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The reactive compatibilization of NBR/EVA blends with oxazoline-modified nitrile rubber

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Abstract

The reactive compatibilization of ethylene-vinyl acetate copolymer (EVA)/nitrile rubber (NBR) blends has been performed using partially hydrolyzed EVA (EVALVA) in combination with oxazoline-functionalized NBR (NBROX). The synthesis of the NBROX has been performed in solution. The presence of 5 wt% of EVALVA in combination with 2.5 wt% of NBROX resulted in a substantial improvement of tensile strength of NBR/EVA (50:50 wt%) vulcanized blends, with a little increase of the elongation at break. The morphologies of these blends were examined by the scanning electron microscopy. A finer morphology has been observed in vulcanized and non-vulcanized blends, compatibilized with the co-reactive EVALVA/NBROX copolymers. Blends of NBROX/EVALVA (50:50 wt%) resulted in insoluble material, constituted by both components, as indicated by Fourier transform infrared analysis. This result indicates the reaction of the co-reactive groups (hydroxyl and oxazoline) during blending.

Keywords: Reactive compatibilization; Oxazoline groups; Rubber blends; NBR and EVA

1. Introduction

Nitrile rubber compounds (NBR) constitute important class of elastomers due to its excellent oil resistance, abrasion resistance and mechanical properties. However, their ozone resistance is poor. Blending ethylene-vinyl acetate copolymers (EVA) and NBR is a good way to develop important class of materials with good elastomeric properties associated to improved tensile strength and ozone and oxygen resistance promoted by the EVA component [1,2]. In addition, it is possible to improve the blend processability due to the known ability of EVA in decreasing the torque and consequently the viscosity of the system, during processing. In spite of good ageing and processing properties, these blends normally present poor mechanical properties because of the immiscibility of the components, which results in gross phase-separated morphology and poor interfacial adhesion. The problems originated from blend incompatibility are normally minimized by the addition of an appropriate interfacial agent. Functional polymers prepared from the blend components have been reported to be a common way to compatibilize such immiscible blends, since the interfacial agent can be formed via interfacial reaction between the corresponding functional groups during blend processing [3,4]. This process, known as reactive compatibilization, is technologically very attractive because several commercial polymers can be easily functionalized using simple organic reactions in solution or in the melt.

Recently, the reactive compatibilization of NBR/EVA blends has been performed in our laboratory using a small amount of mercapto-functionalized EVA [5–7].

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The mercapto groups are able to react with the double bond of the unsaturated rubber component, thus promoting a good interaction between the phases. As a consequence, better mechanical performance has been achieved in both non-vulcanized [5] and vulcanized NBR/EVA blends [7].

Another way to perform the reactive compatibilization of NBR-based blends involves the use of oxazoline group, which can be easily formed by the catalyzed reaction of nitrile group with 2-aminoethanol [8–10]. In addition, this group is reactive toward a relative wide range of other functional groups, as carboxyl, amine, epoxy, anhydride groups, etc. [11,12]. The literature reports several examples of reactive compatibilization of blends containing polyesters, polyamides and polycarbonates using oxazoline-functionalized copolymers [13–18].

This paper deals with the compatibilizating effect of co-reactive functionalized copolymers based on oxazoline-functionalized NBR (NBROX) and partially hydrolyzed EVA (EVALVA), in NBR/EVA blends. The choice of EVALVA as the co-reactive partner was based on the feasibility of its preparation in laboratory and the possibility of being commercially available. In addition, the partial hydrolysis does not change significantly the good flexibility and processability of the EVA precursor and keeps its miscibility with the EVA phase, which is an important requisite for the compatibilization. The compatibilization efficiency has been investigated in both non-vulcanized and vulcanized blends with a composition corresponding to 50:50 wt%. At this composition, the blend morphology presents a co-continuous structure and both components can fully contribute to the properties of the blend.

2. Experimental

2.1. Materials

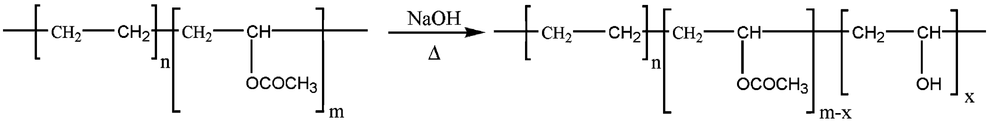
Nitrile rubber (NBR) (33 wt% acrylonitrile; Mooney viscosity (ML 1+4 at 100 °C) = 50) was kindly supplied by Petroflex Ind. Com. S.A., Brazil. EVA copolymers (18 wt% of vinyl acetate (VA); MFI = 2.5 g/10 min at 190 °C) was kindly supplied by Brasken S.A., Brazil. The reagents and solvents employed on the polymer functionalization were used as received (from Merck). Other chemicals employed as the vulcanization components such as zinc oxide (ZnO), stearic acid, sulfur, 2,2′-dithiobisbenzothiazole (MBTS) and tetramethylthiuram disulfide (TMTD) were of the laboratory reagent grade and purchase by the local industries.

2.2. Synthesis and characterization of the functionalized copolymers

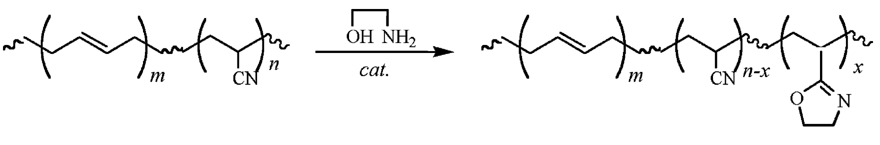
The synthesis of EVALVA, shown in Scheme 1, was performed in toluene solution at 70 °C. In a typical procedure, 100 g of EVA were dissolved into 1000 ml at 70 °C. Then, 20 ml of a methanolic solution of sodium hydroxide (10 wt%) were slowly added. After 1 h reaction, the medium was neutralized with chloridric acid aqueous solution. The formed EVALVA was, then, precipitated into methanol, filtered and dried. The amount of hydroxyl groups was determined from thermogravimetric analysis, by comparing the weight loss corresponding to the acetate groups in EVA and EVALVA samples [19]. At these reaction conditions, an amount of OH groups corresponding to 35 mmol/100 g was obtained.

The functionalization of NBR with oxazoline groups (NBROX), shown in Scheme 2, was performed according to the literature procedure [8,10]. In a typical procedure, NBR copolymer (100 g), 2-aminoethanol (48 g) and zinc acetate in different proportions were dissolved in 1,2-dichlorobenzene. The reaction conditions are described in Table 1. After a pre-established reaction time, the medium was cooled, diluted with chloroform and precipitated into methanol. The functionalized polymer was redissolved in chloroform, reprecipitated into methanol and dried in a vacuum oven for 48 h.

^{13}C-NMR spectra were obtained on a Varian Mercury 300 at 75.4 MHz in deuterated chloroform solution. Fourier transform infrared (FTIR) spectrometry



Scheme 1. The synthesis of partially hydrolyzed EVA (EVALVA).



Scheme 2. The functionalization of NBR with oxazoline groups.

Table 1
The effect of the reaction parameters on the amount of oxazoline groups incorporated into the NBR rubber chain

Amount of zinc acetate (g)	Solvent/NBR (ml/g)	Reaction temperature (°C)	Reaction time (h)	Oxazoline content (mmol/100 g NBR)[a]
6	5	140	**1**	10.7
6	5	140	**2**	20.8
6	**5**	**140**	**4**	**31.0**
6	**5**	**100**	4	3.8
6	5	**160**	4	17.1
6	**10**	140	4	22.7
6	**15**	140	4	9.6
12	5	140	4	19.9
18	5	140	4	20.7

[a] Oxazoline content determined by FTIR quantitative analysis.

was performed on a Perkin–Elmer spectrum one infrared spectrometer, with a resolution of 4 cm^{-1} and 10 scans. The samples were analyzed as a $CHCl_3$ solution at 4 wt% in liquid cell of KBr. The amount of oxazoline group in the NBROX samples was determined from a calibration curve, obtained from a Perkin–Elmer software Spectrum QUANT+version 4.51.

2.3. Blend preparation and measurement of cure parameters

The NBR/EVA blends were prepared in a two-roll mill operating at 110 °C and friction ratio of 1:1.1. Master batches of NBR/NBROX and EVA/EVALVA with different proportions were separately prepared. Then, both master batches in a proportion of 50:50 wt% were blended for 3 min, followed by the other ingredients in this order: ZnO (5.0 phr), stearic acid (0.5 phr), sulfur (1.0 phr), MBTS (2.0 phr) and TMTD (1.0 phr).

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

Non-vulcanized blends were prepared by mixing both master batches of NBR/NBROX and EVA/EVALVA and compression-molded at 160 °C for 15 min.

2.4. Measurement of the mechanical properties

Tensile-strain experiments were performed by means of an Instron 4204 testing machine at room temperature with speed of 200 mm/min, following DIN procedure 53504. The samples were conditioned at 21 °C and 53% of air humidity for 24 h before the testing.

2.5. Blend characterization

Scanning electron microscopy (SEM) was performed on a JEOL 5610 LV equipment with a voltage of 20 kV. For non-vulcanized blends, the samples were cryogenically fractured and the surface was treated with methyl ethyl ketone to selectively etch the NBR phase. The surface was dried, coated with a thin layer of gold an analyzed with a secondary electron detector. The vulcanized samples were also cryogenically fractured and the surface was treated with osmium tetroxide (OsO_4) for 5 min in order to selectively stain the unsaturated phase. The samples were then coated with carbon and analyzed with a backscattered electron detector.

FTIR analysis was performed on a Perkin–Elmer spectrum one infrared spectrometer, at a 4 cm^{-1} resolution averaged over 30 scans, using attenuated total reflectance (ATR) device.

3. Results and discussion

3.1. Synthesis of oxazoline-functionalized NBR (NBROX)

The amount of oxazoline groups in oxazoline-modified NBR (NBROX) was determined from FTIR spectrometry and nuclear magnetic resonance (^{13}C-NMR). Fig. 1 compares the ^{13}C-NMR of NBR and the functionalized copolymer. On can observe the appearance of two new chemical shifts in the NBROX spectrum at 54.4 ppm (peak a) and 67.2 ppm (peak b), which are attributed to the oxazoline heterocyclic function, according to the literature [17,20]. Besides these peaks, another two small peaks at 50.9 ppm (peak c) and 170 ppm (peak d) are also present, which can be attributed to the amide group formed by the reaction of some oxazoline group and 2-aminoethanol, according to Scheme 3.

The FTIR spectra of NBR and NBROX are compared in Fig. 2. The spectrum of NBROX displays two new absorptions at 1663 and 1261 cm^{-1}, related to the (>C=N–) and ($–CH_2–O–$) functions of the oxazoline group, respectively.

The amount of oxazoline group in the NBROX samples was determined using a calibration curve

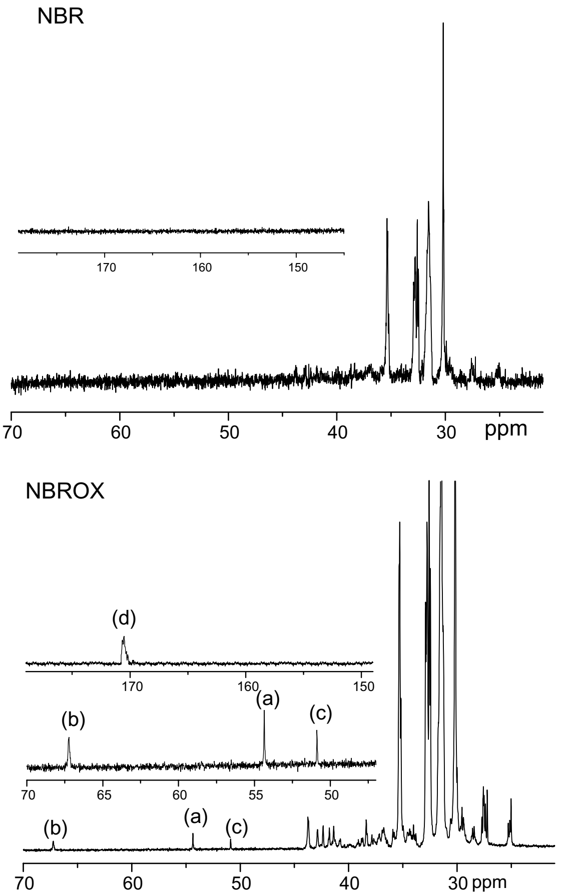


Fig. 1. ^{13}C-NMR of NBR and the oxazoline-functionalized NBR (NBROX).

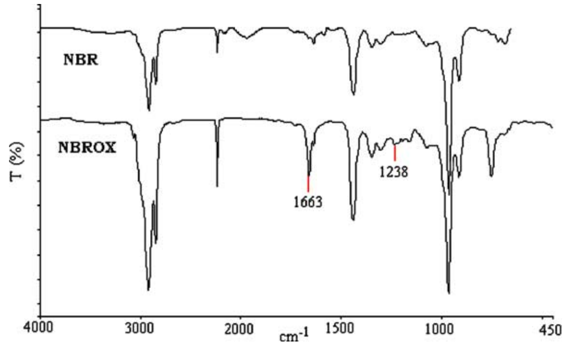


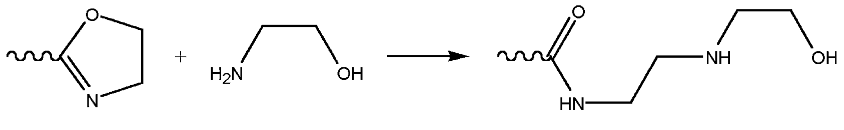
Fig. 2. FTIR spectra of NBR and the oxazoline-functionalized NBR (NBROX).

obtained from FTIR spectra of standard solutions of NBR and 2-methyl-2-oxazoline in different proportion, containing succinic anhydride (as the internal standard) in a 1.4 wt% concentration. The ratios between the characteristic absorptions of the oxazoline group (1663 cm^{-1}) and the anhydride group of the succinic anhydride internal standard (1784 cm^{-1}) were plotted against the concentration of 2-methyl-2-oxazoline present in the standard solution. The experimental error of this method was calculated as 1.33%.

Table 1 summarizes the amount of oxazoline groups in the NBROX samples as a function of the reaction parameters. The oxazoline content in nitrile rubber increased with reaction time. The optimum reaction temperature was found to be 140 °C. Lower temperature decreases the reaction rate and higher temperature contributes for the occurrence of the reaction between the formed oxazoline and the 2-aminoethanol present in the system, according to Scheme 3. From all experimental conditions studied for this functionalization reaction, the best one indicated for the preparation of NBROX in 1,2-dichloro-benzene solution was: reaction time = 4 h; temperature = 140 °C; solvent/rubber ratio = 5.0; 2-aminoethanol/zinc acetate ratio = 8.0. Higher amount of zinc acetate leads to a reduction of 2-oxazoline incorporated into the polymer, probably because of the low dissolution of this catalyst in the reaction system.

3.2. Properties of non-vulcanized NBR/EVA blends

The effect of the functionalized copolymers on the compatibilization of NBR/EVA blends was first investigated for non-vulcanized blends. For this study, a NBROX sample with oxazoline content corresponding to 31 mmol/100 g was employed. The effect of the NBROX concentration on mechanical behavior of these blends containing 2.5 and 5.0 wt% of EVALVA is illustrated in terms of stress–strain curves presented in Figs. 3 and 4, respectively. The ultimate data are also presented in Table 2. The presence of pure EVALVA resulted in tensile behavior very similar to those observed for the non-compatibilized blend when the deformation was lower than around 500%. After this point, the compatibilized blends presented an additional deformation up to break following by an increase on tensile strength. This effect was little higher in blend



Scheme 3. Reaction between oxazoline group and 2-ethanolamine.

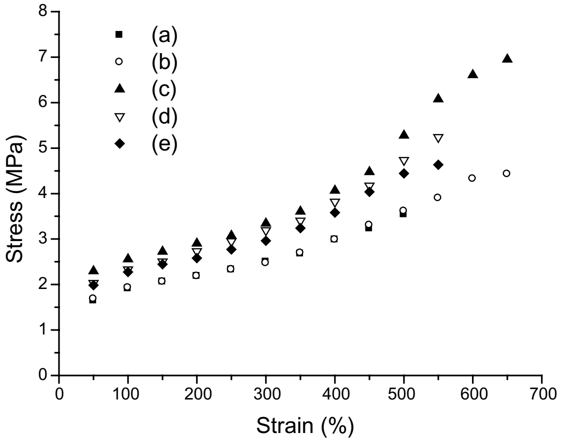


Fig. 3. Stress–strain curves of non-vulcanized NBR/EVA blends (a) without compatibilizer and with (b) EVALVA 2.5%, (c) EVALVA 2.5%/NBROX 2.5%, (d) EVALVA 2.5%/NBROX 5.0%, (e) EVALVA 2.5%/NBROX 7.5%.

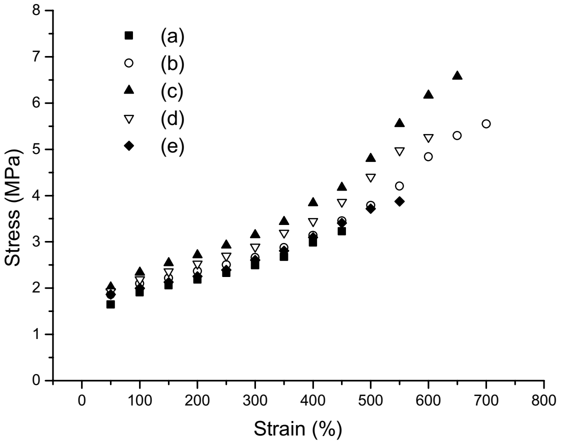


Fig. 4. Stress–strain curves of non-vulcanized NBR/EVA blends (a) without compatibilizer and with (b) EVALVA 5.0%, (c) EVALVA 5.0%/NBROX 2.5%, (d) EVALVA 5.0%/NBROX 5.0%, (e) EVALVA 5.0%/NBROX 7.5%.

containing higher amount of EVALVA and may be related some interaction between the phases, probably originated from hydrogen bond between OH groups of EVALVA and nitrile groups of NBR phase.

The use of NBROX/EVALVA co-reactive copolymers resulted in a significant improvement of tensile strength and elongation at break when 2.5 wt% of NBROX were employed (Figs. 3c and 4c), indicating a better interfacial action of the compatibilizers. The chemical bonds formed during processing promote some crosslinking between the phases and increase substantially the resistance to deformation at the final stage of stress–strain test. Increasing the amount of NBROX resulted in a progressive decrease of tensile strength and elongation at break, probably because of interface saturation and phase embrittlement by excessive reaction.

The effect of EVALVA concentration on the mechanical behavior of the blends at different amount of NBROX is also illustrated in Fig. 5. The use of pure EVALVA resulted in similar properties as compared to non-compatibilized blends, except at the final deformation stage when the tensile strength is higher and depends upon the amount of EVALVA in the blend (Fig. 5a).

Regarding blends compatibilized with the co-reactive copolymers, the use of different amount of EVALVA did not affect the mechanical behavior, except for blends containing 7.5 wt% of NBROX (Fig. 5d). From these results, one can suggest that, for an effective reactive compatibilization, the reactive copolymer must be employed in low proportion, mainly when the functional group is highly reactive, as oxazoline.

Table 2
Tensile properties of non-vulcanized NBR/EVA (50:50 wt %) blends as function of compatibilization

NBROX		EVALVA		Ultimate tensile strength (MPa)	Elongation at break (%)
wt%	mmol OX	wt%	mmol OH		
0	–	0	–	3.5 ± 0.2	460 ± 40
0	–	2.5	0.87	4.4 ± 0.1	620 ± 20
0	–	5.0	1.75	5.4 ± 0.3	650 ± 30
2.5	0.78	2.5	0.87	6.9 ± 0.2	630 ± 30
2.5	0.78	5.0	1.75	6.5 ± 0.1	630 ± 10
5.0	1.55	2.5	0.87	5.1 ± 0.1	550 ± 10
5.0	1.55	5.0	1.75	5.2 ± 0.2	580 ± 20
7.5	2.34	2.5	0.87	4.7 ± 0.3	540 ± 20
7.5	2.34	5.0	1.75	3.9 ± 0.1	540 ± 10

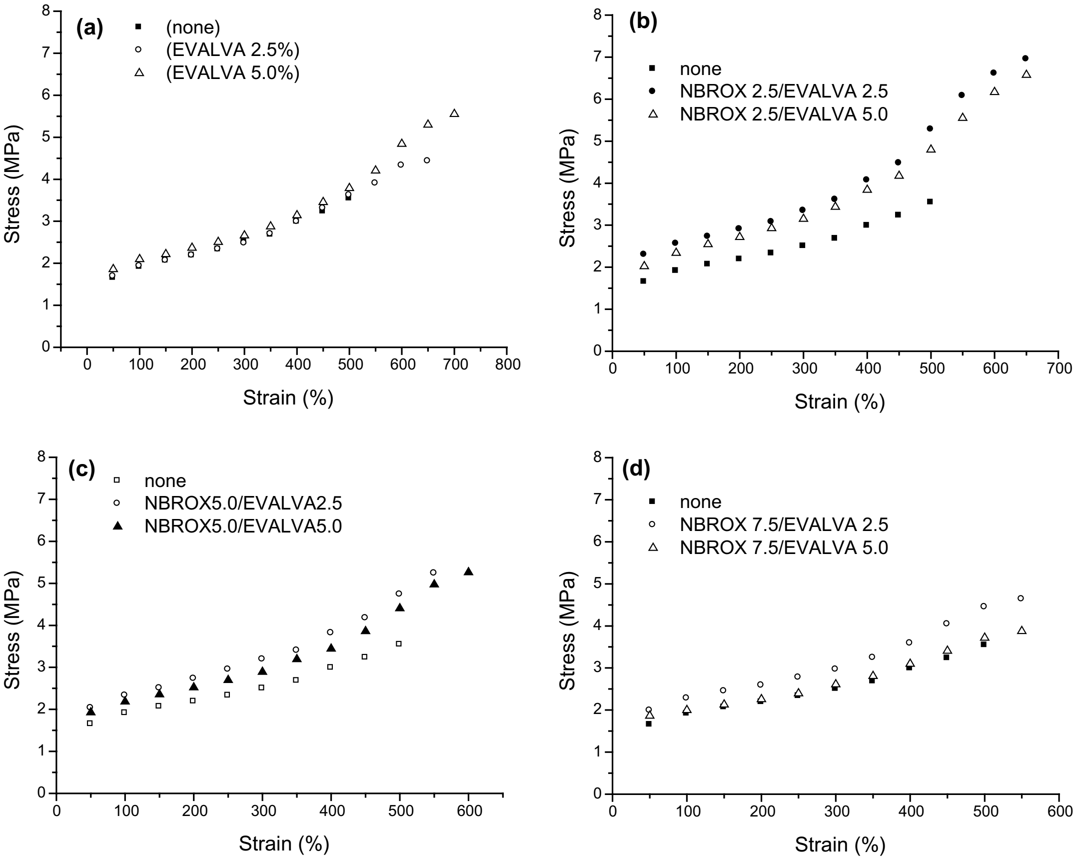


Fig. 5. Stress–strain curves of non-vulcanized NBR/EVA blends with different amount of EVALVA, (a) without NBROX, (b) with NBROX 2.5%, (c) with NBROX 5.0% and (d) with NBROX 7.5%.

The presence of the co-reactive NBROX/EVALVA system also affects the blend morphology. Fig. 6 compares the SEM micrographs of the non-vulcanized blends. The holes in the micrographs are related to the NBR phase, which was extracted by MEK. All these blends present a co-continuous morphology, as expected for this blend composition. The presence of 2.5 wt% EVALVA resulted in a slight reduction of the NBR phase (Fig. 6b), but a better phase dispersion has been achieved with the co-reactive NBROX (2.5 wt%)/EVALVA (2.5 wt%) system (Fig. 6c).

3.3. Properties of vulcanized NBR/EVA blends

The effectiveness of the compatibilization was also evaluated for vulcanized blends. Table 3 presents the main vulcanization parameters. The presence of EVALVA does not affect the curing parameters. The combination of NBROX with EVALVA resulted in a decrease of both scorch time (t_{s1}) and optimum cure time (t_{90}), indicating the participation of the oxazoline group and/or the amide group originated from the reaction between the two co-reactive groups on the curing process. The maximum torque values did not present substantial variations, indicating no influence of the reactive compatibilization on the crosslink density.

The effect of the amount of the co-reactive copolymers on the tensile properties is illustrated in Figs. 7 and 8, for blends containing 2.5 wt% and 5.0 wt% of EVALVA, respectively. Table 4 also summarizes the ultimate data. In all systems studied, the mechanical behavior was quite similar for low deformation degree up to around 400%. Beyond this point, the presence of pure EVALVA (2.5 or 5.0 wt%) resulted in a significant improvement of tensile strength and a little increase of deformation at break. Since this additive does not affect the crosslink density, one may associate this improved performance to the physical interactions between hydroxyl and nitrile groups, as discussed before.

The addition of NBROX in low amount (2.5 wt%) does not affect the tensile properties of vulcanized blends containing 2.5 wt% of EVALVA, but strongly improves the tensile strength when combined with 5.0 wt% of

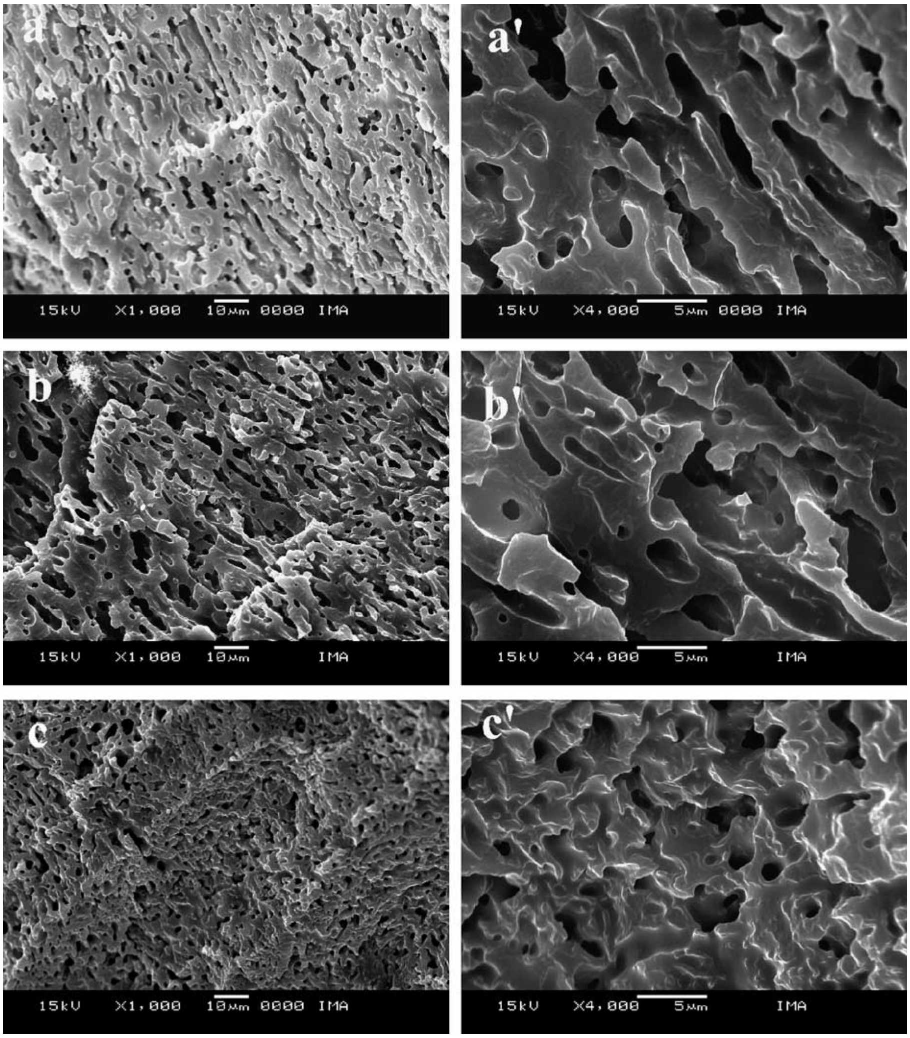


Fig. 6. SEM micrographs of non-vulcanized NBR/EVA (50:50 wt%) blends: (a) pure, (b) with EVALVA (2.5 wt%) and (c) with NBROX (2.5 wt%)/EVALVA (2.5 wt%).

EVALVA (Fig. 8c). At this proportion, the tensile strength has been increased almost 100% followed by a small increasing on the elongation at break, when compared to non-compatibilized blend. The curve profile presents a sharp increase of tensile strength at the final deformation stage indicating an improvement of the reinforcing action promoted by the chemical interaction between the phases. This reinforcing action of the reactive compatibilization associated with the vulcanization process may be responsible for the little increase of the deformation at break in these blends, as compared to the corresponding non-vulcanized blends. As also occurs in non-vulcanized blends, higher amount of NBROX decreases both tensile strength and elongation at break regardless the amount of EVALVA employed.

The morphologies of vulcanized NBR/EVA blends are compared in Fig. 9. The samples were cryofractured, stained with osmium tetroxide and analyzed in a scanning electron microscopy using backscattered detector. The light region in the micrographs corresponds to the NBR phase stained with osmium tetroxide and the black region corresponds to the EVA phase. The co-continuous morphology is also observed in all vulcanized blends, as expected. The blend compatibilized with 5.0 wt% of EVALVA (Fig. 9b) displays higher size of the EVA phase than non-compatibilized blend, in spite of the better mechanical performance of the former. The best morphological situation is clearly observed in blend compatibilized with the co-reactive EVALVA (5.0 wt%)/NBROX

Table 3
Curing parameters of NBR/EVA (50:50 wt%) blends as function of compatibilization

NBROX		EVALVA		M_H (lbf in.)[a]	M_L (lbf in.)[b]	t_{s1} (min)[c]	t_{90} (min)[d]
wt%	mmol OX	wt%	mmol OH				
0	–	0	–	7.5	1.3	5.91	8.91
0	–	2.5	0.87	6.9	1.3	5.27	8.09
0	–	5.0	1.75	6.5	1.2	5.66	8.13
2.5	0.78	2.5	0.87	6.5	1.5	4.41	7.20
2.5	0.78	5.0	1.75	6.7	1.5	4.20	6.73
5.0	1.55	2.5	0.87	6.6	1.7	4.14	6.94
5.0	1.55	5.0	1.75	7.4	1.7	3.96	6.89
7.5	2.34	2.5	0.87	7.2	1.9	3.41	6.00
7.5	2.34	5.0	1.75	5.5	1.8	3.24	5.72

[a] Maximum torque.
[b] Minimum torque.
[c] Scorch time.
[d] Optimum cure time.

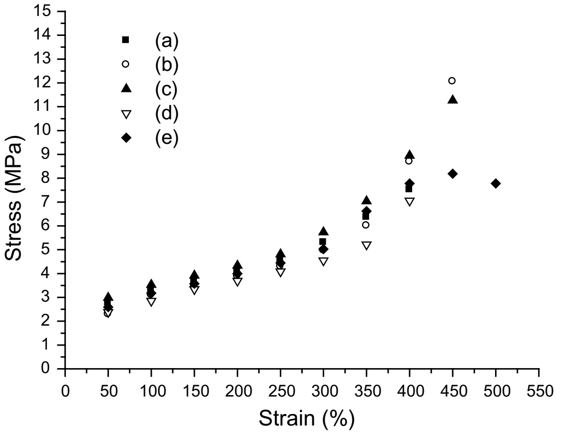


Fig. 7. Stress–strain curves of vulcanized NBR/EVA blends (a) without compatibilizer and with (b) EVALVA 2.5%, (c) EVALVA 2.5%/NBROX 2.5%, (d) EVALVA 2.5%/NBROX 5.0%, (e) EVALVA 2.5%/NBROX 7.5%.

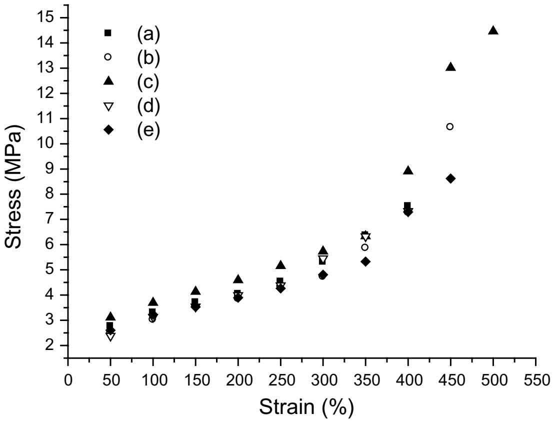


Fig. 8. Stress–strain curves of vulcanized NBR/EVA blends (a) without compatibilizer and with (b) EVALVA 5.0%, (c) EVALVA 5.0%/NBROX 2.5%, (d) EVALVA 5.0%/NBROX 5.0%, (e) EVALVA 5.0%/NBROX 7.5%.

Table 4
Tensile properties of vulcanized NBR/EVA (50:50 wt%) blends as function of compatibilization

NBROX		EVALVA		Ultimate tensile strength (MPa)	Elongation at break (%)
wt%	mmol OX	wt%	mmol OH		
0	–	0	–	7.4 ± 0.1	390 ± 10
0	–	2.5	0.87	11.6 ± 0.5	440 ± 10
0	–	5.0	1.75	11.0 ± 0.3	450 ± 20
2.5	0.78	2.5	0.87	11.0 ± 0.5	450 ± 20
2.5	0.78	5.0	1.75	14.3 ± 0.6	480 ± 10
5.0	1.55	2.5	0.87	7.1 ± 0.2	390 ± 10
5.0	1.55	5.0	1.75	7.2 ± 0.2	390 ± 20
7.5	2.34	2.5	0.87	7.7 ± 0.4	460 ± 30
7.5	2.34	5.0	1.75	8.6 ± 0.6	430 ± 30

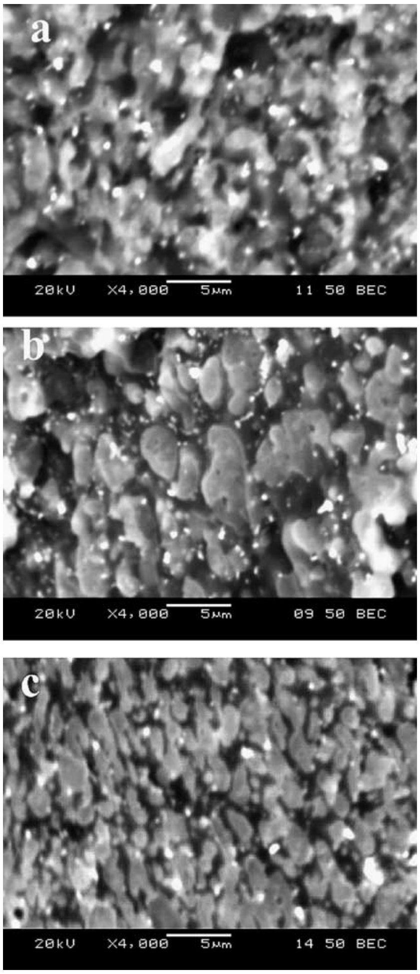


Fig. 9. SEM micrographs of vulcanized NBR/EVA (50:50 wt%) blends: (a) pure, (b) with EVALVA (2.5 wt%) and (c) with NBROX (2.5 wt%)/EVALVA (5.0 wt%).

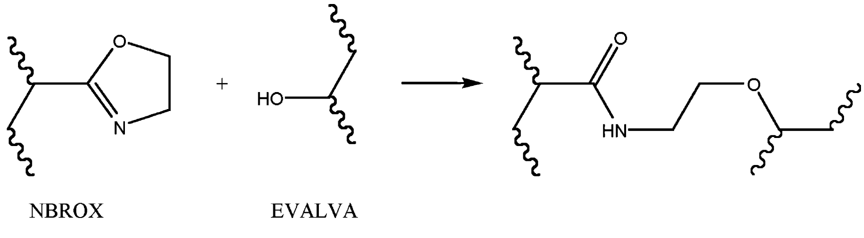
(2.5 wt%) system (Fig. 9c),where a thinner and more elongated EVA phase is present. This morphology is due to the interfacial action of the co-reactive system and must be responsible for the outstanding mechanical performance of the corresponding blend.

3.4. Evidences for the reactive compatibilization

The oxazoline functional groups can react with the hydroxyl groups of EVALVA, according to Scheme 4. In order to evaluate the occurrence of reactions during melt blending, 50 wt% of NBROX were blended with 50 wt% of EVALVA in the two roll-mill at 110 °C and pressed at 160 °C for 15 min. Then, some amount of this non-vulcanized blend was extracted with hot toluene for 24 h. After this treatment, an amount of insoluble material corresponding to 25 wt% have been isolated. A similar treatment has completely dissolved the NBR/EVA blend. These results indicate that the crosslink product was originated from the reaction between the two co-reactive functional copolymers, as illustrated in Scheme 4. The chemical nature of the insoluble material was evaluated by FTIR analysis. Fig. 10 compares the FTIR spectra of NBROX, EVALVA and the insoluble product. The NBROX spectrum displays the characteristic peak at 2237 cm^{-1} related to stretching of nitrile group. In addition, two other peaks at 1666 and 1261 cm^{-1}, related to the C=N and CH_2–O bonds of the oxazoline groups, are also observed.

The EVALVA spectrum presents the characteristic absorptions of the acetate groups: at 1738 cm^{-1}, related to the carbonyl group stretching and at 1238 cm^{-1} related to the C–O bond of the ester. The polyethylene segments are characterized by the absorption at 719 cm^{-1}. The absorption of the OH group at 3450 cm^{-1} is not well defined because of the low concentration of this group in the EVALVA sample.

The spectrum of the insoluble material suggests the presence of both components in the network. The presence of NBROX component is evidenced by the characteristic absorption of the nitrile group at 2230 cm^{-1}, and the EVALVA component is confirmed by the characteristic absorption related to the polyethylene segments at 700 cm^{-1}. Besides these peaks, another set of peaks in the range of 1660–1700 cm^{-1} is observed, which can be attributed to the carbonyl group of ester in the EVALVA component, to amide group formed by the reaction between the oxazoline and OH group, and also to the C=N bond of non-reacted oxazoline group. A better evidence for the reaction between the co-reactive groups is indicated by the presence of the large and



Scheme 4. Reaction between oxazoline group (from NBROX) and hydroxyl groups (from EVALVA).

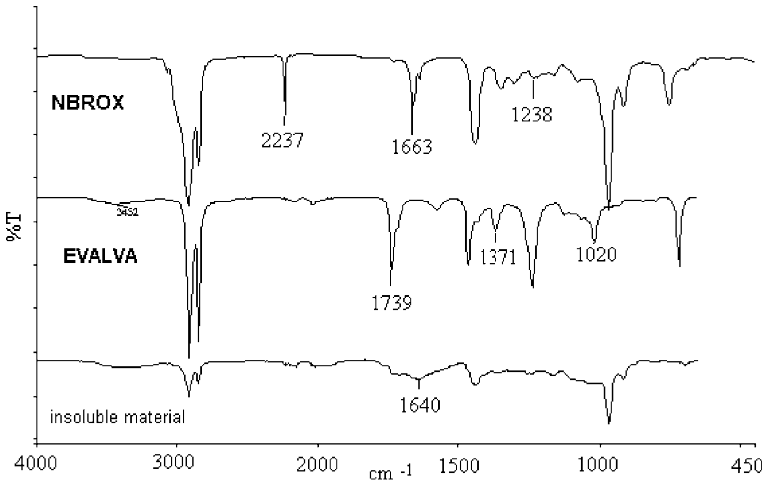


Fig. 10. FTIR spectra of (a) NBROX, (b) EVALVA and (c) the insoluble material isolated from non-vulcanized NBROX/EVALVA (50:50 wt%) blend.

well defined peak at 3350 cm^{-1}, not observable in NBROX or EVALVA, which is attributed to the N–H stretching of the amide group.

4. Conclusions

Mechanical properties of vulcanized or non-vulcanized NBR/EVA blends can be improved by the addition of hydrolyzed EVA alone or better in combination with NBROX. The use of the EVALVA/NBROX co-reactive system is more effective because of the reactivity of the oxazoline group, which favor the formation of true chemical bond between the co-reactive functional groups. The use of low amount of NBROX is good enough to improve both tensile strength and elongation at break of non-vulcanized and vulcanized blends. The effect of the compatibilization on the elongation at break is more pronounce in the case of non-vulcanized blends. The reactive compatibilization was also confirmed by the presence of insoluble material in non-vulcanized blends and by the more uniform morphology.

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References

[1] Varghese H, Bhagawan SS, Rao SS, Thomas S. Eur Polym J 1995;31:957.
[2] Varghese H, Bhagawan SS, Thomas S. J Polym Sci, Phys Ed 1999;37:1815.
[3] Xanthos M, Dagli SS. Polym Eng Sci 1991;31:929.
[4] Liu NC, Baker WE. Adv Polym Technol 1992;11:249.
[5] Jansen P, Soares BG. J Appl Polym Sci 2001;79:193.
[6] Jansen P, Soares BG. J Appl Polym Sci 2002;84:2335.
[7] Jansen P, Gonzalez FG, Soares BG. J Appl Polym Sci 2003;90:2391.
[8] Piglowski J, Gancarz I, Wlazlak M. Polymer 2000;41:3681.
[9] Scaffaro R, Carianni G, La Mantia FP, Zerroukhi A, Mignard N, Granger R, et al. J Polym Sci, Chem Ed 2000;38:1795.
[10] Hseih DT, Pfeiffer DG. J Appl Polym Sci 1995;56:1667.
[11] Frump JA. Chem Rev 1971;71:483.
[12] Nishikubo T, Izawa T, Tokairin A. Makromol Chem, Rapid Commun 1981;2:91.
[13] Saleem M, Baker WE. J Appl Polym Sci 1990;39:655.
[14] Liu NC, Baker WE. Polymer 1994;35:988.
[15] Mäder D, Kressler J, Mülhaupt R. J Appl Polym Sci 1999;73:1685.
[16] Scaffaro R, La Mantia FP, Pentchev IT, Hu GH. Molecular Crystals and Liquid Crystals Sci and Technol; Molecular Crystals and Liquid Crystals 1999;336:169.
[17] Wörner C, Müller P, Mülhaupt R. Polymer 1998;39:611.
[18] Lee S, Park OO. Polymer 2001;42:6661.
[19] Barbosa RV, Soares BG, Gomes AS. J Appl Polym Sci 1993;47:1411.
[20] Müller P, Wörner C, Mülhaupt R. Macromol Chem Phys 1995;196:1917.