



Standard Practice for Stress Relaxation Testing of Raw Rubber, Unvulcanized Rubber Compounds, and Thermoplastic Elastomers¹

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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 transfor-

mation 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:

D 1566 Terminology Relating to Rubber²

D 1646 Test Methods for Rubber—Viscosity, Stress Relaxation, and Pre-vulcanization Characteristics (Mooney Viscometer)²

D 5992 Guide for Dynamic Testing of Vulcanized Rubber and Rubberlike Materials Using Vibratory Methods²

E 328 Methods for Stress Relaxation Tests for Materials and Structures³

¹ This practice is under the jurisdiction of Committee D-11 on Rubber and is the direct responsibility of Subcommittee D11.12 on Processability Tests.

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² Annual Book of ASTM Standards, Vol 09.01.

³ Annual Book of ASTM Standards, Vol 03.01.

3. Terminology

3.1 *Definitions*—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 D 1566, Guide D 5992, or Methods E 328.

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

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

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

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

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

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

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

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

3.1.9 *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.

3.1.10 *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*).

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

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

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

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

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

3.1.16 *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.

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

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

3.1.19 *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: 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.

$\dot{\gamma}$ —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: 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:

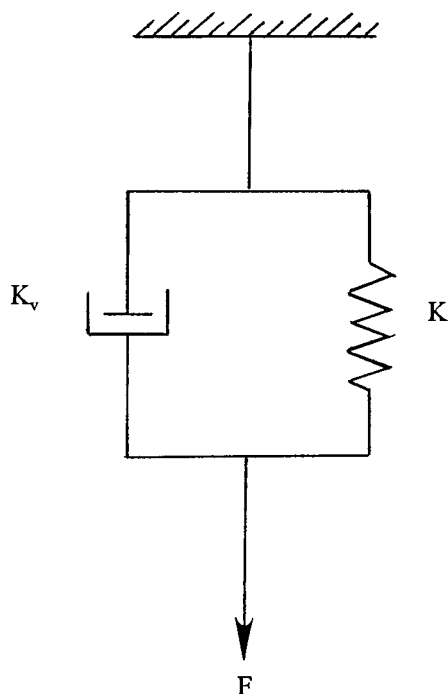
7.1.1 Polymeric materials exhibit both elasticity and viscous resistance to deformation. The materials can retain the recoverable (elastic) strain energy partially, but they also dissipate energy if the deformation is maintained. Mechanical analogues of a viscoelastic solid (Fig. 1) and a viscoelastic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

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



NOTE 1—

F = force,

K_e = spring constant (“e” denotes “elastic”), and

K_v = dashpot constant (“v” denotes “viscous”).

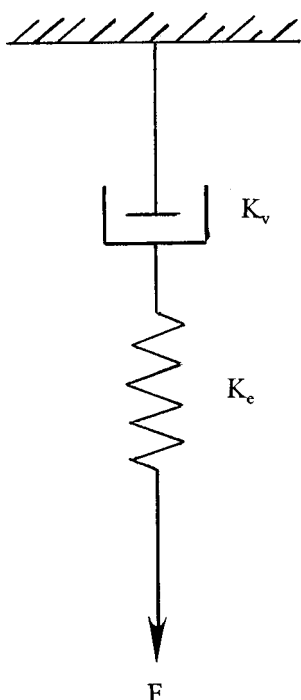
FIG. 1 Voigt Element Representing the Response of a Viscoelastic Solid

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.

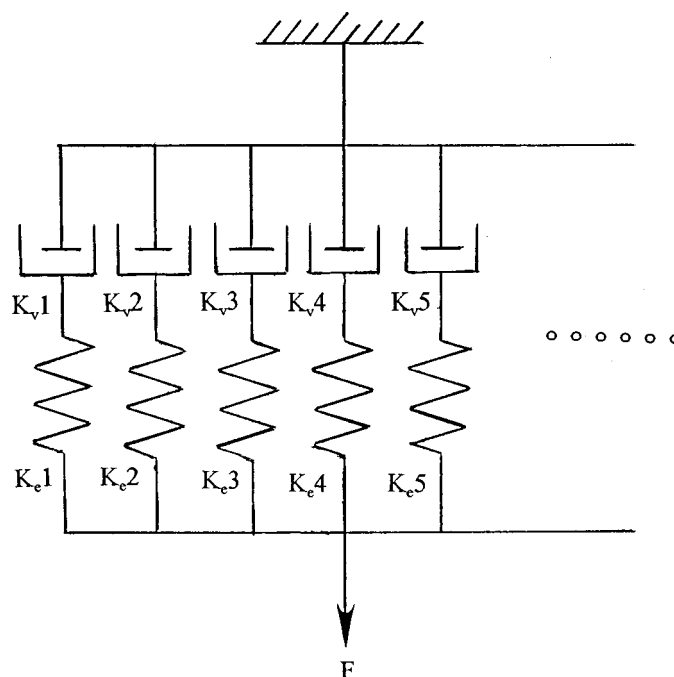
7.2 Molecular Behavior:

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.



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_e = 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

7.2.2 The mechanics of these coil models have been proposed (1)⁴ 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.

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:

$$\frac{F(t)}{\epsilon_0} = \sum_{i=1}^n K_{ei} e^{-t(K_{ei}/K_{vi})} \quad (1)$$

⁴ The boldface numbers in parentheses refer to a list of references at the end of this practice.

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:

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

where:

$G(t)$ = $F(t)/\text{cross-sectional area}/\gamma_0$,

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:

$$G(t) = (\sigma(t)/\gamma) \quad (3)$$

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 of strain ($\dot{\gamma}$), 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:

$$\sigma^{ss}(t) = \gamma \int_{t_0}^{\infty} G(t) dt \quad (4)$$

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

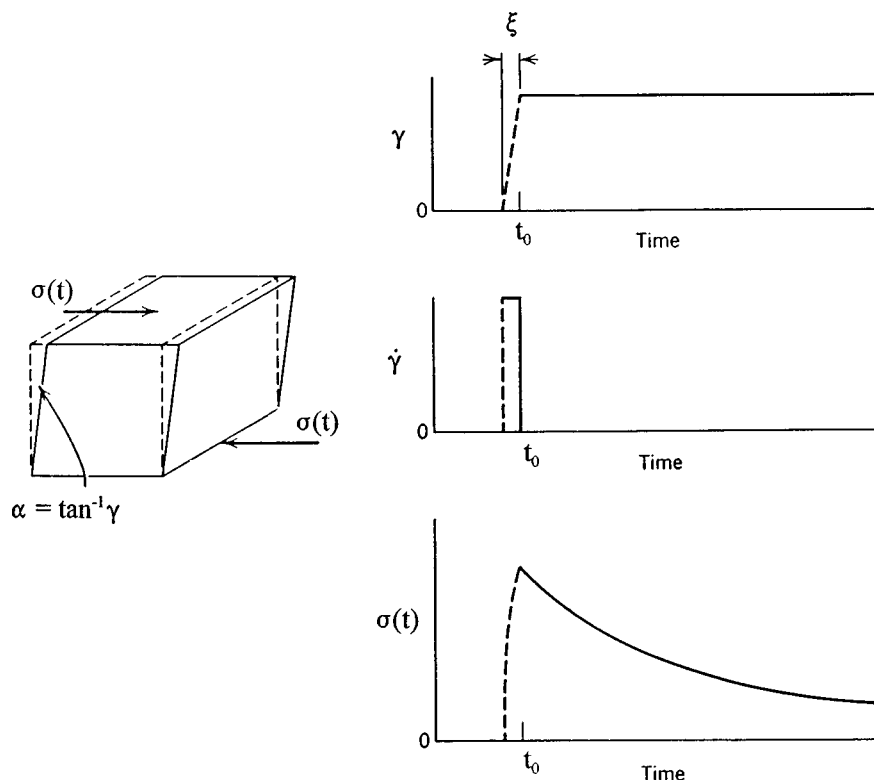


FIG. 4 Geometry and Time Profiles of a Simple Shear Stress Relaxation Experiment Following Sudden Strain