# Ionic Elastomers Based on Carboxylated Nitrile Rubber and Magnesium Oxide

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**ABSTRACT:** The crosslinking of carboxylated nitrile rubber (XNBR) with magnesium oxide (MgO) leads to an ionic elastomer with thermoplastic nature and better physical properties than the ones obtained with other metallic oxides. The crosslinking reaction leads to the formation of a metallic salt as unique product, as it could be seen on the ATR analysis of the samples, prepared at different reaction times. The mechanical properties of the material increase with the amount of crosslinking agent and segregation of an ionic microphase takes place. The presence of this microphase is demonstrated by a relaxation at high temperatures. The apparent activation energy of this relaxation is smaller than the activation energy of the glass transition of the elastomer, the former being more dependent on the amount of metallic oxide than is the latter. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 1894–1899, 2007

**Key words:** carboxylated nitrile rubber; ionic crosslinking; mechanical and dynamic properties

## INTRODUCTION

The carboxylated nitrile rubber (XNBR) is an elastomer with carboxylic groups along the hydrocarbonate chain, able to react with many compounds.[1] One possible reaction of these materials is with metallic oxides, leading to the formation of carboxylic salts, which behave as ionic crosslinks. These carboxylic salts tend to associate as multiplets and clusters.[2] These clusters behave as an ionic microphase immersed on an apolar matrix and are the responsible of the final properties of these materials.

Our research group has been working on the crosslinking of the XNBR with sulfur,[3] which only leads to conventional covalent bonds, with zinc peroxide,[3–5] which produces ionic bonds as well as covalent ones, and a mixed system of sulfur and zinc peroxide.[6] In the present work, the behavior of XNBR crosslinked only with ionic bonds using magnesium oxide (MgO) as the crosslinking agent, is expected to be studied. The election of this oxide as a substitute of zinc oxide is due to the fact that the latter gives problems related to its precocity. The influence of the amount of oxide and crosslinking temperature is analyzed by means of rheometrics curves and mechanical and mechano-dynamic properties.

## EXPERIMENTAL

The nitrile carboxilated rubber, Krynac 7.40 (with 27% content of acrylonitrile, 7 wt % of carboxylic groups and a Mooney viscosity of 40 was supplied by Lanxess (LaWantzenau, Franie). The magnesium oxide (MgO) used was Elastomag 170 Special, supplied by Morton Thiokol Inc. (Chicago, IL). Stearic acid, rubber grade, was also used. All formulations are shown on Table I.

The compounds were prepared on a Gumix laboratory cylinder mixer, with a cylinder diameter of 15 cm and a length of 30 cm. The cylinders were kept cold with cold water circulating through them during the mixing process. The friction relation between them was 1 : 1.15.

The vulcanization curves were obtained with a Monsanto MDR 2000E rheometer, with an oscillation arc of 1°, at different temperatures. The vulcanization reaction was carried out in a hydraulic press heated by thermofluids. Two vulcanization temperatures at 120°C and 150°C were studied.

Tensile tests were performed with an Instron model 4301 dynamometer equipped with a video camera to measure deformations, at a deformation rate of 500 mm/min on Type 2 dumbbell samples according to UNE 53,510.

Tearing tests were carried out on Delft-type samples in agreement with UNE 53,516 Parts 2 at the same deformation rate used for the tensile test. Five samples were tested in each use.

The dynamic properties were determined in a Metravib Viscoanalyser RAC 815, based on a principle of non-resonant forced vibrations. Tests were performed over a wide frequency range (5, 8, 12, 20 Hz) and the temperature programs were run from −60°C to 200°C.

**TABLE I**
**Formulation of Compounds**

|  | Mg-4 | Mg-6 | Mg-8 | Mg-10 | Mg-12 |
|---|---|---|---|---|---|
| XNBR Krynac 7.4 | 100 | 100 | 100 | 100 | 100 |
| Stearic acid | 3 | 3 | 3 | 3 | 3 |
| Magnesium oxide | 4 | 6 | 8 | 10 | 12 |

Infrared spectra were recorded on a spectrophotometer, Nicolet model 520 FTIR, using ATR (Attenuated Total Reflectance) technique, with a scanning rate of 4 cm s$^{-1}$ and a resolution of 4 cm$^{-1}$.

## RESULTS AND DISCUSSION

### The crosslinking reaction

At the vulcanization temperature, reaction between the metallic oxide and the carboxylic groups of the polymeric chain takes place, with the formation of the corresponding metallic carboxylate; any other reaction is also possible. This ionic salt appears as multiplets, and their association, called clusters, leads to the formation of a separated microphase, as mentioned above. Obviously, these associations are thermally labile.

Figure 1 shows the ATR spectra of the sample without crosslinking, and the sample with the composition MgO-8, crosslinked at 150°C. As it can be observed, the signal corresponding to the COOH groups of the polymer, 1698 cm$^{-1}$, disappears and a new peak, corresponding to the metallic salt, appears at a wavelength of 1591 cm$^{-1}$. Moreover, the shoulder that appears at 1419 cm$^{-1}$ is also related with the formation of the salt.

It is considered that the band at 2920 cm$^{-1}$, which corresponds to the asymmetric stretching vibration of CH$_2$ group, does not change during the crosslinking process. Figure 2 shows the variation of the absorbance relation, $A_x/A_{2920}$, with reaction time. In the mentioned relation, $A_x$ defines the absorbance of the bands at a wave length of $x$ cm$^{-1}$, which varies during the crosslinking process (1698, 1591, and 1419 cm$^{-1}$). Regarding the variation of the signals previously mentioned, it is
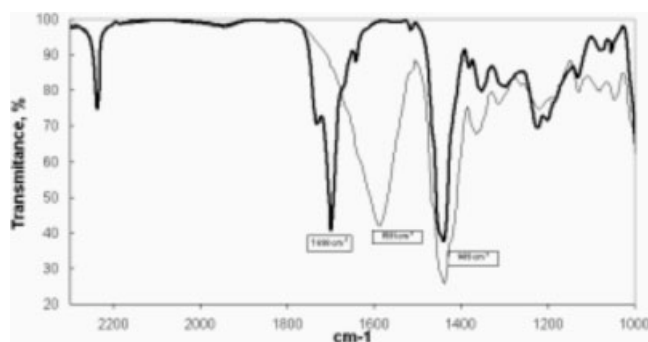
**Figure 1** ATR spectra of compound Mg-8 uncured (—) and cured at 150°C (—).
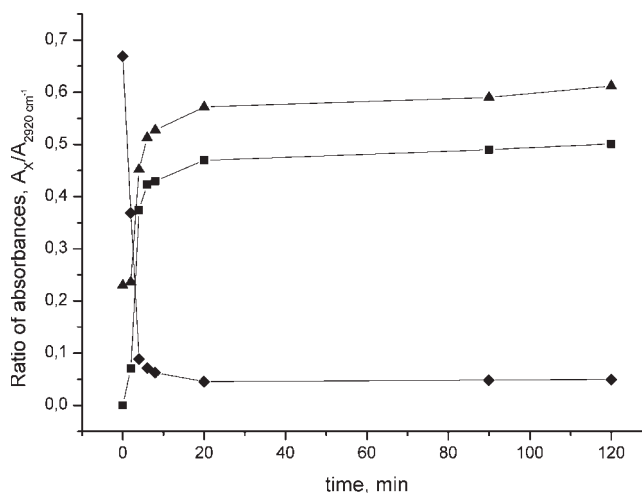
**Figure 2** Ratio of the changing peaks absorbances (($\blacklozenge$) 1698 cm$^{-1}$; ($\blacksquare$) 1591 cm$^{-1}$; ($\blacktriangle$) 1419 cm$^{-1}$) with a non changing peak absorbance (2920 cm$^{-1}$), as a function of time.

possible to conclude that the variation of the different peaks fit in one with the other, i.e., the amount of metallic salt that appears is similar to the amount of carboxylic groups that disappears.

### Vulcanization curves

Table II shows the parameters that describe the vulcanization reaction, at two temperatures and as a function of the amount of MgO utilized. The corresponding values of a mix prepared with 3 phr of MgO, crosslinked at 150°C, have also been included. If the $\Delta S$ parameter is considered, a remarkable difference is found when the samples with 3 and 4 phr of MgO are compared. However, there is no difference between the sample with 4 phr and the others with higher proportion. As it is known, this parameter is related to the crosslinking density and, hence, with the final properties of the vulcanized material. In our opinion, the amount of 3 phr of MgO does not saturate all carboxilic groups. Therefore, the crosslinking density is lower, leading to inferior mechanical properties. This is the reason why the sample with 3 phr has not been included in the present work.

For each temperature, an increase in the level of the metallic oxide leads to an increment of the maximum torque, with no significant differences in the minimum torque. These results mean that the viscosity of the raw mix is smoothly changed with the oxide proportion. The difference between both parameters, which is called Torque increment, $\Delta S$, rises gradually with the content of MgO. This results in an increment of the crosslinking density, hence, an improvement on mechanical properties. Another point that must be emphasized is how the cure index rate (CRI = $100/t_{90}-t_{\Delta 2}$)

**TABLE II**
**Vulcanization Parameters as a Function of MgO Content**

| | 3 phr | 4 phr | | 6 phr | | 8 phr | | 10 phr | | 12 phr | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 150°C | 120°C | 150°C | 120°C | 150°C | 120°C | 150°C | 120°C | 150°C | 120°C | 150°C |
| $S'_H$, (dN m) | 2.66 | 8.44 | 5.77 | 10.47 | 6.70 | 11.71 | 6.90 | 11.77 | 7.32 | 14.93 | 7.95 |
| $S'_L$, (dN m) | 0.57 | 0.89 | 0.60 | 1.0 | 0.61 | 1.12 | 0.61 | 1.05 | 0.62 | 1.15 | 0.63 |
| $\Delta S'$, (dN m) | 2.09 | 7.55 | 5.17 | 9.47 | 6.09 | 10.59 | 6.29 | 10.72 | 6.70 | 13.78 | 7.32 |
| $t_{\Delta 2}$ (min) | – | 36.6 | 6.36 | 20.4 | 4.05 | 12.7 | 3.64 | 12.2 | 2.5 | 7.45 | 2.6 |
| $t_{90}$ (min) | – | 174.8 | 40.73 | 129.1 | 36.16 | 107.5 | 32.63 | 90.15 | 22.84 | 106.2 | 17.21 |
| $t_{90}-t_{\Delta 2}$ (min) | – | 138.2 | 34.37 | 108.7 | 32.11 | 94.8 | 28.99 | 77.95 | 20.24 | 98.75 | 14.61 |
| CRI | – | 0.723 | 2.909 | 0.919 | 3.11 | 1.055 | 3.45 | 1.28 | 4.94 | 1.01 | 6.84 |

has been raised. Up to here, all these results seem to be logical.

However, when the $\Delta S'$ is compared for the same compound at different temperatures, it can be observed that the higher torque increment is obtained when smaller reaction temperature is used. On the other hand, the viscosity of the mix decreases as the temperature rises. These results made us consider the variation of the rheometric curves at different temperatures.

Figures 3 and 4 show the vulcanization curves of the sample with the highest content in MgO (12 phr), in a range of temperatures between 100°C and 150°C, with their elastic ($S'$) and viscous ($S''$) component, respectively.

Regarding the elastic component, which is the one that is usually taken as the vulcanization curve, it can be observed that, at any temperature, the curve rises with reaction time. In the same way, reaction rate (in terms of the slope in the first stage of the curve), increases with the temperature. Therefore, as it was expected, when we rise the temperature, the reaction is enhanced. At low temperatures, e.g., 100°C and 110°C, the reaction is slow and the curves cannot achieve a plateau during the test time employed.

However, as it was mentioned above, the possible maximum torque decreases with the increment in reaction temperature. This fact can be explained if we take into account the chemical bonds formed during the reaction. Obviously, reaction yield and maximum torque possible depend on the amount of metallic oxide added to the compound. Therefore, at any temperature, the same value for the torque, and hence, the same crosslinking density, should be achieved. On the other hand, it cannot be forgotten that ionic bonds, formed during the reaction, are thermally labile, therefore, the number of bonds that remains forming the crosslinked net is variable and it decreases as the temperature rises. As a result of this, the elastic capacity of the compound decreases.

If the curves that correspond to the viscous component, $S''$, are studied, a different behavior can be observed. Firstly, for each temperature, growing curves with reaction time are obtained, which is a characteristic of ionic vulcanization. Furthermore, as the temperature increases, the value for the viscous component increases. This fact leads us to conclude that the thermal lability of the ionic association gives an increment of the viscous component of the compound, i.e., there is a direct proportionality between the loss in
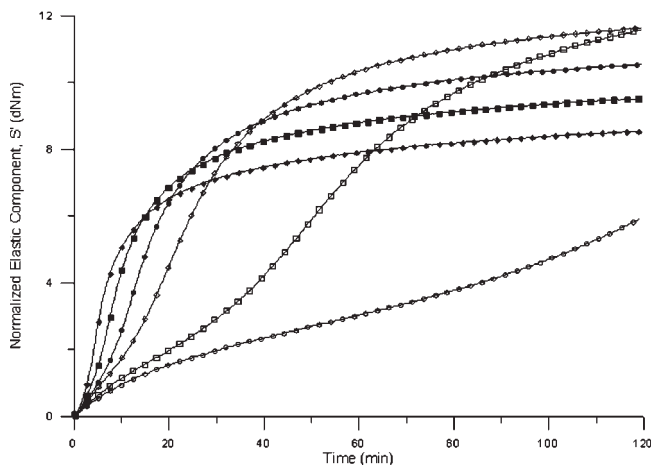


**Figure 3** Normalized elastic component, $S'$, as a function of time at different temperatures: (○) 100°C; (□) 110°C; (◇) 120°C; (●) 130°C; (■) 140°C; (◆) 150°C.
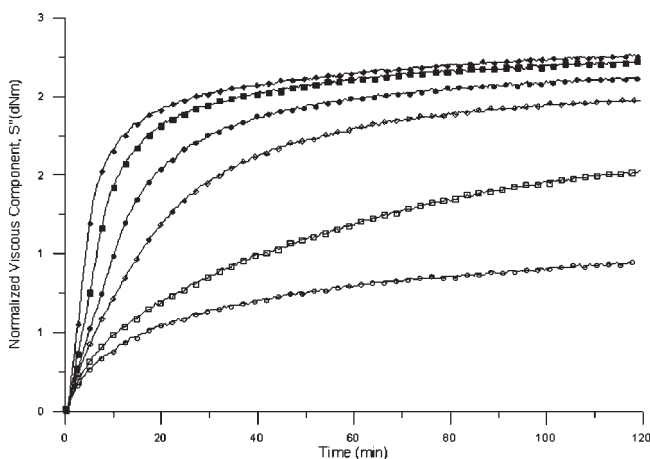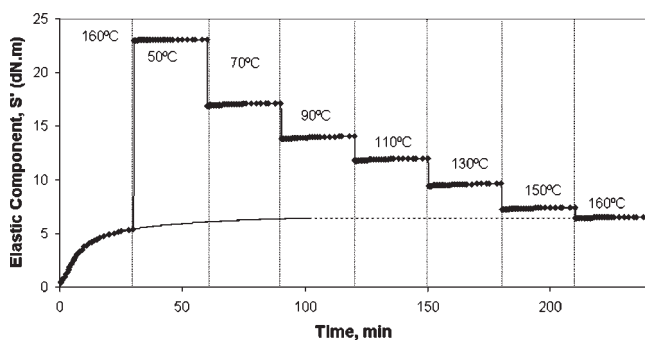


**Figure 4** Normalized viscous component, $S''$, as a function of time at different temperatures. Symbols as in Figure 3.

**Figure 5** Variation of elastic component with temperature: (◆) values of $S'$ (dNm) at different temperatures; (—) continuous curing at 160°C.

elasticity of the sample due to the breakage of the ionic association and the increment of the viscous component.

Figure 5 shows the results for the following experiment: the variation of the elastic component was registered during a certain period of time, at the corresponding vulcanization temperature (160°C for this case) during 30 min. After this time, the rotor is stopped and cooled down to a temperature lower than the vulcanization one and kept at this temperature for the same time utilized before. The torque is registered during the entire process. The mix gently warms up and the compound is kept at this temperature until the initial vulcanization temperature is reached.

When the crosslinking reaction began at high temperatures, as the ionic associations formed are thermally labile, they tend to break down. The breakage of this association directly depends on the temperature. The shape of the curve in this phase is exactly the same as the one obtained for normal vulcanization. When the mix cools down, association of the bonds takes place again, forming ionic associations, according to the amount of oxide added. As the increase in temperature occurs, the breakage of the corresponding bonds takes place at the experiment temperature. When the initial temperature is reached, the elastic torque value is an extension of the original one.

On the other hand, if we look at the normal vulcanization curve (dotted line) of the Figure 5, obtained at 160°C, it can be seen that it agrees with the previous experiment. Both experiments correspond to two different compounds with the same composition; therefore, it is possible to assume that these results are reproducible.

From all these discussions, it can be concluded that the elastomers prepared present thermoplastic properties.

**Physical properties**

Table III shows the physical properties of the different compositions prepared, at two different vulcanization temperatures. From the data obtained, it can be deduced that, for any of the two vulcanization conditions, Shore A hardness, stress at constant strain and tear strength, are enhanced with the content of metallic oxide. However, tensile strength and ultimate elongation do not seem to follow a clear trend and loss abrasion decreases with the content of oxide.

On the other hand, crosslinking density, $v_r$, shows similar values, regardless of vulcanization condition and amount of oxide. It must be considered that the theoretical amount of MgO to saturate the carboxylated

**TABLE III**
**Physical Properties as a Function of Vulcanization Conditions and of MgO Content**

| Property | MgO-4 | MgO-6 | MgO-8 | MgO-10 | MgO-12 |
|---|---|---|---|---|---|
| Vulcanization 180′/120°C | | | | | |
| Shore A hardness | 69 | 70 | 71.4 | 71.7 | 74.3 |
| Stress at 100% strain (MPa) | 2.8 | 3.6 | 4.1 | 3.9 | 5.2 |
| Stress at 300% strain (MPa) | 7.3 | 8.5 | 9.0 | 9.0 | 10.5 |
| Stress at 500% strain (MPa) | 15.0 | 16.4 | 18.1 | 16.8 | 19.3 |
| Tensile strength (MPa) | 43.0 | 42.3 | 42.1 | 40.1 | 40.3 |
| Elongation (%) | 733 | 708 | 713 | 707 | 710 |
| Tear strength (N) | 60.6 | 65.9 | 70.3 | 67.5 | 76.4 |
| Abrasion losses (mm$^3$) | 73 | 75 | 77 | 77 | 78 |
| $v_r$ | 0.441 | 0.444 | 0.445 | 0.449 | 0.458 |
| Vulcanization 50′/150°C | | | | | |
| Shore A hardness | 69 | 72 | 73 | 73.5 | 74.5 |
| Stress at 100% strain (MPa) | 3.5 | 3.3 | 3.6 | 4.8 | 4.9 |
| Stress at 300% strain (MPa) | 7.9 | 9.2 | 10.0 | 10.3 | 11.3 |
| Stress at 500% strain (MPa) | 16.7 | 19.4 | 19.7 | 19.1 | 20.4 |
| Tensile strength (MPa) | 41.8 | 47.1 | 42.2 | 28.8 | 45.8 |
| Elongation (%) | 729 | 710 | 690 | 650 | 700 |
| Tear strength (N) | 61.2 | 61.6 | 61.9 | 64.0 | 65.8 |
| Abrasion losses (mm$^3$) | 73 | 75 | 78 | 80 | 79 |
| $v_r$ | 0.435 | 0.437 | 0.437 | 0.444 | 0.447 |
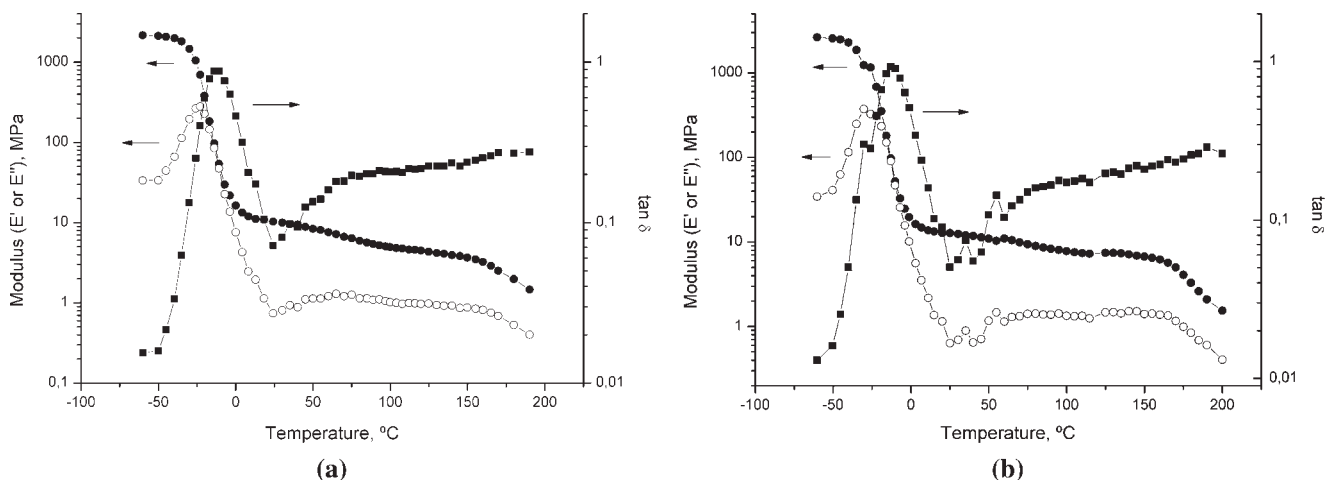
**Figure 6** Variation of storage modulus (●), loss modulus (○) and tan δ (■) as a function of temperature in compound (a) Mg-4 and (b) Mg-12.

groups of the polymer is about 4 phr. Once the oxide is able to saturate the carboxylic groups, the excess present does not have influence on crosslinking density, although it does have a slight reinforcement effect.

Therefore, it can be confirmed that, in general, the properties of these materials are superior to the ones obtained with other oxides, e.g., calcium oxide[7] as the crosslinking agent.

### Dynamical mechanical properties

Figures 6(a) and 6(b) show the variation of the storage modulus, $E'$, the loss modulus, $E''$, and the loss factor, tan δ, versus temperature, for the samples Mg-4 and Mg-12, cured at 150°C, with oscillation frequency of 5 Hz, respectively.

As it can be observed, the oxide content does not affect significantly curves shape. In both cases, it is possible to observe that, at temperatures above room temperature, the values of $E'$ decreases rapidly with a rise of temperature, while $E''$ and tan δ exhibit a peak and an increase, respectively.

Ionic materials are known to present two types of transitions[8]—one at low temperature, associated with the glass transition of the polymer, and a second one

at high temperature associated with the formation of ionic structures, preferably clusters.

To obtain more information about the nature of the ionomeric phase, the effect of plasticizers on their physical properties was studied.[9–11] Plasticizers can be grouped into two types: backbone plasticizers, which mainly act on the nonpolar part of the hydrocarbon chain, and ionic plasticizers, which preferentially affect ionic clusters. In a previous work,[3] we proved that the ionic transition disappears after an extensive treatment with ammonia vapors, which behave as ionic platicizers,[12] decreasing the mechanical properties.

This transition, which is called ionic transition, takes place in a wide range of temperatures; hence, it could be possible to think that it includes, not only the ionic transition, but also the softening of the material. As a result of this, the variation of tan δ with temperature increases progressively. However, this does not happen on the loss modulus curve, where there is a drop on the modulus at high temperatures. This phenomenon is observed on the variation of the storage modulus, where two consecutives drops appeared.

Table IV shows the calculated values for the polymer glass transition and ionic transition, obtained from the loss modulus versus temperature curves. As

**TABLE IV**
$T_g$ and $T_i$ Values at Different Frequencies at 150°C

| Frequency (Hz) | MgO-4 | | MgO-6 | | MgO-8 | | MgO-10 | | MgO-12 | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $T_g$ (°C) | $T_i$ (°C) | $T_g$ (°C) | $T_i$ (°C) | $T_g$ (°C) | $T_i$ (°C) | $T_g$ (°C) | $T_i$ (°C) | $T_g$ (°C) | $T_i$ (°C) |
| 5 | −24.98 | 68.5 | −24.22 | 73.00 | −23.61 | 72.5 | −23.94 | 72.5 | −27.26 | 82.9 |
| 8 | −24.01 | 68.5 | −23.58 | 78.80 | −22.99 | 79.6 | −23.03 | 79.5 | −26.27 | 88.1 |
| 12 | −23.44 | 74.6 | −22.68 | 86.00 | −22.33 | 83.6 | −22.35 | 83.2 | −25.47 | 95.45 |
| 20 | −22.38 | 81.6 | −21.81 | 92.00 | −21.49 | 89.5 | −21.56 | 91.6 | −24.44 | 104.00 |
| Energy[a] (kJ/mol) | 276.12 | 89.57 | 290.13 | 74.37 | 338.35 | 85.52 | 303.16 | 73.38 | 250.32 | 71.47 |
| $T_g$–$T_i$ separation, (°C) | 93.3 | | 93.22 | | 96.11 | | 96.44 | | 110.16 | |

[a] Apparent activation energy of relaxation processes.

well, apparent activation energies for both relaxation processes were evaluated.

The glass transition of the polymer keeps similar values for all mixes, at any oscillation frequency, independently of oxide content, besides for the higher one, where a decrease of ~2°C is observed. On the contrary, the maximum of the ionic transition moves to higher temperatures when the amount of oxide increases. The maximum value is reached for the highest oxide content, with an increase on the temperature of 14°C.

Logically, as the vibration frequency increases, both transition temperatures, glass and ionic, displace to higher values.

The apparent activation energies, obtained from the curves of transition temperatures versus frequency, expose an important difference between both transitions. The ionic transition is correlated to the lower energy and it gradually decreases with the increase in the oxide content. The apparent activation energy of the glass transition, which corresponds to the higher one, goes through a maximum. This occurs for a proportion where the content of oxide is double than the stequiometric amount needed to react with the carboxylic groups of the elastomeric chain.

The distance (in °C units) between the peaks of both transitions is shown in the last row of Table IV. As it was mentioned above, the ionic associations form a segregated microphase within the elastomeric matrix. As the oxide amount is increased, the distance between the peaks rises, i.e., the ionic phase segregation increases.

## CONCLUSIONS

From the above results, it may be concluded that:

- The reaction between the MgO and the carboxilated nitrile rubber (XNBR) leads to the formation of an ionic elastomer with thermoplastic behavior. As a result of the crosslinking, ionic associations are formed. These associations form a segregated microphase, which leads to a relaxation at high temperatures, called ionic transition. These associations are thermally labile.

- As the temperature increases, a decrease in torque increment ($\Delta S$) is observed. This is due to the labile character of the ionic associations, which makes the viscous component to be higher. The increase of the viscous component with temperature is shown in the variation of $S''$ (dNm) with time; these curves are progressively growing.

- The increase in oxide content results in an increase of hardness, stress at constant strain and tear strength, and the segregation of the ionic microphase. This tendency results in a higher separation between the peaks of both transition, glass and ionic.

- The apparent activation energy for the ionic transition is lower than the one obtained for the glass transition. Moreover, the former decreases with the amount of metallic oxide.

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