

Toughening of PP/EPDM Blend by Compatibilization

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ABSTRACT: To improve the mechanical properties of blends of polypropylene (PP) and terpolymer of ethylene-propylene-diene (EPDM), a triblock copolymer, (PP-*g*-MAH)-*co*-[PA-6,6]-*co*-(EPDM-*g*-MAH), was synthesized by coupling reaction of maleic anhydride (MAH)-grafted PP (PP-*g*-MAH), EPDM-*g*-MAH, and PA-6,6. The newly prepared block copolymer brought about a physical interlocking between the blend components, and imparted a compatibilizing effect to the blends. Introducing the block copolymer to the blends up to 5 wt % lead to formation of a β -form crystal. The wide-angle X-ray diffractograms measured in the region of 2θ between 10° and 50° ascertained that incorporating the block copolymer gave a new peak at $2\theta = 15.8^\circ$. The new peak was assigned to the (300) plane spacings of the β -hexagonal crystal structure. In addition, the block copolymer notably improved the low-temperature impact property of the PP/EPDM blends. The optimum usage level of the compatibilizer proved to be 0.5 wt %. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1267–1274, 2000

Key words: polypropylene/EPDM blend; polyamide-6,6-based compatibilizer; impact properties; physical interlocking

INTRODUCTION

PP has good mechanical properties but lacks low-temperature impact properties. Many studies have been carried out on the blends of PP and low-modulus rubbers to obtain good low-temperature properties.^{1–5} Because EPDM has similarity in chemical structure, it has been most intensively tested as the rubber component of the blends.^{6–8} Among PP/rubber blends, the PP/EPDM blend has acquired some commercial success, and finds applications in various industrial fields because the composition-dependent properties of the blends can meet the diverse require-

ments of industrial applications. Despite the structural similarity, however, EPDM itself is not compatible with PP.^{3,6} The EPDM phase exists as separate particles in the PP matrix due to stratification, segregation, and phase inversion.^{9,10} The incompatibility of the blends is signified by poor interface adhesion. The interface instabilities lead to poor and undesirable mechanical properties. To improve the compatibility of the PP/EPDM blends, various compatibilizers have been prepared by molecular design, and incorporated into the blends.^{7–9,11,12}

Recently, numerous polymeric compatibilizers have been reported, which are well summarized in ref. 13. In addition, a very convenient way of preparing compatibilizers has been suggested—the so-called reactive processing methods.¹⁴ Various vinyl monomers can be grafted or block-co-

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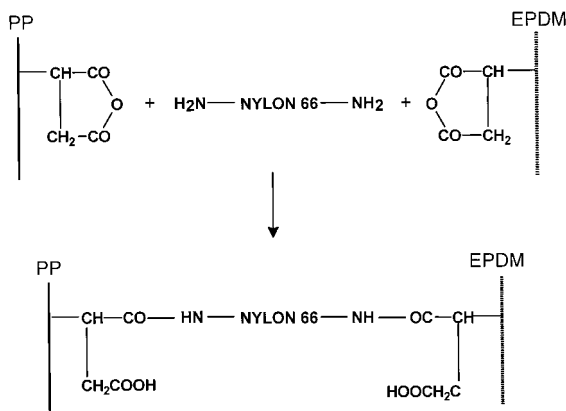


Figure 1 Schematic representation of preparative method of compatibilizer.

polymerized onto the mother polymer such as PP, polyethylene, ethylene-propylene rubber, EPDM, and nitrile rubber. For instance, incorporating PP-grafted maleic anhydride (PP-*g*-MAH) during reactive processing can improve the compatibility of the incompatible nylon-6/PP blend.¹⁵ The compatibility of the EPDM/polyamide (PA)-6,6 blend is improved by incorporating EPDM-*g*-MAH during melt mixing as a result of the reaction of MAH with NH_2 end groups of PA-6,6.¹⁶ For this study we prepared a new compatibilizer for the PP/EPDM blends by coupling (PP-*g*-MAH) and (EPDM-*g*-MAH) to PA-6,6, and the physical properties of the PP/EPDM/compatibilizer blend systems are discussed.

EXPERIMENTAL

Materials

PP and EPDM were supplied by Kumho Petrolchemical Corp. (Korea) and Honam Petrolchemical Corp.

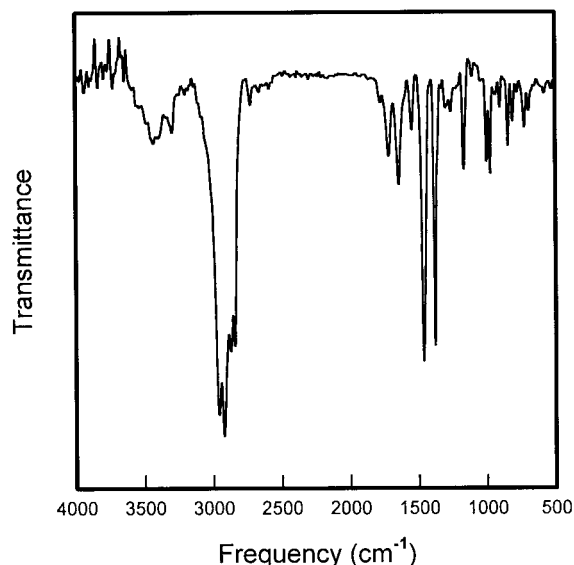


Figure 2 IR spectrum of the prepared compatibilizer.

(Korea), respectively. PP-*g*-MAH and EPDM-*g*-MAH were supplied by Korea Petrolchemical Corp. (Korea). Amine group(- NH_2) end-capped low molecular weight PA-6,6 was purchased from Aldrich Chemical Corp. (Madison, WI). The raw materials were dried at 80°C in a vacuum oven for 24 h prior to use.

The compatibilizer for the PP/EPDM blends, (PP-*g*-MAH)-*co*-[PA-6,6]-*co*-(EPDM-*g*-MAH), was prepared by coupling PP-*g*-MAH and EPDM-*g*-MAH onto PA-6,6 as schematically given in Figure 1. The detailed synthetic procedure is as follows. Twelve grams of PP-*g*-MAH and 12 g EPDM-*g*-MAH were dissolved in 600 mL xylene, and 0.6 g PA-6,6 was dissolved in 180 mL cresol. These solutions were poured into the flask at the same time. The reaction was carried out at 130–140°C for 24 h. The reactants were washed sev-

Table I Crystal Parameters of PP/EPDM/Compatibilizer Blends Measured from WAXS Diffractograms

Composition (wt %)						
PP/EPDM	Compatibilizer	$2\theta = 14^\circ$	$2\theta = 17^\circ$	$2\theta = 18.5^\circ$	$2\theta = 15.8^\circ$	K
65/35	0	1	1.03	0.95	—	—
	0.5	1	0.95	0.93	1.01	0.261
	1	1	1.01	0.97	0.98	0.248
	2	1	0.95	0.95	0.70	0.193
	3	1	0.87	0.92	0.71	0.203
	5	1	0.98	0.91	0.64	0.182

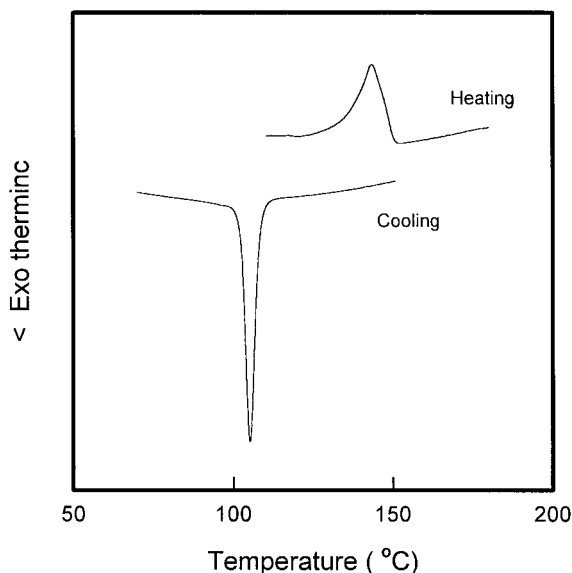


Figure 3 DSC thermograms of the prepared compatibilizer.

eral times with acetone to remove solvents, and dried in the vacuum oven at 60°C for 48 h. The chemical structure of the prepared compatibilizer was identified by FTIR.

The PP/EPDM and PP/EPDM/compatibilizer blends were prepared by melt mixing in a Brabender roller mixer at 30 rpm at 200°C for 30 min. The melt-blended products were cooled in air and dried in the vacuum oven for 24 h at 60°C. In the

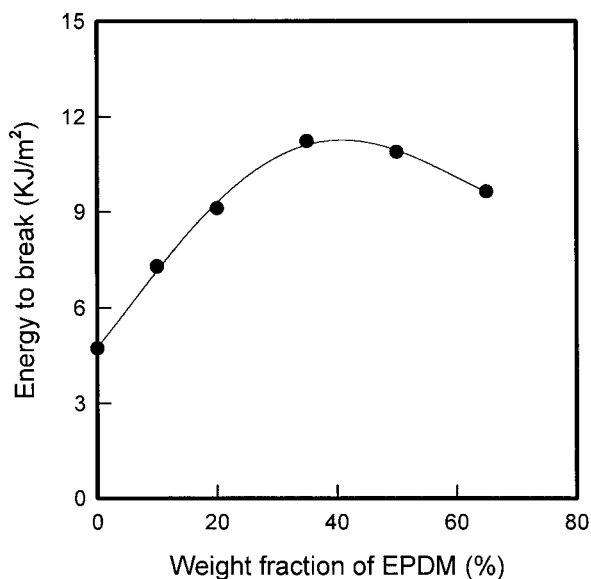


Figure 4 Variation of energy to break of PP/EPDM blends at -40°C,

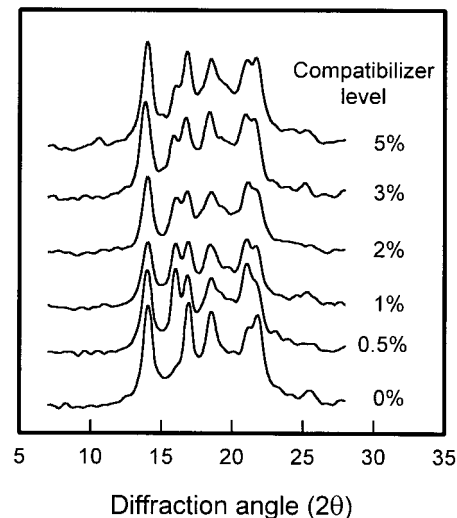


Figure 5 WAXS diffractograms of PP/EPDM/compatibilizer blends at various compatibilizer levels.

PP/EPDM blends the content of the compatibilizer ranged from 0.5 to 5 wt %. The recipes for the blends are listed in Table I.

Measurement of Physical Properties

The thermal properties were measured by differential scanning calorimetry (Perkin-Elmer DSC-7). The heating and cooling rates were 10°C/min, and the temperature range examined was 30 to

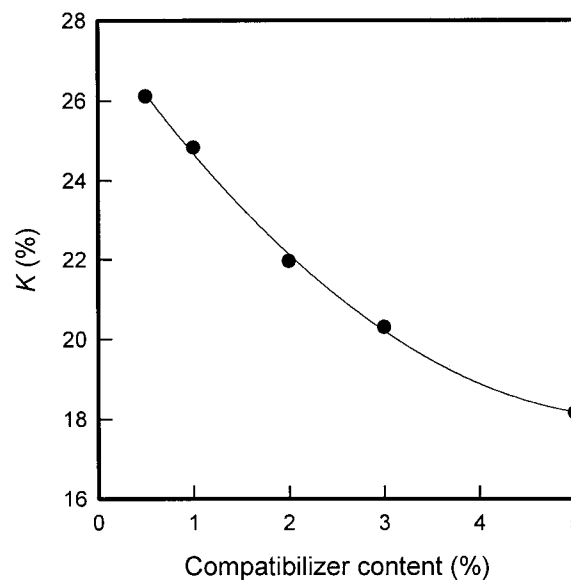


Figure 6 Variation of $K(\%)$ value, proportion of β -form crystal to total crystal, with the compatibilizer content in the PP/EPDM/compatibilizer blends.

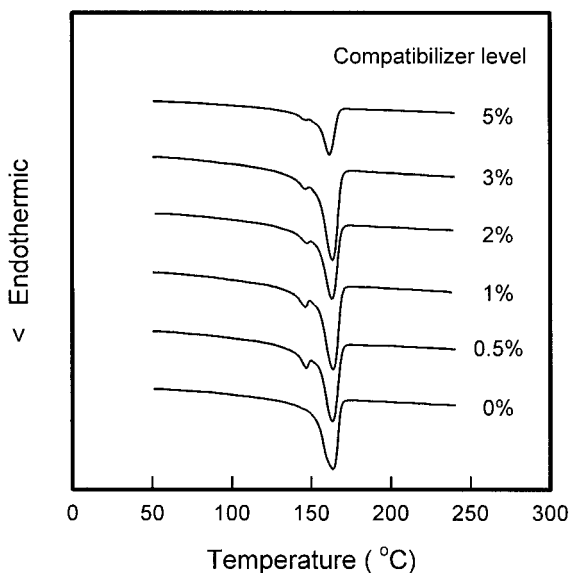


Figure 7 Melting behavior of PP/EPDM/compatibilizer blends at various compatibilizer levels (PP/EPDM is 65/35 by weight).

300°C in nitrogen atmosphere. The rheological properties were measured by the Advanced Rheometric Expansion System (ARES, Rheometric Scientifics). In ARES measurement, a parallel-plate fixture was used. The strain level was 5%, the gap size was 1.2 mm, and the plate diameter was 25 mm. The specimens for RDS measurement were prepared by compression molding at 200°C for 3 min under 200 kg/cm² to minimize errors resulting from residual stresses.

The crystal structure was examined by wide-angle X-ray diffractometry (Mac Science Co.) equipped with Ni filtered Cu-K radiation at 45 kV at 200 mA. The blends were fabricated to films by melt casting at 200°C in nitrogen atmosphere, followed by annealing for 1 h at 100°C. Wide-angle X-ray scattering experiments were carried out over the region of 2θ between 10 and 50°. The blend morphology was observed by scanning electron microscopy (Hitachi SEM S-510). The SEM specimens were prepared by cryogenic impact fracture. The fractured surface of the specimens was etched in *n*-hexane for 2 min to eliminate the EPDM component, then the surface was coated with gold under vacuum.

The tensile properties were measured by an Instron tensile tester 4201 according to ASTM D-638-84 at the crosshead speed of 10 mm/min at 25°C. The impact strength of the blends was measured by an Izod impact tester at -40°C. The impact specimens were prepared by compression

molding. The notch was 2 mm deep. In the cases of mechanical testing, the average value of 10 measurements was taken as datum.

RESULTS AND DISCUSSION

The FTIR spectrum of the prepared compatibilizer is identified in Figure 2. The compatibilizer, (PP-*g*-MAH)-*co*-PA-6,6-*co*-(EPDM-*g*-MAH), gives a —NH stretching band at 3500 cm⁻¹, —CONH bands at 1641 and 1534 cm⁻¹. However, these bands are not observed in the IR spectra of EPDM-*g*-MAH and PP-*g*-MAH, which suggests that the anhydride group of MAH is converted to the amide and carboxylic groups by coupling reaction as given in Figure 1.^{17,18} Figure 3 shows the DSC thermograms of the compatibilizer. A single transition peak is observed in the respective melting and crystallization scans, which also confirms the chemical coupling of EPDM-*g*-MAH and PP-*g*-MAH onto PA-6,6.

To determine the optimum content of EPDM in the PP/EPDM blends for impact strength, the energy to break of the blends was measured at various EPDM contents. Figure 4 exhibits variation of energy to break of PP/EPDM blends with EPDM content. The highest impact strength is acquired at the blend ratio of PP/EPDM, 65/35 by weight. Hence, we fixed the blend ratio of PP/

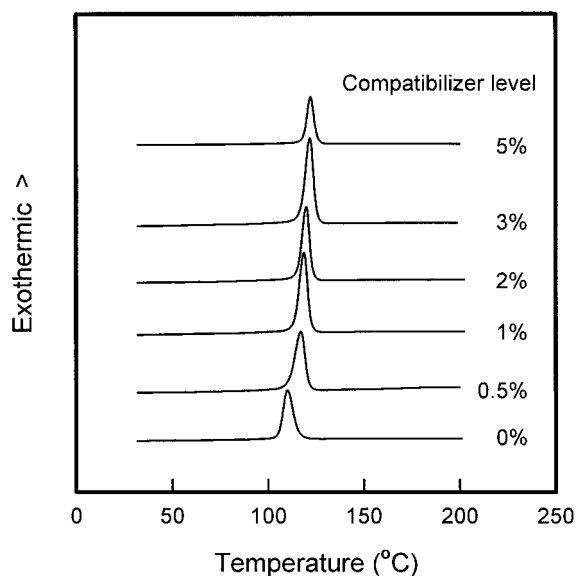


Figure 8 Crystallization behavior of PP/EPDM/compatibilizer blends at various compatibilizer levels (PP/EPDM is 65/35 by weight).

Table II Thermal Parameters of PP/EPDM/Compatibilizer Blends Measured from DSC Thermograms

Composition (wt %)		T_m (°C)	ΔH_m (W/g)	T_c (°C)	ΔH_c (W/g)
PP/EPDM	Compatibilizer				
65/35	0	150.5	46.3	98.8	59.4
	0.5	151.2	41.6	106.6	55.7
	1	152.2	36.1	108.0	53.0
	2	153.3	40.7	110.1	57.5
	3	155.1	42.0	112.1	56.7
	5	155.3	44.9	113.7	55.4

EPDM to be 65/35 for investigating the effect of introducing the compatibilizer on enhancing the impact properties of PP/EPDM blend.

Figure 5 shows the WAXS diffractograms of PP/EPDM and PP/EPDM/compatibilizer blends measured over the region of 2θ between 10 and 50° , and the relative proportion of intensity of the four peaks at $2\theta = 14, 17, 18.5,$ and 15.8° is summarized in Table I. The binary and ternary blends show four sharp reflection peaks assigned to the crystal structures of PP at $2\theta = 14, 17,$ and 18.5° , corresponding to the (110), (040), and (130) planes, respectively. The peak at $2\theta = 21.5^\circ$ represents spacings of the α -monoclinic crystal structure of PP.^{2,11} It should be noted that the ternary blend reveals a new peak at $2\theta = 15.8^\circ$ in addition

to the four peaks identifying the α -monoclinic crystal structure of PP. This peak corresponds to the (300) plane spacings of the β -hexagonal crystal structure of PP. This suggests a very important fact that incorporating the prepared compatibilizer to PP/EPDM blend develops a new β -form crystal structure.

To trace variation of the β -form crystal structure with compatibilizer content, the proportion of β -form crystal to total crystal, $K(\%)$, is calculated by eq. (1).

$$K(\%) = \frac{D_{15.8}}{D_{15.8} + (D_{14} + D_{17} + D_{18.5})} \times 100 \quad (1)$$

in which, $D_{14}, D_{17}, D_{18.5},$ and $D_{15.8}$ represent the intensity of peaks at $2\theta = 14, 17, 18.5,$ and

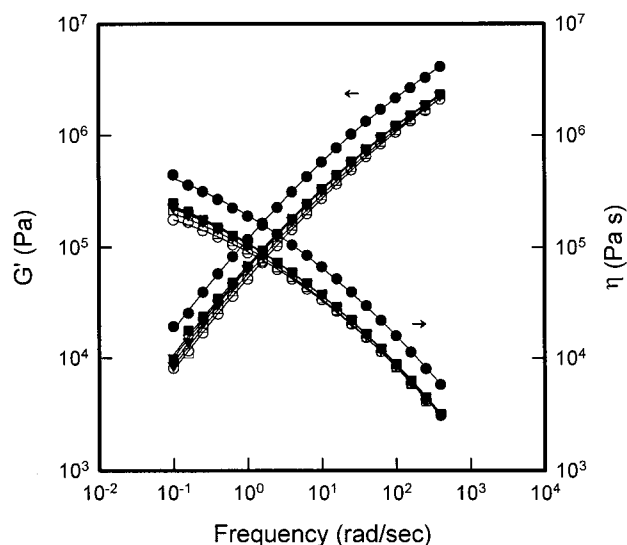


Figure 9 Storage modulus (G') and complex viscosity (η^*) vs. frequency for PP/EPDM/compatibilizer blends at 190°C (blending ratio of PP/EPDM is 65/35 by weight). Compatibilizer level is \circ ; 0, \bullet ; 0.5, ∇ ; 1, \blacktriangledown ; 2, \square ; 3 and \blacksquare ; 5 wt %.

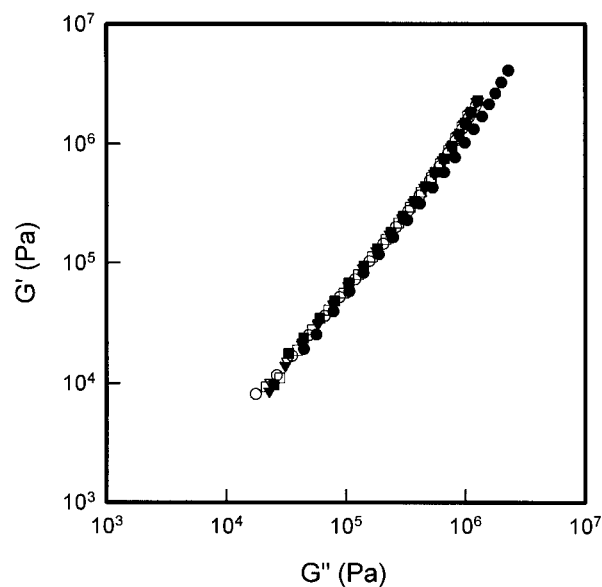


Figure 10 Storage modulus (G') vs. loss modulus (G'') for PP/EPDM/compatibilizer blends at 190°C (PP/EPDM is 65/35 by weight). Symbols are the same as in Figure 9

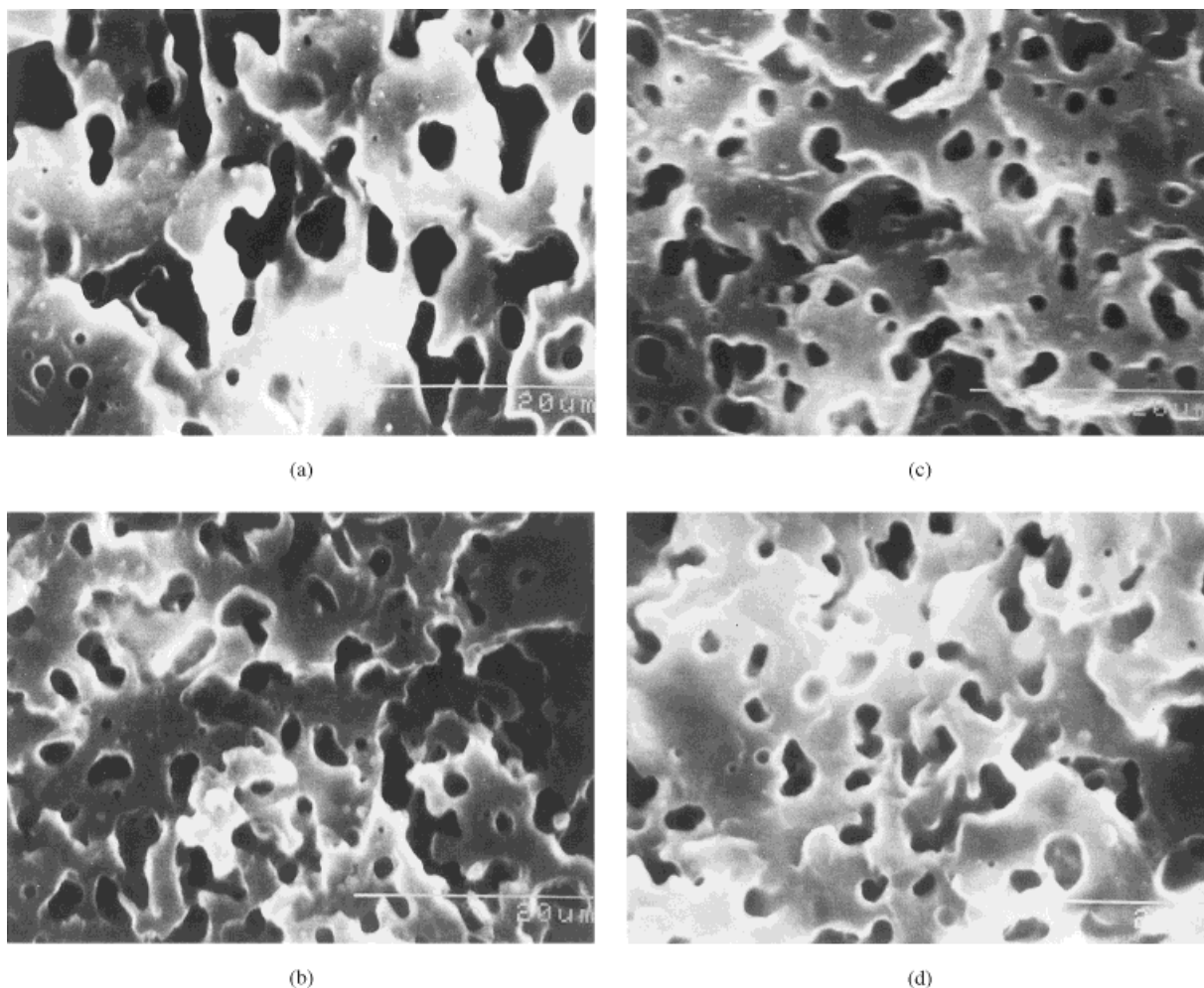


Figure 11 SEM micrographs of cryogenic impact fractured surfaces of PP/EPDM/compatibilizer blends (PP/EPDM is 65/35 by weight). The content of the compatibilizer; (a) 0 wt %, (b) 0.5 wt %, (c) 1 wt %, and (d) 2 wt %.

15.8°, respectively. Figure 6 shows variation of K value with compatibilizer content in PP/EPDM/compatibilizer blends. As the content of the compatibilizer is increased, the K value is decreased.

Figures 7 and 8 present heating and cooling scans of the 65/35 (by weight) PP/EPDM blend at various compatibilizer contents, respectively. The result is summarized in Table II. The thermal properties of the binary blends seem to be largely governed by crystalline PP alone because EPDM is an amorphous polymer. In general, the compatibilizer has little effect on the melting temperature and heat of melting of the blends. This indicates that the compatibilizer has little influence on crystal morphology of PP such as lamella thickness. On the other hand, the crystallization temperature of the blends is increased as the

compatibilizer content is increased. It is noted in Figure 7 that the ternary blends exhibit double melting behavior in the vicinity of 147°C. The secondary peak gets smaller and broader as the compatibilizer content is increased.

Such thermal behavior can be explained by WAXD result. The aforementioned crystal structure of the PP blends changes by incorporating the compatibilizer; a new β -form crystal structure is formed. That is, the compatibilizer may play a role of nucleating agent in the crystallization process of PP. The increased rate of crystallization leads to formation of less stable β -form crystals in the nonisothermal mixing process. Thus, the double melting behavior of the ternary blend may be related to the formation of a new crystal by the compatibilizer. The variation of melting and crystallization temperatures by introducing the com-

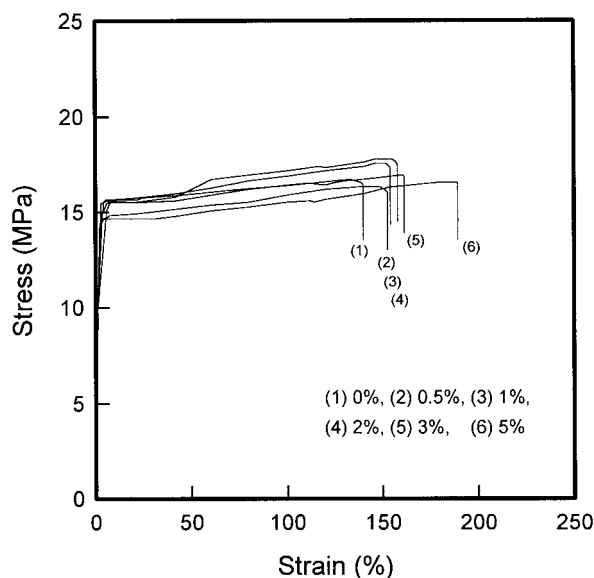


Figure 12 Stress-strain curves of PP/EPDM/compatibilizer blends at -40°C (PP/EPDM is 65/35 by weight).

patibilizer is also caused by change of the crystal structure.

The complex viscosity (η^*) and storage modulus (G') of PP/EPDM and PP/EPDM/compatibilizer blends were plotted against frequency at 190°C in Figure 9. Introducing the compatibilizer generally increases viscosity. This is ascribable to the crosslinking character of the triblock copolymer.¹² That is, introducing the compatibilizer enhances interface adhesion in the PP/EPDM blend because the triblock copolymer, (PP-*g*-MAH)-*co*-[PA-6,6]-*co*-(EPDM-*g*-MAH), promotes physical interlocking between PP and EPDM phases. However, it should be noted that the greatest viscosity is observed at the compatibilizer content of 0.5 wt %, indicating that the most effective physical interlocking between the blend components occurs at this compatibilizer level. G' is increased with increasing compatibilizer content, and gives a maximum at the compatibilizer content 0.5 wt %. This also ascertains that the most effective physical interlocking between the blend components occurs at the compatibilizer content 0.5 wt %.

Figure 10 shows a logarithmic plot of G' against G'' for PP/EPDM and PP/EPDM/compatibilizer blends at 190, 200, and 210°C . On this Cole-Cole-type plot, homogeneous polymer solutions give slopes of 2. However, the binary and ternary blends give slopes of less than 2. This indicates that the blend systems are somewhat heterogeneous, which is the characteristic feature

of block copolymers. It should be noted that among the blends, the blend containing the 0.5 wt % compatibilizer gives the least slope. All the facts, the greatest η^* , the greatest G' , and the smallest slope, indicate the blend systems have the strongest pseudostructure at the compatibilizer level of 0.5 wt %.

Figure 11 shows the SEM micrographs of the cold impact fractured specimens made of PP/EPDM and PP/EPDM/compatibilizer blends. The blend morphology does not notably change with the compatibilizer content. However, incorporation of the triblock copolymer increases the number of dispersed EPDM domains, and improves uniformity of distribution of the EPDM domains. Thus, the triblock copolymer plays the role of an auxiliary compatibilizer in the PP and EPDM phases.

PP/EPDM blends show stress-strain curves typical of elastomers as shown in Figure 12. Introducing the compatibilizer reduces yield stress, but it increases elongation at break.

Figure 13 shows the impact strength of binary and ternary blends were measured by the Izod method at -40°C . As shown in this figure, the impact strength of the ternary blend containing the 0.5% wt of the compatibilizer was highest in the binary and ternary blends, and the impact strength of the other ternary blends was similar with binary blend. This result implies that the

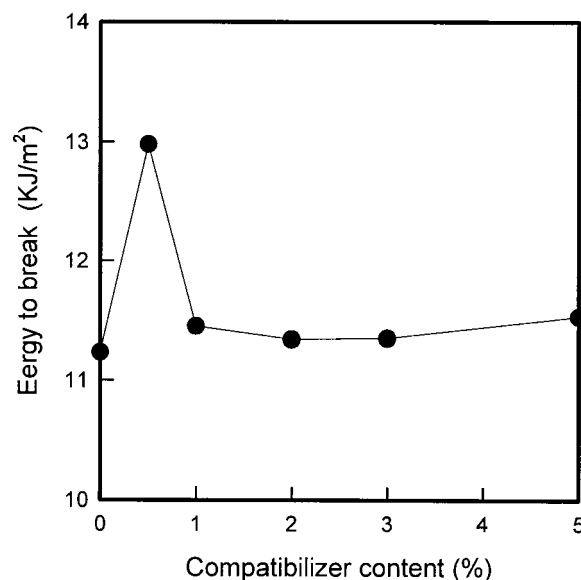


Figure 13 Variation of break of energy with compatibilizer content for 65/35 (by weight) PP/EPDM/compatibilizer blends at -40°C .

impact strength of the ternary blend was related to the formation of new β -form crystal structure as was shown by WAXD and DSC measurements.

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