전단력 하에서 가교된 EPDM과 PP블렌드의
결정 구조 및 몰폴로지

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Crystalline Structure and Morphology
of Dynamically Cured EPDM and PP Blends

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요 약 : 전단력 하에서 가교된 EPDM과 PP 블렌드의 결정구조와 morphology를 연구하였다. EPDM을 가교시키기 위하여 dicumyl peroxide(DCP)를 사용하였고 EPDM과 PP를 동시에 mixer에 혼입한 뒤 shearing force가 가해지는 조건하에서 가교반응과 blending 이 동시에 일어나도록 하는 blend-cure process와 EPDM-DCP mixture를 먼저 curing시키고 전단력 하에서 가교된 EPDM을 2단계로 PP와 혼합시키는 cure-blend process 두가지 방법을 사용하여 시료를 제조하였다. X-선 회절분석에 의해 EPDM은 PP의 결정도를 상승시키나 결정구조는 변화시키지 않고 dynamic curing의 제조방법 역시 PP의 결정구조에는 아무런 영향을 끼치지 않음을 알 수 있었다. EB75 PP25 blend-cure 시료의 경우 SEM 관찰에 의해 EPDM이 microgel 구조를 이루고 있음을 알 수 있었다.

Abstract : Crystalline structure and morphology of the dynamically cured ethylene-propylene-diene terpolymer(EPDM) and polypropylene(PP) blends were investigated. Blends were prepared in a laboratory internal mixer where EPDM was cured with PP under shear by dicumyl peroxide (DCP) (Blend-cure). Blends were also prepared for comparison from EPDM which was dynamically cured without PP and blended later (Cure-blend). The crystalline structrue and morphology were studied by X-ray diffraction, optical microscopy and scanning electron microscopy (SEM). The incorporation of EPDM or dynamic curing process did not alter the crystalline structure of PP used in the study. The microgels of EPDM of about 0.8~1.0 m in size were observed in the dynamically cured EPDM and PP blends of 75 / 25 composition.

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INTRODUCTION

The term thermoplastic vulcanizate (TPV) was adopted to describe a new class of materials which contain a vulcanized rubber phase and a hard thermoplastic phase.[1] These TPV's are based on the initial concepts of Gessler[2] and Fischer[3~5] to produce thermoplastic elastomer which contains fully crosslinked rubber and thermoplastic resin. Fischer reported in his patent of 1973[3] that the blends of partially cured ethylene-propylene-diene terpolymer (EPDM) (or ethylene-propylene rubber (EPR)) and polypropylene (PP) could be applied as good thermoplastic elastomers. In his next patents,[4,5] Fischer used the term "dynamic curing" to describe the preparation route to simultaneously blend and masticate under shear the mixture of PP and EPDM (or EPR) with peroxide in Banbury mixer.

The technology of the dynamic curing is based on the principle of in-situ vulcanization of conventional thermoset rubbers under shear during mixing. The dynamic curing process generates fully cured rubber particles (or microgels) dispersed in a continuous thermoplastic matrix, since the shearing process probably prevents the formation of the three dimensional crosslinked network. This peculiar morphological feature composed of a partly gelled elastomer and a semicrystalline thermoplastic results a final blend which is thermoplastic even though it has a crosslinked rubber as one component.

Table 1. Materials and Their Characteristics.

Materials	Characteristics		Source
PP	MFI	6.0	PP 4017
	$\overline{M}_w$	2.021×10^5	(Korea
	$\overline{M}_n$	2.829×10^4	Petrochem.)
EPDM	$_{inh}$(dl / g)*	1.22	Roy. 521
	I.V.**	15.2	(Uniroyal)
	PE / PP(mol%)	52.0 / 48.0***	
DCP	Granule type		Mitsui Chem.

*0.5g / dl xylene solution at 70℃
**by ICI titration method
***by IR analysis

Studies on the dynamically cured EPDM and polyolefin blends have been carried out by several authors for years.[6~11] Lee and Kim[11] reported on the properties of the dynamically cured EPDM and high density polyethylene (HDPE) blends. They found that the dynamically cured EPDM and HDPE blend had better processability and mechanical properties than those of the linear EPDM / HDPE blend, whereas the press-cured samples, prepared by the conventional compression molding, could not be reprocessed because of their three dimensional network structure.

Recently the rheological properties and crystallization characteristics of the dynamically cured EPDM / PP blends were reported in our previous paper.[12] In the present article, the crystalline structure and morphology of the blends will be reported.

EXPERIMENTAL

The polymers used in this study are listed in Table 1. The polypropylene (PP) and the ethylene-propylene-diene terpolymer (EPDM) with ethylidene norbornene(ENB) as a termonomer were all commercially available grades. The polymers were cured with dicumyl peroxide (DCP).

The EPDM and peroxide were preblended in a 3″ × 7″ research mill (Farrel Co.) at roll temperature of 80℃ for 10 min. DCP contents were fixed 0.67 phr based on the amount of EPDM. The blends of EPDM with polypropylene containing 25, 50 and 75% EPDM by weight were prepared by using the Brabender Roller Mixer (Type w50H) in two different preparative methods. The mixer consists of two removable blades and the sample size in the mixing chamber is approximatedly 60cc (40g / batch).

One method was to blend and cure simultaneously (the blend-cure process). The polypropylene was blended with the EPDM-DCP mixture in the molten state at 190℃ for 15min. The EPDM was dynamically cured under shear in the presence of PP with mixer rpm of 60. Previous analysis of the curing kinetics of EPDM by the dynamic

DSC method[13] established that under such processing conditions the curing reaction was completed.

The other method was to dynamically cure EPDM alone first and then mix the cured EPDM with PP (the cure-blend process). In this process, the EPDM was cured under a constant mixer rpm of 60, as before, without PP at 190℃ for 15 min., followed by blending with PP at the same temperature for 15min. at the same shear condition. Fig. 1 shows the schematic diagram of the experimental procedure. The blend samples prepared and the sample notations are listed in Table 2.

X-ray diffraction patterns of the samples were obtained using a Rigaku Denki X-ray diffractometer with Nickel-filtered CuK radiation at 30kV and 20mA.

Optical observations were made with the American Optics Polarizing Microscope equipped with a heating stage (Mettler FP-2).

Scanning electron microscopy (SEM) was carried out by JEOL JSM-35CF. Samples were cryogenically fractured in liquid nitrogen, followed by gold coating prior to their installation in the SEM chamber. When necessary, in order to determine the state of dispersion and phase continuity, a selective dissolution of a dispersed phase was also attempted.

In this case, the cryogenically fractured samples were etched with n-heptane at room temperature for 2hours to extract EPDM for the linear EPDM /PP blends or with xylene vapor at 130℃ for 30 seconds to extract polypropylene for the dynamically cured EPDM and PP blends. The etched samples were dried under vacuum at 100℃ for 12hours before metallizing with gold.

RESULTS AND DISCUSSION

Crystal Superstructure and X-ray Diffraction

The effects of the EPDM on the crystallinity and crystallization of PP have been recently reported in the literature.[14~18] Incorporation of the elastomer alters the superstructure of PP matrix by changing the average size and number of the spherulites. The chemical structure and molecular weight of the elastomer as well as the crystallization temperature and blend composition are the major factors influencing the morphology.

The crystal superstructure of the EPDM / PP blends has been studied intensively by Martuscelli, et al.[17,18] They observed birefringent spherulitic structures with large interspherulitic amorphous regions in the optical micrographs of the blends. Similar behavior was also observed by the authors
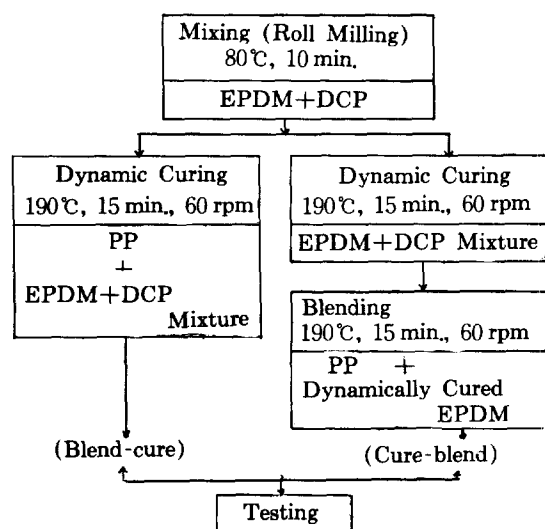
Fig.1. Schematic diagram of experimental procedure.

Table 2. Sample Description.

Sample notation	Composition	
	EPDM	PP
EPDM100	100	0
PP100	0	100
EL75PP25*	75	25
EL50PP50	50	50
EL25PP75	25	75
EB75PP25**	75	25
EB50PP50	50	50
EB25PP75	25	75
EC75PP25***	75	25
EC50PP50	50	50
EC25PP75	25	75

*EL denotes linear EPDM / PP blend
**EB denotes EPDM / PP Blend-cure
***EC denotes EPDM / PP Cure-blend.

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in the case of EPDM / PP blends studied in this experiment.

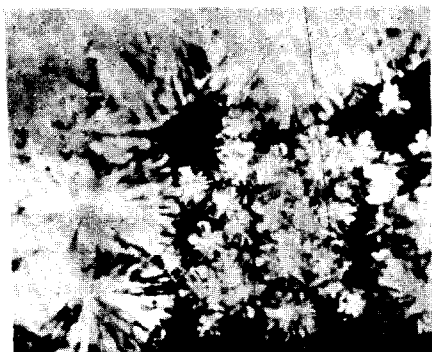Figure 2 shows the typical PP spherulites. As shown in Figure 3, the size of PP spherulites

Fig. 2. Spherulite grown at 131 ℃ in polypropylene, crossed polarizers, ×360.
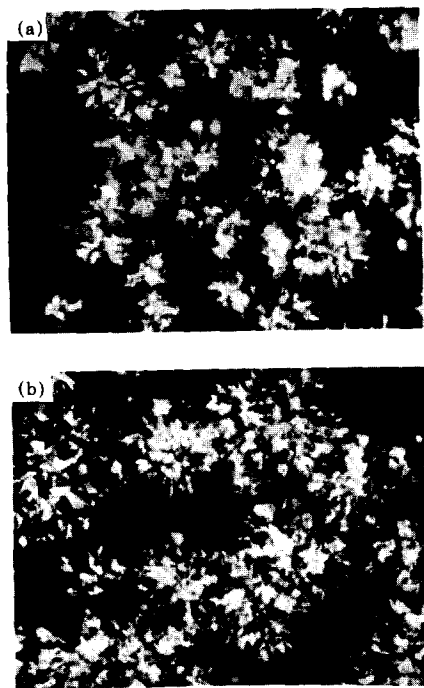

Fig. 3. Spherulite grown at 131 ℃ in (a) EL25PP75 linear blend and (b) EB25PP75 blend-cure, crossed polarizers, ×360.

was decreased by the addition of EPDM for EL 25PP75 linear blend. Similar results were reported by Karger-Kocsis, et al.[14] They reported that the average spherulite size of the sample containing 25wt. % of EPDM elastomer is about 1/3 of the original PP with a 67% reduction. For the dynamically cured blends, the size of the PP spherulite became smaller than those of the linear EPDM / PP blend.

Figure 4 shows the X-ray diffraction scans of PP homopolymer and EPDM / PP blends. The analysis of the relative intensities of the X-ray scattering from all the samples are based on the diffraction pattern of PP homopolymer. For the PP homopolymer, shown in Figure 4, five sharp crystalline reflection peaks, in the region of the Bragg angle (2θ) between 10° and 50° are observed. Those strong diffraction peaks are located at the diffraction angles 2θ of 14.0°, 17.0°, 18.5°, 21.7° and 23.2°. They have been labeled with the indices (110), (040), (130), (131) and (041) respectively.[19] From this diffractogram the PP sample used in this study has the α form or monoclinic structure.[20,21]

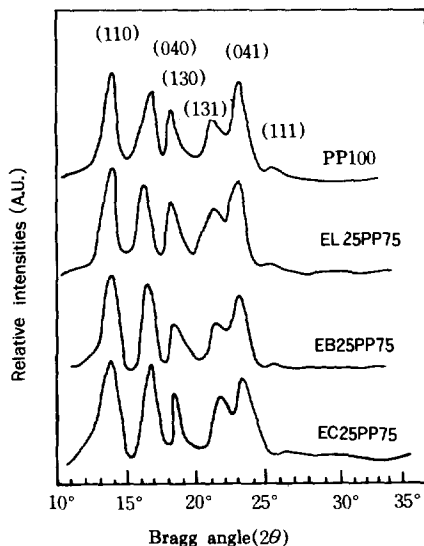Four types of spherulites were observed to grow

Fig. 4. X-ray diffractogram of PP homopolymer and EPDM / PP blends.

from the melt in isotactic polypropylene by Padden and Keith.[22] They explained that type I spherulites exhibited positive birefringence in the radial direction and a simple Maltese cross with a coarse branching radial structure due to the preferred crystalline orientation in the amorphous areas brought about by radial contraction during crystallization at high degree of supercooling. They further reported by X-ray diffraction studies of PP[23] that the most commonly occuring types of spherulites (type I and type II) could be identified as the monoclinic structure whereas type III and type IV spherulites to exhibit negative birefringence were categorized in the second metastable β-crystalline forms. The PP used in this study is categorized in type I spherulite.

The effect of EPDM on the crystal structure of PP is shown in Figure 4. It is seen from the X-ray diffractogram that the incorporation of EPDM did not change significantly the crystal structure of the PP, judging from the fact that the five intensive peaks of PP crystals are observed at the same Bragg angles.

Karger-Kocsis et al.[14] also reported the effect of Ethylene-Propylene Rubber (EPR) on the crystal structure of PP by X-ray diffraction. In contrast to our results, however, the incorporation of EPR leads to an essential changes in the structure of PP from the -form monoclinic crystals to -form hexagonal crystals. The difference may be in part due to the different interactions of EPR and EPDM with PP because of their different chemical structure.

Table 3 shows the characteristic lattice spacing of the PP and EPDM / PP blends. Judging from the relative intensities alone, the degree of crystallinity of the PP phase in the EPDM / PP linear and dynamically cured blends are found to be slightly higher than that of PP homopolymer since the relative intensities at all characteristic peaks of the linear blend are higher than those of PP homopolymer.

This is in accordance with our previous result obtained using differential scanning calorimetry (DSC).[12] It was reported that such result was attributed to the higher rate of crystallization of blend than that of PP homopolymer because of the role of EPDM to selectively extract the defective molecules within PP crystals and increase the mobility of neighboring PP chains by the reduction of glass transition temperatu-re.[12,17] Martuscelli, et al.[17] explained the result by assuming that during blending EPDM were able to dissolve a certain amount of PP molecules having, along the chain, an average higher concentration of chemical defects (steric defects), and molecules with lower molecular mass because the two components are likely to have a certain degree of compatibility in the melt due to their similar structure of the molecules.

Table 3 also shows for comparison the wt.% of crystallinity of PP phase in the blends calculated

Table 3. The Lattice Spacing(d_{hkl}) and Relative Intensities(I_{rel}) of the PP and PP / EPDM Blends.

Sample	Brage angle(2θ)												Weight % crystallinity*
	14.0°		17.0°		18.5°		21.7°		23.2°		25.8°		
	d_{hkl}	I_{rel}	d_{hkl}	I_{rel}	d_{hkl}	I_{rel}	d_{hkl}	I_{rel}	d_{hkl}	I_{rel}	d_{hkl}	I_{rel}	
PP100	6.34	1	5.31	0.71	4.84	0.56	4.12	0.62	3.71	0.17	3.53	0.16	31.1
EL25PP75	6.39	1	5.32	0.94	4.84	0.80	4.13	0.93	3.67	0.21	3.52	0.22	36.0
EB25PP75	6.28	1	5.24	0.94	4.78	0.79	4.09	0.94	3.49	0.22	3.10	0.21	33.8
EC25PP75	6.25	1	5.22	0.95	4.81	0.81	4.11	0.95	3.50	0.23	3.12	0.22	35.7
Miller index	(110)		(040)		(130)		(131)		(041)		(111)		

* The data are taken from Ha, et al, *J. Appl. Polym. Sci.,* **32** 6281 (1986).

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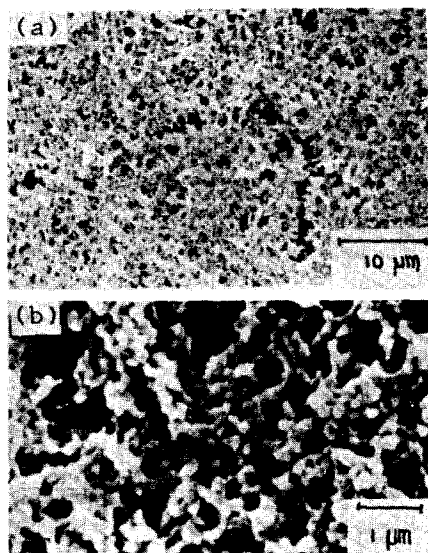Fig. 5. SEM micrographs of PP / EPDM linear blend. (a) EL25PP75 (b) EL50PP50 (c) EL75PP25

Fig. 6. SEM micrographs of EL25PP75 linear blend after etchin with n-heptane for 2 hours.
a) Low magnification (× 2600)
b) high magnification (× 10000)

Fig. 7. SEM micrograph of EB75PP25 blend-cure with DCP concentration of 0.67 phr. (Mixer speed-60 rpm) after etching with hot xylene vapor, high magnification (× 10000)

from the apparent enthalpy of fusion per gram of PP in the blend at the isothermal crystallization temperature of 117℃ on the DSC thermogram. It was found from this study that the processing conditions or preparation method of the dynamic curing did not alter the crystal structure of PP (see Figure 4).

Morphology

The SEM micrographs of the fractured surfaces of EPDM / PP linear blends of three compositions are shown in Figure 5. The SEM micrograph of the fractured surfaces of EL25PP75 blend shows

the presence of hollow spheres representing the removed particles during fracture. The domain size ranged about 0.8~2.0 m in diameter and the domains were regularly distributed throughout the speciman. It can be observed that the adhesion between the dispersed phase and matrix was low.

The phase inversion occurred in EL75PP25 blend and the PP particles are distributed in the EPDM matrix.

Figure 6 shows the SEM micrographs of EL25PP75 linear blend after etching with n-heptane for 2 hours. The higher magnification SEM micrograph shows that the two phases are cocontinuous. The white portions of the micrographs are PP phase and the extracted dark voids are EPDM phase of 0.5~2.0 m in size. PP is clearly a continuous phase resembling an open-cell sponge with micron-sized porosity. Karger-Kocsis et al.[24] explained that the co-continuous network structure might

be formed since the EPDM viscosity is high during the blending process.

Figure 7 shows the SEM micrograph of the fractured EB75PP25 blend-cure sample after etching by hot xylene vapor for 30 seconds. It shows the presence of the EPDM microgel which is very important to impart the processability of the dynamically cured EPDM and PP blend.

It is seen that the microdomains of EPDM have the shape of dumbbell-like microgel of about 0.8~1.0 m in size, where the dark portion represent the PP phase extracted by the hot xylene vapor. Having seen the morphology of the microgel domain of EPDM, one may understand the reason why the dynamically cured blend can be processed and the dynamic aspects prevent the crosslinking of EPDM phase to form three dimensional infinite network.

It should be mentioned that the domain size of EPDM phase is smaller when the blend was prepared by the blend-cure process than when prepared by the cure-blend process, However, in our morphological studies this effect was not clearly shown.

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