Rheological Properties, Tensile Properties, and Morphology of PP/EPDM/Ionomer Ternary Blends

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SYNOPSIS

The rheological and tensile properties and the morphology of polypropylene(PP)/ethylene-propylene-diene terpolymer(EPDM)/ionomer ternary blends were investigated, using a rheometric dynamic spectrometer (RDS), a dynamic mechanical thermal analyzer (DMTA), a tensile tester, and a scanning electron microscope (SEM). Two kinds of poly(ethylene-co-methacrylic acid) (EMA) ionomers, neutralized with different metal ions (Na^+ and Zn^{++}), were used. Blends were melt-mixed, using a laboratory internal mixer at 190°C. The composition of PP and EPDM was fixed at 50/50 by wt % and the EMA ionomer contents were varied from 5 to 20 wt %, based on the total amount of PP and EPDM. It was found that the ternary blends, containing Na-neutralized ionomer, showed considerably different rheological properties and morphology as compared to the PP/EPDM binary blend, due to the compatibilizing effect of the ionomer for PP and EPDM, while the ternary blends, containing the Zn-neutralized ionomer, did not. The compatibilizing effect was most prominent at 5 wt % of ionomer concentration. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Ionomers, which have a small number of ionic groups (up to about 15 mol %), along nonionic backbone chains,[1-3] have attracted interest for many years, because of their unique properties as homopolymers and their ability to compatibilize certain incompatible blends.[4-7] One of the most commonly used ionomers is poly(ethylene-co-methacrylic acid) (EMA) ionomer, where the acid groups are partially or fully neutralized by metal ions.

The EMA ionomers have been used in binary blends in order to improve the toughness of polyamides and poly(ethylene terephthalate), even though the role of the ionomers in those systems is not fully understood.[6-9] The blends of ionomer with polyethylene or ethylene-propylene-diene terpolymer (EPDM) have been studied by us and by Fairley and Prud'homme.[7,8,10]

Blends of PP and EPDM have been extensively studied, since a wide range of properties can be obtained by selecting properly their compositions in the blends.[11-16] It was generally considered that PP and EPDM are incompatible despite their similar molecular structures. Thus, the addition of small amounts of polyethylene has been attempted for PP/EPDM blends in order to enhance the miscibility between the two components, as well as to improve low temperature properties of PP.[17] It has been reported that the addition of a third component into a binary blend changes the morphology and thus affects significantly the mechanical properties of the final blends, such as impact strength.[18,19]

Thus, the object of this work is to investigate the rheological properties and morphology, along with the tensile properties, of the ternary blends of PP, EPDM, and EMA ionomer, in order to better understand the morphology of the ternary blend systems, as well as to shed some light on the compatibilizing effect of the EMA ionomer for a PP/EPDM binary blend. We will focus our investigation to reveal the effect of the metal types used for neutralization in the EMA ionomer and the ionomer contents on those properties and morphology of the PP/EPDM/ionomer ternary blends. The composition of the blend was fixed at a 50/50 PP/EPDM

Table I Materials and Their Characteristics

Material	Properties	Source
PP	$M_n = 2.83 \times 10^4$ $M_w = 2.02 \times 10^5$ $MFI^a = 6.0$ $M_w/M_n = 7.14$	Korea Petrochemical Co. Ltd (PP4017)
EPDM	η_{inh} (dL/g)[b] = 1.22 I.V.[c]: 15.2 PE/PP (mol %)[d] = 52.0/48.0 ENB Type	Uniroyal (Roy. 521)
Ionomer A	Cation Type: Na^+ Ethylene/Methacrylic Acid = 91/9 % Neutralization: 50% Sp. gr[e] = 0.94 $MFI^a = 1.3$	Du Pont (Surlyn 8528)
Ionomer B	Cation Type: Zn^{++} Ethylene/Methacrylic Acid = 91/9 % Neutralization: 50% Sp. gr[e] = 0.95 $MFI^a = 1.1$	Du Pont (Surlyn 9520)

[a] Melt flow index.
[b] 0.5 g/dL xylene solution at 70°C.
[c] By ICl titration method.
[d] By IR analysis.
[e] Specific gravity.

by wt %. The ionomer contents were varied from 5 to 20 wt %, based on the total amount of PP and EPDM.

EXPERIMENTAL

Materials

Table I summarizes the characteristics of the polymers used in this study. The polypropylene (PP) was from Korea Petrochemical PP4017. The eth-ylene-propylene-diene terpolymer (EPDM), with ethylidene-2-norbornene (ENB) as a termonomer, was Royalene 521 by Uniroyal ($M_w = 1.80 \times 10^5$; ethylene content ($C_2 = 52$ mol %). Two kinds of EMA ionomers were supplied from Dupont. The polymers were used as received.

Blend Preparation

Binary PP/EPDM or ternary PP/EPDM/ionomer blends were prepared by melt mixing in a Brabender

Table II Blended Materials and Their Compositions

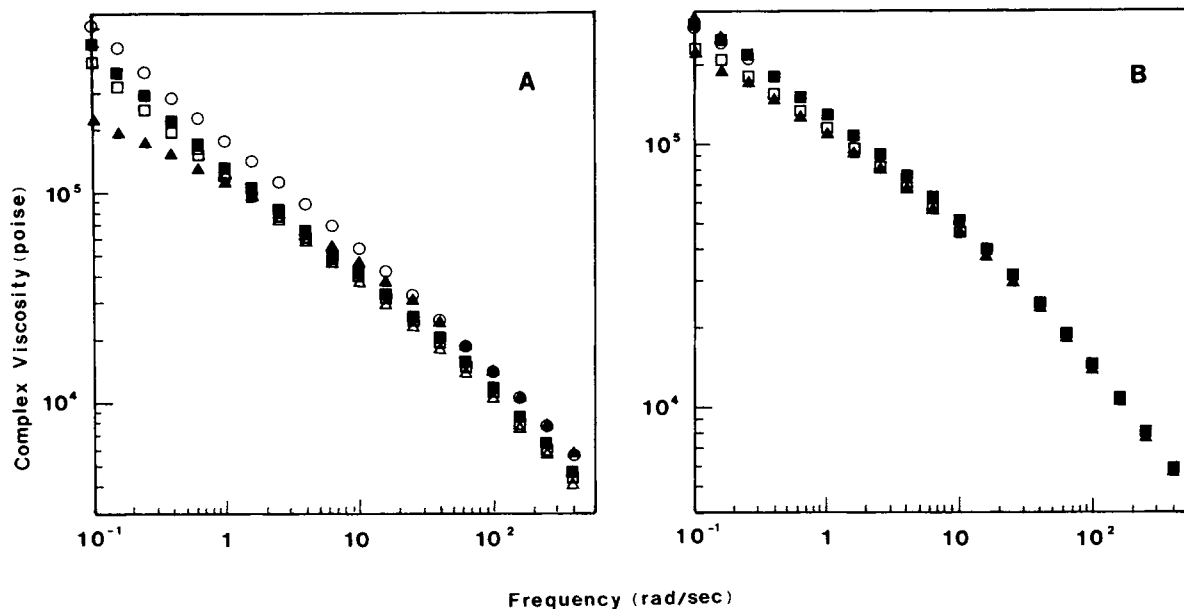| Notation	PP Contents	EPDM Contents	Ionomer Contents
PP50-EP50	50.0 wt %	50.0 wt %	No Ionomers
PP50-EP50/IA5	47.5	47.5	5.0
PP50-EP50/IA10	45.0	45.0	10.0
PP50-EP50/IA15	42.5	42.5	15.0
PP50-EP50/IA20	40.0	40.0	20.0
PP50-EP50/IB5	47.5	47.5	5.0
PP50-EP50/IB10	45.0	45.0	10.0
PP50-EP50/IB15	42.5	42.5	15.0
PP50-EP50/IB20	40.0	40.0	20.0

Figure 1   Complex viscosity vs. frequency for PP/EPDM/ionomer ternary blends: (A) PP50-EP50/IA and (B) PP50-EP50/IB. (▲) 0 wt %, (○) 5 wt %, (□) 10 wt %, (△) 15 wt %, and (■) 20 wt %.

Roller Mixer (Type w50H) at 190°C with a residence time of 15 min at 60 rpm. The composition of the PP and EPDM was fixed at 50/50 by wt %. For the ternary blends, the ionomer contents were varied from 5 to 20 wt %, based on the total amount of PP and EPDM. The sample notations of blends are summarized in Table II.

Measurements

The rheological properties of blends were measured at 200°C, using a RDS [Rheometric Dynamic Spectrometer (RDS 7700)] in a cone-and-plate mode. Cone geometry has 0.1 rad in angle and 1.2 cm in radius. The samples were compression-molded into discs that were 2.5 cm in diameter and 1 mm thick. Strain was maintained at 15% for all samples. Glass transition temperatures of the blends were determined using a Dynamic Mechanical Thermal Analyzer (DMTA; Polymer Laboratory). Measurements were made at a heating rate of 10°C/min and 1 Hz. The sample size was 1.1 mm × 31 mm × 50 mm.

RESULTS AND DISCUSSION

Rheological Properties

The complex viscosities of the PP/EPDM/ionomer ternary blends are shown over three decades of fre-

quencies in Figure 1. It is seen that the viscosities of the ternary blends, containing ionomer A at low frequencies, were higher than those of the PP/EPDM binary blend and that the observed viscosity of the ternary blends, containing 5 wt % of ionomer A, was highest. Of more interest is the fact that the addition of ionomer A to the PP/EPDM binary blend induced viscosity yield. The yield behavior was
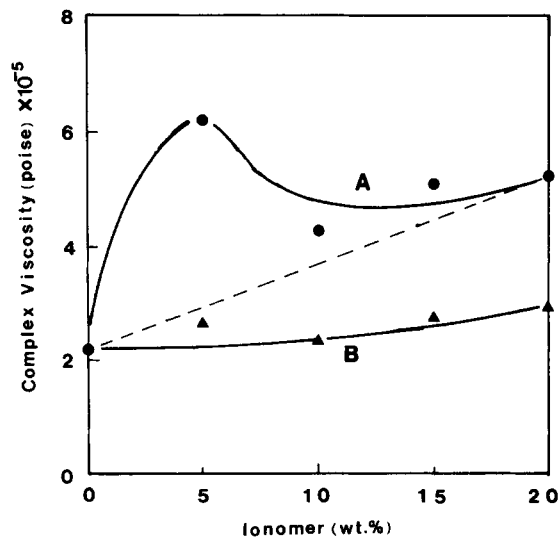

Figure 2   Effect of the content of ionomer on the complex viscosity: (A) PP50-EP50/IA and (B) PP50-EP50/IB.

detected most clearly for the ternary blends containing 5 wt % of ionomer A. In incompatible blends, viscosity yield is normally observed when the component polymers are intimately mixed between droplets, leading to interlocked morphology, and the associated structure has long relaxation times.[20-22] Thus, the result, referred to in Figure 1 for the ternary blends containing ionomer A, implies that mechanical interlocking could be occuring among the three components, due to the inherent ionic cross-linking character of the Na-neutralized ionomer A.

The result is more clearly seen in the plot of complex viscosity against the added ionomer contents at a frequency of 0.1 sec^{-1}, as shown in Figure 2. The viscosity–composition curves show positive deviation from the simple additive rule (dotted line in Fig. 2) with a maximum. Positive deviation of viscosity is often observed when there are strong interactions between droplets, or when the component polymers are intimately mixed.[21-23] The viscosities of ionomer A-containing ternary blends were higher than those of ionomer B-containing ternary blends, regardless of the ionomer contents. The viscosity exhibited a maximum at 5 wt % of ionomer. The result implies that compatibilization was achieved in the presence of 5 wt % of Na-neutralized ionomer A for the PP and EPDM binary blend. A comparison of Figures 1 and 2 indicates, however, that no significantly different viscosity behaviors for the io-

nomer B-containing ternary blends compared to the PP/EPDM binary blend, even though the viscosities of the ternary blends were slightly higher than for the binary blend. It may be thought that the added Zn-neutralized ionomer B did not show any clear compatiblizing effect for the PP/EPDM binary blend.

Figure 3 shows the storage moduli of the PP/EPDM/ionomer ternary blends against the ionomer contents. As in the complex viscosity, the storage moduli (G') of the ternary blends are higher than that of the PP/EPDM binary blend over an extended range of frequencies in the case of the incorporation of ionomer A. It is seen that the ternary blends, containing 5 wt % ionomer A, showed better storage modulus than the other PP/EPDM/ionomer ternary blends or the PP/EPDM binary blends. For the ternary blends containing ionomer A, a plateau began to appear at low frequencies. The tendency of G' to approach a plateau at low frequencies is remeniscent of what was found in other composite systems, such as ABS, acrylonitrile-butadiene copolymer, or filled polymers.[24,25] This again implies the multiphasic morphology of the ternary blends of PP, EPDM, and ionomer. The storage moduli of the ternary blends containing ionomer B, however, show no significant differences.

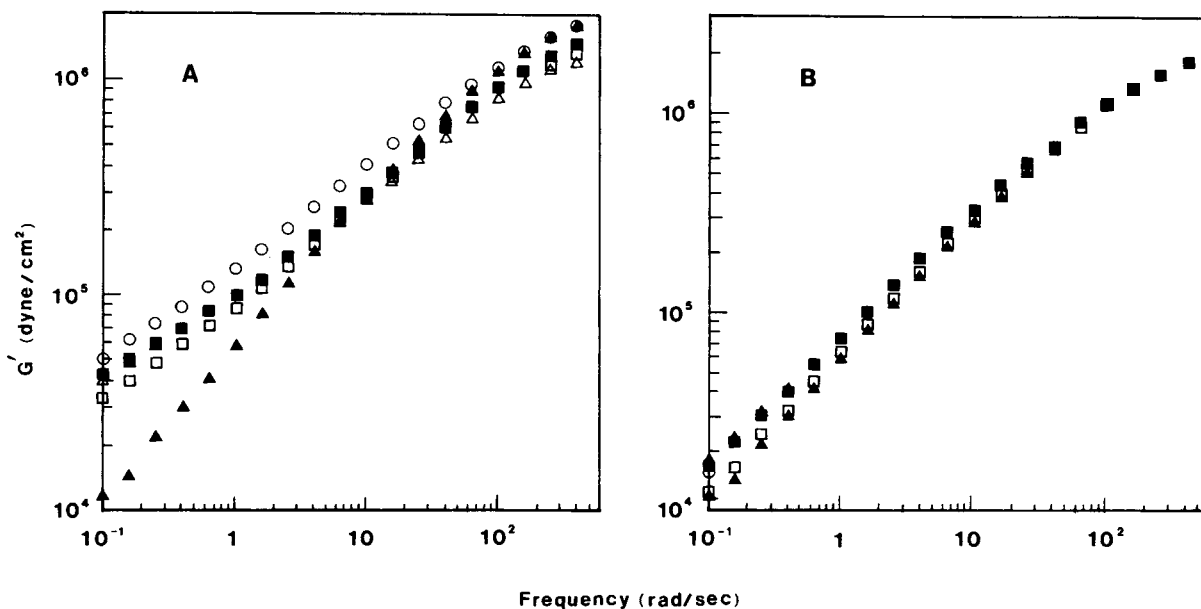Another way to examine this behavior is to plot tan δ as a function of frequency (Fig. 4). Instead of

Frequency (rad/sec)

Figure 3 Storage modulus vs. frequency for PP/EPDM/ionomer ternary blends: (A) PP50-EP50/IA and (B) PP50-EP50/IB. (▲) 0 wt %, (○) 5 wt %, (□) 10 wt %, (△) 15 wt %, and (■) 20 wt %.
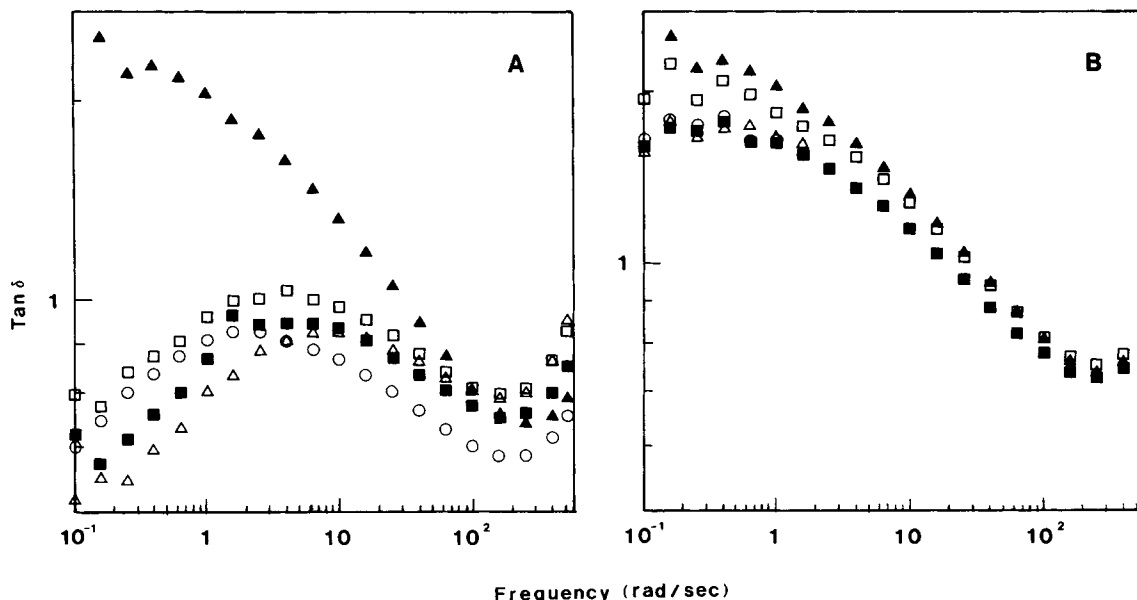
Figure 4   Loss tangent vs. frequency for PP/EPDM/ionomer ternary blends: (A) PP50-EP50/IA and (B) PP50-EP50/IB. (▲) 0 wt %, (○) 5 wt %, (□) 10 wt %, (△) 15 wt %, and (■) 20 wt %.

a relatively monotonic decrease of tan δ as in the PP/EPDM binary blend, maxima were observed in the ternary blends containing ionomer A. This is related to the tendency for the G' and loss modulus (G'') to reach a plateau, both at low and high frequencies. A monotonic decrease of tan δ is usually found in simple polymers. The occurrence of maxima in tan δ in the ternary blends seems to come from the complex multiphasic character, due to the inherent incompatibility among the three components, PP, EPDM, and ionomer.

Ternary blends containing ionomer A had more elastic properties than viscous properties, because than δ was <1 over all the frequency ranges. The effect of ionomer addition was significant when 5 wt % of ionomer A was added. Meanwhile, ternary

blends containing ionomer B, as well as the PP/EPDM binary blend, showed the G'-G'' crossover behavior (i.e., tan δ = 1.0) around the frequency ranges of 20–30 sec^{-1}. This means that the G'' responses dominates over the low range of frequencies, but the G' response dominates over the higher frequency ranges.

Harrell and Nakajima[26] reported that the G' and G'' vs. frequency plot can be used for analyzing the effect of the degree of branching; The low frequency storage modulus increases with the increase in long branching and, thus, for the extreme case, the G' response dominates over the entire range of observed frequencies; that is, no G'-G'' crossover (tan δ = 1) is observed. The above results, in which ionomer A-added ternary blends showed no crossover, suggest

Table III   Tensile Properties of Blends

Sample	Modulus, E (Kgf/cm^2)	Tensile Strength (Kgf/cm^2)	Elongation at Break (%)
PP50-EP50	575.82	105.57	234.75
PP50-EP50/IA5	630.21	109.23	138.60
PP50-EP50/IA10	497.35	88.08	170.02
PP50-EP50/IA15	487.49	74.68	237.00
PP50-EP50/IA20	421.72	56.23	190.43
PP50-EP50/IB5	719.63	112.62	195.18
PP50-EP50/IB10	680.21	93.07	206.33
PP50-EP50/IB15	640.81	85.54	215.45
PP50-EP50/IB20	611.58	65.50	176.66

that the ternary blend has long branches, which form during processing (in melt mixing).[27]

This implies that a mechanical interlocking could be occurring among the three components, due to the inherent ionic crosslinking character of the Na-neutralized ionomer A. Although the Zn-neutralized ionomer B can form mechanical interlocking between PP and EPDM, it seems that the possibility is less than that of ionomer A. It was observed, however, that the three components are mutually incompatible because none of them show a semicircle behavior on the Cole–Cole plot.

Tensile Properties

Tensile properties of the PP/EPDM/ionomer ternary blends are summarized in Table III. Figure 5 shows the tensile strength of the PP/EPDM/ionomer ternary blends vs. ionomer concentration. It was generally observed that the tensile strength decreased with ionomer concentration, regardless of the ionomer types. It should be noted, however, that the tensile strength and modulus of the ternary blend show maxima when 5 wt % of both ionomer A and B were added to the binary PP and EPDM blend, due to their compatibilizing effect in Figures 5 and 6. The ternary blends, containing ionomer B, showed higher tensile strength and modulus than those containing ionomer A.

The addition of ionomer into the PP/EPDM blend reduced the elongation at break, regardless of ionomer types, as shown in Figure 7.
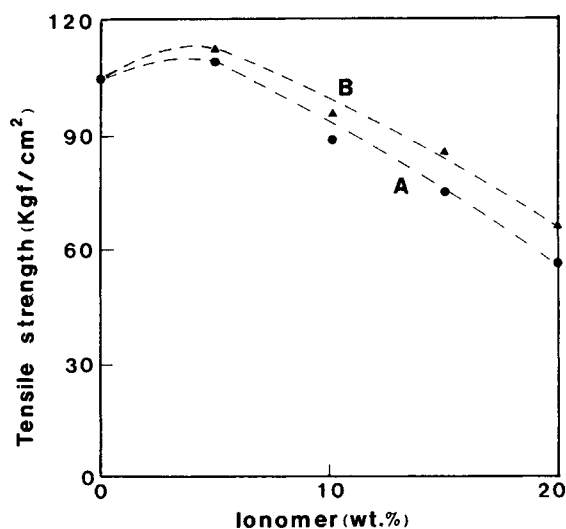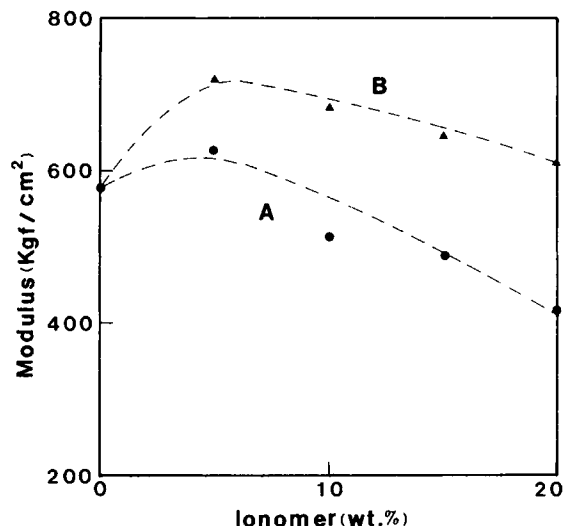

Figure 6 Effect of the added ionomer on the modulus of the PP/EPDM/ionomer ternary blends: (A) PP50-EP50/IA and (B) PP50-EP50/IB.

Morphology

The morphology of the PP/EPDM binary blend, as well as the PP/EPDM/ionomer ternary blends, is analyzed by Scanning Electron Microscopy (SEM). For the PP/EPDM binary blend, as shown in Figure 8, the PP and EPDM are incompatible and their phases are grossly separated. The SEM micrographs show that small EPDM particles peeled off from the continuous matrix of PP when fractured in liquid nitrogen.
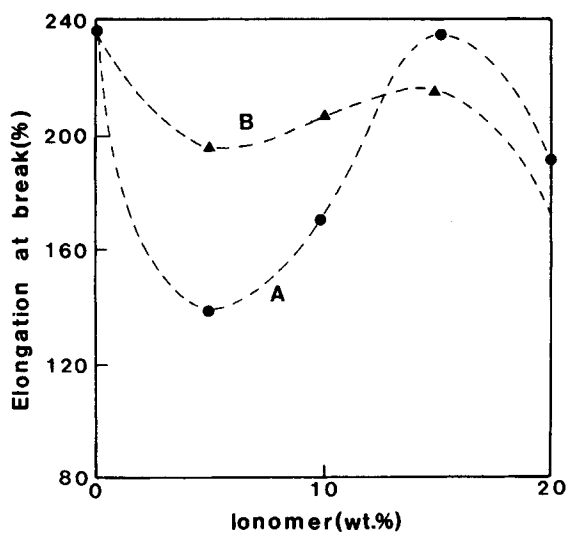

Figure 5 Effect of the added ionomer on the tensile strength of the PP/EPDM/ionomer ternary blends: (A) PP50-EP50/IA and (B) PP50-EP50/IB.

Figure 7 Effect of the added ionomer on the elongation at break of the PP/EPDM/ionomer ternary blends: (A) PP50-EP50/IA and (B) PP50-EP50/IB.
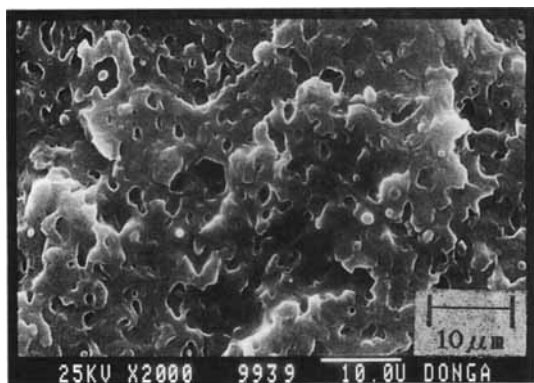
Figure 8 SEM micrograph of the PP/EPDM binary blend, fractured under liquid nitrogen: PP50-EP50.

For the PP/EPDM/ionomer ternary blends, EPDM particles are dispersed in PP matrix (Fig. 9), except when 5 wt % of ionomers are included in the PP/EPDM binary mixtures. When 5 wt % of ionomer A is included, the phase is relatively finer, when compared with that of more than 10 wt % of ionomer inclusion. It is seen that the EPDM particles adhere to the PP matrix, even though the three components are not molecularly mixed. Figure 9 shows that compatibilization was achieved in the presence of 5 wt % of ionomer A for the PP and EPDM phases. Ionomer B did not show any better compatibilizing effect than ionomer A when 5 wt % of each ionomer was added.

These observations agreed with the data of DMTA analysis. Figure 10 shows the mechanical T_g of the PP/EPDM binary and the PP/EPDM/ionomer ternary blends. It is seen that when 5 wt % of ionomers are added to the binary blend, the T_gs are slightly shifted, whereas no shift is observed as more ionomers are added. The shift is more prominent in ionomer A-added blends than in ionomer B-added blends. The result implies that the Na-neutralized ionomer A acts as a compatibilizer when added to a PP/EPDM blend at the concentration of 5 wt %. However, any clear compatibilizing effect is not observed in the ternary blends containing ionomer A with higher concentrations above 10 wt %. Similar trends were observed in the ionomer B-added ternary blends.

Fairley and Prud'homme[8] showed the presence of one phase in the melt in their study on the dy-
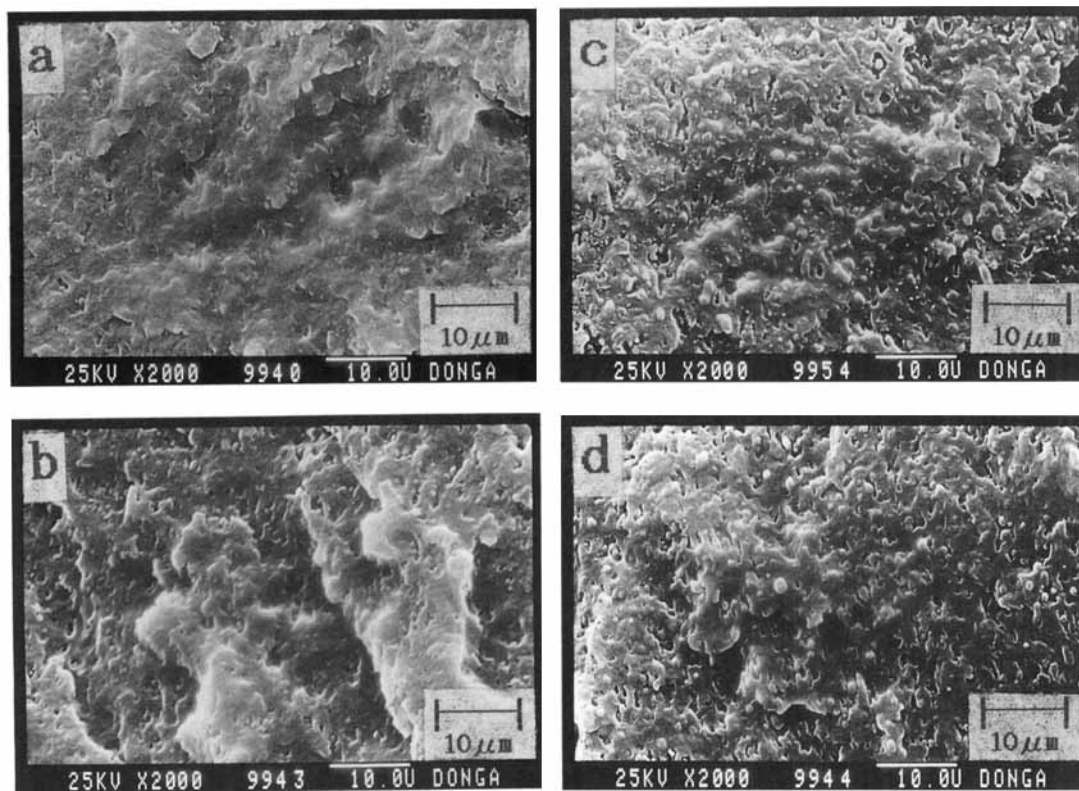

Figure 9 SEM micrographs of the PP/EPDM/ionomer ternary blends, fractured under liquid nitrogen: (a) PP50-EP50/IA5, (b) PP50-EP50/IA10, (c) PP50-EP50/IB5, and (d) PP50-EP50/IB10.
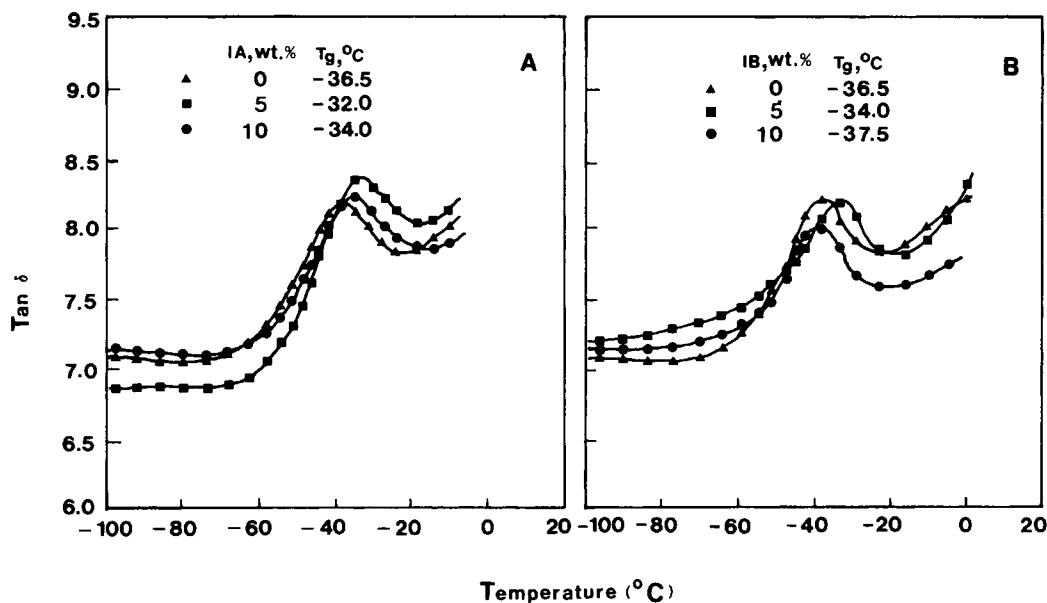
Figure 10 Effect of the added ionomer content on the T_g of the PP/EPDM/ionomer blends: (A) PP50-EP50/IA and (B) PP50-EP50/IB.

namic melt properties of low density polyethylene/ EMA ionomer blends. Taking into consideration the fact that polyethylene is a parent polymer of EPDM, it may be thought that molecular intermixing occurs, to some extent, in the amorphous molten state between the EPDM and ionomer. Thus, the compatibilizing effect of the added ionomer in a PP/ EPDM binary blend can be expected because of the partial miscibility between EPDM and ionomer in the molten state. The reason that ionomer A exhibited better compatibilizing effects than ionomer B, for the mixture of PP and EPDM, may be related to the differences in their interlocking tendencies. It has been established that ionic domains in ionomer act as thermoreversible crosslinks, even though the size and properties of the ionic microdomains are governed by several factors, including the wt % of carboxylic acid, the degree of neutralization of the acid group, and the type of metal cation for neutralization.[28-30] It is assumed that the larger ionization potential character of Na^+, in the Na-neutralized ionomer-containing blends, can provide larger ionic interlocking among the components by its inherent thermoreversible crosslinking role, whereas the smaller ionization potential character of the Zn^{++}, in the Zn-neutralized ionomer B, cannot provide such a larger, favorable interlocking among the components.

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