PP/EPDM 블렌드의 열적성질과 결정구조에 미치는 이오노머 첨가의 영향

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Effect of Ionomer Addition on the Thermal Behavior and Crystalline Structure of the PP/EPDM Blend

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요 약 : 폴리프로필렌(PP)과 에틸렌-프로필렌-디엔 공중합체(EPDM) 블렌드의 열적성질과 결정구조에 미치는 이오노머 첨가의 영향에 대해 시차주사열량계(DSC), 레오미터(RDS) 및 X-선회절계를 사용하여 연구하였다. PP와 EPDM의 조성은 중량비로 50/50으로 고정하였고 중화금속이 다른 두 종류(Na^+ 및 Zn^{++})의 이오노머를 5-20 wt.% 사용하였다. PP/EPDM 블렌드의 열적성질과 결정구조는 Zn^{++}으로 중화된 이오노머의 첨가에는 크게 영향을 받지 않았으나 Na^+로 중화된 이오노머의 첨가에는 크게 영향을 받았으며 특히 5 wt.% 가 첨가될 때 그 영향이 가장 크게 나타났다.

Abstract : The effect of ionomer addition on the thermal properties and crystalline structure of a polypropylene(PP)/ethylene-propylene-diene terpolymer(EPDM) blend was investigated by using Rheometric dynamic spectrometer(RDS), differential scanning calorimeter (DSC), and X-ray diffractometer. Two kinds of poly(ethylene-co-methacrylic acid) ionomers containing different metal ions(Na^+ and Zn^{++}) were compared to find out the effects of the metal ion type for neutralization and the ionomer contents. The composition of PP and EPDM was fixed at 50/50 by weight and the ionomer contents varied from 5 to 20 wt.%. It was found that the thermal behavior and crystalline structure of the PP50-EP50 blend were not affected by the addition of Zn-neutralized ionomer but significantly affected by the addition of Na-neutralized ionomer. The effect of adding Na-neutralized ionomer to PP50-EP50 blend was most prominent at the concentration of 5wt%.

Keywords : PP/EPDM blend, ionomer, crystal structure, thermal property.

INTRODUCTION

The blends of polypropylene(PP) and ethylene-propylene-diene terpolymer(EPDM) have been extensively studied for their commercial importances, since various properties can be ob-tained by proper selection of their compositions in the blends.[1~9] Blending PP with EPDM as its toughening agent is one of the important ways to improve the low temperature brittleness of PP. Similarly, polyolefinic thermoplastic elasto-mers are produced by blending EPDM with PP

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as a reinforcing agent. Thus, addition of small amounts of polyethylene(PE) has been attempted for PP/EPDM blends in order to enhance the poor miscibility between the two components as well to improve PP's low termperature properties. Usually the compatibility of EPDM with PE is known to be better than with PP, even though it depends on the numerous molecular parameters of EPDM such as ethylene content, molecular weight, termonomer type and content, stereoblock length of the ethylene and/or propylene segments, etc.[9] It is also interesting to note that the addition of the third component such as EPDM into PE/PP blends makes changes in morphology and thus affects significantly the mechanical propeties of the final blends such as impact strength.[7,8]

Meanwhile, ionomers, which have a small number of ionic groups(up to about 15mol%) along nonionic backbone chains,[10,11] have attracted much interest for many years, because of their unique properties as homopolymers and their ability to compatibilize certain incompatible blends.[12~14] 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.[14~16] Recently the blends of ionomer with polyethylene or ethylene-propylene-diene terpolymer(EPDM) have been studied by the authors,[16] Fairley and Prud'homme.[17] It was expected that the ionic character of the ionomer used plays an important role to enhance the compatibility between the component polymers.

In the present work, therefore, the effects of adding EMA ionomer to PP/EPDM blend on the thermal behavior and crystalline structure were investigated. Two kinds of EMA ionomers containing different metal ions(Na^+ or Zn^{++})

were used for comparison. Besides, the effect of the metal component for neutralization in the ionomer and the ionomer contents in the PP/EPDM blend were discussed.

EXPERIMENTAL

Materials. Table 1 summarizes the characteristics of the polymers used in this study. The PP used in this work was a Korea Petrochemical PP4017. The EPDM with ethylidene-2-norbornene(ENB) as a termonomer was Royalene 521 produced by Uniroyal. ($M_W = 1.80 \times 10^5$; ethylene content = 52% in moles). Two kinds of EMA ionomers were supplied by Du pont. All the polymers were used as received.

Table 1. Materials Used in Experiments and Their Properties

Meterial	Properties	Source
PP	$Mn = 2.83 \times 10^4$	Korea Petrochemi-
	$Mw = 2.02 \times 10^5$	cal Co. Ltd
	$MFI^a = 6.0$	(PP4017)
	$Mw/Mn = 7.14$	
EPDM	$\eta_{inh}(dl/g)^b = 1.22$	Uniroyal (Roy.521)
	I.V.^{c} : 15.2	
	PE/PP(mol%)^d = 52.0/	
	48.0	
	ENB Type^e	
Na - neu- tralized Ionomer (IA)	Cation Type : Na^+	Du Pont (Surlyn
	Ethylene / Methacrylic	8528)
	Acid = 91/9	
	% Neutralization : 50%	
	Sp.gr = 0.94	
	$MFI^a = 1.3$	
Zn - neu- tralized Ionomer (IB)	Cation Type : Zn^{++}	Du Pont (Surlyn
	Ethylene / Methacrylic	9520)
	Acid = 91/9	
	% Neutralization : 50%	
	Sp.gr = 0.95	
	$MFI^a = 1.1$	

a) melt flow index.
b) 0.5 g/dl xylene solution at 70℃.
c) by ICl titration method.
d) ethylidene-2-norbornene.

Blending. Binary PP/EPDM(PP50-EP50) or ternary PP/EPDM/Ionomer blends have been prepared by melt mixing the polymers in a Brabender Roller Mixer (Type w50H) at 190℃ for 15 minutes at 60 rpm. The composition of the PP and EPDM was fixed at 50/50 by weight. For the ternary blends, the ionomer contents were varied from 5 to 20wt% based on the PP50-EP50 blend.

Measurements. The thermal analysis was performed under nitrogen, with a heating rate of 10℃/min. using a Perkin Elmer differential scanning calorimeter(DSC7). The weight percent crystallinity of PP or ionomer in the blends was evaluated from the ratio of the heat of fusion for the blend to that for the 100% crystalline PP or polyethylene(PE), respectively ($\Delta H_{PP}=$ 209 J/g and $\Delta H_{PE}=277.1$ J/g from the literatures.[18,19] Crystallization kinetics was studied using the dynamic DSC method with six different scan rates of 0.5, 1.0, 2.0, 5.0, 10.0, and 20.0℃/min. Details of the dynamic DSC method are described elsewhere.[20] The weight fraction X_t of the material crystallized at the time t was calculated from the ratio between the heat generated at the time t and the total heat of crystallization. The rheological properties of blends were measured at 200℃ using a Rheometric Dynamic Spectrometer(RDS 7700) in a cone-and-plate type.[21] Cone geometry has 0.1 rad in angle and 1.2 cm in radius. The samples were compression-molded into discs of 2.5 cm in diameter and 1 mm thick. The strain employed for RDS test was maintained to 15% for all of the samples. X-ray diffraction patterns were obtained with a Rigaku Denki X-ray diffractometer using nickel filtered CuKα radiation (30kV, 20mA).

RESULTS AND DISCUSSION

Thermal Behavior. Fig. 1 shows the effect of ionomer added to PP50-EP50 blend on the melting temperature of PP phase. The melting
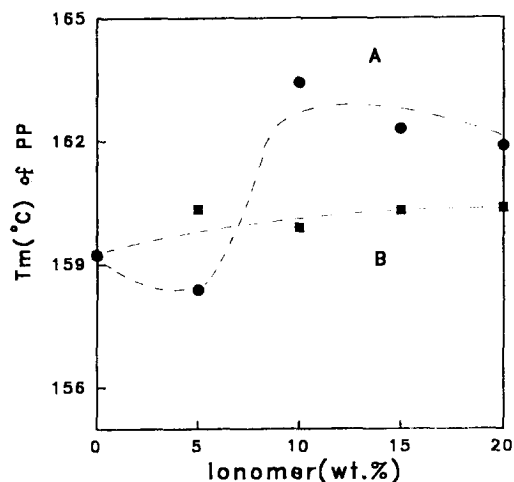

Fig. 1. Melting temperature of PP in PP50-EP50/ Ionomer blends as a function of ionomer contents (wt.%); A:Na-neutralized ionomer, B:Zn-neutralized ionomer.

temperature of PP was not changed significantly with the addition of the Zn-neutralized ionomer. However, the melting temperature of PP increased with the addition of the Na-neutralized ionomer by 2-4℃, except at the concentration of 5 wt%. The initial decrease of melting temperature may come from the compatibilizing effect of the added Na-neutralized ionomer to the PP50-EP50 blend.

It is widely known that presence of certain polymeric species, often referred to as "compatibilizers", improves poor compatibility in the multi-component polymer system by enhancing the interfacial adhesion. Usually, the block or graft copolymers suitably chosen has been reported to show such "compatibilizing" effects for phase separated polymer blends. Role of the compatibilizers has been well reviewed recently.[22,23]

The degree of crystallinity in PP phase as a function of the ionomer content is shown in Fig. 2. The degree of crystallinity in PP phase decreased with ionomer contents, regardless of the ionomer types. The decrease in the degree of
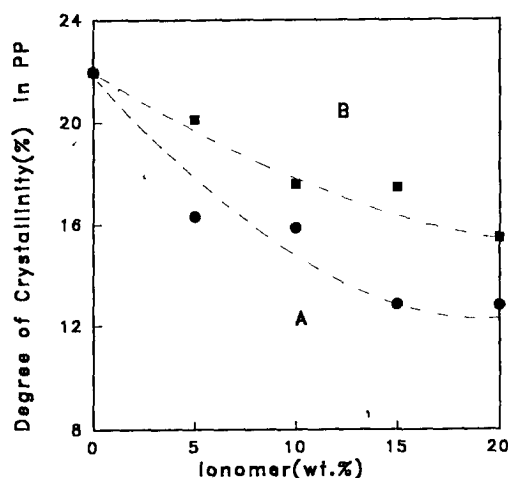
Fig. 2. Degree of crystallinity(%) in PP phase as a function of ionomer contents(wt.%); A:Na-neutralized ionomer, B:Zn-neutralized ionomer.

crystallinity in PP phase became more clear in the case of Na-neutralized ionomer than in the case of Zn-neutralized ionomer.

Table 2 shows the thermal properties of ionomers, PP, and their blends. The melting points of Zn-neutralized ionomer and Na-neu-

tralized ionomer were 107℃ and 102℃, respectively. As expected, the melting temperature of ionomer($T_{m, ionomer}$) and the degree of crystallinity in ionomer phase($X_{m, ionomer}$) increased with increasing ionomer contents, regardless of the ionomer types.

Fairley and Prud' homme[17] reported the presence of one phase in the melt on the dynamic melt properties of low density polyethylene/EMA ionomer blends. Considering that polyethylene is a parent polymer of EPDM, some extent of molecular intermixing may occur in the amorphous molten state between EPDM and ionomer. Thus, the compatibilizing effect of the added ionomer in a PP50-EP50 binary blend can be expected because of the partial miscibility between EPDM and ionomer in the molten state.[24]

It has been established that ionic domains in ionomer act as thermo-reversible crosslinks, even though the size and properties of the ionic microdomains are governed by several factors including the carboxylic acid contents, the neutralization degree of the acid group, and the type of metal cation for neutralization,

Table 2. Thermal Properties of the Linear PP/EPDM and Ionomer Blends

(Scan rate : 10℃/min)

Sample	Composition	$T_{m, ionomer}$(℃)	$T_{m, pp}$(℃)	$X_{m, ionomer}$(%)*	$X_{m, PP}$(%)**
PP50-EP50	50/50	–	159	–	21.98
PP50-EP50/IA5	47.5/47.5/5	100	158	1.20	16.38
PP50-EP50/IA10	45.0/45.0/10	101	163	1.40	15.58
PP50-EP50/IA15	42.5/42.5/15	102	162	1.80	12.88
PP50-EP50/IA20	40.0/40.0/20	102	162	2.40	12.85
PP50-EP50/IB5	47.5/47.5/5	105	160	2.80	20.13
PP50-EP50/IB10	45.0/45.0/10	106	160	2.80	17.57
PP50-EP50/IB15	42.5/42.5/15	106	160	3.20	17.44
PP50-EP50/IB20	40.0/40.0/20	107	160	5.40	15.50
Na-neutralized ionomer (IA)	100	102	–	17.00	–
Zn-neutralized ionomer (IB)	100	107	–	16.00	–

a) Degree of crystallinity of ionomer was calculated based on the 100% crystalline PE ($\Delta H = 277 J/g$)[19]

b) Degree of crystallinity of PP was calculated based on the 100% crystalline PP ($\Delta H = 209 J/g$)[19]

etc.[24~26] It is assumed that a larger ionization potential character of Na^+ in the Na-neutralized ionomer containing blends can provide a larger ionic interlocking among the components by inherent thermo-reversible crosslinking role, whereas a smaller ionization potential character of Zn^{++} in the Zn-neutralized ionomer can not provide such a large favorable interlocking among the components.

In order to explain the thermal behavior of the ionomer added PP50-EP50 ternary blends, viscosity behaviors of the ternary blends were measured by using RDS.

Fig. 3 shows the plot of complex viscosity against the added ionomer contents at a frequency of 0.1 sec.$^{-1}$ The complex viscosities at a frequency of 0.1 sec^{-1} of Na-neutralized ionomer, Zn-neutralized ionomer, and PP50-EP50 blend are 2.58 x 10^4 and 4.25 x 10^4, and 2.20 × 10^5 poise, respectively. The viscosity-composition curves show positive deviation from the simple additive rule(dotted line in Fig. 3) over the ranges of the ionomer contents up to 20wt. %. Positive deviation of viscosity is frequently observed when there are strong interactions between component droplets and in incompatible blends the component polymer droplets are intimately mixed, exhibiting so-called "interlocked morphology".[27~29] The viscosities of Na-neutralized ionomer containing ternary blends were higher than those of Zn-neutralized ionomer containing ternary blends regardless of the ionomer contents. A maximum viscosity was shown at 5wt.% of ionomer. The result proves that compatibilization was achieved in the presence of 5wt.% of Na-neutralized ionomer for the PP50-EP50 binary blend. Note, however, that no significant difference in viscosity behavior was observed for the Zn-neutralized ionomer containing ternary blends compared to the PP50-EP50 binary blend, even though the viscosities of the ternary blends were slightly higher than the binary blend.

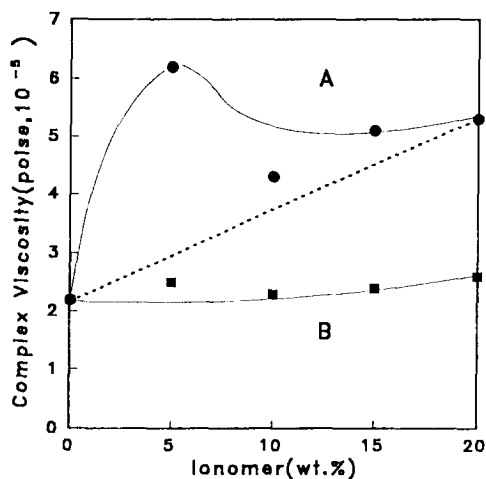Thus, from Fig. 3, it is concluded that a me-

Fig. 3. Effect of the content of ionomers on the complex viscosity of PP50-EP50/Ionomer blends at 200℃; A:Na-neutralized ionomer, B:Zn-neutralized ionomer.

chanical interlocking occurred among PP, EPDM, and ionomer, due to the inherent ionic crosslinking character of the Na-neutralized ionomer. However, a mechanical interlocking of the Zn-neutralized ionomer between PP and EPDM seems to be less than that of Na-neutralized ionomer.

Fig. 4 shows the rate of crystallization for the ternary blends having 5wt% of ionomers and the PP50-EP50 binary blend. In this figure, the crystallization temperature of the blends was 117℃, where PP phases only crystallize. Therefore, it is clear that the crystallization rate of the PP50-EP50 blend containing Zn-neutralized ionomer (PP50-EP50/IB5) is faster than that of the PP50-EP50 blend containing Na-neutralized ionomer (PP50-EP50/IA5) and the PP50 -EP50 binary blend. The PP50-EP50/IA5 blend presents the lowest crystallization rate among the three blends. This means that the compatibilizing effect of Na-neutralized ionomer results in an interpenetrating phase morphology among the three components when 5 wt.% of Na-neutralized ionomer was added to the binary PP50-
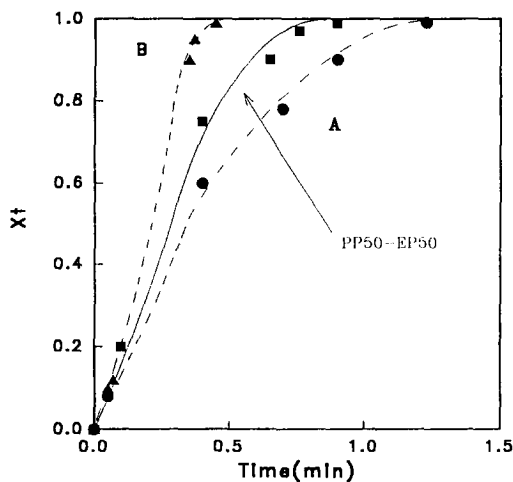
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Fig. 4. Effect of ionomer addition on the crystallization of PP50-EP50 blends at 117℃. The ionomer contents are 5wt.%, respectively.

Table 3. Crystallization Kinetics Parameters of Blends

Sample	Avrami exponent(n)	Avrami constant(k)	Half-life (min)
PP50-EP50	1.17	4.71	0.19
PP50-EP50/IA5	1.33	2.12	0.43
PP50-EP50/IA10	1.17	2.92	0.29
PP50-EP50/IA15	1.16	2.37	0.26
PP50-EP50/IA20	1.28	3.68	0.27
PP50-EP50/IB5	1.14	5.64	0.16
PP50-EP50/IB10	1.25	5.64	0.17
PP50-EP50/IB15	1.57	3.49	0.11
PP50-EP50/IB20	1.28	3.19	0.30

EP50 blend. It was reported that a slower crystallization rate of a polymer blend is one of several indirect evidences of the interpenetrating character of component polymers.[24] The literature, for instance, showed that the interpentrating polymer networks(IPNs), which possess physical interlocking at interfaces, strongly restrict the crystallization of crystalline component.[30]

The crystallization characteristics are reported in Table 3. The half-life of crystallization, $t_{1/2}$, Avrami exponent, n, and kinetic constant, k of the blends are summarized in the table. The PP50-EP50/IA5 blend exhibits smaller k value and higher $t_{1/2}$ value, i.e. lower crystallization rate than any other PP50-EP50 binary blend and ternary blends. There are no significant changes in n values, relating to the dimensions of the crystals, among different blends.

X-ray diffraction. The effect of EPDM or ethylene-propylene rubber(EPR) on the crystal structure of PP has been intensively reported.[5,31,32] The incorporation of the elastomers alters the superstructure of PP matrix by changing the average size and number of the

spherulites, and this change in the superstructure is very important to interpret the function of impact modification of the elastomer with the PP matrix.[2] In order to investigate the effect of adding ionomer to PP50-EP50 binary blend on the crystalline structure, X-ray diffraction studies have been made in this work. It is also believed that the X-ray diffraction study is essential to find how the added ionomer improves the fracture toughness of PP/EPDM/ionomer ternary blends, which will be one of the important subjects in our further works. The X-ray diffraction of the PP50-EP50 binary blend shows four characteristic peaks due to the crystalline structure of PP(EPDM is amorphous and shows no crystalline structure), in the region of the Bragg angle(2θ) between $10°$ and $50°$ (Fig. 5 and 6). Those strong diffraction peaks are located at the 2θ angles $14°$, $17°$, $18.5°$, and $21.7°$ (a doublet). The first three peaks correspond to (110), (040), and (130) planes, respectively, and are characteristic peaks of typical α-form monoclinic structure.[33]

The effects of the added ionomer on the crystal structure of PP50-EP50 blend are shown in Fig. 5 and 6. The diffractograms in Figure 6 show that the incorporation of Zn-neutralized ionomer does not change significantly the crystal structure of the PP and ionomer mixtures. In Fig. 6, the diffraction maxima at $2\theta = 26.5°$
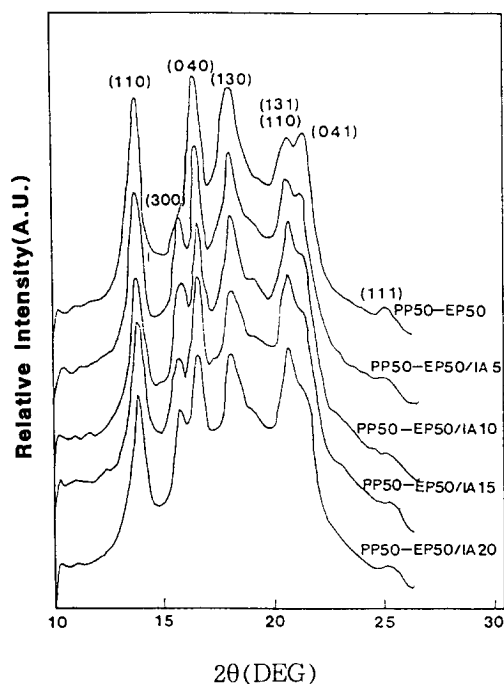
Fig. 5. X-ray diffractograms of PP50-EP50 binary and PP50-EP50/Na-neutralized ionomer(IA) blends; The ionomer contents are varied from 5 to 20wt.%.
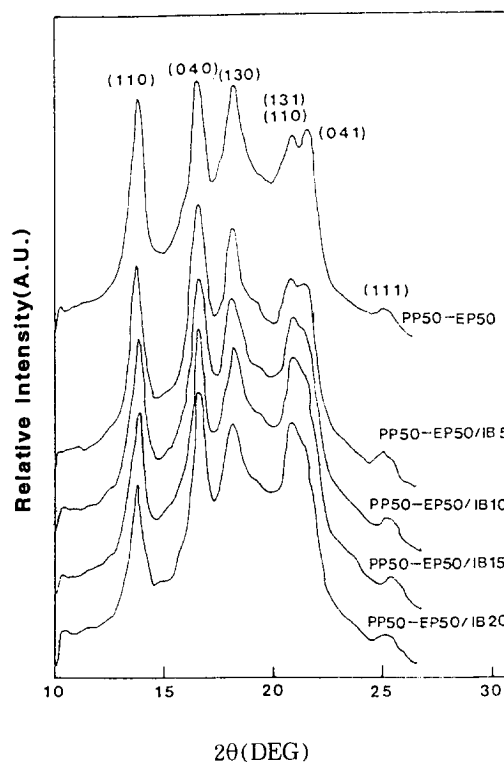

Fig. 6. X-ray diffractograms of PP50-EP50 binary and PP50-EP50/Na-neutralized ionomer(IB) blends; The ionomer contents are varied from 5 to 20wt.%.

correspond to the (111) reflections of the polyethylene pattern of the ionomer homopolymer.[34] At lower Bragg angles than 25° the X-ray diffraction data of the Na-neutralized ionomer and the Zn-neutralized ionomer used in the study are summarized in Table 4.

Of interest, however, is the phenomena for the Na-neutralized ionomer containing ternary blends that the incorporation of Na-neutralized ionomer affects the crystalline structure of PP considerably. In Fig. 5, as the ionomer is added to the PP50-EP50 binary blend, a new sharp peak, which is related to the (300) reflection of the β-form hexagonal phase of PP,[34,35] appears at 2θ=15.8°. This implies that incorporation of Na-neutralized ionomer gives rise to formation of a new crystalline structure associated with β-form of PP crystal. Karger-Kocsis et al.[2] found surch alteration in crystalline structure in

the PP/ethylene-propylene rubber (EPR) blend having 75/25 composition by weight. They explained the structural changes using partial compatibility effect between two components in the molten state due to the EPR selectively extracting the defective molecules in PP. The change in the crystalline structure of PP by the incorporation of EPDM was also reported in the PP/high density polyethylene(HDPE)/EPDM ternary blends having the compositions of 56/19/25 by wt.%.[9]

The relative proportions of α- and β-form, K, can be estimated by the following relationship;

$$K = \frac{H\beta_1}{H\beta_1 + (H\alpha_1 + H\alpha_2 + H\alpha_3)}$$

where $H\alpha$ and $H\beta$ refer to the height of diffrac-

Table 4. X-ray Diffraction Data of the Na- and Zn- neutralized Ionomers

Sample	Bragg angle(2θ)	Lattice spacing($\mathring{A}$)	Remark
Na-neutrali-zed ionomer	5.88°	15.01°	Amorphous peak
	18.01°	4.89°	″
	19.30°	4.59°	″
	21.10°	4.20°	(110)
	23.30°	3.81°	(200)
Na-neutrali-zed ionomer	6.10°	14.48°	Amorphous peak
	18.10°	4.90°	″
	19.50°	4.55°	″
	21.40°	4.15°	(110)
	23.60°	3.77°	(200)

tion peaks and the subscripts 1, 2, and 3 correspond to (110), (040), and (130) planes, respectively. Karger-Kocsis et al[2] and Ha and Kim[9] suggested that the K value should be zero if there was no change in crystalline structure of PP as a result of ionomer addition, since the PP has no β-form crystalline structure before blending. When the compatibilization is achieved by the presence of ionomer for the PP50-EP50 binary blend, however, the ternary blends containing ionomer have finite K values. No change in the crystalline structure of PP was observed in the case of PP50-EP50 binary blend in this study. When the Na-neutralized ionomer was added to the PP50-EP50 blend, however, the K value was maximized (25.2%) at 5wt.% of Na-neutralized ionomer. The proportion decreased in the order of magnitude, 24.5%, 18.3% and 15.4%, as Na-neutralized ionomer was added to the binary blend at 10, 15, and 20wt.%, respectively.

Therefore, the above results of X-ray diffraction indicate that there is a compatibilizing effect of Na-neutralized ionomer for the PP50-EP50 blend.

CONCLUSIONS

It was observed that the thermal behavior and crystalline structure of PP50-EP50 blend were not affected by adding Zn-neutralized ionomer. However, in the case of Na-neutralized ionomer, the effect was significant, especially maximum at 5wt.% of concentration.

The rheological behavior indicated that interpenetrating occured among the three components due to the role of the inherent ionic crosslinking property of the Na-neutralized ionomer. In the X-ray diffraction study of PP50-EP50 blends, a new crystalline structure related to the β-form of PP crystal was indicated and the effect was maximum at 5wt.% of Na-neutralized ionomer.

In conclusion, at the 5wt.% of ionomer concentration, the Na-neutralized ionomer acted as a compatibilizer for the PP50-EP50 blend. However, the Zn-neutralized ionomer showed no clear compatibilizing effect to the blend even at the same concentraion. When the ionomer contents were higher than 10wt%, any PP/EPDM/ionomer ternary blends did not exhibit compatibilizing effect and instead showed complex multiphasic character due to the inherent incompatibility among the three components, PP, EPDM, and ionomer.

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