Structure and Properties of Dynamically Cured EPDM / PP Blends

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Synopsis

The structure and properties of polyolefin blends of ethylene-propylene-diene terpolymer (EPDM) and polypropylene were studied. Blends were prepared in a laboratory internal mixer where EPDM was cured with PP under shear with dicumyl peroxide (DCP) at different shear conditions (blend-cure). Blends were also prepared for comparison from EPDM which were dynamically cured in the absence of PP and blended later (cure-blend). The effect of DCP concentration, intensity of the shear mixing, and rubber/plastic composition were studied. In blend-cure, the melt viscosity increased with increasing DCP concentration in blends of 75% EPDM and 25% PP, but it decreased with increasing DCP concentration in blends of 75% PP and 25% EPDM. In cure-blend, however, the melt viscosity increased with increasing DCP concentration for all compositions. The melt viscosity decreased with increasing intensity of the shear mixing presumably due to the formation of the smaller segregated microdomain of the crosslinked EPDM gels in both blend-cure and cure-blend materials. The crystallization rate was higher in EPDM/PP blends than in PP homopolymer. The crystallization rates for various blending conditions were also compared.

INTRODUCTION

A considerable amount of work has been reported on the blends of polypropylene (PP) and ethylene-propylene-diene terpolymer (EPDM) due to their commercial importance.¹⁻³ There are many ways to combine desired features of each component of the blend. One approach is to prepare the blend in an intensive mixer. The blend of crosslinked EPDM and PP has been prepared in a roll mill or extruder by the "dynamic curing" method where EPDM was cured under shear with peroxide.

The dynamically cured thermoplastic elastomer blends, first described by Fischer,^{4,5} have been widely used in the plastic industry for years.^{6–8} The blends have important technical advantages in processing because the blends can be fabricated by such methods as extrusion and molding, though they possess a crosslinked elastomer as one component. The thermoplastic blend is known to be composed of a partly gelled elastomer and a physically cross-linked plastic and thus exhibits a similar behavior to the thermoplastic IPN (interpenetrating polymer network),⁹ which flows at elevated temperature and yet behaves as a thermoset at use temperature.

Most research has been directed to reveal the mechanical and physical properties of the dynamically cured EPDM/PP blends,^{4,10-12} but no litera-

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ture has been published on the systematic investigation of the effect of shear conditions on the rheological and physical properties of the blends. Moreover, few morphological studies have been reported as yet on the structure of the dynamically cured blends to explain their peculiar thermoplastic processability. Even though Kresge¹³ modelled the EPDM/PP blends to show the morphology of the material after crystallization, this work is not related to the dynamically cured blends but strictly to the thermoplastic IPN and is not sufficient to reveal the relationship between structure and properties of the blends.

The objective of this study is to clarify the effect of the intensity of the shear mixing, peroxide concentration, and rubber/plastic composition on the rheological and thermal properties of the dynamically cured EPDM/PP blend along with the accompanying characteristics in morphology. Blends were prepared in a laboratory internal mixer where EPDM was cured with PP under shear with dicumyl peroxide (DCP) at different shear conditions (blend-cure). Blends were also prepared for comparison from EPDM which were dynamically cured in the absence of PP and blended later (cure-blend).

EXPERIMENTAL

Materials

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

Preparation of Blends

The EPDM and peroxide were preblended in a 3×7 in. research mill (Farrel Co.) at roll temperature of 80°C for 10 min. DCP contents ranged from 0 to 1.33 phr based on the amount of EPDM. The roll-milled strands were blended with polypropylene with compositions of 25, 50, and 75 wt. % EPDM in a 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 60 cc (40 g/batch). The mixer was operated with entrapped air in sealed condition.

Materials PP	Characteristics		Source	
	$ \begin{array}{c} MFI \\ \overline{M}_{w} \\ \overline{M}_{-} \end{array} $	6.0 2.021×10^{5} 2.829×10^{4}	PP4107 (Korea Petrochem.)	
EPDM	$\eta_{inh} (dL/g)^{a}$ IV ^b PE/PP(mol%) ^c	1.22 15.2 52.0/48.0	Roy. 521 (Uniroyal)	
DCP	Granule type		Mitsui	

TABLE I Materials and Their Characteristics

^a0.5 g/dL xylene solution at 70°C.

^bBy ICl titration method.

°By IR analysis.



Fig. 1. Schematic diagram of the experimental procedure.

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 °C for 15 min. The EPDM was dynamically cured under shear in the presence of PP at different shear conditions. During the experimental runs, the shear intensity was controlled by adjusting the rotating speed of the mixer as 20, 40, 60, and 80 rpm. Previous analysis by the dynamic DSC method had already established that under such processing conditions the curing reaction was completed.¹⁴

Sample Description			
	Composition		
Sample Notation	EPDM	PP	
EPDM100	100	0	
PP 100	0	100	
EL75PP25 ^a	75	25	
EL50PP50	50	50	
EL25PP75	25	75	
EB75PP25 ^b	75	25	
EB50PP50	50	50	
EB25PP75	25	75	
EC75PP25°	75	25	
EC50PP50	50	50	
EC25PP75	25	75	

TABLE II Sample Descriptior

^aEL denotes linear EPDM/PP blend.

^bEB denotes EPDM/PP blend-cure.

^cEC denotes EPDM/PP cure-blend.

The other method was to dynamically cure EPDM alone first and then mix the cured EPDM with PP (cure-blend process). In this process, the EPDM was cured under shear at the same four different shear conditions, as before, in the absence of PP at 190 °C for 15 min, followed by blending with PP at the same temperature for 15 min. under a constant mixer rotation of 60 rpm. Figure 1 shows the schematic diagram of the experimental procedure. The blend samples prepared and the sample notations are listed in Table II.

Measurements

The rheological properties were measured with a Capillary Rheometer (Instron Model 3211) in shear rates of $3.5-350.1 \text{ s}^{-1}$ at 200°C. The length and the diameter of the capillary was 5.0851 and 0.1257 cm, respectively; the diameter of the reservoir was 0.9525 cm and the entry angle was 90°. The L/D ratio of the capillary was about 40, and the end effects were considered negligible.

The thermal analysis was performed under nitrogen with a heating rate of 10°C/min using a DuPont 910 DSC Differential Scanning Calorimeter and a DuPont 990 Thermal Analyzer. The wt % crystallinity of PP in the blend was evaluated from the ratio of the amount of heat of fusion of the blend to the heat of fusion of the perfectly crystalline PP ($\Delta H_{PP} = 209 \text{ J/g}$ in the literature¹⁵). The crystallization kinetics were studied with the following dynamic DSC method¹⁶; the samples of about 10 mg were heated to 180°C 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°C/min. The weight fraction X_t of the material crystallized at the time t was calculated from the ratio between the heat ϕ generated at time t and the total heat ϕ_{∞} of crystallization, according to the relation

$$X_{t} = \frac{\phi}{\phi_{\infty}} = \int_{0}^{t} \left(\frac{dH}{dt}\right) dt \bigg/ \int_{0}^{\infty} \left(\frac{dH}{dt}\right) dt$$

Scanning electron microscopy (SEM) was carried out by Autoscan (ETEC equipment). Samples were cryogenically fractured in liquid nitrogen and etched with xylene vapor at 130 °C to extract polypropylene for 30 s and dried for about 12 h at 100 °C under vacuum, followed by platinum coating prior to their installation in the SEM chamber.

RESULTS AND DISCUSSION

Rheological Properties

The rheological behavior for the EPDM/PP linear blends is shown in Figure 2 and the power-law relationship was observed in the shear rate range studied. Values of the exponent n or the flow behavior index of the power-law equation

 $\tau_w = K \dot{\gamma}_w^n$



Fig. 2. Shear stress-shear rate curves for EPDM/PP linear Blends at 200°C: (○) EPDM 100; (□) EL75PP25; (△) EL50PP50; (■) EL25PP75; (●) PP 100.

were calculated from the relation of shear stress and shear rate by linear regression. Table III shows the values of n at 200°C for the EPDM/PP linear blends and n did not change significantly with blend composition. The rheological characterization of the dynamically cured EPDM/PP blends, reported in Figures 3–15, indicates the effect of DCP concentration and shear intensity on the melt viscosity.

Effect of DCP Concentration. Figure 3 shows the viscosity behavior at constant mixer speed of 60 rpm for EB75PP25 blend-cure. It is seen that the viscosity increases with DCP concentration throughout the shear range examined. It is clear that more molecular restrictions are brought about by the formation of chemical crosslinks in EPDM with increasing DCP concentration for EB75PP25 blend-cure.

Figure 4 shows SEM micrograph of EB75PP25 blend-cure fracture surfaces etched by hot xylene vapor. It is seen that the microdomains of EPDM have the shape of dumbbell-like microgel of about 0.8–1.0 μ m in size, where the

Composition	Flow behavior index
EPDM100	0.53
EL75PP25	0.51
EL50PP50	0.50
EL25PP75	0.49
PP100	0.50

TABLE III Values of Flow Behavior Index for EPDM/PP Linear Blends at 200°C



Fig. 3. Effect of DCP concentration (phr) on viscosity for EB75PP25 blend-cure at 200°C (mixer speed; 60 rpm): (\bullet) 0.00; (\bigcirc) 0.33; (\triangle) 0.67; (\square) 1.00; (\bigtriangledown) 1.33.



Fig. 4. SEM micrograph of EB75PP25 blend-cure with DCP concentration of 0.67 phr (dynamically cured at 60 rpm).

dark portions represent the PP phase extracted out by hot xylene vapor. Having seen the morphology of the microgel domain of EPDM, one may understand the reason why the dynamic cured blend can be processed and the dynamic aspects prevent the crosslinking of EPDM phase from truly continuous infinite network.

In contrast to Figure 3, the viscosity decreases with DCP content for EB25PP75 blend-cure, shown in Figure 5. The observed viscosity behavior illustrated in Figure 5 may be attributed to the accelerated mechanochemical



Fig. 5. Effect of DCP concentration on viscosity for EB25PP75 blend-cure at 200°C (mixer speed; 60 rpm): (\bullet) 0.00; (\bigcirc) 0.33; (\triangle) 0.67; (\square) 1.00; (\bigtriangledown) 1.33.

degradation of polypropylene in the presence of peroxide during the dynamic curing. The mechanochemical degradation of thermoplastic polymers during processing was reported in literature,^{18,19} and this phenomenon has been reviewed by Scott.¹⁹ It seems that with compositions of PP greater than 50% this effect becomes predominant whereas, at EB75PP25 composition, the crosslinking effect of EPDM is dominant.

In order to explain the viscosity behavior, the molecular weight of pure PP resin with different DCP concentrations was measured by GPC (gel permeation chromatography) (Fig. 6 and Table IV). The mechanical stress was given to PP at just the same conditions at the temperature 190°C for 15 min at mixer rotation of 60 rpm as when EPDM/PP blend has been prepared. The shift to lower molecular weight with increasing DCP concentration indicates



Log molecular weight

Fig. 6. Effect of DCP concentration on molecular weight distribution of PP (mixer speed; 60 rpm): (---) PP homopolymer; (---) 0.33 phr DCP; (---) 0.67 phr DCP.

HA, IHM, AND KIM

DCP concn (phr)	Mixer rpm	$\overline{M}_n imes 10^{-4}$	$\overline{M}_w imes 10^{-4}$	D_p^{a}	Intrinsic viscosity
0.00	60	2.829	20.207	7.14	1.081
0.33	60	1.709	5.756	3.37	0.472
0.67	.60	1.494	4.473	2.99	0.396
0.00	20	2.977	18.278	6.14	1.029
0.00	40	2.396	17.908	7.48	1.008
0.00	60	2.043	14.147	6.93	0.870
0.00	80	1.218	14.710	12.08	0.847

TABLE IV Molecular Weight Distributions of Polypropylene after Shear

^a D_p means the polydispersity $(\overline{M}_w/\overline{M}_n)$.

that the effect of the peroxide under shear is directly related with the rapid decrease in melt viscosity with increasing concentration of DCP. In his review, Scott¹⁹ reported that, in the mechanochemical degradation of PP during processing, the effect of stress was to give rise to PP chain scission and the effect of peroxide was primarily to increase the rate of formation of hydrogen attached to the tertiary carbon within the chain of polypropylene. The observed viscosity behavior attributed to the formation of PP macroradicals within the blend-cure was different from the viscosity behavior of cure-blend.

For cure-blend, in which EPDM has been dynamically cured separately and blended with PP, the polypropylene is less subjected to the mechanooxidation by peroxide. Thus the viscosity increases with DCP concentration. These results confirm our speculations that the observed reduction in melt



Fig. 7. Comparison of EB25PP75 blend-cure with EC25PP75 cure-blend at 200°C (mixer speed; 60 rpm): (—) EC25PP75; (--) EB25PP75; (●) 0.00; (○) 0.33; (△) 0.67; (□) 1.00.



Fig. 8. Effect of DCP concentration on viscosity for EB50PP50 blend-cure at 200 °C (mixer speed; 60 rpm: (\bullet) 0.00; (\bigcirc) 0.33; (\triangle) 0.67; (\Box) 1.00; (\triangledown) 1.33.

viscosity in blend-cure samples is due in part to oxidative degradation as well as shear degradation (see Fig. 7).

Figure 8 exhibits a different trend from EB25PP75 and EB75PP25 blends. At high shear rates of viscosity measurement the curve for the blend of low DCP concentration crosses that for the blend of high concentration of DCP. The viscosities of the blend of lower DCP concentration are slightly lower than those of highly crosslinked blend at low shear rate, but, increasing the shear rate, the curve for highly crosslinked blend falls down quickly. It is also seen that the blends treated with DCP have lower viscosities than the linear blend of no DCP inclusions over the whole shear rate ranges examined. Taking into consideration that the tendency to form a continuous phase in polymer blends is dominated by concentration and viscosity, Ramos-De Valle²⁰ explained those somewhat unexpected results as follows: When two components having different rheological characteristics flow through capillaries, the components tend to rearrange into a sheath-core configuration, with the component of lower viscosity forming the sheath. This sheath will act as a lubricant between the extrudate and the capillary wall. Such trends are highly plausible at higher shear rate than at lower shear rate. Thus, the more rapid reduction in melt viscosity at higher shear rate with increasing DCP concentration may be caused presumably by the morphological changes in the blend. Such a cross in the viscosity curve plotted against shear rate as observed in blend-cure samples was not observed for EC50PP50 cure-blend (Fig. 9).

Figure 10 shows the flow behavior index of the blends. The decrease of the flow behavior index with increasing DCP concentration shown in the figure implies the higher pseudoplasticity with increasing DCP concentration for the dynamically cured blends except EB25PP75 blend-cure. Such behavior may



Fig. 9. Comparison of EB50PP50 blend-cure with EC50PP50 cure-blend at 200 °C (mixer speed; 60 rpm): (---) EB50PP50; (-) EC50PP50; (Δ) 0.00; (\bigcirc) 0.33; (\bullet) 0.67; (\Box) 1.00.



Fig. 10. Effect of DCP concentration on flow behavior index for EPDM/PP blends [(\triangle) 25/75; (\bigcirc) 50/50; (\square) 75/25] at 200°C (mixer speed; 60 rpm): (---) blend-cure; (---) cure-blend.



Fig. 11. Effect of shear intensity on viscosity for EPDM/PP blend-cure at 200°C (DCP concn; 0.67 phr): (—) EB75PP25; (---) EB50PP50; (---) EB25PP75; (\bigcirc) 20 rpm; (\triangle) 40 rpm; (\Box) 60 rpm; (\bigtriangledown) 80 rpm.

be caused by the decrease of the mobility of polymer chain from the higher chemical crosslink density as the DCP content is increased. It is also shown above that a different type of relationship between the DCP concentration and flow behavior index for EB25PP75 blend-cure. In this case the flow behavior index increased with increasing DCP content. This can be explained by the decreasing molecular weight because of the mechanooxidation of PP during the dynamic curing.

The flow behavior index values in cure-blend samples were low and did not show much change as blend-cure samples. This is due to the fact that the peroxide had little effect on the molecular weight of PP because the dynamic curing was performed in the absence of PP. The flow behavior indices for the EC75PP25 cure-blend showed extremely low values and thus are not included in the figure.

Effect of Shear Intensity. The effect of shear intensity on the rheological properties of the dynamically cured blends are shown in Figures 11–15. The viscosity variations with different shear conditions of the blend-cure are shown in Figures 11–13. In these plots, the blends were cured with the constant concentration of DCP, 0.67 phr, based on the amount of EPDM. As the mixer rotation became faster, the melt viscosity of the blends decreased over all the compositions examined.

The blend-cure (Figs. 12 and 13) clearly showed more distinct reduction in viscosity with increasing shear intensity than cure-blend. This implies that, although the cure-blend has been affected also by the mechanical stress during the dynamic curing, the blend-cure has been subjected more sensitively to the dynamic stress. Thus the reduction in viscosity with increasing



Fig. 12. Comparison of EB50PP50 (---) blend-cure and EC50PP50 (---) cure-blend: (○) 20 rpm; (△) 40 rpm; (□) 60 rpm; (▽) 80 rpm.



Fig. 13. Comparison of EB25PP75 (---) blend-cure and EC25PP75 (---) cure-blend at 200°C (DCP concn; 0.67 phr): (○) 20 rpm; (△) 40 rpm; (□) 60 rpm; (▽) 80 rpm.



Fig. 14. Effect of shear intensity on molecular weight distribution of PP homopolymer (rpm): (--) 20; (---) 40; (---) 60; (----) 80.

shear intensity may be also attributed to mechanical degradation of polypropylene molecules in the blend, along with the oxidative degradation of PP due to the presence of peroxide. It is obvious that the higher shear intensity gives the more rapid reduction in melt viscosity. Comparison of the values of melt viscosity of the blend-cure with that of cure-blend proves well our speculations (see Fig. 12 and 13).



Fig. 15. Effect of shear intensity on flow behavior index for EPDM/PP blends at 200°C (DCP concn; 0.67 phr): (—) blend-cure; (---) cure-blend; (\triangle) EB25PP75, EC25PP75; (O) EB50PP50, EC50PP50; (\Box) EB75PP25, EC75PP25.

It should be mentioned that the probability of forming smaller domain of EPDM is presumed to be higher as the shear intensity increases when the blends were prepared by the blend-cure than when prepared by cure-blend. However, in our morphological studies, the formation of microgel domain of different size with shear intensity was not clearly shown.

Table IV and Figure 14 show the effect of shear intensity on the molecular weight characteristics of polypropylene subjected to mechanical stress. From the gel permeation chromatography analysis, it is obvious that the stronger shear forces with higher mixer rotation speed introduced more mechanical degradation in the polypropylene chain. It is pertinent to note from Figures 6 and 14 that the effect of the peroxide-induced oxidative degradation under shear was higher than the effect of mechanical stress only. The decreasing molecular weight and melt viscosity by mechanooxidative degradation was coincident with the results that the flow behavior index increased as the shear intensity increased. (Fig. 15). It is clear that the flow behavior index was smaller for cure-blend than blend-cure, as may be seen in Figure 15. In this figure, the flow behavior index was not included for their extremely low values for EC75PP25 cure-blend.

Crystallinity and Crystallization Kinetics

The effects of EPDM on the crystal structure of PP have been recently reported.^{3,21-23} The incorporation of the elastomer alters the superstructure of PP matrix by changing the average size and number of the spherulites, and



Fig. 16. Effect of EPDM on crystallization of PP at 117° C: (\triangle) PP homopolymer; (\bigcirc) EL25PP75 linear blend (60 rpm).



Fig. 17. Effect of DCP concentration and shear intensity on crystallization of EL25PP75 linear blend and EB25PP75 blend-cures at 117° C: (\bigcirc) EL25PP75, 60 rpm; (\triangle) EB25PP75, 0.67 phr, 60 rpm; (\Box) EB25PP75, 0.67 phr, 20 rpm.

this change in the superstructure is very important to interpret the function of impact modification of the elastomer with the PP matrix. 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.

In this study, the thermal behavior of dynamically cured EPDM/PP blends was investigated to see the effect of dynamic shear on the crystallinity and the rate of crystallization of PP. Figure 16 shows the effect of the incorporation of EPDM to the rate of crystallization of PP for EL25PP75 linear blend. The isothermal crystallization temperature was $117 \,^{\circ}$ C. It can be seen that the linear blend shows a higher rate of crystallization behavior was attributed to the role of EPDM to selectively extract the defective molecules within PP crystals and also increase the mobility of neighboring PP chains by the reduction of glass transition temperature.²³

In Figure 17 the effect of the shear intensity and DCP concentration on the extent of crystallization of PP is illustrated. It is well demonstrated in Figure 17 that the rate of crystallization of the dynamically cured blend with DCP concentration of 0.67 phr is lower than that of linear EL25PP75 blend but is not affected significantly by the shear intensity. This means that the chemically crosslinked EPDM by DCP restricts the crystallization of PP.

In Figure 18 the rate of crystallization of cure-blend was shown to be higher than the blend-cure sample. This result can be explained if we consider



Fig. 18. Comparison of the rate of crystallization for EB25PP75 blend-cure and EC25PP75 cure-blend at 117°C: (Δ) EB25PP75, 0.67 phr, 60 rpm; (\bigcirc) EC25PP75, 0.67 phr, 60 rpm.

the influence of molecular weight on the crystal growth rate for the two samples at the temperature of maximum crystal growth rate of PP pure resin used in this study, 117 °C.

For cure-blend the PP was not significantly degraded by DCP so that high molecular weight portions of PP tend to be easily crystallized at high temperature around 117 °C, and thus no appreciable decrease might occur in the temperature of maximum crystal growth rate, whereas for blend-cure the reduction of molecular weight of PP due to the peroxide and shear lowered the temperature of maximum crystal growth rate to such an extent that the crystallization rate might be considerably low at about 117 °C. Thus, such interpretations lead to the conclusion that the cure-blend, which had larger fractions of crystallizable high molecular weight of PP at 117 °C, showed a

Sample	$\Delta H (J/g)$ PP	Crystallinity (wt %)
PP homopolymer	65.0	31.1
EPDM/PP (25/75)		
Blend-cure 0.00 phr, 60 rpm	75.3	36.0
0.67 60	70.7	33.8
0.67 20	70.8	33.9
Cure-blend 0.67 60	74.7	35.7

 TABLE V

 Weight % Crystallinity of Polypropylene Phase in EPDM/PP Blends

EPDM / PP BLENDS

Sample		K	n	$t_{1/2}$ (s)
PP homopolymer		1.101	2.226	75.5
EPDM/PP (25/75)				
Blend-cure 0.00 ph	r, 60 rpm	3.909	1.935	24.5
0.67	60	2.221	2.013	33.6
0.67	20	2.014	1.845	33.7
Cure-blend 0.67	60	3.808	2.025	25.9

TABLE VI Crystallization Kinetic Parameters of PP and EPDM/PP Blends

higher rate of crystallization than the blend-cure sample at the isothermal crystallization temperature of PP used in this study.

This result is in accordance with the degree of wt % crystallinity calculated from the apparent enthalpy of fusion per gram of PP in the blend crystallized at 117 °C (Table V). The crystallization characteristics are reported in Table VI. It was also shown again that the wt % crystallinity of PP in the linear and the dynamically cured EPDM/PP blends were always higher than that of PP homopolymer. The half-time of crystallization, $t_{1/2}$, Avrami exponent n and kinetic constant K of the blend and PP homopolymer are summarized in the table.

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