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Impact and tensile dilatometric characteristics of polypropylene/high impact polypropylene blends

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Summary

A series of polypropylene (PP) blends were toughened by various impact modifiers with different mechanical characteristics. The impact, tensile dilatometry and dynamic mechanical behavior of these PP/high impact polypropylene (HIPP) blends was studied. The results showed that the impact strength of PP improves significantly with the addition of a higher content of HIPP which has the lowest flexural modulus and yield strength. This was due to the formation of shear yielding bands in the slow crack growth zone ahead of the notch tip. However, the PP blends modified with HIPP of higher flexural modulus exhibited much lower impact strength owing to these dispersed particles initiate crazes in the slow crack growth zone.

Introduction

Isotactic polypropylene (PP) is used in a wide range of applications because of its attractive properties such as low cost, low specific gravity and good strength. However, poor impact strength of PP, particularly at low temperatures, limits its use in some applications. Thus PP is normally blended with elastomers to improve its low temperature impact strength and brittleness. The dispersed elastomer particles act as stress concentrators favoring the dissipation of the impact energy. An optimum particle size, a low interfacial energy, and good adhesion to the matrix are the necessary requirements for efficient toughening (1). Various elastomers, e.g., ethylene-propylene copolymers, ethylene-propylene diene terpolymer (EPDM) and the nitrile rubber (NBR) system have been added to PP for this purpose (2-6). Several deformation mechanisms have been proposed to explain the toughening of polymers with elastomeric particles. These include stress relief by cavitation around rubber particles, matrix crazing, shear yielding, and combined crazing and yielding (7-11). Among these, some may occur simultaneously or sequentially around the crack tip. In the first case, the dilational deformation mechanism that produce stress-whitening involves both void formation and crazing (1). Crazing associated with the elastomer particles in PP has been observed in the scanning electron microscope (SEM) and transmission electron microscope (2,12). It is worth noting that the toughening effect arises from the cavitation or crazing of the elastomer particles is relatively low. However, the toughness of the PP matrix can be improved significantly through massive shear yielding of the matrix (13).

Numerous studies reported in literature are mainly concerned with the impact toughening of the elastomer-modified PP (2-6,12). However, fewer information is available on the dilational response of rubber-modified PP. In this paper, we report the results on the impact strength and volumetric strain of PP blended with three kinds of thermoplastic olefins. Among these, a newer impact modifier (Himont KS-035P Catalloy process resin) is claimed by the manufacturer to exhibit a unique combination of low temperature impact resistance and flexibility. We correlate the experimental impact energy and dilational response of these HIPP-modified PP blends with the SEM morphological observation in order to determine the mechanisms responsible for the toughening of PP.

Experimental

The PP used in this work was received from the Polyolefin Company (Singapore). Three thermoplastic olefins (KS-035P, KS-059P and RA061) were kindly provided by the Himont Company (Hong Kong). The thermoplastic olefins were ethylene-propylene copolymers with high impact strength. They were designated as E1, E2 and E3 in this paper, respectively. The physical and mechanical properties of PP homopolymer and HIPP copolymers as supplied by the manufacturers are listed in Table 1. Evidently, the E2 impact modifier (KS-059P) has the lowest yield strength and flexural modulus.

Table 1 Physical and mechanical properties of PP homopolymer and HIPP copolymers

	PP	KS-035P	KS-059P	RA061
Density, g/cm^3	0.90	0.88	0.89	0.87
Melt flow rate, g/10 min	12	10	10	0.7
Yield strength, MPa	--	10	5.5	10
Elongation at yield, %	--	15	18	--
Elongation at break, %	640	--	--	760
Flexural modulus, MPa	1440	366	130	310
Notched Izod impact strength, kg.cm/cm^2	2.0	No Break (- 29 °C)	No Break (- 18 °C)	No Break (- 40 °C)

The PP pellets were premixed 10, 20, 30, 40, 50 and 70 wt% of E1, E2 and E3 in a twin-screw Brabender Plasticorder with the barrel temperatures set at 150-210-210 °C. The extrudates were subsequently cut into pellets by a pelletizer. Both standard dog-bone tensile bars (ASTM D638) and plaques were injection molded from these pellets. Izod impact specimens with dimensions of 63.5 x 12.7 x 4 mm were cut from the injection molded plaques. The impact measurements were carried out at room temperature (21 °C) with a Ceast pendulum impact tester. The morphologies of the specimens after impact measurements were observed in a scanning electron microscope (JEOL JSM 820). The fracture surfaces were coated with a thin layer of gold before observation.

Tensile dilatometry measurements were carried out using an Instron tensile testing machine (model 4206) at a displacement rate of 25 mm/min and at 21 °C. Two extensometers were used to measure the axial strain (ε_A) and transverse strain (ε_T) simultaneously during the tests. The volume strain can be determined from the following equation (14),

$$\Delta V/V = (1+\varepsilon_A)(1+\varepsilon_T)^2 - 1 \qquad (1)$$

where ΔV is the change in volume and V is the original volume.

Dynamic mechanical properties of the injection molded specimens were determined by a Du Pont dynamic mechanical analyzer (model 983) at a fixed frequency of 1 Hz. The temperature range studied was from -100 to 100 °C with a heating rate of 2 °C/min.

Results and Discussion

Figure 1 shows the typical storage and loss modulus spectra of the pure PP and its blend containing 10, 20 and 30 wt% E2. The loss modulus spectrum of PP homopolymer clearly indicates that the glass transition temperature (Tg) of PP is located at about 23 °C. The incorporation of HIPP (KS-059) into PP leads to a shift of the Tg to a lower temperature. The Tg of PP is located near 0 °C when the E2 content reaches 30 wt%. It is noticed that a shoulder appears at about -25 °C for the blend containing 30wt% E2. This shoulder corresponds to the Tg of E2 impact modifier. Dynamic mechanical analysis (DMA) senses molecular relaxations arising from local motions of the polymer chain, hence it is widely used to detect the Tgs of polymers. From Fig. 1, the storage modulus of the blends tends to decrease with increasing elastomer content. This is as expected as the elastomer addition generally results in a decrease of the stiffness of polymer blends. Figure 2 shows the variation of the storage and loss moduli with temperature for the blends containing 30 wt% E1 and E3. Apparently, the PP-30wt%E1 blend exhibits additional distinct peak located at about - 53 °C. This means that PP and E1 phases are incompatible. A similar behavior is observed for the PP/30wt%E3 blend.

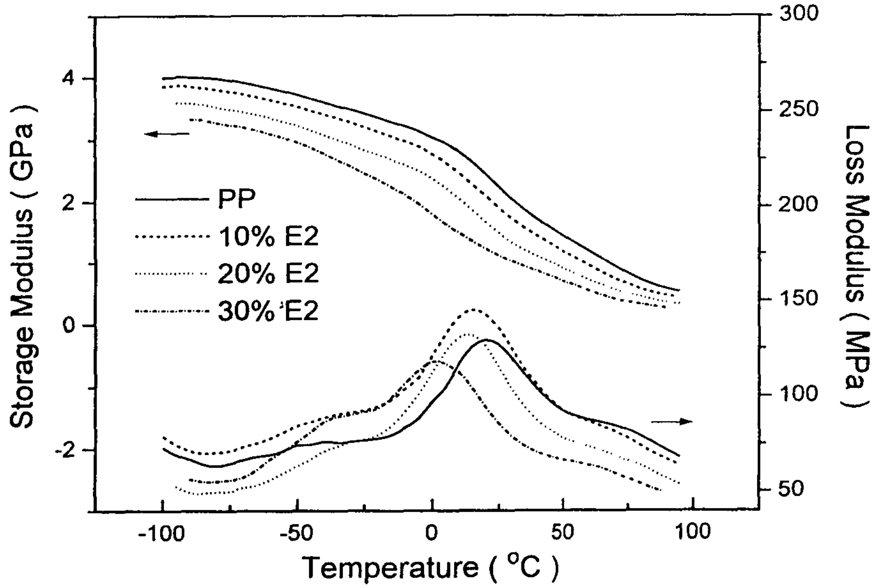

Figure 1. Dynamic mechanical properties of the PP homopolymer and its blends containing 10, 20 and 30 wt% KS-059P impact modifier.

Figure 3 shows the Izod impact strength of the PP blends as a function of the elastomer content. It can be seen that the impact strength of PP improves significantly when the E2 content ≥ 30 wt%. In other words, a brittle-ductile transition occurs for the PP blends containing ≥ 30wt% E2 content. However, the impact strength of PP increases slightly with the additions of E1 or E3 above 30 wt%. Thus only E2 is an effective impact modifier in enhancing the toughness of PP at room temperature. Figure 4a shows the stress-axial strain curves for the PP blends containing E2 additions. The representative volume strain-axial strain curves for these blends are shown in Figure 4b. It is evident

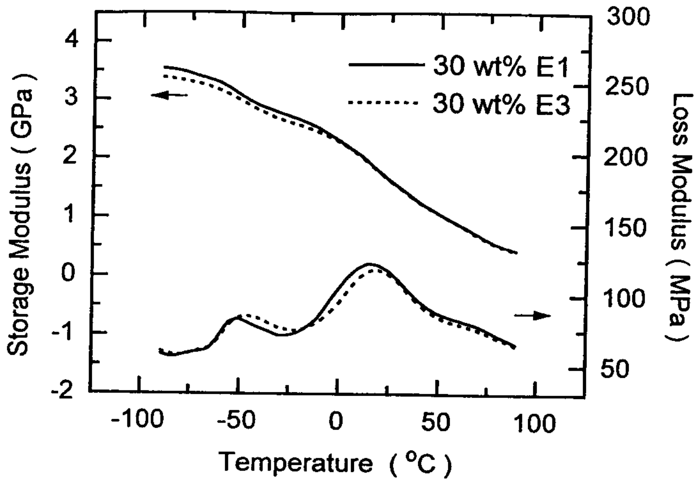

Figure 2 Dynamic mechanical properties of the PP blends containing 30 wt% KS-035P and RA061 impact modifiers.

from Fig. 4a that the yield strength of the PP blends decreases with increasing E2 content. The volume strain due to the dilational response for the PP/10wt%E2 blend is almost linear beyond the yield point indicating that the mechanism of deformation which prevails is crazing. It is generally accepted that pure crazing generally results in a post-yield slope of one in the volume strain-axial strain curves whilst shear yielding with no volume change leads to a nil post-yield slope. It is noticed from Figure 4b that the no volume change is observed beyond the yield point for the PP/30wt%E2 blends, and this indicates a shear yielding process of deformation. Therefore, the addition of 30 wt% E2 to PP leads to a drastic change in the mechanism deformation from crazing/cavitation to the shear yielding. In this regard, the impact toughness of PP improves dramatically for the PP blends containing E2 above 30 wt% as shown in Figure 3. On the other hand, the volume strain is observed to increase almost linearly with axial strain for the PP blends with E1 and E3 additions (Figures 5a-5b). In addition, the higher the elastomer content, the higher is the volume strain. This implies that the elastomer additions have increased the volume strain due to cavitation of elastomer particles or interfacial failure.

The SEM fractograph of the slow crack growth zone ahead of the notch tip for the PP/30wt%E2 blend after impact test is shown in Figure 6. It is evident that the cavities and shear yielding bands are formed in the slow crack growth zone of the PP/30wt%E2 blend. It is worth noting that an earlier cavitation of elastomer particles relieves the plane strain tensile hydrostatic stress during the deformation process, it eventually induces massive shear yielding of the PP matrix. As the shear yielding band formation dissipates a large amount of the impact energy, the PP blends containing E2 content ≥ 30 wt% exhibit good impact strength as shown in Figure 3. With decreasing the E2 content below 30 wt%, the SEM observation shows that cavitation of rubber particles predominates in the slow crack growth zone ahead of the notch. Figures 7a and 7b show the SEM fractographs of the slow crack growth zone for the PP/30wt%E1 and

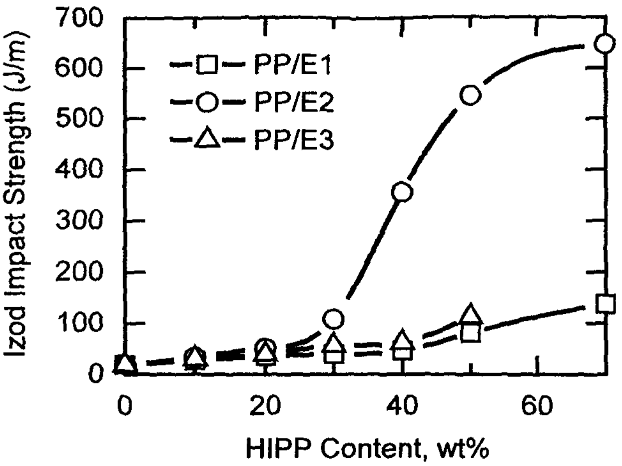

Figure 3 Variation of notched Izod impact strength of PP blends with HIPP content •

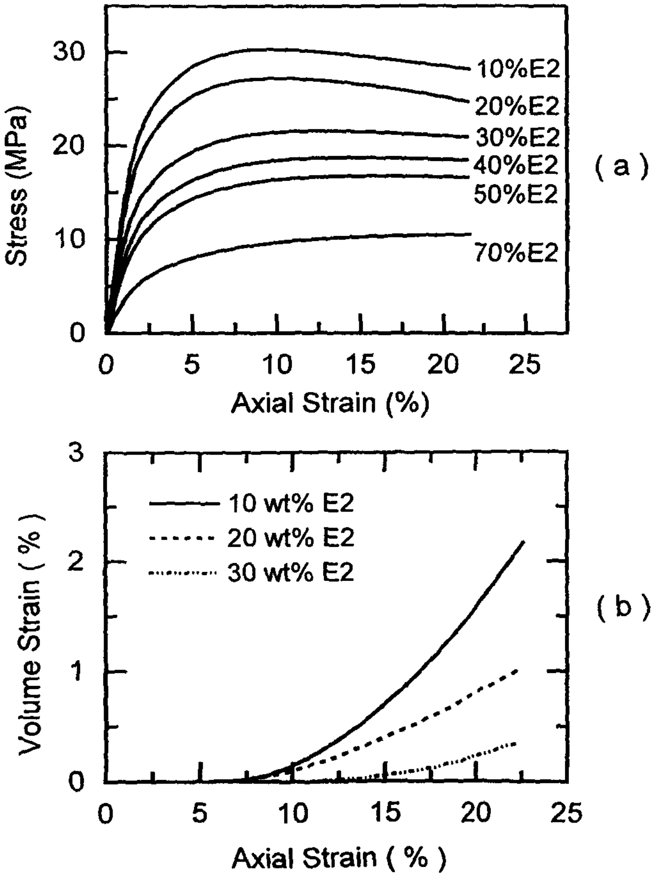

Figure 4 (a) stress - axial strain and (b) volume strain - axial strain for the PP blends toughened by E2 impact modifier •

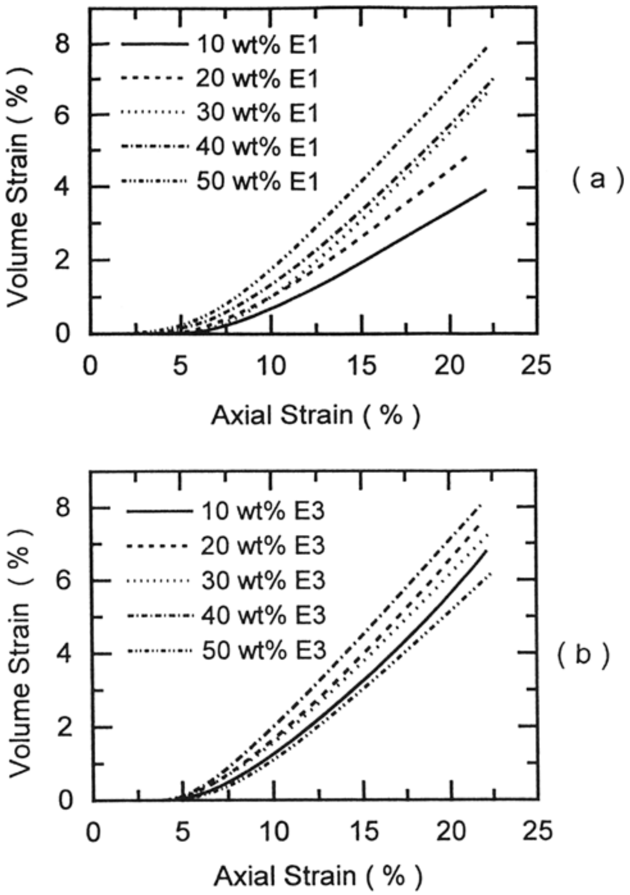

Figure 5 Volume strain - axial strain curves for the PP toughened by (a) E1 and (b) E3 impact modifiers.

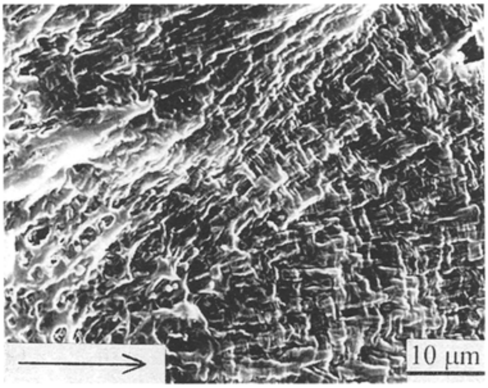

Figure 6 SEM photograph showing the slow crack growth zone of the PP / 30wt% E2 blend after Izod impact test. (The arrow indicates the direction of the slow crack growth zone).

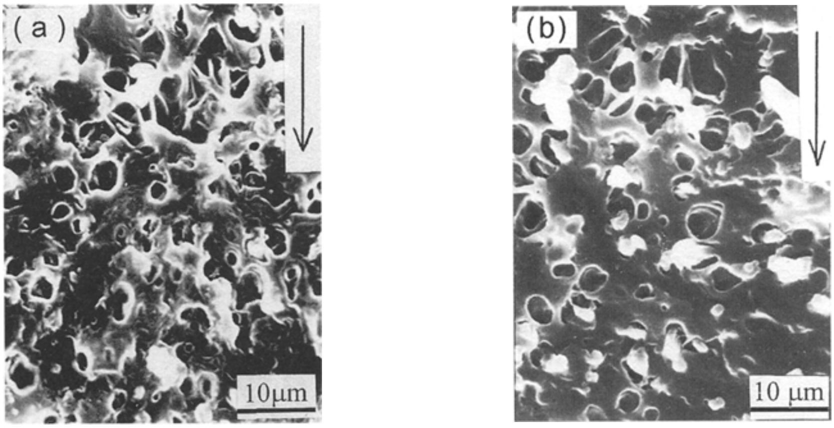

Figure 7 SEM fractographs of the slow crack growth zone of (a) PP/30wt%E1 and (b) PP/30wt% E3 blends. (The arrow indicates the direction of the slow crack growth zone).

PP/30wt%E3 blends. Apparently, only cavities associated with the debonding of elastomers are observed in these micrographs. As the cavitation process dissipates less energy than the shear yielding, the PP blends containing higher concentrations of E1 or E3 exhibit much lower impact strength than the PP blends with higher E2 content. Thus the SEM fractography is in good agreement with the notch Izod impact and tensile dilatometric measurements.

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