

The effect of interfacial adhesion on toughening behaviour of rubber modified poly(methyl methacrylate)*

Kilwon Cho†, JaeHo Yang and Chan Eon Park

Department of Chemical Engineering, Pohang University of Science and Technology, Pohang, 790-784, Korea

(Received 2 September 1996; revised 18 November 1996)

In order to study the effect of interfacial adhesion and particle size on the toughening behaviour of rubber-toughened poly(methyl methacrylate) (PMMA), a systematic model study has been carried out using two different kinds of particles, i.e. 'core' and 'core-shell' type particles. The core particle consists of poly(*n*-butyl acrylate) (PBA), while the core-shell particle has a PBA core and a PMMA outer shell. The prepared particles were blended with matrix PMMA. The values of fracture toughness, K_{IC} , determined by three-point-bending tests at a relatively low strain rate and room temperature, did not show any difference for core blends and core-shell blends. However, the value of K_{IC} at a high strain rate and relatively low temperature and impact strength showed a marked difference between core blends and core-shell blends. These results imply that even though there is no primary chemical bonding between PBA particles and the PMMA matrix for core blends, the interfacial adhesion strength is strong enough to induce matrix deformation at relatively low strain rate, which resulted in similar fracture toughness for both of the blends. However, at a relatively high strain rate, the interfacial failure occurs predominantly, which would not induce much of the matrix PMMA deformation, so the core blends show relatively low fracture toughness. © 1997 Elsevier Science Ltd.

(Keywords: poly(methyl methacrylate); toughening; interfacial adhesion)

INTRODUCTION

It is well known that poly(methyl methacrylate) (PMMA) can be toughened by the addition of a rubbery phase, and the deformation and fracture behaviour of rubber toughened PMMA have been the subject of many previous studies^{1–13}. In commercial applications, significant toughness improvement has been achieved by blending the matrix PMMA with separately prepared toughening particles, and the toughening particles and toughened PMMA have been commercialized successfully during the last two decades. Although many studies have been reported on the mechanical behaviour of rubber-toughened PMMA^{1–13}, there are relatively few reports on the effect of interfacial adhesion and particle size on the toughening behaviour of rubber-toughened PMMA^{10,11}.

In rubber-toughened PMMA, when the rubber phase content and the type of toughening particles are fixed, the toughening behaviour is mainly affected by the rubber particle size and interfacial adhesion. However, these two factors are interrelated with each other, i.e. changing one will change the other. It is, therefore, difficult to separate these variables, and thus determine the true effect of a given factor. Concerning the effect of interfacial adhesion, it is generally accepted that strong interfacial adhesion is essential for the superior

mechanical properties of toughened polymer alloys. However, the strength of interfacial adhesion required for maximum toughness is still unclear, i.e. whether an improvement of the interfacial adhesion between rubber particles and a matrix could further improve the toughness remains unclear. With respect to particle size, the optimum particle size for maximum toughness for rubber toughened PMMA is known to be around $0.3 \mu\text{m}$ ^{10,11,14,15}. However, the reason of existing optimum particle size has not been clearly explained.

The purpose of this paper is to clarify the effect of interfacial adhesion and particle size on the toughening behaviour of rubber toughened PMMA under different mechanical test methods, i.e. impact test and three point bending test. To clarify these effects, a systematic model study has been carried out using two different kinds of toughening particles, i.e. 'core' particles and 'core-shell' type particles. The core particle consists of poly(*n*-butyl acrylate) (PBA), while the core-shell particle has a PBA core and a PMMA outer shell for the compatibilization with matrix PMMA. The prepared particles were blended with the PMMA matrix. The interfacial adhesion between core particles and matrix PMMA is only due to van der Waals attraction, since core particles do not have a PMMA shell, whereas core-shell particles have primary chemical bonding between the PBA core and the PMMA shell. Therefore, core-shell blends are expected to have stronger interfacial adhesion than core blends. The size of the particles can be controlled by seeded emulsion polymerization techniques. In this work, therefore, the effect

* Dedicated to Professor A. N. Gent on the occasion of his 70th birthday, with best wishes

† To whom correspondence should be addressed

Table 1 The information of particle preparation and blending

	Type of particles	
	Core	Core-shell
Initiator	KPS + SBS ^a	KPS + SBS ^a
Ratio of core/shell (%w/w)	No shell	50/50
Crosslinking of PBA core	1 wt% 1,4 BDA	1 wt% 1,4 BDA
Solid content in latex	~ 10 wt%	~ 10 wt%
Blending method	Latex blending	Latex blending

^a Used as redox initiator

KPS, Potassium peroxosulfate
SBS, Sodium bisulfite

of particle size and interfacial adhesion on toughening behaviour can be investigated independently under different mechanical test methods.

EXPERIMENTAL

Materials

The methyl methacrylate (MMA) and butyl acrylate (BA) monomers were used after purification by 10 wt% NaOH solution. Potassium peroxosulfate (KPS) and sodium bisulfite (SBS) were used without further purification. 1,4-Butanediol diacrylate (1,4-BDA) was used as a crosslinking agent for the PBA rubbery core.

Particle preparation and blending

Two kinds of particles were prepared, i.e. 'core' particles and 'core-shell' particles. The rubbery core consists of PBA, and it was slightly crosslinked by 1,4-BDA to retain its spherical morphology and size during the processing and moulding of the blends. The glass transition temperature (T_g) of the core material was about -40°C by dynamic mechanical testing. PMMA was used as a shell material of core-shell particles. These particles were prepared by emulsifier-free emulsion polymerization to eliminate contamination of the particle surface by emulsifier. The particles of desired size (150–600 nm in diameter of the rubbery core) were prepared by sequential emulsion polymerization in which seed particles were first formed and sequentially grown to the desired size. The particle preparation method has been given in detail elsewhere^{10,16}. Information about the prepared particles and their blends with PMMA matrix is given in Table 1.

To study the interfacial adhesion effect, blends containing core particles or core-shell particles (coded 'core blend' and 'core-shell blend', respectively) were prepared by latex blending with PMMA latex, which was also prepared by emulsion polymerization. The rubber-phase concentration in the blends was kept constant, i.e. 10 wt%. In the calculation of rubber phase concentration, the PMMA outer shell of the particles was considered as matrix.

Specimen preparation

The blends were compression moulded into plates 5 mm thick. The moulded plates were machined into Izod impact bars ($12.6 \times 5 \times 64$ mm) and three-point-bend specimens ($5 \times 10 \times 50$ mm) and double-notched four-point-bend test specimens ($5 \times 10 \times 70$ mm).

Fracture toughness and impact strength

The stress intensity factor K_{IC} , was determined using a

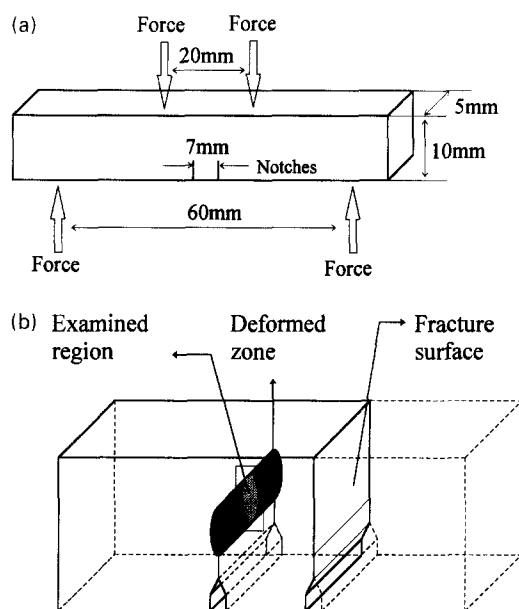


Figure 1 Schematic diagrams of (a) double-notched four-point-bend specimen and (b) regions examined by optical microscopy

single-edge notched specimen by three-point-bending tests (ASTM E399). These specimens were precracked by striking a razor blade previously chilled in liquid nitrogen. At least six specimens were employed in a single derivation of K_{IC} at each test condition. The test was performed using a universal test machine (Instron 4206). Loading rate and temperature were varied to study the interfacial adhesion effect for core blends and core-shell blends. Izod impact strength was determined using a single-edge notched specimen (notch radius 0.25 mm) at room temperature.

Adhesion strength

In order to measure the interfacial adhesion strength between PMMA and PBA at various temperatures and rates, the peel strength of PMMA/PBA adhesive joint was measured. The adhesive joint was constructed of PMMA plate (thickness 1 mm) and PBA plate (thickness 0.1 mm) with a backing cloth on the PBA plate. Peel strength was measured at various temperatures and different peel rates by a 90° peel test, using an universal test machine (Instron 4206). The master curve of peel strength of PMMA/PBA adhesive joint was obtained by shifting peel strengths measured at various peel rates and different temperatures by WLF equation at a reference temperature of -10°C .

Microscopy

The fracture surfaces of the specimens for the three-point-bending test and impact test were examined using a scanning electron microscope (SEM, Hitachi S-570). Samples were coated with a thin layer of gold-palladium. The double-notched four-point-bending test was performed to examine the deformed zone at a crack tip. The well established polishing/sectioning technique^{17–18} was employed. For this purpose, a section thin enough to transmit light was produced using petrographic polishing. The fracture sub-surfaces of the impact and double-notched four-point-bend specimens were examined under the bright field image using a

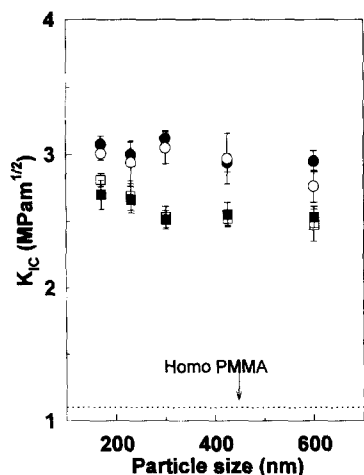


Figure 2 Fracture toughness, K_{IC} as a function of particle size for core blends and core-shell blends (rubber phase content: 10 wt%, tested at room temperature by three-point-bending test). \square , core blends; \blacksquare , core-shell blends at cross-head speed of 1.28 mm min^{-1} ; \circ , core blends; \bullet , core-shell blends at cross-head speed of 450 mm min^{-1}

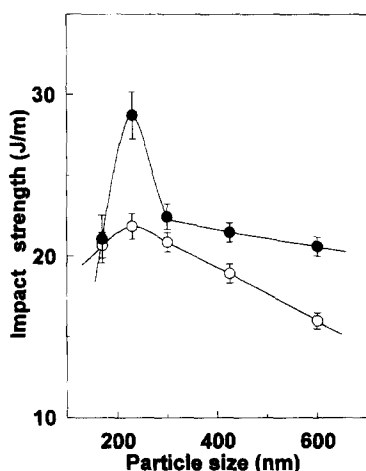


Figure 3 Impact strength as a function of particle size for core blends and core-shell blends (rubber phase content: 10 wt%, tested at room temperature). \circ , core blends; \bullet , core-shell blends

Zeiss optical microscope. A double notched four-point-bend test was employed to produce a sub-critically propagated crack and to get information on the plastic deformation of the specimens. The specimen geometry and the schematic diagram of the deformation region from the double-notched four-point-bend test specimen are shown in *Figure 1*. The test specimen has two identical cracks. During four-point-bend loading, a plastic deformation zone is formed at each crack tip by stress concentration. One of the cracks becomes critical and propagates in an unstable manner, because the cracks can never be identical. Thus the specimen is unloading, and then the other crack immediately becomes stationary. A mature plastic deformation zone at the stationary crack tip was examined by optical microscopy using cutting and polishing techniques as shown in *Figure 1*. The test method of the double-notched four-point-bend test has been given in detail elsewhere¹⁹. All samples examined were the mid parts of specimens, which satisfies the plane strain constraints.

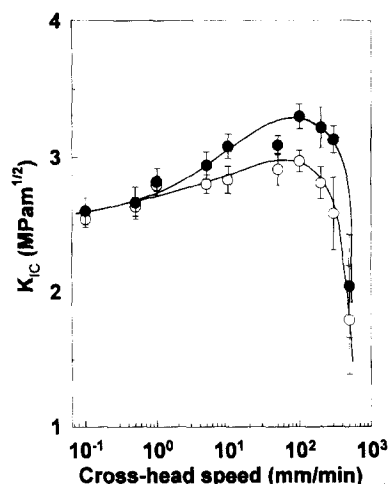


Figure 4 Fracture toughness, K_{IC} as a function of cross-head speed for core blends and core-shell blends (rubber phase content: 10 wt% of 230 nm rubbery particles, tested by three-point-bending test at -10°C). \circ , core blends; \bullet , core-shell blends

RESULTS AND DISCUSSION

The effect of interfacial adhesion and particle size

Interfacial adhesion between rubbery particles and the matrix polymer is regarded as playing an important role in the toughening of rubber-toughened polymers. It is generally accepted that a higher toughness is obtained for better adhesion^{14,15,20,21}. For core-shell particles, the outer shell is composed of PMMA chains which are effectively grafted to the PBA core. Therefore, the fracture toughness of core-shell blends is expected to be higher than that of core blends.

Figure 2 shows the variation of K_{IC} determined by three-point-bending test as a function of particle size for the two different test rates, i.e. cross-head speeds. The PBA rubbery phase content is 10 wt%. The value of K_{IC} for the blends is significantly higher than that of the matrix PMMA. However, K_{IC} values do not show any significant difference for the two different blends, core blends and core-shell blends, irrespective of the cross-head speeds considered. Moreover, there is no significant particle size effect. On the other hand, Izod impact strength results, shown in *Figure 3*, clearly show that the core-shell blends have a higher impact strength than core blends. Furthermore, *Figure 3* clearly shows that there is a maximum toughness around a particle size of 230 nm. The two different toughening behaviours from the two different test methods, i.e. the three-point-bending test and the impact test, as shown in *Figures 2* and *3*, might be due to the difference in the failure mode of matrix PMMA around particles originated from the strain rate difference.

In order to clarify the effects of interfacial adhesion and strain rate on fracture toughness of rubber toughened PMMA, the values of K_{IC} were measured by three-point-bending test with different cross-head speeds at -10°C , and the results are shown in *Figure 4*. The cross-head speed of the universal testing machine is very limited. Therefore the temperature of -10°C was chosen, because the effect of decreasing the test temperature is equivalent to increasing the test rate. As can be seen in *Figure 4*, the two blends show similar fracture toughness at relatively low cross-head speeds, however, at high cross-head speeds a marked difference

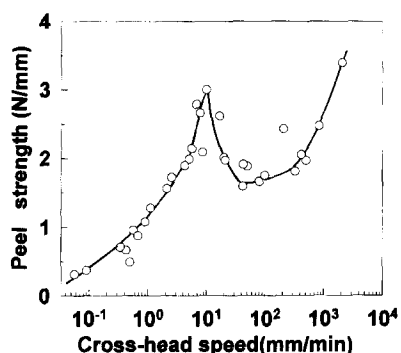


Figure 5 Master curve for peel strength vs cross-head speed (peel rate) for PBA adhesive with a cloth backing on PMMA adherend. (Reference temperature: -10°C)

occurs, i.e. the core-shell blends show a higher fracture toughness. This result correlates quite well with the results of Figures 2 and 3. The different fracture behaviour with strain rate may be due to the difference in failure mode of matrix PMMA around particles.

In order to get some insight into the fracture behaviour around the interface between particles and the matrix polymer with strain rate for core blends, a model adhesion study was conducted by peel test using PMMA/PBA adhesive joints. The model adhesive joints were made up of a PMMA plate and a PBA plate with a backing cloth on a PBA plate. The peel strength of the PMMA/PBA adhesive joints was measured at various temperatures and different peel rates and the results were shifted by WLF equation with a reference temperature of -10°C . As can be seen in Figure 5, the data superpose quite well. Figure 5 shows a quite common pattern for the peeling of viscoelastic adhesives from rigid

adherend²², i.e. a steady rise in peel strength with peel rate up to a critical rate, then an abrupt transition to much lower peel strength. At the same time, the locus of failure changes abruptly from the cohesive failure of adhesive layer to the interfacial failure at the adhesive-adherend interface. Thus it is expected that the failure mode around rubber particles for core blends may be changed from cohesive failure to adhesive failure as the strain rate increases.

From this model peel experiment, it is speculated that even though there is no primary chemical bonding between PBA particles and PMMA matrix for core blends, the interfacial adhesion strength is strong enough to induce matrix deformation at relatively low strain rates, which resulted in similar fracture toughness for both of the blends. However, at relatively high strain rates, the interfacial failure occurs predominantly, which would not induce much of the matrix PMMA deformation, so that the core blends show relatively low fracture toughness, as shown in Figure 4. It is worth noting that the cross-head speed at which the difference in fracture toughness for core blends and core-shell blends occurs in Figure 4, i.e. approximately 10 mm min^{-1} at -10°C , appears to correspond to the cross-head speed at which the transition of cohesive-adhesive failure occurs in Figure 5.

As discussed earlier, it is generally known that in order for the rubbery particles to be effective sites for craze initiation or shear band formation, or to act as energy absorbers, then good particle/matrix interfacial adhesion is required. Typical examples are high impact polystyrene (HIPS) and acrylonitrile butadiene styrene copolymer (ABS)²¹. However, the degree of particle/matrix adhesion to induce matrix deformation is somewhat controversial, and there is a relatively limited number of

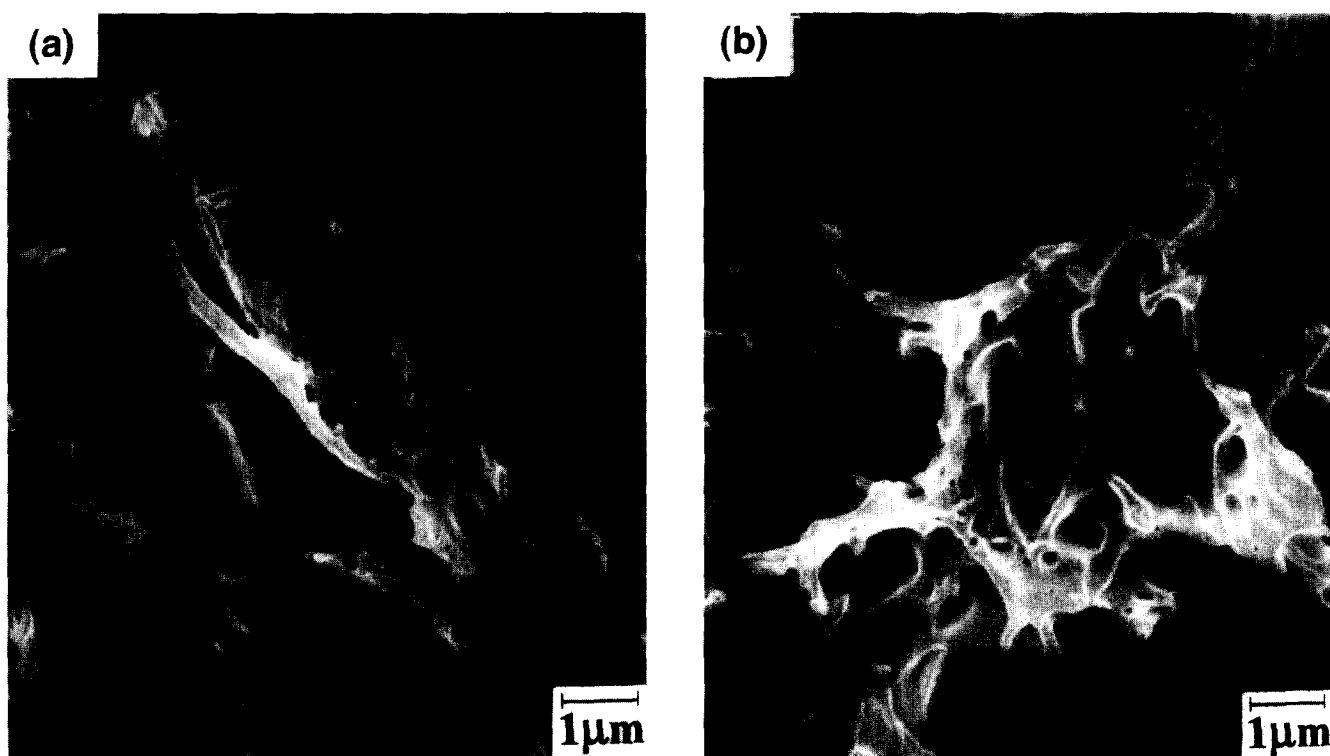


Figure 6 SEM of fracture surface of core blends and core-shell blends (rubber phase content: 10 wt% of 230 nm rubbery particles, tested by three-point-bending test at -10°C and cross-head speed of 100 mm min^{-1}): (a) core-shell blends; (b) core blends

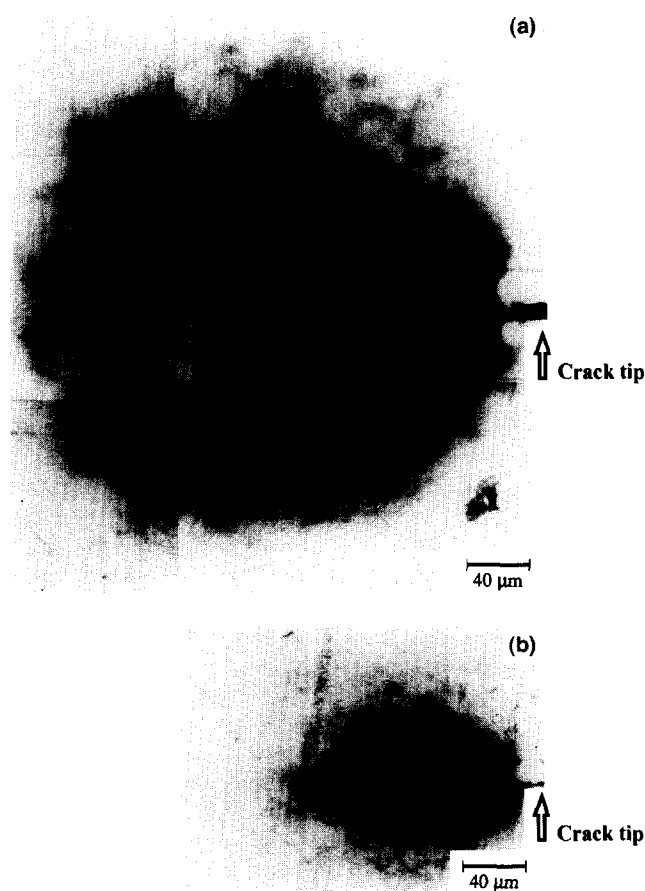


Figure 7 Optical micrograph of thin section of deformed zone in front of the crack tip for core blends and core-shell blends (rubber phase content: 10 wt% of 230 nm rubbery particles, tested by double-notched four-point-bending test at -10°C and cross-head speed of 100 mm min^{-1}): (a) core blends; (b) core-shell blends

reports on this subject^{21,23,24}. Gaymans and coworkers reported that the degree of interfacial adhesion does not much influence the impact toughness of nylon/rubber blends²³. Also Wu has stated that impact toughness of nylon/rubber blends is not much affected by the interfacial adhesion, and only van der Waals attraction is enough for the toughening of nylon, in which the deformation mode is mainly shear yielding²⁴. However, in our study, interfacial adhesion seems to contribute greatly to the fracture toughness, particularly for a high strain rate test such as the impact test, or K_{IC} values at low temperature and high strain rate, as already shown in *Figures 3* and *4*.

Considering the stress around particles, it was suggested that stress concentrated by the addition of rubber particle must be higher than the yield stress or craze stress of the matrix polymer for toughening of multiphase polymers^{6,25}. Therefore, the interfacial adhesion strength should be at least higher than the yield stress or craze stress of the matrix for sufficient toughening. In the case of good interfacial adhesion, the interfacial adhesion strength is strong enough to endure the build-up of sufficient stress around the particles, which induces crazing of the matrix, voiding in the rubber particles or cavity formation around interface at some critical stress level. The voiding or cavity formation transforms the stress field from tri-axial stress to plane stress, which induces shear yielding of the matrix²⁶. In this instance, the tear energy of rubber

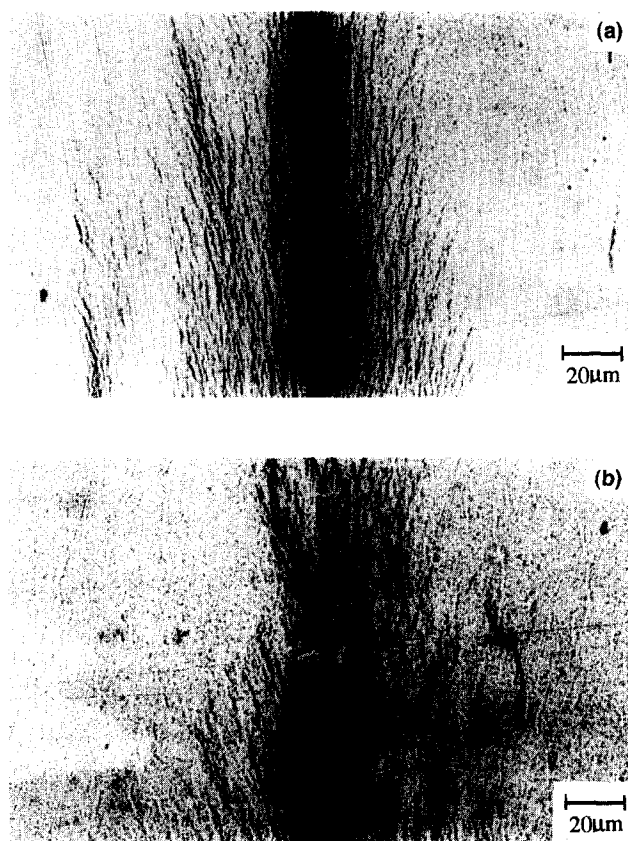


Figure 8 Higher magnification of massively deformed inner region of *Figure 7*: (a) core blends; (b) core-shell blends

particles or interfacial adhesion strength has the window for toughening.

Since the interfacial adhesion strength is highly dependent upon strain rate, as already shown in *Figure 5*, and yield or craze stress of the PMMA matrix is relatively constant compared with interfacial adhesion strength with strain rate, just van der Waals attraction is not enough for toughening of PMMA/PBA blends at high strain rate. In high strain rate tests such as the impact test or the three-point bending test with a high cross-head speed at -10°C , core-shell blends which have stronger interfacial adhesion showed superior toughness to the core blends. On the other hand, at low strain rate, van der Waals attraction between core particles and PMMA matrix seems to be strong enough to induce PMMA matrix deformation. Therefore, the K_{IC} values of both of the alloys do not show any marked difference at low strain rate. These results imply that the effect of interfacial adhesion on fracture behaviour of rubber toughened polymer alloys is strongly dependent upon test rate.

Fractography

SEM of the fracture surface for core blends tested by the three-point-bending test at -10°C shows no big differences in comparison to the fracture surfaces of core-shell blends (*Figure 6*). This result suggests that the deformation mechanism of both blends is essentially the same. The fracture surfaces are very rough and show the presence of holes and dome-like features. The diameter of some holes and dome-like features are slightly bigger than those of PBA rubbery particles, whilst some are much smaller in diameter. The large holes represent the

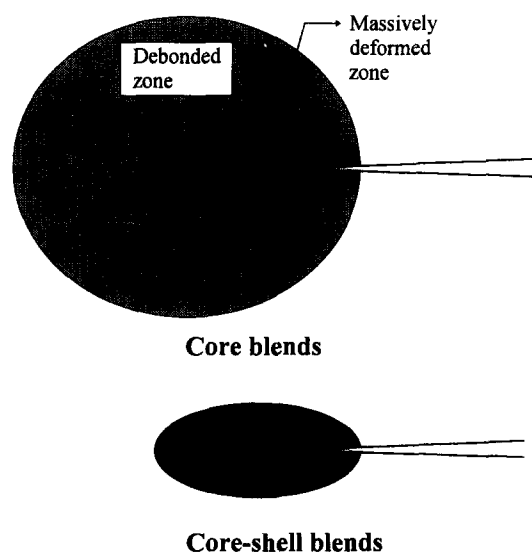


Figure 9 Schematic diagram of deformed zone around crack tip as shown in Figure 7

position occupied by PBA particles. The PBA particles seem to be located deep in the big holes. Therefore, the PBA rubbery particles are hard to see on the fracture surfaces. It seems that severe plastic deformation occurred around the particles, and this drew the particles deep into the surface layer. However, at this moment, the mechanism of formation of small holes is not clear.

In order to get the information of the deformation process at the crack tip, a four-point-bend test was performed, and the optical micrographs obtained are shown in Figure 7 and Figure 8. Figures 7a and 7b are optical micrographs of the deformation zone around the crack tip obtained from the unfractured notch tip of the double-edge notched four-point-bending test specimen. One may identify two deformation zones, i.e. a smaller and darker elliptical zone which is very close to the crack tip, and an outer grey circular zone of a few hundred microns in diameter. The deformation zone in Figures 7a and 7b is represented schematically in Figure 9. Core blends have both the big outer deformation zone and the elliptical zone. On the other hand, core-shell blends have only the inner elliptical zone and no outer deformation zone. Since both core and core-shell particles have the same properties, i.e. the same degree of crosslinking and the same modulus except for interfacial adhesion, the outer region of core blends might be caused by the interfacial failure, i.e. debonding between matrix and rubber particles which occurs at relatively low stress due to the weak interfacial adhesion.

Closer scrutiny of the inner region in both blends by higher magnification shows that fine bands propagate between particles and the bands of both blends are essentially very similar to each other, as shown in Figure 8. These bands are caused by the deformation of the PMMA matrix. Careful examination on the micrographs of the deformation zone in Figures 7a and 7b shows that the inner elliptical region for core-shell blends is slightly bigger than that of core blends, which suggests that more massive deformation occurred for core-shell blends. This microscopic observation is consistent with the K_{IC} trends in Figure 4, i.e. core-shell blends show higher K_{IC} value than core blends. Even though there is no primary chemical bonding between PBA particles and PMMA

matrix, the van der Waals interaction in core blends is sufficient to induce matrix deformation by the three-point-bending test at room temperature. However, it may not be strong enough for a high strain rate test such as the impact test. From these results it is suggested that the role of interfacial adhesion for toughening of phase separated multiphase polymers is strongly dependent upon test method and strain rate. Therefore, good interfacial adhesion is necessary to obtain sufficient toughness, irrespective of strain rate.

CONCLUSIONS

The values of fracture toughness, K_{IC} , did not show any marked difference for core blends and core-shell blends at room temperature. This implies that van der Waals attraction is strong enough for toughening of phase separated multiphase polymers for low strain rate test. However, the values of K_{IC} at -10°C and at high strain rate and impact strength showed a marked difference between core blends and core-shell blends. From these experimental results, it is concluded that the role of interfacial adhesion for toughening of phase separated multiphase polymers is strongly dependent upon test method and strain rate. For sufficient toughness in the high strain rate test, the interface between rubber particles and the matrix polymer should be strong enough to induce much plastic deformation of the matrix. Therefore, good interfacial adhesion is necessary to obtain sufficient toughness, irrespective of strain rate.

ACKNOWLEDGEMENTS

This work was supported in part by a research grant from the Ministry of Education Research Funds for Advanced Materials, 1994. The research grant from the School of Environmental Engineering of Pohang University of Science and Technology is also gratefully acknowledged.

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