

Properties of Dynamically Vulcanized EPDM and LLDPE Blends

KYU-HYUN KIM, WON-JEI CHO, and CHANG-SIK HA*

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

SYNOPSIS

The tensile, rheological, and thermal properties of dynamically vulcanized ethylene-propylene-diene terpolymer (EPDM) and linear low-density polyethylene (LLDPE) blends were reported along with their crystalline structure and morphology. The EPDM/LLDPE blends were prepared in a laboratory internal mixer by simultaneous blending and vulcanization. Vulcanization was performed with dicumyl peroxide. For comparison, linear LLDPE/EPDM blends were also prepared. In comparison to the linear blends, dynamically vulcanized blends showed higher tensile strength and modulus and exhibited improved compatibility. It was found, however, that the crystal structure of LLDPE was not changed by the inclusion of EPDM and the dynamic vulcanization process. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

A considerable amount of work has been reported on the blends of polyolefin 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 blends of crosslinked EPDM and polyolefin were prepared in a roll mill or extruder by the "dynamic vulcanization" method where EPDM was vulcanized under shear with peroxide.

Dynamically vulcanized blends, first described by Fischer,^{4,5} have been widely used in the plastics and thermoplastic elastomer (TPE) industries^{6,7} because of their technical advantages in processing as well as their versatile end-use properties. The blends have important technical advantages in processing because of the thermoplastic nature of the melt, even though they contain a vulcanized rubber as one component. It was found that such thermoplastic nature of the blends might be ascribed to the dynamic aspects of vulcanization to prevent the for-

mation of a three-dimensional infinite network in the rubber phase. They have a number of practical advantages over conventional rubber: a short mixing and processing cycle and low energy consumption; the scrap can be recycled; and properties can be easily manipulated by changing the ratio of the components.

There are several factors affecting the structure and properties of the dynamically vulcanized blends.

1. The composition of rubber and plastic components determines the structure and its potential end-use properties.⁸ The rubber-rich blends can be used as a thermoplastic elastomers, and the plastic-rich blends can be applied as rubber-toughened plastics. The mutual interaction and bulk properties are dependent on the composition.
2. State of the domain is dispersed in a continuous matrix. The morphology is the most important structural feature for the dynamically vulcanized blends, which enables the blends to be processed, even though they have a crosslinked elastomer as one component.

* To whom correspondence should be addressed.

Table I Materials and Characteristics

Material	Properties	Source
LLDPE	M_n 38,000	LLDPE 3120 (Hanyang Chem.)
	M_w 125,000	
	MFI ^a 1.0	
	M_w/M_n 3.29	
EPDM	ML ₁₊₄ ^b (100°C), 47	KEP 430 (Kumho Co.)
	PE/PP (wt %), 51/43	
	ENB type diene	
	content, ^c 6.0 wt %	

^a Melt flow index.

^b Mooney viscosity.

^c By IR analysis.

reported the effect of intensity of the shear mixing, peroxide concentration, and rubber/plastic composition on the rheological and thermal properties of the dynamically vulcanized EPDM/PP (polypropylene) blend along with the accompanying characteristics in morphology. The authors¹³⁻¹⁵ also reported the rheological properties, crystalline structure, and morphology of the dynamically vulcanized EPDM and PP/HDPE (high-density polyethylene) ternary blends as well as EPDM/ionomer blends. Kim and Kim¹⁶ reported the effect of vulcanization conditions on the properties of the dynamically vulcanized EPDM/HDPE blends.

Few papers deal with linear low-density PE (LLDPE)/EPDM blends even though LLDPE has been commercially manufactured for over two decades. The impact of LLDPE and its blend is particularly strong in film blowing technology where it tends to displace LDPE. In terms of total consumption of PE of low density in the U.S., 13% of it was LLDPE in 1981 rising to 38% by 1985.¹⁷ In 1986, LLDPE represented 43% of the North American market and in Europe its share was about 10%.¹⁸

In this article, we will report on the tensile properties, rheology, thermal behavior, crystalline structure, and morphology of dynamically vulcanized EPDM and LLDPE blends. The effect of EPDM/LLDPE composition on the properties of the dynamically vulcanized EPDM/LLDPE blend was investigated.

EXPERIMENTAL

Materials

The polymers used in this study are listed in Table I. The LLDPE and the EPDM with ethylidene-2-

norbornene (ENB) as a termonomer were all commercially available grades. The polymers were vulcanized with dicumyl peroxide (DCP).

Blend Preparation

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 were fixed at 0.67 phr based on the amount of EPDM. The blends of EPDM with LLDPE were prepared by using a Brabender roller mixer (type w50H). The mixer consists of two removable blades. The LLDPE was blended with the EPDM-DCP mixture in the molten state at 150°C for 15 min. The EPDM was dynamically vulcanized under shear in the presence of LLDPE at the mixer rotation speed of 60 rpm. Our previous analyses of the curing kinetics of EPDM by the dynamic differential scanning calorimetry (DSC) method established that under such processing conditions the curing reaction was completed and the crosslinking of EPDM by peroxide was dominant during mixing; whereas the crosslinking of plastic phases such as HDPE and PP as well as LLDPE was negligible.^{12-15,19} For linear LLDPE/EPDM blends (i.e., not vulcanized), the LLDPE was blended with EPDM in the molten state at 150°C for 15 min. In this case, solvent extraction tests and spectroscopic measurements showed that there was no reaction in masticated blends in between the component polymers without peroxide. The samples prepared are listed in Table II and the sample notations are described therein. The investigations on the effects of the intensity of the shear mixing and peroxide concentration on the properties of the dy-

Table II Blended Materials and Compositions

Notation	Contents (wt %)		
	LLDPE	EPDM	DCP
EPDM	0.0	100.0	0.0
LLD10/EP90(L)	10.0	90.0	0.0
LLD25/EP75(L)	25.0	75.0	0.0
LLD50/EP50(L)	50.0	50.0	0.0
LLD75/EP25(L)	75.0	25.0	0.0
LLD90/EP10(L)	90.0	10.0	0.0
LLDPE	100.0	0.0	0.0
LLD25/EP75(v)	25.0	75.0	0.67
LLD50/EP50(v)	50.0	50.0	0.67
LLD75/EP25(v)	75.0	25.0	0.67

^a DCP is in phr based on 100 g EPDM.

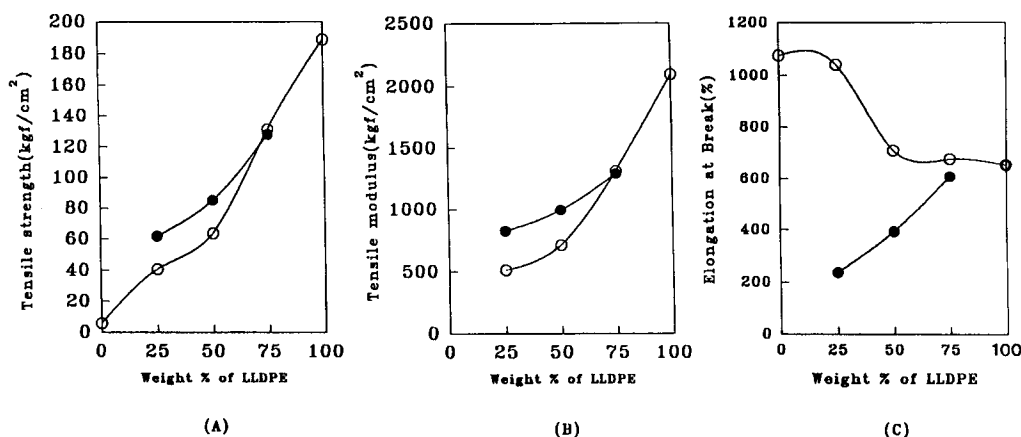


Figure 1 (A) Tensile strength, (B) tensile modulus, and (C) elongation at break of (●) dynamically vulcanized EPDM/LLDPE blends and (○) linear LLDPE/EPDM blends.

namically vulcanized EPDM/LLDPE blend were not carried out in this work, because the match of viscosities at shear conditions for vulcanization as well as mechanical properties of dynamically vulcanized blends with different shear conditions and peroxide contents have been carefully reviewed in our series of previous works dealing with EPDM containing blends.¹²⁻¹⁵

Measurements

Tensile tests were carried out on an Instron tensile tester (model 1127). The specimens were prepared according to ASTM D412-87. The crosshead speed was 500 mm/min and the gauge length is 25 mm. Seven measurements on isotropic samples were averaged.

The rheological properties of blends were measured with a capillary rheometer (Instron model 3211) in shear rates of 6.08–6080 s⁻¹ at 190°C. The length (*L*) and the diameter (*D*) of the capillary was 5.0851 and 0.1257 cm, respectively. 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 Perkin-Elmer differential scanning calorimeter (DSC7). The weight percent crystallinity of LLDPE in the blends was evaluated from the relative ratio of the amount of heat of fusion of the blend to the heat of fusion of LLDPE ($\Delta H_{LLDPE} = 93.979 \text{ J/g}$).

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

The morphology of the blends was observed with a scanning electron microscope (JEOL JSM-35CF). The samples were cryogenically fractured in liquid nitrogen. The fracture topology of the specimen destroyed on fracture were directly observed by gold coating.

RESULTS AND DISCUSSION

Tensile Properties

Figure 1 shows tensile properties of the linear LLDPE/EPDM and the dynamically vulcanized EPDM and LLDPE blends. In general, the tensile strength and modulus are reduced as the EPDM contents increase, both for the linear and the dynamically vulcanized EPDM and LLDPE blends. The reduction in tensile properties should be expected as the result of the rubbery nature of EPDM. At higher LLDPE contents, say 75 wt %, the linear and the dynamically vulcanized EPDM and LLDPE blends showed nearly the same tensile strength and modulus. The tensile strength and modulus of the dynamically vulcanized blends at higher EPDM contents were higher, however, than those of the linear blends due to the chemical crosslinking of EPDM.

The elongation at break for the linear blend increases with increasing EPDM contents, whereas that for the dynamically vulcanized blend decreases with increasing EPDM contents. The reason should be as follows. Although EPDM content increases, the chemical crosslinking of EPDM restricts the mobility of the polymer chain, and the amount of

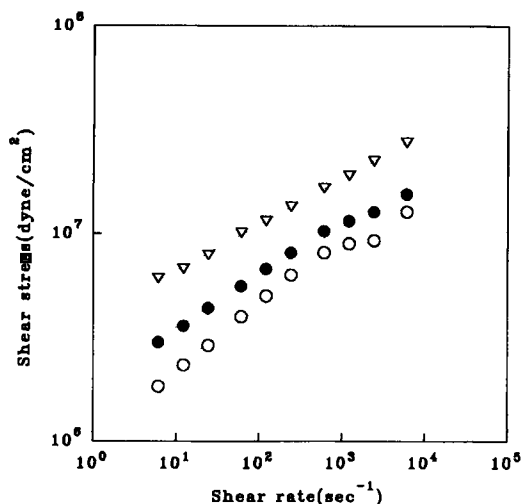


Figure 2 Shear stress-shear rate curves for the dynamically vulcanized EPDM/LLDPE blends at 190°C: (∇) LLD25/EP75, (\bullet) LLD50/EP50, (\circ) LLD75/EP25.

ductile LLDPE decreases. Figure 1 shows that tensile properties sharply change around 50 wt % of composition, implying that the phase of the matrix governing the properties of the blends became inverse at the blend composition.

Rheological Properties

The rheological behavior for the dynamically vulcanized EPDM/LLDPE 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

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

were calculated from the relation of shear stress (τ_w) and shear rate ($\dot{\gamma}_w$) by linear regression. Shear stress is increased as the EPDM contents increase at the same shear rate. The increase in shear stress should be expected as the result of the rubbery nature of EPDM. Similar results were observed for the linear LLDPE/EPDM blends (data not shown).

Figure 3 shows the viscosity behavior at the shear rate of 243.2 s⁻¹ as a function of LLDPE compositions. The dynamically vulcanized blends exhibited higher viscosity than the linear blends over the overall composition ranges. It should be noted, however, that the dynamically vulcanized blends showed the thermoplastic nature, although they contain vulcanized EPDM as one component. It has been reported that the formation of the continuous three-

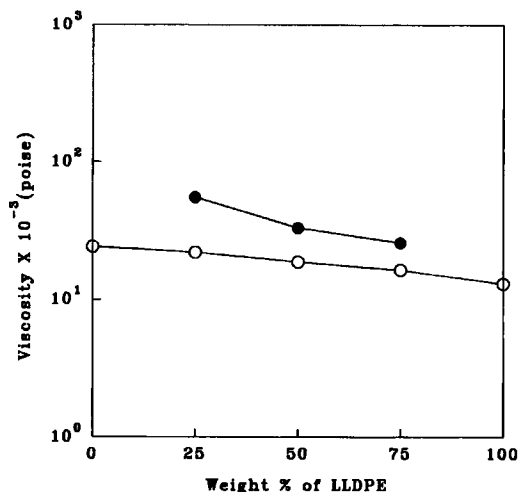


Figure 3 Variation of melt viscosity with different compositions at shear rate 243.2 s⁻¹ (190°C): (\bullet) dynamically vulcanized EPDM/LLDPE blends and (\circ) linear LLDPE/EPDM blends.

dimensional network was constrained effectively, even at low shear intensity.

Figure 4 shows the flow behavior index of the blends at 190°C. The decrease of the flow behavior index with increasing EPDM contents implies the higher pseudoplasticity with increasing EPDM contents for LLDPE/EPDM blends. In comparison to the linear blends, the dynamically vulcanized blends showed much lower flow behavior indices. Such behavior may be caused by the decrease of the mobility of the polymer chain from the higher molecular weight of the EPDM microgel due to the chemical

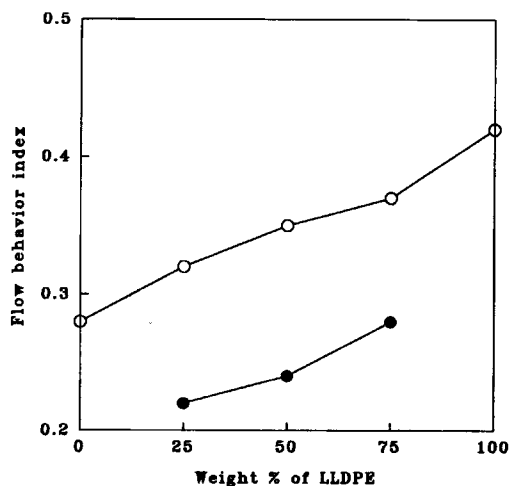


Figure 4 Flow behavior index with different composition at 190°C: (\bullet) dynamically vulcanized EPDM/LLDPE blends and (\circ) linear LLDPE/EPDM blends.

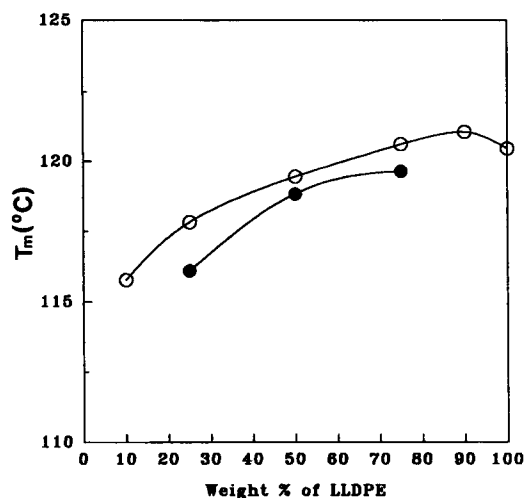


Figure 5 Melting peak temperature (T_m) of (●) dynamically vulcanized EPDM/LLDPE blends and (○) the linear LLDPE/EPDM blends.

crosslink of EPDM. The n behavior indicates that the dynamically vulcanized blends are much more shear sensitive than the linear blends.

Thermal Properties

The effect of EPDM on the thermal properties of LLDPE was determined from DSC. Melting peak temperatures are given in Figure 5. Melting point of blends decreased with increasing EPDM contents for both linear and dynamically vulcanized blends. The inclusion of EPDM causes an LLDPE smaller crystalline domain size for those blends. For the dynamically vulcanized blends, however, the vulcanization of EPDM had a more synergic effect on the decrease of the melt temperature by restricting the mobility of the polymer chain.

Figure 6 shows relative percent crystallinity of the linear and the dynamically vulcanized blends. As LLDPE content increases, relative percent crystallinity monotonically increases. Comparing linear blends with dynamically vulcanized blends, we find nearly the same relative percent crystallinity. The effect of dynamic vulcanization on the wt % crystallinity seems marginal, even though the EPDM chemically cross-linked by DCP restricts the crystallization of LLDPE.

Crystalline Structure

The X-ray diffraction patterns of LLDPE, linear, and dynamically vulcanized EPDM/LLDPE blends at various compositions are shown in Figure 7. The diffraction patterns of the HDPE homopolymer

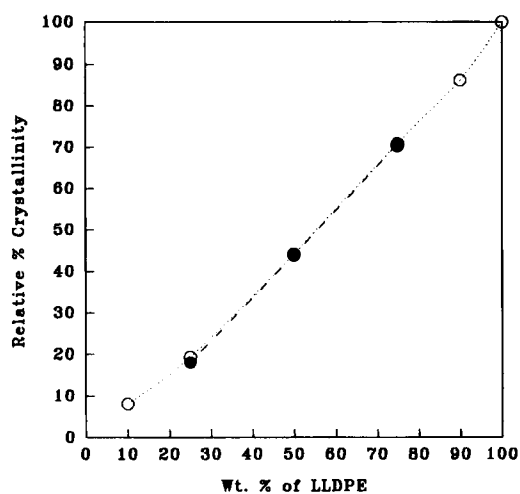


Figure 6 Relative percent crystallinity of (●) dynamically vulcanized EPDM/LLDPE blends and (○) linear LLDPE/EPDM blends.

show 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.²⁰ The diffraction

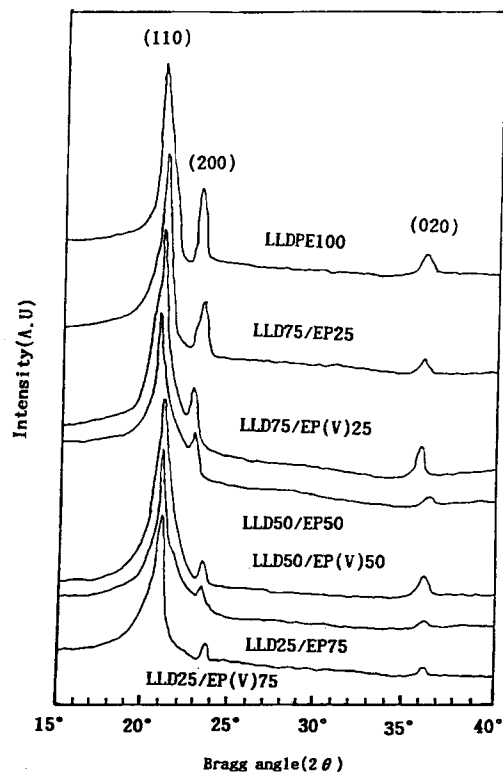


Figure 7 X-ray diffractogram of the dynamically vulcanized EPDM/LLDPE blends and the linear LLDPE/EPDM blends.

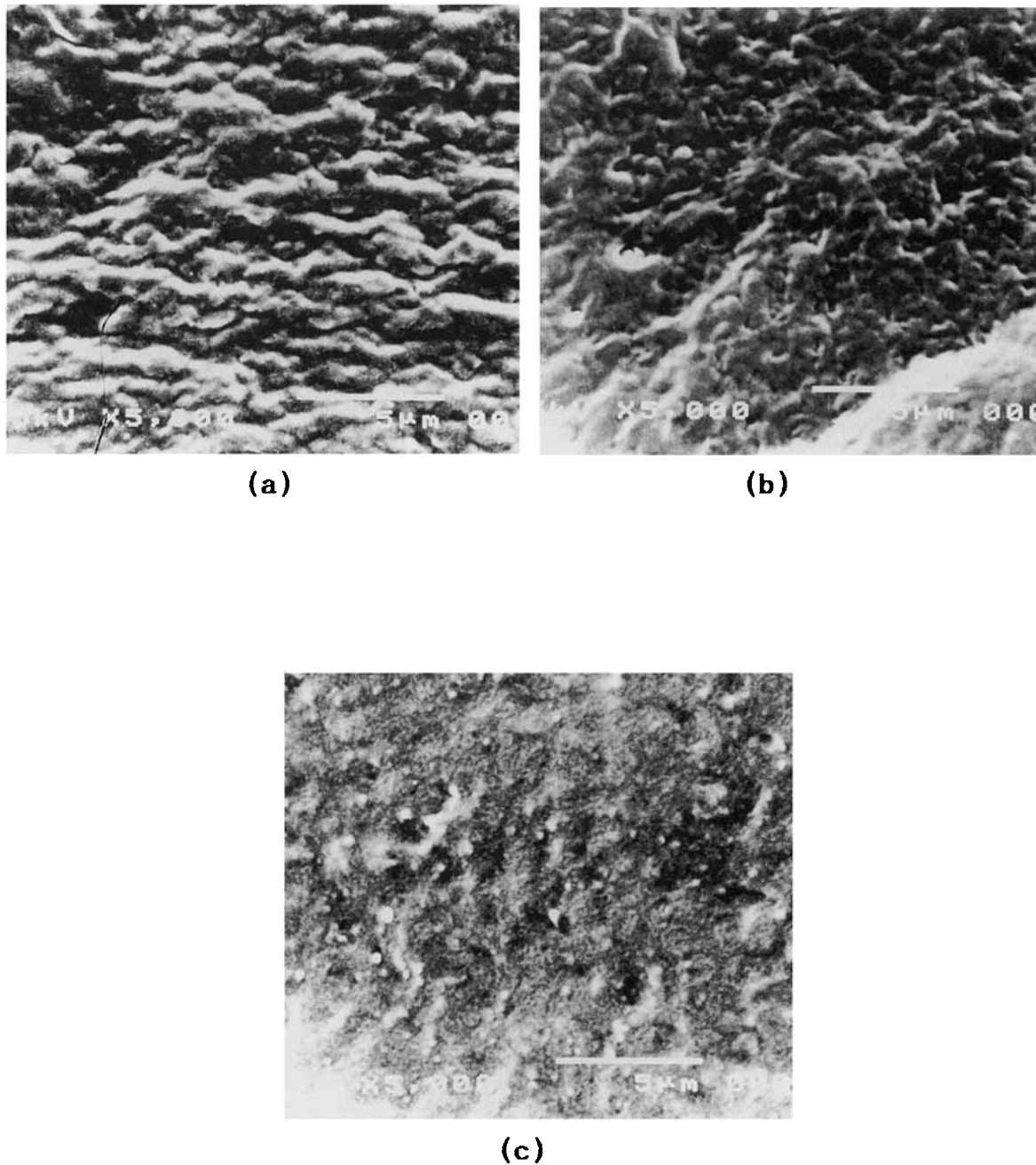


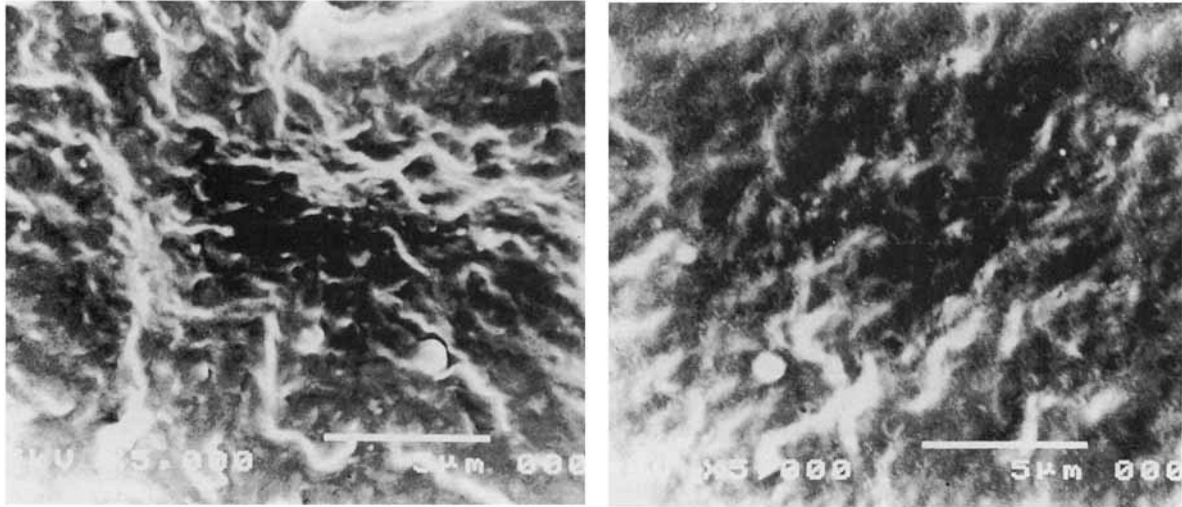
Figure 8 SEM micrographs of the dynamically vulcanized EPDM/LLDPE blends: (a) 25/75, (b) 50/50, (c) 75/25.

patterns of LLDPE exhibited similar features as those of HDPE. Inclusion of EPDM and dynamic vulcanization produce no change in the overall shape of the diffraction patterns. In short, the inclusion of EPDM and the dynamic vulcanization do not significantly change the crystal structure of the LLDPE, judging from the fact that several super-

posed intensity peaks of LLDPE and EPDM blends are observed in the same Bragg angles.

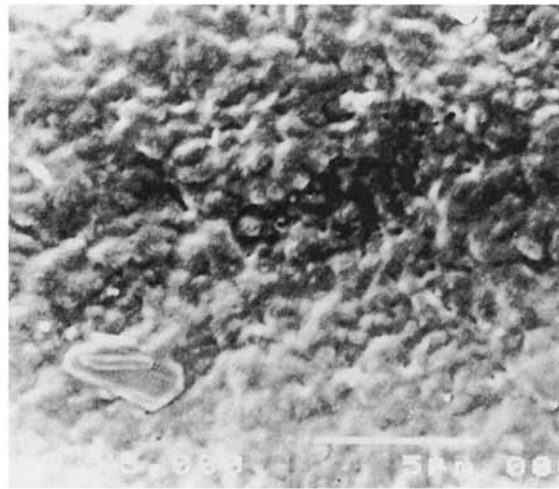
Morphology

The SEM micrographs of the fractured surfaces of the dynamically vulcanized EPDM/LLDPE blends



(a)

(b)



(c)

Figure 9 SEM micrographs of the linear EPDM/LLDPE blends: (a) 25/75, (b) 50/50, (c) 75/25.

of three compositions are shown in Figure 8. The SEM micrograph of the fractured surfaces of LLD75/EP25(v) blend shows the domain of the EPDM. The domain size ranges from 0.2 to 0.4 μm in diameter and the domains are regularly distributed throughout the specimen. The phase inversion occurs in the LLD25/EP75(v) blend and the

LLDPE particles are distributed in the EPDM matrix.

Figure 9 shows the SEM micrographs of the fractured surfaces of the linear LLDPE/EPDM blends of three compositions. The SEM micrographs of the fractured surfaces of the linear blends show nearly the same tendency as those of the dynamically vul-

canized blends. But, careful inspection of Figures 8 and 9 indicates that domain sizes are larger for the linear blends than for the dynamically vulcanized blends except LLD75/EP25(L). The morphology implies that the compatibility of LLDPE and EPDM was improved by the dynamic vulcanization process. The result suggests that the compatibility can be controlled by the application of the dynamic vulcanization. Domain sizes of LLD75/EP25(L) blend are nearly the same as those of LLD75/EP25(V). The result may be closely related to the fact that LLD75/EP25(L) blends have nearly the same tensile property as LLD75/EP25(V). Note that for other compositions, dynamically vulcanized blends have better tensile properties than the linear blends.

CONCLUSIONS

The tensile, rheological, and thermal properties, crystalline structure, and morphology of the linear LLDPE/EPDM and the dynamically vulcanized EPDM/LLDPE blends were studied. Considering all the results, the following conclusions are made.

1. In comparison to the linear blends, dynamically vulcanized blends showed higher tensile strength and modulus due to the chemical crosslinking of EPDM. The elongation at break in the linear blend increased with increasing EPDM contents. But, the elongation at break in the dynamically vulcanized blend decreased with increasing EPDM contents.
2. Viscosity increased monotonically with rubber addition: more in low and less in high shear stress. In comparison to the linear blends, the dynamically vulcanized EPDM/LLDPE blends showed higher viscosity.
3. For the linear blends, melting point was decreased by EPDM inclusion. Comparing with linear blends, the dynamically vulcanized blends showed slightly decreased melting temperatures. In short, the inclusion of EPDM and the dynamic vulcanization caused the LLDPE smaller crystalline domain size. However, the effect was marginal.
4. The inclusion of EPDM and the dynamic vulcanization did not significantly change the crystal structure of LLDPE.
5. The morphological analysis showed that the dynamically vulcanized blends exhibited improved compatibility between EPDM and LLDPE, when compared with the linear blends.

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