

# Dynamic Vulcanization of Polyethylene-Based Thermoplastic Elastomer Blends

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**ABSTRACT:** In this investigation, the effects of blending with ethylene-propylene-diene terpolymer and subsequent dynamic curing with sulfur on the macromolecular structure and properties of pure low-density polyethylene and high-density polyethylene were studied. The crosslinking efficiency of polyethylene-based ethylene-propylene-diene terpolymer blends upon dynamic curing was assessed with torque and gel content measurements. The curing of dispersed ethylene-propylene-diene terpolymer in a polyethylene matrix improved both the mechanical and thermomechanical properties as a result of the formation of a crosslink structure in the rubber phase. In view

of the electrical applications of this cured blend material, the volume resistivity was measured. The thermal stability of vulcanized polyethylene/ethylene-propylene-diene terpolymer blends was found to be superior to that of unvulcanized blends. In scanning electron microscopy analysis, good interface bonding between the polyethylene matrix and dispersed ethylene-propylene-diene terpolymer was observed for the cured blends. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 376–384, 2010

**Key words:** elastomers; morphology; polyethylene (PE); thermal properties; vulcanization

## INTRODUCTION

Nowadays, there is extensive commercial and scientific interest in the development and modification of polyolefin blends because of their relatively low cost and easy processability.<sup>1</sup> However, the use of polyolefins in the industrial sector is limited by their poor impact toughness at low temperatures. Among the different types of polymer blends, thermoplastic elastomers (TPEs) from rubber-thermoplastic blends are finding growing importance in various application sectors as they produce good mechanical properties. It has been suggested that the presence of a small amount of a rubbery phase in a polyolefin matrix could satisfactorily improve the impact resistance and elongation at break but decrease the modulus and toughness of the materials.<sup>2–5</sup> However, the optimum level of the curing agent could lead to controlled crosslinking of the rubber phase and hence improved toughness of TPE blends.

Today, crosslinked polyethylene (PE)-elastomer blends are finding suitable applications in low- and medium-voltage wires and cables because of their excellent dielectric properties.<sup>6–9</sup> The structural modification of such blends is generally achieved by the incorporation of crosslinking agents (e.g., sulfur and

peroxide) and often by  $\gamma$ -irradiation.<sup>10–12</sup> Dynamic vulcanization, first described by Gessler<sup>13</sup> and then developed by Fisher<sup>14</sup> and Coren and coworkers,<sup>15,16</sup> is the most effective method for producing cured elastomeric materials. As proposed by El-Tantawy,<sup>17</sup> uncured butyl rubber/low-density polyethylene (LDPE) blends could find suitable applications in electric current switching, temperature-sensitive sensors, and electromagnetic interference shielding along with good thermal stability. The thermal stability of TPE materials is important for extending the service life and performance level. Ghosh et al.<sup>18</sup> reported the influence of the vulcanizing agents, vulcanizing techniques, and degree of vulcanization on the phase morphology and mechanical properties of ethylene-propylene-diene terpolymer (EPDM) based LDPE blends. Ghosh et al.<sup>19</sup> also studied the thermooxidative degradation of cured EPDM-rich LDPE blends to predict the high-temperature performance of cured insulating materials during their service period. They observed that dynamic curing improved the thermooxidative stability and aging resistance of the blends. Kumer et al.<sup>20</sup> reported that among LDPE/ground tire rubber (GTR)/natural rubber, LDPE/GTR/EPDM, and LDPE/GTR/styrene-butadiene rubber blends (50:25:25), the sulfur-vulcanized LDPE/GTR/EPDM composite had the best mechanical and thermomechanical properties because of LDPE's greater compatibility with EPDM versus natural rubber and styrene-butadiene rubber.

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This investigation dealt with mechanical, electrical, thermal, and thermomechanical properties of PE-based EPDM blends with and without sulfur vulcanization. It also emphasized the effect of the sulfur concentration on the crosslinking characteristics and thermooxidative stability of these blends. The aim of the work was to optimize the degree of improvement of mechanical and dynamic mechanical properties of fresh LDPE and high-density polyethylene (HDPE) by the incorporation of EPDM and subsequent sulfur vulcanization. The volume resistivity of all the formulated PE-EPDM blends was measured. The effect of vulcanization on the morphological properties of the PE-EPDM blends was studied.

## EXPERIMENTAL

### Materials

Fresh LDPE (Indothene HD GC Exp 8A; melt flow index = 4.0 g 10/min at 190°C with a 2.16-kg load, density = 0.922 g/cm<sup>3</sup> at 23°C, gel content = 5.8 g 100 g<sup>-1</sup>, and volume resistivity = 9.3 × 10<sup>15</sup> Ω cm) and HDPE (M6805U; melt flow index = 0.5 g 10/min at 190°C with a 2.16-kg load, density = 0.968 g/cm<sup>3</sup> at 23°C, gel content = 7.2 g 100 g<sup>-1</sup>, and volume resistivity = 7.2 × 10<sup>16</sup> Ω cm), used for making blends with EPDM, were obtained from Indian Petrochemical Corp., Ltd. (Vadodra, India), and Haldia Petrochemical, Ltd. (Haldia, India), respectively. EPDM (Nordel 4570) containing 50 wt % ethylene and 4.9 wt % 5-ethylidene-2-norbornene was procured from DuPont (Borough, New Jersey, USA). The elastomer had a Mooney viscosity of 70 × 10<sup>-1</sup> Pa s (ML<sub>1+4</sub> at 125°C), a weight-average molecular weight of 210,000 g/mol, and less than 1% crystallinity [differential scanning calorimetry (DSC) at 10°C/min]. The sulfur (curing agent) was procured from E. Merck (Darmstadt, Germany). Zinc oxide (ZnO), mercaptobenzthiazyl disulfide (MBTS), and tetramethylthiuram disulfide (TMTD) were obtained from ICI India, Ltd. (Gurgaon, India).

### Methods

#### Preparation of the LDPE-EPDM and HDPE-EPDM blends

The blend formulations (w/w), using fresh LDPE, HDPE, EPDM, sulfur, and additives (ZnO, TMTD, and MBTS), are presented in Table I. Binary 85:15 LDPE-EPDM and 85:15 HDPE-EPDM blends were prepared with a Haake Rheocord 9000 (Karlsruhe, Germany) with an attached Rheomix 600 mixing unit at 140°C for 6.5–7 min at 60 rpm. About 50 g of material was loaded at a time for each batch, and the total loading capacity of the Rheomix mixing chamber was 60 g. The blend of each batch was cooled to room temperature (30°C) and kept at that temperature for 3 h. The change in mixing torque as a function of the blending time, obtained with the torque rheometer, was measured.

#### Compression molding of the blends

Formulated blends were compression-molded to prepare blend sheets (thickness = 3.6 ± 0.2 mm) with a Delta Malikson 100TY pressman (Mumbai, India). The temperature and pressure were maintained at 130°C and 100 kg/cm<sup>2</sup>, respectively, for 15 min. Afterward, the blend sheets were cooled under pressure for 30 min to room temperature. Mechanical test specimens were prepared from these blend sheets per the ASTM standard with a model 6490 counter-cut copy milling machine (Ceast, Italy) with calibrated templates.

### Characterization

#### Gel content determination

The compression-molded cured and uncured samples were tested for the gel content. The gel content percentage was measured by Soxhlet extraction with xylene as the solvent at 140°C for 24 h followed by hot filtration. The weight of the gel fraction (the filtered part) was taken after vacuum drying.

TABLE I  
Formulations of Pure PE and Uncured/Cured PE-EPDM Blends

No.	Sample abbreviation	Blend composition						
		LDPE (wt %)	HDPE (wt %)	EPDM (wt %)	Sulfur (phr)	ZnO (phr)	TMTD (phr)	MBTS (phr)
1	Virgin LDPE	100	0	0	0	0	0	0
2	(LD-EP) <sub>0</sub>	85	0	15	0	0	0	0
3	(LD-EP) <sub>1</sub>	85	0	15	1	3	0.75	0.25
4	(LD-EP) <sub>2</sub>	85	0	15	2	3	0.75	0.25
5	(LD-EP) <sub>3</sub>	85	0	15	3	3	0.75	0.25
6	Virgin HDPE	0	100	0	0	0	0	0
7	(HD-EP) <sub>0</sub>	0	85	15	0	0	0	0
8	(HD-EP) <sub>1</sub>	0	85	15	1	3	0.75	0.25
9	(HD-EP) <sub>2</sub>	0	85	15	2	3	0.75	0.25
10	(HD-EP) <sub>3</sub>	0	85	15	3	3	0.75	0.25

EP = ethylene-propylene-diene copolymer; HD = high-density polyethylene; LD = low-density polyethylene.

### Mechanical properties

Dumbbell specimens (type IV) for tensile tests were prepared according to ASTM D 638. The tensile properties of fresh PE and formulated cured/uncured PE–EPDM blends were measured with an Instron model 3366 tensile test machine (Grove City, PA, USA) with a crosshead speed of 50 mm/min. Samples were conditioned at 23°C with 50% relative humidity for 40 h before testing. The Izod impact strength of notched samples ( $64 \times 12.7 \times 3 \text{ mm}^3$  with a V-notch depth of 2 mm and a notch angle of 45°) was measured with a Davenport Izod impact tester (Hampshire, UK) according to ASTM D 256.

### Electrical properties

The volume resistivity of the blend samples (3.6 mm thick and square) was measured with a Hewlett–Packard model 4329 A high-resistance meter coupled with a model 160084 resistivity cell according to ASTM D 257. The samples were preconditioned at 25°C and 45% relative humidity. In this measurement, the test specimen was placed between the two electrodes, one of which was guarded to prevent surface leakage around the edges. All readings were taken 1 min after the application of a 1000-V direct-current voltage.

### Dynamic mechanical thermal analysis

In the dynamic mechanical analysis, the specimens ( $35 \times 9 \times 2.45 \text{ mm}^3$ ) were clamped between strain gages and subjected to small sinusoidal strain (static strain of 0.2% and dynamic strain of 0.1%) at the frequency of 0.1 Hz. The measurements were carried out from 35 to 150°C at a rate of heating of 3°C/min. The machine used in this measurement was a 2980 DMA V1.7B (TA Instrument, New Castle, DE, USA).

### Thermal analysis

The thermal behavior of fresh PE and formulated cured/uncured PE–EPDM blend samples was measured by DSC and thermogravimetric analysis (TGA) in a nitrogen atmosphere. The DSC analysis was performed from –80 to 200°C at a rate of 5°C/min with a TA 10Q-DSC analyzer (New Castle, DE, USA). The degree of crystallinity ( $X_{cr}$ ) was determined according to the following relation:

$$X_{cr} = 100 \times (\Delta H / \Delta H_0) \quad (1)$$

where  $\Delta H$  is the enthalpy of fusion of the PE component (calculated from the DSC analysis) and  $\Delta H_0$  is the enthalpy of fusion of 100% crystalline PE. In all cases, the heat of fusion of 290 J/g was used for 100% crystalline PE.<sup>21</sup>

TGA was performed with 7–8 mg of a formulated sample at a heating rate of 10°C/min. Each heating scan was performed from 30 to 600°C in a Mettler TG 50 (Mumbai, India) attached to a Mettler TC11 4000 thermal analyzer in a nitrogen flow of 25 mL/min.

### Scanning electron microscopy (SEM)

To study the morphological features of cured and uncured PE–EPDM blends, the tensile test samples were fractured after freezing for 15–20 min in liquid nitrogen. The fractured surfaces were chemically etched to remove uncured EPDM with boiling *n*-hexane for 5 min before being sputtered with gold and analyzed with a scanning electron microscope (JSM 5000, JEOL, Tokyo, Japan).

## RESULTS AND DISCUSSION

The mixing time–torque curves obtained for the formulated LDPE–EPDM and HDPE–EPDM blend samples are shown in Figure 1(a,b), respectively. With the progress of the melt blending, the torque slowly increased up to around 200 s, and this was followed by a rapid rise between 200 and 350 s; it finally reached a constant maximum value (i.e., the torque at the plateau region), the so-called equilibrium mixing torque. The equilibrium torque values, which are indicative of the melt viscosity at that temperature and shear rate, increased with the sulfur concentration increasing in the blends. These results indicate that higher energy input is required for the melt processing of dynamically vulcanized blends versus unvulcanized blends. The increase in torque for dynamically vulcanized blend systems is attributed to the formation of a crosslink network structure (monosulfide, disulfide, or polysulfide linkages between different rubber chains) in the EPDM phase. The equilibrium torque, which reflected the degree of crosslinking in the blends, was shifted to higher values with the sulfur dose increasing from 0 to 3 phr [Fig. 1(a,b)]. The torque observed for the HDPE–EPDM blend systems was higher than that for the LDPE–EPDM blends, and this was due to the higher melt viscosity of the HDPE component versus the LDPE component. The immiscibility of the HDPE and EPDM phases reduced the melt flowability (i.e., increased the melt viscosity) of the blends during mixing.

The gel content was measured to assess the degree of crosslinking in the cured PE–EPDM blends with various sulfur doses. As shown in Figure 2, the gel content of the LDPE–EPDM and HDPE–EPDM blends increased sharply with the sulfur dose increasing from 0 to 2%, and this was followed by a gradual increase at the sulfur concentration of 3%. This indicates the progressive development of crosslinking in the EPDM phase up to a 2% sulfur concentration, beyond which there was little increase in

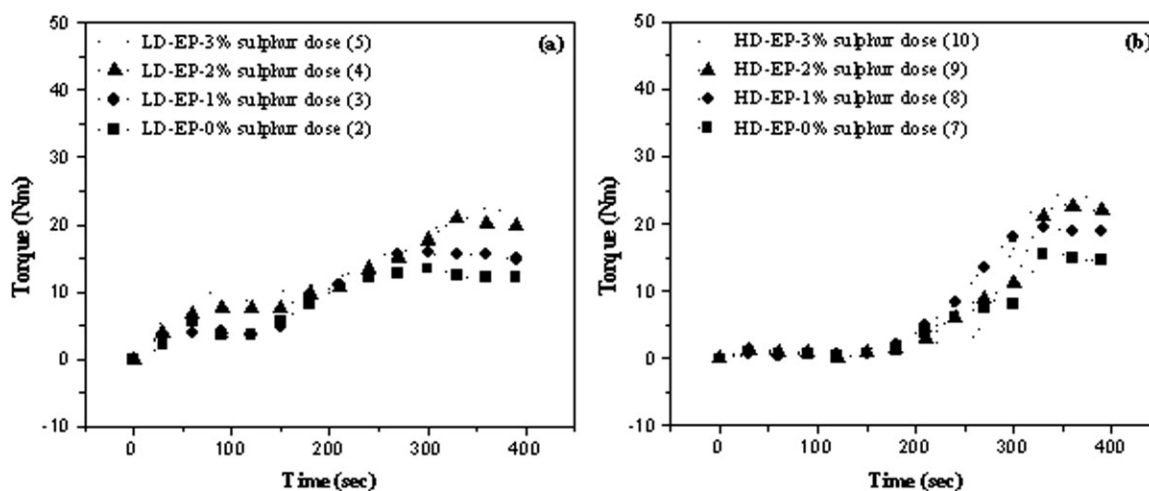


Figure 1 Time-torque mixing curves of (a) LD-EP and (b) HD-EP blends with and without sulfur vulcanization.

the crosslink density of the blends. This observation is in good agreement with the aforementioned mixing torque studies [Fig. 1(a,b)]. The gel content was found to be higher for the HDPE-EPDM blends in comparison with that for the LDPE-EPDM systems. This was probably due to the higher miscibility of the LDPE and EPDM components in the LDPE-EPDM blends, which meant there was less chance for the curing agent to penetrate the rubber phase during vulcanization. The reverse phenomenon might have occurred for the HDPE-EPDM blends because the rubber phase in this system was more exposed to sulfur curing because of the poor miscibility of the highly crystalline HDPE phase and the amorphous EPDM (random copolymer) phase.

The mechanical properties of pure PEs (LDPE and HDPE) and formulated cured/uncured PE-EPDM blends are shown in Figure 3. Both the tensile strength and modulus of fresh LDPE and HDPE drastically decreased upon blending with EPDM [15 wt %; Fig. 3(a,b)], in contrast to the elongation at break, which generally increased [Fig. 3(c)]. In the presence of the elastomeric component, it is reasonable to expect the crystalline particles of the PE component to be predominantly surrounded by the amorphous phase of the elastomer,<sup>22</sup> as reflected in the decrease in the crystallinity in the DSC analysis (Table II). Hence, the amorphous phase increased with the addition of EPDM and, at the same time, reduced its ability to transmit the applied stress to the crystalline particles. Therefore, the mechanical strength of the fresh PEs (LDPE and HDPE) significantly decreased as a result of blending with EPDM.

The tensile strength and modulus of the dynamically vulcanized PE-EPDM blends were higher than those of the unvulcanized blends, increasing with an increase in the sulfur concentration, as shown in Figure 3(a,b). For a cured LDPE-EPDM blend, an

approximately 44% increase in the tensile strength and an approximately 35% increase in the tensile modulus were obtained with the addition of 3% sulfur. Similarly, an approximately 50% increase in the tensile strength and an approximately 41% increase in the tensile modulus were achieved for a cured HDPE-EPDM blend with the same sulfur content. These observations were well corroborated by the results obtained from torque and gel content measurements. The elongation at break (%) of the cured blends was lower than that of the uncured blends, as shown in Figure 3(c). This could be attributed to the reduction of the ductile characteristics of the cured blends as a result of crosslinking.

Figure 3(d) shows that the notched Izod impact strength of pure LDPE and HDPE was significantly increased through blending with EPDM (15 wt %). The dynamic vulcanization of the rubber phase

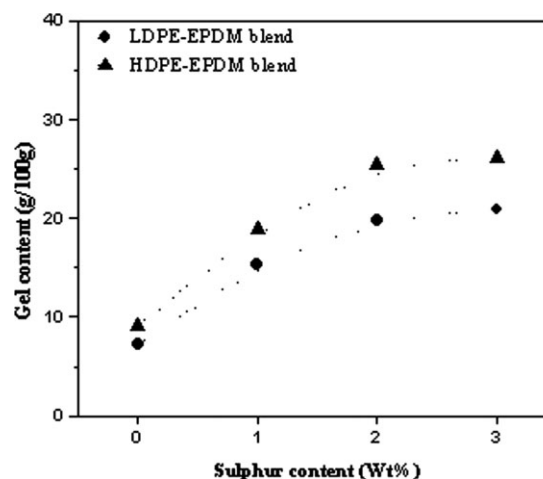


Figure 2 Variation of the gel content as a function of the sulfur content for differently formulated uncured/cured LDPE-EPDM and HDPE-EPDM blends.

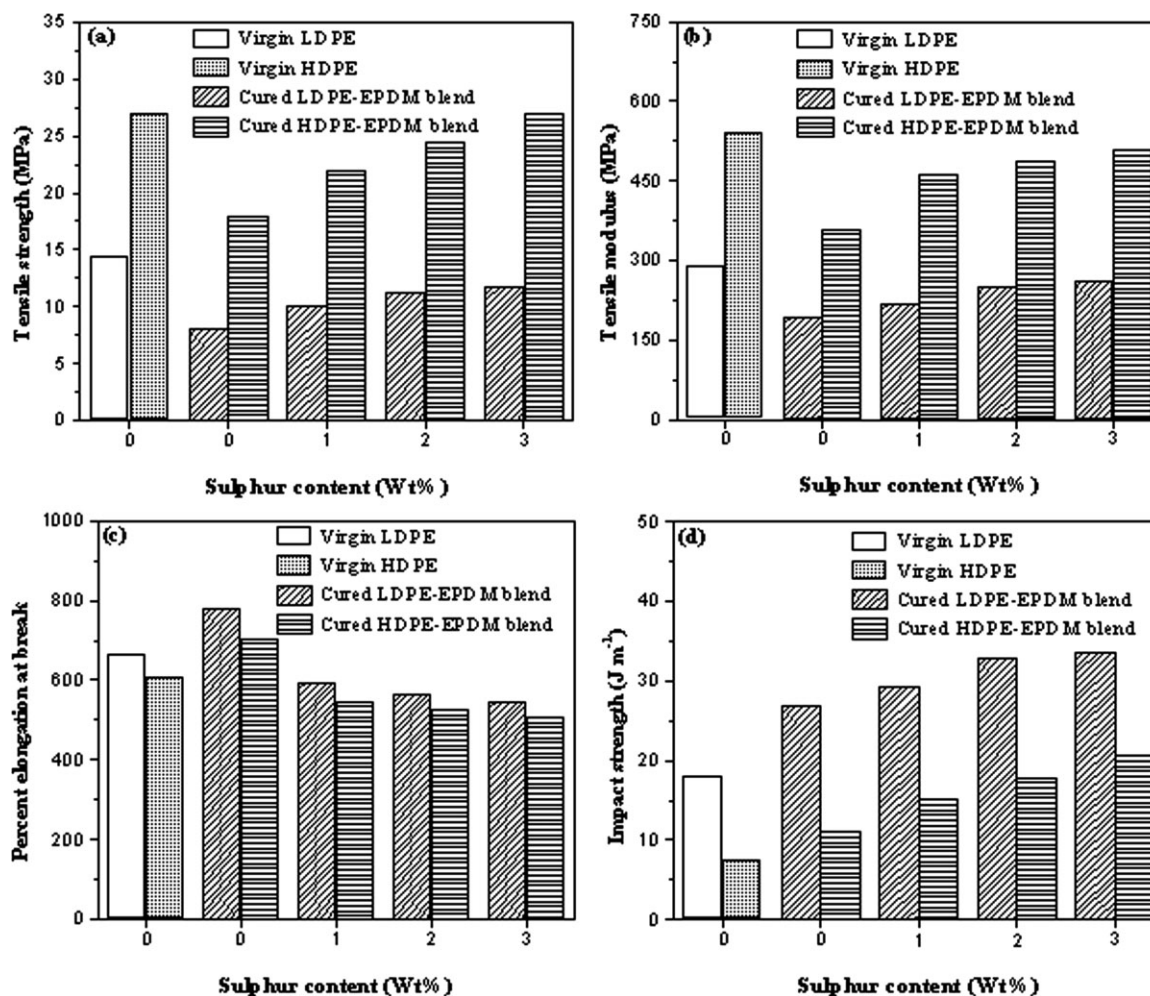


Figure 3 Mechanical properties of pure PE and differently formulated cured/uncured PE-EPDM blends.

further enhanced the impact strength of the PE-EPDM blends. As shown in Figure 3(d), the impact strength of the cured blends increased with the sulfur dose increasing. The maximum impact strengths of 33.6 and 22.6 J/m were recorded for cured LDPE-

EPDM and HDPE-EPDM blends, respectively, at a 3% sulfur concentration. The results indicate that the EPDM rubber acted as a better impact modifier for the LDPE-EPDM blend than for the HDPE-EPDM system, and this was due to better miscibility

TABLE II  
Results from DSC and TGA for Pure PE and Formulated Cured/Uncured PE-EPDM Blends

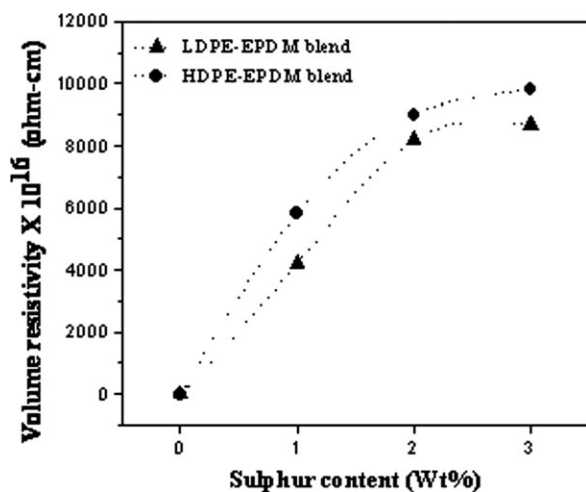
Sample formulation	DSC measurements			TGA measurements			
	$T_g$ (°C)	$T_m$ (°C)	$X_{cr}$	Degradation temperature (°C)		Weight loss (wt %)	Residue (wt %)
				Start	End		
Pure LDPE	-49.7	109.2	34.0	252.7	500.9	97.7	2.3
(LD-EP) <sub>0</sub>	-50.8	108.6	30.4	253.2	497.8	97.3	2.7
(LD-EP) <sub>1</sub>	-47.1	109.4	28.9	276.4	515.5	94.2	5.8
(LD-EP) <sub>2</sub>	-45.9	110.8	28.0	280.2	517.3	91.6	8.4
(LD-EP) <sub>3</sub>	-44.7	110.2	27.1	278.4	515.2	90.2	8.0
Pure HDPE	-44.3	129.7	46.6	300.2	510.2	96.8	3.2
(HD-EP) <sub>0</sub>	-45.2	126.5	38.0	299.6	508.4	96.2	3.8
(HD-EP) <sub>1</sub>	-43.9	127.1	36.8	312.8	530.4	93.4	6.6
(HD-EP) <sub>2</sub>	-40.9	128.4	32.5	325.9	532.7	90.3	9.7
(HD-EP) <sub>3</sub>	-40.3	128.2	31.2	324.7	530.9	88.7	9.1

EP = ethylene-propylene-diene copolymer; HD = high-density polyethylene; LD = low-density polyethylene.

between the LDPE and EPDM components. The impact toughness of TPE blends is significantly dependent on the interfacial adhesion, particle size, and volume fraction of the rubber component.<sup>23</sup> The increase in the impact strength of the dynamically vulcanized blends could be attributed to higher interfacial adhesion between the PE matrix and dispersed EPDM phase.

The volume resistivity is the resistance to leakage of current through the body of a sample material. It depends on several factors, such as the applied voltage, electrification time, and environmental conditions. To make an accurate comparison of the volume resistivity values of the differently formulated samples, all these factors were kept constant. The variation of the volume resistivity of different uncured/cured PE-EPDM blend samples as a function of the sulfur dose is displayed in Figure 4. The volume resistivity of the cured LDPE-EPDM and HDPE-EPDM blends increased sharply with the sulfur dose increasing from 0 to 2%, and this was followed by a little enhancement at a 3% sulfur concentration. The initial increase in the volume resistivity of the blends can be attributed to the effect of crosslinking of the polymer blends by sulfur, which restricted the free mobility of the polymer chain segments and decreased the diene concentration in the EPDM component.

The variations of the dynamic mechanical properties [storage modulus ( $E'$ ), loss modulus ( $E''$ ), and mechanical loss factor ( $\tan \delta$ )] with temperature for differently formulated samples are graphically presented in Figure 5. The  $E'$  values of pure PE, uncured PE-EPDM blends, and cured PE-EPDM (at a 3% sulfur concentration) as a function of temperature are presented in Figure 5(a). The  $E'$  values of the pure LDPE and HDPE components significantly



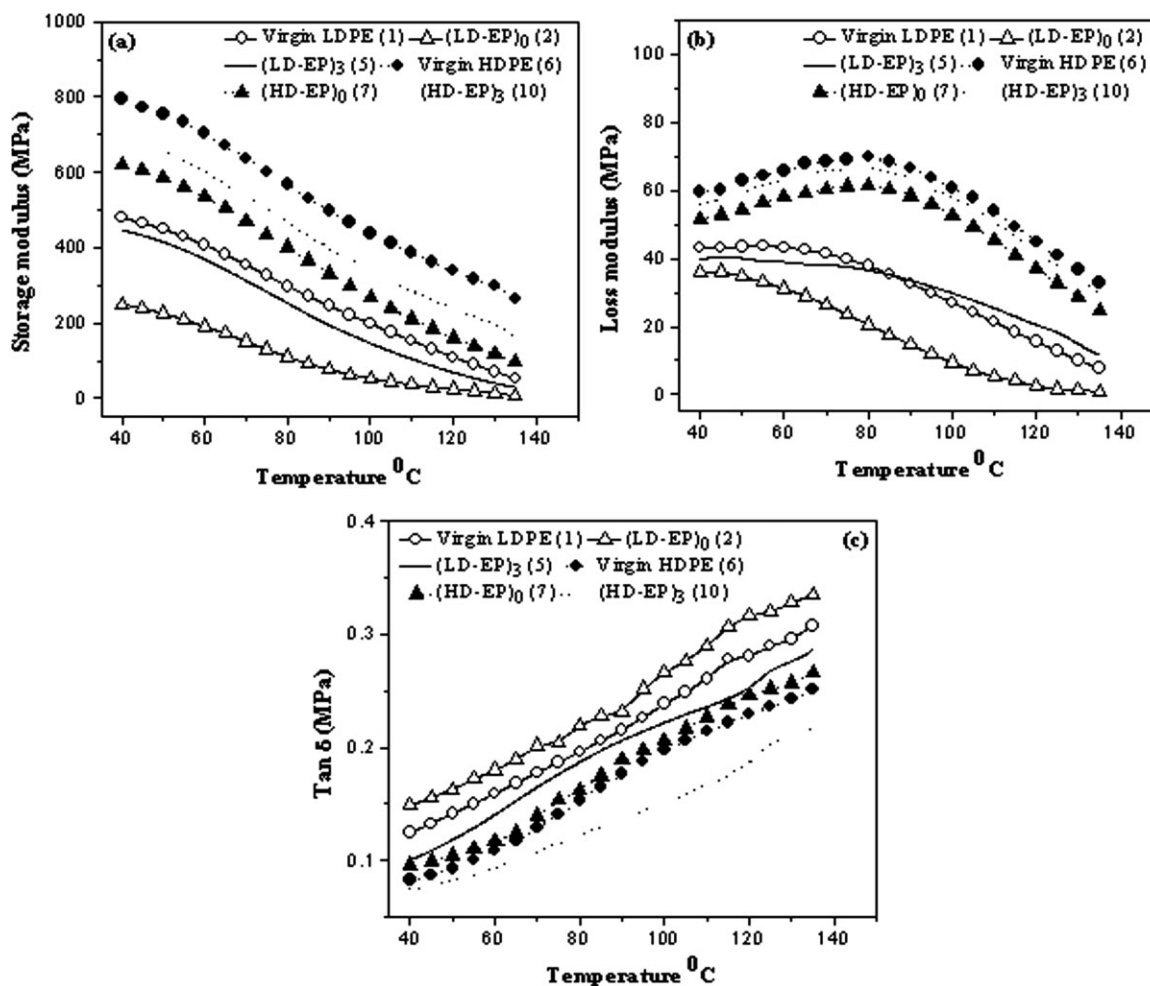
**Figure 4** Volume resistivity versus the sulfur dose for differently formulated uncured/cured PE-EPDM blend systems.

fell with the incorporation of EPDM. However, the dynamic vulcanization with a 3% sulfur concentration increased the  $E'$  values of the PE-EPDM blends. This behavior was due to the increase in stiffness of the blend matrices as a result of crosslinking, which allowed greater stress transfer from the plastic phase to the cured rubber phase at the interface. It also appears that the  $E'$  values of the HDPE-EPDM blends were higher than those of the LDPE-EPDM blends, and this might have been due to the stiffer nature of the highly crystalline HDPE component. However, the rate of reduction of  $E'$  ( $dE'/dT$ ) with the temperature for the cured/uncured HDPE-EPDM blends was higher than that of the LDPE-EPDM systems [Fig. 5(a)]. This could be attributed to greater immiscibility in the HDPE-EPDM blends versus the LDPE-EPDM systems.

The effects of the addition of EPDM and subsequent sulfur curing (by a 3% sulfur dose) on  $E''$  of fresh LDPE and HDPE are shown in Figure 5(b). The  $E''$  curves show an  $\alpha$ -relaxation peak between 60 and 100°C. The  $\alpha$ -relaxation is associated with the chain segment mobility in the crystalline phases, which might be due to reorientation of defect areas in the crystal. As shown in Figure 5(b), the  $\alpha$ -relaxation peak of PE (LDPE and HDPE) was shifted toward a lower temperature region with the incorporation of EPDM, but it moved toward higher temperatures for vulcanized blends. The  $E''$  values in this temperature region were higher for the cured PE-EPDM blends versus the uncured blends [Fig. 5(b)], and this is related to the reduction of the flexibility of the vulcanized materials by the introduction of constraints on the segmental mobility of the polymer chains through the formation of crosslinking networks.<sup>24</sup> The peak broadening was predominant for the cured blends in comparison with the uncured blends [Fig. 5(b)], and this was due to the increase in energy absorption (less viscous dissipation) caused by crosslinking.

The  $E''/E'$  ratio was measured as  $\tan \delta$ . The variation of  $\tan \delta$  as a function of temperature for fresh PE and uncured/cured (at a 3% sulfur concentration) PE-EPDM blends is shown in Figure 5(c). The  $\tan \delta$  values of the cured blends (formulations 5 and 10) were lower than those of the uncured blends (formulations 2 and 7). This could be attributed to the restriction of the chain mobility by a crosslinking effect, which raised the  $E'$  values and reduced the viscoelastic lag between the stress and strain and hence decreased the  $\tan \delta$  values for the cured blends.<sup>25</sup>

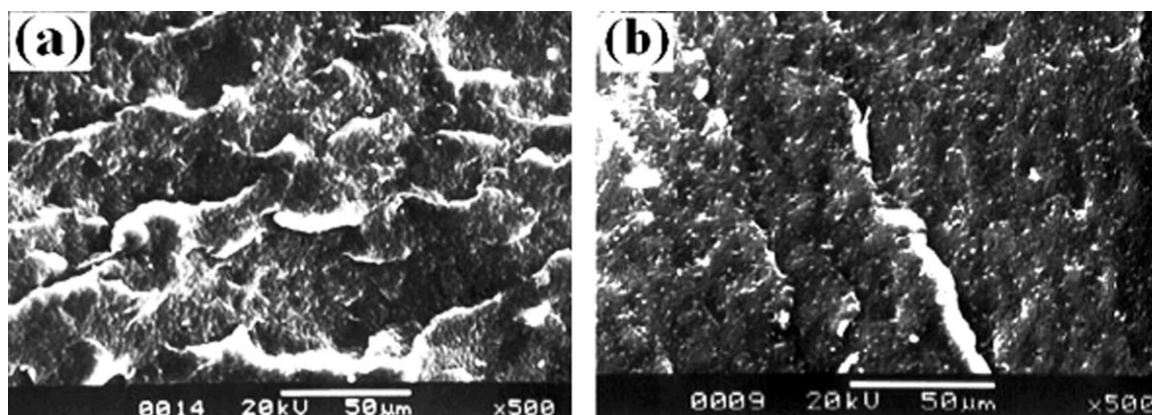
The effects of EPDM incorporation and subsequent sulfur vulcanization on the thermal properties of pure LDPE and HDPE were evaluated with DSC and TGA measurements in an  $N_2$  atmosphere. The detailed results of these thermal analyses for



**Figure 5** Variation of (a)  $E'$ , (b)  $E''$ , and (c)  $\tan \delta$  as a function of temperature for (1,6) pure PE and (2,7) uncured and (5,10) cured PE-EPDM blends.

differently formulated samples are presented in Table II. The glass-transition temperature ( $T_g$ ) of EPDM shifted higher with the sulfur dose increasing in the PE-EPDM blends. The reason is that the crosslinking pulled the polymer chains closer, and this decreased the free volume. As a result of

restricted segmental motion, the  $T_g$  value increased. The crystalline melting temperature ( $T_m$ ) of pure PE decreased with the incorporation of EPDM. However, the melting temperature was slightly increased by sulfur vulcanization. The increase in  $T_m$  for the cured blends was probably due to the fact that the



**Figure 6** SEM microphotographs of (a) uncured and (b) cured (at a dose of 3% sulfur) LDPE-EPDM blends.

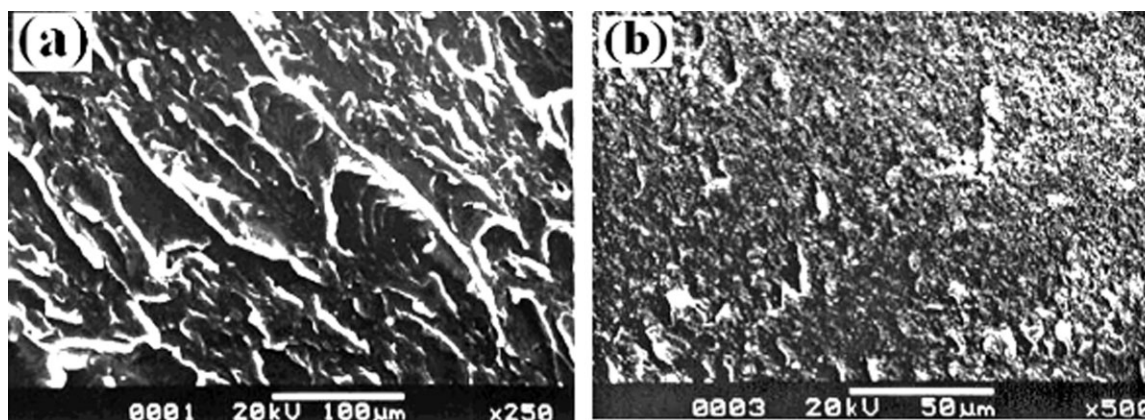


Figure 7 SEM microphotographs of (a) uncured and (b) cured (at a dose of 3% sulfur) HDPE-EPDM blends.

crystalline particles of the PE component were predominantly surrounded by the amorphous cross-linked EPDM phase.<sup>22</sup> The crystallinity percentage of pure LDPE and HDPE decreased with the addition of EPDM, and this was due to the amorphous nature of the rubber phase. Furthermore, the formation of a crosslinked network by sulfur curing created some structural constraints on crystal growth, and this was reflected in the decrease in the crystallinity values of the cured blends (Table II).

To determine and compare the thermal stability of the fresh PE component, uncured PE-EPDM blend, and sulfur-cured PE-EPDM blends, nonisothermal TGA was carried out in an N<sub>2</sub> atmosphere. As observed in Table II, the start and end temperatures of the thermal degradation of the PE component almost remained unchanged in the uncured PE-EPDM blend. However, upon sulfur vulcanization, both the degradation temperatures (start and end) and residual weight of the polymer were remarkably increased with the sulfur concentration increasing from 0 to 2%, and this was followed by a small decrease at a 3% sulfur dose. The initial increase in the residual weight could be attributed to the progressive formation of an infusible crosslinked moiety, whereas the subsequent decrease in the residual weight at a higher sulfur dose (>2%) was probably due to the decomposition of less stable polysulfide linkages at higher temperatures.<sup>19</sup> Moreover, the weight-loss percentage was less in the case of the HDPE-EPDM blend system in comparison with the LDPE-EPDM blends (Table II), and this indicated that the vulcanization occurred predominantly in the EPDM phase of the HDPE-containing blends in comparison with the LDPE blend systems. These results agree well with the aforementioned gel content and torque measurements.

SEM microphotographs of etched and cryogenically fractured surfaces of uncured/cured (3% sulfur) LDPE-EPDM blends (formulations 2 and 5) are shown in Figure 6(a,b). The etching of the fractured

surfaces was performed with *n*-hexane under boiling conditions. As *n*-hexane had no etching action on the LDPE matrix under this condition,<sup>26</sup> the uncured rubber phase dissolved in *n*-hexane and left some voids on the surfaces of the uncured blend sample (LD-EP)<sub>0</sub> [Fig. 6(a)]. The etched surfaces of the vulcanized blend (LD-EP)<sub>3</sub> look even (a less rough surface), and this indicates the absence of an uncured EPDM phase. The results indicate that vulcanization of EPDM by sulfur significantly improved the bonding of the LDPE matrix and dispersed EPDM, and this was reflected in their mechanical performances. A similar morphological phenomenon was also observed for uncured/cured HDPE-EPDM blends (formulations 7 and 10), as shown in Figure 7(a,b).

## CONCLUSIONS

This study evaluated the effect of the dynamic vulcanization of PE (LDPE or HDPE)-EPDM blends by sulfur on the mechanical, dynamic mechanical, electrical, thermal, and morphological properties. The dynamic vulcanization of the EPDM phase dispersed in the PE matrix significantly improved the tensile and impact properties of the blends, and this indicated the formation of a crosslink network structure in the rubber phase. The crosslinking efficiency of the PE-based EPDM blends upon sulfur curing was well evaluated with torque and gel content measurements. However, the HDPE-EPDM blend exhibited a more pronounced curing effect on the properties in comparison with the LDPE-EPDM blends. The sulfur-cured PE-EPDM blends exhibited better dispersion of the EPDM phases in the PE matrix in comparison with the uncured blends. The thermal stability and volume resistivity of the PE-EPDM blends were also significantly improved upon sulfur vulcanization, although the extent of improvement in the properties depended on the variation of the polymeric composition and sulfur dose in the blends. These results indicate that vulcanized blends



of PE with EPDM can be suitable materials for cable insulation and sheathing.

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