

Mercapto-Modified Copolymers in Elastomer Blends. IV. The Compatibilization of Natural Rubber/EPDM Blends

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ABSTRACT: Ethylene—propylene—diene functionalized with mercapto groups (EPDMSH) was employed as compatibilizing agent for natural rubber (NR)/EPDM blends, resulting in a substantial increase of the ultimate tensile strength of these blends without affecting the elongation at break. There is also a decrease of the curing time with the addition of as low as 2.5 phr of EPDMSH, mainly in NR/EPDM (70:30 wt %) blend, indicating the accelerator effect of this functionalized copolymer. This copolymer also increased the crosslink degree and the gel content. From dynamic mechanical analysis (DMTA), it was demonstrated that EPDMSH improves the covulcanization process. The reactive compatibilization of EPDMSH was demonstrated by the presence of insoluble material in nonvulcanized/compatibilized blends and by its thermogravimetric (TGA) analysis. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2892–2900, 2002; DOI 10.1002/app.10283

Key words: elastomer blends; natural rubber; ethylene—propylene—diene; compatibilization; mercapto-modified copolymer

INTRODUCTION

Natural rubber (NR) presents excellent physical properties, but its resistance to heat, oxygen, and ozone is not good. Blending with other less unsaturated elastomer such as ethylene—propylene—diene rubber (EPDM) is an attractive way of developing new rubber materials with better aging resistance.¹ However, these blends usually display inferior mechanical properties mainly at a

composition required for adequate ozone resistance, that is, at an EPDM concentration of 35–40 phr. The decreasing of the mechanical properties is attributed to the difference between the reactivities of the elastomers with the curing agents and/or due to differences in solubilities of the curatives in each elastomer phase.² Such differences are found in blends of rubbers with different unsaturation degree. In these cases, the bulk of the curing system can be consumed by the vulcanization of the more rapidly vulcanizable rubber, usually the higher unsaturated component.^{3,4}

Many efforts have been made to improve the curative distribution in NR/EPDM blends. For example, Suma et al. have first precured the EPDM component to a low degree and then blended it with natural rubber.⁵ This procedure resulted in an improvement of the mechanical

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properties, which was attributed to a covulcanization process as a consequence of a reduction of the migration of the curing agents out of EPDM. Baranwal and Son have reported since three decades ago, the graftization of the accelerators onto the EPDM backbone as a way to improve the covulcanization in NR/EPDM blends.⁶ The functionalization of EPDM with maleic anhydride has been also employed to improve the mechanical properties of these blends.⁷⁻⁹

The addition of a third component, i.e., a compatibilizer, which is able to act at the interface between the phases is also a good approach to obtain polymer blends with a more homogeneous morphology and improved mechanical properties. In this sense, Chang et al. have recently employed trans-polyoctenylene rubber (TOR) as the third polymeric component in NR/EPDM blends.¹⁰ This component has low molecular weight and acts as a processing aid and also as a compatibilizing agent since it is located at the interface between NR and EPDM.

The compatibilization of elastomer blends may be successfully performed by using a functionalized polymer as a reactive compatibilizer. It is well documented in the literature that thiol groups can be added to the carbon-carbon double bond of unsaturated polymers.¹¹⁻¹³ Based on this principle we have started to develop some mercapto-functionalized polymers to be employed as compatibilizing agents of elastomer-based blends. For this purpose, both ethylene-vinyl acetate (EVA) copolymers¹⁴⁻¹⁷ and ethylene-propylene-diene (EPDM) terpolymer¹⁸ have been functionalized with mercapto groups along the backbone. When mercapto groups are introduced along the chain of the less (or not) unsaturated polymer component, it could react with the double bond of the high-diene rubbers and form an effective anchorage between the rubber phases during processing. This should originate in better mechanical performance in addition to good aging and curing properties. Indeed, the use of small amount of mercapto-modified EVA copolymer (EVALSH) in NR/EVA blends increased the ultimate tensile strength and hardness, for blends containing large amount of natural rubber.^{14,15} Similar behavior has been also observed for NBR/EVA blends.¹⁹ Better aging resistance has been also achieved with these compatibilized EVA-based blends.¹⁷

EPDM functionalized with mercapto groups was also employed in NBR/EPDM blends.¹⁸ The improvement of mechanical properties was not

very high in this system but the aging resistance was superior for compatibilized blends. All these systems involve reactive compatibilization through the formation of chemical bond between the unsaturated rubber and the mercapto groups located along the compatibilizing chain. This feature has been indicated by the presence of a great amount of insoluble material after blending the blend components without vulcanization system.¹⁴

This paper describes the influence of mercapto-modified EPDM copolymers (EPDMSH) on the mechanical performance of NR/EPDM blends. The functionalization of EPDM involved two reaction steps.¹⁸ The first step gives rise to thioacetate-modified EPDM (EPDMTA), which was submitted to alkaline hydrolysis, thus obtaining the mercapto-modified EPDM (EPDMSH). Evidence for the reactive compatibilization was obtained by the presence of insoluble material in nonvulcanized blend containing EPDMSH and also by thermogravimetric analysis of this insoluble material.

EXPERIMENTAL

Materials

Natural rubber (NR, *Hevea Brasiliensis*), $M_w = 207,000$, was kindly supplied by Michelin do Brasil S. A. (Rio de Janeiro, Brazil). EPDM rubber samples with two different compositions were kindly supplied by DSM Elastomeros do Brasil S. A. (São Paulo, Brazil). Table I summarizes the characteristics of these EPDM samples. Zinc oxide, stearic acid, sulfur, irganox 245, and 2,2'-dithiobisbenzothiazole (MBTS) were of laboratory reagent grade.

Functionalization of EPDM

The preparation of mercapto-modified EPDM was carried out according to previous report,¹⁸ by using EPDM65 sample. This EPDM sample contains a higher amount of the diene component, which is interesting for obtaining functionalized EPDM with a higher amount of mercapto groups. In addition, the lower Mooney viscosity of this sample may contribute for its location at the blend interface. The reaction involves a free radical addition of thioacetic acid (TAA) to the double bond of the EPDM terpolymer in the presence of azobisisobutyronitrile (AIBN), followed by meth-

Table I Characteristics of EPDM Samples Employed in This Study

	Commercial Grade	
	EP65	EP57C
Number average molecular weight obtained by SEC	150,000	80,000
Density (g/cm ³)	0.837	0.813
Iodine index	29	15
Diene content (mmol/100 g)	114	58.9
Ethylene/propylene weight ratio	60/40	73/27
Mooney viscosity (ML 1 + 4 at 100°C)	77	90

analysis of the acetylthio groups by using methanolic solution of sodium hydroxide. The introduction of thioacetate groups along the EPDM backbone was performed at 70°C in toluene solution for 48 h. The TAA/AIBN and diene/TAA molar ratios were established as 10.0 and 1.0, respectively. The EPDMTA was submitted to an alkaline hydrolysis using 5 wt % solution of NaOH in methanol, giving rise to EPDMSH. The amount of mercapto groups in the functionalized copolymer corresponded to 2.5 mmol/g of polymer. The chemical structures of the functionalized EPDM samples are illustrated in Figure 1.

Preparation of Blends

The EPDM sample used for the blend preparation was EPDM57C, with lower amount of diene. The blends were prepared in a two-roll mill operating at 80°C and at 20 rpm. NR was masticated for 2 min, and then EPDM and the functionalized compatibilizer (EPDMSH) were subsequently added. After the homogenization of the rubber blend (for about 4 min), the other ingredients were added in the following order: zinc oxide (5.0 phr), stearic acid (1.5 phr), irganox 245 (1.0 phr), sulfur (2.5 phr), and 2,2'-dithiobisbenzothiazole (MBTS) (0.8 phr). The processing time after each component addition was about 2 min.

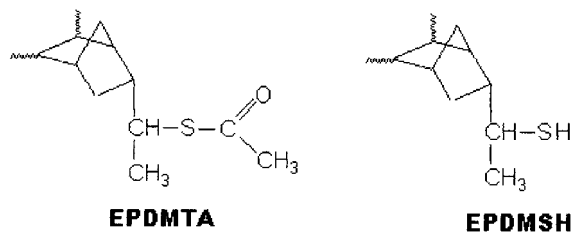


Figure 1 Chemical structures of the functionalized EPDM samples.

The optimum curing time of the blends was established as the necessary time to reach 90% of the maximum torque, which was determined from an oscillating disk rheometer (Monsanto, R-100), operating at 160°C and 1° arc. The blends were then vulcanized up to the optimum curing time in an hydraulic press at 160°C and 1500 lb/in².

Measurements of Physical Properties

For tensile testing, dumbbell-shaped tensile test specimens (ASTM 638—testing number 5) were punched out of the compression molded sheets. Tensile testing was performed on an Instron 4202 Universal Testing Machine with a computerized data acquisition system at a crosshead speed of 100 mm · min⁻¹.

Crosslink densities of the blends were obtained from swelling experiments. Vulcanized samples of about 1 g were accurately weighted (w) and immersed in toluene in closed bottles for 7 days. The surfaces were dried with filter paper and the samples were quickly weighted (w_1). The swollen samples were then dried completely at 60°C for 48 h under reduced pressure and weighted again (w_2). The volume fraction of the polymer in a swollen mass was calculated by the following equation:

$$Vr = \frac{w_2 \cdot (\delta_r)^{-1}}{w_2 \cdot (\delta_r)^{-1} + (w_1 - w_2) \cdot (\delta_s)^{-1}}$$

where δ_r and δ_s are the rubber and solvent densities, respectively.

The insoluble material in unvulcanized and vulcanized blends was determined by submitting a sample of about 1 g to a heating in xylene at 120°C for 24 h.

Thermogravimetric analysis (TGA) were performed in a TGA-7 Perkin Elmer apparatus under

Table II Curing Parameters and Crosslink Degree of NR/EPDM Blends as a Function of Composition and Compatibilization

NR/EPDM (wt %)	80 : 20		70 : 30		60 : 40	
	a	b	a	b	a	b
M_L (in-lb) ^c	1.5	1.9	1.5	2.5	2.0	2.0
M_H (in-lb) ^c	16.5	17.0	19.0	20.3	19.5	20.0
t_{s1} (min) ^d	3.0	2.8	2.8	2.3	3.3	3.0
t_{90} (min) ^d	8.0	8.0	9.5	7.4	10.3	9.5
V_R	0.14	0.20	0.12	0.19	0.12	0.17
Gel content (%)	74	73	66	79	74	81

^a Blends without compatibilizer.

^b Blends with 2.5 phr of EPDMSH.

^c M_L and M_H are the minimum and maximum torque, respectively.

^d The t_{s1} and t_{90} are the scorch time and optimum curing time, respectively.

nitrogen atmosphere and at a heating rate of 10°C/min.

The dynamic mechanical properties of vulcanizates were determined by using a dynamic mechanical thermal analyzer, Rheometric Scientific MKIII, operating in a bending mode at a frequency of 1 Hz and amplitude of 0.1%. The temperature was increased at 2°C/min over the range of -100–20°C.

Scanning electron microscopy (SEM) was performed on a Zeiss DSM 160 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 first coated with carbon.

RESULTS AND DISCUSSION

Curing Characteristics and Mechanical Properties

The effect of EPDMSH on the curing parameters and crosslink degree of NR/EPDM blends is summarized in Table II. For this study, blends with high amount of NR were chosen because there is an interest in developing NR-based blends that could maintain, as much as possible, the good mechanical properties of the NR component. The addition of 2.5 phr of EPDMSH resulted in an increase of both minimum (M_L) and maximum torque (M_H), mainly in blend containing 70 wt % of NR. In addition, there is a decreasing of both scorch time (t_{s1}) and optimum cure time (t_{90}), indicating that the mercapto groups along the

EPDMSH backbone act as accelerator in the curing process. The effect of EPDMSH on the curing parameters is better illustrated in Figure 2, for NR/EPDM (70:30 wt %) blends.

The crosslink degree may be estimated from swelling experiments. The samples have been vulcanized up to the optimum cure time (time to reach 90% of the maximum torque) at 160°C and submitted to swelling experiments in toluene at room temperature, for 7 days. The equilibrium swelling V_r is also indicated in Table II. The addition of 2.5 phr of EPDMSH resulted in a substantial increasing of V_r values, indicating that the mercapto groups in EPDMSH sample are able to increase the crosslink density of the vulcanized rubber blend. In addition, there is a substantial increasing of the amount of insoluble material in compatibilized NR/EPDM blends containing 70 and 60% of NR (see Table II). The amount of the

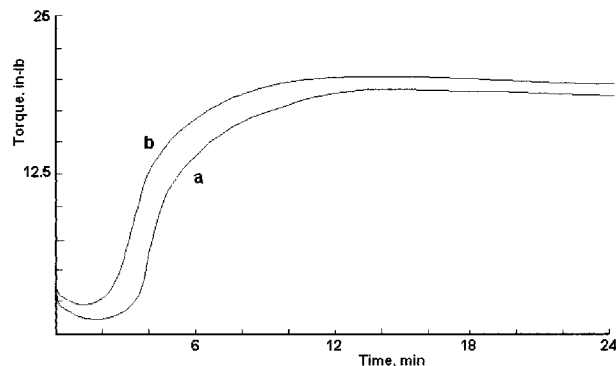


Figure 2 Rheographs of 70:30 NR/EPDM blends cured at 160°C (a) uncompatibilized and (b) compatibilized with 2.5 phr of EPDMSH.

Table III Mechanical Properties of NR/EPDM Blends as a Function of Composition and Compatibilization

NR	EPDM	σ_B (MPa) ^a		ε_B (%) ^b	
		c	d	c	d
100	0	11.5	9.6	750	780
80	20	10.3	13.0	850	830
70	30	10.5	13.5	900	840
60	40	9.4	15.0	600	700
0	100	3.4	5.5	100	200

^a Ultimate tensile strength.^b Elongation at break.^c Blends without compatibilizer.^d Blends with 2.5 phr of EPDMSH.

insoluble material is higher than the amount of the NR component in the blend, indicating that EPDMSH also promotes some crosslinking in the EPDM phase.

The mechanical properties of the blends are compared to those of the pure components in Table III. The ultimate tensile strength of noncompatibilized blends is lower than that of pure NR, as expected since these blends are incompatible. The addition of 2.5 phr of EPDMSH resulted in an improvement of this property for NR/EPDM blends. The values found for the compatibilized blends were even higher than that observed for pure NR, indicating a synergic behavior with the compatibilization. Concerning the elongation at break, the compatibilization did not affect substantially this property, except for the system containing 100% of EPDM, where a significant increase was observed. The improvement of the tensile strength of the blends with the addition of EPDMSH may be attributed to the interfacial action of this component associated to an increase of the crosslink degree.

In spite of the higher tensile strength observed in compatibilized blends, the presence of 2.5 phr of EPDMSH decreases a little this property for system containing 100% of NR. This behavior can be attributed to a decrease of the ability of the NR to crystallize under stress when EPDMSH is dispersed inside it. These features are more important when the matrix is composed of NR. Concerning EPDM pure system, the improvement of the mechanical performance with the addition of EPDMSH may be attributed to the better compatibility between the components and to the reaction between the mercapto groups of the EP-

DMSH and the EPDM matrix. The lower Mooney viscosity of EPDMSH may also be responsible for the increase of the deformation at break.

Morphological Aspects

The phase morphology of NR/EPDM blends of different compositions is illustrated in Figure 3. The light region corresponds to the NR phase, which was stained by OsO₄ and the dark points are related to the unstained EPDM phase. Although the addition of the EPDMSH resulted in an improvement on the mechanical properties, the morphological aspect was not significantly affected. Concerning the NR/EPDM (60:40 wt %) blend, the presence of EPDMSH resulted in a more homogeneous morphology, but the differences are not substantial. Therefore, the improvement of the ultimate tensile strength should be better associated to an improvement on the covulcanization state of the blends and also to an increasing of the crosslink degree. Additional proofs concerning covulcanization are presented later.

Dynamic Mechanical Properties

The dynamic mechanical properties such as storage modulus (E') and damping ($\tan \delta$) of the pure components and the 70:30 NR/EPDM blends were evaluated from -80 to 25°C . Figure 4 shows the variation of $\tan \delta$ and E' vs temperature for the vulcanized homopolymers. The $\tan \delta$ curve of EPDM (curve A) shows a peak at -30°C corresponding to the glass transition temperature (T_g) of this component. Natural rubber exhibits this transition at -52°C with a damping value significantly higher than the EPDM because of the higher rubbery nature of the NR component. Both components exhibit similar storage modulus below the T_g region.

The variations of $\tan \delta$ and E' with temperature for NR/EPDM (70:30 wt %) blends are shown in Figure 5. In spite of the blend incompatibility and also the differences found in the glass transition temperatures of the blend components, the noncompatibilized blend [Fig. 5(a)] displays only one transition at a temperature below that one found in pure NR sample. The extraction experiments with hot xylene revealed that this blend contains a substantial amount of non crosslinked rubber (around 35 wt %). The noncrosslinked rubber should be mainly constituted by the EPDM phase due to its lower cure rate, as compared to

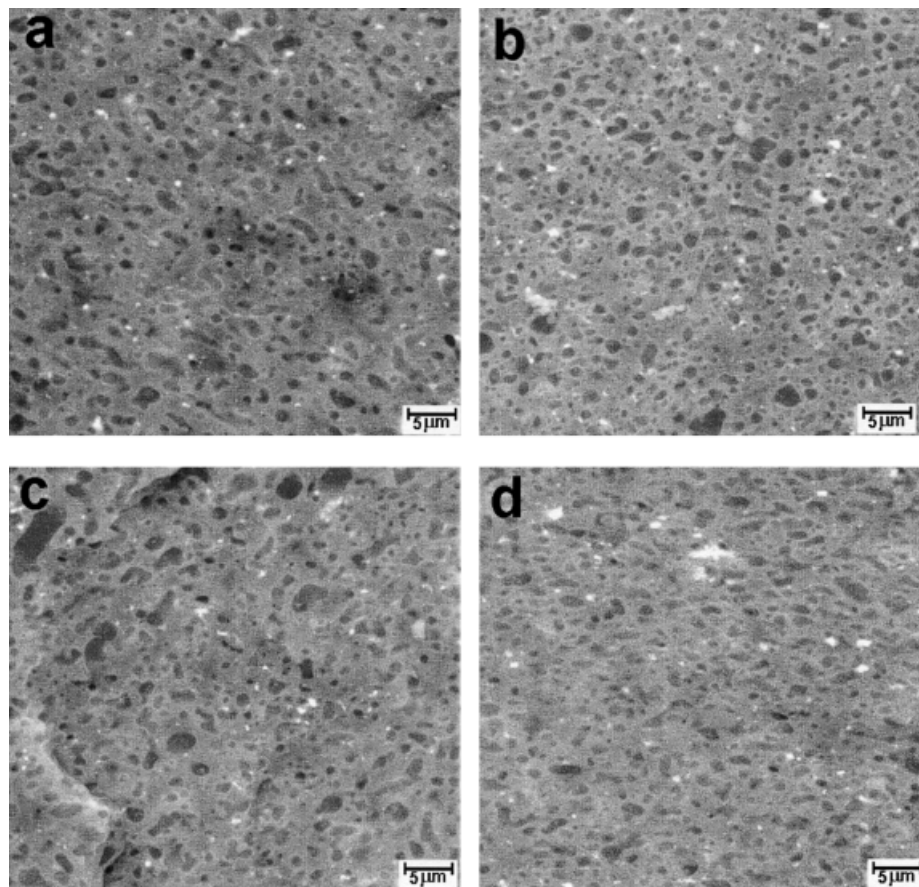


Figure 3 SEM micrographs of NR/EPDM (a and b) 70/30 wt % and (c and d) 60/40 wt % blends. (Micrographs a and b are related to compatibilized blends with 2.5 phr of EPDMSH).

NR phase. Considering the higher chain mobility of the noncrosslinked EPDM, this glass transition temperature is expected to be shifted toward lower temperatures when compared to the same

vulcanized rubber. Therefore, the single tan δ peak in this blend can be attributed to the vulcanized NR phase together with the nonvulcanized

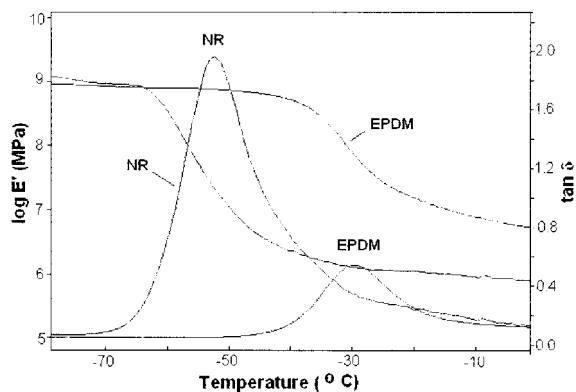


Figure 4 Dynamic mechanical properties of vulcanized NR and EPDM samples.

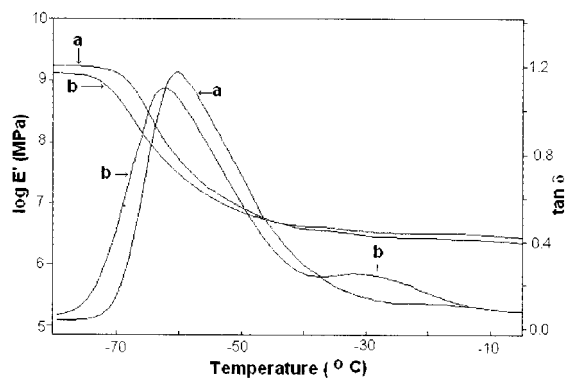


Figure 5 Dynamic mechanical properties of vulcanized NR/EPDM (70:30% wt %) blends: (a) noncompatibilized blend and (b) compatibilized with 2.5 phr of EPDMSH.

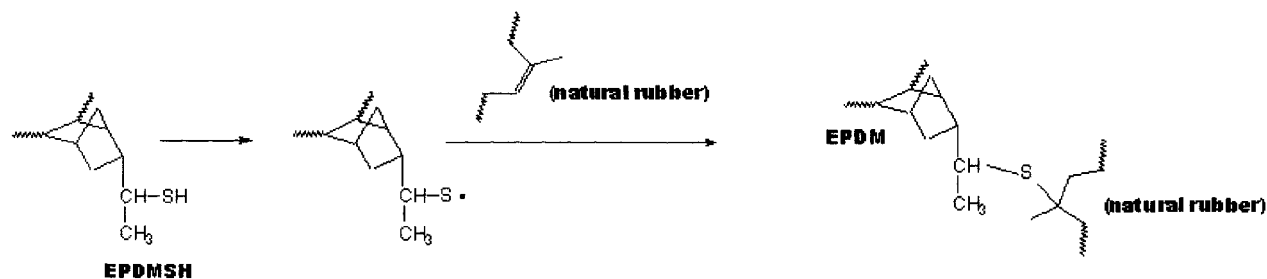


Figure 6 Scheme illustrating the free radical reaction between the double bond of the unsaturated rubber phase and the mercapto groups of EPDMSH.

EPDM phase whose transition should occur at very similar temperatures. The presence of the nonvulcanized EPDM fraction in the blend may also be responsible for the lower glass transition temperature of this blend when compared to the pure NR component.

NR/EPDM blend compatibilized with EPDMSH presents a lower value of the glass transition temperature related to the NR phase and a lower damping [see Fig. 5(b)]. These results may also be attributed to the effective compatibilization of this functionalized copolymer. The strong interactions between the mercapto groups along the EPDMSH backbone and the NR phase decreases the mobility of this phase, giving rise to a decreasing of the damping. In spite of decreasing of damping, this blend displays also a little shift of the glass transition temperature towards lower value. This phenomenon can be attributed to the rubbery nature of the EPDMSH used as compatibilizing agent. As described in experimental part, the EPDM sample used for the preparation of the functionalized EPDM (EPDM65) is less viscous than the EPDM (EPDM57C) used in the blends. The addition of a small amount of this component can plasticize the NR phase thus decreasing the T_g of this phase.

It is important to emphasize that blend compatibilized with EPDMSH displays a second transition [Fig. 5(b)] with low damping at a temperature similar to that found for the vulcanized EPDM sample. This results agree to those concerning gel content and crosslink degree. As observed in Table II, the presence of EPDMSH increased considerably the gel content of the vulcanized sample. The amount of the insoluble material was higher than the proportion of the NR phase, indicating the vulcanization of almost 50% of the EPDM phase in the blend together with the NR phase. The proportion of the vulcanized EPDM phase in the NR/EPDM blend com-

patibilized with EPDMSH may be responsible for the second transition at higher temperature. The damping related to this transition is low because of the low amount of the EPDM as a crosslinked phase and also because of the low damping of the EPDM itself.

Evidence for the Reactive Compatibilization

Reactive compatibilization can be considered when a functionalized polymer, acting as a compatibilizing agent, can react with the blend components, thus forming graft or block copolymer or even a network during the blend processing. In the case of EPDMSH, the reactive processing is believed to occur through a free radical reaction between the double bond of the unsaturated rubber phase and the mercapto groups of the functionalized copolymers, according to the scheme presented in Figure 6.

In order to analyze the effectiveness of the reactive compatibilization, we decided to perform nonvulcanized NR/EPDM blends containing different proportions of the functionalized copolymer, as compatibilizing agent. For this purpose, we have chosen a blend composition of 50:50 wt %. These blends were prepared by melt mixing the components in a two-roll mill at 80°C for 15 min and then compression molded at 160°C for 10 min in a hydraulic press at 6.7 MPa. The samples were submitted to extraction with hot xylene for 24 h in order to determine the amount of insoluble material. As indicated in Table IV, noncompatibilized blend did not present any insoluble material, as expected since there is no vulcanizing system in the formulation and no reaction is expected to occur between NR and EPDM during the blend processing. On the other hand, the presence of EPDMSH resulted in a considerable amount of insoluble material. This proportion is higher than the amount of the functionalized co-

polymer used in the blend, suggesting the formation of a network during the process, as suggested in Figure 6.

The composition of the insoluble fraction obtained from the nonvulcanized blend containing 10 phr of the functionalized copolymer (EPDMSH) was determined by thermogravimetric analysis because both nonvulcanized components, NR and EPDM, display distinct thermal degradation behaviors. Figure 7 compares the thermogram of the insoluble fraction with those of the pure components. As expected, the degradation of NR occurs at a lower temperature than EPDM. The insoluble material obtained from the compatibilized blend [Fig. 7(c)] presents two degradation steps, which can be related to the NR and EPDM phases. The amount of the NR phase in the insoluble material was around 35%, indicating that the network formed during blending is composed by both blend component. Since the amount of EPDM in this insoluble fraction is higher than the amount of the functionalized copolymer added in the blend, we can conclude that the reactive compatibilization involves the reaction of the mercapto groups of the EPDMSH with both NR and EPDM phases in the blend. In other words, the functionalized copolymer is acting as a reactive interfacial agent.

CONCLUSION

EPDMSH resulted in a substantial increase of the ultimate tensile strength of NR/EPDM blends, indicating a compatibilization effect.

EPDMSH also resulted in an increase on the curing time mainly in blends containing 70 wt % of NR. In addition, an increased crosslink degree and higher gel content were observed. Since the EPDMSH sample used in these blends contains mercapto groups in a concentration around 2.5 mmol/g, the addition of 2.5 phr of EPDMSH

Table IV Gel Content of Nonvulcanized NR/EPDM (50 : 50 wt %) Blends Obtained from Extraction in Hot Xylene

EPDMSH phr, 0	Gel Percent %, 0
2.5	23.0
5.0	29.0
10	38.0

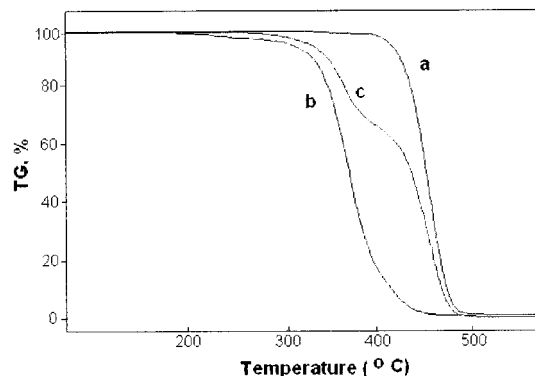


Figure 7 Thermogravimetric analysis of (a) EPDM, (b) NR, and (c) the insoluble material obtained from nonvulcanized NR/EPDM (50:50 wt %) blend compatibilized with 10 phr of EPDMSH.

means that a mercapto content as low as 6 mmol has been introduced in the blend. This low amount of mercapto groups is able to accelerate the curing process and to increase the crosslink density of these blends. This phenomenon was also confirmed by dynamic mechanical analysis. Indeed, a second glass transition temperature related to the vulcanized EPDM phase appears in the blend compatibilized with EPDMSH, indicating that this component is able to promote the vulcanization of the EPDM phase. This transition was not observed in uncompatibilized blend.

By analyzing the insoluble material obtained from nonvulcanized blends, one can confirm the reactive compatibilization of EPDMSH. From all results presented in this work, it is possible to suggest that the EPDMSH acts as compatibilizing agent and helps in the covulcanization process. The efficiency of this compound on the compatibilization and covulcanization of NR/EPDM blends vulcanized with other systems is being investigated, and the results will be reported in a subsequent paper.

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