

Effect of Mercapto-Modified Ethylene–Vinyl Acetate on the Curing Parameters and Mechanical and Dynamic Mechanical Properties of Vulcanized Nitrile Rubber/Ethylene–Vinyl Acetate Blends

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Received 14 October 2002; accepted 11 March 2003

ABSTRACT: The compatibilizing effect of mercapto-modified ethylene–vinyl acetate (EVALSH) was investigated in vulcanized nitrile rubber (NBR)/ethylene–vinyl acetate (EVA) copolymer blends. EVALSH increased the ultimate tensile strength, mainly in blends containing larger amounts of NBR. In addition, an accelerating effect of this functionalized copolymer was observed in blends vulcanized with the sulfur system. This behavior was confirmed with oscillating disk rheometry and differential scanning calorimetry

analyses. The improvement of the mechanical performance was attributed to the interfacial action associated with the increase in the crosslink density of the NBR phase promoted by the mercapto groups in EVALSH. The effects of EVALSH on the morphology and dynamic mechanical properties were also studied. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2391–2399, 2003

Key words: rubber; blends; compatibilization; vulcanization

INTRODUCTION

Blending unsaturated elastomers with ethylene–vinyl acetate (EVA) copolymers is a good way of developing rubbery materials with good ozone and weather resistance. Among several reported EVA-based blend systems, those having nitrile rubber (NBR) as the unsaturated rubber component offer several important advantages because of the excellent oil resistance, abrasion resistance, and mechanical properties promoted by the NBR phase that are associated with the good mechanical and aging performance of EVA. These blends have been reported in the literature several times.^{1–5} Such blends are incompatible and normally result in poor mechanical properties because of gross phase separation and poor interfacial adhesion. This problem can be minimized by the proper control of the phase morphology during processing and by the addition of a compatibilizing agent.

Block and graft copolymers have been extensively employed in blend compatibilization.⁶ However, reactive compatibilization with functional polymers or coupling agents is technologically more interesting because it is often less expensive. In these cases, the block or graft copolymer is formed *in situ* during blend processing.⁶ The success of the reactive compatibilization is based on the nature of the reactive group. Blends of NBR with polyolefins have been compatibilized with the addition of a polyolefin (polypropylene or polyethylene) modified with maleic anhydride or phenolic resin.^{7–12}

The compatibilization of NBR/EVA blends has also been achieved in the presence of a mercapto-modified ethylene–vinyl acetate (EVALSH) copolymer.^{4,5} An improvement in the ultimate tensile strength in non-vulcanized NBR/EVA blends has been observed with the addition of small amounts of EVALSH. EVALSH also exerts some influence on the rheological properties and dynamic mechanical properties of these blends.⁵ The outstanding mechanical performance of these blends has been attributed to reactive compatibilization between the phases, which occurs through the reaction between the mercapto groups along the EVA backbone of the EVALSH component and the double bond of the diene rubber, during melt processing. The probable reaction involved in the reactive compatibilization is illustrated in Figure 1. The efficiency of EVALSH as a compatibilizing agent has also

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Contract grant sponsor: Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq).

Contract grant sponsor: Fundação de Amparo a Pesquisa do Estado do Rio de Janeiro (FAPERJ).

Contract grant sponsor: Coordenação de Aperfeiçoamento de Pessoal de Ensino Superior (CAPES).

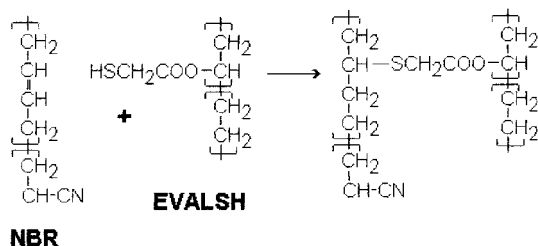


Figure 1 Proposed reaction involved in the reactive compatibilization of the mercapto compound in NBR-based blends.

been observed in natural rubber/EVA^{13,14} and styrene-butadiene rubber (SBR)/EVA blends.^{15,16}

Mercapto-functionalized copolymers also exert a strong influence on the curing parameters of elastomer blends. For example, SBR/EVA blends vulcanized with sulfur-based curing systems present a substantial decrease in the scorch time and optimum cure time, and this suggests an accelerator effect of the mercapto groups.¹⁶ Similar behaviors have also been observed in ethylene-propylene-diene monomer (EPDM)-based elastomer blends containing very small amounts of mercapto-modified EPDM.¹⁷⁻¹⁹

This article describes the influence of EVALSH on the mechanical and dynamic mechanical properties of vulcanized NBR/EVA blends. The effect of this functionalized copolymer on the curing parameters has also been evaluated by oscillatory disk rheometry and differential scanning calorimetry (DSC) analyses.

EXPERIMENTAL

Materials

NBR (NBR615; 33 wt % acrylonitrile, Mooney viscosity = 32) was kindly supplied by Nitriflex S.A. (Rio de Janeiro, Brazil). EVA copolymer (18 wt % vinyl acetate, melt flow index = 2.3 g/10 min at 120°C) was kindly supplied by Petroquímica Triunfo S.A. (Rio Grande de Sul, Brazil). EVALSH was obtained by the esterification of hydrolyzed EVA with mercaptoacetic acid according to the literature procedure.²⁰ The EVALSH used in this study contained 62 mmol % mercapto groups, as determined by Fourier transform infrared spectroscopy and thermogravimetric analysis.

Mixing and measurement of the cure characteristics

The blends were prepared in a Berstoff two-roll mill (Hannover, Germany) at 110°C and 30 rpm. NBR was first masticated for 2 min, and then it was compounded with EVALSH and EVA in that order. After the homogenization of the rubber blend (ca. 4 min), the curatives were added in the following order: zinc oxide (5 phr), stearic acid (1.5 phr), and sulfur (0.3

phr). The accelerators were mercaptobenzothiazole sulfonamide (MBTS; 2.0 phr) and tetramethyl thiuram disulfide (TMTD; 1.0 phr). For curing with peroxide, an amount corresponding to 0.3 phr dicumyl peroxide (DCP) was added after the homogenization of the rubber blend. The total mixing time was 10 min.

The cure characteristics of the mixes were determined with an oscillating disk rheometer (R-100, Monsanto, Lancashire, UK) at 160°C and 1 arc degree according to ASTM D 2084-81.

The specimens (2 mm thick) for mechanical testing were compression-molded at 160°C under 6.7 MPa of pressure and at the optimum cure times (the time corresponding to 90% of the maximum torque.)

Measurements of the mechanical properties

Tensile-strain experiments were performed with an Instron 4204 testing machine (MA) at room temperature and a speed of 100 mm/min according to ASTM D 638-77A.

Degree of equilibrium swelling measurements

Cured test pieces (20 mm × 10 mm × 2 mm) were swollen in toluene until equilibrium swelling. After equilibrium was reached, the swollen test pieces were weighed, dried *in vacuo*, and weighed again. 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:

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

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.

Dynamic mechanical studies

Dynamic mechanical measurements were carried out on a Rheometrics Scientific MKIII dynamic mechanical thermal analyzer (Piscataway, NJ) consisting of a temperature programmer and controller. The experiment was conducted in a bending mode from -60 to 50°C at a frequency of 1 Hz with a programmed heating rate of 2°C/min.

Morphological studies

The molded samples were cryogenically fractured. The surface was immersed in an osmium tetroxide solution for about 5 min to preferentially stain the NBR phase. The samples were then vacuum-dried for

TABLE I
Curing Parameters and Tensile Properties of NBR/EVA (80:20 w/w)^a

Parameter	EVALSH (phr)						
	0	1.5	2.0	2.5	5.0	10	15
M_H (Nm) ^b	1.2	1.8	1.9	1.7	1.6	1.4	1.4
M_L (Nm) ^c	0.31	0.29	0.29	0.34	0.36	0.35	0.69
T_{sI} (min) ^d	6.5	4.7	4.2	3.3	2.3	2.2	2.2
T_{90} (min) ^e	8.8	7.8	7.4	5.8	5.0	5.2	6.2
σ (MPa) ^f	5.7	6.5	7.4	8.6	9.95	10.1	8.1
ϵ (%) ^g	775	701	663	599	549	550	661

^a Blend composition = 5.0 ZnO; 0.5 stearic acid; 0.3 sulfur; 2.0 MBTS; 1.0 TMTD and 5 phr EVALSH.

^b Maximum torque.

^c Minimum torque.

^d Scorch time.

^e Optimum cure time.

^f Ultimate tensile strength.

^g Elongation at break.

48 h. The surface was covered with a thin layer of carbon and analyzed in a scanning electron microscope (DSM 960, Zeiss, Oberkochen, Germany) with backscattered electrons.

RESULTS AND DISCUSSION

Cure parameters and mechanical properties

The studies concerning the effect of EVALSH on the cure parameters and mechanical properties of NBR/EVA blends were initially performed with a sulfur-based vulcanizing system in blends containing 80 wt % NBR. Table I summarizes the results obtained as a function of the amount of EVALSH. Decreases in the both scorch time and optimum cure time were observed as the EVALSH concentration in the blend increased, up to 5 phr EVALSH. This behavior is better illustrated in Figure 2 and indicates an accelerator effect of the cure process, promoted by the mercapto groups in the EVALSH sample. A substantial increase

in the maximum torque was also observed with the addition of as little as 1–2 phr EVALSH, suggesting an increase in the crosslink density. A similar phenomenon has also been observed in other elastomer blends containing mercapto-modified copolymers.^{16,18,19}

In addition to the cure parameters, the presence of EVALSH also affected the tensile properties. As shown in Table I, there was a progressive increase in the ultimate tensile strength with an increase in the EVALSH concentration. The best performance was achieved with an EVALSH concentration of 5–10 phr. After this concentration, the tensile strength decreased, probably as a result of the interface saturation. Similar behavior was found for nonvulcanized NBR/EVA blends,⁴ this being an indication of the compatibilization effect of EVALSH. The interaction between the phases took place because of the ability of mercapto groups to react with the double bond of the unsaturated component, which was associated with the affinity between the EVALSH backbone and the EVA phase.

In addition to the compatibilization, the EVALSH participated during the cure process, as evidenced by the rheometric results. This effect may be related to the ability of mercapto groups in generating free radicals during the blend processing or to some specific interaction between EVALSH and one of the cure components that made up the sulfur-based cure system.

To elucidate the role of EVALSH in the cure process, we also used a peroxide-based cure system. Table II compares the results obtained with both sulfur-based and peroxide-based cure systems. For noncompatibilized blends, the cure with DCP was characterized by a lower scorch time and a higher optimum cure time. The minimum and maximum torque values were not affected by the nature of the cure system, and this indicated no variation in the crosslink densities of these blends. This behavior was confirmed by the V_r values obtained from swelling experiments.

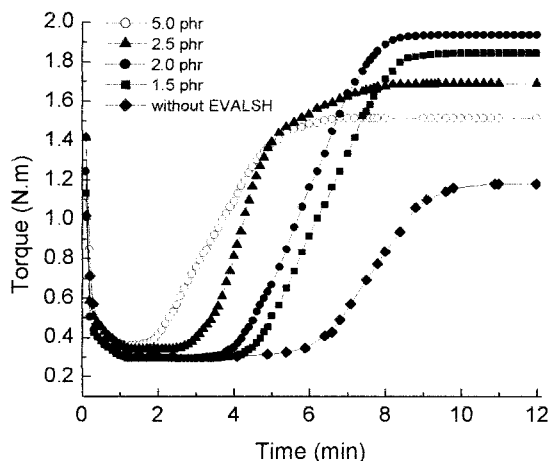


Figure 2 Rheographs of 80:20 NBR/EVA blends cured at 160°C with different amounts of EVALSH.

TABLE II
Influence of the Curing System on the Curing Parameters and Mechanical Properties of NBR/EVA (80:20 w/w) as a Function of the Compatibilization: (A) Without EVALSH and (B) with 5 phr EVALSH

Property	Sulfur system ^a		DCP system ^b	
	A	B	A	B
M_H (Nm) ^c	1.2	1.6	1.2	1.0
M_L (Nm) ^d	0.31	0.36	0.40	0.40
T_{s1} (min) ^e	6.5	2.3	3.0	3.5
T_{90} (min) ^f	8.8	5.0	19.8	19.0
σ (MPa) ^g	5.7	10.0	8.7	8.9
ε (%) ^h	775	549	660	700

^a Sulfur system = 5.0 ZnO; 0.5 stearic acid; 0.3 sulfur; 2.0 MBTS; 1.0 TMTD and 5 phr EVALSH.

^b DCP system = 0.3 phr.

^c Maximum torque.

^d Minimum torque.

^e Scorch time.

^f Optimum cure time.

^g Ultimate tensile strength.

^h Elongation at break.

Concerning tensile properties, the cure with DCP resulted in a substantial increase in the ultimate tensile strength and a decrease in the elongation at break for the noncompatibilized blend, in comparison with that one vulcanized with the sulfur system. The differences in the mechanical performances of the two curing systems were attributed to the ability of DCP to cure both NBR and EVA phases, whereas the sulfur-based system was able to vulcanize only the unsaturated NBR phase. EVALSH exerted no influence on the cure parameters and mechanical properties of the blend cured with DCP. These results indicated that the accelerator effect of EVALSH in the sulfur-based system might have been due to some specific interaction between the curing components and EVALSH.

Studies of the cure process by DSC

The effect of EVALSH on the cure process involving the sulfur-based system was studied by the DSC analysis (in the dynamic mode) of rubber formulations containing the curatives and the mercapto copolymer. Figure 3 compares the DSC curves of these blends containing 80 wt % NBR. Three distinct peaks can be distinguished. The first one at 75–80°C is associated with the crystalline melt transition of the EVA component. The exothermic peak at 175°C is observed only during the first heating cycle and is attributed to the vulcanization process of the NBR phase. This peak is shifted toward a lower temperature (166°C) with the addition of 5.0 phr EVALSH, and this confirms the accelerator action of EVALSH, as also observed in ORD analysis.

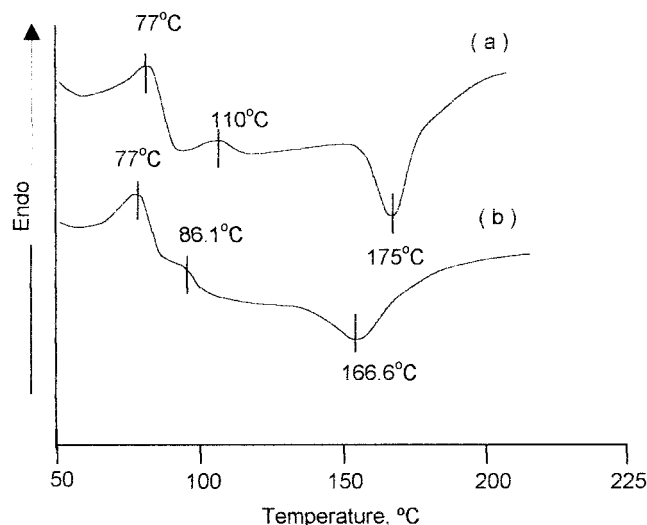


Figure 3 DSC curves of 80:20 NBR/EVA blends: (a) without EVALSH and (b) with 5 phr EVALSH.

Besides these two transitions, there is another endothermic peak at 110°C for the noncompatibilized blend [Fig. 3(a)]. This peak also appears during the second heating stage and could be related to the transition of a component of the vulcanizing system or a particular intermediary species formed before the cure process. It is interesting to observe that in the blend containing EVALSH [Fig. 3(b)], this transition is shifted toward a lower temperature, and this indicates the influence of EVALSH on the formation of this intermediary species.

According to the literature,²¹ the vulcanization process involving sulfur-based systems consists of several intermediary reactions, the first step of which should involve the formation of complexes between the accelerators and the activator system. The activator consists

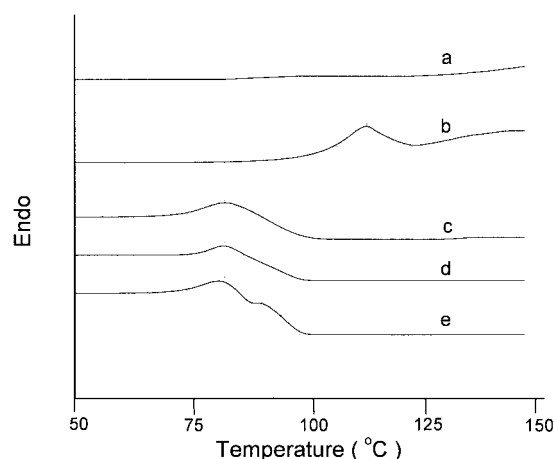


Figure 4 DSC curves of pure NBR containing (a) 2 phr ZnO, (b) 2 phr ZnO and 0.2 phr stearic acid, (c) 2 phr ZnO and 5 phr EVALSH, (d) 5 phr EVALSH and 0.2 phr stearic acid, and (e) 5 phr EVALSH, 2 phr ZnO, and 0.2 phr stearic acid.

TABLE III
Influence of the Blend composition on the Curing Parameters of NBR/EVA as a Function of the Compatibilization: (A) Without EVALSH and (B) with 5 phr EVALSH

Blend composition (wt %)		Curing parameter					
NBR	EVA	M_H (N m) ^a		T_{s1} (min) ^b		T_{90} (min) ^c	
		A	B	A	B	A	B
100	0	2.0	2.2	5.5	4.5	16.5	12.5
80	20	1.2	1.6	6.5	2.3	8.8	6.0
60	40	1.3	1.3	2.0	2.0	6.0	5.0
40	60	0.9	1.0	2.0	1.7	3.5	3.0

^a Maximum torque.
^b Scorch time.
^c Optimum cure time.

of the salt formed by the reaction of zinc oxide and stearic acid (zinc stearate). The resulting zinc stearate acts as an activator for the accelerator system, giving rise to a complex, which is responsible for the curing process together with sulfur.

To elucidate the nature of the species responsible for the transition at 110 or 86°C, we performed some DSC experiments in NBR formulations containing only the activators (without the presence of sulfur and accelerators). Figure 4 illustrates the DSC curves of pure NBR containing different formulations. The NBR sample containing only ZnO did not present any transition [Fig. 4(a)]. ZnO and stearic acid in an NBR sample resulted in a transition at 110°C similar to that observed in a previous system containing the accelerators [Fig. 4(b)]. All NBR samples containing EVALSH displayed an endothermic peak at 77°C related to the melt transition of the crystalline phase of EVALSH. The formulations containing EVALSH/ZnO [Fig. 4(c)] or EVALSH/stearic acid [Fig. 4(d)] did not present any other transition than that corresponding to the melt transition of EVALSH. How-

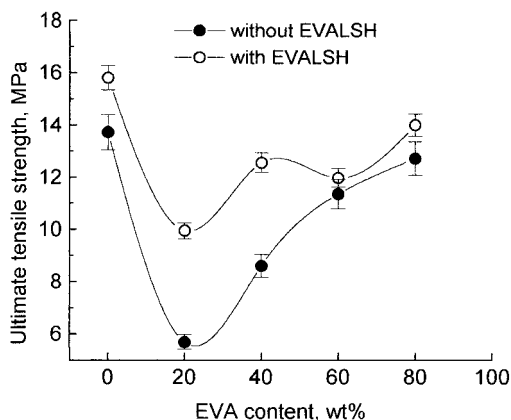


Figure 5 Dependence of the ultimate tensile strength on the blend composition.

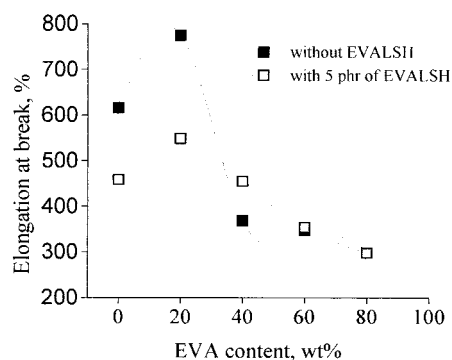


Figure 6 Dependence of the elongation at break on the blend composition.

ever, when EVALSH was combined with the ZnO/stearic acid system [Fig. 4(e)], we could observe the endothermic peak at 86°C and the disappearance of the transition at 110°C.

From these results, we can associate the transition at 110°C with the product resulting from the reaction between ZnO and stearic acid, that is, zinc stearate. EVALSH interacted with the formed zinc stearate, and this resulted in a complex, the transition of which appeared at a lower temperature (86°C). This phenomenon may be responsible for the accelerating effect of EVALSH in the sulfur-based vulcanizing system.

Effect of EVALSH on the NBR/EVA blends as a function of the blend composition

The influence of EVALSH on the curing parameters, mechanical properties, and crosslink density was evaluated as a function of the blend composition. Table III summarizes some of the cure parameters of these blends. The elastomer systems containing large amounts of NBR (100 and 80 wt %) displayed significant decreases in the cure time and scorch time and increases in the maximum torque with the addition of 5 phr EVALSH; this indicated an accelerator effect and an increase in the crosslink density, as previously

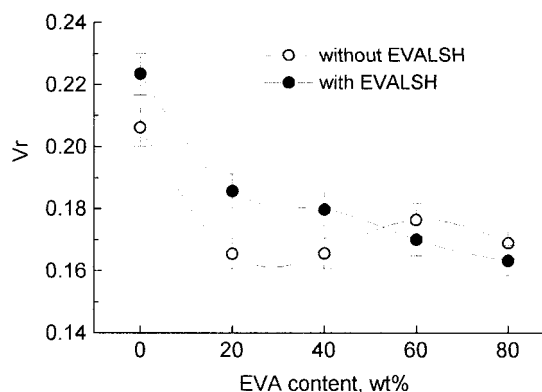


Figure 7 Dependence of V_r on the blend composition.

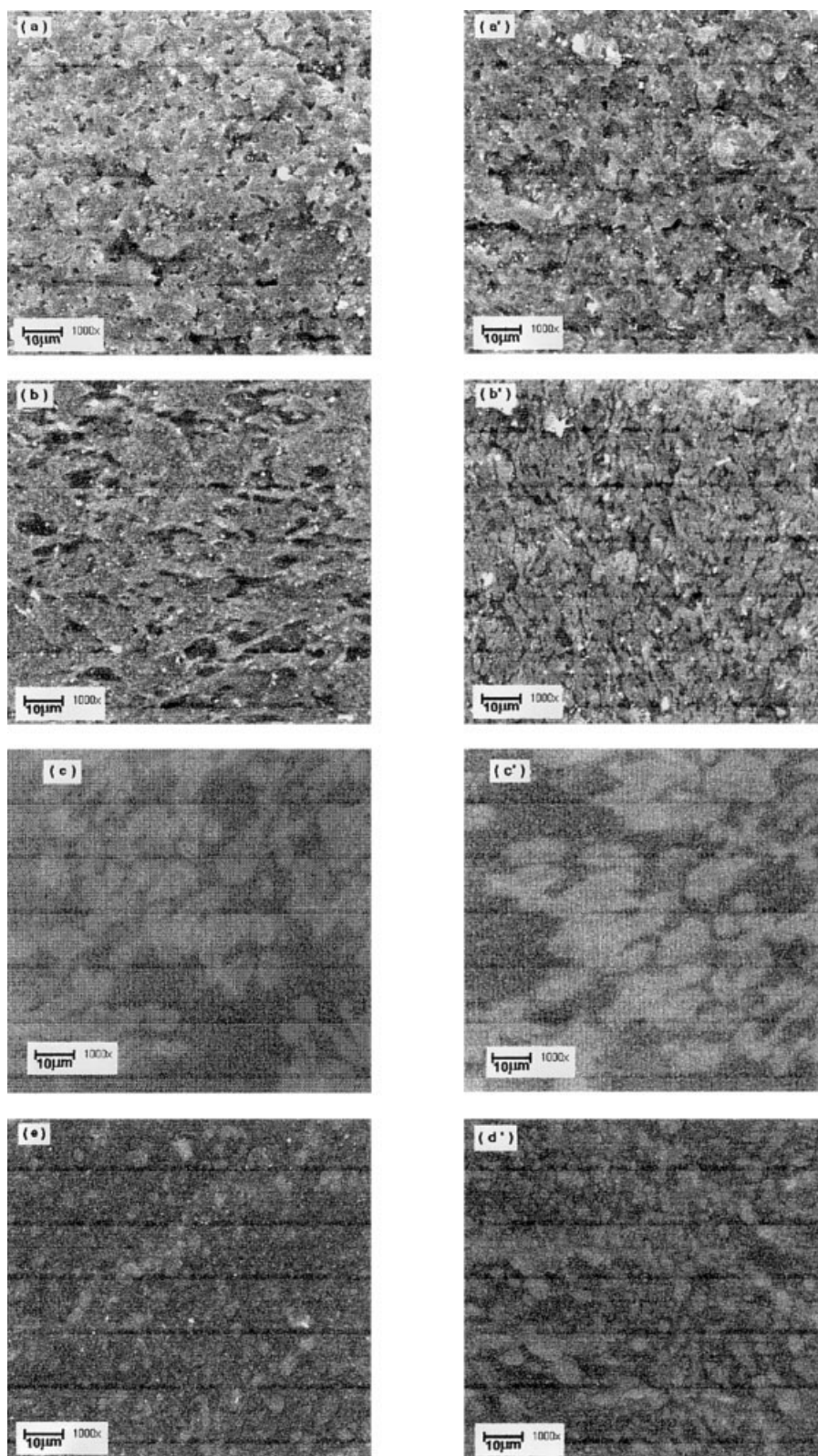


Figure 8 SEM micrographs of NBR/EVA blends with (a) 80, (b) 60, (c) 40, and (d) 20% NBR. The primes correspond to compatibilized blends.

discussed. As the EVA component in the blend increased, the influence of EVALSH on the curing parameters became negligible.

Figures 5 and 6 illustrate the dependence of the ultimate tensile strength and elongation at break, respectively, as a function of the blend composition. The presence of 5 phr EVALSH resulted in an increase in the tensile strength for all blends, but the greatest effect was observed for blends richer in NBR. The elongation at break presented different features: for blends containing large amounts of NBR (80 and 100 wt %), there was a substantial decrease in this property with the addition of EVALSH, probably because of the increase in the crosslink density. For blends richer in EVA, there was no influence on this property. A blend containing 60 wt % NBR presented a slight increase in the elongation at break with the addition of EVALSH.

The improvement in the tensile strength may be associated with an increase in the crosslink density or the interfacial action of EVALSH. The effect of the mercapto-modified copolymer on the crosslink density is illustrated in Figure 7. An increase in this parameter with the addition of EVALSH was observed in all blends containing more than approximately 50 wt % NBR. This behavior was in good agreement with the tensile strength data, indicating that one of the important factors for the improvement of the tensile strength in these compatibilized blends was related to the increase in the crosslink density. The sulfur-based systems were able to vulcanize only the unsaturated NBR phase. Consequently, the action of EVALSH on the cure process was more effective in blends richer in NBR. For blends containing a higher proportion of EVA, there was no significant influence of EVALSH on the crosslink density and on other properties, such as the cure parameters and tensile properties.

Morphological aspects

Scanning electron microscopy (SEM) micrographs of compatibilized and noncompatibilized blends are given in Figure 8. The cryofracture surface was stained with OsO_4 and analyzed with the help of a backscattered detector. The white region corresponds to the stained unsaturated NBR phase. Figure 8(a–d) shows the noncompatibilized blends, and the primes correspond to the compatibilized blends. Blends containing small amounts of NBR (40 or 20 wt %) did not present any morphological difference with the addition of EVALSH [Fig. 8(c,d)]. These results were in good agreement with the tensile properties.

The morphology of an NBR/EVA (80:20 w/w) blend was also not affected by the presence of EVALSH, despite the better tensile strength achieved with the compatibilization. Therefore, we can assume that the main factor responsible for the increasing

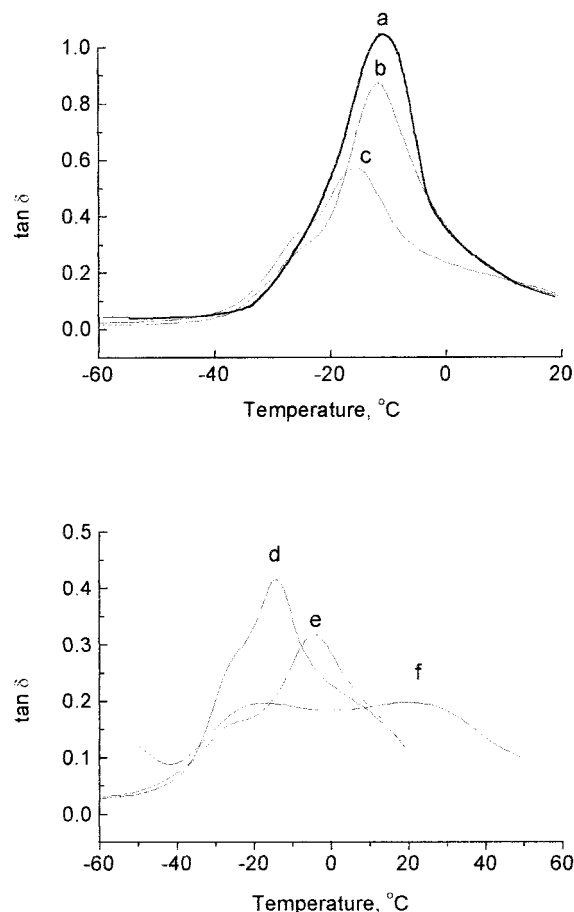


Figure 9 Variation of $\tan \delta$ with the temperature for NBR/EVA blends with (a) 100, (b) 80, (c) 60, (d) 40, (e) 20, and (f) 0% NBR.

mechanical performance of the 80/20 NBR/EVA compatibilized blend was the increase in the crosslink density, rather than some interfacial action of the compatibilizer. For 60/40 NBR/EVA blends, a small influence of EVALSH on the morphology could be observed. At this composition, the EVA phase (dark region) became thinner and more elongated with the compatibilization, and this suggested that the phase coalescence was minimized by the presence of EVALSH. This phenomenon may be an indication of the interfacial action of EVALSH.

Dynamic mechanical properties

The dependence of the loss tangent ($\tan \delta$) on the temperature for the vulcanized blends is illustrated in Figure 9. The vulcanized NBR presented a relaxation peak at -10°C , which corresponded to its glass transition [Fig. 9(a)]. EVA presented two relaxation peaks [Fig. 9(f)], around -20°C and around 20°C , with low damping because of its semicrystalline nature. The blends presented the characteristic relaxation of the NBR phase. It is also possible to distinguish a small

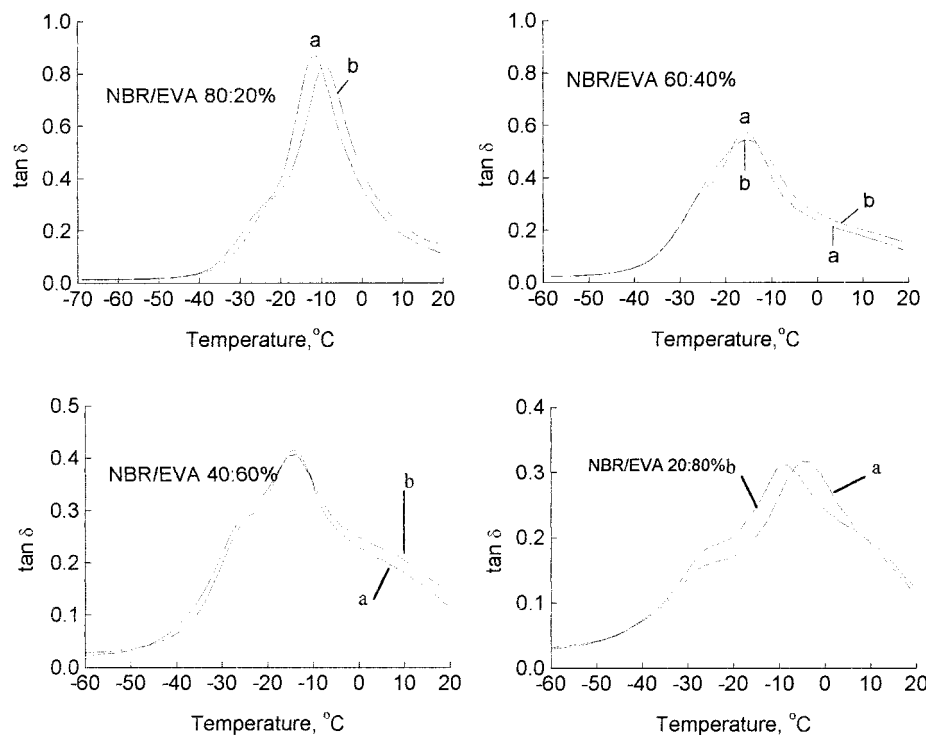


Figure 10 Dependence of $\tan \delta$ on the temperature for NBR/EVA as a function of the blend composition: (a) without EVALSH and (b) with 5 phr EVALSH.

shoulder at a temperature below -20°C in all the blends, which is attributable to the EVA phase. This behavior confirmed the noncompatibility of these blends. This shoulder was not observable in the non-vulcanized blends presented in our previous report⁵ because in those systems the NBR phase was not vulcanized and the glass transition of NBR occurred at a lower temperature, overlapping the EVA transition.

EVALSH exerted little influence on the damping of these blends. As shown in Figure 10, there was little displacement of $\tan \delta$ toward higher temperatures with the addition of EVALSH in blends with 80 wt % NBR, and this indicated a decrease in the chain mobility as a result of the increase in the crosslink density, as also observed in the swelling experiments. In blends with intermediary compositions, EVALSH resulted only in a slight broadening of the damping curve. However, for blends with 20 wt % NBR, the addition of EVALSH resulted in a perceptible displacement of $\tan \delta$ toward a lower temperature. At this composition, EVALSH did not exert an influence on the crosslinking degree, and its effect could mainly be attributed to the interfacial action.

CONCLUSIONS

From the results presented in this work, it is possible to conclude that the mercapto groups in EVALSH act

as accelerators in the curing process, as shown by the decreasing scorch time. In addition, they are able to increase the crosslink density of blends richer in NBR. These characteristics have been observed only in systems vulcanized with sulfur systems. On the basis of the DSC analysis, we can suggest interactions of the mercapto groups with the activators used in the sulfur vulcanizing system. The increase in the crosslinking degree and the interfacial activity of EVALSH may be responsible for the increase in the ultimate tensile strength.

The authors are grateful to Ana C. F. Moreira for her assistance with the dynamic mechanical thermal analysis of the blends.

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