# Compatibilization of Elastomer-Based Blends

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**Summary:** The reactive compatibilization of ethylene-propylene-diene (EPDM)-based dissimilar elastomer blends has been investigated in terms of mechanical properties and swelling degree. The use of mercapto-functionalized copolymers resulted in an improvement of mechanical properties of natural rubber-EPDM blends. The mercapto-groups are able to react with the carbon-carbon double bonds of the high diene rubber, resulting in a good interaction between phases. These interactions were confirmed by the amount of insoluble material obtained in non-vulcanized blends. From dynamic mechanical properties and swelling degree, one can suggest a covulcanization process in these blends cured with sulfur-based system.
Blends composed by nitrile rubber with EPDM displayed good results in terms of mechanical properties when mercapto-functionalized EVA was employed instead of functionalized EPDM, probably because of the higher polarity of the former associated to its lower viscosity. Additionally, an improvement on mechanical properties was also achieved by using EPDM functionalized with mercapto or anhydride groups in combination with nitrile rubber functionalized with epoxy or oxazoline groups.

## Introduction

Blending of two elastomers is carried out for several purposes, such as enhancement of physical properties, improvement of processing characteristics and ageing resistance as well as decreasing compound cost. Most of polymer blends are heterogeneous and incompatible, resulting in a gross-phase separated morphology, poor interfacial adhesion and consequently poor mechanical properties. In the specific case of dissimilar elastomer blends, there is also the problem of cure-rate incompatibility because of differences in unsaturation and polarity of the elastomers. Due to the higher solubility of sulfur in unsaturated rubber, the curatives tend to diffuse into the elastomer phase in which their solubility is highest, resulting in a significant difference on the crosslink density of each rubber phase.[1-3]

 CCC 1022-1360/00/$ 17.50+.50/0

Several approaches have been made to develop vulcanized blends with a single network structure including crosslinked macromolecules of both polymers across the macrodomain interfaces. Most of these studies are related to natural rubber (NR)/ ethylene-propylene-diene (EPDM) rubber blends and include: substitution of zinc oxide by lead oxide as a component of the activation system, [4] halogenation of EPDM to improve sulfur vulcanization, [5] chemical modification of the accelerators to improve their solubility in both phases, [6] grafting of the accelerator onto the phase that present lower solubility with the accelerators, such as EPDM, [7] pre-curing the slower curing rubber (EPDM)[8] and the use of specific accelerators which can react with the EPDM phase, making it more polar and compatible with the curing agents, together with a two-stage vulcanization.[9]

The functionalization of EPDM with maleic anhydride has been also employed by Coran to improve cure compatibility of NR/EPDM blends.[10-11] This functionalization permits the EPDM to be crosslinked independently with the zinc oxide in the accelerated- sulfur vulcanizing system. More recently, the use of poly-trans-octylene (TOR) as compatibilizing agent in NR/EPDM blends has been reported to produce a fine morphology and improve the properties of these blends. [12] TOR acts at the interface between the blend components because of its low viscosity.

The compatibilization and covulcanization of nitrile rubber (NBR)/EPDM blends are even more difficult because the components are different in unsaturation level and polarity. Some reports employ TOR, [13] polybutadiene, [14] polychloroprene, [14-17] chlorinated polyethylene, [14,18] and chlorosulfonated polyethylene. [14,18] All these compounds increased the compatibility of NBR/EPDM blends, although the authors have considered the chlorinated polyethylene as the universal compatibilizer for NBR/EPDM blends. [14,18]

## The reactive compatibilization in elastomer blends

Based on the technological interest of several rubber industries on elastomer blends with good mechanical performance and other interesting properties, we decided to develop new systems able to improve the interfacial adhesion between elastomer phases and, in some cases, impart as much as possible a good crosslink distribution between the phases. Our goal is to incorporate low-unsaturated rubbers (such as EPDM) to high-unsaturated elastomer matrix in order to achieve elastomer materials with outstanding

resistance to the action of heat, oxygen and ozone. For this purpose, we have focused our studies on reactive compatibilization.

The reactive compatibilization is based on the addition of a functionalized polymer that reacts with one or both blend components, thus promoting an effective anchorage between the phases, through chemical linkage.

The first strategy used in our researches to achieve the compatibilization in elastomer-based blends involves the ability of mercapto groups in reacting with carbon-carbon double bonds of unsaturated polymers.[19-21] Therefore, mercapto groups have been introduced along the backbone of the low-unsaturated (such as EPDM) [22] or saturated (such as ethylene- vinyl acetate EVA copolymer) [23] blend component using simple functionalization reactions, as illustrated in Figure 1. An effective interaction between the blend components can be achieved with the addition of small amount of these copolymers, since the mercapto groups react with the double bonds of high-diene rubbers whereas the main chain of the reactive compatibilizing agent may physically interact with the other component, similar in nature. This approach has been profitable for the compatibilization of EVA-based blends, such as NR/EVA,[23-25] NBR/EVA,[26] and SBR/EVA.[27] As it will be discussed in next section, EPDM-based blends have also shown an improvement on the mechanical performance with this kind of compatibilization.

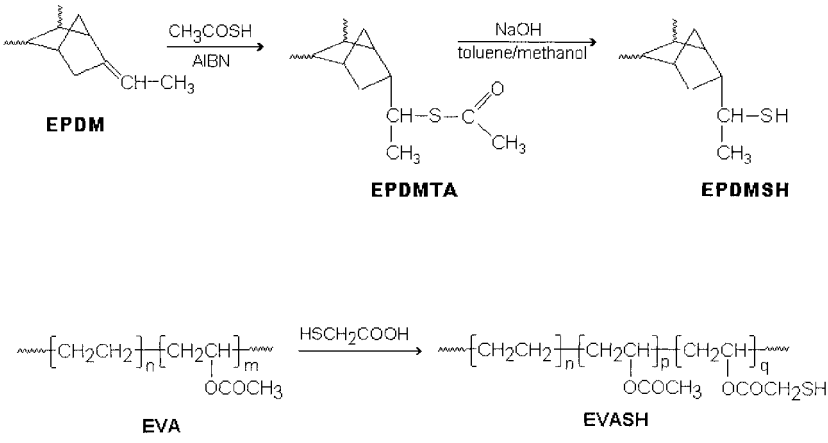
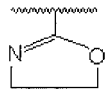
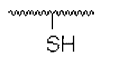
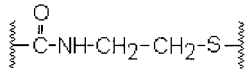
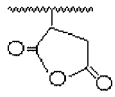
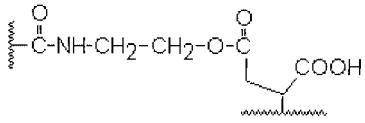
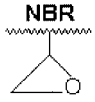
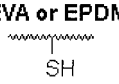
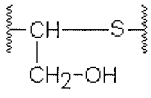
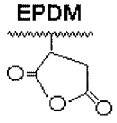
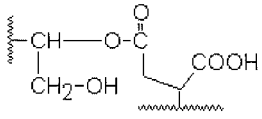



**Figure 1.** Scheme for the mercapto-functionalization of EPDM and EVA

The other strategy involves two different reactive polymers, whose functional groups react each other. A small portion of these compounds are separately blended with each elastomer component and the resulting masterbatches are then blended together to form a compatible blend, whose phases are bounded through a new functional group formed during the mixing process. Some functionalized polymers used in this work are illustrated in Table 1. This procedure was employed in NBR/EPDM because of the possibility of introducing reactive groups along the NBR backbone.

**Table 1.** Examples of reactive compatibilization between elastomer blends

| High-unsaturated rubber | Low-unsaturated rubber | Functional group formed during mixing process |
|---|---|---|
| NBR  | EVA or EPDM  |  |
| | EPDM  |  |
| NBR  | EVA or EPDM  |  |
| | EPDM  |  |

## The compatibilization of NR/EPDM blends

The NR/EPDM blends have been compatibilized with the addition of 2.5 phr of mercapto-modified EPDM (EPDMSH). The curing characteristics and mechanical properties are summarized in Table 2. The first indication of covulcanization was obtained from swelling results. In this Table, Vr corresponds to the volume fraction of the rubber in a swollen network. Higher Vr values mean lower swelling degree. According to Shershnev,[28] if interfacial bonds are formed during covulcanization, the lightly swollen dispersed phase in a blend will restrict the swelling of the swollen

continuous phase. Such interfacial bonds must have been also formed with the addition of EPDMSH in NR/EPDM blends, since a substantial decrease of swelling degree was observed with the compatibilization. This phenomenon is also confirmed by the amount of insoluble material isolated after submitting the vulcanized samples to a extraction with xylene at 120$^0$C for 24h. The amount of insoluble material is higher than the amount of the NR component in blends containing 70 and 60 wt% of NR, indicating that EPDMSH also promotes some crosslinking into the EPDM phase. The compatibilizing effect of EPDMSH can be confirmed from the results concerning ultimate tensile strength. As observed in Table 2, the addition of 2.5 phr of EPDMSH increases this property without affecting significantly the elongation at break.

**Table 2.** Curing parameters and mechanical properties of NR/EPDM blends as a function of composition and compatibilization. [a]

| Properties | NR/EPDM (wt%) | | | | | |
|---|---|---|---|---|---|---|
| | 80:20 | | 70:30 | | 60:40 | |
| | b | c | b | c | b | c |
| $M_L$ (lb.in) [d] | 1.5 | 1.9 | 1.5 | 2.5 | 2.0 | 2.0 |
| $M_H$ (lb.in) [d] | 16.5 | 17.0 | 19.0 | 20.3 | 19.5 | 20.0 |
| $t_{s1}$ (min) [e] | 3.0 | 2.8 | 2.8 | 2.3 | 3.3 | 3.0 |
| $t_{90}$ (min) [e] | 8.0 | 8.0 | 9.5 | 7.4 | 10.3 | 9.5 |
| Vr [f] | 0.14 | 0.20 | 0.12 | 0.19 | 0.12 | 0.17 |
| Gel content (%) | 74 | 73 | 66 | 80 | 74 | 80 |
| $\sigma_B$ (Mpa) [g] | 10.3 | 13.0 | 10.5 | 13.5 | 9.4 | 15.0 |
| $\varepsilon_B$ (%) [h] | 850 | 830 | 900 | 840 | 600 | 700 |

a) 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 compatibilizing (EPDMSH) were subsequently added. After the homogenization of the rubber blend (at 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

b) Blends without compatibilizer

c) Blends with 2.5 phr of EPDMSH

d) $M_L$ and $M_H$ are the minimum and maximum torque obtained from oscillating disk rheometer, respectively.

e) $t_{s1}$ and $t_{90}$ are the scorch time and optimum curing time, respectively.

f) Vr corresponds to the volume fraction of the rubber in a swollen network and is calculated as follows: $Vr = \frac{D \times \rho_r^{-1}}{D \times \rho_r^{-1} + (S - D) \times \rho_s^{-1}}$

where: D = deswollen weight, S = swollen weight, $\rho_r$ = density of rubber blend and $\rho_s$ = density of solvent

g) Ultimate tensile strength.

h) Elongation at break.

In addition of a compatibilizing effect, this functionalized copolymer has also favored the crosslink inside the EPDM phase. This phenomenon was suggested from dynamic mechanical analysis. Figure 2 compares the damping (tan δ) of the vulcanized components with those of the 70:30 NR/EPDM blends, evaluated from -80 to 25$^0$C. The non-compatibilized blend displays only one transition at a temperature below to that one found in pure NR sample, which can be attributed to the vulcanized NR phase together with the non vulcanized EPDM phase whose transition should occur at very similar temperatures. The presence of the non vulcanized 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.

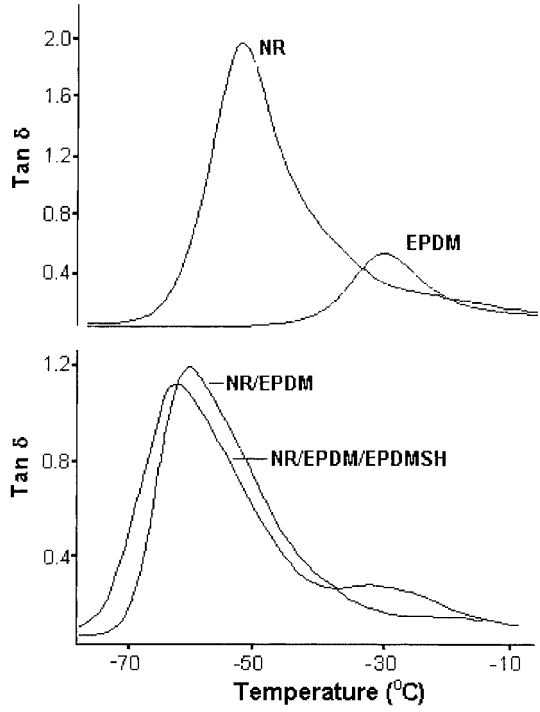



**Figure 2.** Dependence of tan δ with the temperature for vulcanizate samples of NR, EPDM and NR/EPDM (70:30) and NR/EPDM/EPDMSH (70:30:2.5)

NR/EPDM blend compatibilized with EPDMSH presents a lower value of the glass transition temperature related to the NR phase and also a lower damping. 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 decrease the mobility of this phase, giving rise to a decreasing of the damping. It is important to emphasize the presence of a second transition in this blend, at a temperature similar to that found for the vulcanized EPDM sample. This second transition at higher temperature may be related to the proportion of vulcanized EPDM phase in the NR/EPDM blend compatibilized with EPDMSH. These results are in agreement to those concerning gel content.

In order to analyze the effectiveness of the reactive compatibilization, we have studied non-vulcanized NR/EPDM blend containing 10 phr of the functionalized copolymer, as compatibilizing agent. The compatibilized and noncompatibilized NR/EPDM (50:50 %) blends were prepared by melt mixing the components in a two-roll mill at $80^0$C for 15 min and compression-molded at $160^0$ for 10 min in a hydraulic press at 6.7 MPa. The samples were submitted to extraction with hot xylene for 24 hours in order to determine the amount of insoluble material. The 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.

The presence of EPDMSH resulted in a considerable amount of insoluble material (around 40%). This proportion is higher than the amount of the functionalized copolymer used in the blend, suggesting the formation of a network during the process.

The composition of the insoluble fraction obtained from the compatibilized blend was determined by thermogravimetric analysis. Figure 3 compares the Thermogravimetric curves of the insoluble fraction with those of the pure components. As expect, the degradation of NR occurs at a lower temperature than EPDM. The insoluble material obtained from the compatibilized blend (Fig.3c) presents two degradation steps, which can be related to the NR and EPDM phases. 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.

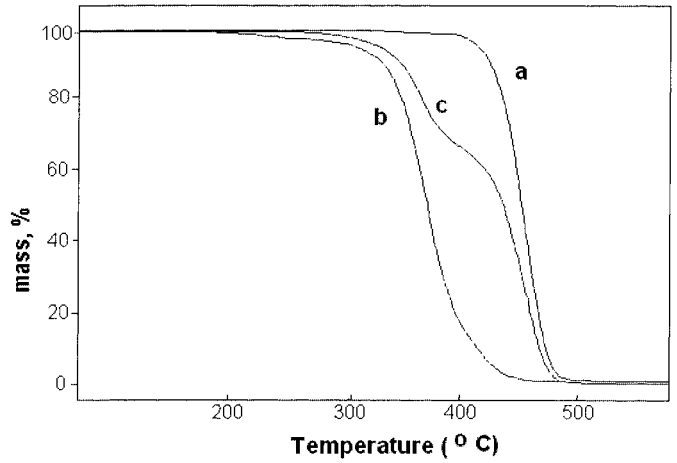



**Figure 3.** Thermogravimetric analysis of (a) EPDM, (b) NR and (c) the insoluble material obtained from non vulcanized NR/EPDM (50:50 wt%) blend, compatibilized with 10 phr of EPDMSH

## The compatibilization of NBR/EPDM blends

NBR/EPDM blends are highly incompatible because of the difference in polarity and unsaturation level between the components. Besides the poor interfacial adhesion and gross-phase separated morphology originated from very different structures, the cure-rate incompatibility is even more significant, specially when sulfur-based curing systems are employed because of the great solubility of the curatives in the polar and unsaturated NBR phase.

In this preliminary study, several reactive compatibilizing systems have been employed in NBR/EPDM (70:30 wt%) blends. Table 3 presents the tensile properties of vulcanized blends containing mercapto-functionalized polymers (EPDMSH or EVASH). A commercial sample of EPDM functionalized with maleic anhydride (EPDM-MA) was also employed in order to compare the compatibilizing efficiency.

**Table 3.** Mechanical properties of vulcanized NBR/EPDM (70:30 wt%) blends, compatibilized with mercapto-functionalized copolymers. [a]

| Compatibilizing agent | Vr | Insoluble material [b] (%) | Mechanical properties | | | |
|---|---|---|---|---|---|---|
| | | | Ultimate tensile strength (MPa) | | Elongation at break (%) | |
| | | | c | d | c | d |
| None | 0.20 | 0 | 2.7 | 2.4 | 600 | 560 |
| EPDMSH | 0.19 | 10 | 2.3 | 2.7 | 580 | 630 |
| EPDM-MA | 0.18 | 26 | 3.2 | 4.0 | 660 | 690 |
| EVA18SH [e] | 0.20 | 8 | 4.2 | 5.6 | 750 | 750 |
| EVA28SH [f] | 0.18 | 5 | 4.3 | 4.4 | 730 | 670 |

a) The blends were prepared in a two roll mill operating at 110°C. NBR was masticated for 2 min and then EPDM and the functionalized compatibilizing were subsequently added. After the homogenization of the rubber blend (at about 4 min), the other ingredients were added in the following order: zinc oxide (5.0 phr), stearic acid (0.5 phr), sulfur (1.0 phr) and 2,2'-dithiobisbenzothiazole (MBTS) (2.0 phr).
b) Insoluble material obtained from non vulcanized blends (before the addition of curatives).
c) Before ageing
d) After ageing in an air circullating oven at 70°C, for 72h.
e) EVA18SH= EVA with 18% of vinyl acetate functionalized with SH.
f) EVA28SH = EVA with 28% of vinyl acetate functionalized with SH.

An increase of tensile properties has been observed with the addition of 5 phr of EPDM-MA or EVASH. EPDMSH does not improve these properties, in spite of being constituted with the same backbone of the EPDM phase and having mercapto groups able to react with the NBR phase.

In order to evaluate the extent of chemical reaction in the presence of these reactive copolymers, a small sample of each blend was withdrawn from the roll-mill before the addition of curatives and submitted to extraction with hot toluene for 24h. As observed in Table 3, all funcionalized copolymers produced insoluble materials, indicating a reactive interaction between the phases. The lower amount of insoluble material obtained with EVA18SH or EVA28SH is due to the low amount of mercapto groups in these samples.

The best results achieved with EVASH may be attributed to its lower melt viscosity and intermediary surface tension. Both characteristics tend to locate this component at the interface. This morphological situation should enhance the interaction of the mercapto groups with the double bonds of both rubber phases, NBR and EPDM. EPDM-MA also improves the tensile properties probably because the anhydride groups interact with zinc

oxide, bringing some amount of the curatives inside the EPDM phase.

Considering that the swelling degree was not affected by the addition of the functionalized copolymers, one can assume that the good mechanical performance may be better attributed to some interfacial action and not to the covulcanization phenomenon.

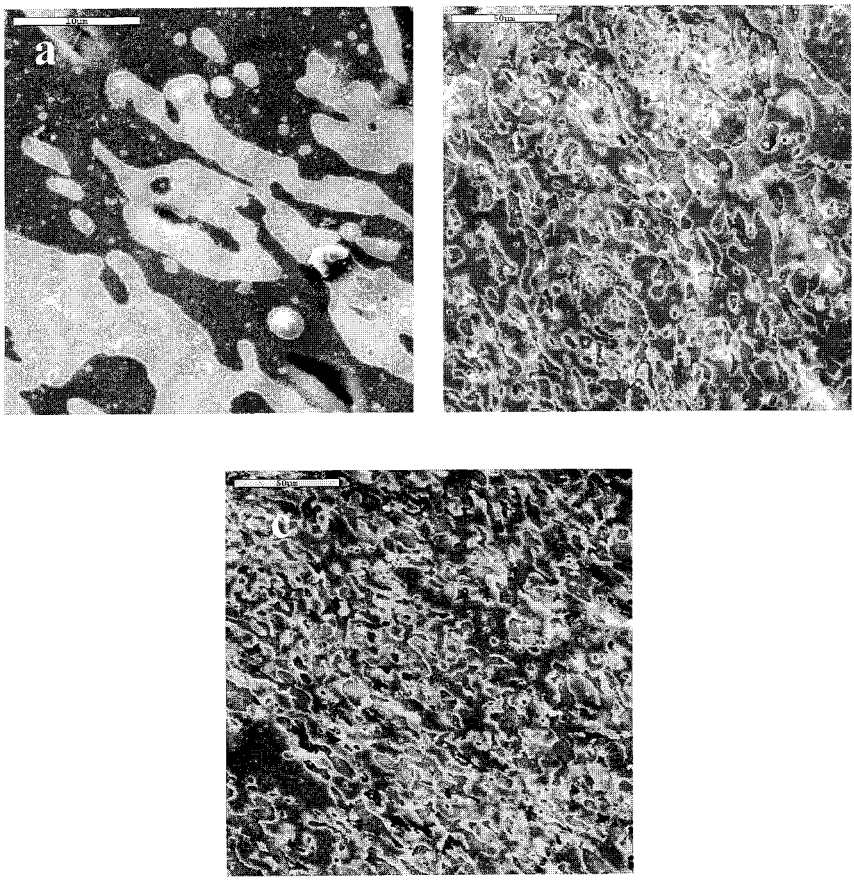



**Figure 4.** SEM micrographs of non vulcanized NBR/EPDM (70:30 wt%) blends: (a) non compatibilized blend; (b) compatibilized with 5 phr of EVA18SH and (c) compatibilized with 5 phr of EVA28SH.

The morphologies of NBR/EPDM blends compatibilized with EVASH are compared to that of non-compatibilized one in Figure 4. These micrographys were taken from non-vulcanized blends, in order to observe the effect of the EVASH as compatibilizing agent without the influence of the curatives. The samples were taken from the roll-mill before the addition of curatives, pressed at 160$^0$C for 15min and analyzed in a ZEISS scanning electron microscope using backscattered detector. The sample surfaces were first stained with osmium tetroxide. The light region in the micrographs presented in Figure 4 corresponds to the NBR phase stained with osmium tetroxide and the black region corresponds to the EPDM phase. The noncompatibilized NBR/EPDM (70:30 wt%) blend presents a gross-phase separated morphology (Fig 4a), whereas the blends compatibilized with 5 phr of EVA18SH (Fig 4b) or EVA28SH (Fig 4c) present a substantial decrease of the phase size, confirming the interfacial action.

In order to increase the interaction between the phases, the NBR component was also functionalized with epoxy groups (NBR-epo) or oxazoline groups (NBR-ox), because these groups present higher reactivity towards mercapto and carboxyl groups than carbon-carbon double bonds. These reactions were summarized in Table 1. For this study, masterbatches of NBR/NBRepo or NBR/NBRox in a proportion of 100:5 phr and EPDM/EPDM functionalized in a proportion of 100:10 phr were separately prepared. Then, 70 parts of the NBR masterbatch and 30 parts of EPDM masterbatch were blended together before adding the curatives. The results are summarized in Table 4. This new procedure resulted in blends with better tensile properties than those without the presence of antagonic reactive groups in the NBR phase. The best results were again achieved with EVASH. Concerning the antagonic reactive group inside the NBR phase, the oxazoline group was more effective on the reactive compatibilization.

Most of the compatibilized blends presented an increase of the ultimate tensile strength after ageing in an air-circulating oven for 72h, indicating a post-curing process during ageing. This phenomenon is accomplished with a small decrease of the elongation at break.

The reaction between the functional groups inside the rubber phases can be suggested from extraction experiments in hot toluene. These experiments were carried out in non vulcanized blends, obtained just before the addition of the curatives. As indicated in Table 4, the amount of insoluble material was significant in all reactive blends. The highest proportion has been achieved in systems containing NBR functionalized with

oxazoline (NBRox), because this group presents higher reactivity than epoxy groups towards mercapto or carboxyl groups located inside the EPDM phase. It is important to emphasize that the amount of these insoluble material is higher than the amount of the functionalized copolymer used in the masterbatches. In NBR masterbatch, the proportion of NBRepo or NBRox corresponds to 5%. Since 70% of these compounded rubbers were used in the blend, the amount of functionalized material corresponds to around 3.7%. On the same way, the EPDM masterbatch contains 10% of the functionalized material, which corresponds to 3% of the functionalized copolymer in the blend. Therefore, one can suggest that the insoluble material also includes some amount of non functionalized rubber, which interacts with the functionalized copolymers through their double bonds.

## Conclusions

Dissimilar elastomer blends can be compatibilized with functionalized copolymers. The components in NR/EPDM blends present different unsaturation level but are similar in polarity. In this case, the use of small amount of mercapto-functionalized EPDM was beneficial for the improvement of mechanical performance. From swelling experiments and dynamic mechanical properties, one can suggest that a covulcanization process occurs in some extent together with the reactive compatibilization.

NBR/EPDM blends are more difficult to be compatibilized because of the differences in both unsaturation level and polarity. Good mechanical performance was achieved only with EVA functionalized with mercapto groups (EVASH), probably because of its location at the interface as a consequence of its lower viscosity and intermediary polarity. This compound resulted in blends with uniform morphology and smaller phase size.

One of the best way to develop NBR/EPDM blends with outstanding properties (good mechanical performance and good ageing resistance) consists of employing antagonic functional groups inside each rubber phase. When part of the NBR phase is functionalized with epoxy or oxazoline groups, the reaction with EPDM functionalized with mercapto or anhydride groups is more effective. With this new system, the use of NBR functionalized with oxazoline groups is much better due to its higher reactivity towards mercapto or carboxyl groups.

**Table 4.** Mechanical properties of vulcanized NBR/EPDM (70:30 wt%) blends, compatibilized with a combination of two functionalized copolymers. [a]

| Blend components | | Vr | b (%) | Mechanical properties | | | |
|---|---|---|---|---|---|---|---|
| | | | | Ultimate tensile strength (MPa) | | Elongation at break (%) | |
| | | | | c | d | c | d |
| NBR | EPDM | 0.20 | 0 | 2.7 | 2.4 | 600 | 560 |
| NBR/NBRepo | EPDM/EPDMMA | 0.21 | 17 | 3.6 | 4.2 | 650 | 620 |
| NBR/NBRepo | EPDM/EPDMSH | 0.19 | 12 | 2.9 | 3.2 | 610 | 590 |
| NBR/NBRepo | EPDM/EVA18SH | 0.21 | 10 | 5.2 | 4.2 | 750 | 700 |
| NBR/NBRox | EPDM/EPDM-MA | 0.21 | 23 | 4.9 | 4.9 | 660 | 630 |
| NBR/NBRox | EPDM/EPDMSH | 0.21 | 26 | 3.3 | 4.0 | 610 | 610 |
| NBR/NBRox | EPDM/EVA18SH | 0.21 | 14 | 6.0 | 6.4 | 760 | 730 |

a) The blends were prepared in a two roll mill operating at 110°C. NBR masterbath was blended with EPDM masterbatch. After the homogenization of the rubber blend (at about 4 min), the other ingredients were added in the following order: zinc oxide (5.0 phr), stearic acid (0.5 phr), sulfur (1.0 phr) and 2,2'-dithiobisbenzothiazole (MBTS) (2.0 phr).
b) Insoluble material obtained from non vulcanized blends (before the addition of curatives).
c) Before ageing
d) After ageing in an air-circulating oven at 70°C, for 72h.

## Aknowledgements

We would like to acknowledge the Conselho Nacional de Desenvolvimento Científico e Tecnológico - CNPq, Coordenação de Aperfeiçoamento de Pessoal de Ensino Superior - CAPES, CEPG-UFRJ, FAPERJ and PADCT/CNPq (proc. nº 620132/98-1) for the financial support and to NITRIFLEX S. A. and Michelin do Brasil for the polymer supplying.

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