

Mercapto-Modified Copolymers in Polymer Blends. III. The Effect of Functionalized Ethylene-Propylene-Diene Rubber (EPDM) on Curing and Mechanical Properties of NBR/EPDM Blends

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ABSTRACT: Ethylene-propylene-diene with ethylene norbornene as the diene (EPDM) samples functionalized with thioacetate (EPDMTA) or mercapto groups (EPDMSH) were employed as compatibilizing agents for nitrile rubber (NBR)/EPDM blends. The cure rate of the blend was affected by the presence of a small portion of these compounds. EPDMTA decreases the cure rate of the blends, whereas EPDMSH was able to decrease the scorch time and increase the cure rate when employed in a proportion as high as 5.0 phr. The compatibilization effect was influenced by the nature of the EPDM employed in the blends. Blends consisting of an EPDM sample with lower viscosity display better dispersion of the EPDM phase inside the NBR matrix and also better mechanical performance with the compatibilization. The compatibilization with EPDMSH is reactive, with the formation of chemical bond between the mercapto groups of the compatibilizing agent and the double bond of the diene rubber. The compatibilization with EPDMTA is also considered to be reactive because the vulcanized blends containing this functionalized copolymer contain a higher amount of cross linked material, as indicated by the lower weight loss after swelling experiments. A scanning electron micrograph demonstrated that these functionalized copolymers led to a finer phase morphology, mainly in NBR/EPDM57C blends. The compatibilization increases the dynamic elastic modulus without affecting the damping. An improvement of thermal aging resistance of the studied blends was also achieved with the presence of the functionalized copolymers. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 38–52, 2001

Key words: elastomer blends; NBR; EPDM; compatibilization; mercapto-modified copolymer

INTRODUCTION

Blending of rubbers is a common practice to produce a vulcanized compound whose physical properties show the desirable features of the compo-

nent elastomers. It is known that the ozone resistance of high-diene rubbers such as natural rubber (NR), styrene-butadiene rubber (SBR), nitrile rubber (NBR), or polybutadiene (BR) can be very greatly improved by the incorporation of low-unsaturated rubbers such as ethylene-propylene-diene rubber with ethylene norbornene as the diene (EPDM). However, some other important properties may be decreased as a consequence of

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Table I Characteristics of Original Elastomers

Material	Commercial Grade	E/P Ratio	Diene Content	MW	Mooney Viscosity	Solubility Parameter (MPa ^{1/2})
Ethylene-Propylene-Diene Terpolymer	EPDM 57C	73/27	58.9 (mmol/100 g)	80,000	90	17.2
	EPDM 65	60/40	114 (mmol/100 g)	230,000	77	16.1
Nitrile rubber	N 615-B	—	67 (wt %)	380,000	48	21.4

incompatibility. In the case of elastomer blends, the incompatibility is due not only to the differences in miscibility between the blend components but mainly to the difference in cure rate. The literature has shown that the difference in unsaturation level of polydiene rubbers and EPDM and the presence of polar groups in some polydiene rubbers, for example, NBR, frequently result in a maldistribution of cross links in the blend system.¹⁻³

Many efforts have been made to solve this problem, including the addition of lead oxide in substitution of zinc oxide,⁴ the halogenation of EPDM to improve sulfur vulcanization,⁵ the chemical modification of the accelerators to improve their solubility in both phases,⁶ and the grafting of the accelerator onto the elastomer in which the solubility is lower.⁷ The functionalization of EPDM with maleic anhydride has been also employed to improve the mechanical properties of NR/EPDM blends.^{3,8,9} More recently, the use of poly-*trans*-octylene (TOR) as compatibilizing agent in NR/EPDM blends has been reported to produce a fine morphology and improvement in the ultimate properties of these blends.¹⁰

The compatibilization of NBR/EPDM blends is also a challenge because the components present differences in unsaturation level and also in polarity. Several approaches have been developed to improve the compatibilization of this blend; such as, the use of TOR,¹¹ polychloroprene,¹²⁻¹⁵ polybutadiene,¹⁵ chlorinated polyethylene,^{15,16} and chlorosulfonated polyethylene.^{15,16} All these compounds increase the compatibility of NBR/EPDM or NBR/EPR. According to Setua et al.,¹⁵ the chlorinated polyethylene has been found to be a universal compatibilizer for all NBR/EPM blends, irrespective of different acrylonitrile concentrations in the NBR, thus producing remarkable improvement in the physicomechanical properties of the vulcanizates.

The addition reactions of thiol groups with the carbon=carbon double bond of unsaturated poly-

mers have been well documented in the literature.¹⁷⁻¹⁹ Based on this principle, we have recently developed mercapto-modified ethylene-vinyl acetate copolymers and employed this functionalized polymer on the compatibilization of NR/EVA blends.²⁰⁻²² The mercapto groups along the EVA backbone were added to the double bonds of the diene rubber during the melt blending process, thus promoting an effective anchorage between the phases. Good aging resistance was also achieved with the compatibilization.²² The efficiency of polymer-carrying mercapto groups in promoting the compatibilization of elastomer blends prompted us to continue our research by introducing mercapto groups along the EPDM backbone and using it as a compatibilizing agent in NR/EPDM²³ and NBR/EPDM blends.²⁴ These preliminary studies revealed that the compatibilization of functionalized EPDM was more effective in NR/EPDM blends, although it also improved the curing parameters and aging properties of NBR/EPDM blends.

In this work, the effects of the functionalized EPDM samples on the curing parameters, mechanical and dynamic mechanical properties, and morphology of NBR/EPDM blends were examined by using EPDM samples with different chemical composition. Both EPDM-carrying thioacetate groups (EPDMTA) and mercapto groups (EPDMSH) were employed as the compatibilizing agents.

EXPERIMENTAL

Materials

Nitrile rubber with 33 wt % of acrylonitrile (NBR) and ethylene-propylene-diene rubber with ethylene norbornene as the diene (EPDM) were kindly supplied by Nitriflex S.A (Brasil) and DSM elastômeros S/A (Brasil), respectively (see Table I for the feature). Mercapto-modified EPDM was obtained in our laboratory, according to literature,²⁴

Table II Formulation of Blend Compounds

Component	phr
NBR/EPDM 57C or EPDM 65	70/30
Zinc oxide	5.0
Stearic acid	0.5
Sulfur	0.3
MBTS	2.0
TMTD	1.0

by a free-radical addition reaction of thioacetic acid to the double bond of the EPDM polymer (EPDMTA) followed by methanolysis of the acetylthio groups with methanolic solution of sodium hydroxide. The EPDM sample used for the synthesis of the functionalized copolymer was EPDM65. The amount of mercapto groups in the functionalized copolymer corresponded to 1.5 wt % of sulfur content, as determined by Fourier transform infrared (FTIR) analysis and coulometric titration. Other chemicals, such as zinc oxide, stearic acid, sulfur, mercaptobenzothiazole sulfonamide (MBTS), and tetramethyl thiuram disulfide (TMTD), were of the laboratory reagent grade.

Mixing and Measurement of Cure Characteristics

Mixing was carried out in a Bersthof two-roll mill at 110 °C. NBR was first masticated for 3 min and blended with the EPDM component, followed by the activators (zinc oxide, stearic acid), sulfur, and accelerators (MBTS and TMTD; see Table II for the amount of each ingredient). The functionalized copolymer was added either after the NBR mastication or after the addition of EPDM. In some experiments, a batch containing the compatibilizing agent and the EPDM component in a proportion of 50:50 wt % was first prepared and added to the NBR/EPDM blend, before the addition of the activator, accelerators, and sulfur.

The cure characteristics of the mixes were determined with an oscillating disk rheometer (Monsanto, R-100) at 160 °C and 1 arc degree, following the ASTM D-2084-81 method. The cure rate was determined by eq. 1:

$$RH = \frac{M_{45} - M_{25}}{t_{45} - t_{25}} \quad (1)$$

where M_{45} and M_{25} are the values of torque at 45 and 25% of cure, respectively, and t_{45} and t_{25} are

the times corresponding to 45 and 25% of cure, respectively. The values corresponding to 45 and 25% of cure were chosen because these data refer to the linear portion of the rheometric curve.

The specimens for mechanical testing were compression-molded at 160 °C under 6.7 MPa pressure and at the optimum cure times (the time corresponding to 90% of the maximum torque, t_{90}) as determined by the rheometric analysis.

Measurement of the Mechanical Properties

Tensile-strain experiments were performed with an Instron 4204 testing machine at room temperature at a speed of 200 mm/min following DIN procedure 53504. The samples were conditioned at 21 °C and 53% air humidity for 24 h before the testing.

Aging Experiments

Accelerated aging of the compression-molded specimens was carried out in an air-circulating oven at 70 °C for 72 h.

Dynamic Mechanical Thermal Analysis

Dynamic mechanical measurements were carried out on dynamic mechanical thermal analyzer Rheometric Scientific MKIII equipment with a temperature programmer and controller. The experiment was conducted in a bending mode from -60 to +20 °C at a frequency of 1 Hz with a programmed heating rate of 2 °C/min.

Degree of Equilibrium Swelling Measurement

Cured test pieces of dimension 20 × 10 × 2 mm were swollen in toluene or in methyl ethyl ketone (MEK) until equilibrium swelling occurred. After reaching the equilibrium, the swollen test pieces were weighed, then dried under vacuum, and again weighed. The swollen and deswollen weights were used to calculate the volume fraction of rubber in the network swollen to equilibrium, V_r , according to the following expression:

$$V_r = \frac{D \times \rho_r^{-1}}{D \times \rho_r^{-1} + (S - D) \times \rho_s^{-1}} \quad (2)$$

where D = deswollen weight, S = swollen weight, ρ_r = density of rubber blend, and ρ_s = density of solvent.

Morphological Studies

The molded samples were cryogenically fractured. The surface was exposed to a methanolic bromine solution (10% v/v) for ~2 h to preferentially stain the NBR phase. The samples were then vacuum dried for 48 h. The surface was covered with a thin layer of gold and analyzed on a JEOL JSM 5800 LV scanning electronic microscope (SEM), using a back-scattered detector.

RESULTS AND DISCUSSION

Curing Parameters

NBR/EPDM (70/30) blends were compounded with EPDM samples with different chemical compositions. Initially, the compatibilized blends were made by adding the functionalized EPDM just after the NBR to enhance the interaction between the mercapto or thioacetate groups of the compatibilizing agent with the double bond of the diene-rubber. The results concerning the curing parameters of these blends as a function of the compatibilization are shown in Table III. The minimum (M_L) and maximum (M_H) torque values were not affected by the addition of EPDMTA in both blend systems. On the other hand, EPDMSH promotes a considerable increase in the minimum torque of both NBR/EPDM57C and NBR/EPDM65 blends, suggesting some interactions between the polymer chains. In spite of an increase in M_L and M_H with the addition of EPDMSH, the differences ($M_H - M_L$) are similar, indicating that the cross linking degree is not affected by the presence of this functionalized copolymer.

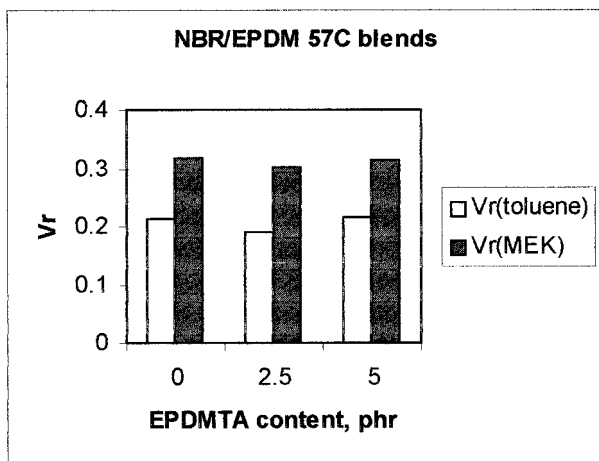
Concerning the cure rate, blends prepared with EPDM65 presented lower cure rate than those prepared with EPDM57C. For blends constituted by EPDM57C, a low amount of EPDMTA (2.5 phr) reduces the scorch time and increases the optimum cure time. As a consequence, there is a retardation of the cure rate. Increasing the amount of EPDMTA results in a scorch protection and an increasing of the cure rate, but the latest value is still lower than that of noncompatibilized blend. The presence of EPDMTA maintains the scorch protection of blends consisting of EPDM 65 samples and also increases the cure rate.

The scorch protection of blends containing EPDMSH was strongly reduced. The cure rate values of blends containing 2.5 phr of EPDMSH decreases substantially in comparison with non-

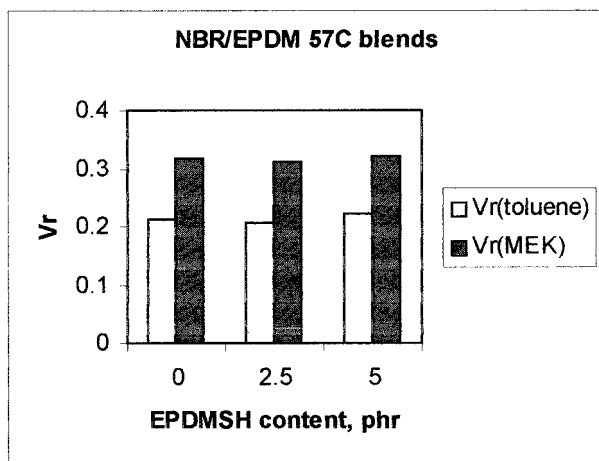
Table III Curing Parameters of NBR/EPDM (70 : 30 phr) Blends

EPDMTA (phr)	EPDMSH (phr)	NBR/EPDM57C Blends					NBR/EPDM65 Blends				
		Minimum Torque, M_L (lb · in)	Maximum Torque, M_H (lb · in)	Scorch Time, t_{s1} (min)	Optimum Cure Time, t_{90} (min)	Cure Rate ^a (lb · in/min)	Minimum Torque, M_L (lb · in)	Maximum Torque, M_H (lb · in)	Scorch Time, t_{s1} (min)	Optimum Cure Time, t_{90} (min)	Cure Rate ^a (lb · in/min)
0	0	4.0	18.0	5.3	8.0	11.2	3.5	17.3	5.3	8.3	6.2
2.5	0	4.5	19.0	3.8	8.8	4.6	4.0	17.5	5.3	8.8	7.2
5.0	0	4.3	19.3	5.8	9.5	8.8	4.5	18.5	5.5	11.5	7.5
0	2.5	7.5	22.5	2.1	5.8	4.4	9.0	24.0	2.5	5.8	2.7
0	5.0	9.0	24.5	2.8	5.3	12.4	10.0	23.5	3.3	5.3	10.8

^a Cure rate, RH = $[(M_{45} - M_{2.5})/(t_{45} - t_{2.5})]$.



(a)



(b)

Figure 1 Degree of equilibrium swelling in toluene and MEK for NBR/EPDM 57C as a function of (a) EPDMTA content and (b) EPDMSH content.

compatibilized blends. However, increasing the amount of EPDMSH resulted in the highest values of cure rate, indicating that the mercapto groups along the EPDMSH backbone act as accelerators in the curing process.

Degree of Equilibrium Swelling

Degrees of equilibrium swelling, V_r , were determined in toluene, which is a good solvent for both NBR and EPDM phases, and in MEK, which can only dissolve or swell the NBR phase. The results concerning the degrees of equilibrium swelling for NBR/EPDM57C blends are illustrated in Figure 1. There is no substantial variation in the V_r values on addition of EPDMTA or EPDMSH in both studied systems, although the values ob-

tained with the compatibilization with EPDMSH are a little higher. These results are in agreement with the torque values observed in rheometric analyses and indicate that neither functionalized copolymers exerts any considerable influence on the cross linking degree. The V_r values obtained in experiments with MEK are higher because this solvent is not able to swell the EPDM phase. The weight loss percentage in experiments performed with toluene are significantly higher than those observed in experiments carried out with MEK. These values are summarized in Table IV. This behavior indicates that the soluble material in experiments with toluene must be mainly constituted by the EPDM phase. This hypothesis has been confirmed by FTIR analysis of the soluble material.

In spite of a small decrease in the cross linking degree, as indicated by the lower values of V_r , the addition of EPDMTA also resulted in an increase in the amount of insoluble material (see Table IV). This phenomenon was only observed when the experiments were performed in toluene, indicating that the EPDMTA increases the amount of the EPDM phase in a cross linked situation. As will be discussed later, the EPDMTA is not able to chemically react with the double bond of the elastomer during the mixing process. Therefore, these intriguing results may be associated to the presence of the vulcanizing agent that should react with the thiocetate groups of the EPDMTA, giving rise to free radical species responsible for the cross linking. This phenomenon occurs mainly in the EPDM phase.

The swelling results for NBR/EPDM 65 blends are presented in Figure 2. The behaviors are quite similar; that is, the addition of EPDMTA leads to lower values of V_r but also lower values of weight loss. On the other hand, the addition of EPDMSH results in better values of V_r and also in a decrease in the weight loss compared with the non-compatibilized blend.

The results from both NBR/EPDM57C and NBR/EPDM65 blends indicate different interaction tendencies. EPDMTA interacts preferentially with the EPDM phase, as shown by the higher reduction of weight loss in the blends. In contrast, EPDMSH interacts preferentially with the NBR phase, exhibiting less of a reduction in weight loss than EPDMTA, producing higher values of V_r , and improving the cross linking of this phase.

Table IV Degree of Equilibrium Swelling and Weight Loss Percentage for Vulcanized NBR/EPDM Blends as a Function of the Compatibilization

		NBR/EPDM57C Blends			
		Swelling Experiments in Toluene		Swelling Experiments in MEK	
EPDMTA, phr	EPDMSH, phr	V_r	Weight Loss, %	V_r	Weight Loss, %
0	0	0.2108	24.4	0.3160	3.8
2.5	0	0.1915	9.0	0.3029	4.2
5.0	0	0.2119	19.0	0.3156	4.3
0	2.5	0.2077	24.5	0.3099	4.4
0	5.0	0.2222	20.4	0.3208	3.8
NBR/EPDM65 Blends					
0	0	0.1924	29.5	0.2609	3.4
2.5	0	0.1874	10.0	0.2826	3.2
5.0	0	0.1789	13.0	0.2930	2.0
0	2.5	0.2055	25.7	0.2618	3.7
0	5.0	0.2055	27.0	0.2844	3.6

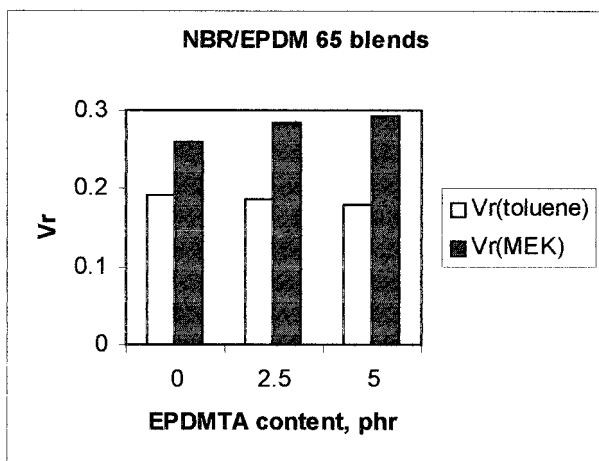
Mechanical Properties

The mechanical properties of these blends are summarized in Table V. The ultimate tensile strength and hardness values for noncompatibilized blends are higher when EPDM57C is used as a blend component because of the higher viscosity and less elastomeric nature of the EPDM57C sample. The addition of the functionalized copolymers (EPDMTA or EPDMSH) resulted in lower values of both ultimate tensile strength and elongation at break. The compatibilization of NBR/EPDM65 blends was more effective. Indeed, both EPDMTA and EPDMSH increased the tensile strength and elongation at break when 5.0 phr of these compound were employed.

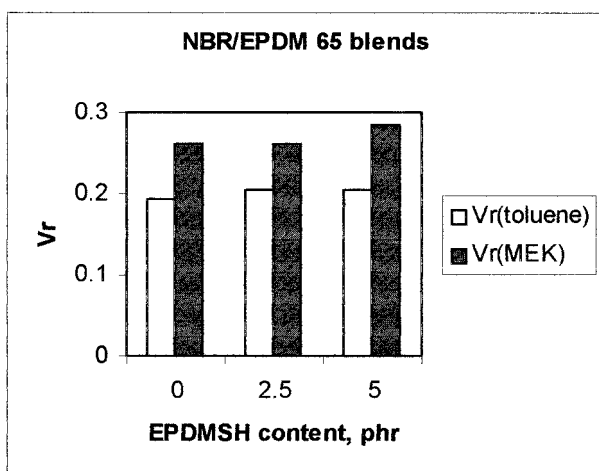
The compatibilization by functionalized EPDM is believed to happen through a chemical reaction of the functionalized groups (thioacetate or mercaptan) with the double bond of the diene rubber during the blending process. This reaction event should give rise to an insoluble material consisting of NBR and EPDM chains. To observe this kind of interaction, small amounts of NBR/EPDMTA and NBR/EPDMSH blends were withdrawn from the roll-mill before the addition of the other blend components. These aliquots were submitted to extraction with hot toluene for 24 h, which can dissolve all blend components. After this treatment, no insoluble material could be detected from the NBR/EPDMTA blend, indicat-

ing that the thioacetate groups were not able to react with the double bond during the blending. In the case of NBR/EPDMSH, a considerable amount of insoluble material was isolated, confirming the chemical reaction between the mercapto groups along the EPDMSH backbone and the double bond of the NBR phase, as shown in Figure 3.

This insoluble material was analyzed by FTIR spectroscopy using the multiple internal reflectance accessory. NBR and EPDMSH samples were prepared by hot-pressing films at 160 °C for few minutes while the insoluble material was dried and then analyzed. The FTIR spectra of NBR, EPDMSH, and the insoluble material obtained from blending NBR and EPDMSH are compared in Figure 4. The NBR spectrum displays characteristic absorptions at 2237 cm^{-1} (related to nitrile groups), 1438 cm^{-1} (related to methylene groups), 968 cm^{-1} (related to 1,2-disubstituted $-\text{CH}=\text{CH}-$) and 918 cm^{-1} (related to vinyl groups, $-\text{CH}=\text{CH}_2$). Concerning EPDMSH, the characteristic peaks are located at 1462 cm^{-1} ($-\text{CH}_2-\text{CH}_3$), 1376 cm^{-1} ($-\text{CH}_3$), and at 720 cm^{-1} ($-\text{CH}_2$). Finally, the spectrum of the insoluble material has absorptions related to both NBR and EPDMSH components; that is, the absorption at 2250 cm^{-1} indicates the presence of NBR and other absorptions that could be attributed to both components. This result confirms the chemical reaction between the mercapto groups of



(a)



(b)

Figure 2 Degree of equilibrium swelling in toluene and MEK for NBR/EPDM 65 as a function of (a) EPDMTA content and (b) EPDMSH content.

EPDMSH and the double bond of the diene rubber component.

In spite of the ability of the mercapto groups to react with the NBR during mixing, there is no improvement in the mechanical performance in the case of NBR/EPDM57C blends. As indicated in Table I, the viscosity of the EPDM57C is substantially higher than that of NBR. Therefore, the dispersion of the EPDM phase into the NBR matrix is poor. In addition, the functionalized copolymer was first blended with the NBR component. This blend procedure contributes to a good dispersion of EPDMSH inside the NBR phase but is not able to bring together the EPDM phase of the blend because of its high viscosity. The distribution of EPDMSH inside the NBR phase may explain the accelerator role of this copolymer on the curing process.

In the case of NBR/EPDM65 blends, the EPDM component presents lower viscosity and can be better dispersed in the NBR matrix. Therefore, the compatibilizer action should be more effective, as indicated by the improvement in the ultimate tensile strength.

Effect of the Mixing Procedure on the Curing Parameters and Mechanical Properties

As discussed in the preceding section, the compatibilization was more effective in NBR/EPDM65 blends, probably because of the lower viscosity of this EPDM sample. However, because NBR has a lower viscosity, this phase tends to encapsulate the EPDMSH (or EPDMTA) and the interfacial action of these functionalized copolymers is not so effective. To overcome these problems, we performed some experiments by modifying the mixing order and also by adding the previously prepared graft copolymer of NBR and

Table V Mechanical Properties of NBR/EPDM (70 : 30 phr) Blends

EPDMTA (phr)	EPDMSH (phr)	NBR/EPDM57C Blends			NBR/EPDM65 Blends		
		σ_B^a (MPa)	ε_B^b (%)	Hardness Shore A	σ_B^a (MPa)	ε_B^b (%)	Hardness Shore A
0	0	3.4	1190	44	2.1	1130	41
2.5	0	2.7	1000	43	2.2	1100	41
5.0	0	3.0	1030	43	2.9	1200	41
0	2.5	2.5	970	45	2.3	1000	40
0	5.0	3.0	850	43	2.9	1230	40

^a Ultimate tensile strength.

^b Elongation at break.

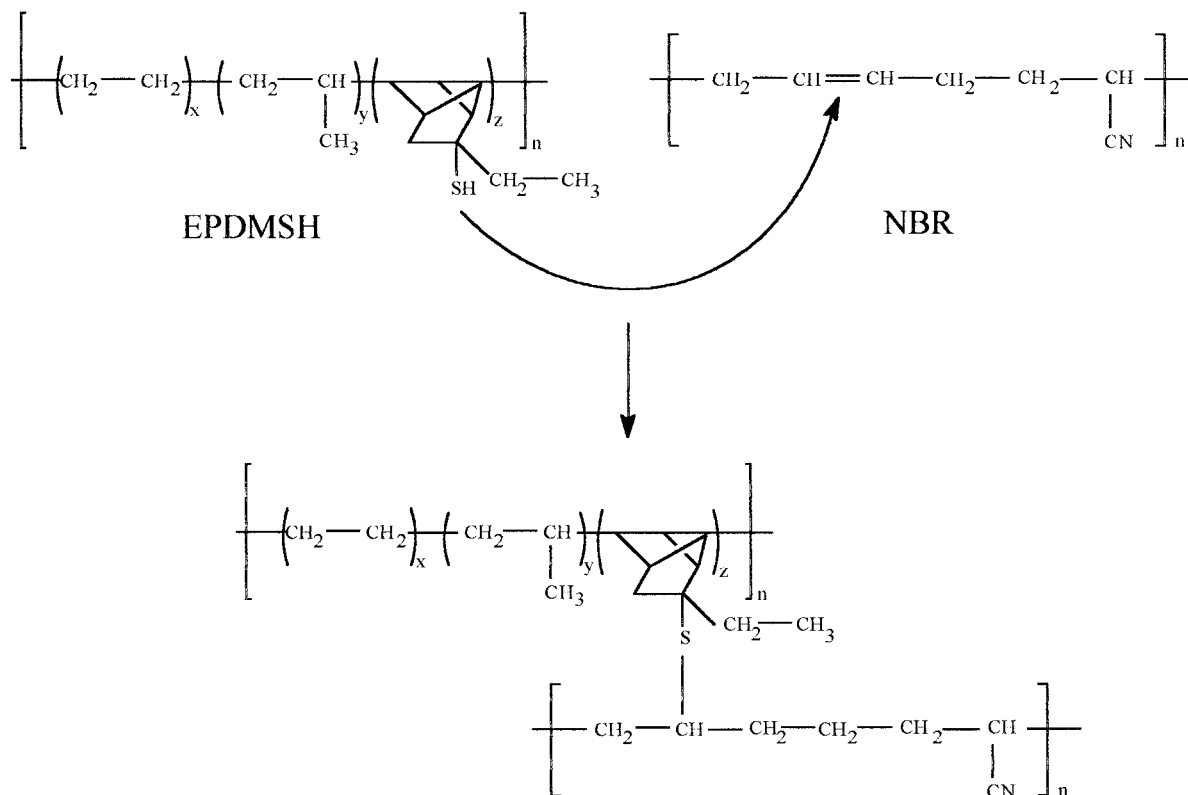


Figure 3 Scheme of the reaction between NBR and EPDMSH.

EPDM. As reported in the literature,¹⁵ when the compatibilizing agents are mixed in advance with the EPM component, they are able to form a skin on the EPM particles and help NBR to adhere to them, thereby producing a fine morphology and better properties.

In a similar manner, the addition of EPDMTA or EPDMSH was made after the mastication of EPDM. Additionally, we have previously prepared a NBR/EPDM graft copolymer by blending NBR/EPDMSH in a proportion of 50:50 wt %. The formation of the graft copolymer was confirmed by the presence of insoluble material, as previously discussed. EPDMTA, EPDMSH, or the graft copolymer were then used in blends with EPDM65 as the blend component, which was added after the EPDM mastication. The blend formulation was the same as that described in Table II, and the amount of EPDMTA or EPDMSH was 5.0 phr, which gave the best results in the earlier studies. The NBR/EPDM graft copolymer was also used in a proportion of 10.0 phr, which corresponds to 5.0 phr of EPDMSH). The curing parameters and mechanical properties of compatibilized NBR/EPDM65 (70:30 wt %) blends

as a function of the mixing procedure are compared in Table VI.

Concerning the rheometric parameters, the addition of the compatibilizing agents after the EPDM does not promote any changes in the minimum or maximum torque, which increases only slightly compared with the noncompatibilized blend. As a consequence, the difference ($M_H - M_L$) increases a little for the compatibilized blends, but not enough to produce great changes in the cross linking degree. The scorch protection is reduced for all compatibilized blends, but EPDMSH exerts the highest influence. Finally, blends containing EPDMTA and EPDMSH cure faster than the noncompatibilized blend, whereas blends compatibilized with the graft copolymer present a lower cure rate. Comparing the two orders of addition of compatibilizers, it can be noted that the addition before the EPDM mastication produces a faster cure for EPDMSH.

All compatibilized blends displayed better ultimate tensile strength compared with the noncompatibilized blend, without substantial changes in the elongation at break. Except for blends compatibilized with EPDMTA, the manner in which

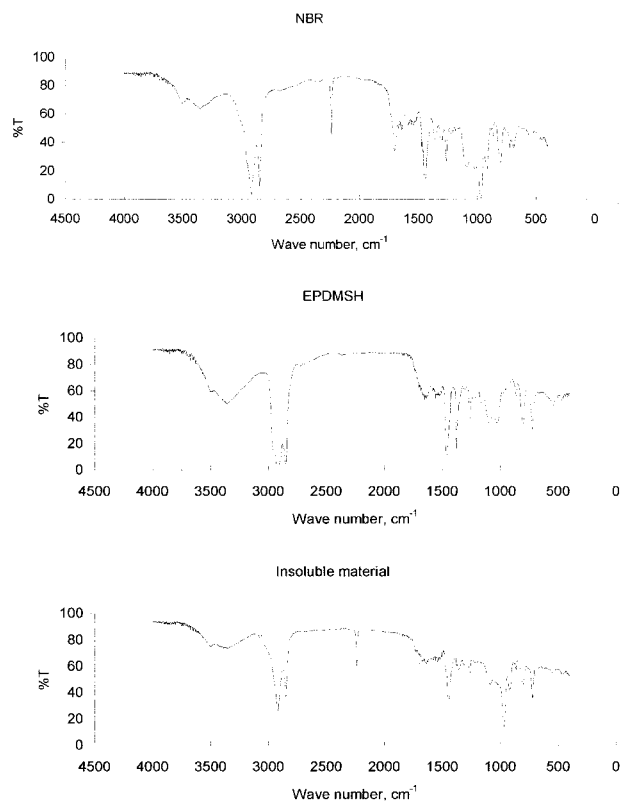


Figure 4 FTIR spectra of NBR, EPDMSH and the insoluble material obtained from NBR/EPDMSH blend.

the compatibilizing is compounded in the mixing did not affect the mechanical properties. In addition, the blend compatibilized with EPDMTA displayed higher values of tensile strength and elongation at break when the compatibilizer was added after the EPDM.

The swelling tests revealed that even in this new order of addition there was weight loss for all compatibilized blends, although both EPDMTA and the graft copolymer greatly reduced this problem compared with the noncompatibilized blend. The values obtained for V_r are very similar in all blends, indicating that the compatibilization did not improve the cross link density regardless of the addition order of the compatibilizers.

Morphology

The effect of the compatibilization on the morphology of the NBR/EPDM blends was studied by scanning electron microscopy. The photomicrographs of NBR/EPDM 57C blends are shown in Figure 5. The dark phase corresponds to the

EPDM phase because this component does not contain enough double bond to be stained with bromine. The addition of 5 phr of both EPDMTA (Figure 5b) or EPDMSH (Figure 5c) resulted in a substantial decrease in the EPDM dispersed phase. The effect of the compatibilization on NBR/EPDM 65 blends is illustrated in Figure 6. In this case, the presence of EPDMTA or EPDMSH does not exert any influence on the dispersion of EPDM phase. The morphology of compatibilized blends prepared by adding the EPDMTA (Figure 7a), EPDMSH (Figure 7b), or the graft copolymer (Figure 7c) after the EPDM mastication is illustrated in Figure 7. In the case of EPDMTA, one can observe a morphology characterized by a more elongated and thinner EPDM phase.

Dynamic Mechanical Properties

Dynamic mechanical analyses were performed on blends whose compatibilizing agents were added after the NBR component. The dynamic moduli and $\tan \delta$ of noncompatibilized blends over the temperature range -60 – -20 °C are shown in Figure 8. Both blends present two damping peaks, confirming the incompatibility of the components. Blend composed of EPDM57C (curve a) displays a higher dynamic elastic modulus (E') than that composed with EPDM65 because of the higher viscosity of the former. The damping peak related to NBR phase appears around -12 °C, whereas that related to the EPDM phase appears in the range -40 – -48 °C. Both transitions are influenced by the nature of the EPDM. The NBR/EPDM65 blend (curve b) present lower glass transition temperatures of both involved phases. The damping corresponding to both transitions are also higher indicating higher mobility of the phases as a consequence of the EPDM nature used in this blend.

The effect of the compatibilization on the dynamic mechanical properties of NBR/EPDM57C and NBR/EPDM65 blends is shown in Figures 9 and 10, respectively. In both blend systems, the addition of the functionalized copolymers increases the dynamic elastic modulus but does not affect significantly the damping. EPDMTA resulted in a higher modulus than EPDMSH probably because of the higher amount of cross linked material, as indicated by the swelling experiments. This variation of dynamic properties implies that the functionalized copolymers increases rigidity of blend vulcanizates without substantial change in hysteresis (determined in terms of $\tan \delta$).

Table VI Curing Parameters and Mechanical Properties of Compatibilized NBR/EPDM65 (70 : 30 wt %) Vulcanizates as a Function of the Mixing Procedure

		NBR/EPDM 65 70/30 Blends					
		Noncompatibilized	5.0 phr of EPDMTA		5.0 phr of EPDMSH		10.0 phr of NBR-g-EPDM
			a	b	a	b	b
Rheometric Parameters							
M_L , lb · in		3.5	4.5	3.4	10.0	3.7	3.4
M_H , lb · in		17.3	18.5	17.7	23.5	19.0	18.1
t_{s1} , min		5.3	5.5	4.8	3.3	1.9	4.0
t_{90} , min		8.3	11.5	8.6	5.3	7.6	8.5
Cure rate		6.2	7.5	7.6	10.8	8.3	5.4
Swelling Tests (toluene)							
V_r^c		0.1924	0.1789	0.1834	0.2055	0.1881	0.2084
Weight Loss, %		29.5	13.0	11.8	27.0	23.6	15.0
Mechanical Properties							
σ^d MPa		2.1	2.9	3.4	2.9	2.8	3.0
ε^e %		1130	1100	1350	1230	1030	990

^a Blend prepared by adding the compatibilizing agent after the NBR mastication.

^b Blend prepared by adding the compatibilizing agent after the EPDM mastication.

^c Rubber volume present in the swollen network.

^d Ultimate tensile strength.

^e Elongation at break.

In the case of NBR/EPDM57C, the addition of EPDMTA or EPDMSH resulted in a small shift of the glass transition temperature of the NBR phase toward lower values. A small increase in damping ($\tan \delta$) of the NBR phase is also observed. Because the compatibilizing agents were obtained from an EPDM sample with higher rubbery characteristic, these behaviors can be associated with an increase in the flexibility of NBR chains as a consequence of the dispersion of the functionalized copolymers inside this phase.

The compatibilized NBR/EPDM 65 blends present a little broadening of the damping peak, as observed in Figure 10. The damping of the NBR phase presents a little decrease, whereas that of the EPDM phase increases a little. The behaviors of the dynamic elastic moduli were similar to that observed with NBR/EPDM57C blends; that is, both compatibilized blends presented higher E' values than the noncompatibilized blend.

Effect of Thermal Aging

The mechanical properties of the NBR/EPDM 57C blends before and after aging are shown in

Figure 11. The noncompatibilized blend shows a decrease in the values of the ultimate tensile strength, σ_B , and elongation at break, ε_B , after aging for 3 days, indicating rubber degradation, as expected. The presence of both EPDMTA and EPDMSH increases the thermal stability of these blends. Concerning the compatibilized blends, both σ_B and ε_B values decrease, but these values are still higher than that of the noncompatibilized blend. The addition of 5.0 phr of EPDMSH to this blend leads to very interesting results. After 3 days of aging in an air circulating oven at 70 °C, the mechanical properties are better than before aging, also indicating a post-curing process during aging. The tensile strength value is also comparable to that value observed for noncompatibilized blend, before aging.

It is well known in the literature that during thermal aging, several phenomena, including main chain scission, more cross link formation, and cross link breakage, can take place. It is also possible that the existing cross links break and a more stable type of cross link, which may be immune to further scission, can be formed. The relative ratio and magnitude of such reactions that

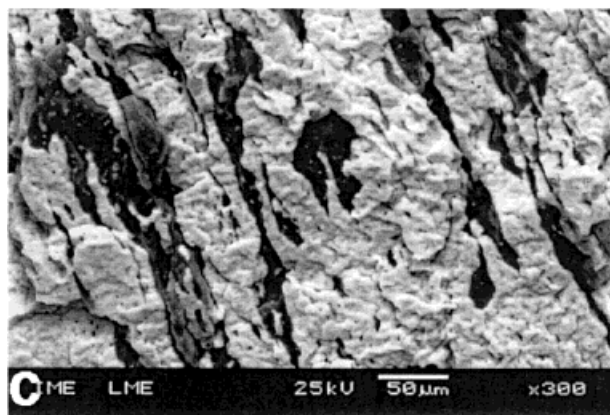
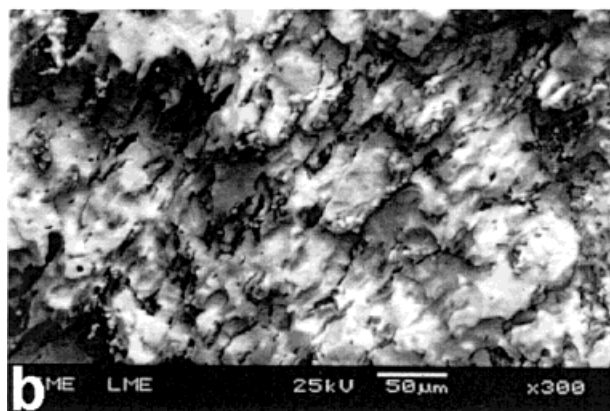
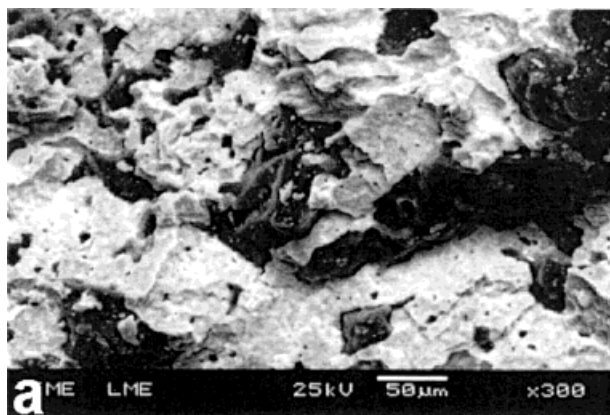


Figure 5 SEM micrographs of NBR/EPDM57C (70:30 wt%) blends (a) without compatibilizer; (b) with 5 phr of EPDMTA, and (c) with 5 phr of EPDMSH (the compatibilizing agents were added after NBR).

take place during aging governs the amount of change in each property. This kind of behavior is commonly reported for NR blends.^{22,25}

The mechanical properties of NBR/EPDM65 blends before and after aging are illustrated in

Figure 12. The behavior of these blends is very similar to that found with NBR/EPDM 57C blends. A decrease in σ_B and ϵ_B values is also observed for noncompatibilized blend during the 3 days of aging, indicating a main chain scission process. The addition of EPDMTA to this blend

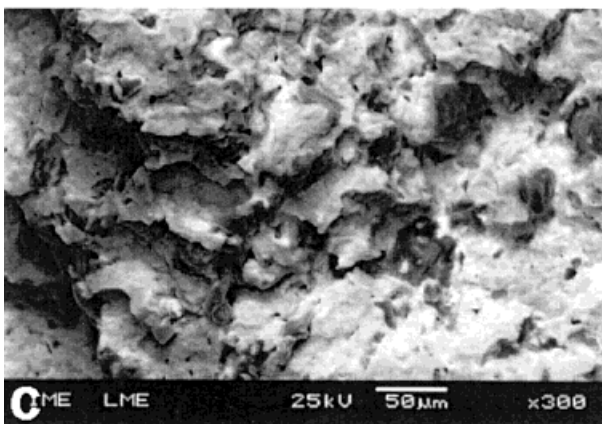
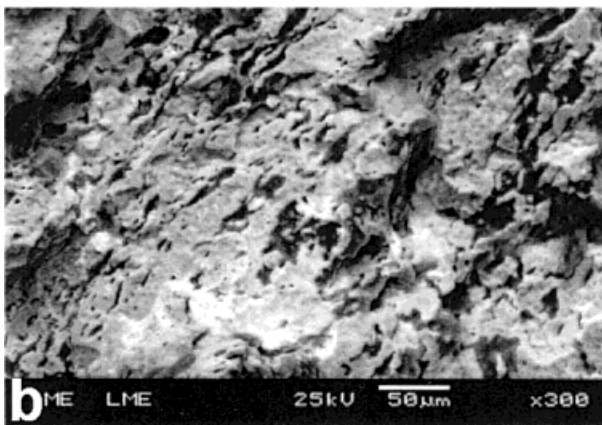
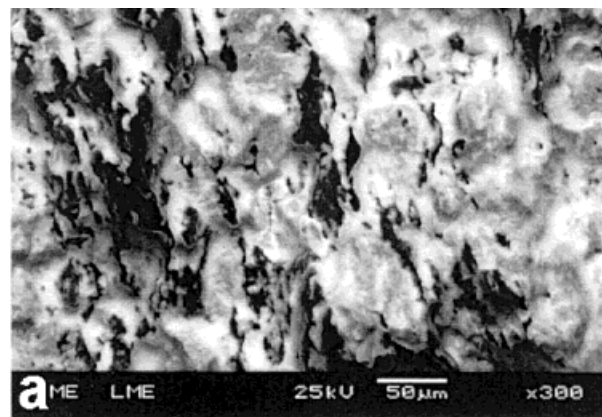


Figure 6 SEM micrographs of NBR/EPDM65 (70:30 wt%) blends (a) without compatibilizer; (b) with 5 phr of EPDMTA, and (c) with 5 phr of EPDMSH (the compatibilizing agents were added after NBR).

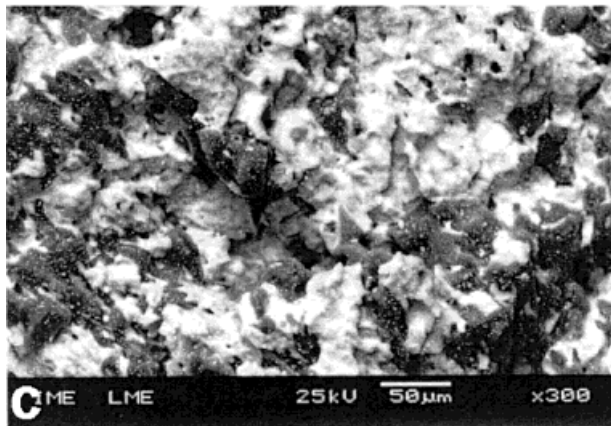
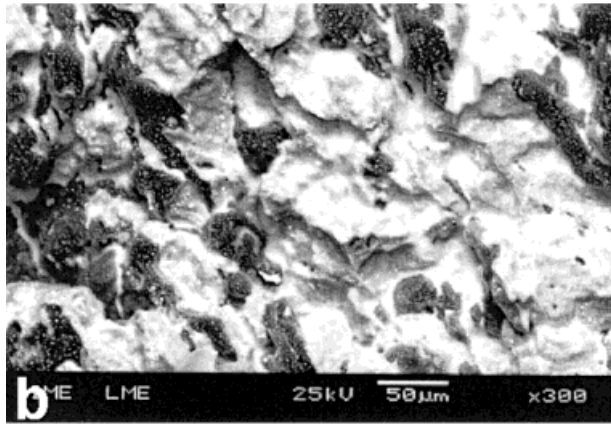
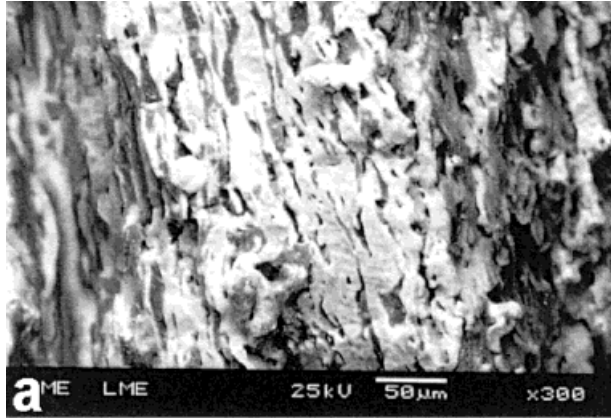


Figure 7 SEM micrographs of NBR/EPDM65 (70:30 wt%) blends (a) with 5 phr of EPDMTA, (b) with 5 phr of EPDMSH, and (c) with 5 phr of NBR/EPDM graft copolymer (the compatibilizing agents were added after EPDM).

reduces the effects of the thermal aging. Indeed, the presence of 2.5 phr of this functionalized copolymer was able to keep the same performance after aging. Increasing the amount of EPDMTA

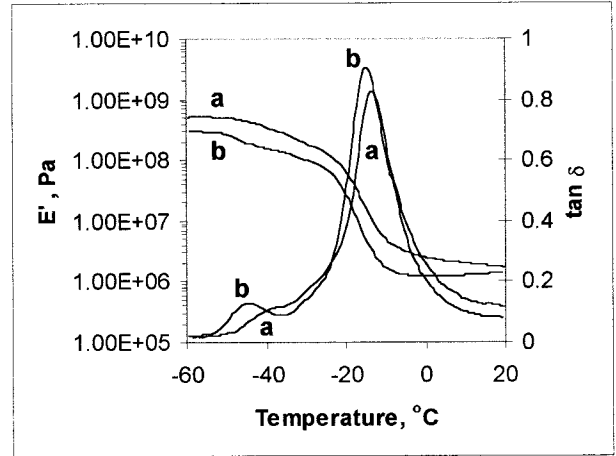


Figure 8 Dynamic elastic moduli (E') and $\tan \delta$ for NBR/EPDM blends prepared with (a) EPDM 57C and (b) EPDM 65 components.

resulted in an increase in the tensile strength as a result of cross linking during the aging process. The effect of EPDMSH on the mechanical properties for aged NBR/EPDM 65 blends is quite similar to that of EPDMTA. In this case, the addition of only 2.5 phr of EPDMSH increases the σ_B value, whereas the ϵ_B value remains almost constant, again as a consequence of a post-curing process. When 5.0 phr of EPDMSH are added both the σ_B and ϵ_B aged values dropped a little. But this drop is less accentuated compared with that for the noncompatibilized blend.

These results indicate that both EPDMTA and EPDMSH increase the thermal stability of these

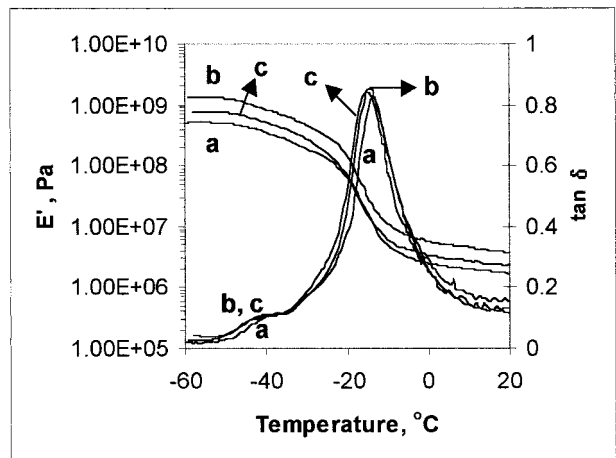


Figure 9 Dynamic elastic moduli (E') and $\tan \delta$ for NBR/EPDM 57C blends (a) noncompatibilized, (b) with 5.0 phr of EPDMTA, and (c) with 5.0 phr of EPDMSH.

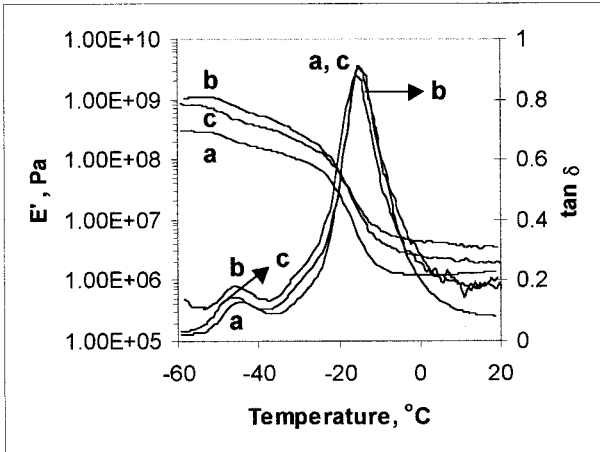


Figure 10 Dynamic elastic moduli (E') and $\tan \delta$ for NBR/EPDM 65 blends (a) noncompatibilized, (b) with 5.0 phr of EPDMTA, and (c) with 5.0 phr of EPDMSH.

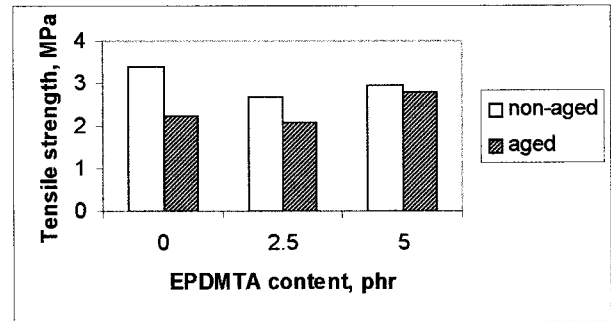
blends. As reported in the literature, antioxidants containing mercapto groups are employed to protect rubber vulcanizates against aging.^{26,27}

The difference in the addition order of the compatibilizing agents on the NBR/EPDM65 blends did not exert any substantial influence on the aging properties. Both EPDMTA, EPDMSH, and the graft copolymer resulted in blends with higher aging resistance than the noncompatibilized blends. This behavior is illustrated in Figure 13.

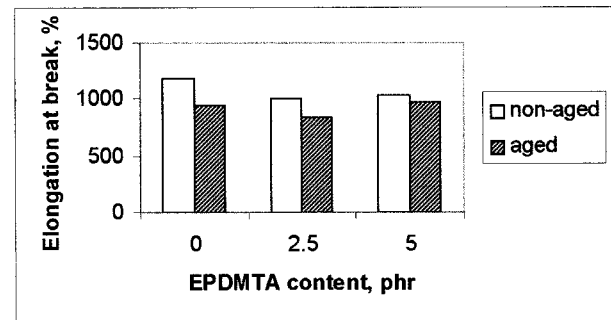
CONCLUSIONS

The addition of both EPDMTA or EPDMSH increases the ultimate tensile strength of NBR/EPDM65 (70:30 wt %) blends without affecting the elongation at break or hardness. The compatibilization effect was not successful when EPDM57C was employed as the blend component, although the morphology of these blends revealed a more uniform phase dispersion of EPDM inside the matrix when the functionalized copolymers are employed. The results concerning mechanical properties obtained with NBR/EPDM57C blends can be attributed to the high difference in viscosity between the blend components. EPDM65 displays lower viscosity, which improves the phase dispersion. In addition, EPDM65 contains a higher amount of unsaturation, which can enhance the covulcanization.

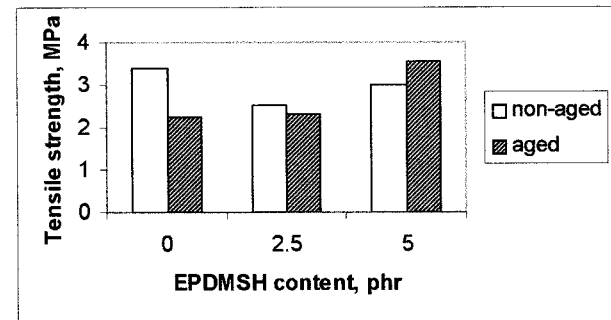
The mechanical properties were not significantly influenced by the order of addition of the



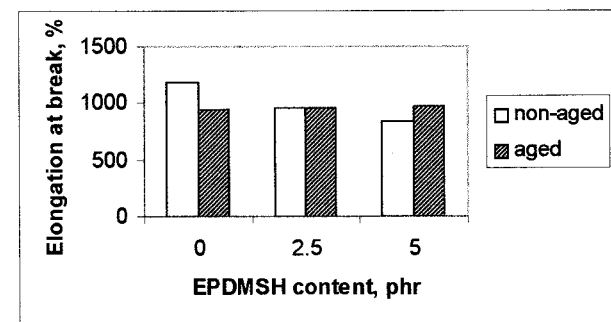
(a)



(b)

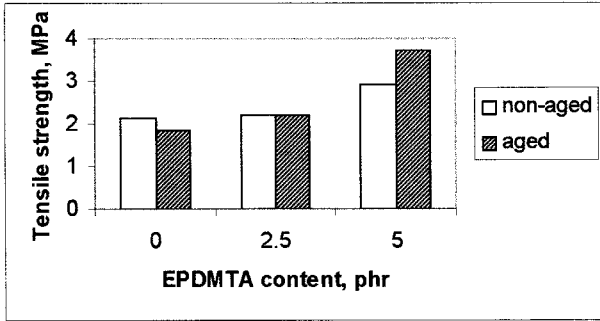


(c)

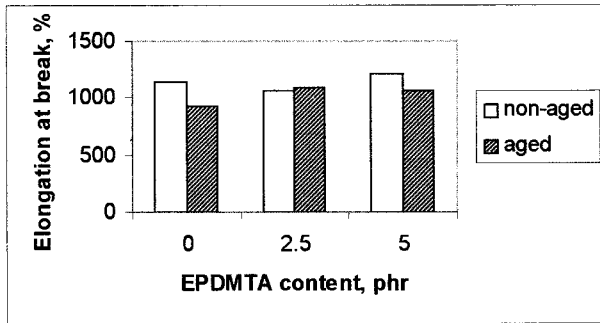


(d)

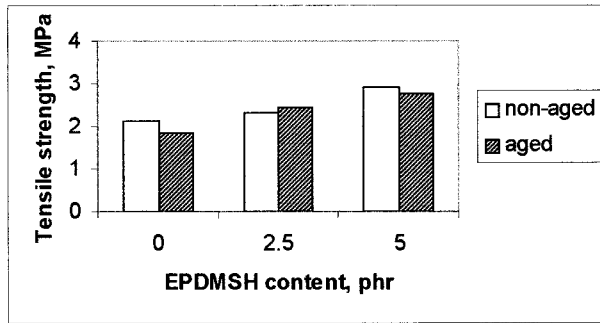
Figure 11 Mechanical properties for NBR/EPDM57C blends before and after aging and with EPDMTA (a and b, respectively) or EPDMSH (c and d, respectively); the compatibilizing agents were added after NBR.



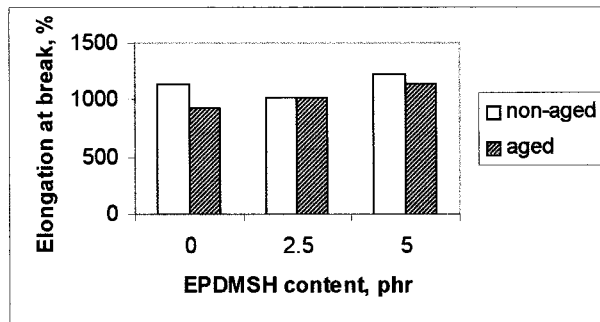
(a)



(b)



(c)



(d)

Figure 12 Mechanical properties for NBR/EPDM65 blends before and after aging with EPDMTA (a and b, respectively) or with EPDMSH (c and d, respectively); the compatibilizing agents were added after NBR).

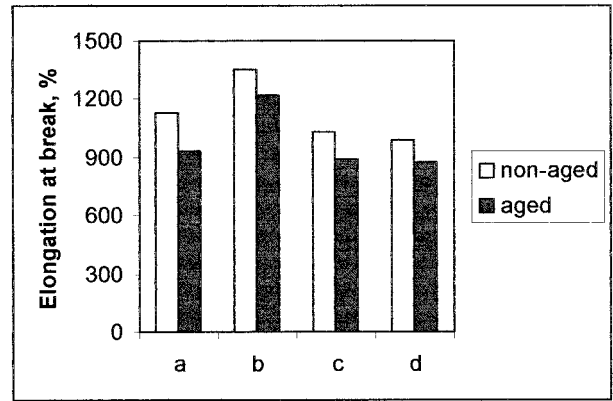
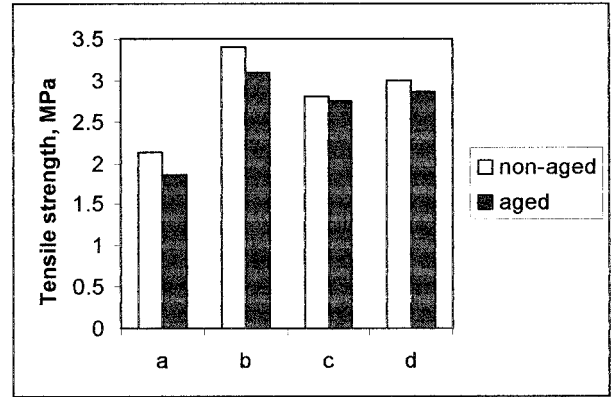


Figure 13 Mechanical properties for NBR/EPDM65 blends before and after aging (a) without compatibilizing agent, (b) with 5 phr of EPDMTA, (c) with 5 phr of EPDMSH, and (d) with 10 phr of NBR-EPDM graft copolymer (the compatibilizing agents were added after EPDM).

compatibilizing agent or by using a previously prepared graft copolymer, except in the case of EPDMTA. In this case, an improvement of both ultimate tensile strength and elongation at break as well as a morphology characterized by a more dispersed EPDM phase inside the NBR matrix have been achieved by adding this compound after the mastication of EPDM. Although EPDMTA has not resulted in the formation of insoluble material when blended with NBR alone, when employed in vulcanized system it was proven, from swelling experiments, to increase the amount of the cross linked material. This result suggests that, during the curing process of the blend, the EPDMTA undergoes degradation with the release of some compounds like thioacetate groups, which, together with the vulcanization system, improve the cross linking of the EPDM phase.

Concerning the curing parameters, blends containing EPDMSH display lower scorch time, indicating an accelerated curing system promoted by the mercapto groups along the EPDMSH backbone. In addition, by adding 5 phr of this compatibilizing agent, an increasing of cure rate is observed.

Although the addition of graft copolymer to the NBR/EPDM 65 blends did not result in a good dispersion of the EPDM phase as well as EPDMTA, the mechanical and aging properties were reasonably good. Finally, the manner in which the compatibilizing agent was added did not affect the aging properties. All compatibilized blends displayed good aging resistance.

To conclude, it is possible to develop NBR/EPDM blends with outstanding mechanical and aging properties by using NBR and EPDM samples of similar viscosities and a mercapto- or thioacetate-functionalized EPDM with a higher proportion of active groups as the compatibilizing agent. Better aging properties have already been achieved in our work, as indicated by the better mechanical properties obtained with the addition of both EPDMTA and EPDMSH.

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