

c. Permanent set

$$\epsilon_2 = \frac{\sigma_0 t}{\eta_2}$$

$$= \frac{(10^8 \text{ N/m}^2)(200 \text{ s})}{5 \times 10^{10} \text{ N.s/m}^2} = 0.4$$

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,

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

(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,

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

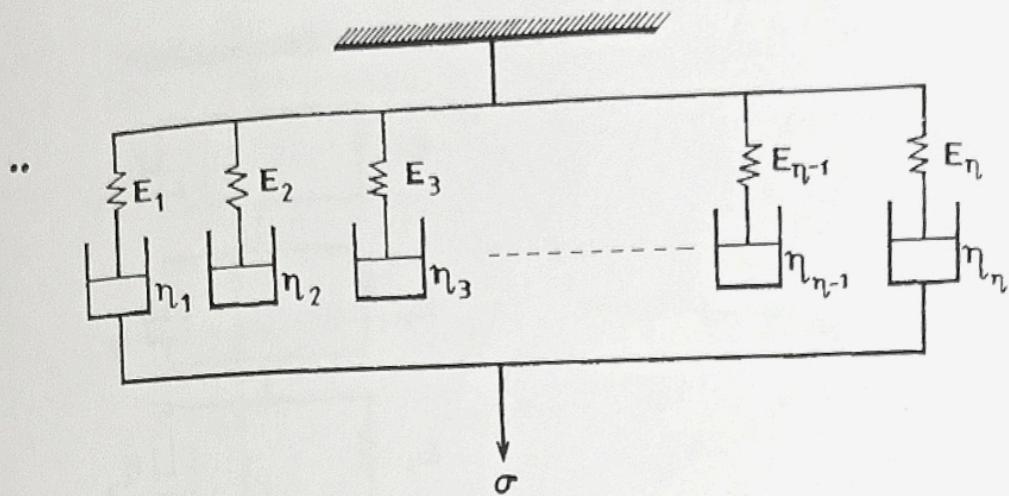


Figure 14.11 The Maxwell-Weichert model.

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 ε_0 as

$$\sigma_i(t) = \varepsilon_0 E_i e^{-t/\tau_i} \quad (14.33)$$

where $\tau_i = \eta_i/E_i$. For the Maxwell-Reichert model under a constant strain, ε_0 ,

$$\sigma(t) = \varepsilon_0 \sum_{i=1}^n E_i e^{-t/\tau_i} \quad (14.34)$$

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 $E(r)$.

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

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

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

or

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

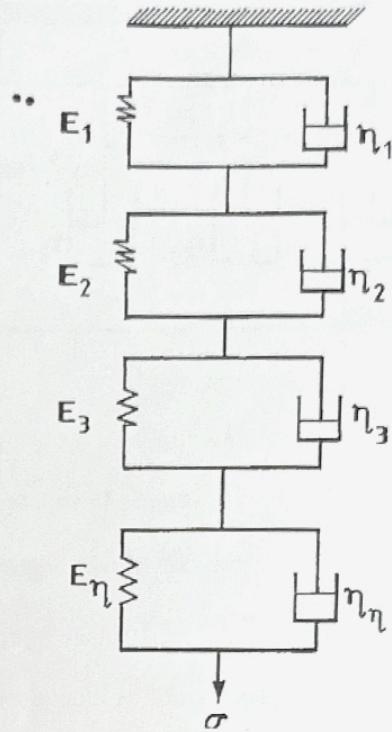


Figure 14.12 Voigt-Kelvin model.

where $J_i = \frac{1}{E_i}$ and is creep compliance. The response of a series of elements subjected to the same constant stress σ_0 becomes

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

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.

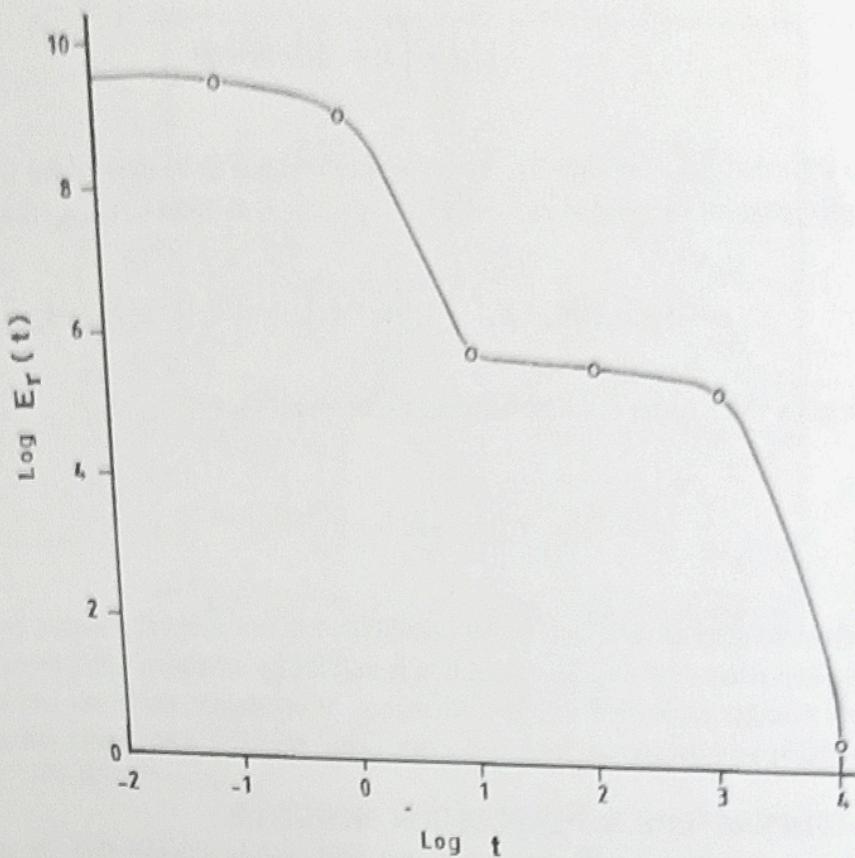


Figure E.14.6 Behavior of a 2-component Maxwell-Reichert model.

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, σ_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

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

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 ε_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