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IMPACT TOUGHENING BEHAVIOUR OF QUATERNARY PP/HDPE/EPDM/EP BLENDS

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Abstract—Quaternary blends of polypropylene (PP), high-density polyethylene (HDPE), ethylene–propylene diene terpolymer (EPDM) and ethylene–propylene block copolymer (EP) were prepared in a twin-screw extruder followed by injection moulding. Izod impact tests were used to determine the impact behaviour of the blends. The results showed that the quaternary blends with EPDM content ≥30 wt% exhibit superior impact strengths at 25 and −30°C. This was due to shear yielding of the matrix in the stress whitening zone of the blends containing 30 wt% EPDM. However, Izod impact tests showed that the impact energies of the blends with 25 wt% EPDM content are dependent on the HDPE concentration at 25°C. With a higher concentration of HDPE (≥15 wt%), the impact strengths at 25°C were comparable to those of the blends containing EPDM content ≥30 wt%. The blends with EPDM ≤25 wt% exhibited low-impact toughness at −30°C as featureless fracture surface and cavitation around the rubber particles were observed in the induction zone ahead of the notch tip. The measured impact strengths generally correlated well with the SEM surface morphologies. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Polyolefins are widely used as structural materials because of their relatively low cost and general availability. However, the use of polypropylene (PP) in the industrial sector is limited owing to its poor impact toughness at low temperatures. The toughness of PP at low temperatures can be improved by blending it with a small amount of polyethylene (PE) and/or rubbery materials [1–5]. Various elastomers have been added to PP, PE and PP/PE blends for this purpose. These include ethylene–propylene [EP] copolymers [5–8], ethylene–propylene diene terpolymer (EPDM) [9–12] and the styrene–butadiene–styrene (SBS) system [13]. In this respect, binary or ternary blends of PP containing PE and elastomers have been developed. It is generally known that PP and PE are immiscible and incompatible despite the fact that both polymers have many similarities in properties [14]. Consequently, the mechanical properties of the PP/PE blends are inferior to those of their pure components. However, the impact performance of PP/PE blends can be enhanced by adding a small amount of ethylene–propylene copolymer [3, 14]. The EP block copolymer, whose segments are compatible with the different phases in the blends, act as an effective compatibilizer or interfacial agent for the PP/PE blends. Flaris and Stachurski [3] reported that the EP block copolymer tends to improve the adhesion between the PP and low-density PE phases, thereby increasing the impact strength of the PP/PE blends. Similarly, PP and EPDM are incompatible at all compositions [10]. It has been reported by Ha and Kim [15] that the addition of a small amount of PE leads to an increase in the miscibility between PP and EPDM. Thus the low-temperature toughness of PP/EPDM blends is improved dramatically due to addition of PE. The work mentioned above is mostly concerned with the morphology and mechanical properties of binary and ternary blends of PP. Little information is available on the mechanical behaviour of quaternary blends of PP containing elastomer particles. This work attempts to prepare the quaternary PP/PE/EPDM/EP blends by means of extrusion followed by injection moulding and to correlate the morphology of the blends with the impact properties.

EXPERIMENTAL

Materials

The isotatic polypropylene (PP 2401) with a melt flow index of 2.5 g/10 min and EP block copolymer with a melt flow index of 1.5 g/10 min were supplied by Yanshan Petrochemical Industry (China). The EPDM rubber was obtained from Mitsui Petrochemical Industries. High-density polyethylene (HDPE) with a melt flow index of 7 g/10 min was produced by Qi Lu Chemical Industry (China).

Blending procedure

All blends were prepared by mixing PP, HDPE, EPDM and EP polymers in a twin-screw extruder (Betol) at appropriate ratios as shown in Table 1. The barrel zone temperatures of the extruder were maintained at 90, 210, 225, 225, 225 and 220°C. The screw speed employed was 320 rpm. The blends were quenched into water upon exit-

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Table 1. Composition of the quaternary blends

Sample	PP (wt%)	EPDM (wt%)	EP (wt%)	HDPE (wt%)
A_1	45	20	20	15
A_2	40	20	20	20
A_3	35	20	20	25
A_4	30	20	20	30
B_1	55	25	20	0
B_2	50	25	20	5
B_3	45	25	20	10
B_4	40	25	20	15
B_5	35	25	20	20
B_6	30	25	20	25
C_1	45	30	20	5
C_2	40	30	20	10
C_3	35	30	20	15
C_4	30	30	20	20
D_1	40	35	20	5
D_2	35	35	20	10
D_3	30	35	20	15
E_1	70	30	0	0
E_2	55	30	0	15
E_3	40	30	0	30

ing the extruder. They were then cut into small granules by a pelletizer. Using these pellets, rectangular plates were injection moulded.

Izod impact test

Notched Izod impact specimens with dimensions of $63.5 \times 12.7 \times 4$ mm were cut from the injection moulding plates. The impact tests were performed with a pendulum-type impact tester at 25 and −30°C, respectively. Five specimens of each composition were tested and the average value reported.

Morphology

The fracture surface of the impact specimens were examined in a Hitachi scanning electron microscope (model S-530). In addition, some specimens were fractured in liquid nitrogen and then etched in *n*-heptane for 5 min prior to SEM observations. The purpose was to dissolve the EPDM particles. All specimens were then coated with a thin layer of gold.

RESULTS AND DISCUSSION

Impact properties

Figure 1(a) and (b) show the variation of Izod impact strength with EPDM content at 25 and −30°C, respectively. At 25°C, the impact energy of the quaternary blends containing 5% HDPE increases from 114 to 136 kJ/m^2 as the EPDM concentration reaches 30 wt%. The impact strength then remains at this level as more EPDM (35 wt%) is incorporated into the blends. For the composition with 10% HDPE, the notched impact strength follows the same trend as for the blends containing 5% HDPE. However, it is noticed that the impact energy increases to a high level of 148 kJ/m^2 for blends comprising 15% HDPE and 25% EPDM. This result implies that the HDPE and EPDM act in synergy to improve the impact toughness of the blends. By contrast, the blends undergo a transition from brittle to ductile behaviour at −30°C [Fig. 1(b)]. It is apparent from Fig. 1(b) that the impact energies of the blends containing 25% EPDM are relatively low, thus they fracture in a brittle mode. At EPDM concentrations of 30% or greater, the blends exhibit high impact energy, hence the ductile mode of failure predominates. Figure 2(a) and (b) show the effect of HDPE content on the notched impact strength of the quaternary blends at 25 and −30°C, respectively. For blends with 20% EPDM, the impact energy is very low, i.e., 94 kJ/m^2 in the presence of 15% HDPE at 25°C. However, the impact energy for these blends is increased to 117 kJ/m^2 as the HDPE content is increased to 20% and above. For blends with 25% EPDM, the impact energies increase with increasing HDPE content. By increasing the EPDM concentrations ≥30%, it is observed that the impact strength of the quaternary blends is independent of the HDPE content at 25°C [Fig. 2(a)]. At −30°C, the blends with 20 and 25% EPDM exhibit low impact energies, but the blend specimens containing 30% EPDM show excellent notched impact toughness. It should be noted from Fig. 2(a) and (b) that the impact energies of the blends containing 20 and 25% EPDM at 25°C are significantly higher than those measured at −30°C. However, the blends with EPDM ≥30% exhibit much higher impact energies at −30°C than at room temperature. In this case, the low-temperature brittleness of PP can be avoided by the incorporation of EPDM content ≥30%.

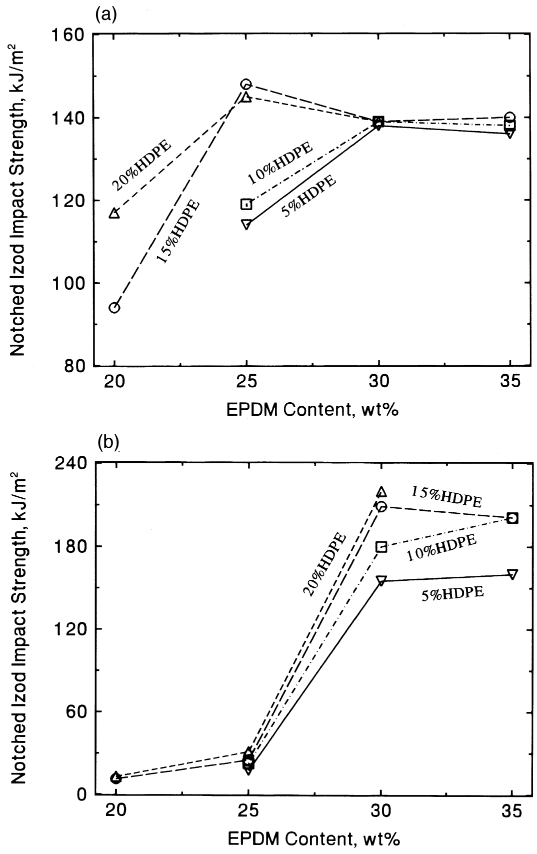

Fig. 1. Variation of impact strength with EPDM content at (a) 25°C and (b) −30°C for quaternary blends containing various HDPE concentrations. All the blends contain 20% EP. ▽, 5% HDPE; □, 10% HDPE; ○, 15% HDPE; △, 20% HDPE.

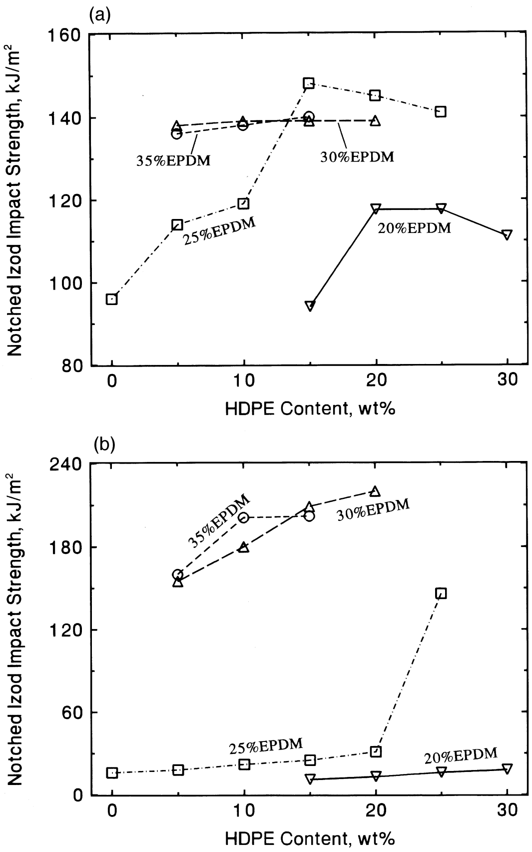

Fig. 2. Variation of impact strength with HDPE content at (a) 25°C and (b) –30°C for quaternary blends containing various EPDM concentrations. All the blends contain 20% EP. ▽, 20% EPDM; □, 25% EPDM; △, 30% EPDM; ○, 35% EPDM.

We now consider the effect of EP block copolymer on the impact strength of the blends containing 30% EPDM at low temperatures. Figure 3 shows the variation of Izod impact strength with temperature for the blends with 30% EPDM. In the absence of EP copolymer, the impact energies of the ternary blends appear to be dependent on the HDPE content. The blend with no HDPE (E_1) exhibits the lowest impact strength, whilst the blends containing 15% HDPE (E_2) and 30% HDPE (E_3) have superior impact toughness at temperatures above –40°C. Figure 4 shows the notched impact strength of the blends with 30% EPDM and 15% HDPE as a function of test temperature. The impact test data of two blend specimens are shown in this figure, i.e. one containing EP block copolymer (C_3) and another without EP copolymer (E_2). It can be seen that the addition of 20% EP block copolymer to the blend (C_3) results in an improvement of toughness over a wide range of test temperatures. It is considered that EP block copolymer addition leads to an improvement in the interfacial adhesion between PP and HDPE, thereby enhancing the impact toughness [3].

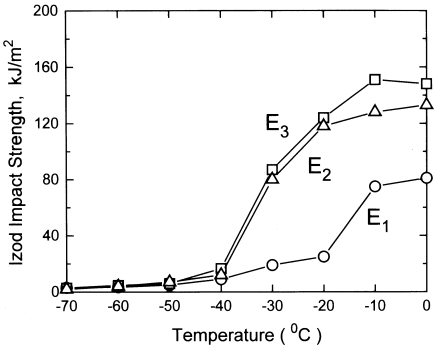

Fig. 3. Variation of impact strength with temperatures for E_1, E_2 and E_3 blends.

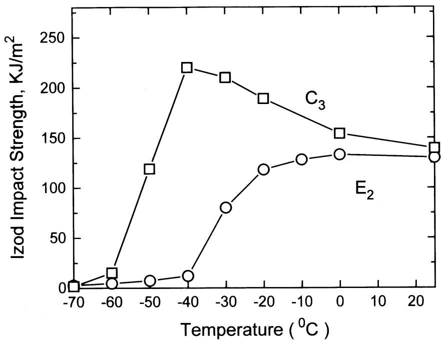

Fig. 4. Variation of impact strength with temperatures for C_3 and E_2 blends.

Morphology

Figure 5(a) shows a typical low-magnification SEM micrograph of the C_3 blend after impact test

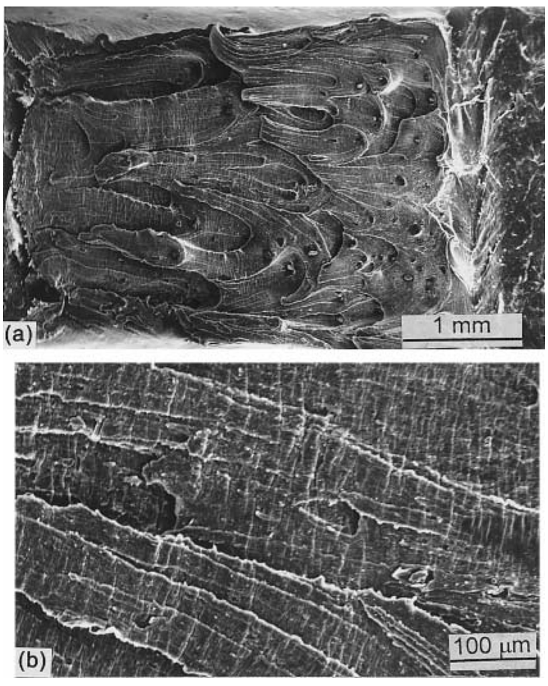

Fig. 5. (a) Low-magnification SEM micrograph showing the fracture surface of C_3 blend after impact testing at –30°C; (b) a higher magnification SEM fractograph of the stress whitening zone ahead of the notch.

at −30°C. Examination of the fracture surfaces of the C_3 blend reveals the formation of an induction zone around the notch showing a stress whitening behaviour. A higher magnification of the stress whitening zone is shown in Fig. 5(b). Apparently, shear bands are formed in the induction zone of the blend containing 30% EPDM, 15% HDPE and 20% EP. As shear yielding dissipates a large amount of impact energy, thus the C_3 blend exhibits superior impact toughness at −30°C. For this super-tough C_3 blend, the Izod impact specimen does not break when tested at −30°C. Similar shear yielding is observed in the induction zones of the blend specimens containing higher EPDM content such as D_2 and D_3 (Fig. 6). To observe the surface morphology of the fast fracture region located further away from the notch, the unbroken Izod specimen was cryofractured in liquid nitrogen. As the matrix in the fast fracture region experiences no plastic deformation, hence the fractograph taken from this region represents the morphology of the sample in the moulded condition. Figure 7(a) shows a typical SEM micrograph of the fast fracture region of the D_3 blend specimen. It can be seen that small and elongated cavities are uniformly distributed in the polymer matrix, and no major agglomeration of rubber particles is observed. Furthermore, some particles can be observed within these cavities. It is considered that these particles are the EPDM surrounding the HDPE inclusions. The particles are well adhered to the matrix, indicating the formation of a stronger interfacial bonding brought about by the EP copolymer incorporation (Fig. 7(b)). When small amounts of HDPE and EPDM are added to PP, they disperse as discrete particles in the PP matrix. As an optimum content of the EPDM is reached, the HDPE particles are likely to be encapsuled by the rubber phase. The compatibility between the EPDM (shell)–HDPE (core) inclusions can be enhanced by the addition of EP copolymer. The formation of a core-shell type rubber modifier effectively toughens the system.

By contrast, there is no shear yielding in the induction zone of the B_3 blend containing 25% EPDM, 10% HDPE and 20% EP after impact testing at −30°C (Fig. 8(a)). The fracture surface appears relative smooth, indicating that little plastic deformation has taken place during the impact tests. The fractograph correlates well with the impact test data as shown in Fig. 2(b) which indicates that the blends with 25% EPDM and HDPE content ≤20% exhibit very low impact energy. On increasing the HDPE content to 25%, the SEM fractograph reveals the formation of cavities in the induction zone of the B_6 blend specimen (Fig. 8(b)). As cavitation, which is associated with debonding of rubber particles from the matrix, dissipates less energy than shear yielding, thus the impact strength of blend B_6 is much smaller than that of blend C_3 at −30°C. On the other hand, the impact energies of the blends with 25% EPDM at 25°C are strongly dependent on the HDPE content (Fig. 2(a)). It is desirable to observe the effect of HDPE content on the morphology of the blends with 25% EPDM content. Figure 9(a) and (b) show the SEM micrographs of the B_1 and B_2 blends after fracture in liquid nitrogen and etching in *n*-heptane solution. The holes represent the sites where the rubber particles are located prior to etching. The blend without HDPE (B_1) shows the formation of larger cavities, whilst the addition of 5% HDPE into the blend (B_2) results in the formation of smaller dispersed particles.

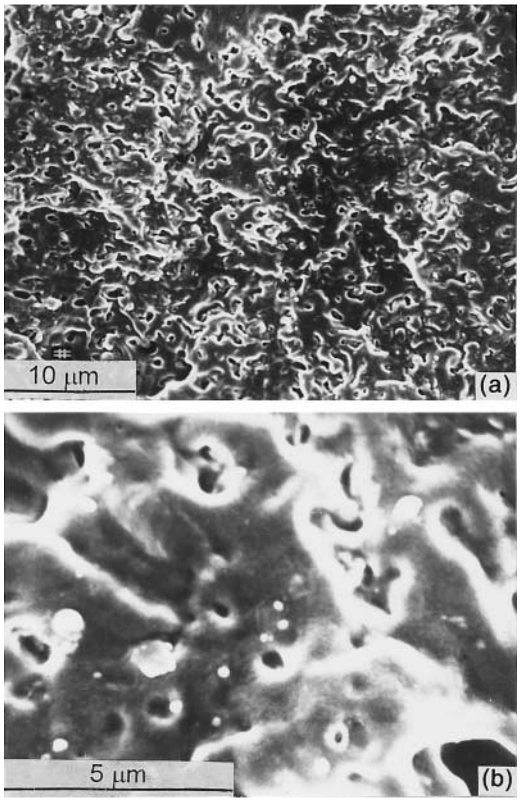

Fig. 7. (a) SEM micrograph showing the fracture surface of the fast fracture zone of D_3 blend and (b) a higher magnification fractograph of (a).

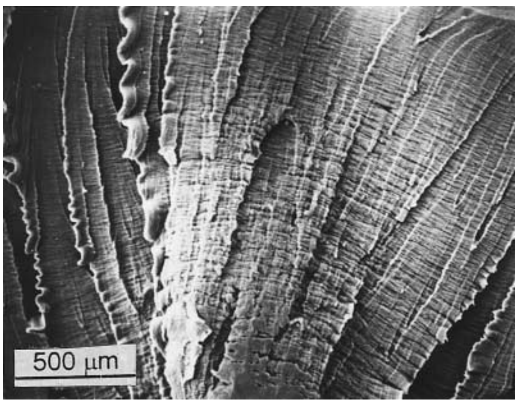

Fig. 6. SEM micrograph showing the fracture surface of the stress whitening zone for D_2 blend after impact testing at −30°C.

Figure 10(a) shows an SEM fractograph of the E_2 blend after impact testing at −30°C. This micrograph indicates that few shear bands are developed in the induction zone of E_2 during impact testing at

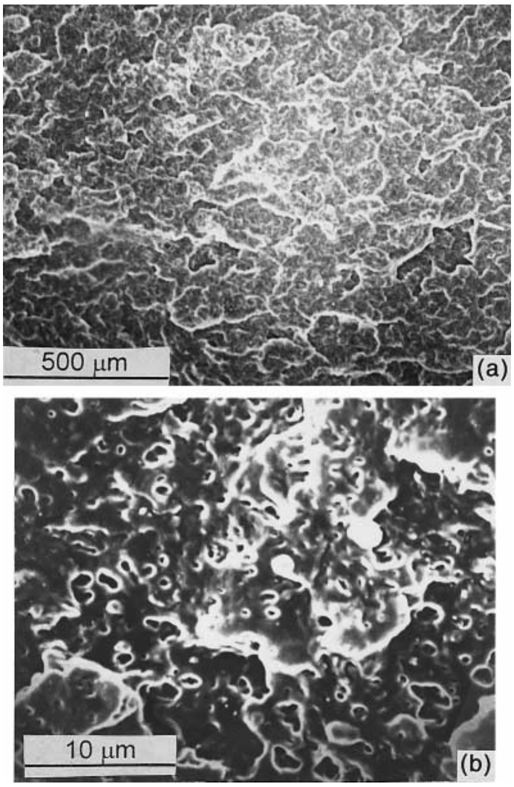

Fig. 8. SEM micrographs showing the fracture surface of the induction zone ahead of the notch for (a) B_3 and (b) B_6 blends.

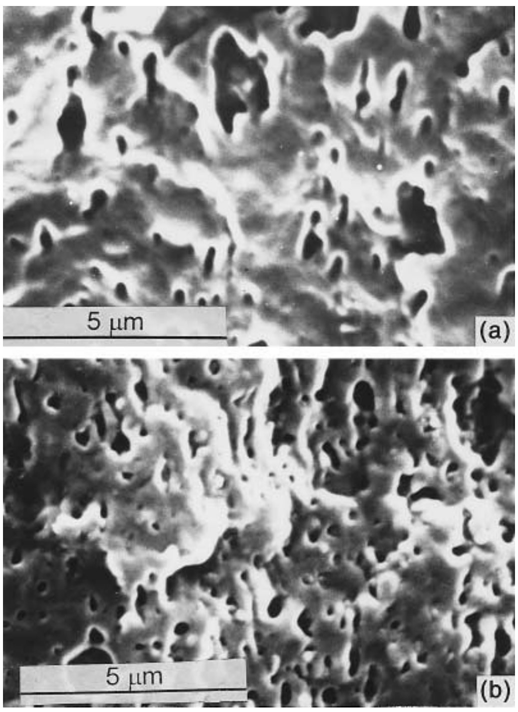

Fig. 9. SEM fractographs of the fast fracture region of (a) B_1 and (B) B_2 blends after fractured in liquid nitrogen and subsequent etching in *n*-heptane solution.

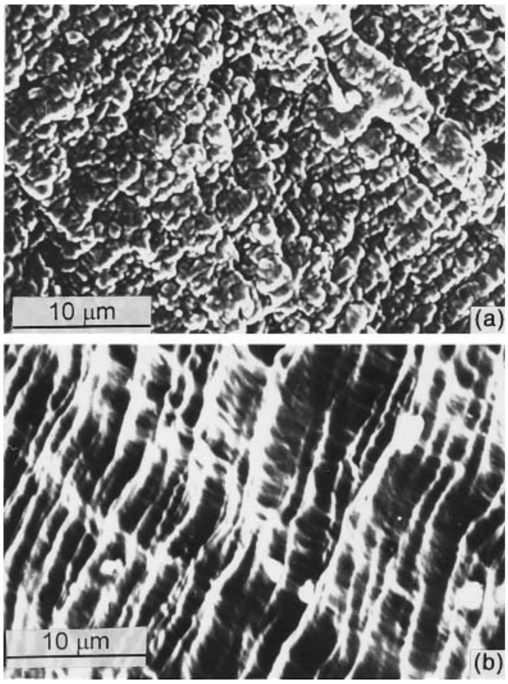

Fig. 10. SEM fractographs of the induction zone for E_2 blend after impact testing at (a) −30°C and (b) 0°C.

−30°C. As the E_2 blend has a transition from brittle to ductile behaviour as shown in Fig. 4, increasing the test temperature to 0°C leads to the formation of shear yielding bands in the entire region of the induction zone (Fig. 10(b)). In this respect, the elastomer-initiated localized shear yielding corresponds to the higher impact strength observed at 0°C as shown in Fig. 4.

It is generally known that the rubber particles act as stress concentrators ahead of the notch tip, thereby promoting crazing or shear yielding of the matrix. The toughening mechanisms depend on the intrinsic ductility of the matrix materials and morphological parameters such as particle size (d), volume fraction of particles (ϕ), and matrix ligament thickness (surface-to-surface interparticle distance) (T) [16, 17]. For binary blends, the relationship between T and d is given by [16]:

$$T_c = d[(\pi/6\phi)^{1/3} - 1] \quad (1)$$

where T_c is the critical particle distance. Wu demonstrated that blends are toughened if T is smaller than T_c. From Equation (1), a small value of T_c can be obtained by reducing d or increasing ϕ. The T_c value of nylon/EPDM blends was determined to be 0.304 μm [16]. For the binary PP/EPDM blends, Qi and co-workers determined the T_c to be 0.15 μm [18]. This implies that shear yielding takes place in binary PP/EPDM blends if T is smaller than 0.15 μm. The presence of HDPE and EP in the PP/EPDM/HDPE/EP blends renders the system more complicated to analyse. Nevertheless, Equation (1) can be used to make a rough estimate for T_c in the quaternary blends, and it indicates that T_c tends to decrease with increasing EPDM volume content. For supertough quaternary blends

Table 2. Impact properties of some blends investigated

Sample	PP (wt%)	EP (wt%)	EPDM/ HDPE ratio	Impact strength at 25°C, kJ/m^2	Impact strength at −30°C, kJ/m^2
A_4	30	20	0.67	111	18
B_6	30	20	1	141	146
C_4	30	20	1.5	139	220
D_3	30	20	2.3	140	201
A_3	35	20	0.8	117	16
B_5	35	20	1.25	145	31
C_3	35	20	2	139	209
D_2	35	20	3.5	138	201
A_2	40	20	1	117	13
B_4	40	20	1.67	148	25
C_2	40	20	3	139	180

with EPDM ≥30 wt%, the rubber particles are closer to each other, thus there is a strong overlap of the stress fields around the particles, thereby inducing shear yielding of the matrix [17].

We can summarize the impact properties of blends of PP with three other olefinic polymers in terms of the EPDM/HDPE ratio (Table 2). This is because the concentration of EP block copolymer is held constant at 20%, except in the case of series E, where it is zero (Table 1). It is more appropriate by comparing sets of blends in which both the PP and EP concentrations are held constant and the EPDM/HDPE ratio is varied. For example, the A, B, C and D series all have materials containing 30%, or 35% or 40% PP, plus 20% EP. Thus all specimens in the A, B, C and D series can be rearranged into three sets of blends with constant concentrations of PP and EP, i.e. 30% PP and 20 EP, 35% PP and 20% EP as well as 40 % PP and 20% EP (Table 2). For the blends containing 30% PP, there is an improvement in the impact strength, particularly at −30°C when the EPDM/HDPE ratio reaches 1 (Table 2). Such low-temperature strength can be further increased by raising the EPDM/HDPE ratio to 1.5 and above. Furthermore, SEM fractographs also indicate that shear yielding tends to occur in the induction zone of the specimens tested at −30°C when the EPDM/HDPE ratio ≥1.5. For blends containing 35% PP, the low-temperature impact strength increases significantly when the EPDM/HDPE ratio approaches 2. Similar shear yielding is observed in these blends with an EPDM/HDPE ratio ≥2. Finally, the low-temperature impact strength of the blends containing 40% PP can be improved when the EPDM/HDPE ratio reaches 3. Thus it is evident that the higher the PP content in the blends, the higher the EPDM/HDPE ratio needed for achieving good impact strength at low temperature.

CONCLUSION

This work demonstrates that the quaternary blends containing EPDM ≥30 wt% exhibit superior impact strengths at low temperatures. SEM observations reveal that shear yielding bands are formed in the stress whitening zone of the blends with EPDM ≥30 wt%. The blends with EPDM ≤ 25 wt% have low impact energies at −30°C, and SEM micrographs show that cavitation around the dispersed particles occurs in the induction zone ahead of the notch tip of such blends. The impact behaviour of the quaternary blends is dependent on the EPDM/HDPE ratio. The higher the PP content in the quaternary blends, the larger the EPDM/HDPE ratio needed for achieving good impact toughness at low temperature.

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