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Effect of matrix composition on the fracture behavior of rubber-modified PMMA/PVC blends

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Summary

PB-g-MMA core-shell impact modifiers were synthesized by seed emulsion polymerization and impact-modified PMMA/PVC blends were prepared by melt blending PMMA, PVC and PB-g-MMA at 160°C. The PB-g-MMA particles were dispersed uniformly in the PMMA/PVC matrix. PMMA/PVC blends were prepared in the blend ratio from 100/0 to 0/100 and the rubber content was kept 16% in all the compositions. The effects of matrix composition on the mechanical properties and morphology of the blends were studied. It was found that when the matrix was a PMMA-rich system, the sample broke in a brittle mode and crazing of the matrix was the main mechanisms of deformation. When the matrix was a PVC-rich system, the sample broke in a ductile mode and the main deformation mechanisms were cavitation of the particle and shear yielding of the matrix. There existed a transition from crazing to shear yielding in the rubber-modified PMMA/PVC blend as the matrix composition varied.

Keywords

PVC, PMMA, crazing, shear yielding, transition

Introduction

Toughness is one of the most important parameters that determine whether a polymer can be used as an engineering material. The toughness of brittle or notch-sensitive polymers can be enhanced by the incorporation of a small quantity of rubber particles with appropriate sizes in the matrix [1]. In rubber-toughened polymer, toughness is affected by many structural variables including the volume fraction [2,3], the internal morphology [7], the size and size distribution of the rubber particles [4-6], the properties of the matrix [8] and the interfacial adhesion of between particles and matrix [9,10].

During the failure process of a rubber-toughened polymer, most of the energy is absorbed by the deformation of the rigid matrix. So the properties and composition of the matrix are therefore of paramount importance in determining the mechanical properties of a rubber-toughened polymer. Jiang [11] has pointed out that the product of the yield stress and yield strain of matrix polymer determined the brittle-ductile transition of rubber-toughened polymers. Wu [12] has investigated the relationship between the chain structure, phase morphology and toughness in thermoplastic polymers and polymer/rubber blends. They pointed out that with the same rubber amount, the extent to which a matrix can be rubber toughened depended on the intrinsic brittleness and ductility of the matrix, as controlled by the entanglement density of matrix. Kim and Paul [13,14] studied the blends of SAN copolymer with a SAN grafted rubber, and they pointed out that the level of attainable toughness of rubber modified polymer was limited by the inherent ductility of polymer matrix.

Knowledge of the miscibility and phase behavior of polymer blends is essential for controlling polymer blends properties. The miscibility of PMMA/PVC blends has been studied by different approaches. Schurer [15] reported that PMMA/PVC is miscible only in blends having PVC contents greater than 60% w/w. Wlochowicz and Janicki [16] concluded that PMMA/PVC blends at all compositions are wholly amorphous two-phase system. Varada [17] investigated the miscibility of PVC with PMMA by ultrasonic and refractive index method. They pointed out that PVC and PMMA are miscible in all compositions. Shen and Torkelson[18] observed that PMMA/PVC blends are miscible at all compositions if they are prepared between Tg and their lower critical solution temperature. This discrepancy is understandable in view of the likelihood of different sample preparation methods, different molecular weights and different sources of the materials, which can significantly affect miscibility. The aim of the current work was to study the effect of matrix composition on the fracture behavior of rubber-modified PMMA/PVC blends. This paper dealt with a transition of deformation mechanism from crazing to shear yielding with a variation of PMMA/PVC weight ratios from PMMA-rich to PVC-rich in the matrix.

Experimental

Materials

PB-g-MMA impact modifiers were synthesized by grafting methyl methacrylate monomer onto polybutadiene (PB) latex rubber particles by seeded emulsion polymerization. In the PB-g-MMA, the weight ratio of PB to MMA is 70/30 and the particle size of PB-g-MMA is about 300 nm.

Both PVC resin, K value 66, M_w = 72,000, M_n= 40,000 (Jilin Petrochemical Company, China) and PMMA resin , M_n = 60 000 were of commercial grade.

Blend preparation

PMMA/PVC blends were produced by compounding PMMA and PVC resin in a two-roll mill at 160°C and 190°C for 5 min., respectively. And rubber-modified PMMA/PVC blends with the constant rubber level of 16 % were also produced by compounding the PB-g-MMA with PMMA and PVC resin in a two-roll mill at 160°C for 5 min. The films obtained were then pressed into sheets by compression molding at 180°C for 10 min. The sheet thickness was set at at 4 mm for the Izod impact tests and 1 mm for the tensile and transparency tests.The compositions of the rubber modified blends were summarized in Table 1.

Table 1. Compositions of rubber-modified PMMA/PVC blends

	rubber content in rubber-modified PMMA/PVC (wt %)	PMMA/PVC in rubber-modified PMMA/PVC
Blend 1	16	100/0
Blend 2	16	80/20
Blend 3	16	60/40
Blend 4	16	40/60
Blend 5	16	20/80
Blend 6	16	0/100

Analysis

TEM samples were microtomed from the PMMA/PVC blends prepared at 160°C and 190°C to observe the morphology and the miscibility of the blends. TEM samples were also microtomed in the stress-whitening zone of impact specimens in order to examine the deformation behavior immediately underneath the fracture surface. The ultrathin sections were parallel to the deformation direction. This allowed for the visualization of crazes, elongated particles, and rubber cavitation whenever presented. All the specimens were cut to 60 nm in thickness using a microtome at –100°C.The specimens were directly observed in a JEM-2000EX TEM without any disposal to investigate the miscibility of PMMA/PVC blends. And the samples from the stress whitening zone were stained by exposing the ultrathin sections in the vapor of 1% OsO_4 solution over night before observation to study the deformation mechanisms.

Deformation mechanisms inside the stress-whitening zone of samples tested in Izod impact were also observed by SEM (JSM-5600). The specimen was prepared by cryogenically splitting the impact-tested sample; the cryogenic fracture surface was perpendicular to the impact fracture surface and passed through the stress-whitening zone.

Mechanical properties

The dimensions of all the specimens obtained for notched Izod impact strength test were 63.5mm×12.7mm×4mm according to ASTM D256. The test was conducted on XJU-22 Impact tester at 23°C.

All tensile specimens were dumb-bell type whose dimension of the parallel part was 30mm in length. Tensile tests were conducted on AGS-H 5kN Electrical Testing Machine at constant crosshead speed of 10mm/min at 23°C according to ASTM D638.

Optical Properties

Transmittances of PMMA/PVC blends were measured by using a Spherical Hazemeter (WGW) at 23°C according to ASTM D1003. The specimens have substantially plane-parallel surfaces free of dust and internal voids. 1 mm thickness Specimens were cut from the compression-molded sheet and the size of each test specimen was large enough to cover the entrance port of the sphere.

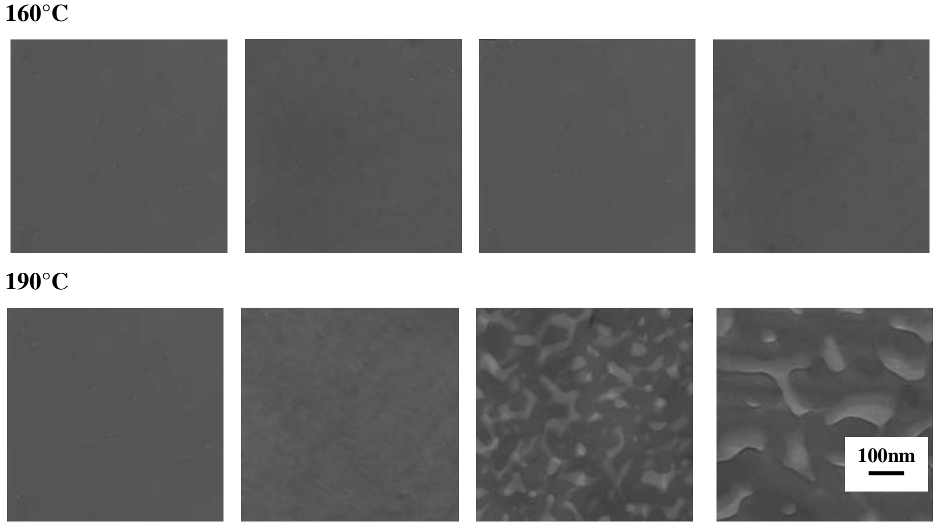
Results and Discussion

Miscibility of PVC and PMMA

The miscibility of amorphous polymers is often deduced from changes in the glass transition temperature (Tg) of the components upon blending. If the blend exhibits a single Tg we assume misciblity, while two glass-transition temperatures indicate partial misciblity or immisciblity of the blend components. However, this method is adequate only for polymer pairs with well-separated glass transition temperature. As for PVC and PMMA used in our study, their Tg is close, so the DMA cannot be used to investigate the miscibility of them. Furthermore, Vesely et.al [19] have pointed out that methods such as DMA and DSC can only measure a macroscopically averaged quantity, and the local fluctuations of composition may exist, in addition to normal density fluctuations. They also pointed that by the TEM a length scale smaller than 5 nm can be detected.

In our study the TEM measurements were used to show some evidence of a microstructure in the PMMA/PVC blends in the observed scale by TEM. Figure 1 gave the morphology of PMMA/PVC blends prepared at 160°C and 190°C. As shown in Figure1, when the blends were prepared at 160°C, the blends were homogeneous over the whole composition range, and no phase separation can be found in the TEM. Wihle TEM of PMMA/PVC blends prepared at 190°C showed significant phase separation,in contrast to the blends prepared at 160°C. The experimental results suggested the PVC and PMMA were miscible in a wide composition in our experiment at 160°C, and there existed phase separation when the blends were prepared at 190°C.

As shown in Figure 2, the light transmittances of the blends prepared at 160°C were kept about 80%, and the transparency was not destroyed by the mixing of the



(a) **(b)** **(c)** **(d)**

Figure 1. TEM micrographs of (a)80/20, (b)60/40, (c)40/60 and (d)20/80 PMMA/PVC blends prepared at 160°C and 190°C

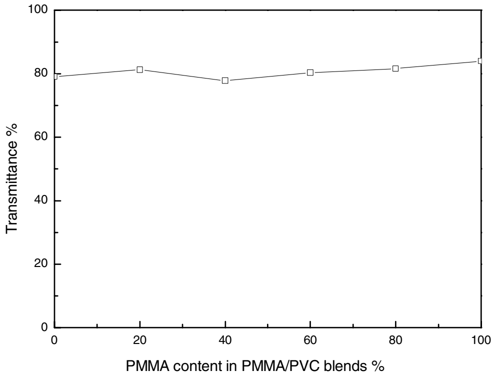


Figure 2. Light transmittance of PMMA/PVC blends prepared at 160°C for a composition of 100/0, 80/20, 60/40, 40/60, 20/80 and 0/100

components, which provided another evidence of the miscibility of the PMMA/PVC blends prepared at 160°C.

Mechanical properties of rubber-modified PMMA/PVC blends

In order to investigate the influence of matrix composition on the fracture behavior of rubber-modified PMMA/PVC blends, the notched Izod impact test was employed. The notched Izod impact strength as a function of PVC content in the matrix for rubber-modified PMMA/PVC blends was depicted in Figure 3. The curve showed that at constant rubber content of 16% the impact strength of the blends increased with the content of PVC in the matrix. The matrix with 20 wt% PVC had impact strength of about 200J/m, and the impact strength was increased to 1000J/m when the PVC content of matrix is 80 wt%. It meant that the increase of PVC content improved the toughness of PMMA/PVC blends greatly.

Polymeric materials under conditions of mechanical deformation such as tensile, fatigue or impact loading have a tendency to exhibit a white appearance, which called stress whitening. It is well known that the impact strength is related to the size of the

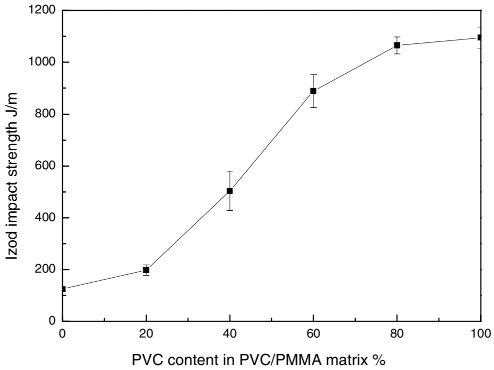


Figure 3. Impact strength of rubber-modified PMMA/PVC blends at constant rubber content of 16wt% with different ratio of PMMA to PVC

stress-whitening zone, and a fractured sample with a large stress-whitening zone usually has higher impact strength. The size of stress whitening zone in Izod impact specimen with different matrix composition were shown in Figure 4. It was clearly found that the size of stress-whitening zone in Izod impact specimens increased with the PVC content in the matrix of the blends. And the results were also according to the impact strength of the blends.

The stress-strain curves of rubber-modified PMMA/PVC blends were given in Figure 5. As the content of PVC in the blends increased, there was a decrease in the yield stress and elastic modulus and an increase in elongation at break. From the stress-strain curve of rubber-modified PVC in Figure 5, it can be found the stress decreased below the yield point, and the phenomenon is known as strain softening. With the increase of the strain, the stress increased again, and the phenomenon is known as strain hardening. It is well known that this strain softening leads to instability of the plastic deformation and the formation of shear bands [20] while the evolution of this localized plastic zone depends on the stabilizing effect of the strain hardening [21]. The toughness enhancement of brittle amorphous polymers can be obtained via microstructural adjustments, resulting effectively in a removal of intrinsic strain softening on the mesoscale via a decrease in yield stress and an increase in strain hardening [22]. It was found that from the Figure 5, the strain softening was suppressed and the strain harden was favored as the increase of PVC content in rubber-modified PMMA/PVC blends, which indicated that the introduction of PVC into the PMMA matrix improved the toughness of the blends. It can be seen from the data that at the same rubber content, the stress-strain behavior were different. It seemed that this difference was caused by the difference in mechanical properties of the two polymers. Ishikawa et.al also pointed out that PMMA with modifier have a lower efficiency of toughening than that of PVC, which is caused by the development of orientation hardening at a lower plastic strain. Vincent [23] has found a correlation between critical tensile strength and the cross-sectional area of the polymer molecules. The high concentration of loading-bearing main-chain chemical bonds enables a polymer to strain harden and reach large strain before fracture. PVC has a high concentration of loading-bearing main-chain chemical bonds of 3.4 bonds per nm^3 and PMMA has a lower concentration of loading-bearing main-chain chemical bonds of 1.50 and bonds per nm^3.These features provided another explanation for the observation that the blends with a PVC-rich matrix had higher strain to break than that with a PMMA-rich matrix.

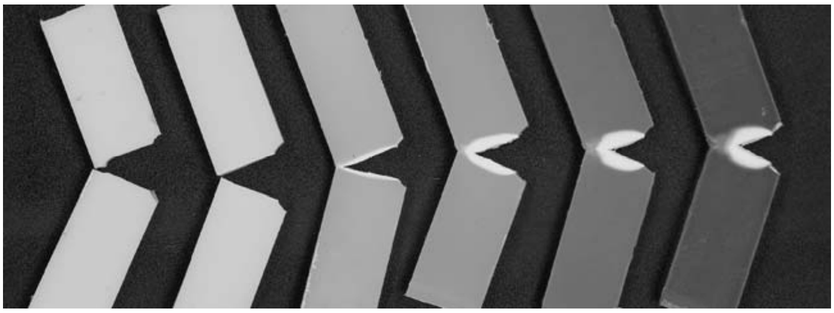


Figure 4. The stress-whitening zone of impact sample of rubber-modified100/0, 80/20, 60/40, 40/60, 20/80, 0/100 PMMA/PVC blends

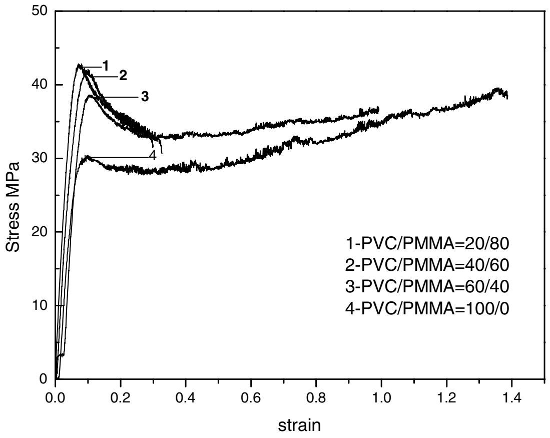
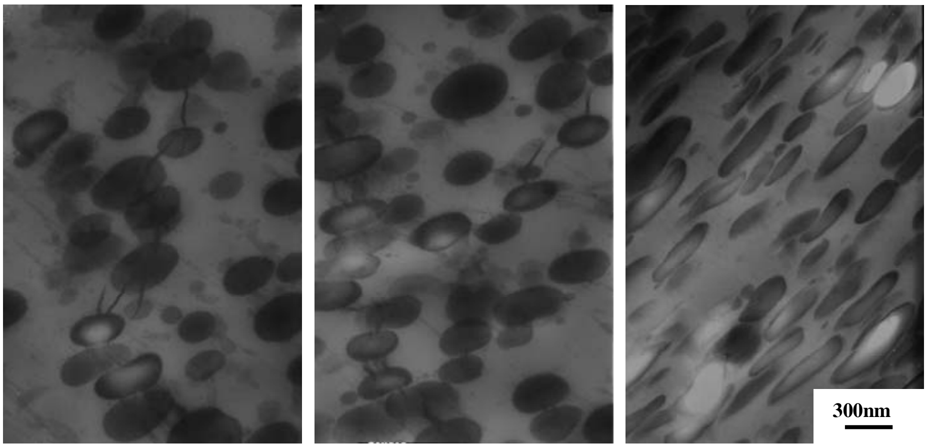


Figure 5. Stress-strain curves for rubber-modified PMMA/PVC blends

Fracture mechanism of rubber-modified PMMA/PVC blends

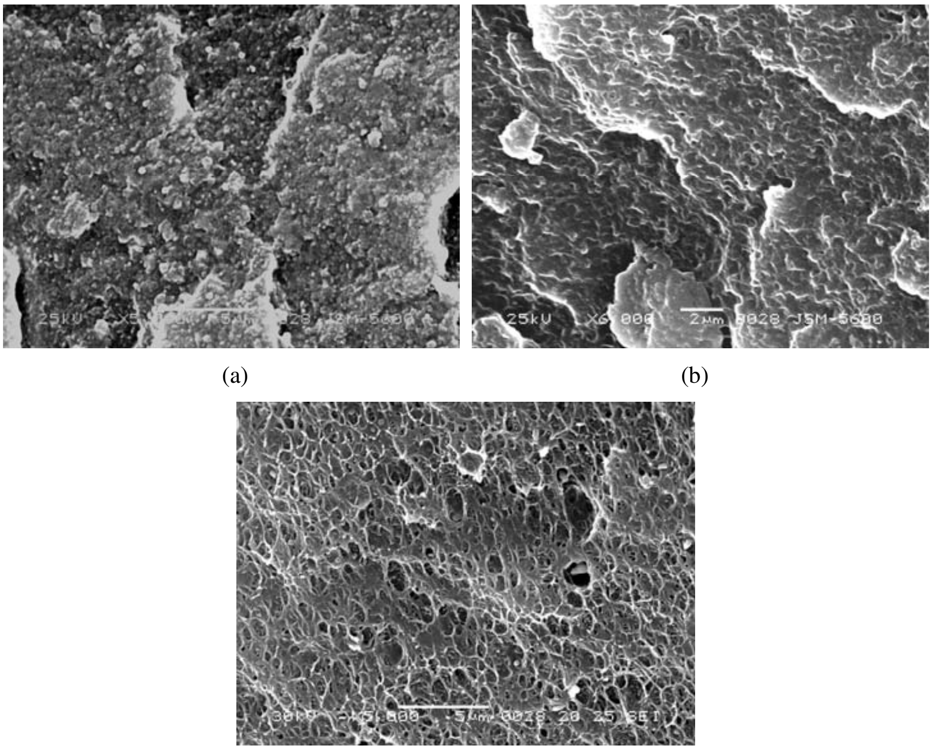
To investigate the influence of matrix composition on the deformation mechanism, the rubber-modified PMMA/PVC blends were studied by TEM. Figure6 showed internal morphology of stress whitening zone in Izod impact specimen by TEM. All the samples had a constant rubber content of 16 wt%, while the matrix varied from PMMA-rich to PVC-rich system. It showed an obvious change in deformation behavior with the composition. At a PMMA-rich system (PMMA/PVC was 80/20, shown in Figure 6(a)), the rubber particles were well dispersed in the matrix. The black crazes showed up clearly against the white background of the undeformed matrix. It was shown that the crazes were initiated from the rubber particles and the propagation direction of crazes was orthogonal to the deformation direction. And the crazes also can be terminated by the rubber particles. As shown in the TEM, there was no sign of elongation of the rubber particles. All these suggested that the main deformation mechanism was crazing of the matrix when the matrix was a PMMA-rich system. At an intermediate composition viz., PMMA/PVC (60/40), shown in Figure 6(b), the TEM showed that some particles cavitated and elongated which indicated that the shear deformation occurs in the matrix. It has been reported that cavitation of rubber particles can relieve the triaxial tension in the front of notch tip, and massive shear yielding in the matrix can occur [24,25]. Besides, few crazes can be found in the sample. It suggested that crazes and shear yielding coexisted in the intermediate composition. In a PVC-rich system, as shown in Figure 6(c), the deformation was clearly different from the PMMA-rich system. There was no evidence of crazing; the matrix deformed almost exclusively by shear deformation. Some rubber particles cavitated and all the particles were elongated by the shear of the matrix.

In order to study the internal deformation mechanisms in the stress-whitening zone, the SEM observations on the cryofractured surface of rubber-modified PMMA/PVC blends was shown in Figure 7. Figure 7(a) showed that there was no sight of any deformation in a PMMA-rich system. It may be seen from figure7(b) that with the increasing of PVC content in the matrix voids and plastic flow can be observed in the sample. Figure7(c) showed massive cavities with plastic flow occurred in PVC-rich system, and most of the cavities in the stress-whitening zone were several times larger than the original rubber particle.



(a) (b) (c)

Figure 6. TEM photographs of stress-whitening zone in impact test specimens of rubber-modified PMMA/PVC blends (a) 80/20 (b) 40/60 (c) 20/80



(a) (b)

(c)

Figure 7. SEM photographs of stress-whitening zone in impact test specimens of rubber-modified PMMA/PVC (a) 80/20 (b) 40/60 (c) 20/80

Combining the results from TEM and SEM, a conclusion can be drawn that transition of deformation mechanism took place with the changing matrix composition in rubber-modified PMMA/PVC with the increase of PVC content, which was from crazing to shear yielding.

The transition of the fracture mechanism with the change of matrix composition

The transition from crazing to shear deformation was found with the increase of PVC content, which reflected the influence of molecular architecture on deformation behavior. Ishikawa et.al [26] pointed out that craze yielding was accompanied by a slippage between oriented molecules around a void as a result of high dilatational stress, while shear plastic deformation was caused by the rotation of small segments in a molecular chain. It is well known that molecular aspects of craze/yield behavior are controlled by entanglement density ν_e. Wu [12] pointed out that a polymer having low entanglement density tends to craze rather than yield. On the other hand, a polymer having high entanglement density tends to yield rather than craze. So as entanglement density of matrix increases in the blends caused by the increase of the amount of PVC in blends, the transition from crazing to shear yielding of matrix takes place, which leads to a higher toughness. Kramer et al. [27-29] introduced a quantitative criterion to predict whether a polymer will undergo crazing or shear yielding when in a certain applied stress field. They pointed out that the generation of the void-fibril structure of a craze involves the chain disentanglement of the polymer, which is not necessary for the production of a shear deformation zone. They found that crazing is the deformation mechanism when the entanglement density of the polymer is below a critical value. At higher entanglement densities both crazing and shear yielding take place, whereas above an upper critical density, disentanglement becomes very difficult. Crazing could thus be suppressed, and only shear deformation zone were observed.

Entanglement density, often described by the molecular weight of a chain between entanglements, can be obtained from the plateau modulus of a high molecular weight melt. It is reported that entanglement density can be adjusted by using miscible blends of glassy polymers with different density of entanglements [30]. The results of Van de Sanden [31] revealed that the entanglement density of miscible PS/PPE blends were linearly increasing with the increase of PPE content. The data from Wu [12] showed that the PMMA have a low entanglement density and PVC has a relative high entanglement density. Despite the fact that no experiment was designed to measure the actual value of entanglement density in blends, one may expect a linear increase of entanglement density of miscible PMMA/PVC blends as the matrix changing from a PMMA-rich system to a PVC-rich system. So it is easily understood that when our rubber-modified PMMA/PVC blends transited from a PMMA rich system to a PVC rich system, the stress of crazing nucleation increased monotonically with increasing PVC content. So in our study, when more PVC was introduced to the blends, the stress of crazing nucleation increased and crazing would be suppressed.

Shear deformation is well known from homopolymer and several rubber-modified polymers. Janet et al. [32] investigated the effect of molecular entanglement density on the shear activation volume of glassy polymers. They found that the same correlation between the shear activation volume V^*_{eq} and the entanglement density ρ_e hold for the blend as well as for various pure glassy polymers: $V^*_{eq} = C\,(\rho_e\,/\mathrm{nm}^{-3})^{\alpha} + V_0$. From the correlation, it can be concluded that with the increasing of entanglement density, the shear activation volume increase and then the shear yielding of matrix will be easily initiated. In our study, since the PVC had a higher entanglement density, with the increase of PVC content in the matrix the blends would deform by shear yielding easily.

Conclusions

The effect of matrix composition on the fracture behavior of rubber-modified PMMA/PVC blends was investigated in this paper. It was found that the deformation behavior of rubber-modified PMMA/PVC depend on the composition of blends. Blend with a PMMA-rich system deformed by the formation of crazes and the blend with a PVC-rich system deformed by shear yielding. There existed a deformation transition from crazing to shear yielding with the changing of PMMA/PVC ratio.

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