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Effect of the orientation hardening of matrix polymers on the toughness of polymer blends

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The effect of orientation hardening of matrix polymers on the toughness of polymer blends was examined. Both poly(methyl methacrylate) (PMMA) and poly(vinyl chloride) (PVC), with different characteristics of orientation hardening were used as matrix polymers and a silicone/acrylic composite rubber graft copolymer was used as the modifier. The efficiency of the improvement in toughness for the blend with PMMA as the matrix polymer, as a result of the addition of the modifier, was lower than that of the blend with PVC. It was suggested that the strain for the initiation of orientation hardening of PMMA was lower than that of PVC. It was concluded that the lower efficiency of toughening for PMMA blended with modifier when compared to that of the PVC blend is caused by the development of orientation hardening at a lower plastic strain. Copyright © 1996 Elsevier Science Ltd.

(Keywords: orientation hardening; toughness; polymer blend)

INTRODUCTION

It is well known that ductile polymers frequently fail in a brittle manner when there is a notch or a crack in the material. The mechanism can be explained by the use of the mechanics of plasticity. As a load is applied to the specimen, the local plastic zone initiates from the tip of the notch. A maximum stress then develops at the tip of the local plastic zone which spreads across the ligament thickness ahead of the notch under the plane strain, which is distinct from the stress distribution ahead of the notch under the elastic state. When the stress ahead of the plastic zone reaches a critical stress by the extension of the plastic zone, the development of the internal craze, in which the plastic strain is locally concentrated between neighbouring voids, occurs at the tip of the local plastic zone. If the stress ahead of the local plastic zone reaches the level of the strength of the fibrils of the craze, then microrupture of the fibrils of the craze leads to the catastrophic brittle fracture[1,2].

It is already known that when a elastomer with a reduced cohesion is blended as a modifier with a matrix polymer, the increase in the applied load preferentially causes the formation of voids. When the production of voids reaches a certain density under such conditions, the phenomenon of 'Poisson shrinkage' occurs between the neighbouring voids. As a result, the strain is released from its restriction so as to reduce the stress concentration. The toughness of polymer blends is clearly improved by the suppression of brittle fracture when the general yielding takes place before the stress ahead of the plastic zone reaches the strength of the craze[3,4].

Based on the above mechanism of toughening, it can be predicted that the criterion for void formation, which depends on the mechanical properties of the modifier, strongly affects the toughening due to the polymer blend. This prediction was validated in the study of the toughness of polycarbonate (PC) blended with acrylonitrile–butadiene–styrene (ABS) copolymer with different strength[5]. From this study, it was suggested that the improvement in toughness is very sensitive to the decrease in the cohesive strength of the modifier and is efficiently accomplished by the addition of a small amount of a modifier of low cohesive strength.

There is a large plastic strain at the tip of a notch in a ductile polymer. In general, the yield stress of the polymer increases with the increase of plastic strain beyond a certain critical strain. This is the well known concept of orientation hardening[6–8]. The orientation hardening of a crystalline polymer takes place at a sufficiently large strain. As an example, the strain for the initiation of the orientation hardening of polypropylene (PP) is ca. 700%[9]. On the other hand, for PMMA[10] and various epoxy resins[11], the strain is less than 30–40%. Because the stress distribution of the plastic zone depends on the yield criterion, it can be logically presumed that orientation hardening affects the stress concentration ahead of the plastic zone.

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The purpose of this present paper is to examine the effect of orientation hardening on the toughness of polymer blends by the use of matrix polymers with different characteristics of orientation hardening.

EXPERIMENTS

Preparation of silicone/acrylic compound rubber graft copolymer

A silicone/acrylic compound rubber graft copolymer was used as the modifier. A mixture of octamethylcyclotetrasiloxane, tetraethoxysilane, and γ-methacryloxypropylmethyldimethoxysilane was added to an aqueous solution of dodecylbenzenesulfonic acid, and then emulsified. The emulsion was heated to achieve polymerization, followed by neutralization to obtain the silicone latex. The silicone latex was mixed with n-butylacrylate, and the latter was then polymerized by the use of a redox polymerization initiator to form the silicone/acrylic rubber graft copolymer. It had previously been estimated from transmission electron microscopy (TEM) of an ultrathin section of a PMMA blend that the diameter of the modifier used is ca. 0.2 μm and that the silicone and acrylate phases are separated in the silicone/acrylic compound rubber[12].

Preparation of compound specimens

The PVC compound used in this study contained 100 parts by weight of PVC resin with a degree of polymerization of 700, 3.5 parts by weight of dibutyltin maleate, 0.8 parts by weight of a poly(hydric alcohol), and 0.4 parts by weight of an acrylic processing aid. The PVC resin compound was mixed with a prescribed amount of the modifier, and extruded by using a single-screw extruder with a diameter of 25 mm to produce a square bar with dimensions of $5 \times 5 \times 12.7\,\mathrm{mm}^3$.

The PMMA used as the matrix polymer was an injection-moulding grade with a molecular weight (M_n) of 60 000. PMMA pellets and modifier were pre-mixed in a mixer and then extruded by using a single-screw extruder with a diameter of 25 mm, with the barrel temperature set at 543 K. Rectangular bars with a thickness of 6.27 mm and a width of 12.6 mm for use in three-point-bending tests were injection moulded at 543 K (molten temperature), with a moulded temperature of 313 K (cooling temperature).

Evaluation of mechanical properties

The variation of toughness upon the addition of modifier was examined by three-point-bending testing on a U-notched specimen with a ligament thickness of 3 mm, a notched-tip radius of 0.5 mm, and a span length of 40 mm. The bending rate was 2 mm min^{-1}.

The process of tensile plastic deformation for the polymer blends was examined by uniaxial tensile testing. The thickness of the specimen used was 2.0 mm for the PMMA blend and 1.0 mm for the PVC blend. The strain rate was 0.2 min^{-1}. The test temperatures were 296 and 313 K for the PVC and PMMA blends, respectively.

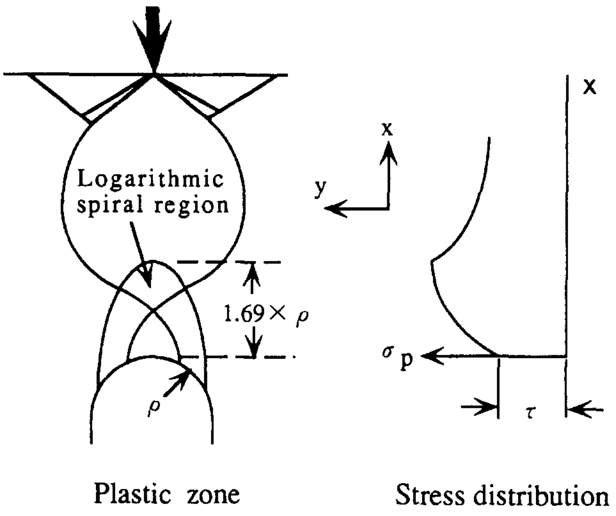
The true stress–strain curves were measured by using plane strain compression tests because PMMA fails in the brittle mode in tensile testing owing to its low molecular weight[13], and furthermore, the plastic deformation of the PVC blend becomes unstable with the development of necking. The die used in the plane strain compression tests had a width of 6 mm and a length of 12 mm; the thickness of the specimen was 2.0 mm. The strain rate was 0.2 min^{-1} and the test temperature was 296 K.

Analysis of the deformation process

In order to investigate the deformation processes of U-notched bars in three-point-bending tests under conditions of plane strain, thin sections were cut normal to the plane of the initial notch by using a microtome for the PVC blend and a microcutter for the PMMA blend on unloaded samples. The morphology of the plastic deform-ation zone was studied with an optical microscope. The fracture surfaces were observed by a scanning electron microscope (Hitachi S-450). The microstructure of the plastic deformation zones containing elastomer were observed with a high-resolution scanning electron microscope of the field emission type (Nihondinshi JSM 6031F) for surfaces of cryogenically fractured samples. Samples for subjection to the bending tests 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 of the epoxy resin, which consisted of 100 parts per hundred of resin (phr) of Epon 828 and 60 phr of Ankamide 506.

RESULTS AND DISCUSSION

The local plastic zone, which is defined by the logarithmic-spiral-line type, is developed from the notch tip when a load is applied by the three-point-bending test on U-notched bars. The size of this local plastic zone increases with an increasing applied load. The general yielding occurs by the propagation of the plastic zone through the ligament thickness, as shown in *Figure 1*. The size of the local plastic zone (logarithmic spiral region) at the general yielding point depends on the length of the span, thickness of the ligament and the yield criterion. For an elastic–plastic material without orientation hardening and the formation of voids, the stress distribution of the local plastic zone (logarithmic spiral region) which developed from the U-notch tip is described by the following equation, which is derived



Plastic zone Stress distribution

Figure 1 Plastic zone of a round notched bar produced at the general yielding point during the three-point-bending test

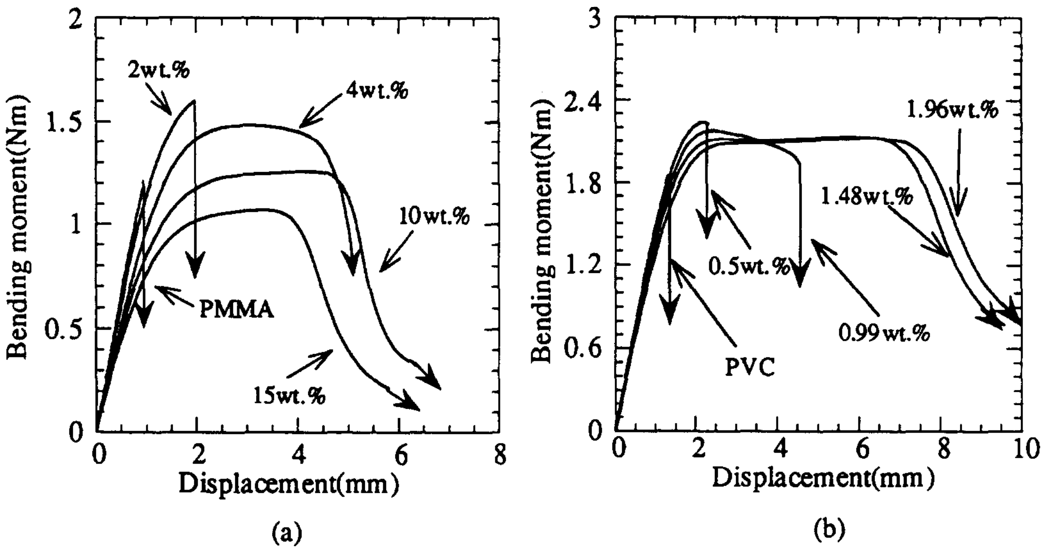


Figure 2 Variation of the bending moment–displacement curves with the addition of modifier for (a) PMMA and (b) PVC

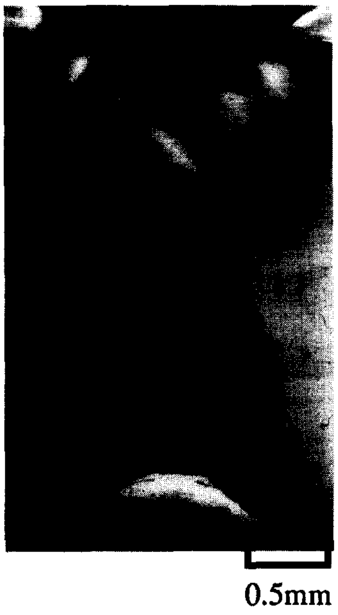


Figure 3 Photomicrograph of microtomed section of PVC blended with 1.48 wt% of modifier in which the general yielding had taken place

by the mechanics of plasticity[14], as follows:

$$\sigma_p = \tau[1 + 2\ln(1 + x/\rho)] \quad (1)$$

where $\sigma_p(= (\sigma_x + \sigma_y + \sigma_z)/3)$ is the mean stress, τ is the shear yield stress, ρ is the notch radius, and x is the distance from the notch tip. It is easily understood from this equation that there is a maximum stress at the tip of this plastic zone.

It has previously been suggested that for PMMA and PVC[2], the stress ahead of the plastic zone reaches a critical stress for nucleation of the internal craze by extending the plastic zone before general yielding takes place. Therefore, the internal craze nucleates and then microrupture of the fibrils in this internal craze leads to catastrophic brittle fracture. If an elastomer with reduced cohesion as the modifier is blended with the matrix polymer described above, the increase in applied load causes the preferential formation of voids. Poisson shrinkage between the neighbouring voids occurs at a certain density, and the strain is released from restriction to reduce the stress concentration. As a result, the toughness is improved by suppression of brittle fracture when the general yielding takes place before the stress ahead of the plastic zone reaches the craze strength.

It has already been indicated that at room temperature internal crazing in PMMA develops at a smaller size of the local plastic zone than that of PVC[2]. In order to compare the effect of toughening by the addition of modifier, the fracture criterion, i.e. the size of the plastic zone required to nucleate internal crazing in PMMA and PVC, should be controlled to be the same value. Therefore, the same ratio of stress for craze nucleation to shear yield stress is required for PMMA and PVC. When the size of the local plastic zone reaches a size of $0.7 \times \rho$ for PVC under a set loading rate and a temperature of 296 K, the internal craze nucleates at the tip of the local plastic zone and then the material breaks. The state of fracture of PMMA at a temperature of 323 K corresponded to that of PVC at a temperature of 296 K under the same loading rate. *Figures 2a* and *2b* show the variation of toughness with the addition of the modifier for PMMA and PVC, respectively. The toughness of the materials can be evaluated from the bending moment–displacement curves. It was previously suggested that the toughness of PVC blended with silicone/acrylic composite rubber is improved to a high efficiency by the addition of a small amount of modifier[15]. As shown in *Figure 2b*, under a low deformation rate, the mode of deformation for the PVC blend changed from brittle fracture to ductile deformation by the addition of only ca. 1 wt% of modifier. On the other hand, in order for general yielding of the PMMA blend to take place, the addition of 4 wt% of modifier was required. As the applied displacement was further increased, the ductile crack initiated at the tip of the notch and then fracture occurred by the propagation of this ductile crack. The displacement for the initiation of the ductile crack propagation was ca. 8 mm for PVC, which was larger than the displacement observed for PMMA (5 mm).

Figure 3 shows a photomicrograph of a microtomed section of PVC, that had been blended with 1.48 wt% of

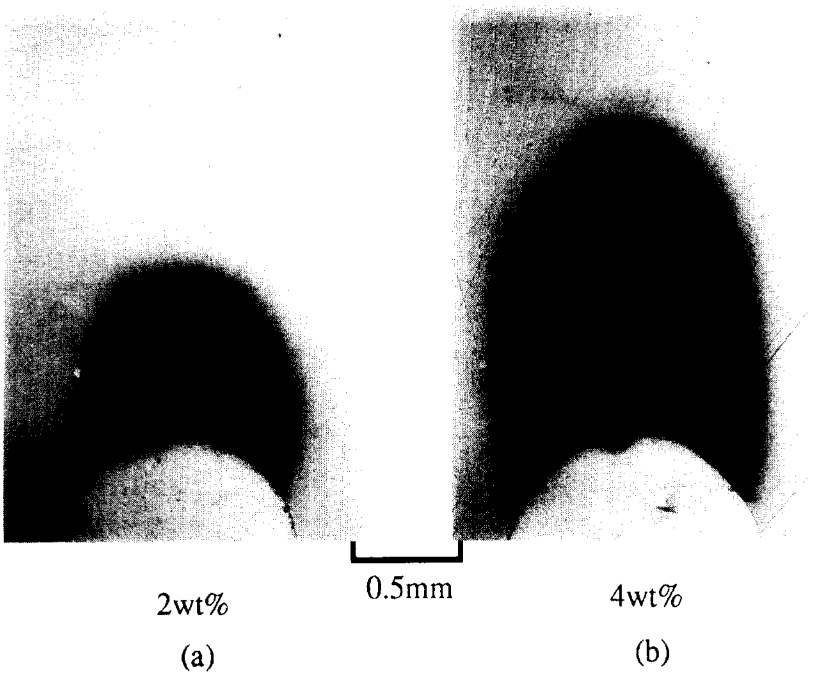


Figure 4 Photomicrographs of (a) a section of PMMA blended with 2 wt% of modifier which was unloaded immediately before brittle fracture and (b) a section of PMMA blended with 4 wt% of modifier which was unloaded immediately before ductile fracture

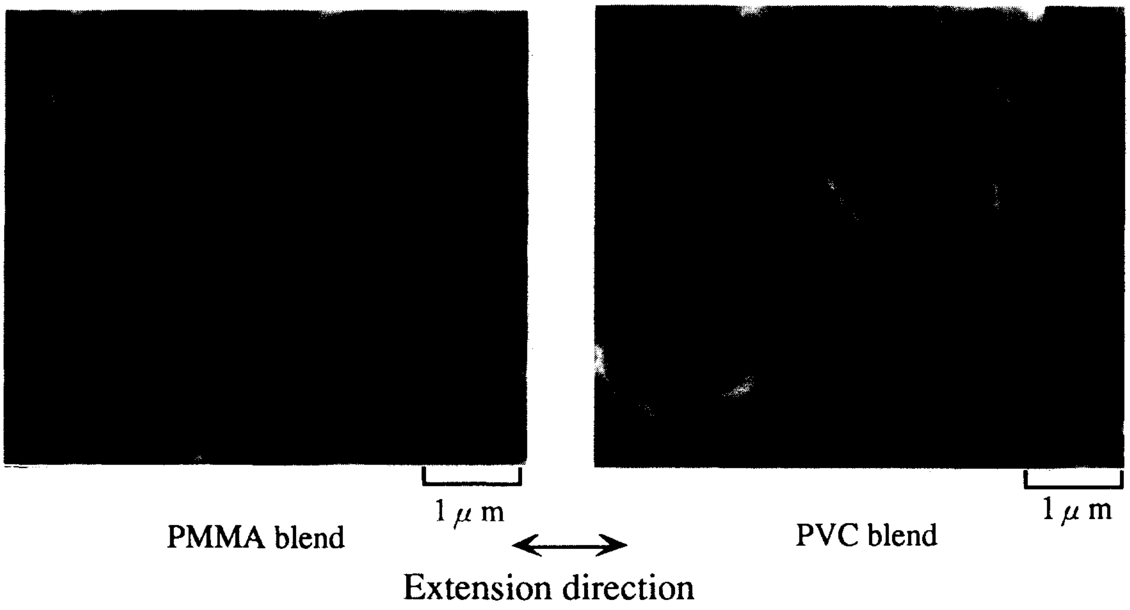


Figure 5 Scanning electron micrographs of the local plastic deformation zones developed from the tip of the U-notch for PMMA blended with 10 wt% of modifier and PVC blended with 4 wt% of modifier. The three-point-bending test was carried out at temperatures of 313 K for the PMMA blend and 296 K for the PVC blend

modifier, for the local plastic zone at the general yielding point. Under the boundary condition of the specimen used, the size of the local plastic zone (logarithmic spiral region) for the perfect plastic–rigid material was $1.69 \times \rho$, which was calculated by the use of the slip-line field theory, as shown in *Figure 1*[14]. The size of the local plastic zone for the PVC blend examined here was $2.60 \times \rho$, as shown in *Figure 3*. The dilatational stress results in the formation of voids in the plastic zone. The numerous voids which had nucleated from the modifier lead to the relaxation of the stress concentration due to Poisson shrinkage between the neighbouring voids. Furthermore, it seems that the shear yield stress decreases with the expanding plastic zone as a result of the formation of voids. Therefore, the size of the local plastic zone at the general yielding point is larger than that of the plastic–rigid material because the stress distribution of the plastic zone containing the numerous voids is similar to that of the plastic zone with a pressure-dependent yield criterion[16].

Figure 4 shows the microphotographs of a section of PMMA blended with 2 wt% of modifier which was unloaded immediately before brittle fracture and of a section of PMMA blended with 4 wt% of modifier which was unloaded immediately before ductile fracture. The

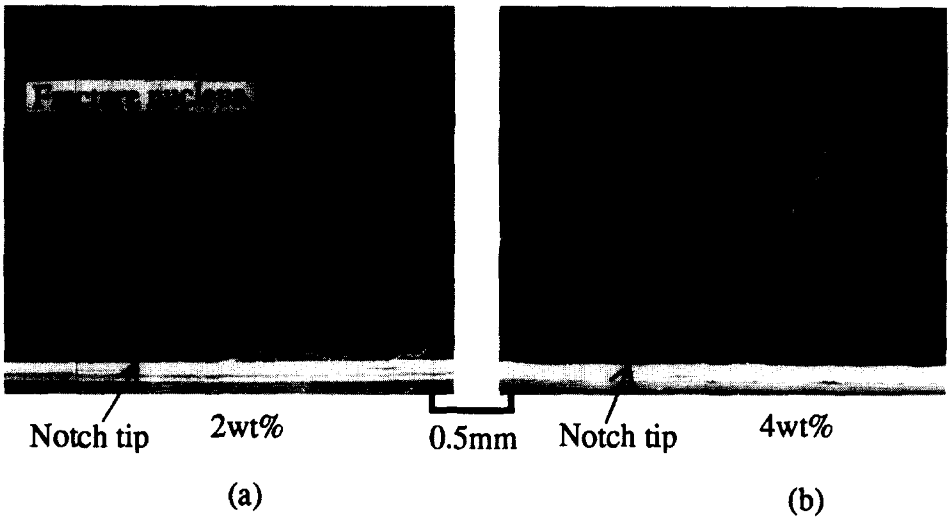


Figure 6 Scanning electron micrographs of fracture surface of PMMA blended with (a) 2 wt% of modifier and (b) 4 wt% of modifier

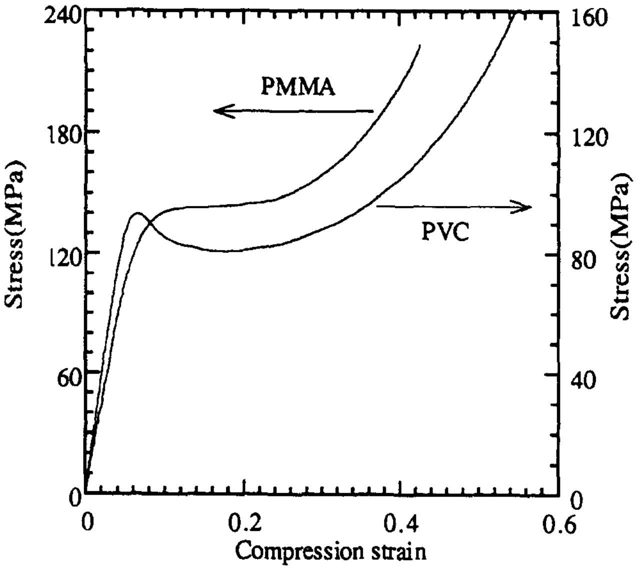


Figure 7 True stress–strain curves of PMMA and PVC, evaluated from plane strain compression tests

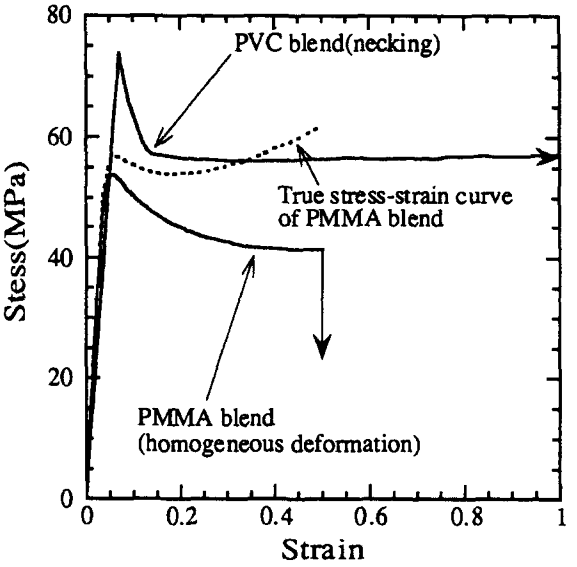


Figure 8 Nominal stress–strain curves of PMMA and PVC blended with 10 wt% of modifier; the tensile tests were carried out at temperatures of 296 and 313 K for the PVC and PMMA blends, respectively

plastic zone was observed as a light-scattering region due to either crazing or the presence of voids. The size of the plastic zone expanded until the brittle fracture was $1.3 \times \rho$ for PMMA blended with 2 wt% of modifier, and until the ductile fracture was $2.4 \times \rho$ for PMMA blended with 4 wt% of modifier.

Figure 5 shows the microstructures of the local plastic deformation zones that had developed from the tip of the U-notch in two polymer blend samples. The contents of the modifier were 10 and 4 wt% for the PMMA and PVC blends, respectively. The three-point-bending test was carried out at temperatures of 313 K for the PMMA blend at 296 K for the PVC blend. The strain was fixed at a displacement of ca. 3 mm by casting of the epoxy resin. The diameter of the modifier used is ca. 0.2 μm, as mentioned above. The scanning electron micrographs show the pronounced extension and expansion of the voids which are developed at the modifier. Although the micrographs shown in *Figure 5* do not provide conclusive evidence that void formation is a result of deformation, because the removal of undeformed particles by cryogenetic fracture may also create these void features on the fracture surface, the formation of voids in this way was also indicated from the diffusion of an immersion liquid (liquid paraffin) into the voids which show up in the cross-sections observed in the optical microscopy studies.

Figure 6 shows scanning electron micrographs of the fracture surfaces of two PMMA blends. A fracture nucleus was observed in PMMA that had been blended with 2 wt% of modifier (*Figure 6a*). The distance from the tip of the notch to the fracture nucleus almost corresponded to the size of the expanded plastic zone immediately before the fracture shown in *Figure 4a*. It was suggested that brittle fracture of this polymer blend initiates at the tip of the local plastic zone at which the stress is a maximum. For PMMA blended with 4 wt% of modifier, the general yielding took place by the relaxation of the stress concentration with the increasing addition of modifier. The ductile fracture of this polymer blend was initiated at the tip of the notch at which the strain is the maximum (*Figure 6b*).

The efficiency of the improvement in toughness for the blend with PMMA as the matrix polymer due to the addition of modifier was lower than that of the blend with PVC. It seems that this difference is caused by the difference in mechanical properties of the two polymers, because the modifier used is the same for both blends. *Figure 7* shows the true stress–strain curves of PMMA and PVC, which were evaluated from plane strain compression tests[12]. The yield stress scale was chosen in such a way that the size of the upper yield stress for PMMA agrees with that of PVC. For PVC, the stress decreased below the yield point, a phenomenon which is known as strain softening[17,18]. It is well known that this strain softening leads to instability of the plastic deformation and the formation of shear bands[18]. When the strain increases beyond 40%, once again the stress increased. This increase in the yield stress is the so-called orientation hardening[6,7]. In contrast, strain softening was not observed for PMMA. The plastic deformation of PMMA without the development of shear bands can be understood by this experimental result. It has been pointed out that for PMMA the strain required for initiation of the orientation hardening is smaller than that of PVC. *Figure 8* shows the nominal stress–strain curves of polymer blends which were evaluated from uniaxial tensile tests. Homogeneous plastic deformation was observed in the PMMA blend although the tensile strain of failure is smaller than that of the PVC blend. The dashed line shows the true stress–strain curve of the PMMA blend, which was calculated on the assumption that the volume during the deformation remains constant. A rise in the yield stress was presumed to occur above a tensile strain of 0.2–0.3. On the other hand, it was difficult to estimate the true stress–strain curves of the PVC blend from the uniaxial tensile test because necking occurs as a result of strain softening. The tensile strain of the necking region was ca. 1.5.

When the yield stress increased due to the orientation hardening, the stress of the plastic zone was increased in comparison to that estimated for an elastic–plastic material with a constant yield stress, as shown by equation (1). Therefore, in order to develop the brittle–ductile transition for U-notched PMMA blend samples, a higher content of modifier than that used for the PVC blend is required. The strain required for the initiation of ductile cracks is also influenced by the orientation hardening as shown in *Figure 8*. Because the stress concentration due to defects at a high plastic strain is amplified by the orientation hardening, it is suggested that the initiation of ductile cracks in the PMMA blends occurs at a lower displacement than that of the PVC blends.

It was suggested from the theory of rubber elasticity that the development of orientation hardening depends on the molecular weight between the entanglements of the molecular chains[20]. For example, since the epoxy resin has a large entanglement density, orientation hardening occurs at a much lower plastic strain when compared with that of the strain of initiation of orientation hardening for thermoplastic polymers. Therefore, it is likely that the origin of the much lower efficiency of the improvement of toughness for an epoxy resin modified by an elastomer is in this strong orientation hardening.

In general, the molecular weight between the entanglements is estimated from the plateau modulus derived from viscoelastic measurements. For PMMA, this molecular weight is slightly larger than that of PVC, and is much higher than that of PC[18]. Needless to say, PC can deform without orientation hardening up to high strain levels (ca. 100%). It seems that at temperatures lower than the glass transition temperature, as a result of the motion of the molecular chains being strongly constrained, the mechanism of orientation hardening in this case differs from that of rubber.

CONCLUSIONS

The effect of orientation hardening on the toughness of polymer blends was examined by the use of matrix polymers with different characteristics of orientation hardening. It was concluded that the lower efficiency of toughening for PMMA blended with a modifier when compared with that of a corresponding PVC blend is caused by the development of orientation hardening at a lower plastic strain of the PMMA.

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