

Ductile–Brittle Transition in Polymers

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Synopsis

Tensile experiments on polypropylene and various rubber-modified polypropylenes, conducted over a wide range of temperatures and strain rates, have shown that the ductile–brittle transition in these highly crystalline polymers is strongly affected by both temperature and strain rate. Such polymers can either craze or shear yield, depending on the temperature and rate of test. High temperatures and low strain rates favor shear yielding, while low temperatures and high strain rates promote crazing. The ductile–brittle transition of these polymers may be understood as due to an alteration in deformation mode, as proposed by Matsushige et al. The competition between crazing and shear yielding dictates the subsequent failure mode. The dependence of the ductile–brittle transition on the test and material parameters (such as temperature, strain rate, pressure, orientation, notching, and plasticizer) may be ascribed to the respective influences of these parameters on crazing relative to shear yielding.

INTRODUCTION

The mechanical properties of polymers are known to be strongly affected by experimental conditions. A change in fracture mode from brittle to ductile with increasing temperature (T) and decreasing strain rate ($\dot{\epsilon}$) is one of the most significant of the observed variations. Despite the great effort directed to examining the effects of T , $\dot{\epsilon}$, and other variables on the ductile–brittle (D–B) transition, the nature of the transition remains poorly understood. Many aspects of D–B behavior in polymers,^{1–3} as in metals, have been explained phenomenologically on the basis of the Ludwik–Davidenkov–Orowan (L–D–O) hypothesis.^{4,5} On this basis, brittle fracture and plastic flow are viewed as independent processes, giving separate characteristic relations for the brittle fracture stress σ_B and the yield stress σ_Y , and the intersection of the σ_B/σ_Y curves defines the transition point.

Vincent¹ proposed that for polymers the yield stress is much more affected by changes in temperature and strain rate than the fracture strength and that the probability of brittle failure can be reduced by (a) increasing the molecular weight, which increases the fracture stress, (b) reducing the crystallinity, which reduces the yield stress, (c) adding plasticizer, which reduces the yield stress more than the brittle strength, (d) adding rubbery polymers, which reduces the yield stress, and (e) reducing crosslinking, which reduces the yield stress more than the brittle strength.

The L–D–O hypothesis^{4,5} and its interpretation by Vincent^{2,6} represent a useful framework for discussing the D–B transition in polymers. The hy-

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† Based in part on a thesis submitted by B. Z. J. in partial fulfillment of the requirements for the PhD degree in Polymerics, MIT, September 1982.

pothesis is subject, however, to a lack of specificity. For example, adding a rubbery phase will lower the macroscopic yield stress of the polymer; but the rationale for rubber toughening arises from the massive generation of crazes/shear bands, thereby dissipating a great amount of mechanical energy. Such microstructural features, which have been identified as critical aspects of the fracture and deformation of glassy polymers, are simply not considered at the level of the L-D-O approach. Recent work by the present authors⁷ has indicated that semicrystalline polymers such as polypropylene (PP) may exhibit similar crazing and shear yielding behavior.

Matsushige et al.⁸ conducted tensile tests over a wide range of pressure and temperature and observed that a brittle-to-ductile transition was induced in polystyrene (PS) and poly(methyl methacrylate) (PMMA) by the superposition of hydrostatic pressure as well as by increases in temperature. Similar behavior was observed in high impact polystyrene (HIPS) under pressure.⁹ These authors^{8,9} explained the D-B transition in terms of a competition between plasticity crazing and shear banding. The two processes respond quite differently to changes of pressure and of temperature, with the D-B transition observed where the craze initiation stress equals the shear band initiation stress.

The main objective of the present paper is to report the results of an extensive study of the effects of temperature and strain rate on the D-B transition in PP and a variety of rubber-modified PPs. The results indicate that the essential feature of the D-B transition in such materials is the competition between crazing and shear yielding, and suggest an explanation for this behavior.

EXPERIMENTAL

Materials and Sample Composition. The materials used in this study encompass polypropylene homopolymer (PP), ethylene/propylene/diene monomer (EPDM) rubber, ethylene/propylene copolymer (EPR), and styrene/butadiene copolymer rubber (SBR). The materials were commercial samples except the SBR samples, which were experimental polymers provided by Dr. Henry Hsieh of Philips Petroleum. The materials, sources, compositions, and processing conditions are listed in Table I. The mixer employed was a Brabender Plasticord single-screw ($L/D = 15$) extruder; the injection molding unit was an Ingersoll-Rand Model V2-18FA. Both are laboratory-scale machines.

Tensile Tests. Standard ASTM D638-76 tensile tests were performed on samples A-1, A-3, B-1, H-2, and H-4. In light of the high sensitivity of polymers to temperature and strain rate, tests were carried out over a wide spectrum of rates and temperatures. A temperature chamber adapted to an Instron universal testing machine was used to provide constant temperatures. The chamber was provided with resistance coils (heat), a coolant source (liquid N₂), and two internal fans, and a bilevel Delta temperature controller. A separate thermocouple was placed in contact with the surface of the specimen being tested to measure the actual test temperature.

Microscopy. A scanning electron microscope (AMR 1000A) was used to investigate the craze and crystalline morphology of microtome-polished sur-

TABLE I
Sample Compositions and Sources

| Designation | Material/composition | Supplier/molding condition | Comment |
|-------------|---|----------------------------|----------------------|
| PP-4 | Polypropylene homopolymer, melt flow rate = 5 | Hercules, Profax 6523 | High ρ |
| PP-12 | Polypropylene homopolymer, MFR = 12 | Hercules, Profax 6323 | Low ρ |
| N-1 | Ethylene-propylene-diene monomer (EPDM) | DuPont, Nordel 1070 | High ρ |
| E-1 | Ethylene-propylene copolymer (EBR) | B. F. Goodrich, Epcar 307 | Low ρ |
| S-2 | Styrene-butadiene copolymer (SBR) | Phillips, Solprene P243S | |
| S-4 | SBR | Phillips, Solprene 4169 | |
| A-1 | PP-4-N-1-15 | Extrusion: | 1. 15 wt % rubber |
| A-3 | PP-12-N-1-15 | Barrell temp = | 2. Sample dimension: |
| B-1 | PP-4-E-1-15 | 220°C, die temp = | 3 × 0.5 × 0.125 |
| H-2 | PP-4-S-2-15 | 200°C $L/D = 15, 80$ | in. dumbbell tensile |
| H-4 | PP-4-S-4-15 | rpm, extruded twice | bar |
| | | Injection molding: | |
| | | T (Zone 1) = 185°C, | |
| | | T (Zone 2) = 200°C, | |
| | | back pressure = | |
| | | 3000-6000 psi, mold | |
| | | temperature = 40°C | |

faces or fracture surfaces of the various samples. Ultrathin sections were stained by standard O_3O_4 treatment and investigated in a transmission electron microscope (Philips EM-300) to determine the craze structure and rubber particle morphology of impact-modified polypropylenes. Visual observation and polarizing light microscopy, in conjunction with electron microscopy, were used to explore the deformation mechanisms in PP and rubber-toughened PP.

Results

Typical temperature- and strain-rate dependencies of the stress-strain (σ - ϵ) behavior of a rubber-modified PP are presented in Figure 1. Curve 10 represents an extreme case where the sample exhibits initial elastic and viscoelastic behavior and breaks rapidly before crazing develops to any appreciable extent. Curves 8 and 9 are examples of plasticity governed primarily by crazing. This was evidenced by the occurrence of pronounced stress whitening in the deformed samples. The samples deformed beyond the initial viscoelastic range and reached a maximum in the σ - ϵ curve. This was followed by a small extent of necking and then fracture without cold drawing. The samples which exhibited σ - ϵ behavior similar to curves 8-10 were tested at relatively low temperatures and high strain rates.

Curves 1-3 are representative of samples which extend far beyond the maximum of the σ - ϵ curves. The samples exhibit a pronounced yield drop

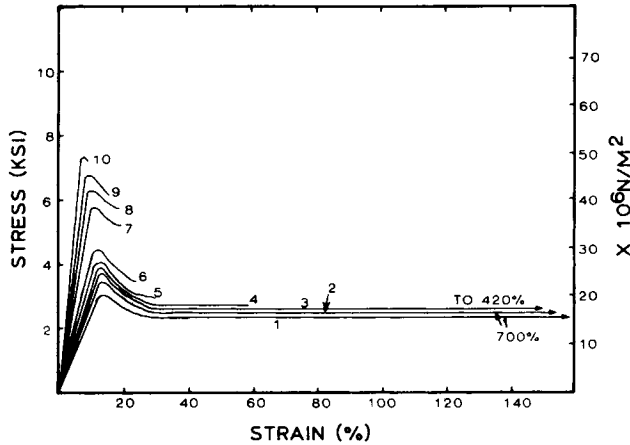


Fig. 1. Tensile stress-strain behavior of H-4 (85% PP-15% SBR):

| Curve | T ($^{\circ}\text{C}$) | $\dot{\epsilon}$ (in./min) |
|-------|----------------------------|----------------------------|
| 1 | 23 | 0.005 |
| 2 | 23 | 0.05 |
| 3 | 23 | 0.5' |
| 4 | 23 | 2.0 |
| 5 | 23 | 5.0 |
| 6 | 23 | 20 |
| 7 | -17 | 0.2 |
| 8 | -17 | 1.0 |
| 9 | -17 | 5.0 |
| 10 | -17 | 20 |

followed by cold drawing. Such behavior is denoted as shear yielding, since the samples exhibit little stress whitening and shear bandlike features were almost always identified near the boundary between drawn and undrawn material.¹⁰ Shear yielding appears to be representative of samples deformed at high temperatures and low rate.

The results of more extensive tensile tests covering a wide range of T and $\dot{\epsilon}$ are presented in Figure 2, where the normalized yield stress, defined as the maximum engineering stress in the σ - ϵ curve divided by the test temperature, is plotted as a function of $\log \dot{\epsilon}$, with each curve representing the behavior at a specific temperature. Again, high strain rate and low test temperature favor crazing while low rate and high temperature promote shear yielding. A transition zone is noted in the spectrum of rates and temperatures where crazes and shear bands coexist and the samples exhibit crazing subsequent to the initial viscoelastic regime, followed by general yielding, a yield drop and a small extent of cold drawing. As the temperature is further decreased or strain rate increased, the extent of cold drawing is reduced and the shear yielding gradually gives way to crazing.

Such a shear yielding-crazing transition is reflected in Figure 2 as the temperature and strain rate where each curve changes its slope. For a given test temperature, there exists a strain rate above which deformation is dominated by crazing, and for a given test rate there exists a temperature

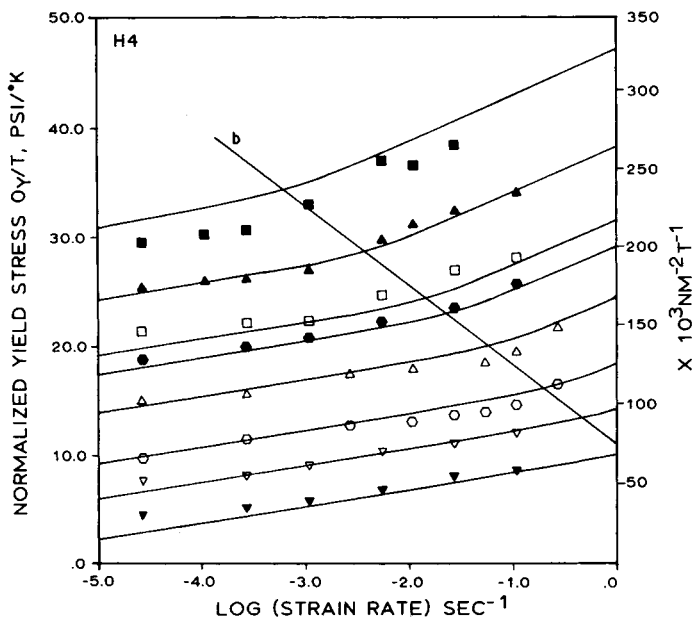


Fig. 2. The yield stress as a function of temperature and strain rate (H-4). Solid curves represent theoretical prediction from a generalized Eyring's theory.²⁰

which demarcates crazing from shear yielding. Similar transitions between crazing and shear yielding are observed for other rubber-modified polypropylenes such as samples H-2, B-1, A-1, and A-3 (Figs. 3-6) as well as PP homopolymers.⁷

The solid curves in Figures 2-6 were drawn according to a generalized Eyring theory of viscous flow¹¹ adapted by Bauwes-Crowet et al.¹² and

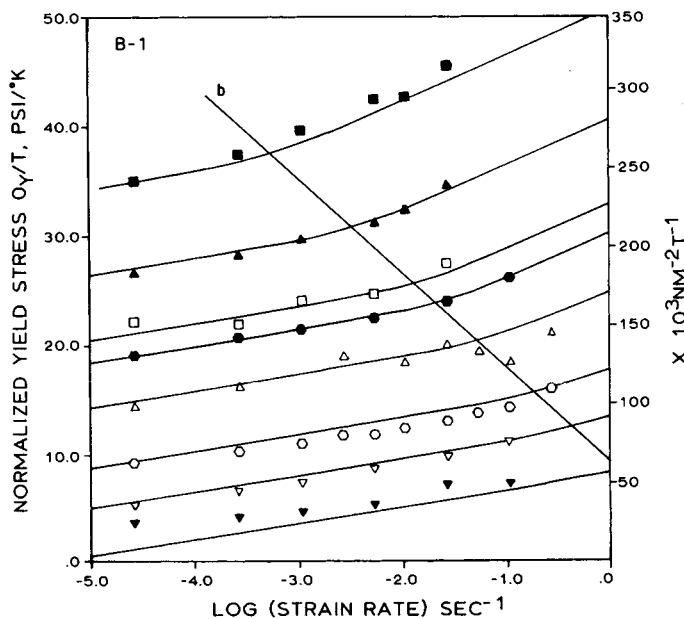


Fig. 3. The yield stress as a function of temperature and strain rate (B-1). Solid curves represent theoretical prediction (see text).

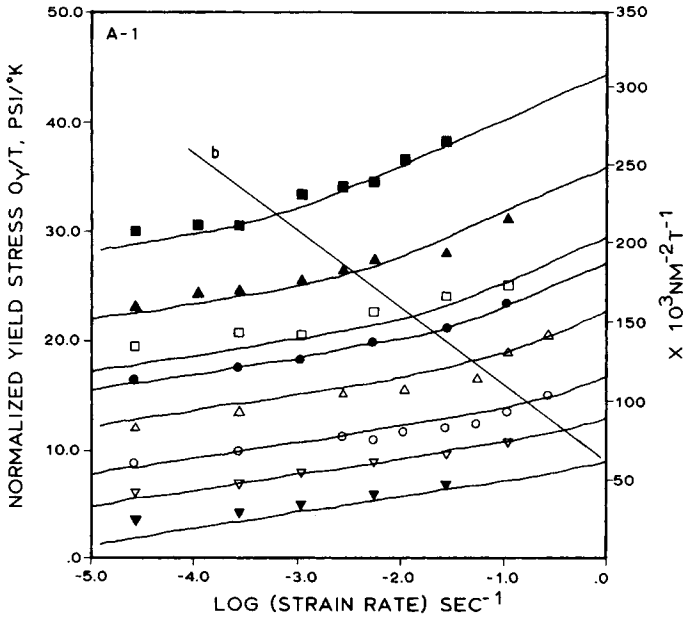


Fig. 4. The yield stress as a function of temperature and strain rate (A-1). Solid curves represent theoretical prediction.

Roetling^{13,14} to explain the tensile yield behavior of polymers. By assuming that two mechanisms of molecular segmental motion are involved during polymer yielding these workers¹²⁻¹⁴ theorized that the yielding stress is the sum of the stresses carried by these two processes, weighted according to the fraction of the shear plane occupied by each type of segment. The normalized yield stress $\sigma_{Y/T}$ is therefore expressed in terms of six fitting

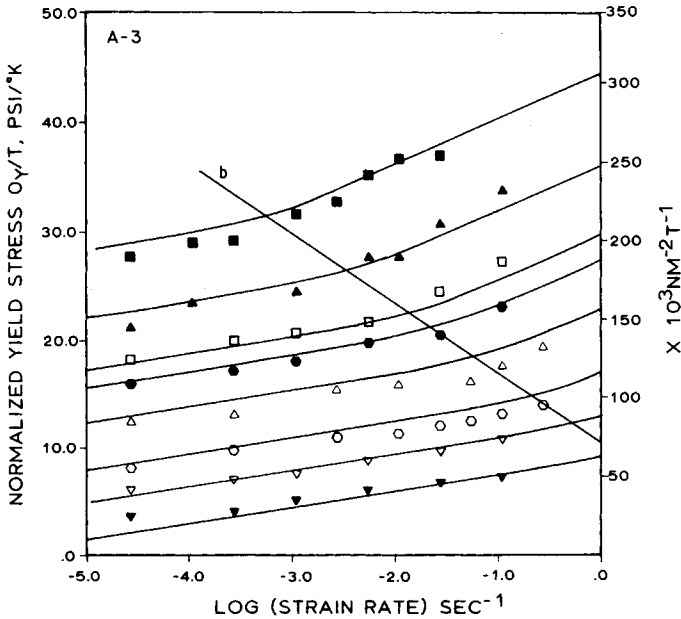


Fig. 5. The yield stress as a function of temperature and strain rate (A-3). Solid curves represent theoretical prediction.

parameters, including activation energy and activation volume for each process.

Various values were assumed for each parameter and input to the computer (HP Model 1000A Minicomputer), which is preprogrammed to perform calculations of normalized stresses and plot solid curves according to the proposed theory. The computer-generated curves are then compared with the experimental data. From this comparison the estimated values of the parameters are revised, and the fitting process is repeated until a reasonably good fit is obtained. The "goodness" of fitting is judged on the basis of the overall matching between the data points and all theoretical curves. As a result, some of the solid curves are not drawn through the data points. However, trying to vary the parameters to best fit these curves will lead to a poorer overall fitting. The values of the final parameters and their interpretation have been given¹⁵ and will be further discussed in a forthcoming paper.¹⁶

A typical rubber-PP morphology and its relationship with crazing are shown in Figure 7. The dark bands which appear to radiate from the more or less spherical rubber particles are crazes; both crazes and the rubbery phase exhibit preferential pickup of the O_3O_4 , providing contrast in the TEM. Detailed discussion of morphological features and crazing behavior in rubber-modified PP is given elsewhere.¹⁶

DISCUSSION

Mechanism of the Ductile-Brittle Transition

The mechanical properties of materials, including polymers, are dependent upon the test conditions, including most notably the temperature and

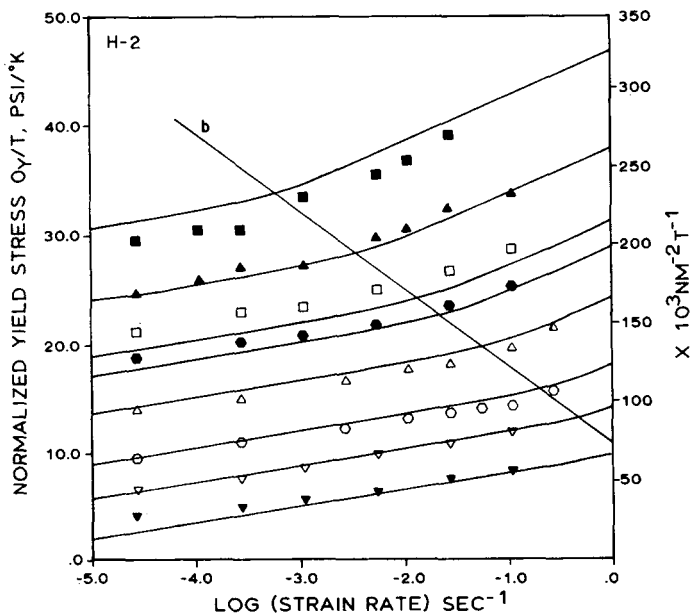


Fig. 6. The yield stress as a function of temperature and strain rate (H-2). Solid curves represent theoretical prediction.



Fig. 7. Typical EPDM rubber-pp morphology and its relationship with crazing.

strain rate. In interpreting the transition between ductile and brittle behavior in polymers, it has been suggested¹ that the yield stress is much more affected by changes in temperature and strain rate than the brittle strength.

For glassy thermoplastics, it is widely recognized that crazing and shear yielding are the two most common modes of deformation. Building upon this, Matsushige et al.⁸ further proposed that the D-B transition is a direct result of the alteration in deformation mode from shear yielding to crazing. Studying the tensile σ - ϵ behavior of PMMA and PS over a range of temperatures, these workers found essentially the same temperature dependencies for both the craze initiation and fracture stresses in the brittle fracture regime. A similar correlation can be seen for the shear band initiation and yield stresses in the ductile regime. The intersection temperature of the relations for craze and shear band initiation delineates the D-B transition (90°C for PS and 50°C for PMMA). A similar D-B transition with respect to hydrostatic pressure was also observed for both polymers.

It was shown in the present work that a shear yielding-to-crazing transition can be induced in various impact-modified PPs, either by decreasing the temperature or by increasing the strain rate. In general, brittle fracture of a polymer (excluding rubber) has been considered to occur when a specimen fails at its maximum load. This definition is extended to include specimens which display a yield drop (in the engineering σ - ϵ curve) and

little or no necking, since in such cases the fracture is caused by the propagation and breakdown of crazes, not shear bands. From the simultaneous observation of the stress-strain and optical behavior, it has been found that the D-B transition in such polymers reflects the change in deformation mode.

Vincent¹ explained the D-B transition by considering that any stress system may be decomposed as the sum of a deviatoric component, which tends to change the specimen shape, and a normal mean stress, which tends to change its volume. As the stress increases, the specimen fails either in shear, if the deviator exceeds the shear fracture stress, or in triaxial tension, if the mean stress exceeds the triaxial tensile breaking strength. Shear failure, which may be characterized by the yield stress in tension, represents a ductile failure, while the triaxial tensile failure represents brittle failure since large deformation is not possible in this mode. Vincent¹ therefore proposed that the D-B transition represents a change from shear to triaxial tensile failure.

Based on the present results and those obtained previously on glassy polymers, this proposal can be modified by suggesting that the specimen will yield in shear if the shear component of the stress exceeds the shear band initiation stress. If the hydrostatic stress component exceeds the stress for craze initiation, the specimen will deform by crazing. The craze initiation stress and the shear band initiation stress are expected to have different sensitivities to temperatures, rate, and pressure of test. The craze initiation stress seems to be a less sensitive function of temperature than the shear band initiation stress, as indicated by data obtained on PS and PMMA.⁸ In contrast, increased pressure affects the shear band initiation process less strongly than crazing,⁸ since the latter is essentially a dilatational process while the former involves little or no volume change. Hydrostatic pressure tends to suppress the cavitation process by raising the stress necessary for the onset of crazing more than that for the formation of shear bands. Similar arguments seem applicable to the deformation of crystalline polymers such as polypropylene and rubber-modified polypropylenes.

Effects of Strain Rate

In obtaining insight into the strain rate sensitivity of crazing and shear banding, it is useful to consider the relative contribution of crazes and shear bands to the overall plastic strain of a specimen. By recognizing the analogies between dislocations in metals and crazes and shear bands in polymers, Kramer¹⁷ has made a useful estimation of the plastic strains contributed by the two mechanisms. Kramer¹⁷ treated the dislocation as a line which bounds a planar area across which there has been a displacement \mathbf{b} . The strain due to a dislocation density ρ moving a distance χ may be expressed as

$$\epsilon = \rho b \chi \quad (1)$$

The shear band was regarded as analogous to a dislocation with a Burgers vector \mathbf{b} in the plane of the band, where

$$b = \gamma t \quad (2)$$

Here γ is the shear strain in the shear band and t is the thickness of the band. Further assuming that a shear band density N_s is nucleated and each grows a distance l in all directions in the plane of the band Kramer obtained

$$\rho \simeq N_s l \quad \text{and} \quad \epsilon_{sb} = N_s \gamma t l^2 \quad (3)$$

By considering the craze as a wedge with a constant wedge angle α and assuming a number density of crazes N_c each of which grows to dimensions l with average b given by $\langle b \rangle = (1 - 1/\lambda)l$, Kramer reached eq. (4) for the macroscopic strain produced by crazing:

$$\epsilon_{\text{craze}} = N_c \alpha (1 - 1/\lambda) l^3 \quad (4)$$

The parameter λ represents the average draw ratio of craze fibrils.

It may be noted from Eq. (4) that if crazes grow linearly with time, the strain due to crazing will accelerate markedly with time due to the l^3 dependence of ϵ_{craze} . By comparison, the strain due to shear bands is proportional to l^2 . It may be inferred from eq. (3) and (4) that, in order for the material to accommodate the rapid increase of plastic strain during high rate loading, crazing should dominate because it provides a faster path for strain increment.

Additional Examples

The discussion of the previous sections suggests that the D-B transition observed in polymers is in general due to an alteration in deformation mode, from distortional (shear banding) to dilational (crazing). On this basis, the experimental parameters and material variables which affect the relative importance of these deformation modes should in turn control the D-B behavior of the polymer. Many other aspects of the mechanical behavior of polymers are also readily explainable on this basis, as illustrated by the following examples:

1. The existence of flaws such as notches, air bubbles, and cracks promotes the formation of crazes by raising the local triaxial stress and strain rate. If not stabilized, the crazes may become cracks, resulting in catastrophic failure. A shift of the D-B transition from -94°C to -4°C by introducing a razor cut in a sample of low density polyethylene¹⁸ may be understood on this basis. Low compression molding temperature or pressure, rough machining, weld lines, and other factors which produce structural irregularities and stress concentrators, should increase the probability of crazing and thus of brittle fracture.

Vincent¹ proposed that, under given conditions, if the ratio of brittle tensile strength to yield strength is not much greater than unity, the material will be notch-sensitive. Based on the arguments outlined above, it is suggested that a material will be notch-sensitive if the ratio of the craze initiation stress to the shear band initiation stress is not much greater than

unity. Under these conditions, a slight increase in the triaxial component relative to the shear component of stress, as a result of notching, may cause the material to craze.

2. Molecular orientation tends to suppress the formation of crazes and promote the shear yielding mode. The resulting material, although stiffer in the direction parallel to the orientation, is usually more ductile. This has also been demonstrated by experiments on styrene-acrylonitrile copolymer (SA) and rubber-modified SA.¹⁹ The present authors have observed that crazes usually do not develop in the highly oriented skin zone of injection-molded PP.²⁰

3. A thermoplastic which exhibits brittle behavior in tension may be ductile in compression, since compressive stress tends to suppress crazing and promote shear yielding.

4. Additions of plasticizer, which reduce the shear yield stress more than the stress for craze formation, should reduce the likelihood of brittle failure.

Many questions remain to be elucidated. It is known that the craze initiation stress of polystyrene is independent of molecular weight, although higher molecular weight material provides higher breaking strength (greater resistance to craze breakdown).²¹ How the shear band initiation stress depends on the molecular weight is not yet clear. Reducing the crystallinity of a semicrystalline polymer may reduce the craze initiation stress as well as the shear band initiation stress. Which one is affected more strongly is still unknown.

CONCLUSIONS

The tensile stress-strain behaviors of polypropylene homopolymer and polypropylenes modified with a variety of rubbers have been studied over a wide range of temperature and strain rate. These crystalline polymers can undergo either crazing or shear yielding depending on the temperature and speed of test. At a given temperature, there appears to exist a critical strain rate above which crazing is the dominant mode of deformation. Similarly, at a given strain rate, there exists a critical test temperature which demarcates crazing from shear yielding behavior.

The present results are in accord with the suggestion of Matsushige et al.⁸ that the D-B transition of a polymer can be associated with an alteration in deformation mode. The competition between craze initiation stress and shear band initiation stress dictates the subsequent failure mode. The effects of temperature, strain rate, hydrostatic pressure, orientation, notching, and adding plasticizer upon the D-B transition of a polymer may be explained on this basis. Each parameter may affect the crazing process and shear banding process to different degrees. The test conditions at which the craze initiation stress equals the shear band initiation stress define the so-called D-B transition.

Financial support for the present work was provided by the Air Force Office of Scientific Research. This support is gratefully acknowledged, as is the assistance of Dr. Henry Hsieh of Phillips Petroleum.

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Received January 25, 1984

Accepted March 5, 1984