NOTE

전단력하에서 가교된 EPDM과 PP/HDPE 삼성분 블렌드의 결정화거동

하 창 식 · 조 원 제 · 김 성 철*

부산대학교 공과대학 고분자공학과 · *한국과학기술원 화학공학과

(1991년 7월 10일 접수)

Crystallization Behavior of Dynamically Cured EPDM and PP/HDPE Ternary Blends

Chang-Sik Ha, Won-Jei Cho, and Sung-Chul Kim*

Department of Polymer Science and Engineering, Pusan National University, Pusan 609-735, Korea

**Department of Chemical Engineering, Korea Advanced Institute of Science and Technology, 373-1,*

Ku-Seung Dong, Yu-Seung Ku, Dae Jeon 305-338, Korea

(Received July 10, 1991)

INTRODUCTION

Dynamic curing is a process of curing rubber under shear stress. Dynamically cured thermoplastic elastomer blends have been widely used in the plastics industry for years.[1~4] The blends have important technical advantages in processing because of the thermoplastic nature of melt even though they have crosslinked elastomer components. It was found that the thermoplasticity results from the dynamic aspect of curing to prevent the formation of three dimensional infinite network in elastomer phase. Well known example of the dynamically cured blends is the blends from ethylene-propylene-diene terpolymer(EPDM) and polyolefin.[1,2,5,6]

Recently, we reported some results concerning the structure and properties of dynamically cured EPDM/Polypropylene(PP)/High density polyethylene(HDPE) ternary blends.[6] In this work,[6] we reported the results from X-ray diffraction studies that the inclusion of small amount of EPDM in the PP-rich ternary PP/HDPE blends changed the crystal structure of PP component in the ternary blends but the preparation methods of dynamic curing did not affect on the crystal structure of PP or HDPE in the blends. We suggested also that more detailed research should be done on the effects of the EPDM/PP/HDPE composition and the preparation method of the dynamic curing to obtain a definitive conclusion about the crystallization behavior of the ternary blends.

In this brief article, therefore, we report more on the crystallization behavior of the dynamically cured EPDM and PP/HDPE ternary blends. The blends were prepared in a laboratory internal mixer by two different methods. In one method blending and curing were performed simultaneously(the blend-cure process.) In blend-cure process, EPDM was cured under shear in the presence of PP and HDPE with dicumyl peroxide (DCP). The other method was to cure EPDM alone first under shear and then mix the cured EPDM with PP/HDPE(The cure-blend process).

The effects of EPDM/PP/HDPE compositions and the preparation methods of the dynamic curing were investigated using Differential Scanning Calorimeter(DSC) and optical microscopy.

EXPERIMENTAL

Materials

The characteristics of the polymers used in this study are summarized in Table 1. The ethylene-propylene-diene terpolymer(EPDM) with ethylidene-2-norbornene(ENB) as a termonomer, polypropylene(PP) and high density polyethylene (HDPE ; PE) were all commercially avialable grades. Dicumyl peroxide(DCP) was used as curing agent.

Preparation of Blends

The binary blends of PP and PE were prepared in the Brabender Roller Mixer(Type w50H) at 190 ℃ 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 and peroxide were

preblended in a 3″×7″ Research Mill(Farrel Co.) at roll temperature of 80℃ for 10 min. DCP contents was fixed at 0.67phr based on the amount of EPDM. The roll-milled strands were blended with PP and PE at a given composition of 25 wt.% in the mixer. The PP(or PE) composition in the PP /PE mixture varied also from 25 to 75 wt.%.

The EPDM-DCP mixture was simultaneously cured and blended with PP and PE under shear in the blend-cure process. The EPDM-DCP mixture was cured alone under shear at 190℃ for 15 min and blended with PP and PE afterward in the cure-blend process. A detailed description of the two methods is given elsewhere.[6] The samples prepared are listed in Table 2 and the sample notations are described therein.

Measurements

The crystallization behavior of the ternary blends was analyzed under nitrogen by following the dynamic differential scanning calorimetry (DSC) using a DuPont 910 DSC and a DuPont 990

Table 1. Characteristics of the Materials Used in the Prparation of the Blends

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

[a] 0.5 g/dL xylene solution at 70℃
[b] by ICl titration method.
[c] by IR method.
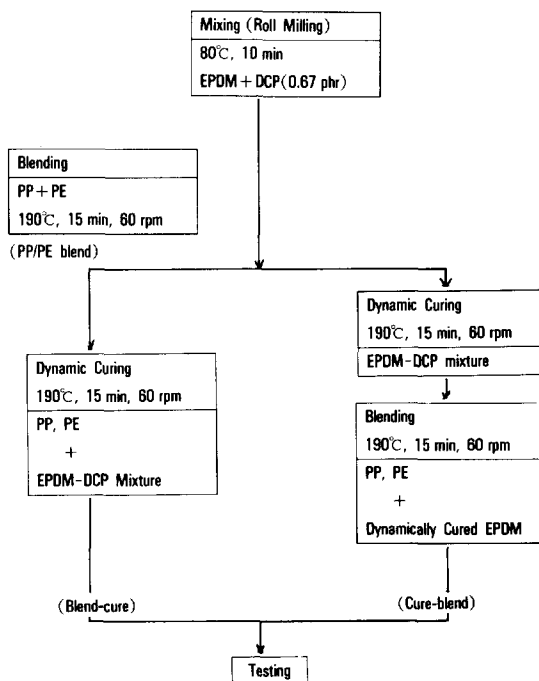
Fig. 1. Schematic diagram of the experimental procedure

Table 2. Blended Sample Description

Sample Notation	Composition(wt.%)			
	EPDM	PP+PE	PP/ (PP+PE)	PE/ (PP+PE)
PP75PE25	0	100	75	25
PP50PE50			50	50
PP25PE75			25	75
RL25P75*	25	75	75	25
RL25S75			50	50
RL25E75			25	75
RB(C)25P75**			75	25
RB(C)25S25			50	50
RB(C)25E75			25	75

* P denotes PP-rich blends ; S denotes same wt.% of PP and PE compositions in the ternary blends ; E denotes PE-rich blends.

** RL means linear EPDM ; RB(C) means Blend-cure(RB) and Cure-blend(RC).

Thermal Analyzer ; the samples of about 10 mg were heated to 180℃ and kept at this temperature for 10 min. for complete melting of crystals. Then the samples were cooled to the room temperature with six different scan rates of 3.6, 5.0, 7.6, 10.0, 15.32 and 20.0℃/min.

Microscopic observations were made with American Optics Polarizing Microscope(POL II) (equipped with a heating stage(Mettler FP-2).

RESULTS AND DISCUSSION

A number of researches have been reported on the crystallization of the PP and PE binary blends.[7~10] The binary blends show different crystallization behavior depending on the composition. In this study, the peak temperature(T_p) of the maximum rate of crystal growth was observed to be 125 ℃ for PP homopolymer and 116℃ for HDPE homopolymer at the cooling rate of 3.6℃/min.

When the scan rate is faster than 10℃/min, the DSC exothermic curve shows a single peak for all the blends regardless of the composition, whereas
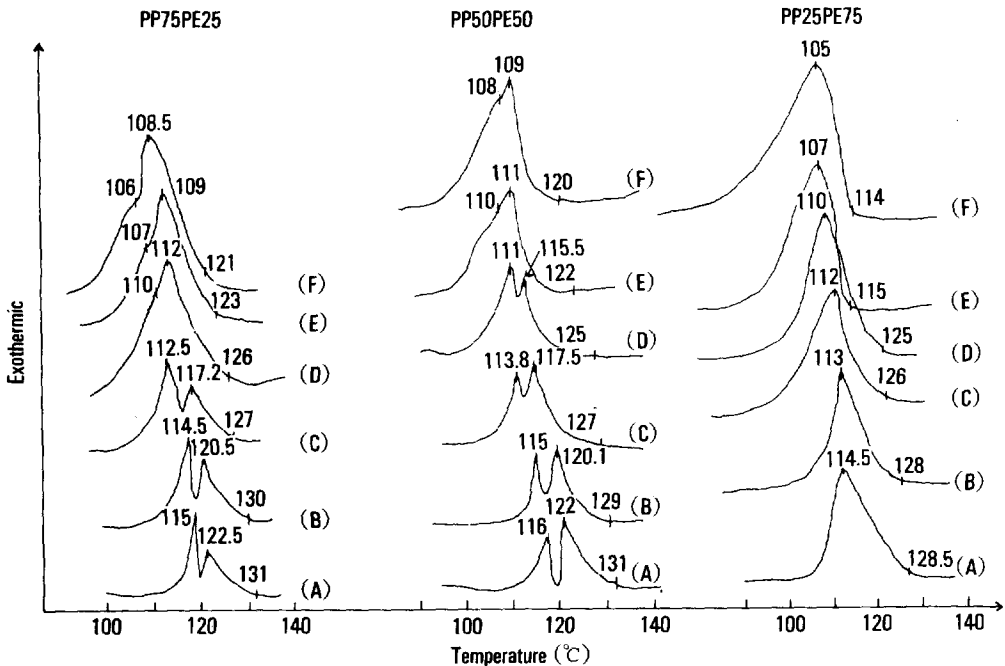
Fig. 2. DSC scans of the crystallization of PP and PE binary blends with different compositions at six different scan rates ; (A) 3.6, (B) 5.0, (C) 7.6, (D) 10.0, (E) 15.32, and (F) 20.0℃/min.

when the scan rate is slower the DSC scan shows two separate exothermic peaks for PP75PE25 and PP50PE50 blends(Figure 2). It is shown in the figure that the peak temperature of PP phase in the blend shows distinct depression compared to PP homopolymer but the peak temperature of the PE phase shows no significant depression in the blends. This result may be attributed to the fact that the polyethylene domain separated from the PP phase in the molten state, plays a defective role to the crystallization of PP. When 25 wt.% of EPDM is included in the PP and PE mixture, the crystallization behavior becomes quite different depending on the composition of PP.

Figure 3 shows the crystallization curve at the scan rate of 3.6℃/min for the RL25P75 ternary blend and the peak temperatures of PE and PP shift to lower temperatures compared to those of the PP and PE binary blends.

This means that both PE and EPDM play defective roles to the crystallization of PP because of their high melt viscosities to restrain the diffusive motion of the PP molecules. However, for the PE-rich ternary blend(RL25E75) the peak temperature was not depressed. This suggests that the in-

clusion of EPDM does not affect significantly the crystallization of the PE-rich blends. It should be noted, however, that the relative intensity of the crystallization exotherm of PP is larger than that of PE in the PP-rich ternary blend whereas the relative intensity of the crytallization exotherm of PP is smaller than that of PE in the PP/PE binary blend of 75/25 composition. Considering that the inclusion of EPDM accelerates the crystallization of PP in PP/EPDM binary blend which was reported previously by the authors,[5] these results may be probably also caused by the accelerating effects of crystallization rate of PP by EPDM even in the presence of PE for the ternary blends.

In Fig. 4, optical micrographs show the phase separation of ternary blends, at a crystallization temperature 128℃, which is high enough to prevent any PE crystallization. The PE and EPDM

(a)

(b)

Fig. 4. Optical micrographs of (a) RL25P75 and (b) RL25E75 blends, taken at 128℃, × 360.
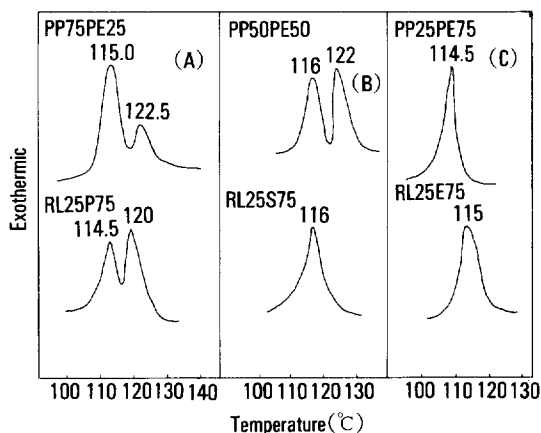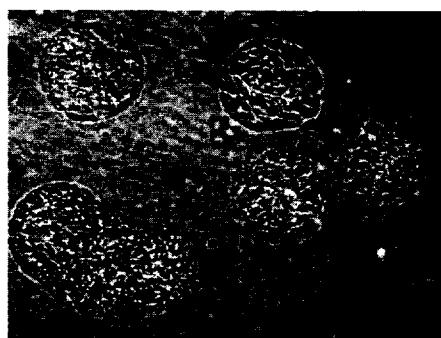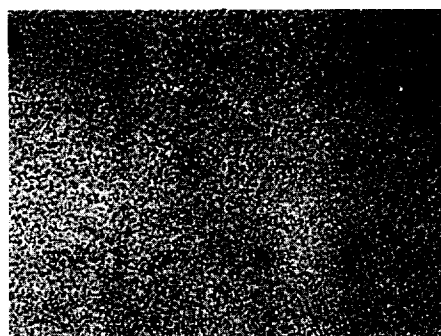

Fig. 3. The effect of EPDM inclusion on the crystallization temperature for EPDM/PP/PE linear ternary blends : (A) PP-rich blend (B) same wt.% of PP and PE-blend and (C) PE-rich blend (DSC scan rate : 3.6 ℃/min.)
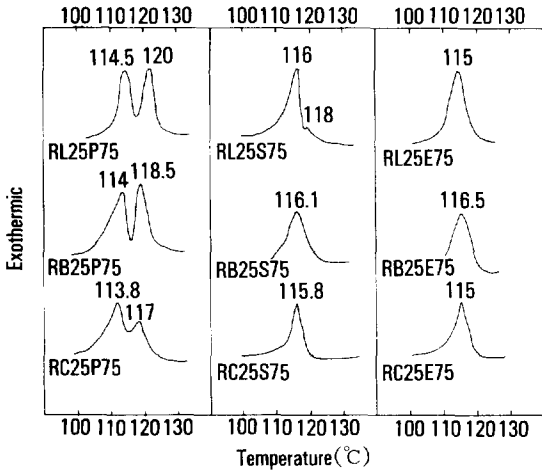
Fig. 5. The effect of EPDM on the crystallization temperature for the dynamically cured blends(scan rate : 3.6℃/min.)

domain is distributed in the amorphous PP at the crystallization temperature for the PP-rich blends (a) while the phase morphology for PE-rich blend is not well defined(b). This may be related to the different compatibilities or segmental solubilities of the EPDM with PP or PE. It may be regarded that the EPDM at the interface of PE and PP plays different roles to determine the final morphology and crystallization behavior of the blend depending on the different compatibilities with PE and PP.[11] But more detailed works should be carried out to interpret the results accurately.

Figure 5 shows the comparison of the crystallization behavior of the ternary blends among linear, blend-cure and cure-blend samples at the scan rate of 3.6 ℃/min. Comparison of the figures shows that the peak temperatures of the blend-cure shift to lower temperature slightly compared to the linear ternary blend in case of PP-rich blend. The peak temperature of the cure-blend sample was shown to be the lowest among the three cases. This result may be attributed to the high viscosity of medium to restrain the diffusive motion of polymer chains. The crystallization of PP is restricted as the degree of crosslinking of EPDM increases in the order of linear, blend-cure and cure-blend

materials.

One can see also that the relative intensity of the crystallization exotherm of PP is larger than that of PE in the PP-rich RL25P75 and RB25P75 ternary blends whereas the relative intensity of the crytallization exotherm of PP is smaller than that of PE in RC25P75 ternary blend, as in the PP/PE binary blend of 75/25 composition(see also Fig. 3). These results mean that the chemically crosslinked EPDM restricts the crystallization of PP and the restricting effect is most clearly seen in case of RC25P75 ternary cure-blend. Comparison of the results of Figures 3 and 5 may prove our speculations that the crystallization of PP is strongly affected by the factor whether EPDM can accelerate the crystallization of PP or not, even in the presence of PE for those EPDM/PP/PE ternary blends.

For PE-rich blends, however, the inclusion of crosslinked EPDM with different preparative route does not affect significantly on the crystallization of the ternary blends when compared to the PP-rich ternary blends.

Even though further studies are required, it has been shown that the crystallization behavior of the ternary blends by DSC studies is in accordance with the result from X-ray diffraction studies reported previously.[6] More precise studies on the crystallization kinetics of the ternary blends are underway and will be reported elsewhere.

REFERENCES

1. W. K. Fischer, U. S. Patent, 3,758,643 (1973).
2. W. K. Fischer, U. S. Patent, 3,862,106 (1975).
3. G. E. O'Conner and M. A. Faith, *Rubber World, Dec.,* 25 (1981).
4. A. Y. Coran and R. Patel, *Rubber Chem. and Technol.,* **56,** 210 (1983).
5. C. S. Ha, D. J. Ihm, and S. C. Kim, *J. of Appl. Polym. Sci.,* **32,** 6281 (1986).
6. C. S. Ha and S. C. Kim, *J. of Appl. Polym. Sci.,* **37,** 317 (1989).
7. M. Paracella, M. Avelda, P. Cresco, and G. Rago-

sta, *Makromol. Chem.*, **181,** 57 (1980).

8. J. Grebowicz and T. Pakula, "Crystallization and Melting of Components in Blends of Polyethylene and Polypropylene", in E. Martuscelli, R. Palumbo and M. Kryszewski, eds. "Polymer Blends-Processing Morphology and Properties", Plenum, New York, 1979.

9. A. J. Lovinger and M. L. Williams, *J. Appl. Polym. Sci.,* **25,** 1703 (1980).

10. O. F. Noel III and J. F. Carley, *Polym. Eng. Sci.,* **24,** 7, 488 (1984).

11. W. J. Ho and R. Salovey, *Polym. Eng. Sci.,* **21,** 9, 839 (1981).