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Stability of plastic deformation and toughness of polycarbonate blended with poly(acrylonitrile–butadiene–styrene) copolymer

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Stability of plastic deformation and toughness of bisphenol-A polycarbonate (PC) blended with poly(acrylonitrile–butadiene–styrene) (ABS) copolymer have been studied by three-point bending tests of U-notched bars under plane strain state. The deformation of PC/ABS blends was transformed into a stable mode by depression of craze nucleation when the content of modifier was increased beyond a certain critical level which was dependent on the cohesive strength of the ABS modifier. It was concluded that the deformation mode of PC/ABS blends could be explained in terms of the theory of instability of plastic deformation in the region of pre-formed voids under dilatational stress. Furthermore, toughness improvement was found to be very sensitive to the decrease of cohesive strength of the modifier and was efficiently accomplished by the addition of a small amount of the modifier of low cohesive strength.

(Keywords: PC/ABS blend; toughness; crazing; instability of plastic deformation; relaxation of strain constraint)

INTRODUCTION

It is now well established that fracture of ductile materials proceeds via the nucleation of numerous voids and then the unstable plastic expansion of these voids. The general yielding between voids is a criterion of fracture for ductile metallic materials[1-4]. In polymeric materials, crazing is an unstable local plastic deformation together with the nucleation of voids, followed by their growth and coalescence[5,6]. The brittle fracture of polymeric materials is developed by the rupture of fibrils in the crazes. The mechanism of crazing is the same as that of ductile metallic materials except for the formation of fibrils.

Recently, we have discussed the deformation and fracture processes of semicrystalline polymers such as polyethylene (PE)[7], polypropylene (PP)[8] and polymethylpentene (PTX)[9]. These examinations suggested that localization of plastic strain, such as occurs during crazing, arises when the stored elastic energy becomes larger than the energy required to propagate the craze under the high dilatational stress caused by the plastic constraint, although the mode of plastic deformation is stable when the plastic constraint is low. Furthermore, these mechanisms were confirmed by finite element analysis for an elastic–plastic material containing a two-dimensional array of cylindrical voids under the presence of expansion stress[9]. It was suggested that the criterion for plastic instability depends on the stress for void nucleation, the density of voids and on boundary conditions such as specimen geometry. Therefore it can be expected that the mode of deformation and toughness will be improved by control of these factors.

It is well known that enhancement of toughness can be achieved by the blending of polymers. We have already discussed the toughening mechanisms of bisphenol-A polycarbonate (PC) blended with poly(acrylonitrile–butadiene–styrene) (ABS) copolymer[10,11]. It was concluded that relaxation of the stress concentration to a lower stress level than the craze strength, due to the formation of voids from the ABS particles, is a basic mechanism for toughening in these polymer blends. The deformation process of polymer blends is the same as that of a ductile material having a heterogeneous structure. Therefore it can be assumed that the mode of deformation and toughness of polymer blends will depend on the density of voids, which is controlled by both the content and cohesive strength of the modifier, and on the molecular weight of the matrix polymer, which relates to the craze strength of the blend.

The purpose of this paper is to examine the effect of ABS composition and molecular weight of matrix polymer (PC) on both the mode of deformation and the toughness of PC/ABS blends on the basis of the instability of plastic deformation in the region of pre-formed voids under dilatational stress.

Table 1 Composition of ABS modifiers

ABS	AN(wt%)	Rubber(wt%)
A	27.6	15.0
B	26.0	25.0
C	25.0	40.0

EXPERIMENTAL

Materials

The matrix materials used were three commercial grades of PC with molecular weight (M_v) of 22 500, 25 000 and 30 000. Three grades of ABS with almost the same content of acrylonitrile (AN) but with different contents of butadiene rubber (*Table 1*) were used as modifier. The AN content was nearly constant regardless of the kind of ABS in order to keep a constant compatibility. The parent PC was blended with ABS at ratios resulting in an ABS volume fraction of 5 to 30 vol%. PC pellets and ABS granules were premixed in a mixer and melt-blended with the barrel temperature set at 513 K.

Specimen preparation

For the tensile tests, sheets 0.5 mm thick were compression moulded at 503–533 K. The cooling temperature was 353 K. Tensile specimens were prepared by milling into a rectangular shape with a width of 6 mm and length of 130 mm. Rectangular bars with thickness of 6 mm and width 12.5 mm for the three-point bending tests were injection moulded at 533 K with a mould temperature of 353 K. A round notch with a radius of 0.5 mm was shaped by machining with a convex milling cutter. The ligament thickness was 4.0 mm. The specimens were cooled with water during machine processing to prevent their rise in temperature.

Mechanical analysis

Material constants such as elastic modulus and yield stress were calculated from uniaxial tensile tests carried out at a strain rate of 0.2 min^{-1} at 296 K. Toughness was measured by three-point bending tests of U-notched bars under plane strain state. The specimens were loaded at a bending rate of 2 mm min^{-1} with a span length of 40 mm in an Instron type testing machine (Auto Graph, Shimadzu DSS-5000). The effect of bending rate on the toughness was examined at rates ranging from 0.125 to 125 mm s^{-1} with an Instron type servohydraulic testing machine (Servo Pular, Shimazu EHF-EB6-10L).

Morphological analysis

To determine the deformation processes of U-notched bars in three-point bending tests under plane strain, thin sections of about 25 μm were cut normal to the initial notch plane using a microtome. The morphology of the craze and plastic deformation zone was studied with an optical microscope for the microtomed sections. Changes in microstructure on the surfaces of cryogenically fractured samples were observed with a scanning electron microscope. Samples, which had been subjected to the bending test, were first immersed in a liquid nitrogen bath for 5 min and then broken normal to the plane of the notch immediately after removal. Because strain recovery on unloading significantly influences the morphology of the deformation zone, the deformation by three-point bending was fixed by casting in an epoxy resin[11], which consisted of 100 parts per hundred of resin (phr) of Epon 828 and 60 phr of Ankamide 506.

RESULTS

Tensile properties

Figure 1 shows the stress–strain curves of PC and the three grades of ABS with different rubber contents. The stress–strain curves of PC were almost independent of the molecular weight. There was a marked drop in the elastic modulus and yield stress of ABS with increasing rubber content. The yielding or so-called craze yielding of ABS is a cavitation process which induces the development of stable crazes. Therefore these results suggest that the cohesive strength of the modifier, which resists the formation of voids, decreased with increasing rubber content in ABS.

Figure 2 shows the variation of the yield stress of PC/ABS blends as a function of ABS content; the molecular weight of the PC matrix was 22 500 in these blends. Both elastic modulus and yield stress became progressively larger with increasing ABS content in the case of a lower content of rubber in ABS; on the contrary, as the content of rubber in ABS was increased, these values decreased with increasing ABS content. The yielding of pure ABS in the tensile tests is by crazing, which induces an expansion of volume. On the other hand, the tensile deformation of PC/ABS blends is mainly governed by pure shear deformation without the expansion of volume. Therefore the development of crazes from the modifier in PC/ABS blends was depressed. As a result, the resistance to deformation of ABS particles was increased in the tensile test of PC/ABS blends.

Toughness

Effect of ABS composition. The effect of modifier content on the toughness of PC/ABS blends was examined by use of a PC matrix with molecular weight of 22 500. *Figure 3* shows the variation of bending moment–displacement curves of U-notched bars of PC/ABS blends as a function of ABS content. In the case

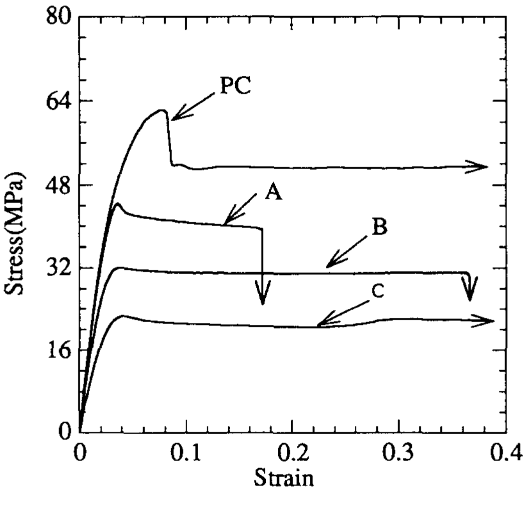


Figure 1 Variation of the stress–strain curves of PC (molecular weight = 22 500) and the three grades of ABS with different rubber contents: A, 15 wt%; B, 25 wt%; C, 40 wt%

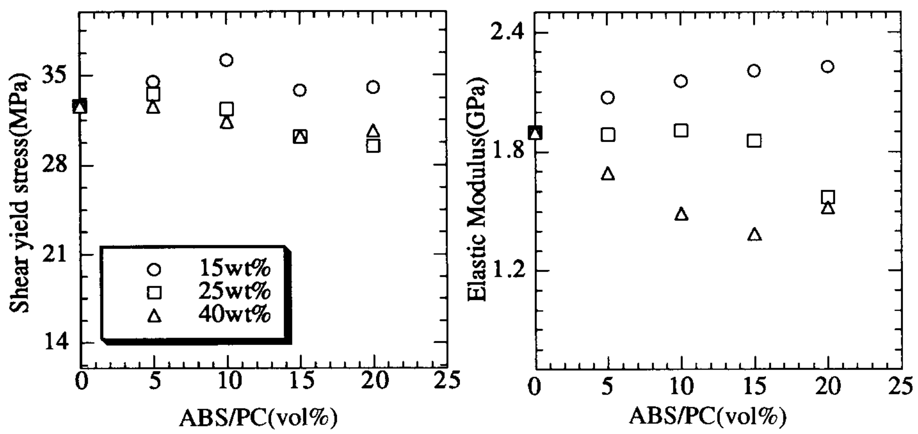


Figure 2 Variation of the yield stress and elastic modulus of ABS/PC blends as a function of ABS content. Molecular weight of PC = 22 500

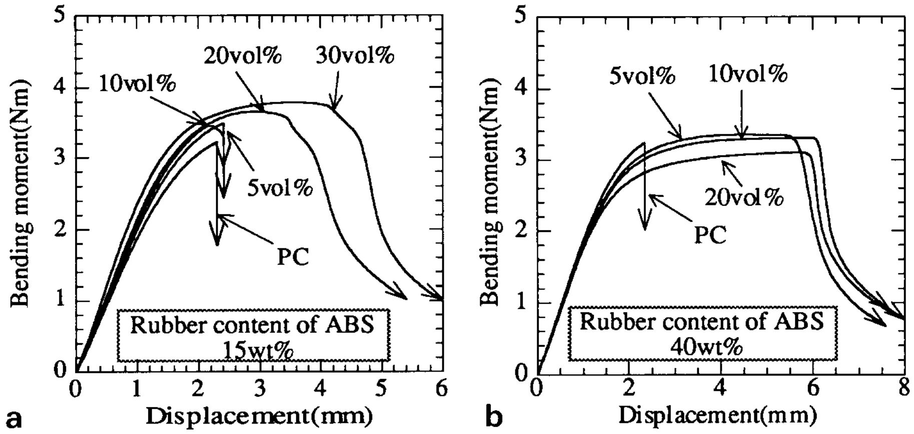


Figure 3 Variation of the bending moment–displacement curves of ABS/PC blends as a function of ABS content. Molecular weight of PC = 22 500. Rubber content of ABS: (a) 15 wt%; (b) 40 wt%

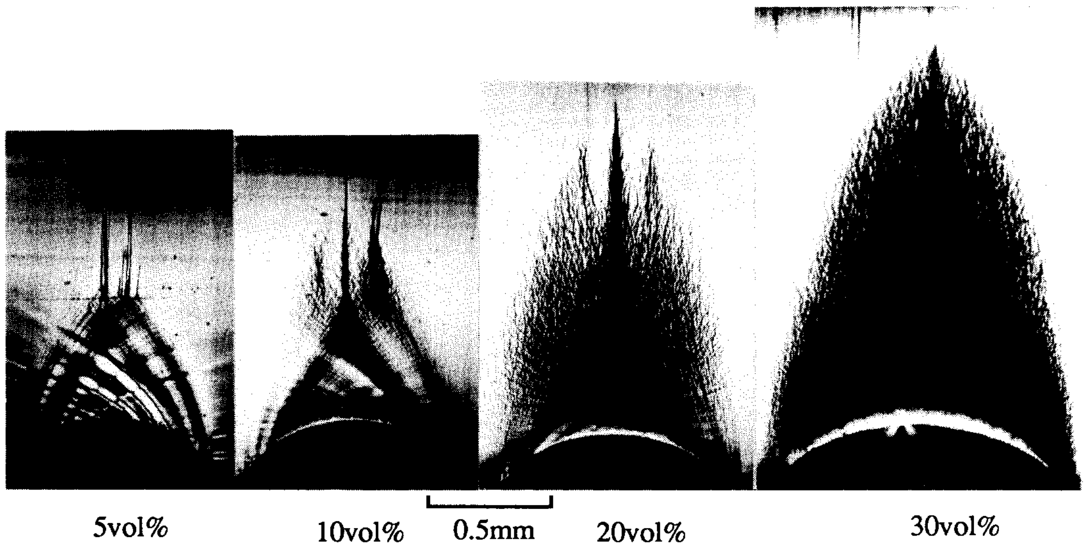


Figure 4 Polarized micrographs of the deformation zone of ABS/PC blends as a function of ABS content. Molecular weight of PC = 22 500; rubber content of ABS = 15 wt%

of the lower content of rubber in ABS, the mode of fracture varied from brittle fracture to ductile plastic deformation as the ABS content increased beyond 15 vol%, as shown in *Figure 3a*. On the other hand, as shown in *Figure 3b*, the addition of only a few per cent of the ABS modifier containing 40 wt% rubber resulted in the brittle to ductile transition in the blends. In this case, when the content of ABS was further increased, the general yield moment (i.e. maximum bending moment) was slightly decreased.

Figure 4 shows polarized micrographs of cross-sections obtained from unbroken samples, which were unloaded immediately before for brittle fracture samples and at the maximum bending moment for ductile fracture samples. The rubber content in ABS was 15 wt% in these cases. A local plastic zone together with the development of shear bands was initiated from the tip of the notch by loading. As this local plastic zone reached a certain critical size, voids were nucleated from the modifier. Numerous crazes or concentrated deformation bands were developed as this plastic zone containing voids was further spread out in the specimen with lower content of ABS (ABS content; 5–15 vol%). Fracture occurred by the nucleation of a crack from the crazes. When the content of modifier was increased beyond a certain critical level, the mode of deformation was transformed into a stable mode by the depression of craze nucleation, as shown in the micrograph of the sample containing 30 vol% of modifier. This stable plastic deformation zone was composed of a shear plastic zone containing the numerous fine voids. It was apparent that the change of deformation mode was easily brought about by the addition of a small amount of the ABS modifier with the higher rubber content.

The effect of the cohesive strength of the modifier on the toughness is shown in *Figure 5*, which presents bending moment–displacement curves of U-notched bars of PC/ABS blend containing 10 vol% of ABS. The improvement of toughness was found to be very sensitive to the decrease of cohesive strength of the modifier. *Figure 6* shows polarized micrographs of cross-sections which illustrate the change of deformation mode with cohesive strength of the modifier. It is clear that the deformation mode became stable as the cohesive strength of the modifier was decreased.

It is well known that the toughness of polymeric materials decreases with increasing loading rate. This mechanism can be illustrated by the slight change of the critical stress of craze nucleation compared with the shear yield stress as the loading rate is increased[12]. The same change due to increasing loading rate also occurred in the PC/ABS blends. *Figure 7* shows the effect of bending rate on the toughness of PC/ABS blends with 30 vol% ABS, the rubber content of the ABS being 15 wt%. It is obvious that increasing the bending rate induced the ductile to brittle transition. Naturally, this transition

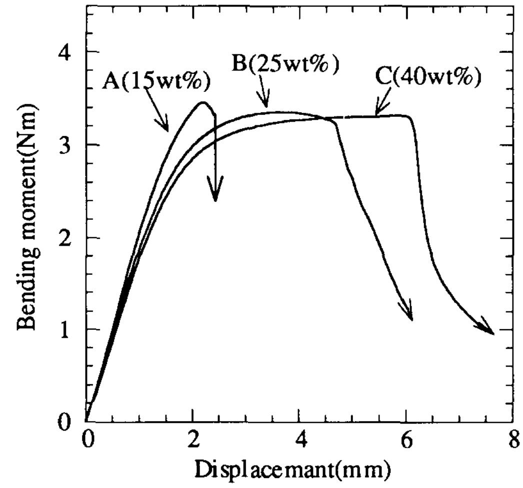


Figure 5 Variation of the bending moment–displacement curves of ABS/PC blends as a function of the rubber content of ABS: A, 15 wt%; B, 25 wt%; C, 40 wt%. Molecular weight of PC = 22 500; ABS content = 10 vol%

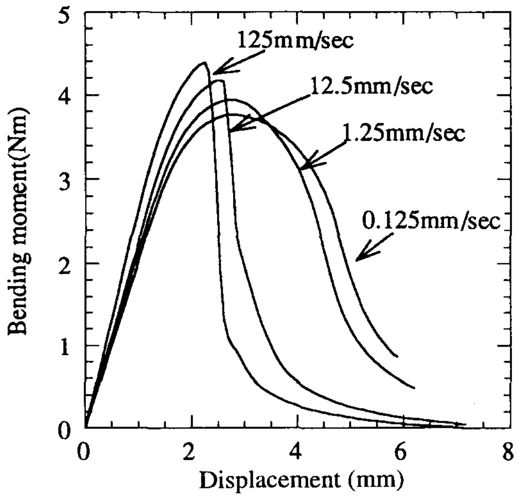
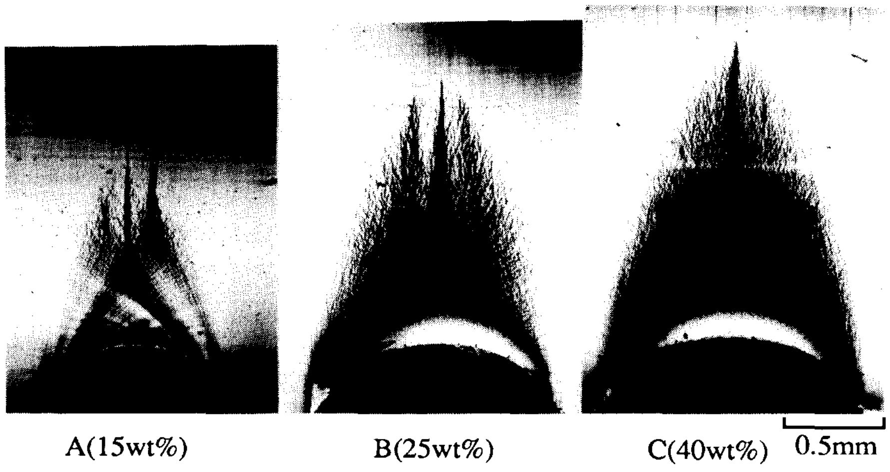


Figure 7 Variation of the bending moment–displacement curves of ABS/PC blends as a function of bending rate. Molecular weight of PC = 22 500; ABS content = 10 vol%; rubber content of ABS = 15 wt%



A(15wt%) B(25wt%) C(40wt%)

Figure 6 Polarized micrographs of the deformation zone of ABS/PC blends as a function of the rubber content of ABS: A, 15 wt%; B, 25 wt%; C, 40 wt%. Molecular weight of PC = 22 500; ABS content = 10 vol%

could be depressed by use of the ABS which contained the higher content of rubber. Because the sensitivity of the mechanical properties of ABS to the loading rate is greater than that of PC, it is suggested that the variation of toughness with loading rate was mainly governed by the mechanical properties of the ABS.

Effect of molecular weight of matrix PC. *Figure 8* shows the variation of bending moment–displacement curves of U-notched bars of PC with molecular weight. The toughness of PC improved with increasing molecular weight because the size of the local plastic zone required to nucleate the internal crazes increased with increasing molecular weight, as shown in *Figure 9*. *Table 2* shows the critical dilatational stresses for craze nucleation estimated from the critical sizes of the local plastic zone required to nucleate internal crazes and the shear yield stresses calculated from the uniaxial yield stresses by dividing by $\sqrt{3}$ using slip-line field theory[13]. These results suggest that the critical stress for nucleation of internal crazes increased with increasing molecular weight of PC although the shear yield stress is independent of the molecular weight.

Figure 10 shows the effect of the molecular weight of the PC matrix on the toughness of PC/ABS blends containing 10 vol% of ABS with a rubber content of 15 wt%. As can be seen, an improvement of the toughness of PC/ABS blends was accomplished by the addition of a small amount of ABS if the molecular weight of the matrix of PC was high. It is easy to infer these results from *Figure 8*.

Figure 11 presents polarized micrographs of cross-sections showing the deformation process of PC/ABS blends; the molecular weight of PC used was 30 000. As the local plastic zone reached a certain critical size, concentrated deformation bands such as crazes were nucleated at the tip of this zone in the same manner as that of PC/ABS blend with lower molecular weight PC. However, these concentrated deformation bands could

Table 2 Variation of critical hydrostatic stress for craze nucleation with molecular weight of PC

Molecular weight	Shear yield stress (MPa)	Critical dilatational stress for craze nucleation (MPa)
L (12 500)	32.9	78.5
M (25 000)	31.4	81.6
H (30 000)	33.2	93.5

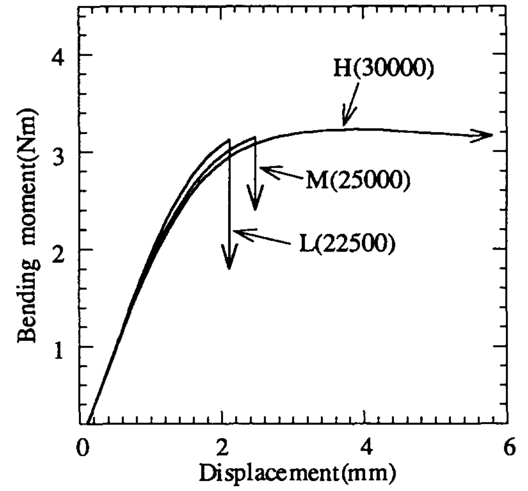


Figure 8 Variation of the bending moment–displacement curves of PC as a function of molecular weight: L, 22 500; M, 25 000; H, 30 000

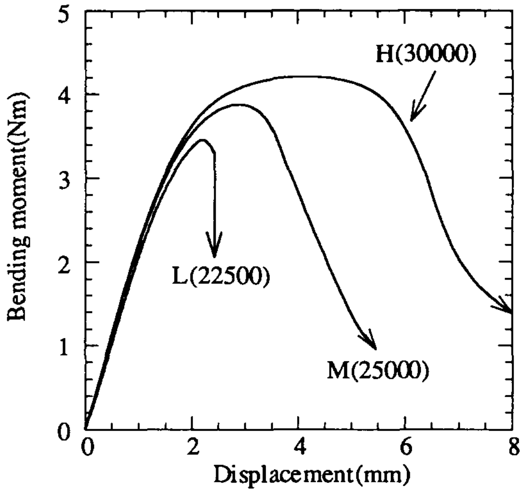


Figure 10 Variation of the bending moment–displacement curves of ABS/PC blends as a function of the molecular weight of the PC matrix: L, 22 500; M, 25 000; H, 30 000. ABS content = 10 vol%; rubber content of ABS = 15 wt%

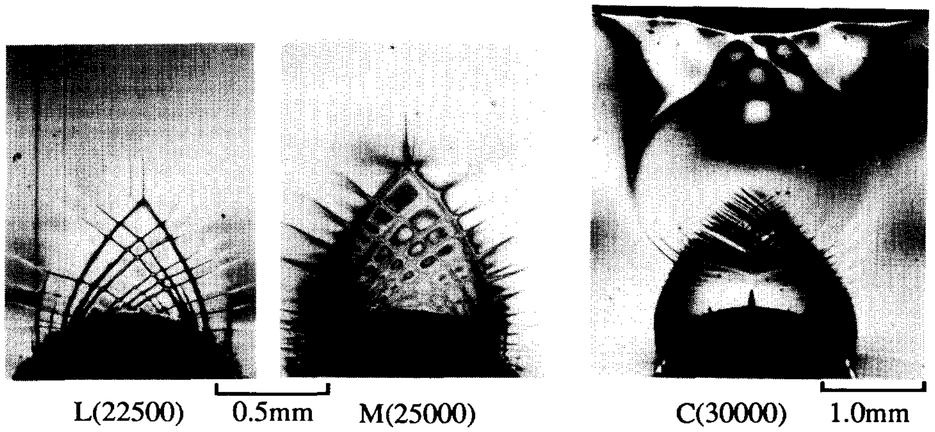


Figure 9 Polarized micrographs of the deformation zone of PC as a function of molecular weight: L, 22 500; M, 25 000; H, 30 000

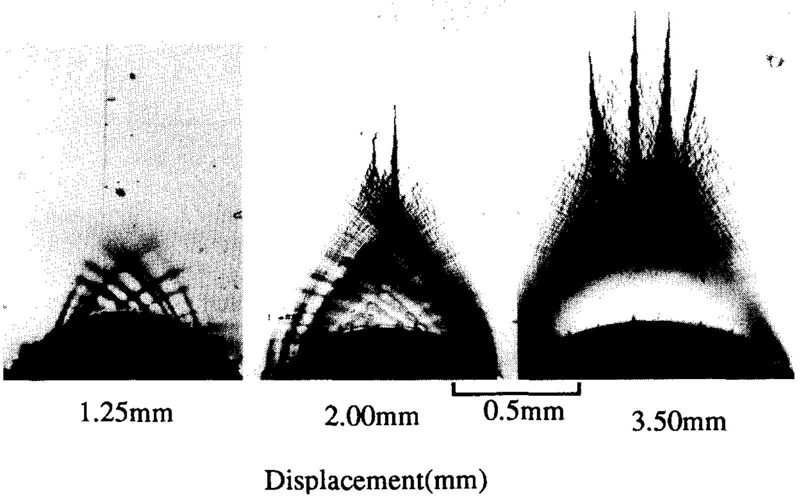


Figure 11 Variation of the deformation zone of ABS/PC blends as a function of displacement. Molecular weight of PC = 30000; ABS content = 10 vol%; rubber content of ABS = 15 wt%

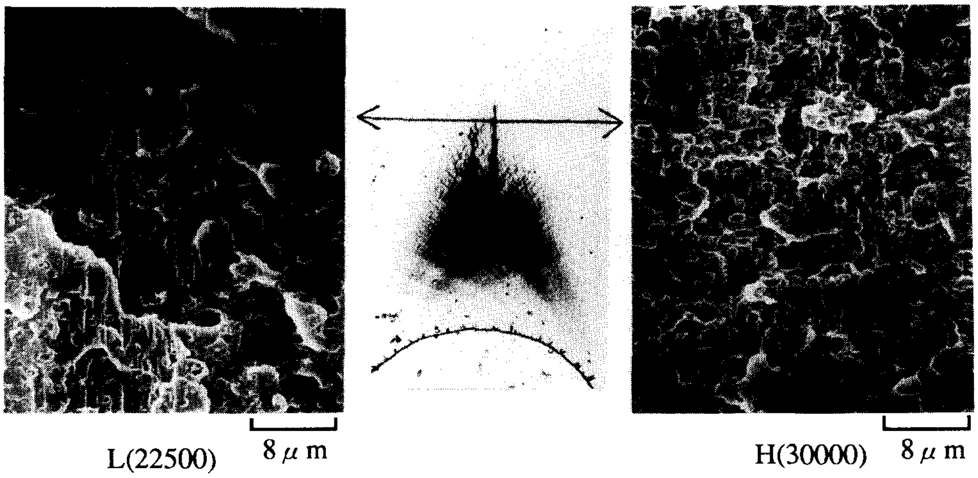


Figure 12 Scanning electron micrographs of unstable concentrated plastic deformation bands. Molecular weight of PC: L, 22500; H, 30000. ABS content = 10 vol%; rubber content of ABS = 15 wt%

be propagated perpendicular to the maximum principal stress over a wide range, as opposed to the case of PC/ABS blend with lower molecular weight PC. It should be noted that this deformation process was independent of the molecular weight of matrix PC, in contrast to the variation of toughness. The brittle fracture of PC/ABS blends composed of lower molecular weight matrix PC was initiated from the concentrated deformation bands shown in the micrographs at displacement of 2.0 mm. Needless to say, as the molecular weight of the PC matrix was increased, the displacement required to fracture was increased and the fracture from these concentrated deformation bands was depressed because of the higher strength of the fibrils. *Figure 12* shows scanning electron micrographs of concentrated deformation bands. In the case of the lower molecular weight PC matrix, internal crazes nucleated between ABS particles were clearly observed. On the other hand, in the case of the PC of higher molecular weight, the deformation zone was composed of voids nucleated from ABS particles and a plastic deformation zone around the voids.

DISCUSSION

Deformation mode of PC/ABS blends

The foregoing results indicate that the stability of plastic deformation is influenced by the content of modifier (ABS) in PC/ABS blends and the rubber content in ABS, and is independent of the molecular weight of the PC matrix. In recent studies[9], we have examined the instability of plastic deformation in the region of pre-formed voids on the basis of the understanding of dilatational yielding. *Figure 13* describes the relations between stability for the growth of voids and the stress condition. If a local stress such as a pure shear stress acts mainly on a region of voids, in which the expansion component of stress is low, the volumeric expansion becomes negligible and the plastic deformation is stable

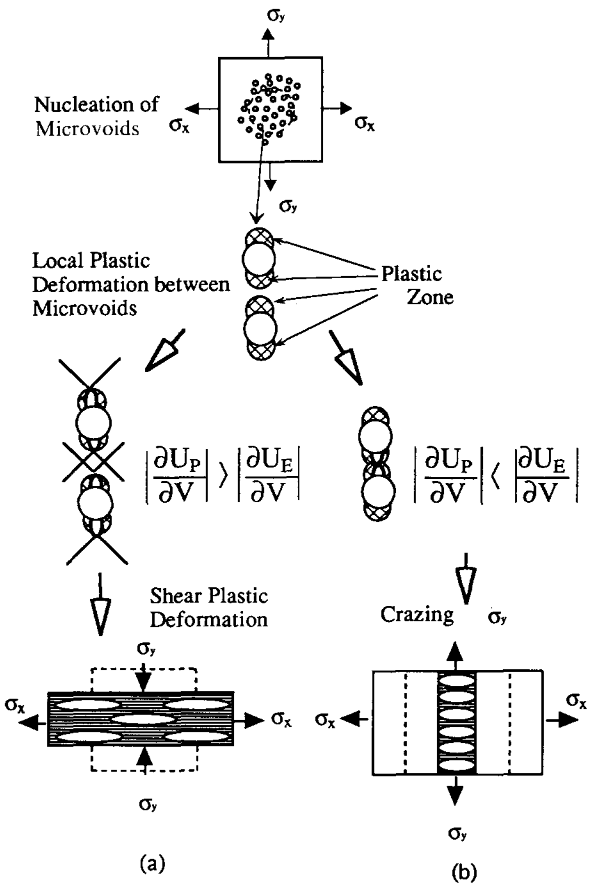


Figure 13 Schematic illustration of the deformation processes of voids

as shown in *Figure 13a*. However, in the presence of dilatational stress, the porosities can be expanded plastically (*Figure 13b*). When the rate of change of the energy for plastic deformation ($|\partial U_P/\partial V|$) by the expansion of holes of volume V is less rapid than the allowable decrease of the elastic strain energy ($|\partial U_E/\partial V|$) for the growth of holes, i.e.

$$\left|\frac{\partial U_P}{\partial V}\right| < \left|\frac{\partial U_E}{\partial V}\right| \tag{1}$$

the plastic strain is spontaneously concentrated into a narrow region. This concentrated unstable plastic deformation is a craze.

It has already been reported that the local radial stress appears to play an important role in the unstable expansion of voids. The criterion for craze nucleation by the unstable concentration of plastic strain generally depends on both dilatational stress and shear stress. Argon[14] has prescribed a condition for an unstable expansion of voids caused by the dilatational stress only, i.e. the craze criterion, as

$$\sigma_P = \frac{2}{\sqrt{3}}\tau \ln\left(\frac{1}{\beta}\right) \tag{2}$$

$$\beta < \frac{1}{1+(2\mu/\sqrt{3}\tau)} \ (=\beta_{crit}) \tag{3}$$

where β is the volumetric ratio of porosities, defined from a ratio of the average diameter of the pores to the average distance between the neighbouring hollow spheres; μ is the shear modulus; and τ is the shear yield stress. When general yielding takes place between the voids below a critical void content (β_{crit}) by the critical dilatational stress ($\sigma_{P_{crit}}$) indicated by equation (2), the rapid growth and concentration of plastic strain occurs by satisfying the condition of equation (1). This example could be observed at the tip of the local plastic zone initiated from the U-notch for PC/ABS blends with a low content of modifier (see *Figure 4*). On the other hand, when the volume fraction of voids is greater than β_{crit}, the plastic deformation is stable even if general yielding occurs between voids. This relation is illustrated in *Figure 14*. The plastic zone of PC/ABS blends with high ABS content (*Figure 4*) and that of blends in which ABS has a higher rubber content (*Figure 6*) are such examples. Even though the volume fraction of voids is below β_{crit}, if the dilatational stress component is less than the value of equation (2), then the plastic deformation in the region of voids is mainly caused by the shear stress beyond the general yield condition and this deformation process is stable. Such a case was observed near the tip of the notch.

Toughness of PC/ABS blends

For a material to have a high toughness, it needs to possess an effective energy-absorbing mechanism. It appears that massive crazing and shear flow are the most frequently encountered energy-absorbing mechanisms[15–18]. Several mechanisms have been proposed to account for the toughness of rubber-modified polymers[19]. For example, the effects of interparticle distance and particle size on toughening were analysed by Wu[20,21].

We have already discussed the energy-absorbing mechanisms of polymer blends based on the fracture mechanism. Brittle fracture originates from the breakdown of fibrillar bundles in the craze. The stress required to break the fibrils is caused, of course, by the constraint of strain. The strength of fibrils and constraint of strain were influenced by both the content and the cohesive strength of the modifier. The fibril strength of PC/ABS blends may decrease with increasing modifier content because the cohesive strength of the modifier is low. Therefore, in order to improve the toughness of PC/ABS blends, sufficient release of the constraint of strain by the development of voids was required to supplement the decrease of strength of fibrils. It can be suggested from the experimental results that the density of voids is sensitive to the cohesive strength of the modifier, and the release of plastic constraint is efficiently accomplished by the addition of a small amount of the modifier with low cohesive strength.

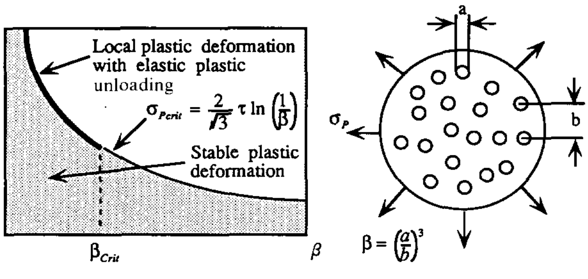


Figure 14 Instability of plastic deformation by elastic unloading

It is obvious that increasing the molecular weight of the PC matrix was effective in improving the toughness of the PC/ABS blend because the nucleation of a crack from the crazes was depressed in the blend with the high molecular weight PC. Therefore, in these samples, the stable crazes could be propagated over a wide range. This type of crazing can be also observed in crystalline polymers. The nucleation of voids in crystalline polymers is easy because the distribution of cohesive strength is wide on account of the heterogeneous structure. As a result, the crazes are initiated at a lower stress level than the fibril strength. Therefore the propagation of crazes in crystalline polymers is stable.

CONCLUSIONS

Stability of plastic deformation and toughness of PC/ABS blends have been studied. It was concluded that the deformation mode of PC/ABS blends can be explained in terms of the theory of instability of plastic deformation in the region of pre-formed voids under dilatational stress. Furthermore, the toughness improvement was found to be very sensitive to the decrease of cohesive strength of the modifier and was efficiently accomplished by the addition of a small amount of the low cohesive strength modifier.

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