

FRACTURE AND TOUGHNESS OF POLYMER SOLIDS

I. Narisawa and M. Ishikawa

*Department of Polymer Materials Engineering, Faculty of Engineering, Yamagata University,
Yonezawa, Japan*

ABSTRACT

The fracture behavior and toughness of glassy polymers under a state of plane strain have been described in relation to two essential types of plastic deformation. From an interpretative analysis of the results in which factors affect the critical stresses for shear yielding and crazing, such as temperature, strain rate, hydrostatic stress and thermal history, it is suggested that the ratio of the critical stress for crazing s to the shear yield stress k is a dominant parameter to characterize toughness of the materials as well as fracture mode. For materials with $s/k \leq 1$ depending on test conditions, brittle fracture occurs without shear yielding. For materials with $1 < s/k < 1 + \pi - \omega$ where ω is the included angle of the notch, quasibrittle fracture occurs with local shear yielding and nucleation of the tip of plastic zone. For materials with $s/k \geq 1 + \pi - \omega$, ductile fracture occurs with general shear yielding.

KEYWORDS

Crazing; shear yielding; brittle fracture; quasibrittle fracture; ductile fracture; slip line field theory; glassy polymers.

INTRODUCTION

The toughness of a material sets limits both to design and safety of engineering components and structures. Therefore, the questions of a criterion for toughness in fracture of glassy polymers have been extensively investigated from both practical and scientific viewpoints.

One of the most practically useful criteria for brittle or quasibrittle fracture is based on linear fracture mechanics. Recent investigations (Williams, 1978) have shown that fracture mechanics analyses are quite successfully applicable to the behavior of glassy polymers in different types of fracture, such as static, impact, fatigue, stress cracking and crazing. More recently, the J energy approach (Rice, 1968) based on nonlinear fracture mechanics has been tried on ductile polymers in which the

considerable amount of energy put into the material is dissipated to create plastic deformation ahead of the crack tip. Results obtained from linear or nonlinear fracture mechanics provide the most satisfactory available parameters characterizing toughness of a material in evaluating and analyzing service failures. However, fracture mechanics approach does not permit fracture of glassy polymers to be interpreted directly in molecular terms, but in terms of only macroscopic continuum properties. It should be noted, furthermore, that the parameters to define fracture toughness are not true material properties, but they are significantly dependent on conditions such as type of loading, specimen geometry, loading rate and temperature.

The object of the present paper is to provide more comprehensive parameters which characterize material toughness in fracture of glassy polymers and parameters which determine a fracture mode, and to enable them to relate directly to fracture processes on both macroscopic and microscopic scales.

APPLICATION OF FRACTURE MECHANICS AND FRACTURE PROCESSES OF GLASSY POLYMERS

The application of linear fracture mechanics to brittle glassy polymers such as polystyrene (PS) and poly methyl methacrylate (PMMA) is now well established. In these glasslike polymers the energy dissipation is considered to be quite local to the crack tip so that the whole system is regarded as a completely elastic body on a macroscopic scale. Toughness is generally defined as material resistance to crack initiation and propagation and it is described by a critical energy input G_c necessary to initiate and grow a crack which leads to final fracture. Essentially, G_c should equal two times the surface energy of the crack, but the value of G_c obtained by application of linear fracture mechanics is usually in much excess of the surface work required for the formation of new surfaces by main chain scission. The reason for this discrepancy is frequently explained by that it is not possible to rupture molecular chains without a modification of the microstructure which is inevitably linked with the work of bond rupture. Many investigators (Berry, 1961; Kambour, 1964; Brown, 1973; Morgan, 1977; Frazer, 1978; Weidmann, 1978) have shown that the energy is dissipated in forming porous structure with ligaments called craze structure as illustrated in Fig. 1.

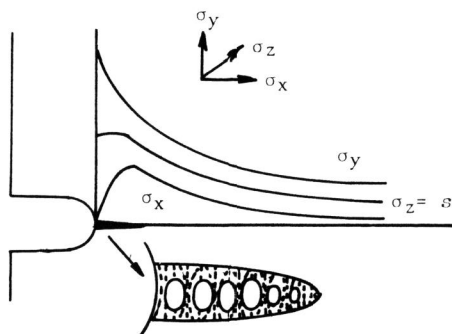


Fig. 1. Surface craze formed by elastic stress concentration at the notch tip.

A considerable amount of research has been conducted on various aspects of crazing, there has been no established agreement on the criterion for craze formation. The most reasonable criterion for craze initiation would be a cavitation criterion in a dilatational stress field, recognizing that crazing requires formation of many fine voids in its structure (Sternstein, 1968; Oxborough, 1974; Gent, 1973; Argon, 1974, 1977; Ishikawa, 1977). In the case of a thick specimen where a state of plane strain prevails, the dilatational stress can be built up to craze initiation at the crack tip, because the lateral contraction of the material is hindered. If Poisson's ratio is 0.5, the dilatational stress is given by

$$s = (\sigma_x + \sigma_y + \sigma_z)/3 = (\sigma_x + \sigma_y)/2 = \sigma_z \quad (1)$$

where the stress components are defined as in Fig. 1.

For quasibrittle polymers such as polycarbonate (PC) and poly vinyl chloride (PVC), the energy dissipation is mainly caused not by crazing, but by forming shear yield deformation at the crack tip which depends on specimen geometry. If the plastic zone is assumed to be small enough not to greatly disturb the elastic stress field near the crack tip, then the linear fracture mechanics can be safely applied to obtain the value of G . In a modest thick specimen, the surface regions of the specimen are always in plane stress while the center tends to be a state of plane strain. The surface shearing results in extra work being necessary for specimen fracture (Parvin, 1975, 1981; Frazer, 1978; Kambour, 1978). Even in such a mixed stress state, the final fracture is produced by craze nucleation at the center of the specimen as typically shown in Fig. 2 in which the microphotographs of the cross-sections of the plastic zone obtained on 0.5mm thick PC sheet (Ishikawa, 1976). As the specimen thickness decreases further

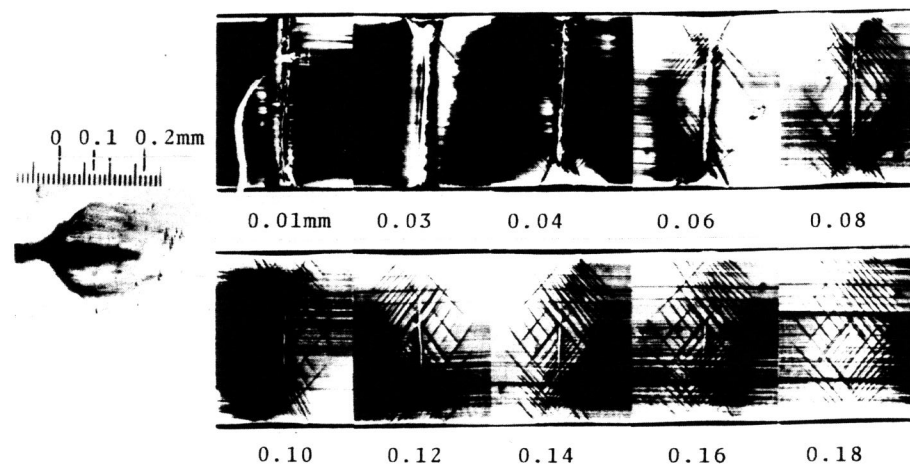


Fig. 2. Microphotographs of an overall view of the plastic zone formed at the tip of the notch in 0.5mm thick PC and successive cross-sections of the plastic zone.

to give through-section yielding, the utility of linear fracture mechanics declines. The value of G for thick specimens, which is often called "plane strain fracture toughness", is practically important because it represents a limit of toughness for quasibrittle polymers.

When the material is sufficiently ductile to form a large plastic deformation at the crack tip, linear fracture mechanics is completely unusable. This problem is encountered particularly in testing rubber-modified polymers such as high impact polystyrene (HIPS), ABS and block copolymers of propylene in which a large stress-whitened deformation area is formed. Fig. 3 shows a typical example of the stress-whitened plastic zone associated with a load-displacement curve of block copolymer of ethylene-propylene subjected to three-point-bending. The J -energy criterion has recently received considerable attention to such

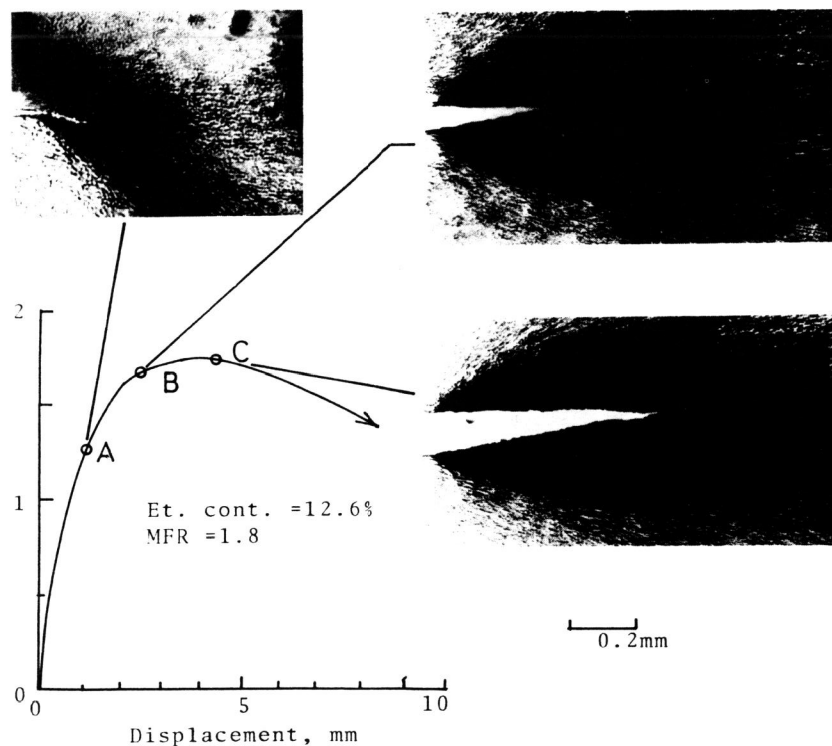


Fig. 3. A typical example of stress-whitened deformation associated with the load-elongation curve of a block copolymer of ethylene-propylene subjected to three-point-bending.

energy dissipating materials, but there has been little amount of published information on the J -integral data of ductile polymers (Williams, 1981). In these circumstances, Fig. 4 shows the experimentally obtained J versus increase of crack length for ethylene-propylene block copolymers. As clearly seen from this figure, the crack does not grow without continuous increase of external work.

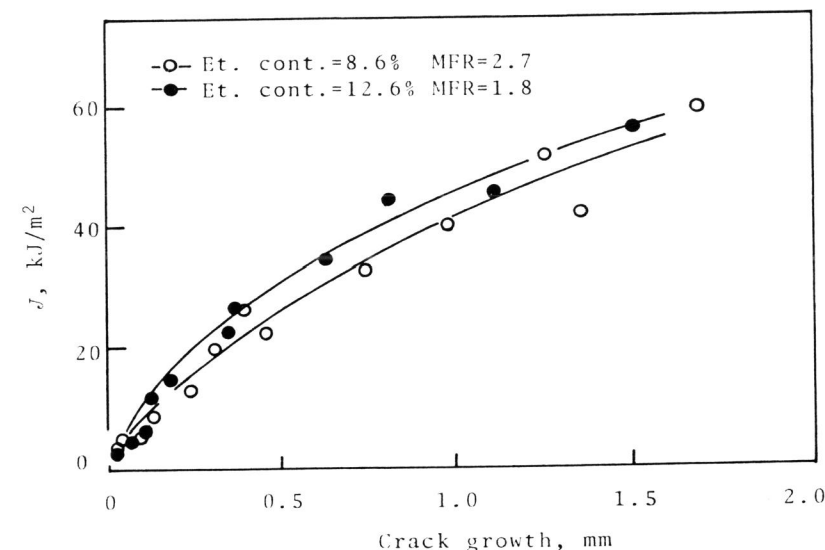


Fig. 4. J -values for block copolymers of ethylene-propylene as a function of crack growth.

BRITTLE AND DUCTILE FRACTURE OF GLASSY POLYMERS

For the particular polymer material which is under consideration, the resistance to plastic deformation and fracture is dependent upon the temperature and strain rate. A pronounced change in the fracture mode is the ductile-to-brittle fracture transition occurring with decreasing temperature and/or increasing strain rate. If a state of stress is chosen so that plane strain is sufficiently maintained for a material which shows shear yielding under tension, it is possible to form both shear yield and craze structures by using a notched thick specimen as shown in Fig. 5 in which shear yielding occurs around the notch root when tensile stress reaches the yield stress of the material. As the applied load is increased, the plastic zone grows into the inside of the material. The stress distribution within the plastic zone is quite different from elastic stress distribution because of constraints caused by undeformed elastic material outside the plastic zone. It is well known that if the material is assumed to be rigid-perfectly-plastic, the stress distribution within the plastic zone can be described by the slip line field theory developed by Hill (1950). On the assumption that the material obeys Mises yield criterion, the maximum principal stress σ_y in the tensile direction within the plastic region of logarithmic spirals at a distance r from the notch tip is given by

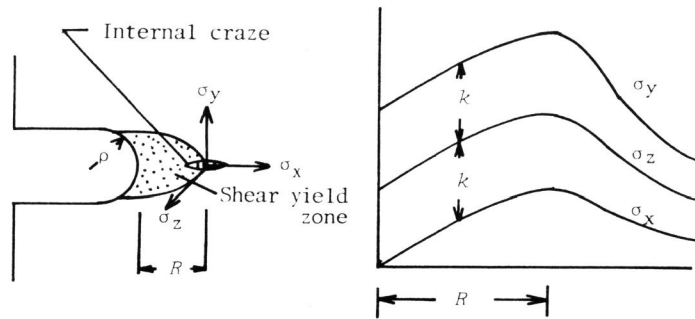


Fig. 5. Stress distribution within the plastic zone.

$$\sigma_y = 2k \{ 1 + \ln(1 + x/\rho) \} \quad (2)$$

where ρ is the notch radius and k is the critical shear stress of the material. The maximum value of σ_y is only dependent on notch geometry:

$$\sigma_{y,\max} = 2k (1 + \pi/2 - \omega/2) \quad (3)$$

where ω is the included notch angle. The maximum size of the plastic zone, given by

$$R_{\max} = \rho \{ \exp(\pi/2 - \omega/2) - 1 \} \quad (4)$$

It is also dependent on the notch geometry. The shear yielding at the notch root provides a dilatational stress concentration ahead of the plastic zone. Using eqs.(1) and (2), and Mises yield criterion, the dilatational stress is given by

$$s = k \{ 1 + 2 \ln(1 + R/\rho) \} \quad (5)$$

where R is the size of the plastic zone.

The fracture steps of such materials in which the local shear yielding occurs at the notch root has been documented (Narisawa, 1980, 1981; Ishikawa, 1981):

- (1) Plastic shear yielding is initiated at the notch root roughly at a stress level of 40-60% of the gross fracture stress.
- (2) As the external load is increased, the plastic zone spreads from the notch root, and when the zone reaches a certain size, a semicircular craze is initiated at the tip of the plastic zone.
- (3) Final fracture is produced by the growth of the internal craze which

converts quickly to a unstable crack when a certain size is reached.

Fig. 6 shows a typical internal craze obtained on PC. The internal craze is observed as a series of concentric interference fringes as shown in Fig. 7 when viewed in the direction indicated by an arrow A. Fig. 8 shows the scanning electron microphotograph of the fracture surface perpendicular to the internal craze broken at 77K. The void content of the internal craze is

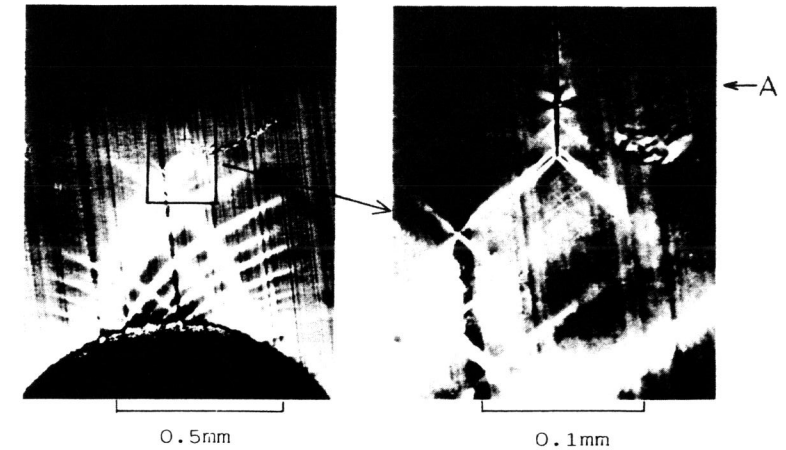


Fig. 6. Microphotographs of the plastic zone and internal craze nucleated at the tip of the plastic zone (PC).

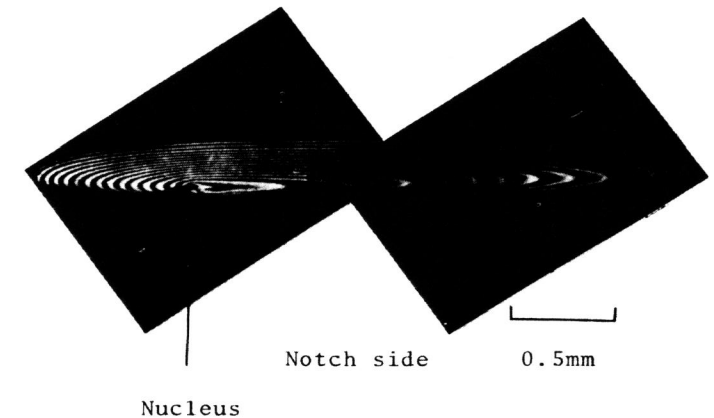


Fig. 7. Fringe pattern of the internal crack.

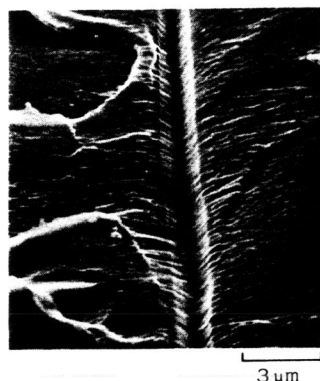


Fig. 8. Scanning electron microphotograph of fracture surface perpendicular to the craze broken at 77K (PC).

calculated to be 40-60% from the critical angle for total reflection on the polymer/craze interface using Lorentz-Lorenz equation (Kambour, 1964). Therefore, the structure of the internal craze is in quite agreement with that of a craze which is nucleated at the crack tip in an elastic stress field.

The process involved in the fracture mentioned above is reflected in the general appearance of the fracture surfaces. As a typical example, optical and scanning electron microphotographs of the fracture surface of PC are shown in Fig. 9. A smooth region around the nucleus corresponds to the semicircular shape in an oblique view. Outside the smooth region the crack is supposed to be unstable and to lead to final fracture of the material.

FACTORS AFFECTING FRACTURE PROCESSES

As shown in the preceding section, shear yielding and crazing, which is often termed as dilatational yielding, are two possible essential types of deformation which determines the fracture process of glassy polymers. The factors affecting critical stresses for shear and dilatational yielding are considered in relation to the problem of ductile-to-brittle fracture transition.

Temperature and Strain Rate

The temperature and strain rate dependence of critical stresses for shear yielding and internal crazing for PMMA, PVC and PS are shown in Figs. 10, 11 and 12 respectively. When both the shear and craze stresses are extrapolated to lower temperatures, they intersect each other at the temperature at which fracture occurs without shear yielding at the notch root, i.e. $R/\rho = 0$ as expected by eq. (4). Such temperatures are estimated to be 293K for PMMA at a bending rate of 100mm/min, 245K for PVC(100mm/min), and 313K for PS(0.1mm/min). It is interesting that these temperatures are nearly equal to

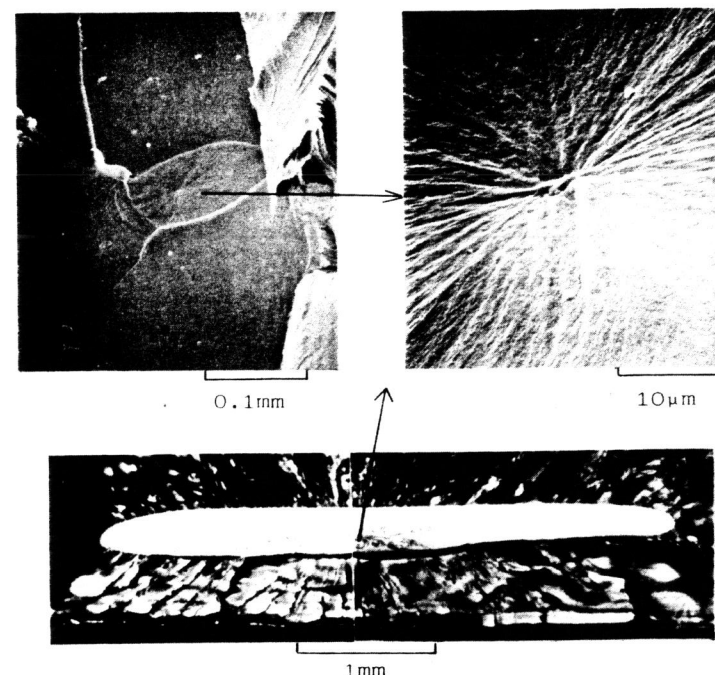


Fig. 9. Optical and scanning electron microphotographs of the fracture surface (PC).

the temperature for β -loss peak of each glassy polymer. In PC, however, the intersected temperature is not observed because the temperature dependence of a critical stress for crazing is nearly equal to that of shear yielding as shown in Fig. 13. In other words, PC requires shear yielding for fracture from an internal craze over a wide range of temperature. This is in agreement with the fact that PC is generally known as one of the most tough polymers in engineering use at low temperatures. As clearly seen from Figs. 10, 11 and 12, the ductile-to-brittle transition temperature at which fracture occurs at the material surface without shear yielding increases with increasing strain rate.

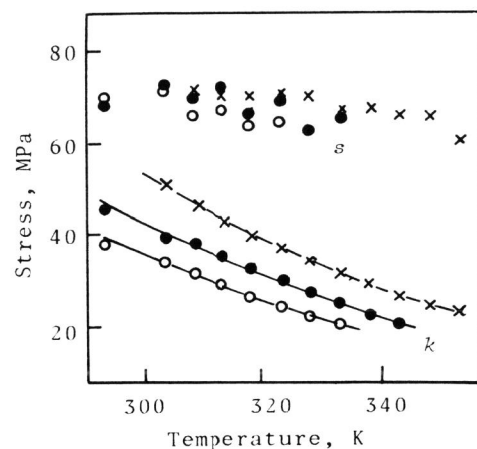


Fig. 10. Variation of the critical hydrostatic stress s for craze nucleation and shear yield stress k in PMMA with temperature at different bending rates: (○) 1mm/min, (●) 10mm/min, (X) 100mm/min.

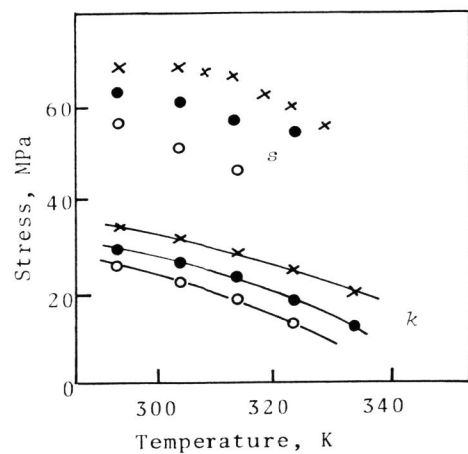


Fig. 11. Variation of the critical hydrostatic stress s for craze nucleation and shear yield stress k in PVC with temperature at different bending rates: (○) 1mm/min, (●) 10mm/min, (X) 100mm/min.

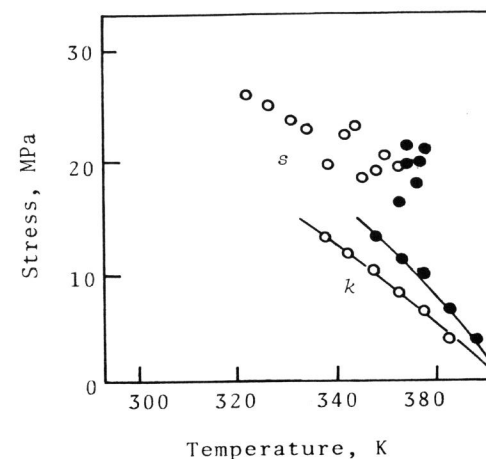


Fig. 12. Variation of the critical hydrostatic stress s for craze nucleation and shear yield stress k in PS with temperature at different bending rates: (○) 0.1mm/min, (●) 0.5mm/min.

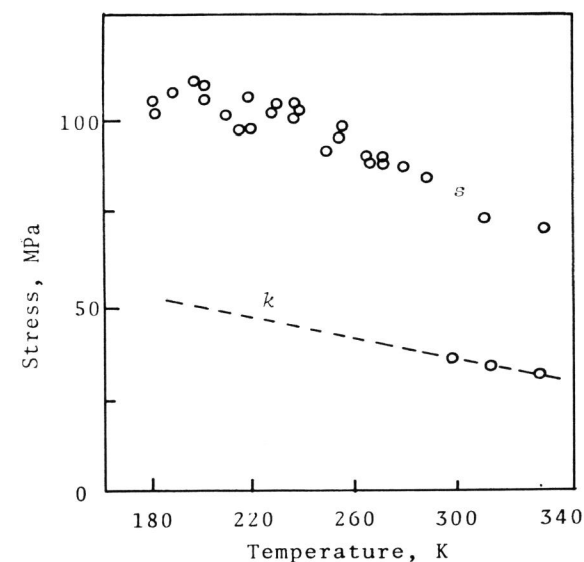


Fig. 13. Variation of the critical hydrostatic stress s for craze nucleation and shear yield stress k in PC with temperature at a bending rate of 10mm/min.

Thermal History

It is the general observation that heat-treatment of glassy amorphous polymers just below their glass transition temperature leads to a significant fall in toughness as shown in Figs. 14 and 15 in which variations of fracture energy of PMMA and PC subjected to three-point-bending with annealing time are shown.

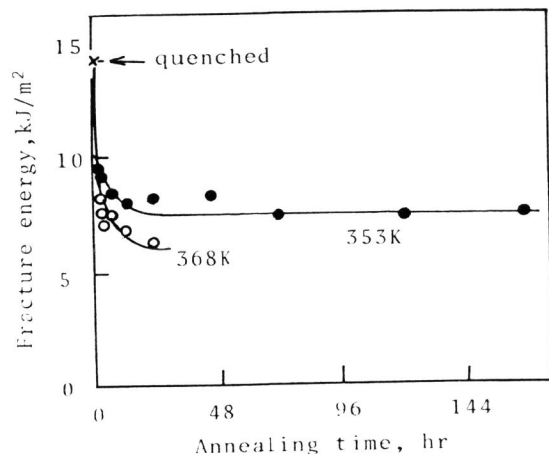


Fig. 14. Fracture energy as a function of annealing time at different temperatures obtained on PMMA.

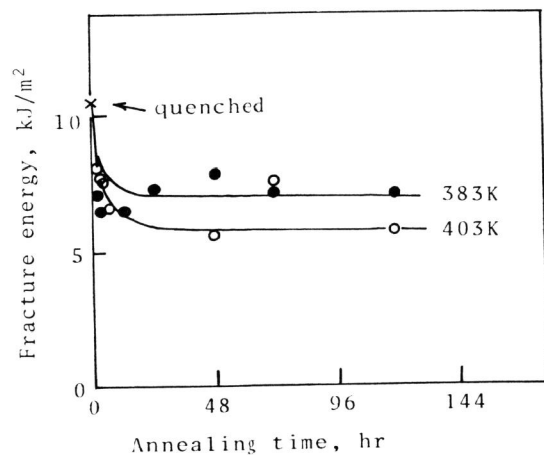


Fig. 15. Fracture energy as a function of annealing time at different temperatures obtained on PC.

There have been several published works which would explain the toughness reduction by annealing based on different mechanisms. Some investigators (Petrie, 1974; Boyer, 1976; Sacher, 1975) have suggested that the submolecular motion which relates to the relaxation process is reduced by annealing, others (Adam, 1975) have suggested that the strain softening effect which is caused by annealing is responsible for embrittlement of the glassy polymers. Thus, there has been no established explanation for the toughness reduction due to annealing.

As shown in Figs. 16 and 17, the maximum extent of the plastic deformation at

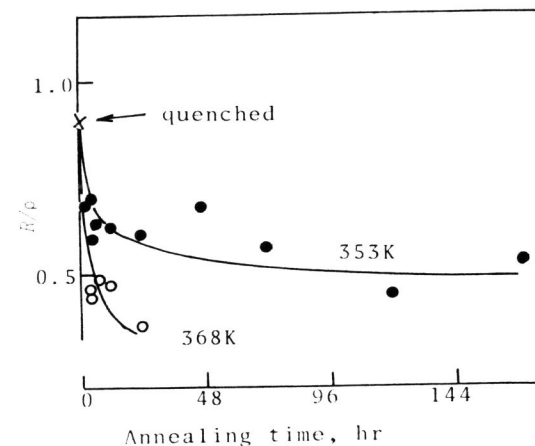


Fig. 16. Variation of the maximum extent of the plastic zone required for internal craze nucleation with annealing time at different temperatures (PMMA).

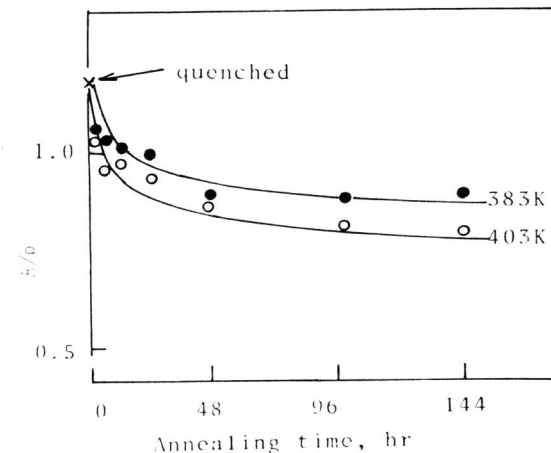


Fig. 17. Variation of the maximum extent of the plastic zone required for internal craze nucleation with annealing time at different temperatures (PMMA).

the notch root decreases with increasing annealing time and, as a result, energy absorption due to plastic deformation decreases by annealing. Figs. 18 and 19 show the variation of the critical stresses for shear yielding and crazing with annealing time. It is suggested from these results that the toughness reduction in glassy polymers by annealing can be interpreted in term of a variation of shear yield stress with annealing and less sensitiveness of the craze stress to heat-treatment.

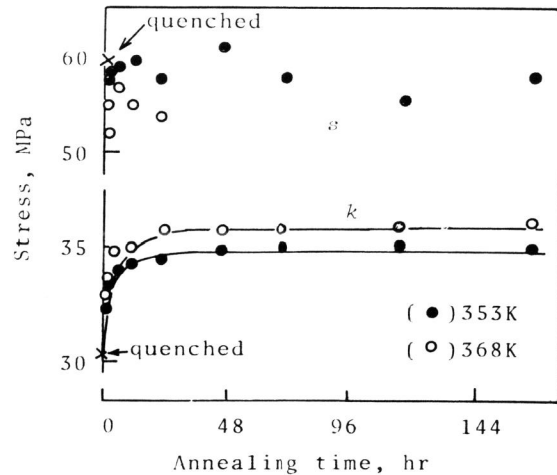


Fig. 18. Variation of the critical hydrostatic stress s for craze nucleation and shear yield stress k with annealing time (PMMA).

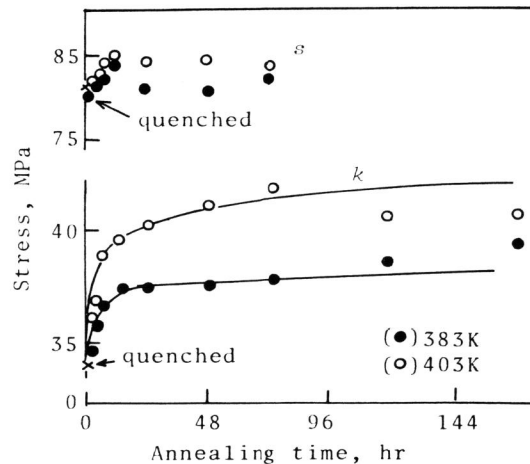


Fig. 19. Variation of the critical hydrostatic stress s for craze nucleation and shear yield stress k with annealing time (PC).

Hydrostatic Pressure

It is well known that glassy polymers, which normally fracture in a brittle manner, can be made to undergo shear yielding by application of hydrostatic pressure as shown in Fig. 20 in which the three-point-bending curves for PC are shown as a function of applied hydrostatic pressure (Matsushige, 1975, 1976). Fig. 21 shows the polarized microphotograph of PC deformed at a pressure at which ductile fracture occurs. General yield through the whole thickness occurs without nucleation of an internal craze. Fig. 22 shows the variation of stress distributions with increasing applied pressure. The size of the plastic deformation necessary for craze formation increases with increasing applied pressure because the dilatational stress is suppressed by application of hydrostatic pressures. As a result, the toughness of PC can be remarkably enhanced and the brittle-to-ductile transition occurs when general yielding takes place through the whole specimen.

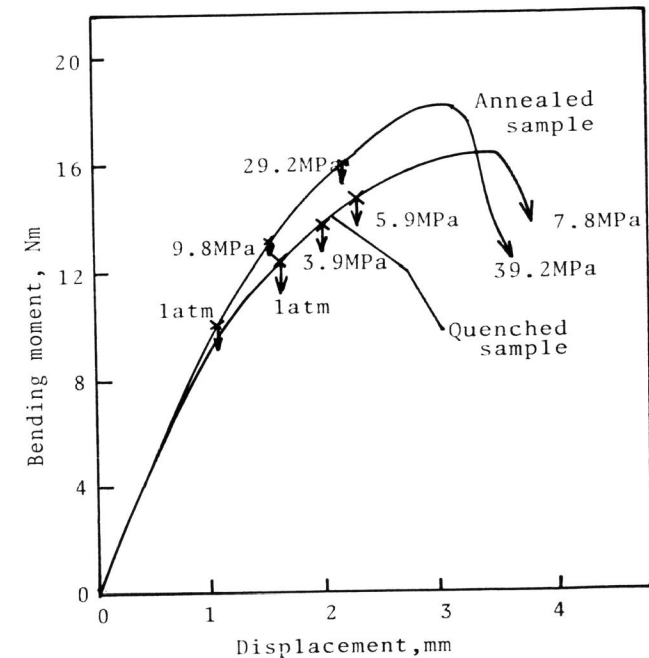


Fig. 20. Bending moment-displacement curves of quenched and annealed PC as a function of applied stress.



Fig. 21. A typical microphotograph of PC deformed at an applied pressure of 12.3 MPa.

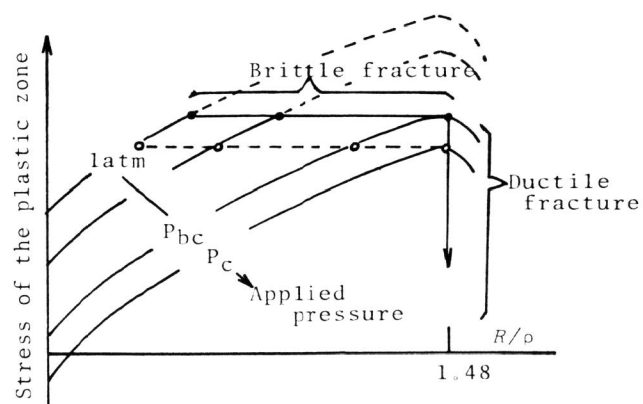


Fig. 22. Variation of the stress distribution in the plastic zone with applied pressure: P_{bc} , brittle to ductile transition pressure. P_c , pressure at which nucleation of craze is suppressed.

Crystalline Structures

With respect to crystalline polymers such as polyethylene (PE), polypropylene (PP) and polyamide (PA) in which inhomogeneous microstructure is well defined, crazing is not so much common as in glassy amorphous polymers. Fig. 23 shows a typical of the deformation zone formed at the notch root of PA-6 plate. The plastic deformation zone is composed of the fine deformation bands which nucleate at the position leaving the notch root (Ishikawa, 1982). The initiation of a crack which leads to final fracture occurs within one of the fine deformation bands as indicated by an arrow. As shown in Fig. 24 the fine deformation bands in which many voids are present pass mainly through the center of the spherulites, but their microstructure is not clear at present. Consequently, it is difficult to apply the slip line

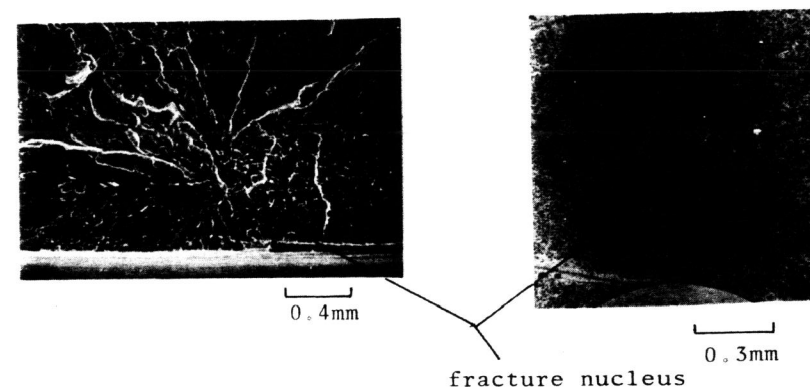


Fig. 23. Plastic deformation formed at the tip of the notch of PA-6 and scanning electron microphotograph of fracture surface.

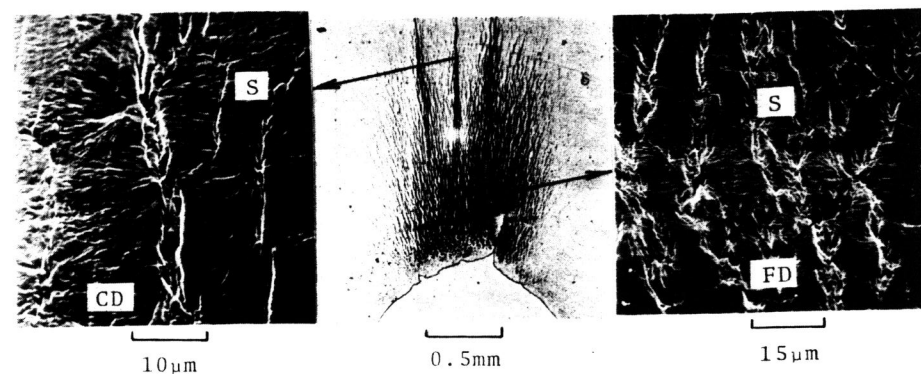


Fig. 24. Scanning electron microphotograph of the deformation bands of PA-6. CD: Concentrated deformation band, FD: fine deformation bands, S: spherulite.

field theory to calculate a critical stress for internal crazing in case of such inhomogenous crystalline polymers because the brittle crack is initiated within the deformation bands. However, the results that the distance of the fracture nucleus increases with increasing temperature as shown in Fig. 25 can be qualitatively explained by the same mechanism established for glassy amorphous polymers.

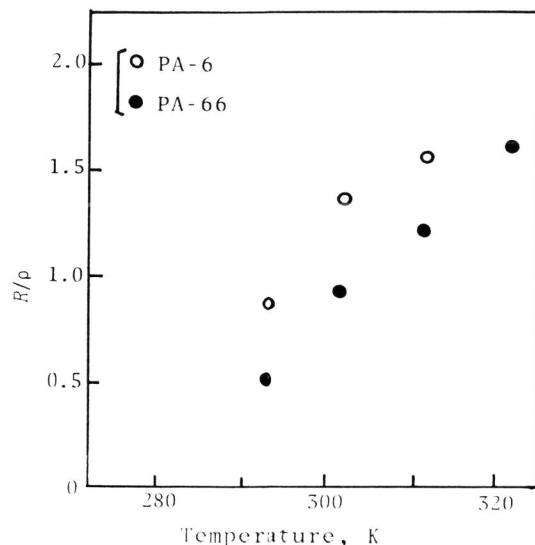


Fig. 25. Variation of the distance of the fracture nucleus from the notch of the PA-6 and PA-66 specimens.

EVALUATION OF FRACTURE TOUGHNESS RELATING TO FRACTURE MECHANISM

Equations (4) and (5) indicate that the dilatational stress at the tip of the plastic zone does not exceed the maximum value given by

$$s = k(1 + \pi - \omega) \quad (6)$$

While the critical stresses for shear yielding and internal crazing are true material properties which are determined independently of tests conditions except temperature and strain rate. Therefore, three types of fracture behavior distinguished in the glass polymers depending on the value of s/k as schematically shown in Fig. 26:

- (a) Ductile fracture with general yield at $s/k \geq 1 + \pi - \omega$
- (b) Quasibrittle fracture with local plastic deformation at $1 < s/k < 1 + \pi - \omega$
- (c) Brittle fracture at specimen surface without shear yield at $1 \leq s/k$.

The plane strain fracture toughness parameters obtained by applying linear fracture mechanics to a fracture type of (b) are expected to increase with increasing value of s/k . Further, it can be seen that the three types of fracture also occur in the case of sharp or line cracks depending on the value of s/k , but in quasibrittle fracture the critical value of s/k can be obtained by a plastic zone of small size because the radius of the crack tip is comparable to the plastic zone length. Therefore, fracture energy decreases with increasing crack sharpness and this is quite in agreement with the general observations. On the contrary, for a plain specimen with no notch or crack, the fracture mode is essentially brittle or ductile depending on the value of s/k .

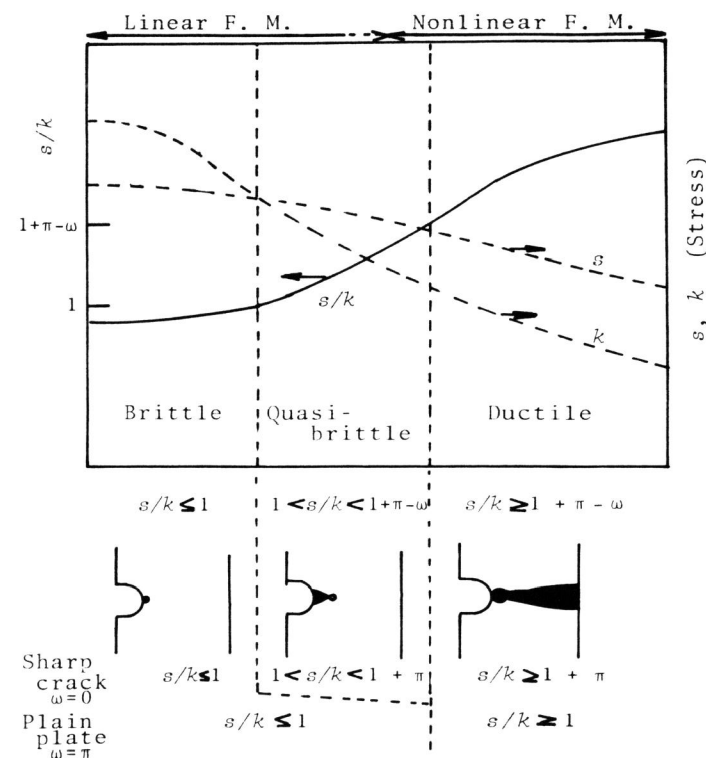


Fig. 26. Schematic illustration of fracture mode depending on the value of s/k .

In the present investigation, multiphase polymers such as rubber-toughened ABS, HIPS and copolymers of PP are excluded because much more inhomogeneity is expected in these polymers than in crystalline polymers. Some experimental results have shown that crazing and/or shear yielding play an important role for their toughness enhancement. Evaluation of s/k for these rubber-toughened polymers will be obtained by application of hydrostatic pressure and by specifying a critical pressure for suppression of so called stress-whitening deformation.

In conclusion, it is suggested that s/k is the most essential material constant which determines the toughness of polymer solids as well as their fracture mode.

REFERENCES

- Adam, A., A. Cross, and R. N. Haward (1975). J. Mater. Sci., **10**, 1582-1590.
- Argon, A. S. (1974). In P. H. Geil, E. Baer, Y. Wada (Eds.) The Solid State of Polymers, Marcel Dekker, New York. pp.573-603.
- Argon, A. S., and J. G. Hannoosh (1977). Phil. Mag., **36**, 1195-1216.
- Berry, J. P. (1961). J. Polym. Sci., **50**, 107-115.
- Boyer, R. F. (1976). Polymer, **17**, 996-1008.
- Brown, H. R., and I. M. WARD (1973). Polymer, **14**, 469-475.
- Frazer, R. A. W., and I. M. WARD (1978). Polymer, **19**, 220-224.
- Gent, A. N. (1973). J. Macromol. Sci., **B8**, 597-603.
- Hill, R. (1950). The Mathematical Theory of Plasticity, Oxford Univ. Press, London.
- Ishikawa, M., I. Narisawa, and H. Ogawa (1976). Polym. J., **8**, 391-400.
- Ishikawa, M., I. Narisawa, and H. Ogawa (1977). J. Polym. Sci. Phys. ed., **15**, 1791-1804.
- Ishikawa, M., H. Ogawa, and I. Narisawa (1981). J. Macromol. Sci., **B19**, 421-443.
- Ishikawa, M., and I. Narisawa (1982). Proc. 20th Jap. Mater. Res., The Soc. Mater. Sci. Kyoto. pp.282-286.
- Kambour, R. P. (1964). Polymer, **5**, 143-155.
- Kambour, R. P. (1966). J. Polym. Sci., A-2, **4**, 349-358.
- Kambour, R. P., A. S. Holik, and S. Miller (1978). J. Polym. Sci. Phys. ed., **16**, 91-104.
- Matsushige, K., E. Baer, and S. V. Radcliffe (1975). J. Macromol. Sci., **B11**, 565-592.
- Matsushige, K., E. Baer, and S. V. Radcliffe (1976). J. Polym. Sci. Phys. ed., **14**, 703-721.
- Morgan, G. P., and I. M. WARD (1973). Polymer, **18**, 87-91.
- Narisawa, I. M., Ishikawa, and H. Ogawa (1979). J. Mater. Sci., **15**, 2059-2065.
- Narisawa, I. M., Ishikawa, and H. Ogawa (1980). Phil. Mag., **41**, 331-351.
- Oxborough, R. J., and P. B. Bowden (1974). Phil. Mag., **30**, 171-184.
- Parvin, M., and J. G. Williams (1975). Int. J. Fract., **11**, 963-972.
- Parvin, M. (1981). J. Mater. Sci., **16**, 1796-1800.
- Petrie, S. E. B. (1974). Polymeric Materials-Relationships Between Structure and Mechanical Behavior, ASM, Ohio. pp.55-118.
- Rice, J. R. (1968). J. Appl. Mech., **35**, 379-386.
- Sacher, E. (1975). J. Appl. Polym. Sci., **19**, 1421-1425.
- Sternstein, S. S., L. Ongchin, and A. Silverman, (1968). Appl. Polym. Symp., **7**, 175-199.
- Weidmann, G. W., and W. DOLL (1978). Int. J. Fract., **14**, R189-R193.
- Williams, J. G. (1978). Advances in Polymer Science **27**, Failure in Polymers, Springer-Verlag, New York. pp.67-120.
- Williams, J. G., and J. M. Hodgkinson (1981). J. Mater. Sci., **16**, 50-56.