Toughening mechanisms of blends of poly(acrylonitrile–butadiene–styrene) copolymer and BPA polycarbonate

M. Ishikawa and I. Chiba
Faculty of Engineering, Yamagata University, Jounan 4-3-16, Yonezawa 992, Japan
(*Received 18 May 1989; revised 17 July 1989; accepted 21 July 1989*)

The toughening mechanisms of blends of poly(acrylonitrile–butadiene–styrene) copolymer (ABS) and bisphenol-A polycarbonate (PC) have been studied by three point bending of round notched bars under plane strain state. The toughness of PC was decreased by adding small amounts of ABS particles, because the voids around the particles of ABS accelerate the development of the internal crazes. For further increase in ABS content, however, the toughness in the polymer blends was improved by the relaxation of stress concentration which increases the stability of craze to the catastrophic crack propagation. Above a certain critical content, which can be estimated from the critical stress for internal craze nucleation and shear yield stress, the shear plastic deformation occurred only in the matrix materials without the nucleation of crazes. It is concluded that the relaxation of stress concentration due to the formation of numerous voids is basic mechanism for the toughening of polymer blends. The energy dissipation by both crazing and shear deformation results from this relaxation of stress.

(**Keywords: polymer blend; toughness; craze; shear plastic deformation; relaxation; stress concentration; polycarbonate; poly(acrylonitrile–butadiene–styrene) copolymer**)

INTRODUCTION

There has been interest in the use of multicomponent polymer composites, because of the possibility of increasing some properties of the polymeric materials. It is well known that the enhancement of toughness in polymers is widely achieved commercially by blending. For example, the resistance of polystyrene to cracking is improved considerably if many small rubber particles are dispersed in the polymer.

The impact modification mechanisms for rubber toughened polymer were generally considered to involve energy dissipation by both crazing initiated from the rubber particles and cavitation of small rubber particles which subsequently promotes localized shear deformation[1–3]. On the other hand, it is well known that the crazing develops into catastrophic crack on polymers in a single component system. Although several principal mechanisms have been proposed to account for the toughness of these rubber modified polymers, a great deal of controversy still exists on the nature of the toughening mechanisms.

In recent studies on the fracture mechanisms of some polymeric materials, we have suggested that the resistance of crack initiation from the notch, that is toughness, is dependent on both shear yield stress and critical stress for craze nucleation[4–9]. Thus, it is necessary to explain the toughening mechanism of polymer blends based on above fracture mechanism.

The purpose of this paper is to examine the fracture processes on the plane strain deformation of polycarbonate (PC) blended with poly(acrylonitrile–butadiene–styrene) copolymer (ABS) and discuss the mechanisms of improvement of toughness.

0032-3861/90/071232–07

EXPERIMENTAL

The materials used were commercial grade of PC with molecular weight (MW) of 25 000 and ABS with acrylonitrile content of 25 wt% and butadiene rubber content of 25 wt%. The parent PC was blended with ABS at ratios resulting in weight fraction of 2.5 and 20%. PC pellets and ABS granules were premixed in a mixer and melt-blended with barrel temperature set at 513 to 523 K.

The materials tested were compression moulded at 523 to 533 K into 1 mm and 6 mm thick sheets. Specimens for tensile mechanical measurements were prepared by milling the 1 mm thick sheets. Three point bending specimens were made from the 6 mm thick sheets. A round notch with radius of 0.5 mm in the specimen was shaped by machining with convex milling cutter. The specimens were loaded in three point bending with a span length 40 mm in an Instron type testing machine (Auto Graph, Shimadzu DSS-5000). Tests were carried out at a bending rate of 2 mm/min at 296 K.

To examine the mechanism of energy dissipation during deformation in three point bending under plane strain, thin sections of about 25 μm were cut normal to the plane of initial notch from unloaded samples as shown in *Figure 1*. The morphology of the craze and plastic deformation was studied in an optical microscope using polarized light and/or dark field light. The changes in microstructure were examined with a scanning electron microscope for surfaces of cryogenically fractured samples. Samples, which were experienced in bending test, were first immersed in liquid nitrogen bath for 5 min, and broken normal to the plane of notch immediately after removal from liquid nitrogen bath (*Figure 1*). When the fracture strain becomes progressively greater with

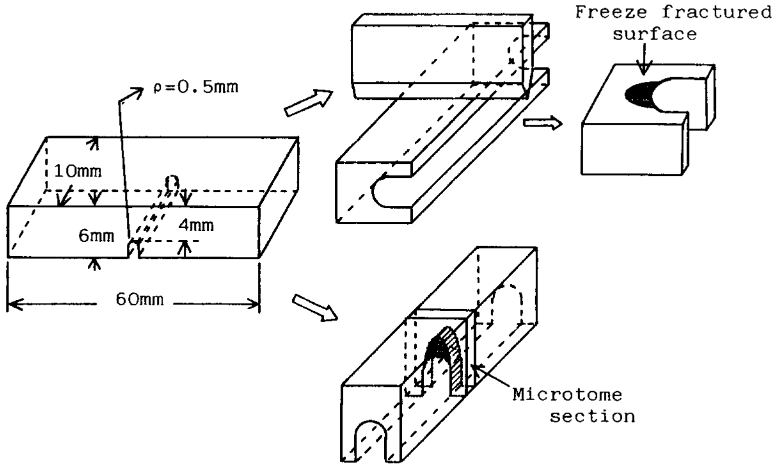

Figure 1 Dimension of test sample and cutting direction for observation of deformation zone

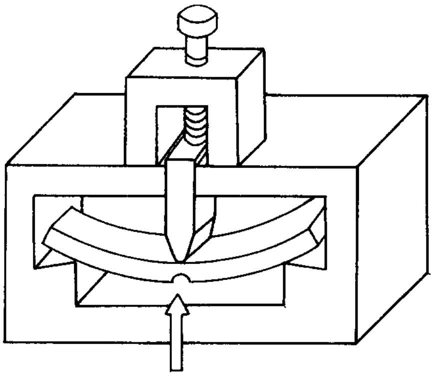

Figure 2 Fixation of strain by casting of epoxy resin

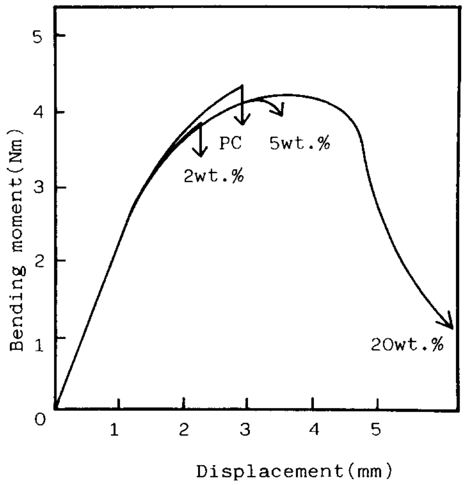

Figure 3 Bending moment-displacement curves of ABS/PC blends deformed at 296 K

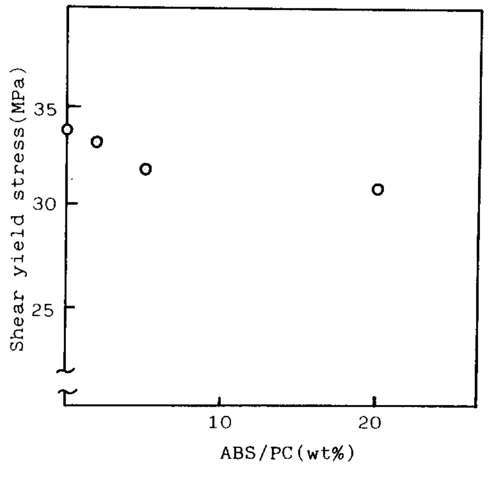

Figure 4 Variation of yield stress as a function of the content of ABS

increasing content of ABS, strain recovery by unloading does influence significantly the morphology of deformation zone. In these cases, the deformation by three point bending was fixed by the casting of epoxy resin, which consisted of 60 parts per hundred of resin (phr) of Epon828, 40 phr of Epon871 and 9 phr of triethylenetetramine, as shown in *Figure 2*.

RESULTS

The bending moment–displacement curves of ABS/PC blends with different contents of ABS, which were tested at 296 K, are shown in *Figure 3*. It is well known that, if a ductile polymer such as PC contains a deep notch and plane strain state is maintained, it fractures in a brittle manner. When ABS was added to PC by 2 wt%, it was found that the toughness was significantly reduced, as can be seen from the bending moment–displacement curve. As the amounts of ABS were further increased, both the maximum moment and the displacement at brittle fracture became larger. The fracture mode was ductile fracture in polymer blends with ABS 5 wt%. Above a critical content of ABS, the toughness of ABS/PC blends was improved in comparison with that of monophase PC. *Figure 4* shows the shear yield stresses, which were experimentally obtained from the uniaxial yield stresses by dividing by $\sqrt{3}$, as a function of the content of ABS. The shear yield stresses were nearly constant regardless of the content of ABS.

Figure 5 shows polarized photomicrographs of the cross sections which were obtained on the unbroken samples, which were unloaded immediately before fracture for brittle fracture samples and at the maximum bending moment for ductile fracture samples. It has been already shown for PC[4] that the brittle fracture occurs from the internal crazes nucleated at the tip of local plastic zone when the size of the local plastic zone, initiated at the notch tip, reaches a certain critical size. In the case of polymer blends with ABS 2 wt%, the local plastic zone

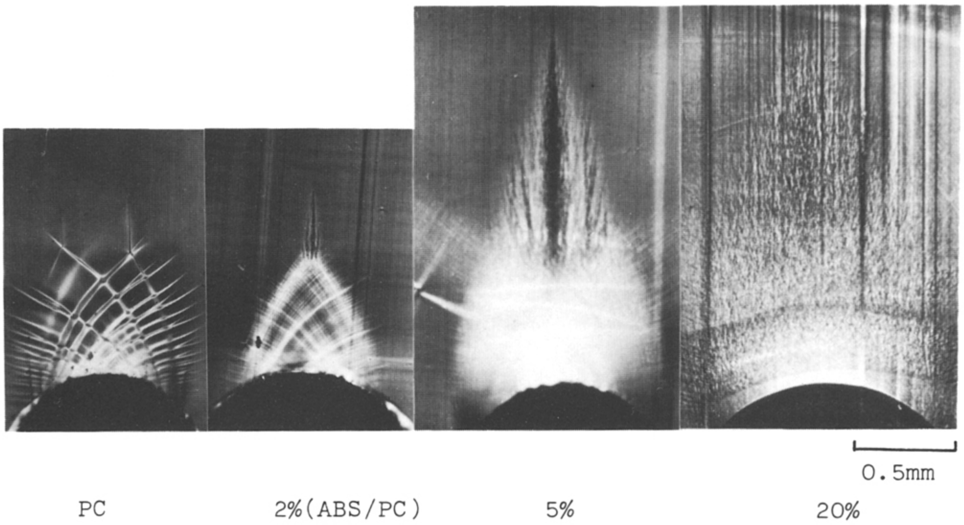

Figure 5 Polarized micrographs of the deformation zone of ABS/PC blends

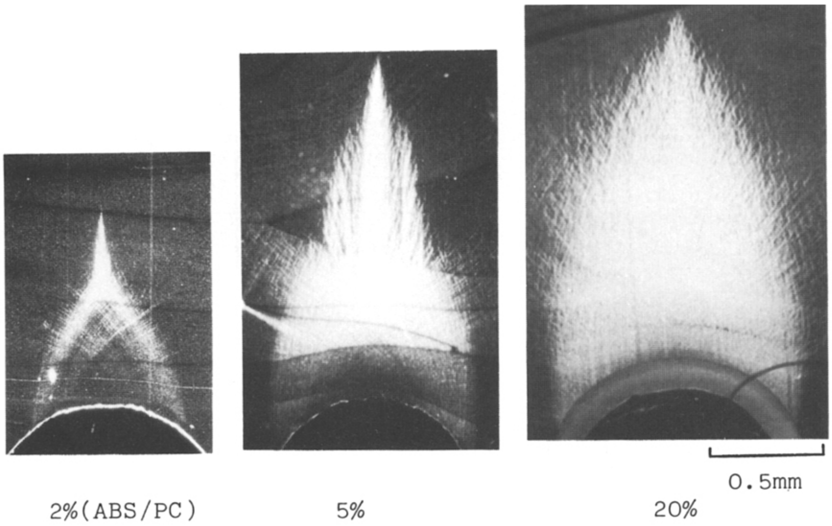

Figure 6 Dark field micrographs of the deformation zone of ABS/PC blends

with the formation of shear bands was initiated from the notch tip in analogy with PC, then the internal crazes were nucleated at tip of this local plastic zone. The size of local plastic zone required to nucleate the internal craze was smaller than that of PC. The formation of voids in the local plastic zone was revealed on the observation of dark field microscope because of the scattering of light due to voids which have larger size than the wavelength of light, as shown in *Figure 6*. Generally, such formation of numerous voids induced by stress is described as stress whitening. The stress whitening appears to be more prominent at the position far apart from the notch tip, that is, in vicinity of the tip of local plastic zone. It was found that a large number of crazes were nucleated at the tip of local plastic zone in comparison with that of PC. The fracture mode of ABS/PC blends was ductile fracture in blends with ABS 5wt%. In this content of ABS, the size of local plastic zone which was measured as the region of higher birefringence on the observation of polarized microscope was similar to that of ABS/PC blends with ABS 2wt%. On the other hand, it was found that the region of stress whitening appears to be wider as compared with that of blends with ABS 2wt%. The formation of numerous crazes was initiated from the tip of the local plastic zone and there was a tendency to concentrate into the narrow bands. The crazes were spread out considerably in form of narrow bands. The crack was nucleated from the internal craze by increasing the strain of deformation zone, after the general yielding was reached. Then the stable propagation of crack induces the ductile fracture of sample. The shear bands, which have a high birefringence as a result of concentration of plastic strain, were observed equivocally, as the content of ABS was increased. In polymer blends with ABS 20wt%, the formation of shear bands was not confirmed, but it was found in dark field microscope that the stress whitening developed over a wide range. The narrow deformation bands which were made by numerous crazes were no longer detectable.

Figure 7 shows the scanning electron micrographs of the surface of cryogenically fractured samples of ABS/PC blends with ABS 2wt%. It was found that the particles of ABS dispersed in PC matrix were slightly deformed in the direction of maximum principal stress ahead of notch tip. The internal crazes which contain the particles of ABS were nucleated at the tip of local plastic zone. The width of the craze in this blend sample is 1–5μm, and slightly narrow in comparison to the value of 2.5μm for PC. The formation of stress whitening was clearly observed in the neighbourhood of plastic zone tip. Although the crazes in the local plastic zone developed from the notch tip also might scatter the light, the crazes were not detached. Therefore, it was concluded that the formation of voids due to the fracture of interface between ABS particle and PC matrix resulted in the stress whitening. *Figure 8* shows the scanning electron micrographs of fracture surfaces for specimens with same ratios of the content of ABS. The nucleus, which is observed inside the elliptical region, is definitely a fracture nucleation site. The morphology of the fracture surface for blends with ABS 2 wt% was similar to that of PC. The ratio of the distance from the notch tip to the position of internal craze nucleation is about 0.96 times as long as the notch radius. This value was slightly smaller than that of PC. The mode of crack propagation was ductile within the internal craze, although the brittle crack was raised when the crack was propagated beyond the region of internal craze.

Figure 9 shows the scanning electron micrographs of the deformation zone of ABS/PC blends with the ABS 5 wt%. It can be seen from the deformation of the particles of ABS in the direction of maximum principal stress ahead of notch tip that the plastic strain was greatly developed at notch tip. The nucleation of crazes was not observed within the local plastic zone. The numerous stable crazes were nucleated at the tip of this plastic zone.

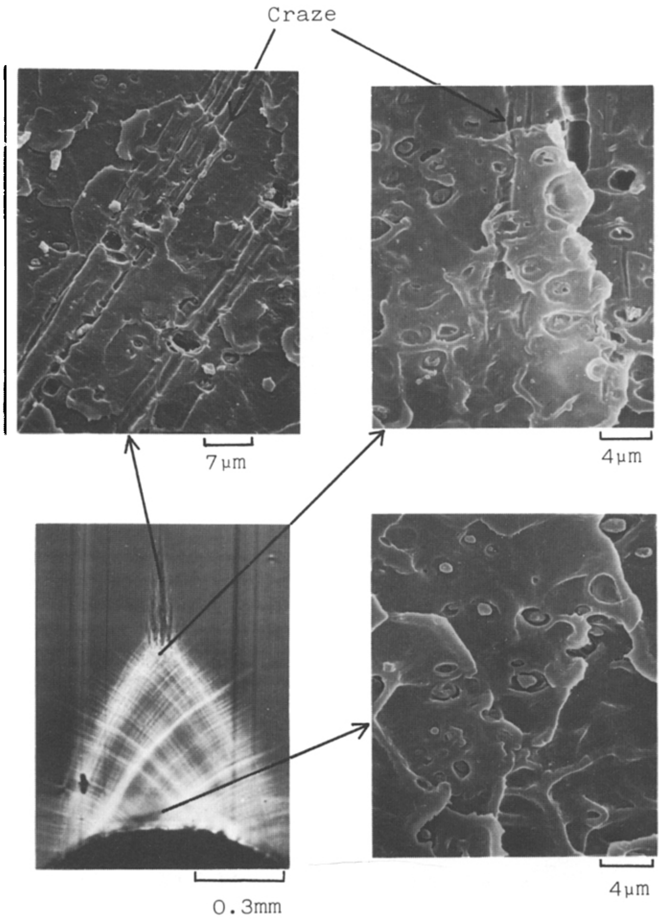

Figure 7 Scanning electron micrographs of the deformation zone of PC blended with 2 wt% ABS

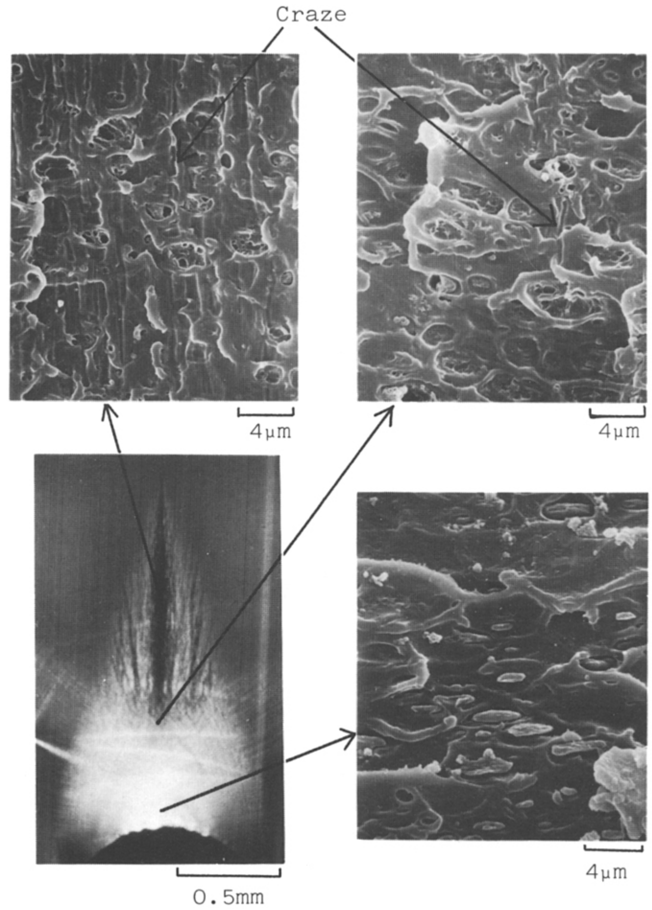

Figure 9 Scanning electron micrographs of the deformation zone of PC blended with 5 wt% ABS

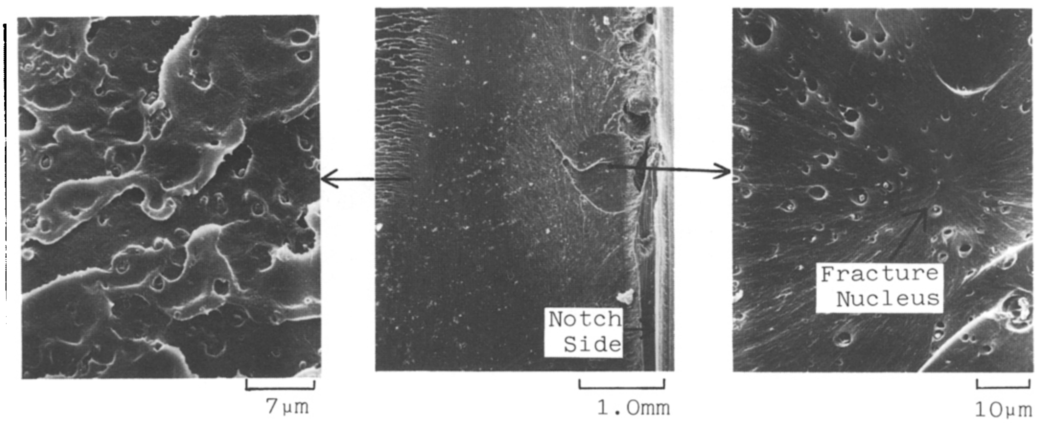

Figure 8 Scanning electron micrographs of the fracture surface of PC

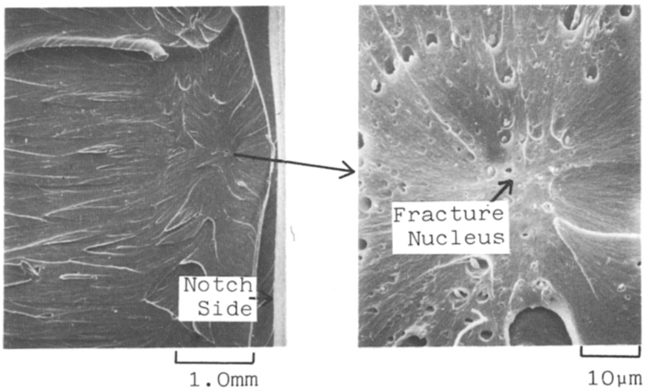

Figure 10 Scanning electron micrographs of the fracture surface of PC blended with 5 wt% ABS

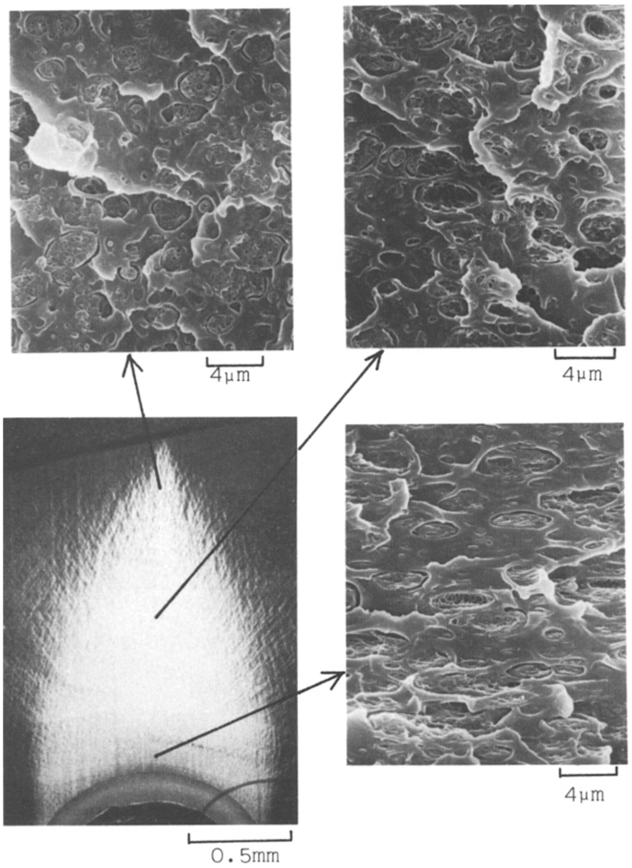

Figure 11 Scanning electron micrographs of the deformation zone of PC blended with 20 wt% ABS

The width of each craze was about 0.6 μm. The scanning electron micrographs of fracture surface for specimen with same ratios of the content of ABS are shown in *Figure 10*.

The fracture was nucleated at the tip of local plastic zone. It was found that the propagation of ductile crack was developed over the fracture surface. *Figure 11* shows the scanning electron micrographs of the deformation zone of ABS/PC blends with ABS 20 wt%. The extremely large plastic strain was developed ahead of notch tip, as can be seen from the deformation of the particles of ABS. It was found that the formation of crazes did not occur. The stress whitening observed was attributed to the voids around the particles of ABS. The plastic deformation occurred by the shear plastic deformation in the PC matrix which contains the voids around the particles of ABS. *Figure 12* shows the corresponding fracture surface. The crack was nucleated at the notch tip when the plastic strain reached a critical strain.

DISCUSSION

It was already known that the brittle fracture of the notched PC bars occurs from the internal crazes which were 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, as shown in *Figure 4*, that is, the stress ahead of plastic zone reaches a critical stress. If it is assumed that PC is a rigid–plastic body and the stress distribution in the local plastic zone ahead of notch tip is calculated from the slip line field theory[4], the stress distribution within the local plastic zone is given by

$$\begin{aligned} \sigma_y &= \sigma_{\text{mean}} + \tau \\ \sigma_x &= \sigma_{\text{mean}} - \tau \end{aligned} \tag{1}$$

where τ is shear yield stress and σ_{mean} is the mean stress (see *Figure 13*). In the plane strain state, the mean stress is expressed by

$$\sigma_{\text{mean}} = \tau(1 + 2\ln(1 + x/\rho)) \tag{2}$$

where x is the maximum plastic zone length and ρ is the notch radius. The critical mean stress (σ_{mean}) for the nucleation of internal craze was 83 MPa, which was calculated from the shear yield stress of 34 MPa for PC and the plastic zone length of 1.06ρ.

It is necessary to understand the stress distribution surrounding the particles in order to explain the mechanism of improvement of toughness. Since the polymer blends with the ABS 2 wt% were fractured when the size of local plastic zone reached a critical length of 0.96ρ,

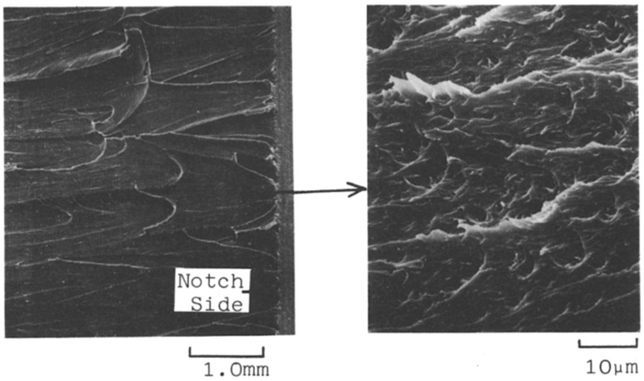

Figure 12 Scanning electron micrographs of the fracture surface of PC blended with 5 wt% ABS

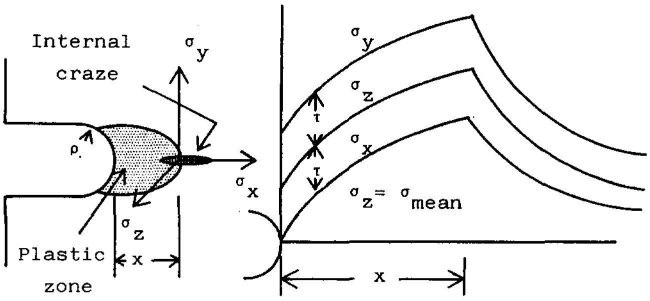

Figure 13 Definition of the stress components

the calculated critical mean stress required to develop the internal crazes in blends with ABS 2 wt% was about 74 MPa. The estimated result was slightly smaller than that of PC. Therefore, it would be surmised that the stress ahead of this plastic zone was increased to the critical stress for craze nucleation of PC by the stress concentration surrounding particle. When the stress ahead of plastic zone reached a cohesive strength of the interface between the particle of ABS and the PC matrix due to the expansion of local plastic zone which initiated at the tip of notch, the voids were formed by the rupture of the interface. Then, the new shape of plastic zone corresponding to the new boundary condition was formed. If the mean stress in the neighbourhood of void is equal to that before the formation of void, the variation of the stress distribution is shown in *Figure 14*. The stress of the elastic plastic boundary at opposite side of the U notch was enhanced in comparison with the mean stress before the rupture of interface. Therefore, the void around the particle of ABS accelerates the development of internal craze. As a result, the internal crazes were nucleated at the small size of plastic zone. Thus the toughness was decreased by presence of the small amounts of ABS particles.

The development of voids was increased with increasing amounts of ABS. The constraint of strain in a direction perpendicular to the maximum principal stress would be relaxed because the transmission of load is inhibited by the presence of voids. Therefore, the yield criterion for the material containing voids is different from that of continuous materials. Berg[10] suggested the yield criterion of ductile materials containing voids as follows:

$$(\sigma_1-\sigma_2)^2+(\sigma_2-\sigma_3)^2+(\sigma_3-\sigma_1)^2=6(\tau_0-g(p)/2)^2 \quad (3)$$

where σ_1, σ_2, σ_3 were principal stresses, τ_0 is shear yield stress of continuous material and $g(p)$ is the parameter which increases with an increase of both content of voids and dilational stress. This equation is formally equivalent to the pressure dependence yield criterion. Thus the stress within the plastic zone initiated from the notch tip is decreased in comparison with that of continuous material as shown in *Figure 15*. Consequently, the stability of craze to catastrophic crack propagation is increased due to the relaxation of stress concentration because the stress required to nucleation of crack in internal craze is greater than the critical stress for internal craze nucleation[7]. In addition, because the stress in the direction of craze propagation could not be borne on the internal craze, the constraint of strain is further decreased and it has become feasible to extend the internal crazes over wide regions.

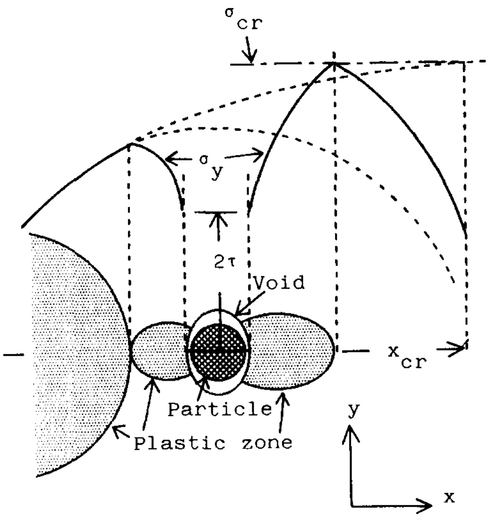

Figure 14 Variation of stress distribution caused by nucleation of void from the particle

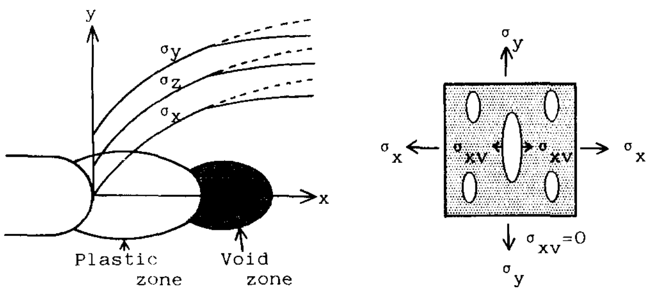

Figure 15 Relaxation of stress concentration due to the formation of voids

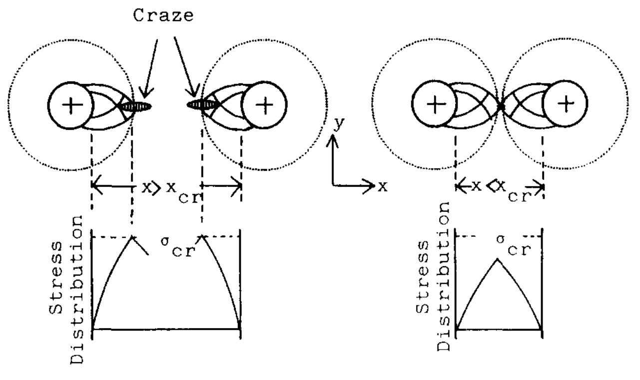

Figure 16 Critical length between voids for plastic deformation due to shear yielding in the matrix material without the nucleation of craze

If it is assumed that there is a plane strain state around the void with ABS particle, the size of the local plastic zone required to nucleate the internal craze at tip of this local plastic zone developed from the void is introduced from equation (1) as follows:

$$x_{cr}=2\rho(\exp(\sigma_{cr}/\tau-1)/2-1) \quad (4)$$

where σ_{cr} is a critical mean stress for the nucleation of internal craze. When the distance between the particle of ABS was decreased beyond this critical value with increasing the content of ABS, the stress within the plastic zone around ABS particle was maintained below the critical stress for craze nucleation as shown in *Figure 16*. Consequently, the nucleation of craze is impossible for the ABC/PC blends which contain the ABS particles above a certain critical content. Therefore, in this case, it is possible to deform with the large plastic strain due to shear yielding in the matrix materials and the pronounced improvement of the toughness is realized.

The critical content (V_{cr}) of dispersed particles for the development of shear plastic deformation between particles without the nucleation of internal craze can be calculated from the critical stress for internal craze nucleation and the shear yield stress in the matrix polymers by using the following equation

$$V_{cr}=0.74\{1/((x_{cr}/2\rho)+1)\}^3 \quad (5)$$

which is obtained on the assumption of regular close packing from the equation (4). The estimated critical content of ABS in blended polymers is about 8.4 vol%.

Although the application of this toughening mechanism to other blended polymers is the subject for a future study, if the critical stress of the matrix polymers for craze nucleation is greater than the shear yield stress, as in nylon[11] and polyetheretherketone[12], and dispersed particles are uniformly distributed, these polymer blends will be tough above the critical contents which are estimated from equation (5).

CONCLUSIONS

It is concluded that the relaxation of stress concentration due to the formation of numerous voids is the basic mechanism of toughening by dispersion of inclusions. The energy dissipation by both crazing and shear deformation results from this relaxation of stress.

ACKNOWLEDGEMENTS

We are grateful to Mr Murayama for his assistance with the experiments. We are also indebted to Teijin Company for supplying PC and to Daiseru Chemical Company for supplying ABS.

REFERENCES

1 Bucknall, C. 'Toughness Plastics', Applied Science, London (1977)

2 Kinoch, A. J. and Young, R. J. 'Fracture Behaviour of Polymers', Applied Science, London (1983)

3 Donald, A. M. and Kramer, E. J. *J. Appl. Polym. Sci.* 1982, **28**, 3719

4 Ishikawa, M., Narisawa, I. and Ogawa, H. *J. Polym. Sci., Polym. Phys. Edn.* 1977, **15**, 197

5 Narisawa, I., Ishikawa, M. and Ogawa, H. *J. Mater. Sci.* 1980, **15**, 2059

6 Ishikawa, M., Ogawa, H. and Narisawa, I. *J. Macromol. Sci. Phys. Edn.* 1981, **B19**, 421

7 Ishikawa, M. and Narisawa, I. *J. Mater. Sci.* 1983, **18**, 1974

8 Ishikawa, M. and Narisawa, I. *J. Mater. Sci.* 1983, **18**, 2826

9 Ishikawa, M. and Narisawa, I. *Jap. Soc. Strength and Fracture Mater.* 1983, **17**, 85

10 Berg, C. A. in 'Inelastic Behavior of Solids' (Eds M. F. Kanninen, W. F. Addler, A. R. Rosenfield and R. I. Jaffer), McGraw-Hill, New York, 1971, 171

11 Ishikawa, M. and Narisawa, I. *Proc. 25th Jap. Cong. on Maters. Res.* 1982, **20**, 282

12 Ishikawa, M. and Narisawa, I. *Polym. Prepr. Japan* 1988, **38**, 3030