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The effect of heat treatment on plane strain fracture of glassy polymers

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The effect of annealing on the plane strain fracture of round-notched polycarbonate and poly(methyl methacrylate) bars has been investigated. Morphological observations of thin sections and fracture surfaces revealed that the fracture initiated from internal crazes which were nucleated at the tip of a local plastic zone. The critical hydrostatic stresses for internal craze nucleation were nearly constant regardless of annealing, while the shear yield stress increased with increasing annealing time. The reduction in toughness by annealing can be ascribed to the decrease of the maximum extent of the plastic zone which gives the critical hydrostatic stress for craze nucleation.

1. Introduction

The mechanical behaviour of glassy amorphous polymers is strongly influenced by heat treatment. For example, it has been shown that the annealing of polycarbonate(PC) just below its glassy transition temperature leads to a significant fall in the notched Charpy impact strength [1, 2]. At the same time, annealing brings about an increase in the tensile strength [3, 4]. It has been also shown that a more drastic change of fracture mode due to annealing occurs in the tensile test of poly(ethylene terephthalate) (PET). Petrie *et al.* [5] and Petrie [6] has shown that the quenched PET, which is a ductile glassy amorphous polymer, varies from ductile to brittle fracture when annealed at a temperature of 324 K for 90 min.

Boyer [7, 8] has suggested that the ductility of glassy amorphous polymers closely relates to the relaxation process due to submolecular motion. In particular, it has been often suggested that the high toughness of PC at low temperature is caused by the relaxation process which occurs at a considerable low temperature of 173 K. Petrie [6] and, independently, Sacher [9–11] pointed out that the submolecular motion is reduced by annealing, and as a result, the toughness of glassy amorphous polymers is decreased. On the other hand, Adam *et al.* [2] have suggested that the reduction in toughness of glassy polymers is due to a larger strain softening effect after yield than untreated materials. Thus, there has been no established explanation for the embrittlement mechanism due to annealing.

In recent studies on the fracture mechanism of glassy amorphous polymers, we [12–14] have shown that the fracture processes of the round-notched bars in the plane strain state above β-transition temperature can be basically explained by the mechanism of "notch brittleness" which was originally proposed by Orowan [15]. Namely, the brittle fracture of the sample occurs from the internal craze which is nucleated at the tip of the local plastic zone when the size of the local plastic zone, initiated at the notch tip, reaches a certain critical size. In these studies, it was pointed out [12] that the maximum extent of the plastic zone for slowly cooled PC is smaller than that for the quenched sample. Therefore, it can be suggested phenomenologically that the reduction in the toughness of glassy amorphous polymers during annealing closely relates to the size of the local plastic zone at the notch root.

The purpose of this paper is to examine the effects of annealing on the plane strain fracture of glassy amorphous polymers in more detail, and to discuss the mechanism of embrittlement due to annealing.

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2. Experimental details

The materials used were commercial grades of poly (methyl methacrylate)(PMMA)(Acrylite) and PC(Panlite) in sheet form of 10 mm thickness. After cutting into a rectangular shape of 15 mm width and 70 mm length, a round notch was introduced in the centre of one edge of the PMMA specimen by drilling a hole of 2.0 mm diameter and then making a saw cut in one side of the specimen. Before making the saw cut, the surface of the hole was polished by conventional metallographic techniques, by using emery paper and a wet polishing cloth with TiO_2. A round notch with radius of 0.5 mm in the PC specimen was shaped 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 due to an increase in temperature, the specimens were cooled with water during machining. These specimens were heated at 403 K for 24 h for PMMA and 433 K for PC to eliminate the residual strain. After heating, all specimens were ice-quenched. The quenched samples were annealed in the silicone oil. The annealing temperatures were 383 and 403 K for PC and 353 and 368 K for PMMA, respectively.

The quenched and annealed specimens were loaded in three-point bending with a span length 50 mm in an Instron type testing machine (Auto Graph, Shimazu DSS-5000). Tests were carried out at a bending rate of 10 mm min^{-1} at 296 K for PC and 323 K for PMMA.

To reveal the structure and morphology of the internal craze and plastic deformation zone, thin sections were cut normal to the plane of the internal craze from the unbroken samples. Furthermore, microscopic observations were made on the fracture surfaces to determine the position of internal craze nucleation.

3. Results and discussion

The bending moment–displacement curves of annealed PC at 403 K for 72 h and annealed PMMA at 368 K for 24 h, which are compared with those of both quenched samples, are shown in Fig. 1. It was found for both samples that the maximum moment and the displacement at fracture were significantly reduced by annealing. Figs. 2 and 3 show the variation of the fracture energy of PC and PMMA with annealing, which were calculated from the bending moment–displacement curves. There was also a reduction in

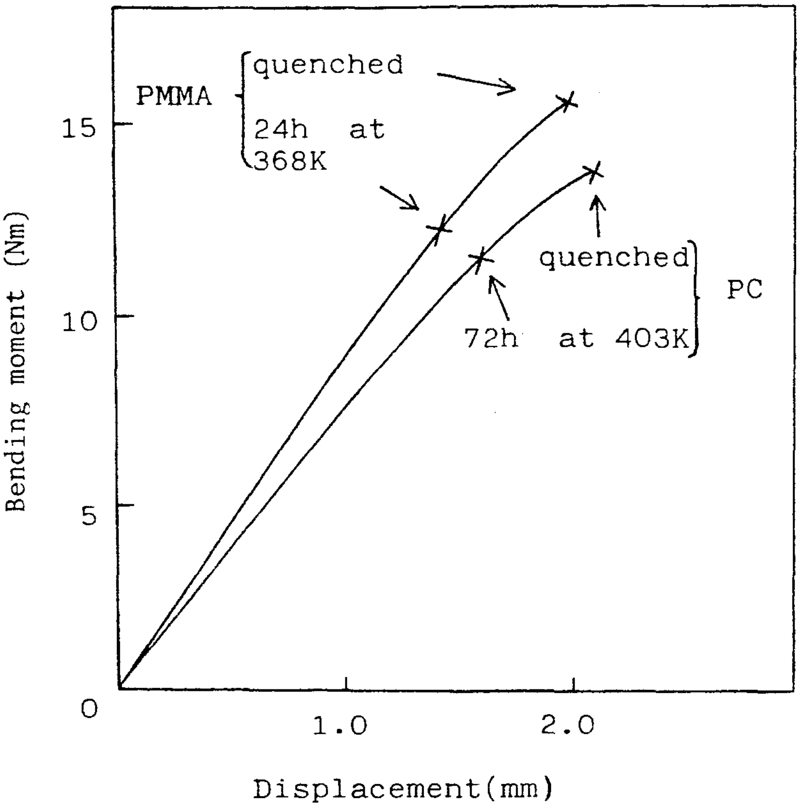

Figure 1 Bending moment–displacement curves of annealed and quenched samples.

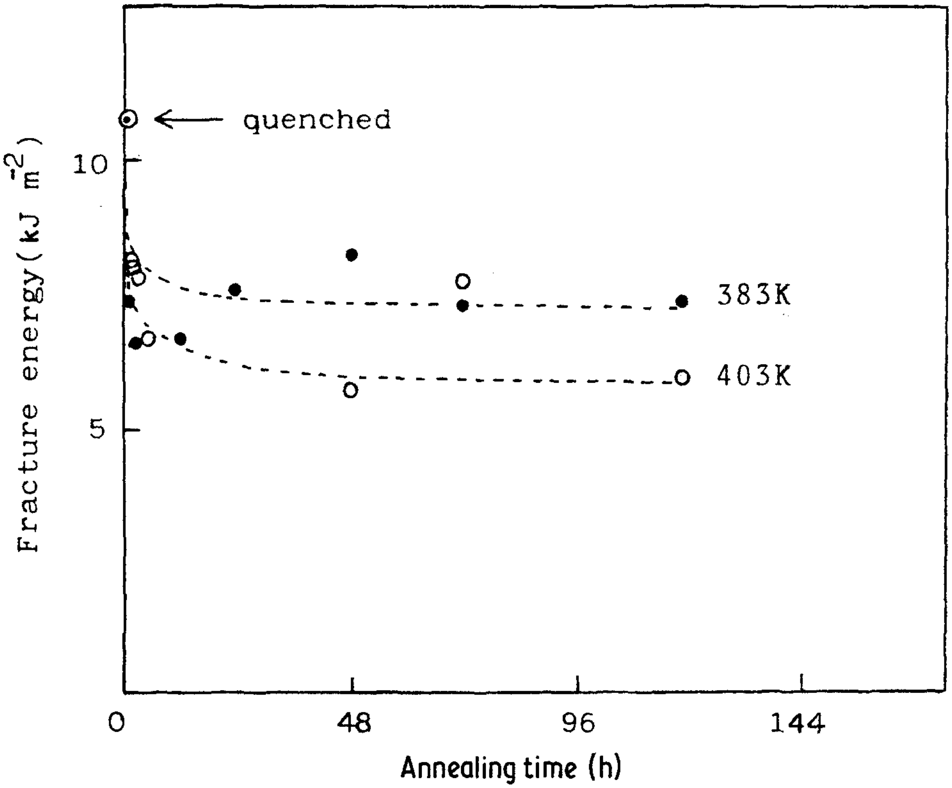

Figure 2 Variation of the fracture energy of PC as a function of time and annealing temperature.

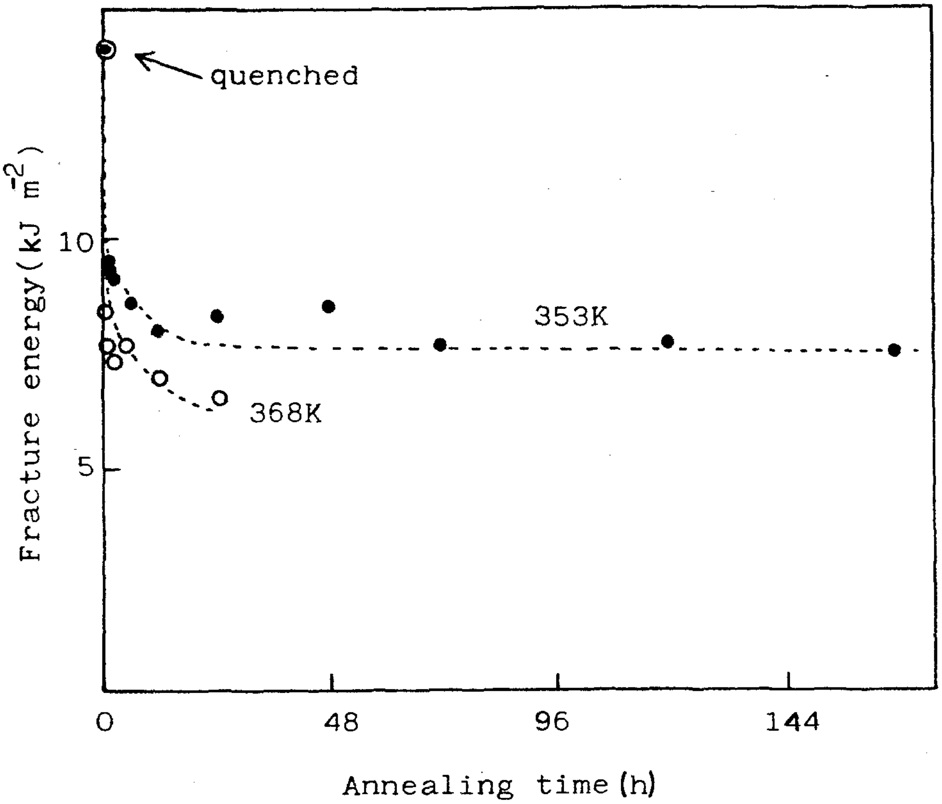

Figure 3 Variation of the fracture energy of PMMA as a function of time and annealing temperature.

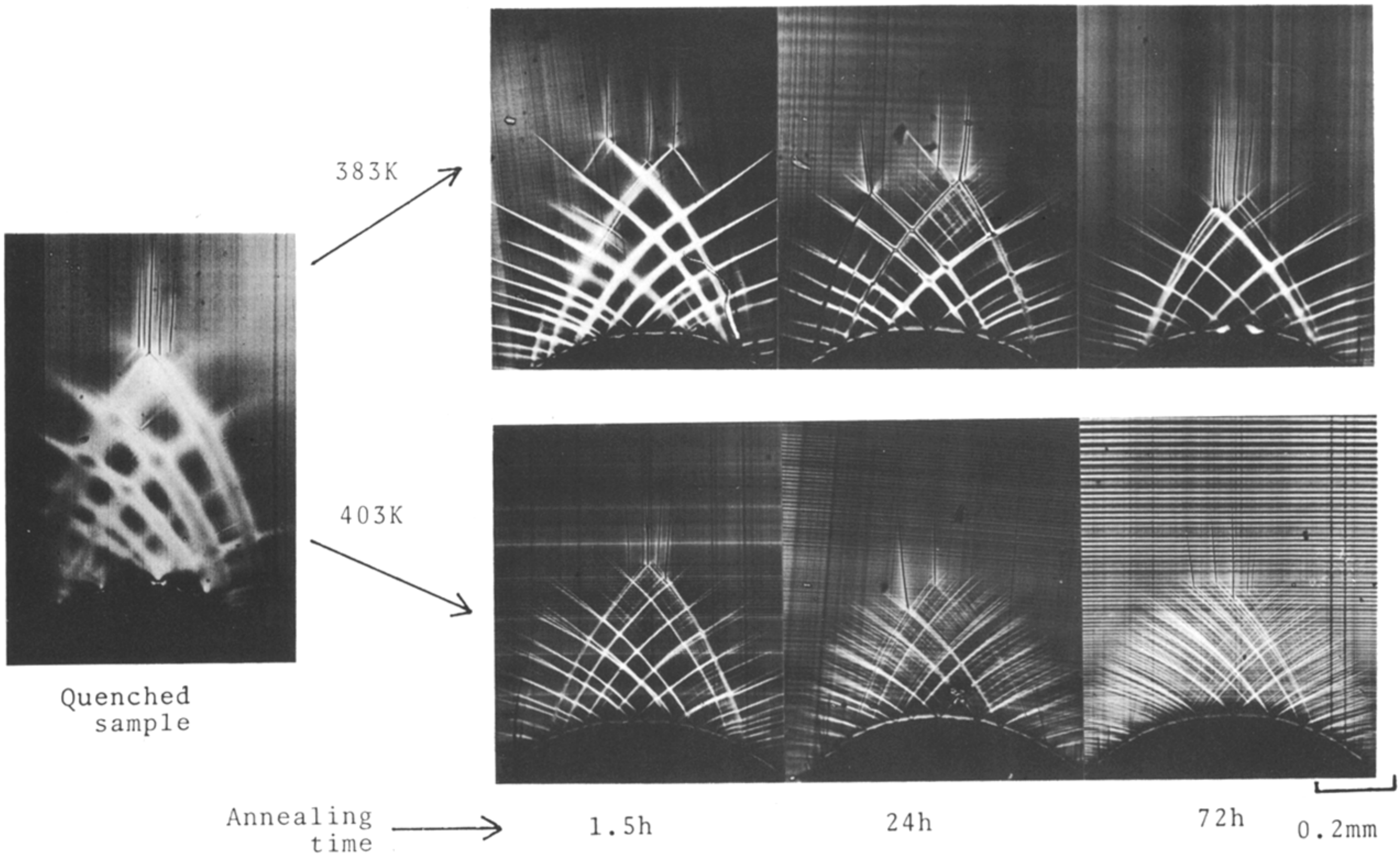

Figure 4 Variation of the plastic zone of PC with time and annealing temperature.

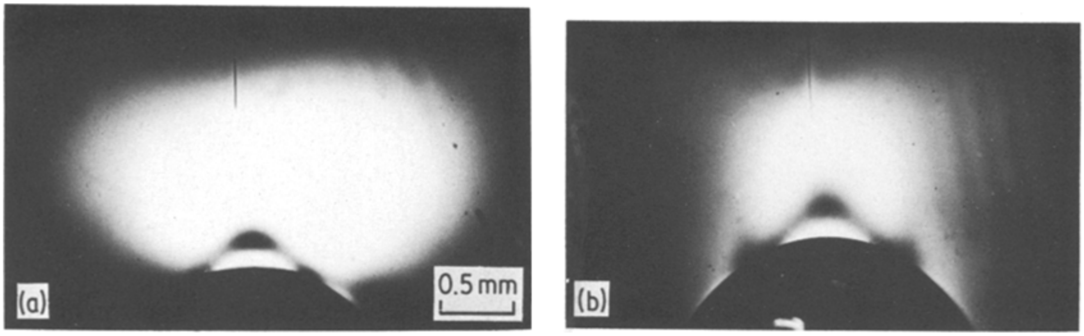

Figure 5 Polarized micrographs of sections obtained on (a) quenched PMMA and (b) PMMA annealed at 368 K for 48 h. Bending tests were carried out at a bending rate of 1 mm min^{-1} at 333 K for annealed samples and 313 K for quenched samples.

the fracture energy with increasing annealing time.

The fracture of the round-notched bars in the plane strain state occurs from the internal craze which is nucleated at the tip of the local plastic zone. To examine the change in the morphology of the plastic zone with annealing, thin sections were cut normal to the plane of the internal craze from the unbroken samples. The broken samples of PC, which contained the internal craze, could be easily obtained by unloading, i.e. reversing the motion of crosshead, immediately prior to the final fracture. The micrographs of the cross-sections of PC are shown in Fig. 4. It was found that the internal crazes were nucleated at the tip of the local plastic zone for all annealed specimens. As already shown in our previous paper [12], the local plastic zone of PC was composed of numerous shear bands. Annealing brought about a change from diffuse shear bands to fine ones. The change in the morphology of the plastic zone corresponds qualitatively to an increase of strain softening by annealing [2]. On the other hand, it was difficult to obtain the unbroken PMMA samples which involved the internal crazes under the usual test condition since the value of the applied moment when the internal craze initiated was extremely close to the fracture moment. Therefore, the bending speed was reduced to a bending rate of 1 mm min^{-1} at 333 K for the annealed samples and at 313 K for the quenched samples, and the unloading condition was found by trial and error. Fig. 5 shows the polarized micrographs of such sections obtained on annealed

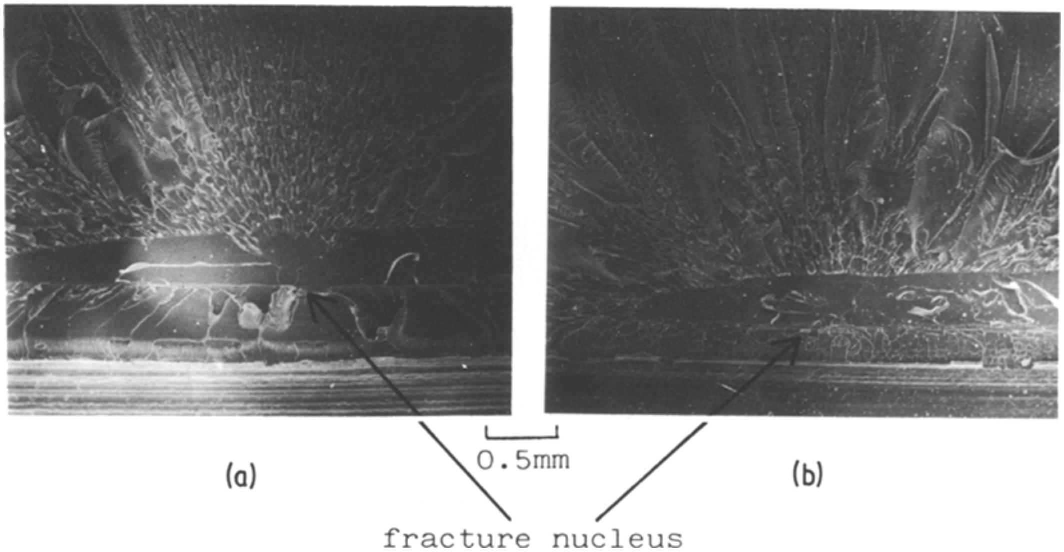

Figure 6 Fracture surfaces of PC (a) quenched and (b) annealed at 403 K for 72 h.

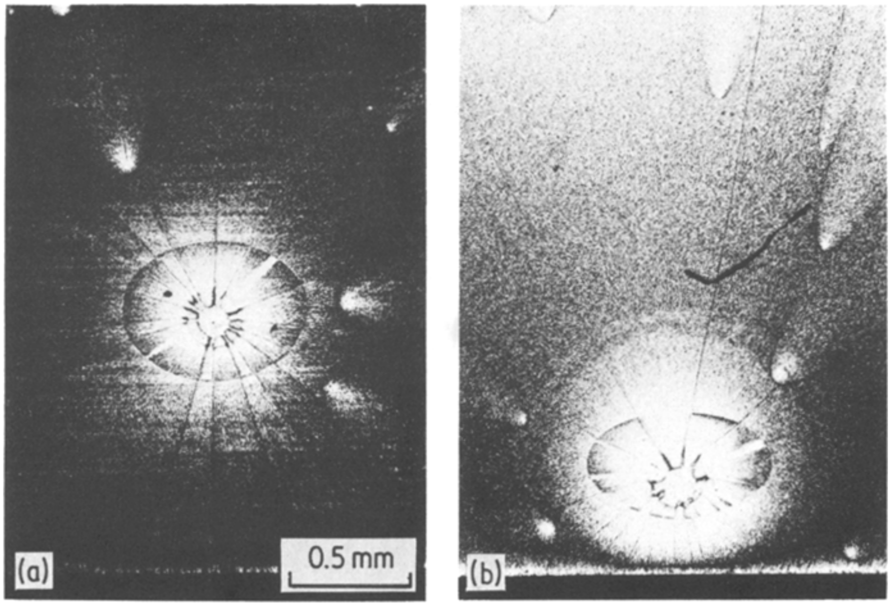

Figure 7 Fracture surfaces of PMMA (a) quenched and (b) annealed at 368 K for 24 h.

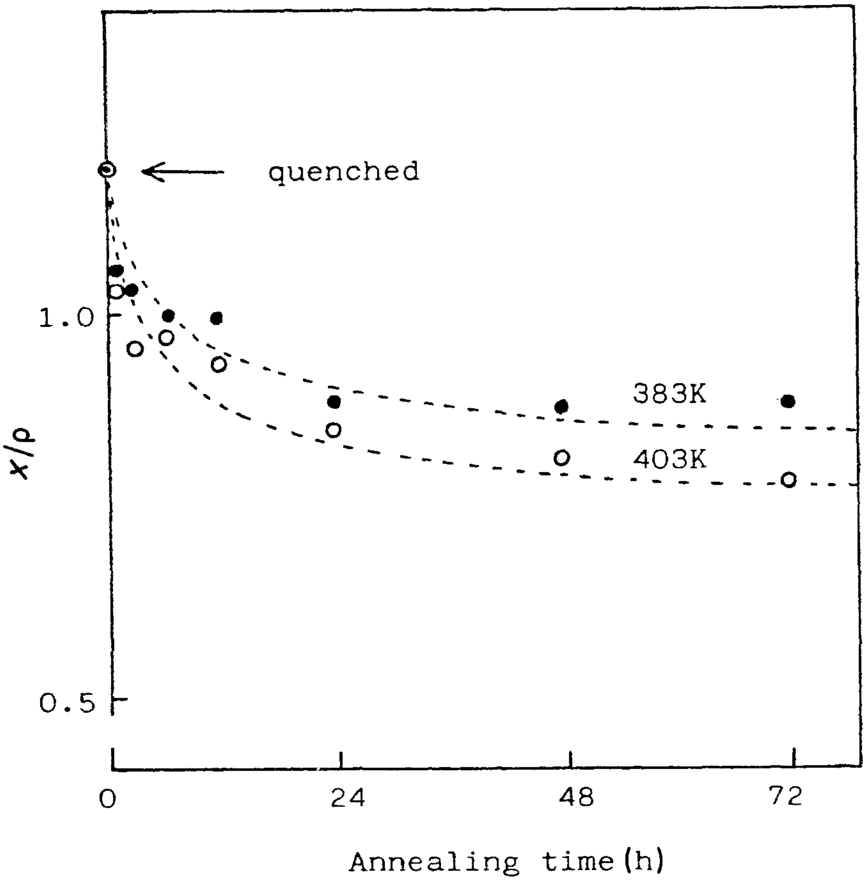

Figure 8 Variation of the ratio (x/ρ) of the maximum extent of the plastic zone (x) to the radius (ρ) of notch root in PC as a function of time and annealing temperature.

and quenched PMMA. There was no change in the morphology of the plastic zone with annealing time in contrast to that of PC. Although, there was a difference in the morphology of the plastic zone between PC and PMMA, it is known that the shear bands in PC do not affect the formation of internal crazes [12].

A critical stress for internal craze nucleation can be calculated from the maximum extent of the plastic zone by applying Hill's slip line field theory [16]. The glassy amorphous polymers are known to obey a pressure-dependent yield criterion. In general, the shear yield criterion under a plane strain state is given by

$$k = k_0 + \cos 2\psi\, s \tag{1}$$

where k_0 is the value of k when the hydrostatic stress component $s = 0$ and $\cos 2\psi$ is constant. The values of $\cos 2\psi$ were -0.07 for PC and -0.15 for PMMA [13]. As stated in detail in the previous paper [13], the hydrostatic stress component ($s(x)$) at the tip of the local plastic zone for the material which obeys the pressure-dependent yield criterion is given by

$$\frac{s(x)}{k_0} = \frac{1}{\cos 2\psi}\left[\left(\frac{1}{1-\cos 2\psi}\right)\left(1+\frac{x}{\rho}\right)^{\frac{2(\cos 2\psi)^2}{1-\cos 2\psi}} - 1\right] \tag{2}$$

The maximum extent of plastic zone required to nucleate the internal craze can be measured from the fracture nucleus on the fracture surface. The fracture surfaces of PC annealed at 403 K for 72 h and of PMMA annealed at 368 K for 24 h, which are compared with each quenched sample, are shown in Figs. 6 and 7, respectively. It can be clearly seen that the maximum extent of the plastic zone of PC and PMMA is reduced by annealing. Figs. 8 and 9 show the ratio (x/ρ) of the maximum extent of the plastic zone (x) to the notch radius (ρ) in PC and PMMA, respectively, as a function of annealing time. It was found that the position of the fracture nucleus gradually approached the notch tip with increasing annealing time. In particular, the fracture in PMMA annealed at 368 K for over 48 h occurred at the notch tip. Equation 2 indicates that an increasing shear yield stress and/or a decreasing critical stress for the

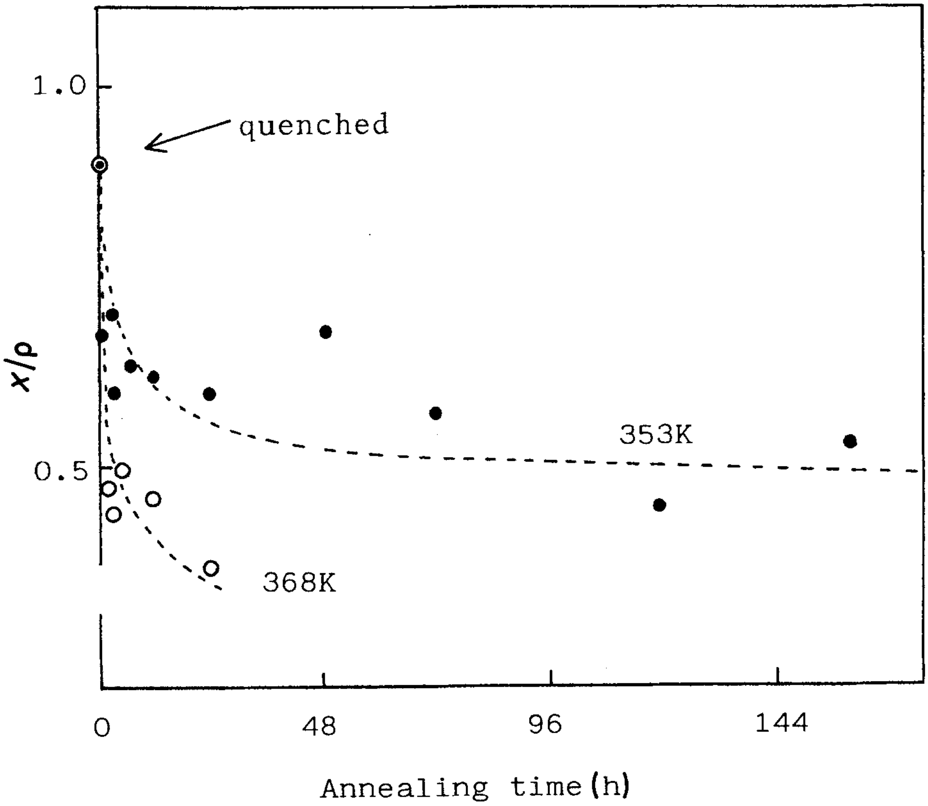

Figure 9 Variation of the ratio (x/ρ) of the maximum extent of the plastic zone (x) to the radius (ρ) of notch root in PMMA as a function of time and annealing temperature.

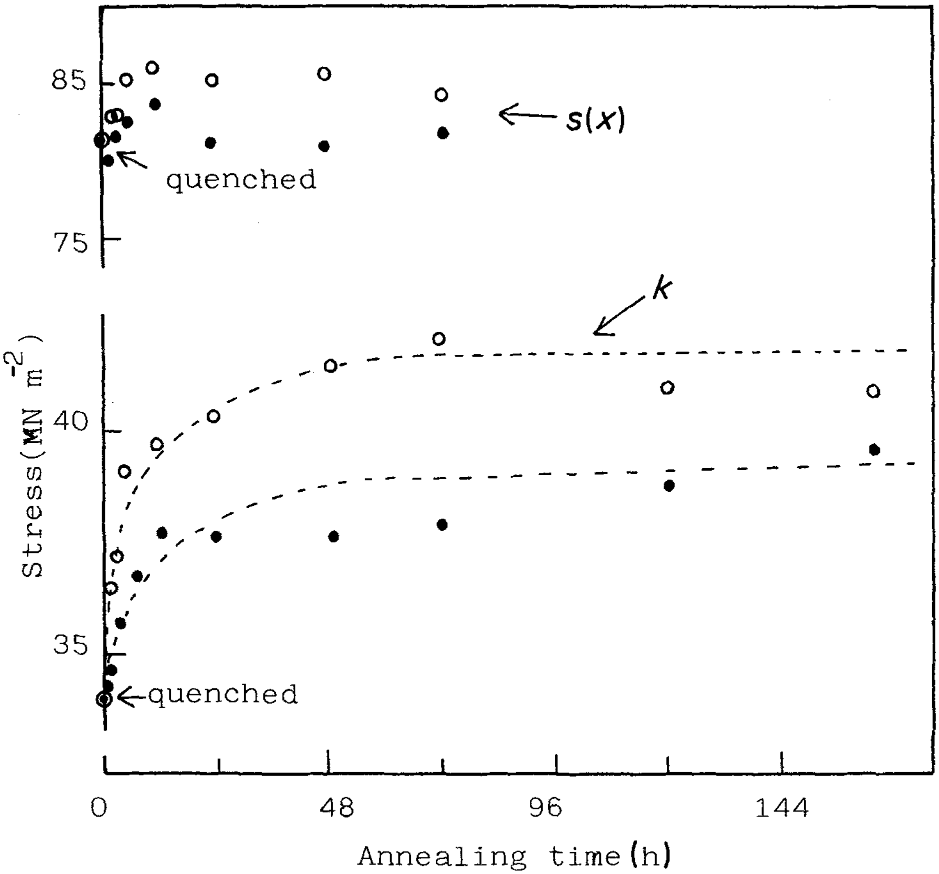

Figure 10 Variation of the critical hydrostatic stress for internal craze nucleation ($s(x)$) and shear yield stress (k) for PC as a function of annealing time: (●) 383 K; (○) 403 K.

internal craze nucleation decreases the maximum extent of the plastic zone, i.e. the energy absorption due to plastic deformation at the notch tip. Figs. 10 and 11 show both critical hydrostatic stress components for nucleation of internal craze and shear yield stresses as a function of the time and temperature of annealing for PC and PMMA, respectively. The shear yield stresses were experimentally obtained from the uniaxial yield stresses by dividing by $3^{1/2}$ on the assumption that the yield criterion is a pressure-dependent Von Mises yield criterion. The tensile tests were carried out at a strain rate of 0.2 mm min^{-1} for both samples. While the shear yield stress increases with an increase of temperature and annealing time, the calculated critical stresses based on Equation 2 are nearly independent of the annealing condition. Although the difference between the molecular mechanism for shear yielding and the internal crazing is obscure, this result is in agreement with the previous [12] results that the critical stress for craze nucleation is less sensitive to thermal histories of the material and test conditions, such as strain rate, than the yield stress is.

4. Conclusions

1. The reduction in toughness by annealing can be ascribed to the decrease of the maximum extent of plastic zone size which gives the critical stress for craze nucleation.

2. The decrease of the plastic zone size is due to the increase of the shear yield stress by annealing. The critical stresses for craze nucleation in PC and PMMA are not affected by annealing.

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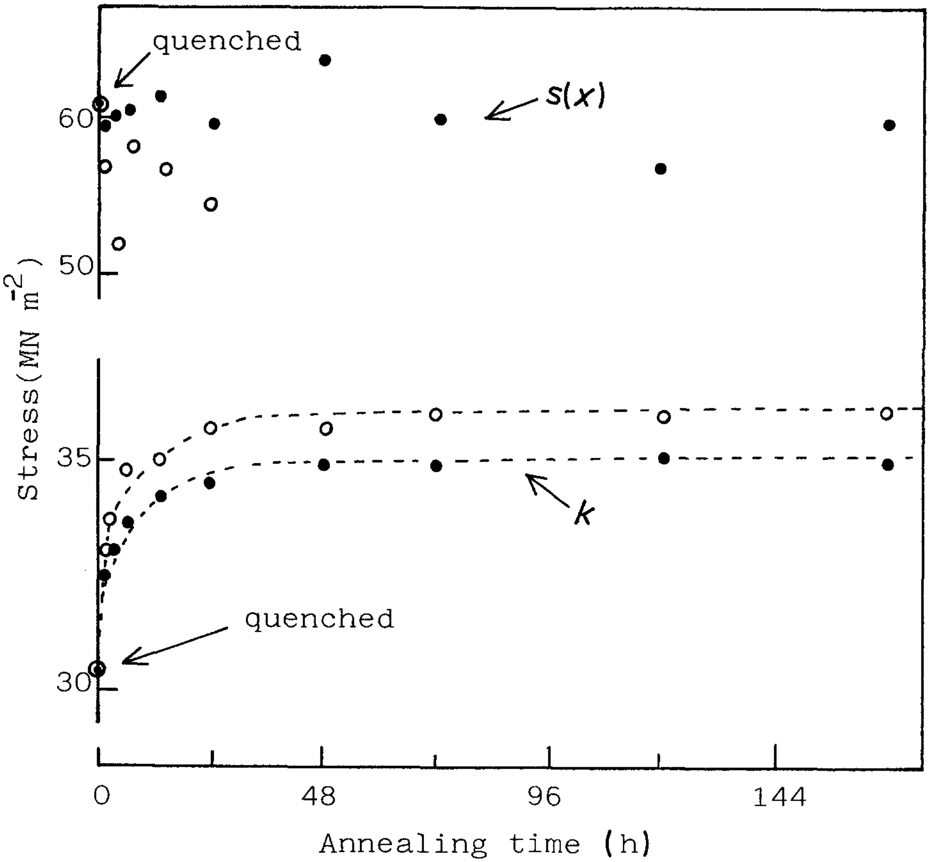

Figure 11 Variation of the critical hydrostatic stress for internal craze nucleation ($s(x)$) and shear yield stress (k) for PMMA as a function of annealing time: (●) 353 K; (○) 368 K.

References

1. G. ALLEN, D. C. W. MORLEY and J. WILLIAMS, *J. Mater. Sci.* 8 (1973) 1449.
2. G. A. ADAM, A. CROSS and R. H. HAWARD, *ibid.* **10** (1975) 1582.
3. K. NEKI and P. H. GEIL, *J. Macromol. Sci.-Phys.* 8 (1973) 295.
4. D. G. LeGRAND, *J. Appl. Polym. Sci.* **13** (1969) 2129.
5. R. M. MININNI, R. S. MOORE, J. R. FLICK and S. E. B. PETRIE, *J. Macromol. Sci.-Phys.* **B8** (1973) 343.
6. S. E. B. PETRIE, "Polymeric Materials–Relationships Between Structure and Mechanical Behavior", edited by E. Baer and S. V. Radcliffe (ASM, Ohio, 1974) p. 55.
7. R. F. BOYER, *ibid.* (ASM, Ohio, 1974) p. 163.
8. *Idem, Polym. Eng. Sci.* 8 (1968) 161.
9. E. SACHER, *J. Macromol. Sci.-Phys.* **B9** (1974) 163.
10. *Idem, ibid.* **B10** (1974) 319.
11. *Idem, ibid.* **B11** (1975) 403.
12. M. ISHIKAWA, I. NARISAWA and H. OGAWA, *J. Polym. Sci. Polym. Phys. Ed.* **15** (1977) 197.
13. I. NARISAWA, M. ISHIKAWA and H. OGAWA, *J. Mater. Sci.* **15** (1980) 2059.
14. M. ISHIKAWA, H. OGAWA and I. NARISAWA, *J. Macromol. Sci.-Phys.* **B19** (1981) 421.
15. E. OROWAN, *Rep. Prog. Phys.* **12** (1948) 185.
16. R. HILL, "The Mathematical Theory of Plasticity", (Oxford University Press, London, 1950).

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