependence is other than sinusoidal seems unlikely to compete with transient and sinusoidal techniques. For the sake of completeness, however, reference is made to the use of a saw-tooth time dependence of strain in connection with direct measurements of stress and strain in elongation of fibers.¹²⁰ This is equivalent to a repeated cycling stress-strain curve at constant rate of elongation, and in principle yields the same information as any of the other time-dependent methods. The use of square wave stress-time pulses has also been discussed.¹²¹ This is equivalent to a repeatedly reversing creep experiment, in which the rate of strain does not attain a constant value before reversal occurs. The ratios of stress to strain in either of these periodic experiments would bear no simple relation to G' and G'' at a comparable frequency. The latter quantities are defined only for sinusoidally varying stress and strain.

V. High-Stress Techniques

1. DYNAMIC STRESS SUPERIMPOSED ON HIGH STATIC STRESS

The behavior of a viscoelastic body in small oscillating deformations, as described by the two components of a complex elastic modulus, can be markedly influenced by the presence of a superimposed static stress; so

¹¹⁶ R. M. Davies, *Phil. Trans. Roy. Soc. (London)* **A240**, 375 (1948).

^{116a} H. Kolsky, *Phil. Mag.* [7] **45**, 712 (1954).

¹¹⁷ J. M. Kendall, *Rheol. Bull.* **12**, 26 (1941).

¹¹⁸ J. H. Dillon, I. B. Prettyman, and G. L. Hall, *J. Appl. Phys.* **15**, 309 (1944).

^{118a} J. P. A. Tillet, *Proc. Phys. Soc. (London)* **B67**, 677 (1954).

¹¹⁹ P. Lupke, *Rubber Chem. Technol.* **7**, 591 (1934).

¹²⁰ F. Breazeale and J. Whisnant, *J. Appl. Phys.* **20**, 621 (1949).

¹²¹ N. A. Tolstoy and P. P. Feofilov, *J. Exptl. Theoret. Phys. (USSR)* **19**, 421 (1949).

that under a given static stress it must be considered as a distinct material.⁶⁵ If the static stress is in the same direction as the dynamic, measurements of the latter will provide a differential dynamic modulus.⁶⁶ The viscoelastic behavior may still be linear with respect to the dynamic deformations if these are small.

In many of the techniques described in the preceding sections, a small static stress is inevitably imposed on the sample when it is mounted in the apparatus, and this is usually ignored. However, some techniques are well adapted for the application of large static stresses and studying their effects. For example, the electromagnetic resonance apparatus with added inertia for deformation of solid samples in shear (Section III-2) can be modified for imposition of static stresses in either shear or compression.¹²² In the case of compression, possible changes in sample shape must be considered^{6, 75} in addition to the obvious dimensional changes. The coaxial cylinder type of resonance device for viscoelastic liquids can also be used with a superimposed shear stress produced by steady rotation of the outer cylinder.⁶⁰ Wave propagation in fibers and strips (Section III-4) can also be carried out with superimposed static tensile stress, and experiments on fibers have been made not only at different degrees of elongation but also during continuously increasing elongation.^{87, 123}

2. HIGH DYNAMIC STRESS

Although in most of the dynamic methods described in Section III an effort is made to keep the stresses and deformations small, to stay within the region of linear viscoelasticity, some of these methods can be adapted to higher stresses so that deviations from linear viscoelasticity can be investigated. Forced resonance vibrations for straining soft solids, as described in Section III-2, have been used^{122, 124} at amplitudes up to 8% shear. For still higher amplitudes,^{44, 47a, 125} and for hard solids,^{126, 127} massive construction and powerful drives are required because of the high energy input; such equipment has been used for deformation in extension-compression. Generation of considerable quantities of heat must be reckoned with in attempting temperature control.

¹²² W. P. Fletcher and A. N. Gent, *Trans. Inst. Rubber Ind.* **26**, 45 (1950).

¹²³ K. W. Hillier and H. Kolsky, *Proc. Phys. Soc. (London)* **62B**, 701 (1949).

¹²⁴ K. E. Gui, C. S. Wilkinson, Jr., and S. D. Gehman, *Ind. Eng. Chem.* **44**, 720 (1952).

¹²⁵ H. McCallion and D. M. Davies, *Proc. Inst. Mech. Engrs. (London)* **169**, 1125 (1956).

¹²⁶ J. A. Sauer, J. Marin, and C. C. Hsiao, *J. Appl. Phys.* **20**, 507 (1949).

¹²⁷ R. D. Spangler, *Phys. Rev.* **86**, 644 (1952).

VI. Derived Calculations

While this chapter is primarily concerned with experimental techniques it is of interest to include some methods for treatment and analysis of experimental data. In particular, it has proved useful to be able to correlate the results of dynamic and transient measurements and to express them in terms of distribution functions of relaxation and retardation times; and also to extend the effective range of either time or frequency by combining measurements at different temperatures (and sometimes at different concentrations) by the use of certain reduced variables. Such derived calculations are described in this section.

1. DISTRIBUTION FUNCTIONS OF RELAXATION AND RETARDATION TIMES

A complete description of the mechanical behavior of a linear viscoelastic body under any kind of time-dependent loading pattern can be given in terms of either a distribution function of relaxation times or a distribution function of retardation times. These may be visualized as corresponding to the mechanical models of springs and dashpots associated with the names of Maxwell and Voigt, respectively (Figs. 22 and 24, Chapter 1 of this volume). In Fig. 22b and 24b, each spring represents a contribution to rigidity (in the case of shear) which is relaxed by a viscous contribution represented by the associated dashpot; the relaxation time is the ratio of the dashpot viscosity to the spring rigidity. In Fig. 22a and 24a, each spring represents a contribution to compliance which is retarded by the associated dashpot, the retardation time being again the ratio of viscosity to rigidity.

The distribution functions for an infinite series of such mechanical elements may be defined in several different ways; a convenient choice is to write $\Phi d \ln \lambda$ as the differential contribution to shear rigidity associated with relaxation times whose logarithms lie between $\ln \lambda$ and $\ln \lambda + d \ln \lambda$; and $L d \ln \lambda$ as the differential contribution to shear compliance associated with retardation times whose logarithms lie between $\ln \lambda$ and $\ln \lambda + d \ln \lambda$.¹²⁸

It must be recognized that recent molecular theories¹²⁹ for linear viscoelastic behavior of polymers predict a discrete rather than a continuous distribution function of relaxation times under certain conditions. In very dilute solutions of a polymer homogeneous with respect to molecular weight, at the long end of the time scale, this is observed and the behavior cannot be described in terms of a continuous distribution. Also, in undiluted poly-

¹²⁸ Distribution functions can also be defined in terms of a differential range $d\lambda$ or $d \log_{10} \lambda$, and can also be defined for contributions to Young's modulus instead of the modulus of rigidity. Normalized, dimensionless functions can also be specified. All of these have been used by various authors.

¹²⁹ P. E. Rouse, Jr., *J. Chem. Phys.* **21**, 1272 (1953).

mers at very short times and hard solids in general, it may be necessary to supplement the continuous distribution, Φ or L , with discrete mechanisms.

If either function Φ or L is known numerically for a linear viscoelastic body over a wide range of values of the variable λ , it is possible to predict its behavior under any kind of time-dependent loading pattern. The equations for the simpler cases of stress relaxation, creep, and sinusoidally varying stress have been given in numerous places.^{130, 131} Equations for more complicated cases, such as constant rate of strain or constant rate of loading, have also been derived.⁵

Although prediction of experimental results from Φ or L is straightforward, the inverse problem of derivation of Φ or L from experimental results is less easy. Data are ordinarily not available over a wide enough time (or frequency) scale to apply the exact integral inversion formulas.²⁻⁴ Accordingly, approximation methods are usually employed, involving differentiation of experimental data, to estimate Φ and L . Of these, Φ is readily obtained from stress relaxation or from either the real or imaginary part of the complex rigidity G^* ; L is readily obtained from creep or from either the real or imaginary part of the complex compliance J^* .

The following first approximation formulas have been widely used:

From stress relaxation after sudden strain,	$\Phi = -(1/\gamma) d\mathfrak{T}/d \ln t$
From stress relaxation after cessation of flow,	$\Phi = -(1/\dot{\gamma}t) d\mathfrak{T}/d \ln t$
From creep,	$L = (1/\mathfrak{T}) d\gamma/d \ln t - t/\eta$
From in-phase rigidity modulus,	$\Phi = G' d \log G'/d \log \omega$
From out-of-phase rigidity modulus,	$\Phi = G''(1 - d \log G''/d \log \omega)$
From in-phase compliance,	$L = J' d \log J'/d \log \omega$
From out-of-phase compliance,	$L = J''(1 + d \log J''/d \log \omega)$

Here, $\mathfrak{T}(t)$ and $\gamma(t)$ are the experimental stress relaxation and creep functions, respectively, $\dot{\gamma}$ is the rate of strain in steady state flow, and η is the steady flow viscosity, if finite (if infinite, the term containing η vanishes). The value of the argument λ to which the estimated values of Φ and L refer is the value of t or $1/\omega$, respectively. When the distributions are broad, these equations provide order of magnitude estimates, but do not give exact agreement when results of stress relaxation G' , and G'' are compared, for example, all for the same material. This is illustrated in the upper half of Fig. 18 for stress relaxation data of Andrews and Tobolsky¹³² and G' and G''

¹³⁰ A. V. Tobolsky and H. Eyring, *J. Chem. Phys.* **11**, 125 (1943).

¹³¹ J. D. Ferry, E. R. Fitzgerald, L. D. Grandine, Jr., and M. L. Williams, *Ind. Eng. Chem.* **44**, 703 (1952).

¹³² R. D. Andrews, *Ind. Eng. Chem.* **44**, 707 (1952)

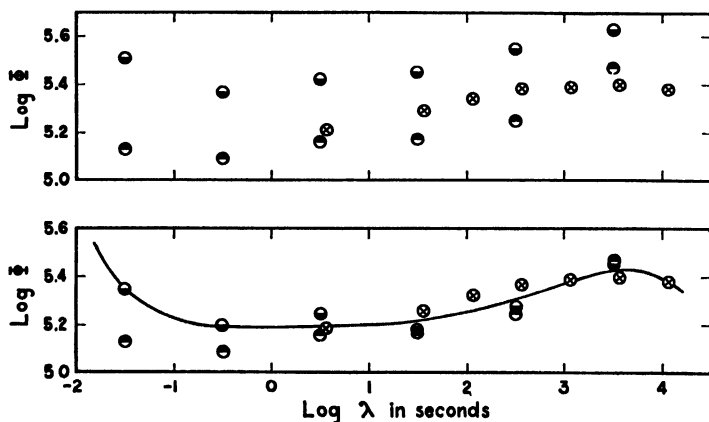


Fig. 18. Distribution function of relaxation times for polyisobutylene (National Bureau of Standards sample, viscosity-average molecular weight 1,350,000), calculated from measurements at 25° C. by methods of first approximation (top graph) and second approximation (bottom graph). Crossed circles, from stress relaxation (reference 132); top and bottom black, from real and imaginary parts, respectively, of the complex shear modulus (reference 47).

data of Philippoff⁴⁷ on a sample of polyisobutylene distributed by Dr. R. S. Marvin of the National Bureau of Standards.¹³³

The importance and versatility of the functions Φ and L have led to various attempts at higher order approximations. The following have been used in the author's laboratory:^{134, 135}

From stress relaxation after sudden strain,	$\Phi = -M(1/\gamma) d \mathfrak{L}/d \ln t$
From stress relaxation after cessation of flow,	$\Phi = -N(1/\dot{\gamma}t) d \mathfrak{L}/d \ln t$
From in-phase rigidity modulus,	$\Phi = AG' \left(1 - \left \frac{d \log G'}{d \log \omega} - 1 \right \right)$
From out-of-phase rigidity modulus,	$\Phi = BG''(1 - d \log G''/d \log \omega)$
From in-phase compliance,	$L = AJ' \left(1 - \left \frac{d \log J'}{d \log \omega} + 1 \right \right)$
From out-of-phase compliance,	$L = BJ''(1 - d \log J''/d \log \omega)$

Here the numerical coefficients A , B , M , and N are functions of the slope of

¹³³ R. S. Marvin, *Proc. 2nd Intern. Congr. Rheol., Oxford* p. 156 (1954).

¹³⁴ J. D. Ferry and M. L. Williams, *J. Colloid Sci.* **7**, 347 (1952).

¹³⁵ M. L. Williams and J. D. Ferry, *J. Polymer Sci.* **11**, 169 (1953).

a log-log plot of Φ or L against λ , determined by a first approximation calculation. Values of these coefficients have been tabulated.¹³⁵ Much better agreement between the values calculated from different sources is obtained in this way, as shown in the lower half of Fig. 18.

Other second approximation formulas may be illustrated by the following ones for determining Φ from stress relaxation:

$$\begin{array}{ll} \text{By Andrews}^{132} & \Phi = -(1/\gamma)[d\mathfrak{T}/d \ln t + 0.58 d^2\mathfrak{T}/d (\ln t)^2] \\ \text{By Schwarzl and} & \Phi = -(1/\gamma)[d\mathfrak{T}(2t)/d \ln t + d^2\mathfrak{T}(2t)/d (\ln t)^2] \\ \text{Staverman}^{136} & \end{array}$$

In the formula of Schwarzl and Staverman, the value of λ to which the estimated Φ refers is not t but $2t$, as indicated.

For moderately sharp distributions, even the second approximation calculations may not suffice. Higher order approximations have been proposed by Schwarzl and Staverman,^{136, 137} and a method for solving the exact integral equations in terms of a Fourier analysis has been devised by Roesler and Pearson.¹³⁸ In some cases, especially at high frequencies, relaxation mechanisms may be associated with discrete relaxation times which cannot be adequately represented by a continuous distribution at all.

Obviously G' and G'' can be predicted from stress relaxation, or J' and J'' from creep, or vice versa in both cases, by using the distribution function Φ or L , respectively, as an intermediary. There is another method for interconversion in which the distribution function enters only as a second-order correction. This has been applied to stress relaxation by Marvin¹³⁹ and to creep by Leaderman.¹⁴⁰

2. REDUCED VARIABLES FOR DESCRIBING EFFECTS OF TEMPERATURE AND CONCENTRATION

Measurements of viscoelastic properties over wide ranges of time (or frequency) and temperature on a single material often yield a family of curves such as shown in Figs. 2, 4, and 11, where the stress-strain ratio varies over several powers of ten. In many cases where the structure of the material is not fundamentally modified by changing the temperature, especially in polymers above their glass transition temperatures, the effects of temperature and time can be interrelated by the use of reduced variables.

The basic assumption¹⁴¹ underlying this treatment is that in a series of

¹³⁵ F. Schwarzl and A. J. Staverman, *Physica* **18**, 791 (1952).

¹³⁷ F. Schwarzl, *Proc. 2nd Intern. Congr. Rheol., Oxford* p. 197 (1954).

¹³⁸ F. C. Roesler and J. R. A. Pearson, *Proc. Phys. Soc. (London)* **B67**, 338 (1954).

¹³⁹ R. S. Marvin, *Phys. Rev.* **86**, 644 (1952).

¹⁴⁰ H. Leaderman, *Proc. 2nd Intern. Congr. Rheol., Oxford* p. 203 (1954).

¹⁴¹ J. D. Ferry, *J. Am. Chem. Soc.* **72**, 3746 (1950).

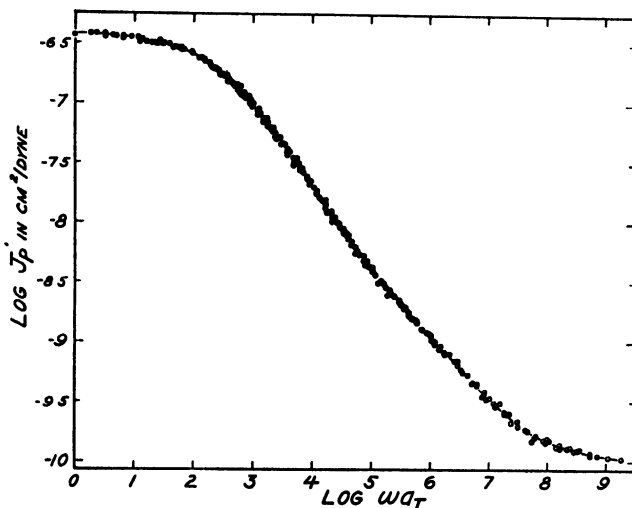


FIG. 19. Real part of complex shear compliance of polyisobutylene, from Fig. 11, plotted with reduced variables to give a single composite curve reduced to 25° C. (from reference 145).

relaxation (or retardation) mechanisms a change of temperature multiplies all relaxation (or retardation) times by the same factor. For polymeric materials whose elasticity is primarily associated with configurational entropy changes, it is usually further assumed that the magnitude of each contribution to rigidity is proportional to the absolute temperature and to the density. Then measurements at a temperature T can be reduced to a standard temperature T_0 by plotting

For stress relaxation,¹⁸ $(\mathfrak{I}/\gamma)(T_0\rho_0/T\rho)$ against t/a_T

For creep,^{25,142} $(\gamma/\mathfrak{I})(T\rho/T_0\rho_0)$ against t/a_T

For modulus of rigidity,¹⁴³ $G'T_0\rho_0/T\rho$ and $G''T_0\rho_0/T\rho$ against ωa_T

For compliance,¹⁴⁴ $J'T\rho/T_0\rho_0$ and $J''T\rho/T_0\rho_0$ against ωa_T

Here, ρ and ρ_0 are the densities at T and T_0 , and a_T is the factor by which all relaxation times change when the temperature is changed from T_0 to T . According to the assumptions, data at all different temperatures should superpose to form a single composite curve when plotted in this way. For some materials this superposition is achieved to a close approximation over rather wide ranges of temperature, as illustrated in Fig. 19 for the dynamic polyisobutylene data¹⁴⁵ of Fig. 11. The resulting curve predicts the proper-

¹⁴² C. A. Dahlquist and M. R. Hatfield, *J. Colloid Sci.* **7**, 253 (1952).

¹⁴³ J. D. Ferry, E. R. Fitzgerald, M. F. Johnson, and L. D. Grandine, Jr., *J. Appl. Phys.* **22**, 717 (1951).

¹⁴⁴ J. D. Ferry and E. R. Fitzgerald, *J. Colloid Sci.* **8**, 224 (1953).

¹⁴⁵ J. D. Ferry, L. D. Grandine, Jr., and E. R. Fitzgerald, *J. Appl. Phys.* **24**, 911 (1953).

ties at the standard temperature T_0 over an extended frequency range, affording the opportunity of calculating distribution functions over a wide range of time scale.

In some applications of this treatment or its equivalent, the factor T_0/T has been omitted, and the factor ρ_0/ρ is often ignored as being unity within experimental error. In materials and under conditions where the compliance is not dominated by configurational (rubberlike) mechanisms, the factor T_0/T is not applicable, but the reduced variables for compliance and creep can be easily modified to take this into account.¹⁴⁴

The factor a_T must be chosen empirically at each temperature, but the requirement of superposition over a range of time (or frequency) does not permit much arbitrary latitude in this choice. Moreover, in dynamic measurements the same choice of a_T must bring both G' and G'' (or J' and J'') into superposition. Analysis of a_T provides an instructive approach to the temperature dependence of the mechanical properties. Its derivative $Rd \ln a_T/d(1/T)$ is an apparent activation energy for the relaxation process; this energy is usually found to be markedly dependent on temperature.

Over very wide ranges of temperature, more than one class of relaxation mechanisms may appear with different values of a_T , so that while the reduction treatment may be successful for a single class, it does not provide superposition for different classes.¹⁴⁶

In viscoelastic solutions over certain ranges of concentration, reduced variables can be used to combine mechanical data at different concentrations as well as temperatures. The basic assumption¹⁴¹ underlying this treatment is that, in a solution of a viscoelastic component in an ordinary viscous liquid, a change in concentration multiplies all relaxation or retardation times by the same factor. It is further assumed that the magnitude of each contribution to rigidity is proportional to the concentration, c , of the viscoelastic component in grams per cubic centimeter. It follows that data at different temperatures and concentrations can be reduced to a standard reference state by plotting:

For modulus of rigidity,

$G'T_0/Tc$ against $\omega\eta T_0/Tc$

and

$G''T_0/Tc$ against $\omega\eta T_0/Tc$

For dynamic viscosity,

η'/η against $\omega\eta T_0/Tc$

Here, by using values of the steady flow viscosity η , arbitrary parameters like a_T are avoided, and the temperature and concentration dependences of the relaxation times are absorbed in those of the viscosity. Application of this treatment to high polymer solutions^{144, 147, 148} has shown that the

¹⁴⁴ J. Heyboer, P. Dekking, and A. J. Staverman, *Proc. 2nd Intern. Congr. Rheol., Oxford* p. 123 (1953).

¹⁴⁷ L. D. Grandine, Jr., and J. D. Ferry, *J. Appl. Phys.* **24**, 679 (1953).

assumption of equal concentration dependence of all relaxation times holds over certain fairly wide regions of concentration. In other regions, however, the long relaxation times are much more strongly concentration-dependent than the short ones.

Nomenclature

a	Coefficient for sample geometry	R_M	Mechanical resistance
a_T	Temperature reduction factor	S_M°	Mechanical elastance of apparatus
c	Concentration	T	Absolute temperature
e	Back e.m.f.	X	Electrical reactance
f	Force	X_0	Electrical reactance at rest
i	$\sqrt{-1}$	X_M	Mechanical reactance
i	Electrical current	Z	Electrical impedance
l	Length (of sample, or of wire in a coil)	Z_0	Electrical impedance at rest
t	Time	Z_M	Mechanical Impedance
v	Velocity	$\mathcal{R}_M$	Characteristic mechanical resistance
x	Amplitude	$\mathcal{X}_M$	Characteristic mechanical reactance
x_0	Critical damping distance	δ_M	Characteristic mechanical impedance
B	Magnetic flux density	$\mathfrak{T}$	Shear stress
E	Young's modulus	γ	Strain
E^*	Complex Young's modulus	$\dot{\gamma}$	Rate of strain
E'	Real part of Young's modulus	η	Viscosity
E''	Imaginary part of Young's modulus	η^*	Complex viscosity
G	Shear modulus	η'	Real part of viscosity
G^*	Complex shear modulus	η''	Imaginary part of viscosity
G'	Real part of shear modulus	λ	Wavelength
G''	Imaginary part of shear modulus	ν	Frequency
J	Shear compliance	π	Circumference/diameter
J^*	Complex shear compliance	ρ	Density
J'	Real part of shear compliance	ρ_0	Density at standard temperature
J''	Imaginary part of shear compliance	φ	Phase difference (optical)
K	Bulk modulus	ψ	Phase angle (mechanical)
K^*	Complex bulk modulus	ω	Circular frequency
L	Distribution function of retardation times	Δ	Logarithmic decrement
M	Mass	$\Delta\omega$	Half width of response curve
R	Electrical resistance	Φ	Distribution function of relaxation times
R_0	Electrical resistance at rest		

CHAPTER 12

FUNDAMENTAL TECHNIQUES: FLUIDS

B. A. Toms

I. Flow through Pipes	475
1. Experiments in Pipe Flow	476
a. Apparatus	476
b. Methods	477
2. Derivation of Pressure Gradient vs. Rate of Flow Relations	479
3. Occurrence of Laminar Flow	481
4. Interpretation of Observed Pressure Gradient vs. Rate of Flow Relations	482
II. Flow Between Coaxial Cylinders	486
1. Apparatus	487
2. Experiments Involving Steady Rotation	493
3. Experiments Involving Oscillatory Motion	496
Nomenclature	535

I. Flow Through Pipes

We are concerned here with the study of the isothermal flow of liquids through straight *narrow* pipes, a type of investigation first introduced, with conspicuous and far-reaching success, by Poiseuille¹ just over a century ago. The motions of liquids, and more especially of non-Newtonian liquids, in wide and in curved pipes are more complicated and less well understood.

If steady laminar flow through a straight pipe of circular section (radius a) be observed, the macroscopic rheological properties of the material can be deduced, in suitable cases, from simultaneous measurements of the volume rate of flow Q and the pressure gradient down the pipe dp/dz .

In the special case of a Newtonian liquid, the relationship between the measured quantities and the characteristic viscosity coefficient η' is expressed by Poiseuille's formula

$$\eta' = \frac{\pi a^4}{8Q} \cdot \frac{dp}{dz} \quad (1)$$

Equation (1) also serves to define an *apparent viscosity coefficient* for a non-Newtonian liquid in a single experiment, but this is an empirical quantity only, since it depends on the rate of flow and on the pipe diameter.

¹ J. L. M. Poiseuille, *Compt. rend.* **11**, 961, 1041 (1840); **12**, 112 (1841); **15**, 1167 (1842); *Mém. Savants Etrangers* **9**, 433 (1846).

When Newtonian behavior does not prevail, or if the rheological properties are unknown (as in the case of a new artificial liquid), a different treatment of the observed Q , dp/dz data is required in order that information of fundamental significance may be procured. In the absence of a definitive method it is appropriate, in the present context, to direct attention to a recently proposed analytical procedure² which merits exploitation, particularly in relation to the flow of suspensions of anisometric particles. In principle, this new method enables the stress vs. rate of strain relation in the bulk of the material remote from boundaries to be deduced when the flow of a non-Newtonian liquid is complicated by a *wall effect*.

We shall now consider some aspects of the conduct and interpretation of *exploratory* experiments in pipe flow.

1. EXPERIMENTS IN PIPE FLOW

a. Apparatus

The restriction that an experimental pipe must be "narrow" is conveniently imprecise, for in practice a variety of bore sizes will usually be needed. Capillary-bore tubes ($a < 0.05$ cm.) are required for most work on low-viscosity liquids ($\eta' < 0.1$ poise, say), and their use is indicated whenever information is sought on flow at large stresses; but flow at small stresses and much of the behavior of liquids of large viscosity ($1 < \eta' < 100$ poise, say) are more easily studied in wider pipes. It is therefore peculiarly difficult to select pipes for an extensive investigation of the flow of a non-Newtonian liquid with widely variable viscosity, and the choice has almost always to be made empirically.

The length l of an experimental pipe is also subject to restriction. This matter will be discussed later (see Section I, 2).

The characteristics of the bore of the pipe must always be known as exactly as possible (determination of the mean radius a , for instance, is especially important, since $Q \propto a^4$). The required observations are facilitated by having the ends of the pipe cut off square with respect to the main axis of the bore: the length of the bore is then well defined, and its true cross section exposed. The shape and principal dimensions of the cross section at both ends can be determined directly with a measuring microscope; but a better indication of the uniformity of the bore, and a more accurate estimate of a , can obviously be secured, after the flow experiments have been completed, by cutting the pipe into several pieces and then examining the ends of these in turn. Destruction of the pipe can, of course, be avoided. In the case of capillary glass pipes, for example, both a and the uniformity of the bore are commonly determined by the classic 'mercurey-thread'

² J. G. Oldroyd, *J. Colloid Sci.* **4**, 333 (1949).

method.³ In the case of pipes which are not of capillary bore a can be deduced by determining the difference in mass between the pipe and a solid cylinder made of the same material and having identical external dimensions; the density of the material must, of course, be known with sufficient accuracy, and the necessary assumption that the bore is a right circular cylinder should be justified.

These topics, and the correction of equation (1) for ellipticity and conicalness of the pipe bore, are discussed by Bingham⁴ and Barr.⁵

Smooth-bore pipes having $0.05 \text{ cm.} < a < 0.5 \text{ cm.}$ will often be satisfactory for the kind of work envisaged here. Such pipes are nowadays manufactured from a variety of metals by methods which ensure that the bore is both unrestricted and very nearly a right circular cylinder; "precision-bore" glass pipes, with internal dimensions accurately specified by the makers, are available.⁶

b. Methods

Fundamentally, every quantitative experiment in pipe flow entails simultaneous observations of the volume rate of flow Q ($\text{cm.}^3/\text{sec.}$) through the pipe and the associated difference of hydrostatic pressure Δp (dynes/cm.^2) between its ends. It is always best to measure these quantities as directly as possible. We shall refer briefly to two general methods, one introduced by Brückner⁷ and the other by Couette:⁸ these are readily applicable, and both have been widely used with a variety of empirical modifications.

It must always be arranged that the liquid enters and leaves the pipe bore in a well-defined (and therefore reproducible) manner: this can be achieved, with the practical advantage of having similar conditions of entry and exit, by fixing the ends of the pipe into two vessels of the same shape and size.

In Brückner's method, this simple assembly, with the pipe horizontal, is partially filled with the experimental liquid and joined in a pneumatic circuit designed so that the air pressure above the liquid surface in one reservoir can be varied independently of that in the other. (For example, it might be arranged, as shown in Fig. 1, that one reservoir is open to the atmosphere while the other is connected to a large vessel in which a constant air pressure, different from atmospheric, is maintained). The liquid can then be caused to flow through the pipe at constant rate, and in either direction;

³ G. Jaeger, *Wiss. Abhandl. physik. tech. Reichsanstalt* **2**, 381 (1895).

⁴ E. C. Bingham, "Fluidity and Plasticity." McGraw-Hill, New York, 1922.

⁵ G. Barr, "A Monograph of Viscosity." Oxford Univ. Press, New York, 1931.

⁶ Anonymous, *J. Sci. Instr.* **22**, 116 (1945).

⁷ H. Brückner, *Wied. Ann.* **42**, 287 (1891).

⁸ M. Couette, *Compt. rend.* **107**, 388 (1888); *Ann. chim. phys.* **21**, 433 (1890).

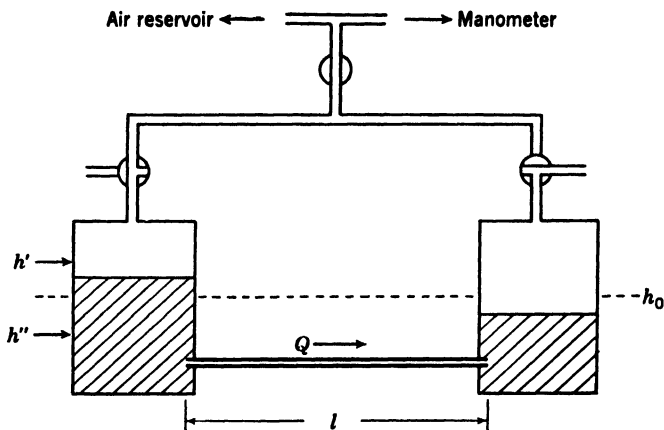


FIG. 1. An experiment in pipe flow. (After Brückner.⁷)

Q is determined by measuring the time required for a known quantity of liquid, indicated by two level marks (h' , h''), to enter or leave one of the reservoirs. If the liquid surface stands midway between the level marks when the air pressure is the same (e.g., atmospheric) in both reservoirs, the net change of hydrostatic pressure resulting from the transference of liquid will be zero: Δp can then be measured directly by means of a suitable manometer in the pneumatic circuit. The principle of this method has found important application in precision viscometry;^{4, 9, 10} it has also been employed in experiments involving relatively large values of Q .¹¹

When data on flow through two (or more) different lengths of pipe having the same radius are required (see Section I, 2), it will often be convenient if the necessary observations can be made in a single experiment. The essential features of Couette's method, which enables this to be done, are represented schematically in Fig. 2. It is seen that the basic vessel-pipe-vessel assembly is repeated so that the mainstream, flowing at constant rate Q , passes through the different pipes successively. (A variety of methods exists for controlling the mainstream, and for measuring Q : several of these are described by Bingham⁴ and Barr,⁵ and there is the noteworthy procedure of Coe¹².) The relevant hydrostatic pressures are indicated by manometers set in this hydraulic circuit: the value of Δp for each pipe can thus be deduced provided the density of the experimental liquid is known. (As indicated in Fig. 2, the working range of the manometers can be extended by uniformly varying the effective atmospheric pressure.) This

⁹ T. Thorpe and J. Rodger, *Phil. Trans. Roy. Soc.* **A185**, 397 (1894).

¹⁰ E. C. Bingham and G. F. White, *Z. physik. Chem.* **80**, 670 (1912).

¹¹ B. A. Toms, *J. Colloid Sci.* **4**, 511 (1949).

¹² J. R. Coe, *Physics* **4**, 274 (1933).

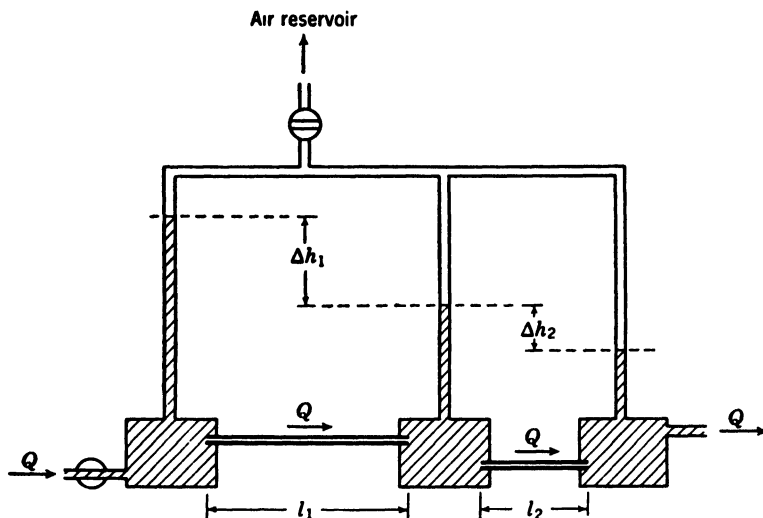


FIG. 2. An experiment in pipe flow. (After Couette.⁸)

method has been used in precision viscometry,^{8, 13} though its application is not restricted in principle to cases in which Q is small.

In every experiment, the temperature of the experimental liquid must be known and maintained constant: this can be achieved by immersing the flow apparatus in a bath of a liquid the temperature of which can be controlled to within, say, $\pm 0.01^\circ$.

2. DERIVATION OF PRESSURE GRADIENT VS. RATE OF FLOW RELATIONS

An experiment in pipe flow yields, in the first instance, related values of the observable quantities Δp and Q (see Section I, 1). If only one pipe is used, the corresponding values of dp/dz and Q , which are required to define the viscosity of the material [see equation (1)], can be deduced directly from the primary data only by assuming (i) that viscous flow prevails uniformly throughout and is confined to the bore of the pipe, and (ii) that energy is expended solely in overcoming the viscous resistance, or friction, of the liquid. But in practice neither of these assumptions is valid, for when a liquid is caused to flow through a pipe from one vessel to another, there occurs (a) relative motion between elements of liquid before they enter the pipe, and (b) anomalous flow which arises at, and persists for some distance downstream of, the pipe entrance (i.e. steady laminar flow does not develop instantaneously); and, of course, the temporary acquisition of kinetic energy by the liquid must also be taken into account. It follows that not

¹³ S. Erk, *Forschungsarb. Ver. deut. Ing.* No. 288 (1927); S. Erk and A. Schmidt, *Physik. Z.* **37**, 489 (1936).

all of the energy expended in an experiment is used to maintain steady laminar flow within the pipe. And so, although the error incurred by putting $dp/dz = \Delta p/l$ may well be negligible if Q is sufficiently small and the pipe is sufficiently long and narrow (cf. Poiseuille¹), it is in principle necessary to correct a crude observation of Δp before evaluation of η' can be undertaken; and, of course, the need for correction grows as Q is increased and l decreased. At the present time, however, it is not known how to make the required correction in the case of a non-Newtonian liquid. Indeed, only approximate solutions of the relevant hydrodynamical problems have so far been achieved in the simpler case of a Newtonian liquid.^{5, 14} The problem of analyzing pipe flow data must therefore be approached in another way if extensive studies in non-Newtonian flow are to be undertaken.

When a liquid flows through a pipe at constant rate, its kinetic energy and the magnitude of the "entrance effects" (more generally, "end effects") are determined by the volume rate of flow; they do not depend upon the length of the pipe. It follows that the difficulties resulting from end effects and the gain of kinetic energy by the liquid can be entirely eliminated by combining suitable observations of Δp and Q obtained from experiments with different separate lengths of pipe, all of the same form and all having the same bore radius. Thus, if the pressure heads required to maintain a volume rate of flow Q in each of two lengths of pipe l' , l'' ($l'' > l'$), both of radius a , are $\Delta p'$, $\Delta p''$, respectively, then the relationship

$$\frac{dp}{dz} = \frac{\Delta p'' - \Delta p'}{l'' - l'} \quad (2)$$

will be valid provided that steady flow is achieved within the length of the shorter pipe. In order to discover whether this essential condition has been satisfied or not, $\Delta p'''(Q)$ must be measured in a third length of pipe l''' ($> l''$); only if

$$\frac{\Delta p'' - \Delta p'}{l'' - l'} = \frac{\Delta p''' - \Delta p''}{l''' - l''} = \frac{\Delta p''' - \Delta p'}{l''' - l'} \quad (3)$$

will it be justifiable to use equation (2) to evaluate $dp/dz(Q)$. It is seen that this ingenious procedure, which was first introduced by Couette,⁸ enables the proper relationship between Q and dp/dz to be constructed for any liquid and for any type of steady flow.

In practice, and particularly in work with non-Newtonian liquids for which entrance effects can be very large, it will sometimes be necessary to increase the lengths of experimental pipes until (3) is satisfied. Pipes for which $100 < l/a < 1000$ are generally serviceable, but optimum lengths have almost always to be fixed empirically.

¹⁴ S. Goldstein (ed.), "Modern Developments in Fluid Dynamics," Vol. 1, Oxford Univ. Press, New York, 1950.

3. OCCURRENCE OF LAMINAR FLOW

When laminar flow prevails in a pipe (i.e., when every particle of the fluid may be assumed to move in a straight line parallel to the axis of the pipe), the pressure gradient is proportional to the first power of the velocity, and the distribution of velocity across a section of the bore is parabolic.¹⁴ This special kind of fluid motion seldom occurs in wide pipes and not always in narrow ones: when it is replaced by nonlaminar flow, none of the conditions mentioned is fulfilled and, of course, (1) ceases to be the relevant relationship between pressure gradient and rate of flow. It is therefore of considerable practical importance to be able to distinguish laminar from nonlaminar flow and also to be apprised of the conditions under which each regime may be expected to persist. These matters have received considerable attention in the literature.

The circumstances of the transition from laminar to nonlaminar flow in pipes were first elucidated by Osborne Reynolds¹⁵ who discovered that the mode of motion can be indicated (in a transparent pipe) by introducing a filament of colored liquid into the mainstream. If laminar flow prevails, the filament extends down the pipe in a straight line, increasing in width only very slowly through diffusion. But if the speed of flow is increased, a stage is reached at which the straight-line motion breaks down: the colored filament then mixes with the mainstream and the pipe appears to be filled with color, while a close examination reveals that the stream is constantly varying, with irregular motions across the bore. By combining this elegant method of detection with appropriate analysis of the corresponding pressure gradient vs. rate of flow data, Reynolds was able to show that the conditions for the change from laminar to nonlaminar flow, and vice versa, can be defined in terms of a dimensionless parameter (the *Reynolds number*),

$$R = \frac{2a\rho}{\eta} \left(\frac{Q}{\pi a^2} \right) \quad (4)$$

which is seen to depend upon the diameter of the pipe bore, the density and viscosity of the fluid, and the mean velocity of flow.

Experiments with Newtonian liquids¹⁵⁻¹⁷ have shown that the type of nonlaminar flow which is ordinarily regarded as turbulence cannot persist in a pipe unless $R > 2000$, approximately. Laminar flow, on the other hand, occurs whenever $R < 1000$, and usually remains the preferred type of motion until $R = 2000$, approximately. Some cases of departure from

¹⁵ O. Reynolds, *Phil. Trans. Roy. Soc.* **174**, 935 (1883); *Sci. Papers*, **2**, 51.

¹⁶ T. E. Stanton and J. R. Pannell, *Phil. Trans. Roy. Soc.* **A214**, 199 (1914).

¹⁷ L. Schiller, *Physik. Z.* **3**, 412 (1920); **25**, 541 (1924); *Forschungsarb. Ver. deut. Ing.* No. 248 (1922).

strictly rectilinear motion when $1000 < R < 2000$ have been reported,^{18, 19} but there is other evidence^{15, 20} that laminar flow can persist at very large values of R (10^4 , or more) if special care is taken to avoid any disturbance in the first reservoir or at the entry to the pipe. However, in ordinary practice breakdown is to be anticipated when $R \geq 2000$.

While it is reasonable to suppose that these conclusions are relevant to the behavior of non-Newtonian liquids, it is not known how R should be calculated for an experiment involving a liquid of variable viscosity coefficient. Nevertheless, there are grounds for thinking that $R = \text{constant}$ can be made a criterion for the breakdown of laminar flow if an apparent viscosity coefficient appropriate to the experimental conditions is substituted for η' in equation (4). Thus the breakdown of laminar flow in certain polymer solutions has been shown to occur at $R_1 = 2000$ (i.e., the same critical Reynolds number as found for the solvent—a Newtonian liquid—under the same conditions) by assuming that the relevant viscosity coefficient was that measured at large rates of shear i.e., η'_1 (see Section I, 4), and a similar result has been obtained in the case of a benzopurpurin sol.²¹

4. INTERPRETATION OF OBSERVED PRESSURE GRADIENT VS. RATE OF FLOW RELATIONS

When the pressure gradient dp/dz in the region of steady laminar flow is known as a function of the volume rate of flow Q for a straight pipe of radius a (see Section I, 2), the characteristic rheological properties of the material remain to be deduced. This is easily accomplished for a Newtonian liquid; but in the case of a non-Newtonian liquid, the possibility that the experimental observations may be complicated by anomalous behavior near the pipe wall has always to be considered, for the wall introduces a preferred direction in the material, and it may happen that the rate of shear near the wall is consequently not a function of shear stress alone. (It is conceivable, for example, that an otherwise isotropic material might behave anisotropically in a thin layer close to a wall if the rotational freedom of rod- or platelike particles in the material were restricted by proximity to a rigid boundary²².) Thus in principle one must be able both to detect and measure a wall effect in pipe flow and to deduce the characteristic rheological properties in the bulk of the material remote from boundaries (i.e., in an isotropic condition) when a wall effect is present.

¹⁸ A. H. Nissan, *J. Inst. Petroleum* **28**, 257 (1942).

¹⁹ R. R. Rothfus and R. S. Prengle, *Ind. Eng. Chem.* **44**, 1683 (1952).

²⁰ H. T. Barnes and E. G. Coker, *Proc. Roy. Soc. (London)* **A74**, 341 (1905).

²¹ A. M. Binnie, *Proc. Phys. Soc. (London)* **57**, 390 (1945); A. M. Binnie and J. S. Fowler, *Proc. Roy. Soc. (London)* **A192**, 32 (1948).

²² F. R. Eirich, H. Margaretha, and M. Bunzl, *Kolloid-Z.* **75**, 20 (1936).

The nature and extent of present achievement in the theoretical treatment of this difficult problem are indicated by Oldroyd;^{22a} the earlier developments have been expounded by Scott Blair²³ and Reiner.²⁴ From the experimental standpoint, we may profitably consider a new analytical procedure suggested by Oldroyd,² for this has certain advantages over others and may replace them.

It is possible to detect anomalous flow of a non-Newtonian liquid near a rigid boundary by plotting the apparent fluidity $1/\eta'$ [as given by equation (1)] against the shear stress at the wall $\tau_a (= \frac{1}{2}a \, dp/dz)$, or some function of τ_a , in laminar flow through pipes of various diameters. If the properties of the liquid in shear are everywhere specified by a unique stress vs. rate of strain relationship (i.e., there is *no* wall effect), all the plotted points should lie on a single curve, $1/\eta' = F(\tau_a)$, *in the region of laminar flow* (the points for the different pipes will, of course, separately depart from this curve at values of τ_a larger than that corresponding to the breakdown of laminar flow in each pipe). A wall effect is indicated if distinct $(1/\eta', \tau_a)$ curves arise from different diameters of pipe; it can be measured by an *effective slip coefficient* $\zeta(\tau_a)$, which is the effective velocity of slip per unit shear stress at a wall, provided the relative displacements of the curves are consistent with the general relation

$$\frac{1}{\eta'} = \frac{4\zeta(\tau_a)}{a} + F(\tau_a) \quad (5)$$

In such a case, and if the curves are sufficiently well defined, equation (5) can be used to obtain $F(\tau_a)$ and $\zeta(\tau_a)$, for if $1/\eta'$ is plotted against $1/a$ for selected constant values of τ_a , the points so obtained should lie on a straight line with slope $4\zeta(\tau_a)$ and intercept $F(\tau_a)$ on the $1/\eta'$ axis. Thus the magnitude of the wall effect can be assessed, and the curve $1/\eta' = F(\tau_a)$ can be constructed and used, as for a liquid not showing wall effects, to obtain the stress vs. rate of strain relationship for the material remote from boundaries. The macroscopic flow properties of the material are then specified completely.

This method of interpreting observed pressure gradient vs. rate of flow relations is laborious, but it has already served to detect and measure a wall effect in solutions of a linear polymer.¹¹ We shall now consider this application, partly to illustrate Oldroyd's method and partly to indicate that results obtained by it are consistent with those deduced by another

^{22a} J. G. Oldroyd, in "Rheology, Theory and Applications" (F. R. Eirich, ed.), Vol. I, Chapter 16, Academic Press, New York, 1956.

²³ G. W. Scott Blair, "Introduction to Industrial Rheology." Churchill, London, 1938.

²⁴ M. Reiner, "Deformation and Flow." Lewis, London, 1949.

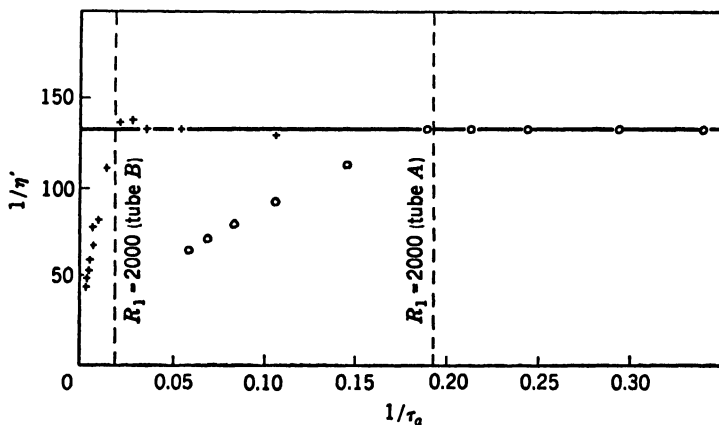


FIG. 3. Observed relations between $1/\eta'$ and $1/\tau_a$ in the case of a Newtonian liquid. (Reproduced by courtesy *J. Colloid Sci.*)

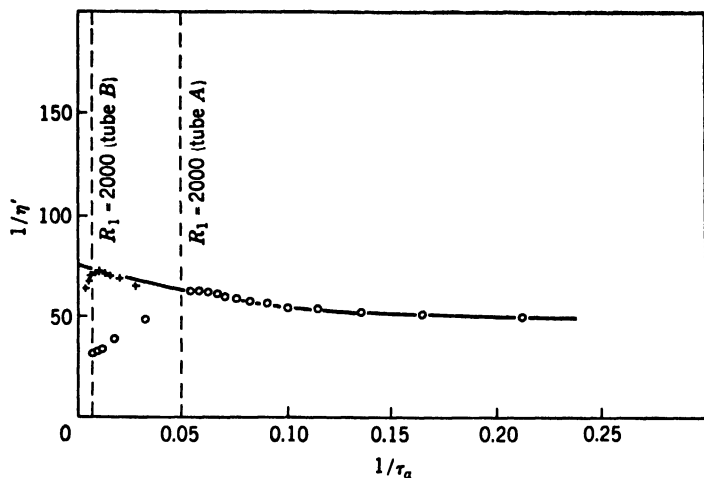


FIG. 4. Observed relations between $1/\eta'$ and $1/\tau_a$ in the case of a non-Newtonian liquid. No wall effect. (Reproduced by courtesy *J. Colloid Sci.*)

procedure of similar scope which was proposed earlier by Schofield and Scott Blair.^{23, 25}

Toms¹¹ observed the flow of dilute solutions of *poly*(methyl methacrylate) in monochlorobenzene [$(\eta) = 39$ liter/gm.] through straight metal pipes of two diameters at 25°. The experimental results, some of which are displayed in Figs. 3 to 5, were represented by plotting $1/\eta'$ against $1/\tau_a$ (i.e., a convenient function of the shear stress at the wall) for *Tube A* ($a = 0.202$ cm.)

²⁵ R. K. Schofield and G. W. Scott Blair, *J. Phys. Chem.* **34**, 248 (1930); **35**, 1212 (1931).

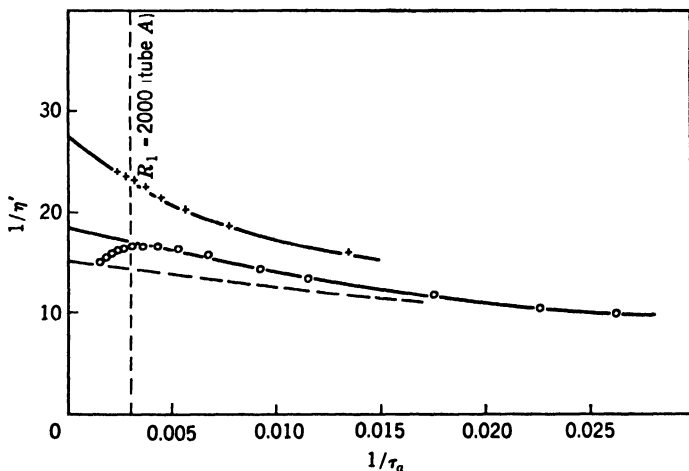


FIG. 5 Observed relations between $1/\eta'$ and $1/\tau_a$ in the case of a non-Newtonian liquid. Wall effect present (Reproduced by courtesy *J. Colloid Sci.*)

and *Tube B* ($a = 0.064_5$ cm.). The accuracy and consistency of results obtained with the two sizes of pipe are indicated in Fig. 3 which refers to experiments with the pure solvent. Monochlorobenzene is seen to be a Newtonian liquid (as is well known), and the observed constant value, $1/\eta' = 132$, is in good agreement with the known fluidity of the material at 25° . It is also evident that breakdown of laminar flow occurred in both pipes at the same Reynolds number, $R_1 = 2000$, and this, of course, is the critical value commonly observed when the ends of the pipe are cut off square as in the present case.

The results obtained with a solution containing 2.5 gm. of polymer per liter are shown in Fig. 4. The fact that a single smooth curve can be drawn through all the points corresponding to laminar flow is evidence that there was no anomalous behavior near a wall; and the significant departure of this curve from the form $1/\eta' = \text{constant}$ is a measure of the extent to which the liquid was not Newtonian. The analytical procedure of Schofield and Scott Blair also indicated the absence of a wall effect and gave the same limiting value, $1/\eta'_1 = 75$, for the fluidity at very large stresses (i.e., $1/\tau_a \rightarrow 0$). It is noteworthy that the critical value of Reynolds number proved to be 2000 in both pipes when the observed value of η'_1 was used in the calculations (see Section I, 3).

The distinct $(1/\eta', 1/\tau_a)$ curves in Fig. 5, which refer to experiments with a solution containing 10 gm. of polymer per liter, are consistent with the occurrence of a wall effect of the type envisaged by Oldroyd. The broken curve in the same figure represents $1/\eta' = F(1/\tau_a)$ and gives $1/\eta'_1 = 15$: as before, when this limiting value is used to calculate Reynolds number, $R_1 = 2000$

marks the breakdown of laminar flow, at any rate in Tube A (the critical conditions were not attained in the narrower pipe). The effective slip coefficient increased with τ_a and attained, at large values of τ_a , a limiting value $\zeta_1 = 0.2$, which means that the effective velocity of slip in these experiments was not bounded but tended to infinity with the shear stress at the wall. It is therefore interesting to note that when the experimental data were analyzed by the method of Schofield and Scott Blair, the presence of a wall effect was confirmed, and their slip parameter σ_0 could be identified with ζ_1 .

II. Flow Between Coaxial Cylinders

We are concerned here with the study of certain aspects of the behavior of a liquid when it is sheared isothermally in a *narrow* annulus between *long* vertical coaxial cylinders. Under these conditions, the material is observed in (as nearly as possible) a simple shearing motion, and it can be arranged that end effects are relatively small.

It is well known that experiments in which one cylinder (preferably the *outer* one²⁶) is rotated at various known constant speeds, and the torque on the other cylinder is measured, can readily be interpreted to give the viscosity of the liquid as a function of rate of shear, or shear stress; moreover, wall effects can be detected and measured by comparing observations on the same liquid in annular gaps of different widths. But a single variable viscosity coefficient associated with an effective slip coefficient (which, of course, may be zero) does not suffice to specify completely the properties in shear of an *elasticoviscous liquid* (a mobile liquid with elasticity of shape is envisaged). It is therefore convenient, and of considerable importance, that liquid elasticity can be detected and measured by maintaining the outer cylinder in forced harmonic oscillations of small amplitude and recording the periodic torque on the inner one, or its motion when constrained by a suitable torsion wire. Experiments of this type, which are not yet practiced widely, depend on the fact that an elastic liquid, unlike an inelastic one, is able to transmit *transverse* elastic waves.^{22a}

Evidently, a suitably designed coaxial-cylinder apparatus has important advantages over a simple pipe, particularly when it is necessary to discover the rheological properties of a liquid, or there is qualitative evidence of elasticity (e.g., in certain polymer solutions, air bubbles can be seen to recoil when stirring is stopped abruptly).

The first coaxial-cylinder viscometer was constructed by Couette,²⁷ and the subsequent development of this type of apparatus can be followed in

²⁶ G. I. Taylor, *Phil. Trans. Roy. Soc.* **A223**, 289 (1922); *Proc. Roy. Soc. (London)* **A157**, 546 (1936).

²⁷ M. Couette, *Ann. chim. phys.* **21**, 433 (1890).

the accounts by Barr⁵ and Merrington.²⁸ The recent introduction of the *coaxial-cylinder elastoviscometer*²⁹⁻³³ is an innovation which promises to enhance our knowledge of the rheological properties of a variety of real liquids. It is therefore appropriate that we should consider here how a liquid, and particularly an elastic liquid, can be characterized in a simple shearing motion by observing its behavior in an apparatus of this kind.

1. APPARATUS

The coaxial-cylinder elastoviscometer described by Oldroyd, Strawbridge, and Toms³² consists essentially of (i) a vertical outer cylinder which can either be rotated steadily at any speed within a wide range or put into forced harmonic oscillations at a wide range of known frequencies, with one of several possible known amplitudes; (ii) an inner cylinder, one of three with slightly different diameters, which can be accurately aligned coaxially with the bore of the outer cylinder. In steady rotation, the torque on the inner cylinder is measured at different speeds. In oscillatory motion, the amplitude of oscillation of the inner cylinder, when constrained by a torsion wire, is measured at different frequencies. (It is less easy to arrange, alternatively, that the inner cylinder remains perfectly stationary while the forces on it are recorded.) In every experiment the temperature of the liquid in the annulus is known and maintained constant.

a. The Coaxial-Cylinder Assembly

The general appearance of this unit and the steel framework in which it is mounted are represented in Fig. 6; important details of the construction are shown in Figs. 7 and 8.

The coaxial-cylinder assembly is held in cross pieces extending between two tall pillars which are set in a bed plate bolted to a concrete block. The cross pieces, which slide upon the pillars, are held apart and in position by steel sleeves of the correct lengths. The top end of each pillar is threaded so that the whole framework can be locked together rigidly by tightening two hexagonal nuts. This method of assembly facilitates adjustment and repair of the apparatus.

The outer cylinder, or "pot," which is made entirely of stainless steel, is mounted in two ball bearings, and the setting is such that its longitudinal

²⁸ A. C. Merrington, "Viscometry," Arnold, London, 1949.

²⁹ J. R. Van Wazer and H. Goldberg, *J. Appl. Phys.* **18**, 207 (1947).

³⁰ H. Goldberg and O. Sandvik, *Anal. Chem.* **19**, 123 (1947).

³¹ T. Nakagawa, *Kagaku* **20**, 327 (1950); *J. Chem. Soc. (Japan)* **72**, 759 (1951). [*From Chem. Abstr.* **46**, 3368, 5933 (1952)].

³² J. G. Oldroyd, D. J. Strawbridge, and B. A. Toms, *Proc. Phys. Soc. (London)* **B64**, 44 (1951).

³³ H. Markovitz, P. M. Yavorsky, R. C. Harper, Jr., L. J. Zapas, and T. W. DeWitt, *Rev. Sci. Instr.* **23**, 430 (1952).

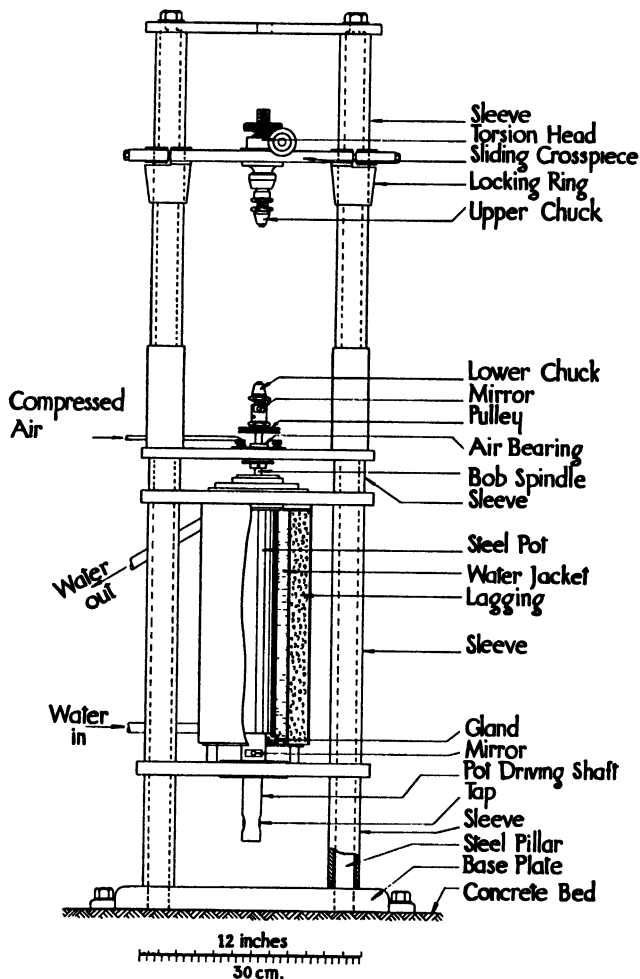


FIG. 6. The coaxial-cylinder assembly and supporting framework. Elevation. (Reproduced from *Proc. Phy. Soc.* by kind permission of the Physical Society.)

axis is as nearly vertical as possible; essentially, it is a tube closed at the bottom end by a plug, a downward extension of which forms the driving shaft (Fig. 7). The interior has the form of a right circular cylinder and is 29.90 cm. in depth measured from rim to floor. Each inner cylinder, or "bob," is basically a solid right circular cylinder of Duralumin alloy, but the bottom end is shaped to a cone of large apical angle terminating in a cylindrical spigot (Fig. 7): this design ensures that the bottom end effect is small and that air bubbles are not trapped when the annulus is filled with liquid (see below). The three inner cylinders differ in diameter (Table I)

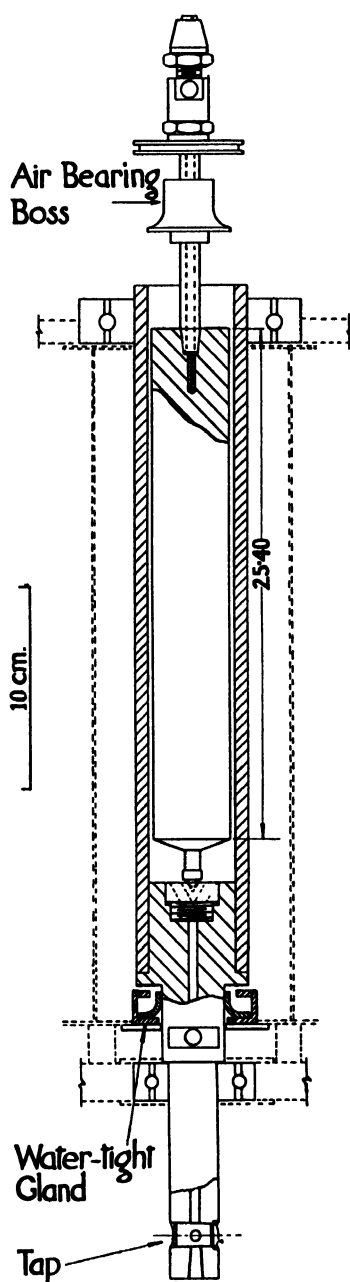


FIG. 7. The coaxial-cylinder assembly. Detail. (After Oldroyd, Strawbridge, and Toms.³²) (Redrawn from *Proc. Phys. Soc.* by kind permission of the Physical Society.)

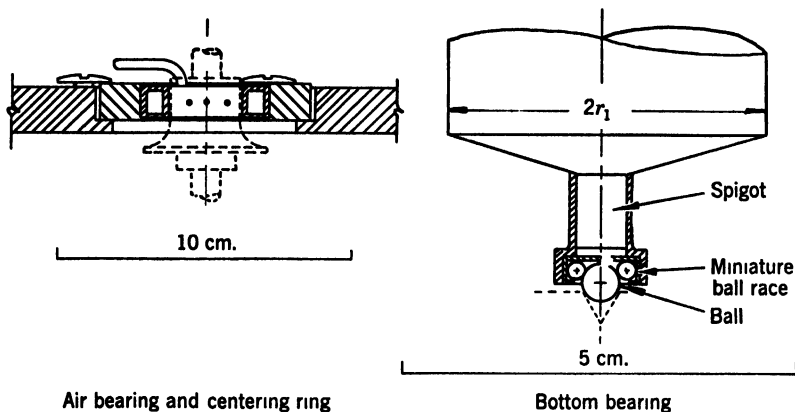


FIG. 8. Details of bearings supporting inner cylinder. (After Oldroyd, Strawbridge, and Toms.²²) (Redrawn from *Proc. Phys. Soc.* by kind permission of the Physical Society.)

but have the same length measured from the top surface to the end of the cylindrical body (25.40 cm.), or to the end of the spigot (26.80 cm.).

- The design and dimensions of the cylinders were chosen so that
- (1) liquids with viscosities between 10^{-2} and 10^2 poise, approximately, could be investigated;
 - (2) the radii of the inner and outer cylinders did not differ by more than 5%, approximately, and annular gaps less than 0.05 cm. in width were avoided (the possible error in the alignment of long cylinders may not be negligible with very narrow gaps and, moreover, these are difficult to fill with liquid);
 - (3) in oscillatory experiments, end effects, and particularly the bottom end effect, could reasonably be ignored (see Section II, 3).

The high degree of precision that was required, and achieved, in making the cylinders is shown by the fact that, when they had been honed smooth, the

TABLE I
CHARACTERISTICS OF CYLINDERS AND ANNULI

Cylinder	Radius (cm.)	Moment of Inertia* (gm. cm. ²)	Annulus Length <i>L</i> (cm.)	Width (cm.)
Outer	2.1712	—	—	—
Inner I	2.1212	2677	25.40	0.0500
Inner II	2.0701	2468	25.40	0.1011
Inner III	1.9691	2098	25.40	0.2021

* With fittings attached (see Fig. 7).

variation of diameter along the length of each was less than 0.0001 in. (the dimensions were specified in inches).

The provision of special bearings (Fig. 8) enables an inner cylinder to be mounted inside the outer so that the vertical axes of the two (very nearly) coincide, and there is almost no hindrance to the proper movement of the inner cylinder. A miniature thrust ball bearing serves to locate the bottom end of the inner cylinder centrally with respect to the bore of the outer; the ball-race is attached to the spigot of the inner cylinder and the steel ball (0.5 cm. diameter) is located in a conical depression at the center of the floor of the outer cylinder. The top end of the inner cylinder is located by means of an air-lubricated bearing which is self-centering and almost ideally frictionless. The air bearing consists of two parts, one a cylindrical boss fitted on a spindle inserted into the top end of the inner cylinder (Fig. 7), and the other, an annular air chamber having twelve radial holes, each 0.08 cm. in diameter, drilled symmetrically around the inner periphery. The air chamber fits a thick brass centering ring which is set in a cross piece (Fig. 6) so that its inner surface is coaxial with the bore of the outer cylinder. The position of the boss on the spindle is adjusted so that the air chamber surrounds it like a collar (Figs. 6 and 8), with an annular gap 0.0064 cm. in width between them. When air is supplied under pressure to the chamber (so that the excess pressure inside is 0.5 atm., approximately), it issues from the holes and impinges on the boss, keeping the spindle in a central position relative to the ring. (The escaping air mingles with the atmosphere above and below the gap, and the down draught is prevented from entering the outer cylinder by a skirt at the bottom of the boss.) There is symmetry about the vertical axis and no resultant torque on the boss.

When a torsion wire has been fitted (see below) the effects caused by friction and minute irregularities in the miniature ball bearing can be virtually eliminated by slightly retracting the chuck attached to the torsion head (Fig. 6) so that the weight of the inner cylinder is entirely supported by the torsion wire. With this improvement in its mounting (which can be achieved, by fine adjustment, without observable detriment to the centering capacity of the bottom bearing), the inner cylinder responds smoothly to very small couples.

Liquid is introduced into the space between the cylinders by forcing it upward through an axial hole in the driving shaft of the outer cylinder (Fig. 7). In the end of the shaft there is a tap, and below this, a tapered socket into which a standard glass cone attached to a pneumatically operated filling apparatus can be inserted. The level of the liquid in the annular gap is deduced from observations of its level in a vertical sight tube attached to the filling apparatus. These arrangements make it possible to

fill the annulus with liquid to any desired level without entrapping air bubbles and without altering the relative positions of the cylinders.

The temperature of the coaxial cylinder assembly is controlled by surrounding the outer cylinder with a lagged jacket (Fig. 6) through which water at known constant temperature is circulated continuously. During an experiment, a removable cover, which encloses the top of the assembly but does not interfere with the movements of the cylinders, serves to improve temperature control within the annulus and to reduce evaporation of the contained liquid.

b. The Driving Mechanism and Measuring Devices

The outer cylinder is moved about its vertical axis by connecting its driving shaft (Fig. 6) with a mechanism actuated by an electric motor. Two kinds of motion are possible, as required. By fixing a pulley on the driving shaft and connecting it, by means of a belt, with a driven pulley, the cylinder can be rotated steadily at any speed between 0.3 and 3000 r.p.m. Alternatively, an angular motion, which is almost exactly simple harmonic, can be maintained at any frequency between 0.25 and 25 c.p.s. with any one of five amplitudes in the ratios 1:2:4:8:16, the smallest of which corresponds to an amplitude of the outer cylinder equal to 0.005 rad. Oscillatory motion is achieved by fixing one end of a relatively long horizontal rigid beam to the driving shaft, and connecting a slot in the other end of the beam to a part of the mechanism which moves with simple harmonic rectilinear motion in a horizontal plane and normal to the length of the beam (for details, see the original paper³²). Speeds and frequencies are determined only when the motion of the outer cylinder is steady or uniformly oscillatory; they are measured stroboscopically.

It is arranged that one of two other observations can be made, depending on the type of motion executed by the outer cylinder. When this is made to oscillate, angular displacement of the inner cylinder is constrained by means of a torsion wire, and the amplitude of the uniform oscillatory motion assumed by the inner cylinder under these conditions is then observed as a function of the frequency. When the outer cylinder rotates steadily, the torque on the inner cylinder is measured at different angular velocities. For each experiment, a suitable torsion wire is chosen from a set of nine with torsional constants approximately in geometrical progression between 0.0037×10^6 and 7.25×10^6 dyne-cm./rad. [The constants of the wires and the moments of inertia of the inner cylinders (Table I) were determined by a dynamical method.] The torsion wires, which are straight and have different diameters and lengths, were made from a beryllium-copper alloy; the ends of each wire are permanently fixed in cylindrical bushes which fit in the collets of chucks attached to the top of the spindle of the inner cylinder and to an adjustable torsion head held in a movable

cross piece (Fig. 6). If the torque on the inner cylinder becomes too large when the outer cylinder rotates and its speed is increased, the restoring force produced by a torsion wire can be supplemented with a suitable couple applied to a pulley on the spindle of the inner cylinder (Figs. 6 and 7). This is done by attaching two threads to the periphery of the pulley and passing them over auxiliary pulleys fixed on opposite sides of the framework: by loading the threads equally, a known axial couple can be applied to the bob spindle without introducing a resultant force tending to displace the vertical axis of the inner cylinder.

Angular movements of the inner cylinder about its vertical axis are observed with the aid of an optical lever 100 cm. in length. A beam of light is reflected from a vertical plane mirror attached to the top of the inner cylinder spindle (Figs. 6 and 7), and is focussed on a horizontal curved scale engraved on a flexible strip of translucent bakelite 100 cm. in length. Angular movements of the outer cylinder can also be observed, and on the same scale, by reflecting a beam of light from a plane mirror fixed to the side of the driving shaft (Fig. 6); thus, in oscillatory experiments, the amplitudes of the inner and outer cylinders can be compared directly once the number of scale divisions corresponding to each fixed amplitude of the outer cylinder has been determined.

2. EXPERIMENTS INVOLVING STEADY ROTATION

The observations made when the outer cylinder is rotating steadily and the flow is laminar can be interpreted to give the viscosity of a liquid as a function of rate of shear (or of shear stress). In addition, wall effects, if present, can be detected and measured.

In order to *eliminate* end effects, two experiments, in which the annular gap is filled to different heights (h' and h'' measured on an arbitrary scale), are performed on each liquid.³⁴ The couples G' , G'' exerted on the stationary inner cylinder in a steady state are recorded as functions of the angular velocity Ω of the outer cylinder, and the relation between torque and angular velocity in each experiment is then defined by drawing a smooth curve through a plot of the observed values (Fig. 9). For a Newtonian liquid, the viscosity η' is given by the formula

$$\eta' = \frac{(r_2^2 - r_1^2)[G''(\Omega) - G'(\Omega)]}{4\pi r_1^2 r_2^2 (h'' - h')\Omega} \quad (6)$$

where r_1 , r_2 are the functional radii of the inner and outer cylinders, respectively (Table I); C.G.S. units are used in all calculations, and Ω is measured in rad./sec., so that η' is obtained in poises. Mean measures of the

³⁴ L. Gurney, *Phys. Rev.* **26**, 98 (1908); G. F. C. Searle, *Proc. Cambridge Phil. Soc.* **16**, 600 (1912).

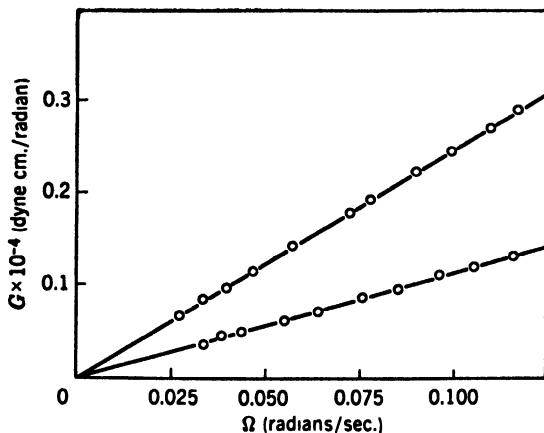


FIG. 9. Relations between G and Ω observed in two experiments at 25° with a solution in pyridine containing 36.40 gm. of *poly*(methyl methacrylate) per liter; Inner cylinder III, $h''-h' = 11.90$ cm. (Redrawn by courtesy *Trans. Faraday Soc.*)

rate of shear D (sec.^{-1}) and the shear stress τ (dyne-cm.^{-2}) are conveniently calculated at $r = (r_1 r_2)^{1/2}$: they are given by

$$D = \frac{2r_1 r_2 \Omega}{r_2^2 - r_1^2} \quad (7)$$

$$\tau = \frac{G''(\Omega) - G'(\Omega)}{2\pi r_1 r_2 (h'' - h')} \quad (8)$$

and, of course, $\eta' = \tau/D$. When the liquid is non-Newtonian and the annular gap is narrow, the same formulas (6) to (8) give the relations between viscosity, rate of shear, and shear stress parametrically, with only a second-order error. In this case τ has the same physical significance as before, and D is a first-order approximation to the rate of shear at $r = (r_1 r_2)^{1/2}$ (reckoning the annulus vs. diameter ratio as a first-order small quantity), so long as wall effects are absent.

Wall effects can be detected by plotting η' against D (or τ), as given by equations (6) to (8), for different annular gaps. Any appreciable wall effect would make the curves for different gaps distinct, but if wall effects are absent the curves should coincide with only a second-order error.^{22a}

The results of some steady-state experiments carried out with the apparatus described in Section II, 1 are displayed in Figs. 9 and 10. These data^{25, 26} refer to a series of elasticoviscous liquids prepared by dissolving *poly*(methyl methacrylate) in pyridine; the solutions contained 2 to 5 % of polymer, and

²⁵ B. A. Toms and D. J. Strawbridge, *Proc. 2nd Intern. Congr. Rheol. Oxford* p. 99 (1953).

²⁶ B. A. Toms and D. J. Strawbridge, *Trans. Faraday Soc.* **49**, 1225 (1953).

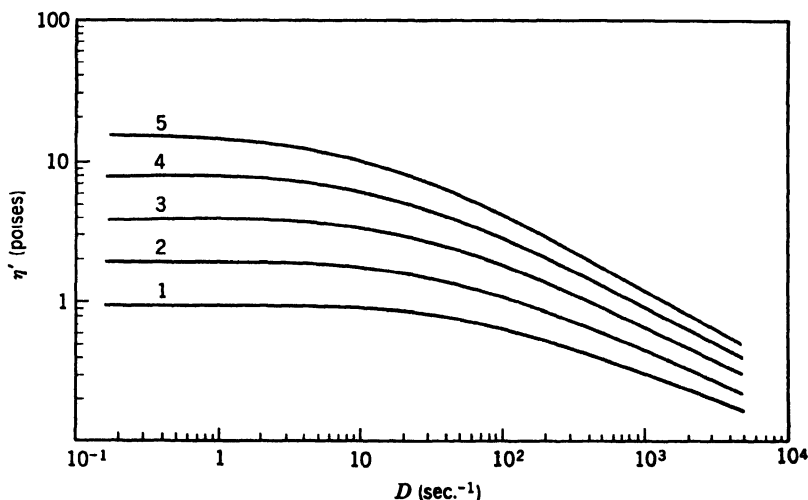


FIG. 10. Observed relations at 25° between viscosity and rate of shear in a series of dilute solutions of *poly*(methyl methacrylate) in pyridine. (Redrawn from *Proc. 2nd Intern. Congr. Rheol.* by courtesy of Butterworths Scientific Publications.)

$[\eta] = 43$ liter/gm. The G against Ω plots in Fig. 9, which refer to solution 3 of Fig. 10, illustrate the above method of determining η' and indicate the consistency of typical experimental observations. The relations deduced between $\log \eta'$ and $\log D$ are represented in Fig. 10. It is seen that the viscosity of each liquid was constant (i.e., Newtonian behavior prevailed) at sufficiently small rates of shear: this fact is important (see Section II, 3), for it means that the behavior in steady shear can be characterized by a limiting viscosity coefficient η_0 . (The value $\eta_0 = 4$ can be deduced from the data of Fig. 9.)

The accuracy of a determination of η' must, of course, be known. The most exact absolute determinations of liquid viscosity yet made with a coaxial-cylinder apparatus are probably those of Leroux,³⁷ who claimed to have measured the viscosity of water at various temperatures with an error not exceeding 1 part in 200. This degree of precision must be regarded as extraordinary for its achievement necessitated extreme experimental precautions. In the present context it is interesting to note that, in testing their coaxial-cylinder elastoviscometer, Oldroyd, Strawbridge, and Toms³² obtained the mean value $\eta' = 0.128$ (standard deviation 0.002) from nine distinct experiments with a Newtonian liquid for which the corresponding value $\eta = 0.130$ had previously been determined by means of a standard capillary viscometer. The degree of precision thus indicated is adequate for work of an exploratory character.

³⁷ P. Leroux, *Ann. phys.* **4**, 163 (1926).

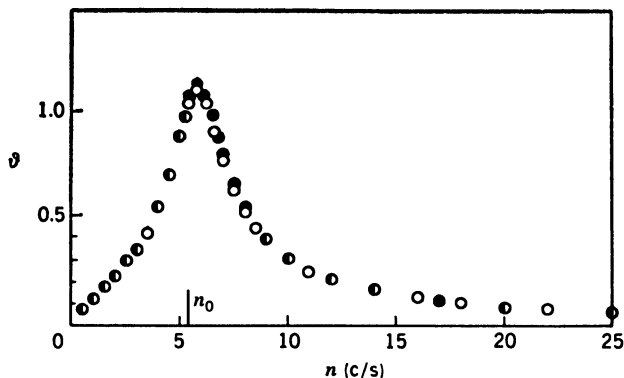


FIG. 11. Relations between ϑ and n observed when the outer cylinder of the elastoviscometer was oscillated with amplitudes 0.01 radian (●) and 0.02 radian (○). Experiments at 25° with the polymer solution referred to in Fig. 9. (Coincident points are denoted ◐.) (Redrawn by courtesy *Trans. Faraday Soc.*)

The stability of laminar flow between relatively rotating coaxial cylinders has been investigated by Taylor;²⁶ the earliest experiments bearing on this matter were those of Couette.²⁷

3. EXPERIMENTS INVOLVING OSCILLATORY MOTION

Results obtained when the outer cylinder is oscillating uniformly are more difficult to interpret. The elastic properties exhibited by any particular liquid are measured by comparing experimental results with appropriate theoretical predictions for a series of idealized liquids characterized by different elastic constants. Since different model liquids can be visualized, agreement between theory and experiment must be rigorously tested: it is to be considered satisfactory only if the deductions from experiments with one inner cylinder and one torsion wire can be used to predict correctly the behavior of the same (real) liquid with different cylinders and wires. In order to illustrate this procedure, we shall follow the method adopted by Toms and Strawbridge^{35, 36} for investigating the elasticity of certain polymer solutions. The theoretical basis of this particular method has been expounded by Oldroyd,³⁸ and its applicability in a real case was first demonstrated by Oldroyd, Strawbridge, and Toms.³²

Oscillatory experiments are carried out with the annular gap completely filled with liquid. The outer cylinder of the elastoviscometer is oscillated with a fixed *small* amplitude (e.g., 0.01 rad.) at different frequencies, and the amplitude of oscillation of the inner cylinder, with a suitable torsion wire in position, is observed as a function of frequency. The results of such an experiment are represented by plotting ϑ , defined as the ratio of the

³⁸ J. G. Oldroyd, *Quart. J. Mech. Appl. Math.* **4**, 271 (1951).

amplitudes of the inner and outer cylinders, against the frequency n measured in cycles per second. The amplitude of the outer cylinder must be small enough for the observed relationship between ϑ and n to be (very nearly) independent of the absolute value of the amplitude (Fig. 11). Several (n, ϑ) curves corresponding to different inner cylinders and wires are obtained for each individual liquid (Fig. 13).

Predicted (n, ϑ) curves appropriate to each experimental setup are obtained by considering a model elasticoviscous liquid whose behavior in oscillatory shearing motion at small amplitudes is characterized by three constants, a coefficient of viscosity η_0 , a relaxation time λ_1 , and a retardation time λ_2 . A linear relation between the shear stress τ , the rate of shear D , and their rates of change $\dot{\tau}$, $\dot{D}$ is assumed:

$$\tau + \lambda_1 \dot{\tau} = \eta_0(D + \lambda_2 \dot{D}). \quad (9)$$

The solution of equation (9) required in calculating $\vartheta(n)$ at different frequencies, with selected values of η_0 , λ_1 , and λ_2 , has been given by Oldroyd.³⁸ The calculation of (n, ϑ) curves is a considerable task, even when η_0 can be assumed constant (cf. Fig. 14); the values of λ_1 and λ_2 which give the best agreement between theory and experiment in the case of a single inner cylinder and torsion wire can be estimated to within about 5%. (In their work on polymer solutions, Toms and Strawbridge were able to limit computation by preparing solutions with selected values of η_0 (cf. Fig. 10): families of predicted (n, ϑ) curves could then be constructed (Oldroyd³⁸), enabling approximate values of λ_1 and λ_2 to be deduced by interpolation.³⁶

In making theoretical predictions, the amplitude of oscillation is supposed

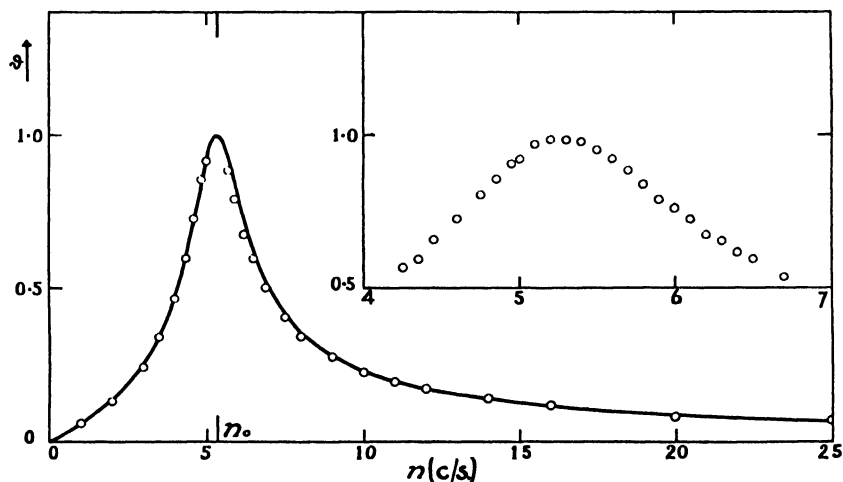


FIG. 12. The relations between ϑ and n in the case of a Newtonian liquid (liquid paraffin B.P.; 25°). (Reproduced from *Proc. Phys. Soc.* by kind permission of the Physical Society).

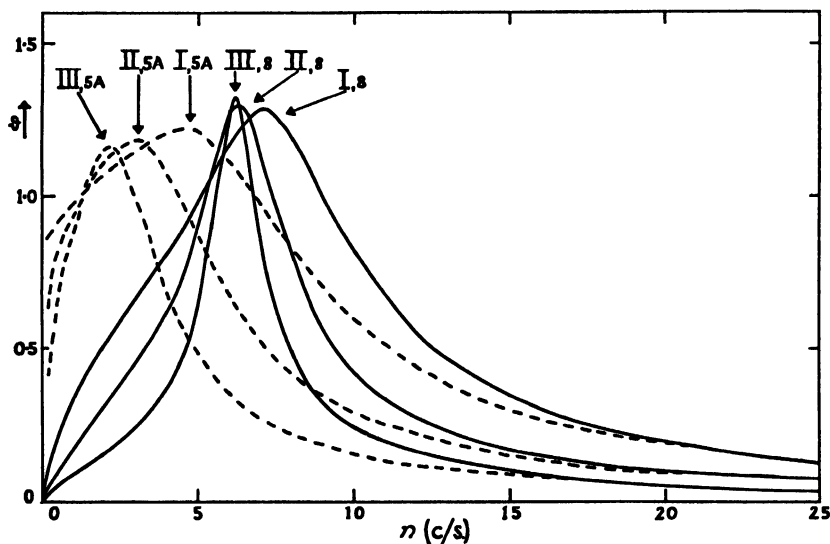


FIG. 13. Observed relations between δ and n in the case of a solution of *poly*-(methyl methacrylate) in pyridine for which $\rho = 0.98$ gm./ml. and $\eta_0 = 7.9$ poises (25°). (Reproduced from *Proc. Phys. Soc.* by kind permission of the Physical Society.)

to be small, so that the ratio of the amplitudes of the inner and outer cylinders is independent of the amplitude, and η_0 can be identified with the viscosity observed in steady rotation at very low rates of shear (see Section II, 2). The full length L of the annulus is assumed filled with liquid, and end effects are ignored.

The relation (9) represents the behavior of a type of material which includes as particular cases the Maxwellian elasticoviscous liquid ($\lambda_2 = 0$) and the Newtonian viscous liquid ($\lambda_1 = 0, \lambda_2 = 0$). It is seen that the relaxation and retardation times have the physical significance that if the motion is suddenly stopped, the shear stress decays as $\exp(-t/\lambda_1)$, and if the stress is removed the rate of strain decays as $\exp(-t/\lambda_2)$.

The agreement between theory and experiment in the case of a Newtonian liquid (liquid paraffin B.P. of density 0.877 gm./ml. and viscosity 1.76 poises at 25°) is illustrated in Fig. 12.³² In this diagram, typical experimental points obtained at 25° using the inner cylinder II (see Table I), with amplitude 0.01 rad. and a torsion wire of restoring constant 2.79×10^6 dyne-cm./rad., are shown in relation to the *theoretical* curve. Inset in the figure are shown some of the individual experimental points near the peak, on an increased frequency scale, as an indication of consistency. The frequency n_0 of free oscillation of the wire and inner cylinder is indicated. It is seen that $\delta(n)$ attains a maximum value, which does not exceed unity, at

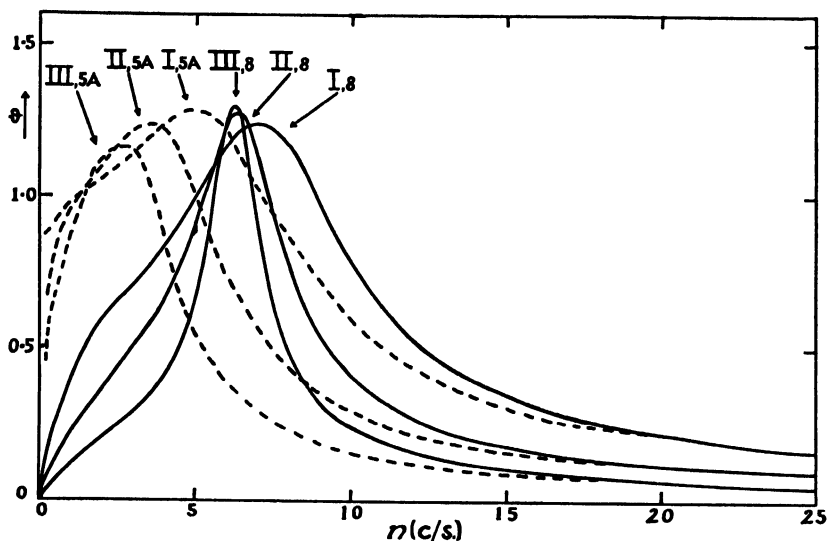


FIG. 14. The predicted relations between ϑ and n in the case of an idealized elasto-viscous liquid for which $\rho = 0.98$ gm./ml., $\eta_0 = 7.9$ poises, $\lambda_1 = 0.065$ sec., $\lambda_2 = 0.015$ sec. (Reproduced from *Proc. Phys. Soc.* by kind permission of the Physical Society.)

a frequency almost exactly equal to n_0 : these are characteristic features of $\vartheta(n)$ in the case of an inelastic liquid;³⁵ moreover, the observed peak height $\vartheta = 1.00$ is consistent with $\eta_0 > 0.5$. The agreement appears to justify the neglect of end effects in the theory of small oscillations, as well as to indicate the accuracy achieved in this kind of experiment with the apparatus described in Section II, 1.

The detection and measurement of elasticity in a real liquid are illustrated by Figs. 13 and 14.³² The experimental results (Fig. 13) refer to a solution of highly polymerized methyl methacrylate in pyridine [$(\eta) = 55$ liter/gm.] containing 30.5 gm. of polymer per liter, and with density 0.98 gm./ml. at 25°. The oscillatory experiments were carried out at 25° with the inner cylinders I, II, and III (Table I) and two torsion wires (numbers 5A and 8) with restoring constants 0.171×10^6 and 2.79×10^6 dyne-cm./rad.; the amplitude of oscillation of the outer cylinder was 0.01 rad. throughout (the curves obtained with amplitude 0.02 rad. did not differ significantly from those of Fig. 13).

The elasticity of the polymer solution is indicated by the fact that, in every experiment, ϑ attained a maximum value exceeding unity [characteristically, the peak of each observed curve occurs at a frequency greater than n_0 , and when $n = n_0$, $\vartheta = 1.00$ (cf. Fig. 11)]. Non-Newtonian behavior was observed in steady-state experiments, but at very small rates of shear the viscosity was constant and equal to 7.9 poises (cf., Figs. 9 and 10).

Assuming $\eta_0 = 7.9$ and $\rho = 0.98$, the theoretical curves shown in Fig. 14 were obtained by determining the values of λ_1 and λ_2 which gave the best "fit" for the experimental curve labeled "II, 8" (Fig. 13) and then using these same values (viz., $\lambda_1 = 0.065$ sec., $\lambda_2 = 0.015$ sec.) to predict curves appropriate to the other experimental conditions. The agreement between theory and experiment appears to justify the conclusion that, to a first approximation, the polymer solution under consideration can be characterized by an equation of state of the form (9)—valid in a simple shearing motion confined to sufficiently small rates of shear—with relaxation time 0.065 sec. and retardation time 0.015 sec. at 25°.

The results of an oscillatory experiment can also be interpreted to give the viscosity coefficient η_0 : the slope of the (n, ϑ) curve is measured at the origin, and then appropriate numerical substitutions are made in the equation

$$\eta_0 = \frac{K(r_2^2 - r_1^2)}{8\pi^2 r_1^2 r_2^2 L} \left[\lim_{n \rightarrow 0} \frac{\vartheta(n)}{n} \right] \quad (10)$$

where (as before) r_1, r_2 are the functional radii of the inner and outer cylinders, respectively, K is the restoring constant of the torsion wire and L is the length of the annulus.³⁸ Toms and Strawbridge³⁶ have shown that values of η_0 determined in this way, though less accurate, are reasonably consistent with those measured by the standard method (see Section II, 2).

Nomenclature

a	Radius of the bore of a pipe.	h	A distance measured vertically on an arbitrary scale
c	Concentration of solute	K	Restoring constant of a torsion wire
D	A measure of rate of shear	l	Length of the bore of a pipe
Δp	Difference of hydrostatic pressure between the ends of a pipe	L	Length of the annulus between coaxial cylinders
dp/dz	Pressure gradient down a pipe	λ_1	Stress relaxation time
η'	Coefficient of viscosity	λ_2	Rate of strain relaxation time, or retardation time
$[\eta]$	Limit $c \rightarrow 0$ (η_{sp}/c), where $(1 + \eta_{sp})$ is the relative viscosity of a polymer solution	n	Frequency of oscillation
G	Couple exerted on the inner, or stationary member, of two relatively moving coaxial cylinders	Ω	Angular velocity of outer of two relatively-moving coaxial cylinders
		Q	Volume rate of flow through a pipe

r_1, r_2	Radii of inner and outer of two coaxial cylinders	ϑ	Ratio of amplitudes (inner/outer) of two coaxial cylinders in relative oscillatory motion.
R	Reynolds number	$\zeta(\tau_a)$	Effective velocity of slip per unit shear stress at a (pipe) wall
ρ	Density		
τ	Shear stress		
τ_a	Shear stress at a pipe wall		

CHAPTER 13

GONIOMETRY OF FLOW AND RUPTURE

A. Jobling and J. E. Roberts

I. Introduction	503
II. Goniometry of Continuous Laminar Shear	506
1. Unidirectional Motion	506
2. Oscillatory Motion	518
3. Normal Pressure Effects	522
4. Future Developments	525
III. Goniometry of the Transition Region between Continuous Flow and Rupture	526
1. Introduction	526
2. Principles of the method	527
a. Irrotational Movements	528
b. Rotational Movements	529
3. Experimental Technique	530
4. Preliminary Results and Discussion	531
Nomenclature	535

I. Introduction

In many stages of industrial processes and in the subsequent use of their products, the flow of materials is of paramount importance. By gaining control of the phenomena governing flow, efficiency can be achieved in the planning of the process, the design of the necessary machinery, and the suitability of the final product for its purpose. The first step in obtaining this control is the development of exact methods for the measurement of all the features in the flow of the material under various types of mechanical action. It is then desirable to be able to correlate these by an adequate theory which can be used to predict the subsequent behavior of the material in any type of instrument and in any desired practical application. Both theoretical and experimental progress in this direction have resulted from the realization of the necessity for *goniometry of flow*, which is the measurement of the distribution of stresses and strains within the flowing material at every instant in time and at every point in space around the full solid angle of directions.

It is clear that goniometric measurements will be required whenever the physical quantity to be measured is anisotropic, that is, that it has a different value in different directions. Stresses and strains are by definition

anisotropic whenever there is a shearing component in the deformation and, since almost all rheological problems involve the consideration of sheared states, it follows that goniometric measurements are essential, at least in principle, even when the material under examination is isotropic in its rest state. This stress-strain anisotropy is important in:

(i) *the definition of the flow phenomena.* Prior to the development of the principles and methods of rheogoniometry, it had been customary to consider the relation between the forces and displacements only in the (tangential) direction of flow. It is now generally agreed that in the flow of viscoelastic fluids additional forces may be generated in other directions and manifest themselves in a number of ways ("normal pressure effects" or "Weissenberg effects"). These general flow phenomena were not clearly shown by the early experimental techniques although they may appear. (For example, in flow through a capillary tube, viscoelastic properties are manifested in a nonparabolic velocity distribution across the tube and an increase in the radius of the jet at the exit.) New techniques for the measurement in a flowing liquid of the pressure distribution around the full solid angle in space have enabled research workers to obtain a much clearer insight into the origin of these effects.

(ii) *the measurement of the mechanical properties.* A knowledge of the mechanical properties of a material may be required for one of two purposes. The chemist requires a knowledge of the properties in the natural or rest state in the hope that he will be able to relate this to the structure of the material and so control its behavior by adjusting its chemical constitution. The physicist and engineer require to know the properties of the material in its flowing state for use in the calculation of transport and handling problems. These mechanical properties are defined generally as the parameters relating the stresses, p , and their time derivatives $\dot{p}$, $\ddot{p}$, $\dots$ to the strains, ϵ , and their time derivatives, $\dot{\epsilon}$, $\ddot{\epsilon}$, $\dots$. Particular cases are Hooke's elasticity, $G(= p/\epsilon)$ and the Newtonian viscosity, $\eta(= p/\dot{\epsilon})$.

In the natural state, if the material to be examined is already anisotropic (e.g. crystals, oriented fibres, drawn wires), the need to measure the mechanical properties in different directions is self-evident. For a material which is isotropic in this state, although the stresses and strains imposed by the mechanical action can be made sufficiently small so as not to disturb this state, they are still anisotropic though the relation between them is isotropic. This means geometrically that their main axes of stress are parallel to those of the strain (and similarly for the time derivatives) and in this case the testing procedure can be simplified. The testing of "natural" states with small strain-amplitude vibrations can be regarded as goniometry in space-time coordinates, as the phase differences between the stresses and

strains appear as phase-angles in the complex plane in which the time-development of the motion is represented.

In the sheared state, it has already been stated that the distribution of stresses and strains and their time derivatives is such that they are always anisotropic and, at least in principle, goniometry is always needed for their quantitative measurement. In the special case of the Newtonian liquid, although the stress and strain velocities are themselves anisotropic, the relation between them is isotropic and characterized by a scalar constant, the viscosity. However, in a sheared general material, whether isotropic or anisotropic in its rest state, the relations between the stresses and strains and their time derivatives may be spatially complex and can only be determined by a complete goniometric investigation.

Recently, goniometric methods have been developed for the testing of materials in the transition region between steady flow and rupture. The movement of the material is controlled by placing it on a deformable substrate and measuring the distribution in space and time of the stresses, strains, and flow disturbances in the material. The principle of the method, illustrated by some preliminary results, is described in Section III.

A theoretical approach to a given problem requires the application of the three fundamental principles of:

- (i) the dynamic equilibrium of forces at every point in the flowing material,
- (ii) the maintenance of continuity, and
- (iii) the stress-strain relation,

and goniometry is of importance in relation to each of these. It is the application of the first principle that has made possible the measurement of the forces in a flowing material across three mutually perpendicular planes without disturbing the motion at the point where the measurements are taken (see Section II). A consideration of the second principle had led to an appreciation of the significance of the directions of lines of zero elongation and planes of zero normal extension in the continuous flow and in the cracking-up patterns that occur in the transition from continuous flow to rupture (see Section III). Finally, goniometry has proved of particular interest in connection with the third principle because it is here that differences of opinion occur as each theorist has made what is, in his view, the simplest assumptions compatible with the physics of the material so that the practical mathematics can be mastered. Though it appears doubtful whether any one theory is yet exact for all materials and all mechanical actions, considerable progress has recently been made. This is discussed in greater detail in the next section, where it is shown that goniometric measurements in certain laminar shearing motions make it possible to determine what theory is most applicable to the real substances so far examined.

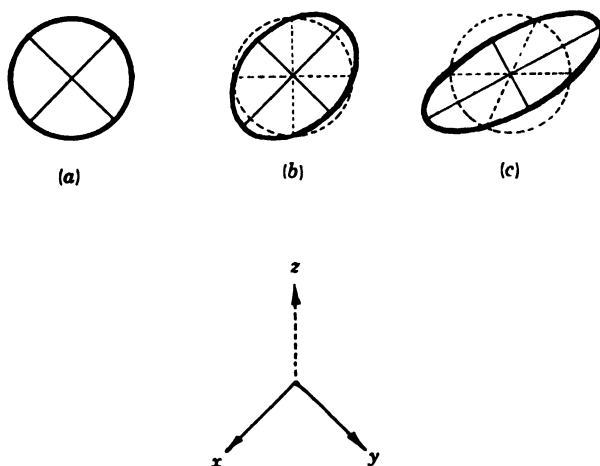


FIG. 1. The strain ellipse in laminar shear.

II. Goniometry of Continuous Laminar Shear

I. UNIDIRECTIONAL MOTION

A number of attempts have been made to derive theoretically the pressure distribution in a flowing liquid. Whereas the predictions of some of these theories are compatible with the behavior of materials which have already been examined others are not, but represent extremely interesting ideas for which practical examples may yet be found.

Weissenberg¹⁻³ has considered initially an ideally elastic material which is isotropic in its ground state but becomes increasingly anisotropic with increasing shear strain. The main axes of strain are parallel to those of the stress, irrespective of the magnitude of the strain velocity. This also applies to viscoelastic media if the elastically recoverable part of the strain is considered. In the laminar shear of both elastic and viscoelastic materials, the orientations of the main axes of the stress may deviate from those of the strain velocity. This is illustrated in Fig. 1, which shows the change in orientation of the strain ellipse. A circle is marked out to denote the unstrained state (a). A small movement changes this into an ellipse with its axes at 45 deg. to the direction of shear (b) but as the recoverable strain increases, the major axis turns more and more into the direction of shear (c). If a circle is marked out in the strained state, an additional small shear results in its transformation into another ellipse at 45 deg. to the direction of shear. Hence the strain velocity is always represented by an ellipse at 45

¹ K. Weissenberg, *Abhandl. preuss. Akad. Wiss. Math. naturw. Kl.* No. 2 (1931).

² K. Weissenberg, *Arch. sci. phys. et nat.* [5] 17, 1 (1934).

³ K. Weissenberg, *Rept. General Conf. Brit. Rheologists' Club* p. 36 (1946).

deg. This angular deviation should increase with the rate of shear as the recoverable strain increases and should produce both normal and tangential stress components.

Reiner⁴ and Rivlin⁵⁻⁷ have assumed a nonlinear relation between stress and strain velocity and no storage of elastically recoverable energy. Garner *et al.*⁸ attribute pressure differences entirely to differences in the rate of shear in different parts of the flowing system. DeWitt⁹ and Fromm¹⁰ have developed mechanical equations of state which are summarized below. Lodge,^{11, 11a} from a consideration of a polymer solution as a network with transient junctions, predicts a simple relation between the stress and refractive index ellipsoids in the flowing material^{11b} and a pressure distribution similar to that of Weissenberg (see above). Oldroyd^{12, 13} obtained a very general equation which allows for the production of normal stresses and contains a sufficient number of empirical constants which can be adjusted to the experimental results and to the theories of Mooney, Weissenberg, and Reiner and Rivlin. Mooney,¹¹⁻¹⁶ by an extension of his theory of rubber-like elasticity, has introduced an elasticity law containing two material characteristics, one the shear modulus, G , and another modulus, H , which allows for normal pressures.

To consider these theories in greater detail, a system of coordinates is required. The trirectangular system used is described in Fig. 2. In this system, the strain velocity tensor is given by

$$\dot{\epsilon} = \begin{vmatrix} 0 & \dot{\epsilon}_{12} & 0 \\ \dot{\epsilon}_{12} & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix} \quad (1)$$

⁴ M. Reiner, *Am. J. Math.* **67**, 350 (1945).

⁵ R. S. Rivlin, *Proc. Roy. Soc. (London)* **A193**, 260 (1948).

⁶ R. S. Rivlin, *Proc. Roy. Soc. (London)* **A200**, 168 (1950).

⁷ R. S. Rivlin, *Trans. Faraday Soc.* **45**, 739 (1949).

⁸ F. H. Garner, A. H. Nissan, and G. F. Wood, *Phil. Trans. Roy. Soc.* **A243**, 37 (1950).

⁹ F. J. Padden and T. W. De Witt, *J. Appl. Phys.* **25**, 1086 (1954).

¹⁰ H. Fromm, *Z. angew. Math. u. Mechanik* **28**, 43 (1948).

¹¹ A. S. Lodge, *Trans. Faraday Soc.* **52**, 120 (1956).

^{11a} A. S. Lodge, Paper read at 9th Intern. Congr. Appl. Mech. Brussels (1956).

^{11b} Lodge's prediction that in a flowing viscoelastic material the stress tensor and the refractive index tensor have the same principal directions and anisotropies in proportion has been confirmed experimentally by Philippoff.^{11c, 11d}

^{11c} W. Philippoff, *J. Appl. Phys.* **27**, 984 (1956).

^{11d} W. Philippoff, *Nature* **178**, 811 (1956).

¹² J. G. Oldroyd, *Proc. Roy. Soc. (London)* **A200**, 523 (1950).

¹³ J. G. Oldroyd, *Quart. J. Mech. Appl. Math.* **4**, 271 (1951).

¹⁴ M. Mooney, *J. Colloid Sci.* **6**, 96 (1951).

¹⁵ M. Mooney, *J. Appl. Phys.* **24**, 675 (1953).

¹⁶ M. Mooney, private communication.

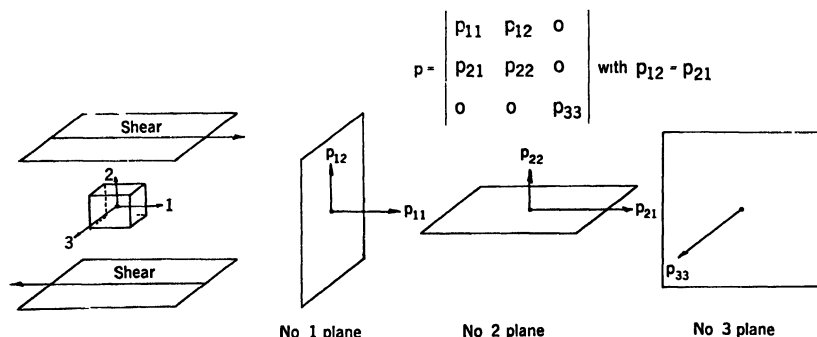


FIG. 2. Resolution of pressures at a point in laminar shear.

where $\dot{\epsilon}_{12}$ is the rate of shear as usually defined.

The stress, p ,^{16a} at any point in the liquid can be resolved into 9 components, p_{jk} , thus:

$$p = \begin{vmatrix} p_{11} & p_{12} & p_{13} \\ p_{21} & p_{22} & p_{23} \\ p_{31} & p_{32} & p_{33} \end{vmatrix} \quad (2)$$

The terms in which $j = k$ are normal stresses and do not contribute to the work done on the liquid. The terms in which $j \neq k$ are shearing stresses. This expression can be simplified since p_{jk} has to satisfy certain conditions of equilibrium and symmetry such that $p_{jk} = p_{kj}$. Further, in a torsional shearing action as employed in the rheogoniometer (described below), there is a digonal symmetry about the No. 3 axis so that $p_{23} = p_{32} = 0$. Equation (2) then reduces to

$$p = \begin{vmatrix} p_{11} & p_{12} & 0 \\ p_{12} & p_{22} & 0 \\ 0 & 0 & p_{33} \end{vmatrix} \quad (3)$$

Later Weissenberg¹⁷ introduced an assumption that, at least as a first approximation, there should be a similitude in the anisotropy of the stress and of the recoverable strain. For planes of any orientation in any flow state, the shearing forces and the elastically recoverable part of the shear

^{16a} The notation adopted here, in contrast to that previously used by Roberts, is the more usual one in that a pull in the liquid has a positive sign and a push a negative sign. This convention has the advantage that it leads to positive values for the elasticity and viscosity but the disadvantage that it represents real pressures (e.g., those balanced by the liquid head in the capillary gages) as *negative* pressures.

The term pressure is used throughout as an abbreviation for pressure density at a point per unit area across a definite plane.

¹⁷ K. Weissenberg, *Nature* **159**, 310 (1947).

strain should have their maxima along the same directions. From this he deduced that for elastic and viscoelastic materials

$$\frac{p_1 - p_2}{\lambda_1^2 - \lambda_2^2} = \frac{p_2 - p_3}{\lambda_2^2 - \lambda_3^2} = \frac{p_3 - p_1}{\lambda_3^2 - \lambda_1^2} = G \quad (4)$$

where p_k are the main values of the stress, λ_1 the main elongation ratios of the recoverable strain, and G a kind of elasticity modulus which may depend on any or all of the invariants of the stresses, strains, and their time derivatives. A special case of this law has been derived by Treloar¹⁸ from a molecular model of rubber.

For a laminar shearing motion equation (4) can be written

$$\begin{vmatrix} p_{11} - p_{22} & p_{12} & 0 \\ p_{12} & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix} = G \begin{vmatrix} \gamma_e^2 & \gamma_e & 0 \\ \gamma_e & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix} \quad (5)$$

where γ_e is the shear component of the recoverable strain and is related to λ by

$$\lambda^2 - 1 = \begin{vmatrix} \gamma_e^2 & \gamma_e & 0 \\ \gamma_e & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix} \quad (6)$$

Weissenberg has also shown¹⁹ that the same equations may be deduced from an alternative assumption that planes will exhibit the same normal forces per unit area if they have undergone the same normal displacements per unit area from their parallel neighboring planes. This applies approximately to the total movement as well as to the recoverable part of it.

For the determination of the shearing component of stress in a viscoelastic fluid in laminar flow, almost any of the conventional viscometric methods can be adapted since the shear stress at a point in a flowing material is determined already by the motion in the immediate vicinity. It is proposed to consider here only those experimental methods which attempt to determine some or all of the other components of stress, and to this end comparatively little work has so far been done.

Early quantitative measurements of normal stresses were those of Russell and Weissenberg²⁰ who measured both the total normal force acting on a plate which formed one boundary of the gap containing the material under test and also the distribution of pressures across this plate by the introduction of a series of capillary gages. At about the same time, Garner *et al.*^{8, 21}

¹⁸ L. R. G. Treloar, "The Physics of Rubber Elasticity." Oxford Univ. Press, New York, 1949.

¹⁹ K. Weissenberg, *Proc. 1st Intern. Rheol. Congr., Scheveningen* p. I-29 (1948).

²⁰ R. J. Russell, Ph.D. thesis, London University (1946).

²¹ F. H. Garner and A. H. Nissan, *Nature* **158**, 631 (1946).

were using a new arrangement consisting of a flat-bottomed cup driven in rotation about its axis with a stationary, centrally mounted circular plate a short distance above the bottom of the beaker. The normal stress on this plate was measured by means of a series of manometer tubes connecting with small portholes at various radial distances. In order to measure the normal pressure in all directions, certain of these gages projected into the gap containing the material and must certainly have produced unsatisfactory disturbances of the flow. These authors also used a series of Couette-type instruments in which the inner member took various forms. Pressures at a series of points on the surface of the inner member were measured, and it was claimed that normal pressure differences were observed only when differences in the rates of shear at various points were also present.

A similar arrangement constructed with greater precision has been described by Rivlin and Greensmith.^{22, 23} The temperature was controlled to within $\pm 0.1^\circ\text{C}$. and the geometry of the gap could be varied, but the use of a parallel gap in which the rate of shear varied from point to point introduced an additional complication. It is considered that the boundary conditions in the last two sets of experiments were such that no clear conclusions can be drawn from the experimental results.

Rivlin and Greensmith considered their observations to provide an experimental check on Rivlin's theory. Subsequent experiments by Roberts^{24, 25} with the same materials in the better defined conditions of the rheogoniometer are in agreement with the theoretical predictions of Weissenberg and Lodge and against those of Rivlin. In particular the negative pressures demanded by Rivlin's theory were not observed^{25a} (see Plate I).

Ward and Lord²⁶ have investigated the way in which the geometry of the system affects a secondary normal pressure effect, the climbing of a viscoelastic fluid up a central rod or cylinder immersed in it when the outer container is rotated. They measured both the torque and the vertical thrust on the inner cylinder, but here again the boundary conditions were varying continuously so that there is no simple method of evaluating the stress distribution from these measurements.

Padden and DeWitt⁹ have described a semiquantitative apparatus in which the height above the free surface to which a liquid rises in a hollow rotating central cylinder is measured as a function of the rate of shear.

²² R. S. Rivlin and H. W. Greensmith, *Nature* **168**, 664 (1951).

²³ H. W. Greensmith and R. S. Rivlin, *Phil. Trans. Roy Soc.* **A245**, 399 (1953).

²⁴ J. E. Roberts, unpublished Ministry of Supply report.

²⁵ J. E. Roberts, *Proc. 2nd Intern. Rheol. Congr. Oxford*, p. 91 (1953).

^{25a} The experiments have been fully discussed with Greensmith. He is of the opinion that the discrepancy between the foregoing experiments and those of Greensmith and Rivlin may be due to extraneous edge effects in the latter case.

²⁶ A. F. H. Ward and P. Lord, *Proc. 2nd Intern. Rheol. Congr., Oxford*, p. 214 (1953).

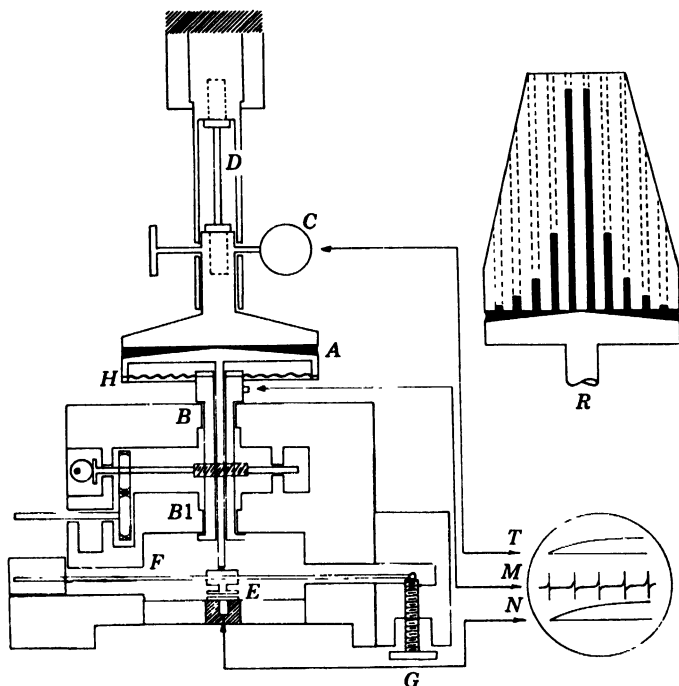


FIG. 3. The Roberts-Weissenberg R8 rheogoniometer

Weissenberg²⁷ has formulated the principles of a testing instrument which he has termed the "rheogoniometer" since, in its ideal form, it would yield a complete specification of rheological data by measuring at every point in the flowing material the development in time of the stresses and strains round the full solid angle in space. The preliminary development of this instrument has been reported by Russell²⁰ and Freeman²⁸ and a modified form for the study of molten plastics has been described by Pollett and Cross.²⁹ Further substantial improvements have been made by Roberts and there are now in existence several instruments of the basic design illustrated in Fig. 3. A number of these have been built by Farol Scientific Instruments, Ltd., Bognor Regis, England.

The basis of the instrument is a slide (not shown) mounted vertically on a steel base. The material under test is held in the gap, *A*, whose form can be varied. The form illustrated is one of the cone-and-plate type introduced by Mooney,³⁰ in which the rate of shear across the gap is constant to within

²⁷ K. Weissenberg, *Proc. 1st Intern. Rheol. Congr., Scheveningen* pp. II-114 (1948).

²⁸ S. M. Freeman, *Rept. General Conf. British Rheologists' Club* p. 68 (1946).

²⁹ W. F. O. Pollett and A. H. Cross, *J. Sci. Instr.* **27**, 209 (1950).

³⁰ M. Mooney and R. H. Ewart, *Physics* **5**, 350 (1934).

$\pm 2\%$. The lower cone can be either rotated continuously, or given an oscillatory motion of variable amplitude, or the oscillatory motion can be superimposed on the continuous rotation so that the material may be examined by vibrational methods in any state of shear. Both rate of rotation and frequency can be varied continuously over a wide range by gearbox and motor controls. In the earliest experiments, the upper boundary of the gap was formed by the capillary head, R . This consists of two glass plates fused very accurately in the form of an inverted T and pierced through the upright of the T with a series of holes. The lower plate is machined to optical limits. The hydrostatic head of the liquid in each tube is taken as a measure of the normal pressure at that point. The capillary head is also pivoted about its vertical axis so that the tangential stress, p_{12} , can be measured by balancing it against a calibrated spring.

Using an apparatus of this type, Roberts^{24, 25} has described an experimental investigation into the stress distribution in a series of flowing viscoelastic materials (solutions of rubber in xylene, aluminum laurate in petrol, and polyisobutylene in *o*-dichlorobenzene) in which all the pressure components were measured. The materials were sheared in gaps of various shapes. p_{22} pressures were determined by balancing them against the height of liquid in the capillary gages. p_{33} pressures were measured by balancing them against pressures exerted by standard Newtonian liquids and, by making these observations at various radii, r ($= 0$ at the center and R at the free boundary) $\delta p_{33}/\delta \ln (r/R)$ was determined. p_{11} pressures were then determined by applying the principle of the equilibrium of forces, according to which they must be in balance (for negligible forces of gravity and inertia) with the experimentally determined quantities, p_{22} , p_{33} , and $\delta p_{33}/\delta \ln (r/R)$ by the equation

$$p_{11} = \frac{\delta p_{33}}{\delta \ln (r/R)} + 2p_{33} - p_{22} \quad (7)$$

Roberts found that in all the systems he investigated

$$p_{22} = p_{33} \quad (8)$$

$$p_{11} - p_{22} = p_{11} - p_{33} = \frac{\delta p_{33}}{\delta \ln (r/R)} \quad (9)$$

The gap must be sufficiently small that the velocity gradient across it is linear; this was checked within the liquid by observing through the glass head, R , with a depth microscope the velocities of small included particles. Cinéphotographs were also taken of the movement of aluminum particles in the edge of Couette-type gaps.

Plate I illustrates the pressure distribution in a tetralin solution of a

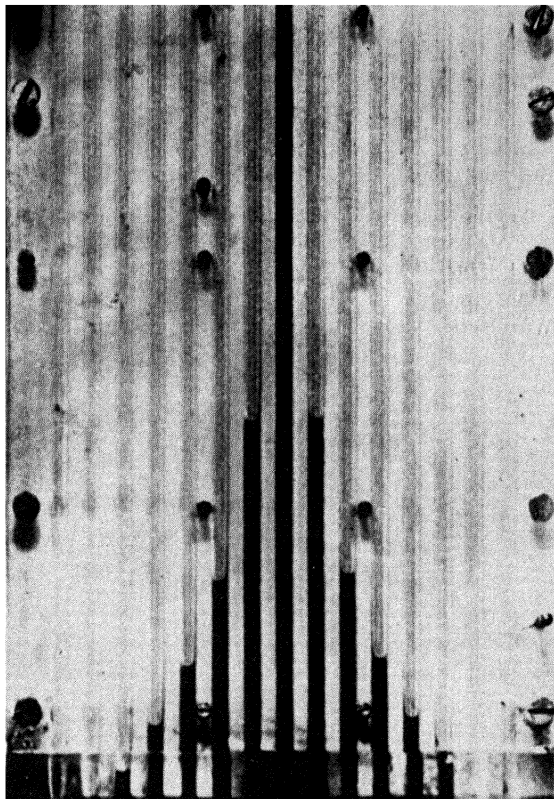


PLATE I. Normal pressure distribution in an 8% solution of polyisobutylene (Op-panol B200) in tetralin.

polyisobutylene sheared in a conical gap and dyed for ease of photography. The equivalence of p_{22} and p_{33} at the free boundary, after correction for surface tension effects, is observed directly and is confirmed by extrapolation to the rim of the measured distribution.

These experimental findings are predicted by the theories of Weissenberg¹⁻³ and Lodge¹¹ but are not compatible with the theories of Garner *et al.*,⁸ Fromm,¹⁰ Padden and DeWitt,⁹ or Reiner⁴ and Rivlin⁵⁻⁷ except in the trivial case where $\delta p_{33}/\delta \ln r/R \rightarrow 0$ when all the theories become indistinguishable. For all values of $\delta p_{33}/\delta \ln r/R > 10^2$ dynes/cm.², the disagreement is beyond the limits of experimental error. There is no indication that, *for these liquids*, the agreement is improved between experiment and Weissenberg's or Lodge's theory by the introduction of an additional constant as suggested by the theory of Mooney.¹⁴⁻¹⁶ Certain special cases of the theories of Mooney and Oldroyd^{12, 13} are consistent with these results.

With a standardized notation, the predictions of these various theories can be summarized as follows:

$$\text{Weissenberg:} \quad p_{11} - p_{22} = p_{11} - p_{33} = \frac{\delta p_{33}}{\delta \ln (r/R)} = p_{12} \gamma_e$$

(where γ_e is the shearing component of recoverable strain)

$$\begin{aligned} \text{Garner, Nissan, and Wood:} \quad p_{11} - p_{33} &= p_{33} - p_{22} \\ &= p_{22} - p_{11} = \frac{\delta p_{33}}{\delta \ln (r/R)} = 0 \\ (\text{i.e., } p_{11} &= p_{22} = p_{33} = 0) \end{aligned}$$

$$\text{Reiner and Rivlin:} \quad 2(p_{22} - p_{33}) = 2(p_{11} - p_{33}) = \frac{\delta p_{33}}{\delta \ln (r/R)}$$

$$\begin{aligned} \text{Mooney:} \quad \frac{2H}{H+G}(p_{11} - p_{33}) &= \frac{2H}{H+G}(p_{22} - p_{33}) = \frac{H}{G}(p_{22} - p_{11}) \\ &= \frac{\delta p_{33}}{\delta \ln (r/R)} \end{aligned}$$

(H and G are constants)

$$\text{Fromm:} \quad p_{11} > p_{22} \neq p_{33}$$

$$\text{Padden and DeWitt:} \quad p_{11} > p_{22} \neq p_{33}$$

$$\text{Lodge:} \quad p_{23} = p_{31} = 0, \quad p_{22} - p_{33} = 0, \quad p_{11} - p_{22} \propto \dot{\epsilon}^2$$

An investigation of the variation with the rate of shear of the normal and tangential stresses in polyethylene has been reported by Pollett.^{31, 32} He also observed that $p_{22} = p_{33}$ in this system within the limits of experimental error.

It follows from equation (5) that

$$G = \frac{\rho_{12}^2}{p_{11} - p_{22}} \quad (10)$$

$$\gamma_e = \frac{p_{11} - p_{22}}{p_{12}} \quad (11)$$

The apparent viscosity, η , is defined in the usual manner by the ratio of the experimentally measured quantities, p_{12} and $\dot{\epsilon}_{12}$, and in most viscoelastic materials it is observed to fall with increasing rate of shear, $\dot{\epsilon}_{12}$. This drop is normally attributed to the onset of a structural breakdown under

³¹ W. F. O. Pollett, *Brit. J. Appl. Phys.*, **6**, 199 (1955).

³² W. F. O. Pollett, *Proc. 2nd Intern. Rheol. Congr. Oxford*, p. 85 (1953).

the action of the shearing motion but may in fact be partly or wholly a geometrical effect resulting from a gradual divergence with increasing recoverable strain of the main directions of stress and strain velocity. When this occurs, only a part of the stress is effective in overcoming the viscous resistance. In order to determine whether or not a true structural breakdown is occurring, it is necessary to compensate for this angular deviation and to calculate an idealized viscosity coefficient, $\eta_{\max}$, which would be obtained if the whole of the stress were effective in overcoming viscous resistance, that is, if the stress and the strain velocity still had the same main directions. It can be shown that the angle, α , between the major axes of stress and strain velocity is given by $\cotan 2\alpha = 2\gamma$, whence

$$\eta_{\max} = \eta \sqrt{1 + \frac{\gamma^2}{4}} = \eta \sqrt{1 + \left(\frac{p_{11} - p_{22}}{2p_{12}} \right)^2} \quad (12)$$

This correction depends only on the directions of the main axes of the stress ellipsoid and not on their magnitudes so that it is independent of the choice of stress quadric. $\eta_{\max}$ could, at least in theory, be determined directly by subjecting the material to an irrotational shear (such as that described in Section III).

Figure 4 provides a striking illustration of the importance of this correction in certain cases. The material is a solution of aluminum laurate in petrol peptized with ethoxyethyl alcohol, and the graphs are obtained by recalculation of the data of Russell.²⁰ Over the initial part of the graph, the geometrical correction fully compensates for the observed drop in η , and

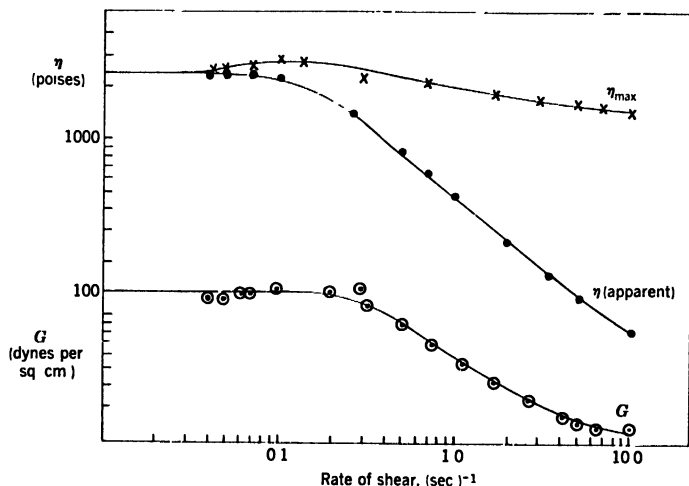


FIG. 4. η , $\eta_{\max}$, and G as functions of the rate of shear (7% Al. laurate in petrol peptized with ethoxyethyl alcohol).

there may even be a slight increase in the true resistance to deformation. The subsequent falling-off of both $\eta_{\max}$ and G may indicate the onset of a true structural breakdown. Thus, if only the tangential stress is measured, not only is some of the available information not collected but that which is obtained cannot be correctly interpreted.

No such angular correction to G is required as both the stress and the recoverable strain have the same main directions at all times.

The definition of η as the constant governing the proportionality of stress and strain velocity is not very satisfactory since, in the general case, this proportionality will be different in different directions in space. η is better regarded as a constant governing the dissipation of energy during flow (energy dissipated per second per unit volume = p_{12}^2/η). From a knowledge of η and G at any given rate of shear, relaxation times, τ ($= \eta/G$) and $\tau_{\max}$ ($= \eta_{\max}/G$) can be calculated. Pilpel^{33, 33a} has studied the variation of these parameters with chemical composition in a series of aqueous soap gels.

For a given material, the logarithmic distribution of normal pressures across the top plate of a conical gap and the equality of p_{22} and p_{33} at the free boundary have first to be established for extreme conditions of flow. For intermediate experiments, it then suffices to measure the total normal pressure on the plate. It can be shown that the relation between this total normal pressure, p , and $p_{11} - p_{22}$ is given by

$$p_{11} - p_{22} = p_{11} - p_{33} = \frac{\delta p_{33}}{\delta \ln (r/R)} = \frac{\delta p_{22}}{\delta \ln (r/R)} = \frac{2p}{\pi R^2} \quad (13)$$

For this purpose, the arrangement on the left-hand side of Fig. 3 is used. The upper plate is constrained from moving vertically and the lower cone is rotated through a special diaphragm, H , which allows a rigid rotational movement to be imparted to the cone but leaves it free to move for a very small distance along the vertical axis. The total normal force, N , is transmitted by a rod to the spring condenser gage, E , F , where it can either be recorded or, if static, measured by a null method using the micrometer screw, G . Tangential stresses, T , are measured by recording the displacement of the condenser gage, C , against the torsion bar, D . In addition to their virtually instantaneous operation, condenser gages have the further advantage that the actual physical displacements may be made very small. This is an approach to the ideal of a null method of measurement. The sensitivities of both condenser gages, C and E , can be varied over wide limits by the use of interchangeable springs, F , and torsion bars, D . The

³³ N. Pilpel, *Trans. Faraday Soc.* **50**, 1369 (1954).

^{33a} N. Pilpel, *Trans. Faraday Soc.* **51**, 1307 (1955).

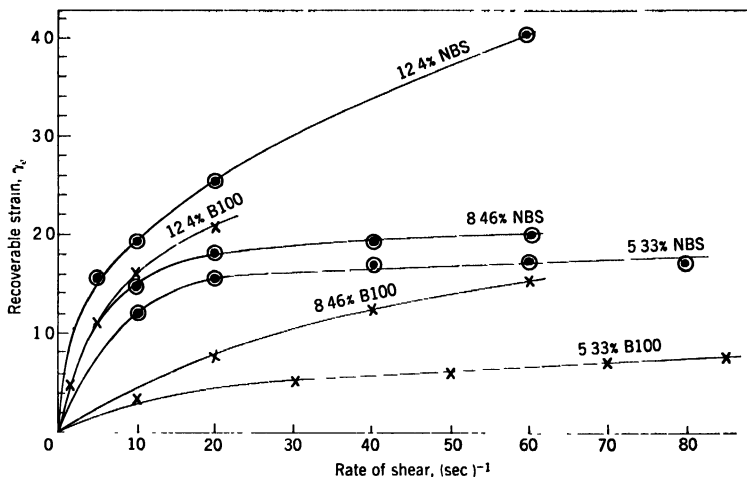


Fig. 5. Recoverable strain as a function of the rate of shear (*m*-xylene solutions of polyisobutylenes).

proximity meter incorporates an additional sensitivity control. The very small capacity changes involved are measured by modified Fielden Model PM4 proximity meters (differential capacity bridges). By coupling these to a double beam cathode-ray oscilloscope with photographic recording, Jobling and Roberts have made an extensive series of measurements of the flow properties of solutions of polyisobutylene in *m*-xylene of varying concentration and molecular weight. Figure 5 shows the variation of the recoverable strain with the rate of shear in some of these systems. The N.B.S. sample is that distributed by Dr. R. S. Marvin of the National Bureau of Standards for a cooperative study and the B100 is an unfractionated commercial product (Oppanol). Their viscosity average molecular weights are, respectively, 1.35×10^6 and 1.3×10^6 . Concentrations are in solute/solution percentages.

The addition of an electromagnetic clutch enables observations to be made of the build-up and decay of the normal and tangential stresses at various predetermined accelerations. These observations are in qualitative agreement with a theoretical prediction of Lodge¹¹ that, in general, the normal stress will decay more slowly than the tangential one. An additional advantage of a clutch and a "hard" type of measurement is that materials which are particularly sensitive to temperature variation may be rapidly and accurately tested since the duration of the experiment may be cut down to 0.1 sec. This method is particularly suited to the testing of some printing inks with which, even in narrow gaps, it is difficult to dissipate the viscous heat at the required rate of shear.

2. OSCILLATORY MOTION

If a material is subjected to an oscillatory laminar shear of sufficiently small strain amplitude, information is obtained about the material in its *natural or ground state*.

It can be shown both experimentally and theoretically that the normal stress components vary with the *even* powers of the strain velocity, $\dot{\epsilon}$, whereas the tangential component of stress varies with the *odd* powers. In the region of the natural state, second and higher terms can be neglected and the normal stresses approximate to zero, whereas the tangential stress becomes linearly related to $\dot{\epsilon}$. Within this region, a large field of investigation has been covered by applying harmonically varying small strains at a series of frequencies and studying the resulting harmonic variation of the tangential and only component of the stress.

The question of what constitutes a sufficiently small strain can be settled experimentally, and has been found to vary with a number of factors including frequency. The two criteria available are (a) the absence of any normal component of stress and (b) the independence of both the measured phase difference between stress and strain, and of the ratio of their amplitudes with respect to the imposed strain amplitude. Mathematically the strain is defined as small if its square is negligible compared with the experimental accuracy. This definition may rule out strains which the two above criteria would admit.

In vibrational tests on viscoelastic materials at large strain amplitudes, the anisotropy of the sheared state shows up in time as well as in space. According to Weissenberg's theory, the normal components of stress should vibrate with twice the frequency of the shear components, and this has been verified experimentally by Weissenberg and Freeman.³⁴

Many authors have assumed that, in the region of the natural state, the stress and its time derivatives are linearly related to the strain and its time derivatives by an equation of the general form (cf. ref. 35)

$$\pi_0 p + \pi_1 \dot{p} + \pi_2 \ddot{p} \cdots = \sigma_0 \epsilon + \sigma_1 \dot{\epsilon} + \sigma_2 \ddot{\epsilon} \cdots \quad (14)$$

where $p = p_{12}$ and $\epsilon = \epsilon_{12}$ but the subscripts are generally dropped since there are now no spatial complications. The coefficients are constants characteristic of the material and for a material which is predominantly liquid, $\sigma_0 = 0$.

Equation (14) contains, as special cases, the mechanical equations of state of the

³⁴ K. Weissenberg and S. M. Freeman, *Nature* **161**, 324 (1948).

³⁵ T. Alfrey, "Mechanical Behaviour of High Polymers." Interscience, New York, 1948.

Hookean solid: $\pi_0 p = \sigma_0 \epsilon$

Newtonian liquid: $\pi_0 p = \sigma_1 \dot{\epsilon}$

And a Maxwell body: $\pi_0 p + \pi_1 \dot{p} = \sigma_1 \dot{\epsilon}$

A four-term equation which may be written

$$\pi_0 p + \pi_1 \dot{p} = \sigma_1 \dot{\epsilon} + \sigma_2 \ddot{\epsilon}$$

has been proposed by Oldroyd^{12, 13} for certain materials.

If a series of stationary vibrational states is now set up in the material, equation (14) may be written

$$p(\pi_0 + (-i\omega)\pi_1 + (-i\omega)^2\pi_2 + \cdots + (-i\omega)^n\pi_n) = \epsilon(\sigma_0 + (-i\omega)\sigma_1 + (-i\omega)^2\sigma_2 + \cdots + (-i\omega)^n\sigma_n) \quad (15)$$

$$\text{since } p = p_A e^{-i(\omega t - p_\phi)} \quad (16)$$

$$\dot{p} = (-i\omega)p_A e^{-i(\omega t - p_\phi)} = (-i\omega)p \quad (17)$$

$$p = (-i\omega)^n p_A e^{-i(\omega t - p_\phi)} = (-i\omega)^n p \quad (18)$$

and similarly for ϵ (where p_A and ϵ_A are the amplitudes and p_ϕ and ϵ_ϕ the phases of the stress and strain, respectively).

Equation (15) can be written

$$p = \Gamma(\omega)\epsilon \quad (19)$$

where

$$\Gamma(\omega) = \frac{(\sigma_0 + (-i\omega)\sigma_1 + (-i\omega)^2\sigma_2 + \cdots + (-i\omega)^n\sigma_n)}{(\pi_0 + (-i\omega)\pi_1 + (-i\omega)^2\pi_2 + \cdots + (-i\omega)^n\pi_n)} \quad (20)$$

$\Gamma(\omega)$ is termed the complex modulus of elasticity and is a function of the frequency and the angular velocity, ω . From the knowledge of Γ as a function of ω gained from vibrational experiments a series of harmonic solutions to equation (14) can be obtained, but Weissenberg has pointed out that vibrational experiments alone cannot uniquely determine the π and σ constants, since $\Gamma(\omega)$ defines only the ratio of the two characteristic functions (20) and not the functions themselves.

It is possible to write down equations of the form of (14) for materials having different π and σ values, but all having the same $\Gamma(\omega)$. These materials would behave identically in vibrational tests but would differ in their behavior in stress relaxation and strain retardation. The ideal relaxation experiment is regarded as one in which ϵ , $\dot{\epsilon}$, $\ddot{\epsilon} \cdots$ are all put equal to zero and the resulting changes of the stress with time are observed (and similarly for the strain retardation with stress and strain transposed in the foregoing). Satisfactory methods for doing either of these experiments have not yet been found, the chief difficulty being that, for example, a rapid movement to bring ϵ to zero is equivalent to a large $\dot{\epsilon}$ term.

With this view it can be seen that the complete characterization of a material in terms of π 's and σ 's requires a knowledge of the results of at least two of the three types of experiment: vibrational, stress-relaxation, and strain-retardation.

This concept is in conflict with the idea that the rheological behavior of a material can be completely described by the mechanical spectrum of relaxation or retardation times derived from either vibrational or stress-relaxation tests only. The fact that mechanical spectra obtained by these two methods do agree fairly well should be regarded as a physical fact rather than a confirmation of the mathematical theory. It is probable that the generalized Maxwell and Voigt models on which this theory is based are not adequate to describe all types of rheological behavior.

For materials whose behavior is predominantly liquid, it is advantageous to express the stress-strain relationship in terms of the reciprocal complex modulus, Λ , where

$$p\Lambda = \epsilon \quad (21)$$

and

$$\Lambda(\omega) = \frac{\pi_0 + (-i\omega)\pi_1 + (-i\omega)^2\pi_2 + \cdots + (-i\omega)^n\pi_n}{\sigma_0 + (i\omega)\sigma_1 + (-i\omega)^2\sigma_2 + \cdots + (-i\omega)^n\sigma_n} \quad (22)$$

Λ can be determined experimentally from the equality

$$\Lambda = \Lambda_A e^{i\Lambda_\phi} = \frac{1}{\Gamma} = \frac{1}{\Gamma_A e^{i\phi}} \quad (23)$$

where

$$\Lambda_A = \frac{1}{\Gamma_A} = \frac{\epsilon_A}{p_A} \quad (24)$$

and

$$\Lambda_\phi = -\Gamma_\phi = \epsilon_\phi - p_\phi \quad (25)$$

At any given frequency, the experimentally determined quantities are the amplitude ratio of strain and stress, ϵ_A/p_A and the phase difference between them, $\epsilon_\phi - p_\phi$.

Additional restrictions on the experimental technique are that the gap size should be small compared with the wavelength of the mechanical wave propagated through the material and that the movement from which p_A is determined should be very small compared with ϵ_A . (In theory it should be zero.)

For a physicochemical interpretation and for comparison with the results of continuous flow tests, it is convenient to express the results in the form of dynamical moduli of viscosity and elasticity as functions of frequency.

The definition of these moduli can be deduced from a calculation of the work done per second and per unit volume and a division of the work into free energy, ϕ , according to an elastic potential and the work of the dissipated energy, H , given out as heat to an isothermal bath. That is,

$$p \cdot \dot{\epsilon} = \frac{d\phi}{dt} + \dot{H} \quad (26)$$

In harmonic shear, the work of the free energy as well as of the dissipated energy will, in general, be different from zero, whereas in the stationary states of continuous unidirectional flow, the work of the free energy, though not necessarily the free energy itself, is always equal to zero, as the whole of the external work done on the material is dissipated as heat. If these energies are expressed in terms of stress (since strain has little meaning in liquid), then

$$p \cdot \dot{\epsilon} = \frac{d}{dt} \left(\frac{p^2}{2G} \right) + \frac{p^2}{\eta} \quad (27)$$

where

$$\frac{1}{G} = \Lambda_A \cos \Lambda_\phi \quad (28)$$

and

$$\frac{1}{\omega\eta} = \Lambda_A \sin \Lambda_\phi \quad (29)$$

At sufficiently low frequencies η and G approach constant values, and in this region, any viscoelastic material approximates to a Maxwell body characterized by a single shear elasticity and a single viscosity. For those materials which have been tested by both vibrational and continuous-flow techniques, these limiting values agree with those obtained from continuous flow measurements extrapolated to zero rate of shear.

Vibrational methods have been very widely used for the mechanical testing of materials because of the applicability of the technique to the whole range of consistencies from solid to liquid. Ferry³⁶ has recently given an excellent extensive review of the subject.

The Roberts-Weissenberg rheogoniometer can be used for vibrational testing since the lower cone can be given a sinusoidal motion of varying frequency and amplitude. The resulting phase and amplitude of stress can be followed by the condenser gage, C (Fig. 3), coupled to the Fielden proximity meter and a cathode-ray oscilloscope as described above. The instrument can be geared down to as low a frequency as is desired and its

³⁶ J. D. Ferry, *Ann. Rev. Phys. Chem.* **4**, 345 (1953).

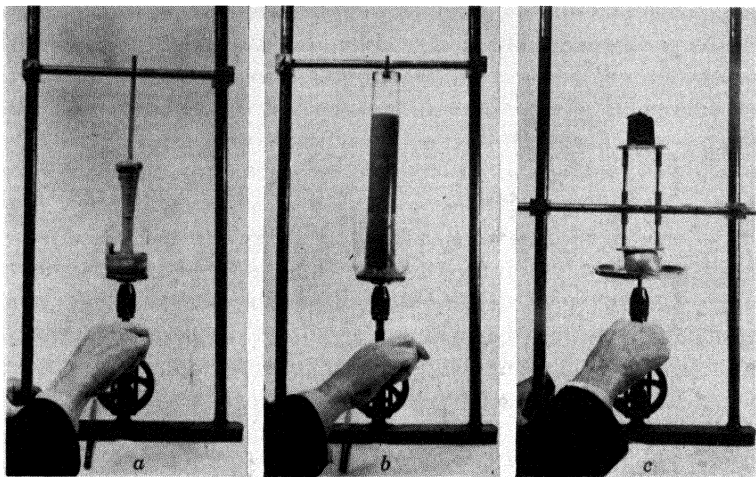


PLATE II. Normal pressure phenomena (outer container rotating). The flow patterns of the general (viscoelastic) liquids in a variety of gaps are compared with that of a special (Newtonian) liquid in Fig. 6.

present upper limit is about 50 c.p.s. The inertia of the upper plate has to be taken into account above about 10 c.p.s. As outlined above, a check on the absence of any normal component of stress provides confirmation that the amplitude of strain is sufficiently small.

Using instruments of this type, Roberts and Jobling have examined a series of polyisobutylene solutions of varying solute molecular weight and concentration and have obtained results in general agreement with those for similar systems reported by Ferry³⁷ and coworkers.

The experimental observation in these materials of a phase difference between stress and strain, varying with the frequency at any chosen strain amplitude, provides further evidence of the inapplicability to these systems of the Reiner-Rivlin assumption that stress and strain velocity are in phase under all conditions.

3. NORMAL PRESSURE EFFECTS

The primary cause of the "normal-pressure effects" or "Weissenberg effects,"^{19, 38, 39} observed in many flow experiments with viscoelastic materials is the presence of the ($p_{11} - p_{33}$) component of stress along the line of flow. If the geometry of flow has a cylindrical symmetry, this becomes a

³⁷ J. D. Ferry, I. Jordan, W. W. Evans, and M. F. Johnson, *J. Polymer Sci.* **14**, 261 (1954).

³⁸ K. Weissenberg and S. M. Freeman, *Proc. 1st Intern. Rheol. Congr. Scheveningen* p. II-12 (1948).

³⁹ K. Weissenberg, *Proc. Roy. Soc. (London)* **A200**, 183 (1950).

“hoop stress,” with a resulting tendency for the material to be constricted toward the cylindrical axis. Three simple experiments illustrating this effect are shown in Plate II.

The climbing of a viscoelastic material up a rod rotating in it provides a simple test for the presence of elastically recoverable strain. Even manual rotation is often sufficient.

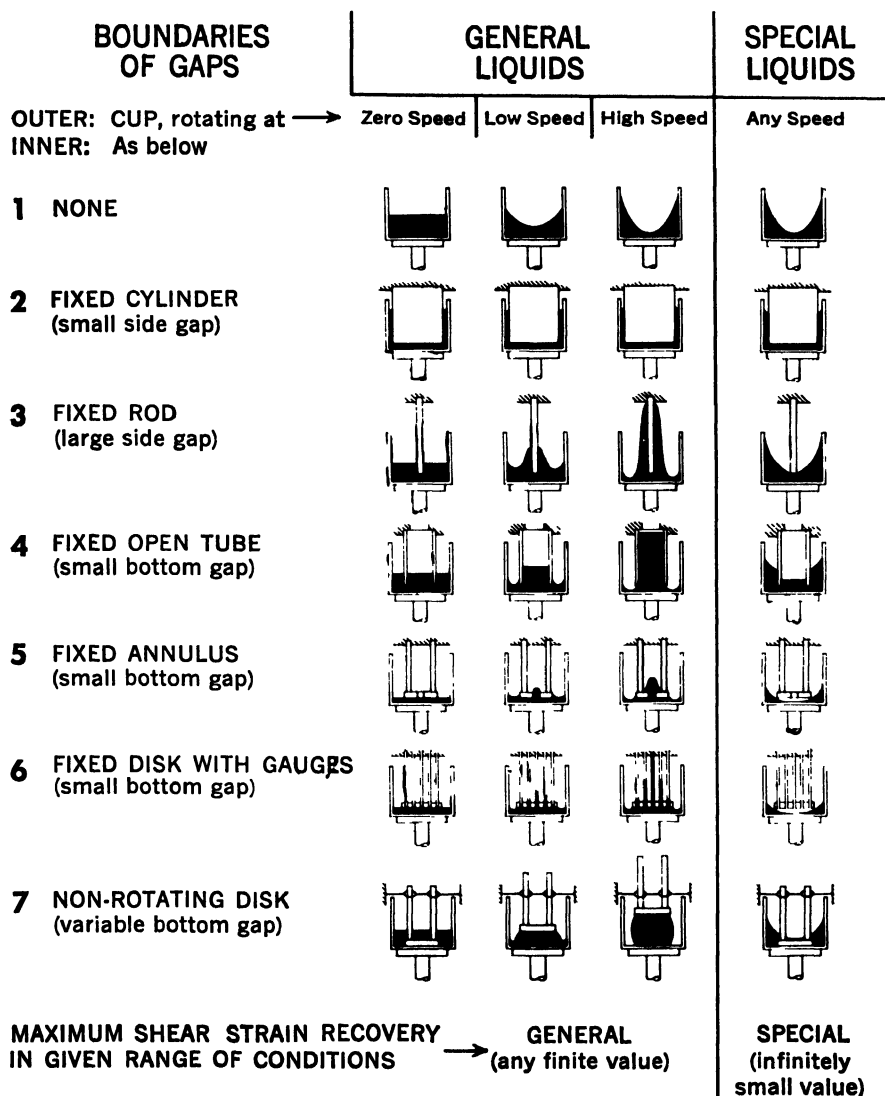


FIG. 6. Flow of liquids under actions of stationary shear in various gaps.

These effects have now been observed in a wide range of materials of both industrial and academic interest. They include many polymer solutions, rubber solutions (though not gutta-percha), molten polyethylene, aqueous gelatin solution in a narrow range of temperature and concentration just above the gel point, hydrocarbon gels of aluminum soaps, certain aqueous soap gels (for example, freshly prepared ammonium oleate solution), some printing inks, and bitumen.

Another type of normal pressure effect which, by contrast, is most marked in the nonelastic, purely plastic materials has been recognized recently. When a ball or flat cylinder of a purely plastic material is rolled between parallel plates under gentle pressure, it forms an elongated cylinder and, at the same time, the ends of the cylinder are sucked in as the action proceeds. In the most favorable case, the two depressions meet and a hollow tube is formed, the central hole being somewhat jagged. The phenomenon was observed by Williamson⁴⁰ in a particular type of Australian clay. He was also able to form a tube in warm plasticine and commented on the resemblance to the Mannesmann process in the steel industry for the production of steel tubes. (Normally a mandrel is used in this process but it has been shown not to be essential.)⁴¹ Weissenberg⁴² concluded that the effect should be a very general one and that the essential features are macroscopic, namely, the consistency of the material as defined by the stress-strain relation and the distribution in time and space of the stresses and strains induced by the rolling action. Moreover, he predicted that tube formation should occur in materials with little or no elastic recovery and that an annulment or even a reversion of the effect (a pressing-out of the ends of the cylinder) should be observed in materials with appreciable amounts of elastic recovery.

These predictions have been confirmed by Egan and Jobling⁴³ in an experimental investigation of a wide range of materials of varying structure and consistency. Plate III illustrates the different behavior of three typical materials. These are, from left to right:

(a) A sample of polyisobutylene with a molecular weight of about 20,000. This exhibits a high degree of elastic recovery and the ends become convex on rolling.

(b) A paste of asbestos fiber in Nujol (liquid paraffin). This is representative of the fibrous pastes in which the tube is formed by the opening up of radial cracks with little or no drawing-in of the ends.

(c) A paste of icing sugar in Nujol. This is typical of the smooth pastes which form tubes by the sucking-in of the ends.

⁴⁰ W. O. Williamson, *Am. J. Sci.* **252**, 129 (1954).

⁴¹ J. Gassen, *Arch. Eisenhüttenwesen* **127**, (1927-8).

⁴² K. Weissenberg, *Bull. Brit. Soc. Rheol.* **No. 43**, 6 (1955).

⁴³ M. J. Egan and A. Jobling, *Nature* **176**, 689 (1955).

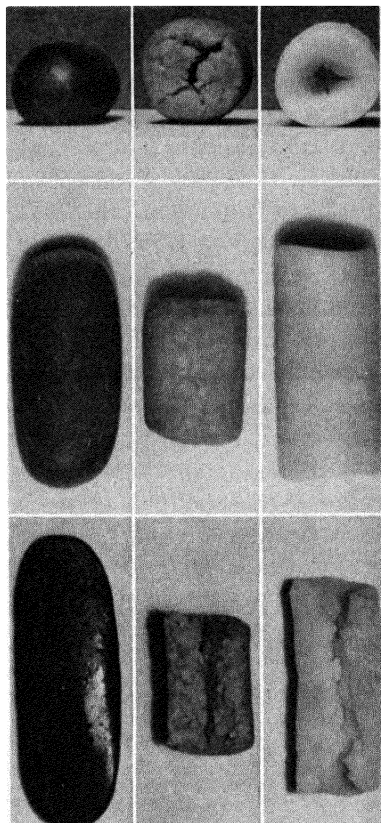


PLATE III. Behavior of different materials in a simple rolling action

Some manifestation of this effect, such as a tendency to suck in air, might be expected to occur in industrial milling or rolling processes with materials of suitable consistency such as concentrated clay or pigment suspensions.

4. FUTURE DEVELOPMENTS

It has been pointed out that the relation between stress and recoverable strain [equation (5)] from which the elasticity modulus, G , is determined in continuous flow experiments depends on an assumption which has not yet been tested by experiment. If, on the continuous shearing motion, an additional oscillatory shear could be imposed, G could be determined independently by the standard vibrational technique and compared with the value calculated at the same rate of shear from equation (10). This additional motion has now been incorporated into the drive of the latest rheogoniometers and experiments to this end are now in progress.

In addition, this movement appears to be fruitful for the study of dilatant materials which tend to flow out of the conical gap in continuous shear.^{44, 45} The well-known shear hardening of dilatant pastes (e.g., many printing inks) has been found to be relaxed by the application of mechanical vibration of sufficiently small amplitude, and a further study of these systems is proceeding.

The use of the glass capillary head (R in Fig. 3) is not always satisfactory for the measurement of normal pressure distributions, some materials taking an excessively long time to reach equilibrium in the tubes. A new type of head in which the normal pressure at a series of points on its surface can be measured with condenser gages has been constructed. It is hoped that this arrangement will enable the true pressure distributions to be determined in a number of materials which exhibit apparently anomalous patterns in the present apparatus.

Further improvements in the experimental method will be achieved by the introduction of automatic null methods of stress measurement. These will simplify the mathematical analysis; for example, corrections for the inertia and movement of the measuring plate will be eliminated. These null methods are particularly advantageous in stress relaxation experiments.

III. Goniometry of the Transition Region Between Flow and Rupture

1. INTRODUCTION

The study of materials in the transition between steady flow and rupture can throw light on a number of subjects of great practical importance such as the breaking and yield strength of materials, fatigue, solid friction, and boundary lubrication. A characteristic of the region is the appearance of perturbations which may range from submicroscopic dislocations of electrons, atoms or molecules to micro- and macroscopic irregularities, such as ridging, crazing, cracking, or twinning, and further on to complete rupture.

Many types of rupture tests are well known. Almost without exception these involve the use of rigid grips to impose the required mechanical action on the material with the resulting serious drawback that, at the boundary where the transmission of the action occurs, there is no deformation. This limits both the type of deformation which can be imposed and the extent to which one has control over it. Recently, Weissenberg has suggested that these objections could be overcome by imposing the mechanical action through a *deformable* boundary member situated in a *main plane* of the deformation, that is, on a plane in which the *maximum* changes in length are occurring. Elastic, viscoelastic, or purely viscous materials can be used for the boundary member, either alone or in conjunction with additional rigid

⁴⁴ R. McKennell, *Proc. 2nd Intern. Rheol. Congr. Oxford* p. 350 (1953).

⁴⁵ E. Bantoft, private communication.

members. In most of the preliminary experiments described here, this material is rubber, either natural or synthetic, in the form of plane sheets, tubes, or balloons.

A general method has been developed by which the chosen boundary material can be given any one of a wide variety of two- or three-dimensional rotational or irrotational shearing movements and the resulting developments in space and time of the stresses, strains, and disturbances propagated through the material under test can be observed *round the full solid angle in space*.

Despite the early state of development of the necessary instruments, a number of very interesting results have already emerged from the preliminary experiments. In addition to the much wider range of mechanical actions which can be applied by the new methods, it is clear from the regularity of the pattern of disturbances which is produced that the action is caused to occur in a very even fashion throughout the material under test. The pattern is so uniform that it should be amenable to quantitative measurement of the periodicity and direction of the disturbances. It is, therefore, possible by this method to obtain much more information about the rupture process than has hitherto been available. By the choice of suitable materials for the boundary members, substances as varied as dry powders, pastes of these in liquid media, polymer films, and vacuum-deposited metal films have been examined and their behavior has been found to exhibit some unexpected common features.

2. PRINCIPLES OF THE METHOD

The new method described here is a kinematic test in which the movement that the material under test is to undergo is prescribed. One then observes the development in time of the distribution round the full solid angle in space of the resulting disturbances to flow and, in the ideal case, also of the stress. The complementary dynamic method in which the stress would be prescribed and the resulting displacements and disturbances observed has not yet been developed.

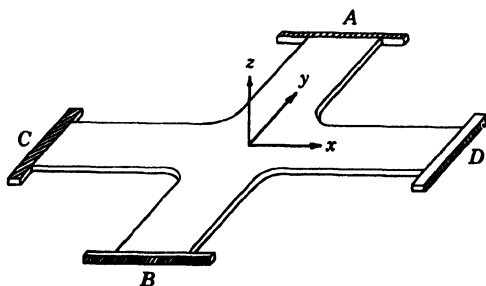


FIG. 7. Form of boundary member used in the general method of rupture testing

a. Irrotational Movements

Consider a boundary member cut from a sheet of an elastic material in the form described in Fig. 7. It is held by four rigid grips at *A*, *B*, *C*, and *D*, whose movement along the radial direction can be controlled. If the material is initially under tension, the dimensions *AB* and *CD* may be either expanded or contracted independently of one another and the ratio of the strains in the two directions and their development in time (for example, at a constant rate of strain, at a constant strain acceleration, with a harmonically varying strain, or with a reciprocating movement) can be varied at will. A certain area in the centre of the cross will undergo a homogeneous deformation; outward along the arms of the cross, the movement will become heterogeneous in a regular fashion that may be determined by ob-

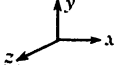
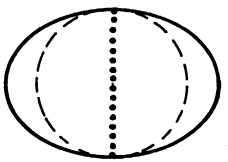
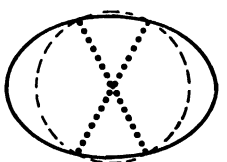
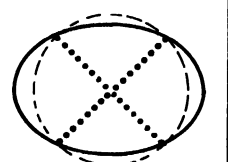
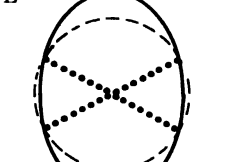
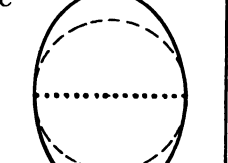
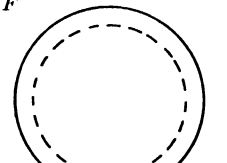
Axes				Axes			
<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>	
1	0	+1	<i>A</i> 	+1	$\frac{1}{2}$	$-\frac{1}{2}$	<i>D</i> 
+1	+1	0	<i>B</i> 	$-\frac{1}{2}$	+1	$-\frac{1}{2}$	<i>E</i> 
0	+1	+1	<i>C</i> 	$-\frac{1}{2}$	$+\frac{1}{2}$	1	<i>F</i> 
<i>G</i> (general)			Any one axis + 1	Other two axes 0 to 1 1 to 0 with sum = 1			

FIG. 8. Table of elongations and contractions occurring in typical pure shearing movements.

serving the deformation of a reference grid imprinted on the surface. With this arrangement, it is possible to produce in the central area the complete range of two and three-dimensional irrotational pure shears. This is better illustrated by a consideration of Fig. 8, which lists the elongations and contractions which occur in the elastic boundary material in a series of typical movements. The table is compiled for a small maximum strain of 1 arbitrary unit (positive for an expansion, negative for a contraction) in any one direction. The strain in the second direction is prescribed and that in the third direction is calculated from the other two on the assumption that the boundary material is incompressible. The accompanying diagrams illustrate the deformation that a circle marked on the material in its initial state (dashed line) would suffer in each of the movements. In all but *F*, it can be seen that there are certain lines in the strain geometry which do not change their length but only their direction during the movement ("lines of zero elongation") and these are shown dotted. Cases *A*, *B*, and *C*, and *D*, *E*, and *F*, respectively, correspond to the same two deformations viewed from three mutually perpendicular directions. Even in the intermediate cases *G*, it is possible to arrange that the boundary member is situated in any one of the three main planes of the three-dimensional movement. The changes from *A* to *C* and from *D* to *E* are, in practice, trivial as they correspond merely to a rotation of Fig. 7 through 90 deg. but they are included for clarity of discussion.

If now a thin film of the material to be examined is spread on the boundary member, the movement of the latter in the common surface is transmitted to it provided that the two adhere throughout the experiment. The transmission of the action is governed by the laws of the equilibrium of forces and of the preservation of continuity. It can be shown that, when the boundary lies in a main plane of the deformation, only stresses normal to and strains in the boundary plane are transmitted from one material to the other.

b. Rotational Movements

The most common rotational action is "simple" or laminar shear. It has been shown in Section II that the stress-strain geometry of laminar shear is complicated by the fact that not only do the main directions of stress and strain rotate in the material as the strain becomes large but they may also deviate from the main directions of their time derivatives. The discussion is therefore limited to the case of small strains where the directions of maximum contraction and extension and zero elongation may be taken as constant since this condition is likely to favor the formation of clear perturbation patterns. With this restriction, the laminar shearing movement then becomes identical with the type *B* movement of Fig. 7.

Some more complicated types of rotational shear are the subject of a continuing investigation.

3. EXPERIMENTAL TECHNIQUE

The method is undoubtedly capable of a large number of variations, developments, and applications and it is proposed to give only a brief account of the examples which have been investigated so far.

Whereas the strains are measured by the actual movement of a grid printed on the substrate, the stresses can be measured by the distortion of this grid from the position it would have taken had there been no test material applied. The stress normal to the substrate may be measured in principle by transferring this stress to a fluid.

A form of the general instrument has already been described but because of their experimental simplicity, it is frequently convenient to use other forms of boundary member, each of which can cover a certain limited range of deformations.

Type *F* movement (Fig. 7) can be produced by inflation and deflation of a balloon of sufficiently large radius. Greater variability is obtained by using a cylindrical balloon with an additional tension along its long axis.

If a disk, prepared by stretching rubber sheets in even tension across a circular wire frame, is given a slight extension or compression across a diameter, the deformation in the centre is of type *B*, with the sheet in the xy -plane. If the circle is first deformed into an ellipse and then given a similar movement, the movements along the x - and y -axes will not now be equal and opposite and their ratio will depend on the eccentricity of the initial ellipse.

If a long strip of elastic sheet is pulled along its greatest length (x -axis), the resulting deformation near the centre of the strip will correspond fairly closely to the type *D*. If the rigid grip holding the strip is orientated along the y -axis, then in the neighborhood of the grip, the deformation resulting from a pull along the x -axis corresponds to type *A* since there can be no movement in the y -direction. Thus there is a continuous transition from type *A* to type *D* as one proceeds from the grip toward the centre.

The ideal requirements of the boundary material are

- (i) It should not react chemically with the material under test.
- (ii) There should be no diffusion into or swelling of one material by the other.
- (iii) The two materials should adhere.
- (iv) The boundary material should deform uniformly without perturbation throughout the transition region where disturbances are appearing in the test sample.
- (v) When it is required to measure forces as well as movements, the resistance to flow in the boundary member should be small compared with that in the material under test.

The swelling of natural rubber by oils and many organic liquids renders

it unsuitable for the testing of many systems. Many synthetic rubbers have a better chemical resistance but their elastic extensibility is not always adequate. In quantitative tests, the possible production by the mechanical action of changes in temperature in the rubber has to be considered and counteracted, if necessary, by isothermal devices. These temperature changes remain negligible in vibrational experiments with small amplitudes over a wide range of frequencies since they are caused by the very small frictional heat of the rubber but in unidirectional deformations, considerable amounts of free energy are added to the heat content of the rubber in extension and subtracted in contraction. The associated temperature changes are then very noticeable.

In a few instances, other boundary materials have been used with success (for example, cellophane film as a substrate for vacuum-deposited aluminum) and one can envisage the possibilities of a number of others, such as a second, more ductile metal as a substrate for a thin film of a brittle metal.

Ideally, the material under test should be sandwiched between two parallel deformable boundaries to improve the homogeneity of the imposed action in the direction perpendicular to the sheet. In the preliminary experiments the second sheet has been omitted to facilitate observation. It is possible that its reintroduction might affect the present results.

4. PRELIMINARY RESULTS AND DISCUSSION

The most marked feature of the early results is the great clarity of both the direction and the periodicity of the rupture pattern which results from the much improved homogeneity of the imposed mechanical action and the similarities observed in the behavior of substances widely different in their chemical and physical properties. This latter point is well illustrated by Plate IV. These patterns were obtained by simple stretching of the materials deposited on rubber sheet (type *D*). From left to right, these are

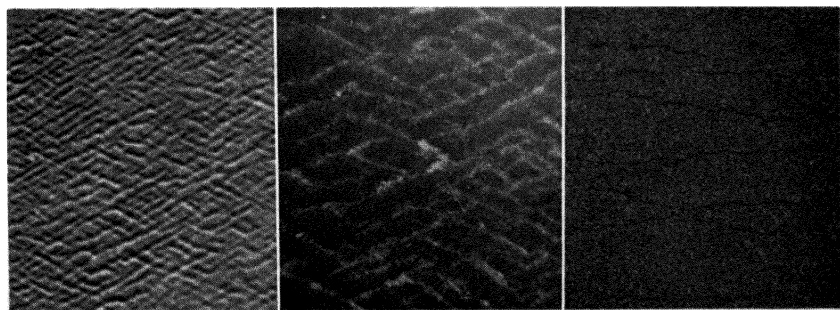


PLATE IV. A comparison of the rupture patterns produced in three different materials by a type *D* action.

corn flour powder, a paste of corn flour in decyl alcohol, and aluminum vacuum-deposited on rubber (for which we are indebted to Messrs. W. Edwards and Co., Crawley, England). The different angle appearing in the last picture may be due to distortion of the rubber by the metal.

The breakup pattern may be regarded as consisting of groups of waves with a statistically well-determined orientation, wavelength, and amplitude. In some instances, there is only a single group of waves with a wave front perpendicular to the direction of maximum contraction (e.g., polystyrene film) and/or elongation.

In general, there occur two or more intersecting groups of waves with wave fronts orientated either perpendicular to the directions of maximum elongation or contraction, and/or perpendicular to the directions of maximum shear, and/or parallel to the lines of zero elongation. The appearance of any one, two, or more groups, simultaneously or in different experiments with the same material, depends on the material and on the mechanical action imposed and can be varied deliberately. The final rupture often occurs in a complex fashion by the opening up of cracks not only along the troughs of the waves of the original perturbation pattern but also along the troughs of a new group of waves appearing at the instant of rupture.

In some materials, the result depends on the rate of deformation. In a sufficiently slow deformation, silicone bouncing putty is able to flow fast enough to maintain continuity and rupture does not occur even at very large strains. At somewhat faster rates of strain, the wave front of disturbances extends perpendicular to the direction in which the major change of length occurs.

To avoid the complications introduced by this time-dependent behavior, most of the investigations so far have been made with dry powders for which the rate of deformation seems to play little part. Plate V illustrates the behavior of corn flour powder in a reciprocating type *B* movement on the flexible disc. Here, as in Plate IV, the disturbances seem to be oriented parallel to the lines of zero elongation in the respective movements.

Although the same perturbation pattern is obtained whether the action is a reciprocating one about the initial position or a unidirectional movement, it has been established, particularly in experiments with powders, that much clearer patterns are obtained by the former technique. In a reciprocating shear, the pattern appears gradually over a period of time which increases as the amplitude of the movement is reduced. It is possible to develop the pattern slowly with a vibrational strain of very small amplitude, a strain many times smaller than that required to produce breakup in a single unidirectional action and the analogy between this behavior and the phenomenon of "fatigue" in metals is a striking one.

The new technique is particularly suited to the examination of dilatant

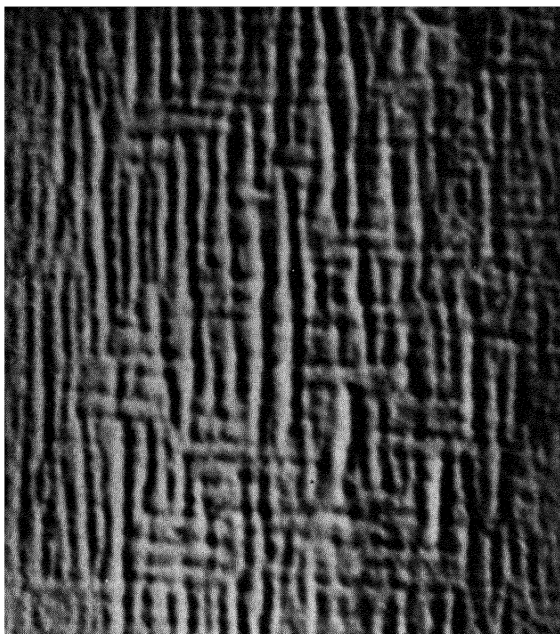


PLATE V. Corn-flour powder in a reciprocating action of type *B*

materials. Thus a highly dilatant corn flour-water paste remains very mobile and deforms freely with the boundary up to very large amounts of strain if the action is sufficiently slow. At a sufficiently high rate of strain, the surface of the material goes dry upon the imposition of a very small strain. If the action is stopped at this point, very rapid relaxation to a mobile fluid takes place but, if the apparently dry material is given a further small strain, rupture occurs, usually normal to the direction of maximum extension if the sample is sufficiently thick and along the lines of zero elongation if the sample is thinly spread. Qualitatively similar results have been obtained with a wide range of dilatant pastes (e.g., metal powders in mineral oils; glass beads in water; corn flour in glycol, glycerol, and decyl alcohol) but in certain of these, relaxation to a mobile fluid on cessation of the shear does not occur immediately as in the corn flour-water system (type I). Sometimes it occurs spontaneously but much more slowly (type II) and this may depend only on the increased viscosity of the liquid phase. In some other instances (type III), spontaneous relaxation does not occur at all, at least within a reasonable time, but the application of a small-amplitude reciprocating shear brings about a rapid return to the mobile state. Even the relaxation of type II materials is greatly speeded by this means. If the amplitude of the strain is increased beyond a certain amount,

relaxation does not take place. It has further been observed that, although a shiny liquid surface may be reformed by the relaxation process, healing of the cracks is not complete and a repetition of the shearing action results in the reappearance of the former cracks. A similar difficulty in annealing stress crazing in polymethyl methacrylate has been reported by Russell.⁴⁶

In materials of sufficient tensile strength, the imposition of the mechanical action through rigid grips frequently produces a distribution of stress and strain which is sufficiently homogeneous over a wide enough region in the material for a clear pattern of disturbances to appear, though the present method is superior in that it offers a much wider choice of the mechanical actions to be applied.

There occur in the literature a number of reports of the formation of perturbation patterns covering a wide range of substances. Most of the investigations refer to single materials or single groups of materials and the generality of these effects and the similarities in the behavior of materials differing greatly in their physical and chemical properties do not appear to have been commented upon previously. The occurrence of regular flow figures ("Luders' lines") has been observed in metals, marble, and wax,⁴⁷ and in tracing paper.⁴⁸ The occurrence of periodic patterns in powder films over which an air stream is passing in a vibratory laminar shearing movement^{49, 50} may be another example of the same phenomenon though the periodicity in this case has been attributed to vortex formation in the air flow. Stress-crazing in high polymers has been shown to be the result of the formation of similar regular patterns,^{46, 51, 52} the cracks in this instance occurring perpendicular to the direction of maximum tension and not at all in the direction of maximum compression. In physical metallurgy a number of examples are known of rupture occurring either in the direction of maximum tension or along shear planes.

All the materials which have been investigated by the present method are isotropic in their initial state. If the material under test is initially anisotropic, then some directions in the material will be weaker than others and these directional properties must be superimposed on those of the stress-strain geometry. Either set may predominate so that the direction in which rupture takes place in these materials may depend either on the geometry of the deformation or on the molecular or crystalline structure of the substance. In crystalline materials, it is probable that the latter set of

⁴⁶ E. W. Russell, *Nature* **165**, 91 (1950).

⁴⁷ A. Nadai, "Theory of Flow and Fracture of Solids." McGraw-Hill, New York, 1950.

⁴⁸ A. H. Nissan, private communication.

⁴⁹ M. Waller, *Nature* **166**, 961 (1950).

⁵⁰ M. Waller, *J. Sci. Instr.* **31**, 410 (1954).

⁵¹ C. C. Hsaio and J. A. Sauer, *J. Appl. Phys.* **21**, 1071 (1950).

⁵² B. Maxwell and L. F. Rahm, *Ind. Eng. Chem.* **41**, 1988 (1949).

properties is most important and deformation occurs along certain crystallographically important directions.

In addition to the obvious utility of the method for determining the mechanical properties of a material at rupture, it is likely to prove a useful tool in a number of other problems. The reproduction in coarse-grained systems, such as pastes and powders, of many of the features of the behavior in deformation of metals should lead to a better understanding of the latter. The paste and powder systems have the great advantage that the determination of the mechanical properties can here be supplemented by microscopic observation of the movement of each unit in the flow process. The study of the changes in mechanical properties which occur when a liquid phase is added to a powder or when the properties of the two phases and the interface in a paste are varied should be fruitful from the viewpoint of lubrication. Even from qualitative experiments, it is easy to distinguish marked differences in the behavior of pastes compounded of the same powder with different liquids.

ACKNOWLEDGEMENTS

The authors are indebted to a number of people for discussions and advice, in particular to Prof. K. Weissenberg and Prof. A. H. Nissan. They also wish to thank Mr. R. A. Awcock and Mr. M. J. Egan for assistance in the preparation of the manuscript.

Nomenclature

α	Angle between the main directions of stress and strain velocity	$\tau_{\max}$	Relaxation time (= $\eta_{\max}/G$)
γ_0	Recoverable strain	ϕ	Free energy
Γ	Complex modulus = $\Gamma_A e^{i\Gamma\phi}$	ω	Angular frequency
ϵ	Strain	G	Elasticity modulus
ϵ_{jk}	Component of strain	G, H	Constants in Mooney's equation
$\dot{\epsilon}, \ddot{\epsilon}, \dots$	First, second, etc. time derivatives of strain	$\dot{H}$	Work of the dissipated energy per unit of time and volume
$\epsilon_A, \epsilon_\phi$	Amplitude and phase of strain	p	Stress, pressure
η	Viscosity coefficient	p_{jk}	Component of stress
$\eta_{\max}$	Idealized viscosity coefficient corrected for the angular divergence of the main directions of stress and strain velocity	p_k	Principal value of stress
λ	Elongation ratio	$\dot{p}, \ddot{p}$	First, second etc. time derivatives of stress
λ_k	Principal elongation ratio	p_A, p_ϕ	Amplitude and phase of stress
Λ	Complex reciprocal modulus = $1/\Gamma = \Lambda_A e^{i\Lambda\phi}$	r	Radius
σ, π	Constants of the stress-strain equation	R	Radius to free boundary of the liquid in the gap of the rheogoniometer
τ	Relaxation time (= η/G)	t	Time
		x, y, z	Coordinate axes
		$\dots$	Double scalar multiplication

AUTHOR INDEX

Numbers in parentheses are footnote numbers and are inserted to enable the reader to locate a cross reference when the author's name does not appear at the point of reference in the text.

A

- Abbott, N. J., 274
 Adams, C. H., 155
 Adams, L. H., 403, 422(4)
 Adler, F. T., 454, 456(78)
 Aiken, W., 179, 439, 440(37)
 Alder, B. J., 99, 137(23)
 Alder, M. G., 307
 Aldrich, R., 55, 57(48)
 Aleksandrov, A. P., 444
 Alexander, A. E., 327, 328, 329, 330, 335(48), 336, 341, 343, 344(48), 345
 Alfrey, T., 46, 47(27), 56, 149, 151(17), 153(17), 159, 161, 179, 274, 275(15), 301, 434, 439, 440(37), 518
 Altenburg, K., 166
 Alder, B. J., 99
 Ames, W. M., 316, 323, 346(19)
 Anderson, F., 287, 293(46), 295, 298(46), 302
 Andrade, E. N. da C., 249, 439
 Andrews, R. D., 45, 46, 48(32), 51, 66, 67, 72, 74, 78, 80(8), 81, 113, 114, 159, 167, 306, 436, 437, 438(18), 468, 469(132), 470, 471(18)
 Andrews, R. D., Jr., 164
 Armstrong, G. M., 258, 436
 Ashworth, J. N., 435, 442(7), 454, 456(7), 463(7)
 Astbury, W. T., 94, 262
 Atkinson, E. B., 247, 248
 Axilrod, B. M., 154
- ### B
- Bander, T., 191
 Backer, S., 285, 289(41), 290
 Bailey, E. D., 460
 Bailey, F., 165
 Baker, E., 156
 Baker, W. O., 169, 457, 458(93), 459, 460
 Ballou, J. W., 157, 456
 Bancroft, D., 461
 Bantoft, E., 526
 Barker, H. D., 308
 Barnes, H. T., 482
 Barr, G., 367, 477, 478, 480(5), 487
 Beaman, R. G., 175
 Bear, R. S., 359
 Beaver, E. W., 205
 Beckwith, R. K., 205
 Behre, J., 190
 Bekkedahl, N., 79
 Belcher, H. V., 110, 125
 Benbow, J. J., 461
 Benioff, H., 423, 425
 Bergmann, L., 457, 458(94)
 Berkley, E. E., 308
 Beste, L. F., 290, 291(54)
 Bestul, A. B., 110, 125, 207, 208, 212
 Beyer, A. E., 231
 Billmeyer, F. W., 291
 Bingham, E. C., 477, 478
 Binnie, A. M., 482
 Birch, F., 410, 411(19), 422, 428(19), 461
 Bird, B. G., 141, 142(72)
 Bischoff, J., 68, 71(12), 75(12)
 Bishop, H. R., 227, 228
 Black, S. A., 197, 207, 208, 209, 217, 231
 Blankenship, E. B., 162
 Blizard, R. B., 444
 Blott, J. F. T., 127
 Blow, C. M., 196
 Boedtker, H., 357, 358, 359
 Bogue, R. H., 328, 331, 354, 356, 361
 Boltzmann, L., 38, 272
 Bott, M. J., 357, 358
 Boyer, R. F., 146, 147, 155, 171(3), 175, 177
 Bradbury, E., 351, 352(60)
 Brauer, P., 155
 Brayant, C. B., 110
 Breazeale, F., 465
 Breuer, G. M., 171
 Breuer, K., 311

Bridgman, P. W., 86, 154
 Brockamp, B., 418
 Brodnyan, J., 55, 452
 Brown, A., 290, 327, 316(29), 350(29)
 Brown, G. M., 65, 78, 79(35), 81(34)
 Brown, K. C., 287
 Browne, H. H., 323
 Bruckner, H., 477, 478(7)
 Bryant, G. M., 299, 300
 Buchdahl, R., 54, 70, 147, 163, 164, 165,
 166, 167, 175(89), 176(8), 177, 179, 248
 Buck, G. S., 292
 Bueche, A. M., 81
 Bueche, F., 131
 Bull, J., 299
 Bullard, E. C., 430
 Bullen, K. E., 406
 Bungenberg de Jong, H. G., 323, 328(18),
 344, 462
 Bunzl, M., 482
 Burbridge, W. N., 227
 Burgers, J. M., 462
 Burleigh, E. G., 302
 Burns, R., 256, 257
 Burr, G. S., 436, 437(22), 464(22)
 Burte, H., 59, 95, 303, 305(93)
 Busse, W. F., 226, 291

C

Cagle, F. W., 98
 Cameron, W. G., 292
 Carlene, P. W., 292
 Carswell, T. S., 154, 155, 156, 255
 Catsiff, E., 45, 46(26), 66(25, 26), 67, 68,
 70, 71, 72(12), 73, 74(25, 26), 75(12,
 13, 25, 26), 76(25, 26), 274, 275
 Chaikin, M., 295
 Chalmers, B., 439
 Chamberlain, N. H., 292, 295, 297
 Chaney, A. L., 205
 Chang, P., 99, 138
 Chasman, B., 256, 257
 Chen, M. C., 293, 295(67)
 Christensen, C. J., 98, 307
 Christiansen, E. B., 127
 Christie, D. G., 456
 Clark, J. F., 300
 Clayton, F. H., 296, 297
 Cleereman, K. J., 163, 164(80), 165
 Codington, R. S., 147
 Coe, J. R., 478

Coker, E. G., 257, 482
 Conant, F. S., 9, 179
 Conrad, C. M., 258
 Cooper, L. V., 192, 213
 Coplan, M. J., 288, 309
 Corey, R. B., 95
 Cotton, F. H., 226
 Cottrell, A. H., 136, 155
 Couette, M., 367, 477, 479, 486, 496
 Courts, A., 320, 324
 Cragg, L. H., 115, 116(47), 118(47),
 119(47), 120(47), 121(47)
 Croft-White, P. Q., 205
 Croome, R. J., 346
 Cross, A. H., 511
 Cuff, F. B., Jr., 136
 Cuff, G., 153
 Cumper, C. W. N., 327, 328, 329, 330,
 335(48), 336, 341, 343, 344(48), 345
 Curtis, C. F., 141, 142(72)

D

Dahlquist, C. A., 439, 440(42), 471
 Daly, R., 413
 Dannis, M. L., 177
 Dart, S. L., 435
 Davies, D. M., 443, 466(41)
 Davies, J. M., 191, 227
 Davies, R. M., 465
 Davies, R. O., 147, 152(7), 156
 Davis, C. E., 323, 328, 330, 356
 de Boer, J. H., 311
 Decker, G. E., 197, 203, 204, 205, 207,
 208, 212(50), 218
 Dekking, P., 54, 472
 Demorest, M. H., 427
 Denham, W. S., 287
 Deutsch, K., 54, 161, 169(71)
 Devonshier, A. F., 141
 de Vries, H., 293, 294(66), 308
 de Vries, O., 191
 de Wissner, W., 191
 De Witt, T. W., 160, 439, 444, 445(52),
 447, 450(52), 487, 507, 510, 513
 Dibblee, T. W., Jr., 428
 Dienes, G. J., 8, 248, 438, 439(32, 33),
 440(32)
 Dieterich, E. O., 191, 227
 Dietz, A. G. H., 153, 154, 167
 Dillon, J. H., 79, 80(40), 95, 190, 192, 212,

213, 215, 216, 231, 294, 295, 306, 435
446(9), 447, 465
Dillon, R. E., 109, 113, 196, 248
Dorn, J. E., 113, 134, 135(38)
Doty, P., 46, 47(27), 357, 358, 359, 434
Drogin, I., 227, 228
Dugger, E., 255
Dunell, B. A., 294, 295, 303, 306
Dusenbury, J. H.,
Dyson, A., 179

E

Eastoe, J. E., 319
Ebers, E. S., 211, 230, 231(86)
Eccher, S., 189, 200, 208, 212
Edelman, S., 452, 453(76)
Edelmann, K., 132, 133, 243, 258
Edgar, O. B., 175
Egan, M. J., 524
Eilers, H., 391
Einstein, A., 101
Eirich, F. R., 243, 435, 436(6), 439, 466(6),
482
Eisenschitz, R., 243, 281
Eldridge, J. E., 338, 339(52), 342(59),
347(52), 348(52), 350
Eley, D. D., 113, 253
Elliott, A., 94, 268
Elliott, F. A., 356
Elsasser, W. M., 430
Elyash, L. J., 439
Enabnit, R. S., 447
Eriksson, R., 400
Erk, S., 479
Evans, E. B., 124, 129
Evans, W. W., 51, 335(47), 336, 435,
436(14), 437(14), 472(118), 473, 522
Ewart, R. H., 511
Ewell, R. H., 86
Ewing, M., 410, 413, 421
Eyring, H., 72, 84, 86, 87, 89, 92, 95,
96(16), 97(1, 2), 98, 99(1b, 18), 101, 104,
113, 114, 119(18), 120(18), 124(18),
128, 129(1b), 130(8), 133, 134(61),
137, 138(1b, 69), 139, 140, 142(1b, 7),
162, 279, 293, 295(67), 301, 302, 303,
307, 468

F

Farrow, B., 285, 289(41a)
Feofilov, P. P., 465

Ferry, J. D., 7(4), 8, 22, 46, 49, 51, 60, 67,
73, 74, 75, 123, 148, 151, 156, 159, 169,
232, 335(47), 336, 337, 338, 339(51),
340, 342, 343(51), 347, 348(51, 52),
350, 354, 355, 357, 435, 436(14)
Ferry, J. D., 437(14), 439, 442(7), 451, 452
(73, 75), 454, 456(7, 78), 463(7), 466
(75), 468, 469, 470, 471, 472, 473, 521,
522
Feughelman, M., 304
Fielding, J. H., 231
Filon, L. N. G., 257
Findley, W. N., 153, 162(27b), 255, 257
Finlayson, D., 311
Fisher, R., 421
Fitzgerald, E. R., 7(4), 8, 22, 46, 67, 73,
74, 159, 169, 451, 452(73, 75), 466(75),
468, 471, 472(144)
Fletcher, W. P., 466
Flory, P. J., 7(4), 8, 53, 113, 123(43),
124(43), 125(43), 147, 165, 177, 210,
225
Fowler, J. S., 482
Fox, G., 286
Fox, J. C., 113, 123(43), 124(43), 125(43)
Fox, K. R., 287
Fox, T. G., Jr., 7(4), 8, 53, 113, 123, 124,
125(43), 147, 165, 167, 210, 225
Franz, E., 311, 312
Freeman, S. M., 511, 518, 522
Fremon, G. H., 284
Frenkel, J., 147
Freudenthal, A. M., 156
Friend, N., 120
Frish, D., 86
Fromm, H., 507, 513
Fujino, K., 295
Fujita, H., 46
Furth, R., 155
Fuoss, R. M., 160, 169
Fysh, D., 317, 361

G

Ganzhorn, G. H., 211
Garner, F. H., 507, 509, 513
Garner, P. J., 205
Garner, T. L., 191
Gassen, J., 524
Gatcombe, E. K., 231
Gearhart, W. M., 248
Gehman, S. D., 435, 446(9), 447, 466

- Gemant, A., 461
 Gent, A. N., 466
 Gerke, R. H., 449
 Gerngross, O., 343, 357, 359
 Gessler, A. M., 228
 Gibbs, J. H., 147
 Glasstone, S., 84, 86(1b), 87(1b), 97(1b),
 99(1b), 129(1b), 137(1b), 142(1b),
 162, 301
 Gloor, W. E., 241, 248(5)
 Gold, T., 420
 Goldberg, H., 447, 466(60), 487
 Goldman, S., 40
 Goldstein, S., 480, 481(14)
 Gonon, W., 268, 299(11)
 Gordon, R. S., 354
 Grabar, P., 330
 Grandine, L. D., Jr., 7(4), 8, 22, 46, 73,
 74, 159, 169, 451, 468, 471, 472
 Grant, N. J., 135
 Green, H. S., 141
 Greensmith, H. W., 510
 Grieco, A., 448
 Griffiths, J. D., 288
 Griffiths, R. W., 190
 Griggs, D. T., 422, 424, 428, 438
 Gross, B., 25, 40, 41(21, 22), 53(16), 150,
 151, 152(21), 434, 468(2-4)
 Grubb, W. T., 81
 Grun, F., 70(15), 71
 Gruntfest, I. J., 155
 Gui, K. E., 466
 Gurnee, E. F., 164
 Gurney, L., 493
 Gutenberg, B., 402, 403, 404, 405, 407,
 410, 412, 413, 414, 416, 417(41), 419
 (31), 420, 423, 424
 Guth, E., 46, 147, 435, 456, 457
 Guthrie, J. C., 296
 Gutowsky, H. S., 147
- H**
- Hagen, H., 191, 226
 Hahn, S. J., 133, 134(61)
 Hall, G. L., 9, 447, 465
 Halsey, G., 59, 95, 301, 302, 303, 305(93),
 464
 Hamburger, W. J., 290, 293(55)
 Hamm, G. G., 189, 200
 Hammerle, W. G., 279, 306
 Hanson, E. E., 81
 Hardtwig, E., 408
 Hargreaves, W. D., 120
 Harper, R. C., Jr., 444, 445(52), 447(52),
 450(52), 487
 Harris, M., 436, 437(16), 464(16)
 Haselbach, C., 268, 299(11)
 Haskell, N. W., 418
 Hastewell, L. J., 439
 Hatfield, M. R., 471
 Hatschek, E., 334, 335, 345, 346
 Haward, R. N., 154, 255, 256, 257
 Hawn, C. Z., 359
 Haycock, E. W., 99, 137(23)
 Heinze, P. N., 191
 Heiskanen, W., 414, 415
 Heiss, J. H., 169, 457, 458(93), 459, 460
 Hencky, H., 243
 Henderson, P., 105
 Hendricks, J. O., 439, 440(32)
 Henneman, J. P., 344
 Henning, H. J., 311
 Henno, M., 280
 Hermann, K., 357, 359
 Hermanne, L., 298
 Hermans, P. H., 262, 263, 285, 308, 312
 Hess, K., 243
 Heuer, W., 226
 Heyboer, J., 54, 161, 169, 170(70), 472
 Hide, R., 430
 Hideshima, T., 160, 161(63), 169
 Hildebrand, J. H., 99, 137(23)
 Hill, M. L., 428
 Hill, R., 175, 262, 263
 Hillier, K. W., 295, 456, 466
 Hindman, H., 287, 436, 437(22), 464(22)
 Hirschfelder, J. O., 141, 142(72)
 Hirvonen, R. A., 414
 Hoekstra, J., 191, 227, 228
 Hoff, E. A. W., 54, 161, 169
 Hoffman, H., 309
 Hoffman, R. E., 99
 Hoffman, R. M., 290, 291
 Hofman Bang, N., 45, 66, 67(6), 72(6), 113
 Holmes, F. F., 67
 Holroyd, L. V., 147
 Holt, W. L., 439
 Holtzschere, J. J., 418
 Hoover, S. R., 300
 Hopkins, I. L., 448
 Horino, T., 295
 Horio, M., 157, 296

Houck, R. C., 323, 328
 Houwink, R., 191
 Howitt, F. O., 262, 263
 Hsiao, C. C., 153, 154, 162(27a), 466, 534
 Huggins, M. L., 243
 Hughes, D. S., 162

I

Ikeda, T., 258
 Irish, E. M., 137, 138(69)
 Ivey, D. G., 46, 457
 Iwayanagi, S., 160, 161(63), 169

J

Jacobs, F., 227
 Jäckel, K., 155
 Jaeger, G., 477
 Jancke, 297
 Jane, R. S., 335
 Janssen, A., 179, 439, 440(37)
 Janus, J. W., 340, 360
 Jeffreys, H., 402, 406, 407, 409, 413, 420, 422, 429
 Jenckel, E., 147, 152, 153, 171(6), 175
 Jenkins, J. A., 308
 Jobling, A., 524
 Johnson, D. H., 81
 Johnson, F. H., 101
 Johnson, M. F., 22, 471, 472(148), 473, 522
 Johnson, N., 216
 Johnson, R., 162
 Johnston, N., 190, 212(13), 215
 Jones, G. O., 147, 152(7), 156
 Jones, H., 177
 Jones, R. W., 8, 12(7), 15(7), 37(7), 38(7), 210, 439, 440(35)
 Jordan, I., 472(148), 473, 522
 Joset, A., 417, 418
 Jurisch, J., 308

K

Kanig, K., 166
 Karam, H. J., 163, 164(80), 165
 Karrer, E., 191
 Kaswell, E. R., 289, 307, 308
 Katchalsky, A., 325
 Kauzmann, W., 113, 146, 147(4)
 Kawai, H., 295
 Ke, T. S., 461
 Keen, W. N., 191

Kenchington, A. W., 320, 322(17), 340, 360
 Kendall, J. M., 465
 Kennedy, G., 404
 Kennedy, W. D., 248, 258, 436
 Khayatt, R. M., 292
 Khera, M. P., 297
 Kimball, A. L., 157, 162
 Kincaid, J. F., 86
 Kinkel, E., 335(46), 336, 339
 Kirkwood, J. G., 151
 Kistler, S. S., 114
 Klein, E., 152
 Klemm, H. F., 248, 438, 439(32), 440(32)
 Knowles, J. K., 153, 154
 Knox, E. O., 439
 Koch, P. A., 311
 Kokes, E. L., 300
 Kolb, H. J., 291
 Kolsky, H., 149, 153, 154, 157(30), 453, 456, 464, 465, 466
 Koorn, V. M., 436, 437(19)
 Koppelman, J., 449, 461(70a)
 Kornfeld, M. O., 448
 Kosten, C. W., 447
 Krimm, S., 71, 146, 147(2)
 Kruse, J., 227
 Kruyt, H. R., 323, 328(18)
 Kunzle, O., 156, 232, 306, 449
 Kuessner, H. O., 428
 Kuhn, W., 70(15), 71, 156, 232, 306, 405, 406, 429, 449
 Kunitz, M., 328, 342, 344(54)

L

Laidler, K. J., 84, 86(1b), 99(1b), 129(1b), 137(1b), 142(1b), 162, 301
 Lamb, H., 221
 Landel, R. F., 75
 Lasater, J. A., 279
 Laughlin, F. R., 161
 Lawton, T. S., 255
 Lazan, B. J., 157, 162, 444, 466(47a)
 Lazurkin, Y. S., 444
 Leaderman, H., 3, 7, 8, 12(6, 7), 15(7), 33(1), 35, 37(7), 38(1, 6, 7), 46, 50, 51(39), 58(2), 59, 67, 150, 151(20), 210, 256, 271, 272, 280(12), 281, 438, 439, 440(35), 470, 471(25)
 Lee, A. R., 389
 Lees, M., 404

Leick, A., 334, 339
 Lennard-Jones, J. E., 141
 Leroux, P., 495
 Leser, W. H., 171
 Lethersich, W., 51, 58(43), 438, 443, 448
 (43), 449(43)
 Leverault, R., 177
 Lewis, G. N., 105
 Lewis, J. P., 456
 Li, J. C. M., 99, 138
 Lieber, P., 408
 Lincoln, B., 296, 312(72)
 Liska, J. W., 179
 Lochner, J. P. A., 296, 311(73)
 Lodge, A. S., 507, 513, 517
 Logan, M. A., 319
 Lonsdale, T., 287
 Lord, P., 510
 Loshak, S., 167
 Lowell, D. E., 162
 Lucas, F., 285
 Lumry, R., 101
 Lundgren, H. P., 436, 437(19)
 Lupke, P., 465
 Luyken, E., 282
 Lyons, W. J., 9

M

McCallion, H., 466
 McCord, F. A., 292
 McCracken, F. A., 205
 McCrackin, F. L., 309
 MacDonald, G., 404
 MacDonald, W. S., 435, 436(11)
 MacGregor, C. W., 135
 MacIness, D. A., 105
 McIntyre, E., 176(112), 177
 McKee, S. A., 190
 McKennell, R., 526
 McKinney, J. E., 452, 453(76)
 MacLeod, A. A., 41(23), 45, 57(23)
 McLoughlin, J. R., 16, 45(12), 64, 65,
 67(2), 68(1), 71, 77, 81, 164, 168, 436
 McSkimin, H. J., 457, 458(93), 459, 460
 Mandel, J., 57
 Mann, J. C., 287
 Mardles, E. W. J., 331
 Margaretha, H., 482
 Marin, J., 153, 162(27a), 466
 Mark, H., 66, 67(5), 108, 109, 147, 171(13),
 179, 275, 290, 310, 439, 440(37)
 Markovitz, H., 439, 444, 445(52), 447,
 450(52), 487
 Markwich, A. H. D., 389
 Markwood, W. H., Jr., 258
 Marriott, R. R., 257
 Martin, C., 351, 352(60)
 Martin, G., 195, 205, 209, 212(33)
 Marvin, R. S., 22, 24(13), 30(13), 35,
 50(13, 15), 51(13, 15), 55, 57(48), 58,
 192, 435, 451, 452, 453(76), 469, 470
 Marzetti, B., 189
 Mason, R., 421
 Mason, W. P., 450, 457, 458(93), 459, 460
 Mattice, H., 408
 Mauersberger, H. R., 262, 263
 Maxwell, B., 154, 161, 444, 534
 Mead, D. J., 169
 Meisser, O., 412
 Melchior, P. J., 406, 420
 Menzel, H., 413
 Meredith, R., 262, 276, 278(22), 285, 286,
 289, 296, 307(39), 308, 309
 Merrington, A. C., 487
 Merz, F. H., 165, 166, 248
 Mesrobian, R. B., 80
 Metz, D., 80
 Meyer, K. H., 236, 262, 263, 268, 299(11)
 Meyer, L. W. A., 258
 Meyers, L. H., 147
 Michelson, A. A., 424
 Miller, C. C., 136
 Miller, M., 342(59), 350
 Mims, R., 162
 Mochulsky, M., 81
 Model, F., 414
 Monck, E., 258
 Montgomery, D. J., 279, 296, 306
 Mooney, M., 108, 109, 184, 185, 186, 187,
 192(2), 197, 200, 205, 206, 207, 208,
 209, 215, 217, 219, 220, 221, 223, 228,
 229, 231, 449, 507, 511, 513
 Moore, S., 318
 Morel, J., 330
 Morton, T. H., 292, 296
 Morton, W. F., 285
 Motz, J., 156, 461
 Mowry, S. C., 457
 Mrowca, B. A., 46, 147, 456, 457
 Müller, F. H., 155, 164, 447
 Mullins, L., 214, 227, 443

N

Nadai, A., 423, 534
 Nakagawa, T., 487
 Nakayama, C., 296
 Nancarrow, H. A., 247, 248
 Nansen, F., 414, 415, 419
 Nason, H. K., 154, 155, 156, 248, 255
 Naunton, W. J. S., 447, 450(56)
 Nederbragt., G. W., 380
 Nelson, J. F., 205
 Neuman, R. E., 319
 Newsome, P. T., 255
 Nielsen, L. E., 54, 70, 147, 156, 163, 164,
 165, 166, 167, 175(89), 176(8, 112),
 177, 178, 179, 248, 449
 Nieman, R. S., 309
 Nijboer, L. W., 389, 394, 395, 397
 Nimer, R. L., 279
 Niskanen, E., 414, 419
 Nissan, A. H., 482, 507, 509, 513(8), 534
 Nobles, L. N., 428
 Nolle, A. W., 157, 160, 448, 449, 450(65),
 456, 457, 461(65), 462(65), 463(65),
 466(65)
 Northrop, J. H., 324, 328, 342, 344(54)
 Nye, J. F., 427

O

Oakes, E. T., 323, 328, 330, 356
 Oberst, H., 456
 O'Connell, R. A., 436, 437(19)
 Oldroyd, J. G., 476, 483, 486(22a), 487,
 489, 490, 492(32), 494(22a), 496, 497,
 498(32), 499(32), 500(38), 507, 513,
 519
 Oliphant, W. F., 157
 Oliver, P. H., 296
 Oncley, J. L., 327, 346(29), 350(29)
 Onogi, S., 157, 296
 O'Shaughnessy, M. T., 273, 274, 275(15)
 Osthoff, R. C., 81
 Ostwald, W., 356/357
 Ott, E., 233, 262, 263

P

Padden, F. J., 507, 510, 513
 Padden, F. J., Jr., 439
 Pannell, J. R., 481
 Park, C., 78
 Parks, G. S., 439
 Parlin, R. B., 101, 104

Patterson, L. T., 164
 Pauling, L., 95
 Pearson, J. R. A., 470
 Peek, R. L., Jr., 195
 Peirce, F. T., 279, 287, 296, 297, 305, 309
 Pelzer, H., 434, 468(4)
 Pepper, D. C., 113, 253
 Permanyer, F., 285
 Perutz, M. F., 427
 Peters, L., 95, 281, 303
 Petersen, R. F., 300
 Pfeiffer, J. P., 366, 386
 Philippoff, W., 55, 132, 133(54), 158, 243,
 443, 447, 452, 469, 507
 Picch, F. E., 241, 248(5)
 Pike, M., 225, 226
 Pilpel, N., 516
 Pinte, C., 280
 Piper, G. H., 187, 188, 193, 196
 Planck, M., 105
 Platt, M. M., 308
 Pleass, W. B., 355
 Podnieks, F., 162
 Poiseuille, J. L. M., 475, 480
 Polissar, M., 101
 Pollard, R., 176(112), 177
 Pollett, W. F. O., 247, 511, 514
 Poole, H. J., 332, 333(40), 334, 335, 339
 Poore, L., 299
 Porter, K. R., 359
 Pouradier, J., 320, 324, 326, 327, 331, 348,
 355
 Powell, R. E., 86, 97(2), 113, 128
 Preissmann, A., 232, 306
 Prengle, R. S., 482
 Press, F., 410, 413, 421
 Press, J. J., 275, 280
 Preston, R. D., 262, 263
 Preston, J. M., 262, 263, 300
 Prettyman, I. B., 79, 80(40), 447, 465
 Prey, A., 420

Q

Quinn, F. A., 110

R

Rabinowitsch, R., 194
 Rahm, L. F., 154, 534
 Raitt, W., 421
 Raub, H. L., 156, 461
 Read, W. T., 436
 Read, W. T., Jr., 136

- Reddish, W., 54, 161, 169(71)
 Ree, T., 89, 92, 98, 99(18), 113, 114, 119
 (18), 120(18), 124(18), 130(8), 133,
 134(61), 142(7), 293, 295(67)
 Rees, W. H., 291
 Reese, C. E., 101, 279
 Reichhardt, C. H., 302, 303
 Reiner, M., 7, 132, 483, 507, 513
 Renquist, H., 413, 417(32)
 Reynolds, O., 481, 482(15)
 Rich, S. R., 460
 Richard, W. R., 175, 177(108)
 Richardson, E. G., 354, 355, 356(61), 462
 Richardson, W. D., 361
 Richter, C. F., 424
 Ricker, N., 413
 Rigby, B. J., 278
 Ripa, O., 276, 304
 Riseman, J., 243
 Ritson, F. J. N., 439
 Rittmann, A., 429
 Rivlin, R. S., 507, 510, 513
 Roberts, J. E., 510, 512
 Robertson, F. M., 157, 162
 Robinson, C., 357, 358
 Robinson, D. W., 161
 Roch, T. W., 429
 Rodger, J., 478
 Roelig, H., 443
 Roesler, F. C., 470
 Rogovin, Z. A., 309
 Rooney, G., 205
 Rorden, H. C., 448
 Rose, L., 288
 Rosevear, E., 86, 97(2)
 Roseveare, W. E., 299
 Rossmassler, S. A., 307
 Roth, F. L., 197, 203, 204, 205, 208, 218,
 439
 Roth, W., 460
 Rothfus, R. R., 482
 Rouse, P. E., Jr., 151, 459, 460, 467
 Rudnick, P., 420
 Runcorn, S. K., 430
 Ruoff, A. L., 95, 96
 Russell, E. W., 534
 Russell, R. J., 509, 511, 515
 Ryan, E. W., 127
- S**
- Saal, R. N. J., 376, 387, 388
 Sack, H. S., 55, 57(48), 156, 461
 Sakurada, I., 311
 Sakurai, T., 258
 Samuel, D. L., 127
 Sandvik, O., 447, 466(60), 487
 Sargent, L. W., 105
 Sato, Y., 258
 Sauer, E., 335(46), 336, 339
 Sauer, J. A., 153, 154, 157, 162(27a), 466,
 534
 Saunders, D. W., 107, 108, 109, 113, 200,
 201, 222
 Saunders, P. R., 327, 333, 336(41), 340
 (41), 341(41), 348(31), 349(31), 355
 (31), 357(31), 358(31)
 Sauramo, M., 413
 Saville, A. K., 282, 283, 287, 289(40),
 309(40)
 Sawyer, W. M., 435, 442(7), 454, 456(7,
 78), 463(7)
 Saylor, C. P., 78
 Scatchard, G., 327, 346, 350
 Schaevitz, H., 156, 436, 437(23)
 Scheidegger, A. E., 423
 Scheirer, J. F., 410, 411(19), 428(19)
 Schetky, L. M.D., 136
 Schiefer, H. F., 286, 309
 Schiller, L., 481
 Schlechtweg, H., 407
 Schmidt, A., 479
 Schmieder, K., 146, 161, 167, 168, 169(69),
 92), 171(92), 172(12), 173(92), 176(92),
 177(92)
 Schoch, T. J., 234
 Schoenfeld-Reiner, R., 132
 Schofield, J. R., 196
 Schofield, R. K., 484
 Schremp, F. W., 51, 335(47), 336, 350,
 435, 436(14), 437(14), 451
 Schwartz, R. T., 255
 Schwarzl, F., 46, 48, 52(20), 56, 150, 151,
 152(22), 159, 161, 435, 470
 Schweydar, W., 420
 Scogin, R. J., 258
 Scott, J. R., 187, 188, 193, 195, 196, 200,
 201, 209, 210, 212(43, 51)
 Scott, J. W., 335
 Scott, R. L., 177
 Scott Blair, G. W., 483, 484
 Searle, G. F. C., 493
 Sen, M. K., 292
 Sens, J., 323, 328(18)

- Servi, I. S., 135
 Sezawa, K., 411
 Shah, S. Y., 278
 Sharp, R. P., 427, 428
 Shaw, J. T. B., 285
 Sheppard, S. E., 255, 323, 328, 332, 335, 339, 345, 354, 356
 Sherby, O. D., 113, 134, 135(38)
 Sherman, L. J., 115, 116, 118, 119(47), 120(47), 121(47)
 Sherman, M. A., 154
 Shriver, G. E., 230, 231(86)
 Shuffler, S. L., 160
 Sieck, P. W., 457
 Siegmann, M. C., 383, 387(8)
 Silverman, S., 456
 Simon, F., 146
 Sinizer, D. I., 135
 Sips, R., 434, 454, 464, 468(5)
 Siren, A., 413, 414
 Sittel, K., 460
 Smallwood, H. M., 206, 219, 220, 222
 Smith, H. de Witt, 281
 Smith, J. C., 153, 157, 309, 456
 Smith, P. A. S., 175, 177(108)
 Smith, R. G., 8, 12(7), 15(7), 37(7), 38(7), 210, 439, 440(35)
 Smith, S. G., 285
 Smith, T. L., 451, 464
 Smith, W. H., 78
 Sones, R. H., 115, 116(47), 118(47), 119(47), 120(47), 121(47)
 Sookne, A. M., 436, 437(16), 464(16)
 Sorge, E., 418
 Sorkin, M., 312
 Spangler, R. D., 466
 Speakman, J. B., 95, 276, 278, 281, 282, 283, 285, 286(40), 287, 289(37, 40), 290, 297, 303, 304, 309(37, 40)
 Spencer, R. S., 109, 110, 113, 114, 124(35), 146, 147, 171(3), 177, 196, 220, 222, 231, 248
 Spicer, H. C., 410, 411(19), 428(19)
 Spurlin, H. M., 258
 Stainsby, G., 324, 325, 326, 327, 328, 329, 348, 349(31), 355(31), 357, 358(31, 58), 435
 Stambaugh, R. B., 447
 Stanford, E. G., 438, 440(28)
 Stanley, G. M., 415
 Stanley, H. E., 291
 Stannett, V., 250
 Stanton, T. E., 481
 Staudinger, H., 226, 308, 312
 Staverman, A. J., 46, 48(29, 30), 52(29), 54, 56, 151, 159, 161, 435, 470, 472
 Stearn, A. E., 137, 138(69), 140
 Steel, R., 94
 Stefan, M. J., 195
 Stein, A. M., 436, 437(19)
 Stein, R., 156
 Stein, R. S., 71, 78, 79, 156, 179(47), 436, 437(17, 23)
 Stein, W. H., 318
 Steinberger, R. L., 279, 280
 Stern, M. D., 79, 81(41)
 Stevens, W. E., 127
 Stone, W. K., 286, 309
 Stout, H. P., 308
 Strawbridge, D. J., 487, 489, 490, 492(32), 494, 496, 497(36), 498(32), 499(32, 35), 500(36)
 Street, A., 94
 Streiff-Becker, R., 427
 Strub, R. A., 231
 Stuart, W. W., 357
 Suda, R., 258
 Sully, A. H., 438
 Susich, G., 285, 289, 290
 Swann, G., 238
 Swanson, D. I., 59, 258
 Sweet, S. S., 332, 335, 339, 345, 354, 356
- T
- Tanaka, M., 258
 Tapsell, H. J., 438
 Taylor, G. I., 153, 157(29), 464, 486, 496
 Taylor, G. S., 195
 Taylor, H. S., 136, 137(68)
 Taylor, N. W., 439, 440(32)
 Taylor, R. H., 231
 Telfair, D., 156
 Thompson, A. B., 160
 Thompson, R. H. K., 311
 Thorpe, T., 478
 Thorsen, W. J., 436
 Thurn, H., 177
 Tillett, J. P. A., 465
 Timmermans, J., 115
 Tipton, H., 293
 Tobolsky, A. V., 16, 45, 46(25, 26), 51, 64, 65, 66, 67, 68, 70, 71, 72, 73, 74, 75

- (12, 13, 25, 26), 76(25, 26), 77, 78, 79,
80, 81, 108, 109, 113, 114, 142, 146,
147, 156, 159, 161, 164, 167, 168, 171
(13), 179(47), 301, 306, 436, 437, 438
(18), 468, 471(18)
- Tolstoy, N. A., 465
- Tomascheck, R., 429
- Toms, B. A., 478, 483(11), 484, 487,
489, 490, 492(32), 494, 496, 497(36),
498(32), 499(32, 35), 500(36)
- Towsley, F. E., 231
- Trail, D., 311
- Treloar, L. R. G., 107, 108, 109, 113, 163,
200, 201, 206, 207, 208, 222, 509
- Trumpler, W. E., Jr., 142
- U
- Überreiter, K., 166
- Ueki, K., 258
- Umstatter, H., 132, 133(54)
- Urquhart, A. R., 262, 263
- Ushakoff, A., 435, 436(11)
- V
- van den Berg, H. J., 462
- van der Meijden, H., 8, 191
- van der Poel, C., 367, 379, 382(2), 383(2),
387(2), 389
- van der Wyk, A. J. A., 268, 299(11)
- Van Dijck, W. J. D., 391
- van Doormaal, P. M., 386
- van Holde, K. E., 12, 15(11), 37(11), 210,
211, 225, 438, 439(29), 440
- Van Oort, W. P., 462
- van Rossem, A., 8, 191, 227, 228
- Van Wazer, J. R., 447, 487
- van Wyk, C. M., 297
- Venet, A. M., 320, 324, 326, 327, 348(24),
355
- Vening-Meinesz, F. A., 419, 423
- Verhoogen, J., 422
- Vielhauer, S., 405, 406, 429
- Vila, G. R., 227
- Villars, D. S., 221
- Voigt, W., 150
- Volterra, E., 464
- Voong, E. T. L., 296
- W
- Wakeham, H., 299, 302
- Wakelin, J. H., 296
- Walker, A. M., 420
- Waller, M., 534
- Walter, J., 87, 139, 140
- Walther, H., 461
- Ward, A. F. H., 510
- Ward, A. G., 249, 257, 314, 316, 320, 322
(17), 327, 333, 336(41), 340, 341(41),
348(31), 349(31), 355(31), 357(31),
358(31), 360, 361, 435
- Waring, J. R. S., 447, 450(56)
- Warner, A. J., 177
- Watson, M. T., 258, 436
- Watson, W. F., 225, 226
- Watts, H., 99
- Weaver, J. V., 187, 227
- Wegel, R. L., 461
- Wegener, W., 276, 277, 282, 306(22)
- Weir, C. E., 171
- Weiss, F., 451
- Weissenberg, K., 243, 506, 508, 509, 511,
513, 518, 524
- Welch, L. M., 205
- Wellmann, H. W., 429
- Wentworth, C. K., 428
- Wert, C. A., 461
- Westbrook, E. L. E., 249
- Whisnant, J., 465
- White, G. F., 478
- White, H. J., 301, 302
- White, H. S., 190, 207, 208(50), 212(50)
- White, L. M., 230, 231
- Whitfield, R., 250
- Whitten, C. A., 428
- Whorlow, R. W., 187, 192, 200, 201, 204,
209, 210, 212, 213, 214, 225, 227
- Wiechert, E., 33, 150, 151(20)
- Wilbourn, A. H., 161
- Wiley, R. H., 171
- Wilkinson, C. S., Jr., 466
- Williams, I., 191
- Williams, J. L., 163, 164(80), 165
- Williams, J. W., 12, 15(11), 37(11), 59,
210, 211, 225, 258, 327, 346(29), 350
(29), 438, 439(29), 440
- Williams, M. L., 46, 49, 73, 75, 232, 468,
469, 470(135)
- Williams, N. L., 151

Williamson, W. O., 524

Wiseman, P., 227, 228

Witte, R. S., 456

Wolcken, K., 418

Wolf, K., 146, 161, 167, 168, 169(69, 92),
171(92), 172(92), 173(92), 176(92), 177

Wolstenholme, W. E., 219, 221, 223

Wood, G. C., 278, 282(24)

Wood, G. F., 507, 509(8), 513(8)

Wood, L. A., 171

Woodbury, J. W., 101

Woodford, D. E., 447

Woods, D. W., 160

Woods, H. J., 94, 262, 263, 281, 295, 299,
300

Work, R. N., 156, 461

Würstlin, F., 175, 176, 177(109)

Wurstlin, F., 171

Y

Yamamoto, K., 296

Yavorsky, P. M., 444, 445(52), 447(52)
450(52), 487

Yerzley, F. L., 449

Yoh-Han Pao, 153

Yorgiadis, A., 157, 162

Young, A., 420

Z

Zagieboylo, W., 289

Zapas, L. J., 160, 444, 445(52), 447(52),
450(52), 487

Zapp, R. L., 228

Zener, C. M., 148, 150(14), 151, 293

Ziffle, H. M., 258

Zwolinski, B. J., 101

Zwikker, C., 447

SUBJECT INDEX

(See also individual Tables of Contents.) Figure in parentheses following page number is equation number; F signifies figure, T signifies table

A

- Absolute compliance, see Elastic compliance
- Absorption coefficient (see also Damping, Attenuation)
 - seismic surface waves, 410
- Acetate (cellulose) rayon, (See also Cellulose acetate) 277
 - creep curves, analysis of, 275, 277, 302
 - creep, humidity and temperature, 279-281
 - dynamic modulus and static strain, 294, 306
 - dynamic properties, effect of frequency, 295
 - instantaneous extension, 273
 - internal friction, 306
 - relaxation, composite curve (master curve, relaxation function), 276, 277
 - rigidity, 292, 297
 - strain recovery, 290
 - strength and rate of extension, 308
 - stress-strain, curve, 284, 285, 296, 303
 - humidity and rate effect, 286, 287
 - stress-strain relaxation, nonlinear, 58
 - superposition principle, 272
- Acetic acid, effect on gelatin, 331
- Acetone, effect on gelatin, 331
- Acid-process gelatin, 341, 344
 - extraction, 360
 - isoionic point (pI), 316
- Acrlan, 265
- Acrylic acid, 170
- Activated complex, 89, 97
 - incomplete equilibrium of, 89
 - volume increase, 141
- Activation energy, activation heat, of
 - flow, viscosity, (see also Flow, Relaxation), 53, 99, 301
 - aluminum and its alloys 134
 - apparent, 68
 - asphalt, 379, 380
 - diffusion, 99
 - free, 85
 - glucose, 153
 - GR-S rubber solutions, 110, 125
 - α -methylnaphthalene, 125
 - molecular rate processes in glasses, 159
 - pressure effect, 86
 - relaxation, apparent, 472
 - torsional, 305
 - rubbers, 108, 109, 206
 - secondary creep, metals, 134
 - Vistanex, 110
 - wool creep, 276
- Activation entropy, negative, due to
 - flow coordination, 109
- Activation, of nonsolvents, 238
- Activity coefficient, 97, 98, 100
- Adhesion, tacky surface, 206
- Adhesives, 241
 - cellulosic, 242
 - gelatin, 359
 - strength, glue, 359
- Adipic acid, 265
- Aftershocks, 423
 - sequences, strain-rebound (recovery), 424
- Aggregation effects, see also Hydrodynamics
 - gelatin, 322, 324, 326, 357-359
- Aging conditions, gelatin, 337
- Airbearing, self-centering, 491
- Alcohols, see also separate listings; e.g.
 - Methyl alcohol, Ethyl alcohol, etc.
 - self diffusion in, 138
- Alfrey
 - method, 46, 50
 - rule, 47
- Alkaline-process gelatin
 - extraction, 316
 - isoionic point (pI), 360
- Alloys, polymer (polyblends), 70

- Alluvium, 404
- Alpha factor, 85
 - temperature independence of, 111, 114
- Aluminum, 531, 532
 - alloys, 113
 - creep secondary of pure, 134
 - of Al-alloys (flow parameters), 134, 135
 - 2S-H₁₈, 135
 - 2S-O, wire, 135
 - soaps, recoverable strain, 524
- Aluminum laurate, 512, 515
 - viscosity coefficient and shear modulus of, 515
- Amorphous polymers, *see* Polymers
- Amorphous regions, 266
 - cellulose, 235
 - wool, 94
- Amplitude
 - coaxial cylinder viscometer, 493
 - large, 466
 - ratio, coaxial cylinders, 496
 - response to imposed stress, frequency dependence, 497
 - of shear strain, sinusoidal, 18
 - stress, 18
- Anelastic, nonelastic
 - behavior, of rock bodies, 425
 - body, 153
 - constants, earth, 409
 - movements, faulting, 429
 - processes, 406, 408
 - properties in oscillatory motion, liquid, 497F, 499
 - tilt, 429
- Anelasticity, inelastic behavior, non-elasticity, (*see also* Creep, Friction, internal, Hysteresis, Viscosity), 148, 150, 153
 - effect of chemical variables, 165
 - of physical variables: temperature, frequency, 157, 158
 - of plasticization, copolymerization, polymer mixture, 175
 - of pressure, stress, orientation, 162
 - of stretch, 163
 - glassy state, fine structure, 161
- Angular vibration frequency, 64
- Anisotropic
 - materials, 504
 - particles, suspension of, 476, 482
 - strain, definition of, 503
 - stress, definition of, 503
- Anisotropy
 - large strain, 518
 - in shear, 506
 - stress and recoverable strain, similitude, 508
 - stress-strain, 504
- Anomalous viscosity, *see* Viscosity
- Non-Newtonian
- Aperiodic
 - element, 95
 - elongation, 95
 - strain, 95
- Apparent
 - activation, polystyrene, relaxation, 165
 - fluidity, viscosity, *see* viscosity
- Ardil, torsional rigidity, 297
- Argon, 140
- Arrhenius law, 80
 - and stress relaxation, 78
- Artificial liquid, 476
- Asbestos fibers, 262
 - paste, radial cracks in rolling, 524
- Asphalt, 363
 - applications, 364
 - blown, 371
 - Borneo, 370, 381
 - breaking strength, 381, 382
 - California, 381
 - compressibility, 380
 - concrete, 388
 - consistency, 365
 - continuous phase, 371
 - disperse phase, 371
 - effect of pressure, 380
 - of temperature, 377
 - elastic deformation, 336, 367, 370-372, 374, 378, 380
 - elastic and viscous behavior, effect of conditions, 366
 - four-parameter model, 375
 - fracture (breaking strength), 399
 - as glass, 373
 - hardness, 365, 376, 377, 382
 - mechanical model representation, 374
 - modulus, 367

- nonlinear elastic model, 376
- preparation, 363
- pure and mixture, stiffness comparison, 396F, 398F
- retarded elasticity, 371
- rheological character, 366, 385, 386T
- softening point, 386
- sol character, 373
- stiffness, effect of temperature and time, 367, 378
- strain recovery, 374
- structure, 364, 371-373
- Venezuela, 370, 381
- viscoelastic properties, 366
- viscous deformation (viscous flow), 367, 378, 380
- Asphalt-mineral aggregate mixture, 388
 - as Bingham material, 391
 - dynamic methods, 389
 - filler-bitumen ratio, 396
 - flow, effect of concentration, 391
 - internal friction, 394, 399
 - stiffness, effect of particle size, 389, 391, 396F, 397
 - strength, 400
 - tests, 393
 - torsional vibration test, 389
 - viscoelastic properties, 389
 - voids, 388, 394
 - yield stress (breaking strength), 389, 399, 400
- Asphaltene, 364, 370, 380
 - effect on flow pattern, 371
- Asphaltic concrete, 388, 396
 - comparison, 399
 - effect of composition, 394T
 - initial resistance, effect of concentration, 395F
- Associated liquid, *see* Liquid
- Attachment
 - between flow units, 221
 - mean life of, 222 (23)
- Attenuation coefficient
 - (*see also* Absorption, Damping, Friction, internal), 184, 149, 409, 448
 - sound wave, 442
- Audio frequencies, resonance methods, soft solids, 448
- B**
- Backbone,
 - influence on secondary mechanical dispersion, 169
 - nature of, 254
- Balata, 212
- Ballistic pendulum, 464
- Balloon inflation, for rupture tests, 530
- Banbury mixer, 182
- Barrier,
 - leakage, 90
 - membrane diffusion, 103
 - potential energy, 90, 97
- Bast fibers, *see also* Cellulose fibers
 - creasing of, 291
 - crystallite size in, 267
 - extensibility, 284
 - relaxation, 278
 - rigidity, flexural, torsional, 292, 297
 - strength, shear, tensile, 310, 311
 - stress-strain curve, 284
 - Young's modulus, 283
- Bearing capacity, limit, asphalt concentration, 395
- Bending (*see also* flexural rigidity), 295
 - modulus, 292
 - resistance, 311
 - rupture, 312
 - of polystyrene, 2
- Benzene, 140
 - as polyisobutylene solvent, 124
 - as polystyrene solvent, 119, 120
- Benzopurpurin sol, 482
- Benzyl cellulose, 234
- Biconical rotor, viscometer, 187
 - shear recovery, 196
 - theory, 193
- Bingham body, 131
 - apparent, nitrocellulose, 252
 - flow, asphalt, 391
- Birefringence, stress, (*see also* Optical anisotropy), 70
 - cellulose derivatives, 243
 - crystalline polymer, 79
 - optical coefficient, 70, 71
 - orientation, 163
 - polyvinyl chloride, 78
 - viscose rayon, 288
- Bismuth, diffusion through lead, 100
- Bitumen,

- asphaltic, 366
 - recoverable strain, 524
 - Weissenberg effects, 524
 - Blending, of gelatine, 342
 - Bloom test, effect of variables, 361
 - Body tides (see also Earth), 420
 - phase angle, 420
 - phase displacement, 419
 - Boltzmann's superposition principle, 2,
38, 64, 77, 153, 272
 - Bond(s), lateral,
 - acting across shear plane, 88
 - breakdown, creep recovery, 271
 - breakdown, rebuilding, Keratin, 281
 - secondary, 250
 - stretching, 271
 - Bone, gelatine, 315
 - glue, 315
 - Borel's theorem, 40
 - Boundary condition
 - surface pressure, 418
 - viscometer, 193
 - Boundary lubrication, 526
 - Boundary material, ideal requirements,
530
 - Boundary member, for rupture test, 526
 - Box type relaxation function, see Relaxa-
tion function.
 - Branching, chain, 226
 - Breaking strength (see also Rupture,
Yield stress), 381, 399
 - asphalt, effect of time and tempera-
ture,
 - asphalt-mineral mixtures, 399
 - compositions, effect of pure asphalt,
400
 - gelatin, 332
 - raw rubber, 182
 - time, 309
 - twist angle, 131
 - Break-up pattern in rupture tests, 532
 - Brittle metal, deposited for rupture
tests, 531
 - Bromoform, diffusion in various sol-
vents, 136
 - Brownian movement, 236
 - Brückner method
 - capillary characterisation, 477
 - Bubbles, oscillations, 462
 - Bulk creep compliance, see Creep com-
pliance
 - Bulk modulus, see Modulus, bulk
 - Bulk stresses, 435
 - Bulk viscosity, see Viscosity
 - Butadiene, copolymer with styrene,
see GR-S
 - Butanone, as polystyrene solvent, 119,
120
 - Butyl rubber, 9
- C**
- Cage model, see Neighbor, nearest
 - Calcium soap in oil, 127
 - Calender, 182
 - shrinkage, 229
 - Calfskin gelatin, fractions rigidity, 348
 - Camphor, as plasticizer, 238, 239
 - Capillary, see also Pipe
 - bore correction, 477
 - bore determination, 476
 - characterisation, 477, 478
 - choice for non-Newtonian liquid, 476
 - dimensions, 476
 - entry conditions, 476
 - flow, see Flow, capillary, Viscometers
 - gages, normal stress, 509
 - viscometers, asphalts, 367
 - Carbon black, 209, 224
 - effect on rubber viscosity, 227
 - on thixotropy, 214
 - Carbon tetrachloride, self diffusion, 99
 - as polyisobutylene solvent, 121
 - Casein fiber,
 - entropy and internal energy, 299
 - stress-strain cycle, entropy contri-
bution, 300
 - Casting box, 241
 - Cell wall, primary, secondary, 268
 - Cellosolve, methyl, 238
 - Celluloid, 239
 - Cellulose, 233
 - crystallite dimensions, 267
 - degree of polymerization, 264
 - β -glucoside linkage, 234
 - melting point, 235
 - molecular structure, 233, 263, 268
 - molecule, average configuration, 237
 - viscosity, 241 (1)
 - Cellulose acetate, 234, 240 (see also
Acetate)
 - creasing of, 291
 - dynamic bending modulus, 246

- impact strength, 258
- injection-molding, 248
- intrinsic viscosity and temperature, 250
- molding powders, flow grades, 241
- rate of shear and temperature, 249
- shear stress, 249
- solvents, 238
- strain recovery, 290
- substitution preferred, 235
- Cellulose aceto-butyrate, 234, 238
 - impact strength, 258
 - pressure, rate of flow, 251
- Cellulose derivatives, 233, 234 (see also Cellulose)
 - degree of crystallinity, 235
 - dependence of flow on stress, 113
 - flow, 243
 - plasticizer swelling, 236
 - solubility, 237
 - solution viscosity, 242
- Cellulose esters (see also individual ester), 234
- Cellulose ethers (see also individual ether), 234
- Cellulose ethyl, see Ethyl cellulose
- Cellulose fibers (see also Cellulose)
 - large strains, internal energy change, 299
 - maximum strength, theoretical strength, 310, 311
 - resilience of, 291
 - stress-strain curves, 284
 - temperature coefficient, 298
 - tensile strength, 308
 - water bound, 297
- Cellulose nitrate, 234, 236
 - cyclohexanone, Weissenberg effect, 244
 - extrusion, flow and recovery, 252, 253
 - impact strength, 258
 - mixed crystal with terpene, 236
 - solubility, 238
 - substitution, preferred, 235
 - wet forming, 252
- Cellulose triacetate, 234, 235
- Cellulose tributyrates, wave of shear-strain, 455
- Cellulose tripropionate, 234
- Cellulosic chains, rigidity, 237
- Cellulosic films, 241
- Cellulosic plastics, 234
 - cold drawn, 256
 - strength, 237
 - determining factors, 255
 - X-ray diffraction, 235
- Cement, ethyl cellulose, 244
- Chain molecules, see also Folding, Configuration, Macromolecules, Segment
 - branching, 266
 - configuration, see Configuration
 - entropy, see Configuration
 - flexibility, mobility (see also Segment), 10, 66, 88, 169, 172
 - heterogeneity of composition, 70
 - jumps, 301
 - length, 242
 - scission, in deformation, 4
 - stiffness, effect on "distinctive" and glass temperature, 69, 70
 - straightening, 271, 276
- Characteristic, see under Noun
- Characterisation complete, rheological requirements, 520
- Charpy impact test, 257
- Chemical potential, 100 (67)
 - gradient, 97, 100
- Chemical stress relaxation 67, 79-81 (see also Chemorheology, Stress relaxation)
- Chemorheology, 5, 79-81
- Chrom alum, gelatin, 331
- Circuit theory, linear, 3, 40
- Clamping absolute, 451
- Classical theory of elasticity, see Elasticity
- Coarse-grained system, 535
- Coaxial, concentric, cylinder viscometer (see also Elastoviscometer, Viscometer, coaxial cylinder, Couette) 192, 244, 248, 435, 445, 493, 500
- asphalt, 367
- design, range, 488, 490
- flow as simple shearing, 486
- gelatin, 335, 350
- impulsive, 465
- oscillatory experiments, 496
- precision, 495
- resonance frequency, 447
- rotating, stability of laminar flow, 496

- Coefficient of friction, see also Friction
particles, asphalt mixture, 390
of viscosity, See Viscosity
of viscous traction, 369
- Cohesion between cellulose chains,
effect of substituents, 235
- Cohesive bonds, breaking in uniform
population, 305
- Cohesive energy density, 70, 238
- Coiling, see Folding, Chain molecules,
Configuration
- Coir fiber, 262, 268
- Cold drawn, cellulosic plastic, 256
- Cold flow, see Flow
- Cold milled rubber, 204
- Collagen, 316-319
conversion to gelatin, 315
low-angle X-ray scattering, 359
sources, 315
structure, 359
- Colloids, in asphalt, 364
- Color test (see also Turbulence), 481
- Combinatorial term, 139
- Comparison of plastometers, visco-
meters, 212
- Compatibility, plasticizer, 238
- Complex compliance, see Elastic com-
pliance
- Complex formation, plasticizer, 238
- Complex modulus, see Modulus
- Complex reciprocal modulus, 520 (see
also Elastic compliance, complex)
- Complex shear modulus, resonance
frequency, apparatus, 446
- Compliance, see Elastic compliance
- Compressibility, 452, 456
and free volume, asphalt, 380
- Compression, see also Plastometers
cellulose derivatives, 245, 253
gelatin, 335
unilateral, 435
recovery, 197
viscometers, 190, 195
and wave propagation, 456
- Compressive transient, 465
- Concentration, effect on viscosity, see
Viscosity
- Concentric-cylinder apparatus, see Co-
axial cylinder viscometer
- Condensed systems, potential energy, 87
- Condenser gages, 516
- Conductivity
electric, earth, 404
thermal, earth, 404
- Configurations, 70 (see also Chain
molecules, Macromolecules, Relaxa-
tion mechanism, Solvent)
cellulose molecule, 237
polymer in solution, 243
elastic deformation, 10, 220, 254
entropy, rubber elasticity, 10, 70, 71,
298, 471
state of glasses, 147
- Consistency
asphalt, 365
material, 463
- Continuity principle, 505
- Continuous phase, asphalt, 364, 371, 381
- Convection currents
earth, 422
earth core, 430
- Coordination of the segmental motion,
109
- Copolymer, see Polymer, also individual
copolymer
- Copolymerization, effect on glass transi-
tion, 175
- Cordite, 239
- Core, see Earth, Core.
- Corn flour
paste, 532
powder, 532, 533F
fatigue and failure of, 531F
- Cortex, cystine content, 209
- Cotton, 262, 268
breaking velocity, 309
creasing of, 291
dynamic bending modulus, 296
dynamic modulus and static strain,
294
elastic moduli, 283
extensibility, 284
fibers, reaction to acids and alkalis,
279
flow units, 302
moisture regain, 270
molecular orientation, 267
nitrated, 133
relaxation, 278, 279, 302
strain recovery, 290
stress-strain, curve, 283, 284

- effect of humidity and temperature, 287, 288
- tensile strength, 308
- torsional rigidity, 297
- Cotton strength, see also Cotton
 - degree of polymerization and, 308, 312
 - flexing, 312
 - limiting breaking velocity, 309
- Couette method, 486 (see also Coaxial-cylinder viscometer)
 - capillary, pipe characterization, 478
 - flow analysis, 480
- Crazing, 154, 526
- Creasing
 - effect of crystal limits, 291
 - of side groups, 292
 - geometry of, 291
 - recovery from larger strains, 291
- Creep, 6-10, 25, 38, 63, 150, 271, 408, 434
 - acetate, 302
 - analysis, 11, 25, 97, 275, 280, 302, 304, 437
 - asphalt, 246, 256
 - cellulose derivatives, 246, 258
 - curve, aluminum and alloys, 134, 136, 440
 - Andrade's equation, 257
 - fibers, 270, 272, 273
 - humidity and temperature, 13, 279, 281
 - effect of time, 11
 - experiment, 25, 437
 - formed elastomers, 184
 - gelatin gels, 332, 335, 351
 - latex rubber, 114
 - lead, 113
 - linear portion, 152
 - master curve, 274, 275f
 - metals 113, 134, 136, 276
 - methods, 438
 - models, equivalence, 302
 - molecular interpretation, 275, 96
 - nylon, 274
 - organic glass, polystyrene, 152
 - plasticized system, 179
 - primary, 6-10, 96, 152, 271, 302, 437
 - protein fibers, 272, 276
 - recovery, 38, 59, 272, 424
 - recovery, bond breakdown, 271
 - relaxation spectrum and, 151
 - rigid materials, 156
 - secondary, 96, 134
 - silk, 302
 - steel, 113
 - strain, 38, 257, 424
 - elastic tectonic, 426
 - studies by compression, extension
 - simple shear, torsion, 438
 - temperature-time, reduced variables, 471
 - tertiary, 96
 - test, 14, 271, 426
 - tin, 113
 - viscose rayon, 302
 - wool, 59
 - zinc, 113
- Creep compliance, 26, 29, 30, 50 (3)
 - bulk, 56
 - butyl rubber, normalized, 9
 - calculation from relaxation modulus, 41
 - comparison, 20, 21T
 - elastic, 14, 35, 47
 - experimental, 30
 - longitudinal, 56
 - natural rubber, normalized, 9
 - noncross-linked polymer, 13
 - normalized, 9
 - plastic in tension, 57
 - shear, definition, 7
 - from longitudinal creep and stress relaxation tests, 57
 - vulcanized rubber, 8
- Creep function, 151, 274
 - model representation, 301
- Crepe, see Rubber
- Creslan, 205
- Critical constants, 401
- Critical damping distance, 457
- Critical dimension, sample, 442, 453, 461
- Cross elasticity (see also Weissenberg effect), cellulose derivatives, 243
- Crossing potential barrier, 90
- Cross-linked polymer, see Polymer
 - cross-linked, Rubber
- Cross-linking, 226, 246
 - in deformation, 4, 79
 - by oxidation, 80
- Cross-section area changes, 439
- Crustal layers, earth, 403
- Crystalline

- materials, pattern of rupture, 534
 - micelles, cellulose, 235
 - polymer, *see* Polymer
 - regions, cross links, 236
 - Crystallinity, 235
 - Crystallites, network structure, 267
 - Crystallization
 - in creep, 276
 - of glasses, 147
 - rate in stress relaxation, 79
 - Cuprammonium rayon, 234, 262
 - creep, 276, 279
 - dynamic properties, effect of frequency, 295
 - internal friction, 295
 - stress relaxation, 278
 - torsional rigidity, 297
 - Curing, raw elastomer, 182
 - Currents
 - convection, 422
 - in core, 430
 - Cyclic stress energy dissipation, 162
 - Cyclohexyl methacrylate, 170
 - Cystine, 267
- D**
- Dacron, Terylene, Polyethylene Terephthalate,
 - breaking extension, 288
 - dynamic modulus, 294, 296
 - moisture regain, 270
 - prerupture flow, 288
 - rigidity, 296, 297
 - strain recovery, 290
 - strength, effect of temperature, 308, 310
 - stress-strain curve, 284, 285, 288
 - yield stress, 288
 - Young modulus, 288, 289
 - Damping, (*see also* Absorption, Attenuation, Friction, internal, Hysteresis), 145, 148, 409 (12), 454f
 - capacity specific, 293
 - distance critical 453, 454
 - effect of humidity and temperature, 286
 - of orientation, 164
 - extremely high, 460
 - gelatin gels, characteristics of, 336
 - increase below glass transformation, 164
 - logarithmic, 148, 448, 461
 - longitudinal waves, 429
 - maxima, discrete, 175
 - rheometer, 192
 - seismic waves, 409
 - severity of, 454
 - Dashpots, in mechanical model, 26, 467
 - Debye temperature, 139
 - Decay law of nerve impulse, 104
 - Decay modulus, *see* Modulus
 - Decay stress, *see* Stress
 - Decrement, *see* Attenuation, Damping
 - Defo method, 191
 - Defo plastometers, 192
 - Deformation, 253 (*see also* Displacement, Strain)
 - amplitude, 148
 - asphalt, 367
 - bulk, 22
 - dynamic, 4
 - elastic, large, theory, 2
 - non linear, 7
 - versus viscous, asphalts, 367
 - homogeneous, 528
 - instantaneous, 9
 - internal energy increase by, 9
 - irreversible, non-recoverable, permanent, viscous, 7, 39, 84, 145, 152, 153, 165
 - irreversible, set, fiber, 81, 271
 - main plane, 529
 - non-recoverable, effect of chemical variables, 165
 - nonsinusoidal, 465
 - residual, *see* irreversible
 - shear (*see also* Shear, Shearing), 22
 - sinusoidal, 3, 367
 - translation and rotation in, 5
 - Degradation
 - cellulose derivatives, 237
 - gelatin, 323
 - Degree of crystallinity, Dacron, 266
 - Degree of freedom
 - activated complex, 89, 90
 - translational, 90
 - Degree of order, glasses, 147, 266
 - Degree of orderliness, 266
 - Degree of packing, function of temperature, 53
 - Degree of polymerization, *see* Molecular weight

- Degree of substitution, preferred, cellulose derivatives, 235
- Delayed, Retarded, see also Elasticity, retarded
extension (see also Creep), 273
- Delta function, approximations for relaxation and retardation spectra, 47
- Demineralized gelatin, concentration effect, 341
- Denaturation, 264
- Denotation impulse, 465
- Dense road carpet mixtures, 388
- Density
earth, 401, 405
earth, change with depth, 421
fluid, 481
- Descaling of fibers, 292
- Detector coil driver, 451
- Deviator components, 55
- Dialysis, gelatin, 318
- Dibutylphthalate, effect on polyvinyl-chloride damping, 178
- Dibutylsebecate, effect on polyvinyl-chloride damping, 178
- Dielectric behavior, time effects, 3, 169
- Diethyl phthalate, effect on polyvinyl-chloride damping, 178
- Differential transformer, 436
- Differential viscosity, asphalt mixture, 390, 394, 399 (19)
- Diffusion, translational and general, see also self-diffusion
benzene, 138
biological, 101
cross-surface, grain boundary, 136, 225
free, 99
free energy, in liquid or solid state, 102
generalized, theory of, 97
heterogeneous systems, 100
hydrogen bonding solvents, 138
membrane, 101
multiple relaxation, 84
net rate of, 98 (53a) (53b) (54)
relation to viscosity, 97
relaxation of the solvent, 101
self, 99, 138
solution, 136
of spheres, 101
steady state, 100
water, 138
- Diffusion coefficient, 98 (55)
standard membrane, 103
- Diffusion, rotational, see Orientation, Birefringence
- Diisobutylene, as polyisobutylene solvent, 124
- Dilatancy, 94, 131
effect of rate, 533
printing inks, 526
reversal, 533
- Dilatant pastes, 533
shear hardening, 526
- Dilatation, waves of, 453
- Dilatometric glass, transition temperature, 167
- Dilauryl phthalate, effect on polyvinyl-chloride, damping, 178
- Dillon extrusion plastometer, 190F
- Dimethyl formamide, 95
- Diethylphthalate, effect on polyvinyl-chloride damping, 178
- Dipole moment of macromolecules, side group, 172
- Discrete relaxation, molecular theory, 36, 52
- Discriminating power, 213
- Disentanglement, see Entanglement
- Disk viscometer, 186
theory, 193
- Dislocation, 526
edge, 136
movement of, 136
screw, 136
- Disperse phase, asphalt, 364, 371, 381
- Dispersion region
moduli, 161
multiple, 161, 162, 175
secondary, 167, 169, 170
solubility effect, 176
temperature effect, 161
- Displacements, see also Deformation, Strain
measurements of, 516
normal, 509
- Disruptive force, shear planes, 221 (22)
- Dissipation energy, see Energy dissipation
- Distinctive temperature, 68-70, 75

- GR-S, 69
 - Paracryl, 69
 - polyisobutylene, 69, 72
 - polymethylmethacrylate, 69
 - Distortion, waves of, 453
 - Distribution,
 - box, 72-74
 - distribution function, 151
 - of equilibrium positions, 139
 - molecular weight, 65-68, 72
 - relaxation or retardation times, 72, 73, 467
 - relaxation times, calculation from experimental measurements, 468-70
 - wedge, 72, 73
 - Disulfide
 - bonds, effect of humidity on relaxation, 282
 - in Keratin, 94
 - cross links, Keratin fibers, 276
 - linkages, 299
 - hydrolysis, 279
 - Divergence, 514
 - Double refraction, strain, 454
 - Downwarping sediments, geological, 421
 - Drawing during spinning, 266
 - Driving force, complex, dynamic measurements, 446
 - Dry process, cellulose acetate, 240
 - Ductility, 154
 - amorphous glasses, 155
 - Duralumin, creep, 440
 - Dynamic, complex modulus, see Modulus, complex, dynamic
 - Dynamic
 - deformation, 4, 25
 - experiment, volume viscoelasticity, 56
 - internal friction, 293
 - measurements (see also Dynamic response), 157
 - methods, viscoelasticity, 434
 - moduli interdependence (see also Dynamic modulus), 23
 - properties, fibers, effect of amplitude, 294
 - rigidity, dispersion, gelatin, 336
 - stress, high, 466
 - superimposed on high static, 465
 - tests, asphalt mixture, 391
 - frequency, 52
 - and transient measurements, correlation, 467
 - viscosity, 44, 192, 244
 - Dynamic modulus (see also Modulus),
 - 21 T, 64, 72, 192, 293, 306, 444
 - differential, 466
 - fibers, 294, 306, 307
 - rigidity, gelatin, 351
 - versus static strain, fibers, 294
 - Dynamic response, mechanical measurements, 18, 28
 - classification, 442
 - comparison of, 20, 21T, 463
 - criteria for selection of, 442, 463
 - critical dimension, 442
 - high stress, 466
 - limitation and advantages, 462, 463T
 - non-sinusoidal, 465
 - parameter relation, 21
 - procedures, 24
 - resonance methods, 445
 - sample size comparison with wave length, 442, 446
 - superimposed static stress, 465
 - Dynel, 265
- E**
- Earth, see also Earth, Core, Crust, Mantle
 - absorption coefficient, 410
 - axis, gyroscopic motion, 401, 420
 - begin, 401
 - body tides, 401, 406, 420
 - boundaries, 401
 - breaking strength, 403
 - circulation, 422
 - density, 401, 421
 - elastic constants, 401-405
 - elastic motion, retarded, 406, 408, 409
 - electric conductivity, 404
 - fault, see Fault
 - firmoviscosity, 406
 - flow, in the core, 429
 - flow, speed, 406, 413, 417, 423
 - friction internal, 406, 409
 - heat flow, 404
 - interior of, 401, 409
 - interior convection, 405
 - latitude and viscosity, 420
 - magnetic field of, 429

- nonelastic constants (see also Viscous, Dissipating), 409
- nonelastic processes, 406, 408
- phase change, 404, 422
- pressure, 403
- radioactive process, 404
- radius, 421
- relaxation time, 409, 419, 423
- rigidity, 402, 405
- rotational velocity of, 421
- shearing strain, 406
- strain accumulation, 423
- strain-rebound, 423
- subcrustal currents, 422
- surface of, 404, 409
- viscosity, 409, 418, 420, 421
 - with depth, 418, 419
- viscous flow, resisting strength, 409
- viscous recoil, 419
- Earth, core, 401, 402, 406
 - boundary, 429
 - composition, 402
 - convection currents, 430
 - flow, 402, 429
 - seismic surface, 410
 - viscosity, 405, 429
- Earth, crust
 - bulk modulus, 404T
 - model, 428
 - movement along faults, 428
 - rigidity, 404
 - rocks, 404
- Earth, mantle, 402, 403
 - flow process, 418, 419, 422
 - relaxation time, 418
 - transition to core, 429
 - viscosity, 421
- Earthquakes, 403, 423, 426
 - amplitude decrease, 410
 - cycles, 426
 - deep focus, 423, 426
 - energy, 424
 - magnitude, 424 (30)
 - research, 411
 - rupture, 420, 423
 - series, 423, 425
 - strain, post glacial uplift, 417
 - strain-rebound characteristics, 423, 425
 - strain-release, 426
 - waves, 405, 409
- Echoes, seismic recording, 418
- Efflux, reduced, 195
- Einstein's formula, asphalt mixtures, 392
- Einstein-Stokes equation, 100
- Elastance, 446
- Elastic, see also under noun, Elasticity
 - afterworking, earth, 406, 408
 - body, 84, 509
 - constants, earth, 401, 403, 405, 422
 - deformation, see Deformation
 - distortion, extrusion, nitrocellulose, 252
 - effects, cellulose derivatives, 243
 - energy, in flow, 92
 - force, fiber, 272
 - hysteresis, Coulomb type, 59
 - limit, gelatin gels, 345
 - materials (bodies), 509
 - motion, delayed, retarded, in earth, 406-408, 411
 - rebound (see also Elastic recovery, Strain rebound), 424-429
 - recoil, cellulose derivatives, 243
 - shrinkage, calendered sheet, 229
 - stiffness, 448 (see also Modulus, rigidity, Modulus Young's)
 - straining, ordinary, 253
 - waves, earth, 421, 422, 429
- Elastic compliance, reciprocal modulus, 150
 - absolute, 20
 - bulk, 55
 - complex, dynamic, 20, 28, 150, 441, 468
 - delayed, 13, 25
 - equilibrium, 8, 44
 - loss, mechanical model, 28, 29 (6b), 43
 - not experimentally accessible, 11
 - steady state, 13, 17
 - storage (see also Energy, Modulus elastic), 23, 43, 50
 - mechanical model, 28, 29 (6a), 35
 - temperature dependence, 7
 - temperature-time, reduced variables, 471
- Elastic modulus, see Elastic, Elasticity, Moduli, Modulus
- Elastic recovery, rebound, 14, 187, 228 (12), 248, 289, 370, 371, 424
- calendered sheet, 229

- curve, rheometer, 192
- formed elastomers, 184
- function of rate of extrusion, 216
- glasses, 152
- plastomer, 191
- and pressure, 524
- relation to stress, 374
- retarded, 2, 12, 24
- rheometer, 185, 187, 215
- stock, shrinkage, 183
- strain, 289, 291
- time dependend, 2
- Elastic response, deformation
 - elastic waves, retarded, earth, 409
 - in phase (immediate), 6, 443, 444
 - out of phase, 6, 443, 444
- Elasticity
 - cellulose derivatives, 253
 - complex modulus, 519 (20)
 - configurational, 254
 - cross (see also Weissenberg effect), 243
 - delayed, see retarded, see also Friction, internal, Voigt body
 - dynamic, see Four parameter model, Maxwell body, Voigt body
 - evanescent, 243
 - gelatine gel, 342
 - gelatine film, effect of temperature, humidity, 351
 - general and theory, 2, 40, 243, 253
 - glasslike, at high frequencies, 59
 - liquid, 496-499
 - harmonic oscillations, 486
 - modulus, see Elastic compliance, Moduli, Modulus
 - ordinary, 253, 254
 - perturbation upon flow, 52
 - retarded (see also Viscoelastic), 2, 6, 10, 32, 41, 407-409
 - asphalt, 370-375
 - fibers, 290
 - shear, 509, 519, 521
- Elastico-viscosity, 406, 407
- Elastico-viscous liquids (see also Elasticity, Maxwell body, Non-Newtonian liquids), 11-15, 92-96, 105-131, 215, 243, 445, 486, 504, 510
- characterization (detection), 486, 497, 499
- flow in pipes, 484
- Maxwellian, 498
- properties in oscillatory motion, 498F, 499
- in steady flow, 484, 494
- relaxation and retardation times, 497-500
- rheological model, 496-498, 499F
- solution of polymethyl methacrylate, 484, 494, 499
- viscosity and fluidity, 484, 494, 500
- wall effect, 485
- Elastomer, see Rubbers, Chain molecules
- Elastoviscosimeter, coaxial-cylinder, 487
- air-lubricated bearing, 490F, 491
- design, 487-492
- end effects, 490, 493, 498, 499
- motion of, 492
- oscillatory experiments, 496
- rate of shear, 494, 495F
- relaxation and retardation times, determination, 497, 499
- shear stress, 494
- steady-rotation experiments, 493
- torsion wires, 492
- torsional head, 491
- viscosity coefficient determination, 493-495F
- wall effect, 494
- Elastoviscous, see Elasticoviscous
- Electrical
 - capacity, mechanical dynamic measurement, 450
 - reactance, 450
 - resistance, mechanical dynamic measurement, 450
 - transport, membrane diffusion, 104
- Electromagnetic transducer relation, 460
- Ellipse geometry, 444
- Elongation (extension)
 - at break, cellulose plastic, effect of temperature, 256
 - lines of zero, 505, 529, 532
 - spontaneous, see Spontaneous elongation
- Enamels, cellulosic, 241
- End effects, 189
 - coaxial cylinders, 480, 490, 493, 499
 - non-Newtonian liquids, 480
 - oscillatory experiments, 490
 - pipes, 479, 480
- End groups, effect on mechanical properties, 167

- Energy, see also Configurations, Degrees of freedom
absorbed in impact, 257
activation, see Activation energy
barrier, two-state system, deformation, 304
density, cohesive, 238
earthquakes, 424
formation of holes, 87
internal, increase by deformation, 9, 298
loss, 444, 456
storage (see also Elastic compliance), 4, 424, 444
stored, dynamic measurements, 441
vaporization and number of holes, 88
wells, steepness, 84
- Energy dissipation (see also Damping, Dynamic loss), 4, 148, 150, 293, 448
comparison, 521
cyclic stress, 162
dynamic measurements, 441
impact, 465
viscosity and, 516
- Entangled, Entanglement (see also Macromolecules), 88, 92, 93, 276
flow unit, 88
- Entrance pressure drop
rubber extrusion, 194
thixotropy, 208
- Enthalpy as function of temperature, 53
- Entropy, (see also Configurational), 111
stressing contribution, 300
- Equation of motion (see also Navier-Stokes), 418 (25)
Ostwald-de Waele, 108
Stokes-Einstein, 100
Vibrations, 149 (2)
- Equation of state
flow units, 90
liquids, 140 (107)
viscoelastic behavior, reduced, 72
- Equilibrium
amorphous regions, cellulose, 236
compliance, see Elastic Compliance
constant at zero stress, 93
crystalline regions, cellulose, 236
of forces, 505
mechanical of glass transformation, 146
modulus, see Modulus
position, gaslike, solidlike, 139
rate of approach to, 30
site, empty (see also Holes), 84, 87, 141, 142
- Equivalence, temperature and frequency (see also Scale Factor), 158
- Equivalent loading time,
asphalt, penetration, 383
Ring and Ball test, 386
- Ethyl alcohol, effect on gelatin, 331, 345
- Ethyl cellulose, 234, 235, 246, 247
apparent viscosity and temperature, 250
as binder, 244
hot dip, 242, 244
impact strength, 258
plastic range, 247
substitution, 235
- Ethylene glycol, 266
- Euler's constant, 306
- Evanescent elasticity, cellulose derivatives, 243
- Experimental data, analysis, 467
- Explosions, elastic waves, 421
- Extension, see also Creep
gelatin gels, 335T
fibers, 272-276
- Extension breaking, see Rupture
- External forces, 149
- Extraction, gelatine, 315, 316
- Extruder
power consumption, 227
screw, 182
- Extrusion, 239
compound (nitro cellulose), 252
critical pressure and speed, cellulose aceto-butyrate, 251
method, rotation method comparison, 208
plastometer, 189, 190, 194, 207, 208, 248
swell, 196, 251
time of, 190
- Eyring,
creep rate, theory, 85
hyperbolic sine function, 85, 113, 123
shear rate, theory, 85
theory, revised for rheological units, 220
viscous flow, theory, 85, 206, 225

F

- Factory ratings, processability, 230
Failure (see also Breaking, Yielding), 526
Failure, brittle, see Rupture
Falling cylinder viscometer, 210
Fatigue, 257, 526
 powder aggregates, 532
 strength, and strain amplitude, 162
Fault, Earth
 displacement, 428
 nonelastic movement, 429
 zone, viscous distortion, 428
Fennoscandia,
 depression, 415
 rate of uplift, 415
 uplift, 413, 414, 419
Ferry and Williams approximation method, 49
Fibers
 conditioning, 270
 convolutions, cotton, 268
 immersed, 437
 longitudinal waves, 456
 strength, 308-310
 polyethylene, 293, 306, 308
 polyvinyl, 265, 294, 300, 307, 308
 structure, 262
 wave propagation superimposed, tensile stress, 466
Fibrils, cell wall, 268
Fibrin spacings, 359
Fibroin, 264
Filler-bitumen ratio, 396
Fillers
 aiding Hooke's law, 58
 viscosity effects in rubbers, 227
Films, cellulose, 238, 241
Filtration, 101
Final stress, fiber deformation, 302
Fine structure
 anelastic properties, 161
 fibers, 268
Firmoviscosity, 406, 407
Fish collagens and gelatins, 319, 320
Fitzgerald, apparatus of, 451
Five element model, 30-32
 operator equation, 31
Fixed shear rates in molding, 250
Flax, 262, 268, 311
 molecular orientation, 267
 tensile strength, 308
 torsional rigidity, 297
 twisting resistance, 311
 yarns, 278
Flexural, resonance vibrations for compound systems, 462
Flexural rigidity, see Rigidity
Flexural waves, 456
Flooring composition, 246
 ethyl cellulose, 244
Flow, fluid, irreversible, viscous (see also Flow, curve, plane, plastic, process, Hydrodynamics, Viscosity), 4, 72, 79, 84, 152, 242, 333, 407, 413, 422
 activation energy, 53
 anomalous, analysis, 483
 between coaxial cylinders, 486
 birefringence, see Optical anisotropy
 capillary, 479
 cellulose acetate, effect of plasticizer, 251
 cellulose derivatives, 242
 cold, cellulose derivatives, 246
 organic glasses, 155, 165
 data, pipe, analysis, 475, 480
 earth, across mantle, 422
 earth's core, 429
 equation, generalized, 113
 general in pipes, 483 (5)
 geological periods, 422
 small scale, 427
 goniometry, 503F
 heat, see Heat
 ice in glaciers, 427
 laminar, breakdown, 481, 485
 at large stresses, 476
 liquids, 504, 506F, 523
 lava, 428
 melt, polyethylene, 517
 polyisobutylene, 517
 polystyrene, 113
 nonlaminar, 481
Newtonian, 12, 13, 209, 413, 414, 427
Non-Newtonian, see anomalous, Non-Newtonian
parameters, aluminum and its alloys, 135
 concentration dependence, 119
patches, 88
pressure distribution, 504, 506F

- properties, ethyl cellulose, effect of time, 247F
- relaxation time, 72
- rubbery, 66, 71-74, 77
- secondary (see also Creep, Cross, Elasticity, Weissenberg effect), 243
- solution, polyisobutylene, 517
- steady, 12, 93, 475, 480
- steady state stress-dependent phenomena, 92
- at stresses below strength, 422
- subcrustal, 413, 417
- suspensions of anisometric particles, 476
- thermoplastic suppressed by chemical cross links, 79
- transition to rupture, 526
- viscoelastic liquid, see Elastico-viscous
- with structural change, 92, 94, 96
- wall, anomalous near, 482, 483
- Flow curve
 - classification of, 131, 132, 209, 210
 - cellulose acetate, 249
 - determination, 193, 479
 - dilatant system, 131
 - elastomers, 200, 206, 210
 - with structural change, 131
 - without structural change, 131, 132
- Flow, plastic, 89, 247
 - asphalt composition, 391
 - boundary condition, 390 (18)
 - earth, 413
 - gelatin gels, 332, 335, 350, 352
- Flow process, 85
 - earth, 406, 413
 - earth's mantle, 419, 422
 - natural rubber, 109
- Flow units, Rheological flow units, 84, 88, 114, 222-225
 - carbon black, 227
 - change with polymer concentration, 130
 - cross-sectional area, diameter, 130, 219-224
 - deformable, 92
 - (dislocations) in metals and in plastics, 136
 - dynamic viscosity, 224
 - elastic modulus, 221
 - elastomers, 220
 - equation of state for, 90, 91
 - friction of, 220
 - hair, 95
 - heterogeneity of, 88
 - mean life of an attachment, 222
 - Newtonian, 105, 109, 114, 127, 129
 - Non-Newtonian, 105, 109, 127, 129
 - number of, 302
 - parameter of, 111, 112
 - polystyrene solution, 116
 - probability of occurrence of, 89
 - relaxation time of, 88
 - rotational velocity, 221
 - temperature dependence, 111
 - types, for high molecular weights, 129, 133
 - vibration, 91
- Fluid dynamics, 480
- Fluidity
 - elastomers, 200, 219
 - power law, 193, 194, 214
 - rubbers, temperature effects, 211
- Flux density, magnetic, 450
- Folding, Coiling, Curling, polymer molecules, (see also Chain molecules, Configuration), 10, 129, 130
- Folds geological, 428
- Forces
 - descriptive, 210 (22)
 - dynamic equilibrium, in flow, 505
 - restoring (tension, inner), 298
 - transmission through deformable agent, 526F.
- Formaldehyde
 - effect on gelatin, 331, 346
- Formamide, effect on gelatin, 331
- Forming operations, 227
 - of raw elastomer, 182
- Four parameter (term) equation, 519
- Fracture, see Breaking strength, Rupture, Strength
- Free energy, curves
 - diffusion in liquid or solid state, 102
 - elastic potential, 521
 - entanglement-disentanglement transition, 93
 - gradient, 97
 - Helmholtz, 106, 140
 - membrane diffusion, 103
 - perfect gas, 140

- transition α - β in wool, 95
- well, minimum, 84
- Free radicals, by mechanical rupture, 226
- Free rotation, 237
- Free volume, 139, 177
 - effect on glassy modulus, 69
 - loss, under pressure, 55
 - relation to compressibility, asphalt, 380, 381
- Freezing, cellulose aceto butyrate, 251, 252
- Frequency, see also Jump frequency, Sinusoidal, Vibrations
 - circular, 442
 - coaxial cylinders, 496
 - dispersion, in glasses, 161
 - dynamic response, tests, 19, 52
 - effect on damping, 162
 - on mechanical behavior, 442
 - on moduli, 19, 35, 44
 - master curve (see also Scale factor), 67, 73-75
 - ordinary, 442
 - range, scale, 22, 158
 - extended by reduced variables, 472
 - mechanical measurements, 157
 - response, curve, 447, 461
 - elasticoviscous liquid, 497
 - rheometer, 192
 - spurious effects, 464
 - time scale, time-temperature superposition, (see also Scale factor) 4, 22, 67, 74-77
 - temperature and, comparison of effects on organic glasses, 159
 - vibrations, 64, 149
- Friction anelastic, see Friction internal
- Friction force, 100
- Friction internal (see also Coefficient, Damping, Delayed (retarded), Viscoelasticity, Voigt model) 161, 293, 295, 307, 408, 412
 - asphalt, 394, 399
 - earth, 406-411
 - effect on compressional motion, 412
 - on seismic waves, 412
 - fibers, 295, 306
 - stress dependence, 157, 306
 - triaxial test, 400
- Frictional resistance, aggregates particles, 390
- Fringe, cellulose, 235
- Fusion,
 - entropy of, 142
 - random mixing, 141
- G**
- Gaslike equilibrium position in liquids, 139
- Gaussian error function, 71
- Gel, see also Gelation
 - asphalt, 274
 - ethylcellulose, 244
 - formation, theories, 357
 - forming power, gelatin, 315, 316
 - GR-S, 226
 - sol, transition temperature, gelatin, 322
- Gelatin, Gelatine, 314, 316
 - acid process, 317, 320, 350
 - adhesive, 359
 - aggregation, 322, 324, 326, 358, 359
 - aging, 335
 - alkali process, 320, 328, 333, 349, 350
 - amide groups, 316-319
 - amino acid analysis, composition, 318, 319T
 - amino end groups, 320T, 321T, 324
 - apparent viscosity, effect of rates of shear, see Gelatin, viscosity of solutions
 - blends, 317, 342
 - Bloom-gelometer, 317T, 333, 360, 361
 - calfskin, 325, 331, 333
 - carboxyl groups, 316, 321T
 - chain folding, 326
 - chemical differences, 321
 - chrome alum, 331
 - counter ions, 326
 - degradation, 315-317, 324, 329, 330, 339, 347, 350, 352, 358
 - deionization, dialysis, demineralisation, 318, 324, 340, 341
 - drum drying, 351
 - effect of phenol, urea, 346
 - of temperature, 346
 - electrolyte effect on elasticity, 344
 - electrostatic interaction, 359
 - extracted, properties of, temperature, 315, 317T
 - family, 314
 - fish collagens, 319

- formaldehyde hardening, 331, 332
- fractionation, fractions, 317, 327, 328, 348, 349
- gel formation, power (see also Gelatin gels), 321, 346, 350, 351, 360
- gelation, region, 353
 - viscosity and elasticity, 356F
- heterodisperse, 320
- Hooke's law, 332
- hydrogen bonds, 353, 358
- hydrolysis, see degradation
- ice point, 332
- impurities, 316
- intermolecular bonding, 331
- intramolecular bonding, 331
- intrinsic viscosity, 323
- ionizing groups, 320, 321
- isoelectric point, (pI), opalescence, 316, 359
 - viscosity minimum, 329
- isoionic point, 316
- jelly strength, 333
- light scattering, 320, 357-359
- loci of gel bonds, 357
- longitudinal shearing, 336
- manufacture, see gelatin, manufacture
- mean residue weight, 319
- melting point, see Gelatin melting
- molecular weight, 320, 321, 327, 330, 347, 348, 357, 360
- molecule, net charge, 325
- mucopolysaccharides, 316
- muta-rotation, 357, 358
- osmometry, 320, 327
- ossein, fractions, 315, 318, 328, 348
- pigskin, 341
- polypeptide chain structure, 321, 359
- precooling, 338
- prevention of setting, 346, 355
- properties, thermal and mechanical
 - history, 332, 350, 353
- proteolytic enzymes, 314
- raw material, pretreatment, 316
- setting point (see also melting point), 314, 353
- sizing, 360
- solutions, light scattering, 358
 - recoverable strain, 524
 - viscosity, see Gelatin, viscosity of solutions
- specification, 360
- square law of concentration dependence, 338-341
- sugar-acid mixture, 359
- table jellies, 359
- thiotropic effects, 357
- titration curve, 320, 322F
- transition temperature, 356
- ultrasonics, 330
- viscosity, see Gelatin, viscosity of solutions
- viscosity and rigidity at melting point, 355
- Weissenberg effect in aqueous solutions of, 524
- X-ray low angle scattering, 359
- Young's modulus, 332, 334
- Gelatin film, sheet,
 - cold dried, 351, 352
 - elasticity, 342, 351
 - extension at break, strength, 351, 352
 - hot dried, 351, 352
 - load-extension curve, 352F, 353F
 - plastic flow, 351
 - structure difference, 351
 - yield point, 352
 - Young's modulus, 352
- Gelatin gels
 - bonds, 358
 - compression, 335, 346
 - creep, 332, 336, 351
 - damping, 336
 - effect of formaldehyde, 346
 - of viscosity, 355, 356
 - elasticity, 254, 342, 343, 345
 - extension, 334T, 335T
 - flow, 334
 - formation of, (see also Gelation), 330, 350, 353-357
 - gel-formation power, 315-317, 320, 346, 360
 - Hooke's law, 332
 - jelly strength, 333
 - load-strain curve, 333F, 352, 353
 - mechanical history, 354
 - mechanical testing, 335, 361
 - moduli, dynamic, 351
 - of elasticity, 332, 334, 346, 347, 351
 - hardened, 346
 - nonelectrolytes, effect of, 345
 - orientation, 332, 353
 - plastic flow, 332, 335, 350, 352

- Poisson's ratio, 332
- relaxation time, 351
- rigidity, see Gelatin rigidity
- rupture, 332, 335, 345
- secondary bonds, 357
- shearing stress, 333, 336
- strain relaxation, 332, 333, 335, 350, 351
- structure, 345, 350, 351, 352, 357
- thermal history, 314, 332, 350, 353
- time dependent effects, 332, 357
- transverse vibration, 336
- van der Waals forces, 357
- yield point, 332, 352
- Young's modulus, 332-335, 351
- Gelatin manufacture, 315
 - acid process, 317, 318T, 320T, 323, 326, 344, 360
 - alkaline process, 316-320T, 322F, 323, 326T, 360
 - extraction temperature, 315-317T, 320
 - pretreatment, 316, 317
- Gelatin, melting point, 314, 322, 337, 346, 349, 354, 358
 - concentration dependence, 353, 354
 - effect of electrolyte, 355
 - molecular weight dependence, 355
- Gelatin, rigidity, modulus of gels, 332, 335, 343F, 345F
 - additives, effect, 344, 346
 - concentration dependence, 338, 339 341F, 342T
 - dispersion with frequency, 336
 - effect of strain, 333
 - ionic strength effect, 341, 345
 - isoelectric point, 344
 - melting point region, 338, 355, 356F
 - mixtures, 342
 - molecular weight dependence, 346-348F
 - pH dependence, 343, 344F
 - temperature effect, 337, 340, 346
 - time effect, 336, 340F
- Gelatin sheet, see Gelatin film
- Gelatin, viscosity of solutions, 316-331
 - anomalous, effect of rate of shear (see also Non-Newtonian liquids), 323, 353, 355, 356F, 357
 - chain folding, 326, 358
 - concentration effects, 328
 - effect of pH, ionic strength, salts, 324-326T, 328, 329
 - molecular weight, 360
 - and rigidity at melting point, 355
 - temperature effect, 326, 329, 330T
- Gelatine, (see also Gelatin), 314
- Gelation, see also Gel, Gelatin gel
 - effect of viscosity, 355, 356
 - region, rheological properties, 330, 353
 - theory, 315, 332, 357
- Geodetic measurements of movements, 348
- Geological
 - flow, 422, 427
 - folds, 428
 - sediments, downwarping, 421
 - trenches, (graben) 421, 428
- Geometry, sample, dynamic measurements, 446, 463
- Glaciated area, 413
- Glacier ice, Newtonian flow, 427
- Glass, 146, 451
 - elastic body, ideal, 4
 - fibers, 462
 - fibers, twisting resistance, 311
 - forming liquids, 145
 - modulus (see also Modulus), 68, 69
 - organic, see Organic glasses
 - relaxation, 54
 - state, region, 65, 69, 71, 76, 145, 146
 - temperature, distinctive, 68-70, 75, 76F
 - torsional relaxation, 279
 - viscous flow, 100
 - waves in, transverse, longitudinal, 458
- Glass compliance (see also Compliance), 9, 44
 - Hookean, 25
 - non cross-linked polymer, 13
- Glass, pipes, precision bore, 477
- Glass transformation, transition (see also Glass, state, temperature), 146, 161
 - diffusion-controlled relaxation, 147
 - configurational elasticity, 254
 - effect of chain interaction, 173
 - of concentration, 176
 - of monomer structure, 167, 172
 - of plasticizer, 177
 - glucose, 152
 - mechanical, 167
 - polyisobutylene, 37

- region (see also Dispersion, region, secondary), 145, 167
 - rubber transition, 3, 4, 70
 - temperature, 53, 54, 68-70, 75, 167, 171, 236
 - effect of copolymer composition, 177, 178
 - Glasslike
 - behavior, side group movement, 54
 - elasticity, see Elasticity, glass compliance
 - material, 5
 - Glassy modulus, rate of annealing, 65
 - Global strain, 426
 - Globular protein, denaturation, 264
 - Glucose
 - activation energy, 153
 - glass transformation, 152
 - residue, 263
 - viscosity, 152
 - Glucoside ring, hydroxyl groups, 234
 - Glue, see also Gelatine
 - adhesive strength, 359
 - bone, 315, 317, 320, 321
 - hide, 315, 317, 318
 - sizing effect of viscosity, 360
 - tack, 360
 - viscosity, 317, 359
 - Glycerine, effect on gelatine, 346
 - Glycine, 267
 - Glycol dimethacrylate, effect as cross linking agent, 170
 - Goniometry of Flow and Rupture, 503
 - space-time coordinates, 504
 - Gradient, chemical potential, 100
 - Gradient, velocity, see Shear rate
 - Grain boundary, diffusion through, 136
 - Granite, 404
 - Gravity
 - anomalies, 414, 415, 421
 - reduction, 421
 - Grease, lime-base, 127
 - Great Lakes, water level, 415, 416
 - Greenland
 - ice, 417
 - profile, 417
 - rock depression, 417
 - rock surface, 417, 418
 - Grid, reference, 530
 - GR-I, 212
 - rheological units, 220
 - rheometer flow curves, 204
 - Group velocity, seismic waves, 413
 - GR-S, 72, 110, 114, 169, 209, 212, 224
 - bond formation, 230
 - concentration effects, 126, 127
 - dissolved in α -methylnaphthalene, 125, 129, 132
 - distinctive temperature, 69
 - extrusion viscometers, entrance pressure drop, 207
 - fluidity, flow curves, power law, 207, 210
 - gel formation, 226
 - processability, 230
 - rheological units, 220
 - rheometer, flow curves, 205
 - shear rate vs. shear stress in α -methylnaphthalene, 126
 - solutions, values of parameters in α -methylnaphthalene, 125
 - stress relaxation, 69, 76
 - X-518, 110
 - X-672, 110
 - Growth of plants, 101
- H
- Hair, human, 276
 - dynamic properties, 295
 - Hair, natural wool, see Wool
 - Hard solid, dynamic mechanical measurements, 463
 - Hardness, 84
 - asphalt, 365, 377
 - gelatine, 331
 - penetration test, asphalts, 382
 - Harmonic oscillator, see Oscillator
 - Heat
 - activation, flow of GR-S, 206
 - flow through the earth, 404
 - fusion, polyamides, 175
 - specific, liquids, 140 (107) (108)
 - vaporization, 86
 - Helium II, frictionless flow, 90
 - Helix, in Keratin, 95
 - Hemp, 262, 268
 - tensile strength, 308
 - Hencky, evanescent elasticity, 243
 - Hevea, 114
 - breakdown in processing, 226
 - compression viscosity, 209
 - elastic recovery, 215

- extrusion viscometers, entrance pressure drop, 207
- fluidity, effect of temperature, rheometer, flow curve, 203-205
- Pale Crepe, flow curve, 200
- thixotropy, 202
- rheological units, 220
- rubber flow, 210
- temperature effect on viscosity, 213
- Hexagonal close-packed system, 98
- Hexamethylene diamine, 265
- Hide
 - gelatin, 328
 - lined, 319T
 - glue, 315, 317, 318
- High energy radiation, changes in polymers, 80
- High polymer, see Macromolecule, Polymer
- Higher order approximations, dynamic measurements, 469
- Holes
 - energy for formation of, 87
 - liquids (see also Equilibrium, empty sites), 87
 - nature of, 138
 - size of, volume, 87, 142
 - volume, estimates, 142
- Hooke, Hookean
 - elasticity, elastic solid, 63, 504, 519
 - law, 84, 96, 332, 407
 - springs in mechanical model, 26
- Hooke stress, 523
- Hot dip composition, 242
- Hot milled rubber, 205
- Hot wire anemometer, 462
- Hudson Bay uplift, 416
- Humidity and
 - creep, 279
 - dynamic modulus, 295
 - stress-strain curves, 286
 - tensile strength, 309
 - torsional rigidity, 296
- Hydrated lime, 127
- Hydrogen bonds, 94, 95
 - between chain molecules, 264
 - cellulose, 235
 - effect on diffusion, 99, 138
 - gelatin, 253, 258
 - silk, 267
- Hydrolysis, gelatin, 314, 315, 323
- Hydrolytic reaction types, 314
- Hydrostatic stress, pressure (see also Stress), 5, 55
- Hydroxyl groups
 - cellulose, 237, 247
 - glucoside ring, 234
- Hyperbolic sine function (law)
 - fibers, 303
 - metals, 113
- Hysteresis loop, 158
 - Coulomb type, 59
- I
- Ice
 - flow in glaciers, 427
 - Greenland, 417
 - load decrease, 417
 - point, gelatin, 332
 - sheet, 413
 - thickness, iceage, 414
- Ice cap, North America, 415
- Ideal, see under noun
- Imaginary moduli, see Modulus
- Immediate strain recovery, fibers, 290
- Impact strength, see Strength
- Impact, yarn, longitudinal, 309
- Impedance, viscoelastic
 - bridge, 451
 - characteristic, 463
 - electrical, 450 (6)
 - mechanical, 446, 450 (2), 458
- Impressed frequency, see Frequency, vibrations
- Impulse methods, 464
 - detonation, 465
 - rebound, 465
- Incompressible systems, 436
- Incompressibility of ions, 104
- Index of fiber modification, 290
- Industrial rheology, 483
- Industrial testing methods, gelatin, 359
- Inelastic behavior, see Anelasticity
- Inertia, 148, 463
 - correction, 452
 - resonance, 445, 461
- Inflexion point, in flow curves, 131
- Inherent viscosity (see also Viscosity), 115-120
- Initial resistance, stress
 - asphalt, 389, 394, 395, 399

- effect of temperature, 397
 - fiber deformation, 302
 - Injection molding, 183, 241, 248
 - cellulose acetate, 240
 - powders, 240
 - Inorganic glasses, defined as supercooled liquids, 146
 - In-phase (see also Viscoelasticity), 18
 - compliance, 468
 - modulus, see Modulus
 - Instruments, see under name of instrument
 - stress-strain, dynamic, 443, 496, 518
 - Integral inversion formulas, 468
 - Interaction between solute molecules, 243 (1)
 - Interchange reaction
 - chemical stress relaxation, 81
 - silicone, 81
 - sulfide, 79
 - Intermittent modulus, 80
 - Intermolecular bonds, forces, 147, 298
 - Internal see also under noun
 - energy changes and restoring forces, 298
 - Internal friction, see Friction, internal
 - Intrinsic viscosity (see also Macromolecules, Particles, Polymer, Viscosity), 115
 - molecular weight relationship, 242 (2)
 - Iodine, diffusion of, 99, 136
 - Ionic strength, effect on gelatin strength, 341
 - Ions, as flow units in metals, 87
 - Irreversible flow, 242 (see also Flow)
 - Irrotational movements, 528
 - Isoborneol, as plasticizer, 238
 - Isoelectric point, pI
 - gelatin, 316, 344, 360
 - minimum viscosity, 329
 - Isofenchone, as plasticizer, 238
 - Isoionic point, gelatin, 328
 - Iso free-volume state, 177
 - Isostasy, 421
 - Isoviscous state (see also Viscosity), 177
 - Izod impact test, 257
- J**
- Jelly strength, see Gelatin gel
 - Jute, 262
 - flexural rigidity, 292
 - molecular orientation, 267
 - tensile strength, 308
- K**
- Kapok, 262
 - fiber torsion, 296
 - torsional rigidity, 297, 94
 - Keratin fiber, 264, 267, 281, 299
 - creep behavior, 59, 304
 - form- α , 94, 267
 - form- β , 94, 268
 - helix in α -form, 95
 - long range elasticity, 294
 - network, 264
 - set, setting agent, 281
 - transformation reversible, 268
 - Kinked chain molecules, see Chain molecules, Macromolecules
 - Krypton, 140
 - Kuralon, 265, 308
- L**
- Lacquers, cellulose derivatives, 258
 - Lacuna (see also Holes), 87
 - Lamé constants (see also Modulus), 411
 - Laminar flow
 - coaxial cylinders, 493, 496
 - pipes, 475, 481
 - Poiseuille's equation, 475
 - Reynolds number, 481
 - strain ellipse, 506F
 - transition to nonlaminar flow, 481
 - wall effects, 482, 483, 494
 - Laminar shear
 - goniometry, 506
 - resolution of pressures, 508F
 - stress-strain geometry, 529
 - Land rising, 413
 - Laplace transforms
 - inversion, 41
 - relating creep compliance and relaxation modulus, 40 (21)
 - Latex, creep of, 114
 - Latitude variation, 429
 - Lattice distance, 98, 142
 - Lattices of liquids, 84
 - Lava flow, 428
 - Lead, diffusion of bismuth through, 100
 - Leather cloth, synthetic, 241
 - Leathery state, 65
 - Lethersich, apparatus of, 433, 448

- Light-scattering, gelatin, 320, 357-359
Lime base grease
 effect of shear rate, 128
 flow parameters, 127
Limed hide, amino acid analysis, 319T
Limiting intrinsic viscosity, 115
Linear, see also under noun
 circuit theory, 3, 40
 response theory, 3
 viscoelastic behavior, degree of approximation, 33
 specifications, 53
 viscoelasticity, deviations, 466
Lines of zero elongation, 529
Liquid, Liquids, (see also Flow, Viscosity associated, non-associated), 86, 141
 elasticoviscous, 486
 junction potential, 105
 inelastic (anelastic, viscous), 141, 145, 499
 measurement of elasticity, 499
 resin, 463
 self diffusion in, 99
 solid and gas, comparison of, 139
 specific heat, 140 (108)
 structure of, 86, 89, 138
 theories of state and viscosity, 140 (107), 407
 volume of, 140
LM-S polyisobutylene, 110, 112
Load extension curves (see also Stress-Strain relations), 283
Load measurements, 436
Loading history, 39, 272
Locking of faults, tectonic, 426
Logarithmic decrement (see also Attenuation), 149, 293
Longitudinal, see also under noun
 creep compliance, 56
 extension, gelatin gels, 333
 relaxation modulus, time scale, 56, 57
 shearing of gels, 336
 stress, strain, 56, 57
 waves, 454
 earth's, 401, 410, 411, 429
Loss, see also Phase angle
 angle, factor, phase angle, tangent, 19, 20, 293, 448, 461, 463
 compliance, see Compliance
 mechanical, 461
 moduli, (see also Modulus), 28, 43
Low loss systems, 462
Lubricant, 237 (see also Plasticizer)
 extrusion, 238
 internal, 228
Luders' lines, 534

M
Macromolecules, macromolecular, see also Chain molecules
 chain bulkiness, 172
 chain stiffness, effect of, 70
 crystallites, 77
 entanglement, 66, 77, 88
 flexibility, see Chain molecules
 segment, length, 71
 solution flow, 472
 solution system, 114
Macrostress, 90
Magnetic flux density, 450
Magnetrostrictive
 oscillator, transverse waves, 460
 rod, 448
Maltenes, 364
 effect of flow pattern, 371
Mannesmann process, tube formation by rolling, 524
Manometer, pipe flow, 478F
Marble, Luders' lines in, 534
Markovitz and DeWitt, apparatus of, 444
Mason, apparatus of, 457, 459
Mass deficit, postglacial, 414
Master curve, composite, normalized curve (see also Scale factor), 8, 67, 75, 168, 471
 creep, Nylon, 275
 stress-strain, acetate rayon, 277
 viscose rayon, 277
Mastication, 182
 effect on chain branching, 246
 on cross-linking, 246
 on molecular weight distribution, 246
Mastics, 388, 391
 stiffness, effect of concentration and temperature, 397F
Maxwell body, element, model, unit (see also Elasticoviscous liquids, Rheological models), 27, 28, 38, 51, 92, 442, 467, 498, 519, 541
 earth, 406
 equation for stiffness, 368

- five-element model, 30
- six-element model, 34
- McKee Worker viscometer, thixotropic breakdown, 190
- Mechanical, see also under noun
 - dissipation factor, 150
 - history, gelatin gels, 354
 - impedance, variation, 451
 - models, see Rheological models
 - properties, temperature dependence, 472
 - resonance, 445
 - testing, 521
- Melt viscosity, see Viscosity
- Melting, see also Softening point, Setting point
 - gelatin, see Gelatin melting point
 - point, constant, 140, 141
 - points, rocks earth interior, 405
- Melts, cellulose derivatives, 241
- Membrane
 - diffusion, 101
 - nerve, 104
 - thickness of standard, 103
- Mercury self-diffusion, 99
- Mercury threat method, 476
- Metabolism, 131
- Metals
 - analogy to pastes, 535
 - creep of, 134
 - films, failure of, 532
 - vacuum-deposited, 527
 - flow parameters, 113
 - fusion of, 141
 - liquid, 87
 - Luder's lines, 534
 - unit for viscous flow, 86, 141
 - vaporization unit, 86
- Methyl acrylate, 170
- Methyl methacrylate, 170
- N-Methyl methacrylamide, 170
- Micelles (crystalline), 235
- Microstress, 90
- Milling, 182
- Mineral aggregate asphalt mixture, 391
 - (see also Asphalt mixtures)
- Mineral oil, 246
- Mixed crystals, 256
- Mixing
 - breakdown and, 246
 - entropy of, 141
 - raw elastomer, 182
 - raw rubber, 182
- Model rheological, see Rheological models
- Moduli, 21T, 75, 149, 157, 435, 446, 468, 509
 - definition, polymer, 44, 45, 54
 - electrical measurements, 451
 - and energy wells, 84
 - frequency and temperature dependence, 44, 160
 - imaginary, real, (see also Modulus) 148, 149, 461
 - mechanical model, 34
 - storage, see Modulus, storage
- Modulus (see also Elastic compliance, Elasticity, Moduli), 63, 84, 243
 - absolute, 20, 441
 - asphalt, 367, 380
 - attenuation, 454 (82)
 - complex (see also Dynamic modulus), 20, 64, 73-75, 148, 150, 293, 319, 367, 441, 461, 519 (20)
 - reciprocal, 520 (21)
 - comparison, interconversion, 75, 435, 425
 - creep, 63
 - decay, 27, 29, 31, 32
 - dynamic, and distribution of relaxation times, 72
 - imaginary, loss, out-of-phase, 19, 22, 28, 43, 148, 149, 293, 444
 - real part, in phase part of complex elastic, storage, unrelaxed elastic, 19, 64, 72-74, 192, 294, 306, 444-448, 461, 468
 - earth, 404, 405
 - effect of amorphous region, 236
 - elastic, equilibrium, limiting, see Modulus, elastic
 - evanescent, Hencky, 243, 244 (4)
 - gelatin gels, 332-335, 346
 - glass, glassy (see also elastic, ordinary), 16, 17, 44, 65, 68, 69
 - intermittent, 80, 83
 - liquid, solution, 54, 243, 244 (4)
 - ordinary, see Modulus, elastic
 - rubber, 66, 68
- Modulus, bulk, 55, 380
 - complex, 452, 456
 - earth, 404-406, 435

- effect on viscosity, 405
- Modulus, elastic, equilibrium, limiting, ordinary, (see also Modulus, dynamic, real, glass, Modulus, rigidity), 16, 28, 43, 54, 254, 255, 509, 515, 525
- function of frequency, 19
- models, 32, 35
- modulus relaxation, relationship, 50, 51
- polyisobutylene, 36
- polymethylmethacrylate, 36
- real material, 35
- Modulus, relaxation, 15, 29, 32, 38 (11 α), 63, 64, 71, 73, 81
 - bulk, 55
 - calculation from creep compliance, 41
 - comparison, 20, 21T
 - longitudinal, 56, 57
 - mechanical model (generalized), 27, 42
 - molecular weight effect, 16
 - polymer, 15, 17
 - storage modulus, relationship, 50
- Modulus, rigidity, shear, stiffness, 19, 64, 75, 84, 145, 148, 367, 435, 507, 509, 515, 521, 525
 - aluminum laurate, 515
 - complex, see Modulus
 - effect of frequency, 17, 19, 521
 - evanescent, 244 (4)
 - gelatin, 335
 - imaginary, see Modulus, loss
 - rate dependence, 515, 521
 - real, see Modulus, dynamic, real
 - relation to Young's modulus, 75, 435
 - strain dependence, 335
 - temperature-concentration superposition, 471, 472
- Modulus, Young's (Stiffness in elongation), 63, 64, 75, 332, 366 (1), 367, 435
 - asphalt, 380
 - asphalt mixture, 392
 - complex, 293, 441
 - Dacron, 288
 - fiber bending, 292
 - fibers, 283, 286, 306
 - gelatin gels, 332, 334, 351
 - humidity and, 287
 - for perfect elastic solid, 435
 - rate of extension and, 286
 - shear modulus, relation to, 435
 - stone, 392
 - temperature and, 289
 - viscose rayon, 284
- Mohorovičič discontinuity, 402, 403
- Mohr stress circle, diagram
 - asphalt, 389
 - triaxial shear, 390
- Moisture, see under noun, effect of as plasticizer, 241
- Molecular, see also Chain molecules, Configuration, Macromolecule, Relaxation mechanism
 - aggregation, gelatin, 326
 - mechanism of stretching, 71
 - orientation, 252, 294
 - effect on extension at break, strength, 307
 - in glasses, 162
 - fiber, effect on modulus and extension, 284
 - flow in molding, 249
 - patch, see Flow unit
 - structure, see under noun, Structure
 - theories, linear viscoelastic behavior, 52, 60, 467
 - theory of liquids, see Liquid, theory of flow and viscosity
 - volume, 87
- Molecular weight, molecular weight
 - average, molecular weight distribution, degree of polymerization (DP), 210, 226, 242
 - between entanglements, 66
 - cellulosic, 264
 - effect on fiber strength, 308
 - on glasses, 167, 168F
 - on processing, 225
 - on stress relaxation, 65-68, 72
 - on viscosity, 115-117, 242 (2), 327
 - gelatin, 320, 347, 357, 358
 - minimum, effect on mechanical properties, 165
 - polyisobutylene, 67, 68, 72
 - relaxation, effect on, 66, 68
 - and rigidity, 349
 - viscosity-averaged, 110
- Molding, injection, 241, 248
 - blow, vacuum, 256
- Molding strain, cellulose derivatives, 258
- Monomer-units, see also Segment
 - effect on the mechanical behavior, 145, 167, 172

- Monochlorbenzene, fluidity, 485
 Mooney
 rheometer, 185
 viscometer, 186, 187, 218
 Motion, 418 (25) (see also Equation of motion)
 unidirectional, 506
 Mountain support, strength, 422
 Movement
 faults, earth's crust, 428
 geodetic measurements, 428
 glacier, 427
 irrotational, 528
 polar, 420
 three-dimensional, 529
 Multiplication factor, see Scale factor
 Mucopolysaccharides, gelatin, 316
 Mudflows, 428
 Mutarotation, gelatin, 357, 358
- N**
- Napalm, flow rates, 127
 Native asphalts, 363
 Native cellulose fibrils, 268
 Natural rubber, see Rubber
 Natural state, 504, 518
 Natural wool, see Wool
 Nearest neighbor, see Neighbor nearest
 Necking (of tensile test pieces), 254, 256
 Neighbor, nearest
 effect, Cage model, 98
 number in shear plane, 98, 99
 relaxing in diffusion, 101, 136, 137
 Neon, 140
 Neoprene
 crystallinity, 78
 GN, 212
 spontaneous elongation, 78
 stress relaxation, 78, 80
 Nerve
 action, 101
 decay law of, impulse, 104
 Network structure, gels, 357
 Newtonian flow, liquid (see also Flow, fluid, Liquids), 12, 23, 106, 131, 371, 382, 413, 414, 481, 498, 519
 end effects, 480
 flow, deviation from, turbulence, 123, 481-484
 of glacier ice, 427
 flow units, see Flow units
 fluidity and stress at wall, 481F
 laminar flow, 481
 Poiseuille's equation, 475
 properties in oscillating motion, 497
 rate of shear, 497F, 499
 shear stress, 494
 viscosity, 85, 92 (8), 475, 193, 504, 519
 Nielsen, apparatus of, 451
 Nitrated cotton, in butyl acetate, 133
 Nitrocellulose, see Cellulose nitrate
 Nitrocotton, dough processing, 239
 Nitrogen, 140
 Noncross-linked polymer, see Polymer, noncross-linked
 Nonelastic, see Anelastic
 Non-laminar flow, see Turbulence
 Nonlinear elasticity, theory, 301
 Non-Newtonian liquids (see also Elastic-viscous liquids, Maxwell body, Weissenberg effect), 106, 131, 509, 515
 apparent viscosity coefficient, 475, 497
 breakdown of laminar flow, 482
 cellulose derivatives, 244
 end, entrance, effects, 480
 flow, parameters from viscosity-shear rate plots, 107
 theory, 113, 210, 249, 497, 509, 521
 through channels, 231
 units, see Flow units
 fluidity, shear stress and wall effect, 483-485
 molecular weight effect, 129
 polyisobutylene, 123
 steady flow, 485, 494
 viscosity, 85, 92 (2), 494
 Non-normalized relaxation, retardation, function, 41
 Non-recoverable deformations, see Deformation
 Non-sinusoidal deformation, see Deformation
 Normal extension, planes of zero, 505
 Normal stress (pressure) effect (see also Weissenberg effect), 504, 516, 518, 522F, 524
 decay, 517
 Normal, transversal, stress (see also Stress), 3, 5, 55, 508
 asphalt, 390
 delayed elastic motion, 411
 frequency, strain velocity, 518

- Hooke's law, 411 (17)
and lateral deformation, 57
measurements, 509
plastic, viscoelastic materials, 524
rheogoniometer, 512
- Normal and tangential tractions, 5
- North America uplift, 417
- Nuclear magnetic resonance of glasses, 147
- Nylon, Nylon-66, 265
breaking velocity, 308, 309
creep, 272, 274, 280
dynamic properties, 294-296
elastic, 266
instantaneous extension, 273
internal friction, 306, 307
moisture regain, 270
p-phenylene copolymers, 175
relaxation, and temperature, 283, 307, 310
resilience of, 291
strain recovery, 290
strength, 308-312
stress-strain curve, 59, 285, 288
effect of conditions, 286-288
stressing, entropy contribution, 300
structure, 265
superposition principle, 272
torsional rigidity, 297, 311
Young's modulus, initial, dry, wet, 289
- O
- Operator equation, 26
definite integration, 407
five element (parameter) model, 31
order, 32
shear response, 26
six element (parameter) model, 34
viscoelastic response, parameters, 28
- Oppanol, dissolved in decalin, 133
- Optical anisotropy (see also Birefringence, streaming, stress), 92, 507
cellulose derivatives, 243
orientation, 163
- Optical rotation, polypeptide chain, 358
- Orientation, molecular (see also Birefringence, streaming, stress, Hydrodynamics, Particles), 163, 249, 252, 299
- Ordering, side groups in glasslike behavior, 54
- Ordinary elastic deformation, see Modulus, elastic
- Organic glasses (see also Glass, Glass transformations), 145, 160, 170T
copolymer, 160
defined as supercooled liquids, 146
effect of variables, 153, 154
experimental techniques, 155
low-molecular weight, 153, 168
- Orientation, see also Molecular birefringence, 163
effect on organic glasses, 162
extent influencing factors, 163
freezing, 252
partly oriented state, 266
ultimate-strength, 165
- Orlon, 265
initial Young's modulus, effect of temperature, 289
moisture regain, 270
strength, 308
stress-strain curves, 285, 288
torsional rigidity, 297
- Orthocortex, 269
- Oscillating motion, linear and angular (see also Frequency, Vibrations), 446, 450, 490, 496, 518
- Oscillating plate, 454
- Oscillator
average energy of, 90
partition function, 130
- Oscillographic recording, 436
- Ossein gelatin, 315, 318, 328, 340, 342, 354
degraded, 338
- Ostwald-deWaele equation, 108
- Ostwald, flow curve, 132
- Out-of-phase, 18 (see also Viscoelasticity)
compliance, 468
modulus, see Modulus
rigidity modulus, 468
- Overtones, 461
- Oxidation
cleavage, 79, 80
during mastication, 182
rubber processing, 226
- P
- Paper, Luder's lines in, 534
- Paracril B, Paracril-26
distinctive temperature, 69

- rheological units, 220
- stress relaxation, 69, 70
- Paracortex, 269
- Paraffin B. P., liquid, 498
- Parallel plate, see also Compression, Plastometer
 - ethyl cellulose, 245
 - nitrocellulose, 253
- Parameters
 - characteristic of relaxation, 72
 - comparison of model and material, 28, 35
 - diffusion equation, 98
 - operator equation, 28, 34
 - rheological flow units, 224
 - viscosity formula, determination of, 106, 112, 135
- Particles, see also Ellipsoids, Hydrodynamics, Interaction, Macromolecules, Orientation, Rods
 - rod- or platelike, 476, 482
 - spheres, diffusion, 101
 - suspension, 476
- Partition function, 139
- Pastes, 534
 - mechanical behavior of, 533
- Peak
 - displacement, 447
 - force, 446
 - half width of resonance, 148
- Penetration test, index, 364, 370, 377
 - asphalt, 371, 382
 - effect of conditions, 383, 385, 387
 - of stiffness, 382-385 (15)
 - Newton's law, 365
- Peptide bonds (linkage), 264, 265
 - gelatin, 321, 395
- Perbunan, 212
- Permeability, 103, 104
- Permanent set, see Deformation, irreversible
- Permanent waving, 282
- Perturbation pattern, 534
 - analogy to fatigue, 532
- Phase angle, see Loss, angle, Viscoelasticity,
 - body tides, 420
 - dynamic measurements, 441, 444
 - rhegoniometry, 505
- Phase change, in earth, 404, 422
- Phase difference, see Birefringence
- Phase displacement, body tides, 419
- Phase lag, asphalt, 368, 394
- Phase separation
 - plasticized systems, 175
 - polyblends, 175
- Phase transition, 94 (see also Transition, Glass transformation)
 - α - β , rate, 303
- Phenomenological theory of viscoelasticity, 60
- Philippoff, apparatus of, 443, 447
- Photoelastic pattern, 456
- Photoelasticity, cellulose derivatives, 258
- Piezoelectric crystal, torsional, 154
- pick-up, 456
- Pipes
 - bore characterization, 476
 - bore correction, precision, 477
 - dimensional requirements, 476, 480
- Pipe (capillary) flow, 475-479
 - characterisation, laminar flow, 477, 478, 480, 481
 - interpretation of data, 482
 - kinetic energy correction, end effects, 479
 - monochlorobenzene, 484F, 485
 - Poiseuille's equation, 475
 - polymethylmethacrylate solutions, 484
 - pressure gradient, 479, 481
 - Reynold's number, turbulence, 481
 - shear stress at wall, 483
 - slip coefficient, 483
 - temperature control, 479
 - wall effect, 482
- Plastic, dynamic mechanical measurements, 463
- Plastic flow, see Flow, plastic
- Plastic materials, nominal stress, 521
- Plastic range of ethyl cellulose, 247
- Plasticator, 182
- Plasticine, 524
- Plasticity, Plastic range (see also Flow, plastic, Yielding), 247
 - measurements, thixotropic effects, rubber, 209
 - power law, 195 (11), 209
- Plasticization, plasticizers, 182, 236-238, 250
 - cellulose derivatives, 237

- effect on glass transition, 171, 175, 177
 - on the rheology of elastomers, 227
- impact strength, 258
- viscosity, 177
- Plastics molten, rheogoniometer, 511
- Plastics viscosity, see Flow, plastic, Viscosity
- Plastometer, 245, 247
 - comparison, 248
 - compression, plate, 195
 - extrusion, 189, 194, 207, 217
 - parallel plate, recovery, nitrocellulose, 253
 - shearing cone, 188
 - Stefan formula, 195 (9)
- Poisseuille's equation, 475
- Poisson's constant, ratio, 157, 162, 332
 - asphalt, 367
- Polar movement, 420
- Polyacenaphthalene, glass temperature, 70
- Polyacrylonitrile, 173
- Polyamides, heat of fusion (see also Nylon, Polypeptides), 175
- Polyblends, Polymer mixtures, 175-178
 - glass temperature, 70
- Polyester rubber, 80
- Polyethylacrylate rubber, 80
- Polyethylene, Polythene, 172
 - crystallinity, 175
 - fibers, 295, 306, 308
 - moisture regain, 170
 - molten, recoverable strain, 524
 - relaxation, 306
 - strength, 308
 - stress normal and tangential, 514
 - structure, 264
- Polyethylene terephthalate, 266
- Polyisobutylene, 35, 64, 75, 110, 112, 114, 172, 173, 211, 225
 - behavior in rolling, 524, 525
 - complex shear compliance, real part, 453F
 - composite curve, see Master curve
 - distinctive temperature, 69
 - distribution function of relaxation times, 469F
 - dynamic shear modulus, 73-75
 - flow, melt, viscosity, 210, 517
 - glass-rubber transition, 37
 - master relaxation curve, 67, 68, 471
 - molecular weight effect, 167, 211
 - retardation spectrum, 46
 - rubbery flow region, 72
 - secondary mechanical dispersion, 169
 - shear moduli, damping, 168
 - solution, 124, 522
 - flow, recoverable strain, 517
 - non-Newtonian behavior, 119, 124
 - stress distribution in flowing, 517
 - solvent effect, 124, 125
 - storage modulus, 36
 - stress relaxation, 64, 66, 69, 76, 438
 - effect of molecular weight distribution, 67, 68, 72, 168
 - viscosity, specific, 123
 - wedge and box distribution, relaxation, 46
 - Weissenberg effect, 513F
- Polymer, see also Chain molecules, Configurations, Hydrodynamics, Macromolecules, Viscosity
 - alloy, see Polyblend
 - amorphous, linear, 64, 70, 75-78, 244
 - chains, entropy change, ordering, configurations, 10, 55
 - chains, side groups in glasslike behavior, 54
 - characteristic parameters, Master curve, 68, 69T
 - chemical cross linking, 66, 79, 81
 - cross-linked, see Polymer cross-linked
 - crystalline, 64, 72, 76-78, 244
 - decay of stress, 79
 - films, 527
 - noncross-linked, see Polymer noncross-linked
 - orientation, effect of frequency, 53
 - plastic flow, 247
 - plasticizer compatibility, effect of damping, 176
 - solutions, dilute, 463
 - elasticity, 499
 - flow, 113
 - nonlaminar, 482
 - recoverable strain, 524
 - rheological equation of state, 500
 - wall effect, 483
 - stress-crazing of, 534
 - unfolding at high temperatures, 130
 - Weissenberg effect, 524

- Polymer cross-linked, amorphous, 4, 31, 70, 78
moduli, definition, 45, 54
non-linear behaviour, 58
relaxation modulus, 15
sinusoidal testing, 18
temperature effects, 9
viscoelastic, 5
- Polymer mixtures, see Polyblends
- Polymer noncross-linked, amorphous, 33, 51
creep compliance, 13
glass compliance, state, 13, 53
non-linear behavior, 58
relaxation modulus, 15
sinusoidal testing, 18
temperature effect, 13
time effect, 11, 44
viscosity, 51 (37 α)
- Polymethylacrylate, 173
- Polymethylmethacrylate, 64, 147, 173, 484
comparison of methods, 161
damping, 146
distinctive temperature, 69
effect of pressure, 162
elasticity, 499
electrical dispersion, 169
flow through pipes, fluidity, 484, 485
in monochlorobenzene, 484
nonlaminar flow, 485
pyridine solutions, 494, 498F, 499
relaxation and retardation times, 500
Reynolds number, 482, 485
secondary mechanical dispersion, 169
slip coefficient, wall effect, 485, 486
storage modulus, 36
strength of, effect of rate of strain, 154
stress relaxation, 64, 65, 69, 76
viscosity, 494, 495F, 499
- Polypeptides, 94
chains, optical rotation, 358
unfolding, 303
fibers, 264
- Polysaccharides, 233
- Polystyrene, 15, 109, 112, 115, 147, 163, 172
activation energy, 53
bending, 2
bulk modulus (Poisson's ratio), 162
cyclohexane solutions, 122, 129
damping, dissipation factor, 161-166
ductile under compression, 154
fractions solvent, shear rate effects, 116
glass state, effect of molecular weight, 146, 162, 165
glass temperature, 70, 165
internal stress relaxation, 165
moduli, effect of pressure, 162
modulus, effect of orientation, 164
rubbery state, 146
solutions, effect of concentrations, 118
of temperature, 130
solvent effects, 119, 120
thermal expansion, 53, 166
time effects at high temperature, 3
toluene solutions, 117, 118
unfolding chains with temperature, 129
xylene solutions, 123
Young's modulus, effect of molecular weight, 165
- Polystyrene-GR-S mixture, 176
- Polysulfide rubber, Thiocol rubber
chemical stress relaxation, 80, 81
spontaneous elongation, 78
- Polyvinyl acetate, stress relaxation, 114
- Polyvinyl alcohol, 265
- Polyvinylbenzoate, 176
- Polyvinyl-n-butylether, 173
- Polyvinyl carbazole, 169, 172
- Polyvinylchloride
glass transition, 167
plasticized, 78, 178
polycrystallinity, 78
secondary mechanical dispersion, 169
stress relaxation, 78
- Polyvinyl ethers, secondary mechanical dispersion, 169
- Polyvinyl ethyl ether, 173
- Polyvinyllic fibers
rubberlike elasticity, 300
strength, 308
structure, 265
- Polyvinyl fluoride, 173
Polyvinyl formal, structure, 237
- Polyvinylidene fibers
dynamic modulus, 294
internal friction, 307
structure, 265
- Polyvinylisobutylether, 173
- Polyvinylmethylether, 173

- Postglacial mass deficit, uplift, 413, 414
 Potential energy, barriers (see also Interaction, Interatomic), 53, 54, 85, 87 (13)
 across nerve membrane, 104
 gradient, 100
 group movement, 54
 liquid junction, 105
 solid, 139
 succession of, 101
 Powder aggregates, deformation and failure of, 531F
 Powder corn-flour, 533F
 Powder films, periodicity, 535
 Power consumption in rubber forming, 226, 227
 Power law
 fluidity, Porter-Rao, 193 (3), 194
 plasticity, 195 (11), 209
 Prerupture flow, Dacron, 288
 Pressure
 critical extrusion, 251
 density, 508
 distribution in flowing liquids, 504, 506F
 earth, interior, 403, 430
 effect on asphalt, 381, 381T
 on organic glasses, 162
 on viscosity, 86
 entrance, 191, 207, 208
 estimate of hole volume, 142
 gradient, pipe, 481
 hydrostatic, determination, 476
 mechanical work, 183
 negative, 508, 510
 normal, rheogoniometer, 512
 secondary, 510
 Printing inks
 dilatancy, 526
 flow testing of, 517
 recoverable strain, 524
 Weissenberg effect in, 524
 Processibility, Processing, 230, 231
 difficulties in rubbers, 225, 226
 Propagation of waves, 149
 Protective coatings, asphalt, 388
 Protein fibers, see also Polyamides, Polypeptides
 resilience of, 291
 structure, 264, 267, 269
 Protein globular, 264
 Puerto Rico deep, 421
 Pulse propagation, fibers, 294
 Pyroxylin, 239
- Q**
- Quality
 calendering, 229
 processing, 230
 Quantum effect at low temperature, 90
 Quartz
 surface, reflecting a shear wave, 460
 wedge, double, 455
- R**
- Ramie, 262, 268
 acetylated, breaking load, 311
 molecular orientation, 267
 tensile strength, 308
 Random distribution of molecules, 139
 Rate constant, see Rate process theory
 Rate of extrusion, influences, 228
 Rate process theory, Reaction rate theory, (see also Liquid state, theories, Viscosity, theories), 83, 91, 301
 determining step, solution viscosity, 129
 flow, rate, constant, 85, 89, 93 (19), 97, 102
 state α - β transition, 303
 two state theory, 303, 304
 Rate of strain, of shear, see Shear rate
 Raw elastomers, Raw rubber, see also Rubber
 flow mechanism, 232
 mixing and forming of, 182
 rheological testing, rotational instruments, 184
 Reactance
 mechanical, 446, 450 (76)
 mechanical, characteristic, 458 (96)
 Reaction rate theory, see Rate process theory
 Real moduli, see Moduli, Modulus
 Rebound tests, 465
 Recovery, see Elastic recovery
 Reduced, Reducibility
 temperature, 9
 variables, 159-470-472
 viscosity, 114, 128, 129
 lower limit, gelatine, 357
 Reference grid, 529

- Reference temperature, 15
Refractive index ellipsoids, and stress, 507
Regelation, 427
Regenerated cellulose, 234
Regenerated protein fibers (see also Protein fibers), 262
Relative humidity, 270
 plasticizing properties, 255
 viscosity, 114
Relaxation, Relaxation Mechanism (see also Creep, Rheological models, Viscosity), 55, 519
 constant strain, 435
 effect of reducing agents, 279
 fibers, 270, 276, 278, 279, 306
 master curve, 67-69, 72-75
 modulus, see Modulus, relaxation
 paste, 534
 process, influence of pH, 278
 temperature dependence, in glasses, 146, 160
 stress, 114
 tensile, 63, 65F, 68F, 69T, 72, 302
 cellulose fibers, 276, 306
 composite master curve, 277
 effect of humidity, temperature, 282, 283
 tests, 271
 theory of transport phenomena, 83
 torsional, 279, 305
Relaxation function, 31
 box type, 45, 72
 fibers, model representation, 301
 non-normalized, 41
 wedge type, 45, 72
Relaxation spectrum, 32, 42, 43, 151, 295, 305, 476
 approximation methods, 46, 49, 152
 asphalt, 376
 calculation, 45
 continuous, discrete, 52
 power function, 49
 wedge and box, polyisobutylene, 46
Relaxation time, 26, 27, 32-34, 72, 73, 92, 93, 419, 421, 423, 497, 498, 516
 average, 88
 characteristics, 68, 69
 as a function of temperature, 75
 core boundary, 429
 discrete, 32, 52, 305, 467, 470
 distribution, (see also Relaxation spectrum), 72-74, 279, 305
 earth, 409
 entropy and heat of activation, 111
 fitting, number required, 52, 305
 flow units, 88, 111, 125
 gelatin, 351
 Maxwell element, 369
 natural, 91
 polymethylmethacrylate solution, 500
 soap gels, 516
 spectrum, see distribution
 spread effect, 36, 52
 temperature dependence, 159
 theoretical concept, 27, 52, 151
 viscous flow, 406
Residual deformation, see Deformation residual
Residual stress, see Stress residual
Resilience (see also Elastic recovery), 148, 290, 291
 effect of amorphous region, 236
 fiber, 290, 291
 type, 291
Resistance
 mechanical, 446, 450
 characteristic, 458 (92)
Resonance
 frequency 150, 293, 442, 446, 461
 asphalt, 368, 389
 half-width, 148
 method, fibers, 294, 448, 462
 peak, 150
 vibrations, forced, 445, 448
 free, 442, 448, 461, 463, 496-500
 viscoelastic liquids, 462
Restoring force, 148
Restriction of free rotation, cellulose, 237
Retardation, Retarded (delayed) elasticity, see Elasticity, retarded
Retardation function, 30
 box type, 45
 non-normalized, 41
Retardation spectrum, 42, 43, 151, 467
 approximation methods, calculation, 45, 46, 49
 asphalt, 376
 continuous, discrete, 52
 molecular theory, 52

- Retardation time (see also Friction, internal, Rheological models), 32, 33, 42, 151, 375, 407, 467, 497
characteristic, 274
earth, 409
molecular weight dependence, 37
number and magnitude, 37
polymethylmethacrylate solution, 500
wool, 59, 290
- Reynolds number, 481
critical, 482, 485
- Rheogoniometer, 508, 510, 511F, 516F, 521, 525
- Rheological
bodies, see Rheological models
curves, see Flow curve
equations, liquid, elastico-viscous, 91, 92, 497, 514, 518, 519
flow units, see Flow units
inhomogeneity, 88, 230
- Rheological models (see also Macromolecules), 25-37, 105, 151, 375, 467
asphalt, 374, 375
elastico viscous liquid, 497
Maxwell body, 368, 369, 374
nonlinear elastic, 376
Voigt element, 374, 375
- Rheological unit, see Flow units
- Rheometer, 184-186, 192
- Rigidity, see also Elastic compliance, Macromolecules, Modulus, rigidity, Stiffness
earth, 402, 404-406
flexural, 292, 295
gelatin, 332, 340-343
gelatin glue, 318
temperature, time effect, 407, 471
torsional fibers, 296, 297
- Ring and Ball, see Softening point
- Rocks
bodies, nonelastic behavior, 425
earth's crust, 404
energy stored, 424
flow, 428
melting point, 405
- Roeling apparatus, 443
- Rolling action
comparison of effect, 525F
paste of asbestos fiber, 524
of icing sugar, 524
polyisobutylene, 524
- Rossi-Peake
flow temperature, 248
temperature, cellulose acetate, 241
- Rotating cylinder, hollow, 510
- Rotating cylinder viscometer, see Coaxial cylinder viscometer
- Rotating vector, representation of stress-strain, 19
- Rotation in solid state, 142
- Rotational waves, 460
- Roth-Rich Viscotron, 460
- Roughness, Rugosity, 226, 228, 230
- Rouse pendulum, 460
- Rubber, Elastomers, Rubberlike bodies, 1, 31, 145, 181, 206, 210
Buna N, 80
Buna S, 80
butyl, 9, 80
cross-linked, 4, 14-16, 31, 70, 78, 79
cooled, time effect, 3
flow curves, 132, 200, 204
GR-S, see GR-S
milled, 105, 108, 112, 182, 205
natural, 9, 78-80, 107, 114
stress relaxation in crystallizing region, 79
polyester, see Polyester rubber
polyethylacrylate, see Polyethylacrylate rubber
polysulfide, see Polysulfide rubber
processing difficulties, 226
raw, 4, 225, 255
rheological testing, 183
rheometer, 184, 186, 192
shear oscillations, viscosity, 192
silicone, 81
softening, oil, 225
solutions, recoverable strain, 524
Weissenberg effect, 524
in xylene, 512
stock, 183
thixotropic, in extrusion, 194, 213
vulcanized (see also cross linked), 14-16
- Rubberlike elastic, Rubbery
effects, nitrocellulose, 253
flow, 66, 67, 71-76
gelatin, 254
plateau, 65-67, 70, 71, 76-79
polymer, dynamic mechanical measurements, 463

- region, effect of molecular weight, 167
- state, 146
- synthetic fibers, 265
- Rupture (see also Breaking strength, Strength), 154, 254
 - asphalt, 282, 399
 - and bending, 311
 - cellulose derivatives, time effect, 257
 - effect of strain rate, 523
 - elastic rebound (recovery), 424
 - in extension, 309
 - along fault surfaces, 423
 - goniometry of, 503, 526, 527F
 - and isotropy, 534
 - maximum, 534
 - patterns, comparison, 531F, 532
 - rubber flow, 221, 226
 - of tacky mass, 182
 - testing, general method, 526-532
 - transition region, 526
 - work of (toughness), fibers, 308
- S**
- Sample
 - geometry, dynamic measurements, 446
 - size, elastic wavelength ratio, 442, 463
- Sandsheet mixtures, comparison, 399
- Sandwich shearing viscometer, 210
- Saran, 265
 - dynamic modulus, effect of frequency, static strain, 294, 295
 - moisture regain, 270
 - relaxation times, 307
- Scale factor, Shifting factor, along time axis (see also Master curve, Time-temperature superposition), 8, 15, 22, 75, 158, 159, 274, 472
- Scattering, seismic waves, 413
- Schwarzl method, 52
 - relaxation and retardation spectra, 48
- Scission-crosslinking reaction, Chemo-rheology, 5, 79, 80
- Scorch
 - rubber stock, 227
 - test, rubber rheometer, 187
- Scott testers, 188, 464
- Screw
 - dislocations, 136
 - extruder, 182
 - Newtonian materials, 231
 - extrusion, cellulose nitrate, 230
- Second-order transition (glass) temperature, see Glass transformation
- Sediments, downwarping, 421
- Sea-level changes, 416
- Segment, Segmental
 - flexibility (chain mobility), 10, 169, 172
 - glass transformation, 171
 - motion, coordination of, 109, 111
- Seismic waves, 401, 402
 - absorption dispersion, 410
 - change with distance, 412 (24)
 - constants, form, period, 412, 413
 - laboratory experiments, companion, 411, 412
 - surface, absorption, 410
 - velocity, 412
 - wavelength, 430
- Self-diffusion, see Diffusion
- Sericin, 269
- Serine, 267
- Set, breakdown of bond network (see also Deformation, irreversible), 271
- Setting point (temperature) (see also Melting point), gelatin, 314
- Shear, Shearing (see also Deformation, Strain), 22
 - compliance (see also Creep compliance, Elastic compliance), 20, 467
 - creep test, 6
 - disk viscometer, 244
 - displacement, 97, 454
 - elasticity, see Modulus, rigidity
 - goniometry, 504
 - harmonic, 521
 - irrotational, pure, 528F, 529
 - laminar, oscillatory, 192, 448, 518
 - simple, rotational, 6, 438, 506-509, 529
 - layers, plane, 84, 88
 - loss modulus, 19, 20
 - plane, glacier, 427
 - response, operator equation, 26
 - rigidity, see Rigidity
 - simple, see laminar
 - stiffness, see Stiffness
 - storage modulus, function of frequency (see also Modulus rigidity), 19
 - strain, see Strain
 - strength, see Strength, shear

- volume, 85, 111, 114 (see also Alpha factor)
- waves, damped, 411, 454, 460
- Shear modulus, see Modulus, rigidity
- Shear rate, rate of deformation, strain rate, velocity gradient (see also Anelasticity, Creep, Rate process theory, Viscosity), 85 (1 α), 192, 243, 249, 250, 256, 508
- aluminum laurate, 515F
- axes, 506
- cellulose derivatives, 243
- coaxial rotating cylinders, 494 (7)F
- decay, 498
- dynamic measurements, 442, 497
- effect on recoverable strain, 14, 165, 196, 251, 274, 517F
 - on strength, 154
- Eyring's equation, 85, 91
- fiber, 95
- gelatin solutions, 323, 356
- measurements, see individual Tables of Contents
- polystyrene, 110
- reduced, 108, 109 (1), 110
- steady, 193 (3), 464, 468
 - limiting viscosity coefficient, 495
- temperature effect, 13F, 85, 153, 249-252
- tensor, 507 (1)
- viscosity, effect on, see Non-Newtonian liquids
- at wall, 483
- at wall, Hevea, 208
- Shear stress, 6, 12, 26, 84, 192, 195, 243, 249, 336, 439, 441, 483, 493, 508, 514
- amplitude, 18, 19F, 436, 441F, 497, 520
- coaxial rotating cylinders, 494 (8)
- components, 5, 18, 441, 508
- computation, slip velocity, 200, 202
- decay, 498
- flow units, assuming, 222
- in mechanical model, 26
- pipes, 195, 483
- retarded, Hooke's law, 411 (19)
- total, 91 (31)
- upper limit, in rheometer, 204
- vicinity determined, 509
- variation with strain velocity, 518
- at wall, 195, 208, 483
- Shifting factor, see Scale factor
- Shrinkage, longitudinal
 - from elastic recovery of the stock, 183
 - in forming, 228
- Side group, influence on secondary mechanical dispersion, 169
- Silica network, sodium ion diffusion, 100
- Silicone bouncing putty, rupture of, 532
- Silicone rubbers, stabilized, 81
- Silk, 262, 264
 - creasing of, 291
 - creep, 270, 302
 - dynamic modulus, 295
 - gum, sericine, 269
 - instantaneous extension, 273
 - internal friction, 295, 306
 - moisture regain, 270
 - rigidity 292, 297
 - strain recovery, 290,
 - strength, 308, 312
 - stress-strain curves, 285-288
 - structure, 264, 267
 - superposition principle, 272
 - torsional relaxation, 279
 - Young's modulus, and temperature, 289
- Similitude, anisotropy of stress and recoverable strain, 508
- Single crystals, 155
- Sinusoidal, see also Frequency, Vibrations
 - deformation, 3
 - methods, 434, 440
 - strain, 28 (4)
 - stress, 28, 468
- Six element model, 33
 - creep compliance, 35
 - numerical values, 36
- Sizing, glue, 360
- Skin, gelatin, 315
- Slip, Slippage
 - effect of capillary diameter, 217
 - mechanism, 218, 483, 486, 494
 - plastometer, 191
 - rheometer, 184
 - screw extruder, 184
- Slip bands in plastics, 256
- Slip velocity, 197, 198 (14) (16), 199, 201 (13), 483
 - computation, 199, 218
- Hevea, extrusion viscometer, 217

- power law, 197, 218
- wetting of surface, 218
- Soap gels
 - aqueous, 516
 - recoverable strain, 524
 - relaxation times in, 516
- Sodium carboxymethyl cellulose, 127
- Sodium ion, diffusion through silica, 100
- Softening point, Ring and ball, 245, 247, 386
 - asphalt, 364, 380, 386-388
 - equivalent loading time, 386, 387
 - rate of heating, 387, 388
- Sol type asphalt, 373-375, 377
- Solid, solids, see also Glass, Rheological models
 - friction, 526
 - hard, 461, 463
 - melting, see Melting
 - monatomic, 142
 - plastic, 105, 112
 - soft, 456, 461, 464
 - stress waves, 149
 - viscoelastic, see Viscoelastic
- Solidlike equilibrium position in liquids, 139
- Solute interaction, cellulose derivatives, 243
- Solutions, see also under respective solvent, Bire fringence, Colloidal, Macromolecular, etc.
 - cellulose derivatives, 241, 258
 - high polymers, 114
 - viscosity, 114, 258
 - solvent, temperature effect, 119, 120, 130
- Solvation, 238
- Solvent
 - effect on viscosity, 119, 129, 130
 - molecules, trapped, 129
 - for polystyrene, good, 119, 122
 - power, 124
 - temperature effect, 130
- Sound velocity, 91
- Specific
 - heat, liquids, 140 (107) (108)
 - volume, effect of molecular weight, 165
 - as function of temperature, 53
- Spectrum, relaxation and retardation, see Relaxation spectrum, Retardation spectrum
- Spinning, dry, 241
- Spiral structure, cellulose fibrils, 268
- Spontaneous elongation, 78
- birefringence, 79
- Spring constant, 93, 148, 467 (see also Modulus, Elasticity, Young's modulus)
- Spring line, two-state theory, 304
- Standard
 - atmosphere, 270, 272
 - membrane, diffusion coefficient, 103
 - state, concentration, 272
 - temperature, 471, (see also Scale factor)
- Starch, α -glucoside linkage, 234
- State
 - isoviscous, 177
 - natural, 518
 - α - β transition, rate, 303
- Static
 - rigidity modulus, gelatin, 351
 - strain superimposed, 456
 - stress, compression, 466
 - shear, 466
 - superimposed on dynamic, 465
- Steady state
 - compliance, 17, 23 (376)
 - noncross-linked polymer, 51
 - elastic compliance, 13, 44
 - flow (see also Viscosity theories), 12
 - flow curve in rheometer, 185
 - viscosity of elastomers, 183
- Steel, stress relaxation, 114, 142
- Step function
 - experiments, 17, 24, 56
 - relaxation and retardation spector, approximations, 47
 - response, 26
- Stiffness, see also Modulus
 - shear, 7, 17, 169
 - tension, 63, 367
- Stiffness of asphalt, 367, 371, 380
 - dynamic measurements, moduli, 367-369
 - effect of conditions, 367, 370F, 376-384
 - graphic representation, 368
 - mastics, 391
 - maximum value, 380, 382
 - mixture and volume concentration, 392
 - and penetration, 383, 384F, 385F

- softening point, 387, 388
- sol asphalt, 382
- static measurements, 367, 368
- stress dependence, 372, 373
- time-temperature equation, 368, 386
- torsion, 389
 - and Young's modulus, 67
- Stiffness, asphalt-mineral aggregate mixtures, 389, 391-397, 397 (20), 398
- Stirling's approximation, 141
- Stokes-Einstein equation, 101
- Stokes' law, 100, 221
- Storage compliance, see Elastic compliance
- Storage moduli, see Modulus, elastic
- Strain, relative Displacement, see also Deformation
 - accumulation, earth, 423
 - amplitude, 18-20, 162, 441F, 455, 496, 520
 - anisotropic, definition, 503
 - aperiodic, 95
 - creep, 38, 280, 426
 - double refraction, 336, 454
 - dynamic measurements, 18, 293, 336, 442, 496, 518
 - effect of finite, 18
 - of orientation in glasses, 163(F)
 - elastic creep, tectonic, 426
 - ellipse, laminar flow, 506F, 508
 - energy, 58, 293, 424
 - gage, 435, 436
 - global, 426
 - history, integral equation, 39
 - interval, 280
 - lagging, out of phase, 19F, 441F
 - longitudinal, 56, 63, 367
 - measurements, see individual Tables of Contents
 - periodic, saw-tooth, 465
 - recoverable (see also Strain-rebound), 38, 196, 253, 254, 289-291, 374, 509, 514, 523
 - effect of rate of shear, 517F
 - relaxation function, 151
 - retardation, 519
 - shear, 26, 38
 - shear ratio, transducer measurements, 156
 - shear wave, cellulose tributyrates, 455F
 - sinusoidal (see also Sinusoidal), 28 (4)
 - small, criteria, 518
 - and spring, autographic devices, 443
 - stress ratio (see also Elastic compliance, Stress-strain), 273
 - tectonic process, 423, 426
 - tensile (see also Creep), 2, 63, 273, 437
 - tensor, 55
 - wall, 525
- Strain rate, see Shear rate
- Strain rebound, see also Strain, recovery
 - aftershock sequences, 424, 425F
 - amplitude, 425
 - characteristics, 425-427
 - earthquakes, increments, sequence, 423, 426F, 427F
 - elastic, tectonic, 424, 429
- Strained state, axes, 506
- Straining, van der Waals bonds, 253
- Straining of streamlines, 244
- Strength, shear (see also Breaking, strength, Rupture, Yielding), 311
 - breaking, earth, 403
 - cellulose plastics, 237, 255
 - fatigue, 162
 - fibers, 311
 - flexing of fibers, 312
 - gelatine, 333
 - impact, mechanism, 255, 257, 258
 - test, deformable boundary, 526
 - ultimate, glasses, 153, 155, 175, 179
 - wet, 311
 - yield, for flow in earth, 421
- Strength tensile, 307
 - asphalt, 381
 - bending, 311
 - effect of conditions, 308, 311
 - fibers, 307, 310
 - gelatin, 351
 - glass transformation, 155
 - rayon, 308
 - test length, 308
 - theoretical, 311
 - time factor, 308
 - ultimate, metals, 134
- Stress, 55, 92, 527
 - amplitude, 19F, 20F, 441F, 520
 - anisotropic, definition, 503, 504
 - components, 18, 418, 508
 - constant rate of increase, 464
 - crazing, patterns, 534

- decay, see Stress relaxation
- distribution in flow, 516, 517
- dynamic, 18, 20, 28, 162, 442, 466, 496, 518
- effect on damping, 162
- ellipsoid, 515
- on flow units, 91-93
- gravitational, earth, 418
- history, increments, superposition (see also Superposition principle), 37, 39, 43
- limits, permissible, asphalt, rubber, 202, 225, 228, 382, 482
- in liquids, 11, 84, 480, 483, 497, 508 (2). 521 (27)
- longitudinal, 56
- measurement, see Individual Table of Contents
- Mohr circle, 389, 390
- optical coefficient (see also Birefringence), 70
- phases, with strain, 18, 20, 441, 496
- and refractive index ellipsoids, 507
- residual, 40, 89
- secondary normal, see Normal stress effect
- shear, see Shear, Shear stress
- sinusoidal, see dynamic
- static, in dynamic mechanical measurements, 465
- system, deep earthquakes, 426
- tangential, 411, 512, 518
- tensile, 3, 64, 134, 273, 298, 437
- tensor, 508
- time pulses, square wave, 465
- transversal, see Normal stress
- ultimate, see Strength
- waves, propagation in solids, 9, 149, 453, 460, 463T
- Stress relaxation, 3, 15, 16, 25, 63-78, 114, 150, 196, 214, 434, 517, 519 (see also Tension, recovery)
 - after flow, 468
 - apparatus, experiment, 25, 435, 437
 - Buna N, 81
 - Butyl rubber, 81
 - cellulose derivatives, 258
 - chemical, 79-81
 - by crystal growth, 78
 - experiment, 25, 435
 - fibers, distribution of relaxation times, 306
 - function, see Relaxation function
 - gelatin, 332, 335, 350, 351
 - glass, 168
 - GR-S, 69, 76
 - Mooney viscometer, 196
 - natural rubber, 78, 79, 81
 - Neoprene, 78, 81
 - Paracril 26, 69, 76
 - plasticized system, 179
 - polyester rubber, 81
 - polyisobutylene, 66, 68, 69, 75, 76
 - polymethylmethacrylate, 65, 69, 76, 81
 - polysulfide rubber, 78, 81
 - polytrifluorochloroethylene, 77
 - second approximation formulas, 470
 - temperature effect, 16, 437, 471
- Stress-strain (see also Creep, Deformation, Stress-strain curves), 12, 15, 84, 255, 463, 505
 - amplitude ratio, see phase ratios
 - asphalt, 366, 394
 - distribution in flowing material, 503
 - effect of time scale, (see also Time scale, Scale factor) 408
 - ellipse, recording, 443
 - fibers, effect of conditions, 283, 286
 - gelatin, 333
 - general equation, 518 (14)
 - geometry, sample, 436, 439
 - global system, 426
 - measurements (see also individual Table of Contents), 155, 443
 - nonlinear, 58, 303, 374
 - organic glasses, 153
 - peak, 20, 444
 - phase ratios, projections, 20F, 441F, 435, 451, 470, 520
 - ratio, asphalts, 367
 - frequency effect, 18, 441
 - Maxwell element, 368 (7) (8)
 - transduces measurements, 449
 - in rolling action, 524
 - rotating vector representation, 19, 441
 - summation, history (see also Superposition principle), 37, 43
 - time derivatives, 504
 - time effect, 2, 3
 - torsional, see Torque, twist

- velocity, divergence of directions, 515
 nonlinear, 507
 and viscosity, 516
- Stress-strain curves, 6, 11
 cellulose derivatives, 255, 284, 303
 constant rate of loading, 464
 deduction of viscoelastic properties
 from, 464
 gelatin, 352F, 353F
 GR-S, 111
 humidity and, 287
 polyisobutylene, 111
 protein fibers, 285
 rate of extension and, 286
 synthetic fibers, 284
 temperature and, 288
 wool, effect of humidity, 287
- Stretching, see Deformation, Strain
- Structural breakdown, change (see also
 Thixotropy), 96, 129, 514, 516
 in flow, 92
 flow curves, 132
- Structure
 asphalt, 364, 371-373
 cellulose, 233, 263, 268
 collagen, 359
 fibers, 262, 264, 265, 267, 269
 fine, anelastic properties, 161
 fibers, 268
 gelatin gels, 345, 350-352, 357
 liquids, 138
 network, gels, 357
 Nylon, 265
 polyethylene, 264
 polyvinyl fibers, 265
 polyvinylidene fibers, 265
 protein fibers, 264, 267, 269
 silk, 264, 267
 synthetic fibers, 264
 wool, 59, 264, 267, 269
- Styrene-isobutylene, glass transition,
 176
- Subcrustal, earth, see also Earth, etc.
 current, flow, 413, 417, 422
- Substitution, degree of, 234, 235
- Sugar, effect on gelatin, 346
- Sugar paste, 524
- Sulfur, curing of raw rubber, 182
- Supercontraction, 282
- Superposition equation, principle (see
 also Boltzmann, Hydrodynamic,
 Stress), 43 (17 α), 64, 68, 74, 78, 272,
 471
- Surface
 pressure, 418
 roughness, 228, 229
 slip, 197, 217, 228
 waves absorption (see also Earth,
 etc.), 410
- Suspension, see Particles
- Swelling, 236
- Syneresis, asphalt, 273
- Synthetic fibers, structure, 264
- T
- Table jellies, 359
- Table plastometer, 195
- Tachometry, 447
- Tack, 205, 360
- Tangential and normal tractions, 5, 508
 (see also Stress)
- Tangential stress, see Shear stress
- Tearing, in extrusion, 226
 internal, flowing rubbers, 205
- Tectonic, see also Earth, etc.
 process, rheology, 428
 strain, 423
 theories and viscous flow, 422
- Temperature
 asphalt, 378
 axis, shift, see Scale factor, Time scale
 change, rubber testing, 531
 control, 479, 481
 earth, 403, 404
 effect on dispersion region, 161
 on fiber strength, 309
 on flow properties, 211, 249, 250, 128
 on moduli (see also Modulus), 44
 on strength, 155
 on toughness, 258
 on viscosity (see also Viscosity),
 120, 128, 212, 326, 330
 glass, transition, see Glass transforma-
 tion
 range, mechanical measurements, 24,
 158, 472
- Ring and Ball, effect of rates of heat-
 ing, 388T
- reduced (see also Scale factor), 24

- rise by energy dissipation, 155, 201, 204, 531
- Rossi-Peake, 241, 248
- second order transition, see Glass transition
- standard, see Scale factor, Master curve
- and tension, 298
- and time interrelation (see also Scale factor), 470
- Tenasco, 289, 309
- Tensile strength, see Strength, tensile
- Tensile stress, see Stress, tensile
- Tensile-test, 366, 436-438
 - necking, 254
 - plastic yielding, 254
- Tension
 - decay (see also Stress relaxation), 3, 15, 64, 270, 278, 434
 - inner, see Forces
 - recovery, 271
 - along stream lines (see also Weissenberg effect), 243
- Tertiary sandstone, 404
- Terylene, see Dacron
- Test, Testing, see Creep, Dynamic, Relaxation, Viscosimetry, etc.
- Test instruments, discriminating power, 25, 213, 463T
- Thermal hydrolytic reaction, gelatin, 314
- Thermodynamic
 - activity, see Activity
 - equilibrium, 236
 - estimate of hole volume, 142
 - function for liquids, 140
- Thiokol rubber, see Polysulfide rubber.
- Thixotropic, Thixotropy, 92-94 (41), 132, 185, 224
 - asphalt, 336, 371, 377
 - behavior, 303
 - effect, gelatin, 357
 - elastomers, 183, 192, 213
 - fibers, 305
 - increased by carbon black, 214
 - neglect in plastometer, 195
 - recovery, 185, 200, 214
 - units (see also rheological units), 219
- Three-element model, 27, 29, 31, 33, 300
 - fiber deformation, 301
- Three-state theory, fiber deformation, 305
- Tidal forces, earth's body tides, 418
- Tide gages, 414, 415
- Tide, semi-daily, earth, 421
- Tilt, nonelastic, 429
- Time
 - dependence, see Creep, Energy dissipation, Frequency, Rheological equation of state, Shear rate, etc.
 - effects, 3, 17, 20, 441
 - monotonic change of stress-strain, 464
 - of relaxation, see Relaxation time
 - of retardation, see Retardation time
- Time scale, 4, 53, 64, 67, 301
 - asphalt, 377, 378
 - creep test, 14
 - experimental, 16
 - glass modulus, 17
 - longitudinal experiments, 57
 - molecular rearrangement, 53
 - shift, 8, 274, 281
 - viscoelastic measurements, 434
- Time-temperature superposition (see also Scale factor, Master curve), 64, 281, 471
- factor, 472
- limit, 77
- principle, 67
- range of validity, 68
- temperature limit, 71
- Tin foil, torsional relaxation, 279
- Toluene
 - as polyisobutylene solvent, 124
 - as polystyrene solvent, 119, 120
- Tonga Deep, 421
- Torque, Twist (see also Stress-strain, torsional), 192, 311, 335, 494F, 516
- acetate rayon, 285
- nylon, 285
- periodic, 448
- viscose rayon, 285
- Torsion, see also Coaxial cylinder viscosimeter
 - bars, 516
 - gelatin, 335
 - head, elastoviscometer, 491
 - pendulum, 156, 449, 459
- Torsional, see under individual noun
- Toughness (see also Rupture, work of), 253
 - cellulose derivatives, 253, 258
 - determining factors, 255

- impact-test, 257
 - plastic materials, 257
 - Tractions, see Stress
 - Tracing, Luder's lines, 534
 - Trans* configuration, ester groups, Dacron, 266
 - Transducer, 459, 460
 - double (Fitzgarald), 451, 452F
 - electromagnetic, 450, 452
 - electromechanical, 449
 - measurements of, 156, 463
 - methods, 451, 459
 - Transformation, α - β , reversible, Kera-tins, 268
 - Transient methods, viscoelasticity, 434, 435
 - Transient phenomena, 97
 - Transition, see also Glass transforma-tion
 - entanglement-disentanglement, 92
 - from mantle to core, 429
 - state, 65, 71, 72, 76
 - temperature, gelatin, 356
 - glass, 171
 - Transition α - β , (see also Gelatin, Ker-atin, Wool) 94, 95
 - Translation and rotation in deforma-tion, 5
 - Transmission coefficient, 90
 - Transmission of force through deforma-ble agent, 526F
 - Transport phenomena (see also Diffu-sion, Relaxation theory of trans-port phenomena), 83
 - electrical, membrane diffusion, 104
 - facilitation in melting, 141
 - Transverse force, stress, see Normal stress
 - Transverse waves
 - absorbed, earth core, 402
 - longitudinal, 405
 - propagation, gelatin, 336
 - Trenches, tectonic, 421
 - Triaxial test
 - asphalt, 399
 - asphalt mixture, 389, 393
 - Tricresylphosphate, polyvinylchloride damping, 178
 - Trouton's rule, 156, 369
 - Tube formation by rolling, 524
 - Tuning fork, apparatus, 448
 - Turbulence (see also Reynolds number), 123
 - coaxial cylinders, 496
 - color test, 481
 - in pipe flow, 481, 485
 - polymer solutions, 484F, 485F
 - Twinning, 526
 - Two-state theory, fibers, 303, 304
 - Type, asphalts, 365
 - Tyrosine, 267
- U
- Ultimate-strength, see Strength
 - Ultimate stresses, see Strength
 - Ultrasonics, gelatin solution, 330
 - Umst tter viscometer, 244
 - Unidirectional motion, 506
 - Unilateral compression, 435
 - Uplift postglacial, 413-419
 - center of, 415
 - Newtonian flow, 414
 - viscous process, 418
- V
- Valence angles, bending of, 71, 253
 - van der Waals forces, potential (see also Molecular interaction), 9, 71, 238, 253
 - gel formation, 357
 - between flow units, 88
 - between polymer chains, 53
 - organic glasses, 169
 - Vaporization heat, relation with activa-tion free energy for flow, 86
 - Vapor pressure of solids, 140
 - Variation of latitude, effect of earth's viscosity, 420
 - Velocity, see also Flow, Shear rate
 - color front, 219
 - earthquakes waves, 405
 - group, 413
 - rotational, earth, 421
 - seismic, 401
 - slip, see Slip, velocity
 - Velon, 265
 - Vibrating-reed method, 156, 461, 462
 - Vibrating system, mass of, 148
 - Vibrations (see also Frequency, Waves), 19, 64, 441
 - forced, impressed, 150, 155, 293, 445, 461

- free, 156, 468
- free, decrement, 410
- longitudinal, dilational, compressional, 453-461
- resonance, see Resonance
- shear, transverse, 19, 64, 441-460, 496
- testing, 504, 518F (see also Dynamic response)
- torsional, 389, 448, 462, 517
- Vibrational states, stationary, 519
- Vinyl alcohol, 265
- Vinylchloride, fibers, 265
- Vinylchloride-methacrylate, 176, 178
- Vinylchloride-vinylacetate, glass transition, 176
- Vinylidene chloride, 265
- Vinyon, 265
 - entropy contribution, 300
 - moisture regain, 270
 - strength, 308
 - stress-strain curves, 285, 288
- Vinyon N
 - entropy contribution, 300
 - strength, 308
- Virial
 - coefficient, second, 140
 - estimate of hole volume, 142
 - theorem, 90, 112, 114
- Viscoelastic, viscoelasticity, firmo-viscosity, 4, 5 (see also Anelasticity, Creep, Friction, internal, retarded, Rheological models, Voigt body)
- body, 151, 181, 434, 506, 509, 514, 523
- cellulose derivatives, 258
- cordite, 253
- deformation, mechanism, 6-10, 70, 92-96, 504
- elastomer flow, see Elastico-viscous liquids
- fluid, liquid, see Elastico-viscous liquids
- glasslike behavior, 41, 58
- linear, 11, 33, 60, 64, 69, 76
- measurements, 433, 440, 435, 509-512, 517, 522
- parameters of operator equation, 28, 34
- polycrystalline polymer, 76
- properties, asphalt, and penetration index (P.I.), 365
- response, types of, 6-10, 53, 57, 65
- shear and volume equations, 56 (38) theory, 6, 22, 40, 513
- versus glass relaxation, 55
- volume versus shear, 55
- Weissenberg effect, theories, 513, 514, 523
- Viscometers, Viscosimeters
 - biconical rotor, 187, 193
 - coaxial-cylinder, see Coaxial cylinder viscometer
 - comparison, 212
 - compression, 190, 195
 - cone and plate, 511
 - disk, 186
 - extrusion, 189, 194, 207, 217
 - falling cylinder, 210
 - Mooney, 186, 187
 - Newtonian, 209, 482, 486
 - precision, 478, 479, 495
 - sandwich shearing, 210
- Visco-plastic solid, see Bingham body
- Viscose rayon, 262, 277
 - core, 269
 - creasing of, 291
 - creep, 272-275
 - curve analysis, recovery 275, 280, 281
 - dynamic modulus and static strain, 294, 295
 - flexural rigidity, 292
 - flow units, 302
 - instantaneous extension, 272
 - internal friction, 295, 306
 - moisture regain, 270, 282, 295
 - molecular orientation, 267
 - nonlinear stress-strain relation, 58
 - relaxation, 277, 282
 - rigidity flexural, 292, 297, 311
 - skin, 269
 - solutions, 234
 - strain recovery, 290
 - strength, Henning, 309-312
 - stress-strain curve, 284-287
 - superposition principle, 272
- Viscosimeters, see Viscometers
- Viscosity (see also Friction internal, Intrinsic viscosity, Viscometers, Viscosity equations and theories, Viscosity measurements) 12, 17, 51 (37 α), 148, 152, 407, 475-479, 481, 515

- activation energy, see Activation energy
- anomalous, see Non-Newtonian Liquids
- apparent, 249, 475, 514F, 515F
- bulk, see volume
- coefficient, see also Viscosity equations, individual materials
 - calculation from rate of creep, 156
 - effect of variables, 153
 - elasticoviscous model, liquid, 497
 - idealized, 515 (12)
 - from oscillatory experiment, 500 (10)
- complex, see dynamic
- concentration, effect of, 117, 118, 124, 242, 328, 524
- decrease, with depth, earth, 419
- definition, see Viscosity equations
- dynamic, complex, 44, 244, 442, 520, 521
 - temperature-concentration superposition, 472
- effect of frequency, 521
 - of pressure, 86
- formulas, see Viscosity equations
- high pressure, 86
- infinite shear rate, 106
- inherent, effect of conditions, 115-120
- internal, cellulose, 258
- intrinsic, limiting, 115, 242
- lava, 428
- mechanical model, 26, 28, 34
- melt, 12-14, 131, 141, 244, 445, 524
- of mixture, effect of asphalt viscosity, 399F
- molecular weight, average, 110
- molecular weight effect, 116, 242 (2), 327
- Newtonian, see Newtonian flow
- oscillatory, equivalence with steady flow, 500
- pH curve, gelatin, 324
- in pipes, see Pipe flow
- plastics, 105 (86), 244, 524
- relative, 114
- as scalar, 505
- shear rate (see Non-Newtonian Liquids)
- shifting factor and, 15
- short duration, 517
- solvent, effect of, 119, 129, 130
- specific, 115
- steady flow, 145, 468, 472, 498
 - as stiffness x time, 367 (4)
 - temperature effect (see Temperature, effect)
 - from tensile experiment, 366
 - total, 105
 - volume, 74
- Viscosity coefficient, see Viscosity
- Viscosity, equations and theories, (see also Flow, Hydrodynamics, Liquids), 44, 85, 114, 152, 192, 406, 421, 504, 516
 - generalized equations, 105 (86), 194 (8), 300-306, 514
 - Mooney, 226
 - reduced for temperature, 128
 - rubber, Eyring's, 206, 220, 225
- Viscosity measurements, Viscosity of
 - aluminum laurate, 515
 - asphalt, 366
 - asphalt sol, 382
 - cellulose, 242
 - earth, 405, 406, 409, 418, 420, 421, 423, 429
 - gelatin, 316-318, 322-328, 353, 355, 356F
 - gelatin glue, 318, 359
 - glucose, 152
 - lava, mud, 427, 428
 - liquid paraffin, 498
 - monochlorobenzene, 485
 - polymethylmethacrylate, 485, 494F, 495, 498
 - water, 495
- Viscotron, 460
- Viscous (see also Viscosity, Flow viscous)
 - deformation, 145
 - distortion, fault zone, 428
 - flow, activation heat, 87
 - earth, 413
 - relaxation time, 406
 - in solids, 407, 408
 - strength resisting in earth, 409, 420
 - in tectonic theories, 422
 - fluid, action of radial load, 418
 - recoil, earth, 419
 - type process, 408
- Vistanex LMS, 110
- Voidage, effect of, in asphalt mixture, 394
- Voigt body, element, model, Kelvin body (see also Rheological models, Visco-

- elasticity), 26, 27, 30, 34, 58, 374, 376, 442, 467
 - degenerate, 37
 - in series, 37
 - Voltage-current ratios, 450
 - complex, 451
 - Volume, see also Free volume, Solutions, concentrated, Viscosity, volume change, retarded elastic wave, 411 (20)
 - compliance, bulk, 56 (38)
 - flow rate, 477
 - increase, accompanying activation for flow, 86, 87
 - accompanying melting of solids, 141
 - relation with size of holes, 87
 - per molecule, 88
 - specific, 53, 165
 - temperature curve, for glasses, 147
 - Vulcanized rubber, 14, 15
 - creep compliance, 8
 - departure from linearity, 58
- W**
- Wall effects, 476, 483
 - coaxial cylinder, 494
 - pipes, 482
 - polymethylmethacrylate, solutions, 483, 485
 - slip, coefficient and velocity of, 483, 486
 - suspensions of anisometric particles, 482
 - Walter-Eyring volume function, 140 (110)
 - Water, viscosity, 495
 - Waves, see also Damping, Frequency, Vibrations
 - bulk, 454, 456
 - dilatation, longitudinal, 429, 453, 454
 - distortion, 453
 - flexural, 456, 452
 - period change, 413
 - propagation, 453, 454, 456, 458, 463
 - impedance, 458
 - rotational, 460
 - seismic, 401, 412, 430
 - shear-strain, cellulose tributyrates, 455F
 - spherical, absorption coefficient, 410
 - standing, 457
 - surface, absorption, 410
 - transverse, elastic, shear, 19, 64, 441, 454, 486, 496
 - velocity, 412 (24)
 - viscoelastic, 442
 - Wax, Luder's lines, 534
 - Weak spots, fibers, 308
 - Wedge relaxation function, 45, 72
 - Weissenberg effect (see also Normal-stress effect), 244, 504, 522F
 - Bitumen, 524
 - cellulose derivatives, 243
 - gelatin aqueous solutions, 524
 - polymers, 524
 - printing inks, 524
 - rubber solutions, 524
 - soap gels, 524
 - Wet process, cellulose acetate, 240
 - Wet state network, 298
 - Wet strength, fibers, 311
 - Williams plastometer, 191
 - Wool, wool fibers, 59, 94, 95, 262, 264, 267, 296
 - cortex, 269
 - creasing of, 291
 - creep, extension, 59, 96, 276, 304
 - cuticle, 269
 - dynamic properties, 295, 296
 - epicuticle, 269
 - medulla, 269
 - moisture regain, 270
 - nonlinear stress-strain relation, 50
 - recovery, 290
 - relaxation, 278, 282, 297
 - retardation time, 59
 - rigidity, 292, 296, 297, 311
 - set, 281
 - strength, 308-311
 - stress-strain curve, 285, 287, 299
 - structure, 59, 264, 267, 269
 - thermodynamic model, 283
 - α - β transformation, 285
 - in water, stress-strain cycle, entropy contribution, 299
 - Young's modulus, 283, 289
 - Work, conversion into heat, 3
 - Work hardening, 96
 - Work recovery, 289, 291
 - World strain, tectonic, 425

X

Xanthate, see Viscose
Xenon, 140
X-518 GR-S rubber (see also GR-S), 110,
112, 125, 129
X-672 GR-S rubber (see also GR-S), 110,
112
Xi-factor in diffusion, 98, 101-103
X-ray
 diffraction, cellulosic plastics, 235
 glasses, 147
 pattern, 94
 low angle scattering, gelatin, 359
 scattering, of polymers, 64
Xylonite, 239

Y

Yield, Yielding, see also Flow, plastic
 intergranular, glaciers, 427

 point, apparent, nitrocellulose, 252
 gelatin gels, 332, 352
 large recoverable strains, 254
 in oriented glasses, 165
 rubber extrusion, 194
 strength (see also Strength), 526
 stress, asphalt, 372, 389
 Dacron, 288
 effect of rate of strain, 256
 organic thermoplastics, 256
 reduced by hydrostatic tension, 256
 solution, crystallizable polymers, 244
 value, raw rubber, 209
Young's modulus, see Modulus, Young's

Z

Zein, 262
Zero elongation
 lines of, 528F
 failure along, 531F

