

## Polymer Viscoelasticity

### I. INTRODUCTION

Traditional engineering practice deals with the elastic solid and the viscous liquid as separate classes of materials. Engineers have been largely successful in the use of materials like motor oil, reinforced concrete, or steel in various applications based on design equations arising from this type of material classification. However, it has become increasingly obvious that elastic and viscous material responses to imposed stresses represent the two extremes of a broad spectrum of material behavior. The behavior of polymeric materials falls between these two extremes. As we said in [Chapter 13](#), polymers exhibit viscoelastic behavior. The mechanical properties of solid polymers show marked sensitivity to time compared with traditional materials like metals and ceramics. Several examples illustrate this point. (1) The stress–strain properties of polymers are extremely rate dependent. For traditional materials, the stress–strain behavior is essentially independent of strain rate. (2) Under a constant load, the deformation of polymeric material increases with time (creep). (3) When a polymer is subjected to a constant deformation, the stress required to maintain this deformation decreases with increasing time (stress relaxation). (4) The strain resulting from a polymer subjected to a sinusoidal stress has an in-phase component and an out-of-phase component. The phase lag (angle) between the stress and strain is a measure of the internal friction, which in principle is the mechanical strain energy that is convertible to heat. Traditional materials, for example, metals close to their melting points, exhibit similar behavior. However, at normal temperatures, creep and stress relaxation phenomena in metals are insignificant and are usually neglected in design calculations. In choosing a polymer for a particular end-use situation, particularly structural applications, its time-dependent behavior must be taken into consideration if the polymer is to perform successfully.

Our discussion of the viscoelastic properties of polymers is restricted to the linear viscoelastic behavior of solid polymers. The term *linear* refers to the mechanical response in which the ratio of the overall stress to strain is a function of time only and is independent of the magnitudes of the stress or strain (i.e., independent of stress or strain history). At the onset we concede that linear viscoelastic behavior is observed with polymers only under limited conditions involving homogeneous, isotropic, amorphous samples under small strains and at temperatures close to or above the  $T_g$ . In addition, test conditions must preclude those that can result in specimen rupture. Nevertheless, the theory of linear viscoelasticity, in spite of its limited use in predicting service performance of polymeric articles, provides a useful reference point for many applications.

To aid our visualization of viscoelastic response we introduce models that represent extremes of the material response spectrum. This is followed by the treatment of mechanical models that simulate viscoelastic response. These concepts are developed further by discussion of the superposition principles.

### II. SIMPLE RHEOLOGICAL RESPONSES

#### A. THE IDEAL ELASTIC RESPONSE

The ideally elastic material exhibits no time effects and negligible inertial effects. The material responds instantaneously to applied stress. When this stress is removed, the sample recovers its original dimensions completely and instantaneously. In addition, the induced strain,  $\epsilon$ , is always proportional to the applied stress and is independent of the rate at which the body is deformed (Hookean behavior). [Figure 14.1](#) shows the response of an ideally elastic material.

The ideal elastic response is typified by the stress–strain behavior of a spring. A spring has a constant modulus that is independent of the strain rate or the speed of testing: stress is a function of strain only. For the pure Hookean spring the inertial effects are neglected. For the ideal elastic material, the mechanical response is described by Hooke's law:

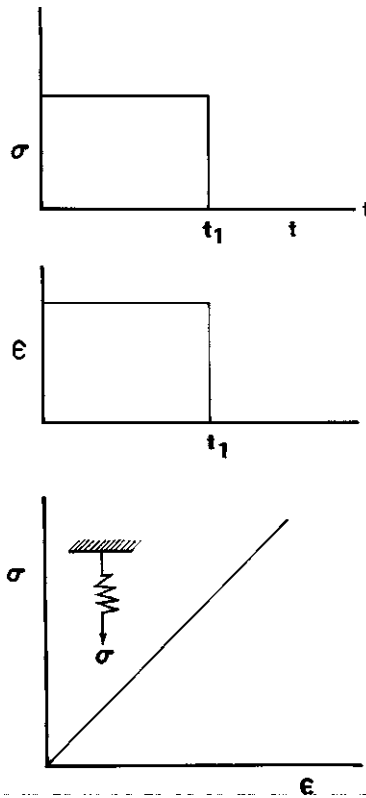


Figure 14.1 *Ideal elastic response.*

$$\sigma = E\epsilon \quad (14.1)$$

where  $\sigma$  is the applied stress,  $\epsilon$  is the strain, and  $E$  is Young's modulus.

## B. PURE VISCOUS FLOW

Fluids have no elastic character; they cannot support a strain. The dominant characteristic of fluids is their viscosity, which is equivalent to elasticity in solids. According to Newton's law, the response of a fluid to a shearing stress  $\tau$  is viscous flow, given by

$$\tau = \eta \frac{d\gamma}{dt} \quad (14.2)$$

where  $\eta$  is viscosity and  $d\gamma/dt$  is strain rate. Thus in contrast to the ideal elastic response, strain is a linear function of time at an applied external stress. On the release of the applied stress, a permanent set results. Pure viscous flow is exemplified by the behavior of a dashpot, which is essentially a piston moving in a cylinder of Newtonian fluid (Figure 14.2). A dashpot has no modulus, but the resistance to motion is proportional to the speed of testing (strain rate).

However, no real material shows either ideal elastic behavior or pure viscous flow. Some materials, for example, steel, obey Hooke's law over a wide range of stress and strain, but no material responds without inertial effects. Similarly, the behavior of some fluids, like water, approximate Newtonian response. Typical deviations from linear elastic response are shown by rubber elasticity and viscoelasticity.

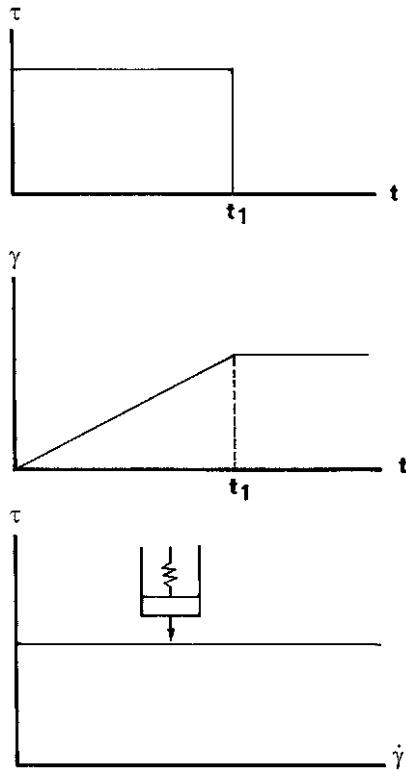


Figure 14.2 *Pure viscous behavior.*

### C. RUBBERLIKE ELASTICITY

The response of rubbery materials to mechanical stress is a slight deviation from ideal elastic behavior. They show non-Hookean elastic behavior. This means that although rubbers are elastic, their elasticity is such that stress and strain are not necessarily proportional (Figure 14.3).

### III. VISCOELASTICITY

Viscoelastic material such as polymers combine the characteristics of both elastic and viscous materials. They often exhibit elements of both Hookean elastic solid and pure viscous flow depending on the experimental time scale. Application of stresses of relatively long duration may cause some flow and irrecoverable (permanent) deformation, while a rapid shearing will induce elastic response in some polymeric fluids. Other examples of viscoelastic response include creep and stress relaxation, as described previously.

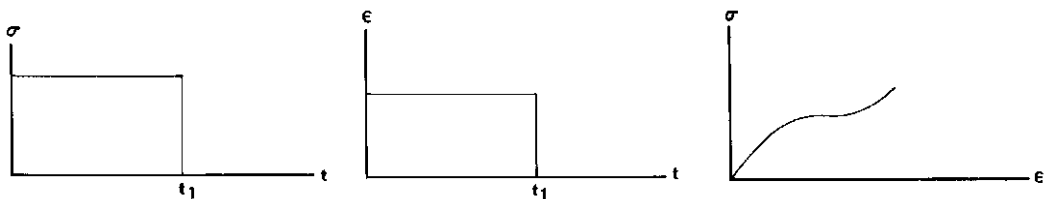


Figure 14.3 *Rubber elasticity.*

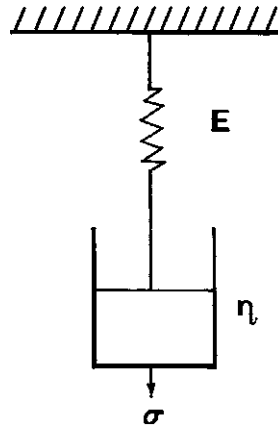


Figure 14.4 The Maxwell element.

It is helpful to introduce mechanical elements as models of viscoelastic response, but neither the spring nor the dashpot alone accurately describes viscoelastic behavior. Some combination of both elements is more appropriate and even then validity is restricted to qualitative descriptions; they provide valuable visual aids. In most polymers, mechanical elements do not provide responses beyond strains greater than about 1% and strain rates greater than  $0.1 \text{ s}^{-1}$ .

#### IV. MECHANICAL MODELS FOR LINEAR VISCOELASTIC RESPONSE

##### A. MAXWELL MODEL

To overcome the poor description of real polymeric materials by either the spring or the dashpot, Maxwell suggested a simple series combination of both elements. This model, referred to as the Maxwell element, is shown in Figure 14.4. In the Maxwell model,  $E$ , the instantaneous tensile modulus, characterizes the response of the spring while the viscosity,  $\eta$ , defines viscous response. In the following description we make no distinction between the types of stress. Thus, we use the symbol  $E$  even in cases where we are actually referring to shearing stress for which we have previously used the symbol  $G$ . This, of course, does not detract from the validity of the arguments.

In the Maxwell element, both the spring and the dashpot support the same stress. Therefore,

$$\sigma = \sigma_a = \sigma_d \quad (14.3)$$

where  $\sigma_s$  and  $\sigma_d$  are stresses on the spring and dashpot, respectively. However, the overall strain and strain rates are the sum of the elemental strain and strain rates, respectively. That is,

$$\epsilon_T = \epsilon_s + \epsilon_d \quad (14.4)$$

or

$$\dot{\epsilon}_T = \dot{\epsilon}_s + \dot{\epsilon}_d \quad (14.5)$$

But

$$\dot{\epsilon}_s = \frac{\dot{\sigma}}{E} \text{ and } \dot{\epsilon}_d = \dot{\sigma}/\eta \quad (14.6)$$

where  $\dot{\epsilon}_T$  is the total strain rate, while  $\dot{\epsilon}_s$  and  $\dot{\epsilon}_d$  are the strain rates of the spring and dashpot, respectively. The rheological equation of the Maxwell element on substitution of Equation 14.6 in 14.5 becomes

$$\dot{\epsilon}_T = \frac{1}{E} \dot{\sigma} + \frac{1}{\eta} \sigma \quad (14.7)$$

As Equation 14.7 shows, the Maxwell element is merely a linear combination of the behavior of an ideally elastic material and pure viscous flow. Now let us examine the response of the Maxwell element to two typical experiments used to monitor the viscoelastic behavior of polymer.

### 1. Creep Experiment

In creep, the sample is subjected to an instantaneous constant stress,  $\sigma_0$ , and the strain is monitored as a function of time. Since the stress is constant,  $d\sigma/dt$  is zero and therefore, Equation 14.7 becomes

$$\dot{\epsilon}_T = \frac{1}{\eta} \sigma_0 \quad (14.8)$$

Solving the equation and noting that the initial strain is  $\sigma_0/E$ , the equation for the Maxwell element for creep can be written as

$$\epsilon(t) = \frac{\sigma_0}{E} + \frac{\sigma_0}{\eta} t \quad (14.9)$$

$$\epsilon(t) = \sigma_0 \left[ \frac{1}{E} + \frac{t}{\eta} \right] \quad (14.10)$$

On removal of the applied stress, the material experiences creep recovery. Figure 14.5 shows the creep and the creep recovery curves of the Maxwell element. It shows that the instantaneous application of a constant stress,  $\sigma_0$ , is initially followed by an instantaneous deformation due to the response of the spring by an amount  $\sigma_0/E$ . With the sustained application of this stress, the dashpot flows to relieve the stress. The dashpot deforms linearly with time as long as the stress is maintained. On the removal of the applied stress, the spring contracts instantaneously by an amount equal to its extension. However, the deformation due to the viscous flow of the dashpot is retained as permanent set. Thus the Maxwell element predicts that in a creep/creep recovery experiment, the response includes elastic strain and strain recovery, creep and permanent set. While the predicted response is indeed observed in real materials, the demarcations are nevertheless not as sharp.

### 2. Stress Relaxation Experiment

In a stress relaxation experiment, an instantaneous strain is applied to the sample. The stress required to maintain this strain is measured as a function of time. When the Maxwell element is subjected to an

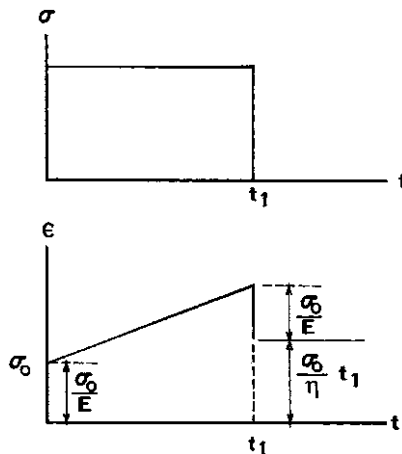


Figure 14.5 Creep and creep recovery behavior of the Maxwell element.

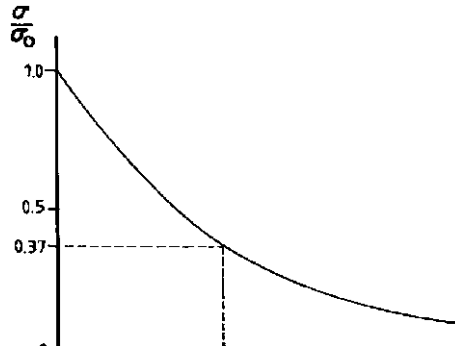


Figure 14.6 Relaxation time for the Maxwell element.

instantaneous strain, only the spring can respond initially. The dashpot will relax gradually, and consequently, the stress decreases with increasing time.

The rheological equation for the Maxwell element from Equation 14.7 is

$$\dot{\epsilon}_r = \frac{1}{E} \dot{\sigma} + \frac{1}{\eta} \sigma \quad (14.7)$$

Since the strain is constant,  $\dot{\epsilon}_r$  is zero, thus Equation 14.7 is reduced to

$$\frac{1}{E} \dot{\sigma} + \frac{1}{\eta} \sigma = 0 \quad (14.11)$$

The solution to this first-order differential equation with the boundary condition that  $\sigma = E\epsilon_0$  at  $t = 0$  is

$$\sigma = \sigma_0 \exp\left(-\frac{E}{\eta} t\right) \quad (14.12)$$

We define the quantity  $\tau$  as the relaxation or response time and it is given as the ratio  $\eta/E$ . Equation 14.12 thus becomes

$$\sigma = \sigma_0 \exp(-t/\tau) \quad (14.13)$$

The relaxation time from Equation 14.13 is the time required for the stress to decay to  $1/e$  or 37% of its initial value (Figure 14.6). If we divide the stress by the constant strain,  $\epsilon_0$ , Equation 14.13 becomes

$$\frac{\sigma(t)}{\epsilon_0} = \frac{\sigma_0}{\epsilon_0} e^{-t/\tau}$$

or

$$E_r(t) = E e^{-t/\tau} \quad (14.14)$$

$E_r$  is the relaxation modulus. For the Maxwell element in a stress relaxation experiment, all the initial deformation takes place in the spring. The dashpot subsequently starts to relax and allows the spring to contract. For times considerably shorter than the relaxation time, the Maxwell element behaves essentially like a spring; while for times much longer than the relaxation time, the element behaves like a dashpot. For times comparable to the relaxation time, the response involves the combined effect of the spring and the dashpot.

**Example 14.1:** A polystyrene sample of  $0.02/\text{m}^2$  cross-sectional area is subjected to a creep load of  $10^5 \text{ N}$ . The load is removed after 30 s. Assuming that the Maxwell element accurately describes the behavior of polystyrene and that viscosity is  $5 \times 10^{10} \text{ P}$ , while Young's modulus is  $5 \times 10^5 \text{ psi}$ , calculate:

- The compliance
- The deformation recovered on the removal of the dead load
- The permanent

**Solution:** a. The creep equation for the Maxwell element is

$$\epsilon(t) = \sigma_0 \left[ \frac{1}{E} + \frac{t}{\eta} \right] \quad \text{or}$$

$$\frac{\epsilon(t)}{\sigma_0} = \left[ \frac{1}{E} + \frac{t}{\eta} \right] \text{ or compliance.}$$

$$\begin{aligned} E &= 5 \times 10^5 \text{ psi} = 5 \times 10^5 \text{ psi} \times 6.894 \times 10^3 (\text{N}/\text{m}^2/\text{psi}) \\ &= 3.45 \times 10^9 \text{ N}/\text{m}^2 \end{aligned}$$

$$\eta = 5 \times 10^{10} \text{ P} = 5 \times 10^9 \frac{\text{N} \cdot \text{s}}{\text{m}^2}$$

$$J = \frac{1}{3.45 \times 10^9} + \frac{30}{5 \times 10^9} \text{ m}^2/\text{N} = 6.29 \times 10^{-9} \text{ m}^2/\text{N}.$$

- b. The deformation recovered on the removal of load is due to the spring  $\epsilon_s$ ,

$$\epsilon_s = \frac{\sigma_0}{E}$$

$$\sigma_0 = \frac{P_0}{A} = \frac{10^5}{0.02} \text{ N}/\text{m}^2 = 5 \times 10^6 \text{ N}/\text{m}^2$$

$$\epsilon_s = \frac{5 \times 10^6}{3.45 \times 10^9} = 1.45 \times 10^{-3}$$

- c. The permanent set is due to the viscous flow  $\epsilon_d$ .

$$\epsilon_d = \frac{\sigma_0}{\eta} t$$

$$= \frac{5 \times 10^6 (\text{N}/\text{m}^2)}{5 \times 10^9 (\text{Ns}/\text{m}^2)} \times 30 (\text{s})$$

$$= 0.03$$

### 3. Dynamic Experiment

Let us consider the response of a Maxwell element subjected to a sinusoidal stress. The corresponding strain will be sinusoidal but out of phase with the stress by an angle  $\delta$ , as discussed in [Chapter 13](#). Thus,

$$\sigma = \sigma_0 \sin \cdot \omega t \tag{14.15}$$

Now the rheological equation for the Maxwell element is

$$\begin{aligned}\epsilon(t) &= \frac{1}{E} \sigma + \frac{1}{\eta} \int \sigma dt \\ \frac{d\epsilon}{dt} &= \frac{\sigma_0 \omega}{E} \cos \omega t + \frac{\sigma_0}{\eta} \sin \omega t\end{aligned}\tag{14.16}$$

Integration of Equation 14.16 between two time limits and noting that  $\epsilon(0)$  is not necessarily zero yields

$$\begin{aligned}\tan \delta &= \frac{1}{\tau \omega} \\ E' &= \frac{E \tau^2 \omega^2}{1 + \omega^2 \tau^2}\end{aligned}\tag{14.17}$$

$$E'' = \frac{E \tau \omega}{1 + \omega^2 \tau^2}\tag{14.18}$$

where  $\tau = \eta/E$ .

## B. THE VOIGT ELEMENT

Since, as we saw above, the Maxwell element is not perfect, it seems logical to consider a parallel arrangement of the spring and the dashpot. This is the so-called Voigt or Voigt–Kelvin element (Figure 14.7).

The Voigt element has the following characteristics:

- The spring and the dashpot always remain parallel. This means that the strain in each element is the same.
- The total stress supported by the Voigt element is the sum of the stresses in the spring and the dashpot.

$$\sigma_T = \sigma_s + \sigma_d\tag{14.19}$$

Thus, the rheological equation for the Voigt element is given by

$$\sigma_T = E\epsilon + \eta \frac{d\epsilon}{dt}\tag{14.20}$$

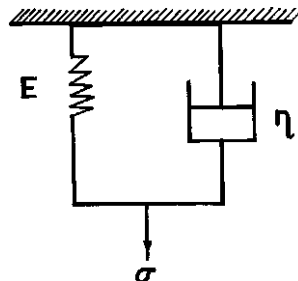


Figure 14.7 The Voigt element.



## 1. Creep Experiment

In a creep experiment, the applied stress is constant; consequently, Equation 14.20 becomes

$$\sigma_0 = E\varepsilon + \eta \frac{d\varepsilon}{dt} \quad (14.21)$$

This is a linear differential equation with solution [integrate between the limits  $\varepsilon(0) = 0$  and  $\varepsilon(\tau) = \varepsilon(t)$ ]:

$$\begin{aligned} \varepsilon(t) &= \frac{\sigma_0}{E} [1 - e^{-Et/\eta}] \\ \varepsilon(t) &= \frac{\sigma_0}{E} [1 - e^{-t/\tau}] \end{aligned} \quad (14.22)$$

or

$$J(t) = \frac{\varepsilon(t)}{\sigma_0} = J [1 - e^{-t/\tau}]$$

where

$$J = \frac{1}{E} = \text{reciprocal of modulus}$$

The creep and creep recovery curves for the Voigt elements are shown in Figure 14.8.

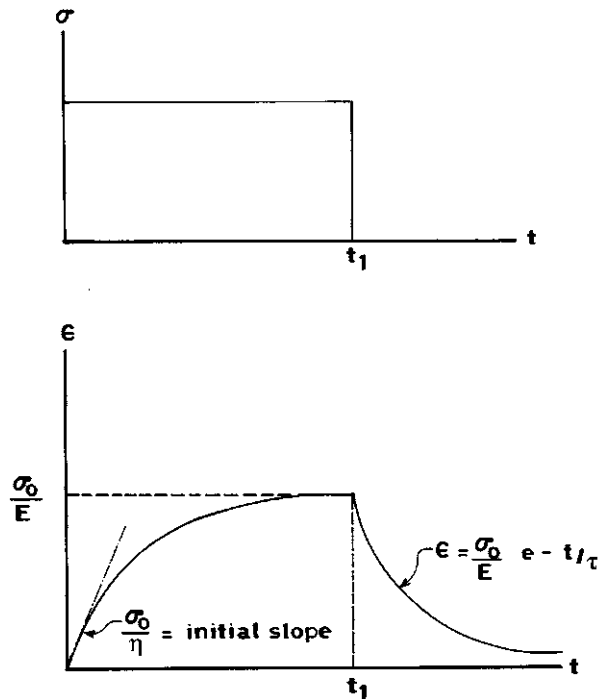


Figure 14.8 Creep and creep recovery curves for the Voigt element.

On the application of a sudden constant stress in a creep experiment, only the spring offers the initial resistance to deformation; the spring would elongate instantaneously if possible, but its deformation is constrained by that of the dashpot. Recall that for the Voigt element both the spring and the dashpot have equal strains. Therefore, the initial total stress is borne by the dashpot. Under the influence of the constant force, the dashpot begins to flow thus transferring part of the load to the spring. The transfer of load to the spring results in a concomitant decrease in the stress on the dashpot and hence a decrease in the strain rate, which is proportional to the magnitude of the stress experienced by the dashpot. Eventually, the element comes to its equilibrium strain. At this point the strain rate is zero; the resistance of the dashpot is therefore also zero which means that the entire stress is now supported by the spring. The equilibrium strain is simply the strain due to the spring ( $\sigma_0/E$ ). If the load is removed after equilibrium, the strain decays exponentially.

We note that the Voigt model predicts that strain is not a continuous function of stress; that is, the element does not deform continuously with the sustained application of a constant stress. The strain approaches an asymptomatic value given by ( $\sigma_0/E$ ). The strain of the element at equilibrium is simply that of an ideal elastic solid. The only difference is that the element does not assume this strain instantaneously, but approaches it gradually. The element is shown to exhibit retarded elasticity. In creep recovery, the Maxwell element retracts instantaneously but not completely, whereas the Voigt element exhibits retarded elastic recovery, but there is no permanent set.

## 2. Stress Relaxation Experiment

In a stress relaxation experiment ( $\epsilon = \text{constant}$ ), the rheological equation for the Voigt element reduces to

$$\sigma(t) = E\epsilon \quad (14.23)$$

This is essentially Hooke's law. The Voigt model is not suited for simulating a stress relaxation experiment. The application of an instantaneous strain induces an infinite resistance in the dashpot. It would require an infinite stress to overcome the resistance and get the dashpot to strain instantaneously. This is obviously unrealistic.

## 3. Dynamic Experiment

Now consider the response of a Voigt element subjected to a sinusoidal strain:

$$\epsilon = \epsilon_0 \sin \omega t$$

The stress response of the Voigt element is

$$\sigma = \sigma_s + \sigma_d$$

$$\sigma_s = E\epsilon_0 = E\epsilon_0 \sin \omega t, \text{ and } \sigma_d = \eta \dot{\epsilon} = \eta \omega \epsilon_0 \cos \omega t \quad (14.24)$$

$$\sigma = E\epsilon_0 \sin \omega t + \eta \omega \epsilon_0 \cos \omega t$$

Since the sine term is the component in phase with the strain and the cosine term denotes the 90° out-of-phase term, then

$$\sigma' = E\epsilon' \text{ and } \sigma'' = \eta \omega \epsilon'' \quad (14.25)$$

Consequently,

$$E' = \frac{\sigma'}{\epsilon'} = E'' = \frac{\sigma''}{\epsilon''} = \eta \omega$$

$$\tan \delta = \frac{E''}{E'} \quad (14.26)$$

$$\tan \delta = \frac{\eta \omega}{E} = \tau \omega$$

**Example 14.2:** Comment on the physical significance of the quantities measured in dynamic mechanical (oscillating) experiments.

**Solution:** To appreciate the physical significance of the quantities measured in oscillatory experiments, we consider the energy changes in a sample undergoing cyclic deformation. We start by noting that in viscoelastic and purely viscous materials, the stress and strain are out of phase. Figure E.14.2 shows stress–strain representation of a viscoelastic material. The oscillatory strain is  $\epsilon = \epsilon_0 \sin \omega t$ .

a. *Purely elastic body:* the work per unit volume is

$$W = \sigma d\epsilon$$

$$d\epsilon = \epsilon_0 \cos \omega t d(\omega t)$$

For purely elastic body,

$$\sigma = E\epsilon = E\epsilon_0 \sin \omega t$$

Therefore, the work done over the first quarter cycle of applied strain is given by

$$\begin{aligned} W &= \int_0^{\pi/2} E\epsilon_0 \sin \omega t \epsilon_0 \cos \omega t d(\omega t) \\ &= E\epsilon_0^2 \int_0^{\pi/2} \sin \omega t \cos \omega t d(\omega t) \\ W &= \frac{E\epsilon_0^2}{2} \end{aligned}$$

For the second quarter (i.e., integrating from  $\pi/2$  to  $\pi$ , the result is exactly the same except that the sign is negative. Thus for a full cycle, in the case of an elastic body, the energy stored in the first and third quarter cycles is recovered completely in the second and fourth cycles.

b. *Completely viscous flow:* in this case,

$$\sigma = \eta \dot{\epsilon}$$

$$\begin{aligned} W &= \int_0^{2\pi} \eta \epsilon_0 \omega \cos \omega t \epsilon_0 \cos \omega t d(\omega t) \\ &= \pi \eta \omega \epsilon_0^2 \end{aligned}$$

For a viscous body, the energy imparted is completely dissipated over the full cycle.

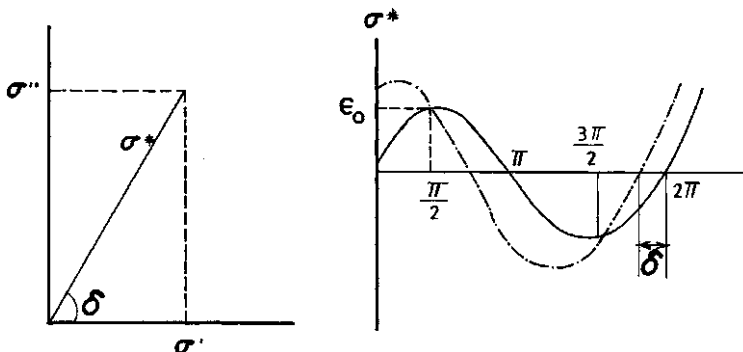


Figure E.14.2 Quantities in oscillatory experiments.

c. *Viscoelastic material:* here there is a phase angle  $\delta$  between the stress and strain. Thus,

$$\sigma = \sigma^* \sin(\omega t + \delta)$$

Therefore,

$$W = \int_0^{2\pi} \sigma d\varepsilon = \sigma^* \varepsilon_0 \int_0^{2\pi} \sin(\omega t + \delta) \cos \omega t d(\omega t)$$

Integration of this equation shows that for the elastic component of the work per unit volume, there is no net energy lost or gained. The viscous component becomes

$$W = \pi \varepsilon_0^2 E'' = \pi \varepsilon_0^2 E' \tan \delta$$

This is the net energy loss through viscous heat generation in material.

**Example 14.3:** A Voigt element has parameters  $E = 10^8 \text{ N/m}^2$  and  $\eta = 5 \times 10^{10} \text{ N} \cdot \text{s/m}^2$ . Sketch the creep curve for this element if the imposed constant stress is  $10^8 \text{ N/m}^2$ .

**Solution:**

$$J(t) = \frac{\varepsilon(t)}{\sigma_0} = J(1 - e^{-t/\tau})$$

$$J = \frac{1}{E} = \text{compliance} = 10^{-8} \text{ m}^2/\text{N}$$

$$\tau = \eta/E = \text{retardation time} = \frac{5 \times 10^{10} \text{ Ns/m}^2}{10^8 \text{ N/m}^2}$$

$$= 500 \text{ s}$$

$$J(t) = \frac{\varepsilon(t)}{\sigma_0} = 10^{-8} (1 - e^{-t/500})$$

$$E(t) = \sigma_0 10^{-8} (1 - e^{-t/500})$$

$$= 1 - e^{-t/500} \text{ since } \sigma_0 = 10^8$$

Using this equation a creep curve for several decades of time is shown in Figure E14.3.

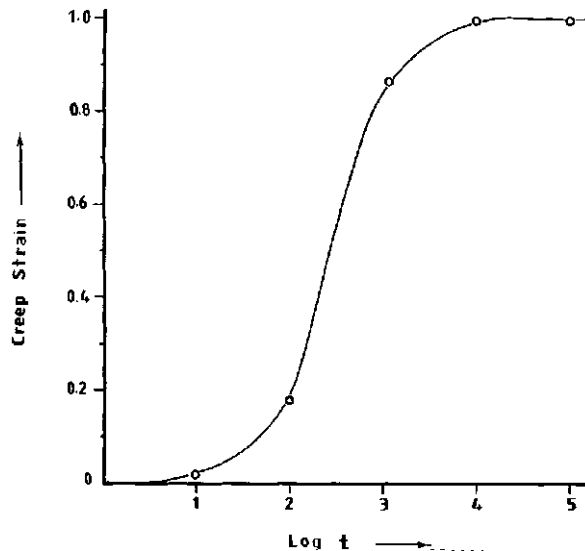
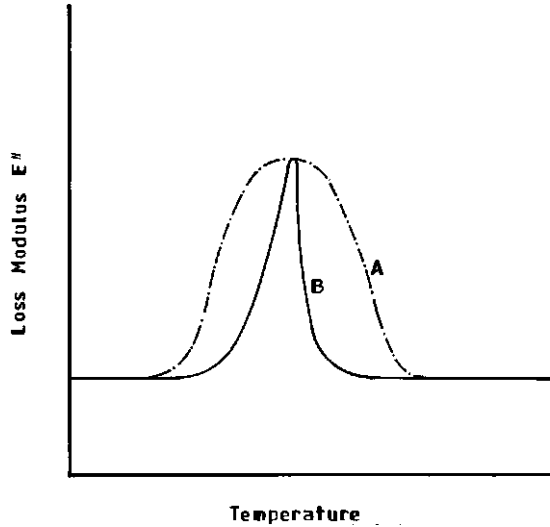


Figure E.14.3 Creep curve for Voigt element.

**Example 14.4:** Figure E.14.4 shows the loss modulus–temperature curves for the two materials A and B. Select either A or B for use as

- a. Car tire
- b. Engine mount

Explain the basis of your selection.



**Figure E.14.4** Energy absorption profiles for two materials.

**Solution:** The area under the loss modulus–temperature curve is a measure of the damping capacity or ability to absorb energy of the material. Obviously, A has a higher damping capacity than B.

- a. In car tires, temperature buildup contributes to rapid deterioration and wear of tire and loss of traction. Consequently, material B will be more suitable for use as a car tire since it will absorb less energy and hence result in less temperature buildup.
- b. A critical requirement for an engine mount is the ability to absorb the vibrational loads from the engine. In this case, a material with the ability to dissipate the vibrational energy as heat would be preferable; that is, material A.

### C. THE FOUR-PARAMETER MODEL

Neither the simple Maxwell nor Voigt model accurately predicts the behavior of real polymeric materials. Various combinations of these two models may more appropriately simulate real material behavior. We start with a discussion of the four-parameter model, which is a series combination of the Maxwell and Voigt models (Figure 14.9). We consider the creep response of this model.

Under creep, the total strain will be due to the instantaneous elastic deformation of the spring of modulus  $E$ , and irrecoverable viscous flow due to the dashpot of viscosity  $\eta_2$ , and the recoverable retarded elastic deformation due to the Voigt element with a spring of modulus  $E_3$  and dashpot of viscosity  $\eta_3$ . Thus, the total strain is the sum of these three elements. That is,

$$\epsilon(t) = \epsilon_1 + \epsilon_2 + \epsilon_3 \quad (14.27)$$

$$\epsilon(t) = \frac{\sigma_0}{E_1} + \frac{\sigma_0 t}{\eta_2} + \frac{\sigma_0}{E_3} \left[ 1 - \exp^{-t/\tau_3} \right] \quad (14.28)$$

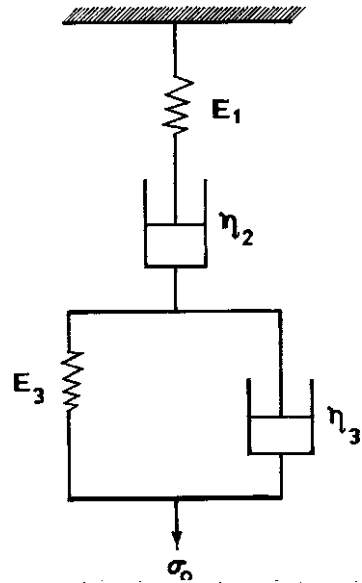


Figure 14.9 Schematic of the four-parameter model.

where  $\sigma_0$  is the imposed constant stress and  $\tau_3$  equals  $\eta_3/E_3$  and is referred to as the retardation time.

In creep recovery, say, the load is removed at time  $t_1$ ; the deformation,  $\sigma_0/E_1$ , due to the spring of modulus  $E_1$  is recovered instantaneously. This will be followed by the retarded elastic creep recovery due to the Voigt element given by  $\epsilon_3$  or

$$\epsilon_3 = \frac{\sigma_0}{E_3} [1 - \exp(-t_1/\tau_3)] \quad (14.29)$$

Only the deformation due to the dashpot of viscosity  $\eta_2$  is retained as a permanent set. The creep and creep recovery curve of this model is shown in Figure 14.10.

The four-parameter model provides a crude qualitative representation of the phenomena generally observed with viscoelastic materials: instantaneous elastic strain, retarded elastic strain, viscous flow, instantaneous elastic recovery, retarded elastic recovery, and plastic deformation (permanent set). Also, the model parameters can be associated with various molecular mechanisms responsible for the viscoelastic behavior of linear amorphous polymers under creep conditions. The analogies to the molecular mechanism can be made as follows.

1. The instantaneous elastic deformation is due to the Maxwell element spring,  $E_1$ . The primary valence bonds in polymer chains have equilibrium bond angles and lengths. Deformation from these equilibrium values is resisted, and this resistance is accompanied by an instantaneous elastic deformation.
2. Recoverable retarded elastic deformation is associated with the Voigt element. This arises from the resistance of polymer chains to coiling and uncoiling caused by the transformation of a given equilibrium conformation into a biased conformation with elongated and oriented structures. The process of coiling and uncoiling requires the cooperative motion of many chain segments, and this can only occur in a retarded manner.
3. Irrecoverable viscous flow is due to the Maxwell element dashpot  $\eta_3$ . This is associated with slippage of polymer chains or chain segments past one another.

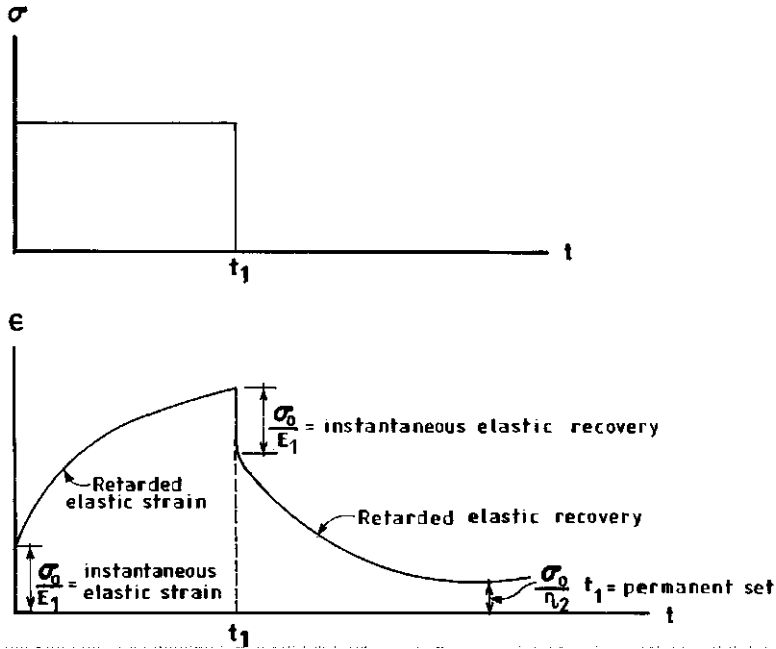


Figure 14.10 Creep response of the four-parameter model.

**Example 14.5:** The constants for a four-parameter model are

$$E_1 = 5 \times 10^8 \text{ N/m}^2, \eta_2 = 5 \times 10^{10} \text{ N} \cdot \text{s/m}^2, E_3 = 10^8 \text{ N/m}^2, \text{ and } \eta_3 = 5 \times 10^8 \text{ N} \cdot \text{s/m}^2$$

For creep and creep recovery experiments calculate:

- The instantaneous elastic strain
- The recoverable retarded elastic strain
- The permanent set

Assume that the creep experiment lasted for 200 s and that the imposed stress is  $10^8 \text{ N/m}^2$ .

**Solution:**

- Instantaneous elastic strain

$$\begin{aligned} \epsilon_1 &= \frac{\sigma_0}{E_1} \\ &= \frac{10^8 \text{ N/m}^2}{5 \times 10^8 \text{ N/m}^2} = 0.2 \end{aligned}$$

- Recoverable retarded elastic strain given by

$$\epsilon_3 = \frac{\sigma_0}{E_3} [1 - e^{-t/\tau_3}]; \quad \tau_3 = \frac{\eta_3}{E_3} = \frac{5 \times 10^8 \text{ N} \cdot \text{s/m}^2}{10^8 \text{ N/m}^2} = 5 \text{ s}$$

$$\begin{aligned} \epsilon_3 &= \frac{10^8}{10^8} [1 - e^{-200/5}] \\ &= 1.0 - 4.25 \times 10^{-18} = 1.0 \end{aligned}$$

c. Permanent set

$$\begin{aligned}\epsilon_2 &= \frac{\sigma_0 t}{\eta_2} \\ &= \frac{(10^8 \text{ N/m}^2)(200 \text{ s})}{5 \times 10^{10} \text{ N}\cdot\text{s/m}^2} = 0.4\end{aligned}$$


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## V. MATERIAL RESPONSE TIME — THE DEBORAH NUMBER

A physical insight into the viscoelastic character of a material can be obtained by examining the material response time. This can be illustrated by defining a characteristic time for the material — for example, the relaxation time for a Maxwell element, which is the time required for the stress in a stress relaxation experiment to decay to  $e^{-1}$  (0.368) of its initial value. Materials that have low relaxation times flow easily and as such show relatively rapid stress decay. This, of course, is indicative of liquidlike behavior. On the other hand, those materials with long relaxation times can sustain relatively higher stress values. This indicates solidlike behavior. Thus, whether a viscoelastic material behaves as an elastic solid or a viscous liquid depends on the material response time and its relation to the time scale of the experiment or observation. This was first proposed by Marcus Reiner, who defined the ratio of the material response time to the experimental time scale as the Deborah number,  $D_n$ . That is,

$$D_n = \frac{\text{material response time}}{\text{experimental time scale (observation time)}} \quad (14.30)$$

A high Deborah number that is a long response time relative to the observation time implies viscoelastic solid behavior, whereas a low value of Deborah number (short response time relative to the time scale of experiment) is indicative of viscoelastic fluid behavior. From a conceptual standpoint, the Deborah number is related to the time one must wait to observe the onset of flow or creep. For example, the Deborah number of a wooden beam at 30% moisture is much smaller than that at 10% moisture content. For these materials the onset of creep occurs within a reasonably finite time. At the other extreme, the Deborah number of a mountain is unimaginably high. Millions of years must elapse before geologists find evidence of flow. This apparently is the genesis of Marcus Reiner’s analogy (“The mountains flowed before the Lord” from the Song of Deborah, Book of Judges V).

It must be emphasized, however, that while the concept of the Deborah number provides a reasonable qualitative description of material behavior consistent with observation, no real material is characterized by a simple response time. Therefore, a more realistic description of materials involves the use of a distribution or continuous spectrum of relaxation or retardation times. We address this point in the following section.

## VI. RELAXATION AND RETARDATION SPECTRA

Real polymers are not characterized by a simple response time. Instead, a distribution or continuous spectrum of relaxation or retardation times is required for a more accurate description of real polymers. Many complex models have been proposed to simulate the viscoelastic behavior of polymeric materials. We discuss two of these models.

### A. MAXWELL–WEICHERT MODEL (RELAXATION)

The generalized model consists of an arbitrary number of Maxwell elements in a parallel arrangement (Figure 14.11).

Consider the generalized Maxwell model in a stress relaxation experiment. The strain in all the individual elements is the same, and the total stress is the sum of the stress experienced by each element. Thus,

$$\sigma = \sigma_1 + \sigma_2 + \sigma_3 + \dots + \sigma_{n-1} + \sigma_n \quad (14.31)$$



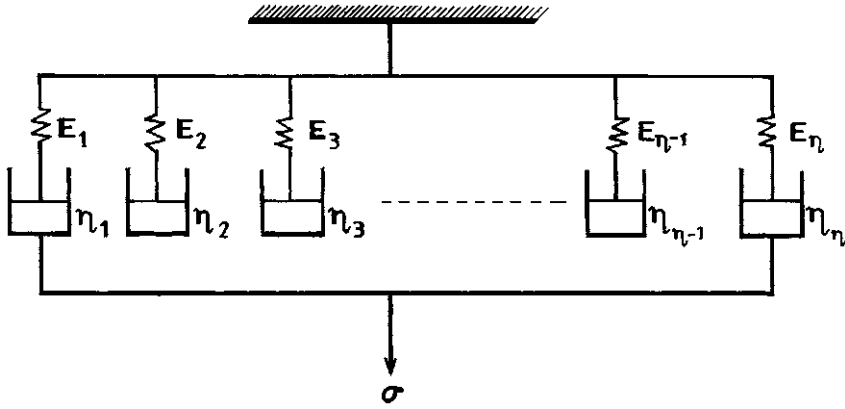


Figure 14.11 The Maxwell–Weichert model.

The individual stress in each element is given by

$$\sigma_i = \sigma_0 e^{-t/\tau_i} \quad (14.32)$$

This gives the stress relaxation of an individual element under a constant strain  $\epsilon_0$  as

$$\sigma_i(t) = \epsilon_0 E_i e^{-t/\tau_i} \quad (14.33)$$

where  $\tau_i = \eta_i/E_i$ . For the Maxwell-Reichert model under a constant strain,  $\epsilon_0$ ,

$$\sigma(t) = \epsilon_0 \sum_{i=1}^n E_i e^{-t/\tau_i} \quad (14.34)$$

or

$$E(t) = \sum_{i=1}^n E_i e^{-t/\tau_i} \quad (14.35)$$

If  $n$  is large, the summation in the equation may be approximated by the integral of a continuous distribution of relaxation times  $E(\tau)$ .

$$E(t) = \int_0^{\infty} E(\tau) e^{-t/\tau} d\tau \quad (14.36)$$

If one of the Maxwell elements in the Maxwell–Weichert model is replaced with a spring or a dashpot of infinite viscosity, then the stress in such a model would decay to a finite value rather than zero. This would approximate the behavior of a cross-linked polymer.

## B. VOIGT–KELVIN (CREEP) MODEL

The generalized Voigt element or the Voigt–Kelvin model is a series arrangement of an arbitrary number of Voigt elements (Figure 14.12). Under creep, the creep response of each individual element is given by

$$\epsilon_i(t) = \sigma_0 J_i (1 - e^{-t/\tau_i}) \quad (14.37)$$

or

$$J_i(t) = \frac{\epsilon_i(t)}{\sigma_0} = J_i (1 - e^{-t/\tau_i}) \quad (14.38)$$

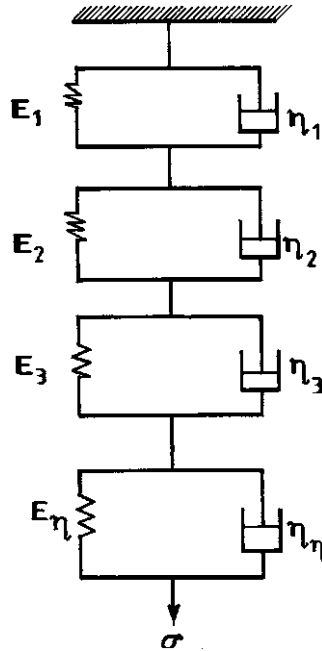


Figure 14.12 Voigt-Kelvin model.

where  $J_i = \frac{1}{E_i}$  and is creep compliance. The response of a series of elements subjected to the same constant stress  $\sigma_0$  becomes

$$J(t) = \frac{\epsilon(t)}{\sigma_0} = \sum_{i=1}^n J_i (1 - e^{-t/\tau_i}) \quad (14.39)$$

For a large value of  $n$  (i.e.,  $n \rightarrow \infty$ ), the discrete summation in Equation 14.39 may be replaced by an integration over all the retardation times:

$$J(t) = \int_0^\infty J(\tau) (1 - e^{-t/\tau}) d\tau \quad (14.40)$$

where  $J(t)$  is the continuous distribution of retardation times. If the generalized Voigt model is to represent a linear polymer (viscoelastic liquid), then the modulus of one of the springs must be zero. This element has infinite compliance and represents a simple dashpot in series with all the other Voigt elements.

**Example 14.6:** A polymer is represented by a series arrangement of two Maxwell elements with parameters  $E_1 = 3 \times 10^9 \text{ N/m}^2$ ,  $t_1 = 1 \text{ s}$ ,  $E_2 = 5 \times 10^5 \text{ N/m}^2$ , and  $t_2 = 10^3 \text{ s}$ . Sketch the stress relaxation behavior of this polymer over several decades (at least seven) of time.

**Solution:**

$$E_r(t) = \sum_{i=1}^2 E_i e^{-t/\tau_i}$$

Determining  $\log E_r(t)$  when  $t$  varies from 0.01 to  $10^4$ , a plot of  $\log E_r(t)$  vs.  $\log t$  is shown in [Figure E14.6](#).

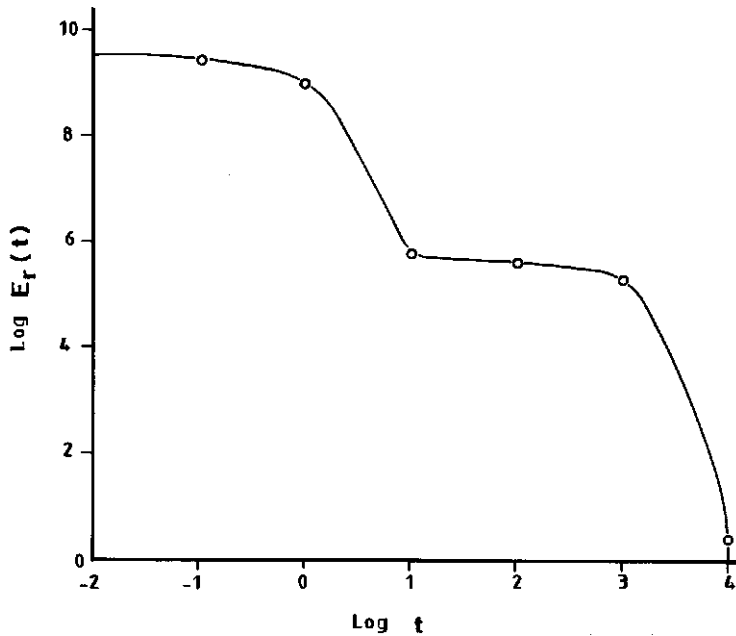


Figure E.14.6 Behavior of a 2-component Maxwell-Reichert model.

## VII. SUPERPOSITION PRINCIPLES

In the following sections we discuss the two superposition principles that are important in the theory of viscoelasticity. The first is the Boltzmann superposition principle, which is concerned with linear viscoelasticity, and the second is time-temperature superposition, which deals with the time-temperature equivalence.

### A. BOLTZMANN SUPERPOSITION PRINCIPLE

As discussed earlier for a Hookean solid, stress is a linear function of strain, while for a Newtonian fluid, stress is a linear function of strain rate. The constants of proportionality in these cases are modulus and viscosity, respectively. However, for a viscoelastic material the modulus is not constant; it varies with time and strain history at a given temperature. But for a linear viscoelastic material, modulus is a function of time only. This concept is embodied in the Boltzmann principle, which states that the effects of mechanical history of a sample are additive. In other words, the response of a linear viscoelastic material to a given load is independent of the response of the material to any load previously on the material. Thus the Boltzmann principle has essentially two implications — stress is a linear function of strain, and the effects of different stresses are additive.

Let us illustrate the Boltzmann principle by considering creep. Suppose the initial creep stress,  $\sigma_0$ , on a linear, viscoelastic body is increased sequentially to  $\sigma_1, \sigma_2, \dots, \sigma_n$  at times  $t_1, t_2, \dots, t_n$ , then according to the Boltzmann principle, the creep at time  $t$  due to such a loading history is given by

$$\varepsilon(t) = J(t)\sigma_0 + J(t-t_1)[\sigma_1 - \sigma_0] + \dots + J(t-t_n)[\sigma_n - \sigma_{n-1}] \quad (14.41)$$

Here  $J$  is compliance, whose functional dependence on time is denoted by the parentheses. The square brackets denote multiplication. For a continuous loading history, then, the creep is expressed by the integral:

$$\varepsilon(t) = \int_0^t J(t-\theta) [\dot{\sigma}(\theta)] d\theta \quad (14.42)$$

where  $\dot{\sigma}(\theta)$  describes the stress history. A similar expression can be derived for stress relaxation. In this case, the initial strain is changed sequentially to  $\varepsilon_1$ ,  $\varepsilon_2$ , and  $\varepsilon_n$  at times  $t_1$ ,  $t_2 \dots t_n$ ; then the resultant stress is

$$\sigma(t) = E_r(t)\varepsilon_0 + E_r(t-t_1)[\varepsilon_1 - \varepsilon_0] + \dots + E_r(t-t_n)[\varepsilon_n - \varepsilon_{n-1}] \quad (14.43)$$

For a continuous strain history, the Boltzmann expression becomes

$$\sigma(t) = \int_0^t E_r(t-\theta) [\varepsilon(\theta)] d\theta \quad (14.44)$$

Linear viscoelasticity is valid only under conditions where structural changes in the material do not induce strain-dependent modulus. This condition is fulfilled by amorphous polymers. On the other hand, the structural changes associated with the orientation of crystalline polymers and elastomers produce anisotropic mechanical properties. Such polymers, therefore, exhibit nonlinear viscoelastic behavior.

## B. TIME-TEMPERATURE SUPERPOSITION PRINCIPLE

Structural engineering design with engineering materials usually requires that the structures maintain their integrity for long periods of time. In such designs the elastic modulus of structural components is an important parameter for relating design stresses to component dimensions. We know, of course, that the modulus of polymeric materials decreases with increasing time. Therefore, to ensure a safe and proper design, it is necessary to know the lower limit of modulus. Ideally, the most reliable information on modulus changes of a polymeric material should be developed over a long period in which test samples are subjected to conditions comparable to those that will be experienced by the material in real-time service. Accumulation of such long-term data is obviously inconvenient, expensive, and indeed hardly practical. Consequently, in engineering practice, reliance has to be placed necessarily on short-term data for the design for long-term applications.

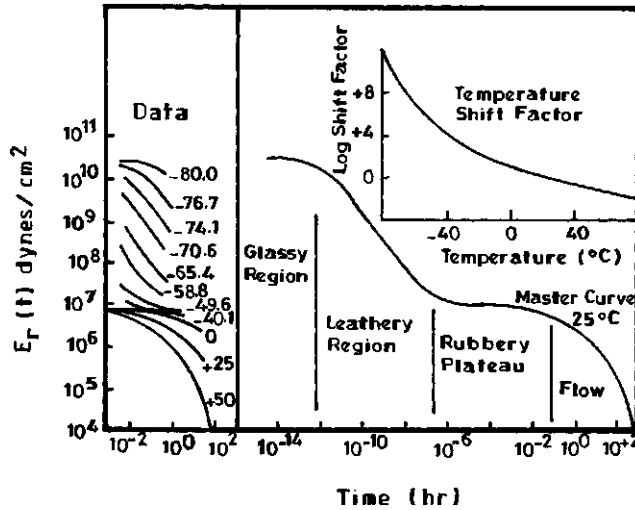
Fortunately for linear amorphous polymers, modulus is a function of time and temperature only (not of load history). Modulus–time and modulus–temperature curves for these polymers have identical shapes; they show the same regions of viscoelastic behavior, and in each region the modulus values vary only within an order of magnitude. Thus, it is reasonable to assume from such similarity in behavior that time and temperature have an equivalent effect on modulus. Such indeed has been found to be the case. Viscoelastic properties of linear amorphous polymers show time–temperature equivalence. This constitutes the basis for the time–temperature superposition principle. The equivalence of time and temperature permits the extrapolation of short-term test data to several decades of time by carrying out experiments at different temperatures.

Time–temperature superposition is applicable to a wide variety of viscoelastic response tests, as are creep and stress relaxation. We illustrate the principle by considering stress relaxation test data. As a result of time–temperature correspondence, relaxation curves obtained at different temperatures can be superimposed on data at a reference temperature by horizontal shifts along the time scale. This generates a simple relaxation curve outside a time range easily accessible in laboratory experiments. This is illustrated in [Figure 14.13](#) for polyisobutylene. Here, the reference temperature has been chosen arbitrarily to be 25°C. Data obtained at temperature above 25°C are shifted to the right, while those obtained below 25°C are shifted to the left.

The procedure for such data extrapolation is not arbitrary. The time–temperature superposition principle may be expressed mathematically for a stress relaxation experiment as

$$E_r(T_1, t) = E_r(T_2, t/a_T) \quad (14.45)$$

This means that the effect on the modulus of changing the temperature from  $T_1$  to  $T_2$  is equivalent to multiplying the time scale by a shift factor  $a_T$ , which is given by



**Figure 14.13** Time-temperature superposition for polyisobutylene. (From Tobolsky, A.V. and Catsiff, E., *J. Polym. Sci.*, 19, 111, 1956. With permission.)

$$a_T = t_T/t_{T_0} = \tau_T/\tau_{T_0} = \eta_T/\eta_{T_0} \quad (14.46)$$

where  $t_T$  is the time required to reach a particular mechanical response (modulus in this case) at temperature  $T$ , and  $t_{T_0}$  is the time required to produce the same response at the reference temperature  $T_0$ . An important empirical relation correlating the shift factor with temperature changes has been developed by Williams, Landel, and Ferry, the so-called WLF equation.<sup>3</sup> The WLF equation, which is valid between  $T_g$  and  $T_g + 100^\circ\text{C}$ , is given by the general expression

$$\log_{10} a_T = \frac{-C_1(T - T_0)}{C_2 + T - T_0} \quad (14.47)$$

where  $T_0$  is the reference temperature and  $C_1$  and  $C_2$  are constants to be determined experimentally. The temperatures are in degrees Kelvin. It is common practice to choose the glass transition temperature,  $T_g$ , as the reference temperature. In this case, the WLF equation is given by

$$\log_{10} a_T = \frac{-17.44(T - T_g)}{51.6 + T - T_g} \quad (14.48)$$

Before shifting the curves to generate the master curve, it is necessary to correct the relaxation modulus at each temperature for temperature and density with respect to the reference temperature. That is,

$$E_{\text{reduced}}^{(t)} = \left(\frac{T_0}{T}\right) \left(\frac{\rho_0}{\rho}\right) E_r(t) \quad (14.49)$$

$\rho_0$  = density at  $T_0$   
 $\rho$  = density at  $T$

This correction is based on the theory of rubber elasticity, which postulates that the elastic modulus of rubber is proportional to the absolute temperature  $T$  and to the density of the material. It can be argued, of course, that this correction may only be necessary in the rubbery region, where the predominant

response mechanism is chain coiling and uncoiling. It may not apply in the glassy region, where the mechanical response is governed essentially by the stretching of bonds and deformation of bond angles, or the viscous region, which involves chain slippage.

**Example 14.7:** In a stress relaxation experiment conducted at 25°C, it took 10<sup>7</sup> h for the modulus of the polymer to decay to 10<sup>5</sup> N/m<sup>2</sup>. Using the WLF equation, estimate how long will it take for the modulus to decay to the same value if the experiment were conducted at 100°C. Assume that 25°C is the T<sub>g</sub> of the polymer.

**Solution:**

$$\log_{10} a_T = \log \frac{t_{100}}{t_{25}} = \frac{-17.44(100 - 25)}{51.6 + 100 - 25}$$

$$= -10.33$$

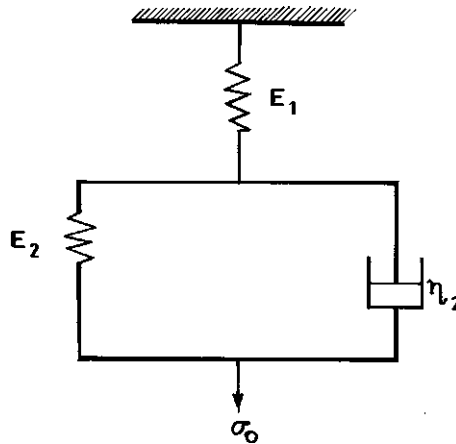
$$\frac{t_{100}}{t_{25}} = 4.66 \times 10^{-11} \text{ h}$$

$$t_{100} = 4.66 \times 10^{-11} \times 10^7 \text{ h}$$

$$= 4.66 \times 10^{-4} \text{ h}$$

## VIII. PROBLEMS

14.1. The following three-parameter model is assumed to simulate the behavior of a certain polymer:



In a creep and creep recovery experiment:

- What is the rheological equation that describes this model?
  - Sketch the creep and creep recovery curve.
- 14.2. Calculate the relaxation modulus after 10 s of the application of stress for a polymer represented by three Maxwell elements in parallel where:

$$E_1 = 10^5 \text{ N/m}^2, \tau_1 = 10 \text{ s}$$

$$E_2 = 10^6 \text{ N/m}^2, \tau_2 = 20 \text{ s}$$

$$E_3 = 10^7 \text{ N/m}^2, \tau_3 = 30 \text{ s}$$

14.3. A Voigt–Kelvin model consists of four elements with the following parameters:

Element No.	$E(\text{N/m}^2)$	$\eta (\text{N.s/m}^2)$
1	$5 \times 10^8$	$5 \times 10^{10}$
2	$10^{10}$	$5 \times 10^{10}$
3	$5 \times 10^8$	$5 \times 10^9$
4	$10^8$	$5 \times 10^{10}$

In a creep experiment, if the imposed stress is  $10^8 \text{ N/m}^2$ , determine the strain after 100 s.

- 14.4. The initial stress on a polymer in a creep experiment is  $10^8 \text{ N/m}^2$ . This load is increased by  $10^7 \text{ N/m}^2$  and  $10^6 \text{ N/m}^2$  after  $10^2$  and  $10^3$  s, respectively. Assuming that the Boltzmann superposition principle holds for this material, find the strain after  $10^4$  s. The creep compliance for the material is given by  $10^{-8} (1 - e^{-10^{-4}t})$ .
- 14.5. In a stress relaxation experiment the modulus of polyisobutylene relaxed to  $10^6 \text{ N/m}^2$  in  $10^4$  h at  $0^\circ\text{C}$ . If it is desired to cut the experimental time to 10 h, use the WLF equation to estimate the temperature at which the experiment must be conducted. The  $T_g$  for PIB is  $-70^\circ\text{C}$ .
- 14.6. The relaxation time for a material that obeys the WLF equation at  $0^\circ\text{C}$  is  $10^4$  s. Its relaxation time at  $T_g$  is  $10^{13}$  s. What is the relaxation time of this material at  $25^\circ\text{C}$ ?
- 14.7. In a forced vibration experiment, the damping peak for polycarbonate occurred at  $150^\circ\text{C}$  at a frequency of 1 Hz. What would be the location of this peak if the frequency were 1000 Hz? Polycarbonate has a  $T_g$  of  $150^\circ\text{C}$ .
- 14.8. A tactic polystyrene has a  $T_g$  of  $100^\circ\text{C}$ . What are the relative rates of stress relaxation of this polymer at  $150^\circ\text{C}$  and  $125^\circ\text{C}$ ?

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