Dynamic Mechanical Properties of Polypropylene-g-Maleic Anhydride and Ethylene–Propylene–Diene Terpolymer Blends: Effect of Blend Preparation Methods

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ABSTRACT: In this work, we attempted two different ways of processing to improve interfacial adhesion of polypropylene (PP) and ethylene–propylene–diene terpolymer (EPDM) by introducing maleic anhydride (MAH); In one way, the *in situ* grafting and dynamic vulcanization (ISGV) were performed simultaneously from PP and EPDM with MAH in the presence of dicumyl peroxide (DCP) in an intensive mixer. In another way, PP was first grafted with MAH and then the PP-g-MAH was blended with EPDM in the intensive mixer in the presence of DCP by the dynamic vulcanization (DV). It was found that the glass transition temperatures (T_gs) of both PP and EPDM phases were shifted to higher temperature as the EPDM content increased for the blends prepared by both IGSV and DV methods, mainly due to the crosslinking of EPDM. The higher T_gs and larger storage moduli were observed for the blends prepared by the ISGV method than those prepared by the DV method, while the morphology showed that the size reduction of dispersed particles in latter blends was larger than that of the former blends. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 2777–2784, 2000

Key words: *in situ* grafting and dynamic vulcanization; dynamic vulcanization; polypropylene/ethylene–propylene–diene terpolymer blends; dynamic mechanical properties; interfacial adhesion improvement; reactive blending

INTRODUCTION

The miscibility in polymer blend systems has been extensively studied for many years. In most of polymer blends, the components are immiscible because of the negligibly small entropy gain on mixing. The components are easily phase separated and show weak interfacial characteristics, resulting in poor mechanical properties. For this reason, many attempts have been made to enhance the miscibility by introducing specific interactions between components that provide a negative enthalpy of mixing that can overcome a small entropy gain of mixing enough for the Gibbs free energy to be negative.[1] In many cases, the introduction of polar groups into the repeating unit of one of the components gives miscibility to the blends that otherwise are not miscible.[2,3] The reactive blending technique or in-situ compatibilization has been widely applied nowadays to improve the interfacial adhesion in blends.[3,4] The use of maleic anhydride (MAH) is one of the most common ways in the reactive blending in order to improve the interfacial adhesion in immiscible polymer blends.[5]

Table I Characteristics of the Polymers Used in this Work

Designation	Description	Source
PP	MI (230°C) = 3.5 MW = 105,000	LG Caltex Oil Co. (H430)
PP-g-MAH	MAH (wt %) = 0.8 MW = 124,000	Synthesized
EPDM	Propylene (wt %) = 45 Diene (wt %) = 5 Diene type = ethylidene 2-norbornen	Keumho Polychem (KE-570)

Another way to improve the interfacial adhesion in blends is to use compatibilizers, either block or graft copolymers generated *in situ* at the interface between two components of the blends during melt mixing.[3,6,7] These compatibilizers generated at the interface act as emulsifiers and reduce the interfacial tension, at some level of compatibilizer, drop to zero, so there is some finite, equilibrium size of the domains. Even when the interfacial tension is not zero, a finer dispersion of the phases can be achieved during intensive mixing when the interfacial tension is very small.[7]

One of the largest classes of polymer blends in use today are the mixtures of polypropylene (PP) and ethylene–propylene–diene terpolymer (EPDM). Over almost entire composition ranges, useful materials can be obtained.[8–10] Blends with a small percentage of EPDM are a toughened version of PP, while those with a majority of EPDM are thermoplastic elastomers. EPDM can be used as toughening agent to solve the problem of low-temperature brittleness of PP in the PP/EPDM blends. In spite of similar molecular structures, however, the PP/EPDM blend is immiscible system in general. To improve the interfacial adhesion in the blend, there have been a lot of attempts using a third component whose molecular structure is similar to PP or EPDM as a compatibilizer.[11–13] It has been reported that introducing an ethylene ionomer neutralized with metal cation to PP/EPDM blends showed much enhanced mechanical properties and morphology.[11]

On the other hand, thermoplastic polyolefins (TPO) based on PP/EPDM blends have increased in popularity in recent years. Especially, the TPO prepared by the "dynamic vulcanization" process has important technical advantages in processing because of the thermoplastic nature of melt even though they contain a crosslinked elastomer as one component.[14] In general, vulcanized elastomer can not be reprocessible because of the network structure formed. The use of the dynamic vulcanization process has been reported to effectively enhance the miscibility of PP and EPDM as well as to assure the thermoplastic nature of melt.[12]

In this work, we attempted two different ways of processing to enhance the miscibility of PP and EPDM by introducing MAH; In one way, the *in situ* grafting and dynamic vulcanization (ISGV) were performed simultaneously from PP and EPDM with MAH in the presence of dicumyl peroxide (DCP) in an intensive mixer. In another way, PP was first grafted with MAH and then the PP-g-MAH was blended with EPDM in the intensive mixer in the presence of DCP by the dynamic vulcanization (DV). The objective of this work is to investigate the effect of the blend preparation methods on the dynamic mechanical properties of blends thus obtained in order to give insight on the improvement of interfacial adhesion in PP/EPDM blends.

EXPERIMENTAL

Materials

Table I summarizes the characteristics of the polymers used in the present study. The PP used in this study was H430 grade purchased from the LG Caltex Oil Co. (Yeochon, Korea). EPDM was obtained by Keumho Polychem (Yeochon, Korea). Maleic anhydride (Aldrich, Milwaukee, Wisconsin, USA) and DCP (Mitsui Chem. Yokohama, Japan) were used as received.

Synthesis of PP-g-MAH

The composition of the reaction mixture was 40 g PP, 10 phr MAH, and 0.1 phr DCP. The temper-

Table II T_gs of Various Blends Having Different PP or PP-g-MAH and EPDM Compositions

Preparation Method	Content (PP/EPDM)	T_g (°C)	
		PP Phase	EPDM Phase
ISGV	90/10	7.5	−47.3
	75/25	12.2	−42.1
	50/50	15.6	−39.0
DV	75/25	2.1	−46.3
	50/50	12.1	−44.2
	25/75	—	−38.9

ature of the mixing chamber was set at 200°C. MAH was added prior to DCP for preventing the chain scission of PP chain due to DCP at elevated temperature. And then DCP was added consequently. After 15 min, the product was removed from the chamber. The amount of MAH grafted on PP was estimated as 0.8% by weight using the KOH titration method.[15] PP-g-MAH synthesized by melt grafting was identified by observing new peaks at 1863 and 1786 cm^{-1} on IR spectra, which were not shown in the PP used for synthesizing the PP-g-MAH. The peaks at 1863 and 1786 cm^{-1} are assigned as asymmetric and symmetric stretching vibration peaks of carbonyl group in anhydride, respectively.

Blend Preparation

Blends for this work were prepared by two different methods: ISGV and DV.

In situ *Grafting and Dynamic Vulcanization*

PP and EPDM were mixed in the Brabender Roller Mixer (Type w50H) at 200°C for 5 min at 60 rpm. Then, 10 phr of maleic anhydride was poured into the mixer and 0.3 phr of dicumyl peroxide was introduced sequentially. The final products were pulled out from the chamber after about 15 min. The content of EPDM was varied from 10 to 50 wt % based on the PP/EPDM blend. The product was rapidly compression molded to prepare samples for measurements.

Dynamic Vulcanization

Prior to dynamic vulcanization of PP-g-MAH and EPDM, EPDM was preblended with 0.3 phr dicumyl peroxide using a home-made roll mill at

80°C. The blending and curing were done simultaneously in the presence of PP-g-MAH and EPDM in the roller mixer at 200°C for 15 min at 60 rpm. The content of EPDM was varied from 25 to 75 wt % based on the PP-g-MAH/EPDM blend. The product was rapidly compression molded to prepare samples for measurements.

FTIR Measurements

FTIR spectra were taken using a Polaris/FTIR spectrometer. At least 32 scans at a resolution of 2 cm^{-1} were signal averaged.

Dynamic Mechanical Properties

The tan δ and storage modulus (E') were measured using a dynamic mechanical thermal analysis (Gabo-Qualimeter 3031). The scan rate was 3°C/min and the frequency was 1 Hz. The sample size for measurement was $1.5 \times 6 \times 20$ mm. The glass transition temperature (T_g) was obtained directly by selecting the point showing the highest value among the shoulder in the tan δ-temperature data.

Morphology

The samples were cryogenically fractured in liquid nitrogen into two pieces. The fracture surface was coated with gold in vacuum and observed by
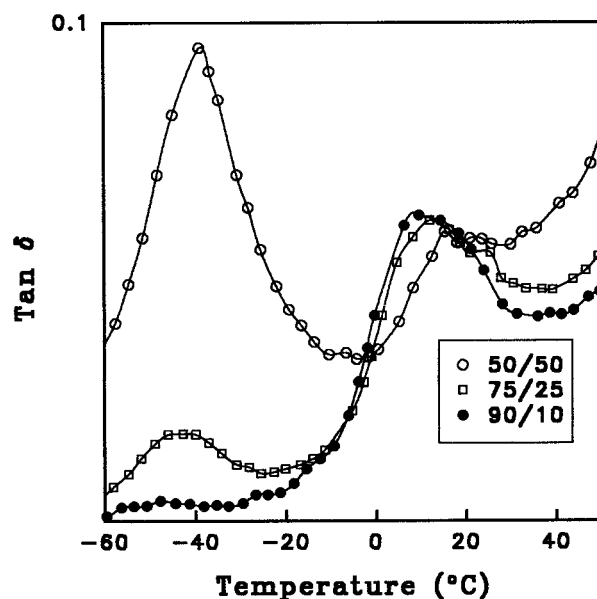

Figure 1 Tan δ of PP/EPDM blends prepared by the ISGV method as a function of temperature. Blend compositions are 90/10, 75/25, and 50/50 by weight.
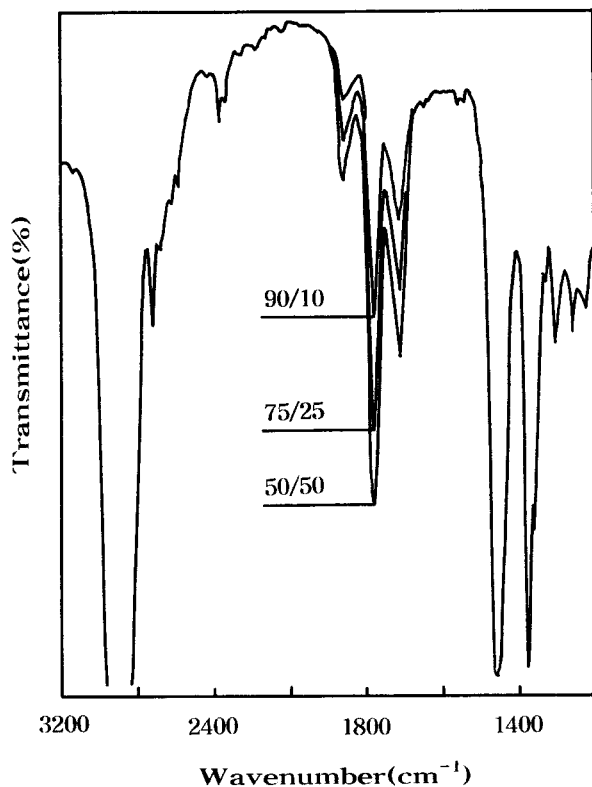
Figure 2 Infrared spectra of the PP/EPDM blends prepared by the ISGV method. Blend compositions are 90/10, 75/25, and 50/50 by weight.

a scanning electron microscope (SEM) (JEOL, JSM-35CF).

RESULTS AND DISCUSSION

Tan δ Behavior

Figure 1 shows the tan δ of blends having different PP/EPDM compositions as a function of temperature, which has been prepared by the ISGV method. In the 90/10 PP/EPDM blend, the T_gs of PP and EPDM phases were 7.5 and -47.3°C, respectively. In the 75/25 blend, the T_gs of PP and EPDM phases were 12.2 and -42.1°C, respectively. In the case of the 50/50 blend, the T_gs of each phase were found at 15.6 and -39.0°C, respectively.

As the content of EPDM increases, the T_gs of PP and EPDM phases were shifted to higher temperature. The trend of the T_g shift at different PP/EPDM compositions can be accounted for various complicated reaction mechanisms. Grafting of MAH onto both PP and EPDM, chain scission of

PP chain, and crosslinking of EPDM can arise during the reaction. Figure 2 shows the infrared spectra of the blends having different compositions, which were prepared by the ISGV method. The spectra show that the peak intensities around 1863 and 1786 cm^{-1} are increased with increasing the EPDM content, meaning that the total degree of grafting of MAH onto polymer chains increases as the content of EPDM increases. It may be assumed that the grafting of MAH onto the EPDM chain takes place competitively and simultaneously with the formation of PP-g-MAH. In case of the PP/EPDM blend having a 90/10 composition, the grafting of MAH onto EPDM and/or PP chains as well as the crosslinking of EPDM chains by DCP take place preferentially, while the mechanochemical degradation of PP by DCP cannot be neglected.[14]

As the content of EPDM increases, however, the crosslinking of EPDM and the grafting of MAH onto EPDM or PP take place predominantly and the mechanical degradation of PP by DCP is not significant so much. For these reasons, the T_gs of both EPDM and PP phases would have shifted to higher temperatures. And there may be another possibility of increasing the T_g of PP phase in the viewpoint of miscibility. In general, the T_gs of each phase approach gradually and shows a single T_g that is the midpoint of those of each components as the miscibility of the system
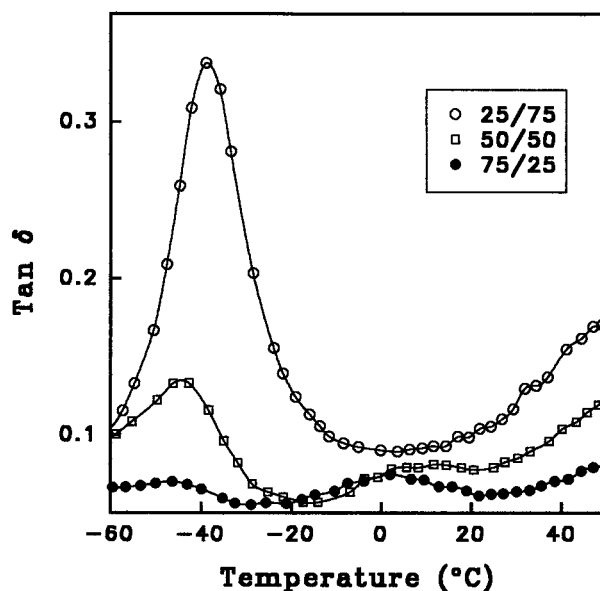

Figure 3 Tan δ as a function of temperature for the PP-g-MAH/EPDM blends prepared by DV. Blend compositions are 75/25, 50/50, and 25/75 by weight.
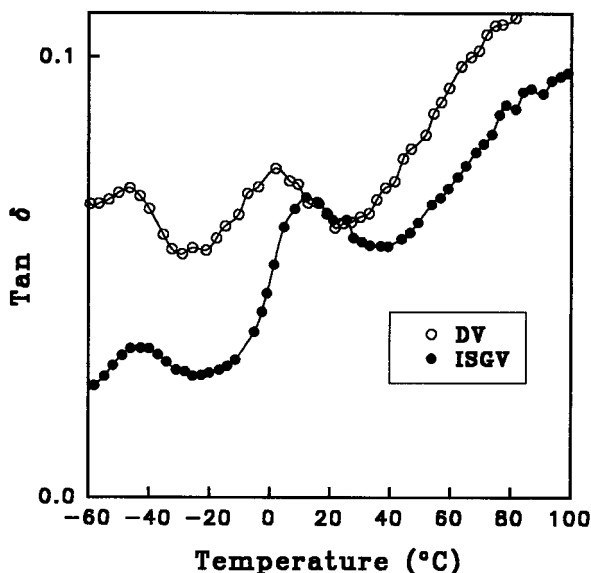
Figure 4 Comparison of tan δ of blends prepared by different preparation methods as a function of temperature. The composition of EPDM is 25 wt % for both blends prepared by the ISGV and the DV methods.

Figure 6 Storage moduli of the PP/EPDM blends prepared by the ISGV method as a function of temperature. Blend compositions are 90/10, 75/25, and 50/50 by weight.

increases. Due to the electrostatic repulsion between the polar groups, maleic anhydride, which attached superfluously to the PP and EPDM main chain, the miscibility of the blends having higher EPDM content would be decreased compared to that of the blends having smaller EPDM content.
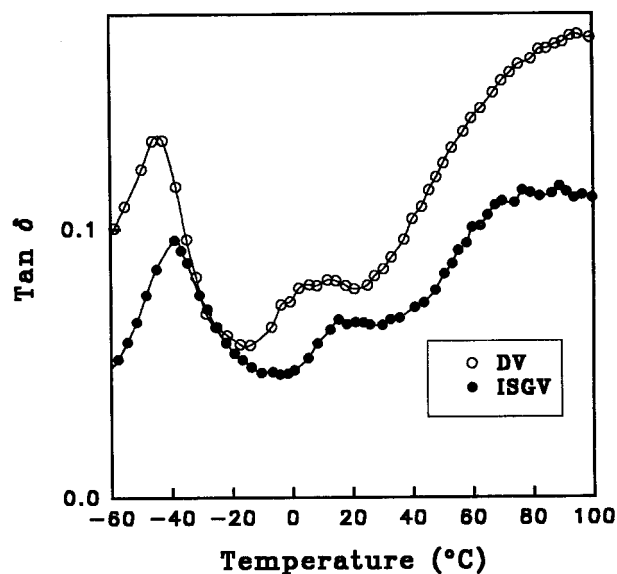
The network structure resulted from the chemical crosslinking between the EPDM molecules by DCP can also decrease the interfacial adhesion with PP.

Figure 3 shows the tan δ as a function of temperature for the dynamically vulcanized blend

Figure 5 Comparison of tan δ of blends prepared by different preparation methods as a function of temperature. The composition of EPDM is 50 wt % for both blends prepared by the ISGV and the DV methods.
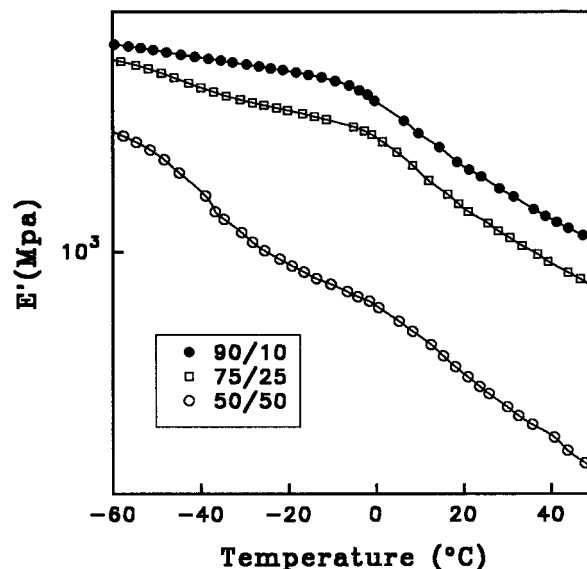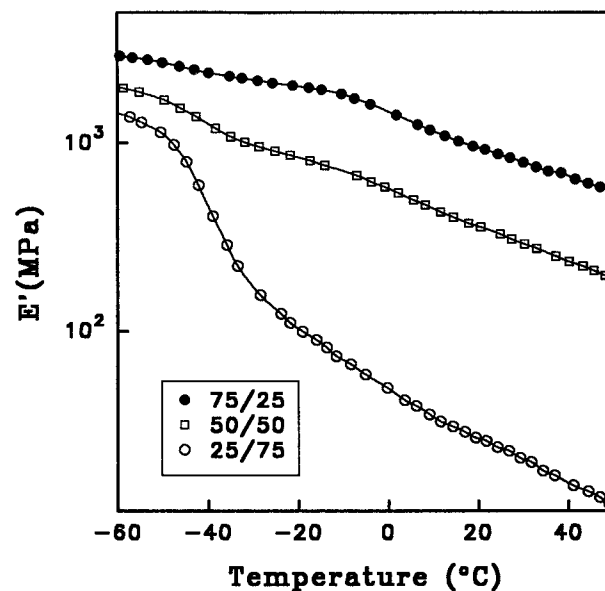

Figure 7 Storage moduli of PP-g-MAH/EPDM blends prepared by the DV method as a function of temperature. Blend compositions are 75/25, 50/50, and 25/75 by weight.
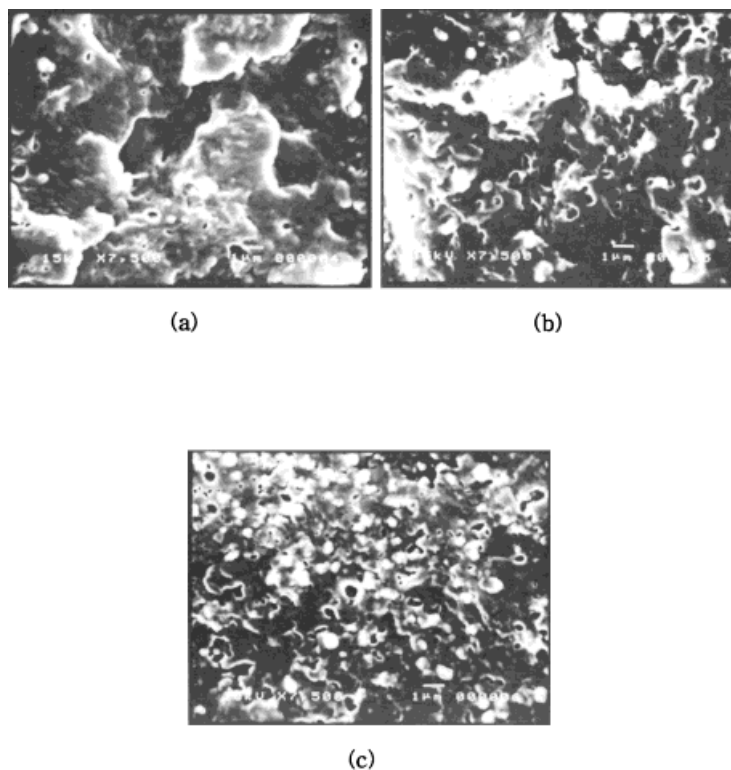
Figure 8   SEM micrographs of PP/EPDM blends prepared by the ISGV method. Blend compositions are (a) 90/10, (b) 75/25, and (c) 50/50 by weight.

with different contents of PP-g-MAH and EPDM. The T_gs of blends having 75/25 composition by weight were detected at −46.3 and 2.1°C. In the case of the blend having a 50/50 composition, the T_gs were −44.2 and 12.1°C. And the T_g of EPDM phase in the 25/75 blend was −38.9 °C. The T_g of PP for this blend was not clearly detected. The increase of T_g of EPDM phase can be ascribed to the effect of crosslinking. The cured EPDM particles by the dynamic vulcanization process confine the segmental mobility of PP, and thus the T_g of PP phase would also be shifted to higher temperature.

From the result obtained from the tan δ behavior of blends prepared by two different preparation methods, it can be known that the T_gs of both EPDM and PP phases increase to higher temperature as the EPDM content increases, regardless of the blend preparation methods. Due to the crosslinking of EPDM phase, the shift of T_gs to higher temperature would have occurred.

The tan δ behavior of blends prepared by different preparation methods having the same PP/EPDM contents are compared in Figures 4 and 5. The T_gs of both EPDM and PP phases of blends prepared by the ISGV method were higher compared to those of blends prepared by the DV method, regardless of the blend compositions. The result can be explained from the fact that the degree of crosslinking and the degree of grafting of polar maleic anhydride group onto polymer chains during vulcanization by the ISGV method are higher than those by the DV method. The T_gs of blends having different compositions prepared by different preparation methods are summarized in Table II.

Modulus of Blends

Figure 6 shows the storage moduli of the blends having different PP/EPDM composition, prepared by the ISGV method. The tendency of having lower modulus on increasing the content of EPDM is shown. This is not unusual, since the semicrystalline PP possesses inherently higher modulus than the elastomeric EPDM. Even the crosslinked EPDM particle can not be comparable to PP.

The storage moduli of PP-g-MAH/EPDM blends prepared by the DV method are shown in Figure 7. For the same reason as mentioned above, the modulus of blends was lowered as the content of EPDM
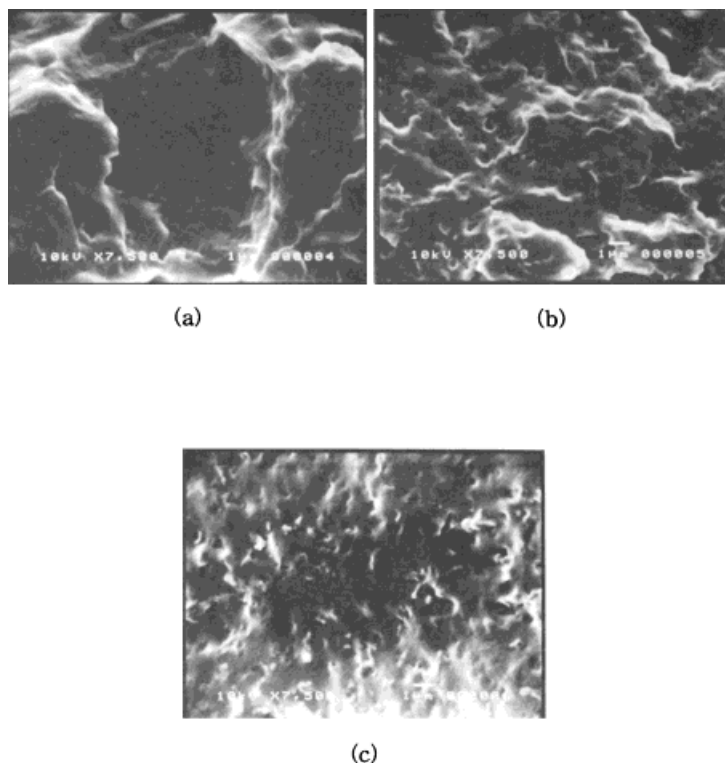
Figure 9   SEM micrographs of PP-g-MAH/EPDM blends prepared by the DV method. Blend compositions are (a) 75/25, (b) 50/50, and (c) 25/75 by weight.

increased. Careful inspection of Figures 6 and 7 indicates that the storage moduli of the blends prepared by the ISGV method are higher than those prepared by the DV method, regardless of the blend compositions. The result is closely related to the higher T_gs of components for the blends prepared by the ISGV method in comparison to those by the DV method, as shown in Table II.

Morphology of Blends

Figure 8 shows the SEM micrographs of PP/EPDM blends prepared by the ISGV method. In this case, due to the deficiency of interfacial adhesion between the two phases, the morphology were quite rough and coarse EPDM particles are distributed in the PP matrix.

The morphologies of the PP-g-MAH/EPDM blends prepared by the DV method are shown in Figure 9. The fractured surfaces were quite smooth throughout all the blend compositions. It can be known from the SEM micrographs that the cured EPDM particles are finely dispersed with very small particle size in the PP-g-MAH matrix. This fine morphology resembles that of the thermoplastic interpenetrating polymer network

(IPN), as already reported for the dynamically vulcanized EPDM and ionomer blends.[13] The blend prepared by the DV method would have the IPN structure where cured elastomer particles are dispersed finely across the olefinic matrix homogeneously.[13] In his review, Sperling attributed combinations of physically crosslinked polymers, including multiblock copolymers, semicrystalline polymers and ionomers—especially where both polymers attained some degree of dual-phase continuity—to a new class of IPNs designated "thermoplasic IPNs."[16]

CONCLUSIONS

In the studies of the dynamic mechanical properties of the blends by two different blend preparation methods such as the ISGV and the DV, the T_gs of both PP and EPDM phases were shifted to higher temperature as the EPDM content increased. The shift can be attributed in part to the crosslinking of EPDM by DCP. It was found that the blends prepared by the ISGV method showed higher T_gs and larger storage moduli in compar-

ison to the blends prepared by the DV method. The SEM morphology, however, showed that the size reduction of dispersed particles in the blends prepared by the DV method is larger than that of the blends prepared by the ISGV method.

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