Chapter 13

Mechanical Properties of Polymers

I. INTRODUCTION

In Chapter 1, we observed that plastics have experienced a phenomenal growth since World War II, when they assumed enhanced commercial importance. This explosive growth in polymer applications derives from their competitive costs and versatile properties. Polymers vary from liquids and soft rubbers to hard and rigid solids. The unique properties of polymers coupled with their light weight make them preferable alternatives to metallic and ceramic materials in many applications. In the selection of a polymer for a specific end use, careful consideration must be given to its mechanical properties. This consideration is important not only in those applications where the mechanical properties play a primary role, but also in other applications where other characteristics of the polymer such as electrical, optical, or thermal properties are of crucial importance. In the latter cases, mechanical stability and durability of the polymer may be required for the part to perform its function satisfactorily.

The mechanical behavior of a polymer is a function of its microstructure or morphology. Polymer morphology itself depends on many structural and environmental factors. Compared with those of metals and ceramics, polymer properties show a much stronger dependence on temperature and time. This strong time and temperature sensitivity of polymer properties is a consequence of the viscoelastic nature of polymers. This implies that polymers exhibit combined viscous and elastic behavior. For example, depending on the temperature and stress levels, a polymer may show linear elastic behavior, yield phenomena, plastic deformation, or cold drawing. An amorphous polymer with T_g below ambient temperature may display nonlinear but recoverable deformation or even exhibit viscous flow. Given the complexity of polymer response to applied stresses or strains, it is imperative that, for their judicious use, those who work with polymers have an elementary knowledge of how polymer behavior is influenced by structural and environmental factors. We have already dealt with the structures of polymers in earlier chapters. We devote succeeding sections to discussing the mechanical properties of polymers in the solid state.

II. MECHANICAL TESTS

Polymer components, like other materials, may fail to perform their intended functions in specific applications as a result of

1. Excessive elastic deformation
2. Yielding or excessive plastic deformation
3. Fracture

Polymers show excessive elastic deformation, particularly in structural, load-bearing applications, due to inadequate rigidity or stiffness. For such failure, the controlling material mechanical property is the elastic modulus. As we shall see in subsequent discussions, the elastic moduli of some polymers are subject to some measure of control through appropriate structural modification.

Failure of polymers in certain applications to carry design loads or occasional accidental overloads may be due to excessive plastic deformation resulting from the inadequate strength properties of the polymer. For the quantification of such failures, the mechanical property of primary interest is the yield strength and the corresponding strain. The ultimate strength, along with the associated strain, also provides useful information.

Cracks constitute regions of material discontinuity and frequently precipitate failure through fracture. Fracture may occur in a sudden, brittle manner or through fatigue (progressive fracture). Brittle fracture occurs in materials where the absence of local yielding results in a build-up of localized stresses, whereas fatigue failure occurs when parts are subjected to alternating or repeated loads. Fatigue fractures occur without visible signs of yielding since they occur at strengths well below the tensile strength of the material.

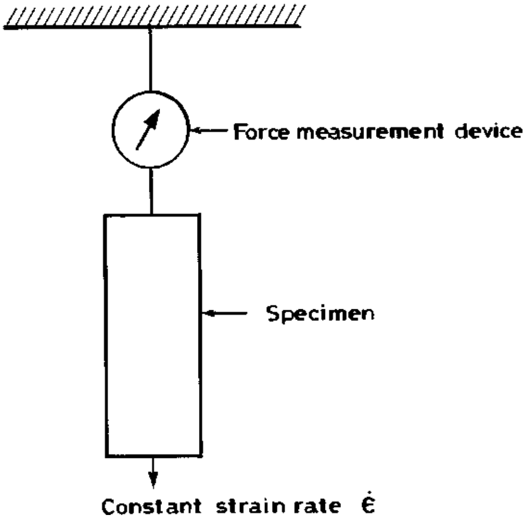


Figure 13.1 *Schematic of stress–strain test.*

As we said earlier, polymers will continue to be used in a variety of end-use situations. Therefore, to ensure their successful performance in these applications, it is necessary to clearly understand their mechanical behavior under a variety of stress conditions. Particular cognizance must be taken of the relatively high sensitivity of polymer failure modes to temperature, time, and loading history. For good design, it is important to be able to relate design load and component dimensions to some appropriate material property that defines the limits of the load-bearing capability of the polymer material. A variety of test methods exist for predicting mechanical performance limits under a variety of loading conditions. These range from simple tension, compression, and shear tests to those designed to test complex stress states and polymer time–temperature response. Elaborate treatment of polymer deformation behavior under complex stress states would require complex mathematical analysis, which is beyond the scope of this volume. Our discussion emphasizes problems of a one-dimensional nature, and cases of nonlinear deformation will be treated in an elementary fashion.

A. STRESS–STRAIN EXPERIMENTS

Stress–strain experiments have traditionally been the most widely used mechanical test but probably the least understood in terms of interpretation. In stress–strain tests the specimen is deformed (pulled) at a constant rate, and the stress required for this deformation is measured simultaneously (Figure 13.1). As we shall see in subsequent discussions, polymers exhibit a wide variation of behavior in stress–strain tests, ranging from hard and brittle to ductile, including yield and cold drawing. The utility of stress–strain tests for design with polymeric materials can be greatly enhanced if tests are carried out over a wide range of temperatures and strain rates.

B. CREEP EXPERIMENTS

In creep tests, a specimen is subjected to a constant load, and the strain is measured as a function of time. The test specimen in a laboratory setup can be a plastic film or bar clamped at one end to a rigid support while the load is applied suddenly at the other end (Figure 13.2). The elongation may be measured at time intervals using a cathetometer or a traveling microscope. Measurements may be conducted in an environmental chamber.

Creep tests are made mostly in tension, but creep experiments can also be done in shear, torsion, flexure, or compression. Creep data provide important information for selecting a polymer that must sustain dead loads for long periods. The parameter of interest to the engineer is compliance (J), which is a time-dependent reciprocal of modulus. It is the ratio of the time-dependent strain to the applied constant stress [$J(t) = \varepsilon(t)/\sigma_0$]. Figure 13.3 shows creep curves for a typical polymeric material.

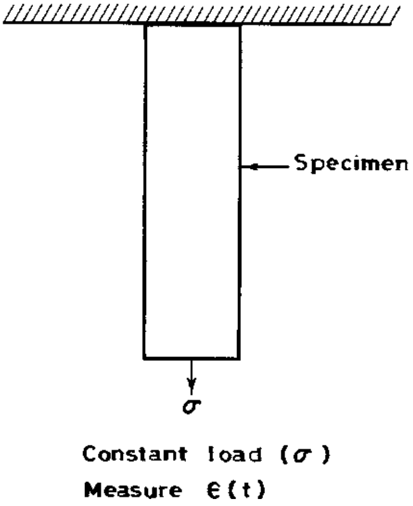


Figure 13.2 *Schematic representation of creep experiment.*

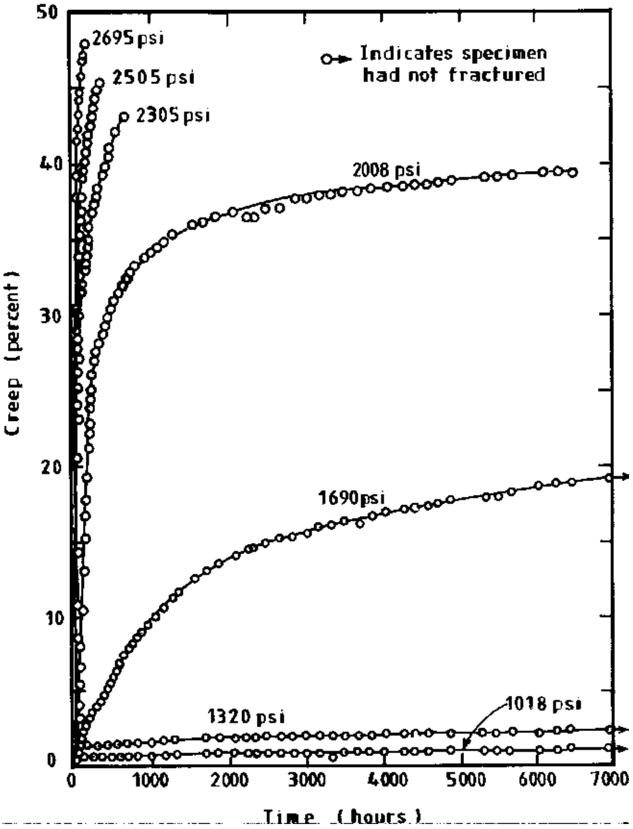


Figure 13.3 *Creep of cellulose acetate at 45°C. (From Findley, W.N., Mod. Plast., 19(8), 71, 1942. With permission.)*

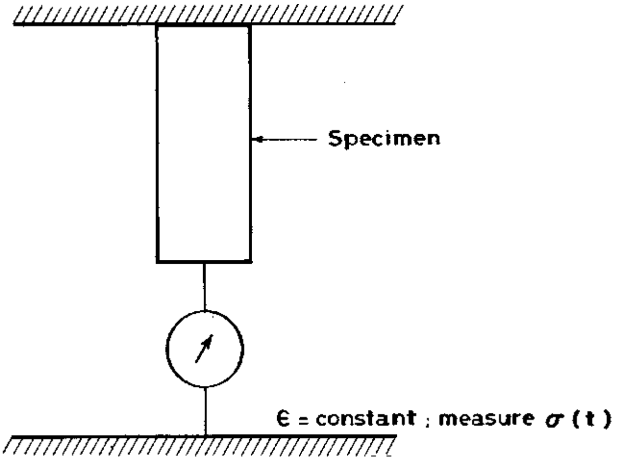


Figure 13.4 *Schematic of stress relaxation experiment.*

C. STRESS RELAXATION EXPERIMENTS

In stress relaxation experiments, the specimen is rapidly (ideally, instantaneously) extended a given amount, and the stress required to maintain this constant strain is measured as a function of time (Figure 13.4). The stress that is required to maintain the strain constant decays with time. When this stress is divided by the constant strain, the resultant ratio is the relaxation modulus ($E_r(t,T)$), which is a function of both time and temperature. Figure 13.5 shows the stress relaxation curves for PMMA at

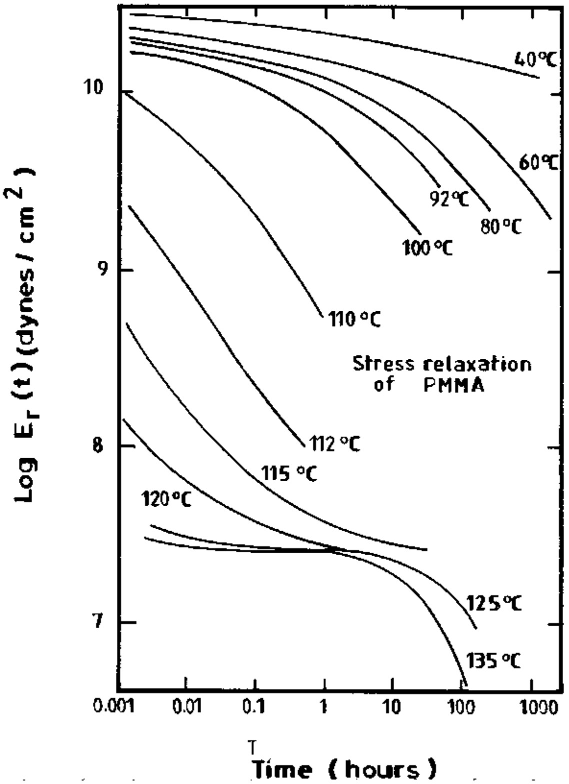


Figure 13.5 *Log $E_r(t)$ vs. log t for unfractionated poly(methyl methacrylate). (From McLoughlin, J.R. and Tobolsky, A.V., J. Colloid Sci., 7, 555, 1952. With permission.)*

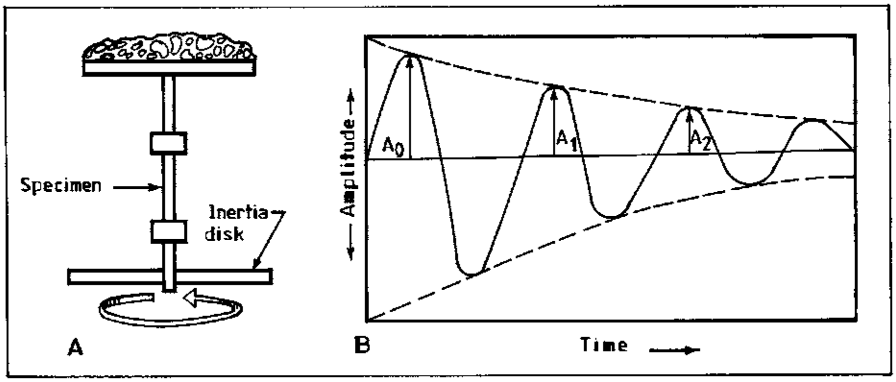


Figure 13.6 *Torsion pendulum (A) is used to get data for typical response curve (B), indicating decreasing amplitude of oscillation. (From Fried, J.R., Plast. Eng., 38(7), 27, 1982. With permission.)*

different temperatures. Stress relaxation data provide useful information about the viscoelastic nature of polymers.

D. DYNAMIC MECHANICAL EXPERIMENTS

In dynamic mechanical tests, the response of a material to periodic stress is measured. There are many types of dynamic mechanical test instruments. Each has a limited frequency range, but it is generally possible to cover frequencies from 10^{-5} to 10^{6} cycles per second. A popular instrument for dynamic mechanical measurements is the torsion pendulum (Figure 13.6A). A polymer sample is clamped at one end, and the other end is attached to a disk that is free to oscillate. As a result of the damping characteristics of the test sample, the amplitude of oscillation decays with time (Figure 13.6B).

Dynamic mechanical tests provide useful information about the viscoelastic nature of a polymer. It is a versatile tool for studying the effects of molecular structure on polymer properties. It is a sensitive test for studying glass transitions and secondary transitions in polymer and the morphology of crystalline polymers.

Data from dynamic mechanical measurements can provide direct information about the elastic modulus and the viscous response of a polymer. This can be illustrated by considering the response of elastic and viscous materials to imposed sinusoidal strain, ε:

$$\varepsilon = \varepsilon_0 \sin(\omega t) \tag{13.1}$$

where ε_0 is the amplitude and ω is the frequency (in radians per second, $\omega = 2\pi f$; f is in cycles per second). For a purely elastic body, Hooke's law is obeyed. Consequently,

$$\sigma = G\varepsilon_0 \sin(\omega t) \tag{13.2}$$

where G is the shear modulus. It is evident from Equations 13.1 and 13.2 that for elastic bodies, stress and strain are in phase.

Now consider a purely viscous fluid. Newton's law dictates that the shear stress is given by $\sigma = \eta\dot{\varepsilon}$, that is,

$$\sigma = \eta\varepsilon_0\ \omega \cos(\omega t) \tag{13.3}$$

In this case, the shear stress and the strain are 90° out of phase. The response of viscoelastic materials falls between these two extremes. It follows that the sinusoidal stress and strain for viscoelastic materials are out of phase by an angle, say δ. The behavior of these classes of materials is illustrated in Figure 13.7.

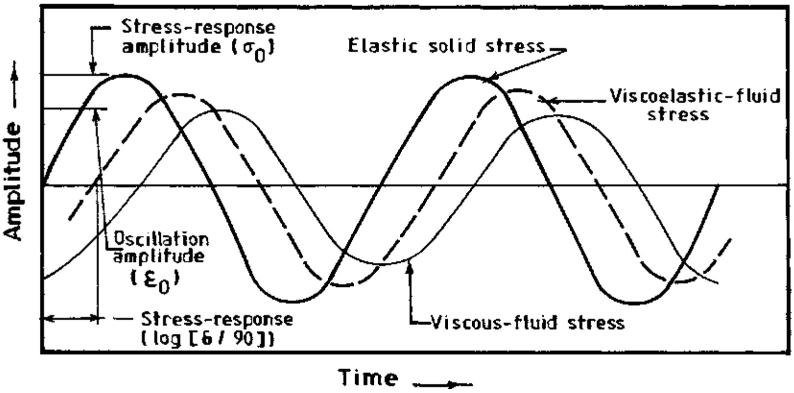


Figure 13.7 *The phase relation is shown between dynamic strain and stress for viscous, elastic, and viscoelastic materials.*

The lag angle between stress and strain is defined by the dissipation factor or tan δ given by

$$\tan \delta = \frac{G''}{G'} \tag{13.4}$$

where G′ is the real part of the complex modulus (G″ = G′ + iG″), and G″ is the imaginary part of the modulus. In physical terms, tan δ denotes material damping characteristics. It is a measure of the ratio of the energy dissipated as heat to the maximum energy stored in the material during one cycle of oscillation.

A convenient measure of damping is in terms of quantities determined from experiment. Thus,

$$\tan \delta = \frac{1}{\pi} \ln \frac{A_1}{A_2} \tag{13.5}$$

where A_1, and A_2 are the amplitudes of two consecutive peaks (Figure 13.7). Alternatively, this may be expressed in terms of log decrement (Δ) for free vibration instruments like the torsional pendulum.

$$\Delta = \ln \frac{A_1}{A_2} = \ln \frac{A_2}{A_3} = \frac{1}{n} \ln \frac{A_i}{A_{i+n}} \tag{13.6}$$

It follows from Equations 13.5 and 13.6 that

$$\Delta = \pi \tan \delta \tag{13.7}$$

E. IMPACT EXPERIMENTS

Polymers may also fail in service due to the effects of rapid stress loading (impact loads). Various test methods have been proposed for assessing the ability of a polymeric material to withstand impact loads. These include measurement of the area under the stress–strain curve in the high-speed (rapid) tensile test; the measurement of the energy required to break a specimen by a ball of known weight released from a predetermined height, the so-called falling ball or dart test; and the Izod and Charpy tests. The most popular of these tests methods are the Izod and Charpy impact strength tests. Essentially, the Izod test involves the measurement of the energy required to break a H × H in. notched cantilever specimen that is clamped rigidly at one end and then struck at the other end by a pendulum weight. In the case of the Charpy test, a hammerlike weight strikes a notched specimen that is rigidly held at both ends. The energy required to break the specimen is obtained from the loss in kinetic energy of the hammer

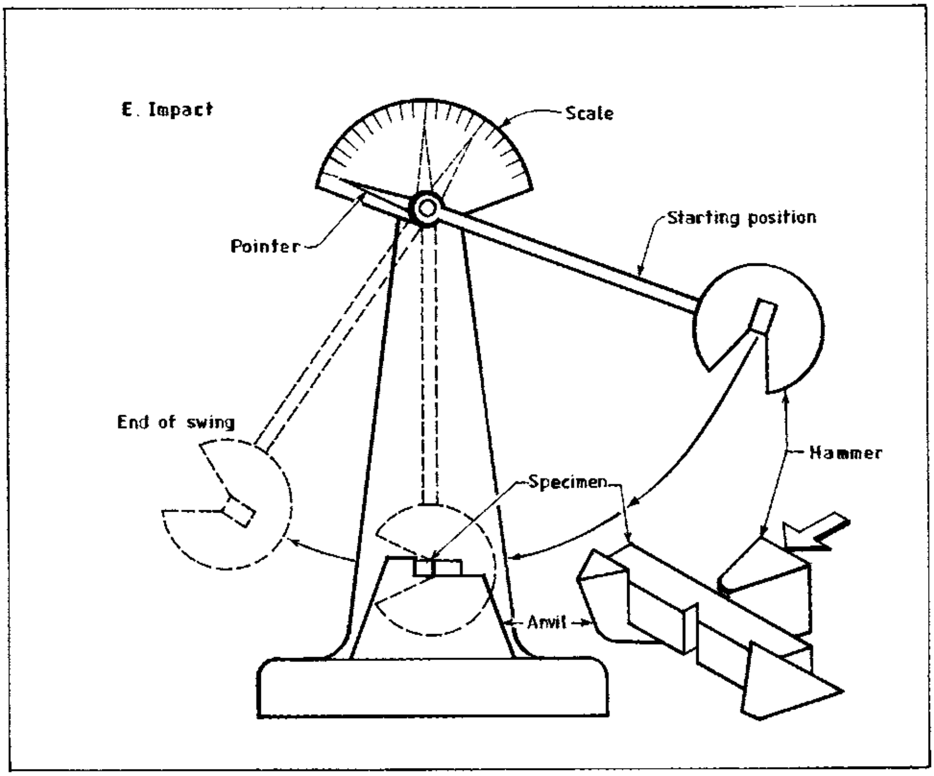


Figure 13.8 *Schematic representation of impact test. (From Fried, J.R., Plast. Eng., 38(7), 27, 1982. With permission.)*

(Figure 13.8). Another test that is emerging as a substitute for the impact test is the measurement of fracture toughness, which in essence measures the resistance to failure of a material with a predetermined crack.

Impact tests provide useful information in the selection of a polymer for a specific application, such as determining the suitability of a given plastic as a substitute for glass bottles or a replacement for window glass. Table 13.1 gives values of impact energies for some polymers. It can be seen that, in

Table 13.1 *Impact Energies of Some Polymers*

Polymer	Grade	Impact Energy (J)
Polystyrene	General purpose	0.34–0.54
Polystyrene	Impact	0.68–10.80
Poly(vinyl chloride)	Rapid	0.54–4.07
Poly(vinyl chloride)	Plasticized	1.36–20.33
Polypropylene	Unmodified	0.68–2.71
Poly(methyl methacrylate)	Molding	0.41–0.68
Poly(methylmethacrylate)	High impact	1.90
Polyoxymethylene		1.90–3.12
Nylon 6,6		1.36–3.39
Nylon 6		1.36–4.07
Poly(propyleneoxide)		6.78
Polycarbonate		16.26–24.39
Polyethylene	Low density	21.70
Polyethylene	High density	0.68–27.10
Polytetrafluoroethylene		4.07
Polypropylene		0.68–2.71

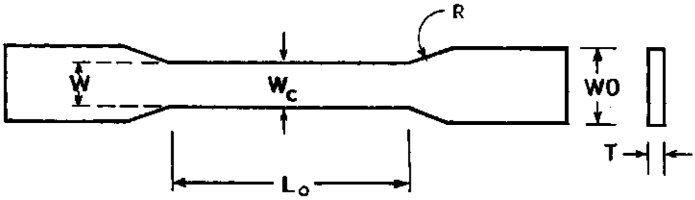


Figure 13.9 *Typical tensile specimen.*

general, brittle polymers like general-purpose polystyrene have low impact resistance, while most engineering thermoplastics like polyamides, polycarbonate, and polyoxymethylene and some commodity thermoplastics like polyethylene, polypropylene, and polytetrafluoroethylene have high impact strength.

III. STRESS–STRAIN BEHAVIORS OF POLYMERS

In stress–strain experiments, a polymer sample is pulled (deformed) at a constant elongation rate, and stress is measured as a function of time. Figure 13.9 shows a typical tensile specimen (ASTM D638M). Generally the polymer specimen, which may be rectangular or circular in cross-section, is molded or cut in the form of a dog bone. It is clamped at both ends and pulled at one of the clamped ends (usually downward) at constant elongation. The shape of the test specimen is designed to encourage failure at the thinner middle portion. The central section between clamps is called the initial gauge length, L_0. The load or stress is measured at the fixed end by means of a load transducer as a function of the elongation, which is measured by means of mechanical, optical, or electronic strain gauges. The experimental data are generally stated as engineering (nominal) stress (σ) vs. engineering (nominal) strain (ε). The engineering stress is defined as

$$\sigma = \frac{F}{A_0} \tag{13.8}$$

where F = the applied load
A_0 = the original cross-sectional area over the specimen

The engineering strain is given by

$$\varepsilon = \frac{L - L_0}{L_0} = \frac{\Delta L}{L_0} \tag{13.9}$$

where L_0 = original gauge length
ΔL = elongation or change in the gauge length
L = instantaneous gauge length

Engineering stress and strain are easy to calculate and are used widely in engineering practice. However, engineering stress–strain curves generally depend on the shape of the specimen. A more accurate measure of intrinsic material performance is plots of true stress vs. true strain. True stress σ_t is defined as the ratio of the measured force (F) to the instantaneous cross-sectional area (A) at a given elongation, that is,

$$\sigma_t = F/A \tag{13.10}$$

True strain is the sum of all the instantaneous length changes, dL, divided by the instantaneous length L.

$$\varepsilon_t = \int_{L_0}^{L} \frac{dL}{L} = \ln \frac{L}{L_0} \tag{13.11}$$

Some relation exists between true strain and engineering strain and between true stress and engineering stress. From Equation 13.11,

$$\varepsilon_t = \ln\frac{L}{L_0} = \ln\frac{L_0 + \Delta L}{L_0} = \ln(1+\varepsilon) \tag{13.12}$$

Up to the onset of necking, plastic deformation is essentially a constant volume process such that any extension of the original gauge length is accompanied by a corresponding contraction of the gauge diameter. Thus,

$$AL = A_0L_0 \tag{13.13}$$

That is,

$$\frac{L}{L_0} = \frac{A_0}{A} \tag{13.14}$$

But from Equation 13.12 it follows that

$$\varepsilon_t = \ln\frac{A_0}{A} \text{ and } \frac{A_0}{A} = 1+\varepsilon \tag{13.15}$$

Now

$$\sigma_t = \frac{F}{A} = \frac{F}{A_0}\cdot\frac{A_0}{A}$$

That is,

$$\sigma_t = \sigma(1+\varepsilon) \tag{13.16}$$

For small deformations, true stress and engineering stress are essentially equal. However, for large deformations the use of true strain is preferred because they are generally additive while engineering strain is not.

A. ELASTIC STRESS–STRAIN RELATIONS

When a material is subjected to small stresses, it responds elastically. This means that

1. The strain produced is reversible with stress.
2. The magnitude of the strain is directly or linearly proportional to the magnitude of the stress for material that exhibits Hookean behavior. This relation between stress and strain is known as Hooke's law and may be written as

$$\frac{\text{Stress}}{\text{Strain}} = \text{Constant} \tag{13.17}$$

Since stress may act on a plane in different ways, this constant is defined in different ways depending on the applied force and the resultant strain. Two of the most important types of stress are shear stress, which acts in a plane, and tensile stress, which acts normally or perpendicular to the plane. Normal stresses may be tensile or compressive.

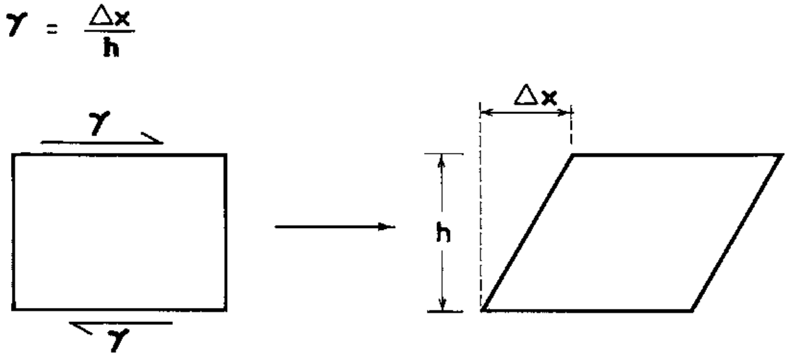


Figure 13.10 *Generation of shear strain from simple shear.*

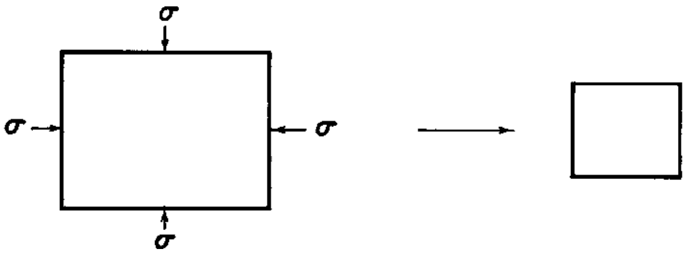


Figure 13.11 *Pure dilatation.*

Consider a parallelepiped that has been deformed by application of a force τ (Figure 13.10). The elastic shear strain γ is the amount of their ΔX divided by the distance, h, over which the shear has occurred:

$$\gamma = \frac{\Delta x}{h} \tag{13.18}$$

For small strains, this is simply the tangent of the angle of deformation. In pure shear, Hooke's law is expressed as

$$\tau/\gamma = G \tag{13.19}$$

where τ is the shear stress and G is the shear modulus. Deformation due to pure shear does not result in a change in volume, but produces a change in shape.

Now suppose the parallelepiped is subjected to equal normal pressure (compressive stress, $^{-}\sigma$) in such a way that its shape remains unchanged but the volume, V, is changed by the amount ΔV (Figure 13.11). Deformation of this type is called pure dilatation, and Hooke's law for elastic dilatation is written as

$$\sigma = KD \tag{13.20}$$

where K is the bulk modulus and D is the dilatation strain given by $\Delta V/V$. We reemphasize that pure dilatation does not produce a change in shape but produces a change in volume.

In a majority of cases, a body under stress experiences neither pure shear nor pure dilatation. Generally, a mixture of both occurs. Such a situation is exemplified by uniaxial loading which, of course, may be tensile or compressive. Here a test specimen is loaded axially resulting in a change in length, ΔL. The axial strain, ε, is related to the applied stress in an elastic deformation by Hooke's law:

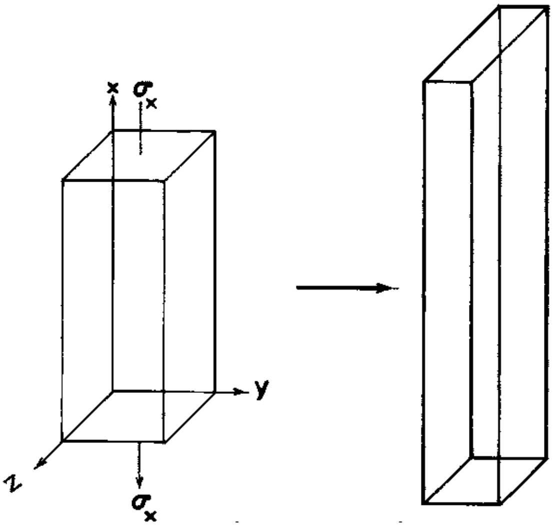


Figure 13.12 *Axial elongation accompanied by transverse contractions.*

$$\sigma = E\varepsilon \tag{13.21}$$

where E is Young's modulus (modulus of elasticity).

During extension, specimen elongation in the axial or longitudinal direction is accompanied by a contraction in the perpendicular transverse directions, given by the compressive strains $\varepsilon_y = \varepsilon_z$ as shown in Figure 13.12. Poisson's ratio, denoted by the parameter ν, is the ratio of the induced transverse strains to the axial strain.

$$\nu = -\frac{\varepsilon_y}{\varepsilon_x} = -\frac{\varepsilon_z}{\varepsilon_x} \tag{13.22}$$

The negative sign indicates that the strains ε_z and ε_y are due to contractions.

For incompressible materials, the volume of the specimen remains constant during deformation, and ν is 0.5. This is generally not true, although it is approached by natural rubber with ν = 0.49. For most polymeric materials, there is a change in volume ΔV, which is related to Poisson's ratio by

$$\Delta V = (1 - 2\nu)\,\varepsilon V_0 \tag{13.23}$$

or, in general,

$$\nu = \frac{1}{2}\left[1 - \frac{1}{V}\,\frac{\partial V}{\partial \varepsilon}\right]$$

where V_0 is the initial (unstrained) volume and ΔV is the difference between the volume V at a given strain ε and the initial volume.

For materials that are isotropic and under deformations where Hooke's law is valid, the elastic constants and ν are related according to the following equations:

$$E = 2G(1 + \nu) \tag{13.24}$$

$$E = 3K(1 - 2\nu) \tag{13.25}$$

Example 13.1: In a tension test, a brittle polymer experienced an elastic engineering strain of 2% at a stress level of 35 MN/m^2. Calculate

a. The true stress
b. The true strain
c. The fractional change in cross-sectional area

Solution: Under elastic conditions, deformation is a constant-volume process, hence:

$$\sigma_t = \sigma(1+\varepsilon)$$

$$\varepsilon = 0.02$$

$$\sigma_t = 35\,(1+0.02)\ \mathrm{MN/m^2}$$

$$= 35.7\ \mathrm{MN/m^2}$$

$$\varepsilon_t = \ln\,(1+\varepsilon)$$

$$= \ln\,(1+0.02)$$

$$= 0.0198$$

$$\frac{A_0 - A}{A_0} = 1 - \frac{A}{A_0} = 1 - \frac{1}{1+\varepsilon}\ \text{ since }\ \frac{A_0}{A} = 1+\varepsilon$$

$$= 1 - \frac{1}{1.02}$$

$$= 0.0196$$

Example 13.2: Polypropylene has an elastic modulus of 2 × 10^5 psi and Poisson's ratio of 0.32. For a strain of 0.05, calculate the shear stress and the percentage change in volume.

Solution:

$$E = 2G\,(1+\nu)$$

$$G = \frac{E}{2(1+\nu)}$$

$$\tau = G\gamma = \frac{E}{2(1+\nu)}\gamma$$

$$= \frac{2\times10^5}{2(1+0.32)} \times 0.05$$

$$= 3.79\times10^3\ \text{psi}$$

$$\Delta V = (1-2\nu)\,\gamma V_0$$

$$\frac{\Delta V}{V_0} = (1-2\nu)\gamma$$

$$= [1-2(0.32)]\ 0.05$$

$$= 1.8\%$$

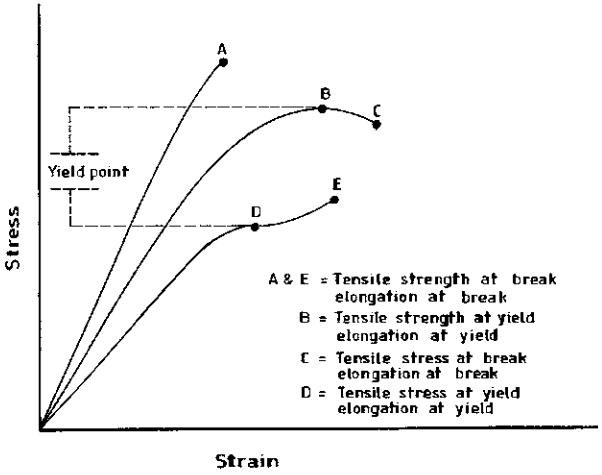


Figure 13.13 *Engineering data from stress–strain tests.*

IV. DEFORMATION OF SOLID POLYMERS

To relieve stress, all materials under the influence of external load undergo some deformation. In some cases, this deformation may be quite large and perceptible, like the boughs of a mango tree under the weight of its fruit. In some other cases, deformation may be imperceptibly small, for example, a fly perching uninvitedly on the dining table. Irrespective of our ability to observe it, some deformation always occurs when stresses are imposed on a material.

It is known that up to a certain limiting load, a solid will recover its original dimensions on the removal of the applied loads. This ability of deformed bodies to recover their original dimensions is known as elastic behavior. Beyond the limit of elastic behavior (elastic limit), a material will experience a permanent set or deformation even when the load is removed. Such a material is said to have undergone plastic deformation. For most materials, Hooke's law is obeyed within the elastic limit, that is, stress proportional to strain. However, proportionality between stress and strain does not always hold when a material exhibits elastic behavior. A typical example is rubber, which is elastic but does not show Hookean behavior over the entire elastic region.

Figure 13.13 illustrates the basic data on mechanical properties that are obtainable from stress–strain experiments. The gradient of the initial linear portion of the curve, within which Hooke's law is obeyed, gives the elastic, or Young's, modulus. The determination of the elastic limit is tedious and very frequently depends on the sensitivity of the strain-measuring devices employed. Consequently, it is common practice to replace it with the proportional limit, which defines the point where the nonlinear response is observed on the stress–strain curve. The maximum on the curve denotes the yield strength. For engineering purposes, this marks the limit of usable elastic behavior or the onset of plastic deformation. The stress at which fracture occurs (material breaks apart) is referred to as the ultimate tensile strength or, simply, tensile strength σ_B. The strains associated with the yield point or the fracture point are referred to as the elongation at yield and elongation at break, respectively. Typical values of these mechanical properties for selected polymers are shown in Table 13.2.

To emphasize the usefulness of stress-strain measurements, it is necessary to highlight the physical significance of the parameters defined above or the mechanical quantities derivable from these parameters:[4]

- Stiffness — Defines the ability to carry stress without changing dimension. The magnitude of the modulus of elasticity is a measure of this ability or property.
- Elasticity — Stipulates the ability to undergo reversible deformation or carry stress without suffering a permanent deformation. It is indicated by the elastic limit or, from a practical point of view, the proportional limit or yield point.
- Resilience — Defines the ability to absorb energy without suffering permanent deformation. The area under the elastic portion of the stress-strain curve gives the resilient energy.

Table 13.2 *Typical Mechanical Properties of Selected Polymers*

Polymer	Poisson Ratio	Elastic Modulus (10^3 psi)	Yield Strength (10^3 psi)	Ultimate Strength (10^3 psi)	Elongation to Fracture (%)
Polypropylene	0.32	1.5–2.25	3.4	3.5–5.5	200–600
Polystyrene	0.33	4–5	—	5.5–8	1–2.5
Poly(methylmethacrylate)	0.33	3.5–5	7–9	7–10	2–10
Polyethylene (LDPE)	0.38	0.2–0.4	1–2	1.5–2.5	400–700
Polycarbonate	0.37	3.5	8–10	8–10	60–120
Poly(vinyl chloride (PVC), rigid	0.40	3–6	8–10	6–11	5–60
Polytetrafluoroethylene	0.45	0.6	1.5–2	2–4	100–350

From Fried, J.R., *Plast. Eng.*, 38(7), 27, 1982. With permission.

- Strength — Indicates the ability to sustain dead load. It is represented by the tensile strength or the stress at which the specimen ruptures σ_B.
- Toughness — Indicates the ability to absorb energy and undergo extensive plastic deformation without rupturing. It is measured by the area under the stress-strain curve.

The response of material to applied stress may be described as ductile or brittle depending on the extent to which the material undergoes plastic deformation before fracture. Ductile materials possess the ability to undergo plastic deformation. For engineering purposes, an appropriate measure of ductility is important, because this property assists in the redistribution of localized stresses. On the other hand, brittle materials fail with little or no plastic deformation. Brittle materials have no ability for local yielding; hence local stresses build up around inherent flaws, reaching a critical level at which abrupt failure occurs. Figure 13.14 shows the broad spectrum of stress-strain behavior of polymeric materials, while Table 13.3 lists the general trends in the magnitude of various mechanical parameters typical of each behavior.

From the preceding discussion (Figure 13.14 and Table 13.3), it is obvious that polymers have a broad range of tensile properties. It is therefore instructive to examine these properties more closely and present current molecular interpretation at the observed properties. Figure 13.15 is a schematic representation of the macroscopic changes that occur in polymers that exhibit cold drawing during a tensile test.

At small strains, polymers (both amorphous and crystalline) show essentially linear elastic behavior. The strain observed in this phase arises from bond angle deformation and bond stretching; it is recoverable on removing the applied stress. The slope of this initial portion of the stress–strain curve is the elastic modulus. With further increase in strain, strain-induced softening occurs, resulting in a reduction of the instantaneous modulus (i.e., slope decreases). Strain-softening phenomenon is attributed to uncoiling

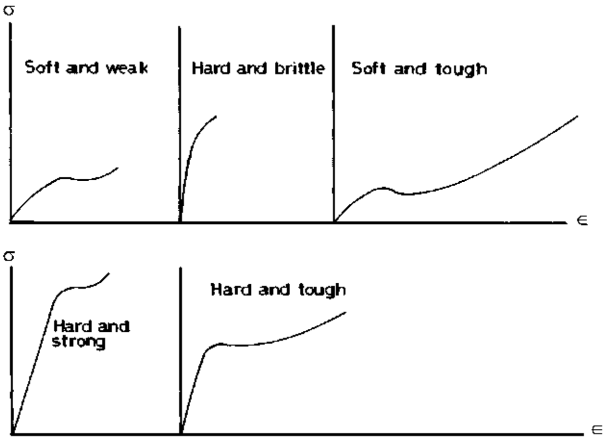


Figure 13.14 *Typical stress–strain curves for polymeric materials. (From Winding, C.C. and Hiatt, G.D., Polymer Materials, McGraw-Hill, New York, 1961. With permission.)*

Table 13.3 *Characteristic Features of Polymer Stress–Strain Behavior*

Material Stress-Strain Behavior	Elastic Modulus	Yield Point	Tensile Strength	Elongation at Break
Soft and weak (polymer gels)	Low	Low	Low	Moderate
Hard and brittle (PS)	High	Practically nonexistent	High	Low
Hard and strong (PVC)	High	High	High	Moderate
Soft and tough (rubbers and plasticized PVC)	Low	Low	Moderate	High
Hard and tough (cellulose acetate, nylon)	High	High	High	High

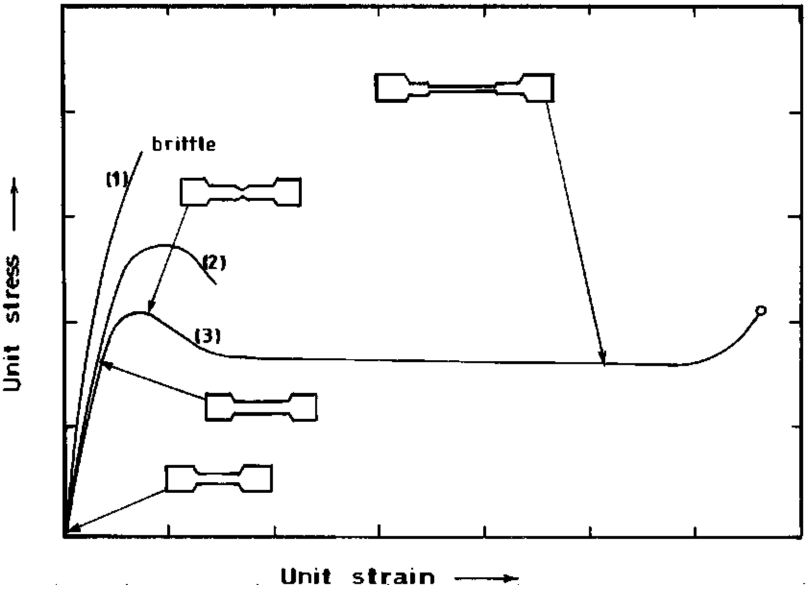


Figure 13.15 *Schematic representation of macroscopic changes in tensile specimen shape during cold drawing. (From Fried, J.R., Plast. Eng., 38(7), 27, 1982. With permission.)*

and straightening of polymer chains, and the associated strain is recoverable. For hard, rigid polymers like polystyrene that show little or no yielding, a further increase in stress results in brittle failure (curve 1). In the case of ductile polymers, including engineering thermoplastics (polyamides, high-impact polystyrene), the stress–strain curve exhibits a maximum: the stress reaches a maximum value called the yield stress (more precisely, upper yield stress) and then decreases to a minimum value (drawing stress or lower yield stress). At this point, the sample may either rupture or experience strain hardening before failure. At the drawing stress, polymers that strain-harden require no further increase in applied stress to induce further elongation. It is believed that at the yield stress some slippage of polymer chains past each other occurs. The attendant deformation is recovered partially and slowly on the removal of the applied stress. What happens after the upper yield stress depends on the ability of the polymer material to strain-harden. The onset of necking is associated with an increase in the local stress at the necked region due to the reduction in the load-bearing cross-sectional area. This results in extensive deformation of the polymer material in the vicinity of the necked region, and the polymer chains in the amorphous regions undergo conformational changes and become oriented (stretched) in the direction of the applied tensile stress. The extended chains resist further deformation. If this orientation-induced hardening or resistance is sufficiently high to sustain or overcome the increased stress due to the reduction in the cross-sectional area (following the onset of necking), then further deformation (extension) of the specimen will occur only through the propagation of the neck along the sample. On the other hand, if the increased stress at the neck region increases faster than orientation hardening, then the necked region deepens continuously, leading ultimately to local failure at that region.

The molecular orientation of polymer chains is reflected in the observed changes of shape of the specimen (curve 3, Figure 13.15). Up to the yield stress, specimen deformation is essentially homogeneous. This means that deformation occurs uniformly over the entire gauge length of the specimen. At the yield stress, local instability ensues and the specimen begins to neck at some point along its gauge length. For specimens that exhibit orientation hardening before failure, the neck stabilizes; that is, the specimen shows no further reduction in cross-sectional area, but the neck propagates along the length of the gauge section until the specimen finally ruptures. The process of neck propagation is referred to as cold drawing.

Example 13.3: The mechanical properties of nylon 6,6 vary with its moisture content. A nylon specimen with a moisture content (MC) of 2.5% has an elastic modulus of 1.2 GN/m^2, while that for a sample of moisture content of 0.2% is 2.8 GN/m^2. Calculate the elastic energy or work per unit volume in each sample subjected to a tensile strain of 10%.

Solution:

$$\text{Work} = [\text{Force, (F)}][\text{increment of extension, (dL)}]$$

$$\text{Work per unit volume} = \frac{\text{FdL}}{\text{AL}} = \int_0^\varepsilon \sigma d\varepsilon$$

In the elastic region, Hooke's law holds, i.e., $\sigma = E\varepsilon$.

$$\text{Work per volume} = \int_0^\varepsilon E\varepsilon d\varepsilon = \frac{E\varepsilon^2}{2}$$

Sample 1 (2.5% MC):

$$\text{Elastic energy} = \frac{(1.2 \times 10^9\ \text{N/m}^2)(0.1)^2}{2}$$

$$= 0.6 \times 10^9 \times 10^{-2}\ \text{N-m/m}^3$$

$$= 6\ \text{MJ/m}^3$$

Sample 2 (0.2% MC):

$$\text{Elastic energy} = \frac{(2.8 \times 10^9\ \text{N/m}^2)(0.1)^2}{2}$$

$$= 14\ \text{MJ/m}^3$$

Example 13.4: Two nylon samples of moisture contents 2.5% and 0.2% have ε_B of 300% and 60%, respectively. Calculate the toughness of each sample if the stress-strain curve of nylon for plastic deformation is given by

$$\sigma = 8500\ \varepsilon^{0.1}\ \text{psi}$$

Comment on your results.

Solution:

$$\text{Work per unit volum (toughness)} = \int_0^{\varepsilon_B} \sigma d\varepsilon$$

$$= \int_0^{\varepsilon_B} 8500\varepsilon^{0.1} d\varepsilon$$

$$= 7727\varepsilon^{1.1} \text{ in.-lb/in.}^3$$

$$\text{Nylon 2.5\% MC, toughness} = 7727(3)^{1.1}$$

$$= 25{,}873 \text{ in.-lb/in.}^3$$

$$\text{Nylon 0.2\% MC, toughness} = 7727(0.6)^{1.1}$$

$$= 4405 \text{ in.-lb/in.}^3$$

As MC increased from 0.2 to 2.5%, toughness increased by about 500%.

V. COMPRESSION VS. TENSILE TESTS[6]

Recall that normal stresses can be either tensile or compressive. However, the main focus of our discussion so far has been on tensile tests. Let us now examine the behavior of polymers in compression.

Figures 13.16 and 13.17 are plots of the compressive stress–strain data for two amorphous and two crystalline polymers, respectively, while Figure 13.18 shows tensile and compressive stress–strain behavior of a normally brittle polymer (polystyrene). The stress–strain curves for the amorphous polymers are characteristic of the yield behavior of polymers. On the other hand, there are no clearly defined yield points for the crystalline polymers. In tension, polystyrene exhibited brittle failure, whereas in compression it behaved as a ductile polymer. The behavior of polystyrene typifies the general behavior of polymers. Tensile and compressive tests do not, as would normally be expected, give the same results. Strength and yield stress are generally higher in compression than in tension.

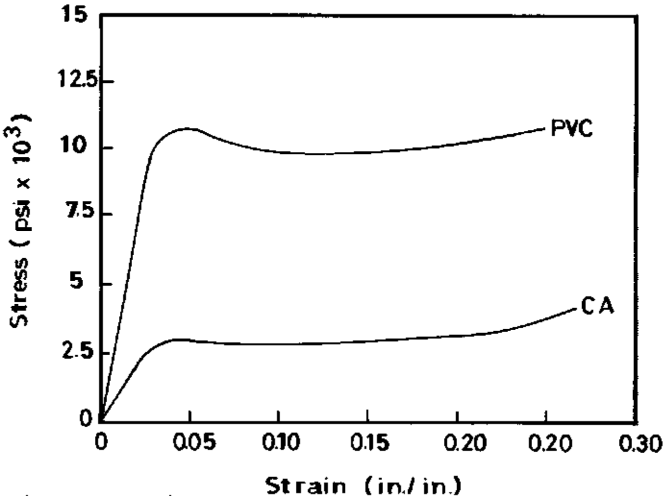


Figure 13.16 *Compressive stress–strain data for two amorphous polymers: polyvinyl chloride (PVC) and cellulose acetate (CA). (From Kaufman, H.S. and Falcetta, J.J., Eds., Introduction to Polymer Science and Technology, John Wiley & Sons, New York, 1977. With permission.)*

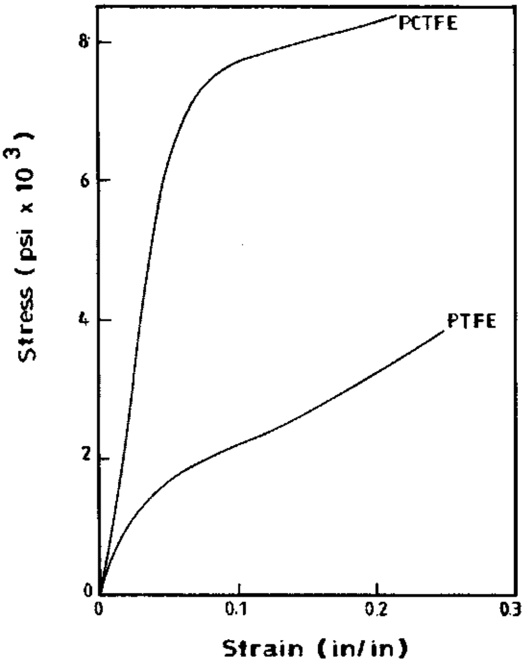


Figure 13.17 *Compressive stress–strain data for two crystalline polymers: polytetrafluoroethylene (PTFE) and polychlorotrifluoroethylene (PCTFE). (From Kaufman, H.S. and Falcetta, J.J., Eds., Introduction to Polymer Science and Technology, John Wiley & Sons, New York, 1977. With permission.)*

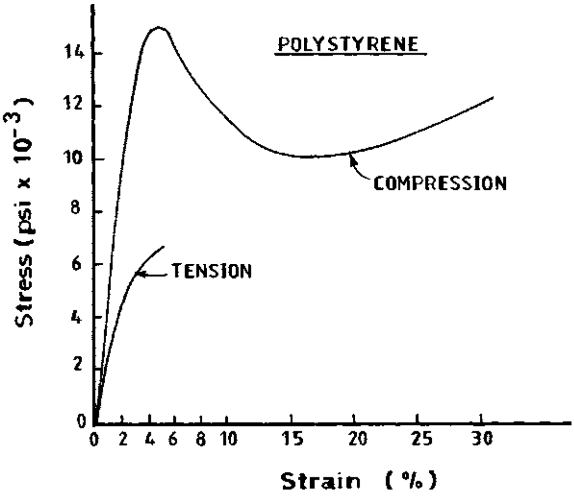


Figure 13.18 *The stress–strain behavior of a normally brittle polymer, polystyrene, under tension and compression. (From Nielsen, L.E., Mechanical Properties of Polymers and Composites, Vol. 2, Marcel Dekker, New York, 1974. With permission.)*

The tensile properties of brittle materials depend to a considerable extent on the cracks and other flaws inherent in the material. As we shall see later, for a material in tension, brittle fracture occurs through the propagation of one of these cracks. Since load cannot be transmitted through free surfaces, the presence of cracks essentially creates concentrations of stress intensity. When this tensile stress exceeds the fracture strength of the material, fracture occurs. It is apparent, therefore, that in contrast to tensile stresses, which open cracks, compressive stresses tend to close them. This could conceivably enhance the tensile strength.

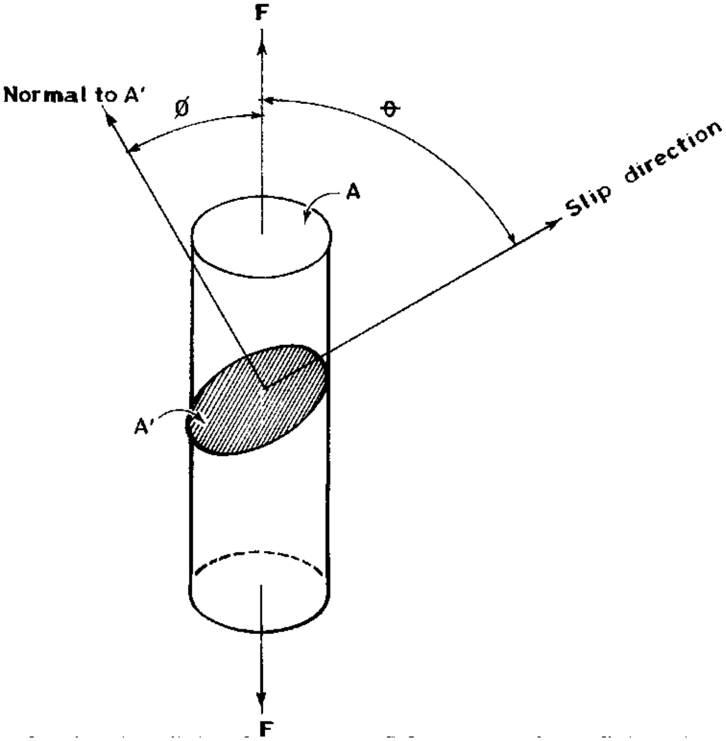


Figure 13.19 *Generation of shear stress due to uniaxial loading.*

The conditions for fracture are dictated by the magnitude of the imposed tensile stresses. On the other hand, the extent of permanent (plastic) deformation produced by a given load depends primarily on the magnitude of the shear stresses induced by the load. For example, the application of a uniaxial load, F, on a material generates shear stresses, τ, in certain geometric planes in particular directions. The magnitude of the generated shear stresses depends on the orientations of the planes and directions to the tensile axis. This can be illustrated by considering Figure 13.19.

Let us compute the shear stresses generated on the sectional plane A′ in a direction of angle θ to the tensile axis.[8] The normal to plane A′ makes an angle ϕ with the tensile axis. The load on A′ in the direction of deformation (slip) is F cos θ. Therefore, the stress generated on A′ is given by

$$\tau = \frac{F\cos\theta}{A/\cos\phi} \tag{13.26}$$

But by definition, F/A = σ, hence

$$\tau = \sigma\cos\theta\cos\phi \tag{13.27}$$

For a fixed value of ϕ, the minimum value of θ is $\pi/2 - \phi$. Thus Equation 13.27 becomes

$$\tau = \sigma\cos\phi\cos\left(\frac{\pi}{2} - \phi\right) = \sigma\cos\phi\sin\phi \tag{13.28}$$

The maximum value of τ occurs when $\phi = \pi/4$, that is,

$$(\tau)_{\max} = \sigma\,(0.707)^2 = \frac{\sigma}{2} \tag{13.29}$$

Plastic deformation occurs when τ_{max} is at least equal to the yield strength of the material, i.e., for yielding to occur.

$$\tau_{max} \geq \sigma_y \tag{13.30}$$

The yield criterion for simple uniaxial stress dictates theoretically that for plastic deformation to occur, the imposed tensile stress must be at least twice the magnitude of the shear stresses generated. In other words, the tensile strength must be at least twice the shear strength. This is often not the case in practice; tensile strength is generally less than twice the shear strength. Also, the fact that contrary to theoretical prediction, the yield value for a given material is not the same in tension and in compression suggests that for polymers, plastic deformation may not be due entirely to shear stresses alone.

VI. EFFECTS OF STRUCTURAL AND ENVIRONMENTAL FACTORS ON MECHANICAL PROPERTIES

As we saw in the preceding discussion, several mechanical parameters can be derived from stress-strain tests. Two of these parameters are of particular significance from a design viewpoint. These are strength and stiffness. For some applications, the ultimate tensile strength is the useful parameter, but most polymer products are loaded well below their breaking points. Indeed, some polymers deform excessively before rupture and this makes them unsuitable for use. Therefore, for most polymer applications, stiffness (resistance to deformation under applied load) is the parameter of prime importance. Modulus is a measure of stiffness. We will now consider how various structural and environmental factors affect modulus in particular and other mechanical properties in general.

A. EFFECT OF MOLECULAR WEIGHT

In contrast to materials like metals and ceramics, the modulus of polymers shows strong dependence on temperature. Figure 13.20 is a schematic modulus–temperature curve for a linear amorphous polymer like atactic polystyrene. Five regions of viscoelastic behavior are evident: a hard and glassy region followed by a transition from the glassy to rubbery region. The rubbery plateau, in turn, is followed by a transition to the melt flow region. The glassy-to-rubbery transition is denoted by T_g, while the rubber-to-melt-flow transition is indicated by T_{fl}. There is a drop in modulus of about three orders of magnitude near the T_g. There is a further modulus drop at T_{fl}. If the T_g is above room temperature, the material will be a rigid polymer at room temperature. If, however, the T_g occurs below room temperature, the material will be rubbery and might even be a viscous liquid at room temperature.

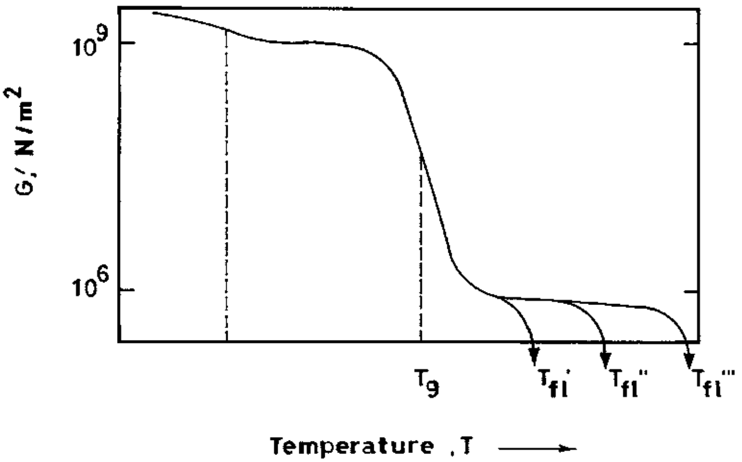


Figure 13.20 *Schematic representation of the effect of molecular weight on shear modulus–temperature curve. T_g is the glass transition temperature while T_{fl} is the flow temperature. T_{fl}', T_{fl}'', $T_{fl'''}$ represent low-, medium-, and high-molecular-weight materials, respectively.*

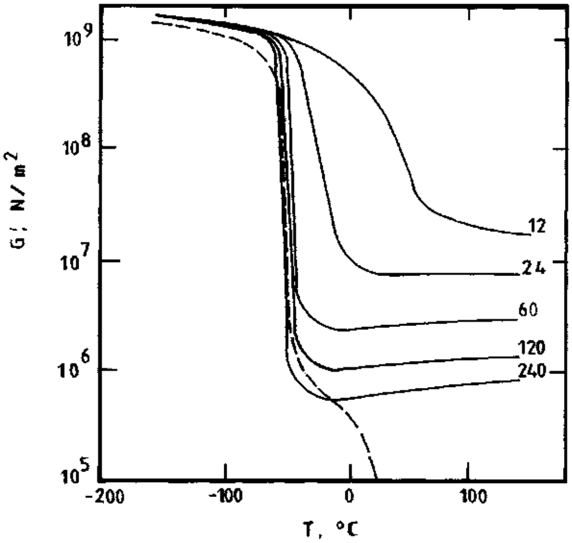


Figure 13.21 *Effect of cross-linking on shear modulus of natural rubber: (———) cross-linked, the approximate mean number of chain atoms between successive cross-links is indicated; (– – – –) noncross-linked. (From Heijboer, J., Br. Polym. J., 1, 3, 1969. With permission.)*

The molecular weight has practically no effect on the modulus in the glassy region (below T_g); the drop in modulus and the location of the T_g are also almost independent of the molecular weight. We recall that T_g is the onset of cooperative motion of chain segments. It is therefore to be expected that the number of chain entanglements (which increases with increasing molecular weight) will hardly affect such segmental mobility, and consequently T_g is independent of molecular weight. In contrast to the T_g, T_{fl} is strongly dependent on the molecular weight. Movement of entire molecules is associated with viscous flow. This obviously will depend on the number of entanglements. The higher the molecular weight (the higher the number of entanglements), the higher must be the temperature at which viscous flow becomes predominant over rubbery behavior. Consequently, for high molecular weight polymer, T_{fl} is high and the rubbery plateau long, whereas for low-molecular-weight polymers the rubbery plateau is absent or very short.

B. EFFECT OF CROSS-LINKING

Figure 13.21 shows the effect of cross-linking on the modulus of natural rubber cross-linked using electron irradiation. M_c is the average molecular weight between cross-links. It is a measure of the cross-link density; the smaller the value of M_c, the higher the cross-link density. In the glassy region, the increase in modulus due to cross-linking is relatively small. Evidently the principal effect of cross-linking is the increase in modulus in the rubbery region and the disappearance of the flow regions. The cross-linked elastomer exhibits rubberlike elasticity even at high temperature. Cross-linking also raises the glass transition temperature at high values of cross-link density. The glass-to-rubber transition is also considerably broadened.

Cross-linking involves chemically connecting polymer molecules by primary valence bonds. This imposes obvious restrictions on molecular mobility. Consequently, relative to the uncross-linked polymer, cross-linking increases polymer ability to resist deformation under load, i.e., increases its modulus. As would be expected, this effect is more pronounced in the rubbery region. In addition, the flow region is eliminated in a cross-linked polymer because chains are unable to slip past each other. Since T_g represents the onset of cooperative segmental motion, widely spaced cross-links will produce only a slight restriction on this motion. However, as the cross-link density is increased, the restriction on molecular mobility becomes substantial and much higher energy will be required to induce segmental motion (T_g increases).

Example 13.5: The densities of hard and soft rubbers are 1.19 and 0.90 g/cm^3, respectively. Estimate the average molecular weight between cross-links for both materials if their respective moduli at room temperature are 10^6 and 10^8 dynes/cm^2.

Solution: The average molecular weight between cross-links, M_c is given by

$$M_c = \rho \frac{RT}{G}$$

where ρ = density, R = gas constant, T = absolute temperature, and G = shear modulus.

$$\begin{aligned} M_c &= \frac{\left(1.19\ \mathrm{g/cm^3}\right)\left(8.31 \times 10^7\ \mathrm{erg/mol\ K}\right)\left(300\ \mathrm{K}\right)}{\left(10^8\ \mathrm{dyne/cm^2}\right)} \\ &= 300 \left(\frac{\mathrm{g}}{\mathrm{mol}}\right)\left(\frac{\mathrm{erg}}{\mathrm{cm^2}}\right)\left(\frac{\mathrm{cm^3}}{\mathrm{dyne}}\right) \\ &= 300 \left(\frac{\mathrm{g}}{\mathrm{mol}}\right)\left(\frac{\mathrm{erg}}{\mathrm{cm^3}}\right)\left(\frac{\mathrm{cm^3}}{\mathrm{dyne\text{-}cm}}\right) \\ &= 300\ \mathrm{g/mol} \end{aligned}$$

Soft rubber:

$$\begin{aligned} M_c &= \frac{\left(0.90\ \mathrm{g/cm^3}\right)\left(8.31 \times 10^7\ \mathrm{erg/mol\ K}\right)\left(300\ \mathrm{K}\right)}{10^7\ \mathrm{dyne/cm^2}} \\ &= 2250\ \mathrm{g/mol} \end{aligned}$$

C. EFFECT OF CRYSTALLINITY

Crystallinity in a polymer is the result of ordered molecular aggregation, with molecules held together by secondary valence bonds. Therefore, crystallinity may be viewed as a form of physical cross-linking which is thermoreversible. Since crystallites have much higher moduli than the amorphous segments, crystallites can also be regarded as rigid fillers in an amorphous matrix. The effect of crystallinity on modulus becomes readily understandable on the basis of these concepts. Figure 13.22 is an idealized modulus–temperature curve for various degrees of crystallinity. We observe that crystallinity has only a small effect on modulus below the T_g but has a pronounced effect above the T_g. There is a drop in modulus at the T_g, the intensity of which decreases with increasing degree of crystallinity. This is followed by a much sharper drop at the melting point. Crystallinity has no significant effect on the location of the T_g, but the melting temperature generally increases with increasing degree of crystallinity. These features are evident for two polyethylenes of different crystallinities (Figure 13.23). Alkathene is branched with a density of 0.92 g/cm^3, while the Ziegler polyethylene is linear and has a density of 0.95 g/cm^3. The greater crystallinity of the Ziegler polyethylene results in a higher modulus, especially above 0°C.

D. EFFECT OF COPOLYMERIZATION

In discussing the effect of copolymerization on modulus, it is necessary to make a distinction between random and alternating copolymers and block and graft comonomers. Random and alternating copolymers are necessarily homogeneous, while block and graft copolymers with sufficiently long sequences exhibit phase separation. Random and alternating copolymers show a single transition that is intermediate between those of the two homopolymers of A and B (Figure 13.24). Copolymerization essentially shifts

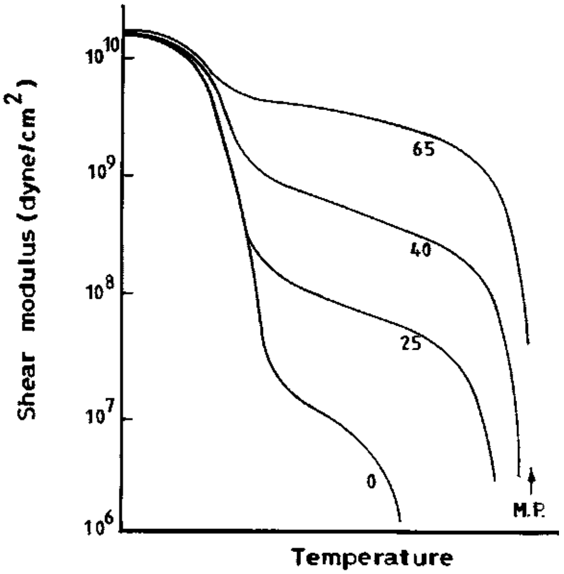


Figure 13.22 *Effect of crystallinity on the modulus–temperature curve. The numbers of the curves are rough approximations of the percentage of crystallinity. Modulus units = dynes/cm^2. (From Nielsen, L.E., Mechanical Properties of Polymers and Composites, Vol. 2, Marcel Dekker, New York, 1974. With permission.)*

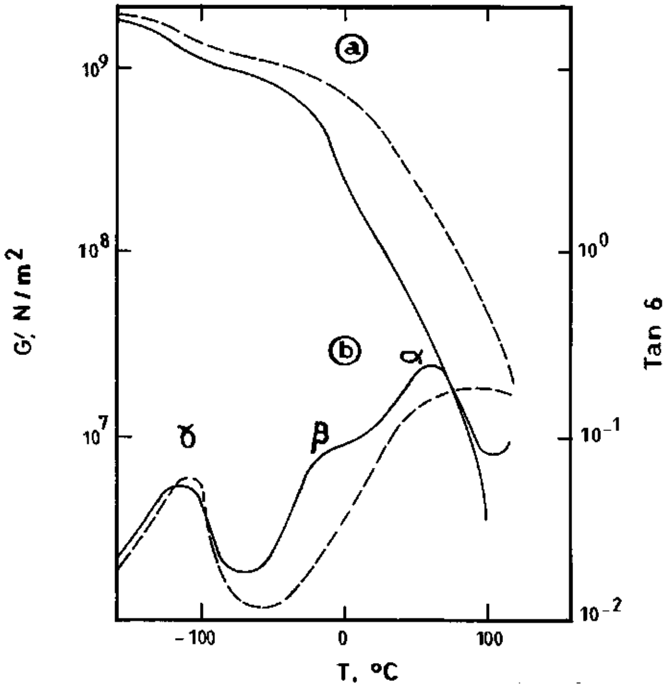


Figure 13.23 *Shear modulus (a) and damping (b) at I Hz as a function of temperature for a branched and a linear polyethylene: (––––) Ziegler polyethylene; (———) Alkathene. (From Heijboer, J., Brit. Polymer J., 1, 3, 1969. With permission.)*

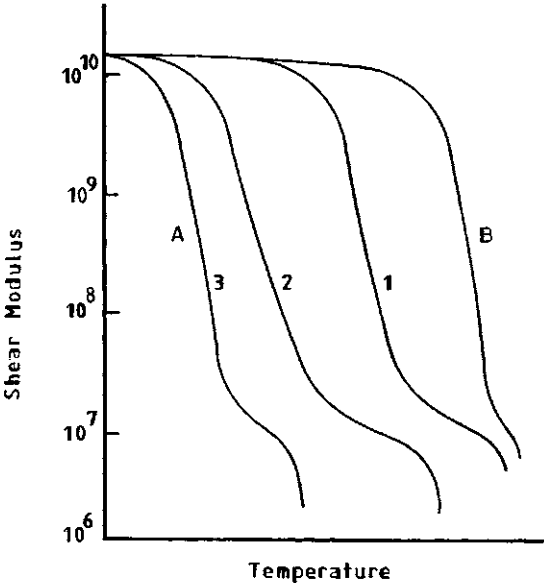


Figure 13.24 *Effect of plasticization or copolymerization on the modulus–temperature curve. The curves correspond to different copolymer compositions. (B) Unplasticized homopolymer; (A) either a second homopolymer or plasticized B. (From Nielsen, L.E., Mechanical Properties of Polymers and Composites, Vol. 2, Marcel Dekker, New York, 1974. With permission.)*

the modulus–temperature curve the same way as T_g. In addition, there is a broadening of the transition due to polymer composition heterogeneity. We recall that in copolymer the reactivities of the monomers are generally different. Consequently, the initial polymer formed is richer in the more reactive monomer while that formed later is richer in the less reactive monomer. This leads overall to a polymer of heterogeneous composition and consequently a distribution of glass transitions (broad transition region).

Block and graft copolymers, which exist as a two-phase system, have two distinct glass transitions, one for each of the homopolymers. Consequently, the modulus–temperature curve shows two steep drops. The value of modulus in the plateau between the two glass transitions depends upon the ratio of the components and upon which of the two phases is dispersed in the other. These features are illustrated in Figure 13.25 for a styrene–butadiene–styrene block copolymer. The glass transition of the butadiene phase near –80°C and that for the styrene phase near 110°C are clearly evident. Between the T_g of butadiene and the T_g of styrene, the value of the modulus is determined by the amount of polystyrene; the rubbery butadiene phase is cross-linked physically by the hard and glassy polystyrene phase. It is noteworthy that while styrene–butadiene–styrene block copolymers have high tensile strength, butadiene–styrene–butadiene copolymers have a very low tensile strength, showing that strength properties are dictated by the dispersed phase.

In both cases of copolymerization, there is a noticeable decrease in the slope of the modulus curve in the region of the inflection point. This, in essence, means a decrease in the modulus in the rubbery region. This contrasts with the chemically cross-linked systems where the modulus in the rubbery region shows some increase with increasing temperatures. In the copolymer system, the molecules are interconnected by physical cross-links due to secondary forces. These cross-links can be disrupted reversibly by heating, and this forms the basis of the new class of copolymers referred to as thermoplastic elastomers.

E. EFFECT OF PLASTICIZERS

Plasticizers are low-molecular-weight, usually high boiling liquids that are capable of enhancing the flow characteristics of polymers by lowering their glass transition temperatures. Modulus, yield, and tensile strengths generally decrease with the addition of plasticizers to a polymer. In general, on

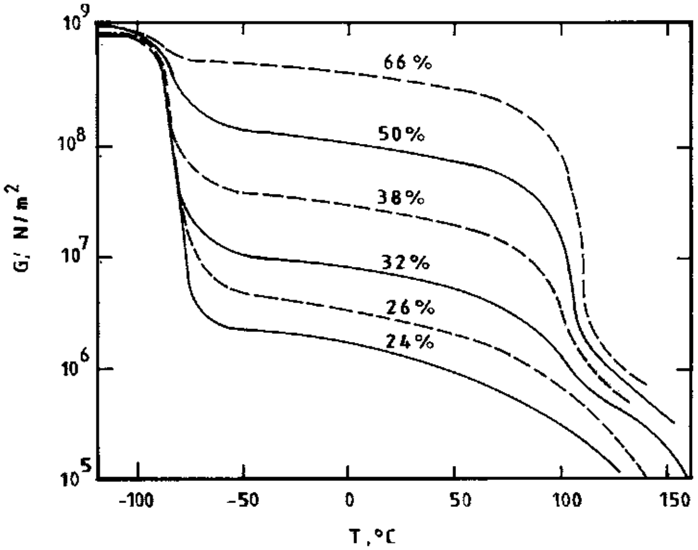
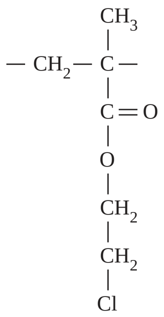


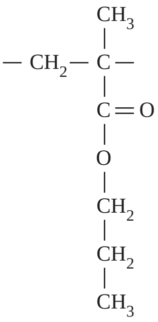
Figure 13.25 *Shear modulus as a function of temperature for styrene–butadiene–styrene block copolymers. Wt.% styrene is indicated on each curve. (From Heijboer, J., Br. Polymer J., 1, 3, 1969. With permission.)*

plasticization a polymer solid undergoes a change from hard and brittle to hard and tough to soft and tough. This is exemplified by the use of dioctylphthalate to convert poly(vinyl chloride) from a rigid material, such as PVC pipes, to a soft one, as in car seat covers or a raincoat. Plasticization and alternating or random copolymerization have similar effects on modulus (Figure 13.24). In this case B is the unplasticized homopolymer, while curves 1, 2 and 3 represent increasing plasticization of B.

F. EFFECT OF POLARITY

The effect of polarity is shown in Figure 13.26, which compares poly(vinyl chloride) with polypropylene. The T_g of the polar poly(vinyl chloride) is about 90°C higher than that of the nonpolar polar polypropylene. As the methyl group and chlorine atom occupy about the same volume, the differences in mechanical behavior can only be due to the relative polarities of the two polymers. However, the effect of the substitution of the chlorine atom for the methyl group depends on the molecular environment of the chlorine atom. The further the chlorine atom is from the main chain, the smaller its effect on the T_g. This is illustrated in Figure 13.27, which compares the mechanical behavior of the following polymers:

Polymer	**Structure**
Poly(2-chloroethyl methacrylate)	 $-CH_2-\overset{\substack{CH_3\\ \vert}}{\underset{\substack{\vert\\ C=O\\ \vert\\ O\\ \vert\\ CH_2\\ \vert\\ CH_2\\ \vert\\ Cl}}{C}}-$

Polymer	Structure
Poly(*n*-propyl methacrylate)	 $-CH_2-\overset{\overset{\displaystyle CH_3}{\vert}}{\underset{\underset{\underset{\underset{\underset{\displaystyle CH_3}{\vert}}{\underset{\displaystyle CH_2}{\vert}}}{\underset{\displaystyle CH_2}{\vert}}}{\underset{\displaystyle O}{\vert}}}{\underset{\displaystyle C=O}{\vert}}}{C}}-$

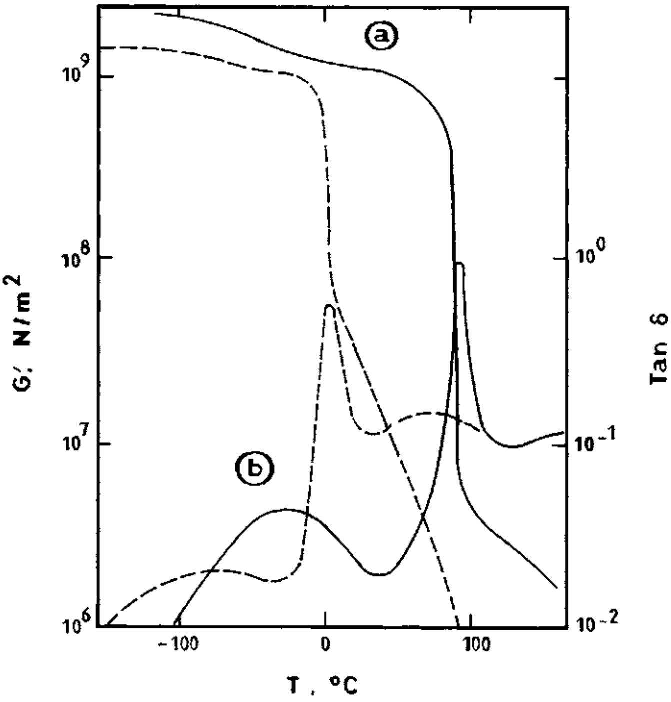


Figure 13.26 *Shear modulus (a) and damping (b) as a function of temperature: (———) poly(vinyl chloride); (– – – –) polypropylene. (From Heijboer, J., Br. Polym. J., 1, 3, 1969. With permission.)*

In this case, the T_g of poly(2-chloroethyl methacrylate) is only 20°C higher than that of poly(*n*-propyl methacrylate). However, with the secondary transitions, which represent the movement of the side chains (chloroethyl and *n*-propyl groups, respectively), the effect on the location of the glass temperature is much larger. Also, the modulus of the polar polymer is much higher. In the glassy region, the magnitude of the modulus is determined primarily by secondary bonding forces. It is therefore to be expected that the modulus will be increased by the introduction of polar forces. Indeed, polarity is generally the most effective means for increasing modulus in the glassy region.

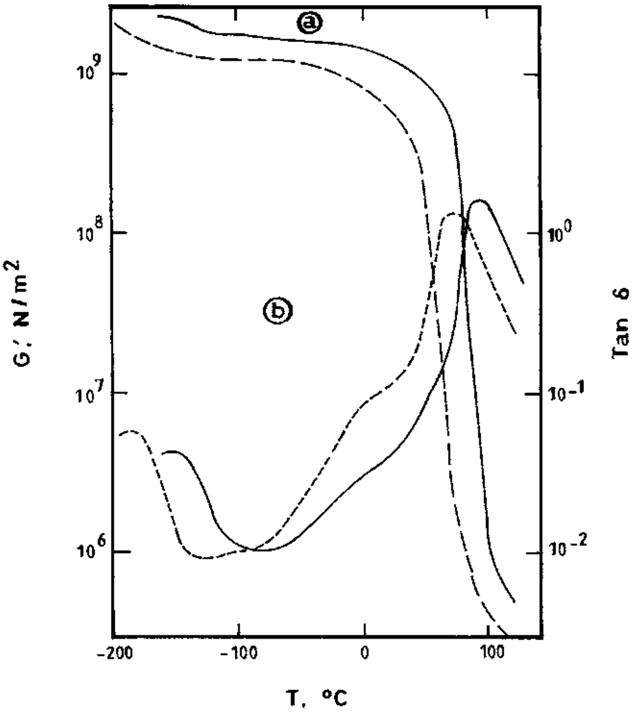


Figure 13.27 *Shear modulus (a) and damping (b) at 1 Hz as a function of temperature: (———) poly(2-chloroethyl methacrylate); (– – – –) poly(n-propyl methacrylate). (From Heijboer, J., Br. Polym. J., 1, 3, 1969. With permission.)*

Example 13.6: Both polyoxymethylene (DuPont Delrin 550) and polyethylene (Calanese Fortiflex A70) show similar mechanical behavior but the glass transition temperature of polyoxymethylene is about 50°C higher than that of polyethylene. Explain.

Solution:

Polymer	Structure
Polyoxymethylene	$–CH_2–O–$
Polyethylene	$–CH_2–CH_2–$

The presence of the oxygen atom in the main chain of polyoxymethylene might have been expected to enhance its flexibility compared with polyethylene and hence reduce its T_g relative to that of polyethylene. However, we note that the dipole character of the C–O–C group produces polar forces between adjacent chains, which act over a longer range and are stronger than van der Waals forces. Thus, for polyoxymethylene the induced flexibility is more than offset by the increased bonding forces resulting from polarity.

G. STERIC FACTORS

In discussing the influence of steric features on mechanical properties, it is convenient to consider the side chains and the main chain separately. The effects of flexible side chains differ completely from those of stiff side chains. Long, flexible side chains reduce the glass transition temperature, while stiff side chains increase it. Long, flexible side chains increase the free volume and ease the steric hindrance from neighboring chains and as such facilitate the movement of the main chain. Figure 13.28 illustrates

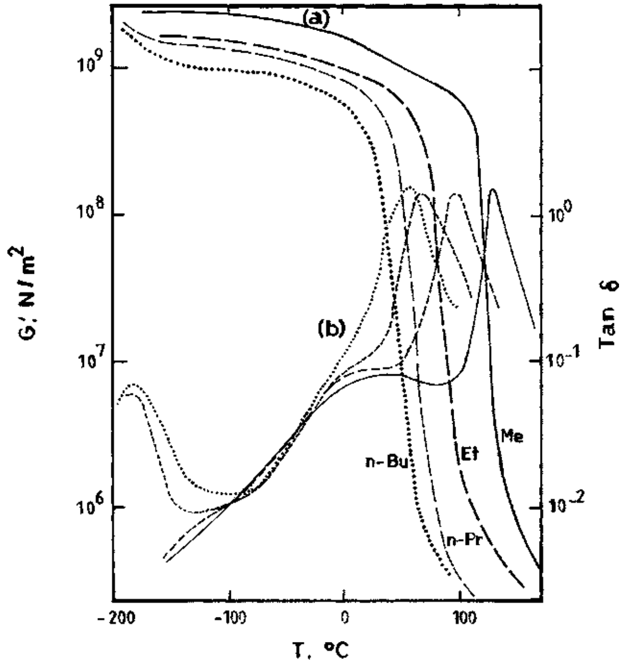


Figure 13.28 *Shear modulus (a) and damping (b) at 1 Hz as a function of temperature for poly(n-alkyl methacrylate). (––––) Polymethyl methacrylate; (– – –) polyethyl methacrylate; (— — —) poly(n-propyl methacrylate); (· · ·) poly(n-butyl methacrylate). (From Heijboer, J., Proc. Int. Conf. Physics Non-crystalline Solids, North-Holland, Amsterdam, 1965, 231. With permission.)*

the reduction in T_g and the increase in modulus in the glassy region with increase in length of the alkyl group for poly(*n*-alkyl methacrylate).

Branched side chains, particularly if the branched point is located close to the main chain, increase the glass transition temperature. This is illustrated in Figures 13.29 and 13.30 for a series of polyacrylates and polyolefins with branched side chains, respectively.

Structural changes within or near the main chain, even if minor, can produce a drastic effect on the mechanical properties of a polymer. Table 13.4 shows the increase in T_g and T_m (for the crystallizable polymers) by the introduction of rings into the main chain.

In spite of the possible increase in chain flexibility due to the elongation of the diacid by two methylene groups, polycyclamide has higher T_g and T_m than nylon 6,6 as a result of the substitution of stiff cyclohexylene 1,4 for four methylene groups in nylon 6,6. Trogamid T does not crystallize. However, the additional stiffening of the main chain due to the presence of methyl side groups leads to a further increase in the T_g. In general, the introduction of rings into the main chain provides a better structural mechanism for toughening polymers than chain stiffening by bulky side groups. For example, polycarbonate, polysulfone, and polyphenylene oxide all have high impact strength whereas poly(vinyl carbozole) with comparable T_g is brittle (Table 13.5).

H. EFFECT OF TEMPERATURE

The mechanical properties of polymers are generally more susceptible to temperature changes than those of ceramics and metals. As discussed in Section 12.5.1, the modulus of a polymer decreases with increasing temperature. However, the rate of decrease is not uniform; the drop in modulus is more pronounced at temperatures associated with molecular transitions. As the temperature is increased to a level that can induce some form of molecular motion, a relaxation process ensues and there is a drop in modulus. At temperatures below the T_g, the polymer is rigid and glassy. In the glassy region, there are usually one or more secondary transitions that are related either to movements of side chains or to restricted movements of small parts of the main chain. For the secondary transitions, the drop in modulus is about 10 to 50%, while primary transitions like T_g and T_m, which involve large-scale main chain

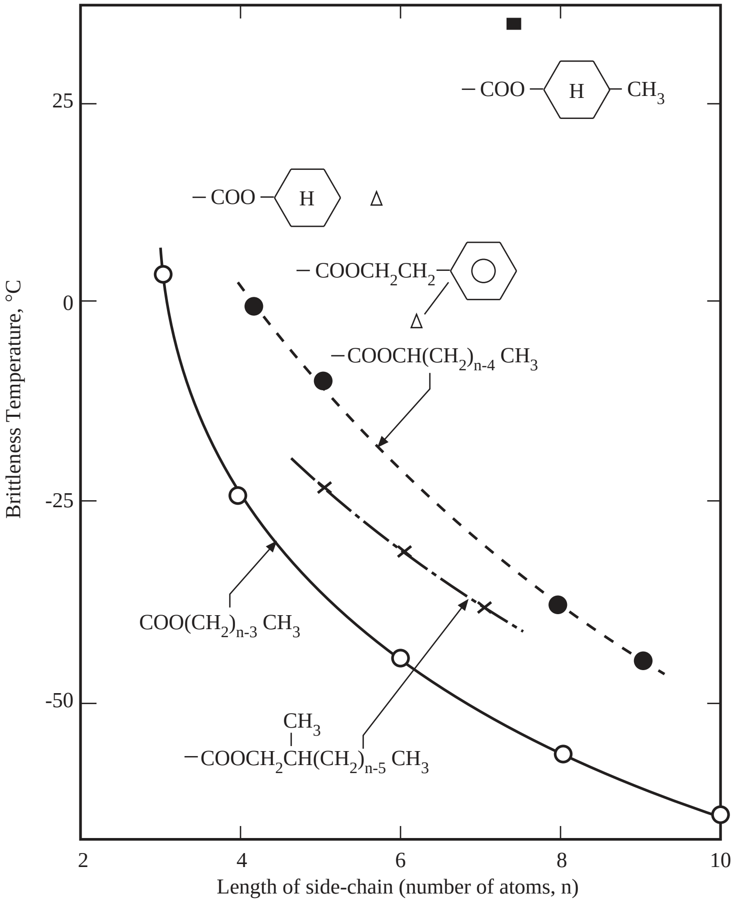


Figure 13.29 *Brittleness temperatures for polyacrylates as a function of the total length of the side chain. (From Heijboer, J., Br. Polym. J., 1, 3, 1969. With permission.)*

motions, the drop in modulus varies from one to three orders of magnitude depending on the type of polymer. If no molecular relaxation process occurs over a particular temperature range, the modulus decreases rather slowly with increasing temperature. In this case, the decrease in modulus is due to the normal reduction in intermolecular forces that occurs with an increase in temperature.

The general effect of temperature on the stress-strain properties of a polymer is illustrated in Figure 13.31. Below the T_g, the modulus is high, as discussed above; there is essentially no yield point and consequently the polymer is brittle (i.e., has low elongation at break). The yield point appears at temperatures close to the T_g. As we shall see in the next section, a high speed of testing requires higher temperatures for the appearance of the yield point. In some polymers with pronounced secondary transitions, the yield point appears in the neighborhood of this transition temperature rather than at T_g. For example, in spite of a high T_g of 150°C, polycarbonate is remarkably tough at room temperature, and this is associated with a secondary transition at about –100°C. In general, therefore, as the temperature is increased, the modulus and yield strength decrease and the polymer becomes more ductile.

I. EFFECT OF STRAIN RATE

Polymers are very sensitive to the rate of testing. As the strain rate increases, polymers in general show a decrease in ductility while the modulus and the yield or tensile strength increase. Figure 13.32 illustrates this schematically. The sensitivity of polymers to strain rate depends on the type of polymer: for brittle polymers the effect is relatively small, whereas for rigid, ductile polymers and elastomers, the effects can be quite substantial if the strain rate covers several decades.

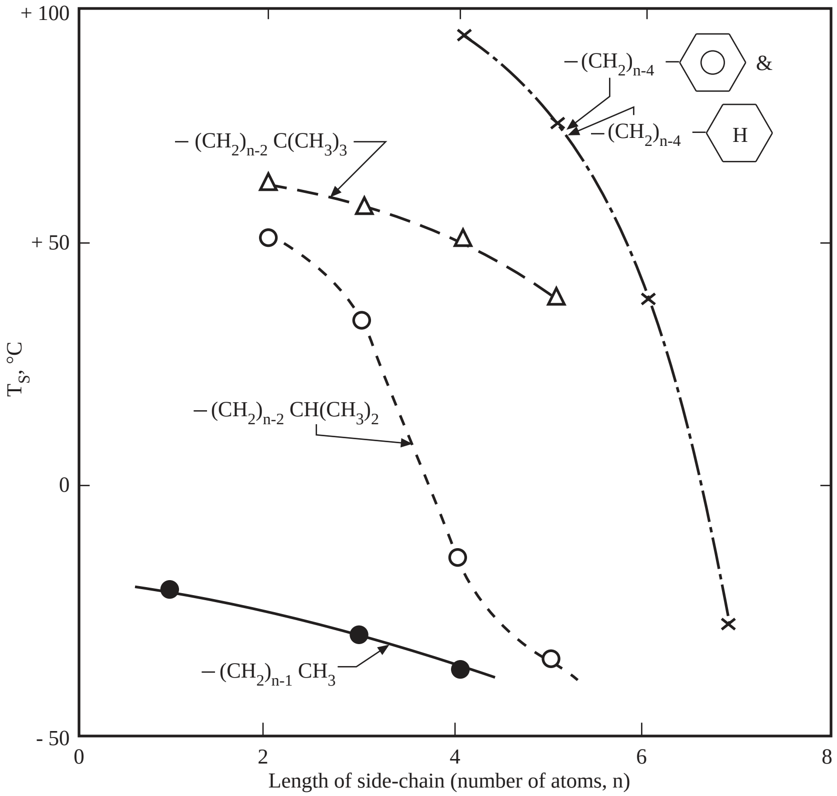


Figure 13.30 *Softening temperature of polyolefins with branched side chains. (From Heijboer, J., Br. Polym. J., 1, 3, 1969. With permission.)*

Table 13.4 *Effects of the Introduction of Rings into the Main Chain of Some Polyamides*

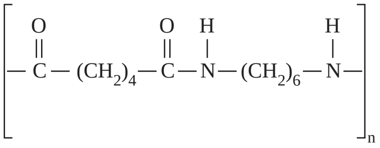
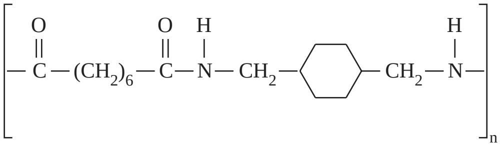
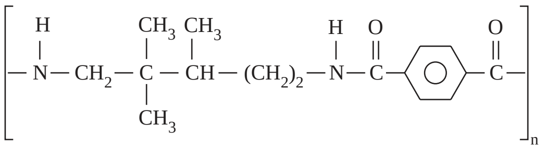
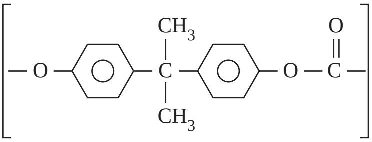
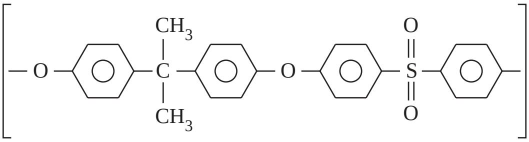
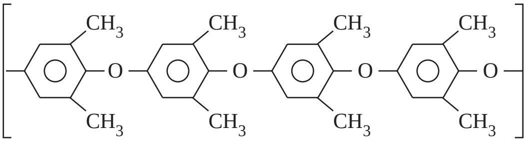
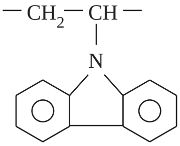
Polymer	Structure	T_g °C	T_m °C
Nylon 6.6 (Zytel, Du Pont de Nemours)	 $\left[-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{\mid}{N}}-(CH_2)_6-\overset{H}{\overset{\mid}{N}}-\right]_n$	75	260
Polycyclamide (Q.2 Tennessee Eastman Co.)		125	300
Trogamid T (Dynamit Nobel A.G.)		145	none

Table 13.5 *Polymer Stiffening Due to the Introduction of Rings into the Main Chain*

Polymer	Structure	T_g °C
Polycarbonate		150
Polysulfone		190
Poly(phenylene oxide)		220
Poly(vinyl carbazole)		208

Polymers show a similar response to temperature and strain rate (time), as might be expected from the time–temperature superposition principle (compare Figures 13.31 and 13.32). Specifically, the effect of decreasing temperature is equivalent to that of increasing the strain rate. As has become evident from our previous discussions, low temperature restricts molecular movement of polymers, and consequently they become rigid and brittle. Materials deform to relieve imposed stress. High strain rates preclude such deformation and therefore result in brittle failure.

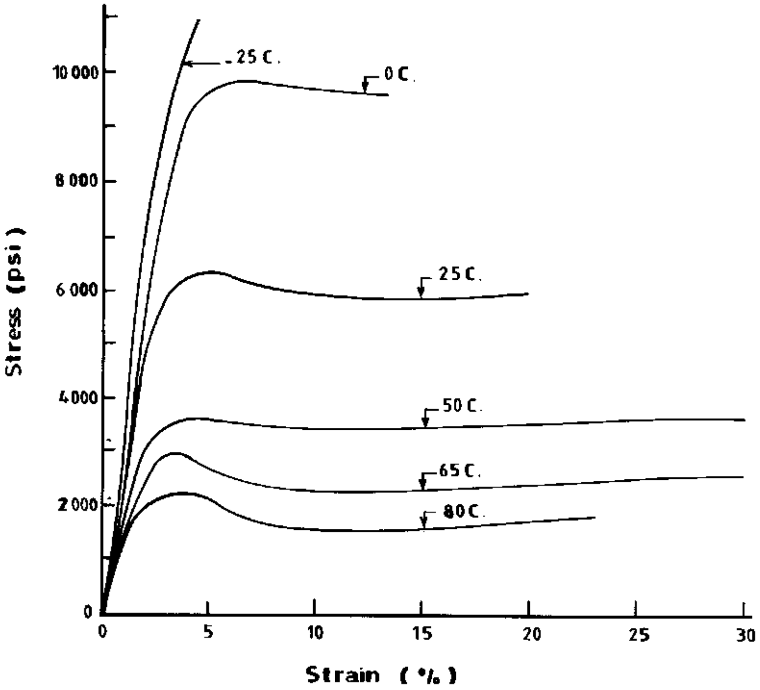


Figure 13.31 *The stress–strain behavior of cellulose acetate at different temperatures. (From Carswell, T.S. and Nasor, H.K., Mod. Plast., 21(6), 121, 1944. With permission.)*

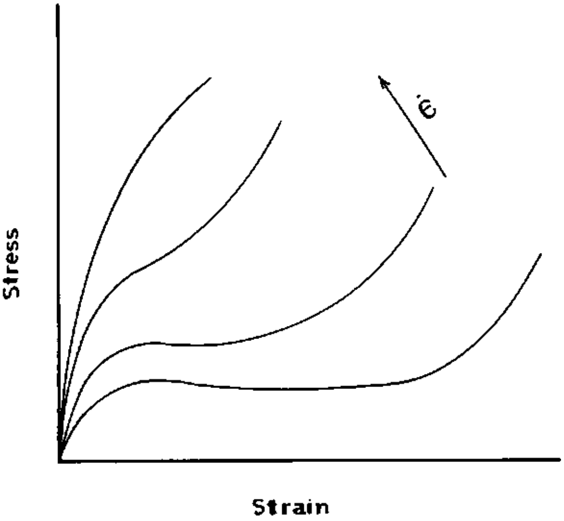


Figure 13.32 *Schematic illustration of the effect of strain rate on polymers.*

Example 13.7: Explain the observed differences in the tan δ of polystyrene tested at the two different frequencies shown in Figure E13.7.

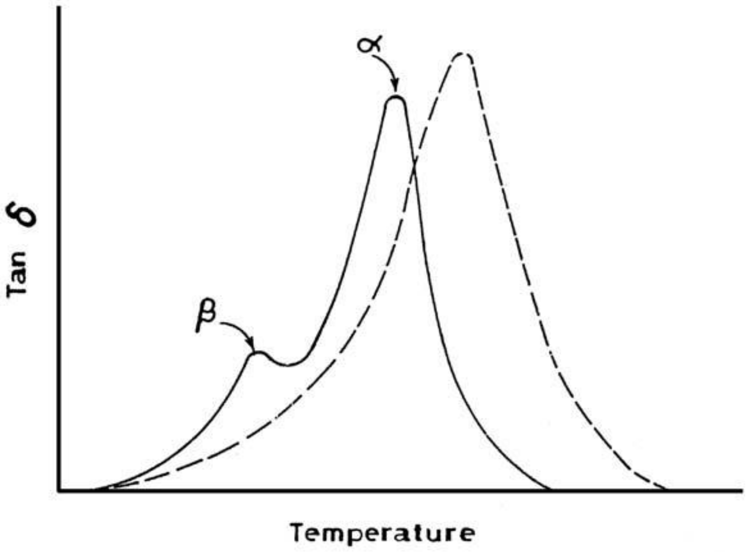


Figure E.13.7 *Schematic representation of the variation of tan δ with temperature for atactic polystyrene tested at 0.1 Hz (——) and 50 Hz (– – –).*

Solution: The mechanical properties of polymers depend on time and temperature. The time dependence is usually expressed as a frequency dependence, which to a first approximation is related to time by $2\pi \upsilon = 1/t$ where υ is the frequency. The combined dependence of molecular processes of viscoelastic materials on frequency and temperature can be described by an activation energy E_a. E_a is about 100 kcal/mol and 10 kcal/mol for primary and secondary transitions, respectively. This implies that the relaxation processes associated with the molecular motions shift to higher temperatures at higher frequencies; however, the secondary transition shifts more than the primary transition. Therefore, if tests are conducted at high frequencies, the resolution between the energy absorption peaks for primary and secondary transitions that are close to each other is poor. Thus, in this case, the β and α peaks, which are relatively distinct at 0.1 Hz, merge at 50 Hz, and there is a shift in the peak to higher temperatures.

J. EFFECT OF PRESSURE

The imposition of hydrostatic pressure on a polymer has a tremendous effect on its mechanical properties, as demonstrated by the stress–strain behavior of polypropylene in Figure 13.33. The modulus and yield stress increase with increasing pressure. This behavior is general for all polymers. However, the effect of pressure on the tensile strength and elongation at break depends on the polymer. The tensile strength tends to increase for ductile polymers, but decrease for some brittle polymers. The elongation at break increases for some ductile polymers, but decreases for most brittle polymers and polymers such as PE, PTFE, and PP, which exhibit cold drawing at normal pressures. In some brittle polymers like PS, brittle-ductile transition is induced beyond a certain critical pressure.

The increase in modulus and yield stress with increase in pressure is to be expected on the basis of the available free volume. An increase in pressure decreases the free volume (i.e., increases the packing density) and as such enhances the resistance to deformation (modulus) or delays the onset of chain

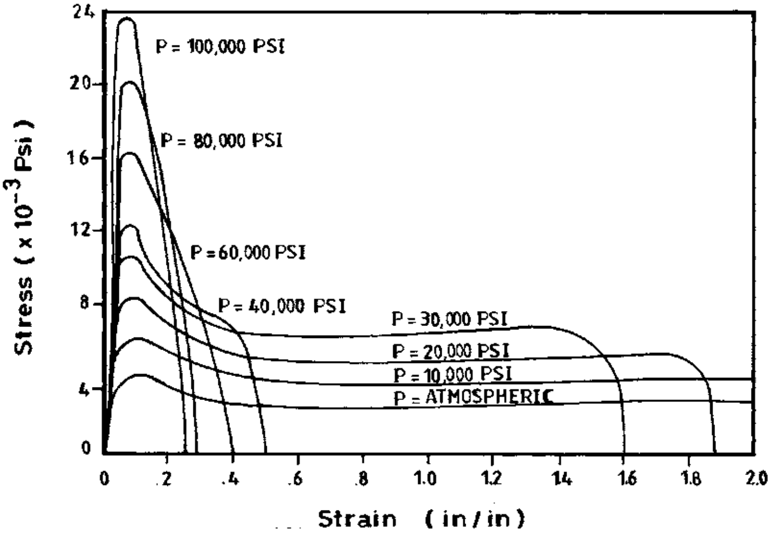


Figure 13.33 *The stress–strain behavior of polypropylene at different pressures. (From Nielsen, L.E., Mechanical Properties of Polymers and Composites, Vol. 2, Marcel Dekker, New York, 1974. With permission.)*

slippage or plastic deformation (yielding). The embrittlement of polymers capable of cold drawing with increase in pressure can be rationalized on the basis of the reduction in chain mobility associated with the decrease in free volume. Also, with an increase in pressure, the occurrence of relaxation processes responsible for the cold drawing phenomenon is delayed to higher temperatures. In other words, subjecting a polymer to increasing pressure at a given temperature has an effect on its mechanical behavior equivalent to reducing its temperature at a given pressure.

VII. POLYMER FRACTURE BEHAVIOR

Structural members can fail to perform their intended functions in three general ways: (1) excessive elastic deformation, (2) excessive plastic deformation, and (3) fracture. Modulus is a measure of the resistance to elastic deformation. We discussed the effects of various factors on modulus in the previous section. The stress levels encountered in most end-use situations preclude excessive plastic deformation. Although polymers are noted generally for the ductility, they are susceptible to brittle failure under appropriate conditions. Brittle fracture is usually catastrophic and involves very low strains. The major conditions responsible for brittle failure include low temperature, high rates of loading such as during shock or impact loading, and alternating loads. A polymer can rupture at loads much lower than would be dictated by its yield or tensile stress if subjected to alternating loads or to static loads for long duration. Therefore, to utilize a polymer properly, careful consideration must be given to possible brittle failure that can arise from environmental conditions and/or stress levels imposed on the polymer in use. We now discuss very briefly the fracture behavior in polymers.

A. BRITTLE FRACTURE

The theoretical fracture strength of a material can be deduced from the cohesive forces between the component atoms in the plane under consideration from a simple energy balance between the work to fracture and the energy require to create two new surfaces. It can be shown that the theoretical cohesive strength is given by

$$\sigma_c = \sqrt{\frac{E\gamma_s}{a_0}} \tag{13.31}$$

where σ_C = theoretical cohesive strength
E = Young's modulus
γ_S = surface energy per unit area
a_0 = equilibrium interatomic spacing of atoms in the unstrained state

Engineering materials, including polymers, generally have low fracture strengths relative to their theoretical capacity. The lower-than-ideal fracture strengths of engineering materials are generally attributed to the presence of flaws such as cracks, scratches, and notches inherent in these materials.

The first explanation of the discrepancy between observed fracture strength of crystals and the theoretical cohesive strength was proposed by Griffith.[12] He utilized an earlier analysis by Inglis,[13] who showed that the applied stress, σ_o, was magnified at the ends of the major axis of an elliptical hole in an infinitely wide plate (Figure 13.34) according to the following relation:

$$\sigma_t = \sigma_0 \left(1 - 2\sqrt{a/\rho}\right) \tag{13.32}$$

where ρ is the radius of curvature of the tip of the hole, 2a is the length of the major axis of the hole, and σ_t is the stress and the end of the major axis.

Griffith proposed that a brittle material contains a population of cracks and that the amplification of the local stresses at the crack tip was such that the theoretical cohesive strength was reached at nominal stress levels much below the theoretical value. The high stress concentrations lead to an extension of one of the cracks. The creation of two new surfaces results in a concomitant increase in surface energy, which is supplied by a decrease in the elastic strain energy. Griffith established the following criterion for the propagation of a crack: "A crack will propagate when the decrease in the elastic strain energy

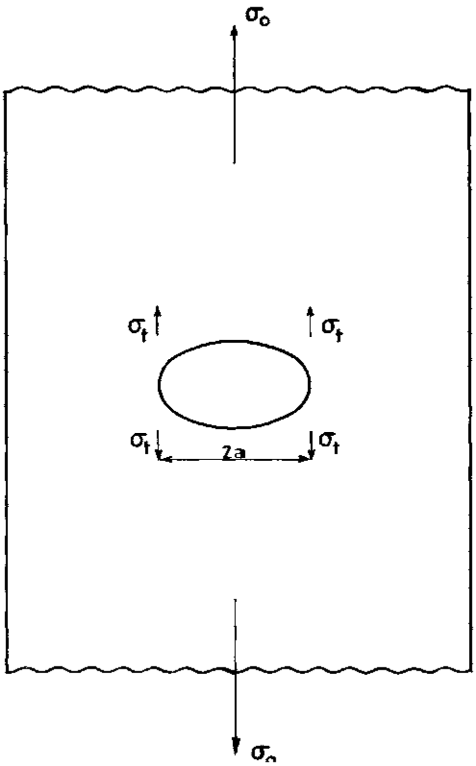


Figure 13.34 *Model of an elliptical crack of length 2a subjected to a uniform stress* σ_0 *in an infinite plate.*

is at least equal to the energy required to create the new surface."[12] He showed that the stress required for crack propagation is given by the relation:

$$\sigma_f = \sqrt{\frac{2E\gamma_s}{\pi a}} \quad \text{for plane stress} \tag{13.33}$$

$$\sigma_f = \sqrt{-\frac{2E\gamma_s}{(1-\nu^2)(\pi a)}} \quad \text{for plane strain} \tag{13.34}$$

where E is Young's modulus, γ_s is the surface energy per unit area, ν is Poisson's ratio and a is half crack length.

The Griffith relation was derived for an ideally brittle material and the theory satisfactorily predicts the fracture strength of a material like glass, where the work to fracture is essentially equal to the increase in surface energy. On the other hand, the theory is inadequate for describing the fracture behavior of materials like polymers and metals, which are capable of extensive plastic deformation (i.e., materials whose fracture energies are several orders of magnitude greater than surface energy). A substantial amount of local plastic deformation invariably occurs at the crack tip.

To obviate this inadequacy, Griffith's equation had to be modified to include the energy expended in plastic deformation in the fracture process. Accordingly, Irwin[14] defined a parameter, G, the strain-energy-release rate or crack extension force, which he showed to be related to the applied stress and crack length by the equation:

$$\sigma = \sqrt{\frac{EG}{\pi a}} \tag{13.35}$$

At the point of instability, the elastic energy release rate G reaches a critical value, G_C, whereupon a previously stationary crack propagates abruptly, resulting in fracture.

A different approach from the strain-energy-release rate in the study of the fraction process is the analysis of the stress distribution around the crack tip. This gives the stress intensity factor or fracture toughness K, which for a sharp crack in an infinitely wide and elastic plate is given by

$$K = \sigma\sqrt{\pi a} \tag{13.36}$$

The stress intensity factor K is a useful and convenient parameter for describing the stress distribution around a crack. The difference between one cracked component and another lies in the magnitude of K. If two flaws of different geometries have the same value of K, then the stress fields around each of the flaws are identical. Since K is a function of applied load and crack size, it increases with load. When the intensity of the local tensile stresses at the crack tip attains a critical value, K_C, failure occurs. This critical value, K_C, defines the fracture toughness and is constant for a particular material, since cracking always occurs at a given value of local stress intensity regardless of the structure in which the material is used. K_C is a function of temperature, strain rate, and the state of stress, varying between the extremes of plane stress and plane strain. In addition, K_C also depends on the failure mode. The stress field surrounding a crack tip can be divided into three major modes of loading depending on the crack displacement, as shown in Figure 13.35. Mode I is the predominant mode of failure in real situations involving cracked components. This is the mode of failure that has received the most extensive attention. For mode I, G and K are related according to Equations 13.37 and 13.38.

$$G_{Ic} = \frac{K_{IC}^2}{E} \quad (\text{plane stress}) \tag{13.37}$$

$$G_{IC} = \frac{K_{IC}^2}{E}(1-\nu^2) \quad (\text{plane strain}) \tag{13.38}$$

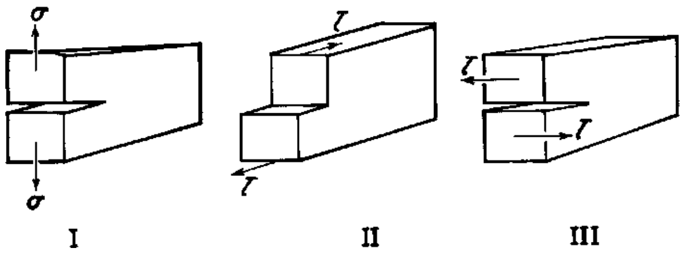


Figure 13.35 *Basic modes of failure of structural materials: (I) opening or tensile mode; (II) sliding or in-plane shear mode; (III) tearing or antiplane shear mode.*

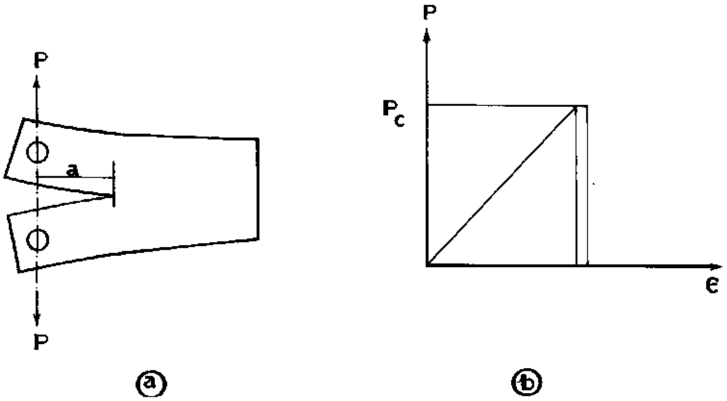


Figure 13.36 *(a) Schematic of a specimen loading in mode I in Figure 13.35; (b) schematic of a corresponding load-displacement diagram.*

B. LINEAR ELASTIC FRACTURE MECHANICS (LEFM)

Our discussion thus far has focused in a rather superficial way on the general evolution of the important area of fracture mechanics. The basic objective of fracture mechanics is to provide a useful parameter that is characteristic of the given material and independent of test specimen geometry. We will now consider how such a parameter, such as G_{Ic}, is derived for polymers. In doing so we confine our discussion to the concepts of linear elastic fracture mechanics (LEFM). As the name suggests, LEFM applies to materials that exhibit Hookean behavior.

To determine G_{Ic}, consider a precracked specimen (Figure 13.36a). In order to obtain the energy lost to a growing crack, we should examine the energy stored in the system before and after crack extension. This can be done by using the load (P)–displacement (ε) diagram (Figure 13.36b) and calculating the total energy before and after a finite amount of crack motion. This difference becomes, in the limit, the value of G_{Ic}.

The total energy $U(a_1)$ available to the specimen for an initial crack length, a, and a critical load, P_c, is given by

$$U(a_1) = \frac{P_c\,\varepsilon(a_1)}{2} \tag{13.39}$$

where ε is the displacement. The reciprocal of the slope of P–ε line is defined as the compliance of the specimen

$$C(a_1) = (a_1)/P_c \tag{13.40}$$

Substituting (13.40) into (13.39) we obtain

$$U(a_1) = \frac{P_c^2\, C(a_1)}{2} \tag{13.41}$$

Assuming the crack extends infinitesimally at constant load, the expression for the energy lost to the growing crack per unit area for a width, b, is

$$G_{IC} = \frac{dU}{dA} = \frac{1}{b}\frac{dU}{da} = \frac{P_c^2}{2b}\left(\frac{\partial C}{\partial a}\right) \tag{13.42}$$

Equation 13.42 is general and can be used to determine the cohesive fracture behavior of polymers. To do this, a large number of specimen geometries have been devised. However, we illustrate the use of Equation 13.42 in the assessment of the strength of adhesive joints using tapered double-cantilever beam (TDCB) specimen geometry. Most adhesive materials are thermosets, which are usually highly cross-linked and brittle. Thermosets are therefore ideally suited for the application of the principles of linear elastic fracture mechanics. As indicated earlier, structural members can fail to perform their intended functions by excessive elastic deformation, excessive plastic deformation, or fracture. Adhesive joints constitute a minute fraction of the total volume of a structure. Consequently, even large elastic or inelastic deformation within the bond line is not hazardous since their contribution to the overall deformation of the structure would be insignificant. However, rigid structural adhesives are particularly susceptible to brittle failures; hence, prevention of brittle fracture is the critical problem in adhesive-bonded structures.

Fracturing in brittle materials, we have seen from theories discussed above, is associated with the occurrence of preexisting flaws. These initial flaws, introduced in manufacture or service, may be dust particles, bubbles, and nonbonded areas in the case of adhesive joints. Fractures usually occur by a progressive extension of the largest of these flaws. Furthermore, structural adhesives are inherently brittle when tested uniaxially, a characteristic that is accentuated when they are used in thin layers where deformation is further restricted because of the multiaxial stress state imposed by the proximity of high modulus adherends. The combination of fracturing with very little permanent deformation and crack growth from preexisting flaws suggests that fracturing of adhesive joints can be described by the techniques of fracture mechanics. Using the concepts of linear elastic fracture mechanics and with a knowledge of the largest flaw contained in these materials, one can establish minimum toughness standards for structural adhesive joints. Mostovoy et al.[15,16] and Ripling et al.[17–19] have developed and applied the tapered double-cantilever beam (TDCB) to study strength and durability characteristics of adhesives and adhesive joints with metal adherends. Using beam theory from strength of materials, they established the following relation between specimen compliance and crack length.

$$\frac{\partial C}{\partial a} = \frac{8}{Eb}\left[\frac{3a^2}{h^3} + \frac{1}{h}\right] \tag{13.43}$$

where E = Young’s modulus
ν = Poisson’s ratio (assumed to be 1/3)
b = specimen width
h = beam height at the distance a from the point of loading

From Equations 13.42 and 13.43,

$$G_{IC} = \frac{4P_c^2}{EB^2}\left[\frac{3a^2}{h^3} + \frac{1}{h}\right] \tag{13.44}$$

From Equation 13.44, it can be seen that as the crack gets longer, i.e., as *a* increases, P_c decreases to maintain a constant value of G_{Ic}. Obviously, the calculation of G_{Ic} requires monitoring both P_c and a for each calculation of G_{Ic}. Testing can be simplified, however, if the specimen is contoured so that the

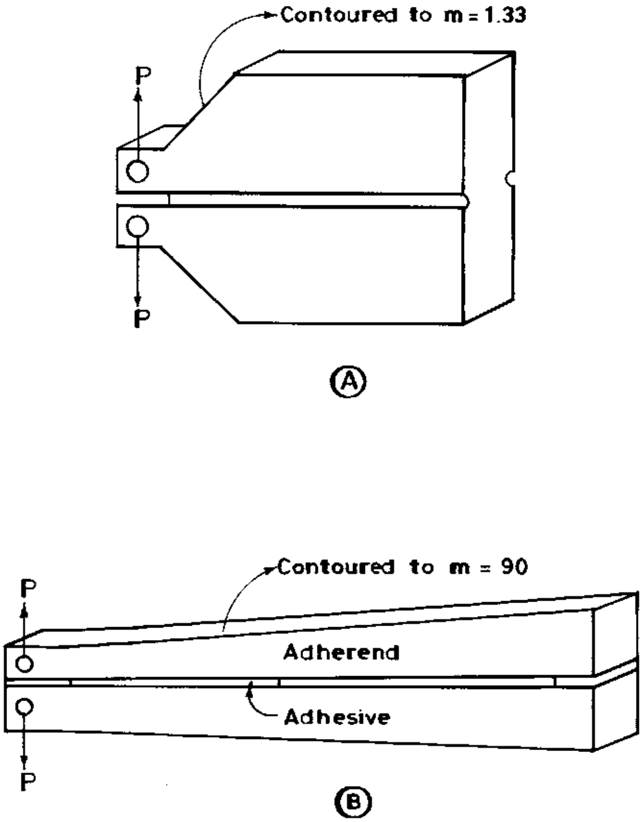


Figure 13.37 *Schematic representation of TDCB specimens for testing of A) bulk materials and B) adhesives.*

compliance changes linearly with crack length. If dC/da is a constant, the relation between G_{Ic} and P_c is independent of a and, hence, only P_c needs to be followed for the evaluation of G_{Ic}. To develop a linear compliance specimen, its height is varied so that the quantity ($3a^2/h^3 + 1/h$) in Equation 13.44 is constant. Hence

$$\frac{3a^2}{h^3} + \frac{1}{h} = m\ (\text{a constant}) \tag{13.45}$$

so that

$$G_{IC} = \frac{4P_c^2}{Eb^2} \cdot m \tag{13.46}$$

This type of contoured specimen is known as the tapered-double-cantilever beam (TDCB) specimen.

There are, of course, an infinite number of m values that can be chosen to satisfy Equation 13.46. The determination of m is governed by a basic assumption that the entire energy supplied to the specimen is concentrated on the crack line for crack extension. Thus the choice of m is such that the bending stresses on the adherend are minimized. This, in turn, depends on the modulus of the adherends relative to the adhesive. This necessitates an empirical determination of the appropriate m value through a procedure known as compliance calibration. Figure 13.37 is a schematic of the specimen geometries of TDCB for the determination of G_{Ic} for bulk adhesives and adhesive joints.

The shape of the load–displacement curves using this specimen geometry can reveal interesting information about the intrinsic nature of the adhesive. Generally, in evaluating G_{Ic}, a continuously increasing load is applied to the specimen and a P–ε diagram is obtained with the extensometer mounted directly on the sample. Two types of P–ε diagrams are usually obtained (Figure 13.38). Curves of type A are typical of rate-insensitive materials, while type B curves exemplify rate-sensitive ones. For type

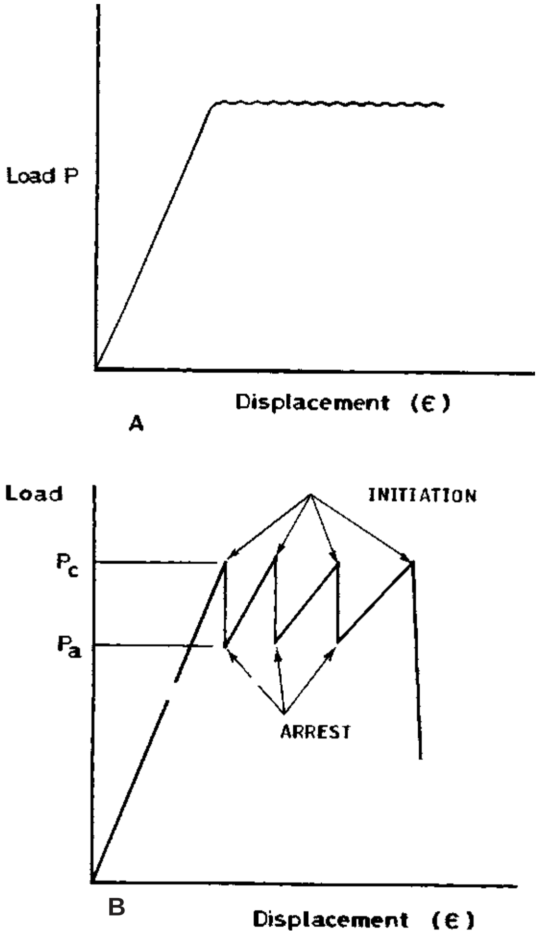


Figure 13.38 *Load–displacement (P–ε) diagrams typical of (A) stable ("flat") propagation; (B) unstable ("peaked") propagation.*

B curves, two load values are exhibited: P_c, the crack initiation load at the point of instability used in the calculation of G_{Ic}; and P_a, the crack arrest load used for estimating G_{Ia}. For rate-insensitive materials, G_{Ic} and G_{Ia} are identical, and the crack growth a is dictated by the cross-head speed, $\dot{\varepsilon}$.

On a given test machine and at a given cross-head speed, the difference between initiation and arrest fracture energies, $G_{Ic} - G_{Ia}$ indicates the energy released during crack propagation; it is a measure of the brittleness or resistance to catastrophic failure of the adhesive system. Figure 13.39 shows different adhesive joint failure modes for TDCB specimens. We notice that the systems A and B have about the same crack initiation loads. However, the two systems are different in their resistance to crack propagation. A is a hard and very brittle adhesive. Unlike A, B has an internal mechanism for arresting crack propagation; at the onset of instability the material undergoes plastic deformation, blunts the crack, and consequently prevents catastrophic failure. B is therefore not only hard but also tough. Using these arguments, the adhesive system C is hard and strong while D is soft and weak. D is characteristic of systems with a spongy adhesive layer.

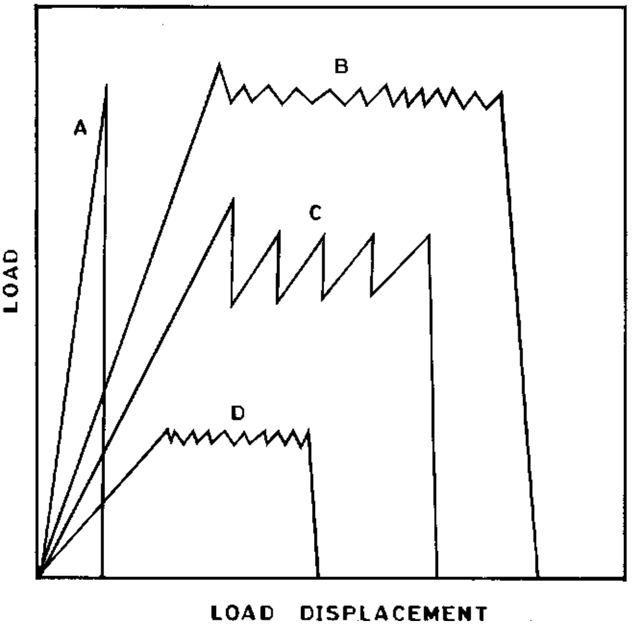


Figure 13.39 *Possible adhesive joint failure modes for TDCB specimens tests.*

Example 13.8: Urea–formaldehyde (UF) adhesive used in bonded wood products was modified by copolymerizing 10 mol% urea derivative of dodecanediamine (DDDU). The fracture energies of wood joints made with the unmodified and DDDU-modified adhesives were found to be 130 and 281 J/m^3, respectively. Explain the enhanced fracture energy of the wood joint bonded with the modified adhesive.

Solution:

$$H_2N-CO-NH-(CH_2)_{12}-NH-CO-NH_2$$

$$\text{urea derivative of dodecanediamine (DDDU)}$$

Cured urea–formaldehyde adhesive is characterized by the presence of methylene bridges between strongly hydrogen-bonded urea linkages. Consequently, cured UF adhesives are inherently stiff and brittle. Incorporation of DDDU with its 12 methylene groups into the resin structure results in cured UF adhesive with a more flexible network. The increased flexibility decreases internal stress and the associated flaws, and hence the fracture energy increases.

VIII. PROBLEMS

13.1. Calculate the resilience of polycarbonate with yield strength 62.05×10^6 N/m^2 and elastic modulus 24.13×10^8 N/m^2.

13.2. A polymer, T, when tested in uniaxial tension has its cross-sectional area reduced from 2.00 cm^2 to 1.0 cm^2. The cross-sectional area of a second polymer, S, under the same test changed from 20 cm^2 to 18 cm^2. Which of these two polymers would you choose for making children's toys, assuming other qualities are comparable for both polymers?

13.3. Explain the observed trend in the mechanical properties of the polymers shown in the following table.

Polymer	**Elastic modulus (MN/m^2)**	**Tensile Strength (MN/m^2)**	**Elongation of Break %**
Low-density polyethylene	138–276	10.3–17.2	400–700
High-density polyethylene	414–1034	17.2–39.9	100–600
Polytetrafluoroethylene	414	13.8–27.6	100–350
Polypropylene	1034–1551	24.1–37.9	200–600
Polystyrene	2758–3447	37.9–55.2	1–2.5
Poly(vinyl chloride)	2068–4436	41.4–75.8	5–60
Nylon 6,6	1241–2760	62.0–82.7	60–300
Polycarbonate	1243	55.2–68.9	60–120

13.4. Figure Q13.4 shows the stress–strain curve for a polymer material under uniaxial loading. The material deformed uniformly until N, where necking ensued. If the material obeys the relation $\sigma = K\varepsilon^n$ up to the point N, calculate the strength, σ_N, of the material at the onset of necking. $K = 10^6$ N/m^2, $\varepsilon = 0.5$.

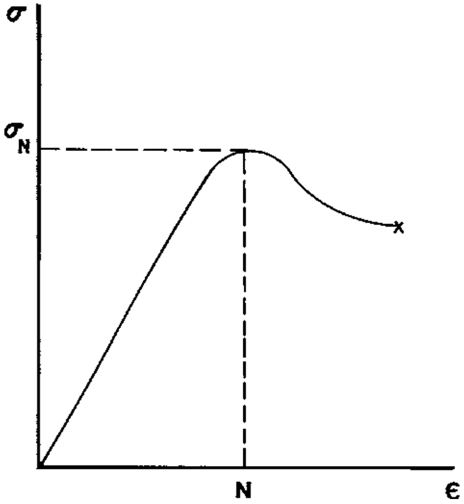


Figure Q13.4 *Stress–strain curve for a polymer.*

13.5. Calculate the maximum load a polymer sample in uniaxial tension can sustain before yielding when the maximum resolved shear stress (τ_{max}) is 10^6 N/m^2. The cross-sectional area of the sample is 10^{-4} m^2.

13.6. Suppose that yielding occurs in a polyethylene crystal when the critical resolved shear stress, $\tau_{max} \approx 27.58 \times 10^6$ N/m^2 is produced on the {110} type slip plane along a <111> type direction. If the tensile axis coincides with the <110> direction, what maximum axial stress must be applied to cause yielding on a {110} plane in a <111> direction?

13.7. Explain the following observations:

a. Although the refractive indices of polystyrene and polybutadiene differ considerably, materials derived from styrene–butadiene–styrene copolymers are transparent and have high tensile strength.
b. When natural rubber with chains of poly(methylmethacrylate) grafted to it is isolated from ethylacetate, it is hard, stiff, and nontacky. On the other hand, when the same polymer is isolated from hexane it is limp, flabby, and tacky.
c. Block copolymers of styrene and vinyl alcohol are soluble in benzene, water, and acetone.
d. Both poly(hexamethylene sebacamide) (nylon 6,10) and poly(hexamethylene adipamide) (nylon 6,6) are fiber-forming polymers. A copolymer consisting of hexamethylene terephthalamide and hexamethylene adipamide retains the qualities of nylon 6,6 fiber, whereas a copolymer consisting of hexamethylene sebacamide and 10 mol% hexamethylene terephthalamide is elastic and rubbery with drastic reductions in stiffness and hardness.

13.8. Two polypropylene materials have densities 0.905 and 0.87 g/cm^3. Sketch the modulus–temperature curves for these materials on the same graph.

13.9. Explain the difference in the glass transition temperatures between the following pairs of polymers.

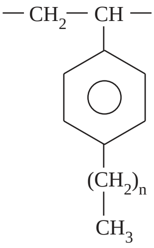
a. Poly(vinyl methyl ether) and poly(vinyl formal)

$T_g = 13°C$ $\qquad$ $T_g = 105°C$

b. Poly(*t*-butyl methacrylate) and poly(ethyl methacrylate)

$T_g = 135°C$ $\qquad$ $T_g = 100°C$

13.10. How would you expect the stiffness of the series of poly(*p*-alkylstyrene) shown below to vary with n? Explain your answer very briefly.



(Str. 11)

13.11. Two materials formed by reaction injection molding have the following tensile and fracture properties:[26]

Material	E(MPa)	σ_u(MPa)	ε_u(%)	G_c(kJ/m^2)
S	266	16.8	222	7.12
H	532	15.3	17	0.06

Estimate the intrinsic flaw size in these materials assuming they were tested under (a) plane stress and (b) plane strain. Assume $\nu = 0.3$. Comment on your result. Which of these two materials will be more suitable for use in an application where the ability to withstand extensive abuse is a requirement?

13.12. Figure Q13.12 shows the mechanical properties of two urea–formaldehyde (UF) resins cured with NH_4Cl: (bottom) variation of the shear strength of bonded wood joints with cyclic wet–dry treatments of joints; (middle) development of internal stress with duration of resin cure at room temperature; (top) dynamic mechanical properties of resins. Discuss the interrelationships between the observed mechanical properties.

13.13. Figure Q13.13 shows the variation of fracture initiation (G_{Ic}) energies with cure of phenol–formaldehyde adhesive cured at 85°C. It is known that during cure of phenolic resins, dimethylene ether linkages are formed initially from the condensation of methylol groups. These ether linkages decompose subsequently according to the scheme shown. How do these reactions provide a possible explanation for the trend in G_{Ic}? A and B represent two different states of cure of the phenolic resin with the same fracture energy. What is the major difference in the fracture characteristics of materials in these states?

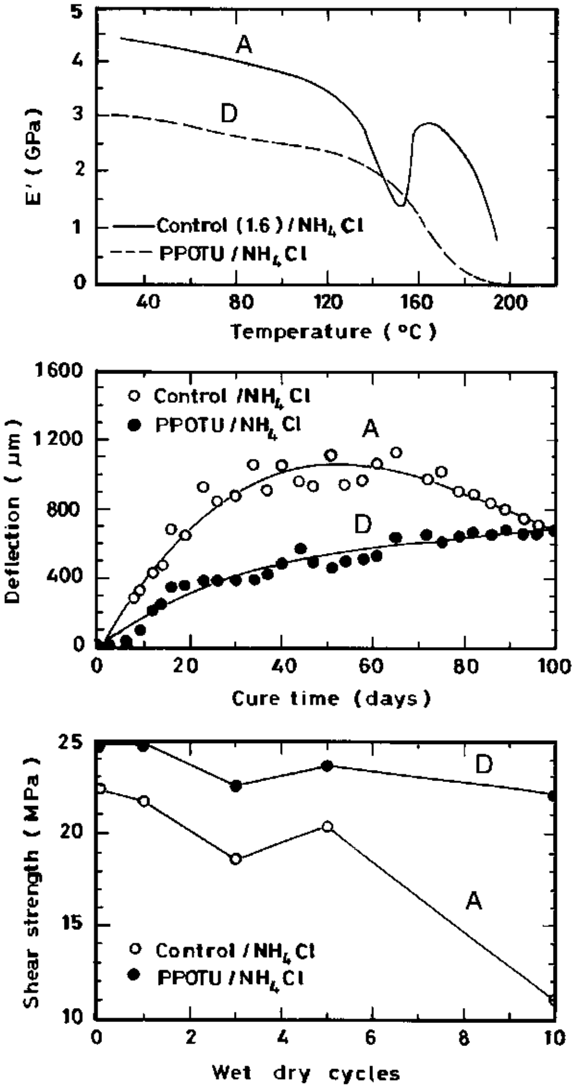


Figure Q13.12

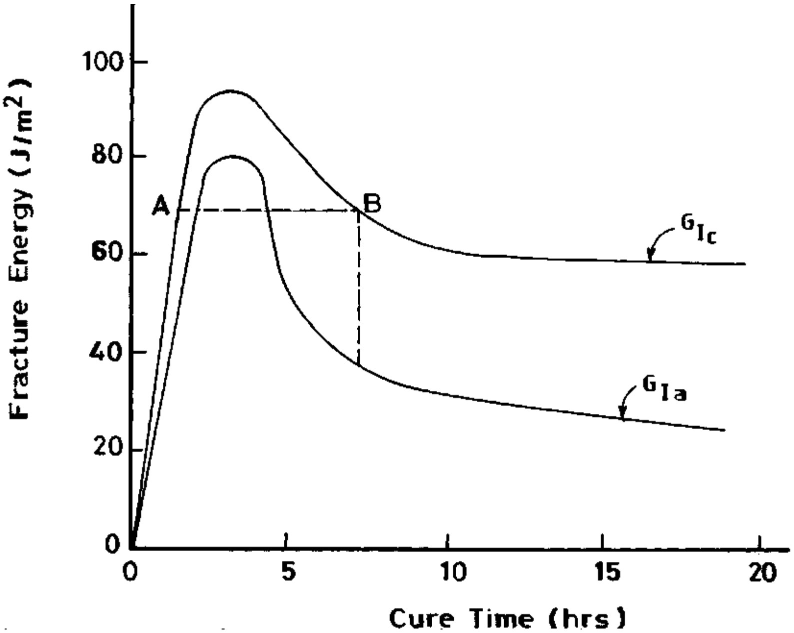


Figure Q13.13 *Variation of fracture initiation and arrest energies with cure time for phenolic resin cured at 85° ( ).*

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