films. Thick specimens generally do not tear and moderately thick specimens produce spurious bending loads. The actual limit of specimen thickness varies with the material and the test conditions. (2) The method cannot be used on brittle materials as they fracture uncontrollably across the specimen at right angles to the initial cut. (3) The result depends on the thickness of the specimen. Figure 14, for example, shows γ (= $2L/t$) as a function of thickness for samples of amorphous, isotropic poly(ethylene terephthalate) film (28). Clearly, it cannot be assumed for thermoplastic films that γ is a material property, independent of thickness. Apparently no work has been published concerning the effect of sample thickness on γ for any rubbery polymer.

Compression. If a specimen is compressed uniaxially at constant speed, the load developed can be recorded as a function of the deformation (29). This can be converted into a true stress–strain curve. A compression test has the following two advantages over a tensile test for determination of deformation: (1) When a material is brittle in a tensile test, the tensile yield stress cannot be measured directly. It may be that such a material is not brittle in a compression test; it is then possible to measure the yield stress in compression. (2) When a specimen fails by necking rupture in a tensile test, the true stress–strain curve can be obtained only in a limited range of strains. Since such a material is generally more ductile in compression, the compressive true stress–strain curve can be obtained up to higher strains.

The main difficulty with compression tests lies in ensuring that the stress is uniform. Long thin specimens buckle and short fat specimens barrel because of friction between the loading plates and the specimen ends. A preferable form of compression test was devised by Watts and Ford (30) for metal sand has been applied to thermoplastics by Williams and Ford (31). This test uses a technique in which the center of a specimen is compressed between two dies. When the dies are moved together with constant speed, the specimen is compressed in one direction and expands outward at right angles. Because of frictional restraint there is no strain in the third orthogonal direction except for relatively small end errors. Because the strains are thus confined to a single plane, this is called a plane-strain compression test. The curve of load against deformation can be recorded and, because the area of contact is constant throughout the test, the curve can be converted directly into a true stress–strain curve; the load recorded is proportional to the true stress, unlike the situation in uniaxial tensile and compressive tests where the loads must be corrected to allow for the changing cross-sectional areas. Of course, this test is not designed to give a direct measure of fracture but its particular value is that it provides a true stress–strain curve directly, even when this is difficult in tension because of necking and fracture. It has the following two disadvantages: (1) The results are not extended reliably beyond nominal strains of about 70%, which is the equivalent of a tensile draw ratio of about 3. Behavior at much higher draw ratios than this can be investigated in tension in the favorable cases when the specimens do not break. (2) It may be necessary to make tests with a series of different dies of varying length-to-width ratios to overcome experimental errors caused by friction and specimen geometry (30, 31).

Mechanism

It is usual to start a discussion on the mechanism of fracture by pointing out that the measured tensile strengths of solids are much lower than the theoretical strengths as calculated from the atomic binding forces. For organic polymers, the maximum theoretical strength is that of a carbon–carbon bond, which has been given by de

Boer (32) as about 4×10^{11} dynes/cm^2 and by Mark as about 1.5×10^{11} dynes/cm^2 (33). In comparison, the usual tensile strengths quoted for elastomers and plastics are much lower, lying in the neighborhood of 10^8 to 10^9 dynes/cm^2. However, this simple comparison is too superficial because the measured tensile strength can be varied considerably by changes in the test temperature and the molecular orientation in the sample (34) and these factors are not considered in the calculations of de Boer and Mark; in practice, the tensile strength of a carbon–carbon bond cannot be approached unless the molecules are highly oriented in the direction of the applied tensile force. The highest polymer tensile strength published is about 2.3×10^{10} dynes/cm^2, given by Milagin and Shishkin (35) for a drawn nylon fiber tested in liquid nitrogen. If the test specimen had been quite perfect, presumably it would have extended until all the molecules were fully oriented and then have broken at a true stress at least six times higher. This leads to the conclusion that this fiber did not have a perfectly uniform structure and that the stress at the point where fracture originated was higher than the average measured stress. It is therefore assumed that all other polymer samples whose fracture stresses have been recorded to date also contain structural irregularities at which the local stress and strain are higher than the average measured stress and strain.

If fracture originates at a structural irregularity or fault in the specimen, it is necessary to consider how a crack propagates from the fault. Griffith (14) suggested that, for glass, the faults had the form of sharp cracks (length c) and that they propagated when the stress reached a value $\alpha\sqrt{Y\gamma/c}$ (see the section on Natural Cracks). According to Griffith's original idea, γ, the surface energy controlling fracture, was the same as the normal surface energy, but this idea is no longer accepted. Orowan (36) demonstrated that, for metals an overwhelmingly larger contribution to the fracture surface energy came from plastic deformation localized on the fracture surface. Berry (37) demonstrated that even for brittle fractures in plastics, the fracture surface energy is on the order of 10^5 ergs/cm^2 compared with about 50 ergs/cm^2 for the normal surface energy and about 200 ergs/cm^2 calculated from the assumption that the only energy-absorbing mechanism was the rupture of carbon–carbon bonds. Like Orowan, Berry attributed this large discrepancy to the "energy dissipated in inelastic processes which occur under the influence of the high stresses at the tip of the flaw." In other words, even in a fracture which appears brittle by the criterion given above (p. 303) (since the average strain does not reach the yield strain) there is localized yielding and extension to strains beyond yield. These considerations suggest that there are significant similarities between brittle fracture and necking rupture and, indeed, these two types of failure have four important features in common:

1. In both cases the yield strain has been exceeded in part of the specimen.

2. As Kambour (38,39) has shown, the material on brittle fracture surfaces consists partly of oriented polymer molecules. It is readily shown that the material in the necked region of a specimen which has failed by necking rupture also consists partly of oriented polymer molecules.

3. Kambour has also shown that the material on brittle fracture surfaces is partially void. This is also often true of the material in the necked region of a specimen which has failed by necking rupture (see the section on Necking Rupture and Fig. 8). The occurrence of voids can be understood by considering the stresses on the fracture surface. When the yield stress is reached locally, the material extends and, in order to keep the volume constant, it is necessary for the extension to be accompanied by side-

ways contractions. However, restraining forces from neighboring material, which has not yielded, tend to prevent these contractions; the locally yielded material, therefore, becomes subjected to tensile stresses in all directions. This triaxial tensile stress naturally tends to cause cavitation or microvoiding. This provides the fourth feature common to brittle fracture and necking rupture.

4. In both cases the stress system has a high triaxial tensile component because of the restraining influence of the neighboring material.

On the other hand, there are two major differences between brittle fracture and necking rupture: (a) In brittle fracture the yielding and deformation beyond yield are not observed in the macroscopic load–deformation curve. (b) The depth of material in which the strain exceeds the yield strain is very much smaller in brittle fracture than in necking rupture. Kambour (39) estimated that the depth of residual deformation in a slow brittle crack in a sample of poly(methyl methacrylate) was $0.68\ \mu$. In necking rupture, the depth of residual deformation is often several thousand times greater than this.

It seems, therefore, that brittle fracture can be considered to be an extremely localized form of necking rupture. In the section on Cold Drawing it was shown that necking was an instability of deformation caused by the reduction in slope of the true stress–strain curve. Williams and Turner (40) have performed an approximate analysis of the state of stress at the tip of the crack and have concluded that "in many, if not most, problems of fracture of interest to the engineer, a plastic instability precedes separation of the material." In other words, the mechanism of fracture involves an instability of the type discussed in connection with necking in cold drawing.

Williams and Turner assumed a stress–strain law of the form given in equation 22 where $\bar{\sigma}$ and $\bar{\epsilon}$ are equivalent stress and strain, and deduced that fracture toughness

$$\bar{\sigma} = A\bar{\epsilon}^n \qquad (22)$$

(K_c or G_c) should increase as the strain-hardening exponent n increases. Because the analysis is only approximate, and because the stress–strain relation used is not generally true for polymers, the quantitative conclusions of their approach cannot be applied directly. However, as a matter of principle, it follows that the details of fracture behavior depend upon the details of deformation behavior beyond yield. In particular, it is to be expected that the fracture toughness tends to increase as the rate of orientation-hardening increases.

To summarize the foregoing, four points may be listed: (a) Observed fracture stresses are less than theoretical fracture stresses and therefore fracture must originate at flaws. (b) Observed fracture surface energies are greater than theoretical fracture surface energies and therefore there are localized inelastic deformations even in brittle fractures. (c) Brittle fractures are extremely localized necking ruptures and therefore involve instabilities of deformation. (d) Instability of deformation and fracture toughness are dependent on the rate of orientation hardening beyond the yield point.

Factors Affecting Fracture

Fracture and Deformability. The remainder of this article will be devoted to consideration of the effects of a variety of changes, either in experimental conditions or in the material under examination, on the fracture behavior. Fracture is always preceded by some general deformation of the test specimen and, as shown in the discussion in the section above, fracture is preceded or accompanied by higher local de-