

Compatibilization Efficiency of Carboxylated Nitrile Rubber and Epoxy Pre-polymer in Nitrile/Acrylic Rubber Blends

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Abstract: An investigation has been made of the effects from a compatibilizer, viz. carboxylated nitrile rubber (XNBR), on several properties of nitrile rubber (NBR) and acrylic rubber (ACM) blends, including curing characteristics, mechanical, dynamic mechanical and dielectric properties. The presence of XNBR until 10 phr resulted in an improvement of the ultimate tensile properties, especially elongation at break. The mechanical properties associated to the volume fraction of rubber in the network (V_r) and torque values suggest the co-vulcanization phenomenon imparted by the compatibilization. The oil resistance of NBR/ACM (50:50 wt. (%)) blends (compatibilized and non compatibilized) was similar to that observed for pure ACM and significantly higher than NBR. The addition of small amounts of epoxy pre-polymer in combination with XNBR resulted in an additional improvement of the tensile properties. The dynamic mechanical and dielectric properties of the blends were also investigated. The loss modulus values of the compatibilized blends were significantly lower indicating an increase of the elastic characteristics. All blends presented two dielectric relaxation peaks confirming the heterogeneity of the compatibilized blends.

Keywords: *Acrylic rubber, nitrile rubber, blends, compatibilization, mechanical properties, dynamic mechanical properties, dielectric properties.*

Introduction

Polar rubbers are extensively employed on the development of seals and gaskets which are in contact with oil and fuels. One of the most popular classes of these special elastomers is nitrile rubber (NBR) because of its good resistance to oil, fuel and abrasion. However it presents limited resistance to ozone and heat, due to the presence of unsaturation in the chain. Acrylic rubbers (ACM) are also an important polar elastomer and present excellent resistance to oil, heat, ageing and ozone. They usually present a better combination of oil and heat resistance than nitrile rubber because of the polarity and absence of unsaturation in the main chain. The polarity and consequently the swelling resistance and flexibility depend upon the acrylic ester used as the monomer^[1]. The presence of these polar group in the pendent position also results in poor gum strength. The best way to achieve commercially viable products with outstanding properties is through the addition of filler and/or blending with other thermoplastic or rubber. Several researchers have reported the use of ACM rubbers in blends with some thermoplastic as nylon^[2-5], poly (vinyl chloride)^[6-7], ethylene – vinyl acetate (EVA) copolymers^[8], poly(vinylidene fluoride) (PVDF)^[9], poly (ethylene terephthalate)^[10], chlorinated polypropylene^[11] and polypropylene^[12], as well as with few rubbers as fluorocarbon rubber^[13-17] and natural rubber^[18-20]. Recently we have reported some results involving mechanical and dynamic mechanical properties of ACM/NBR blends aiming to develop a system with better heat and oil resistance than pure NBR elastomer and better mechanical performance than ACM^[21]. For curing the NBR phase we have studied the influence of peroxide or sulfur-based system. Peroxide combined with m-phenylene-bis-maleimide (BMI) was shown to be an effective curing system for NBR phase^[22] and a compatibilizing system for the ACM/NBR blends^[21].

ACM rubbers are commercialized with different type of cure-site monomers, introduced in the polymer chain during the polymerization^[23]. Some of them include chlorine, carboxyl and epoxide groups. The ACM used in this work contains double

active cure-site based on chlorine and carboxyl groups. These groups may also act as reactive compatibilizers when blended with other functional polymers.

The aim of the present work is to evaluate the efficiency of carboxylated NBR (XNBR) alone or in combination with epoxy pre-polymer as the compatibilizing system for ACM/NBR blends. XNBR may participate in the curing process together with the ACM because of the presence of carboxyl groups in both rubber components. In addition, the epoxy pre-polymer should react with these carboxyl groups improving the interaction between the components. Consequently they should improve the interfacial adhesion between NBR and ACM phases and improve the mechanical performance. The efficiency of the epoxy pre-polymer as the compatibilizing agent may be attributed to its low viscosity, which tends to be located at the interface, and also because of the reactivity of the oxirane groups with several other functional groups as carboxyl, amine, etc.

In the present work, the compatibilization effect of XNBR and epoxy pre-polymer was evaluated by means of mechanical, dynamic mechanical and dielectrical properties.

Experimental

Materials

Nitrile rubber (NBR) [33 wt. (%) acrylonitrile, Mooney viscosity (ML 1 + 4 at 100 °C) = 60], acrylic rubber, Hicryl 1540, (ACM), [derived from the polymerization of ethyl acrylate and containing carboxyl and chlorine as the double cure site groups; Mooney viscosity (ML 1+4 at 100 °C) = 40] and carboxylated Nitrile rubber (XNBR) (NX43G), [28 wt. (%) acrylonitrile; carboxyl content = 4%; Mooney viscosity (ML 1+4 at 100°C) = 48] were kindly supplied by Petroflex Ind. Com. S.A. Rio de Janeiro, Brazil. Diglycidyl ether of bisphenol A (DGEBA) – based epoxy prepolymer (EPON 828) was purchased from Shell

Química do Brasil and presents the following characteristics: viscosity = 110-150 P; epoxide equivalent = 185-192 g/equiv, and hydroxyl groups around 0.05 mol/100 g. WB 222, a processing agent based on aliphatic fatty acid esters, used for the ACM, was supplied by Struktol. Chemac Park 50, a hexamethylenediamine carbamate, (HMDAC) was supplied by Chemicon Ind. Quim. S.A. N,N'-m-phenylene-bis-maleimide (HVA-2) (BMI) was purchased by Dupont Dow Elastomers. Other ingredients such as stearic acid, dicumyl peroxide (DCP) and sodium stearate (Na stearate) were laboratory reagent grade.

Blend preparation

The blends were prepared in a two roll mill operating at room temperature, with friction ratio of 1:1.1. NBR and XNBR were masticated for 3 minutes and blended with ACM and epoxy resin together with processing aids for the ACM component (WB 222 and stearic acid). After the homogenization of the rubber blend (for about 5 minutes) the other ingredients were added. The basic formulation are listed in Table 1, obeying the addition sequence. The processing time after each component addition was about 2 minutes.

After mixing, the samples were compression molded between pieces of aluminum foil in a two-plates hydraulic press at 170 °C at pressure of 7,5 MPa. The molding time was adjusted according to the optimum cure time (ASTM D 2084-81 method), as determined from an oscillating disk rheometer (ODR; Tecnologia Industrial – model T100) with an oscillating angle of 1°. The optimum cure time (t_{90}) as established as the time to reach 90% of the maximum torque.

The cure rate index (CRI) is calculated using the following equation:

$$CRI = 100 / (t_{90} - t_{s1}) \quad (1)$$

where t_{90} and t_{s1} are the time to achieve 90% of the maximum torque and the scorch time, respectively.

The test specimens for tensile measurements and dynamic mechanical analysis were cut from the molded slabs approximately 2.0 mm thick.

Testing

Tensile testing of the samples was done at 25 °C, using dumb bell-shaped test specimens according to DIN 53504 – type S2 method. The measurements were performed in a Universal testing machine, Instron model 5569, at a crosshead speed of 200 mm/min. The average value of five tests for each sample is reported here.

The compression set test was done under a constant strain of 25% according to ASTM D 395-85 at 100 °C for 22 hours. The specimens for this test were compression molded for $2xt_{90}$, in order to obtain circular disk samples 6.0 mm thick and 12.5 mm diameter.

Degree of equilibrium swelling

The degree of equilibrium swelling was determined in toluene, which could swell both NBR and ACM 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 vacuum*, and weighed again. The swollen and deswollen weights were used to calculate the volume fraction of rubber in the network (V_r):

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

where D is the deswollen weight, S is the swollen weight, ρ_r is the density of the rubber blend, and ρ_s is the density of the solvent.

Table 1. Curing parameters and physic-mechanical properties of NBR/ACM (50:50 wt. (%)) blends as a function of XNBR as the compatibilizing agent.

Ingredients (phr)	mix 1	mix 2	mix 3	mix 4	mix 5	mix 6	mix 7
ACM	100	-	50	50	50	50	50
NBR33	-	100	50	47.5	45	40	25
XNBR				2.5	5.0	10	25
stearic acid	1.0	-	0.5	0.5	0.5	0.5	0.5
WB 222	2.0	-	1.0	1.0	1.0	1.0	1.0
sodium stearate	4.0	-	2.0	2.0	2.0	2.0	2.0
Chemac Park50	1.5	-	0.75	0.75	0.75	0.75	0.75
BMI	-	3.0	1.5	1.5	1.5	1.5	1.5
DCP	-	0.3	0.15	0.15	0.15	0.15	0.15
Cure characteristics from ODR							
t_{s1} (min)	2.0	1.6	1.5	3.1	2.3	2.5	2.0
t_{90} (min)	16	7.5	16	18	18	18.5	19
M_L (dN.m)	2.3	2.9	2.4	0.5	2.4	2.3	3.1
M_H (dN.m)	11.5	31	15.5	11.1	10.5	9.7	9.8
$M_H - M_L$ (dN.m)	9.2	28.1	13.1	10.6	8.1	7.4	6.8
CRI	7.0	17	6.9	6.7	6.4	6.25	5.9
Physical properties							
σ_B (MPa)	1.66	3.84	2.5	3.8	3.5	4.6	3.4
ϵ_B (%)	360	148	546	625	750	1020	800
CS (%)	17.6	12	25	58	43	52	51
S (%)	7.8	18	8.1	9.7	9.4	9.3	9.4
V_r	0.1570	0.2198	0.2540	0.2600	0.2235	0.2124	0.2123

M_H = maximum torque; M_L = minimum torque; t_{90} = optimum curing time; t_{s1} = scorch time; σ_B = ultimate tensile strength; ϵ_B = elongation at break; CS = compression set; S = Swelling in mineral oil; V_r = volume fraction of rubber in the network.

Oil uptake

The test specimens were immersed in a mineral oil at 100 °C for 70 hours. The test specimens were then removed from the oil, wiped with tissue paper to remove the excess oil from the surface and weighted. Percentage mass swell was then calculated as follow:

$$\text{change in mass} = \frac{W_2 - W_1}{W_1} \times 100 \quad (3)$$

where W_1 and W_2 are the weight of the samples before and after immersion, respectively.

Dynamic mechanical analysis

The dynamic mechanical analyses of the blends were obtained by using the DMA analyzer (Q800; TA Instrument). The sample specimens (25 × 12 × 2 mm) were analyzed in single cantilever mode at a constant frequency of 10 Hz, strain amplitude of 30 μm and temperature ranging from -60 to +60 °C, with a heating rate of 2 °C/min. The temperature corresponding to the maximum peak in loss modulus versus temperature plot was taken as the glass-to-rubber transition temperature (T_g).

Dielectric analysis

The dielectric measurements were performed using a Thermal Dielectric Analyzer DETA (TA Instruments Model 2970) with parallel plate electrodes. The DETA was used to measure the dielectric permittivity (ϵ') and dielectric loss (ϵ'') on a thin film of vulcanized rubber specimens cured by compression molding at 170 °C. A maximum force of 150N was applied to the sample to achieve a minimum spacing of 0.25 mm. Measurements were taken in the frequency range from 1 to 10⁵Hz and through a temperature range of -50 to 150 °C, under dry nitrogen gas purging.

Results and Discussion

Curing characteristics and physical-mechanical properties

The effect of XNBR on the curing parameters and tensile properties of ACM/NBR (50:50 wt. (%)) blends is summarized in Table 1. ACM was cured by sodium stearate combined with HMDAC, whereas NBR was cured by DCP-based peroxide together with BMI as the co-agent. The cure of ACM was not so fast and the crosslink density (indicated by the lower ΔM ($M_H - M_L$) value) was also lower than that observed for pure NBR. Of course, these differences are associated to the lower curing site concentration in the ACM rubber and the different curing process in each rubber, which should also present different reactivities. NBR/ACM blend presented a delay of the curing process, whose value was comparable to that of pure ACM. The maximum torque and the ΔM values stayed in between those of the pure components, indicating that the crosslink density of the system was decreased by the presence of ACM. The addition of XNBR in the blend resulted in an increase of both scorch (t_{s1}) and optimum curing time (t_{90}), suggesting an additional delay of the curing process. In addition, the ΔM values also decreased suggesting a decrease of the crosslink density. These results indicated that the carboxyl groups of XNBR consumed part of the curing system designed for the ACM component, contributing for a decrease of the overall crosslink density of the blends.

The addition of up to 10 phr of XNBR resulted in an increase of ultimate tensile properties especially the elongation at break. These results suggest that XNBR acts as a compatibilizing agent,

promoting an effective anchorage between NBR and ACM through the carboxyl groups of the XNBR component which should participate on the curing process together with the carboxyl curing site of the ACM phase. On the other hand, the peroxide system is able to promote the cure of both the NBR and XNBR phases, because of the double bonds present in both components.

The V_r values related to ACM/NBR blends without XNBR (mix 3) and with 2.5 phr of XNBR (mix 4) are higher than those found for the pure rubbery components. This phenomenon is due to the lower swelling ability of the rubber vulcanizates. Since the ΔM values are lower, one can attribute this behavior as a co-vulcanization phenomenon, in which both rubber components take part in the network. According to some reports in the literature, the lightly swollen rubber phase restricts swelling of the highly swollen phase because of the interfacial crosslinking^[24-27]. This phenomenon is possible because the BMI used as the co-agent for the peroxide curing system may also react with the hexamethylenediamine formed through the decomposition of the Chemac Park 50 (HMDAC), which is used for curing the ACM phase^[21]. The probable reactions that occur at the ACM/NBR interface during the curing process is illustrated in Figure 1.

The compression set (CS) value of ACM/NBR blend is higher than those corresponding to the pure rubbery components, probably because of the lower crosslink density in this blend, as indicated by the ΔM values. The presence of XNBR contributes for an additional increase of CS because of the lower crosslink density in these blends. It is very interesting to point out that the oil resistance of the blends containing 50 phr of NBR is comparable or slightly lower than the pure ACM and significantly higher than NBR. This result is very interesting under the technological and economical point of view since it is possible to develop rubber systems with outstanding mechanical performance and good oil resistance and lower cost.

The effect of the epoxy pre-polymer in combination with XNBR on the ultimate tensile properties of NBR/ACM blends are illustrated in Figure 2, as functions of epoxy pre-polymer and XNBR contents. For blends containing 2.5 and 5.0% of XNBR, the presence of epoxy resin resulted in a significant improvement of both tensile strength and elongation at break, confirming the compatibilizing effect. The oxirane groups of the epoxy resin are able to react with the carboxyl groups of both XNBR and ACM, improving the adhesion between them. This reaction is also illustrated in Figure 1.

Dynamic mechanical properties

Dynamic mechanical analysis constitutes a convenient tool for studying polymer/polymer compatibility and also determining some important parameters as glass transition temperature, damping behavior, modulus, etc. Figure 3 shows the temperature dependence of the loss modulus for NBR, ACM and their blends containing different amounts of XNBR. The maximum of the loss modulus was considered as the glass transition temperature. For pure NBR and ACM rubbers, the T_g values corresponded to -22 °C and -8 °C, respectively. The ACM/NBR blend displayed a broad transition with a maximum at -25 °C, corresponding to the NBR phase transition, and a shoulder at around -12 °C, which was related to the ACM phase transition. This broad transition and the shift of the ACM phase transition towards lower temperature indicate that the blend is partially compatible, with the formation of an interphase between the rubbers^[28]. The loss modulus profiles of the blends containing XNBR displayed similar trends. Nevertheless, the maxima of the loss modulus were shifted towards higher temperature than

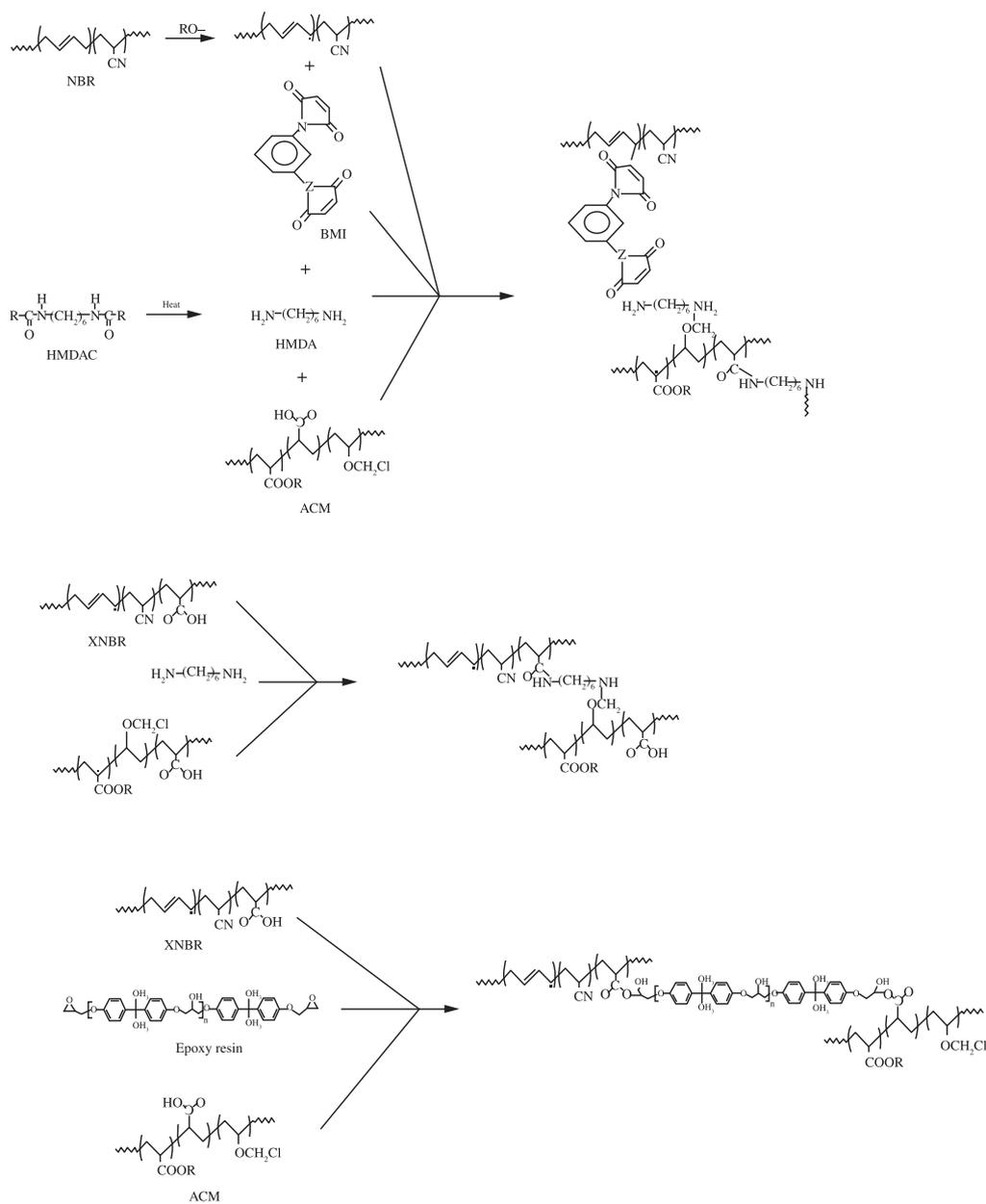


Figure 1. Probable reactions which occur at the ACM/NBR interface during the compatibilization and curing process.

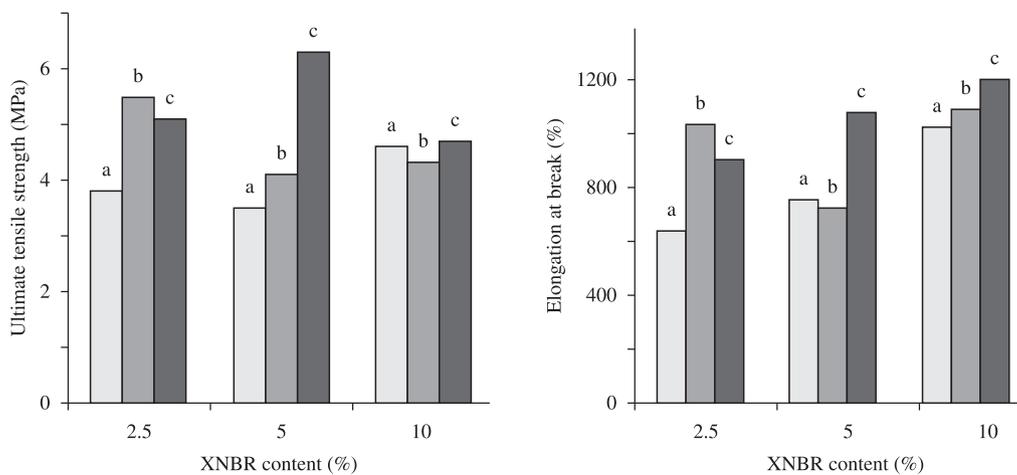


Figure 2. Tensile properties of NBR/ACM blends as a function of the epoxy resin content: (a) 0%, (b) 0.5% and (c) 1.0%.

the pure NBR, staying at an intermediary values between those of both individual rubbers. Additionally, the area under the loss modulus curves for the XNBR – containing blends is significantly lower indicating an improvement of the elastic properties of these materials, probably because of the increasing of the interactions between the phases through either grafting of crosslinking at the interface. This behavior is in agreement with the tensile properties, confirming the compatibilizing effect of the XNBR.

The effect of the epoxy pre-polymer as the compatibilizing agent on the storage (E') and loss (E'') moduli of NBR/ACM blends is illustrated in Figure 4. The presence of the epoxy pre-polymer resulted in a shift of the loss modulus towards higher temperature and an additional decrease of loss modulus, suggesting an increase of the interaction between rubbers as a consequence of the compatibilization. Also the storage modulus in the rubbery state increased with the addition of the epoxy pre-polymer as the compatibilizing agent, confirming the reinforcing action of the chemical crosslinkings that occur at the interface region.

Dielectric analysis

Dielectric relaxation technique complements DMA for the characterization of heterogeneous systems. This technique deals with the evaluation of changes in ionic and dipolar mobilities of a material when it is submitted to an alternating electric field^[29]. The two most important parameters which are possible to evaluate are: dielectric permittivity (ϵ') related to the amount of dipole alignment,

and dielectric loss (ϵ''), which corresponds to the energy required for aligning dipoles and moving ions.

Figure 5 illustrates the isochronal curves of permittivity and loss of NBR, ACM and the non compatibilized NBR/ACM (50:50 wt. (%)) blend, as a function of temperature. All ϵ' isochrones display similar pattern, characterized by one step at lower temperature, which shifts towards higher temperature as the frequency measurements increases. This step-wise increase of ϵ' and a sharp maximum in ϵ'' are due to the glass-rubber relaxation process. Moreover, the strong increase in ϵ'' at lower frequencies and/or higher temperatures is also observed, which is attributed to the onset of ionic conduction, as reported by other authors^[29].

The dielectric response of pure NBR is higher than pure ACM and those corresponding to the NBR/ACM blend stay in between. This behavior suggests a higher polarity of the NBR rubber. The NBR/ACM blend displays two relaxation peaks in the loss curves, which are only observed at low frequency (1 and 10 Hz). These relaxations, at lower and higher temperatures, are related to the glass-rubber transitions of the NBR and ACM phases, respectively, and indicate that the blend is not miscible, as expected.

The dielectric relaxation processes at lower frequencies are strongly influenced by the interfacial polarization and ionic conductivity contributions. In order to avoid such interferences, many authors use the electrical modulus formalism to describe the relaxation of the dipole that exists in different energy environment, without the effects of the conductivity^[30-31]. The complex electric modulus is derived from the complex permittivity, according to the relationship defined by Macedo et al.^[32]:

$$M' = \frac{\epsilon_1}{(\epsilon')^2 + (\epsilon'')^2} \quad M'' = \frac{\epsilon''}{(\epsilon')^2 + (\epsilon'')^2} \quad (4)$$

Figure 6 illustrates the dependence of M'' with the temperature for the NBR/ACM blends as a function of the XNBR content. The pure rubbers exhibit two relaxation peaks. The relaxation at higher temperature may be attributed to the conductivity relaxation, according to the literature^[30]. The blends present two main relaxation peaks related to the different rubber domains, confirming that the blends are immiscible. Additionally, there is another small relaxation in between the main peaks, which can be related to the interphase. According to the insert of Figure 6, the presence of

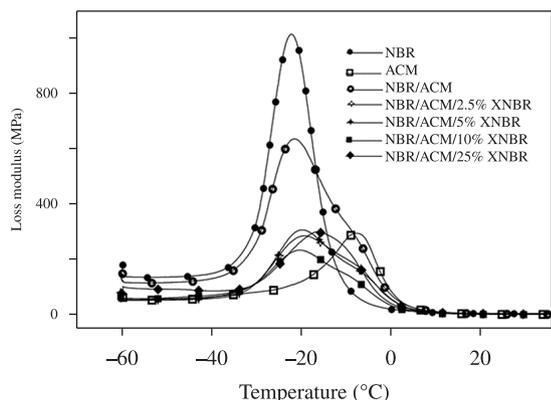


Figure 3. Dependence of loss modulus with temperature for NBR/ACM blends as a function of the XNBR content.

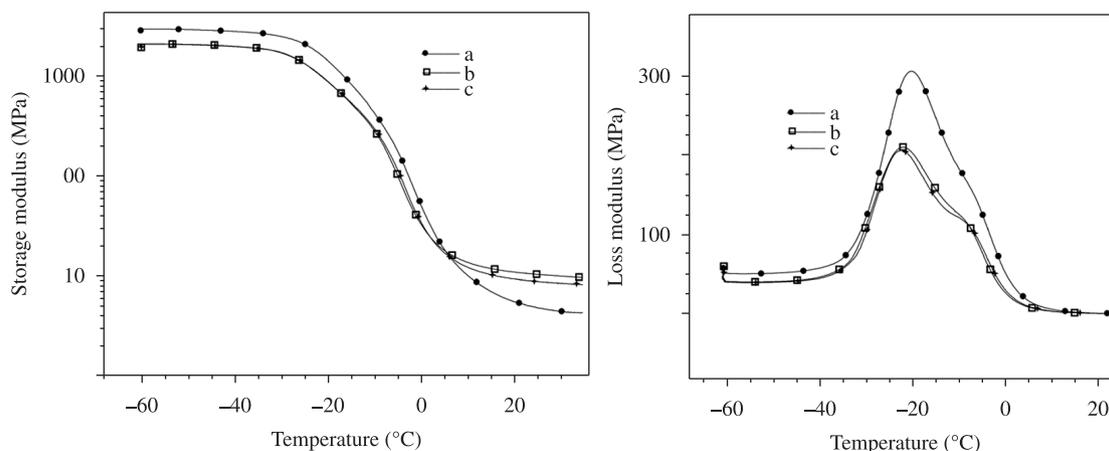


Figure 4. Dependence of storage and loss moduli with temperature for NBR/ACM blends containing 2.5% of XNBR, as a function of the epoxy pre-polymer content. (a) 0%; (b) 0.5 and (c) 1% of epoxy pre-polymer.

XNBR resulted in a slight increase of the dielectric loss modulus, suggesting a more polar interphase.

The effect of the epoxy pre-polymer on the dielectric loss modulus (M'') of NBR/ACM blends containing 5% of XNBR is illustrated in Figure 7. The presence of epoxy resin resulted in a

broadening of the relaxation at higher temperature and a shift of this relaxation towards higher temperature. This may indicate some additional interaction between ACM and the XNBR promoted by the epoxy pre-polymer located at the interface.

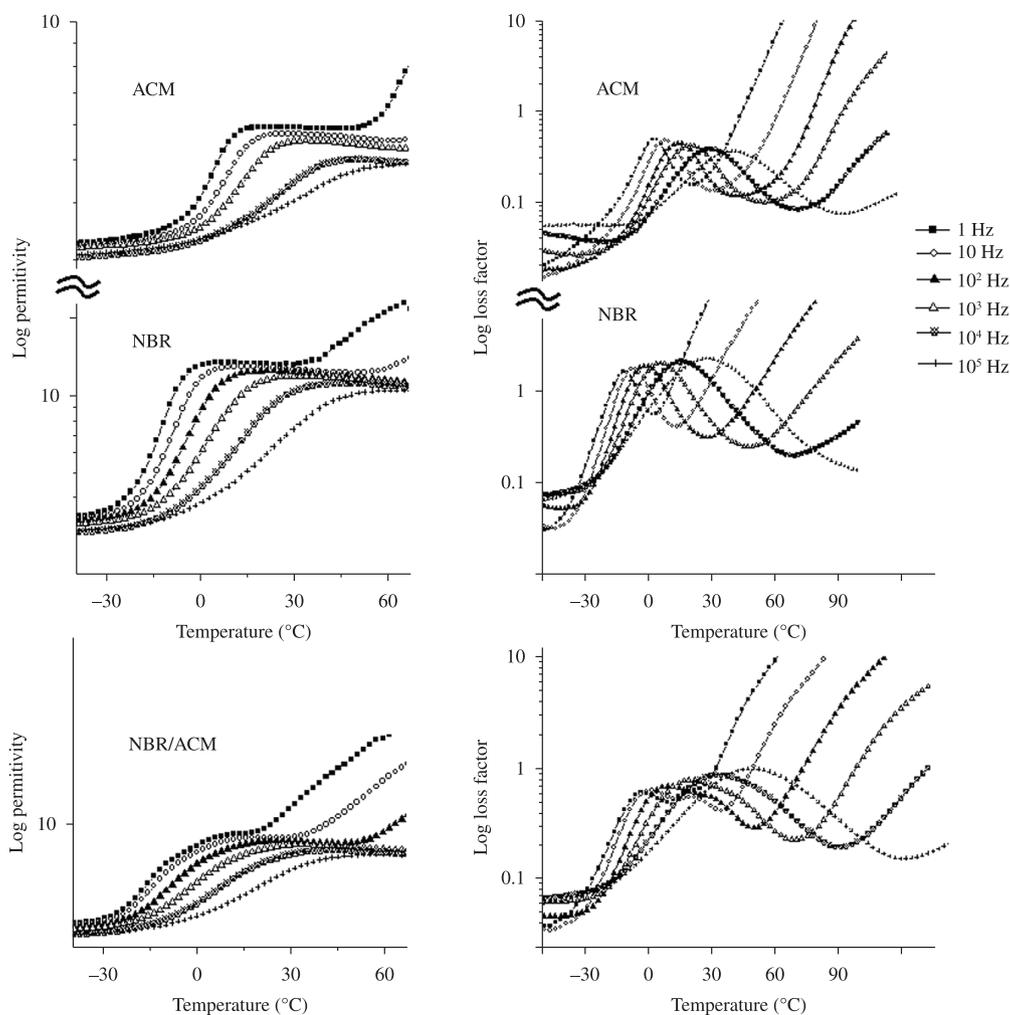


Figure 5. Temperature dependence of permittivity (ϵ') and Loss factor (ϵ'') at various frequencies for the pure NBR, ACM and the non compatibilized NBR/ACM blend.

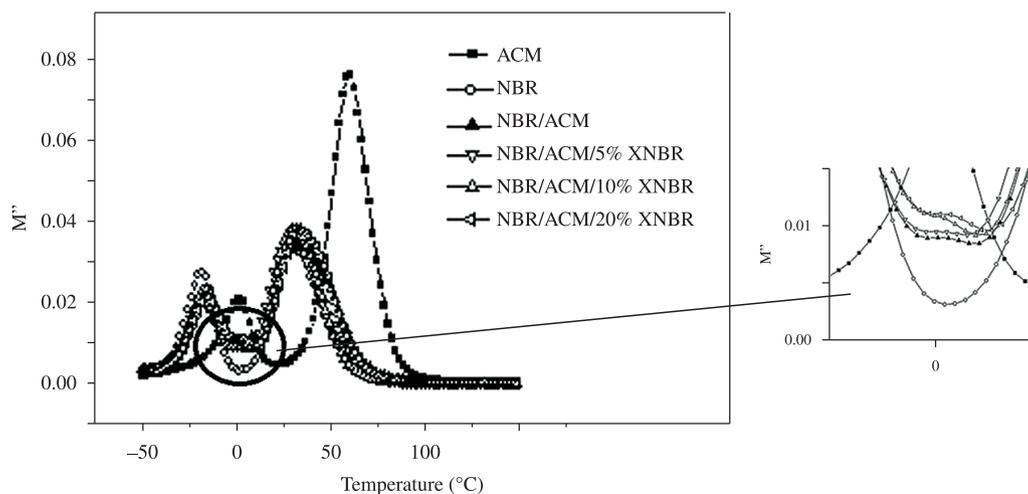


Figure 6. Dependence of M'' with the temperature for the NBR/ACM blends as a function of the XNBR content.

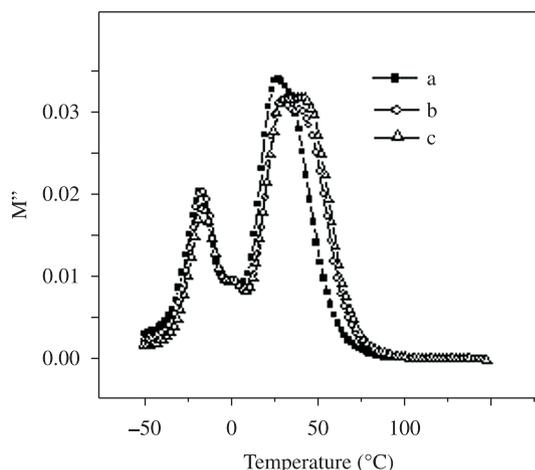


Figure 7. Dependence of M'' with the temperature for the NBR/ACM blends containing 5% of XNBR, as a function of the epoxy pre-polymer content. (a) 0%; (b) 0.5 and (c) 1% of epoxy pre-polymer.

Conclusions

The effect of carboxylated nitrile rubber was investigated as compatibilizing agent for ACM/NBR blends. The presence of up to 10 phr of XNBR resulted in a significant improvement of the tensile properties especially the elongation at break. The ACM/NBR blends developed in this work presented oil resistance comparable or a little lower than the ACM, which is a very promising result since the ACM/NBR blends present outstanding mechanical performance when compared to the pure rubber components and are less expensive than pure ACM. The addition of small amount of epoxy pre-polymer resulted in an additional improvement of the ultimate tensile properties. The efficiency of the compatibilization was evidenced by dynamic mechanical properties. The loss modulus curves of the blends were broad and appeared at intermediary transition temperatures related to the rubber components, indicating compatibilization. All blends presented two dielectric relaxation peaks confirming the heterogeneity of the compatibilized blends

Acknowledgments

We would like to acknowledge the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPERJ), for the financial support.

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Received: 04/01/12

Revised: 30/04/12

Accepted: 06/06/12