

9th Edition

Materials Science and Engineering

AN INTRODUCTION

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Front Cover: Depiction of a unit cell for iron carbide (Fe_3C) from three different perspectives. Brown and blue spheres represent iron and carbon atoms, respectively.

Back Cover: Three representations of the unit cell for body-centered cubic iron (α -ferrite); each unit cell contains an interstitial carbon atom.

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Chapter 6 Mechanical Properties of Metals

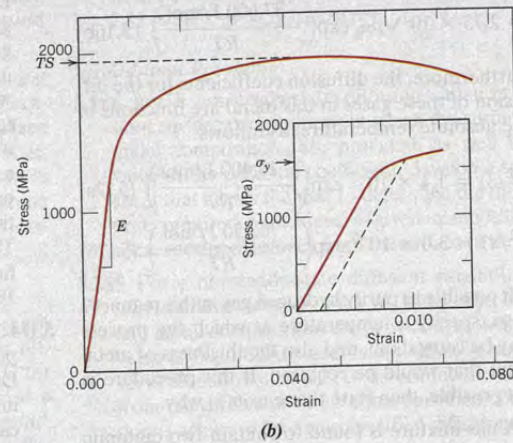
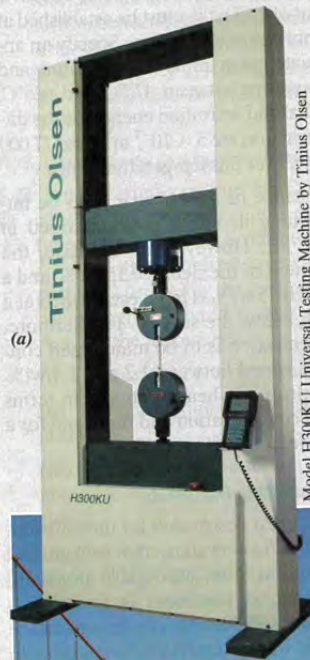


Figure (a) shows an apparatus that measures the mechanical properties of metals using applied tensile forces (Sections 6.3, 6.5, and 6.6). Figure (b) was generated from a tensile test performed by an apparatus such as this on a steel specimen. Data plotted are stress (vertical axis—a measure of applied force) versus strain (horizontal axis—related to the degree of specimen elongation). The mechanical properties of modulus of elasticity (stiffness, E), yield strength (σ_y), and tensile strength (TS) are determined as noted on these graphs.

Figure (c) shows a suspension bridge. The weight of the bridge deck and automobiles imposes tensile forces on the vertical suspender cables. These forces are transferred to the main suspension cable, which sags in a more-or-less parabolic shape. The metal alloy(s) from which these cables are constructed must meet certain stiffness and strength criteria. Stiffness and strength of the alloy(s) may be assessed from tests performed using a tensile-testing apparatus (and the resulting stress-strain plots) similar to those shown.

WHY STUDY The Mechanical Properties of Metals?

It is incumbent on engineers to understand how the various mechanical properties are measured and what these properties represent; they may be called upon to design structures/components using predetermined

materials such that unacceptable levels of deformation and/or failure will not occur. We demonstrate this procedure with respect to the design of a tensile-testing apparatus in Design Example 6.1.

Learning Objectives

After studying this chapter, you should be able to do the following:

1. Define engineering stress and engineering strain.
2. State Hooke's law and note the conditions under which it is valid.
3. Define Poisson's ratio.
4. Given an engineering stress-strain diagram, determine (a) the modulus of elasticity, (b) the yield strength (0.002 strain offset), and (c) the tensile strength and (d) estimate the percentage elongation.
5. For the tensile deformation of a ductile cylindrical specimen, describe changes in specimen profile to the point of fracture.
6. Compute ductility in terms of both percentage elongation and percentage reduction of area for a material that is loaded in tension to fracture.
7. Give brief definitions of and the units for modulus of resilience and toughness (static).
8. For a specimen being loaded in tension, given the applied load, the instantaneous cross-sectional dimensions, and original and instantaneous lengths, be able to compute true stress and true strain values.
9. Name the two most common hardness-testing techniques; note two differences between them.
10. (a) Name and briefly describe the two different microindentation hardness testing techniques, and (b) cite situations for which these techniques are generally used.
11. Compute the working stress for a ductile material.

6.1 INTRODUCTION

Many materials are subjected to forces or loads when in service; examples include the aluminum alloy from which an airplane wing is constructed and the steel in an automobile axle. In such situations it is necessary to know the characteristics of the material and to design the member from which it is made such that any resulting deformation will not be excessive and fracture will not occur. The mechanical behavior of a material reflects its response or deformation in relation to an applied load or force. Key mechanical design properties are stiffness, strength, hardness, ductility, and toughness.

The mechanical properties of materials are ascertained by performing carefully designed laboratory experiments that replicate as nearly as possible the service conditions. Factors to be considered include the nature of the applied load and its duration, as well as the environmental conditions. It is possible for the load to be tensile, compressive, or shear, and its magnitude may be constant with time, or it may fluctuate continuously. Application time may be only a fraction of a second, or it may extend over a period of many years. Service temperature may be an important factor.

Mechanical properties are of concern to a variety of parties (e.g., producers and consumers of materials, research organizations, government agencies) that have differing interests. Consequently, it is imperative that there be some consistency in the manner in which tests are conducted and in the interpretation of their results. This consistency is accomplished by using standardized testing techniques. Establishment

and publication of these standards are often coordinated by professional societies. In the United States the most active organization is the American Society for Testing and Materials (ASTM). Its *Annual Book of ASTM Standards* (<http://www.astm.org>) comprises numerous volumes that are issued and updated yearly; a large number of these standards relate to mechanical testing techniques. Several of these are referenced by footnote in this and subsequent chapters.

The role of structural engineers is to determine stresses and stress distributions within members that are subjected to well-defined loads. This may be accomplished by experimental testing techniques and/or by theoretical and mathematical stress analyses. These topics are treated in traditional texts on stress analysis and strength of materials.

Materials and metallurgical engineers, however, are concerned with producing and fabricating materials to meet service requirements as predicted by these stress analyses. This necessarily involves an understanding of the relationships between the microstructure (i.e., internal features) of materials and their mechanical properties.

Materials are frequently chosen for structural applications because they have desirable combinations of mechanical characteristics. The present discussion is confined primarily to the mechanical behavior of metals; polymers and ceramics are treated separately because they are, to a large degree, mechanically different from metals. This chapter discusses the stress-strain behavior of metals and the related mechanical properties, and also examines other important mechanical characteristics. Discussions of the microscopic aspects of deformation mechanisms and methods to strengthen and regulate the mechanical behavior of metals are deferred to later chapters.

6.2 CONCEPTS OF STRESS AND STRAIN

If a load is static or changes relatively slowly with time and is applied uniformly over a cross section or surface of a member, the mechanical behavior may be ascertained by a simple stress-strain test; these are most commonly conducted for metals at room temperature. There are three principal ways in which a load may be applied: namely, tension, compression, and shear (Figures 6.1*a*, *b*, *c*). In engineering practice many loads are torsional rather than pure shear; this type of loading is illustrated in Figure 6.1*d*.

Tension Tests¹

One of the most common mechanical stress-strain tests is performed in *tension*. As will be seen, the tension test can be used to ascertain several mechanical properties of materials that are important in design. A specimen is deformed, usually to fracture, with a gradually increasing tensile load that is applied uniaxially along the long axis of a specimen. A standard tensile specimen is shown in Figure 6.2. Normally, the cross section is circular, but rectangular specimens are also used. This “dogbone” specimen configuration was chosen so that, during testing, deformation is confined to the narrow center region (which has a uniform cross section along its length) and also to reduce the likelihood of fracture at the ends of the specimen. The standard diameter is approximately 12.8 mm (0.5 in.), whereas the reduced section length should be at least four times this diameter; 60 mm (2½ in.) is common. Gauge length is used in ductility computations, as discussed in Section 6.6; the standard value is 50 mm (2.0 in.). The specimen is mounted by its ends into the holding grips of the

¹ASTM Standards E8 and E8M, “Standard Test Methods for Tension Testing of Metallic Materials.”

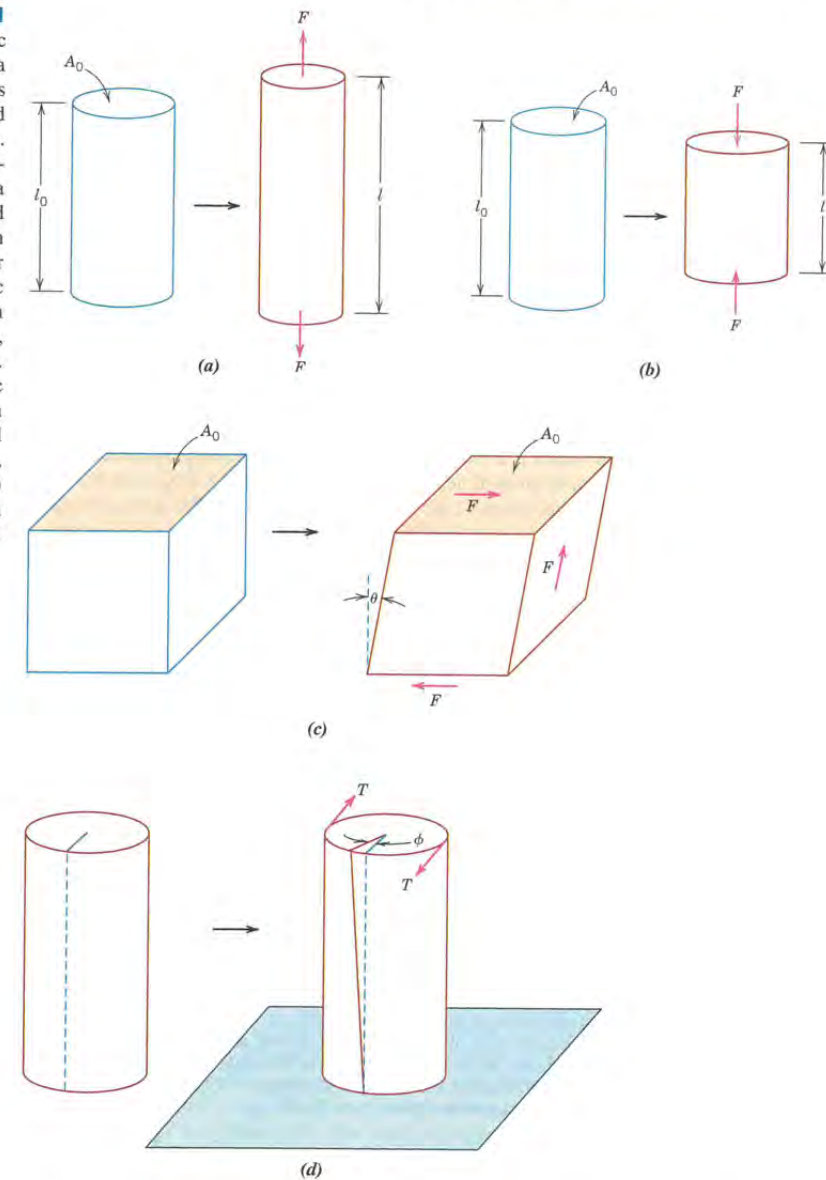
Figure 6.1

(a) Schematic illustration of how a tensile load produces an elongation and positive linear strain.

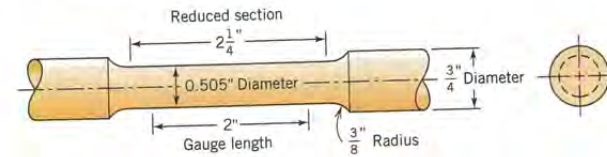
(b) Schematic illustration of how a compressive load produces contraction and a negative linear strain.

(c) Schematic representation of shear strain γ , where $\gamma = \tan \theta$.

(d) Schematic representation of torsional deformation (i.e., angle of twist ϕ) produced by an applied torque T .



testing apparatus (Figure 6.3). The tensile testing machine is designed to elongate the specimen at a constant rate, and to continuously and simultaneously measure the instantaneous applied load (with a load cell) and the resulting elongations (using an extensometer). A stress-strain test typically takes several minutes to perform and is destructive; that is, the test specimen is permanently deformed and usually fractured. [Photograph (a) opening this chapter is of a modern tensile-testing apparatus.]

Figure 6.2 A standard tensile specimen with circular cross section.

The output of such a tensile test is recorded (usually on a computer) as load or force versus elongation. These load–deformation characteristics depend on the specimen size. For example, it requires twice the load to produce the same elongation if the cross-sectional area of the specimen is doubled. To minimize these geometrical factors, load and elongation are normalized to the respective parameters of **engineering stress** and **engineering strain**. Engineering stress σ is defined by the relationship

$$\sigma = \frac{F}{A_0} \quad (6.1)$$

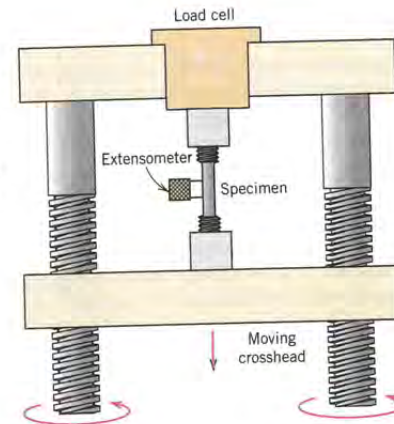
in which F is the instantaneous load applied perpendicular to the specimen cross section, in units of newtons (N) or pounds force (lb_f), and A_0 is the original cross-sectional area before any load is applied (m² or in.²). The units of engineering stress (referred to subsequently as just *stress*) are megapascals, MPa (SI) (where 1 MPa = 10⁶ N/m²), and pounds force per square inch, psi (customary U.S.).²

Engineering strain ϵ is defined according to

$$\epsilon = \frac{l_i - l_0}{l_0} = \frac{\Delta l}{l_0} \quad (6.2)$$

in which l_0 is the original length before any load is applied and l_i is the instantaneous length. Sometimes the quantity $l_i - l_0$ is denoted as Δl and is the deformation elongation or change in length at some instant, as referenced to the original length. Engineering strain (subsequently called just *strain*) is unitless, but meters per meter or inches per inch is often used; the value of strain is obviously independent of the unit system. Sometimes strain is also expressed as a percentage, in which the strain value is multiplied by 100.

Figure 6.3 Schematic representation of the apparatus used to conduct tensile stress–strain tests. The specimen is elongated by the moving crosshead; load cell and extensometer measure, respectively, the magnitude of the applied load and the elongation. (Adapted from H. W. Hayden, W. G. Moffatt, and J. Wulff, *The Structure and Properties of Materials*, Vol. III, *Mechanical Behavior*, p. 2. Copyright © 1965 by John Wiley & Sons, New York.)



engineering stress
engineering strain

Definition of
engineering stress
(for tension and
compression)

Definition of
engineering strain
(for tension and
compression)

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Tutorial Video:

Tensile Test

What are the
Differences between
Stress and Strain?

²Conversion from one system of stress units to the other is accomplished by the relationship 145 psi = 1 MPa.

Compression Tests³

Compression stress–strain tests may be conducted if in-service forces are of this type. A compression test is conducted in a manner similar to the tensile test, except that the force is compressive and the specimen contracts along the direction of the stress. Equations 6.1 and 6.2 are utilized to compute compressive stress and strain, respectively. By convention, a compressive force is taken to be negative, which yields a negative stress. Furthermore, because l_0 is greater than l_i , compressive strains computed from Equation 6.2 are necessarily also negative. Tensile tests are more common because they are easier to perform; also, for most materials used in structural applications, very little additional information is obtained from compressive tests. Compressive tests are used when a material's behavior under large and permanent (i.e., plastic) strains is desired, as in manufacturing applications, or when the material is brittle in tension.

Shear and Torsional Tests⁴

For tests performed using a pure shear force as shown in Figure 6.1c, the shear stress τ is computed according to

$$\tau = \frac{F}{A_0} \quad (6.3)$$

where F is the load or force imposed parallel to the upper and lower faces, each of which has an area of A_0 . The shear strain γ is defined as the tangent of the strain angle θ , as indicated in the figure. The units for shear stress and strain are the same as for their tensile counterparts.

Torsion is a variation of pure shear in which a structural member is twisted in the manner of Figure 6.1d; torsional forces produce a rotational motion about the longitudinal axis of one end of the member relative to the other end. Examples of torsion are found for machine axles and drive shafts as well as for twist drills. Torsional tests are normally performed on cylindrical solid shafts or tubes. A shear stress τ is a function of the applied torque T , whereas shear strain γ is related to the angle of twist, ϕ in Figure 6.1d.

Geometric Considerations of the Stress State

Stresses that are computed from the tensile, compressive, shear, and torsional force states represented in Figure 6.1 act either parallel or perpendicular to planar faces of the bodies represented in these illustrations. Note that the stress state is a function of the orientations of the planes upon which the stresses are taken to act. For example, consider the cylindrical tensile specimen of Figure 6.4 that is subjected to a tensile stress σ applied parallel to its axis. Furthermore, consider also the plane $p-p'$ that is oriented at some arbitrary angle θ relative to the plane of the specimen end-face. Upon this plane $p-p'$, the applied stress is no longer a pure tensile one. Rather, a more complex stress state is present that consists of a tensile (or normal) stress σ' that acts normal to the $p-p'$ plane and, in addition, a shear stress τ' that acts parallel to this plane; both of these stresses are represented in the figure. Using

Definition of shear
stress

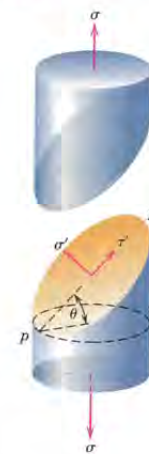


Figure 6.4 Schematic representation showing normal (σ') and shear (τ') stresses that act on a plane oriented at an angle θ relative to the plane taken perpendicular to the direction along which a pure tensile stress (σ) is applied.

³ASTM Standard E9, "Standard Test Methods of Compression Testing of Metallic Materials at Room Temperature."

⁴ASTM Standard E143, "Standard Test Method for Shear Modulus at Room Temperature."

mechanics-of-materials principles,⁵ it is possible to develop equations for σ' and τ' in terms of σ and θ , as follows:

$$\sigma' = \sigma \cos^2 \theta = \sigma \left(\frac{1 + \cos 2\theta}{2} \right) \tag{6.4a}$$

$$\tau' = \sigma \sin \theta \cos \theta = \sigma \left(\frac{\sin 2\theta}{2} \right) \tag{6.4b}$$

These same mechanics principles allow the transformation of stress components from one coordinate system to another coordinate system with a different orientation. Such treatments are beyond the scope of the present discussion.

Elastic Deformation

6.3 STRESS-STRAIN BEHAVIOR

Hooke's law—relationship between engineering stress and engineering strain for elastic deformation (tension and compression)

modulus of elasticity
elastic deformation



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Metal Alloys

Table 6.1
Room-Temperature
Elastic and Shear
Moduli and Poisson's
Ratio for Various
Metal Alloys

Metal Alloy	Modulus of Elasticity		Shear Modulus		Poisson's Ratio
	GPa	10 ⁶ psi	GPa	10 ⁶ psi	
Aluminum	69	10	25	3.6	0.33
Brass	97	14	37	5.4	0.34
Copper	110	16	46	6.7	0.34
Magnesium	45	6.5	17	2.5	0.29
Nickel	207	30	76	11.0	0.31
Steel	207	30	83	12.0	0.30
Titanium	107	15.5	45	6.5	0.34
Tungsten	407	59	160	23.2	0.28

⁵See, for example, W. F. Riley, L. D. Sturges, and D. H. Morris, *Mechanics of Materials*, 6th edition, Wiley, Hoboken, NJ, 2006.

⁶The SI unit for the modulus of elasticity is *gigapascal* (GPa), where 1 GPa = 10⁹ N/m² = 10³ MPa.

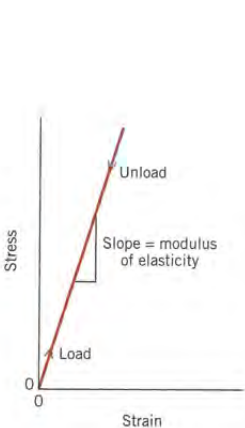


Figure 6.5 Schematic stress-strain diagram showing linear elastic deformation for loading and unloading cycles.

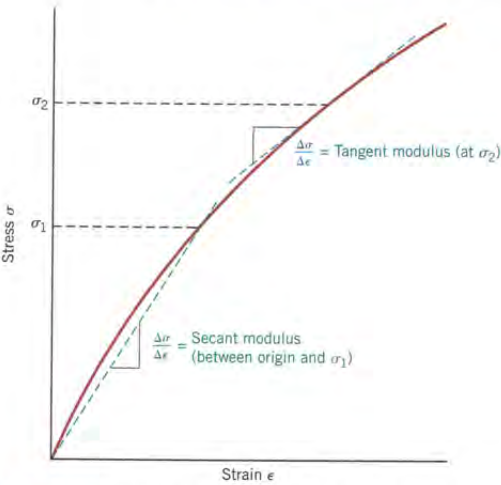


Figure 6.6 Schematic stress-strain diagram showing nonlinear elastic behavior and how secant and tangent moduli are determined.

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Calculations
Calculating Elastic
Modulus Using a
Stress vs. Strain Curve

from the application of a given stress. The modulus is an important design parameter for computing elastic deflections.

Elastic deformation is *nonpermanent*, which means that when the applied load is released, the piece returns to its original shape. As shown in the stress-strain plot (Figure 6.5), application of the load corresponds to moving from the origin up and along the straight line. Upon release of the load, the line is traversed in the opposite direction, back to the origin.

There are some materials (i.e., gray cast iron, concrete, and many polymers) for which this elastic portion of the stress-strain curve is not linear (Figure 6.6); hence, it is not possible to determine a modulus of elasticity as described previously. For this nonlinear behavior, either the *tangent* or *secant modulus* is normally used. The tangent modulus is taken as the slope of the stress-strain curve at some specified level of stress, whereas the secant modulus represents the slope of a secant drawn from the origin to some given point of the σ - ϵ curve. The determination of these moduli is illustrated in Figure 6.6.

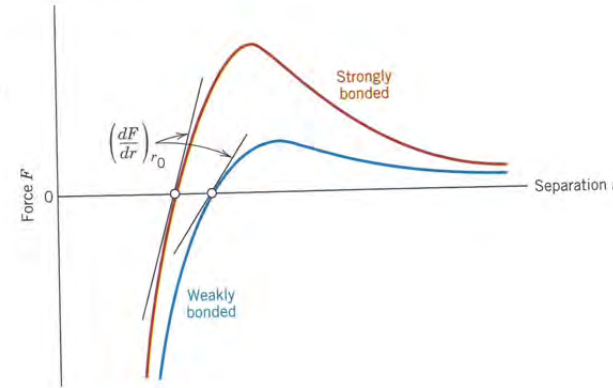
On an atomic scale, macroscopic elastic strain is manifested as small changes in the interatomic spacing and the stretching of interatomic bonds. As a consequence, the magnitude of the modulus of elasticity is a measure of the resistance to separation of adjacent atoms, that is, the interatomic bonding forces. Furthermore, this modulus is proportional to the slope of the interatomic force-separation curve (Figure 2.10a) at the equilibrium spacing:

$$E \propto \left(\frac{dF}{dr} \right)_{r_0} \tag{6.6}$$

Figure 6.7 shows the force-separation curves for materials having both strong and weak interatomic bonds; the slope at r_0 is indicated for each.

Values of the modulus of elasticity for ceramic materials are about the same as for metals; for polymers they are lower (Figure 1.5). These differences are a direct consequence of the different types of atomic bonding in the three materials types.

Figure 6.7 Force versus interatomic separation for weakly and strongly bonded atoms. The magnitude of the modulus of elasticity is proportional to the slope of each curve at the equilibrium interatomic separation r_0 .



Furthermore, with increasing temperature, the modulus of elasticity decreases, as is shown for several metals in Figure 6.8.

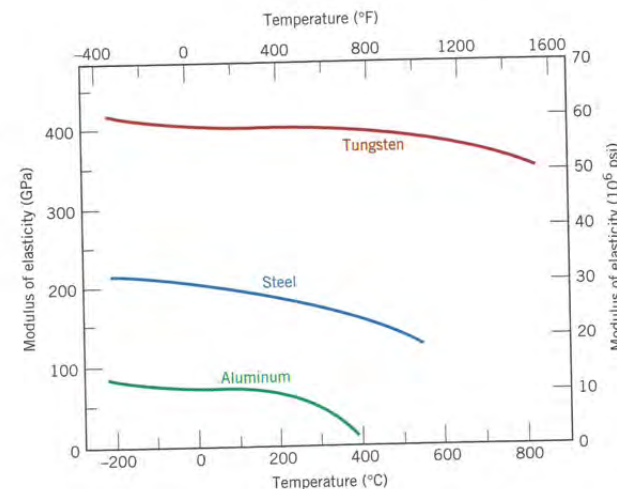
As would be expected, the imposition of compressive, shear, or torsional stresses also evokes elastic behavior. The stress-strain characteristics at low stress levels are virtually the same for both tensile and compressive situations, to include the magnitude of the modulus of elasticity. Shear stress and strain are proportional to each other through the expression

$$\tau = G\gamma \quad (6.7)$$

where G is the *shear modulus*, the slope of the linear elastic region of the shear stress-strain curve. Table 6.1 also gives the shear moduli for a number of common metals.

Relationship
between shear stress
and shear strain for
elastic deformation

Figure 6.8 Plot of modulus of elasticity versus temperature for tungsten, steel, and aluminum.
(Adapted from K. M. Ralls, T. H. Courtney, and J. Wulff, *Introduction to Materials Science and Engineering*. Copyright © 1976 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)



6.4 ANELASTICITY

anelasticity

To this point, it has been assumed that elastic deformation is time independent—that is, that an applied stress produces an instantaneous elastic strain that remains constant over the period of time the stress is maintained. It has also been assumed that upon release of the load, the strain is totally recovered—that is, that the strain immediately returns to zero. In most engineering materials, however, there will also exist a time-dependent elastic strain component—that is, elastic deformation will continue after the stress application, and upon load release, some finite time is required for complete recovery. This time-dependent elastic behavior is known as **anelasticity**, and it is due to time-dependent microscopic and atomistic processes that are attendant to the deformation. For metals, the anelastic component is normally small and is often neglected. However, for some polymeric materials, its magnitude is significant; in this case it is termed *viscoelastic behavior*, which is the discussion topic of Section 15.4.

EXAMPLE PROBLEM 6.1

Elongation (Elastic) Computation

A piece of copper originally 305 mm (12 in.) long is pulled in tension with a stress of 276 MPa (40,000 psi). If the deformation is entirely elastic, what will be the resultant elongation?

Solution

Because the deformation is elastic, strain is dependent on stress according to Equation 6.5. Furthermore, the elongation Δl is related to the original length l_0 through Equation 6.2. Combining these two expressions and solving for Δl yields

$$\sigma = \epsilon E = \left(\frac{\Delta l}{l_0} \right) E$$

$$\Delta l = \frac{\sigma l_0}{E}$$

The values of σ and l_0 are given as 276 MPa and 305 mm, respectively, and the magnitude of E for copper from Table 6.1 is 110 GPa (16×10^6 psi). Elongation is obtained by substitution into the preceding expression as

$$\Delta l = \frac{(276 \text{ MPa})(305 \text{ mm})}{110 \times 10^3 \text{ MPa}} = 0.77 \text{ mm (0.03 in.)}$$

6.5 ELASTIC PROPERTIES OF MATERIALS

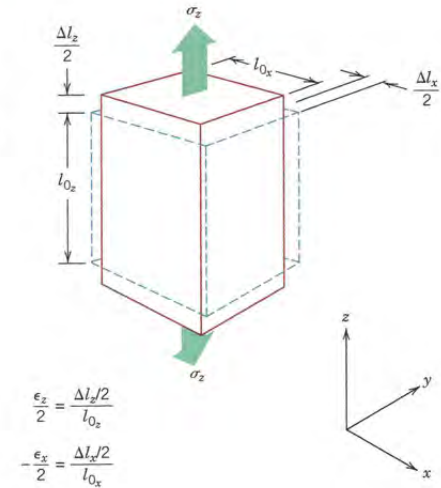
Poisson's ratio

Definition of
Poisson's ratio in
terms of lateral
and axial strains

When a tensile stress is imposed on a metal specimen, an elastic elongation and accompanying strain ϵ_z result in the direction of the applied stress (arbitrarily taken to be the z direction), as indicated in Figure 6.9. As a result of this elongation, there will be constrictions in the lateral (x and y) directions perpendicular to the applied stress; from these contractions, the compressive strains ϵ_x and ϵ_y may be determined. If the applied stress is uniaxial (only in the z direction) and the material is isotropic, then $\epsilon_x = \epsilon_y$. A parameter termed **Poisson's ratio** ν is defined as the ratio of the lateral and axial strains, or

$$\nu = -\frac{\epsilon_x}{\epsilon_z} = -\frac{\epsilon_y}{\epsilon_z} \quad (6.8)$$

Figure 6.9 Axial (z) elongation (positive strain) and lateral (x and y) contractions (negative strains) in response to an imposed tensile stress. Solid lines represent dimensions after stress application; dashed lines, before.



For virtually all structural materials, ϵ_x and ϵ_z will be of opposite sign; therefore, the negative sign is included in the preceding expression to ensure that ν is positive.⁷ Theoretically, Poisson's ratio for isotropic materials should be $\frac{1}{4}$; furthermore, the maximum value for ν (or the value for which there is no net volume change) is 0.50. For many metals and other alloys, values of Poisson's ratio range between 0.25 and 0.35. Table 6.1 shows ν values for several common metallic materials.

For isotropic materials, shear and elastic moduli are related to each other and to Poisson's ratio according to

$$E = 2G(1 + \nu) \quad (6.9)$$

In most metals, G is about $0.4E$; thus, if the value of one modulus is known, the other may be approximated.

Many materials are elastically anisotropic; that is, the elastic behavior (i.e., the magnitude of E) varies with crystallographic direction (see Table 3.4). For these materials, the elastic properties are completely characterized only by the specification of several elastic constants, their number depending on characteristics of the crystal structure. Even for isotropic materials, for complete characterization of the elastic properties, at least two constants must be given. Because the grain orientation is random in most polycrystalline materials, these may be considered to be isotropic; inorganic ceramic glasses are also isotropic. The remaining discussion of mechanical behavior assumes isotropy and polycrystallinity because this is the character of most engineering materials.

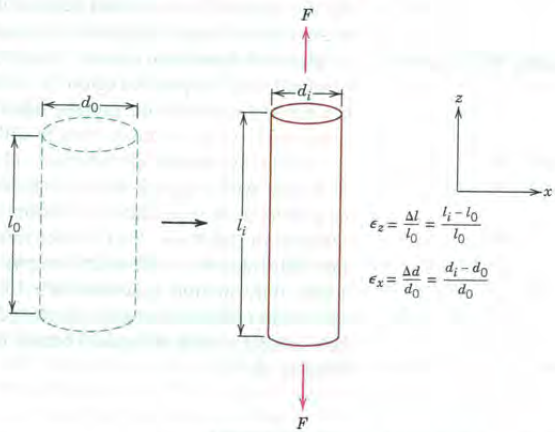
Relationship among elastic parameters—modulus of elasticity, shear modulus, and Poisson's ratio

⁷Some materials (e.g., specially prepared polymer foams) when pulled in tension actually expand in the transverse direction. In these materials, both ϵ_x and ϵ_z of Equation 6.8 are positive, and thus Poisson's ratio is negative. Materials that exhibit this effect are termed *auxetics*.

EXAMPLE PROBLEM 6.2

Computation of Load to Produce Specified Diameter Change

A tensile stress is to be applied along the long axis of a cylindrical brass rod that has a diameter of 10 mm (0.4 in.). Determine the magnitude of the load required to produce a 2.5×10^{-3} -mm (10^{-4} -in.) change in diameter if the deformation is entirely elastic.



Solution

This deformation situation is represented in the accompanying drawing.

When the force F is applied, the specimen will elongate in the z direction and at the same time experience a reduction in diameter, Δd , of 2.5×10^{-3} mm in the x direction. For the strain in the x direction,

$$\epsilon_x = \frac{\Delta d}{d_0} = \frac{-2.5 \times 10^{-3} \text{ mm}}{10 \text{ mm}} = -2.5 \times 10^{-4}$$

which is negative because the diameter is reduced.

It next becomes necessary to calculate the strain in the z direction using Equation 6.8. The value for Poisson's ratio for brass is 0.34 (Table 6.1), and thus

$$\epsilon_z = -\frac{\epsilon_x}{\nu} = -\frac{(-2.5 \times 10^{-4})}{0.34} = 7.35 \times 10^{-4}$$

The applied stress may now be computed using Equation 6.5 and the modulus of elasticity, given in Table 6.1 as 97 GPa (14×10^6 psi), as

$$\sigma = \epsilon_z E = (7.35 \times 10^{-4})(97 \times 10^3 \text{ MPa}) = 71.3 \text{ MPa}$$

Finally, from Equation 6.1, the applied force may be determined as

$$\begin{aligned} F &= \sigma A_0 = \sigma \left(\frac{d_0}{2} \right)^2 \pi \\ &= (71.3 \times 10^6 \text{ N/m}^2) \left(\frac{10 \times 10^{-3} \text{ m}}{2} \right)^2 \pi = 5600 \text{ N (1293 lb}_f\text{)} \end{aligned}$$

Plastic Deformation

plastic deformation

For most metallic materials, elastic deformation persists only to strains of about 0.005. As the material is deformed beyond this point, the stress is no longer proportional to strain (Hooke's law, Equation 6.5, ceases to be valid), and permanent, nonrecoverable, or **plastic deformation** occurs. Figure 6.10a plots schematically the tensile stress-strain behavior into the plastic region for a typical metal. The transition from elastic to plastic is a gradual one for most metals; some curvature results at the onset of plastic deformation, which increases more rapidly with rising stress.

From an atomic perspective, plastic deformation corresponds to the breaking of bonds with original atom neighbors and then the re-forming of bonds with new neighbors as large numbers of atoms or molecules move relative to one another; upon removal of the stress, they do not return to their original positions. The mechanism of this deformation is different for crystalline and amorphous materials. For crystalline solids, deformation is accomplished by means of a process called *slip*, which involves the motion of dislocations as discussed in Section 7.2. Plastic deformation in noncrystalline solids (as well as liquids) occurs by a viscous flow mechanism, which is outlined in Section 12.10.

6.6 TENSILE PROPERTIES

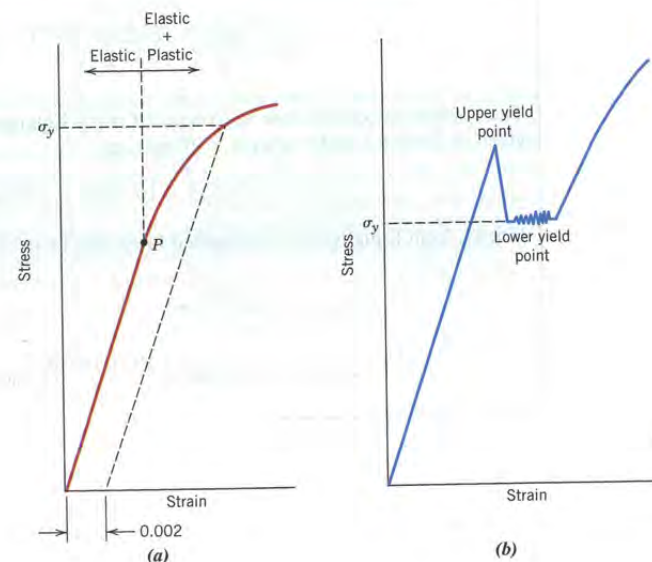


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Metal Alloys
yielding

Yielding and Yield Strength

Most structures are designed to ensure that only elastic deformation will result when a stress is applied. A structure or component that has plastically deformed—or experienced a permanent change in shape—may not be capable of functioning as intended. It is therefore desirable to know the stress level at which plastic deformation begins, or where the phenomenon of **yielding** occurs. For metals that experience this gradual

Figure 6.10 (a) Typical stress-strain behavior for a metal showing elastic and plastic deformations, the proportional limit P , and the yield strength σ_y , as determined using the 0.002 strain offset method. (b) Representative stress-strain behavior found for some steels demonstrating the yield point phenomenon.



proportional limit

yield strength

elastic-plastic transition, the point of yielding may be determined as the initial departure from linearity of the stress-strain curve; this is sometimes called the **proportional limit**, as indicated by point P in Figure 6.10a, and represents the onset of plastic deformation on a microscopic level. The position of this point P is difficult to measure precisely. As a consequence, a convention has been established by which a straight line is constructed parallel to the elastic portion of the stress-strain curve at some specified strain offset, usually 0.002. The stress corresponding to the intersection of this line and the stress-strain curve as it bends over in the plastic region is defined as the **yield strength** σ_y .⁸ This is demonstrated in Figure 6.10a. The units of yield strength are MPa or psi.⁹

For materials having a nonlinear elastic region (Figure 6.6), use of the strain offset method is not possible, and the usual practice is to define the yield strength as the stress required to produce some amount of strain (e.g., $\epsilon = 0.005$).

Some steels and other materials exhibit the tensile stress-strain behavior shown in Figure 6.10b. The elastic-plastic transition is very well defined and occurs abruptly in what is termed a **yield point phenomenon**. At the upper yield point, plastic deformation is initiated with an apparent decrease in engineering stress. Continued deformation fluctuates slightly about some constant stress value, termed the **lower yield point**; stress subsequently rises with increasing strain. For metals that display this effect, the yield strength is taken as the average stress that is associated with the lower yield point because it is well defined and relatively insensitive to the testing procedure.¹⁰ Thus, it is not necessary to employ the strain offset method for these materials.

The magnitude of the yield strength for a metal is a measure of its resistance to plastic deformation. Yield strengths may range from 35 MPa (5000 psi) for a low-strength aluminum to greater than 1400 MPa (200,000 psi) for high-strength steels.



Concept Check 6.1 Cite the primary differences between elastic, anelastic, and plastic deformation behaviors.

[The answer may be found at www.wiley.com/college/callister (Student Companion Site).]

tensile strength

Tensile Strength

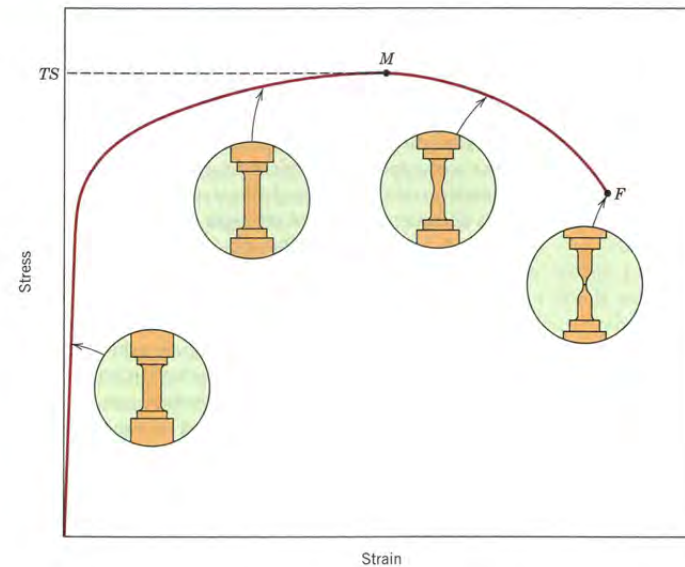
After yielding, the stress necessary to continue plastic deformation in metals increases to a maximum, point M in Figure 6.11, and then decreases to the eventual fracture, point F . The **tensile strength** TS (MPa or psi) is the stress at the maximum on the engineering stress-strain curve (Figure 6.11). This corresponds to the maximum stress that can be sustained by a structure in tension; if this stress is applied and maintained, fracture will result. All deformation to this point is uniform throughout the narrow region of the tensile specimen. However, at this maximum stress, a small constriction or neck begins to form at some point, and all subsequent deformation is confined at this neck, as indicated by the schematic specimen insets in Figure 6.11. This phenomenon is termed **necking**,

⁸Strength is used in lieu of stress because strength is a property of the metal, whereas stress is related to the magnitude of the applied load.

⁹For customary U.S. units, the unit of kilopounds per square inch (ksi) is sometimes used for the sake of convenience, where 1 ksi = 1000 psi.

¹⁰Note that to observe the yield point phenomenon, a "stiff" tensile-testing apparatus must be used; by "stiff," it is meant that there is very little elastic deformation of the machine during loading.

Figure 6.11 Typical engineering stress–strain behavior to fracture, point *F*. The tensile strength *TS* is indicated at point *M*. The circular insets represent the geometry of the deformed specimen at various points along the curve.



and fracture ultimately occurs at the neck.¹¹ The fracture strength corresponds to the stress at fracture.

Tensile strengths vary from 50 MPa (7000 psi) for an aluminum to as high as 3000 MPa (450,000 psi) for the high-strength steels. Typically, when the strength of a metal is cited for design purposes, the yield strength is used because by the time a stress corresponding to the tensile strength has been applied, often a structure has experienced so much plastic deformation that it is useless. Furthermore, fracture strengths are not normally specified for engineering design purposes.

EXAMPLE PROBLEM 6.3

Mechanical Property Determinations from Stress–Strain Plot

From the tensile stress–strain behavior for the brass specimen shown in Figure 6.12, determine the following:

- The modulus of elasticity
- The yield strength at a strain offset of 0.002
- The maximum load that can be sustained by a cylindrical specimen having an original diameter of 12.8 mm (0.505 in.)
- The change in length of a specimen originally 250 mm (10 in.) long that is subjected to a tensile stress of 345 MPa (50,000 psi)

Solution

- The modulus of elasticity is the slope of the elastic or initial linear portion of the stress–strain curve. The strain axis has been expanded in the inset of Figure 6.12 to facilitate

¹¹The apparent decrease in engineering stress with continued deformation past the maximum point of Figure 6.11 is due to the necking phenomenon. As explained in Section 6.7, the true stress (within the neck) actually increases.

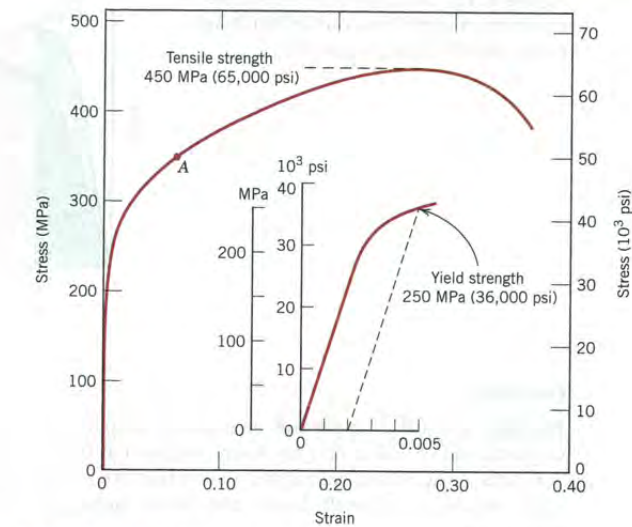


Figure 6.12 The stress–strain behavior for the brass specimen discussed in Example Problem 6.3.

this computation. The slope of this linear region is the rise over the run, or the change in stress divided by the corresponding change in strain; in mathematical terms,

$$E = \text{slope} = \frac{\Delta\sigma}{\Delta\epsilon} = \frac{\sigma_2 - \sigma_1}{\epsilon_2 - \epsilon_1} \quad (6.10)$$

Inasmuch as the line segment passes through the origin, it is convenient to take both σ_1 and ϵ_1 as zero. If σ_2 is arbitrarily taken as 150 MPa, then ϵ_2 will have a value of 0.0016. Therefore,

$$E = \frac{(150 - 0) \text{ MPa}}{0.0016 - 0} = 93.8 \text{ GPa } (13.6 \times 10^6 \text{ psi})$$

which is very close to the value of 97 GPa (14×10^6 psi) given for brass in Table 6.1.

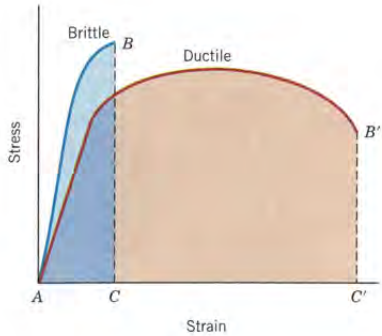
- The 0.002 strain offset line is constructed as shown in the inset; its intersection with the stress–strain curve is at approximately 250 MPa (36,000 psi), which is the yield strength of the brass.
- The maximum load that can be sustained by the specimen is calculated by using Equation 6.1, in which σ is taken to be the tensile strength, from Figure 6.12, 450 MPa (65,000 psi). Solving for F , the maximum load, yields

$$\begin{aligned} F &= \sigma A_0 = \sigma \left(\frac{d_0}{2} \right)^2 \pi \\ &= (450 \times 10^6 \text{ N/m}^2) \left(\frac{12.8 \times 10^{-3} \text{ m}}{2} \right)^2 \pi = 57,900 \text{ N } (13,000 \text{ lb}_f) \end{aligned}$$

- To compute the change in length, Δl , in Equation 6.2, it is first necessary to determine the strain that is produced by a stress of 345 MPa. This is accomplished by locating the stress point on the stress–strain curve, point *A*, and reading the corresponding strain from the strain axis, which is approximately 0.06. Inasmuch as $l_0 = 250$ mm, we have

$$\Delta l = \epsilon l_0 = (0.06)(250 \text{ mm}) = 15 \text{ mm } (0.6 \text{ in.})$$

Figure 6.13 Schematic representations of tensile stress–strain behavior for brittle and ductile metals loaded to fracture.



Ductility

ductility

Ductility is another important mechanical property. It is a measure of the degree of plastic deformation that has been sustained at fracture. A metal that experiences very little or no plastic deformation upon fracture is termed *brittle*. The tensile stress–strain behaviors for both ductile and brittle metals are schematically illustrated in Figure 6.13.

Ductility may be expressed quantitatively as either *percent elongation* or *percent reduction in area*. Percent elongation (%EL) is the percentage of plastic strain at fracture, or

Ductility, as percent elongation

$$\%EL = \left(\frac{l_f - l_0}{l_0} \right) \times 100 \quad (6.11)$$

where l_f is the fracture length¹² and l_0 is the original gauge length as given earlier. Inasmuch as a significant proportion of the plastic deformation at fracture is confined to the neck region, the magnitude of %EL will depend on specimen gauge length. The shorter l_0 , the greater the fraction of total elongation from the neck and, consequently, the higher the value of %EL. Therefore, l_0 should be specified when percent elongation values are cited; it is commonly 50 mm (2 in.).

Percent reduction in area (%RA) is defined as

Ductility, as percent reduction in area

$$\%RA = \left(\frac{A_0 - A_f}{A_0} \right) \times 100 \quad (6.12)$$

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Tutorial Video:
Tensile Test
How do I determine ductility in percent elongation and percent reduction in area?

where A_0 is the original cross-sectional area and A_f is the cross-sectional area at the point of fracture.¹² Values of percent reduction in area are independent of both l_0 and A_0 . Furthermore, for a given material, the magnitudes of %EL and %RA will, in general, be different. Most metals possess at least a moderate degree of ductility at room temperature; however, some become brittle as the temperature is lowered (Section 8.6).

Knowledge of the ductility of materials is important for at least two reasons. First, it indicates to a designer the degree to which a structure will deform plastically before

¹²Both l_f and A_f are measured subsequent to fracture and after the two broken ends have been repositioned back together.

Table 6.2
Typical Mechanical Properties of Several Metals and Alloys in an Annealed State

Metal Alloy	Yield Strength, MPa (ksi)	Tensile Strength, MPa (ksi)	Ductility, %EL [in 50 mm (2 in.)]
Aluminum	35 (5)	90 (13)	40
Copper	69 (10)	200 (29)	45
Brass (70Cu–30Zn)	75 (11)	300 (44)	68
Iron	130 (19)	262 (38)	45
Nickel	138 (20)	480 (70)	40
Steel (1020)	180 (26)	380 (55)	25
Titanium	450 (65)	520 (75)	25
Molybdenum	565 (82)	655 (95)	35

fracture. Second, it specifies the degree of allowable deformation during fabrication operations. We sometimes refer to relatively ductile materials as being “forgiving,” in the sense that they may experience local deformation without fracture, should there be an error in the magnitude of the design stress calculation.

Brittle materials are *approximately* considered to be those having a fracture strain of less than about 5%.

Thus, several important mechanical properties of metals may be determined from tensile stress–strain tests. Table 6.2 presents some typical room-temperature values of yield strength, tensile strength, and ductility for several common metals. These properties are sensitive to any prior deformation, the presence of impurities, and/or any heat treatment to which the metal has been subjected. The modulus of elasticity is one mechanical parameter that is insensitive to these treatments. As with modulus of elasticity, the magnitudes of both yield and tensile strengths decline with increasing temperature; just the reverse holds for ductility—it usually increases with temperature. Figure 6.14 shows how the stress–strain behavior of iron varies with temperature.

Resilience

resilience

Resilience is the capacity of a material to absorb energy when it is deformed elastically and then, upon unloading, to have this energy recovered. The associated property is the *modulus of resilience*, U_r , which is the strain energy per unit volume required to stress a material from an unloaded state up to the point of yielding.

Computationally, the modulus of resilience for a specimen subjected to a uniaxial tension test is just the area under the engineering stress–strain curve taken to yielding (Figure 6.15), or

Definition of modulus of resilience

$$U_r = \int_0^{\epsilon_y} \sigma d\epsilon \quad (6.13a)$$

Assuming a linear elastic region, we have

Modulus of resilience for linear elastic behavior

$$U_r = \frac{1}{2} \sigma_y \epsilon_y \quad (6.13b)$$

in which ϵ_y is the strain at yielding.

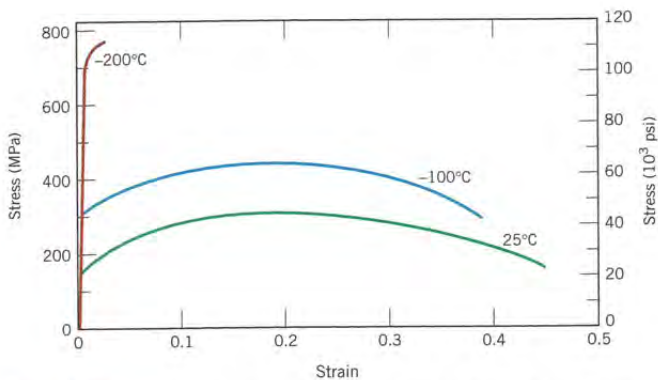


Figure 6.14 Engineering stress-strain behavior for iron at three temperatures.

The units of resilience are the product of the units from each of the two axes of the stress-strain plot. For SI units, this is joules per cubic meter (J/m^3 , equivalent to Pa), whereas with customary U.S. units it is inch-pounds force per cubic inch (in.-lb/in.^3 , equivalent to psi). Both joules and inch-pounds force are units of energy, and thus this area under the stress-strain curve represents energy absorption per unit volume (in cubic meters or cubic inches) of material.

Incorporation of Equation 6.5 into Equation 6.13b yields

$$U_r = \frac{1}{2} \sigma_y \epsilon_y = \frac{1}{2} \sigma_y \left(\frac{\sigma_y}{E} \right) = \frac{\sigma_y^2}{2E} \quad (6.14)$$

Thus, resilient materials are those having high yield strengths and low moduli of elasticity; such alloys are used in spring applications.

Toughness

Toughness is a mechanical term that may be used in several contexts. For one, toughness (or more specifically, *fracture toughness*) is a property that is indicative of a material's resistance to fracture when a crack (or other stress-concentrating defect) is present (as discussed in Section 8.5). Because it is nearly impossible (as well as costly) to manufacture materials with zero defects (or to prevent damage during service), fracture toughness is a major consideration for all structural materials.

Another way of defining toughness is as the ability of a material to absorb energy and plastically deform before fracturing. For dynamic (high strain rate) loading conditions and when a notch (or point of stress concentration) is present, *notch toughness* is assessed by using an impact test, as discussed in Section 8.6.

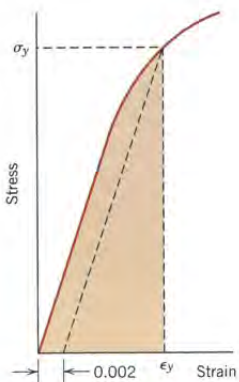


Figure 6.15 Schematic representation showing how modulus of resilience (corresponding to the shaded area) is determined from the tensile stress-strain behavior of a material.

Modulus of resilience for linear elastic behavior, and incorporating Hooke's law

toughness

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Tensile Test
What is toughness and how do I determine its value?

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Mechanical Property Calculations from Tensile Test Measurements

For the static (low strain rate) situation, a measure of toughness in metals (derived from plastic deformation) may be ascertained from the results of a tensile stress-strain test. It is the area under the σ - ϵ curve up to the point of fracture. The units are the same as for resilience (i.e., energy per unit volume of material). For a metal to be tough, it must display both strength and ductility. This is demonstrated in Figure 6.13, in which the stress-strain curves are plotted for both metal types. Hence, even though the brittle metal has higher yield and tensile strengths, it has a lower toughness than the ductile one, as can be seen by comparing the areas ABC and $AB'C'$ in Figure 6.13.

Concept Check 6.2 Of those metals listed in Table 6.3,

- (a) Which will experience the greatest percentage reduction in area? Why?
- (b) Which is the strongest? Why?
- (c) Which is the stiffest? Why?

[The answer may be found at www.wiley.com/college/callister (Student Companion Site).]

Table 6.3 Tensile Stress-Strain Data for Several Hypothetical Metals to Be Used with Concept Checks 6.2 and 6.4

Material	Yield Strength (MPa)	Tensile Strength (MPa)	Strain at Fracture	Fracture Strength (MPa)	Elastic Modulus (GPa)
A	310	340	0.23	265	210
B	100	120	0.40	105	150
C	415	550	0.15	500	310
D	700	850	0.14	720	210
E	Fractures before yielding			650	350

6.7 TRUE STRESS AND STRAIN

From Figure 6.11, the decline in the stress necessary to continue deformation past the maximum—point M —seems to indicate that the metal is becoming weaker. This is not at all the case; as a matter of fact, it is increasing in strength. However, the cross-sectional area is decreasing rapidly within the neck region, where deformation is occurring. This results in a reduction in the load-bearing capacity of the specimen. The stress, as computed from Equation 6.1, is on the basis of the original cross-sectional area before any deformation and does not take into account this reduction in area at the neck.

Sometimes it is more meaningful to use a true stress-true strain scheme. **True stress** σ_T is defined as the load F divided by the instantaneous cross-sectional area A_i over which deformation is occurring (i.e., the neck, past the tensile point), or

$$\sigma_T = \frac{F}{A_i} \quad (6.15)$$

true stress

Definition of true stress

Chapter 15 Characteristics, Applications, and Processing of Polymers

Photograph (a) shows billiard balls made of phenol-formaldehyde (Bakelite). The Materials of Importance piece that follows Section 15.15 discusses the invention of phenol-formaldehyde and its replacement of ivory for billiard balls. Photograph (b) shows a woman playing billiards.



(a)



(b)

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WHY STUDY the Characteristics, Applications, and Processing of Polymers?

There are several reasons why an engineer should know something about the characteristics, applications, and processing of polymeric materials. Polymers are used in a wide variety of applications, such as construction materials and microelectronics processing. Thus, most engineers will be required to work with polymers at some point in their careers. Understanding the mechanisms by which polymers

elastically and plastically deform allows one to alter and control their moduli of elasticity and strengths (Sections 15.7 and 15.8). Also, additives may be incorporated into polymeric materials to modify a host of properties, including strength, abrasion resistance, toughness, thermal stability, stiffness, deteriorability, color, and flammability resistance (Section 15.21).

Learning Objectives

After studying this chapter, you should be able to do the following:

1. Make schematic plots of the three characteristic stress-strain behaviors observed for polymeric materials.
2. Describe/sketch the various stages in the elastic and plastic deformations of a semicrystalline (spherulitic) polymer.
3. Discuss the influence of the following factors on polymer tensile modulus and/or strength: (a) molecular weight, (b) degree of crystallinity, (c) predeformation, and (d) heat treating of undeformed materials.
4. Describe the molecular mechanism by which elastomeric polymers deform elastically.
5. List four characteristics or structural components of a polymer that affect both its melting and glass transition temperatures.
6. Cite the seven different polymer application types and note the general characteristics of each type.
7. Briefly describe addition and condensation polymerization mechanisms.
8. Name the five types of polymer additives and, for each, indicate how it modifies the properties.
9. Name and briefly describe five fabrication techniques used for plastic polymers.

15.1 INTRODUCTION

This chapter discusses some of the characteristics important to polymeric materials and the various types and processing techniques.

Mechanical Behavior of Polymers

15.2 STRESS-STRAIN BEHAVIOR

The mechanical properties of polymers are specified with many of the same parameters that are used for metals—that is, modulus of elasticity and yield and tensile strengths. For many polymeric materials, the simple stress-strain test is used to characterize some of these mechanical parameters.¹ The mechanical characteristics of polymers, for the most part, are highly sensitive to the rate of deformation (strain rate), the temperature, and the chemical nature of the environment (the presence of water, oxygen, organic solvents, etc.). Some modifications of the testing techniques and specimen configurations used for metals (Chapter 6) are necessary with polymers, especially for highly elastic materials, such as rubbers.

¹ASTM Standard D638, "Standard Test Method for Tensile Properties of Plastics."

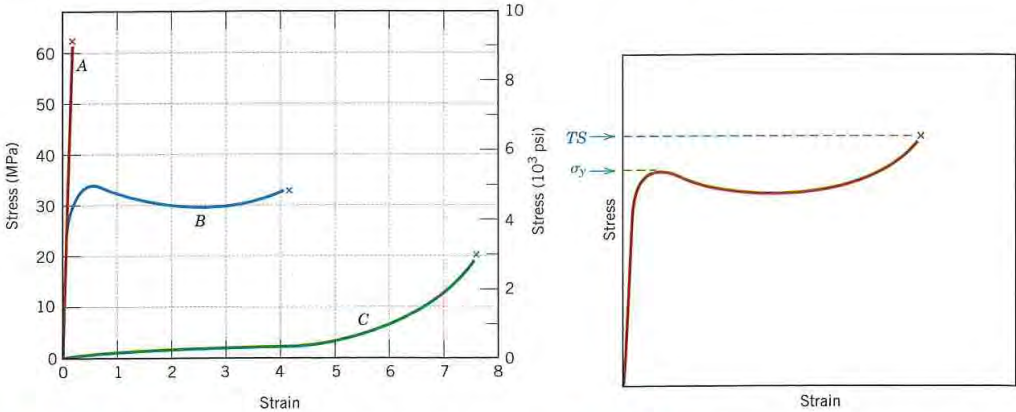


Figure 15.1 The stress-strain behavior for brittle (curve A), plastic (curve B), and highly elastic (elastomeric) (curve C) polymers.


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Polymers
elastomer

Three typically different types of stress-strain behavior are found for polymeric materials, as represented in Figure 15.1. Curve A illustrates the stress-strain character for a brittle polymer, which fractures while deforming elastically. The behavior for a plastic material, curve B, is similar to that for many metallic materials; the initial deformation is elastic, which is followed by yielding and a region of plastic deformation. Finally, the deformation displayed by curve C is totally elastic; this rubber-like elasticity (large recoverable strains produced at low stress levels) is displayed by a class of polymers termed the **elastomers**.

Modulus of elasticity (termed *tensile modulus* or sometimes just *modulus* for polymers) and ductility in percent elongation are determined for polymers in the same manner as for metals (Sections 6.3 and 6.6). For plastic polymers (curve B, Figure 15.1), the yield point is taken as a maximum on the curve, which occurs just beyond the termination of the linear-elastic region (Figure 15.2). The stress at this maximum is the yield strength (σ_y). Furthermore, tensile strength (TS) corresponds to the stress at which fracture occurs (Figure 15.2); TS may be greater than or less than σ_y . For these plastic polymers, strength is normally taken as tensile strength. Table 15.1 gives these mechanical properties for several polymeric materials; more comprehensive lists are provided in Tables B.2 to B.4, Appendix B.

In many respects, polymers are mechanically dissimilar to metals (Figures 1.5, 1.6, and 1.7). For example, the modulus for highly elastic polymeric materials may be as low as 7 MPa (10^3 psi), but it may run as high as 4 GPa (0.6×10^6 psi) for some very stiff polymers; modulus values for metals are much larger and range between 48 and 410 GPa (7×10^6 to 60×10^6 psi). Maximum tensile strengths for polymers are about 100 MPa (15,000 psi), whereas for some metal alloys they are 4100 MPa (600,000 psi). Furthermore, whereas metals rarely elongate plastically to more than 100%, some highly elastic polymers may experience elongations to greater than 1000%.

In addition, the mechanical characteristics of polymers are much more sensitive to temperature changes near room temperature. Consider the stress-strain behavior for poly(methyl methacrylate) (Plexiglas) at several temperatures between 4°C and 60°C (40°F and 140°F) (Figure 15.3). Increasing the temperature produces (1) a decrease in elastic modulus, (2) a reduction in tensile strength, and (3) an enhancement of ductility—

Figure 15.2 Schematic stress-strain curve for a plastic polymer showing how yield and tensile strengths are determined.

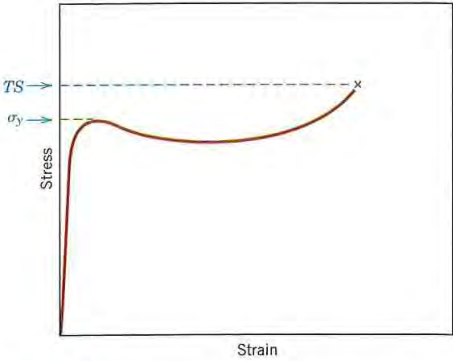


Table 15.1 Room-Temperature Mechanical Characteristics of Some of the More Common Polymers

Material	Specific Gravity	Tensile Modulus [GPa (ksi)]	Tensile Strength [MPa (ksi)]	Yield Strength [MPa (ksi)]	Elongation at Break (%)
Polyethylene (low density)	0.917–0.932	0.17–0.28 (25–41)	8.3–31.4 (1.2–4.55)	9.0–14.5 (1.3–2.1)	100–650
Polyethylene (high density)	0.952–0.965	1.06–1.09 (155–158)	22.1–31.0 (3.2–4.5)	26.2–33.1 (3.8–4.8)	10–1200
Poly(vinyl chloride)	1.30–1.58	2.4–4.1 (350–600)	40.7–51.7 (5.9–7.5)	40.7–44.8 (5.9–6.5)	40–80
Polytetrafluoroethylene	2.14–2.20	0.40–0.55 (58–80)	20.7–34.5 (3.0–5.0)	13.8–15.2 (2.0–2.2)	200–400
Polypropylene	0.90–0.91	1.14–1.55 (165–225)	31–41.4 (4.5–6.0)	31.0–37.2 (4.5–5.4)	100–600
Polystyrene	1.04–1.05	2.28–3.28 (330–475)	35.9–51.7 (5.2–7.5)	25.0–69.0 (3.63–10.0)	1.2–2.5
Poly(methyl methacrylate)	1.17–1.20	2.24–3.24 (325–470)	48.3–72.4 (7.0–10.5)	53.8–73.1 (7.8–10.6)	2.0–5.5
Phenol-formaldehyde	1.24–1.32	2.76–4.83 (400–700)	34.5–62.1 (5.0–9.0)	—	1.5–2.0
Nylon 6,6	1.13–1.15	1.58–3.80 (230–550)	75.9–94.5 (11.0–13.7)	44.8–82.8 (6.5–12)	15–300
Polyester (PET)	1.29–1.40	2.8–4.1 (400–600)	48.3–72.4 (7.0–10.5)	59.3 (8.6)	30–300
Polycarbonate	1.20	2.38 (345)	62.8–72.4 (9.1–10.5)	62.1 (9.0)	110–150

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at 4°C (40°F) the material is totally brittle, whereas there is considerable plastic deformation at both 50°C and 60°C (122°F and 140°F).

The influence of strain rate on the mechanical behavior may also be important. In general, decreasing the rate of deformation has the same influence on the stress-strain characteristics as increasing the temperature; that is, the material becomes softer and more ductile.

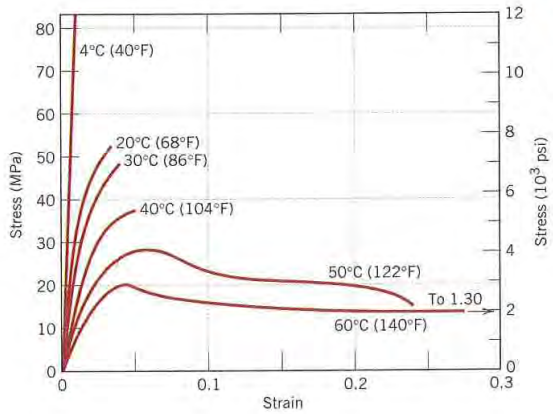
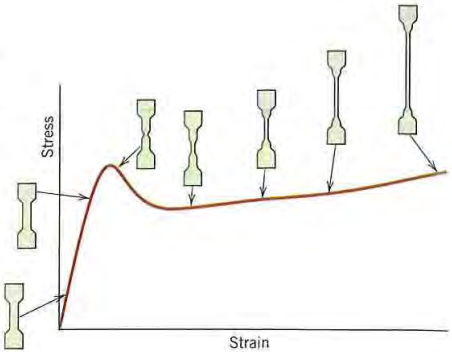


Figure 15.3 The influence of temperature on the stress-strain characteristics of poly(methyl methacrylate). (Reprinted with permission from T. S. Carswell and H. K. Nason, "Effect of Environmental Conditions on the Mechanical Properties of Organic Plastics," in *Symposium on Plastics*. Copyright ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428.)

Figure 15.4 Schematic tensile stress-strain curve for a semicrystalline polymer. Specimen contours at several stages of deformation are included. (From Jerold M. Schultz, *Polymer Materials Science*, copyright © 1974, p. 488. Reprinted by permission of Prentice Hall, Inc., Englewood Cliffs, NJ.)



15.3 MACROSCOPIC DEFORMATION



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Polymers

Some aspects of the macroscopic deformation of semicrystalline polymers deserve our attention. The tensile stress-strain curve for a semicrystalline material that was initially undeformed is shown in Figure 15.4; also included in the figure are schematic representations of the specimen profiles at various stages of deformation. Both upper and lower yield points are evident on the curve, which are followed by a near horizontal region. At the upper yield point, a small neck forms within the gauge section of the specimen. Within this neck, the chains become oriented (i.e., chain axes become aligned parallel to the elongation direction, a condition that is represented schematically in Figure 15.13d), which leads to localized strengthening. Consequently, there is a resistance to continued deformation at this point, and specimen elongation proceeds by the propagation of this neck region along the gauge length; the chain orientation phenomenon (Figure 15.13d) accompanies this neck extension. This tensile behavior may be contrasted to that found for ductile metals (Section 6.6), in which once a neck has formed, all subsequent deformation is confined to within the neck region.

Concept Check 15.1 When citing the ductility as percent elongation for semicrystalline polymers, it is not necessary to specify the specimen gauge length, as is the case with metals. Why is this so?
[The answer may be found at www.wiley.com/college/callister (Student Companion Site).]

15.4 VISCOELASTIC DEFORMATION

An amorphous polymer may behave like a glass at low temperatures, a rubbery solid at intermediate temperatures [above the glass transition temperature (Section 15.12)], and a viscous liquid as the temperature is further raised. For relatively small deformations, the mechanical behavior at low temperatures may be elastic—that is, in conformity to Hooke’s law, $\sigma = E\epsilon$. At the highest temperatures, viscous or liquid-like behavior prevails. For intermediate temperatures, the polymer is a rubbery solid that exhibits the combined mechanical characteristics of these two extremes; the condition is termed **viscoelasticity**.

Elastic deformation is instantaneous, which means that total deformation (or strain) occurs the instant the stress is applied or released (i.e., the strain is independent of time).

viscoelasticity

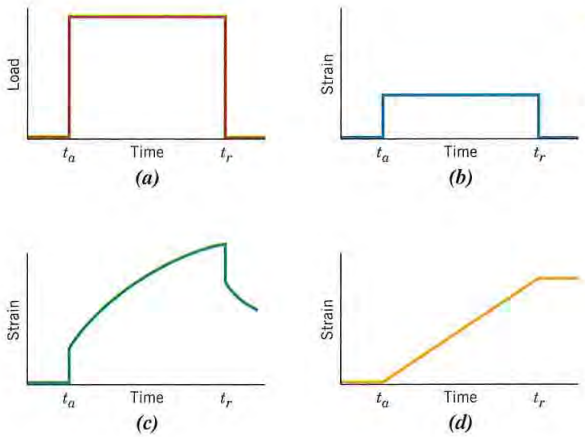


Figure 15.5 (a) Load versus time, where load is applied instantaneously at time t_a and released at t_r . For the load-time cycle in (a), the strain-versus-time responses are for totally elastic (b), viscoelastic (c), and viscous (d) behaviors.

In addition, upon release of the external stress, the deformation is totally recovered—the specimen assumes its original dimensions. This behavior is represented in Figure 15.5b as strain versus time for the instantaneous load-time curve, shown in Figure 15.5a.

By way of contrast, for totally viscous behavior, deformation or strain is not instantaneous; that is, in response to an applied stress, deformation is delayed or dependent on time. Also, this deformation is not reversible or completely recovered after the stress is released. This phenomenon is demonstrated in Figure 15.5d.

For the intermediate viscoelastic behavior, the imposition of a stress in the manner of Figure 15.5a results in an instantaneous elastic strain, which is followed by a viscous, time-dependent strain, a form of anelasticity (Section 6.4); this behavior is illustrated in Figure 15.5c.

A familiar example of these viscoelastic extremes is found in a silicone polymer that is sold as a novelty and known by some as Silly Putty. When rolled into a ball and dropped onto a horizontal surface, it bounces elastically—the rate of deformation during the bounce is very rapid. However, if pulled in tension with a gradually increasing applied stress, the material elongates or flows like a highly viscous liquid. For this and other viscoelastic materials, the rate of strain determines whether the deformation is elastic or viscous.

Viscoelastic Relaxation Modulus

The viscoelastic behavior of polymeric materials is dependent on both time and temperature; several experimental techniques may be used to measure and quantify this behavior. *Stress relaxation* measurements represent one possibility. With these tests, a specimen is initially strained rapidly in tension to a predetermined and relatively low strain level. The stress necessary to maintain this strain is measured as a function of time while temperature is held constant. Stress is found to decrease with time because of molecular relaxation processes that take place within the polymer. We may define a **relaxation modulus** $E_r(t)$, a time-dependent elastic modulus for viscoelastic polymers, as

$$E_r(t) = \frac{\sigma(t)}{\epsilon_0} \quad (15.1)$$

where $\sigma(t)$ is the measured time-dependent stress and ϵ_0 is the strain level, which is maintained constant.

relaxation modulus

Relaxation modulus—ratio of time-dependent stress and constant strain value

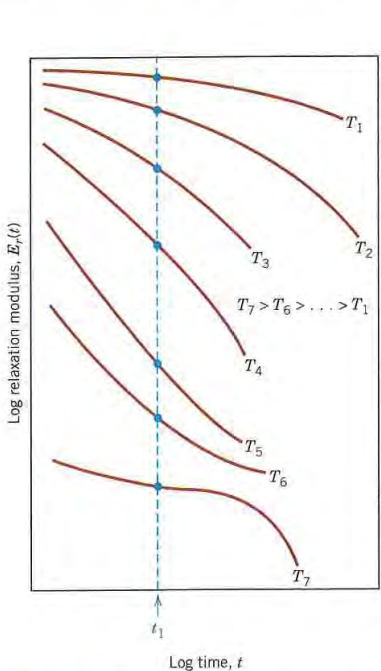


Figure 15.6 Schematic plot of logarithm of relaxation modulus versus logarithm of time for a viscoelastic polymer; isothermal curves are generated at temperatures T_1 through T_7 . The temperature dependence of the relaxation modulus is represented as $\log E_r(t_1)$ versus temperature.

Furthermore, the magnitude of the relaxation modulus is a function of temperature; to more fully characterize the viscoelastic behavior of a polymer, isothermal stress relaxation measurements must be conducted over a range of temperatures. Figure 15.6 is a schematic $\log E_r(t)$ -versus- $\log$ time plot for a polymer that exhibits viscoelastic behavior. Curves generated at a variety of temperatures are included. Key features of this plot are that (1) the magnitude of $E_r(t)$ decreases with time (corresponding to the decay of stress, Equation 15.1), and (2) the curves are displaced to lower $E_r(t)$ levels with increasing temperature.

To represent the influence of temperature, data points are taken at a specific time from the $\log E_r(t)$ -versus- $\log$ time plot—for example, t_1 in Figure 15.6—and then cross-plotted as $\log E_r(t_1)$ versus temperature. Figure 15.7 is such a plot for an amorphous (atactic) polystyrene; in this case, t_1 was arbitrarily taken 10 s after the load application. Several distinct regions may be noted on the curve shown in this figure. At the lowest temperatures, in the glassy region, the material is rigid and brittle, and the value of $E_r(10)$ is that of the elastic modulus, which initially is virtually independent of temperature. Over this temperature range, the strain-time characteristics are as represented in Figure 15.5b. On a molecular level, the long molecular chains are essentially frozen in position at these temperatures.

As the temperature is increased, $E_r(10)$ drops abruptly by about a factor of 10^3 within a 20°C (35°F) temperature span; this is sometimes called the *leathery*, or *glass*

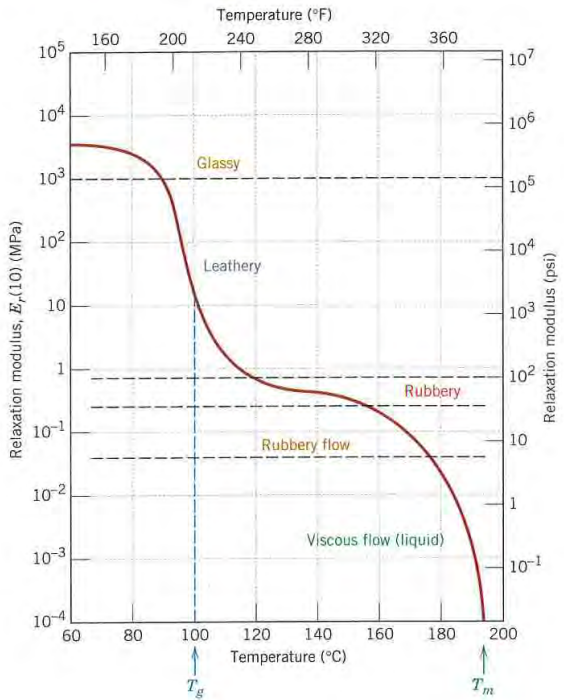


Figure 15.7 Logarithm of the relaxation modulus versus temperature for amorphous polystyrene, showing the five different regions of viscoelastic behavior. (From A. V. Tobolsky, *Properties and Structures of Polymers*. Copyright © 1960 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

transition region, and the glass transition temperature (T_g , Section 15.13) lies near the upper temperature extremity; for polystyrene (Figure 15.7), $T_g = 100^\circ\text{C}$ (212°F). Within this temperature region, a polymer specimen will be leathery; that is, deformation will be time dependent and not totally recoverable on release of an applied load, characteristics that are depicted in Figure 15.5c.

Within the rubbery plateau temperature region (Figure 15.7), the material deforms in a rubbery manner; here, both elastic and viscous components are present, and deformation is easy to produce because the relaxation modulus is relatively low.

The final two high-temperature regions are rubbery flow and viscous flow. Upon heating through these temperatures, the material experiences a gradual transition to a soft, rubbery state, and finally to a viscous liquid. In the rubbery flow region, the polymer is a very viscous liquid that exhibits both elastic and viscous flow components. Within the viscous flow region, the modulus decreases dramatically with increasing temperature; again, the strain-time behavior is as represented in Figure 15.5d. From a molecular standpoint, chain motion intensifies so greatly that for viscous flow, the chain segments experience vibration and rotational motion largely independent of one another. At these temperatures, any deformation is entirely viscous and essentially no elastic behavior occurs.

Normally, the deformation behavior of a viscous polymer is specified in terms of viscosity, a measure of a material's resistance to flow by shear forces. Viscosity is discussed for the inorganic glasses in Section 12.10.

The rate of stress application also influences the viscoelastic characteristics. Increasing the loading rate has the same influence as lowering the temperature.

The $\log E_r(10)$ -versus-temperature behavior for polystyrene materials having several molecular configurations is plotted in Figure 15.8. The curve for the amorphous material (curve C) is the same as in Figure 15.7. For a lightly crosslinked atactic polystyrene (curve B), the rubbery region forms a plateau that extends to the temperature at which the polymer decomposes; this material will not experience melting. For increased crosslinking, the magnitude of the plateau $E_r(10)$ value will also increase. Rubber or elastomeric materials display this type of behavior and are ordinarily used at temperatures within this plateau range.

Also shown in Figure 15.8 is the temperature dependence for an almost totally crystalline isotactic polystyrene (curve A). The decrease in $E_r(10)$ at T_g is much less

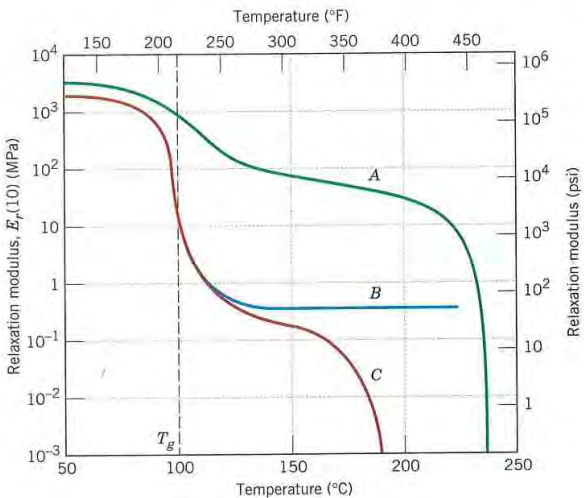


Figure 15.8 Logarithm of the relaxation modulus versus temperature for crystalline isotactic (curve A), lightly crosslinked atactic (curve B), and amorphous (curve C) polystyrene. (From A. V. Tobolsky, *Properties and Structures of Polymers*. Copyright © 1960 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

pronounced than for the other polystyrene materials because only a small volume fraction of this material is amorphous and experiences the glass transition. Furthermore, the relaxation modulus is maintained at a relatively high value with increasing temperature until its melting temperature T_m is approached. From Figure 15.8, the melting temperature of this isotactic polystyrene is about 240°C (460°F).

Viscoelastic Creep

Many polymeric materials are susceptible to time-dependent deformation when the stress level is maintained constant; such deformation is termed *viscoelastic creep*. This type of deformation may be significant even at room temperature and under modest stresses that lie below the yield strength of the material. For example, automobile tires may develop flat spots on their contact surfaces when the automobile is parked for prolonged time periods. Creep tests on polymers are conducted in the same manner as for metals (Chapter 8); that is, a stress (normally tensile) is applied instantaneously and is maintained at a constant level while strain is measured as a function of time. Furthermore, the tests are performed under isothermal conditions. Creep results are represented as a time-dependent *creep modulus* $E_c(t)$, defined by²

$$E_c(t) = \frac{\sigma_0}{\epsilon(t)} \quad (15.2)$$

where σ_0 is the constant applied stress and $\epsilon(t)$ is the time-dependent strain. The creep modulus is also temperature sensitive and decreases with increasing temperature.

With regard to the influence of molecular structure on the creep characteristics, as a general rule the susceptibility to creep decreases [i.e., $E_c(t)$ increases] as the degree of crystallinity increases.

✓ Concept Check 15.2 An amorphous polystyrene that is deformed at 120°C will exhibit which of the behaviors shown in Figure 15.5?

[The answer may be found at www.wiley.com/college/callister (Student Companion Site).]

15.5 FRACTURE OF POLYMERS

The fracture strengths of polymeric materials are low relative to those of metals and ceramics. As a general rule, the mode of fracture in thermosetting polymers (heavily crosslinked networks) is brittle. In simple terms, during the fracture process, cracks form at regions where there is a localized stress concentration (i.e., scratches, notches, and sharp flaws). As with metals (Section 8.5), the stress is amplified at the tips of these cracks, leading to crack propagation and fracture. Covalent bonds in the network or crosslinked structure are severed during fracture.

For thermoplastic polymers, both ductile and brittle modes are possible, and many of these materials are capable of experiencing a ductile-to-brittle transition. Factors that favor brittle fracture are a reduction in temperature, an increase in strain rate, the presence of a sharp notch, an increase in specimen thickness, and any modification of the polymer structure that raises the glass transition temperature (T_g) (see Section 15.14). Glassy thermoplastics are brittle below their glass transition temperatures. However, as the temperature is raised, they become ductile in the vicinity of their T_g s and experience plastic yielding prior to fracture. This behavior is demonstrated by the stress-strain characteristics of poly(methyl methacrylate) (PMMA) in Figure 15.3. At 4°C, PMMA is totally brittle, whereas at 60°C it becomes extremely ductile.

²Creep compliance, $J_c(t)$, the reciprocal of the creep modulus, is also sometimes used in this context.

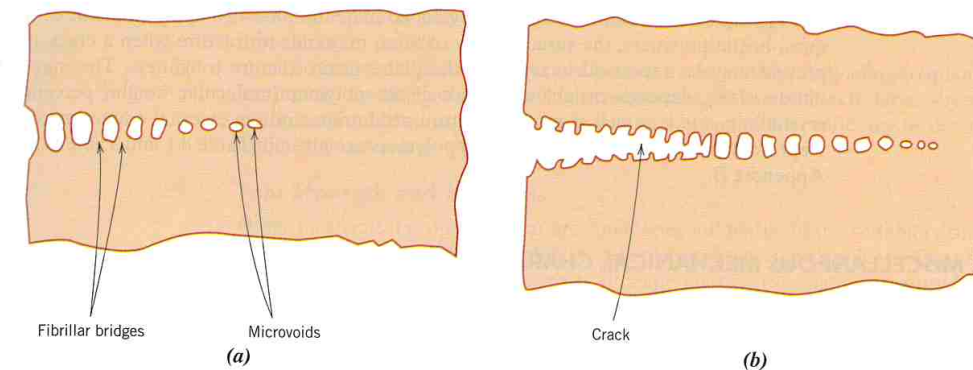


Figure 15.9 Schematic drawings of (a) a craze showing microvoids and fibrillar bridges and (b) a craze followed by a crack.

(From J. W. S. Hearle, *Polymers and Their Properties*, Vol. 1, *Fundamentals of Structure and Mechanics*, Ellis Horwood, Ltd., Chichester, West Sussex, England, 1982.)

One phenomenon that frequently precedes fracture in some thermoplastic polymers is *crazing*. Associated with crazes are regions of very localized plastic deformation, which lead to the formation of small and interconnected microvoids (Figure 15.9a). Fibrillar bridges form between these microvoids wherein molecular chains become oriented as in Figure 15.13d. If the applied tensile load is sufficient, these bridges elongate and break, causing the microvoids to grow and coalesce. As the microvoids coalesce, cracks begin to form, as demonstrated in Figure 15.9b. A craze is different from a crack in that it can support a load across its face. Furthermore, this process of craze growth prior to cracking absorbs fracture energy and effectively increases the fracture toughness of the polymer. In glassy polymers, the cracks propagate with little craze formation, resulting in low fracture toughnesses. Crazes form at highly stressed regions associated with scratches, flaws, and molecular inhomogeneities; in addition, they propagate perpendicular to the applied tensile stress and typically are 5 μm or less thick. The photomicrograph in Figure 15.10 shows a craze.

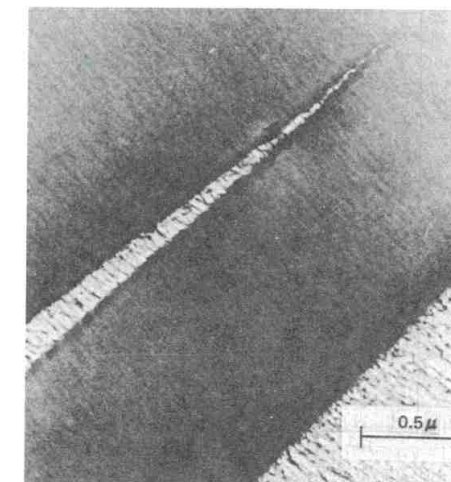


Figure 15.10 Photomicrograph of a craze in poly(phenylene oxide). (From R. P. Kambour and R. E. Robertson, "The Mechanical Properties of Plastics," in *Polymer Science, A Materials Science Handbook*, A. D. Jenkins, Editor. Reprinted with permission of Elsevier Science Publishers.)

Principles of fracture mechanics developed in Section 8.5 also apply to brittle and quasi-brittle polymers; the susceptibility of these materials to fracture when a crack is present may be expressed in terms of the plane strain fracture toughness. The magnitude of K_{Ic} depends on characteristics of the polymer (molecular weight, percent crystallinity, etc.), as well as on temperature, strain rate, and the external environment. Representative values of K_{Ic} for several polymers are given in Table 8.1 and Table B.5, Appendix B.

15.6 MISCELLANEOUS MECHANICAL CHARACTERISTICS

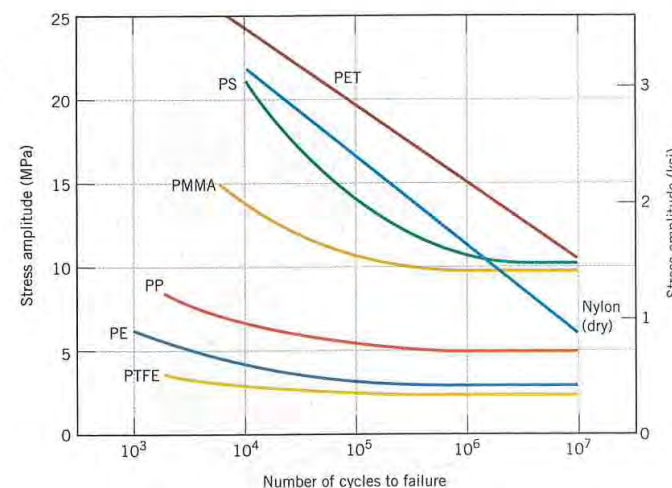
Impact Strength

The degree of resistance of a polymeric material to impact loading may be of concern in some applications. Izod or Charpy tests are ordinarily used to assess impact strength (Section 8.6). As with metals, polymers may exhibit ductile or brittle fracture under impact loading conditions, depending on the temperature, specimen size, strain rate, and mode of loading, as discussed in the preceding section. Both semicrystalline and amorphous polymers are brittle at low temperatures, and both have relatively low impact strengths. However, they experience a ductile-to-brittle transition over a relatively narrow temperature range, similar to that shown for a steel in Figure 8.13. Of course, impact strength undergoes a gradual decrease at still higher temperatures as the polymer begins to soften. Ordinarily, the two impact characteristics most sought after are a high impact strength at the ambient temperature and a ductile-to-brittle transition temperature that lies below room temperature.

Fatigue

Polymers may experience fatigue failure under conditions of cyclic loading. As with metals, fatigue occurs at stress levels that are low relative to the yield strength. Fatigue testing in polymers has not been nearly as extensive as with metals; however, fatigue data are plotted in the same manner for both types of material, and the resulting curves have the same general shape. Fatigue curves for several common polymers are shown in Figure 15.11 as stress versus the number of cycles to failure (on a logarithmic scale). Some polymers have a *fatigue limit* (a stress level at which the stress at failure becomes independent of the number of cycles); others do not appear to have such a limit. As

Figure 15.11 Fatigue curves (stress amplitude versus the number of cycles to failure) for poly(ethylene terephthalate) (PET), nylon, polystyrene (PS), poly(methyl methacrylate) (PMMA), polypropylene (PP), polyethylene (PE), and polytetrafluoroethylene (PTFE). The testing frequency was 30 Hz. (From M. N. Riddell, "A Guide to Better Testing of Plastics," *Plastics Engineering*, Vol. 30, No. 4, p. 78, 1974. © Society of Plastics Engineers.)



would be expected, fatigue strengths and fatigue limits for polymeric materials are much lower than for metals.

The fatigue behavior of polymers is much more sensitive to loading frequency than for metals. Cycling polymers at high frequencies and/or relatively large stresses can cause localized heating; consequently, failure may be due to a softening of the material rather than a result of typical fatigue processes.

Tear Strength and Hardness

Other mechanical properties that are sometimes influential in the suitability of a polymer for some particular application include tear resistance and hardness. The ability to resist tearing is an important property of some plastics, especially those used for thin films in packaging. *Tear strength*, the mechanical parameter measured, is the energy required to tear apart a cut specimen that has a standard geometry. The magnitude of tensile and tear strengths are related.

As with metals, hardness represents a material's resistance to scratching, penetration, marring, and so on. Polymers are softer than metals and ceramics, and most hardness tests are conducted by penetration techniques similar to those described for metals in Section 6.10. Rockwell tests are frequently used for polymers.³ Other indentation techniques employed are the Durometer and Barcol.⁴

Mechanisms of Deformation and for Strengthening of Polymers

An understanding of deformation mechanisms of polymers is important to be able to manage the mechanical characteristics of these materials. In this regard, deformation models for two different types of polymers—semicrystalline and elastomeric—deserve our attention. The stiffness and strength of semicrystalline materials are often important considerations; elastic and plastic deformation mechanisms are treated in the succeeding section, whereas methods used to stiffen and strengthen these materials are discussed in Section 15.8. However, elastomers are used on the basis of their unusual elastic properties; the deformation mechanism of elastomers is also treated.

15.7 DEFORMATION OF SEMICRYSTALLINE POLYMERS

Many semicrystalline polymers in bulk form have the spherulitic structure described in Section 14.12. By way of review, each spherulite consists of numerous chain-folded ribbons, or lamellae, that radiate outward from the center. Separating these lamellae are areas of amorphous material (Figure 14.13); adjacent lamellae are connected by tie chains that pass through these amorphous regions.

Mechanism of Elastic Deformation

As with other material types, elastic deformation of polymers occurs at relatively low stress levels on the stress-strain curve (Figure 15.1). The onset of elastic deformation for semicrystalline polymers results from chain molecules in amorphous regions elongating in the direction of the applied tensile stress. This process is represented schematically for two adjacent chain-folded lamellae and the interlamellar amorphous material as Stage 1 in Figure 15.12. Continued deformation in the second stage occurs by changes

³ASTM Standard D785, "Standard Testing Method for Rockwell Hardness of Plastics and Electrical Insulating Materials."

⁴ASTM Standard D2240, "Standard Test Method for Rubber Property—Durometer Hardness"; and ASTM Standard D2583, "Standard Test Method for Indentation Hardness of Rigid Plastics by Means of a Barcol Impressor."

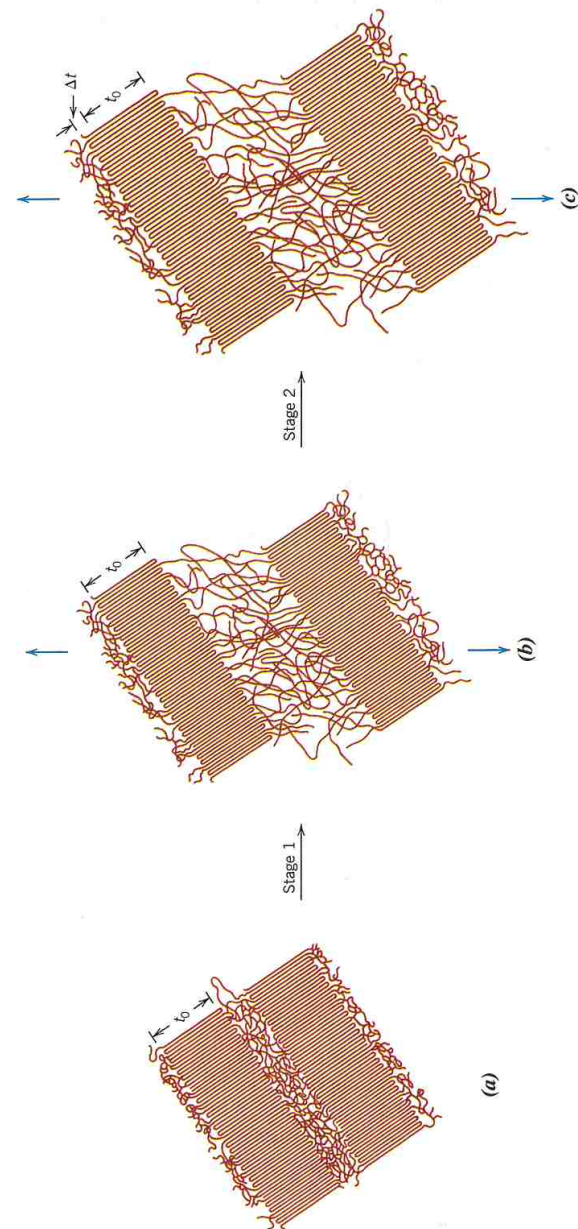


Figure 15.12 Stages in the elastic deformation of a semicrystalline polymer. (a) Two adjacent chain-folded lamellae and interlamellar amorphous material before deformation. (b) Elongation of amorphous tie chains during the first stage of deformation. (c) Increase in lamellar crystallite thickness (which is reversible) due to bending and stretching of chains in crystallite regions. (From SCHULTZ, POLYMER MATERIALS SCIENCE, 1st Edition, © 1974, Reprinted by permission of Pearson Education, Inc., Upper Saddle River, NJ.)

in both amorphous and lamellar crystalline regions. Amorphous chains continue to align and become elongated; in addition, there is bending and stretching of the strong chain covalent bonds within the lamellar crystallites. This leads to a slight, reversible increase in the lamellar crystallite thickness as indicated by Δl in Figure 15.12c.

Inasmuch as semicrystalline polymers are composed of both crystalline and amorphous regions, they may, in a sense, be considered composite materials. Therefore, the elastic modulus may be taken as some combination of the moduli of crystalline and amorphous phases.

Mechanism of Plastic Deformation

The transition from elastic to plastic deformation occurs in Stage 3 of Figure 15.13. (Note that Figure 15.12c is identical to Figure 15.13a.) During Stage 3, adjacent chains in the lamellae slide past one another (Figure 15.13b); this results in tilting of the lamellae so that the chain folds become more aligned with the tensile axis. Any chain displacement is resisted by relatively weak secondary or van der Waals bonds.

Crystalline block segments separate from the lamellae in Stage 4 (Figure 15.13c), with the segments attached to one another by tie chains. In the final stage, Stage 5, the blocks and tie chains become oriented in the direction of the tensile axis (Figure 15.13d). Thus, appreciable tensile deformation of semicrystalline polymers produces a highly oriented structure. This process of orientation is referred to as **drawing**, and is commonly used to improve the mechanical properties of polymer fibers and films (this is discussed in more detail in Section 15.24).

During deformation, the spherulites experience shape changes for moderate levels of elongation. However, for large deformations, the spherulitic structure is virtually destroyed. Also, to a degree, the processes represented in Figure 15.13 are reversible. That is, if deformation is terminated at some arbitrary stage and the specimen is heated to an elevated temperature near its melting point (i.e., is annealed), the material will recrystallize to again form a spherulitic structure. Furthermore, the specimen will tend to shrink back, in part, to the dimensions it had prior to deformation. The extent of this shape and structural recovery depends on the annealing temperature and also the degree of elongation.

15.8 FACTORS THAT INFLUENCE THE MECHANICAL PROPERTIES OF SEMICRYSTALLINE POLYMERS

A number of factors influence the mechanical characteristics of polymeric materials. For example, we have already discussed the effects of temperature and strain rate on stress-strain behavior (Section 15.2, Figure 15.3). Again, increasing the temperature or diminishing the strain rate leads to a decrease in the tensile modulus, a reduction in tensile strength, and an enhancement of ductility.

In addition, several structural/processing factors have decided influences on the mechanical behavior (i.e., strength and modulus) of polymeric materials. An increase in strength results whenever any restraint is imposed on the process illustrated in Figure 15.13; for example, extensive chain entanglements or a significant degree of intermolecular bonding inhibit relative chain motions. Even though secondary intermolecular (e.g., van der Waals) bonds are much weaker than the primary covalent ones, significant intermolecular forces result from the formation of large numbers of van der Waals interchain bonds. Furthermore, the modulus rises as both the secondary bond strength and chain alignment increase. As a result, polymers with polar groups will have stronger secondary bonds and a larger elastic modulus. We now discuss how several structural/processing factors [molecular weight, degree of crystallinity, predeformation (drawing), and heat-treating] affect the mechanical behavior of polymers.

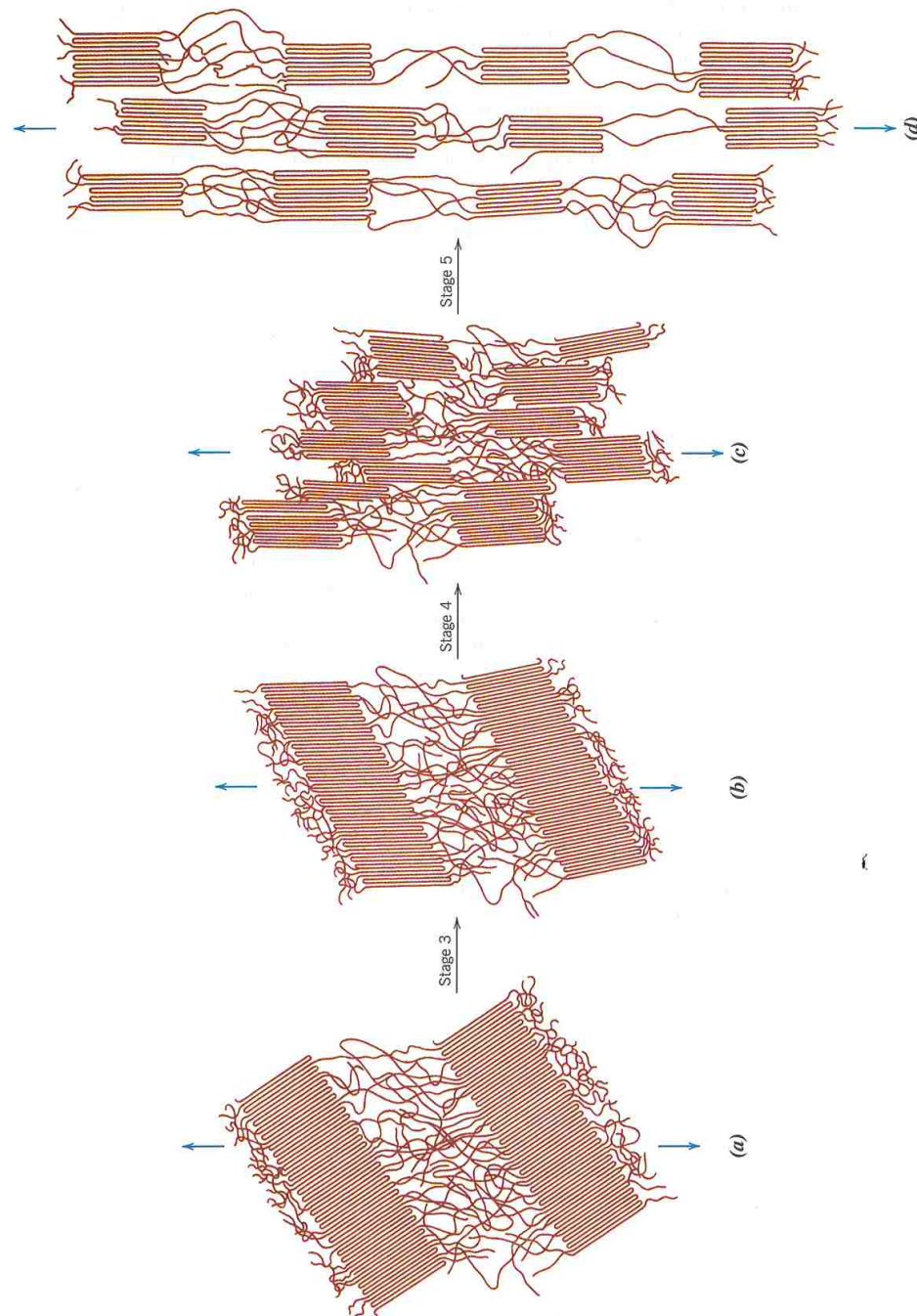


Figure 15.13 Stages in the plastic deformation of a semicrystalline polymer. (a) Two adjacent chain-folded lamellae and interlamellar amorphous material after elastic deformation (also shown as Figure 15.12c). (b) Tilting of lamellar chain folds. (c) Separation of crystalline block segments. (d) Orientation of block segments and tie chains with the tensile axis in the final plastic deformation stage. (From SCHULTZ, POLYMER MATERIALS SCIENCE, 1st Edition, © 1974. Reprinted by permission of Pearson Education, Inc., Upper Saddle River, NJ.)

Molecular Weight

The magnitude of the tensile modulus does not seem to be directly influenced by molecular weight. On the other hand, for many polymers it has been observed that tensile strength increases with increasing molecular weight. TS is a function of the number-average molecular weight,

$$TS = TS_{\infty} - \frac{A}{M_n} \quad (15.3)$$

where TS_{∞} is the tensile strength at infinite molecular weight and A is a constant. The behavior described by this equation is explained by increased chain entanglements with rising M_n .

Degree of Crystallinity

For a specific polymer, the degree of crystallinity can have a significant influence on the mechanical properties because it affects the extent of the intermolecular secondary bonding. For crystalline regions in which molecular chains are closely packed in an ordered and parallel arrangement, extensive secondary bonding typically exists between adjacent chain segments. This secondary bonding is much less prevalent in amorphous regions, by virtue of the chain misalignment. As a consequence, for semicrystalline polymers, tensile modulus increases significantly with degree of crystallinity. For example, for polyethylene, the modulus increases approximately an order of magnitude as the crystallinity fraction is raised from 0.3 to 0.6.

Furthermore, increasing the crystallinity of a polymer generally enhances its strength; in addition, the material tends to become more brittle. The influence of chain chemistry and structure (branching, stereoisomerism, etc.) on degree of crystallinity was discussed in Chapter 14.

The effects of both percent crystallinity and molecular weight on the physical state of polyethylene are represented in Figure 15.14.

Predeformation by Drawing

On a commercial basis, one of the most important techniques used to improve mechanical strength and tensile modulus is to permanently deform the polymer in tension. This procedure is sometimes termed *drawing* and it corresponds to the neck extension process illustrated schematically in Figure 15.4. In terms of property alterations, drawing is the polymer analogue of strain hardening in metals. It is an important stiffening and strengthening technique that is employed in the production of fibers and films. During drawing the molecular chains slip past one another and become highly oriented; for

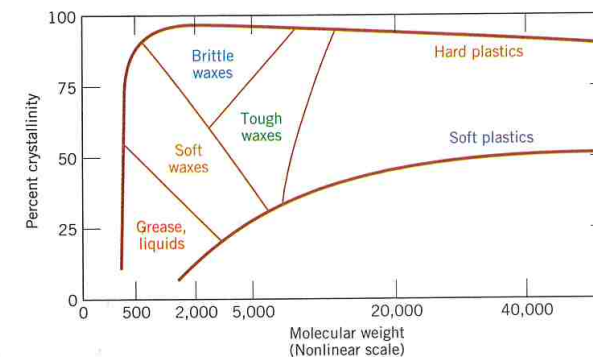


Figure 15.14 The influence of degree of crystallinity and molecular weight on the physical characteristics of polyethylene. (From R. B. Richards, "Polyethylene—Structure, Crystallinity and Properties," *J. Appl. Chem.*, **1**, 370, 1951.)

semicrystalline materials the chains assume conformations similar to that represented schematically in Figure 15.13*d*.

Degrees of strengthening and stiffening depend on the extent of deformation (or extension) of the material. Furthermore, the properties of drawn polymers are highly anisotropic. For materials drawn in uniaxial tension, tensile modulus and strength values are significantly greater in the direction of deformation than in other directions. Tensile modulus in the direction of drawing may be enhanced by up to approximately a factor of three relative to the undrawn material. At an angle of 45° from the tensile axis, the modulus is a minimum; at this orientation, the modulus has a value on the order of one-fifth that of the undrawn polymer.

Tensile strength parallel to the direction of orientation may be improved by a factor of at least two to five relative to that of the unoriented material. However, perpendicular to the alignment direction, tensile strength is reduced by on the order of one-third to one-half.

For an amorphous polymer that is drawn at an elevated temperature, the oriented molecular structure is retained only when the material is quickly cooled to the ambient temperature; this procedure gives rise to the strengthening and stiffening effects described in the previous paragraph. However, if, after stretching, the polymer is held at the temperature of drawing, molecular chains relax and assume random conformations characteristic of the predeformed state; as a consequence, drawing will have no effect on the mechanical characteristics of the material.

Heat-Treating

Heat-treating (or annealing) of semicrystalline polymers can lead to an increase in the percent crystallinity and crystallite size and perfection, as well as to modifications of the spherulite structure. For undrawn materials that are subjected to constant-time heat treatments, increasing the annealing temperature leads to the following: (1) an increase in tensile modulus, (2) an increase in yield strength, and (3) a reduction in ductility. Note that these annealing effects are opposite to those typically observed for metallic materials (Section 7.12)—weakening, softening, and enhanced ductility.

For some polymer fibers that have been drawn, the influence of annealing on the tensile modulus is contrary to that for undrawn materials—that is, the modulus decreases with increased annealing temperature because of a loss of chain orientation and strain-induced crystallinity.

✓ Concept Check 15.3 For the following pair of polymers, do the following: (1) state whether it is possible to decide if one polymer has a higher tensile modulus than the other; (2) if this is possible, note which has the higher tensile modulus and then cite the reason(s) for your choice; and (3) if it is not possible to decide, state why not.

- Syndiotactic polystyrene having a number-average molecular weight of 400,000 g/mol
- Isotactic polystyrene having a number-average molecular weight of 650,000 g/mol

✓ Concept Check 15.4 For the following pair of polymers, do the following: (1) state whether it is possible to decide if one polymer has a higher tensile strength than the other; (2) if this is possible, note which has the higher tensile strength and then cite the reason(s) for your choice; and (3) if it is not possible to decide, state why not.

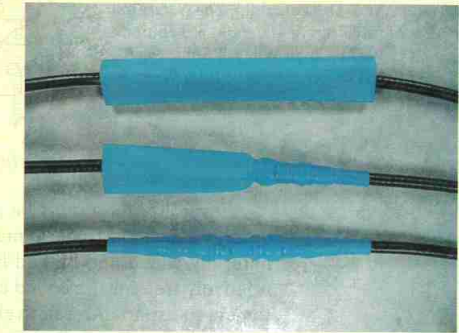
- Syndiotactic polystyrene having a number-average molecular weight of 600,000 g/mol
- Isotactic polystyrene having a number-average molecular weight of 500,000 g/mol

[The answers may be found at www.wiley.com/college/callister (Student Companion Site).]

MATERIALS OF IMPORTANCE

Shrink-Wrap Polymer Films

An interesting application of heat treatment in polymers is the shrink-wrap used in packaging. Shrink-wrap is a polymer film, usually made of poly(vinyl chloride), polyethylene, or polyolefin (a multilayer sheet with alternating layers of polyethylene and polypropylene). It is initially plastically deformed (cold drawn) by about 20% to 300% to provide a prestretched (aligned) film. The film is wrapped around an object to be packaged and sealed at the edges. When heated to about 100°C to 150°C, this prestretched material shrinks to recover 80% to 90% of its initial deformation, which gives a tightly stretched, wrinkle-free, transparent polymer film. For example, CDs and many other consumer products are packaged in shrink-wrap.



Top: An electrical connection positioned within a section of as-received polymer shrink-tubing. Center, Bottom: Application of heat to the tubing caused its diameter to shrink. In this constricted form, the polymer tubing stabilizes the connection and provides electrical insulation. (Photograph courtesy of Insulation Products Corporation.)

15.9 DEFORMATION OF ELASTOMERS

One of the fascinating properties of the elastomeric materials is their rubber-like elasticity—that is, they have the ability to be deformed to quite large deformations and then elastically spring back to their original form. This results from crosslinks in the polymer that provide a force to restore the chains to their undeformed conformations. Elastomeric behavior was probably first observed in natural rubber; however, the past several decades have brought about the synthesis of a large number of elastomers with a wide variety of properties. Typical stress-strain characteristics of elastomeric materials are displayed in Figure 15.1, curve C. Their moduli of elasticity are quite small, and, they vary with strain because the stress-strain curve is nonlinear.

In an unstressed state, an elastomer is amorphous and composed of crosslinked molecular chains that are highly twisted, kinked, and coiled. Elastic deformation upon application of a tensile load is simply the partial uncoiling, untwisting, and straightening and resultant elongation of the chains in the stress direction, a phenomenon represented in Figure 15.15. Upon release of the stress, the chains spring back to their prestressed conformations, and the macroscopic piece returns to its original shape.

Part of the driving force for elastic deformation is a thermodynamic parameter called *entropy*, which is a measure of the degree of disorder within a system; entropy increases with increasing disorder. As an elastomer is stretched and the chains straighten and become more aligned, the system becomes more ordered. From this state, the entropy increases if the chains return to their original kinked and coiled contours. Two intriguing phenomena result from this entropic effect. First, when stretched, an elastomer experiences a rise in temperature; second, the modulus of elasticity increases with increasing temperature, which is opposite to the behavior found in other materials (see Figure 6.8).