JOURNAL OF MATERIALS SCIENCE **35** (2000) 4833–4840

Effect of high density polyethylene addition and testing temperature on the mechanical and morphological properties of polypropylene/ethylene-propylene diene terpolymer binary blends

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High density polyethylene (HDPE) was added to the polypropylene (PP)/ethylene-propylene diene terpolymer (EPDM) binary blend, and the effect of testing temperatures on the modulus of elasticity, impact behavior and corresponding fracture morphology was analyzed. Modulus of elasticity generally decreased as the EPDM content increased regardless of the testing temperatures. However, it was found that the modulus of elasticity of PP/EPDM/HDPE ternary blend increased compared to PP/EPDM binary blend when tested at −30 and −60 °C. Notched Izod impact strength changed depending on the testing temperatures, however, there was not much difference between binary and ternary blends up to 20 wt% EPDM. However, at more than 30 wt% EPDM content, ternary blends showed higher impact strength compared to binary blends. Especially, at −30 °C, brittle-ductile transition was observed between 20 and 30 wt% EPDM. Subsurface morphology was also analyzed, and the relationship between the impact strength and the stress whitening zone was investigated. Scanning electron microscopy observation of impact fractured surfaces was conducted, and overall morphology was analyzed with respect to HDPE addition and testing temperature change. © *2000 Kluwer Academic Publishers*

1. Introduction

Since the first successful stereoregular synthesis by Natta in 1954, polypropylene (PP) has been widely used in a variety of applications. PP has many advantages such as low density, good moldability, high softening point as well as good mechanical properties, however, it has poor impact strength at low temperature. In order to overcome this disadvantage, ethylene-propylene-diene terpolymer (EPDM) was incorporated into PP, and there have been many studies regarding crystallization, mechanical and rheological behaviors [1–8]. Even though PP/EPDM blends can increase the low temperature impact strength, it also results in a decrease of modulus and tensile strength. Thus, in order to overcome this behavior, high density polyethylene (HDPE) is occasionally added to the PP/EPDM binary blend. Regarding these PP/EPDM/HDPE ternary blends, Choudhary *et al.* studied the morphological, rheological and mechanical behavior with changing EPDM content added to a PP/HDPE binary blend with fixed composition [9]. They found that by adding EPDM to the PP/HDPE binary blend, EPDM can act as a lubricant as well as compatibilizer, and form a core-shell structure within the PP matrix. Meanwhile, D'Orazio *et al.* studied the changes in mechanical properties and fracture mechanisms on adding EPDM to the PP/HDPE binary blends [10]. They found that EPDM can act as an interfacial agent to increase the interfacial bonding between the PP matrix and dispersed HDPE particles. Stehling *et al.* studied the fracture morphology of PP/EPDM/HDPE ternary blends, and examined the state of dispersed phase quantitatively as well as impact and modulus of elasticity behavior [11]. They concluded that the melt residence time during processing affected the phase morphology. These previous studies on the PP/EPDM/HDPE ternary blends covered the mechanical and morphological properties, but there have been no systematic studies covering the test temperature effect on the modulus of elasticity, impact strength and the corresponding fracture morphology with HDPE addition.

Thus, in this investigation, a fixed amount of HDPE was added to the PP/EPDM binary blend, and systematic studies correlating the modulus of elasticity, impact strength and corresponding fracture morphologies were conducted. The testing temperature was carefully selected by considering the glass transition temperature (T_g) of each component (PP = −9.8 °C, EPDM = −45.4 °C, and HDPE = −105.7 °C), thus the testing temperatures were set at −60 °C, −30 °C and 23 °C in order to investigate the T_g effect on the above properties.

2. Experimental

2.1. Materials

Polypropylene (PP) and high density polyethylene (HDPE) used in this investigation are commercial grades H730F (M.I. = 3.5g/10 min) and JH910 (M.I. = 7.5g/10 min) manufactured by SK Co., respectively. Ethylene-propylene diene terpolymer (EPDM) used in this investigation is a commercial grade KEP570P (M.I. = 0.14g/10 min) manufactured by Kumho Polychem. Co.

2.2. Sample preparation

PP/EPDM binary and PP/EPDM/HDPE ternary blends were manufactured using a twin screw extruder (Brabender Plasticorder PLE 651). The processing temperature was between 200–220 °C, and screw speed was 65 rpm. All blends were treated identically during the processing. Specimens for mechanical property tests were manufactured using injection molder (Engel ES 240/75P), and all injection molded specimens were conditioned in an oven at 50 °C to remove any residual stress before the test. Compositions of the PP/EPDM binary blends were 100/0, 90/10, 80/20, 70/30 and 50 wt% PP/50 wt% EPDM, respectively. The compositions of the PP/EPDM/HDPE ternary blends were the same as the PP/EPDM binary blends except for an additional 20 phr of HDPE.

2.3. Mechanical property test

ASTM D-638 type specimens were used for the tensile tests. Tensile tests were performed using Lloyd Instruments Co. (model LR50K). Testing temperatures were chosen considering the glass transition temperatures of PP, EPDM and HDPE, thus the chosen testing temperatures were −60, −30 and 23 °C. All tests were performed using the environmental chamber, and liquid nitrogen was used as a coolant. All specimens were stored at least for 5 hours, and at least 10 specimens were used and the average values were used for the data plot except maximum and minimum values.

Notched Izod impact tests were performed using ASTM D-256 type specimens and the impact tester was Testing Machines Inc. (model 43-02, notched Izod type). The same testing temperatures were used as in the tensile tests, low temperature tests were performed using an attached environmental chamber. Carbon dioxide was used as a coolant. At least 10 specimens were used and the average values were used for the data plot except maximum and minimum values.

2.4. Morphology observation

In order to observe the cross sections in a plane perpendicular to the notch root of impact fractured specimens, they were ground and polished using sand papers (240, 320, 400 and 600 grit) and alumina paste (1.0 and 0.3 μm). The final thickness of the polished specimens was about 100–150 μm . Then, the impact fractured notch tip areas were examined to observe the plastic deformation such as crazes using transmission optical microscopy. Also, impact fractured surfaces of PP/EPDM binary and PP/EPDM/HDPE ternary blends were observed using the SEM (scanning electron microscope, JEOL model JSM-5200). In the case of PP/EPDM/HDPE ternary blend, in order to observe the fracture morphology change according to EPDM content and HDPE addition, EPDM was selectively etched using xylene at 23 °C for 10 min in an ultrasonic cleaner (Bransonic Co., 2210R-DTH). Impact fractured surfaces were coated with gold before the SEM observation, and the operating voltage was 20 kV.

3. Results and discussion

3.1. Mechanical test results

Fig. 1 shows the modulus of elasticity of PP/EPDM binary and PP/EPDM/HDPE ternary blends at three different testing temperatures. Generally, all binary and ternary blends showed a modulus decrease with increasing EPDM content. At 23 °C, the modulus shows little change with the HDPE addition, however, at −30 and −60 °C (below the T_g of PP), the modulus of the binary blend is much higher. Also, the modulus of the ternary blend is about twice that of the binary blend at −30 and −60 °C. In the case of the binary blend at −30 and −60 °C, this behavior is because the testing temperature is below the T_g of the PP matrix, thus the matrix is in a glassy state and results in a higher modulus. However, in the case of the ternary blend at the same testing temperatures, the modulus is much higher than that of the binary blend. At −30 °C, the added HDPE and

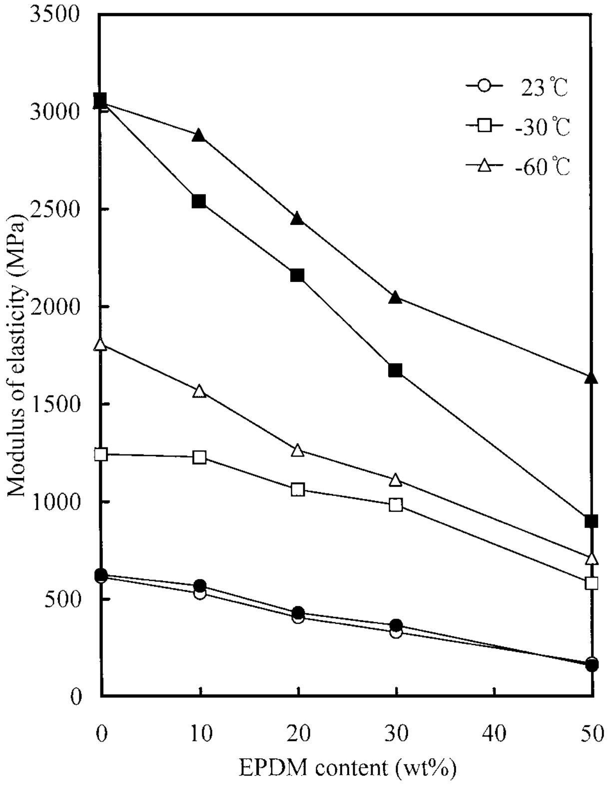


Figure 1 Modulus of elasticity vs. EPDM content of PP/EPDM binary and PP/EPDM/HDPE ternary blends at various testing temperatures (unfilled symbol : binary blend, filled symbol : ternary blend).

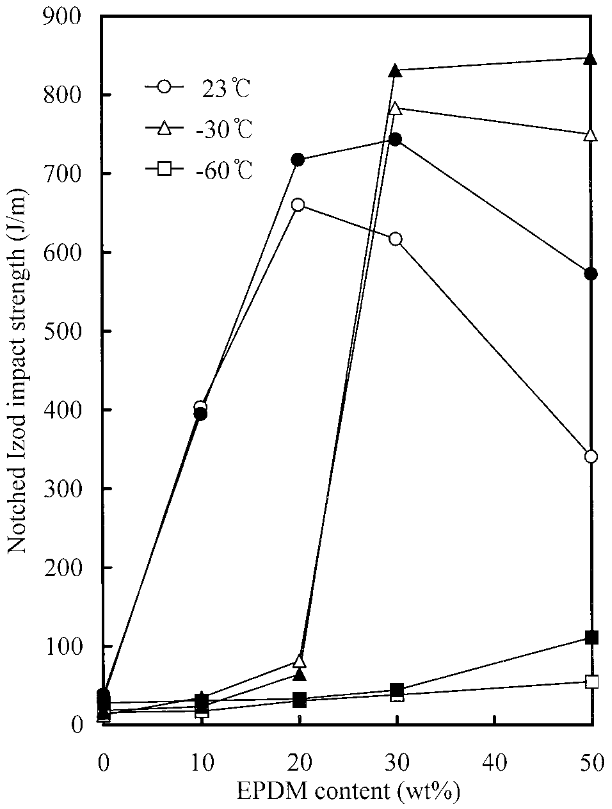


Figure 2 Notched Izod impact strength vs. EPDM content of PP/EPDM binary and PP/EPDM/HDPE ternary blends at various testing temperatures (unfilled symbol : binary blend, filled symbol : ternary blend).

EPDM are still in rubbery state, but the material still can have higher modulus due to the rule of mixtures relationship since the added HDPE has higher modulus than EPDM at this testing temperature. At −60 °C, EPDM is in a glassy state, thus it has higher modulus compared to that at −30 °C, and results in a still higher modulus in a ternary blend.

Fig. 2 shows the impact strength of PP/EPDM binary and PP/EPDM/HDPE ternary blends at three different testing temperatures. At 23 °C, the notched Izod impact strength increased up to 20 wt% EPDM regardless of the HDPE addition. However, at more than 20 wt% EPDM, the ternary blend has a much higher impact strength compared to the binary blend. At more than 30 wt% EPDM, the impact strength of both binary and ternary blends started to decrease, but the impact strength of the ternary blend was still higher than that of the binary blend.

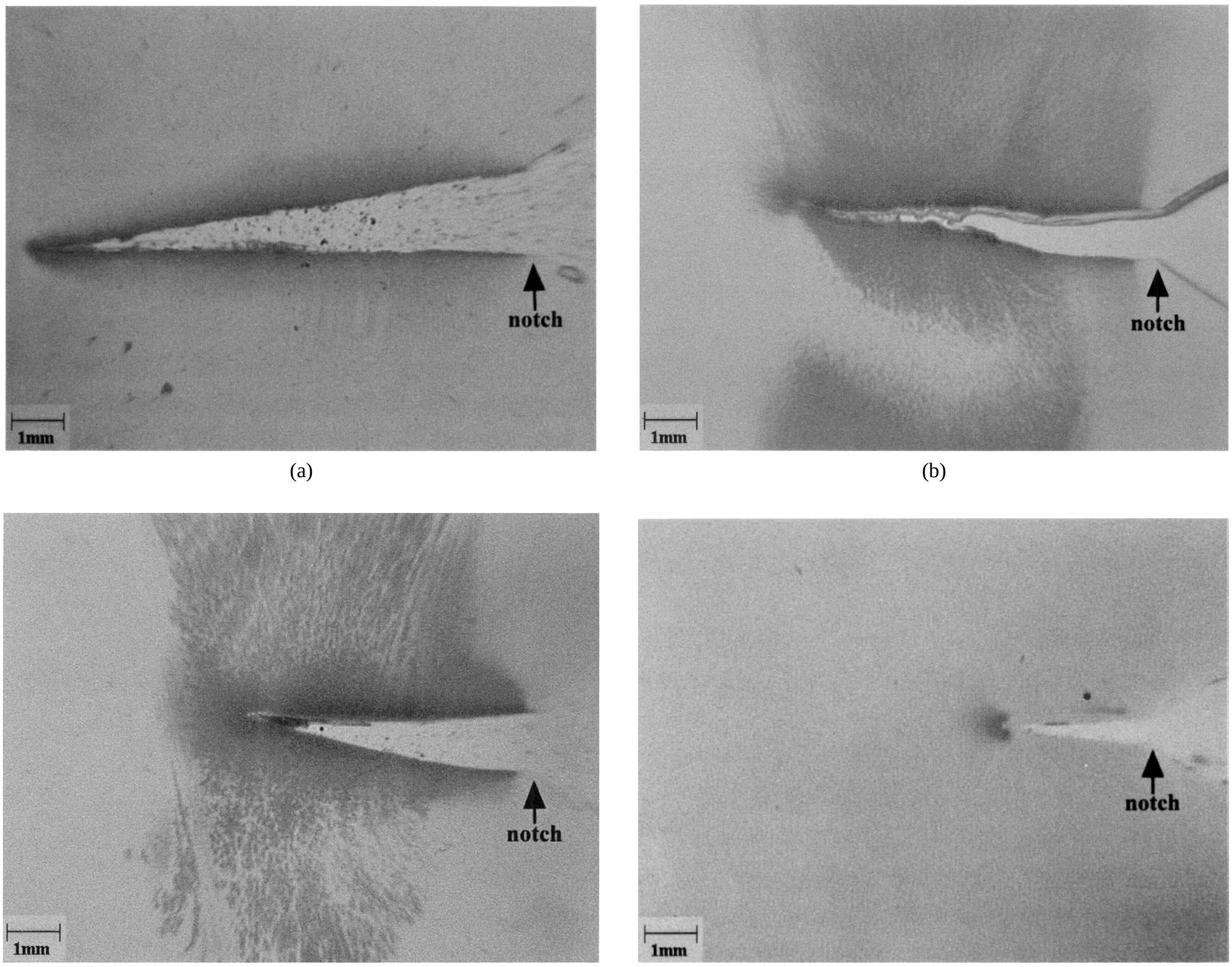
At −30 °C, very low impact strength was observed up to 20 wt% EPDM, however, at 30 wt% EPDM, the impact strength increased more than ten times. Since the T_g of PP is about −10 °C, at −30 °C testing condition, the PP matrix is in a glassy state, but the HDPE and EPDM is still in a rubbery state, thus, the PP matrix will have brittle behavior. However, between 20–30 wt% EPDM, an abrupt brittle-to-ductile transition is observed, and this is probably due to the formation of dispersed particles of critical size which will be discussed in the morphology observation section of impact fractured specimens. Generally brittle-ductile transition depends on the rubber type, dispersed particle size and interfacial bonding between matrix and rubber, and in the case of rubber reinforced glassy amorphous thermoplastic, it is known that there exists an optimum particle size for this transition occur. Also, the impact strength of the ternary blend was higher than that of the binary blend at more than 30 wt% EPDM, but the difference was not great considering the impact test nature.

However, at −60 °C, which is a temperature below the T_g of PP and EPDM, all blends showed low impact strength regardless of composition. In the case of the binary blend, this phenomenon is expected since both PP and EPDM are in a glassy state. In the case of the ternary blend, EPDM can envelop the dispersed HDPE particles which will be discussed in the morphology observation of impact fractured specimens. Thus, at this temperature, the dispersed phase and the PP matrix are also in a glassy state, and result in low impact strength. Also, the addition of HDPE brings very little effect in increasing the impact strength at low EPDM content due to the above reason, but starts to show the effect at higher EPDM content (50 wt% EPDM), and at this composition, the ternary blend has about two times higher impact strength compared to the binary blend.

3.2. Fracture subsurface morphology observation

Figs 3 and 4 show transmission optical micrographs of cross sections in a plane perpendicular to the notch root of impact fractured PP/EPDM/HDPE ternary blend tested at 23 and −30 °C, respectively. As can be seen in Fig. 3, as the EPDM content increased, the crack length from the notch tip decreased, and a stress whitening zone area proportional to the impact strength was observed. Fig. 3a shows the subsurface fracture microstructure of the ternary blend with 10 wt% EPDM, and the crack propagates about 9 mm from the notch tip and a localized stress whitening zone was observed along the crack surface. In Fig. 3b and c which are for ternary blends with 20 and 30 wt% EPDM, an expanded stress whitening zone is observed centered on the crack, and the crack length also decreased from about 5.5 to 4.5 mm as the EPDM content increased. From this investigation, we can conclude that the impact strength is related to the size of stress whitening zone as well as crack length. Normally, the appearance of the stress whitening zone in an impact fractured PP/EPDM binary blend is due to the occurrence of numerous multicrazes near the notch tip, and this phenomenon was not observed in a pure PP, and as the EPDM content increased, the stress whitening zone increased. This tendency is also clearly observed in Fig. 3a through 3c. However, as is shown in Fig. 3d, in the case of 50 wt% EPDM, only a localized stress whitening zone was observed ahead of the notch tip since at this composition, phase inversion probably took place.

Fig. 4 shows the subsurface fracture microstructure of impact fractured ternary blends tested at −30 °C. All ternary blends up to 20 wt% EPDM broke, but the specimens with more than 30 wt% EPDM did not break during the impact testing. This result is in good agreement with the observed brittle–ductile transition in the impact test results, and the subsurface morphology of the specimens with 20 and 30 wt% EPDM (Fig. 4a



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

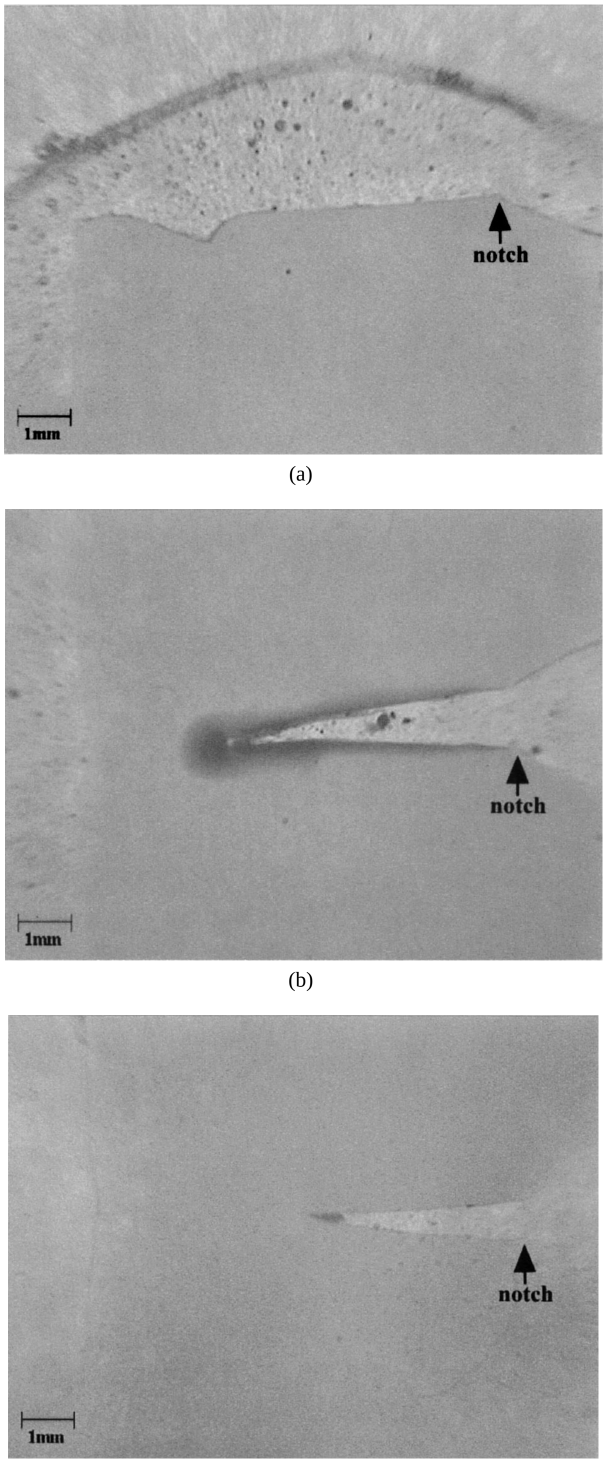
Figure 3 Transmission optical micrographs of notched Izod impact tested specimens near the crack tip region at 23 °C of (a) 90 wt% PP/10 wt% EPDM/20 phr HDPE ternary blend, (b) 80 wt% PP/20 wt%/EPDM/20 phr HDPE ternary blend, (c) 70 wt% PP/30 wt% EPDM/20 phr HDPE ternary blend, (d) 50 wt% PP/50 wt% EPDM/20 phr HDPE ternary blend.

and b). Fig. 4a shows the subsurface morphology of 20 wt% EPDM, and no stress whitening zone is observed near the fracture surface which is in good agreement with the observed low impact strength. Fig. 4b shows subsurface morphology after the brittle-ductile transition at −30 °C, and it shows the dark colored stress whitening zone along the crack surface and ahead of the crack tip, and at this composition, it did not break from the impact test and its crack length was about 4.5 mm which is almost the same as in 23 °C testing condition. In the case of 50 wt% EPDM, similar morphology was observed as for the 23 °C test condition. Also, as in a 23°C test condition, the crack length from the notch tip decreased as the EPDM content increased. And, the crack length from the notch tip seems to be almost the same for 30 and 50% EPDM if the specimen does not break from the impact test regardless of the test temperature change.

3.3. Impact fractured surface morphology observation

Fig. 5a shows the impact fractured surface morphology of PP/EPDM/HDPE ternary blend with 30 wt% EPDM tested at −60 °C, after etching EPDM with xylene. As can be seen, ternary blends do not consist of EPDM particles and HDPE particles separately imbedded in the PP matrix. Rather there are partly filled holes in the micrograph of the ternary blend. It shows a dense residue with some attachment to the PP matrix. According to Stehling *et al.* [11] when PP rich ternary blends are mixed, EPDM and HDPE combine to form composite particles dispersed in PP. At short melt residence time, EPDM does not completely surround the HDPE particles and HDPE is partly attached to the PP matrix.

Upon subsequent extraction, the HDPE particles are retained in the partly empty cavity by the PP-HDPE attachments. At long melt residence time, however, the PP-HDPE attachments are displaced, and the HDPE particles become completely enveloped by EPDM. When EPDM is extracted from the fracture surface, the insoluble but unattached HDPE particles are flushed away, leaving an empty hole. The tendency for EPDM to envelop HDPE, rather than vice versa, in a PP matrix is reasonable from interfacial energy considerations. If PP, EPDM and HDPE are completely insoluble, then the HDPE-within-EPDM structure(HDPE core-EPDM shell structure) will be thermodynamically favorable over an EPDM-within- HDPE structure if $\gamma_{\mathrm{PP\text{-}EPDM}} < \gamma_{\mathrm{PP\text{-}HDPE}}$, where γ is the interfacial energy. As can be seen in Fig. 5a, HDPE particles are observed with some HDPE attachment to the PP matrix. D'Orazio et al. also observed this structure in their



(a)

(b)

(c)

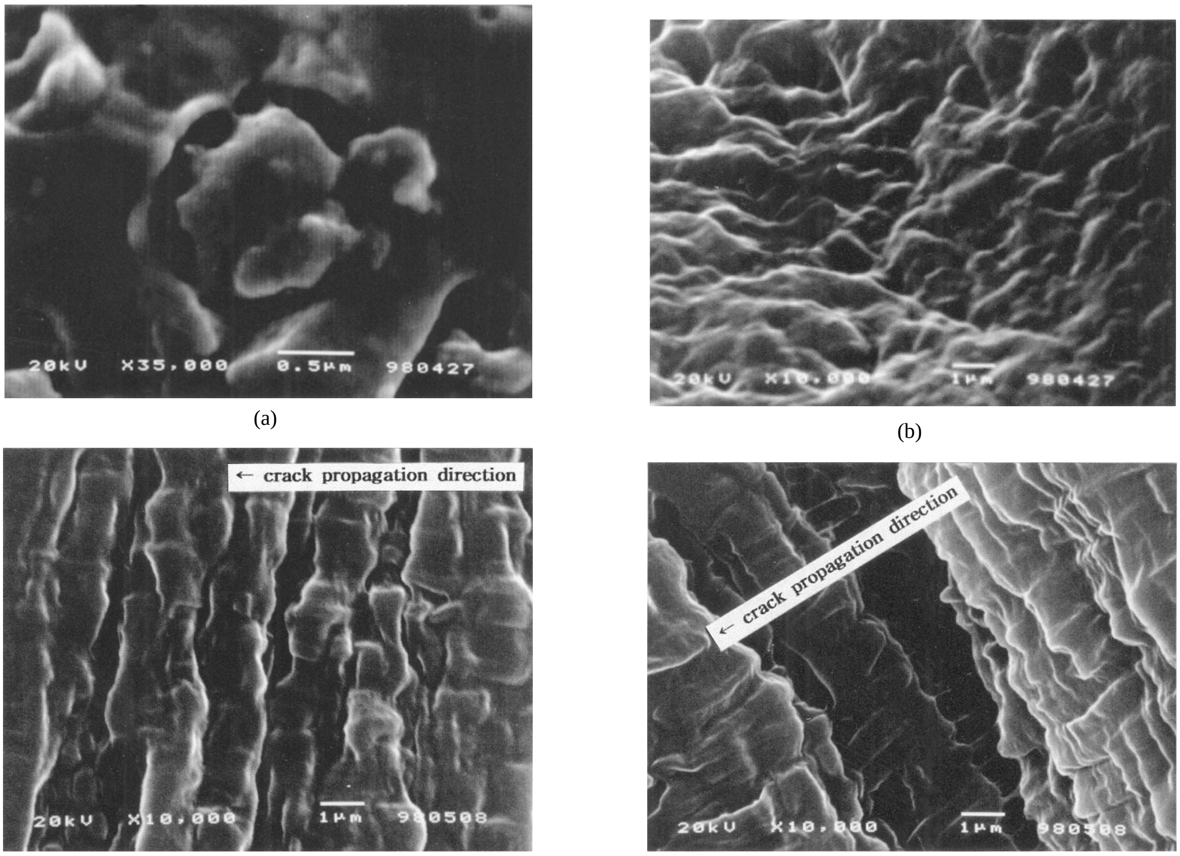
Figure 4 Transmission optical micrographs of notched Izod impact tested specimens near the crack tip region at −30 °C of (a) 80 wt% PP/20 wt%/EPDM/20 phr HDPE ternary blend, (b) 70 wt% PP/30 wt% EPDM/20 phr HDPE ternary blend, (c) 50 wt% PP50 wt% EPDM/ 20 phr HDPE ternary blend.

study of the PP/EPDM/HDPE ternary blend [10]. They found that the matrix and dispersed particles are interconnected by the HDPE attachment as in our observation, and in this case, EPDM acts as an interfacial agent which can promote the interfacial bonding between the PP and HDPE.

Fig. 5b–d show the impact fractured surface of PP/EPDM/HDPE ternary blend tested at 23 °C. Fig. 5b shows the fracture surface of ternary blend with 20 wt% EPDM, and severe plastic deformation is observed. Fig. 5c shows a fracture surface of the ternary blend with 30 wt% EPDM. As can be seen, striations perpendicular to crack propagation direction is observed, and overall fracture surface is not greatly different from Fig. 5b. Fig. 5d shows the etched surface of Fig. 5c, and extended HDPE attachments are observed within the PP matrix. Flaris and Stachurski studied the toughening mechanism of PP/EPDM/LLDPE ternary blend [12]. They found that EPDM and LLDPE can form a skin-core microstructure and be dispersed within the PP matrix, and proposed two toughening models for this behavior. One is the toughening effect via the extension of dispersed LLDPE particles and the other is the toughening effect by the addition of EPDM to the brittle matrix. In our system, by adding HDPE to the PP/EPDM binary blend, dispersed HDPE particles are surrounded by EPDM and form a skin-core microstructure. Then, the partially enveloped HDPE particles can be extended perpendicular to the crack propagation direction, thus it can effectively dissipate the impact energy and result in an increase of impact strength in a ternary blend.

Fig. 6 shows the impact fractured surface of a ternary blend tested at −30 °C. Fig. 6a shows the fracture surface of ternary blend with 20 wt% EPDM, and compared to the 23 °C condition (Fig. 5b), matrix plastic deformation is not observed. Generally, when the matrix is brittle, severe plastic deformation on the fracture surface is not observed on impact failure, and a relatively glass like clean fracture surface is obtained. If the interfacial bonding between the matrix and dispersed phase is weak, then the dispersed phase will separate from the matrix. From the observation of the fracture surface, even though the EPDM is not etched, separation of the dispersed phase from the matrix is observed. Fig. 6b shows the etched surface of 6a, and the fracture surface is clean as a glass, and a very inhomogeneous dispersed phase is observed. Some of the dispersed phase is completely empty which indicates that EPDM enveloped the HDPE particles completely. But, some of the dispersed phase shows HDPE phases in the hole still attached to the PP matrix via HDPE attachment. Fig. 6c shows the fracture surface of the ternary blend with 30 wt% EPDM which shows ten times higher impact strength compared to the ternary blend with 20 wt% EPDM. Even though the test was performed below the T_g of PP, severe plastic deformation can be found on the fracture surface. Wu differentiated the fracture mechanism during impact tests depending on the nature of matrix, and when the matrix is brittle, the main fracture mechanism occurs by matrix crazing, whereas in the case of a ductile matrix, the main fracture mechanism is by matrix yielding [13].

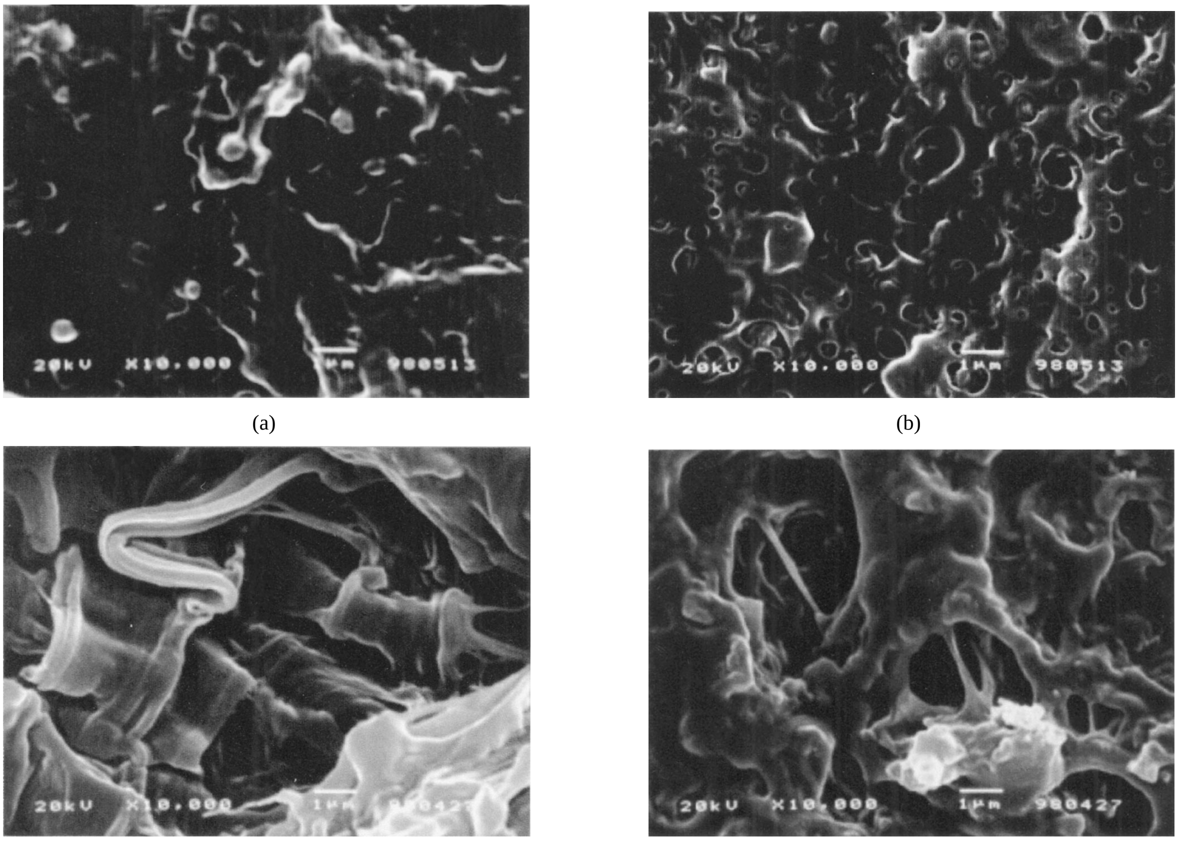
When the matrix is brittle, abrupt brittle-ductile transition occurs at a specific critical distance between the dispersed particles or particle size. From our observation, the average particle diameter of the dispersed phase was about 1.4 μm at 30 wt% EPDM with a fairly homogeneous particle size distribution compared to less than 1.0 μm at 20 wt% EPDM with a very



(a) (b)

(c) (d)

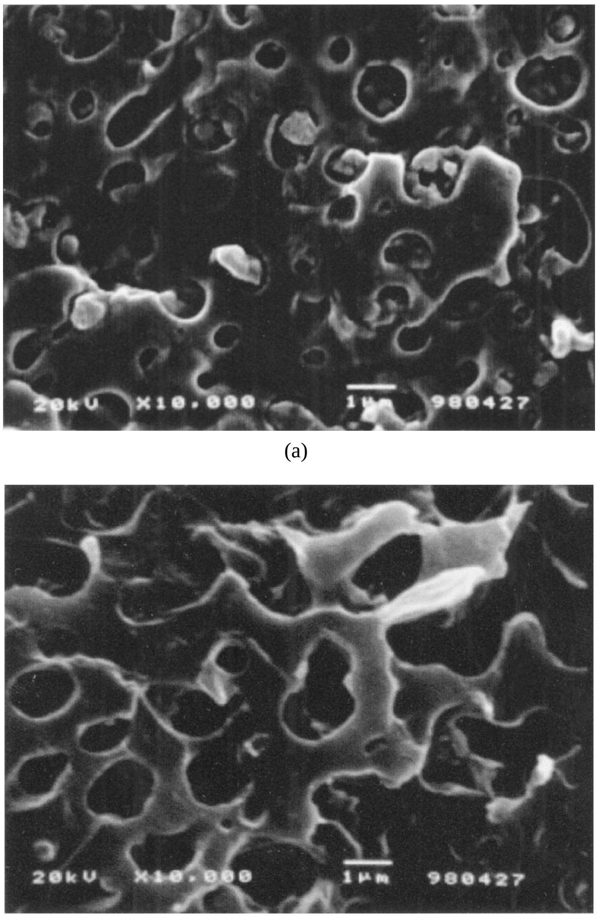
Figure 5 SEM micrographs of notched Izod impact fractured surfaces of (a) 70 wt% PP/30 wt% EPDM/20 phr HDPE ternary blend tested at −60 °C (fracture surface was treated with xylene at 23 °C, 10 min), (b) 80 wt% PP/20 wt% EPDM/20 phr HDPE ternary blend tested at 23 °C, (c) 70 wt% PP/30 wt% EPDM/20 phr HDPE ternary blend tested at 23 °C, (d) 70 wt% PP/30 wt% EPDM/20 phr HDPE ternary blend tested at 23 °C (fracture surface was treated with xylene at 23 °C, 10 min).



(a) (b)

(c) (d)

Figure 6 SEM micrographs of notched Izod impact fractured surfaces at −30 °C of (a) 80 wt% PP/20 wt% EPDM/20 phr HDPE ternary blend, (b) 80 wt% PP/20 wt% EPDM/20 phr HDPE ternary blend (fracture surface was treated with xylene at 23 °C, 10 min), (c) 70 wt% PP/30 wt% EPDM/20 phr HDPE ternary blend, (d) 70 wt% PP/30 wt% EPDM/20 phr HDPE ternary blend (fracture surface was treated with xylene at 23 °C, 10 min).



(a)

(b)

Figure 7 SEM micrographs of notched Izod impact fractured surfaces at −60 °C of (a) 80 wt% PP/20 wt% EPDM/20 phr HDPE ternary blend (fracture surface was treated with xylene at 23 °C, 10 min), (b) 70 wt% PP/30 wt% EPDM/20 phr HDPE ternary blend (fracture surface was treated with xylene at 23 °C, 10 min).

inhomogeneous particle size distribution as shown in Fig. 7a and b. And, there occurs an abrupt brittle-ductile transition between these compositions. Thus, in our system, the critical dispersed particle size for a brittle-ductile transition is about 1.4 μm at −30 °C testing condition. Fig. 6d shows an identical specimen as Fig. 6c except for the EPDM etching, and it shows severe PP matrix plastic deformation along with highly extended HDPE attachment within the HDPE/EPDM dispersed phase. This severe matrix deformation along with the extension of dispersed HDPE probably accounted for its high impact strength at −30 °C.

Fig. 7 shows the impact fractured surfaces of ternary blends at −60 °C which is below the T_g of PP and EPDM, and the fracture surfaces are etched with xylene. In the case of 20 wt% EPDM (Fig. 7a), partially aggregated HDPE particles are observed with some HDPE attachments to PP matrix, but the matrix fracture surface is very clean with little plastic deformation. Fig. 7b also reveals the very clean fracture surface, and it shows that etching resulted in an extraction of EPDM particles as well as HDPE in the majority of dispersed phases since at this composition EPDM can surround the dispersed HDPE particles more easily, thus aggregated HDPE particles are not easily observed as in 20 wt% EPDM (Fig. 7a).

4. Conclusion

A fixed amount of HDPE was added to PP/EPDM binary blends, and the effects of testing temperature on the modulus of elasticity, impact behavior and corresponding fracture morphologies were observed and the following conclusions could be made.

From the tensile tests, the modulus of elasticity decreased as the EPDM content increased at all testing temperatures, and the addition of HDPE did not bring any change at 23 °C. However, at −30 and −60 °C which are temperatures below the T_g of PP, the addition of HDPE results in a modulus increase about twice that of the binary blend. Impact tests showed that there was not much difference between the binary and ternary blends up to 20 wt% EPDM, and at more than 30 wt% EPDM, ternary blends showed a higher impact strength, and as the testing temperature increased, the difference between the binary and ternary blend increased further. At 23 °C, impact strength increased up to 30 wt% EPDM, however, it started to decrease beyond this content. At −30 °C, very low impact strength was observed at 20 wt% EPDM, but at 30 wt% EPDM, it exhibited very high impact strength which indicated that the brittle-ductile transition occurred in this composition range. At −60 °C, all binary and ternary blends showed a low impact strength regardless of composition, and this was because the test temperature was below the T_g of PP matrix and dispersed EPDM.

Subsurface microstructure observation of ternary blends after the impact test showed that at 23 °C, the crack length from the notch tip decreased as the EPDM content increased. At 10 wt% EPDM, a small localized stress whitening zone was observed adjacent to the fracture surface, but at 20–30 wt% EPDM, a comprehensive stress whitening zone proportional to EPDM content was observed.

This is due to the occurrence of numerous crazes, and it can dissipate the impact energy via new surface creation. Also, the crack length from the notch tip decreased with increasing EPDM, and the absolute crack length was also similar at the same composition regardless of testing temperature changes. SEM observation of impact fractured ternary blends showed that by adding HDPE to the 70 wt% PP/30 wt% EPDM binary blend, the dispersed EPDM and HDPE could form skin-core microstructures and the PP matrix was partly connected by the extended HDPE attachment within the dispersed EPDM/HDPE particles.

References

1. V. CHOUDHARY, H. S. VARMA and I. K. VARMA, *Polymer* **32** (1991) 2534.
2. L. D'ORAZIO, C. MANCARELLA, E. MARTUSCELLI and F. POLATO, *ibid.* **32** (1991) 1186.
3. B. Z. JANG, D. R. UHLMANN and J. B. VANDER SANDE, *Polym. Eng. Sci.* **25** (1985) 643.
4. K. NITTA, K. OKAMOTO and M. YAMAGUCHI, *Polymer* **39** (1998) 53.
5. D. W. BARTLETT, J. W. BARLOW and D. R. PAUL, *J. Appl. Polym. Sci.* **27** (1982) 2351.
6. C. S. HA and S. C. KIM, *ibid.* **37** (1989) 317.
7. Z. S. PETROVIC, J. BUDINSKI-SIMENDIC, V. DIVJAKOVIC and Z. SKRBIC, *ibid.* **59** (1996) 301.
8. N. HOLZ, G. S. GOIZUETA and N. J. CAPIATI, *Polym.*

Eng. Sci. **36** (1996) 2765.

9. V. CHOUDHARY, H. S. VARMA and I. K. VARMA, *Polymer* **32** (1991) 2541.
10. L. D'ORAZIO, R. GRECO, E. MARTUSCELLI and G. RAGOSTA, *Polym. Eng. Sci.* **23** (1991) 489.
11. F. C. STEHLING, T. HUFF, C. S. SPEED and G. WISSLERS, *J. Appl. Polym. Sci.* **26** (1981) 2693.
12. V. FLARIS and Z. H. STACHURSKI, *ibid.* **45** (1992) 1789.
13. S. WU, *Polymer* **26** (1985) 1855.

Received 11 August 1999
and accepted 3 March 2000