Inasmuch as the presence of unsaturation in the polymer has been demonstrated on several occasions, initiation under these conditions is by acrylamide anion.

**L. W. Bush and D. S. Breslow**

*Research Center*
*Hercules Incorporated*
*Wilmington, Delaware 19899*
*Received January 31, 1968*

## Craze Formation Yield Stress and the So-Called Ductile–Brittle Transition in Glassy Polymers

The purpose of this communication is to add to the growing body of evidence favoring the view that the so-called ductile–brittle transition in glassy polymers is in reality a transition between two alternate modes of ductility both of which, prior to specimen fracture, can involve large amounts of straining in large amounts of polymer. We also wish to suggest that accumulated evidence makes difficult the view that gross polymer ductility is fully explained by the hypothesis that under stress $T_g$ is caused to be equal to or lower than the actual temperature of the deforming polymer.

Below their $T_g$'s linear amorphous polymers like polystyrene, polymethyl methacrylate, polycarbonate, and poly-2,6-dimethylphenylene oxide (PPO®)[2] resin commonly exhibit ductile failure by a shear deformation mechanism over temperature ranges which vary from 15 to 300°. Little or no density change is involved. The temperature range over which this behavior can be observed can be extended (a) by careful choice of testing rate;[1] (b) by preorientation of the specimen at $T > T_g$;[3a] or (c) by conducting the test under hydrostatic pressure.[3b]

Below the so-called ductile–brittle transition temperature the common mode of failure is apparently brittle in that no maximum is observed in the stress–strain curve. Crazing initiates at low stress, fracture initiates in one of the crazes,[4] and more craze material is produced as the crack propagates.[5] The high energy of crack propagation is associated with the viscoelastic strains involved in the craze formation and breakdown.[6]

**Experimental Section.** In the course of studies of the role of organic agents in promoting craze formation and breakdown in glassy polymers, we have noticed large differences in mechanical response of PPO films tested in the presence of small-molecule organic agents. These differences depend on whether the agent is applied at the initiation of the tensile test or is allowed to absorb in the specimen to equilibrium prior to test initiation.

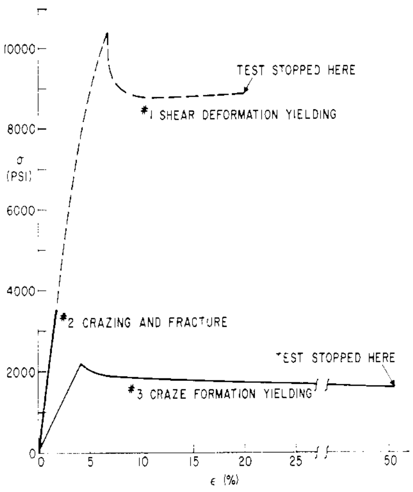

Figure 1. Engineering stress–strain curves for PPO film at 0.05 in./min extension rate: test 1, dry film; test 2, film immersed in acetone at start of test; test 3, film equilibrated with acetone vapor prior to test initiation.

In Figure 1, for example, we show three Instron stress–strain curves at 0.05 in./min elongation rate for 2.5-mil thick annealed film specimens of PPO of $[\eta] = 0.71$ dl/g. Specimens had the conventional dogbone shape with a gauge length of 1.25 in. Curve 1 is the engineering tensile stress–strain curve of the dry film; a yielding of the well known type involving response to the shear component of stress[7,8] occurs at 10,400 psi. Curve 3 exhibits apparently brittle fracture at 3500 psi, the crack having initiated at a single preformed craze; for this test the film specimen was mounted in a special jig which allowed simultaneous initiation of straining and immersion of the film in liquid acetone.

Curve 3 was obtained from testing a specimen which had been mounted in the same jig with a few cubic centimeters of acetone in the bottom of the glass envelope enclosure and left in contact with the saturated vapor for 24 hr prior to test initiation. (From separate sorption kinetic experiments this film is known to reach sorption equilibrium in acetone in 24 hr; equilibrium solubility is 0.16 g/g of polymer. The equilibrated film is still glassy at room temperature as evidenced by its lack of plasticizer-induced crystallinity[9] and its modulus of $4 \times 10^9$ dyn/cm$^2$.) Crazes were observed to initiate at low stresses and grow very rapidly, each tending to cover the entire cross section. Craze formation accelerated with stress increase, and it was apparent that the yield stress observed (2200 psi) was to be construed as that stress at which plastic deformation by craze formation equaled the rate of crosshead extension. The test was continued to about 50% elongation of the test section and then stopped because of limitations in the testing jig. At no time were there observed any signs of deformation bands at angles other than 90° to the tensile stress direction; thus shear deformation is ruled out as contributing significantly to the ductile failure observed here.

Figure 2 is a photomicrograph of the test section of specimen 3 subsequent to testing. The corrugations running perpendicular to the stress direction are the edge grooves of crazes. It is apparent that the fraction of the area taken up by crazes $F \simeq 0.5$. We may estimate crudely the fraction $f$ of the original test section which has been converted into crazes as follows. From craze refractive index measure-

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(1) R. E. Robertson, private communication.

(2) Registered trademark of the General Electric Co.

(3)(a) R. D. Andrews and W. Whitney, Massachusetts Institute of Technology Textile Division Report No. TD-123-64, May 1, 1964. (b) L. Holliday, J. Mann, G. Pogany, H. Pugh, and D. Gunn, *Nature*, **202**, 381 (1964).

(4) J. P. Berry, *J. Polym. Sci.*, **50**, 107, 313 (1961).

(5) R. P. Kambour, *ibid., Part A-2*, **4**, 4165 (1964).

(6) R. P. Kambour, *ibid., Part A-2*, **4**, 17, 349 (1966).

(7) W. Whitney, *J. Appl. Phys.*, **34**, 3633 (1963).

(8) R. E. Robertson, *J. Chem. Phys.*, **44**, 3950 (1966).

(9) R. P. Kambour, F. E. Karasz, and J. H. Daane, *J. Polym Sci., Part A-2*, **4**, 327 (1966).

ments results of which will be reported elsewhere the void content $V$ of the individual craze in PPO polymer is calculated[10] to be about 60%. Since $V = \epsilon_c/(1 + \epsilon_c)$, where $\epsilon_c$ is the strain developed in the individual craze, $\epsilon_c \simeq 1.5$. The total length attained by unit length of original test section is $1 + f\epsilon_c$ where $f$ is the fraction of polymer in the test section transformed into crazes. Therefore

$$F = f(1 + \epsilon_c)/(1 + \epsilon_c) \simeq 0.5$$

Substituting $\epsilon_c \simeq 1.5$ yields $f \simeq 0.3$ so that roughly 30% of the test section has been transformed into craze material in the drawing process.

The same phenomenon has been observed in PPO resin equilibrated with other liquids and also in polystyrene and in Lexan polycarbonate films equilibrated in a similar way.

**Conclusions.** We conclude the following from these observations and related knowledge.

1. Glassy polymers can sometimes undergo craze formation so easily by comparison with craze fracture and with shear deformation that a craze formation yield stress is exhibited followed by gross amounts of drawing. In our case this is effected by incorporation of weak plasticizer. Proper incorporation of rubber particles, as in high-impact polystyrene, can bring about the same effect although probably not by quite the same mechanism.[11,12]

2. Whether few or many crazes form before fracture occurs depends on the relative values of stress for craze formation and craze failure.

3. Whether a shear deformation yielding occurs before craze formation depends essentially on which of these competing modes of ductility is easier under the particular condition.

4. Consequently, the so-called ductile–brittle transition is a misnomer and in reality should be viewed basically as a ductile–ductile transition in that only a transition from one ductile mode to another is involved.

5. There may well be no low-temperature limit on the crazing mode of ductility; fracture studies[13] indicate that in polymethyl methacrylate, for example, crazing occurs under stress at least down to 100°K, which is 250° below the ductility transition temperature normally cited. Therefore, since large-strain ductility is probably involved in failure under all conditions (only the amounts of polymer involved varying widely), the traditional view that the temperature of the ductility transition in glassy polymers is the lower limit of stress-induced flow is no longer tenable.

6. Finally we suggest that the hypothesis of stress-lowering of $T_g$[14] is insufficient, by itself at least, as an explanation of flow in glassy polymers. On the macroscopic scale the elemental step in shear deformation appears to be the propagation in the direction of maximum shear stress of discrete, sharply bounded, thin shear bands each of fixed degree of strain.[7] Crazes are sharply bounded to a similar degree but by contrast propagate in a direction perpendicular to the maximum tensile stress.[10,15] $T_g$-lowering hypotheses are not capable alone of rationalizing the existence of such strikingly different deformation modes.

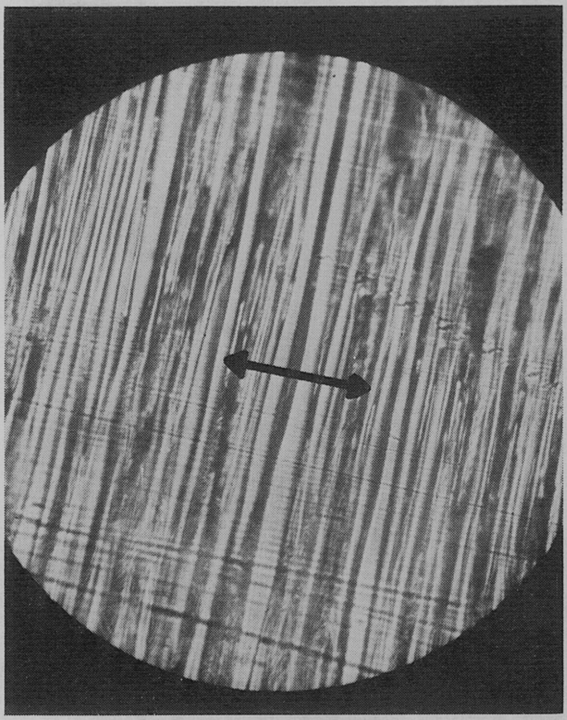

Figure 2. Photomicrograph of surface of film test section subsequent to test 3 showing large-scale craze formation perpendicular to tensile stress direction (arrow). Field diameter is 0.05 cm.

By analogy with well-established theories of the deformation of crystalline substances,[16] and in agreement with Robertson,[8,17] we expect that a fully satisfactory explanation of glassy polymer deformation requires an understanding of supramolecular organization and its interaction with allowed chain conformations in imposing restrictions on cooperative motion in the glassy state.

**R. P. Kambour and G. A. Bernier**

*General Electric Research and Development Center*
*Schenectady, New York*

*Received February 19, 1968*

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(11) C. B. Bucknall and R. R. Smith, *ibid.*, **6**, 437 (1965).

(12) M. Matsuo, *ibid.*, 7, 421 (1966).

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(14) See, *e.g.*, M. H. Litt and P. Koch, *ibid.*, *Part B*, **5**, 251 (1967).

(15) S. Sternstein, L. Ongchin, and A. Silverman, Symposium on Polymer Modification of Rubbers and Plastics, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967 [see *Polym. Preprints*, **8**, No. 2, 1495 (1967)].

(16) See, *e.g.*, A H. Cottrell, "Dislocations and Plastic Flow in Crystals," Oxford University Press, London, 1953.

(17) R. E. Robertson, Symposium on Polymer Modification of Rubbers and Plastics, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967 [see *Polym. Preprints*, **8**, No. 2, 1501 (1967)].