

# Effect of Anhydride-Modified Ethylene–Propylene–Diene Rubber and Ethylene–Vinyl Acetate Copolymers on the Compatibilization of Nitrile Rubber/Ethylene–Propylene–Diene Rubber Blends

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**ABSTRACT:** The effects of maleic anhydride modified ethylene–propylene–diene rubber (EPDMMA) and maleic anhydride modified ethylene–vinyl acetate (EVAMA) on the compatibilization of nitrile rubber (NBR)/ethylene–propylene–diene rubber (70:30 w/w) blends vulcanized with a sulfur system were investigated. The presence of EPDMMA and EVAMA resulted in improvements of the tensile properties, whereas no substantial change was detected in the degree of crosslinking. The blend systems were also analyzed with scanning electron microscopy and dynamic mechanical thermal analysis. The presence of EVAMA resulted

in a blend with a more homogeneous morphology. The compatibilizing effect of this functional copolymer was also detected with dynamic mechanical analysis. A shift of the glass-transition temperature of the NBR phase toward lower values was observed. The presence of EPDMMA and EVAMA also increased the thermal stability, as indicated by an improvement in the retention of the mechanical properties after aging in an air-circulating oven. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2408–2414, 2003

**Key words:** compatibilization; rubber; blends

## INTRODUCTION

Blending nitrile rubber (NBR) with a suitable amount of ethylene–propylene–diene rubber (EPDM) is an attractive way of developing rubber materials with good oil resistance imparted by the NBR component and associated with improved heat and ozone resistance.<sup>1</sup> However, this blend is immiscible and generally exhibits a gross-phase-separated morphology and poor interfacial adhesion, which contribute to a decrease in the mechanical performance. In addition, the differences in the reactivities of the elastomer components toward the curing agents and solubilities of the curatives in the elastomer phases also result in a maldistribution of crosslinks in the blend system.<sup>2–5</sup> The curing system is normally con-

sumed by the more rapidly vulcanizable rubber, that is, the NBR phase, because of its higher unsaturation degree and higher polarity.<sup>5–7</sup>

Many efforts have been made to improve the compatibilization of this blend, including the use of low-molecular-weight compounds such as poly(*trans*-octylene) (TOR)<sup>8</sup> or polar polymers such as polychloroprene,<sup>9–12</sup> chlorinated polyethylene,<sup>12,13</sup> and chlorosulfonated polyethylene.<sup>12,13</sup> The use of a liquid elastomer normally results in a more homogeneous morphology and a better mechanical performance because of its lower viscosity, which contributes to its location at the interface of the heterogeneous blend. In addition, it is believed that it participates in the network because of the presence of double bonds in its structure, which improve the interfacial adhesion and contribute to the covulcanization.<sup>8,14</sup> Polar chloro-containing polymers are considered very good compatibilizing agents because of their better affinity toward the NBR component.<sup>12</sup>

The reactive compatibilization of NBR/EPDM blends has also been performed in our laboratory with mercapto-modified EPDM<sup>15</sup> and mercapto-modified ethylene–vinyl acetate (EVA) copolymers.<sup>16</sup> The mercapto groups along the functionalized copolymer backbone are able to react with the double bond of the diene rubber during the melt-blending process, promoting an effective anchorage between the phases.

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Polymers containing anhydride groups constitute the most versatile reactive compatibilizing agents for several polymer blends because of the high reactivity of the anhydride group and the easy functionalization process, based on the free-radical addition of maleic anhydride (MA) onto the polymer backbone, usually by a melt-mixing process including reactive extrusion.<sup>17-19</sup> For elastomer-containing blends, some reports in the literature discuss the effects of MA-modified polypropylene and MA-modified polyethylene on the compatibilization of either nonvulcanized or dynamically vulcanized NBR-polypropylene blends<sup>20-22</sup> and NBR-polyethylene blends.<sup>23</sup> Both functionalized polymers have also been employed on for compatibilization of blends containing natural rubber and polyethylene or polypropylene.<sup>24</sup> EPDM functionalized with MA has also been employed by Coran<sup>5</sup> in blends based on vulcanized natural rubber.

Considering the versatility of MA-modified polymers as reactive compatibilizers for several polymer blends, we decided to investigate the effects of two different functionalized polymers on the mechanical performance of vulcanized NBR/EPDM blends. This article compares the efficiency of maleic anhydride modified ethylene-propylene-diene rubber (EPDMMA) and maleic anhydride modified ethylene-vinyl acetate copolymer (EVAMA) on the mechanical, dynamic mechanical, and morphological properties of NBR/EPDM blends. EPDMMA is employed because its structure is similar to that of the EPDM blend component. However, EVAMA should give good results because its polarity is higher than that of EPDMMA. Therefore, a better affinity with the NBR phase is expected.

## EXPERIMENTAL

### Materials

NBR [33 wt % acrylonitrile; Mooney viscosity ( $M_L$  1+4 at 100°C) = 48] was kindly supplied by Nitriflex Industries (Rio de Janeiro, Brazil). EPDM with ethylene norbornene as the diene (ethylene/propylene weight ratio = 60/40; 114 mmol of ethylene norbornene/100 g) was kindly supplied by DSM Elastomeros do Brasil S.A. (Sao Paulo, Brazil). EPDMMA (0.5 wt % MA) was kindly supplied by Uniroyal S.A. (USA) EVAMA was synthesized in our laboratory, as described in the literature.<sup>25</sup> The MA content in the EVAMA sample corresponded to 2.1 wt %, as determined by titration with an ethanolic KOH standard solution. Other chemicals, such as zinc oxide (ZnO), stearic acid, sulfur (Vetec Ind. Quim., Rio de Janeiro, Brazil), and 2,2'-dithiobisbenzothiazole (MBTS), were laboratory-reagent-grade.

TABLE I  
Formulation of the NBR/EPDM Blends

	System composition
NBR (wt %)	70
EDPM (wt %)	30
EPDMMA or EVAMA (phr)	5.0
ZnO (phr)	5.0
Stearic acid (phr)	0.5
Sulfur (phr)	1.0
MBTS (phr)	2.0

### Mixing and measurement of the cure characteristics

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

The cure characteristics of the mixes were determined with an oscillating disk rheometer (ODR; Tecnologia Industrial, Buenos Aires, Argentina) operating at 160°C and a 1° arc according to the ASTM D 2084-81 method. The cure rate (RH) was determined as follows:

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

where  $M_{45}$  and  $M_{25}$  are the values of torque at 45 and 25% cure, respectively, and  $t_{45}$  and  $t_{25}$  are the times corresponding to 45 and 25% cure, respectively. The values corresponding to 45 and 25% cure have been chosen because these data refer to the linear portion of the rheometric curve.

The blends were then vulcanized up to the optimum cure time [i.e.,  $t_{90}$ , the time corresponding to 90% of the maximum torque ( $M_H$ ), or the torque value of the highest part of the cure curve given by the ODR] in a hydraulic press at 160°C and 15,000 lb/in.<sup>2</sup>.

### Degree of equilibrium swelling

The degree of equilibrium swelling was determined with experiments performed in toluene, which could swell both NBR and EPDM in the crosslinked states. Cured test pieces (20 mm × 10 mm × 2 mm) were swollen until equilibrium swelling was achieved. Then, 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 ( $V_r$ ):

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

TABLE II  
Vulcanization Parameters of the NBR/EPDM (70:30 w/w) Blends as a Function of Compatibilization

Compatibilizer (5 phr)	$M_L$ (lbf in.)	$M_H$ (lbf in.)	$M_H - M_L$	$t_{s1}$ (min)	$t_{90}$ (min)	RH (lbf in./min)	$V_r$
None	2.5	19.0	16.5	15	29	1.2	0.21
EPDMMA	3.3	19.7	16.4	16	30	1.2	0.18
EVAMA	3.1	19.2	15.9	13	26	1.2	0.20

where  $D$  is the deswollen weight,  $S$  is the swollen weight,  $\rho_r$  is the density of the rubber blend, and  $\rho_s$  is the density of the solvent.

### Measurement of the mechanical properties

Tensile-strain experiments were performed with an Instron 4204 testing machine (MA) at room temperature at a speed of 200 mm/min according to 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. The retention of mechanical properties was calculated as follows:

Retention(%)

$$= \frac{(\text{Mechanical property})_{\text{after aging}}}{(\text{Mechanical property})_{\text{before aging}}} \times 100 \quad (3)$$

### Dynamic mechanical analysis

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

### Morphological studies

Scanning electron microscopy (SEM) was performed on a JEOL 5610 LV instrument (Tokyo, Japan) with a backscattered electron detector and a voltage of 20 kV. The samples were cryogenically fractured, and the surface was treated with osmium tetroxide ( $\text{OsO}_4$ ) for 5 min to selectively stain the unsaturated phase. The stained surfaces were then washed with water, dried, and coated with carbon.

## RESULTS AND DISCUSSION

### Curing characteristics and swelling degree

The vulcanization characteristics of NBR/EPDM blends as a function of compatibilization, together

with the degree of equilibrium swelling of the vulcanized blends, are presented in Table II. The presence of EPDMMA or EVAMA resulted in a small increase in the minimum torque ( $M_L$ ; i.e., the torque value at the lowest part of the cure curve measured by the ODR) during the scorch-delay period, which can be related to an increase in the blend viscosity. This behavior may be attributed to the formation of an ionic crosslink network by the action of ZnO on pendant succinic anhydride groups of the functionalized copolymers. According to Coran,<sup>5</sup> this kind of network forms rapidly under mixing and milling conditions. In addition, the anhydride groups could also react with the double bond of the elastomer phase similarly to those processes related by Choudhury and Bhowmick<sup>24</sup> in natural rubber/polyethylene blends compatibilized with MA-modified polyethylene.

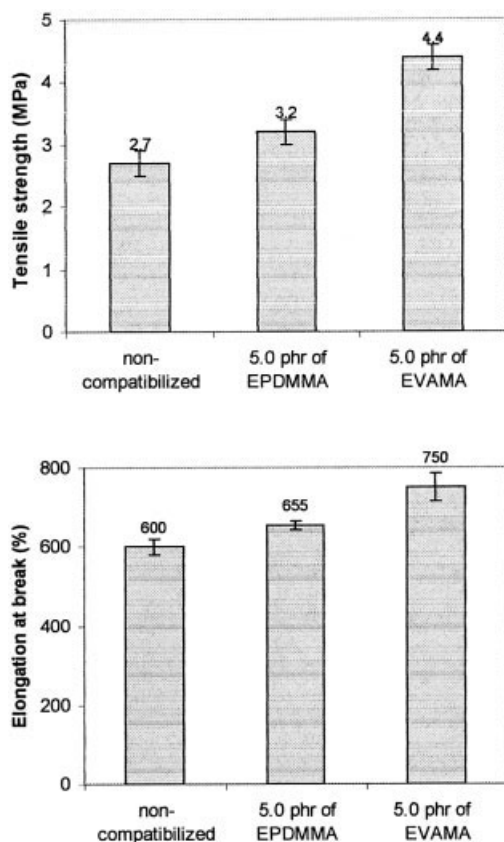
The difference between  $M_H$  and  $M_L$  ( $M_H - M_L$ ) and the overall RH were not significantly affected by the presence of the functionalized copolymers, and this indicated no influence of these components on the crosslink density.

The effect of the functionalized copolymers on the crosslink density could also be estimated from swelling experiments. As presented in Table II, there was little or no decrease in the  $V_r$  values with the addition of EPDMMA or EVAMA; this was also an indication that the crosslink density of the vulcanized blends was not affected by the compatibilization.

Concerning the scorch resistance, the addition of EPDMMA resulted in a slight increase in the scorch time ( $t_{s1}$ ) and  $t_{90}$ , whereas EVAMA reduced these parameters. As reported by McGill and Shelver,<sup>26</sup> in the presence of ZnO, the anhydride groups can be rapidly converted into their zinc salts, and these salts have a positive effect on crosslinking, reducing the induction period. This effect was more pronounced in EVAMA because of the larger number of succinic anhydride groups and the better affinity of EVAMA toward the polar NBR medium.

### Mechanical properties

The effect of compatibilization on the tensile properties of NBR/EPDM blends is illustrated in Figure 1. The addition of 5.0 phr EPDMMA resulted in a small improvement in both the ultimate tensile strength and elongation at break. Nevertheless, the values found for the blends compatibilized with EVAMA were supe-



**Figure 1** Tensile properties of vulcanized NBR/EPDM (70:30 w/w) blends.

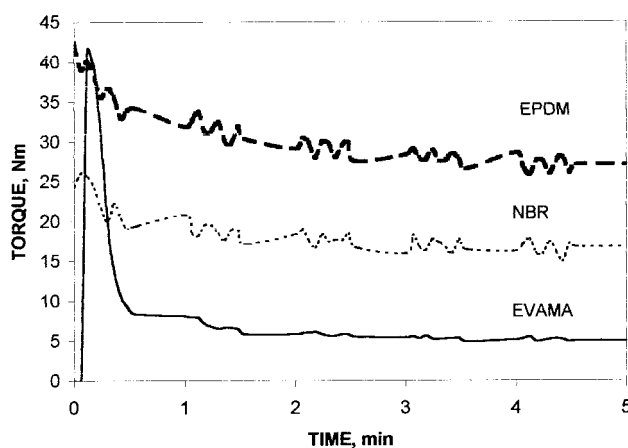
rior, despite the similar structures of the EPDMMA and EPDM blend components. Considering that the swelling degree was not significantly affected by the addition of MA-modified copolymers, we can assume that the good mechanical performance may be better attributed to the interaction between the functionalized copolymers and the rubber components and not to a covulcanization process. The outstanding performance of EVAMA may be related to its more polar nature (which increases its affinity toward the NBR phase), which is associated with its lowest melt viscosity. Both characteristics contribute to its location at the interface, which makes easier its interaction with both NBR and EPDM phases.

The lowest viscosity of EVAMA can be confirmed from the torque values obtained by the processing of each blend component in a Haake internal mixer (Hannover, Germany) at 110°C with cam rotors. Figure 2 compares the torque curves, and it is possible to observe the lowest value of the torque (which is related to the melt viscosity) for the EVAMA component, in comparison with the NBR and EPDM components. An increase in the tensile properties and a more uniform morphology have also been observed with the addition of TOR (a low-viscosity component) in NR/EPDM<sup>14</sup> and NBR/EPDM<sup>8</sup> blends.

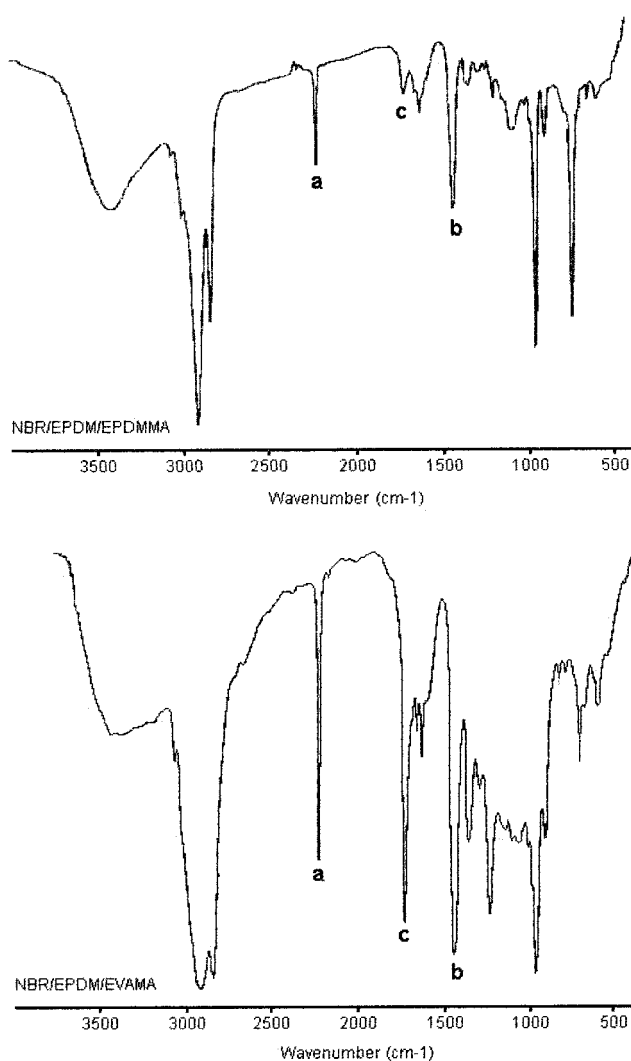
A literature survey reveals that there are three possibilities explaining the action of MA-modified polymers on elastomer blends. As discussed earlier by Coran,<sup>5</sup> the improvement of the mechanical properties in natural rubber/EPDMMA blends can be attributed to the formation of an ionic network resulting from the reaction between the anhydride groups and ZnO. According to Thomas et al.,<sup>21</sup> MA-modified polypropylene should promote the compatibilization of NBR/polypropylene blends through dipolar interactions between the anhydride groups and the polar NBR phase. Finally, Choudhury and Bhowmick,<sup>24</sup> studying the compatibilization of natural rubber/polyethylene blends by the addition of MA-modified polyethylene, proposed that mechanoradicals could be generated during the blend processing, which could promote the reaction between the succinic anhydride pendant groups and the double bonds of the natural rubber phase.

To establish the nature of compatibilization by MA-modified copolymers, we withdrew a small amount of each blend from the roll mill before the addition of the curatives and submitted it to extraction with hot toluene for 24 h to dissolve all blend components. After this treatment, no insoluble material could be detected from the noncompatibilized blend, and this indicated that NBR and EPDM were not able to react with each other. For compatibilized blends, a considerable amount of an insoluble material was isolated (ca. 20%), confirming the occurrence of a chemical reaction during milling and mixing.

The insoluble materials obtained from the nonvulcanized blends containing EPDMMA and EVAMA were analyzed with Fourier transform infrared spectroscopy, the spectra of which are compared in Figure 3. Both spectra display characteristic absorptions at 2237 (peak a, related to nitrile groups) and 1450  $\text{cm}^{-1}$  (peak b, related to methylene groups), which confirm the presence of the NBR component in the insoluble



**Figure 2** Torque curves of EPDM, NBR, and EVAMA obtained with a Haake internal mixer.



**Figure 3** FTIR spectra of the insoluble material isolated from nonvulcanized blends compatibilized with EPDMMA and EVAMA.

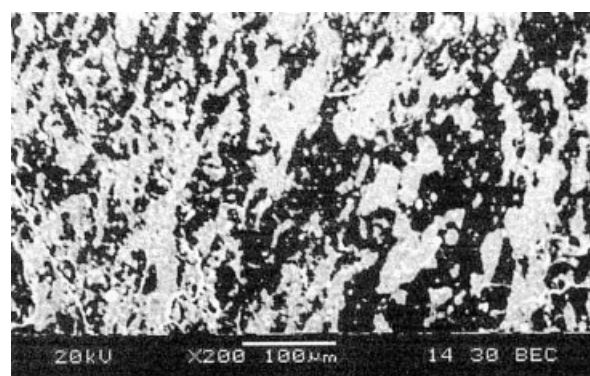
materials. Among these peaks, the spectra also display the characteristic absorption around  $1730\text{--}1740\text{ cm}^{-1}$  (peak c, related to the carbonyl groups). Of course, this absorption is very strong for the blend compatibilized with EVAMA because of the great number of carbonyl groups in the EVA sample. These results provide evidence of the reaction between the pendant succinic groups along the EPDMMA or EVAMA backbone and the double bond of the NBR phase.

These experimental observations suggest the reactive compatibilization of NBR/EPDM blends by MA-modified copolymers but do not refute the occurrence of dipolar interactions, mainly with EVAMA because of its more polar nature.

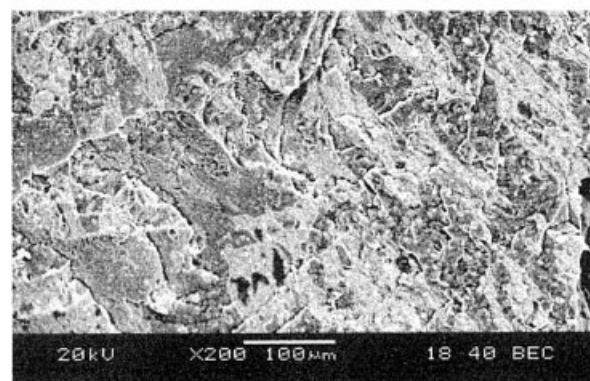
### Morphological aspects

The morphologies of noncompatibilized and compatibilized NBR/EPDM blends are compared in Figure 4.

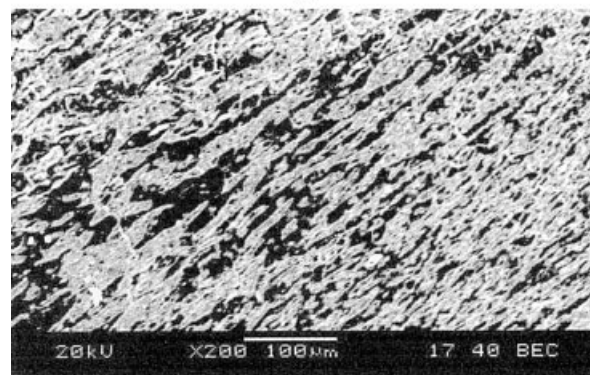
The sample surfaces were first stained with  $\text{OsO}_4$ . The light regions in the micrographs correspond to the NBR phase that was stained with  $\text{OsO}_4$ , and the black regions correspond to the EPDM phase. The noncompatibilized blend presented a gross-phase-separated morphology [Fig. 4(a)], as expected for a noncompatibilized blend. The addition of EPDMMA reduce a little the size of the EPDM domains (darker regions), but the morphology was still heterogeneous [Fig. 4(b)]. The blend compatibilized with EVAMA [Fig.



(a)

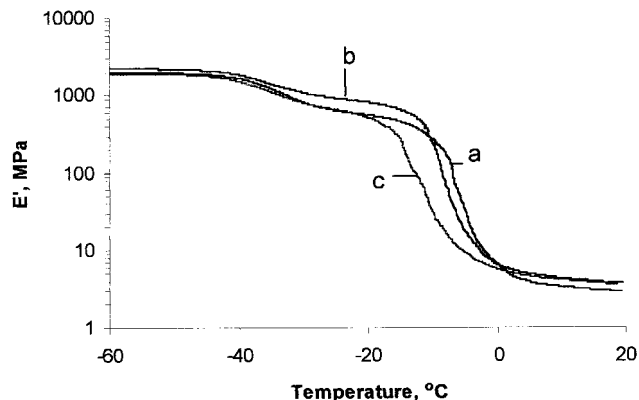


(b)



(c)

**Figure 4** SEM micrographs of NBR/EPDM (70:30 w/w) blends vulcanized with a sulfur-based system: (a) noncompatibilized blend, (b) EPDMMA-compatibilized blend, and (c) EVAMA-compatibilized blend.



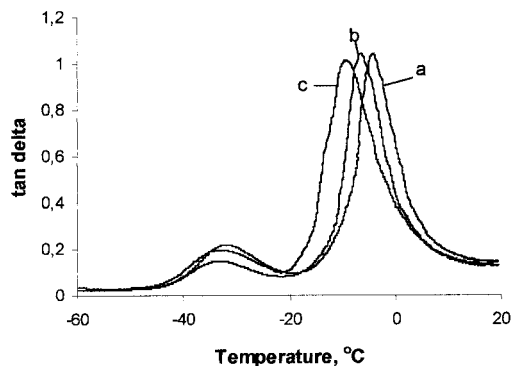
**Figure 5** Curves of  $E'$  versus the temperature for NBR/EPDM (70:30 w/w) blends as a function of compatibilization: (a) noncompatibilized blend, (b) EPDMMA-compatibilized blend, and (c) EVAMA-compatibilized blend.

4(c)] was characterized by a substantial decrease in the EPDM phase size, which confirmed the influence of this functional copolymer on the morphology. The observed morphological aspects of the NBR/EPDM blends are in agreement with the mechanical properties.

#### Dynamic mechanical properties

The dynamic mechanical properties, such as the storage modulus ( $E'$ ) and damping ( $\tan \delta$ ), of vulcanized NBR/EPDM (70:30 w/w) blends were evaluated from  $-60$  to  $20^\circ\text{C}$ . Figure 5 illustrates the variation of  $E'$  versus the temperature as a function of compatibilization. In all the blends, we can distinguish two transitions, as expected for an immiscible blend: the first transition starting around  $-40^\circ\text{C}$  is related to the glass-rubber transition of the EPDM phase, and the second at a higher temperature corresponds to the transition of the NBR phase. The addition of 5.0 phr EPDMMA resulted in a slight increase in the modulus in the region between the two transitions. In this temperature range, the EPDM phase reached its rubbery nature. Therefore, the increase in the modulus in this region indicates that EPDMMA reduced the mobility of the EPDM phase. This phenomenon was not observed with EVAMA probably because of the lower affinity of this component toward the EPDM phase.

Figure 6 illustrates the dependence of  $\tan \delta$  on the temperature for the compatibilized and noncompatibilized blends. The noncompatibilized blend displayed a loss tangent peak around  $-34^\circ\text{C}$ , which corresponded to the glass transition of EPDM, and another around  $-4^\circ\text{C}$  related to the transition of the NBR phase. The presence of EPDMMA or EVAMA resulted in a shift of the glass-rubber transition of the NBR phase toward a lower temperature. This behavior indicates a better interaction of the EPDM phase (the

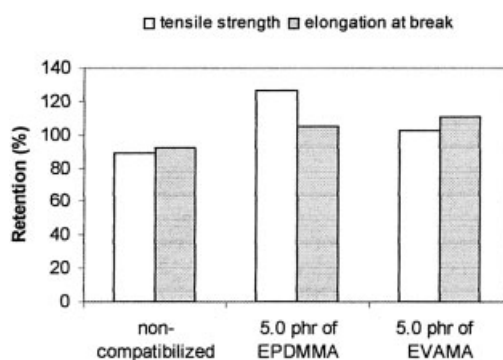


**Figure 6** Curves of  $\tan \delta$  versus the temperature for NBR/EPDM (70:30 w/w) blends as a function of compatibilization: (a) noncompatibilized blend, (b) EPDMMA-compatibilized blend, and (c) EVAMA-compatibilized blend.

transition of which occurred at a lower temperature) with the NBR phase. The displacement of the transition temperature of the NBR phase by the addition of EVAMA was even more accentuated, indicating a better interfacial action of this compatibilizing agent. This phenomenon was also confirmed with SEM micrographs, as discussed before.

#### Aging properties

The effects of EPDMMA and EVAMA on the aging properties were also investigated for NBR/EPDM (70:30 w/w) blends vulcanized with a sulfur system. Figure 7 illustrates the variation of the tensile properties of blends after aging in an air-circulating oven at  $70^\circ\text{C}$  for 72 h. The noncompatibilized blend presented a decrease in the ultimate tensile strength and elongation at break after aging for 3 days, which indicated rubber degradation, as expected. The presence of both EPDMMA and EVAMA increased the thermal stability of these blends. Concerning the compatibilized blends, both the ultimate tensile strength and elongation at break increased, and this indicated a postcuring process during aging.



**Figure 7** Retention of the tensile properties of NBR/EPDM (70:30 w/w) blends after aging as a function of compatibilization.

## CONCLUSIONS

NBR/EPDM blends are difficult to compatibilize because of the differences in both the unsaturation level and polarity. Good mechanical performance was achieved with copolymers functionalized with MA, mainly EVAMA. The crosslinking degree of the NBR/EPDM (70:30 w/w) blends was not significantly affected by the presence of EPDMMA and EVAMA. Therefore, the better mechanical performance achieved with the addition of MA-modified copolymers should be related to the interaction of EPDMMA or EVAMA with the blend components. The morphology of the compatibilized blends was more homogeneous as a result of the lower phase segregation. This morphological situation was more pronounced in blends compatibilized with EVAMA, probably because of its preferential location at the interface as a result of its lower viscosity and intermediary polarity.

The dynamic mechanical results confirmed the compatibilizing effects of both EPDMMA and EVAMA. These copolymers were able to shift the glass transition of the NBR phase toward lower temperatures. Because EPDM displayed lower  $T_g$  values, these results indicated a better interaction between the phases, mainly with EVAMA.

The outstanding aging properties of the compatibilized blends could also be related to the more uniform distribution of the vulcanized EPDM phase, which could act as a physical barrier against the action of heat aging because of its saturated backbone, preventing the propagation of free radicals.

In conclusion, the presence of EPDMMA and EVAMA resulted in a compatibilization process that probably occurred through an interaction between the pendant succinic anhydride groups along the EPDM or EVA backbone and the NBR phase. Such interactions resulted in an improvement of the mechanical performance as a result of a more homogeneous morphology.

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