

Compatibilization of Nitrile-Butadiene Rubber/Ethylene-Propylene-Diene Monomer Blends by Mercapto-Modified Ethylene-Vinyl Acetate Copolymers

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ABSTRACT: Mercapto-modified ethylene-vinyl acetate (EVASH) has been employed as a reactive compatibilizing agent for nitrile-butadiene rubber (NBR)/ethylene-propylene-diene monomer (EPDM) blends vulcanized with a sulfur/2,2'-dithiobisbenzothiazole (MBTS) single accelerator system and a (sulfur/MBTS/tetramethylthiuram disulfide (TMTD) binary accelerator system. The addition of 5.0 phr EVASH resulted in a significant improvement in the tensile properties of blends vulcanized with the sulfur/MBTS system. In addition to better mechanical performance, these functionalized copolymers gave rise to a more homogeneous morphology and, in some cases, better aging resistance. The compatibilization was not efficient in blends vul-

canized with the S/MBTS/TMTD binary system, probably because of the faster vulcanization process occurring in this system. The good performance of these EVASH samples as compatibilizing agents for NBR/EPDM blends is attributed to the higher polarity of these components that is associated with their lower viscosity. Dynamic mechanical analysis also suggested a good interaction between the phases in the presence of EVASH. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1404–1412, 2004

Key words: reactive compatibilization; mercapto groups; rubber blends; nitrile-butadiene rubber; ethylene-propylene-diene monomer

INTRODUCTION

Nitrile-butadiene rubber (NBR) is well known for its good oil resistance; but its resistance to heat, oxygen, and ozone is relatively poor. In order to minimize the oxidative degradation of NBR during service at high temperature, it is interesting to blend it with a saturated or low unsaturated polymer.¹ Ethylene-propylene-diene terpolymer (EPDM) may be a good partner for developing new rubber materials with better aging resistance because of its unsaturated backbone. However, NBR/EPDM blends are highly incompatible because of the difference in polarity and unsaturation level between the two components.^{2–7} Besides the poor interfacial adhesion and gross-phase separated morphology originating from very different structures, the cure rate incompatibility is even more significant, especially when sulfur-based curing systems are employed, because of the great solubility of the curatives in the polar and unsaturated NBR phase.^{8–10}

A common way to improve the interfacial adhesion and mechanical properties of heterogeneous polymer blends consists of the addition of a small amount of a compound, which is a compatibilizing

or interfacial agent. Block and graft copolymers whose segments are miscible with each polymer phase are normally employed for this purpose.¹¹ However, such copolymers may be formed *in situ* by the addition of appropriate reactive or functional compounds during melt mixing under conditions of high temperature and shearing. This process is known as reactive compatibilization. It is technologically more versatile and economical because of the facility of developing functional polymers as compared to the synthetic processes used for the preparation of graft and block copolymers with a desired macromolecular architecture. In addition, the efficiency of reactive compatibilization in improving interfacial adhesion is much better than common physical compatibilizers.^{11,12}

Several functional polymers have been developed by grafting vinyl monomers such as vinyl silane, acrylic acid, or maleic anhydride on the main chain of commercial polymers.^{13–15} The use of these functional polymers in blends containing polymers with other functional groups (e.g., hydroxyl, carboxyl, or amine groups) gives rise to polymer materials with improved mechanical performance, more uniform morphology, and higher interfacial adhesion because of the effective anchorage between the phases, which is

achieved by the *in situ* formation of the graft or block copolymer.¹⁶

In the case of elastomer-based blends, mercapto-modified copolymers have been proved to be good reactive compatibilizing agents because of the ability of mercapto groups to react with the double bond of high-diene rubbers.^{17,18} Several studies on the compatibilization of elastomer-based blends by using mercapto-modified copolymers have been developed in our laboratory. For example, vulcanized and nonvulcanized blends of ethylene-vinyl acetate (EVA) copolymer with natural rubber NR,^{19–23} nitrile rubber,^{24,25} and styrene-butadiene rubber^{26,27} presented improved mechanical performance and better aging resistance with the addition of a small amount of mercapto-modified, EVA (EVASH). Mercapto-modified EPDM (EPDMSH) was also effective in the compatibilization of natural rubber/EPDM blends.^{28,29} In all systems, a large amount of insoluble material could be isolated from nonvulcanized, compatibilized blends, indicating that the mercapto groups have reacted with the double bonds of high-diene rubbers during blending, which characterizes the reactive compatibilization.

EPDMSH has been also employed in NBR/EPDM blends, but the improvement of the mechanical properties was not considerable.³⁰ This blend is not easy to compatibilize because of the difference in unsaturation level and polarity between the components. In spite of the presence of mercapto groups along the EPDMSH backbone, this functional copolymer still presents low polarity, which makes its interaction with the NBR phase difficult.

In order to improve the interfacial action of the mercapto-functionalized copolymer in NBR/EPDM blends, we decided to employ EVASH copolymer in these blends. EVASH presents some interesting characteristics that can be useful in the compatibilization of these blends: its more polar nature improves its interaction with the NBR phase, the large amount of ethylene units in its backbone may impart some affinity toward the EPDM phase, its lower viscosity compared to those of the blend components facilitates its preferential location at the interface, and the presence of mercapto groups should provide a good anchorage between the phases. Preliminary studies on this subject revealed that EVASH was more efficient than EPDMSH as a compatibilizing agent for NBR/EPDM blends.^{31,32} Therefore, the aim of this article is to discuss the effect of this mercapto compound on the mechanical, dynamic mechanical, and morphological properties of vulcanized NBR/EPDM blends. For this purpose, two different sulfur-based curing systems and two different EVASH samples were employed. The efficiency of reactive compatibilization was also investigated in nonvulcanized blends.

TABLE I
Formulations of NBR/EPDM Blends

	Accelerator system	
	Single	Binary
NBR (wt %)	70	70
EPDM (wt %)	30	30
EVA18SH or EVA28SH (phr)	5.0	5.0
Zinc oxide (phr)	5.0	5.0
Stearic acid (phr)	0.5	0.5
Sulfur (phr)	1.0	1.0
MBTS (phr)	2.0	2.0
TMTD (phr)	0	1.0

EXPERIMENTAL

Materials

The NBR [33 wt % acrylonitrile, Mooney viscosity (ML 1 + 4 at 100°C) = 48] was kindly supplied by Nitriflex Ind., Brazil. EPDM rubber with ethylidene-norbornene as the diene (ethylene/propylene weight ratio = 60/40, 114 mmol ethylene norbornene/100 g) was kindly supplied by DSM Elastomeros do Brasil S. A. EVA copolymers [containing 18 and 28 wt % VR; melt flow index (MFI) = 2.3 and 2.5 g/min at 120°C, respectively] were kindly supplied by Petroquímica Triunfo, Brazil, and Politeno S.A., Bahia, Brazil. The EVASH copolymers were synthesized in our laboratory by a transesterification reaction between EVA copolymer and mercaptoacetic acid according to the literature.³³ The functionalized copolymers obtained from EVA copolymers containing 18 and 28% VA were denoted as EVA18SH and EVA28SH, respectively. The mercapto content in these copolymers was found to be 0.13 and 0.33 mmol/g, respectively, as determined by coulometric titration.³³ Other chemicals, such as zinc oxide, stearic acid, sulfur, 2,2'-dithiobisbenzothiazole (MBTS) and tetramethylthiuram disulfide (TMTD) were laboratory reagent grade.

Mixing and measurement of cure parameters

The blends were prepared in a two-roll mill operating at 110°C and with a friction ratio of 1:1.1. NBR was masticated for 3 min and blended with EPDM and the functionalized compatibilizer (EVA18SH or EVA28SH). After the homogenization of the rubber blend (for about 7 min), the other ingredients were added (see Table I for addition order and quantities). The processing time after each component addition was about 2 min.

The cure characteristics of the mixes were determined by using an oscillating disk rheometer (ODR; Tecnologia Industrial—Argentina) operating at 160°C with a 1° arc, according to the ASTM D 2084-81 method. The blends were vulcanized up to the optimum curing time in a hydraulic press at 160°C and 15,000 lb/in.²

Degree of equilibrium swelling

Cured test pieces (20 × 10 × 2 mm) were swollen in toluene or methyl ethyl ketone (MEK) until equilibrium swelling occurred. After reaching equilibrium, the swollen test pieces were weighed, dried under a vacuum, and reweighed. The swollen and deswollen weights were used to calculate the volume fraction of rubber in the network swollen to equilibrium (V_r), according to eq. (1):

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

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

Measurement of mechanical properties

Tensile-strain experiments were performed by means of an Instron 4204 testing machine at room temperature with a speed of 200 mm/min, following DIN 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. The retention of mechanical properties was calculated as expressed in eq. (2).

$$\text{retention(\%)} = \frac{(\text{mechanical property})_{\text{after aging}}}{(\text{mechanical property})_{\text{before aging}}} \times 100 \quad (2)$$

Dynamic mechanical analysis

Dynamic mechanical measurements were carried out on a dynamic mechanical thermal analyzer (DMA 2980, TA Instruments). The experiment was conducted in bending mode at a frequency of 1 Hz. The temperature was increased at 2°C/min over the range from -60 to 20°C.

Morphology characterization

Scanning electron microscopy was performed on JEOL 5610 LV equipment using a backscattered electron detector and a voltage of 20 kV. The samples were cryogenically fractured and the surface was treated with osmium tetroxide (OsO₄) for 5 min in order to selectively stain the unsaturated phase. The samples were then coated with carbon.

TABLE II
Curing Parameters of NBR/EPDM (70:30 wt %) Blends as Function of Curing System and Compatibilization

EVA18SH (phr)	EVA28SH (phr)	MH (lb ft in.)	ML (lb ft in.)	t_{s1} (min)	t_{90} (min)
S/MBTS/TMTD1.0/2.0/1.0					
0	0	24.4	3.6	3.5	6.1
5.0	0	22.7	3.5	2.5	5.4
0	5.0	22.0	3.3	2.5	4.4
S/MBTS1.0/2.0					
0	0	19.0	2.5	15.0	29.4
5.0	0	17.1	2.8	11.4	27.6
0	5.0	16.8	2.6	11.4	28.2

MH, Maximum torque. *ML*, Minimum torque; t_{s1} , scorch time; t_{90} , optimum cure time

RESULTS AND DISCUSSION

Curing characteristics

Table II presents the vulcanization parameters of NBR/EPDM (70:30 wt %) blends as a function of the curing system and compatibilization. Blends were vulcanized with a S/MBTS single accelerator system and a S/MBTS/TMTD binary accelerator system. Blends containing MBTS as a single accelerator displayed longer cure times and more scorch safety than those employing MBTS/TMTD. This was expected because MBTS is classified as a delayed-action semiultra accelerator whereas TMTD acts as an ultraaccelerator and vulcanizing agent.³⁴ The maximum torque values, measured at low strain, are normally proportional to the number of crosslinks formed per unit volume of rubber (i.e., to the crosslink density). In the binary MBTS/TMTD system, the maximum torque values were higher than in the MBTS single accelerator system, suggesting a lower crosslink density in blends vulcanized with the latter system.

The addition of EVASHs resulted in a decrease of the maximum torque. Because the maximum torque is normally related to the crosslink density, these results suggest a decrease of the crosslink density. However, EVA is a known processing aid, because of its reduced viscosity. Therefore, the decrease of the maximum torque should also be related to the decrease of the overall viscosity of the sample with the presence of EVASH. Indeed, in both vulcanizing systems, the maximum torque decreases slightly with the increase of the acetate group content in the EVASH sample, because of the lower viscosity (higher MFI value) of the EVA28 sample.

The presence of EVASH decreases both the scorch time and optimum cure time, indicating an accelerating effect for the curing process that is promoted by the mercapto groups. This behavior has been observed in other sulfur-cured blends compatibilized with mercapto-modified copolymers.^{26,29,30}

TABLE III
Results Obtained from Swelling Experiments on NBR/EPDM (70:30 wt %) Blends as Function of
Compatibilization and Curing System

EVA18SH (phr)	EVA28SH (phr)	MEK		Toluene		$WL_{\text{tol}} - WL_{\text{MEK}}$ (%)
		V_r	WL (%)	V_r	WL (%)	
S/MBTS/TMTD1.0/2.0/1.0						
0	0	0.34	3.1	0.23	10.0	6.9
5.0	0	0.34	4.4	0.24	15.8	11.4
0	5.0	0.33	4.1	0.24	17.6	13.5
S/MBTS1.0/2.0						
0	0	0.27	3.1	0.21	5.2	2.1
5.0	0	0.28	3.8	0.21	5.8	2.0
0	5.0	0.28	5.2	0.19	9.6	4.4

WL, weight loss (soluble material).

Swelling degree

The crosslink density of the vulcanizates can be estimated from swelling experiments by measuring the volume fraction of rubber in the gel (V_r) according to eq. (1) in the Experimental section. The swelling experiments were carried out in MEK, which can only dissolve or swell the NBR phase, and toluene, which can dissolve both the NBR and EPDM phases. Table III summarizes the results concerning the V_r and the amount of noncrosslinked rubber (soluble material) for NBR/EPDM (70:30 wt %) blends. In both systems, the V_r values obtained from swelling experiments in MEK were always higher because this solvent is not able to swell the EPDM phase. The nonswollen EPDM phase would limit the swelling of the NBR matrix in the same way as carbon black restricts the swelling of a compound. The amount of nonvulcanized NBR phase was very small in both curing systems that were employed, as indicated by the amount of soluble materials isolated after extraction with MEK. Blends vulcanized with the binary MBTS/TMTD accelerator system presented higher V_r values from experiments performed either in MEK or in toluene, suggesting a higher crosslink density achieved with the binary accelerator system. The addition of 5 phr EVASHs did not substantially affect the V_r values obtained in both curing systems and in both swelling experiments (MEK or toluene). These results are in good agreement with those for the maximum torque obtained from ODR measurements, indicating that these functionalized copolymers did not change the crosslink density of the blends.

The amount of soluble material from extraction with MEK is related to the fraction of nonvulcanized NBR. Because hot toluene should extract all nonvulcanized components, the weight loss (WL) difference ($WL_{\text{tol}} - WL_{\text{MEK}}$) is related to the fraction of nonvulcanized EPDM; and, for compatibilized blends, the fraction of

EVASH not chemically bonded into the rubber phase. In spite of the higher crosslink density achieved with the binary accelerator system, the total amount of soluble material (from extraction with hot toluene) is higher than in blends vulcanized with the MBTS single accelerator system. Nevertheless, in both curing systems, the ($WL_{\text{tol}} - WL_{\text{MEK}}$) values were lower than the EPDM content in the blends (30 wt %), indicating that a large part of the EPDM was also vulcanized. This phenomenon was more pronounced in blends vulcanized with the S/MBTS system.

Concerning the compatibilized blends, those vulcanized with the S/MBTS/TMTD binary accelerator system presented a substantial increase of ($WL_{\text{tol}} - WL_{\text{MEK}}$). This result suggests a decrease of the EPDM fraction as a vulcanized situation, probably because of the very fast vulcanization process in this system. In addition, there should be a large amount of the EVASH sample not chemically bonded to the rubber matrix. In the case of the S/MBTS single accelerator system, there is no substantial difference in the ($WL_{\text{tol}} - WL_{\text{MEK}}$) values for compatibilized or noncompatibilized blends, which indicates that EVASH remained chemically bonded to the rubber matrix after the curing process.

Mechanical properties

The effect of the curing system on the tensile properties of NBR/EPDM (70:30 wt%) blends is illustrated in Figure 1 as a function of blend compatibilization. For noncompatibilized blends, the one vulcanized with the S/MBTS/TMTD binary accelerator system presented a small increase in the ultimate tensile strength and a considerable decrease in the elongation at break, probably because of the higher degree of crosslinking.

The addition of 5.0 phr EVA18SH and EVA28SH resulted in an increase of the tensile strength and

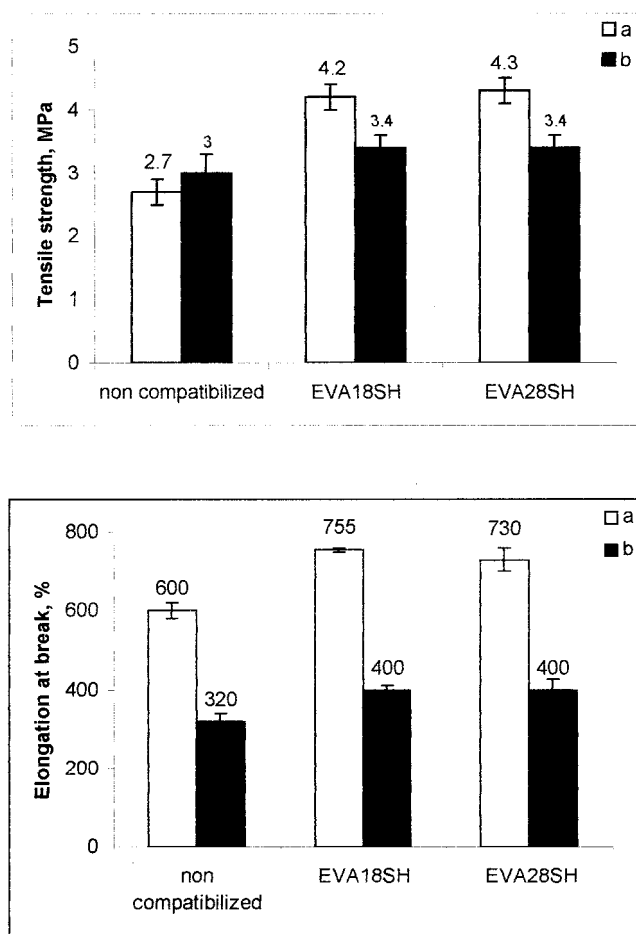


Figure 1 The mechanical properties of NBR/EPDM (70:30 wt %) blends as a function of compatibilization and cured with (a) S/MBTS and (b) S/MBTS/TMTD systems.

elongation at break of blends vulcanized with the S/MBTS single accelerator system. The improvement of the tensile properties of these blends may be attributed to the interfacial action of EVA18SH and EVA28SH, as a consequence of the reactions between the double bonds of the NBR phase and the mercapto groups of the compatibilizing agent, which occur during the blending process.

In the blends vulcanized with the S/MBTS/TMTD accelerator system, the addition of either EVA18SH or EVA28SH resulted in a small improvement of the mechanical properties, related to the noncompatibilized blend. However, these values were lower than those obtained with the single accelerator system.

In order to evaluate the extent of the chemical reaction between the EVASHs and the rubber matrix, a small amount of each blend was withdrawn from the roll mill before the addition of curatives and submitted to extraction with hot toluene for 24 h. As observed in Table IV, the addition of EVA18SH and EVA28SH produced an amount of insoluble material, indicating a reactive interaction between the phases.

Therefore, before adding the curatives, reactive compatibilization is achieved.

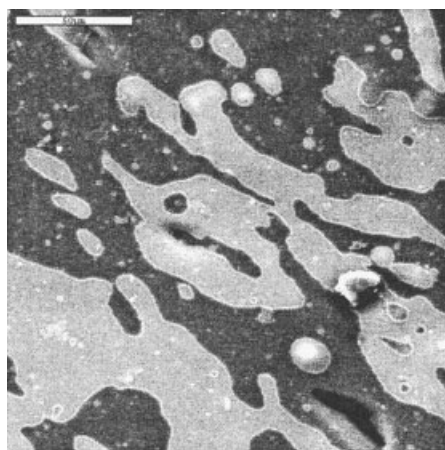
After the vulcanization process, the chemical interaction between EVASH and the rubber components is maintained in the case of the S/MBTS single accelerator system, as indicated by the low amount of extracted material in vulcanized blends (see Table III) and by improved mechanical performance. In the case of the binary accelerator system, the vulcanization process probably destroys the chemical interaction between EVASH and the rubber, resulting in a higher amount of extractable material from the corresponding blend. This phenomenon probably occurs through the combined action of TMTD and MBTS and may be the cause of the marginal improvement of the mechanical performance.

Morphological aspects

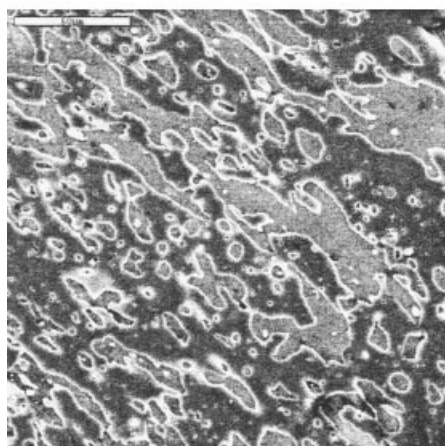
The morphologies of NBR/EPDM (70:30 wt %) blends compatibilized with EVASHs are compared to that of a noncompatibilized one in Figures 2, 3, and 4. The micrographs shown in Figure 2 were taken from nonvulcanized blends in order to observe the effect of EVA18SH and EVA28SH as compatibilizing agents without the influence of the curatives. The samples were withdrawn from the two-roll mill before the addition of curatives and pressed at 160°C for 15 min. Then, they were cryofractured, stained with osmium tetroxide, and analyzed in a scanning electron microscope using a backscattered detector. The light region in the micrographs corresponds to the NBR phase stained with osmium tetroxide and the black region corresponds to the EPDM phase. The noncompatibilized blend presents a gross-phase separated morphology [Fig. 2(a)] whereas the NBR/EPDM blends compatibilized with 5.0 phr EVA18SH [Fig. 2(b)] or EVA28SH [Fig. 2(c)] present a substantial decrease of the phase size, confirming the interfacial action of these compounds. The best morphological situation achieved with EVASHs may be attributed to their lower viscosities and intermediary surface tensions. Both characteristics tend to locate these components at the interface. In addition, the reaction between mercapto groups and the rubber phase, occurring at the

TABLE IV
Insoluble Material Obtained from Nonvulcanized NBR/EPDM (70:30 wt %) Blends (Before Addition of Curatives) as Function of Compatibilization

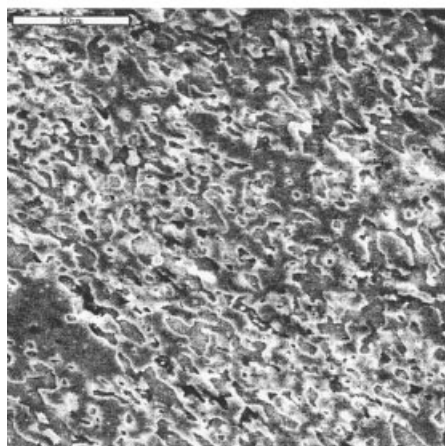
EVA18SH (phr)	EVA28SH (phr)	Insoluble material (%)
0	0	0
5.0	0	8.0
0	5.0	5.0



(a)



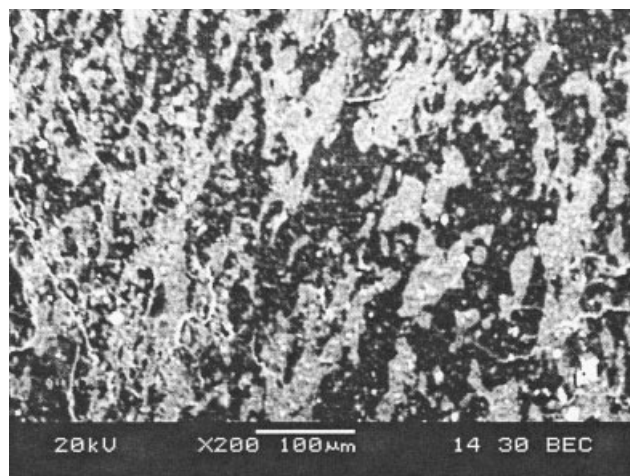
(b)



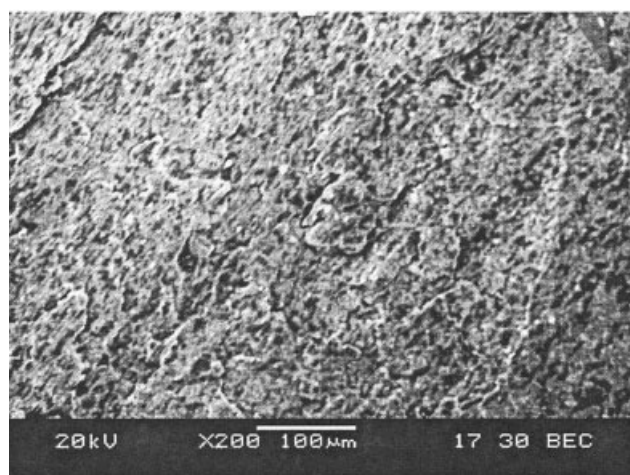
(c)

Figure 2 Scanning electron microscopy micrographs of nonvulcanized NBR/EPDM (70:30 wt %) blends: (a) non-compatible and compatibilized with 5.0 phr (b) EVA18SH and (c) EVA28SH.

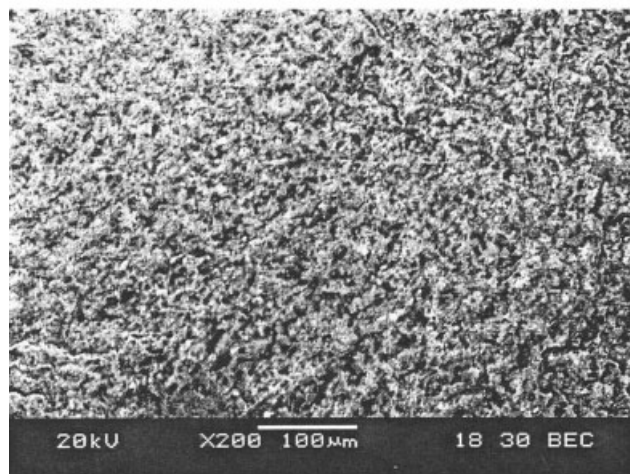
interface, diminishes the chance of phase coalescence. The most uniform morphology was achieved with EVA28SH, probably because of its lower viscosity



(a)

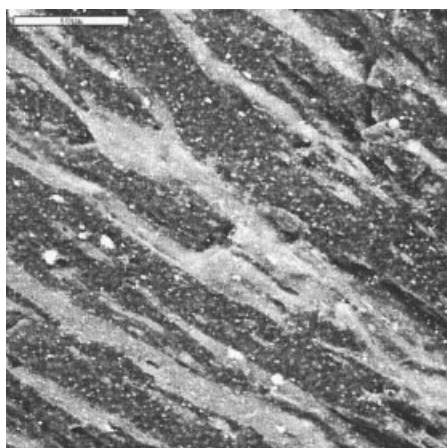


(b)

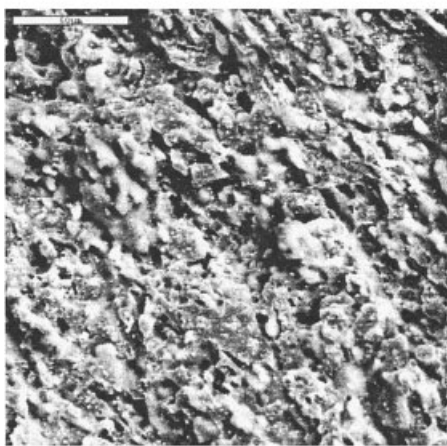


(c)

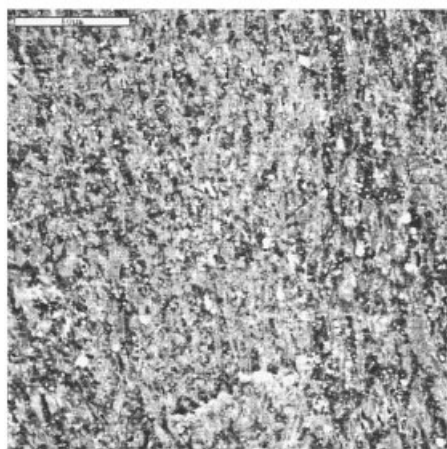
Figure 3 Scanning electron microscopy micrographs of NBR/EPDM (70:30 wt %) blends vulcanized with the S/MBTS single accelerator system: (a) noncompatible and compatibilized with 5.0 phr (b) EVA18SH and (c) EVA28SH.



(a)



(b)



(c)

Figure 4 Scanning electron microscopy micrographs of NBR/EPDM (70:30 wt %) blends vulcanized with the S/MBTS/TMTD binary accelerator system: (a) noncompatibilized and compatibilized with 5.0 phr (b) EVA18SH and (c) EVA28SH.

compared to EVA18SH. The morphological difference between both compatibilizing agents did not affect the mechanical properties.

Figures 3 and 4 show the micrographs of NBR/EPDM (70:30 wt %) blends cured with single and binary accelerator systems, respectively. As observed in Figures 3(a) and 4(a) the vulcanization process does not change the morphological situation of the noncompatibilized blend (i.e., there is still gross-phase segregation). However, the domain sizes decrease with the vulcanization process.

The addition of EVASHs produced a more uniform morphology for blends cured with both single and binary accelerator systems, thus reducing phase segregation [see Fig. 3(b, c), 4(b, c)]. This morphological aspect was early observed in nonvulcanized blends.

Comparing both curing systems, one can observe smaller phase segregation in blends vulcanized with the S/MBTS single accelerator system, which can be attributed to a better reticulation of the EPDM phase. This characteristic is also observed in compatibilized blends, as a consequence of the better interaction between the phases, which still remains after the vulcanization.

Dynamic mechanical properties

Figure 5 shows the variation of $\tan \delta$ versus the temperature for the NBR/EPDM (70:30 wt %) blends vulcanized with the S/MBTS single accelerator system as a function of the compatibilization. For this study, the compatibilized blend with EVA18SH was chosen as an example. Two damping peaks are observed in both blends, confirming the incompatibility of the blend components. Considering the noncompatibilized blend, the damping peak related to the glass transition of the NBR phase appears at around -4°C whereas that related to the glass transition of the EPDM phase appears in the range of -30 to -33°C . The addition of EVA18SH promoted a substantial shift of the glass-transition temperature (T_g) related to the NBR phase toward a lower one in the direction of the T_g of the

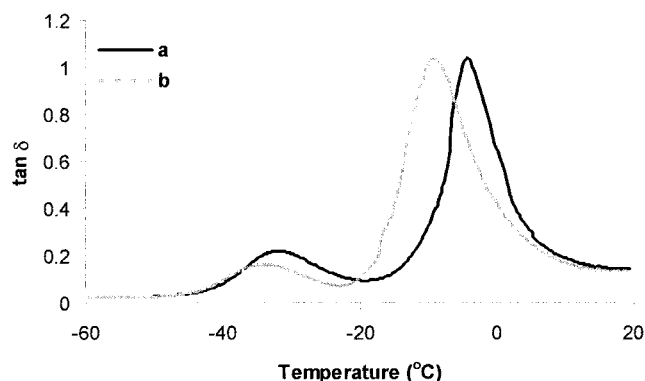


Figure 5 Curves of the damping ($\tan \delta$) versus temperature for NBR/EPDM (70:30 wt %) blends vulcanized with the S/MBTS single accelerator system: (a) noncompatibilized and (b) compatibilized with 5.0 phr EVA18SH.

EPDM phase. This behavior suggests the interaction between EPDM and NBR that is promoted by reactive compatibilization. In addition to the displacement of the transition, the damping curve of the compatibilized blend is a little broader, probably because of interfacial interactions promoted by the compatibilizers, which favors a better dispersion of the EPDM phase inside the NBR phase. Moreover, the broadening of the damping curve also suggests the presence of another phase, which is probably constituted of a NBR–EVASH network formed during the reactive compatibilization through the reaction between the mercapto groups and double bonds of NBR. The damping value related to the EPDM phase decreases with the compatibilization. Because the damping value is also related to the concentration of the polymer responsible for the corresponding transition, one can suggest that a lower fraction of this phase is involved in this transition and another fraction should be dispersed inside the NBR phase, as a consequence of the compatibilization.

Effect of thermal aging

Above room temperature, many polymers degrade in air via various oxidation processes. Therefore, the determination of the mechanical properties of NBR/EPDM blends after storage for 72 h in an air oven at 70°C was monitored. Figure 6 presents the results related to the retention of the tensile strength and elongation at break of the blends after aging. The noncompatibilized blend displays a slight decrease in the tensile strength after aging. This behavior was similar in both sulfur-curing systems and indicates the ability of the EPDM component to promote better thermal stability in the rubber system.

The presence of EVA18SH and EVA28SH in blends vulcanized with the S/MBTS/TMTD binary accelerator system resulted in similar retention values of the tensile strength but lower retention values of the elongation at break compared to those of the noncompatibilized blend. This behavior indicates a stiffening of the compatibilized blends.

Concerning blends vulcanized with S/MBTS single accelerator system, one can observe better thermal stability of the NBR/EPDM blend with the addition of EVASHs, mainly EVA18SH. As observed in Figure 6, there is even an increase in the tensile strength after aging, indicating a postcuring process. The elongation at break values did not change after aging.

CONCLUSIONS

EVASH copolymers are effective in improving the tensile properties of NBR/EPDM blends vulcanized with the S/MBTS single accelerator system. Because the crosslink density was not significantly affected by

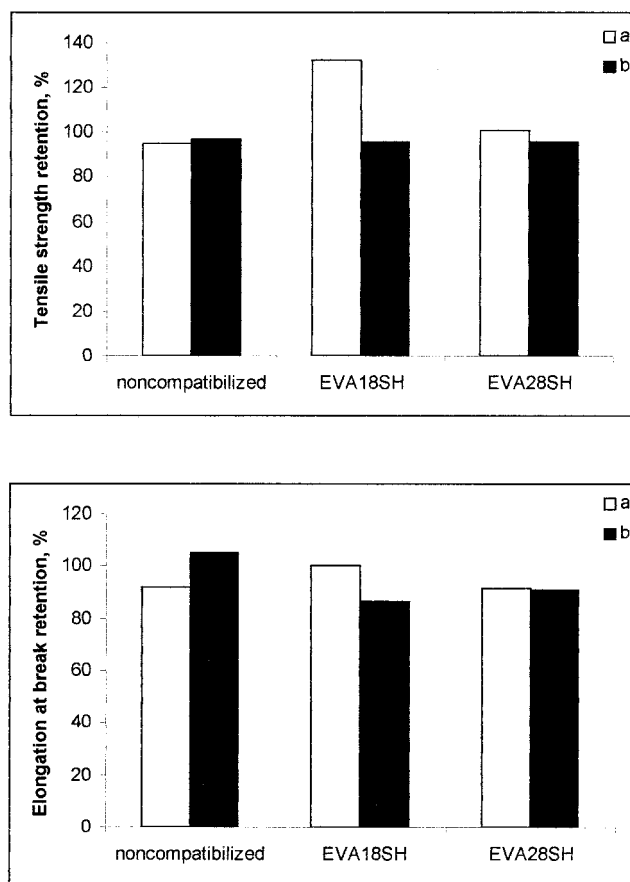


Figure 6 The retention of the tensile properties of NBR/EPDM (70:30 wt %) blends with thermal aging: (a) cured with the S/MBTS single accelerator system and (b) cured with the S/MBTS/TMTD binary accelerator system.

the presence of EVA18SH or EVA28SH, one can suggest that the better mechanical performance can be attributed to the anchorage between the phases, which is promoted by the chemical bonds formed between the mercapto groups of the EVASH component and the double bonds of the rubber matrix. This phenomenon was confirmed by the presence of insoluble materials in the corresponding nonvulcanized blends. In addition, it is believed that EVASH is preferentially located at the interface because of its lower viscosity, intermediary interfacial tension, and moderate polarity. The interfacial action of EVASH resulted in better mechanical performance and more homogeneous morphology of the blends.

Dynamic mechanical analysis of blends vulcanized with the S/MBTS single system confirmed the compatibilizing effect of EVASH. Indeed, a significant shift of the T_g related to the NBR phase toward lower temperature was observed, indicating a better dispersion of the EPDM phase inside the NBR matrix. The corresponding damping peak was a little broader for the compatibilizing blend, suggesting the presence of a third phase, probably comprising a NBR–EVASH network formed during mixing.

The inefficiency of EVASH in improving the mechanical performance of blends vulcanized with the S/MBT/TMTD system may be attributed to the faster vulcanization process (which diminishes the chance of the vulcanization of the EPDM phase) and to the possible action of the combined accelerators (MBTS with TMTD) in destroying the NBR–EVASH network formed before the curing process.

To summarize, NBR/EPDM blends with a combination of good mechanical performance, improved aging resistance, and more homogeneous morphology can be developed by using a low amount of an appropriate EVASH and a S/MBTS vulcanized system. The main drawback of this system is the slow curing process. The addition of EVASH decreases the scorch and optimum curing times (but not too much) compared to the S/MBTS/TMTD system.

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