Chapter 14

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, ε, 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:

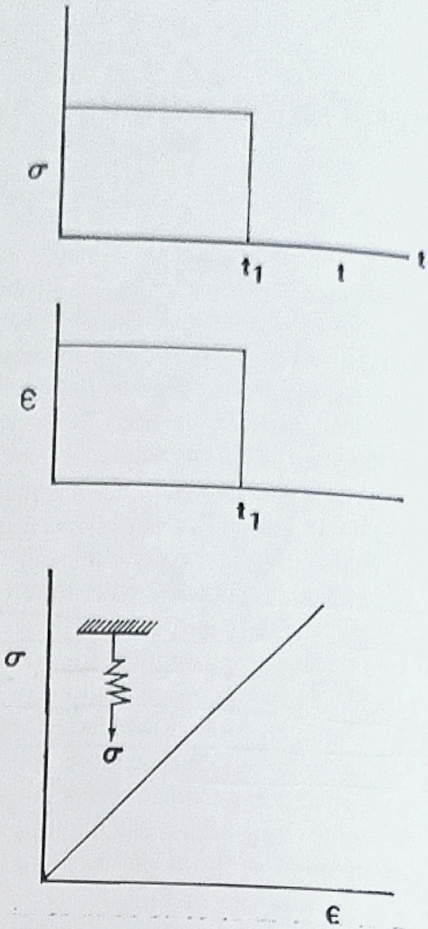

Figure 14.1 *Ideal elastic response.*

$$\sigma = E\varepsilon \tag{14.1}$$

where σ is the applied stress, ε 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 τ is viscous flow, given by

$\left(\frac{dy}{dt}\right) = f(t)$ linear

$$\tau = \eta \frac{d\gamma}{dt} \tag{14.2}$$

where η 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.

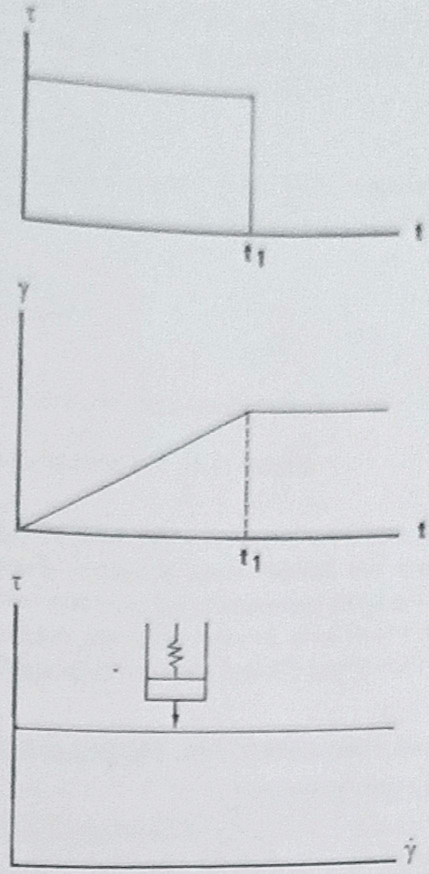

Figure 14.2 *Pure viscous behavior.*

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.

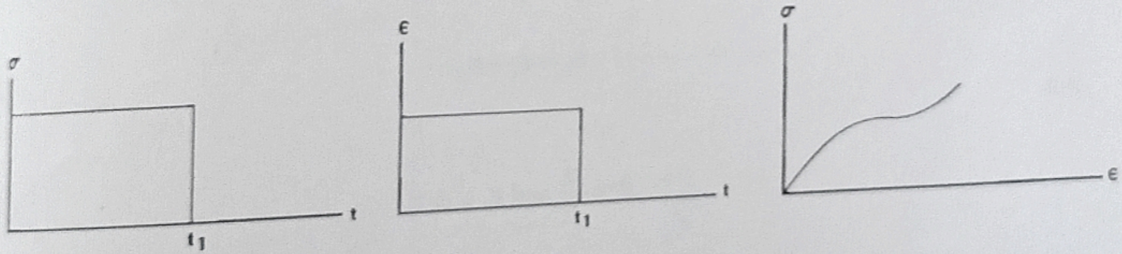

Figure 14.3 *Rubber elasticity.*

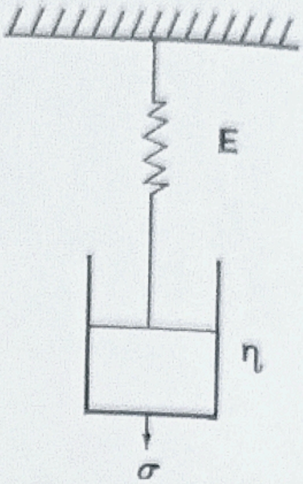

Figure 14.4 *The Maxwell element.*

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 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, η, 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,

$$\sigma = \sigma_s = \sigma_d \tag{14.3}$$

where σ_s and σ_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,

$$\varepsilon_T = \varepsilon_s + \varepsilon_d \tag{14.4}$$

or

$$\dot{\varepsilon}_T = \dot{\varepsilon}_s + \dot{\varepsilon}_d \tag{14.5}$$

But

$$\dot{\varepsilon}_s = \frac{\dot{\sigma}}{E} \text{ and } \dot{\varepsilon}_d = \sigma/\eta \tag{14.6}$$

where $\dot{\varepsilon}_T$ is the total strain rate, while $\dot{\varepsilon}_s$ and $\dot{\varepsilon}_d$ 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

$$\dot{\varepsilon}_T = \frac{1}{E}\dot{\sigma} + \frac{1}{\eta}\sigma \tag{14.7}$$

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, σ_o, 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

$$\varepsilon_T = \frac{1}{\eta}\sigma_0 \tag{14.8}$$

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

$$\varepsilon(t) = \frac{\sigma_0}{E} + \frac{\sigma_0}{\eta}t \tag{14.9}$$

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

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, σ_o, is initially followed by an instantaneous deformation due to the response of the spring by an amount σ_o/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

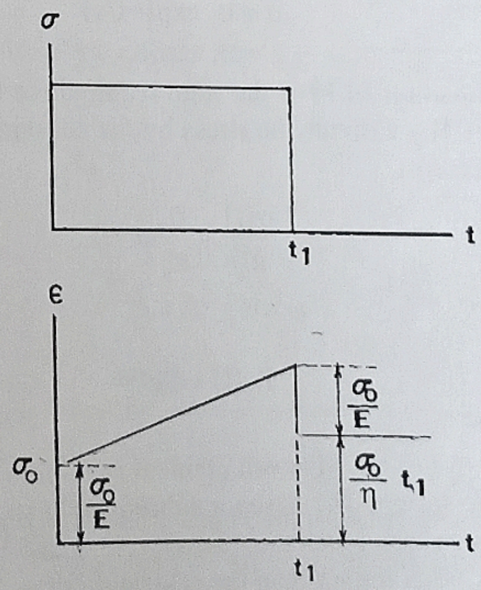

Figure 14.5 *Creep and creep recovery behavior of the Maxwell element.*