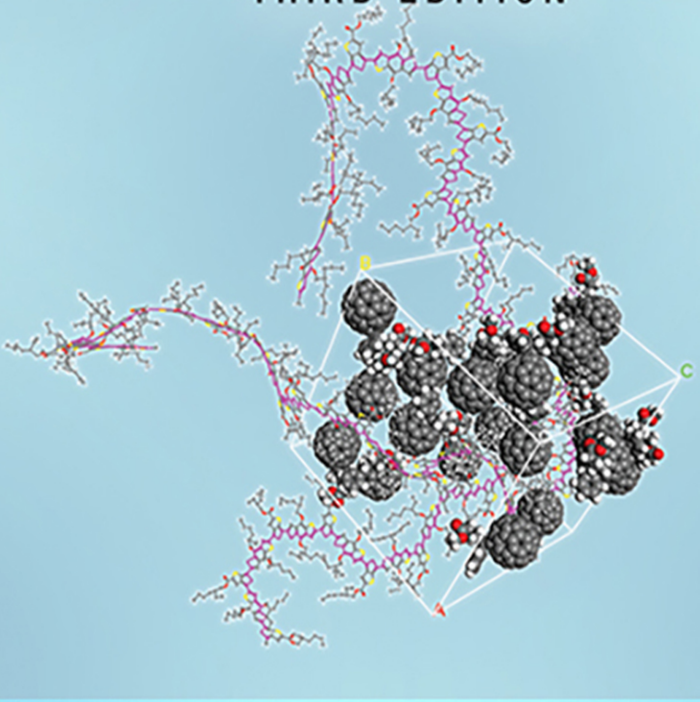
POLYMER SCIENCE & TECHNOLOGY

THIRD EDITION



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lationship. Another commonly used empirical relation that can be derived from eq. (4.32) is the *logarithmic rule of mixtures* given as

$$\boxed{\ln T_{\mathrm{g}} = W_1 \ln T_{\mathrm{g},1} + W_2 \ln T_{\mathrm{g},2}}\,. \tag{4.36}$$

Pressure Dependence. Compared to effects of molecular weight and plasticization, T_g is relatively insensitive to pressure. The glass-transition temperature will increase with increasing pressure at a rate of approximately 25 K per kbar of pressure. The pressure dependence can be estimated from the compressibility and thermal expansion coefficients as

$$\frac{dT_{\mathrm{g}}}{dp} = \frac{\Delta\beta}{\Delta\alpha}\,. \tag{4.37}$$

Effect of Heating Rate. The T_g has a small dependence on the heating or cooling rates in DSC and other methods of thermal characterization. Samples that are slowly heated through the glass transition exhibit a lower T_g than those that are rapidly heated due to the non-equilibrium state of the glass (see Section 4.1.2). The relationship between T_g (K) and the heating rate, q (K min^{-1}), is given in the form [25, 26]

$$T_{\mathrm{g}} = a + b \ln q \tag{4.38}$$

where a and b are polymer-specific parameters (e.g., a = 372.5 K and b = 4.02 K for PS; a = 383 K and b = 4.23 K for PMMA).

Effect of Crosslinks. As a result of the restriction of long-range segmental motion, crosslinking elevates T_g. The form of the relationship between T_g and crosslink density is often given by the Fox–Loshaek equation [27]

$$T_{\mathrm{g}}^{\mathrm{c}} = T_{\mathrm{g}}^{\mathrm{o}} + k_{\mathrm{c}}\rho_{\mathrm{c}} \tag{4.39}$$

where $T_{\mathrm{g}}^{\mathrm{c}}$ is the glass-transition temperature of the crosslinked polymer, $T_{\mathrm{g}}^{\mathrm{o}}$ is the glass-transition temperature of the uncrosslinked polymer, k_c is a polymer-specific constant, and ρ_c represents the number of crosslinks per gram.

4.4 Mechanical Properties

4.4.1 Mechanisms of Deformation

At low strain (i.e., <1%), the deformation of most polymers is elastic, meaning that the deformation is homogeneous and full recovery can occur over a finite time. At higher strains, the deformation of glassy polymers occurs by either *crazing*, characteristic of brittle polymers, or by a process called *shear banding,* which is the dominant mechanism for ductile polymers. Such deformations are not reversible unless the polymer is heated above its glass-transition temperature.

Crazing. The term *crazing* owes it origin to the Middle English word *crasen*, which means "to break." It was originally applied to describe a network of fine cracks appearing on the surface of ceramics and glasses. When some polymers such as polystyrene are deformed to a certain level, the critical strain (ε_c), what appear to be small cracks develop in a direction *perpendicular* to the principal direction of deformation. Some typical values of critical strains are given in Table 4-12. These crazes reflect light and result in visual cloudiness or whitening of the sample. Crazes developed in a polycarbonate tensile bar are shown in Figure 4-15.

Table 4-12 Critical Strains for Craze Initiation in Glassy Polymers

Polymer	Critical Strain (%)
Polystyrene	0.35
Styrene–acrylonitrile copolymer (SAN)	0.49
Poly(methyl methacrylate)	0.8–1.30
Poly(2,6-dimethyl-1,4-phenylene oxide)	1.5
Polycarbonate	1.8
Polysulfone	2.5

A craze is a unique morphological feature of polymers and is morphologically different from a true crack. A craze, which can be nanometers to a few micrometers in thickness, consists of polymer microfibrils (0.6 to 30 nm in diameter) stretched in the direction of tensile deformation. The microfibrils are surrounded by void space, which can represent as much as 90% of the total volume of the craze. This anisotropic morphology of a craze results in the scattering of light. An electron micrograph of typical craze structures is shown in Figure 4-16.

The time for the initiation of a craze depends upon many factors, including the magnitude of the applied stress, temperature, and the presence of low-molecular-weight liquids, which may act to promote craze development (see Section 6.1.3). Although the reasons for craze initiation are still uncertain and several different theories have been proposed, it is recognized that crazes constitute the defects from which brittle cracks initiate. Mechanical fracture of a sample that has begun crazing is initiated by the breakdown of the fibrillar microstructure to form additional voids that grow slowly until some critical size has been reached. Beyond this point, the craze will rapidly propagate as a crack. As the crack propagates, crazes are formed at the crack tip and act to retard its advance.

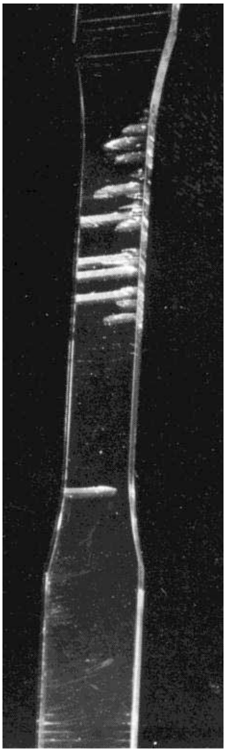

Figure 4-15 Visual view of crazes developed perpendicular to the tensile direction in a polycarbonate dogbone. Courtesy of R. P. Kambour.

Shear Banding. While some polymers such as polystyrene will readily craze when strained in tension, crazes may not develop in other polymers such as polycarbonate under identical conditions. Instead, these polymers will form regions of localized shear deformation. These regions are called shear bands, which develop at angles of 45° to the stretch direction. Other polymers such as SAN can exhibit both modes of deformation. In general, shear-band formation is a dominant mode of deformation during tensile yielding of ductile polymers.

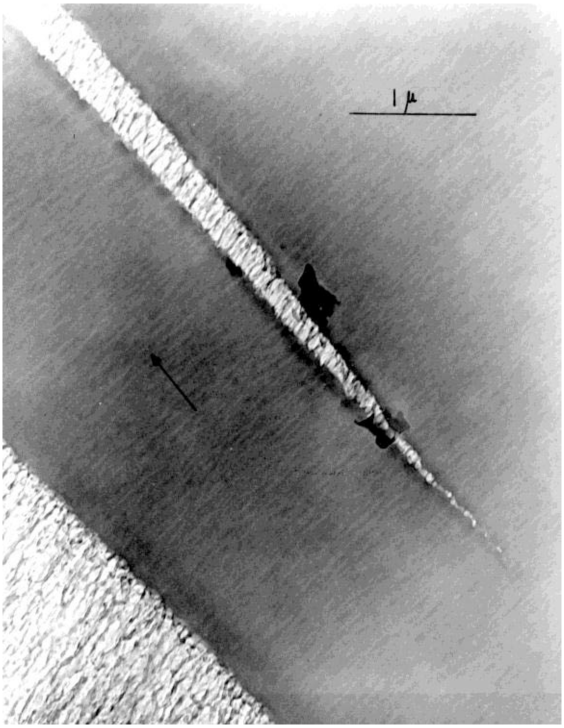

Figure 4-16 Scanning electron micrograph of craze structures in poly(2,6-dimethyl-1,4-phenylene oxide) [28]. The craze structure was preserved prior to microtoming by infusion of liquid sulfur. Courtesy of R. P. Kambour.

4.4.2 Methods of Testing

As the HDT indicates the temperature limits within which a plastic may be used, a variety of methods are used to determine mechanical performance under a variety of loading conditions. These may be classified as static (i.e., tensile and shear), transient (i.e., creep and stress relaxation), impact (Izod and Charpy), and cyclic (i.e., fatigue tests). Static tests are used to measure the force response when a sample is strained, compressed, or sheared at a constant rate. These provide a means to characterize the mechanical properties of a polymer in terms of modulus, strength, and elongation to failure. Transient tests measure the time response of the force (or stress) on a polymer sample when it is rapidly stretched to a given length (*stress relaxation*) or the time response of strain when a load (stress) is rapidly applied (*creep*). Impact tests measure the energy required for a sample to fail under different loading histories, while fatigue tests determine the number of cycles of applied stress required for failure.

Static Testing. Static tests refer to those for which the deformation rate is steady in time. While tensile, compressive, or shear modes may be employed, tensile testing is the most common. In a typical tensile test, a polymer sample, in the form of a dogbone (e.g., Figure 4-17), is clamped at one end and pulled at a constant rate of elongation at the other clamped end.* The thinner portion of the tensile specimen encourages the sample to fail at the center of the bar, where the stress is the highest, and not at the grip sites, where stress concentration may otherwise result in premature failure.

As indicated in Figure 4-17, the initial length of a central section contained within the narrow region of the tensile specimen is called the initial *gage length*, L_o. During deformation, force, F, is measured as a function of elongation at the fixed end by means of a transducer. Usually, the tensile response is plotted as *engineering* (nominal) *stress*, σ, versus *engineering* (nominal) *strain*, ε, where

$$\sigma = \frac{F}{A_o} \tag{4.40}$$

and

$$\varepsilon = \frac{\Delta L}{L_o}. \tag{4.41}$$

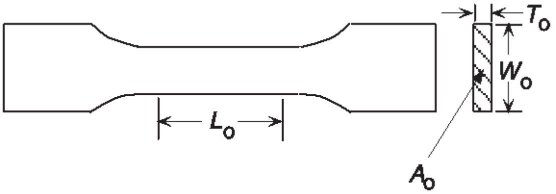

Figure 4-17 Illustration of a typical tensile-dogbone sample. The overall length of the specimens may vary from 63.5 to 246 mm. During tensile measurement, the sample is gripped at the wide ends. Specimen parameters include L_o, gage length (distance between test marks or extensometer span, ca. 50 mm); W_o, initial width (19 or 29 mm); T_o, initial thickness (4 to 14 mm); and A_o, initial cross-sectional area.

In eq. (4.40), A_o is the original (undeformed) cross-sectional area of the gage region and ΔL in eq. (4.41) is the change in sample gage length ($L - L_o$) due to the defor-

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* Conditions and sample dimensions for tensile tests are specified by ASTM D 638, "Tensile Properties of Plastics." For specimens of thickness up to 3.2 mm (1/8 in.), conditions and sample dimensions are given by ASTM D 1708, "Tensile Properties of Plastics by Use of Microtensile Specimens."

mation. Sample length can be determined from instrumental settings of the mechanical-testing instrument or by an extensometer, which is a strain gage that is attached to the gage-length region of the tensile specimen.

Alternatively, the stress-strain response of a sample may be reported in terms of true stress and true strain. The *true stress* is defined as the ratio of measured force to the *actual* cross-sectional area, A, at a given elongation

$$\sigma^{\mathrm{T}} = \frac{F}{A} . \tag{4.42}$$

Since the actual cross-sectional area decreases as the sample is elongated, the true stress will always be larger than the engineering stress. Assuming that the volume of the sample remains constant during deformation, it can be shown (see Problem 4-1) that the true stress is simply related to the engineering stress as

$$\sigma^{\mathrm{T}} = \sigma \frac{L}{L_{\mathrm{o}}} . \tag{4.43}$$

The *true strain*, ε^{T}, is defined as

$$\varepsilon^{\mathrm{T}} = \int_{L_{\mathrm{o}}}^{L} \left(\frac{1}{\ell} \right) d\ell = \ln \left(\frac{L}{L_{\mathrm{o}}} \right) . \tag{4.44}$$

With the exception of elastomers, the assumption of a constant volume during deformation is not strictly correct, because the volume of glassy polymers increases, or dilates, during extension. This change in volume, ΔV, at a given strain may be calculated from the relation

$$\Delta V = V = V_{\mathrm{o}} = (1 - 2\upsilon)\varepsilon V_{\mathrm{o}} \tag{4.45}$$

where V_0 is the initial (unstrained) volume, ε is *true* strain, and υ is called *Poisson's ratio*, which is defined as the ratio of *true* strain in the transverse direction, ε_{T}, to the *true* strain in the longitudinal direction, ε_{L}, and is calculated as

$$\boxed{\upsilon = -\frac{\varepsilon_{\mathrm{T}}}{\varepsilon_{\mathrm{L}}} = \frac{1}{2}\left[1 - \frac{1}{V}\left(\frac{\partial V}{\partial \varepsilon} \right) \right]} . \tag{4.46}$$

For the majority of glassy polymers, $\upsilon \approx 0.4$, as shown by data for polystyrene, poly(methyl methacrylate), and poly(vinyl chloride) in Table 4-13. For completely incompressible materials, for which the term $(\partial V/\partial \varepsilon)$ within brackets in eq. (4.46) is zero, υ obtains its maximum value of 0.5 as approached by natural rubber and low-density polyethylene ($\upsilon = 0.49$).