Standard Practice for
Stress Relaxation Testing of Raw Rubber, Unvulcanized Rubber Compounds, and Thermoplastic Elastomers[1]

This standard is issued under the fixed designation D6048; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

INTRODUCTION

There are a number of techniques used to identify the processability of raw rubber, unvulcanized rubber compounds, and thermoplastic elastomers (rubber and rubberlike materials). Most measure a single averaged value of non-Newtonian viscosity with some doing so after a period of steady shear. These techniques may not provide sufficient information with regards to the processability of a selected material, as they: (*1*) fail to provide a measure of the viscoelastic behavior, and (*2*) destroy structure of the selected material through the steady shearing.

Stress relaxation testing provides a measure of the viscoelastic response of a material over a period of time without destroying the structure of the sample. In such testing both the instantaneous and time-dependent response to an applied deformation are measured. The information from this single experiment can then be used to examine a material's reaction to various different process conditions.

There are several different techniques for measuring stress relaxation properties of rubber and rubberlike materials. This practice serves to provide the reader with some background information about those techniques in terms of the theory of testing and the interpretation of results. Many concepts are put forward that are not discussed in depth, for to do so would require a textbook, not a practice. The reader is therefore encouraged to consult the identified references.

1. Scope

1.1 This practice covers several different techniques for determining the stress relaxation characteristics of rubber and rubberlike materials and for the possible interconversion of this stress relaxation information into dynamic mechanical properties.

1.2 The techniques are intended for materials having stress relaxation moduli in the range of 10^3 to 10^8 Pa (0.1 to 1.5×10^4 psi) and for test temperatures from 23 to 225°C (73 to 437°F). Not all measuring apparatus may be able to accommodate the entire ranges. These techniques are also intended for measurement of materials in their rubbery or molten states, or both.

1.3 Differences in results will be found among the techniques. Because of these differences, the test report needs to include the technique and the conditions of the test. This information will allow for resolving any issues pertaining to the test measurements.

1.4 The generalized descriptions of apparatus are based on the measurement of force as a function of time. Mathematical treatment of that relationship produces information that can be representative of material properties. Mathematical transformation of the force measurements will first yield stress relaxation moduli with subsequent transformation producing dynamic mechanical properties.

1.5 The values stated in SI units are to be regarded as the standard. The values given in parentheses are provided for information only.

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1566 Terminology Relating to Rubber

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[1] This practice is under the jurisdiction of Committee D11 on Rubber and is the direct responsibility of Subcommittee D11.12 on Processability Tests.

Current edition approved May 1, 2012. Published July 2012. Originally approved in 1996. Last previous edition approved in 2007 as D6048 – 07. DOI: 10.1520/D6048-07R12.

[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

D1646 Test Methods for Rubber—Viscosity, Stress Relaxation, and Pre-Vulcanization Characteristics (Mooney Viscometer)

D5992 Guide for Dynamic Testing of Vulcanized Rubber and Rubber-Like Materials Using Vibratory Methods

E328 Test Methods for Stress Relaxation for Materials and Structures

3. Terminology

3.1 *Definitions:*

3.1.1 Each of the following terms applies to linear viscoelastic behavior. The terms have been arranged logically so that simple basic terms are defined first and are then used to define more complex terms that either contain the simple terms or depend upon the simple terms for comprehension. Some terms in this section have been excerpted from Terminology D1566, Guide D5992, or Test Methods E328.

3.1.2 *stress, n*—the force per unit area that acts on the face of a cubical element that is perpendicular to the force.

3.1.3 *strain, n*—the change in the size or shape of a body due to force when referred to its original size or shape.

3.1.4 *initial stress, n*—the stress occurring in a specimen immediately upon achieving the given input strain.

3.1.5 *damping, n*—a material property that results in the conversion of mechanical energy to heat when the material is subjected to deformation.

3.1.6 *modulus, n*—a material property that is the ratio of stress to strain.

3.1.7 *stress relaxation, n*—the time-dependent decrease in stress under constant strain at constant temperature.

3.1.8 *relaxation curve, n*—a plot of the force, stress, or relaxation modulus as a function of time.

3.1.9 *relaxation time, n*—the time required for a body to relax after deformation (synonym: *time constant*).

3.1.10 *relaxation spectrum, n*—the response of a group of bodies to deformation, each having a unique relaxation time; normally defined as a mathematical function, an integral over which describes linear viscoelastic behavior.

3.1.11 *elastic, adj*—the tendency for a material to return to original shape after release of stress; specifically, descriptive of that component of the complex force in phase with dynamic deflection that does not convert mechanical energy to heat and that can return energy to an oscillating mass-spring system (synonym: *storage*).

3.1.12 *loss, adj*—descriptive of that fraction of energy absorbed by a strained object that is converted to heat, that is, that which is hysteretic.

3.1.13 *viscous, adj*—descriptive of that type of energy loss in which the damping component of stress is proportional to the rate of deformation.

3.1.14 *compression, n*—the type of strain parallel to the direction of displacement that results in a decrease in the height of the strained body.

3.1.15 *shear, n*—the type of strain that is perpendicular to the direction of displacement.

3.1.16 *shape factor, n*—for disks or cylinders to be tested in compression, the ratio of the diameter of the specimen to its height.

3.1.17 *compression modulus, n*—a material property of resistance to change in height when subjected to a compressive force; a ratio of compressive stress to compressive strain.

3.1.18 *viscoelasticity, n*—a unique response to deformation characterized by both the storage and loss of energy; the response is dependent on time and temperature.

3.1.19 *linear viscoelasticity, n*—a unique response to deformation characterized by both the storage and loss of energy where modulus is independent of strain.

3.1.20 *reptation, n*—the mechanism by which the motion of a polymer molecule is restricted by the proximity of segments of other polymer molecules.

3.2 *Symbols:*

G—shear modulus.
$G(t)$—shear relaxation modulus as a function of time.
$P(t)$—pressure (in compression) as a function of time.
τ—characteristic relaxation time.
t_0—zero time.
σ—stress.
ε—extensional strain.
γ—shear strain.
γ—rate of shear strain.
Δ—compressive strain (in bulk).
$\dot{\Delta}$—rate of compressive strain (in bulk).
t—running time.
K_e—spring constant (elastic).
K_v—dashpot constant (viscous).

3.3 *Symbols for Dynamic Properties:*

G^*—complex shear modulus.
E^*—complex extensional modulus in either tension or compression.
$G' = G^* \cos\delta$—shear storage modulus; the in-phase component of G^*.
$G'' = G^* \sin\delta$—shear loss modulus; the component of G^* out of phase by 90°.
$E' = E^* \cos\delta$—extensional storage modulus, the in-phase component of E*.
$E'' = E^* \sin\delta$ —shear loss modulus; the component of E^* out of phase by 90°.
η—viscosity.
η'—dynamic viscosity.
ω—angular frequency.

4. Summary of Practice

4.1 The methods covered in this practice are divided into four general categories.

4.1.1 Shear stress relaxation after sudden step strain,

4.1.2 Compressive stress relaxation after sudden step strain,

4.1.3 Shear stress relaxation after cessation of steady shear flow, and

4.1.4 Shear stress relaxation after sudden stress application.

4.2 Descriptions of these methods are given in Section 8. Sufficient mathematical formulae are also provided to indicate how results are calculated.

5. Significance and Use

5.1 The processing behavior (processability) of rubber or rubberlike materials is closely related to their viscoelastic properties. The viscoelastic properties as well as the mechanical properties are related to the polymeric, including macromolecular and micromolecular structure. Therefore, a determination of the viscoelasticity of a material will provide information to predict processing and service performance.

5.2 Stress relaxation testing provides a methodology for investigating the viscoelasticity of rubber or rubberlike materials. Certain structural characteristics that have been demonstrated to be evaluated by this test method are: (*1*) average molecular weight, (*2*) molecular weight distribution, (*3*) linearity or chain branching, (*4*) gel content, and (*5*) monomer ratio.

5.3 This practice is intended to describe various methods of measuring the stress relaxation properties of raw rubber, unvulcanized rubber compounds, or thermoplastic elastomers for determining the processability of these materials through viscoelastic measurements. Factory performance characteristics that this methodology may correlate with include die swell or shrinkage, extrusion rate, mill banding, carbon black incorporation time, and mold flow.

6. Hazards

6.1 There are no hazards inherent to the techniques to be described. There is no use of reagents or hazardous materials. The design of the various different test apparatus may have created possible pinch points; caution shall be exercised and a guard shall be provided for these sites.

6.2 Normal safety precautions and good laboratory practice should be observed when using any equipment. This is especially true when performing tests at elevated temperatures where electrical heaters are used.

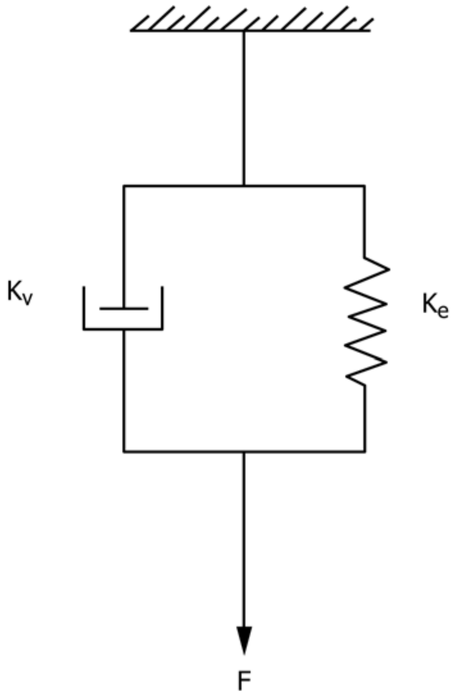
7. Theory of Stress Relaxation

7.1 *Mechanical Models of Viscoelasticity:*

7.1.1 Polymeric materials exhibit both elasticity and viscous resistance to deformation. The materials can retain the recoverable (elastic) strain energy partially, but they also dissipate energy if the deformation is maintained. Mechanical analogues of a viscoelastic solid (Fig. 1) and a viscoelastic liquid (Fig. 2) help identify this behavior.

7.1.2 In Fig. 1, a dashpot is connected in parallel with a spring. This is known as a Voigt element. If deformed, the force in the spring is assumed to be proportional to the elongation of the assembly, and the force in the dashpot is assumed to be proportional to the rate of elongation of the assembly. With no force acting upon it, the assembly will return to its reference state that is dictated by the rest length of the spring.

7.1.3 In this example, if a sudden tensile force is applied, some of the work performed on the assembly is dissipated in the dashpot while the remainder is stored in the spring. The applied force is analogous to the deforming stress and the elongation is analogous to the resulting strain. The viscous resistance to deformation represented by the dashpot introduces time dependency to the response of the assembly where this dependency is dictated by the spring and dashpot constants. The assembly cannot respond instantaneously to changes in stress; this indicates that the viscoelastic solid has a time dependency.



NOTE 1—
F = force,
K_e = spring constant (“e” denotes “elastic”), and
K_v = dashpot constant (“v” denotes “viscous”).

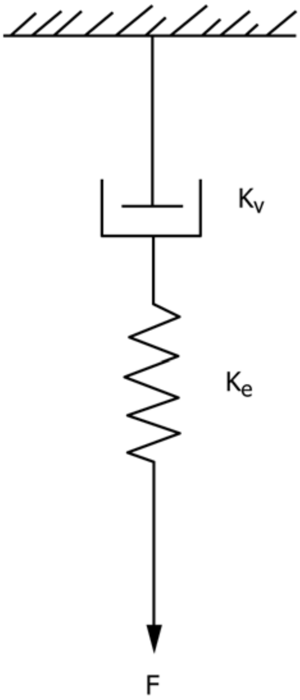
FIG. 1 Voigt Element Representing the Response of a Viscoelastic Solid

7.1.4 In Fig. 2, a dashpot is connected in series with a spring. This is called a Maxwell element. Unlike the Voigt element, there is no dictated reference state so that the assembly will deform indefinitely under the influence of an applied force, assuming that the dashpot has infinite length, a characteristic of a viscoelastic fluid.

7.1.5 In this example, if a sudden tensile force is applied, it is the same in both the spring and the dashpot. Some of the work performed on the assembly is dissipated in the dashpot while the remainder is stored in the spring. The total displacement experienced by the element is the sum of the displacements of the spring and the dashpot. As with the Voigt element representing a viscoelastic solid, the Maxwell element represents a combination of viscous and elastic properties. This indicates that the viscoelastic liquid is also time-dependent and has a characteristic time constant. However, as the time constant becomes smaller and smaller, the elastic quality of the liquid becomes less and less and appears to behave more like a purely viscous material.

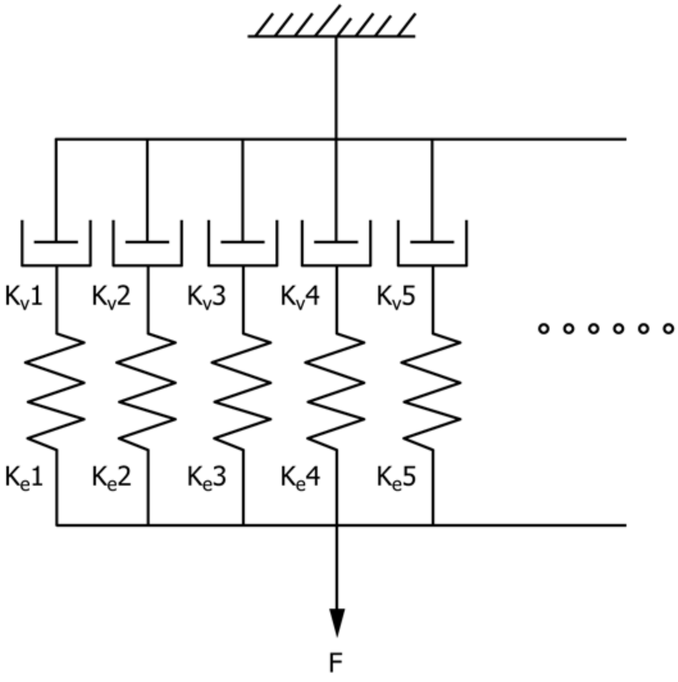
7.1.6 The response of polymers to changes in stress or strain is actually a combination of multiple elements of both mechanical models; one such example is illustrated in Fig. 3. The response is always time-dependent and involves both the elastic storage of energy and viscous loss.

7.2 *Molecular Behavior:*



NOTE 1—
F = force,
K_e = spring constant (“e” denotes “elastic”), and
K_v = dashpot constant (“v” denotes “viscous”).

FIG. 2 Maxwell Element Representing the Response of a Viscoelastic Liquid



NOTE 1—
F = force,
K_c = spring constant (“e” denotes “elastic”), and
K_v = dashpot constant (“v” denotes “viscous”).

FIG. 3 Parallel Maxwell Elements, Each Having Its Unique K_e and K_v, Represent the Rate of Decay in a Stress Relaxation Experiment

7.2.1 In the rubbery or molten state, the polymer molecules are flexible and can be considered like entangled coils. Under small deformation, the coils change shape. The coils will return to their original shape when the deformation is removed. That return is retarded by molecular friction as the coils overlap; the density of the molecules in the space that they occupy at any given instant is much less than the observed density. This overlapping or entanglement strongly affects the motion of neighboring molecules.

7.2.2 The mechanics of these coil models have been proposed (**1**)[3] and modified (**2**) but only explain polymer behavior in dilute solution where there is little or no interaction between individual polymer coils. A theory (**3**) of reptation better considers the interaction between polymer molecules. This theory places the molecule within a tube of known diameter and length. Under deformation, and at very short times, the only reaction that occurs within an entangled molecule is the redistribution of segments between the constraining points of entanglement. Once the maximum strain energy that can be reduced by this rearrangement is obtained, the molecules further relieve the stress by diffusion out of their tubes.

7.2.3 A modification (**4**) of the tube theory gives a better description of polydispersed polymers that may also have long-chain branching in which relaxation through retraction of the molecules within their tubes is the dominant mechanism.

7.2.4 In any of these models of molecular behavior under deformation, the qualitative behavior of flexible polymers is predicted. The quantitative behavior, the magnitude of the viscous and elastic characteristics, depends upon the detailed chemical structure of the polymer molecules.

7.3 *Stress Relaxation:*

7.3.1 As this practice deals with raw rubber, unvulcanized rubber compounds, and thermoplastic elastomers, either in their rubbery or molten state, the discussion on relaxation modulus will be limited to the plateau and terminal zones (see Annex A1). These relaxation mechanisms are illustrated in Fig. A1.1. If the rubber or rubberlike material is suddenly deformed and the ability of the instrumentation is sufficient to measure immediate relaxation response, the material will appear to act like a solid. The submolecular units of the polymer cannot rearrange fast enough to begin dissipating the strain energy. With increasing time, the polymer begins relaxing to a reduced free energy state. A period called the plateau zone is then achieved due to the presence of a transient entanglement network. As relaxation time increases, the polymer reaches lower and lower states of free energy as the molecular chains begin to re-orient to an equilibrium distribution of segments with the longest chains re-orienting at the longest times. At this point there is a rapid reduction of modulus, the terminal zone.

7.3.2 Stress relaxation is the time-dependent decrease in stress under constant strain at constant temperature. The rate of decay can be expressed by a first-order equation since the rate of decay for the perturbed portion of the sample being measured is proportional to the total amount of remaining perturbed sample.

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[3] The boldface numbers in parentheses refer to a list of references at the end of this practice.

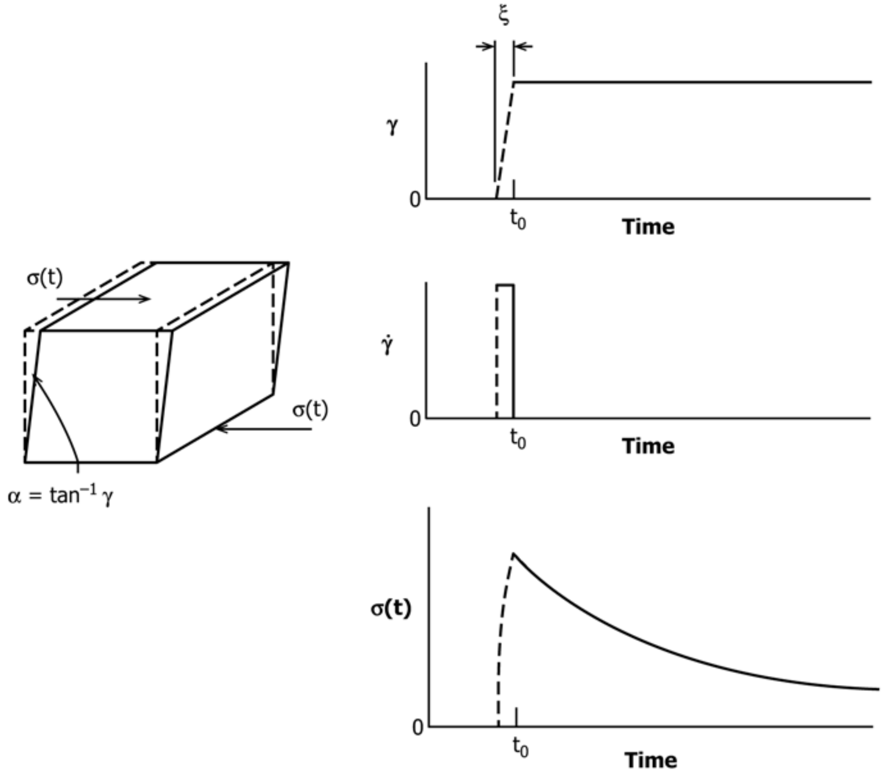

FIG. 4 Geometry and Time Profiles of a Simple Shear Stress Relaxation Experiment Following Sudden Strain

7.3.3 A combination of parallel Maxwell elements serves to represent this behavior (**5**) for molten polymers as illustrated in Fig. 3. Each Maxwell element represents a certain contribution to the relaxation property of the viscoelastic material. Mathematically, this is represented by:

$$\frac{F(t)}{\varepsilon_0} = \sum_{i=1}^{n} K_{ei} e^{-t(Ke/Kv)i} \tag{1}$$

where:

$F(t)$ = force as a function of time,
ε_0 = initial extensional strain,
K_e = spring constant,
K_v = dashpot constant, and
i = number of element(s).

Representing Eq 1 in terms of material properties, in shear:

$$G(t) = \sum_{i=1}^{n} G_i e^{-t/\tau i} \tag{2}$$

where:

$G(t)$ = $^{\text{F(t)/cross-sectional area}}/_{\gamma 0}$,
G = K_e,
τ = K_v/K_e, and
γ_0 = initial shear strain.

A plot of relaxation modulus against time has certain characteristic features. These features can be associated with different kinds of molecular responses and can be influenced by the molecular weight, molecular weight distribution, and long chain branching of the viscoelastic material, whether it is amorphous or crystalline and whether the material has been reinforced with filler or diluted with some form of low molecular weight material acting as a plasticizing agent.

8. Test Techniques (5)

8.1 *Shear Stress Relaxation after Sudden Step Strain:*

8.1.1 This technique involves the application of a shear strain at a constant rate within a very brief period of time. A schematic diagram of this deformation is found in Fig. 4. The stress required to maintain the shear strain as a function of time is then measured beginning at t_0.

8.1.2 If the stress is measured at times much longer than the time required to apply the maximum strain, then:

$$G(t) = (\sigma(t)/\gamma) \tag{3}$$

8.1.3 In simple shear, the change in shape of the test specimen is not accompanied by any change in volume which allows for interpretation of the resulting behavior in molecular terms.

8.2 *Compressive Stress Relaxation after Sudden Step Strain:*

8.2.1 This technique involves the application of a compressive strain at a constant rate within a very brief period of time on an unconstrained cylinder. A schematic diagram of simple compression is found in Fig. 5. The stress required to maintain the compressive strain as a function of time is then measured beginning at t_0.

8.3 *Shear Stress Relaxation after Cessation of Steady Shear Flow:*

8.3.1 After attaining steady-state viscosity conditions during the steady shear deformation of a material at constant rate

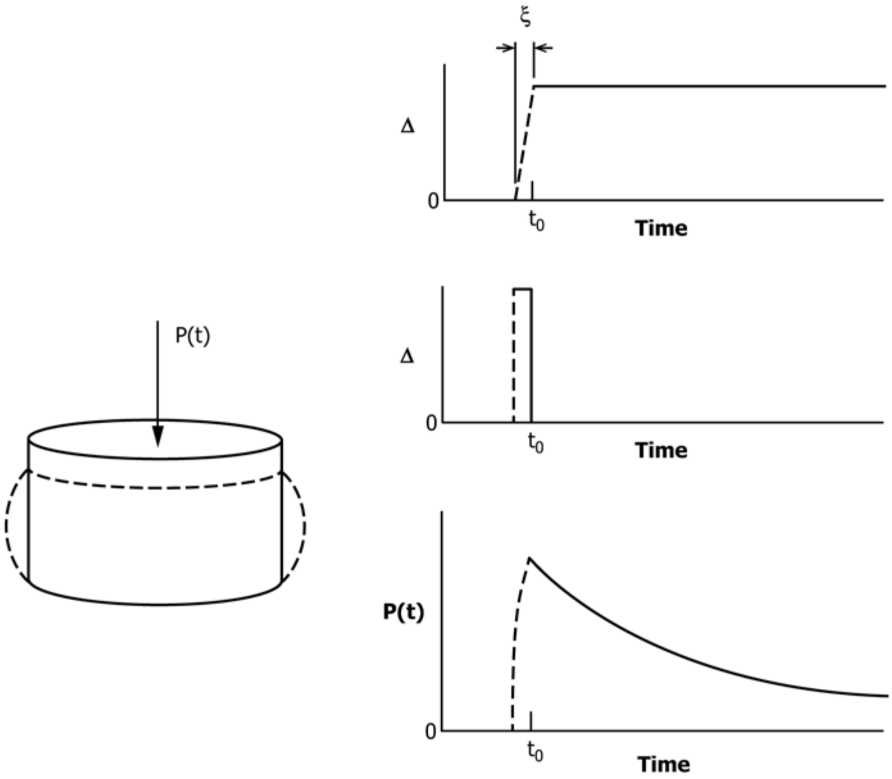

FIG. 5 Geometry and Time Profiles of a Simple Compressive Stress Relaxation Experiment Following Sudden Strain

of strain (γ), the shearing action upon the material is abruptly stopped. The steady-state stress (σ^{ss}) will then gradually decrease and be measured as a function of time beginning at t_0, where:

$$\sigma^{ss}(t) = \gamma \int_{t_o}^{\infty} G(t)\,dt \qquad (4)$$

A schematic diagram of this test profile is found in Fig. 6.

8.3.2 The difference in this technique of relaxation from that of 8.1 can be identified in terms of Fig. 6. If the strain is suddenly imposed as in 8.1, the force is initially distributed among the single elements in proportion to the spring constants. If relaxation follows the attainment of steady-state flow, the force is initially distributed in proportion to the dashpot constants. The relaxation times between the two techniques will be the same but the magnitude of the individual relaxing force contributions will be different, producing a different overall relaxation history for the polymer. Also, short relaxation responses are occurring during the steady shear flow portion of the test, dependent upon the shear rate, where these responses are not recovered when $G(t)$ is measured.

8.4 *Shear Stress Relaxation after Sudden Stress Application:*

8.4.1 Capillary rheometers are normally used to measure shear stress-shear rate relationships under steady, laminar flow conditions. It is also possible to increase shear stress by applying a deformation (d) at a constant rate (d) within a brief period of time, developing an increase in barrel pressure (P). A schematic of this stress condition is shown in Fig. 7. The relaxation of the barrel pressure as a function of time, $P(t)$, is then measured beginning at t_0.

8.4.2 Relaxation of applied stress in a capillary rheometer can involve shear flow through the capillary as well as stress relaxation without shear flow. For test times much longer than the time to apply the maximum stress, the shear stress as a function of time may be calculated by:

$$\sigma(t) = (P(t))/4(L/D) \qquad (5)$$

where:

$\sigma(t)$ = shear stress as a function of time,
L = length of the die orifice, and
D = diameter of the die orifice.

9. Factors Influencing Measurements

9.1 *Sample Preparation/Handling:*

9.1.1 The processing that rubber or rubberlike materials may experience in preparing a test piece may alter the physical state of the material, affecting the relaxation properties. Standardization and adherence to well defined procedures of sample preparation must be followed.

9.1.2 The instrumentation may also uniquely form material into a test piece. The test piece must be fully relaxed when performing a step strain experiment, otherwise there may be relaxation processes being measured in addition to those intended.

9.1.3 When testing low viscosity or sticky materials, a protective film may be used between the test piece and the metal surfaces of the test fixture(s). This will assist in easy and rapid removal after completion of the test. However, if the film used is polymeric it will have relaxation properties. Though the film is thin and virtually negligible in comparison to the

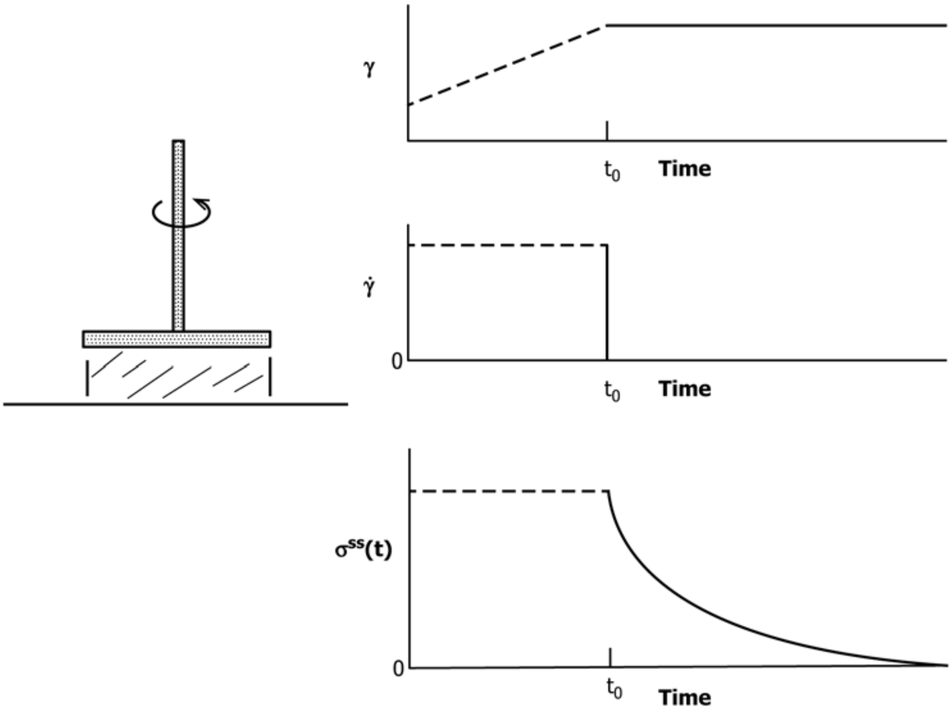

FIG. 6 Geometry and Time Profiles of a Simple Shear Stress Relaxation Experiment Following Cessation of Steady-State Flow

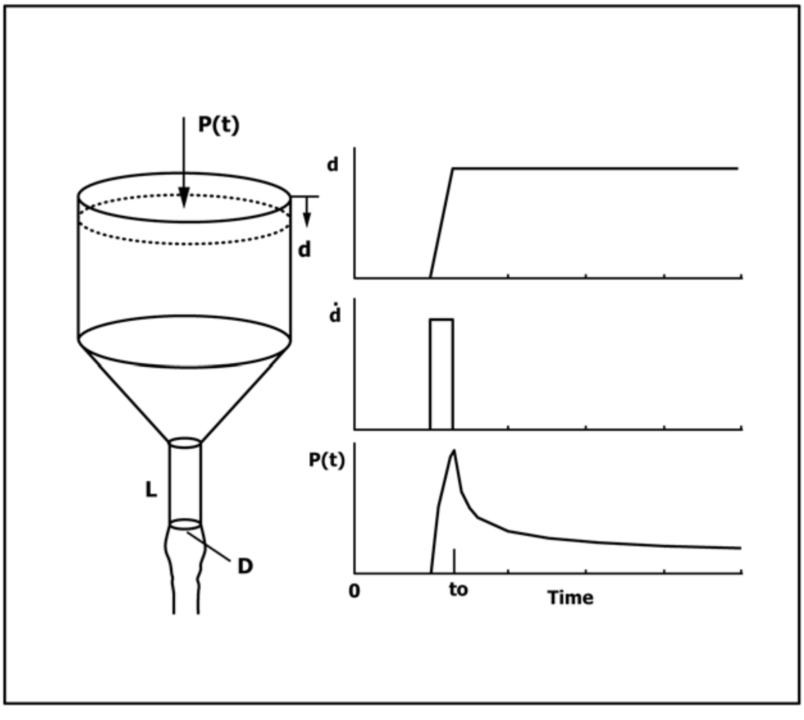

FIG. 7 Geometry, Displacement, and Pressure Profiles for a Rapid Application of Stress Through Piston Displacement (d) in a Capillary Rheometer

thickness of the test piece, both the type and thickness of the film should be standardized to minimize its influence on test measurements.

9.2 *Thermodynamic Factors*—There are two thermodynamic factors that can act on the rubber or rubberlike test piece: thermal-related factors and mechanical forces. Both factors involve a rise in internal temperature of the test piece.

9.2.1 *Thermal-Related Factors:*

9.2.1.1 Temperature is one of the principal variables that influences viscoelastic behavior. Each molecular contribution to the measurement of relaxation properties is associated with a relaxation time that is proportional to temperature. Testing at different temperatures will therefore explore different mechanisms of relaxation.

9.2.1.2 Relaxation properties change drastically with increasing temperature. The techniques presented here consider testing under isothermal conditions where the room-temperature material is placed within the test fixtures that are at some elevated temperature. The physical state of the material may well change from rubbery to a soft viscous material. The rate of this change is dependent upon the thermal transfer between test fixtures and test piece, that is, due to the thermal conductivity of the material, the construction of the test fixtures or the contact surface area between the fixtures and the test piece.

9.2.2 *Mechanical Forces:*

9.2.2.1 Mechanical forces are the stress and strain exerted on the test piece. The recoverable portion of the deformation influences the elastic energy of the rubber or rubberlike material. The nonrecoverable portion of the deformation influences the viscosity of the material. The magnitude of the deformation will influence the instantaneous measurement of resistance offered by the rubber or rubberlike material to that deformation and all subsequent measurements of relaxation. Standardization among instruments that deform the test piece in a specific way is needed to minimize the influences; agreement among instruments that deform the test piece in different ways cannot be expected.

9.3 *Mechanical and Instrumentation Factors:*

9.3.1 Viscoelastic properties are dependent upon the rate of applied strain or the rate of applied stress, or both, depending upon the material. Because of these dependencies, the components that control the deformation and measure the response need to be standardized and then periodically verified among like instrumentation.

9.3.2 *Stress Relaxation after Sudden Strain:*

9.3.2.1 For instruments that measure stress relaxation properties after sudden application of strain, maximum displacement and the time to maximum displacement should be highly repeatable.

9.3.2.2 For instruments that measure in compression, the variation in volume from test piece to test piece must be very small so as to not confound the true relaxation properties of the material.

9.3.2.3 The strain rate history during deformation can cause differences in the subsequent immediate relaxation of the polymer. Typically, classical stress relaxation experiments try to impose the deformation on the material as instantaneously as possible. The data obtained at relaxation times approximately 10 times greater than the time required to impose the deformation are essentially equivalent to those obtained from an ideal instantaneous deformation. Data obtained immediately after imposition of the total deformation should be discarded to remove any effects of strain rate.

9.3.3 *Stress Relaxation after Cessation of Steady Shear Flow:*

9.3.3.1 For instruments that measure stress relaxation properties after a steady-state viscosity has been reached under constant rate of strain, for example, per Test Methods D1646, high precision is necessary for both rotation speed and the cessation of rotation. The maintenance of rotation speed is important as the viscosity of non-Newtonian fluids is dependent upon the shearing rate. Repeatability in cessation of rotation is important in that relaxation of the test piece begins as soon as the rate of shearing begins to slow so that a constant and rapid means of bringing the moving test fixture to rest be incorporated to minimize influence on the resultant relaxation properties of the material. Frictional factors during flow and after cessation must be minimized.

9.3.4 *Geometry:*

9.3.4.1 Because stress is the force per unit area exerted on the test piece, an accurate representation of the geometry of the test piece is critical.

9.3.5 *Shape Factor:*

9.3.5.1 Shape factor is a critical variable that influences the measurement of compressive modulus. It must be accounted for if different sizes of test pieces are used (**6**). Standardization of the size of the piece would avoid this effect and improve reproducibility. However, it must be remembered that the calculated compressive modulus is representative only of the size of the test piece.

10. Types of Analysis and Their Influences on Results

10.1 Any of the described techniques of stress relaxation involve the measurement of a decaying force as a function of time. Results can then be reported in terms of the physical measurement of force or they can be transformed into material properties.

10.2 *Force Measurements:*

10.2.1 The methods of stress relaxation are straightforward when expressed as the measurement of force as a function of time, provided that the influencing factors of 9.3.2 and 9.3.3 are considered. If a characteristic relaxation time(s) is to be measured, the initial stress will significantly influence the determination. Zero time must be the same from test to test.

10.2.2 The terminal relaxation curve may fit a power law equation:

$$F(t) = At^n + B \tag{6}$$

The coefficients A and n characterize the time-dependence (viscosity) of the polymer, while B represents the equilibrium force maintained by the polymer after complete relaxation from the imposed deformation; it is quite possible that a non-zero value of B may be obtained by this purely empirical equation even for an uncrosslinked melt. If data are treated in this manner, there is no need to transform force measurements to material properties. However, the number of data points collected to characterize the relaxation curve as well as the beginning and end points will affect the fit of the nonlinear equation. Therefore, data collection and handling, as well as the reduction technique, need to be standardized.

10.3 *Conversion to Material Properties:*

10.3.1 The conversion from force relaxation values to relaxation modulus values requires accurate knowledge of the geometry of the test specimen at deformation and the amount of the deformation.

11. Keywords

11.1 compression; elastomer; polymer; relaxation; rubber; shear; strain; stress; viscoelasticity

ANNEX

(Mandatory Information)

A1. CHARACTERIZATION OF MOLECULAR PARAMETERS BY STRESS RELAXATION

A1.1 The characterization of raw rubber, unvulcanized rubber compounds, and thermoplastic elastomers in their rubbery or molten states necessitates measurement of their relaxation mechanisms in the plateau or terminal zones, or both (7.3). The plateau zone (G^0_N, the plateau shear modulus) occurs when molecular weights are at and above a critical entanglement composition. The width and the height of the plateau are related to the number of entanglements per molecule. An approximate value of the entanglement molecular weight can be obtained at the $G(t)$ inflection point leading into the plateau zone by:

$$M_e = dRT/G \tag{A1.1}$$

where:

M_e = entanglement molecular weight,
d = density, g/cm^3,
R = gas constant, l·atm/mol·°K, and
T = absolute temperature, °K.

A1.2 The terminal zone occurs after the raw rubber, etc. has relaxed for sufficiently long times that the molecules begin to disentangle. This zone occurs after the plateau zone (Fig. A1.1). These longest of relaxation times are determined by long-range motions of the molecules of greatest molecular weight.

A1.3 Fig. A1.2 provides an example of the effect of weight-average molecular weight ($\bar{M}_W$). The definition of the plateau depends upon the molecular weight distribution (MWD). This effect on $G(t)$ is illustrated in Fig. A1.3.

A1.4 Many polymers contain branches with lengths comparable to the critical entanglement length of a linear polymer chain. The effect of branching depends on the length of the branches, their geometrical arrangement along the main chain, and on their distribution among the main chains. The occurrence of branching is often accompanied by a broadening of the MWD. An example of the effect of branching in Fig. A1.4 illustrates very similar $G(t)$ behavior to the MWD effects depicted in Fig. A1.3.

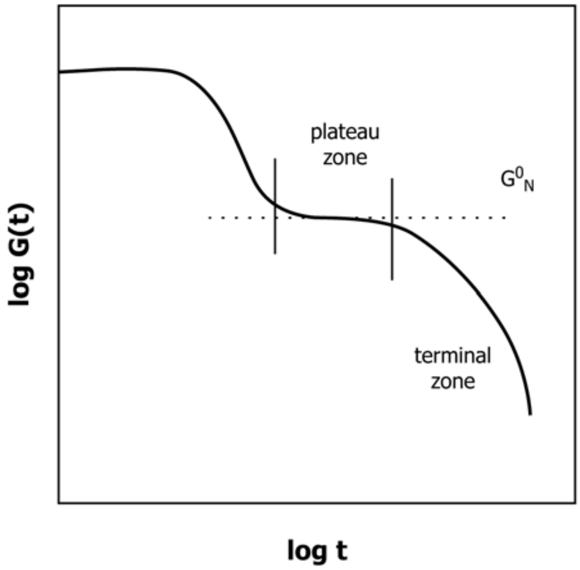

FIG. A1.1 Shear Stress Relaxation Modulus as a Function of Time Covering Behavior from Solid-like Through the Plateau Zone (G^0_N) to the Terminal Zone

A1.5 The presence of branching serves to reduce the number of entanglements and to lower viscosity because the branch points tie together chain segments that might normally be widely spaced according to the random motion of linear main chains. Branching also serves to extend the relaxation spectrum to much longer times.

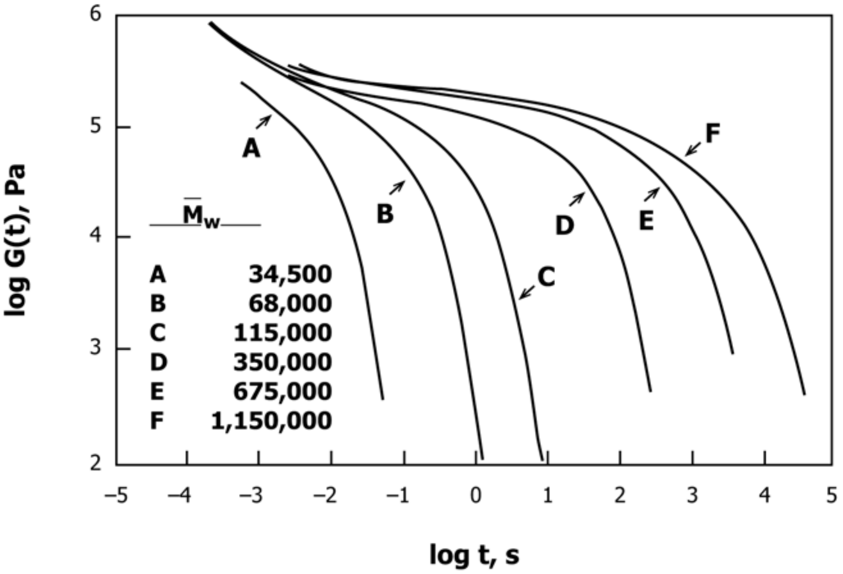

FIG. A1.2 An Example of the Effect of Molecular Weight on *G(t)* (7)

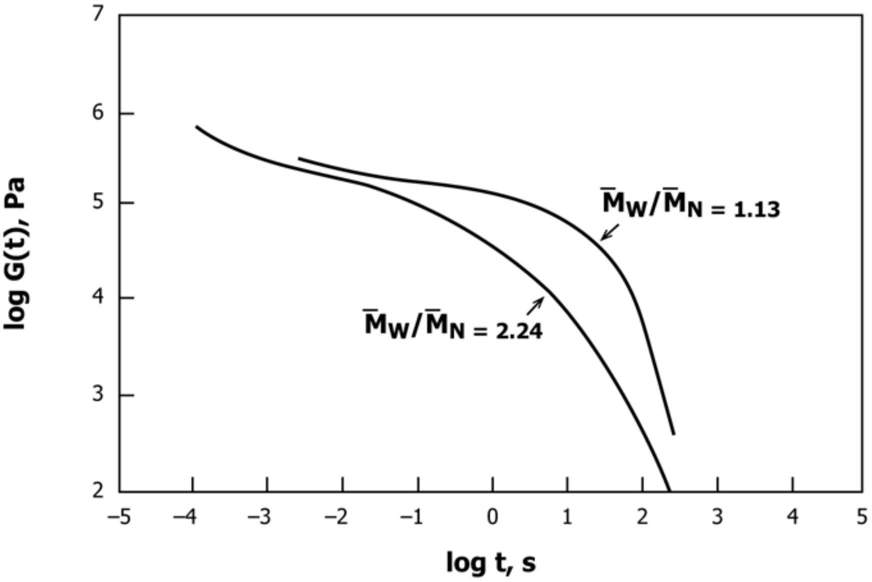

FIG. A1.3 An Example of the Effect of MWD on *G(t)* Wher M_N is the Number-Average Molecular Weight (7)

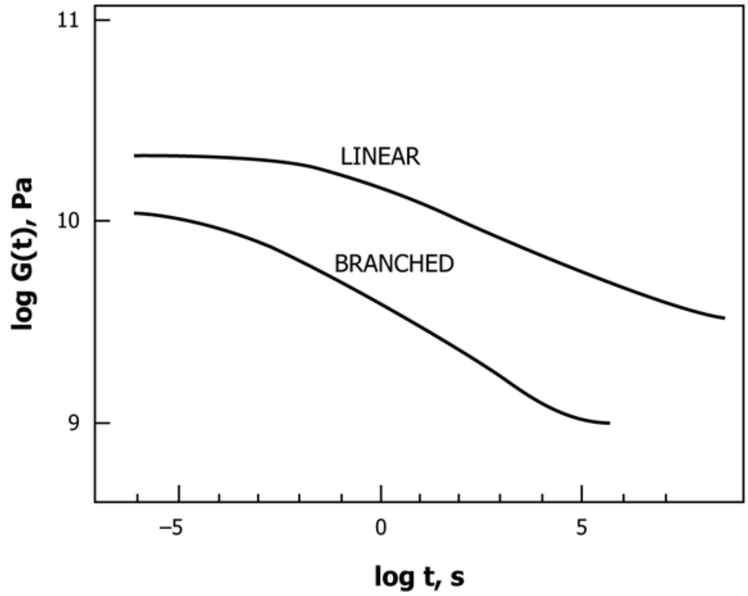

FIG. A1.4 An Example of the Effect of Chain Branching on *G(t)* (8)

APPENDIXES

(Nonmandatory Information)

X1. CONVERSION OF STRESS RELAXATION PROPERTIES TO DYNAMIC PROPERTIES

X1.1 Interrelationship

X1.1.1 The time-dependent stress relaxation modulus reflects the relaxation time spectrum, or viscoelastic properties. As such, the relaxation modulus is affected by the polymer's molecular weight, molecular weight distribution, molecular structure, etc. These molecular parameters are often more easily separated and therefore identified by examining the viscoelastic behavior in the frequency domain. There is considerable evidence (**8**) that a difference in the manifestation of entanglements exists in the elastic and viscous components, again more easily separated in the frequency domain.

X1.1.2 It is possible to determine exact relations for calculating any viscoelastic function in shear as a function of either time or frequency from the relationship:

$$\sigma(t) = \int_{-\infty}^{t} G(t-t')\gamma(t')dt' \quad \text{(X1.1)}$$

X1.1.3 An example of the interrelationships among relaxation mechanisms is represented by a flow chart in Fig. X1.1. This chart is close-looped if viscoelastic behavior is linear; note the presence of Eq X1.1 in the loop.

X1.1.4 Derivations of the equations supporting these interrelationships can be found in Ref (**9**). The development of the unique interrelationships will also be referred to the literature (**10–11**).

NOTE X1.1—Relationships are analogous for bulk compression.

X1.2 Symbols

X1.2.1 Definitions of symbols for dynamic properties are found in 3.3. These symbols apply to linear viscoelastic behavior.

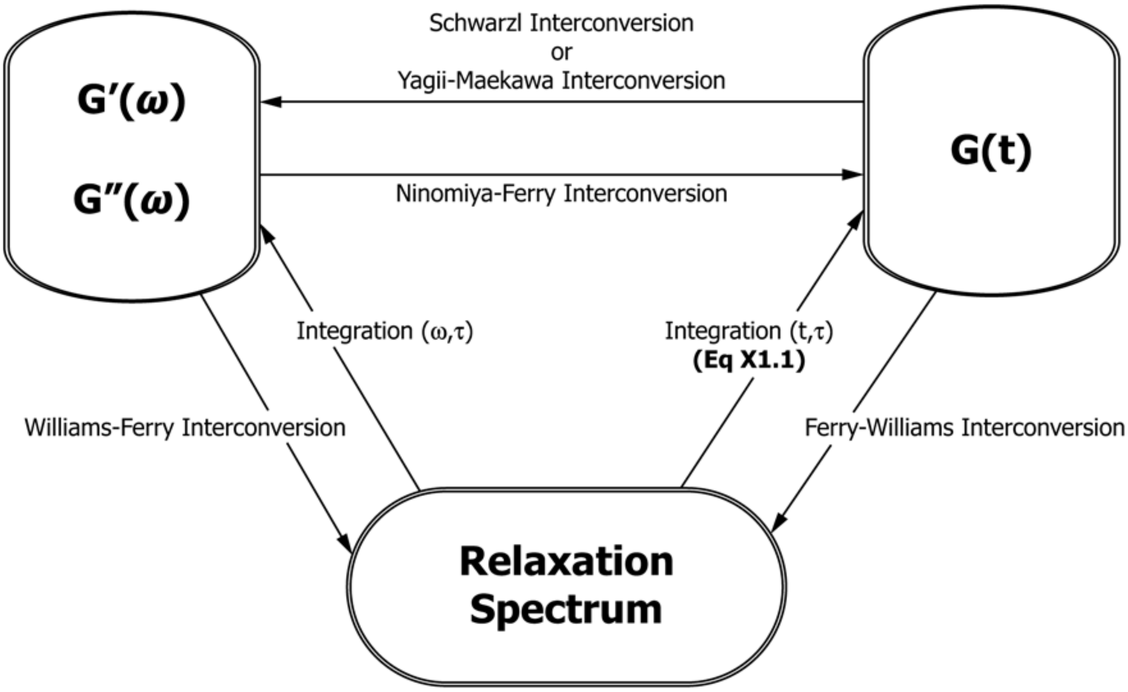

FIG. X1.1 The Interrelationships Among the Various Different Relaxation Mechanisms

X2. CHARACTERIZATION OF MOLECULAR PARAMETERS BY DYNAMIC PROPERTIES

X2.1 Characterization

X2.1.1 A dynamic measurement at frequency ω is qualitatively equivalent to a transient one at $t = 1/\omega$. By being able to investigate the separate elastic and viscous responses ($G'(\omega)$ and $G''(\omega)$, respectively) and certain relationships between them, polymer differences can be related to distinct molecular parameters.

NOTE X2.1—$E'(\omega)$ and $E''(\omega)$ are analogous relationships for any type of extensional deformation.

X2.1.2 The dynamic viscosity can be calculated from the loss modulus by:

$$\eta'(\omega) = G''(\omega)/\omega \tag{X2.1}$$

Because $\eta'(\omega)$ closely resembles $\eta(\gamma)$ (**12**), identifications of molecular weight and MWD can be made. The example (**13**) of Fig. X2.1 shows how three samples (A, B, C) of different $\bar{M}_W$ but similar MWD are distinguished by this measurement. Also distinguished by this example is the difference in MWD for two samples of similar $\bar{M}_W$ (B, D). The differences at low ω reveals relaxation processes of larger molecules while η' at higher ω is dominated by the relaxation processes of smaller molecules and segments of the larger molecules.

X2.1.3 The degree of entanglement, influenced strongly by the type and amount of chain branching, can be distinguished by a plot of $G'(\omega)$ or by a combination plot of both $G'(\omega)$ and $G''(\omega)$. Fig. X2.2 and Fig. X2.3 show such examples (**14**), (**15**) where Fig. X2.2 displays the effect of increasing entanglement and where Fig. X2.3 displays a contrast in properties for a linear sample and an extensively branched sample.

X2.1.4 Another relationship, G' plotted versus G'' (**16**) or G'' versus G' (**15**), provides corroboration to the assignment of differences due to $\bar{M}_W$ or MWD as well as provides better clarification of long-branching differences. Fig. X2.4 plots G'' vs G' for the two samples of Fig. X2.3. This analysis can also provide insight into the miscibility of blends. The example (**17**) of Fig. X2.5 shows a distinctly inflected region where the maximum at the lower G' value is representative of the lower molecular weight fraction of an immiscible blend and the maximum at the higher G' value is representative of the higher molecular weight fraction.

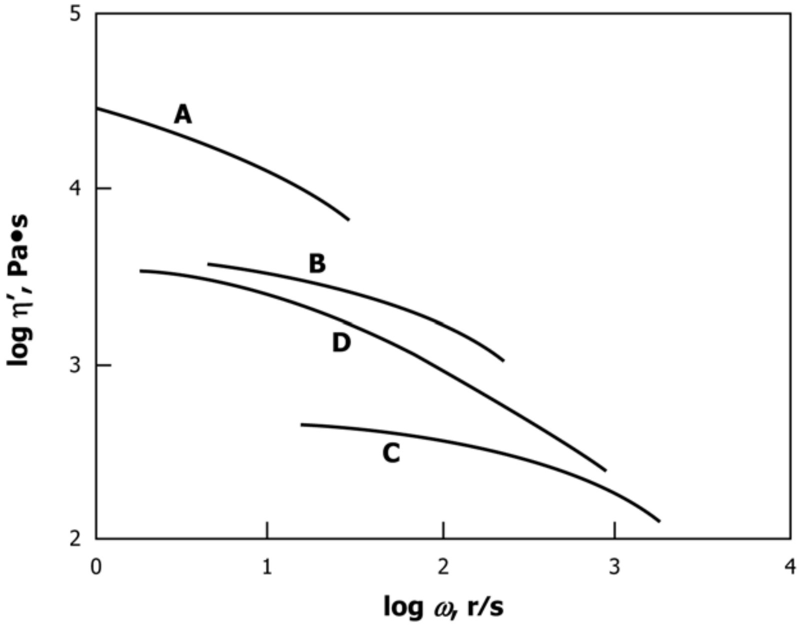

FIG. X2.1 A Log-Log Plot of Dynamic Viscosity Versus Angular Frequency Separates Out Both the Effect of M_W (Samples A, B, C) and MWD (Samples B, D)

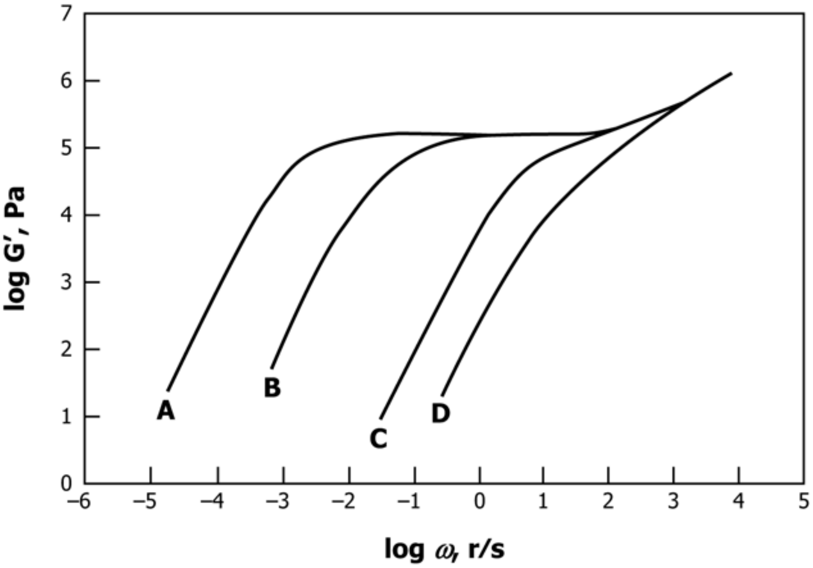

FIG. X2.2 A Log-Log Plot of G' (ω) Identifies the Effect of Entanglement Where Sample A is the Most Highly Entangled Sample and Sample D is the Least Entangled

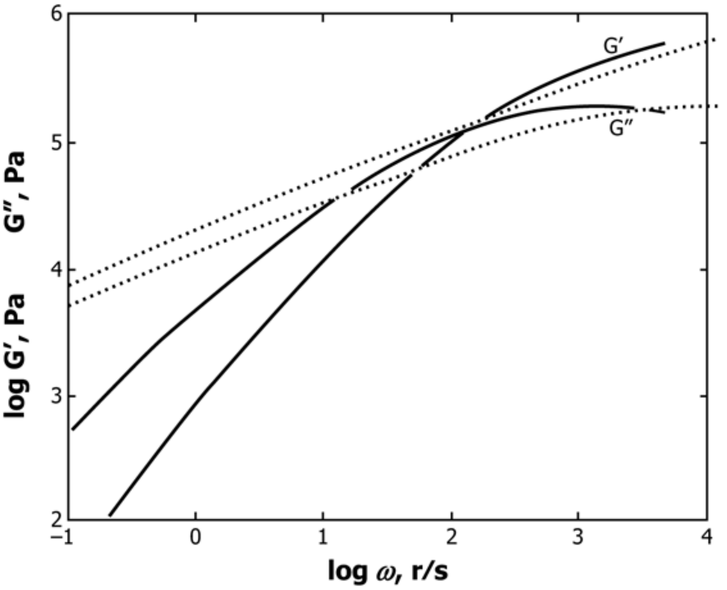

FIG. X2.3 A Log-Log Plot of G' (ω) and G'' (ω) Identifies the Specific Effect of Branching Where the Solid Lines are for a Linear Sample and the Dotted Lines are for a Highly Branched Sample

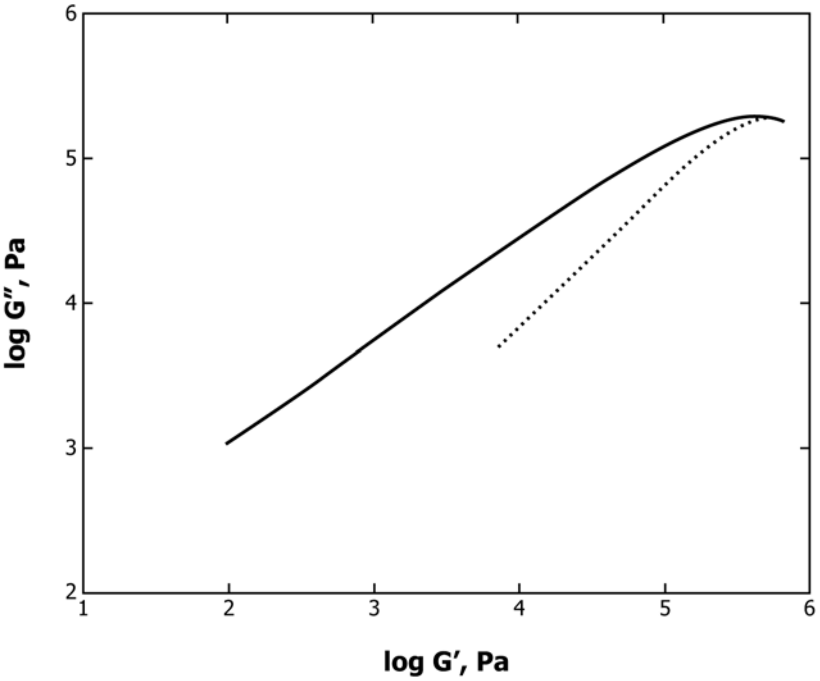

FIG. X2.4 A Log-Log Plot of G'' vs G' Identifies the Specific Effect of Branching Where the Solid Line is for a Linear Sample and the Dotted Line is for a Highly Branched Sample.

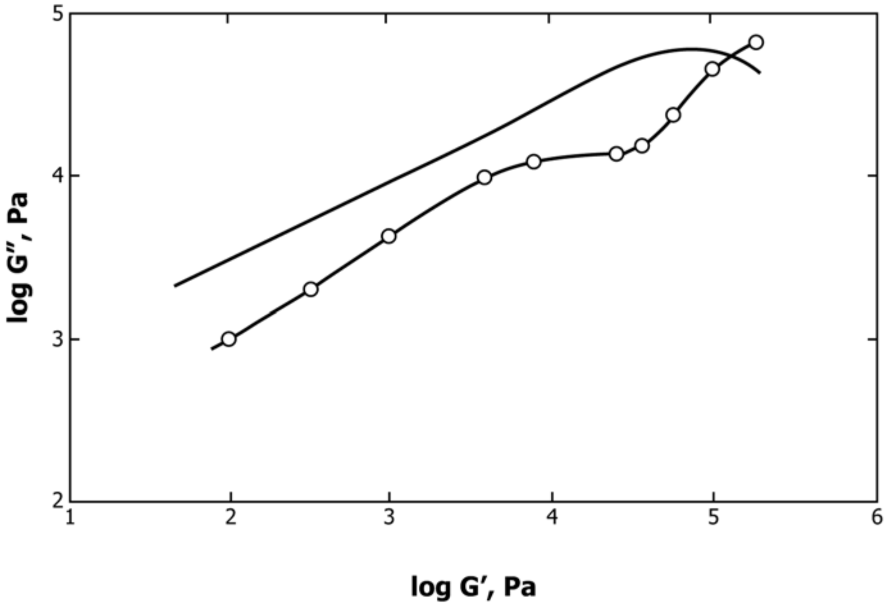

FIG. X2.5 A Log-Log Plot of G'' vs G' Identifies the Ability to Detect Immiscibility of Blends. The Solid Line Represents a Miscible Blend While the Line Containing Open Circles Represents an Immiscible Blend

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