

Rheological Properties and Crystalline Structure of the Dynamically Cured EPDM and PP / HDPE Ternary Blends

CHANG SIK HA, *Department of Polymer Science and Engineering, Pusan National University, Pusan 609-735, Korea*, and SUNG CHUL KIM, *Department of Chemical Engineering, Korea Advanced Institute of Science and Technology, Seoul 130-650, Korea*

Synopsis

The rheological properties and crystalline structure of the polyolefin ternary blends of EPDM/polypropylene/high density polyethylene were studied. Blends were prepared in a laboratory internal mixer by two different methods. In blend-cure process, blending and curing were performed simultaneously and EPDM was cured by dicumyl peroxide (DCP) in the presence of PP/HDPE under shear. The cure-blend was to cure EPDM alone first under shear (dynamic curing) and then mix the cured EPDM with PP and HDPE. The effect of DCP concentration, intensity of the shear mixing, and the rubber/plastic composition were studied using capillary rheometer and X-ray diffractometer. The PP-rich ternary blends showed the effect of the mechanooxidative degradation of PP by shear and peroxide. The melt viscosity increased with increasing DCP concentration in blends of EPDM-rich compositions. X-ray diffraction studies revealed that the inclusion of 25 wt % of linear EPDM in the PP/HDPE mixture for the PP-rich ternary blends changed the crystal structure of polypropylene component in the ternary blends. However, the dynamic curing did not alter the crystal structure of PP or HDPE in the blends.

INTRODUCTION

The blends of polypropylene, high density polyethylene, and ethylene-propylene-diene terpolymer (EPDM) have been intensively studied due to their commercial importance.¹⁻⁵ The blends were prepared sometimes in an intensive mixer, through a roll mill or an extruder by the "dynamic curing" method where EPDM was cured under shear with peroxide.

The dynamically cured blends, first described by Fischer,^{6,7} have been widely used in the plastics industry for years.^{8,9} The blends have important technical advantages in processing because of the thermoplastic nature of melt even though they contain a crosslinked elastomer as one component. It was found that such thermoplastic nature of the blends might be ascribed to the dynamic aspects of curing to prevent the formation of three-dimensional infinite network in elastomer phase.

Studies on the dynamically cured EPDM and polyolefin blends have been carried out by several authors.^{6,7,10,11} Recently we also published a paper on the structure and properties of the dynamically cured EPDM/PP blends and observed the rheological properties and crystallization characteristics of the blends.¹²

The objective of this research is to examine the rheological properties and crystalline structure of the dynamically cured EPDM and PP/HDPE ternary

TABLE I
Materials

Materials	Characteristics		Source
PP	MFI	6.0	PP4107 (Korea Petrochem.)
	M_w	2.201×10^5	
	M_n	2.829×10^4	
HDPE	MFI	0.8	E308 (Korea Petrochem.)
	M_w	1.002×10^5	
	M_n	1.310×10^4	
EPDM	η_{inh} (dL/g) ^a	1.22	Roy.521 (Uniroyal)
	IV ^b	15.2	
	PE/PP (by mol. %) ^c	52.0/48.0	
DCP	Granule type		Mitsui Chem.

^a0.5 g/dL xylene solution at 70°C.

^bBy ICl titration method.

^cBy IR analysis.

blends. The effect of rubber/plastic compositions, peroxide content, and shear conditions of the blends were studied using a capillary rheometer and X-ray diffractometer.

EXPERIMENTAL

Materials

The commercial grade polypropylene (PP), high density polyethylene (HDPE), and ethylene-propylene-diene terpolymer (EPDM) with ethylidene-2-norbornene (ENB) as a termonomer were used in the study (Table I).

Preparation of Blends

The binary blends of PP and HDPE were prepared in the Brabender Roller Mixer (Type w50H) at 190°C for 15 min at 60 rpm. The composition of the blend was varied from 25 to 75 wt %. The ternary blends of PP, HDPE, and EPDM were prepared by two different methods (Fig. 1), the blend-cure and cure-blend process. The EPDM-DCP mixture prepared by a Farrel Research Mill (3 × 7 in.) were simultaneously cured and blended with PP/HDPE preblends under shear in the blend-cure process. The EPDM-DCP mixture was cured alone under shear at 190°C for 15 min and blended with PP/HDPE preblends afterward in the cure-blend process. A detailed description of the two methods is given elsewhere.¹²

The samples prepared are listed in Table II and the sample notations are described therein.

Measurements

The rheological properties were measured with a capillary rheometer (Instron Model 3211) at 200°C. The length and the diameter of the capillary were 5.0851 and 0.1257 cm, respectively, and the L/D ratio of the capillary

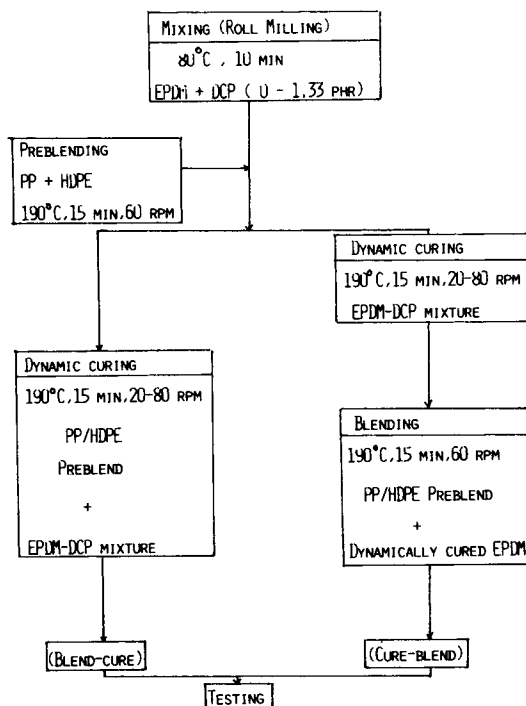


Fig. 1. Schematic diagram of the experimental procedure.

was about 40. X-ray diffraction patterns were obtained with the Rigaku Denki X-ray diffractometer using nickel filtered CuK_α radiation (30 kV, 20 mA).

RESULTS AND DISCUSSION

Rheological Properties

Figure 2 shows the melt viscosity change with shear stress at 200°C for the linear EPDM/PP/HDPE ternary blends. It is seen from these figures that the viscosity of the blends with equal amount of PP and HDPE component at a given EPDM concentration are the lowest. The viscosity difference is most distinct for the blends of 50 wt % of EPDM [see Fig. 2(b)].

The rheological behavior of the ternary blends may be attributed to the complex interactions between the components. The minimum viscosity observed in the blends with equal amount of PP and HDPE components may be ascribed to the phase separation between the components due to the inherent heterogeneity. It seems that HDPE-EPDM has slightly better compatibility than the PP-EPDM pair.

The rheological behavior of the dynamically cured ternary blends of the EPDM-rich compositions are shown in Figure 3. The mixer rotation speed was at 60 rpm. In the EPDM-rich blends the viscosity increases with increasing DCP concentration regardless of the relative composition of PP and HDPE due to the chemical crosslinking of EPDM during the curing process even under shear. These trends are similar to those of the dynamically cured

TABLE II
Sample Description

Samples Notation	Composition (wt %)			
	EPDM	PP + HDPE	PP/(PP + HDPE)	HDPE/(PP + HDPE)
PP75PE25	0	100	75	25
PP50PE50	0	100	50	50
PP25PE75	0	100	25	75
RL25P75 ^a	25	75	75	25
RL25S75	25	75	50	50
RL25E75	25	75	25	75
RB(C)25P75 ^b	25	75	75	25
RB(C)25S75	25	75	50	50
RB(C)25E75	25	75	25	75
RL50P50	50	50	75	25
RL50S50	50	50	50	50
RL50E50	50	50	25	75
RB(C)50P50	50	50	75	25
RB(C)50S50	50	50	50	50
RB(C)50E50	50	50	25	75
RL75P25	75	25	75	25
RL75S25	75	25	50	50
RL75E25	75	25	25	75
RB(C)75P25	75	25	75	25
RB(C)75S25	75	25	50	50
RB(C)75E25	75	25	25	75

^aP denotes PP-rich composition; S denotes same wt % of PP and HDPE compositions; E denotes HDPE-rich composition in the ternary blends.

^bRL means linear EPDM; RB(C) means blend-cure (RB) and cure-blend (RC).

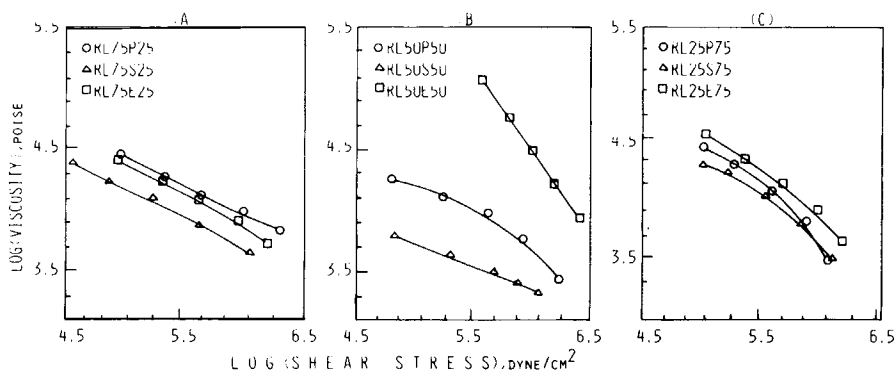


Fig. 2. The rheological characteristics of the EPDM/PP/HDPE ternary blends: (A) EPDM-rich composition [(O) RL75P25; (Δ) RL75S25; (\square) RL75E25]; (B) composition of 50 wt % EPDM [(O) RL50P50; (Δ) RL50S50; (\square) RL50E50]; (C) compositions of 25 wt % EPDM [(O) RL25P75; (Δ) RL25S75; (\square) RL25E75]. Mixer speed 60 rpm, 200°C.

EPDM-PP or EPDM-HDPE binary blends of the same compositions reported in our previous studies.^{11,12}

It is interesting to point out, however, that for RB75P25 blends the viscosity of the blends with higher DCP content changes rapidly with shear stress and crosses the viscosity curve of the linear blend [see Fig. 3(a)]. The

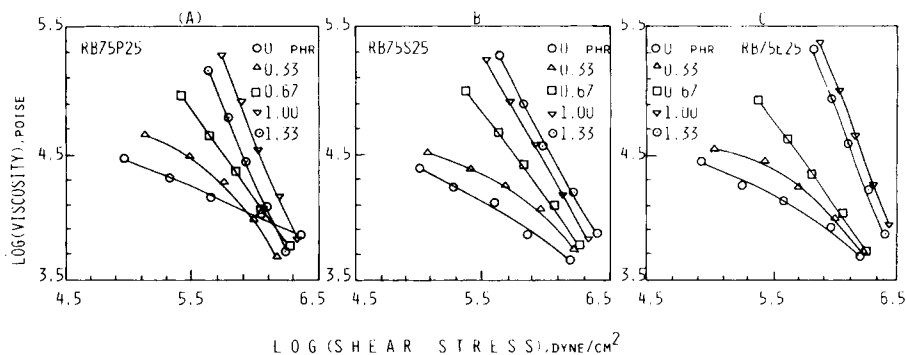


Fig. 3. The effect of DCP concentration on the viscosity of the dynamically cured ternary blends (blend-cure of the EPDM-rich composition: (A) RB75P25; (B) RB75S25; (C) RB75E25. Mixer speed 60 rpm, 200°C. phr: (○) 0; (△) 0.33; (□) 0.67; (▽) 1.00; (⊙) 1.33.

shear thinning effect becomes higher as the molecular weight and molecular weight distribution are increased in the EPDM component with crosslinking. In the ternary blends, the viscosity sometimes decreases with increasing DCP concentration above the concentration of 1.0 phr due to the combined effect of the peroxide-induced degradation of PP under shear and the chemical crosslinking of EPDM [see Figs. 3(a) and (c)].

The effect of the peroxide-induced mechanochemical degradation of polypropylene is clearly shown in the case of the PP-rich ternary blends of lower EPDM content (25 wt %). Figure 4(a) shows the plot of the melt viscosity of RB25P75 blends against shear stress with different DCP concentration. The marked reduction in viscosity with increasing DCP concentration is mainly to be ascribed to the influence of peroxide and shear on the mechanochemical degradation of PP. Similar results were already reported for the dynamically cured EPDM/PP binary blends in our previous paper.¹²

The viscosity behavior of RB25E75 blends is similar to that of the dynamically cured EPDM/HDPE binary blends of 25/75 composition, reported by Lee and Kim.¹¹ The viscosity drops initially at lower DCP concentration due to the incompatibility of the crosslinked EPDM and HDPE but increases at high DCP content due to the high viscosity of EPDM [Fig. 4(c)].

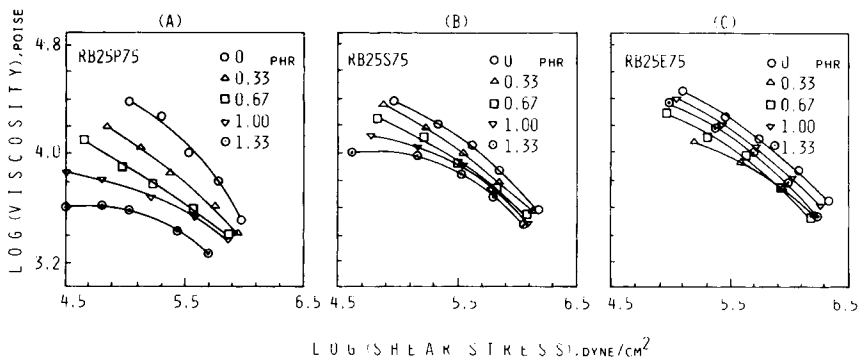


Fig. 4. The effect of DCP concentration on the viscosity of the dynamically cured ternary blends (blend-cure of the composition of 25 wt % EPDM: (A) RB25P75; (B) RB25S75; (C) RB25E75. Mixer speed 60 rpm, 200°C. phr: (○) 0; (△) 0.33; (□) 0.67; (▽) 1.00; (⊙) 1.33.

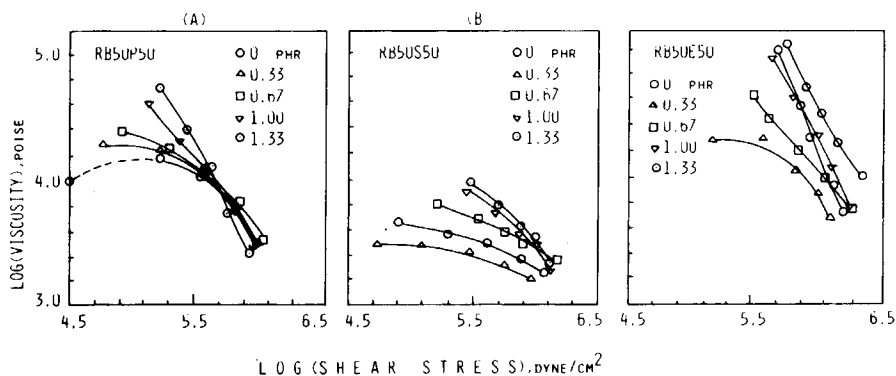


Fig. 5. The effect of DCP concentration on the viscosity of the dynamically cured ternary blends (blend-cure of the composition of 50 wt % EPDM: (A) RB50P50; (B) RB50S50; (C) RB50E50. Mixer speed 60 rpm, 200°C. phr: (○) 0; (△) 0.33; (□) 0.67; (▽) 1.00; (○) 1.33.

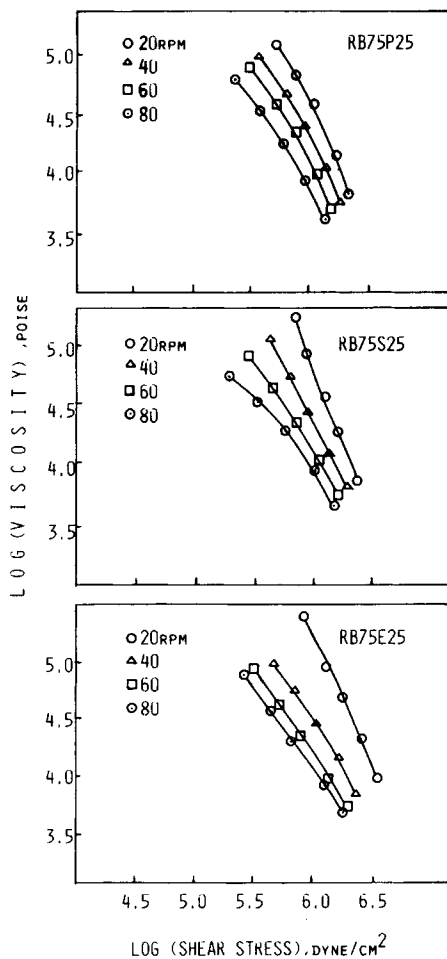


Fig. 6. The effect of shear intensity on the melt viscosity of the dynamically cured EPDM-rich ternary blends. DCP 0.67 phr, 200°C. rpm: (○) 20; (△) 40; (□) 60; (○) 80.

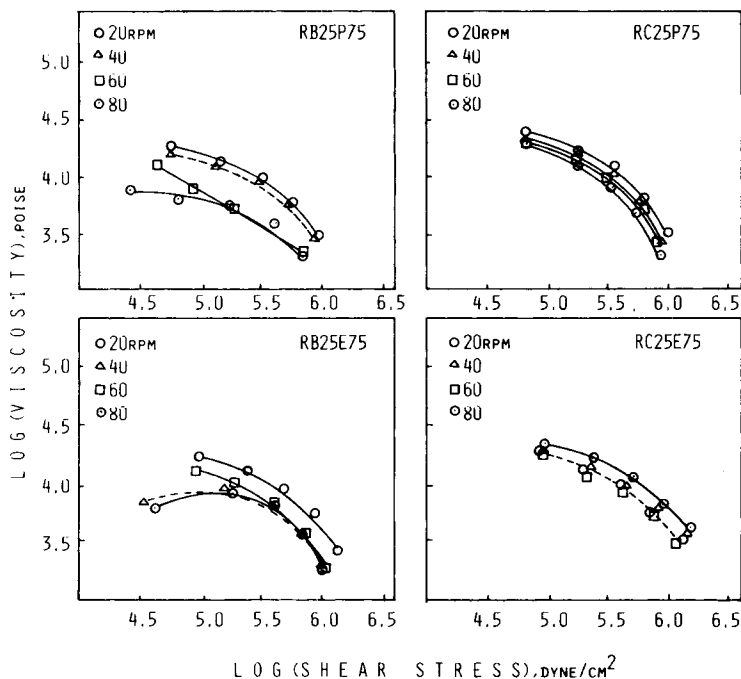


Fig. 7. The effect of shear intensity on the melt viscosity of the dynamically cured ternary blends. Comparison of the blend-cure and the cure-blend at two different compositions. DCP 0.67 phr, 200°C. rpm: (○) 20; (△) 40; (□) 60; (○) 80.

For RB25S75 blends, the viscosity behavior shows both the influence of the peroxide and the mutual interaction between components under shear. The general trend is similar to that of RB25P75 blend [Fig. 4(b)].

In the case of the ternary blends with EPDM composition of 50 wt % (Fig. 5), more complex rheological behavior was observed. For both RB50S50 and RB50E50 blends, at DCP content of 0.33 phr, the viscosity is lower than that of the linear blend of the same composition but increased with further increase of the DCP content. This behavior is very similar to that of the dynamically cured EPDM and HDPE binary blends of 25/75 composition where the initial reduction in melt viscosity is observed at lower DCP content due to the incompatibility between the slightly crosslinked EPDM and HDPE.¹¹

In contrast to the two figures, the RB50P50 blend shows increased shear thinning effect at high DCP concentration. This is similar to the dynamically cured EPDM and PP binary blends of the same composition in our previous study.¹²

The effect of the shear intensity on the rheological properties of the dynamically cured ternary blends is shown in Figures 6 and 7. For all the compositions, the concentration of DCP was fixed at 0.67 phr. The viscosity decreased with increasing shear intensity in the blends with EPDM-rich compositions in Figure 6, mainly due to the formation of the microgel domain of smaller size.

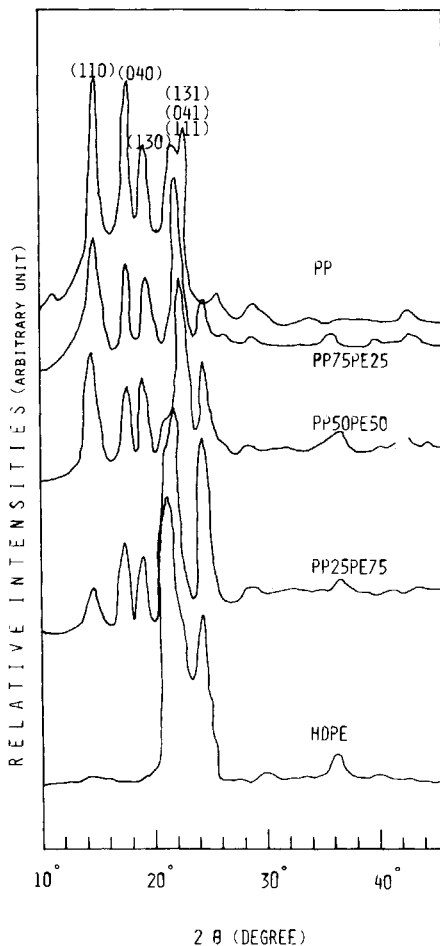


Fig. 8. X-ray diffractograms of PP/HDPE binary blends with different compositions.

It can be noted that the decrease of viscosity with shear intensity is more distinct when the blends are prepared by the blend-cure process than when prepared by the cure-blend process (see Fig. 7) and that the EPDM-rich blends show significantly lower viscosity as shear intensity is increased both for the blend-cure materials and for the cure-blend materials. These findings strongly suggest that the effect of the mechanochemical degradation of PP becomes predominant for the compositions of EPDM less than 50 wt % whereas at the EPDM-rich composition the formation of smaller microgels of EPDM is dominant.

X-Ray Diffraction

The X-ray diffraction of the PP homopolymer shows four sharp crystalline reflection peaks, in the region of the Bragg angle (2θ) between 10° and 50° (Fig. 8). Those strong diffraction peaks are located at the diffraction angles 2θ of 14.0° , 17.0° , 18.5° , and 21.7° (a doublet), of which the fore three peaks correspond to (110), (040), and (130) planes, respectively, and are characteristic of typical α -form monoclinic structure.¹³ The α -form of polypropylene has been extensively investigated.¹⁴⁻¹⁷

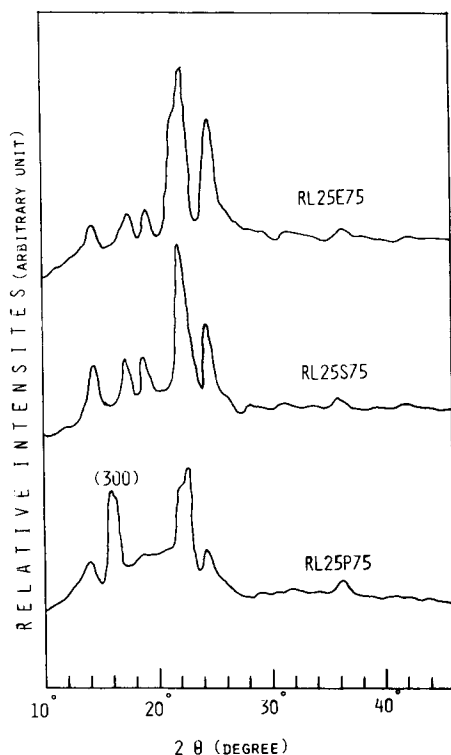


Fig. 9. X-ray diffractograms of EPDM/PP/HDPE linear ternary blends of 25 wt % EPDM composition.

The diffraction pattern of the HDPE homopolymer shows three diffraction maxima at 2θ values of 21.8° , 24.3° , and 36.5° , which correspond to (110), (200), and (020) planes, respectively, and is characteristic of a typical orthorhombic structure.¹⁸ The diffractogram of the binary PP and HDPE blend shows superpositions of each characteristic peak of the PP and HDPE homopolymer in Figure 8 with no additional peaks.

The effect of the EPDM on the crystal structure of PP and HDPE mixture is shown in Figure 9. For the RL25S75 and RL25E75 ternary blends, it is seen from the diffractograms that the incorporation of EPDM does not change significantly the crystal structure of the PP and HDPE mixtures, judging from the fact that several superposed intensity peaks of PP and HDPE crystals are observed in the same Bragg angles.

Of interest, however, is the phenomena for RL25P75 ternary blends that the incorporation of EPDM affects considerably the structure of PP crystals in the presence of HDPE in the ternary blends.

In the diffraction patterns of the composition, shown in Figure 9, the diffraction maxima of PP crystal at $2\theta = 17.0^\circ$ and 18.5° disappear and a new sharp peak at $2\theta = 16.0^\circ$ corresponding to the (300) reflection of the β -form hexagonal phase¹⁹ appears, whereas the maxima of HDPE crystal at $2\theta = 21.8^\circ$, 24.3° , and 36.5° remain unchanged even though the intensities of the peak decrease. This result means that the incorporation of EPDM leads to an essential change in the structure of PP from α -form to β -form. The change in the structure of PP by the incorporation of ethylene-propylene-rubber (EPR)

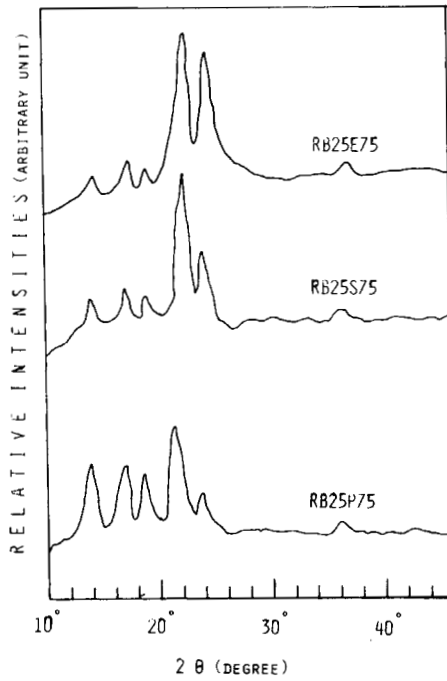


Fig. 10. X-ray diffractograms of the dynamically cured EPDM and PP/HDPE ternary blends (blend-cure of 25 wt % EPDM composition).

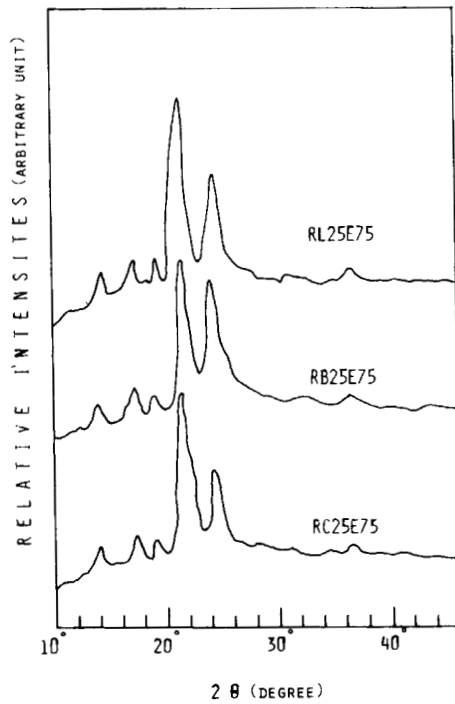


Fig. 11. X-ray diffractograms of the dynamically cured EPDM and PP/HDPE ternary blends for the HDPE-rich compositions with different preparation methods.

was also reported by Karger-Kocsis et. al.³ They reported that in the PP/EPR blends the proportion of the hexagonal phase of PP decreased with increasing concentration of EPR.

It seems that with inclusion of EPDM in the blend the EPDM extracts selectively the amorphous fractions of PP, which leads to alteration of the crystalline structure. The addition of the EPDM copolymer to the binary PP and HDPE blends have been also reported to change the fracture mechanism and the overall surface morphology in the literature.^{20,21}

The X-ray diffraction patterns of the dynamically cured ternary blends are given in Figure 10. Most of the figures show almost the same diffraction patterns at the same 2θ regardless of the composition or preparation route for the blend except that the intensities were slightly different.

It was found from these results that the processing conditions or preparation method of the dynamic curing did not alter the crystal structure of PP and HDPE in the ternary blends both for the PP-rich blends (Fig. 10) and the HDPE-rich blends (Fig. 11). From these X-ray diffraction patterns it was very difficult to determine the absolute degree of crystallinity and the unit cell constants because of the superposed diffraction patterns of the binary PP and HDPE crystals.

The authors wish to thank Prof. Jang Hyun Sung of Dong-A University for his help in the X-ray diffraction experiments and Mr. Young Sam Hur for his help in the preparation of blend samples.

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Received July 29, 1987

Accepted September 21, 1987