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Fracture of notched polycarbonate under hydrostatic pressure

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The brittle fracture behaviour and plastic deformation of round-notched polycarbonate bars subjected to three-point bending under hydrostatic pressure have been studied. Below a certain critical pressure, the brittle fracture initiated from an internal craze nucleated at the tip of the local plastic zone ahead of the notch root. The position of the nucleation of the craze receded from the tip of the notch with increasing applied pressure. When the pressure was increased over a critical value, general yielding occurred by passage of the plastic zone across the notched cross-section, that is, the brittle to ductile transition took place. A qualitative analysis of the stress distribution within the plastic zone explains that the brittle to ductile transition under hydrostatic pressure occurs when the general yield takes place before a critical stress for brittle crack propagation is reached.

1. Introduction

Mechanical behaviour of glassy polymers is strongly influenced by hydrostatic pressure. A pronounced change in the fracture mode is that the material, which normally fractures in a brittle manner, can be made to undergo yielding by the application of hydrostatic pressure. Such examples have been reported for various polymers, i.e. polystyrene (PS) [1–3], poly(methyl methacrylate) (PMMA) [4, 5], polyimide (PI) [6] and polysulphone (PSF) [7]. Avoiding the environmental effect of the pressure transmitted fluid, Matsushige *et al.* [2, 5] have shown that the brittle to ductile transition of PMMA and PS occurs at hydrostatic pressures of 0.25 kbar for PMMA and 0.35 kbar for PS, respectively. They have conclusively suggested that the stresses for craze and shear band initiation have different pressure dependent curves, and the brittle to ductile transition occurs when a material undergoes shear deformation before a critical stress for the initiation of a craze is reached. While in a recent study of Trent *et al.* [8] for PS and high-impact polystyrene (HIPS), it was suggested that the principal stress required to initiate the craze shows almost no pressure dependency.

The mechanism for the nucleation of a craze at atmospheric pressure has been extensively investigated on the basis of the recognition that crazing is the direct precursor of brittle fracture in glassy polymers. Generally, the crazes chosen as the subject of these studies are surface ones which are initiated from the surface inhomogeneities at well below the uniaxial yield stress. In previous papers [9, 10], it has been shown that if several glassy polymers contain a deep notch and the plane strain state is maintained at the notch root during loading, they fracture in a brittle manner due to the nucleation of internal crazes. The internal crazes can be nucleated ahead of the plastic deformation zone which is initiated at the notch root, and the void contents are about 40 to 50% and nearly equal to those obtained on surface crazes. More recently, we [11] have shown that the brittle fracture processes of PMMA, PS, and PVC above the β transition temperature are quite similar to those of polycarbonate (PC). Namely, notch brittleness in ductile glassy polymers can be explained by the mechanism originally proposed by Orowan [12] for metals; if ductile materials contain a deep notch, the tensile stress required to produce a given amount of shear stress ahead of the local plastic zone is increased by intro-

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ducing a state of triaxial tension, and therefore, if the tensile stress ahead of the local plastic zone reaches the stress required to initiate the internal craze before the development of general yield across the notch section, brittle fracture occurs, following the nucleation of an internal craze.

If the nucleation of an internal craze occurs when a certain critical dilatational stress is reached, it can be expected that the nucleation of an internal craze is suppressed by the hydrostatic pressure, and as a result the material can be plastically deformed above a certain critical hydrostatic pressure.

The purpose of this paper is to examine the effects of the hydrostatic pressure on the nucleation of the internal craze ahead of the plastic zone at the base of a round notch, and to discuss the mechanism of notch brittleness in glassy polymers.

2. Experimental details

The experiments were performed on PC supplied by Teijin Co. Ltd., in the form of pellets. The average molecular weight was 30 000. The pellets were first dried under vacuum at a temperature of 393 K for 48 h, then the sheets of 10 mm thickness were compression moulded at a temperature of 553 K and a pressure of 20 MPa. After cutting into a rectangular shaped specimen, a rounded notch of 0.5 mm radius was shaped in one side of the specimen by machining with a convex milling cutter. In order to avoid the development of a layer of oriented polymer on the surface of the notch tip by an increase of temperature, the specimens were cooled with water during machining. Fig. 1 shows the shape and dimensions of the test samples. The dimensions were chosen so that they fully maintain the plane strain condition under loading. The quenched samples were obtained by ice-quenching after heating at 433 K for 24 h, and the annealed samples were obtained by heating the quenched samples at 408 K for 48 h.

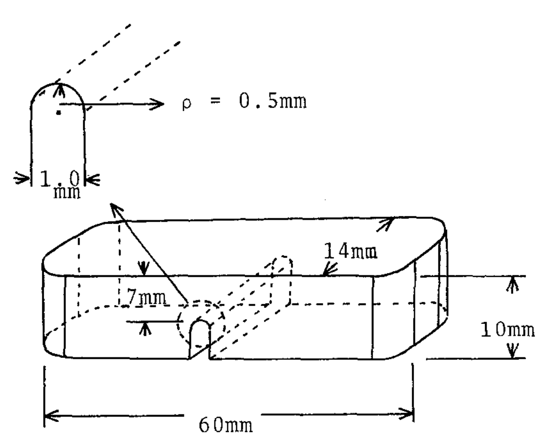

Figure 1 Shape and dimensions of test samples.

The apparatus used for three-point bending tests under hydrostatic pressure is shown in Fig. 2. The hydrostatic pressure was applied to the specimen by a hand plunger pump and controlled by a balancing weight. The maximum hydrostatic pressure in this apparatus was 68 MPa. Silicon oil (Shinetsu Chemical Co. Ltd., KF54. 500 cs) was used as the pressure-transmitting fluid. The three-point bending tests in the pressure chamber were performed by driving the rod into an Instron-type testing machine (Auto Graph. Shimazu DSS-5000). The tests were carried out at a bending rate of 1 mm min^{-1} at a temperature of 296 K. The span length was 40 mm. Since the preliminary experiments showed that the silicon oil used here had no environmental effects on PC, the test samples were not sealed from the pressure-transmitting fluid.

Microscopic observations were made on the specimen unloaded during deformation. Thin sections were cut normal to the plane of notch for examination in the microscope. The fractured specimens were washed in an ultrasonic bath several times before observing the fracture surface.

3. Results

Although PC is known to be a typical ductile polymer under conditions where the plane stress state prevails [13], it can be demonstrated also that under conditions where dimensions of the samples are sufficient to maintain the plane strain state they fracture in a relatively brittle manner. Notches in the thick samples enhance such an embrittlement due to the limited plastic deformation around the notch and to the triaxial stress concentrations in the centre of the materials [9, 10, 14, 15].

Application of hydrostatic pressure will suppress the triaxial stress components within the material and, as a result, the fracture mode of the notched samples can be changed from brittle to ductile again, as will be observed on the bending moment–displacement curves obtained with increasing hydrostatic pressure.

The bending moment–displacement curves for quenched and annealed samples are shown in Fig. 3 as a function of applied hydrostatic pressure. At a region of low applied pressure, the fracture

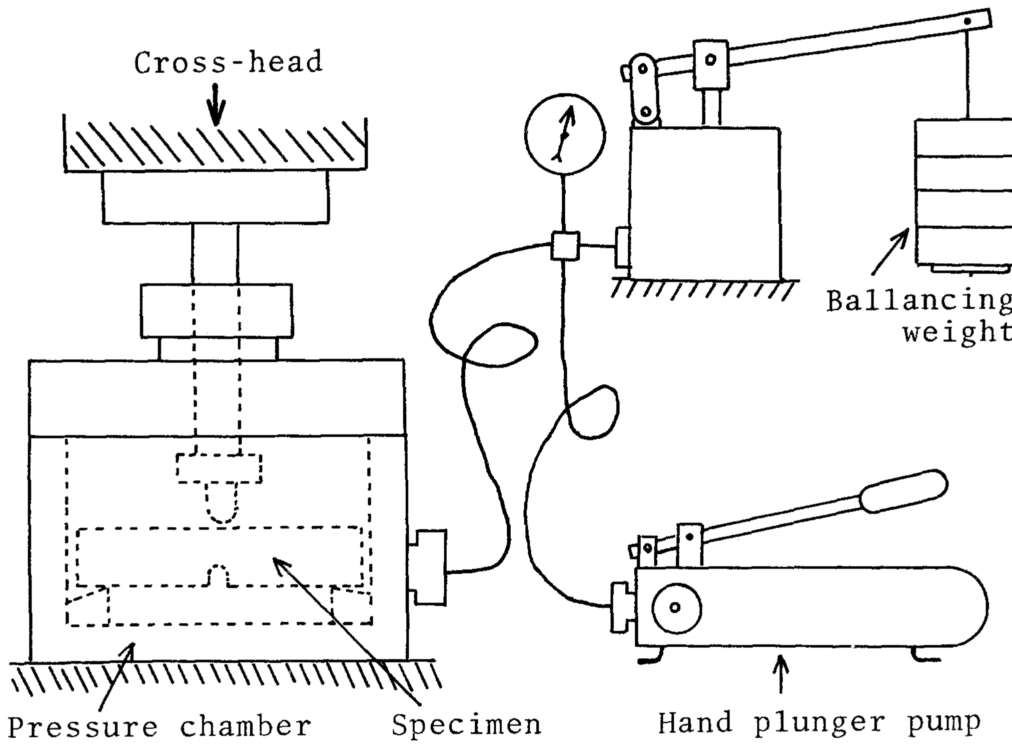

Figure 2 Schematic diagram of the apparatus used in the three-point bending test under hydrostatic pressure.

mode was brittle fracture as seen in the bending moment–displacement curves. In this region, the maximum bending moment (or fracture bending moment) and the displacement at fracture were rapidly increased with increasing applied pressure. As the applied pressure was further increased over a critical applied pressure, the fracture mode varied from brittle to ductile fracture. Above a critical applied pressure, the bending moments for both samples fell gradually with increasing displacement, after the maximum bending moment was reached.

The maximum bending moment in the bending moment–displacement curves for both quenched and annealed samples are shown in Fig. 4 as a function of the applied pressure. The pressure dependence of the maximum bending moment in the region of brittle fracture evidently differs from that in the region of ductile fracture. Therefore, the pressure at which the two curves intersect defines the brittle to ductile transition pressure. The brittle to ductile transition pressures of quenched and annealed samples were about 7.8 MPa for quenched samples and about 34.3 MPa for annealed samples, respectively. The maximum bending moment at brittle to ductile transition pressure was 1.5 times that at atmospheric pressure for quenched samples, and 2.0 times for the annealed samples.

Matsushige *et al.* [2, 5] showed in uniaxial tensile tests under the hydrostatic pressure for PS and PMMA sealed from the pressure-transmitted fluid that the craze and shear band initiation stresses have different pressure-dependent curves which intersect at the brittle to ductile transition pressure. The pressure-dependence of the maximum bending moment obtained here is similar to their results.

The polarized microphotographs of the sections which are obtained on a quenched sample deformed at an applied pressure of 5.9 MPa and on an annealed sample deformed at 24.5 MPa are compared with those deformed at atmospheric pressure as shown in Fig. 5. These applied pressures are slightly lower than brittle to ductile transition pressures. The internal craze nucleated at the elastic–plastic boundary can be clearly observed in these microphotographs. The general characteristics of the brittle fracture under hydrostatic pressure associated with the microphotographs are similar to those fractured under atmospheric pressure except that the distance from the notch tip to the position of craze nucleation is increased with increasing applied pressure. Fig. 6 shows

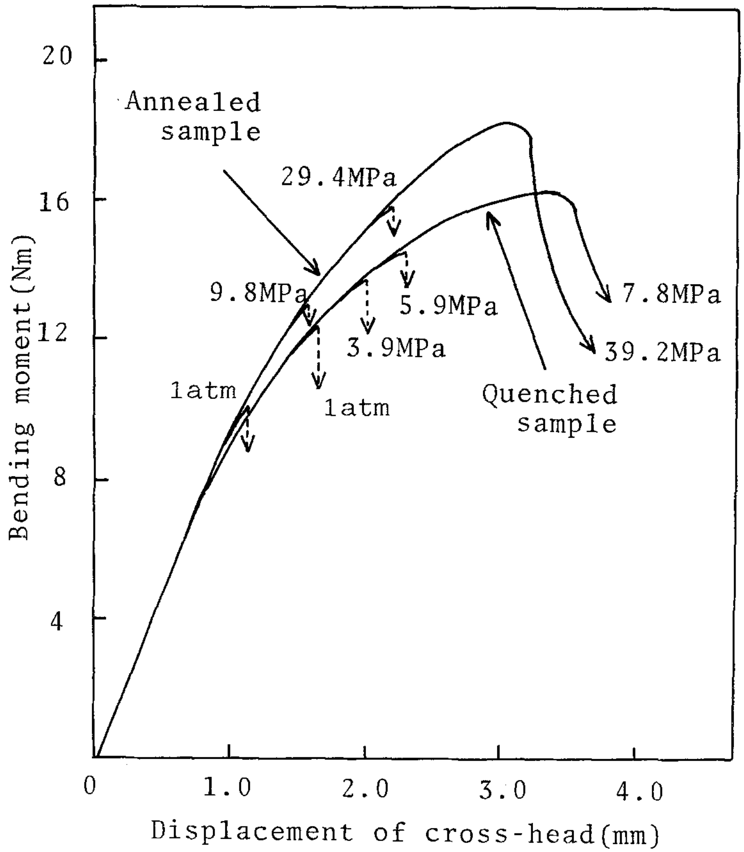

Figure 3 Bending moment–displacement curves of quenched and annealed samples as a function of applied hydrostatic pressure.

polarized microphotographs of sections which are obtained on quenched and annealed samples, deformed under applied pressures of 9.8 MPa for the quenched sample and 39.2 MPa for the annealed sample, respectively, and unloaded immediately after the maximum bending moments in each case were reached. These applied pressures are slightly higher than the brittle to ductile

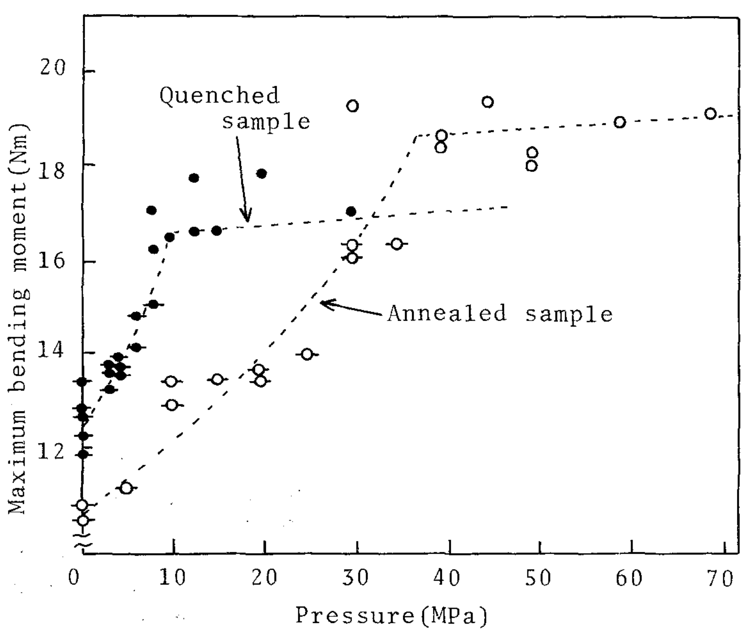

Figure 4 Pressure dependence of fracture bending moment (–○– –●–) and general yield moment (○ ●) in quenched and annealed samples.

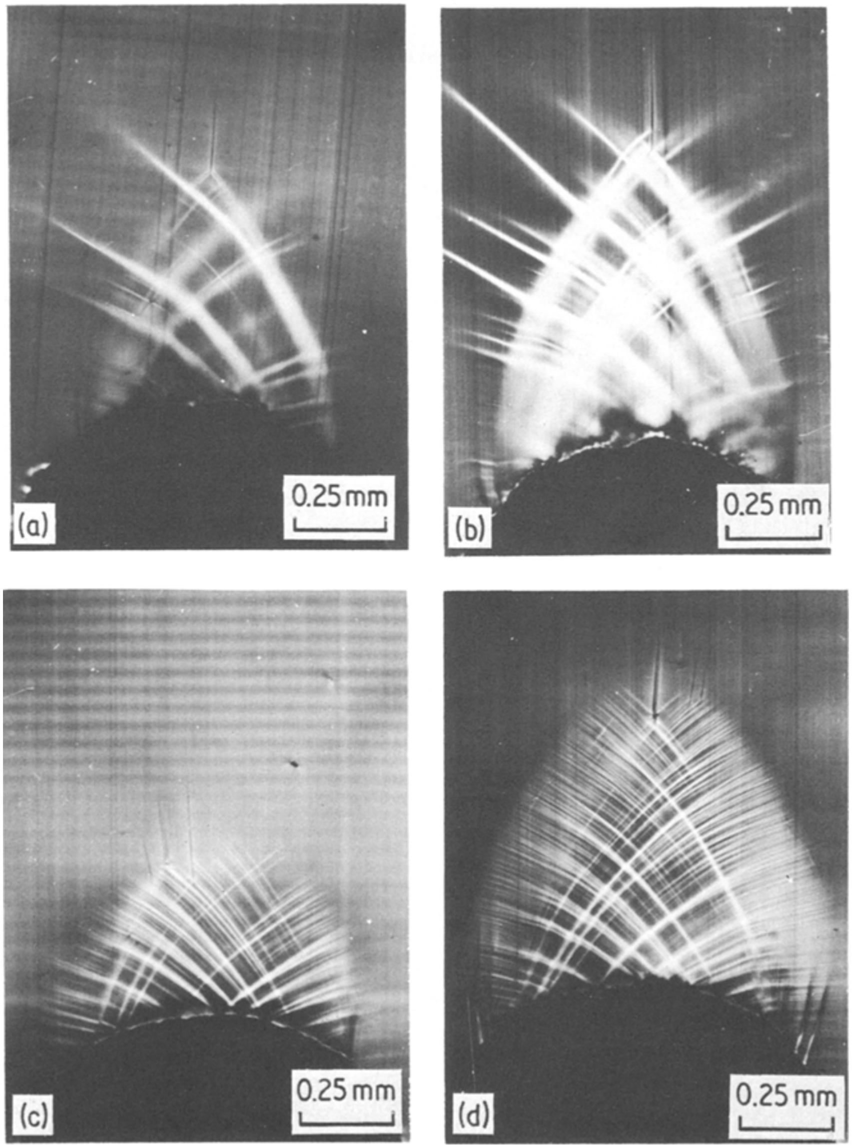

Figure 5 Variation of the plastic zone with the application of hydrostatic pressure for (a) and (b) quenched PC at 1 atm and 5.9 MPa, respectively, and (c) and (d) annealed PC at 1 atm and 24.5 MPa, respectively.

transition pressure for each sample. The deformation bands spread across the notched cross-section to leave an elastic enclave located on the symmetry axis. It is evident that the samples were deformed plastically. The enlarged microphotographs of each sample in Fig. 6 show that the internal craze is initiated ahead of the local plastic zone directly below the notch root. Although the brittle to ductile transition pressures were about 7.8 MPa for quenched samples and 34.3 MPa for annealed samples, the nucleation of internal crazes for both samples were still observed at pressures of 9.8 MPa for quenched samples and 44.1 MPa for annealed samples. However, these internal crazes did not lead to brittle fracture. Fig. 7 shows the polarized microphotographs of sections which were obtained on a quenched sample deformed at an applied pressure of 12.3 MPa and on an annealed sample deformed at 44.1 MPa. These pressures are higher than the critical applied pressures required to prevent the nucleation of internal crazes in each sample. Evidently, under these applied pressures, each sample was deformed plastically without the nucleation of internal crazes. It is found that, in the enlarged microphotographs of the sections, the ductile crack propagates through the local plastic

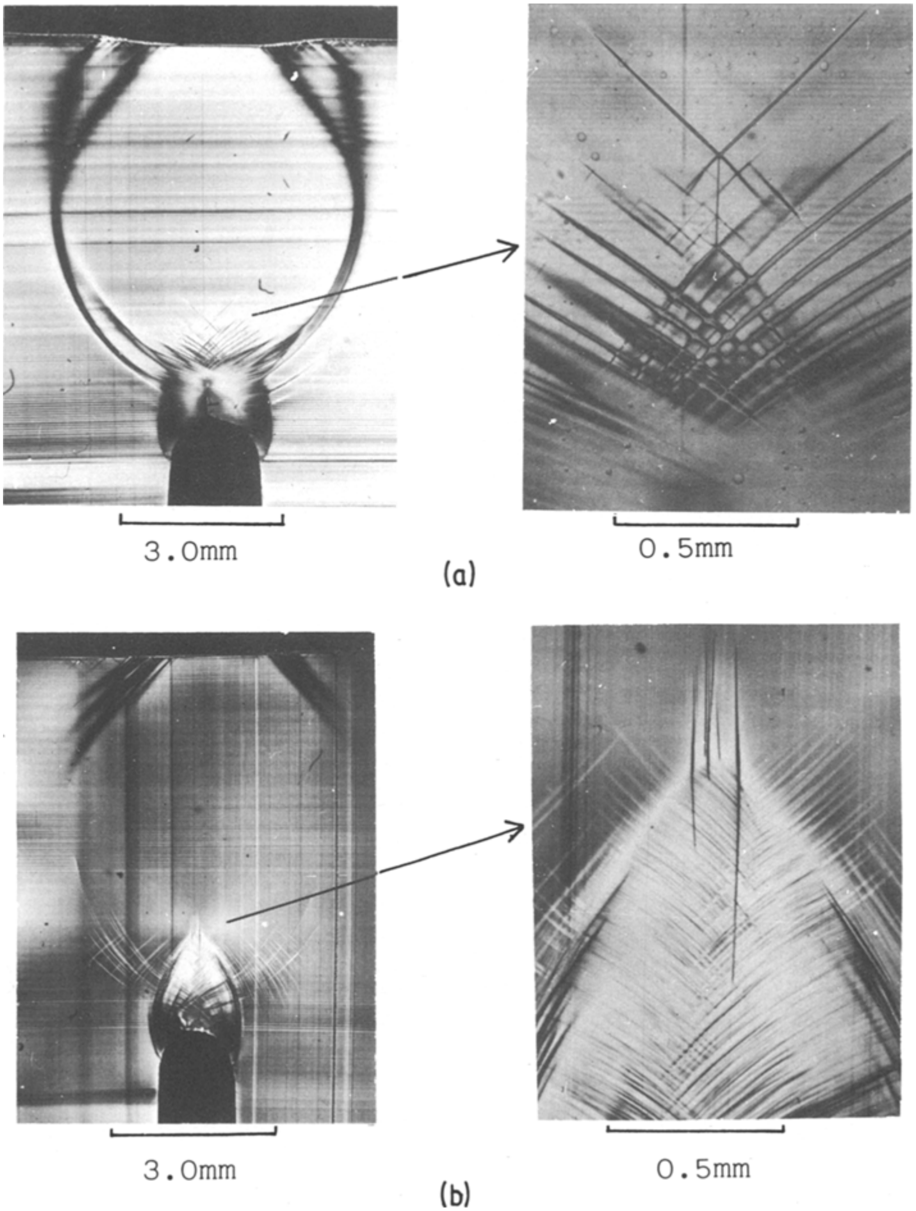

Figure 6 Polarized micrographs of sections obtained on quenched (a) and annealed (b) PC, which are deformed under applied pressure of 9.8 MPa for quenched sample and 39.2 MPa for annealed sample.

zone. The reduction of the bending moment beyond the general yield point was caused by the propagation of this ductile crack.

Fig. 8 shows the fracture surfaces at a pressure of 5.9 MPa for a quenched sample and 24.5 MPa for an annealed sample. In our previous paper [10], it was pointed out that the maximum extent of the plastic zone can be measured from the fracture nucleus on the fracture surfaces. Fig. 9 shows the ratio (x/ρ) of the maximum extent of the plastic zone (x) to the radius (ρ) of the notch root as a function of the applied pressure. The ratios for both quenched and annealed samples increase with increasing applied pressure. On the other hand, under applied pressures higher than brittle to ductile transition pressure, it is found that the size of the local plastic zone remains nearly constant, regardless of the applied pressure as can be seen from Figs. 6 and 7.

4. Discussion

When the round notched PC bar is deformed by an

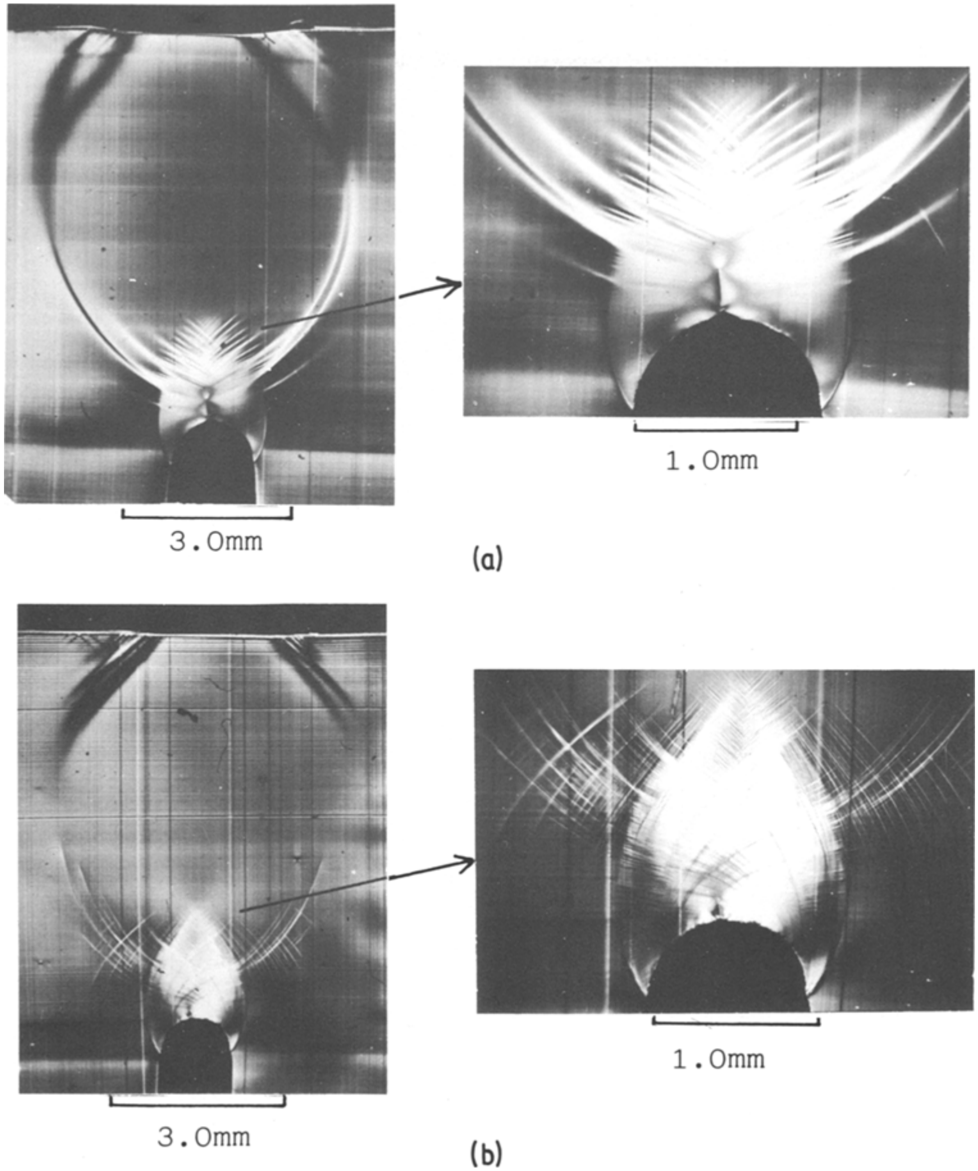

Figure 7 Polarized micrographs of sections obtained on quenched (a) and annealed (b) PC, which are deformed under applied pressure of 12.3 MPa for quenched sample and 44.1 MPa for annealed sample.

applied bending moment, the local plastic zone is initially formed at the tip of the notch prior to brittle fracture. If it is assumed that PC is a rigid–plastic body, the stress distribution in the local plastic zone ahead of the notch tip is calculated from the slip-line field theory developed by R. Hill [16]. The slip-line for the local plastic zone ahead of the notch root in the plane strain state is shown in Fig. 10 together with the definition of stress components and coordinates. These slip-lines are expressed by logarithmic spirals. Therefore, the stress distribution within the local plastic zone is given by

$$\begin{aligned} \sigma_y &= \sigma_p + k \\ \sigma_y &= \sigma_p + k \end{aligned} \tag{1}$$

where k is the shear yield stress and σ_p is the mean stress ($\sigma_p = (\sigma_y + \sigma_x + \sigma_z)/3$). In the plane strain state, the mean stress is equal to σ_z, and is expressed by

$$\sigma_p = k\left[1 + 2\ln\left(1 + \frac{x}{\rho}\right)\right] \tag{2}$$

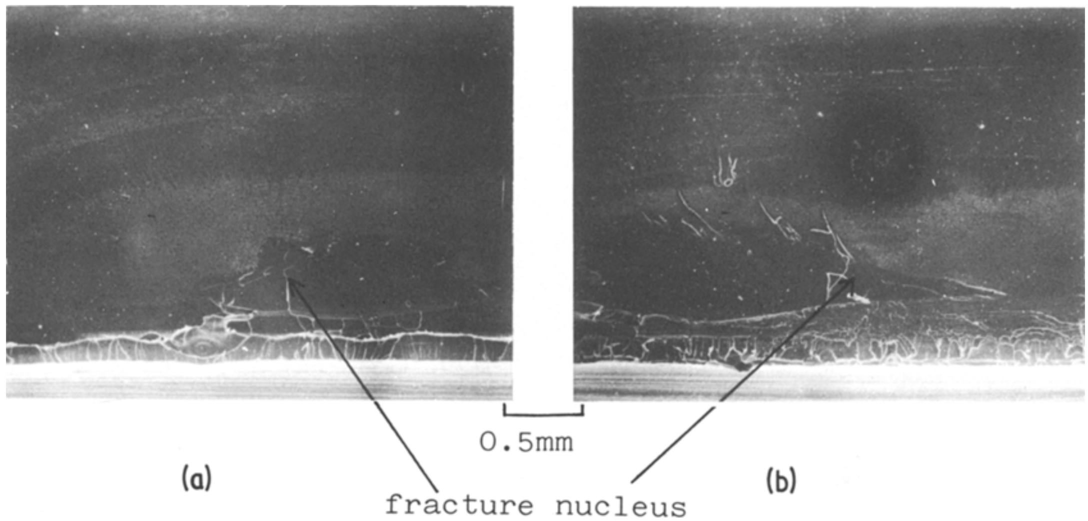

Figure 8 Fracture surfaces of quenched PC (a) deformed at pressure of 5.9 MPa and of annealed PC (b) deformed at pressure of 24.5 MPa.

where x is the maximum plastic zone length. The maximum triaxial stress occurs at the tip of the local plastic zone and its value increases as the local plastic zone spreads. At atmospheric pressure, the brittle fracture of the round-notched bar is initiated from the internal craze when the size of this plastic zone reached a certain critical size and the stress ahead of the local plastic zone reaches a certain critical value of the material.

On the other hand, at a region of applied pressure below the brittle to ductile transition pressure, the experimental results suggested that the size of the local plastic zone increased with increasing applied pressure, and the bending moment at brittle fracture also increased. In order to qualitatively understand the mechanism of the brittle fracture under hydrostatic pressure, we discuss the stress distribution within the local

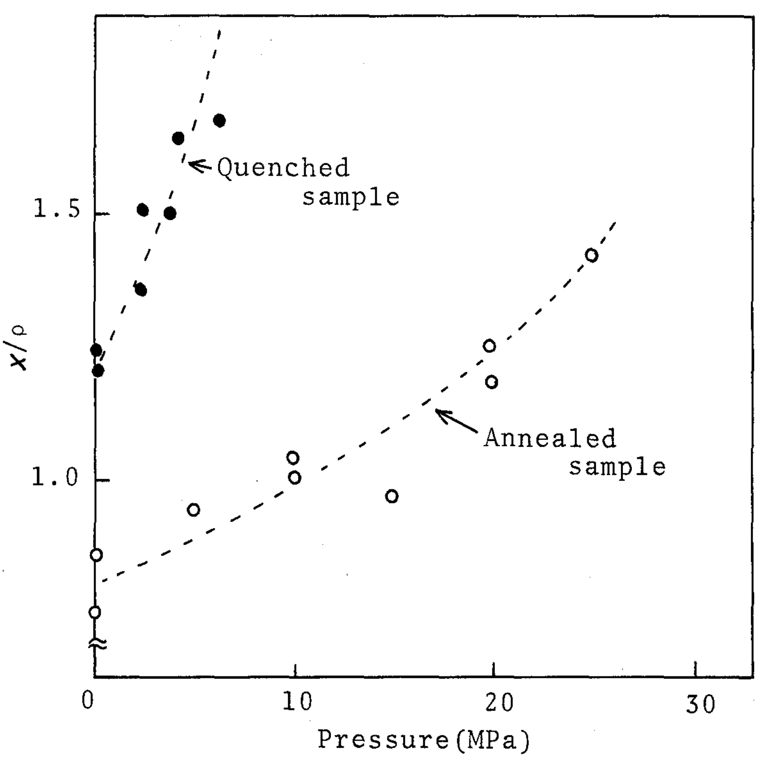

Figure 9 Pressure dependence of ratio (x/ρ) of the maximum extent of the plastic zone (x) to the notch radius (ρ).

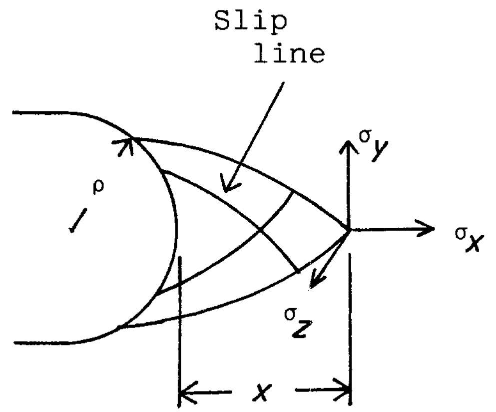

Figure 10 Definition of stress components.

plastic zone formed under hydrostatic pressure for the rigid–plastic body. Since the hydrostatic pressure does not affect the slip-line field, the slip-line of the local plastic zone formed under hydrostatic pressure is the same as that formed at atmospheric pressure. Therefore, the mean stress of the local plastic zone formed under hydrostatic pressure is given by

$$\sigma_p = k\left[1 + 2\ln\left(1 + \frac{x}{\rho}\right)\right] - P \qquad (3)$$

where P is the applied pressure. Fig. 11 shows the variation of the stress distribution in the local plastic zone with increasing applied pressure. It is shown that the size of the local plastic zone required to introduce a stress which is equal to the stress ahead of the local plastic zone formed under atmospheric pressure increased with increasing applied pressure. Therefore, if the critical stress required to nucleate the internal craze is independent of the applied pressure, the size of the local plastic zone required to nucleate the internal craze should increase with increasing applied pressure. Consequently, the expansion of the local plastic zone below the notch root due to an increase of applied pressure induces the increase of the maximum bending moment.

Fig. 12 shows the slip-line field at general yield for a round-notched bar subjected to three-point bending. The slip-lines are calculated on the assumption that the material is obeying Von Mises yield criterion. This solution is roughly in agreement with the shape of plastic zone for both samples shown in Fig. 6 and Fig. 7. The shape of the plastic zone at general yield is not influenced by the application of hydrostatic pressure since the solution of the slip-line field depends only on the geometry of the sample, such as notch radius, notch depth, and span length. Therefore, the maximum size of logarithmic spiral region formed at the notch root is that formed at general yield. The size of the logarithmic spiral region at general yield can be calculated to be $1.475 \times \rho$ for the geometry of the samples used in this experiment. The stress ahead of logarithmic spiral region decreases with further increasing applied pressure after the size of logarithmic spiral region reaches this critical value by an increase of the applied pressure, as can be seen from Fig. 11. As a result,

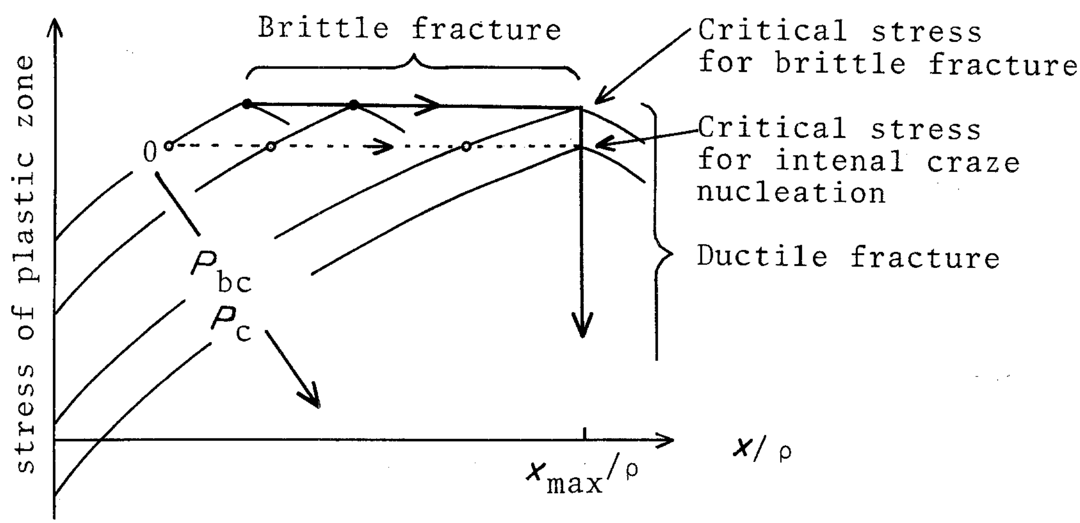

Figure 11 Variation of the stress distribution in the local plastic zone with increasing applied pressure. P_{bc} is the brittle to ductile transition pressure. P_c is the pressure for the prevention of an internal craze.

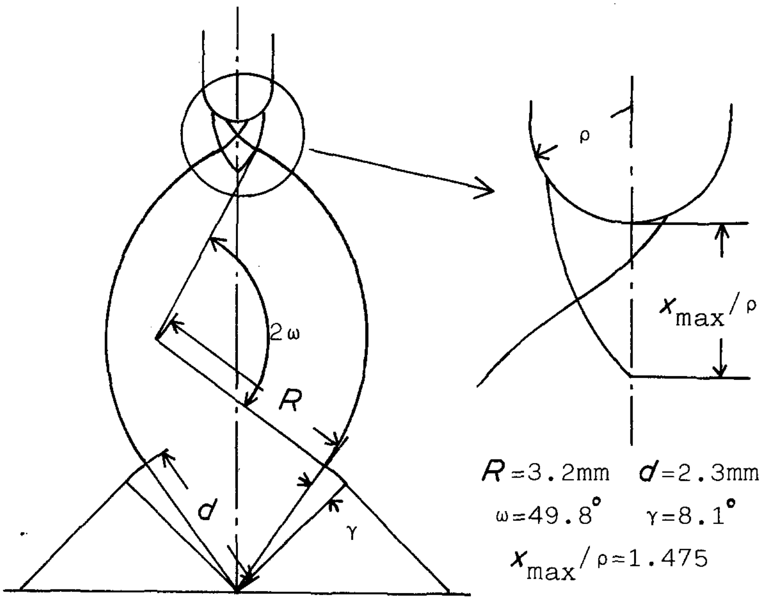

Figure 12 Slip-line field at general yield for a round-notched bar subjected to three-point bending.

the general yield takes place before the stress for brittle crack propagation from an internal craze is reached, and the fracture mode varies at a brittle to ductile transition pressure.

The results obtained here have shown that the heat treatment of PC has a singificant effect on the brittle to ductile transition, that is, quenching brought about a large decrease in the transition pressure. This means that the toughness of PC can be remarkably enhanced by quenching from near its glass transition temperature. There have been several attempts to explain the toughness enhancement of PC on quenching and/or embrittlement on annealing. Adam *et al.* [13] have proposed the mechanism that the reduction in toughness during annealing can be ascribed to greater plastic instability and to the consequent reduction in volume of the zone plastic yielding. So and Broutman [17] have suggested that crazing of quenched PC can be suppressed by compressive residual stresses having a maximum value near 20 MPa at the surface.

In the previous results [9], the shape and dimensions of the plastic zone for both quenched and annealed PC samples are quite reasonably described by the logarithmic spirals of the slip-line field theory. No effect of heat treatment on the pattern of the plastic region when it fully develops ahead of the notch tip has been observed. Generally, annealing of PC brings about an increase in the yield strength with a small change in density as observed by many investigators [18–20]. The difference of the critical pressure for a brittle to ductile transition between quenched and annealed samples can be explained by this change. According to Equation 3, the brittle to ductile transition pressure, i.e. critical applied pressure required to extend the size of the local plastic zone below the notch root up to $1.475 \times \rho$, depends on both critical stresses for the internal craze nucleation and shear yield. The critical shear stress for the internal craze nucleation was about 88 MPa regardless of the heat treatment, while the shear yield stress for quenched PC (34.3 MPa) was smaller than that for a slowly cooled sample (40.4 MPa). Using these values with Equation 3, the brittle to ductile transition pressures were calculated to be 7 MPa for the quenched sample and 26 MPa for a slowly cooled sample. The calculated value for a quenched sample is approximately in agreement with that of the experimental result. Therefore, it can be undoubtedly suggested that the change in the brittle to ductile transition pressure during annealing closely relates to the increase in the shear yield stress.

The microphotographs of the sections obtained on the sample deformed above the brittle to ductile transition pressure shows that the hydrostatic pressure which is higher than the brittle to ductile transition pressure is needed to prevent the nucleation of the internal craze. Therefore, it is suggested that the critical stress for brittle crack propagation from an internal craze is larger than the critical stress required to nucleate the internal craze.

5. Conclusions

The following conclusions are drawn from the present work.

(i) The brittle to ductile transition of a round notched PC bar under hydrostatic pressure occurs when general yield takes place before a critical stress for brittle crack propagation due to an internal craze.

(ii) The critical stress for brittle crack propagation is slightly higher than the critical stress for nucleation of the internal craze.

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