

Polyamide-Reinforced Ethylene–Propylene–Diene Rubber Compatibilized with Chlorinated Polyethylene

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ABSTRACT: Vulcanizates of blends of ethylene–propylene–diene rubber and polyamide copolymers were prepared by reactive compatibilization. A reactive route was employed for compatibilizing these blends with the addition of chlorinated polyethylene (CPE). The influence of the compatibilizers, crosslinking agents, blend compositions, and addition modes of the compatibilizers on the mechanical properties of the blends was investigated. The morphologies of the blends were determined with scanning electron microscopy. The addition of CPE was found to reduce the particle size of the dispersed phase remarkably. The stability

of the blends with compatibilizers was measured by high-temperature thermal aging. The mechanical properties were examined by stress–strain measurements and dynamic mechanical thermal measurements; the addition of polyamide copolymers caused significant improvements in the tensile properties of these blends. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1727–1736, 2003

Key words: polyamides; rubber; polyethylene (PE); compatibilization

INTRODUCTION

Until now, most research into polyamide (PA)/rubber blends has been directed toward improving the impact properties of PA. Rubber/PA blends can be sorted into three groups according to the blend composition or processing technology. First, the toughness of PA can be improved by its proper blending with small amounts of suitable rubbery polymers. Important reviews have extensively described the technology of the rubber toughening of brittle plastics.^{1,2} Second, a thermoplastic vulcanizate (TPV) can be prepared by the melt mixing of PA and rubber in the presence of crosslinking agents for the rubber. With a suitable compatibilizer and crosslinking of the rubber phase during the melt mixing, up to 60 wt % rubber can be dispersed in the PA matrix, and this can improve the mechanical properties markedly.^{3–7} These TPV materials exhibit good elastic properties with thermoplastic processability. The original investigations into the dynamic vulcanization of TPVs were performed on polypropylene with different rubber compositions and were initiated by Fisher⁸ and Coran and Patel.⁹ Third, reinforcing rubber by melt mixing with PA is a new subject of research in this field. Only a few studies have been reported on PA-reinforced ethylene–propylene–diene rubber (EPDM).^{10–12}

EPDM is well known for the excellent heat resistance attributed to its saturated backbone structure

and nonpolarity. However, the poor mechanical properties of EPDM vulcanizates, especially those cured by sulfur, are obstacles to the expansion of EPDM's applications. It is difficult to reinforce EPDM with a high melting point nylon such as nylon 6 or nylon 66 because of the differences in the processing temperatures. However, the nylon terpolymer has a low melting temperature and a glass-transition temperature (T_g) of 30–50°C. These characteristics are suitable for nylon copolymer blending with EPDM. Maleated elastomers have widely been used in rubber-toughening PA research. In this work, many maleated elastomers and chlorinated polyethylene (CPE) were used as compatibilizers. All of them contained functionalities that could form graft copolymers *in situ* during the melt with nylon. The pioneering work of EPDM reinforced by PA and carbon black was performed by Luo and Liang.¹⁰ However, to our knowledge, EPDM reinforced totally by PA has not been researched in detail. The purpose of this study was to determine a suitable method for reinforcing EPDM by PA. The experimental results indicate that vulcanized EPDM/PA blends with suitable compatibilizers can display attractive mechanical properties and heat resistance.

EXPERIMENTAL

Materials

EPDM (EP4045) was produced by Jilin Petroleum Chemical Co., Ltd. (Jilin, China) and had as a diene component 5-ethylidene-2-norbornene, a propylene content of 35.9 mol %, and a Mooney viscosity

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ML₁₊₄(100°C) value of 42. A copolymer of PA 1010, PA 66, and PA 6 (70 wt % PA 1010, 20 wt % PA 66, and 10 wt % PA 6) with a melting point of 150°C was produced by the Shanghai Celluloid Factory (Shanghai, China). Maleic anhydride grafted ethylene-propylene rubber (MAH-g-EPR; Exxelor VA 1801; grafting degree = 0.7%) was produced by Exxon Co., Ltd. (NY). Maleic anhydride grafted ethylene-propylene-diene rubber (MAH-g-EPDM; CMG9802; grafting degree = 0.8%) was produced by Sunrise Chemical Cooperation (Shanghai, China). CPE with a chlorine content of 36% was a product of Jiangsu Dongtai Chemical Factory (Jiangsu, China). Carboxylated nitrile rubber (XNBR; Krynac X7.50) was produced by Bayer Co., Ltd. (Berlin, Germany). Carbon black (HAF N330) was provided by Cabot Shanghai Co., Ltd. (Shanghai, China). Zinc oxide (ZnO), stearic acid (SA), tetramethylthiuram disulfide (TMTD), *N,N'*-*m*-phenylene bismaleimide (HVA-2), dicumyl peroxide (DCP), dibenzothiazyl disulfide (MBTS), and sulfur (S) were used as received.

Blend preparation

Before all the melt processing steps, PA was dried in a vacuum oven at 80°C for at least 12 h. The compositions were prepared by a method called *two-step mixing*. In these experiments, both EPDM and a compatibilizer were treated as rubber components, and their total content was 100 phr. The EPDM/PA/CPE blends were prepared at 180°C and 60 rpm in the mixing chamber of a Hakke RC90 rheometer (Berlin, Germany). One minute after the melting of the CPE/PA blends in the chamber, EPDM was added. Fourteen minutes later, the blend batch was dumped. The batch was passed once through a cold roll mill; this yielded a sheet about 2 mm thick. After cooling to room temperature, the batch was reloaded onto the cold miller, and all the crosslinking agents were incorporated into it to give a blend. All the blends were vulcanized at 160°C for 12 min for the preparation of samples for the testing of the mechanical properties.

Measurements

Mechanical properties

The mechanical properties of vulcanized EPDM/CPE/PA blends were measured according to an ASTM D 412 die with an Instron 4465 tensile tester (NY). The Shore A hardness was determined with a Shore A durometer according to ASTM D 2240-91.

Scanning electron microscopy (SEM)

The blend samples were cryogenically fractured in liquid nitrogen into two pieces or tensile-fractured into two pieces at room temperature on the tensile

tester. For the dissolution of the dispersed phase, the fractured surfaces were etched in formic acid for 24 h. After being coated with gold, the fractured surfaces of the samples were observed with a Hitachi S-2150 scanning electron microscope (Tokyo, Japan). Micrographs were obtained at a magnification of 1000×.

Differential scanning calorimetry (DSC)

A PerkinElmer DSC Pyris 1 (NY) was used to study the thermal behavior. T_g 's were obtained by the heating of samples over a temperature range of -60 to 100°C at 20°C/min.

Dynamic mechanical properties

The dynamic mechanical thermal analysis (DMTA) properties of the vulcanized blends were determined on a Rheometric Scientific DMTA IV instrument (Houston, TX). The samples were all tested under a multiwave dynamic tension mode at a frequency of 10 Hz. The temperature range was -100 to 100°C at a heating rate of 3°C/min. The specimen dimensions were 12 × 4 × 1 mm³.

RESULTS AND DISCUSSION

Effects of the compatibilizers and crosslinking agents

It is well known that EPDM and PA are immiscible. For a fine dispersion of the rubber phase or the plastic phase to be achieved in the matrix, for thermoplastic/rubber combinations with a high interfacial tension between the components, it is necessary to for the blend to be compatibilized by the addition of a compatibilizer. Several compatibilizers, such as MAH-g-EPR, MAH-g-EPDM, CPE, malenic anhydride grafted octene-ethylene copolymer (MAH-g-POE), and XNBR, were used in the EPDM/PA blends. The effects of the compatibilizers on the mechanical properties of EPDM/PA vulcanizates are shown in Table I.

The vulcanized EPDM/PA blends compatibilized by MAH-g-EPR, MAH-g-EPDM, and CPE all showed improved mechanical properties in comparison with the EPDM/PA blends vulcanized without compatibilizers when EPDM was cured by sulfur. However, MAH-g-EPDM and CPE led to the best mechanical properties. In this article, we mainly report our studies on EPDM/CPE/PA blends; EPDM/MAH-g-EPDM/PA will be reported elsewhere.

The mechanical properties of the EPDM/PA blends with the aforementioned compatibilizers cured by DCP were also measured in addition a sulfur crosslinking system. The results are shown in Table II. The blends compatibilized by MAH-g-EPR, MAH-g-EPDM, MAH-g-POE, and XNBR showed improved mechanical properties. However, for the blends cured by DCP, compared

TABLE I
Effects of Compatibilizers on the Mechanical Properties of Vulcanized EPDM/PA Blends

	Compatibilizer				—
	MAH-g-EPR	MAH-g-EPDM	CPE	XNBR	
Tensile strength (MPa)	11.2	14.1	14.2	4.0	6.8
Elongation at break (%)	336	384	366	120	269
Tensile set at break (%)	30	31	28	30	20
Shore A hardness	65	68	72	63	70

Formulation: EPDM, 86; compatibilizer, 14; PA, 40; S, 2; TMTD, 1; MBTS, 0.5; SA, 2; and ZnO, 5.

with the uncompatibilized samples in Table I, the tensile strength increased only about 50%.

From the results listed in Tables I and II, the conclusion can be drawn that both MAH-g-EPDM and CPE are suitable compatibilizers for vulcanized PA/EPDM blends. When the blends were cured by DCP, they had relatively high elongations at break (ca. 450%). When the blends were cured by sulfur vulcanizing agents, they had relatively high tensile strengths (ca. 14 MPa). The results also indicate that there is a matching relationship between the compatibilizers and crosslinking agents.

Effect of the CPE content on the mechanical properties of the vulcanized EPDM/PA blends

The effect of CPE as a compatibilizer on the mechanical properties of vulcanized EPDM/CPE/PA blends

is shown in Figure 1. It can be seen in Figure 1(a) that the tensile strength and elongation at break increased with increasing CPE contents at concentrations of up to 20 phr and then leveled off at higher concentrations. In this blending system, the compatibilization is considered to occur through chemical bonds between CPE and PA molecules. Coran and Patel¹³ researched this work and confirmed that chemical interactions between phases could give high strength to CPE-PA compositions. Even a small amount of chemical bonding between PA molecules and those of CPE rubber might greatly improve the mechanical properties of the blends;¹ for example, a graft formation might be the result of aminolysis of the halogenated polymer by a terminal amine group of the PA copolymer. The proposed reaction pattern can be schematically represented as follows:

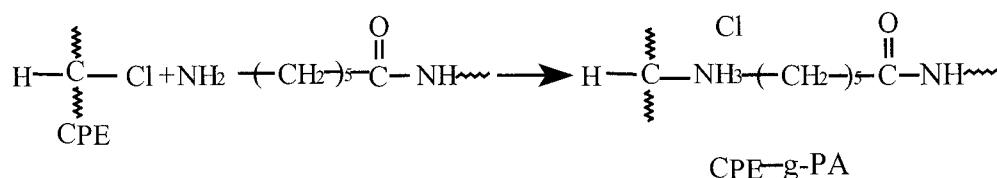


Figure 1(b) shows the relationship between the compatibilizer content and the tensile set at break and hardness. The results show that the tensile set at break increased with the CPE content from 0 to 60 phr in the EPDM/PA blends, but the hardness was little changed.

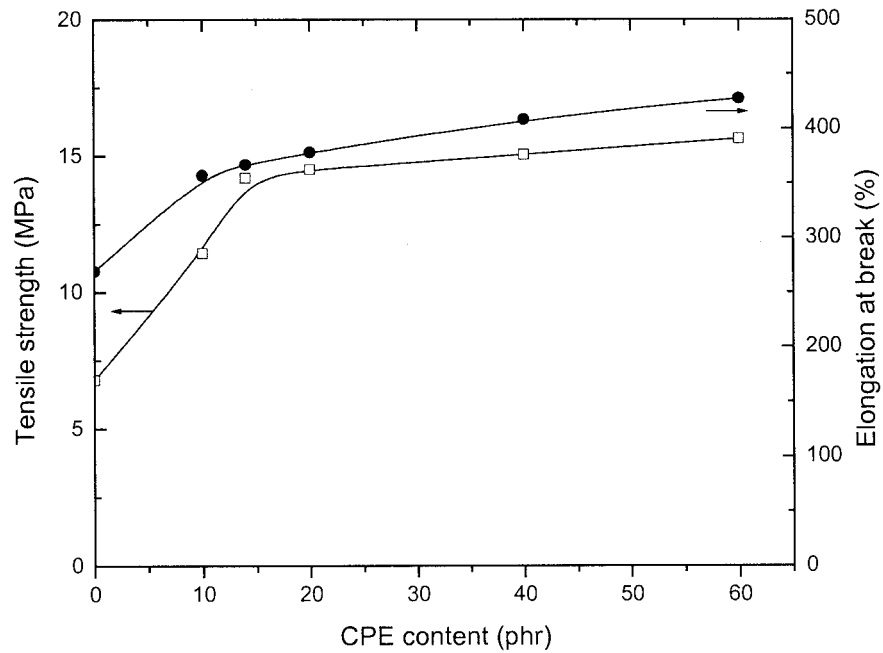
Effect of the addition mode of the compatibilizer

To study the influence of the addition mode of CPE, we performed the blending operations in four different ways:

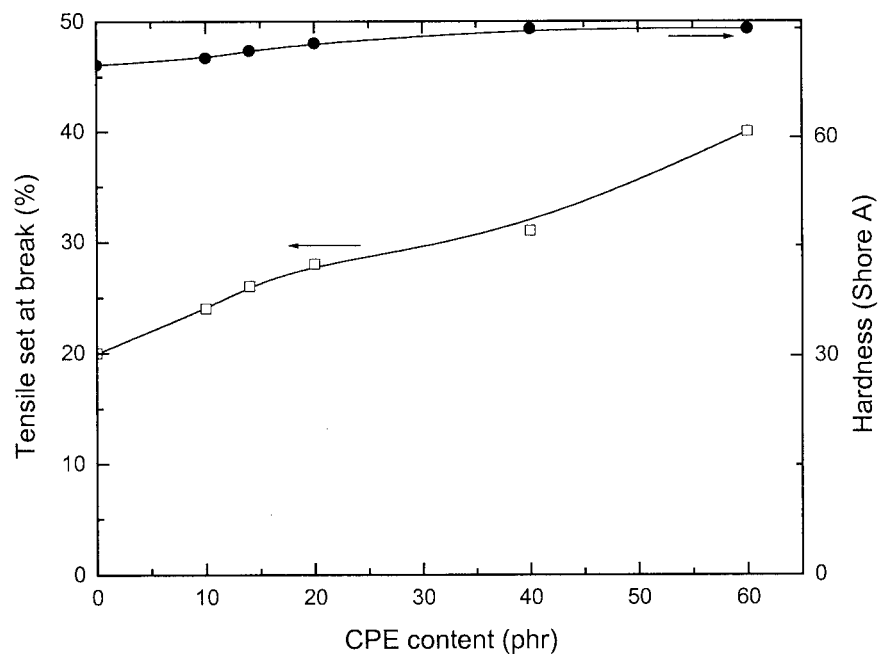
TABLE II
Effect of Compatibilizers on the Mechanical Properties of Vulcanized EPDM/PA Blends

	Compatibilizer				
	MAH-g-EPR	MAH-g-EPDM	CPE	MAH-g-POE	XNBR
Tensile strength (MPa)	8.4	8.6	6.8	9.3	9.9
Elongation at break (%)	455	448	367	398	407
Tensile set at break (%)	40	20	32	20	28
Shore A hardness	54	57	58	59	69

Formulation: EPDM, 86; compatibilizer, 14; PA, 40; S, 1; DCP, 4; HVA-2, 1; SA, 1; and ZnO, 5.



(a)



(b)

Figure 1 Effect of the CPE content on the mechanical properties of vulcanized EPDM/PA blends (formulation: rubber, 100; PA, 40; EPDM/CPE, 100/0, 90/10, 86/14, 80/20, 60/40, or 40/60; S, 2; TMTD, 1; SA, 2; MBTS, 0.5; and ZnO, 5).

TABLE III
Effect of the Addition Modes of CPE on the Mechanical Properties of Vulcanized EPDM/PA Blends

	Addition mode			
	1	2	3	4
Tensile strength (MPa)	12.9	14.2	8.7	10.3
Elongation at break (%)	363	367	307	329
Tensile set at break (%)	20	28	12	20
Shore A hardness	72	72	67	72

Formulation: EPDM, 86; CPE, 14; PA, 40; S, 2; SA, 2; TMTD, 1; MBTS, 0.5; and ZnO, 5.

1. PA, EPDM, and CPE were added together into the mix chamber.
2. CPE was preblended with PA for 3 min and then mixed with EPDM.
3. CPE was preblended with EPDM for 3 min and then mixed with PA.
4. EPDM and PA were preblended for 3 min, and then CPE was added to the blend.

The mechanical properties of the vulcanized (86/14/40) EPDM/CPE/PA blends for these four cases are given in Table III.

The best mechanical properties were obtained when CPE was preblended with PA. The mechanical properties increased in the following order: 3 < 4 < 1 < 2. Case 3 was the worst. Apparently, preblending CPE and PA was beneficial for obtaining a graft copolymer of CPE and PA, which was the actual compatibilizer in the EPDM/PA blends. From a comparison of the results listed in Table III, the simultaneous addition of all the components seems to be the most feasible method on an industrial scale.

Effect of the PA content

It is well known that rubbers are generally reinforced by carbon black. In this study, PA was used as a reinforcing agent for EPDM. To investigate the effect of the PA content on the mechanical properties of vulcanized EPDM/CPE/PA blends, we prepared a series of EPDM/CPE/PA blends with different PA contents. The results for the mechanical properties are shown in Figure 2.

The PA contents affected the properties of the blends significantly. As shown in Figure 2, the tensile strength and elongation at break increased with increasing PA contents and achieved a maximum at the PA content of 60 phr; this was followed by a descending curve. The tensile set at break and hardness increased steadily with the PA content at 0–100 phr. For the rubber/PA mass ratio of 100/40, the tensile strength was 14.2 MPa, and the elongation at break was 368%, whereas the Shore A hardness was only 72; this indicated that the 86/14/40 EPDM/CPE/PA

blend was an elastomer with excellent mechanical properties.

Typical stress–strain curves of EPDM/CPE/PA vulcanizates with various PA contents are shown in Figure 3. The strain–stress curves of the vulcanizates exhibit the characteristic of rubber tensile curves over the whole range of PA contents. No tensile yield appears in the curves with PA content of 0–100 phr; this indicates that rubber was the continuous phase.

Aging resistance of the vulcanized EPDM/CPE/PA blends

Table IV shows the aging resistance of vulcanized EPDM/CPE/PA blends and the EPDM vulcanizate reinforced by carbon black. The EPDM/CPE/PA vulcanizates maintained relatively high tensile strengths and elongations at break even after aging at 135°C for 168 h; this indicates that the vulcanizate had good aging resistance, the same as that of the carbon black reinforced EPDM vulcanizates.

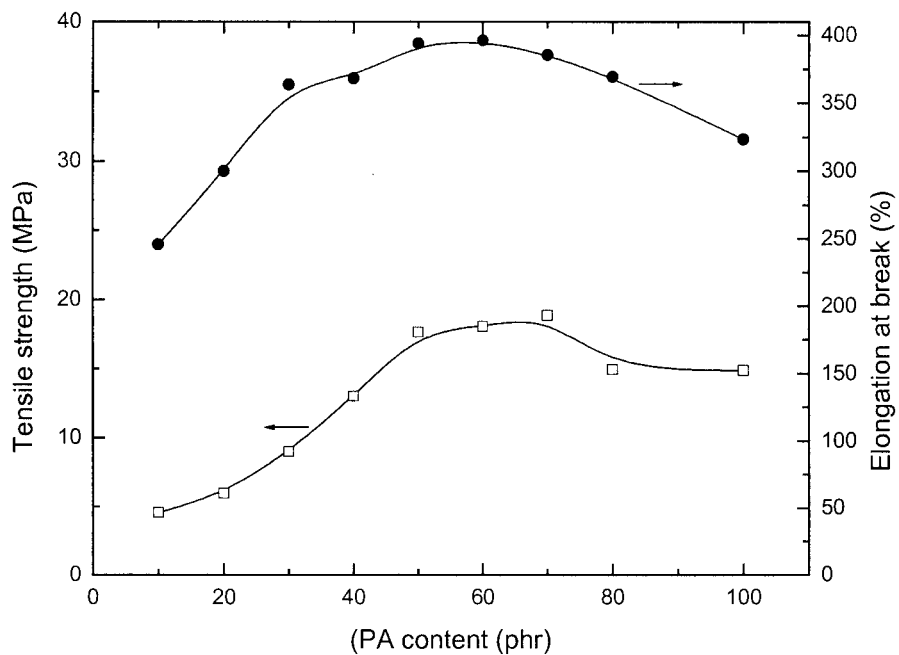
DSC

We performed DSC experiments to investigate the compatibility between EPDM and PA before and after the addition of CPE in the EPDM/PA blend. Table V shows the effect of the addition of CPE to the blending system on T_g 's of EPDM and PA.

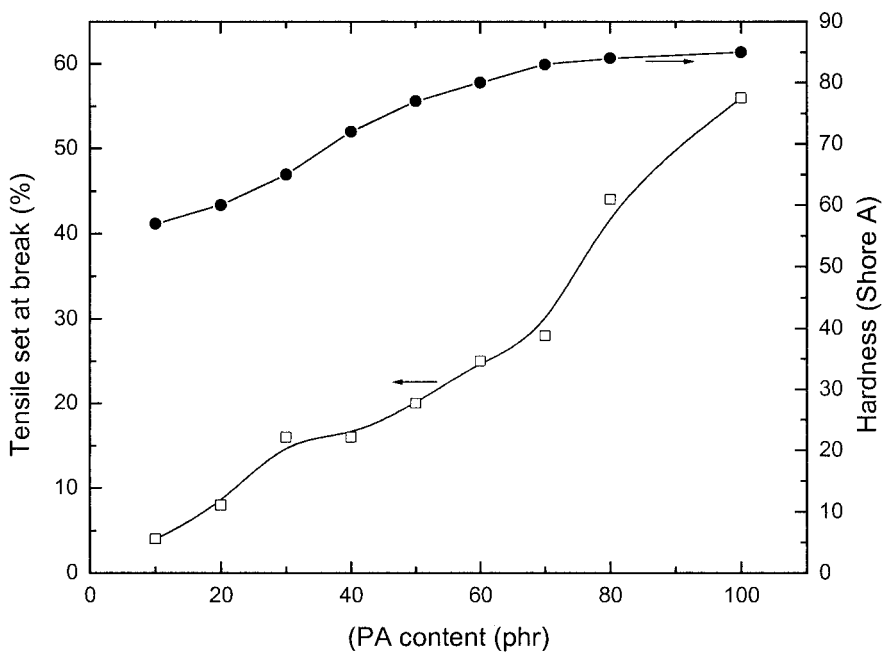
The blend was still a two-phase system. The T_g 's of pure EPDM, pure PA, and pure CPE were -50 , 20 , and -21 °C, respectively. T_g of EPDM in the simple EPDM/PA blends was the same as that of pure EPDM. However, T_g of PA in the simple EPDM/PA blends was 5°C higher than that of pure PA. The reason for this increase in T_g of PA is not known. In Table V, it can be seen that T_g of PA in the blends decreased 7°C when 14 phr CPE was added to the EPDM/PA blends. It has been reported that the segmental motion in chains of a polymer, when the polymer is attached to more components (i.e., lower T_g), is enhanced in the blend with respect to that in the homopolymer.¹⁴ This can be caused by the chemical reaction between PA and CPE. Moreover, the addition of CPE does not affect T_g of EPDM at all.

DMTA

The T_g 's (α transition) determined by DMTA for EPDM (cured with sulfur) and CPE (not cured but containing sulfur) were -36 and 6 °C, respectively [Fig. 4(a)]. T_g of PA was 34°C, and at low temperatures, a β peak (-67 °C) with a small intensity could be observed that was probably due to the relatively fast cooling process of the test specimen. This resulted in the preservation of weak hydrogen bonds between the carbon amide groups. A similar β peak



(a)



(b)

Figure 2 Effect of the PA content on the mechanical properties of vulcanized EPDM/PA blends (formulation: EPDM, 86; CPE, 14; S, 2; SA, 2; TMTD, 1; MBTS, 0.5; and ZnO, 5).

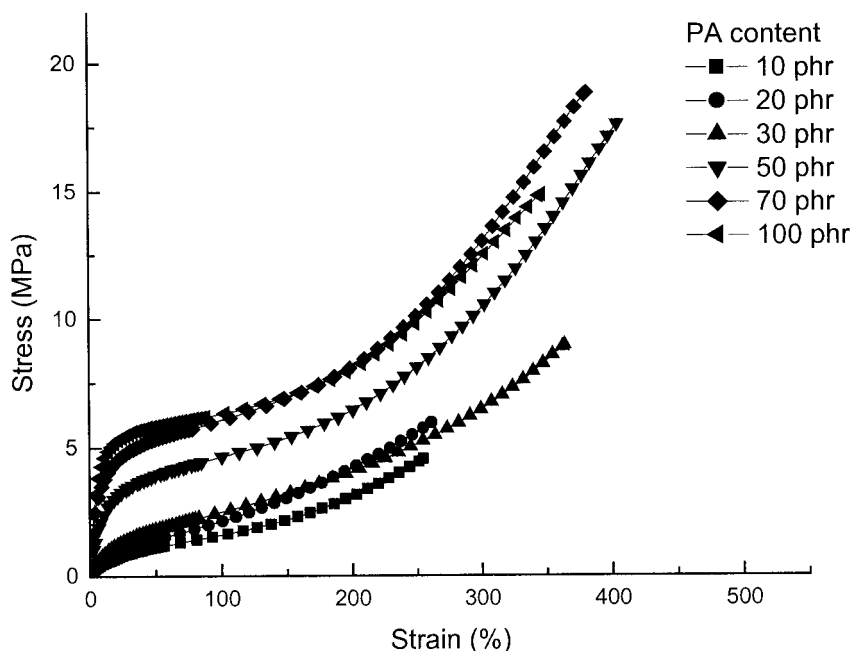


Figure 3 Strain–stress curves of vulcanized EPDM/PA blends with different PA contents (formulation: EPDM, 86; CPE, 14; S, 2; SA, 2; TMTD, 1; MBTS, 0.5; and ZnO, 5).

of PA could also be observed in the relaxation behavior of other kinds of PA, such as PA 6 or PA 66.¹⁵ The temperature dependence of the storage modulus for EPDM, CPE, and PA is shown in Figure 4(b). As expected, PA has a relatively high value in comparison with EPDM and CPE at a given temperature range.

The $\tan \delta$ values of blends for uncompatibilized and compatibilized EPDM/PA vulcanizates are shown in Figure 5. In 100/40 EPDM/PA blends, the T_g 's of EPDM and PA were -36 and 41°C , respectively. In the 86/14/40 EPDM/CPE/PA blend, the T_g 's of EPDM

and PA were -35 and 36°C , respectively. T_g of PA in the blends decreased by 5°C after 40 phr CPE was added to the blends. This indicated that the segmental motion of the PA chains occurred at lower temperatures in the ternary blend than in the EPDM/PA blend. T_g of EPDM in the blends remained unaltered, regardless of whether the blends were compatibilized or not. Figure 6 shows the storage modulus of blends having different EPDM/CPE/PA vulcanizates with different PA contents. The tendency of a high modulus with an increasing content of PA was reasonable. Therefore, the modulus of the blends could easily be controlled by adjustments to the PA contents in the EPDM/CPE/PA blends.

TABLE IV
Aging Resistance of PA-reinforced EPDM Vulcanizates and Carbon-Reinforced EPDM Vulcanizates (Aging at 135°C)

Sample	Time (day)	Tensile				Shore A hardness
		strength (MPa)	Elongation at break (%)	Tensile set at break (%)		
1	0	18.5	325	4	72	
	1	17.8	186	4	73	
	3	17.0	179	4	74	
	5	14.1	149	4	76	
	7	13.1	96	4	80	
2	0	14.2	367	28	72	
	1	14.0	142	24	75	
	3	13.8	141	18	75	
	5	13.7	119	18	74	
	7	13.5	99	17	78	

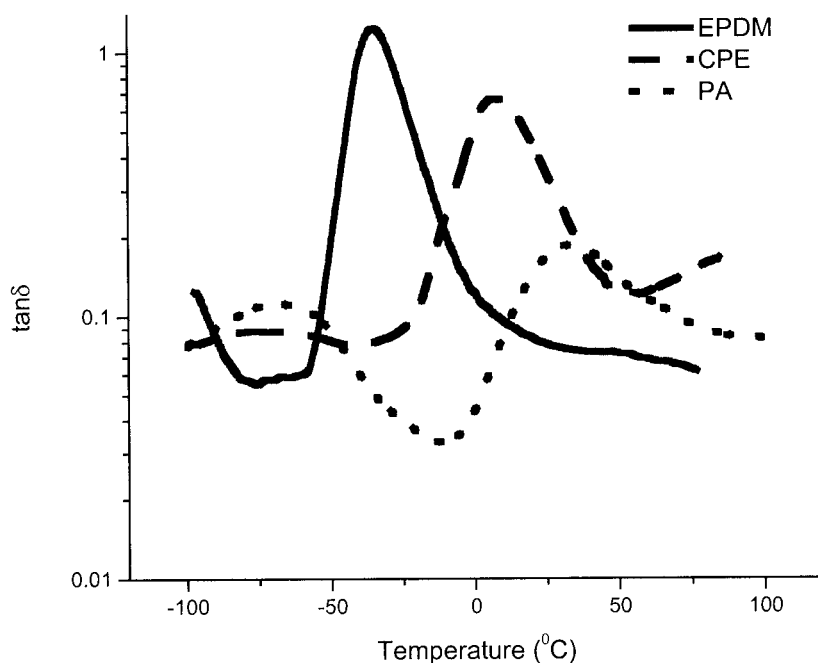
Formulation: 1. EPDM, 100; HAF N330, 40; S, 2; SA, 2; TMTD, 1; MBTS, 0.5; and ZnO, 5. 2. EPDM/CPE/PA, 86/14/40; S, 2; SA, 2; TMTD, 1; MBTS, 0.5; and ZnO 5.

Morphology of the vulcanized blends

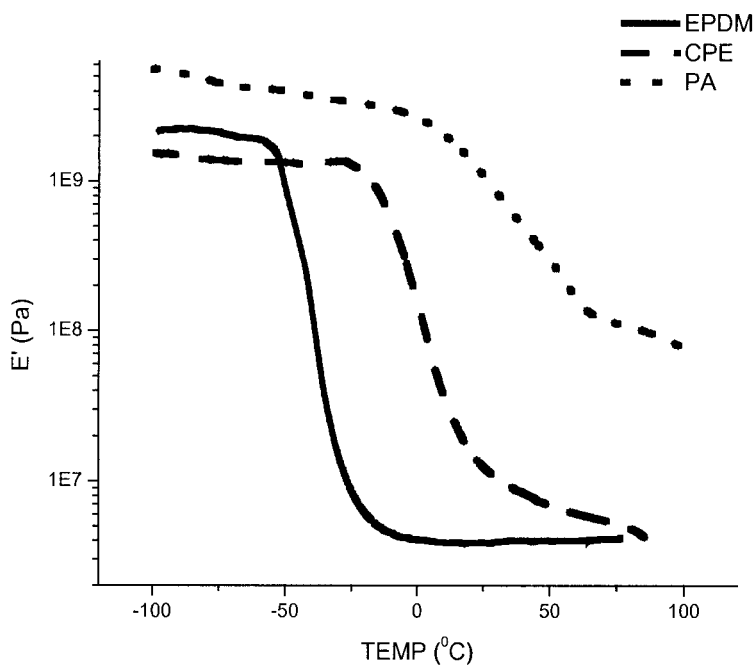
To determine the effect of the addition of CPE on the morphology of the vulcanized EPDM/PA blends,

TABLE V
Effect of the Addition of CPE in the Blend System on the T_g 's of EPDM and PA

Sample	T_{gEPDM} ($^\circ\text{C}$)		T_{gPA} ($^\circ\text{C}$)		T_{gCPE} ($^\circ\text{C}$)	
	DSC	DMTA	DSC	DMTA	DSC	DMTA
Pure EPDM	-50	-36*				
Pure PA			20	34		
Pure CPE					-21	6
100/40 EPDM/PA						
EPDM/CPE/PA blends (86/14/40)	-50	-36	25	41		
	-50	-35	13	36		



(a)



(b)

Figure 4 DMTA results for EPDM, PA, and CPE: (a) $\tan \delta$ and (b) the storage modulus (E').

we observed a series of samples with SEM. The tensile-fractured surfaces of the 100/40 EPDM/PA and 86/14/40 EPDM/CPE/PA blends are shown in Figure 7. The dispersed PA phase was pulled out

from the rubber matrix under stress, and the fractured surface was smooth on the EPDM/PA micrograph. The surface was smooth, and the dispersed nylon particles were not uniform. In comparison

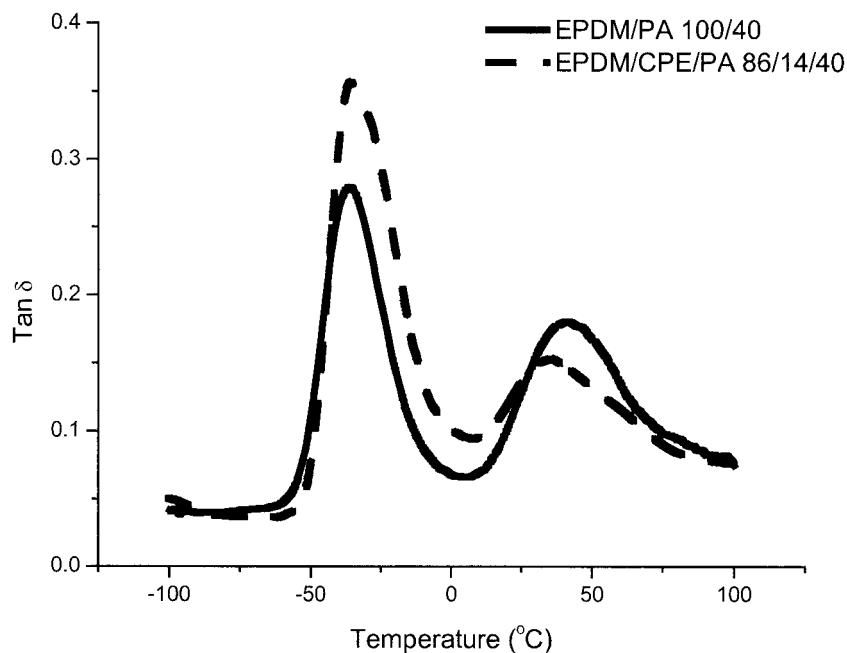


Figure 5 Tan δ as a function of temperature for EPDM/PA and EPDM/CPE/PA blends.

with the EPDM/PA micrograph, the tensile-fractured surface of EPDM/CPE/PA was rough and coarse.

The brittle failure surfaces of 100/40 EPDM/PA and 86/14/40 EPDM/CPE/PA blends are shown in Figure 8. The hole formed by the etching of the dispersed PA phase from the EPDM matrix was not uniform within the range of 5–50 μm on the EPDM/PA micrograph. In comparison with the EPDM/PA micro-graph, the hole on the EPDM/CPE/PA micrograph was more

uniform within the range of 3–10 μm . This proved that the addition of CPE made the dispersed phase smaller and well distributed and, therefore, improved the mechanical properties of the compatibilized vulcanizates.

CONCLUSIONS

An *in situ* compatibilized EPDM/CPE/PA vulcanizate with excellent mechanical properties was prepared. In comparison with other compatibilizers, both CPE and

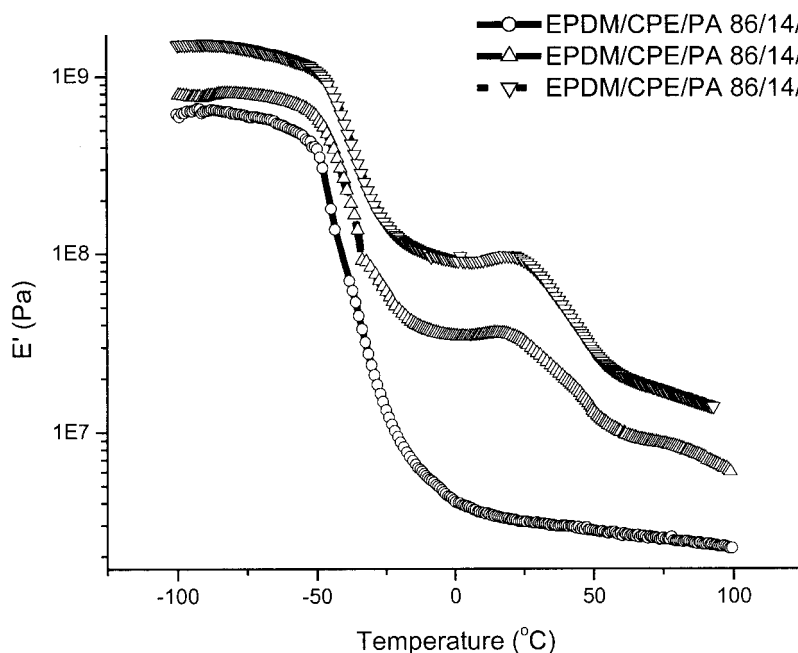
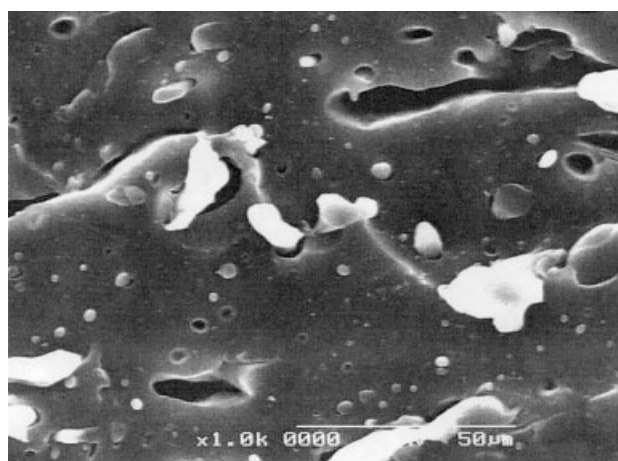
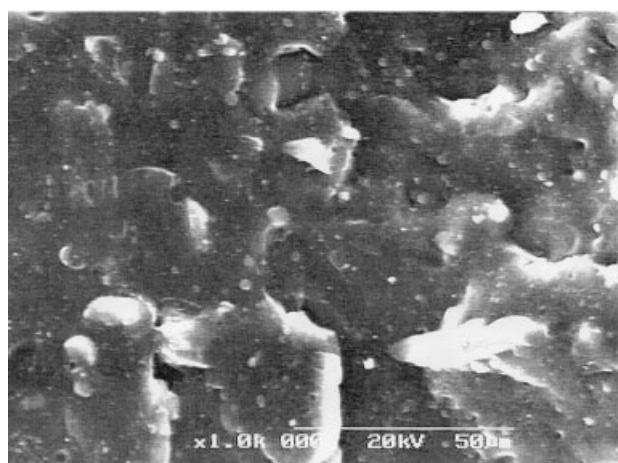


Figure 6 Storage modulus (E') of EPDM/CPE/PA blends of different compositions.

MAH-g-EPDM had better performance in compatibilizing EPDM/PA blends. The vulcanized EPDM/CPE/PA blend with sulfur as a curative had a higher tensile strength than EPDM/CPE/PA cured by DCP. However, the vulcanized EPDM/compatibilizer/PA blend with DCP as a curative had a higher elongation than the vulcanized blend with sulfur as a curative. Both the tensile strength and elongation at break increased with increasing CPE contents in the EPDM/CPE/PA blends. A suitable CPE content was about 14–20 phr. The tensile strength and elongation at break of the vulcanized EPDM/CPE/PA blends achieved a maximum at a PA content of 60 phr, and this was followed by a decrease. The stress–strain curves of the EPDM/PA vulcanizates exhibited characteristic rubber tension over the whole range of PA contents. Both DSC and DMTA experiments indicated that the addition of CPE did not affect T_g of EPDM but did reduce T_g of PA. The SEM results showed that the addition of CPE could reduce the particle size of the

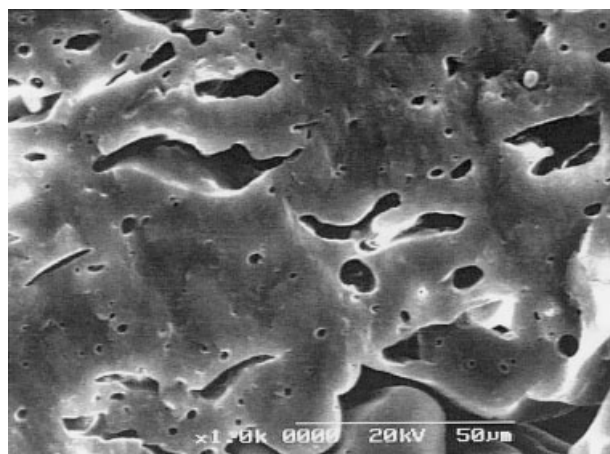


(a)

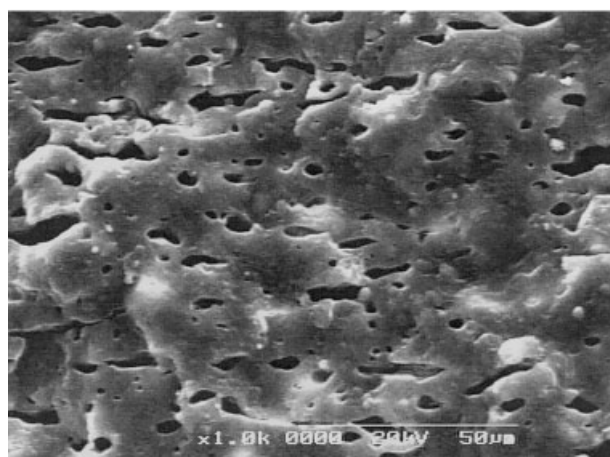


(b)

Figure 7 SEM micrographs of (a) 100/40 EPDM/PA and (b) 86/14/40 EPDM/CPE/PA blends (tensile-fractured surface).



(a)



(b)

Figure 8 SEM micrographs of (a) 100/40 EPDM/PA and (b) 86/14/40 EPDM/CPE/PA blends (brittle failure surface).

PA phase that existed at an average size of 5 μm in the vulcanized EPDM/CPE/PA blends. The EPDM/CPE/PA blends had good thermal aging resistance.

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