R. W. Hertzberg "Deformation and Fracture of Eng. Mater. Struct."
4th ed., John Wiley, 1996.

6.3 VISCOELASTIC RESPONSE OF POLYMERS AND THE ROLE OF STRUCTURE   225

ficial changes occur while stiffness and maximum service temperature decrease. Consequently, the extent of polymer plasticization is determined by an optimization of processability, ductility, strength, and stiffness, and service temperature requirements. It is interesting to note that nylon 66 is inadvertently plasticized by the moisture it picks up from the atmosphere (Table 6.3).

Blowing Agents.   These substances are designed to decompose into gas bubbles within the polymer melt, producing stable holes. (In this way, expanded or foamed polymers are made.) The timing of this decomposition is critical. If the viscosity of the melt is too high, the bubbles will not form properly. If the viscosity is too low, the gas bubbles burst with the expanding polymer mass collapsing like an aborted soufflé.

Cross-linking Agents.   The basic difference between thermoplastic and thermosetting polymers lies in the nature of the intermolecular bond. In thermoplastic materials, these bonds are relatively weak and of the van der Waals type. Consequently, heating above T_g or T_m provides the thermal energy necessary for chains to move independently. This is not possible in thermosetting polymers, since the chains are rigidly joined with primary covalent bonds. Sulfur is a classic example of a cross-linking agent as used in the vulcanization of rubber.

From this very brief description of polymer additives, it is clear that a distinction should be made between a pure polymer and a polymer plus assorted additives; the latter is often referred to as a *plastic*, though rubbers also may be compounded. Although the terms *plastic* and *polymer* are often used synonymously in the literature, they truly represent basically different entities.

6.3   VISCOELASTIC RESPONSE OF POLYMERS AND THE ROLE OF STRUCTURE

The deformation response of many materials depends to varying degrees on both time-dependent and time-independent processes. For example, it was shown in Chapter 5 that when the test temperature is sufficiently high, a test bar would creep with time under a given load (Fig. 6.12a). Likewise, were the same bar to have been stretched to a certain length and then held firmly, the necessary stress to maintain the stretch would gradually relax (Fig. 6.12b). Such response is said to be *viscoelastic*. Since T_g and T_m of most polymeric materials are not much above ambient (and in fact may be lower as in the case of natural rubbers), these materials exhibit viscoelastic creep and relaxation phenomena at room temperature. When the elastic strains and viscous flow rate are small (approximately 1 to 2% and 0.1 s^{-1}, respectively), the viscoelastic strain may be approximated by

$$\epsilon = \sigma \cdot f(t) \tag{6-7}$$

That is, the stress–strain ratio is a function of time only. This response is called *linear* viscoelastic behavior and involves the simple addition of linear elastic and linear viscous (Newtonian) flow components. When the stress–strain ratio of a material varies with time and *stress*
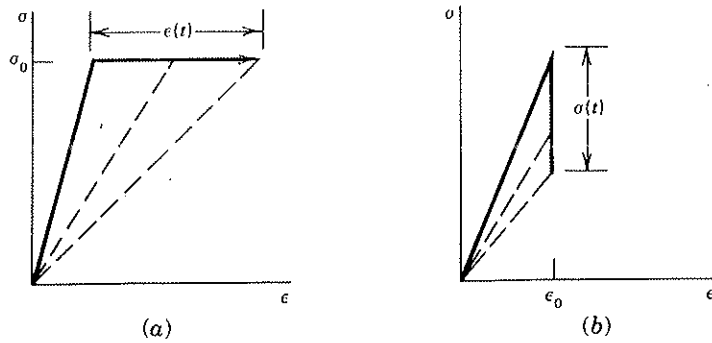
$$\epsilon = g(\sigma, t) \tag{6-8}$$

FIGURE 6.12 Time-dependent stress–strain response in polymers: (*a*) creep and (*b*) relaxation behavior.

the viscoelastic response is nonlinear. A comparison of creep behavior between metals and polymers is summarized in Table 6.4.

On the basis of the simple creep test it is possible to define a creep modulus

$$E_c(t) = \frac{\sigma_0}{\epsilon(t)} \tag{6-9}$$

where $E_c(t)$ = creep modulus as a function of time

σ_0 = constant applied stress

$\epsilon(t)$ = time-dependent strain

Note different values of $E_c(t)$ in Fig. 6.12*a*. Likewise, in a stress relaxation test where the strain ϵ_0 is fixed and the associated stress is time dependent, a relaxation modulus $E_r(t)$ may be defined

$$E_r(t) = \frac{\sigma(t)}{\epsilon_0} \tag{6-10}$$

Figure 6.12*b* illustrates the change in E_r with time. These quantities can be plotted against log time to reveal their strong time dependence, as shown schematically in Fig. 6.13*a* for $E_r(t)$. (For small strains and up to moderate temperatures, corresponding to linear viscoelastic behavior, $E_r \approx E_c$.) It is clear that material behavior changes radically from one region to another. For very short times, the relaxation modulus approaches a maximum limiting value where the material exhibits glassy behavior

TABLE 6.4 Comparison of Creep Behavior in Metals and Polymers

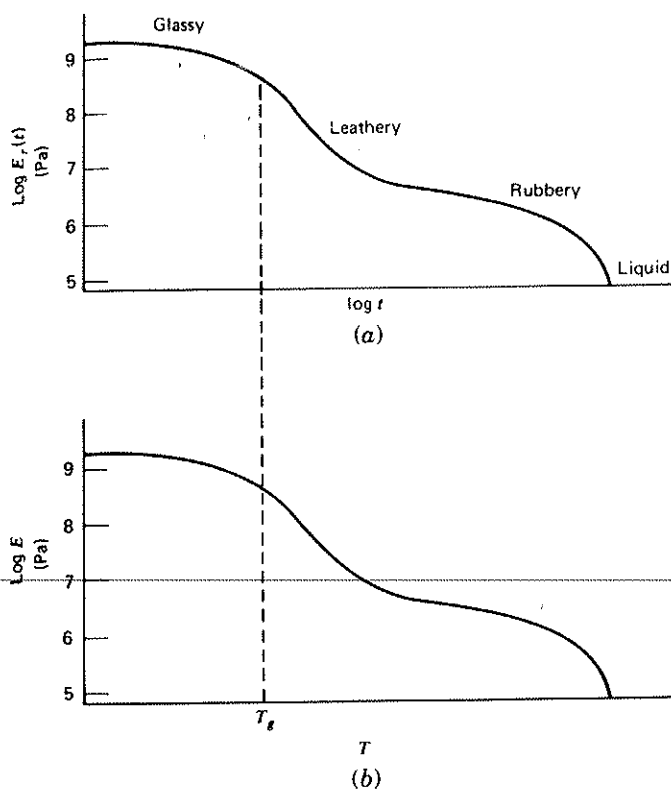| Creep Behavior	Metals	Polymers
● Linear elastic	No	Sometimes
● Recoverable	No	Partially
● Temperature range	High temperatures above ~ $0.2\ T_h$	All temperatures above ~ $-200°C$

FIGURE 6.13 Time–temperature dependence of elastic modulus in thermoplastic polymeric solids: (*a*) change in relaxation modulus $E_r(t)$ as function of time; (*b*) change in tensile modulus as function of temperature.

associated with negligible molecule segmental motions. At longer times, the material experiences a transition to leathery behavior associated with the onset of short-range molecule segmental motions. At still longer times, complete molecule movements are experienced in the rubbery region associated with a further drop in the relaxation modulus. Beyond this point, liquid flow occurs. It is interesting to note that the same type of curve may be generated by plotting the modulus (from a simple tensile test) against test temperature (Fig. 6.13*b*). In this instance, the initial sharp decrease in E from its high value in the glassy state occurs at T_g. The shape of this curve can be modified by structural changes and polymer additions. For example, the entire curve is shifted downward and to the left as a result of plasticization (Fig. 6.14*a*). As $\overline{M}$ increases, the rubbery flow region is displaced to longer times (Fig. 6.14*b*), because molecular and segmental molecular movements are suppressed when chain entanglement is increased. Molecular weight has relatively little effect on the onset of the leathery region, since T_g is relatively independent of $\overline{M}$ except at low $\overline{M}$ values (Fig. 6.15). The effect of $\overline{M}$ on T_g is believed to be related to the chain ends.[1] Since the ends are freer to move about, they generate a greater than average amount of free volume. Adjacent chains are then freer to move about and contribute to greater
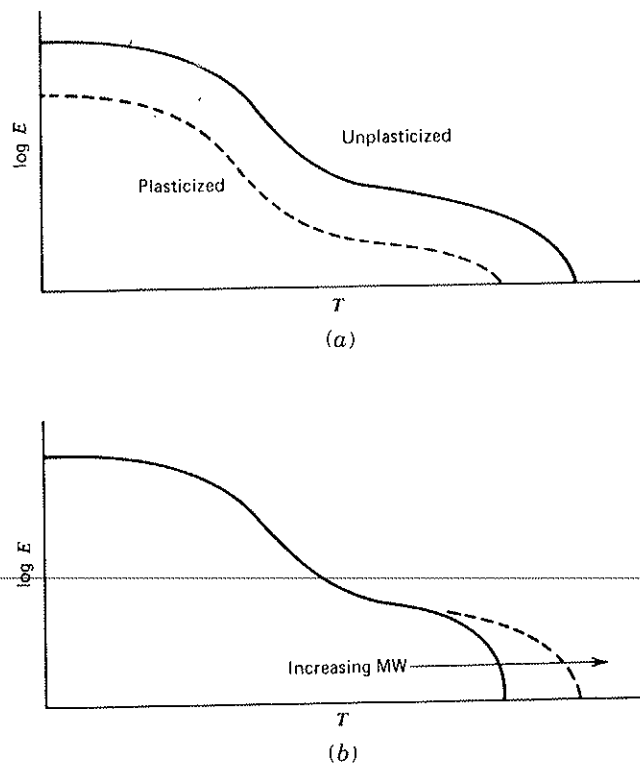
FIGURE 6.14   Effect of (a) plasticization and (b) molecular weight on elastic modulus as function of temperature.
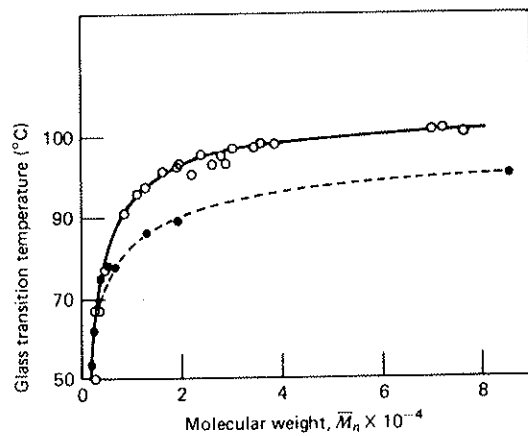

FIGURE 6.15   Glass transition temperature in PMMA (○) and polystyrene (●) as a function of $\overline{M}_n$.[19] (M. Miller, *The Structure of Polymers*, © 1966 by Litton Educational Publishing by permission of Van Nostrand Reinhold.)

mobility of the polymer. Since the chain ends are more sensitive to $\overline{M}_n$ than $\overline{M}_w$, T_g is best correlated with the former measure of molecular weight. The leathery region is greatly retarded by cross-linking, while the flow region is completely eliminated, the latter being characteristic of thermosetting polymers (Fig. 6.16).

The temperature–time (i.e., strain rate^{-1}) equivalence seen in Fig. 6.13 closely parallels similar observations made in Chapter 5. It is seen that the same modulus value can be obtained either at low temperatures and long times or at high test temperatures but short times. In fact, this equivalence is used to generate E_r versus log t curves as shown in Fig. 6.13a. The reader should appreciate that since such plots extend over 10 to 15 decades of time, they cannot be determined conveniently from direct laboratory measurements. Instead, relaxation data are obtained at different temperatures over a convenient time scale. Then, after choosing one temperature as the reference temperature, the remaining curves are shifted horizontally to longer or shorter times to generate a single master curve (Fig. 6.17). This approach was first introduced by Tobolsky and Andrews[22] and was further developed by Williams et al.[23] Assuming that the viscoelastic response of the material is to be controlled by a single function of temperature (i.e., a single rate-controlling mechanism), Williams et al.[23] developed a semiempirical relation for an amorphous material, giving the time shift factor a_T as

$$\log a_T = \log \frac{t_T}{t_{T_0}} = \frac{C_1(T - T_0)}{C_2 + T - T_0} \tag{6-11}$$

where a_T = shift factor that is dependent on the difference between the reference and data temperatures $T - T_0$

t_T, t_{T_0} = time required to reach a specific E_r at temperatures T and T_0, respectively

C_1, C_2 = constants dependent on the choice of the reference temperature T_0

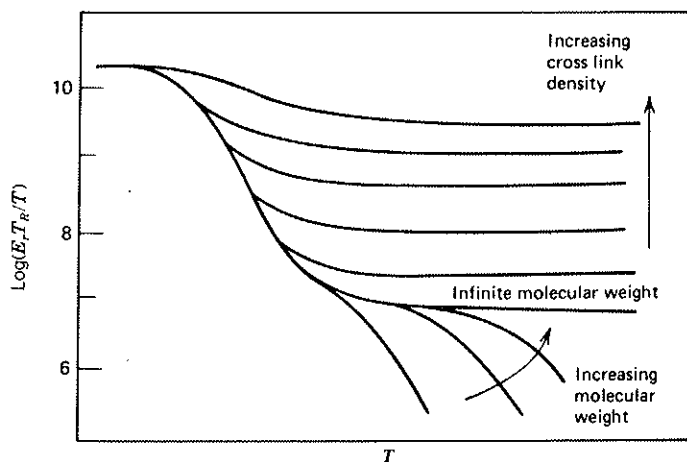T = test temperatures where relaxation data were obtained, K

FIGURE 6.16 Effect of molecular weight and degree of cross-linking on relaxation modulus.[20] (Reprinted with permission from McGraw-Hill Book Company.)
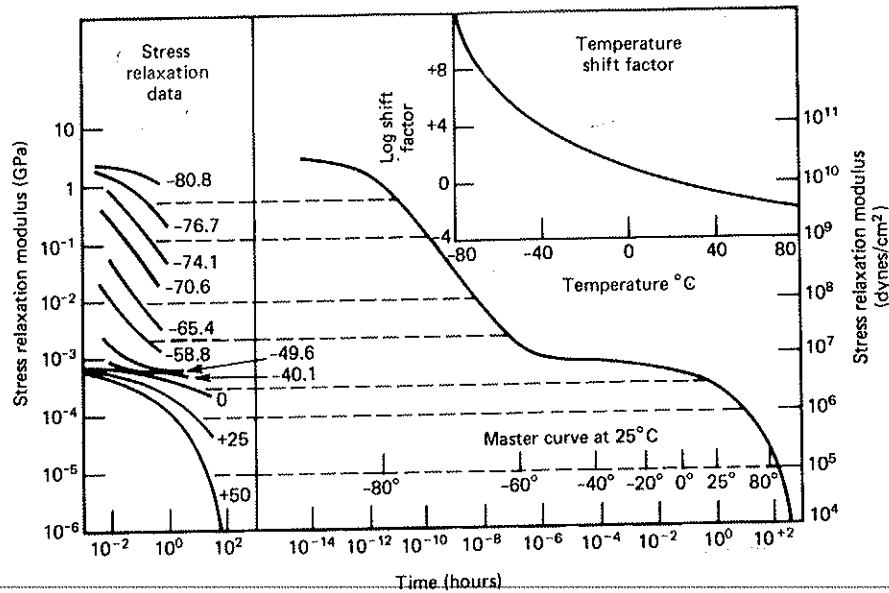
FIGURE 6.17 Modulus–time master plot for polyisobutylene based on time–temperature superposition of data to a reference temperature of 25°C. (From Catsiff and Tobolsky,[21] with permission from John Wiley & Sons, Inc.)

This relation is found to hold in the temperature range $T_g < T < T_g + 100$ K, but is sometimes used beyond these limits on an individual basis as long as time–temperature superposition still occurs. This would indicate that the same rate-controlling processes were still operative. Two reference temperatures are often used to normalize experimental data—T_g and $T_g + 50$ K—for which the constants C_1 and C_2 are given in Table 6.5.

The shift function may be used to normalize creep data,[4] enabling this information to be examined on a single master curve as well. Furthermore, by normalizing the creep strain results relative to the applied stress σ_0, the normalization of both axes converts individual creep–time plots into a master curve of creep compliance versus adjusted time (Fig. 6.18). These curves can be used to demonstrate the effect of MW and degree of cross-linking on polymer mechanical response much in the manner as the modulus relaxation results described in Figs. 6.14 and 6.16. Note that viscous flow is eliminated and the magnitude of the creep compliance reduced with increasing cross-linking in thermosetting polymers. For the thermoplastic materials, compliance decreases with increasing viscosity, usually the result of increased MW.

As previously noted (e.g., see Eqs. 6-9 and 6-10), the elastic modulus of engineering

TABLE 6.5 Constants for WLF Relationship

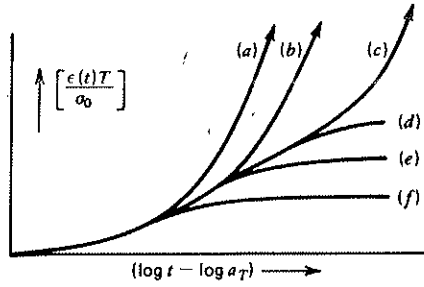| Reference Temperature	C_1	C_2
T_g	−17.44	51.6
$T_g + 50$ K	−8.86	101.6

FIGURE 6.18 Master creep curve revealing effect of increasing MW ($a{\rightarrow}b{\rightarrow}c$) and degree of cross-linking ($d{\rightarrow}e{\rightarrow}f$) on creep strain. (T. Alfrey and E. F. Gurnee, *Organic Polymers*, © 1967. Reprinted by permission of Prentice-Hall Inc., Englewood Cliffs, NJ.)

plastics varies with time as a result of time-dependent deformation. For this reason, the designer of a plastic component must look beyond basic tensile data when computing the deformation response of a polymeric component. For example, if a designer were to limit component strain to less than some critical value ϵ_c, the maximum allowable stress would be given by $E\epsilon_c$ so long as the material behaved as an ideally elastic solid. Since most engineering plastics experience creep, the level of strain in the component would increase with time as noted in Fig. 6.19a. To account for this
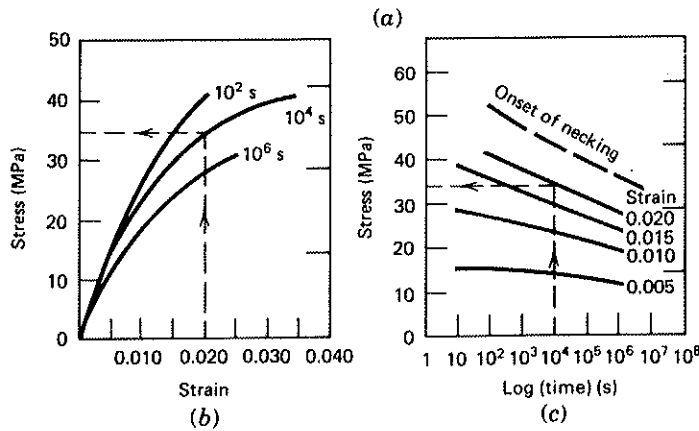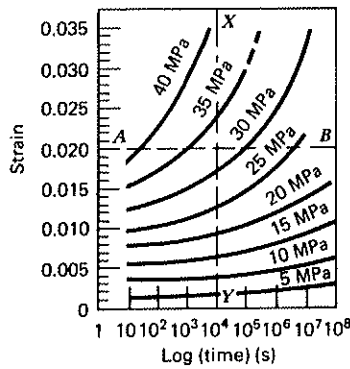

FIGURE 6.19 Creep response in PVC pipe resin at 20°C. (*a*) Creep curve; (*b*) isochronous stress–strain curves; (*c*) isometric stress–time curves.[2] (By permission of ICI Ltd.)

additional deformation, designers often make use of *isochronous* stress–strain curves which are derived from such creep data (e.g., see line *xy*). Figure 6.19*b* shows three isochronous stress–strain curves corresponding to loading times of 10^2, 10^4, and 10^6 s, respectively. To illustrate the use of these curves, we see that to limit the strain in a component to no more than 0.02 after 10^4 s, the allowable stress must not exceed 32 MPa.

The creep data shown in Fig. 6.19*a* can be analyzed in alternative fashion by considering the stress–time relation associated with various strain levels (e.g., line *AB*, Fig. 6.19*a*). The resulting *isometric* curves provide stress–time plots corresponding to different strain levels (Fig. 6.19*c*). For example, if a component were designed that would strain less than 0.02 after 10^4 s, the maximum permissible stress level would again be 32 MPa.

EXAMPLE 6.1

A PVC rod experiences a load of 500 N. An acceptable design calls for a maximum strain of 1% after one year of service. What is the minimum allowable rod diameter?

We will assume that the creep characteristics of the PVC pipe are identical to data shown in Fig. 6.19. Since one year is equal to 3.15×10^7 s, we see from Fig. 6.19*a* that an allowable strain of 1% would correspond to a stress of approximately 15 MPa. A similar result could have been identified with an isometric stress–time curve corresponding to 1% strain or with an isochronous stress–strain curve, corresponding to 3.15×10^7 s. The minimum rod diameter is then found to be

$$\sigma = \frac{P}{\frac{\pi}{4}d^2}$$

$$15 \times 10^6 = \frac{500}{\frac{\pi}{4}d^2}$$

$$\therefore d \sim 6.5 \text{ mm}$$

6.3.1 Mechanical Analogs

The linear viscoelastic response of polymeric solids has for many years been described by a number of mechanical models (Fig. 6.20). Many, including this author, have found that these models provide a useful physical picture of time-dependent deformation processes. The spring element (Fig. 6.20*a*) is intended to describe linear elastic behavior

$$\epsilon = \frac{\sigma}{E} \quad \text{and} \quad \gamma = \frac{\tau}{G} \tag{1-7}$$

such that resulting strains are not a function of time. (The stress–strain–time diagram for the spring is shown in Fig. 6.21*a*.) Note the instantaneous strain upon application