

# Miscibility of Blends of Ethylene-Propylene-Diene Terpolymer and Polypropylene

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Received 27 June 2000; accepted 5 April 2001

**ABSTRACT:** The miscibility of polymers is not only an important basis for selecting a proper blending method, but it is also one of the key factors in determining the morphology and properties of the blends. The miscibility between ethylene-propylene-diene terpolymer (EPDM) and polypropylene (PP) was explored by means of dynamic mechanical thermal analysis, transmission electron microscopy (TEM), and differential scanning calorimetry (DSC). The results showed that a decrease in the PP content and an increase of the crosslinking density of EPDM in the EPDM/PP blends caused the glass-transition temperature peaks of EPDM to shift from a lower temperature to higher one, yet there was almost no variance in the glass-transition temperature peaks of PP and the degree of crystallinity of PP decreased. It was observed that the blends prepared with different mixing equipment, such as a single-screw extruder and an open mill, had different mechanical properties and blends prepared with the former had better mechanical properties than those prepared with the latter. The TEM micrographs revealed that the blends were composed of two phases: a bright, light PP phase and a dark EPDM phase. As the crosslinking degree of EPDM increased, the interface between the phases of EPDM and PP was less defined and the EPDM gradually dispersed in the PP phase became a continuous phase. The results indicated that EPDM and PP were both partially miscible. The mechanical properties of the blends had a lot to do with the blend morphology and the miscibility between the blend components. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 315–322, 2002

**Key words:** miscibility; polypropylene; ethylene-propylene-diene terpolymer; glass-transition temperature; crystallinity degree; morphology

## INTRODUCTION

Studies on ethylene-propylene-diene terpolymer and polypropylene (EPDM/PP) blends began in the 1960s.<sup>1</sup> These dynamically cured blends first described by Fischer<sup>2</sup> have been widely used in the plastics industry for years. The blends are prepared in an open mill or extruder by the “dynamic curing” method where EPDM is cured under shear with curing agents. The miscibility of

amorphous polymers can usually be judged by whether the solubility parameter ( $\delta$ ), critical surface tensions ( $r_c$ ), and interaction parameter ( $\chi_{AB}$ ) approach each other.<sup>3</sup> The compositions, except for a few polymers<sup>4</sup> that are constituted of amorphous and crystalline polymers or two kinds of crystalline polymers, are generally immiscible. In the EPDM/PP blends, EPDM is an amorphous polymer and PP is a semicrystalline polymer. It seems that the miscibility between PP and EPDM can be determined by  $\delta$ ,  $\chi_{AB}$ , or  $r_c$ . Yet the  $\delta$  values usually vary with the measurement methods, the solvents that are used, and the experimenters. The  $\delta$  values of EPDM and PP [8.04 and 7.86

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*Journal of Applied Polymer Science*, Vol. 83, 315–322 (2002)  
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**Table I** Characteristics of Polymers and Cure Agents

Materials	Trade Name	Source	Comments
PP	T300	Shanghai Petroleum Chemical Co., Ltd., China	MFR = 2.5, (230°C, 2.16-kg load), homopolymer
EPDM	EP35	Japan Synthetic Rubber Co.	ML <sub>1'+8'</sub> <sup>127°C</sup> = 56 Diene type ENB
Phenolic resin SnCl <sub>2</sub> · 2H <sub>2</sub> O	2402	Jingmei Chemical Factory, Wubei, China Jiaozhui Chemical Factory, Henan, China	C.P. A.R.

(cal/cm<sup>3</sup>)<sup>1/2</sup>, respectively] were obtained by the Kraus calculation method and approached each other,<sup>5</sup> which indicated that the EPDM and the amorphous portions of PP were both partially miscible. Yin et al.<sup>6</sup> investigated the interfacial penetration of EPDM and the amorphous portion of PP in the blends by means of wide angle X-ray diffraction, differential scanning calorimetry (DSC), and a torsion pendulum; they concluded that there was interfacial penetration between the two amorphous phases. The present study sought to interpret the relation of its miscibility to the glass-transition temperature ( $T_g$ ), crystallinity, morphology, and mechanical properties of the blends. Moreover, the  $T_g$  and crystallinity degree of the blends at four different ratios of rubber to plastic and the tensile strength and morphology of the blends prepared with two kinds of mixing equipment were investigated.

## EXPERIMENTAL

### Materials

The base materials (polymers and curing agents) used in this study are commercially available. Table I lists the main characteristics of the polymers and curing agents.

### Processing and Specimen Preparation

Melt blending of the constituents in various portions was carried out in an open mill (SK-160B, Wuhan) at 180 ± 10°C for 10 min. Then the molten mass was taken out of the open mill. After cooling, the mass was remelted and mixed for another 2 min in the open mill. The mass was again removed from the open mill and molded into a 2 mm thick milled sheet. The sheet was then cut, compression molded in a frame (2.0 mm thick) between plates in a platen press at 210°C, and cooled under pressure. Appropriate test spec-

imens were cut from the molded sheet and used after at least 24-h storage at room temperature.

The extruder employed in the experiment was a 30-mm diameter single-screw extruder with a length to depth ratio of 25. Melt blending of the constituents in various portions was conducted at a speed of 60 rpm and at a barrel temperature of 180–200°C. The residual time of the blends in the extruder was kept at 1 min by adjusting the extruder rate. The same extrusion conditions were used throughout the research. The samples were extruded and pelletized twice. In the first extrusion the PP and EPDM were melt blended. The purpose of the second extrusion was to thoroughly disperse the EPDM particles in the PP matrix. The tensile behaviors were examined according to GB528-82 on an AG-2000A apparatus at a cross-head speed of 100 mm/min. The tests were carried out at 23 ± 2°C. All data were recorded and processed automatically.

### Morphological Characteristics

Samples were cryogenically cut with glass knives (V-LKB, Swiss) and stained with OsO<sub>4</sub>, which reacted with the double bonds of EPDM and darkened it. Then the samples were examined using a TEM microscope (H-806).

### Dynamic Mechanical Thermal Analysis (DMTA)

All samples were compression-molded sheets (0.1-mm thickness, 3-mm width) prepared in a heated press at 200°C with a pressure of 15 MPa. The experiments were carried out with DMTA (MkIII, version 5.41, Rheometric Scientific Ltd.) at a rate of 10°C/min and a frequency of 5 Hz.

### Thermal Analysis

The melting and recrystallization behavior of the EPDM/PP blends were analyzed by DSC (DSC7,

**Table II Mechanical Property of Uncured EPDM/PP Blends Prepared with Various Mixing Equipment**

EPDM-PP	Tensile Strength (MPa)	
	Single-Screw Extruder	Open Mill
80 : 20	7.2	4.6
70 : 30	15.8	13.7
60 : 40	18.4	16.6
50 : 50	20.8	19.6

Perkin–Elmer). The DSC tests were run at heating and cooling rates of 10°C/min.

The melting temperature ( $T_m$ ), crystallization temperature ( $T_c$ ), and heat of fusion ( $\Delta H_f$ ) were obtained. The following equation was used to calculate the crystallinity ( $X_c$ ) of the PP homopolymer<sup>7</sup>:

$$X_c = 100\Delta H_f/\Delta H_c$$

where  $\Delta H_c$  is the heat of fusion for a perfect crystal (209 J/g).

## RESULTS AND DISCUSSION

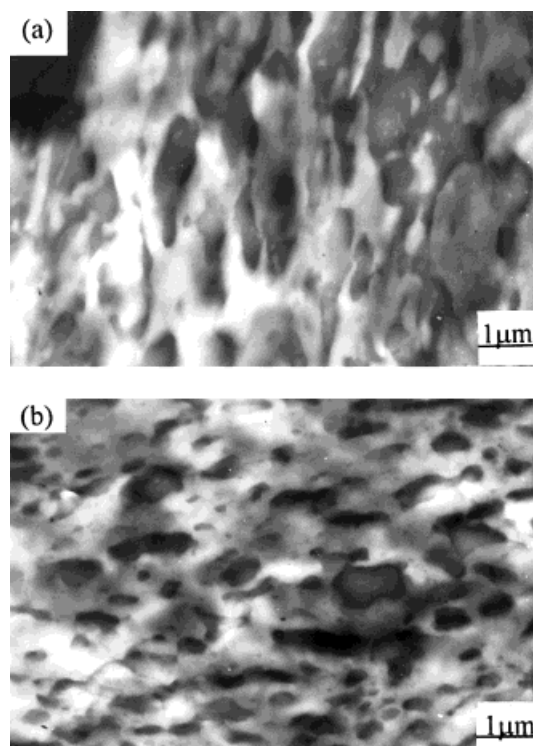
### EPDM/PP Blends Prepared with Different Mixing Equipment

A previous article<sup>8</sup> demonstrated that the EPDM/PP blends prepared in the single-screw extruder had better mechanical properties than those prepared with the open mill. The mechanical properties of the blends prepared with the internal mixer and the open mill were studied by Zhu et al.<sup>9</sup> This article continued the studies on the mechanical properties of the blends by analyzing both the morphology and miscibility. The tensile strengths of the blends prepared with two types of mixing equipment are shown in Table II. It is obvious that the blends prepared in the single-screw extruder presented higher tensile strength, a higher proportion of EPDM in the blends, and an apparent difference in the tensile strength; the major reason for this was that there was weaker shear force in the open mill, which cannot separate rubber into smaller particles at elevated EPDM content. The micrographs of the blends are shown in Figures 1 and 2. Their morphological features were similar, and they consti-

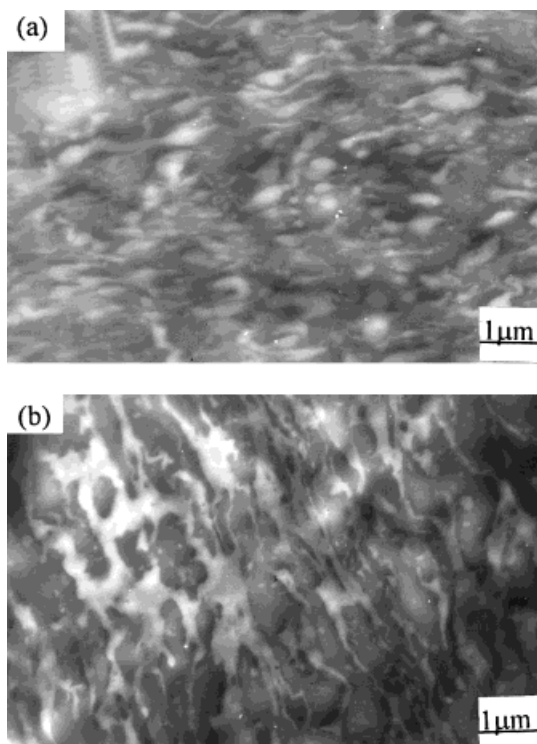
tuted two phases: a bright PP phase and a dark EPDM phase. Contrary to the similarity of the whole morphology, a remarkable difference in the EPDM phase was observed. In the blends prepared in the single-screw extruder, the EPDM particles were smaller than those prepared in the open mill and they were finely dispersed in the PP phase. These observations can be explained. The single-screw extruder exerted intensive shear force on the blends, producing smaller rubber particles under intensive shear. On the other hand, EPDM or PP could form a graft or block copolymer, which would improve the miscibility between the polymers. These results were consistent with the conclusion<sup>10</sup> that intensive shear can improve the miscibility of the blends. If these two effects were taken into account, it could be inferred that there was good agreement between the micrographs and mechanical properties.

### Dynamically Cured EPDM/PP Blends with Different Proportions of Rubber and Plastic

The DMTA technique is a versatile tool to study miscibility in blends, particularly at elevated



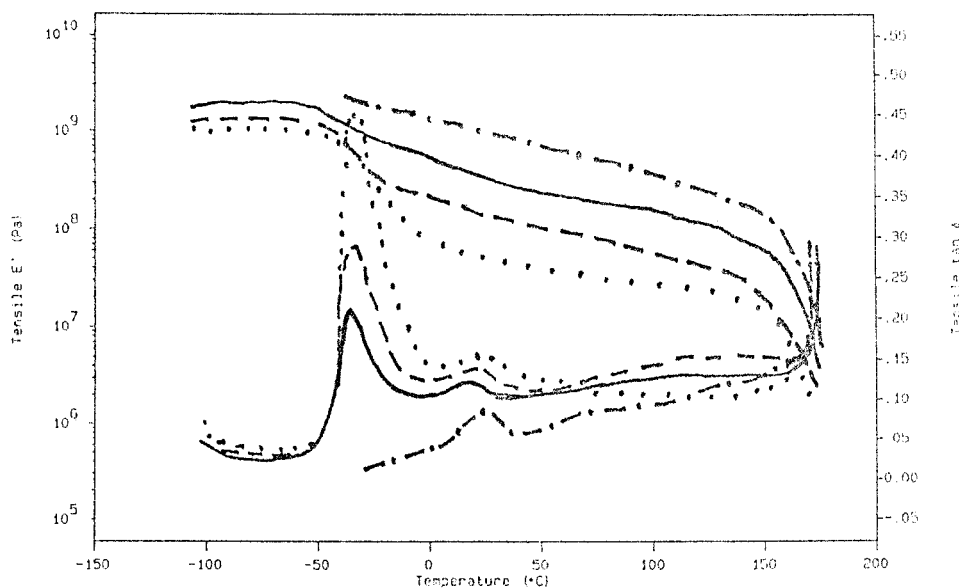
**Figure 1** TEM micrographs of the uncured EPDM/PP blends prepared in the single-screw extruder: (a) EPDM 60 PP 40 and (b) EPDM 50 PP 50.



**Figure 2** TEM micrographs of the uncured EPDM/PP blends prepared in the open mill: (a) EPDM 60 PP 40 and (b) EPDM 50 PP 50.

temperature.<sup>11</sup> Figure 3 gives the shear modulus and  $\tan \delta$  values versus the temperature. The plots indicate that there were two transitions

from a glassy state to a rubbery state with the progressive heat of the sample. The  $\tan \delta$  peaks of the blends indicate the  $T_g$  of the blends. In the EPDM case, the  $\tan \delta$  peaks decreased and became broadened as the PP content increased in the blends. This behavior was observed earlier in uncured EPDM/PP blends.<sup>6</sup> However, the present study was focused on the  $T_g$  of cured EPDM/PP blends. The DMTA curves of different compositions of rubber and plastic (70/30, 60/40, 50/50, or pure PP) are shown in Figure 3. It can be seen that, without the exception of pure PP, the blends showed two apparent peaks (i.e., the blends presented two  $T_g$  values). The higher temperature corresponded to the  $T_g$  of PP and the lower one to the  $T_g$  of EPDM, which was lower than that of pure EPDM, as shown in Figure 4. This indicated that two components in the blends were immiscible. Further, as the PP content in the blends increased, the  $T_g$  of EPDM was shifted toward a lower temperature. This result was not in agreement with the results obtained by Yin et al.<sup>6</sup> that different behaviors need further investigation. According to the fact that the  $T_g$  of pure PP corresponds to the  $T_g$  in the amorphous regions,<sup>12</sup> as the EPDM content was increased in the blends, there was almost no variance in the  $T_g$  of PP. The peak shifts of EPDM and PP both approached each other. The phenomenon of the peak shift of EPDM demonstrated that, although the supermolecular structure of the aggregation state in



**Figure 3** DMTA curves of EPDM/PP blends with 5 phr of phenolic resin. The mass ratios of rubber to plastic were (— · —) 0/100, (—) 50/50, (- - -) 60/40, and (· · ·) 70/30.

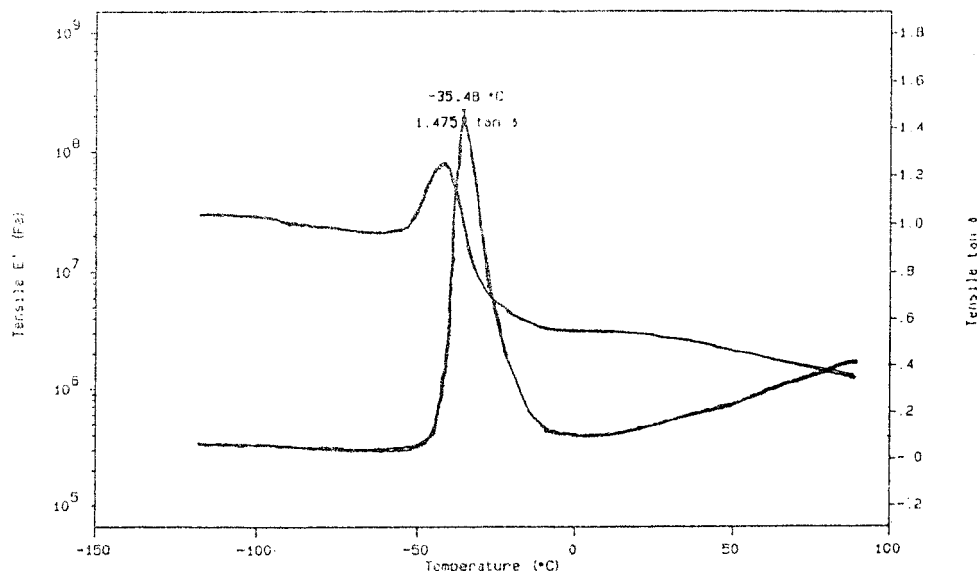


Figure 4 A DMTA curve of pure EPDM.

EPDM and PP made a great difference, there was an interpenetration between the noncrystalline portion of PP and the interface of EPDM that indicated that the two components had a certain degree of miscibility.

The DSC cooling and heating curves illustrating the melting and recrystallization behavior of the EPDM/PP blends are shown in Figures 5 and 6, respectively. Note that as the PP content was increased in the blends, the melting peak of the polymer blends shifted to a lower temperature

while the crystalline peaks of PP shifted to a higher temperature. As the PP crystallized, its crystalline temperature (Fig. 6) was far below its melting temperature (Fig. 5) because of undercooling. As EPDM was added to the blends, the phenomena of undercooling decreased. Karger-Kocsis et al. observed similar phenomena when they studied PP/EPDM blends.<sup>13</sup> The incorpora-

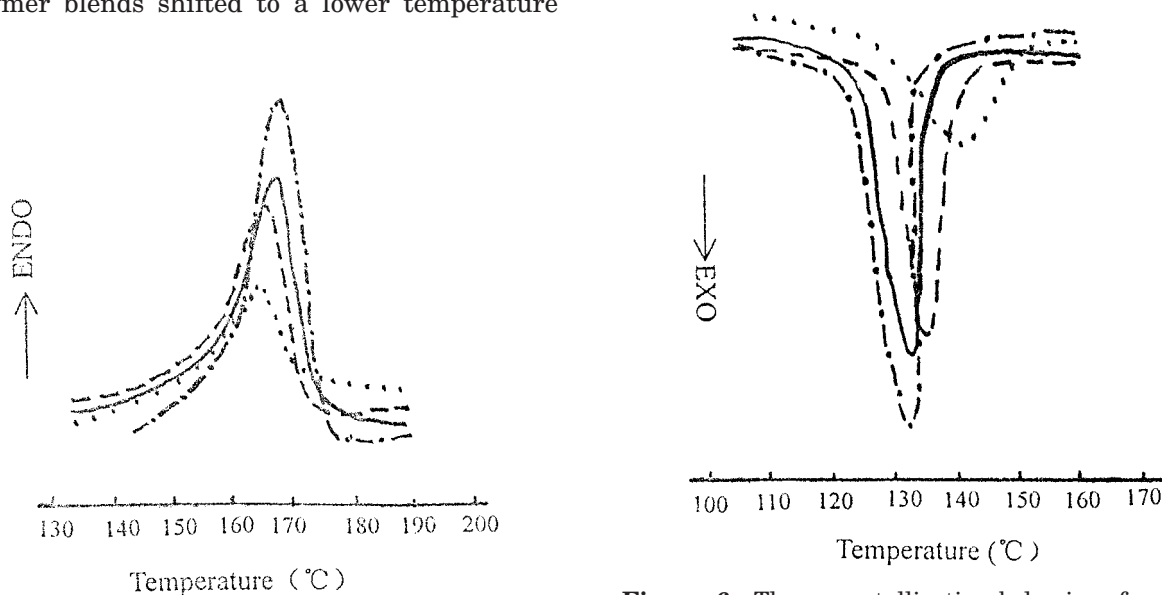


Figure 5 The melting behavior of pure PP and dynamically cured EPDM/PP blends with 5 phr of phenolic resin. The mass ratios of rubber to plastic were (— · —) 0/100, (—) 50/50, (- - -) 60/40, and (· · ·) 70/30.

Figure 6 The recrystallization behavior of pure PP and dynamically cured EPDM/PP blends with 5 phr of phenolic resin. The mass ratios of rubber to plastic were (— · —) 0/100, (—) 50/50, (- - -) 60/40, and (· · ·) 70/30.



**Table III Physical Properties of EPDM/PP Blends**

Properties	Rubber/Plastic <sup>a</sup>				Amount of Cure Agents <sup>b</sup>			
	70/30	60/40	50/50	0/100	0.03	0.12	0.21	0.30
$T_c$ (°C)	137	134	132	122	139	137	135	134
$T_m$ (°C)	161	161	163	164	159	160	160	161
$\Delta H_f$ (J/g)	24	30	33	92	36	34	32	30
$X_c$ (%)	11	14	16	44	17	16	15	14

<sup>a</sup> With 5 phr curing agents.

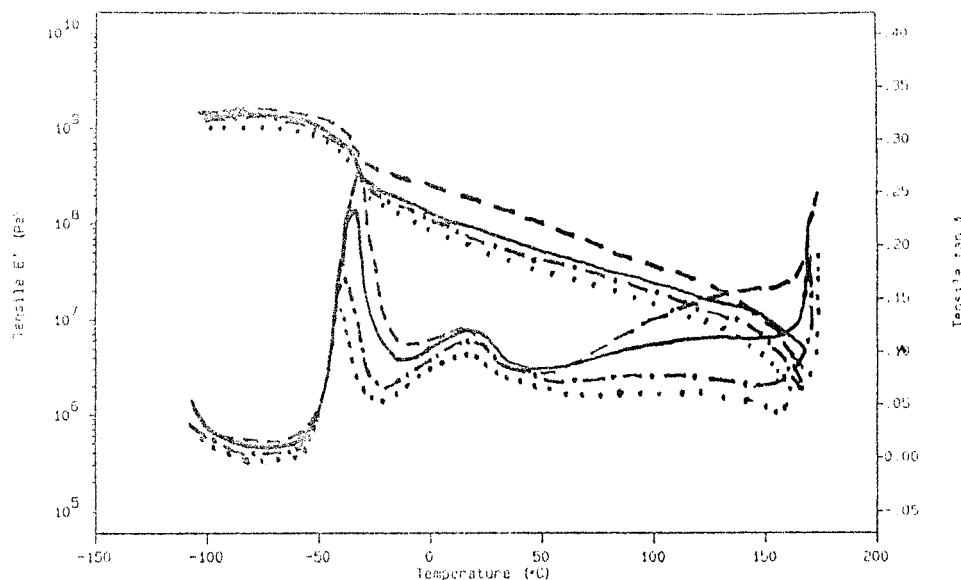
<sup>b</sup> EPDM 60PP40.

tion of EPDM resulted in the formation of  $\alpha$ -form spherulites (i.e., the EPDM acted as a nucleated agent and decreased the degree of undercooling). The EPDM acted as a nucleated agent in the PP phase, which demonstrated that there was interpenetration between the amorphous portion of the PP and the interface of the EPDM in the blends.

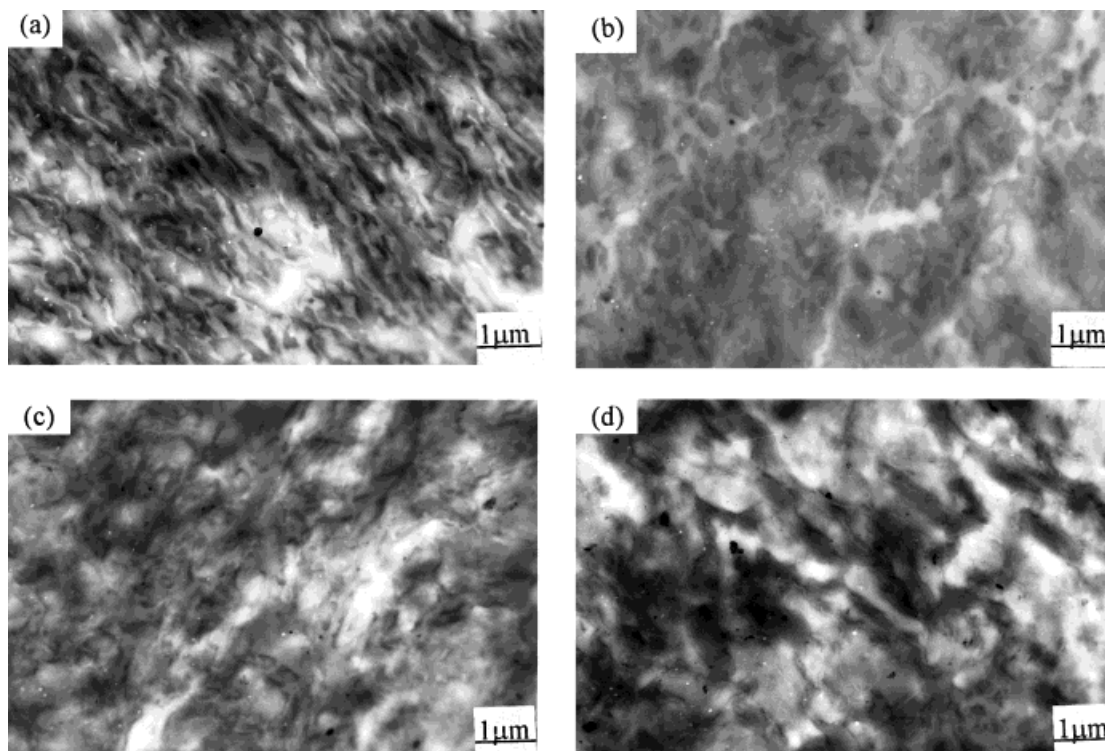
The thermal properties of the EPDM/PP blend are summarized in Table III. The  $X_c$  of PP was measured by DSC. It was apparent that the crystallinity of PP was suppressed by EPDM (i.e., the aggregation of the molecular chains and rearrangement were impeded by EPDM); as a result, the crystalline defects in the PP increased.

#### Dynamically Cured EPDM/PP Blends with Various Amounts of Curing Agents

The DMTA curves of the EPDM/PP blends cured with various amounts of curing agents (60/40 mass ratio of rubber/plastic) are shown in Figure 7. All blends presented two distinct peaks, indicating the immiscibility between the components of these blends. The results also showed that the  $T_g$  peak of EPDM shifted toward a higher temperature and the peaks broadened. One possible explanation was that the higher degree of crosslinking prevented the alignment of chains in a crystal lattice, hindering crystallization and leading to the decrease of the degree of crystallinity of PP (Table III). Crosslinking restricted the chain mo-



**Figure 7** DMTA curves of the EPDM/PP blends with a 60/40 mass ratio of rubber to plastic. The amounts of curing agents were (···) 0.5, (— · —) 2.0, (—) 3.5, and (---) 5.0 phr.



**Figure 8** TEM micrographs of the dynamically cured EPDM/PP blends with a 60/40 ratio of rubber to plastic. The amounts of curing agents were (a) 0.5, (b) 2.0, (c) 3.5, and (d) 5.0 phr.

bility and caused an increase in the apparent  $T_g$  as the amount of curing agents was increased. The  $T_g$  peaks of PP remained almost unchanged; the  $T_g$  peaks of the two components gradually approached each other as the amount of curing agents was increased. This demonstrated that the miscibility of EPDM and PP was improved. We believed that the increase in miscibility was caused by the graft copolymer of PP and EPDM at the interface. It was quite possible that the graft copolymer was produced by the coupling of EPDM radicals and the PP radical or with participation of curing agent radicals (PP–curing agents–EPDM type) under dynamic crosslinking. It is recognized that the miscibility in EPDM/PP blends is increased by the presence of a graft or block polymer of the blend components.<sup>14</sup>

Figure 8 shows TEM micrographs of the dynamically cured EPDM/PP blends with varied amounts of curing agents. The morphology of the blends depended on the composition, shear rate, and location of the cross section<sup>15,16</sup> of the blends. In spite of the difference in the degree of crystallinity of PP arising from the degree of crosslinking, the blends were composed of two inhomoge-

neous phases: a white PP phase and a dark EPDM phase. An EPDM-rich phase was distributed in the PP phase. Although the miscibility of the two components could be completely determined from the morphology of the blends, if the TEM micrographs were correlated with the DMTA results, a conclusion could be drawn that the two components in the EPDM/PP blends were immiscible. Meanwhile, Figure 8 shows that as the amount of curing agents was increased, the EPDM changed from a dispersed phase to a continuous one and the interface between the PP and EPDM phase became more vague, which indicated that the miscibility of the two components was improved.

## CONCLUSION

It was confirmed that the EPDM/PP blends prepared in a single-screw extruder presented better mechanical properties than those prepared with an open mill. That effect on the mechanical properties was partially attributed to the improved mixing of the two components in the EPDM/PP

blends prepared in the single-screw extruder, which was verified by TEM micrographs. It was found that the blends prepared with different ratios of rubber to plastic and with varied amounts of curing agents presented two  $T_g$  values, suggesting that the components of the blends were immiscible. All of the TEM micrographs were in accordance with the above conclusion. The  $T_g$  peaks of EPDM shifted in all blends, indicating a certain degree of miscibility between the two components. As the ratios of rubber to plastic and the amount of curing agents increased, the  $T_g$  peaks of the two components approached each other (i.e., the miscibility between the two components was improved).

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