

# Ionic Elastomers Based on Carboxylated Nitrile Rubber (XNBR) and Zinc Peroxide: Influence of Carboxylic Group Content on Properties

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**ABSTRACT:** The properties of ionic elastomers formed in the crosslinking with zinc peroxide are studied in compounds with varying proportions of carboxylic groups in the elastomeric matrix. At the temperature used, 150°C, preferentially ionic bonds were formed. The crosslinking densities and, correspondingly, the physical properties, increased with the acid group content and with the reaction time. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 605–615, 2002; DOI 10.1002/app.10313

**Key words:** ionomers; crosslinking; infrared spectroscopy; DSC

## INTRODUCTION

Ionomeric modification of elastomers consists of introducing small amounts (<10%) of ionic functionalities (e.g.,  $\text{COO}^-$ ,  $\text{SO}_3^-$ ) in the skeleton of the elastomeric chain. These ionic groups can unite to form ion-rich aggregates in an elastomeric matrix. The ionic domains have a marked effect on the physical and mechanical properties of the elastomers. Elastomeric ionomers have been reviewed by Macknight and Lundberg.<sup>1</sup>

Crosslinking of carboxylate groups can occur via a large number of chemical reactions,<sup>2</sup> but the most common method is via salt formation, especially using divalent metal oxides.

Crosslinking in carboxylated nitrile rubbers (XNBR) can take place via conventional methods based on sulphur accelerators or by metallic oxides, preferentially zinc oxide.<sup>3</sup> One disadvantage of the crosslinking by zinc oxides is that the com-

pounds are produced very early on, making its practical application difficult. This drawback is overcome by using vulcanization agents such as metal peroxides either in a masterbatch with the polymer or in special preparations.<sup>4,5</sup>

During the molding process of carboxylated nitrile rubber in the presence of metallic oxide, a carboxylic acid salt is formed that results in the formation of ionic elastomers or ionomers with greatly improved physical properties.<sup>6,7</sup> The crosslinks produced by the zinc ion from the zinc oxide or peroxide are ionic as opposed to those produced by conventional vulcanization with sulphur accelerators or organic peroxides that are covalent.

The present work reveals the influence of carboxyl group content ( $-\text{COOH}$ ) on the properties of ionic elastomers. The different carboxyl contents are achieved by diluting commercial XNBR with NBR of the same acrylonitrile content (Krynac 2750).

## EXPERIMENTAL

The carboxylated nitrile rubber used in this study was XNBR Krynac 7.40, which has an acryloni-

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**Table I** Formulation of the Compounds (in pphr)

	C-1	C-2	C-3	C-4	C-5	C-6
XNBR 7.40	14.28	28.57	42.85	57.14	71.43	85.71
Krynac 2750	85.75	71.43	57.15	42.86	28.57	14.29
Stearic acid	1	1	1	1	1	1
Struktol ZP1410 <sup>a</sup>	20	20	20	20	20	20
% COOH (theo)	1	2	3	4	5	6

<sup>a</sup> Struktol ZP1014 contents correspond to 10 parts of active agent (50/50 O<sub>2</sub>Zn/O<sub>2</sub>Zn).

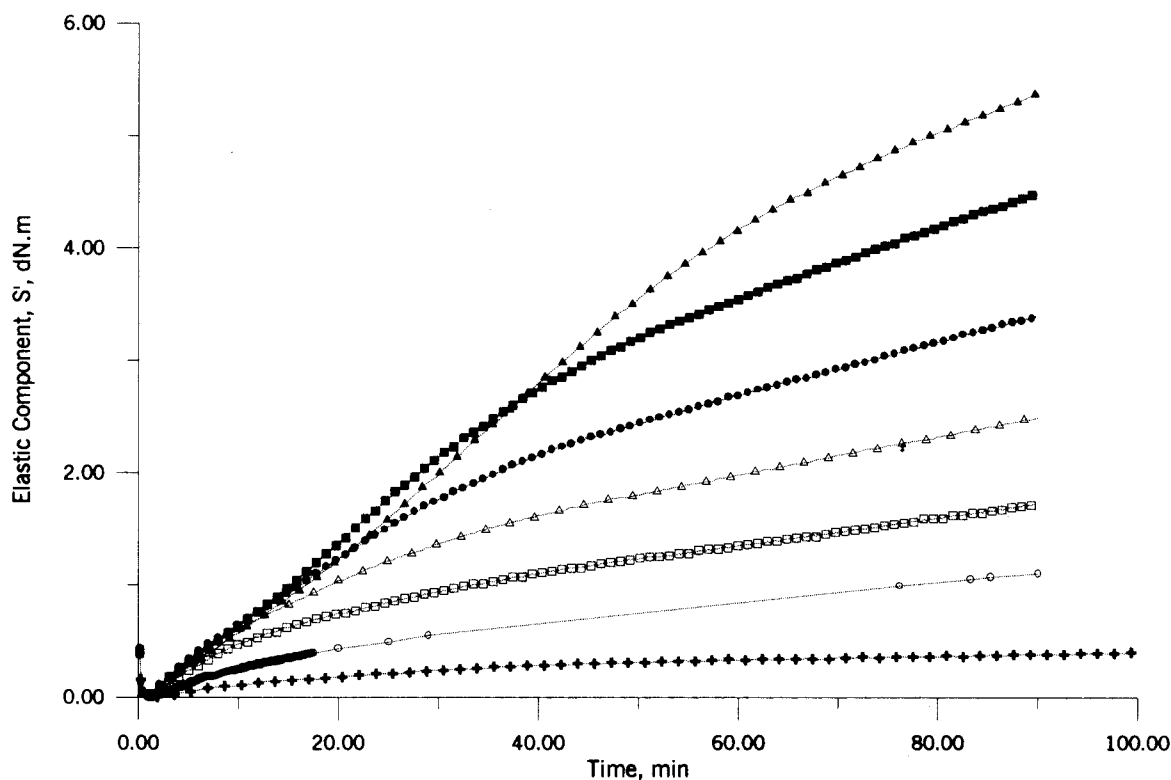
trile content of 27 and 7% of carboxyl groups. To obtain a specific amount of carboxyl groups, the XNBR was diluted with NBR Krynac 2750. The recipes are shown in Table I.

The zinc peroxide used was Struktol ZP1014, a preparation based on 50% active compounds (50/50 O<sub>2</sub>Zn/O<sub>2</sub>Zn), 30% inorganic dispersants and 20% organic dispersants with a total zinc peroxide content of 29% and a specific weight of 2.3 g/cm<sup>3</sup>.

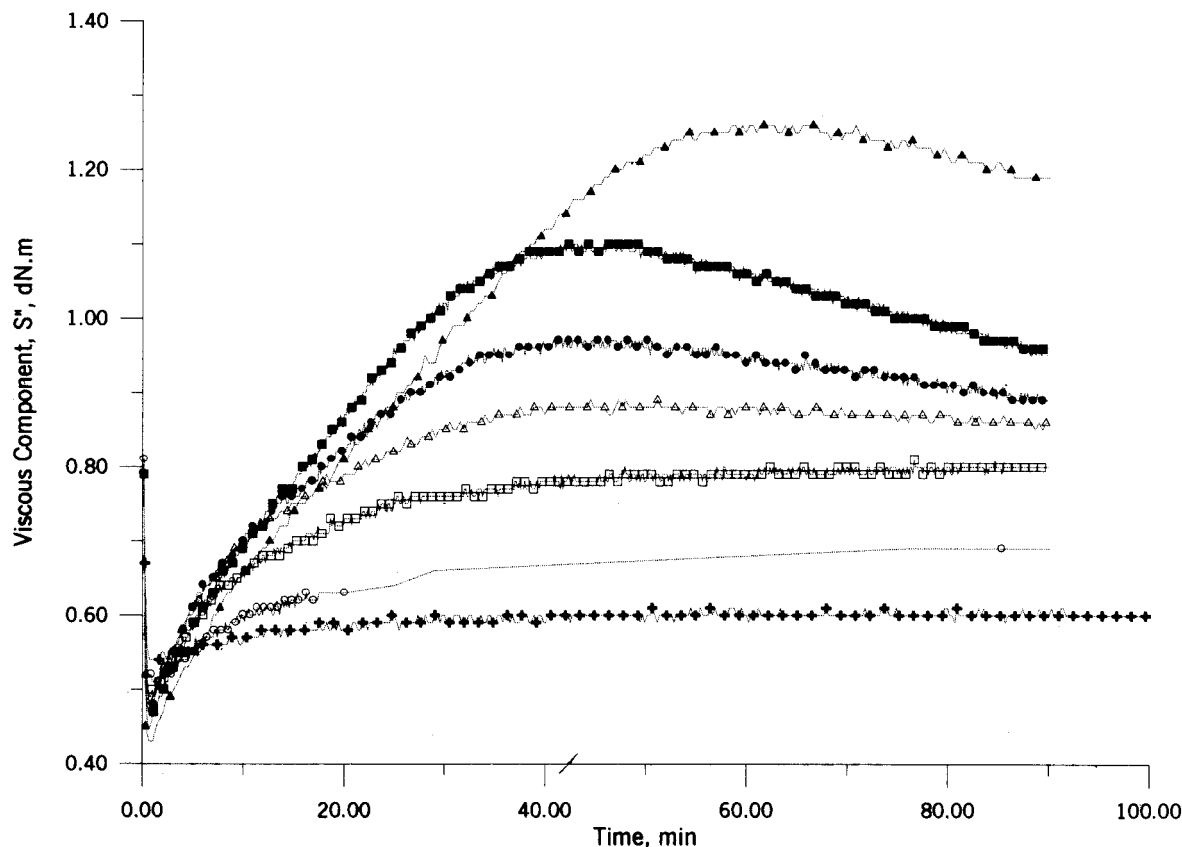
The compounds were prepared in a laboratory cylinder mixer with a friction ratio of 1 : 1.25, maintained cool by cold circulating water.

The vulcanization curves were obtained using a rotorless Monsanto rheometer, model MDR 2000E, at a temperature of 150°C, with an oscillation arch of 1°. The compound was vulcanized in a hydraulic press heated by thermofluid to the vulcanization temperature for a specific vulcanization time.

To measure the tensile properties and tear strength an Instron Dynamometer, model 4301, equipped with a video system to determine the deformations produced was used. Dumb-bell test pieces and Delft-type test pieces, respectively, were used and a deformation rate of 500 mm/min



**Figure 1** Variation of elastic component,  $S'$ , as a function of time: (○) sample C-1; (□) sample C-2; (△) sample C-3; (●) sample C-4; (■) sample C-5; (▲) sample C-6; (+) NBR.



**Figure 2** Variation of the viscous component  $S''$  as a function of time: Symbols as in figure 1.

was applied. The crosslinking density was determined by stress-deformation measurements, T-type straight test pieces were used and a deformation rate of 0.5 mm/min was applied.

The dynamic properties were determined in a Metravib Viscoanalyser PAC 815, based on a principle of nonresonant forced vibrations. Measurements were made at variable deformation, room temperature, and a vibration frequency of 11 Hz, and also with a dynamic deformation of 5  $\mu\text{m}$ , at variable temperature and a vibration frequency of 5 Hz. In both cases, test pieces of approximately  $20 \times 9 \times 2$  mm were used.

Infrared spectra on uncrosslinked and crosslinked materials were taken using a Perkin-Elmer Spectrum One instrument and a Perkin-Elmer Universal ATR amplifying accessory. Absorbances were calculated with the software Omnic ESP as peak height of the bands always choosing the same baseline for a determined peak.

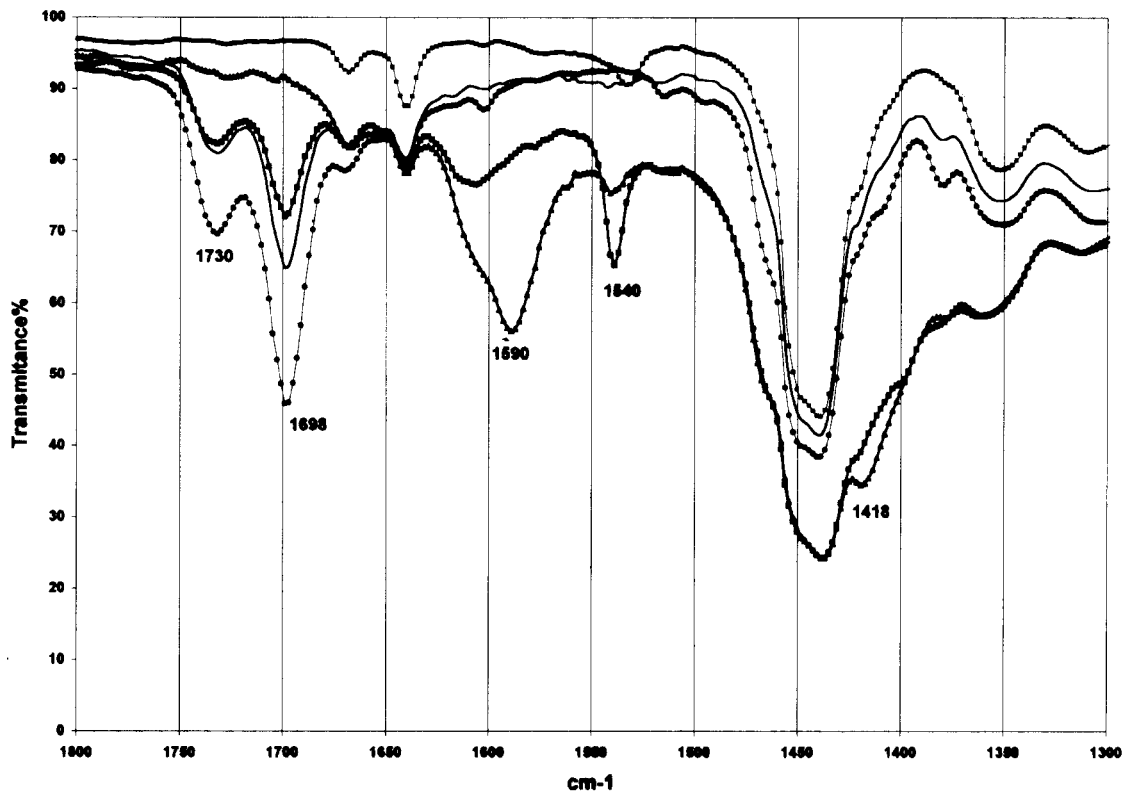
The DSC curves were obtained from uncured and cured samples by using a Perkin-Elmer DSC 7 instrument, at a heating rate of  $10^\circ\text{C}/\text{min}$ .

## RESULTS AND DISCUSSION

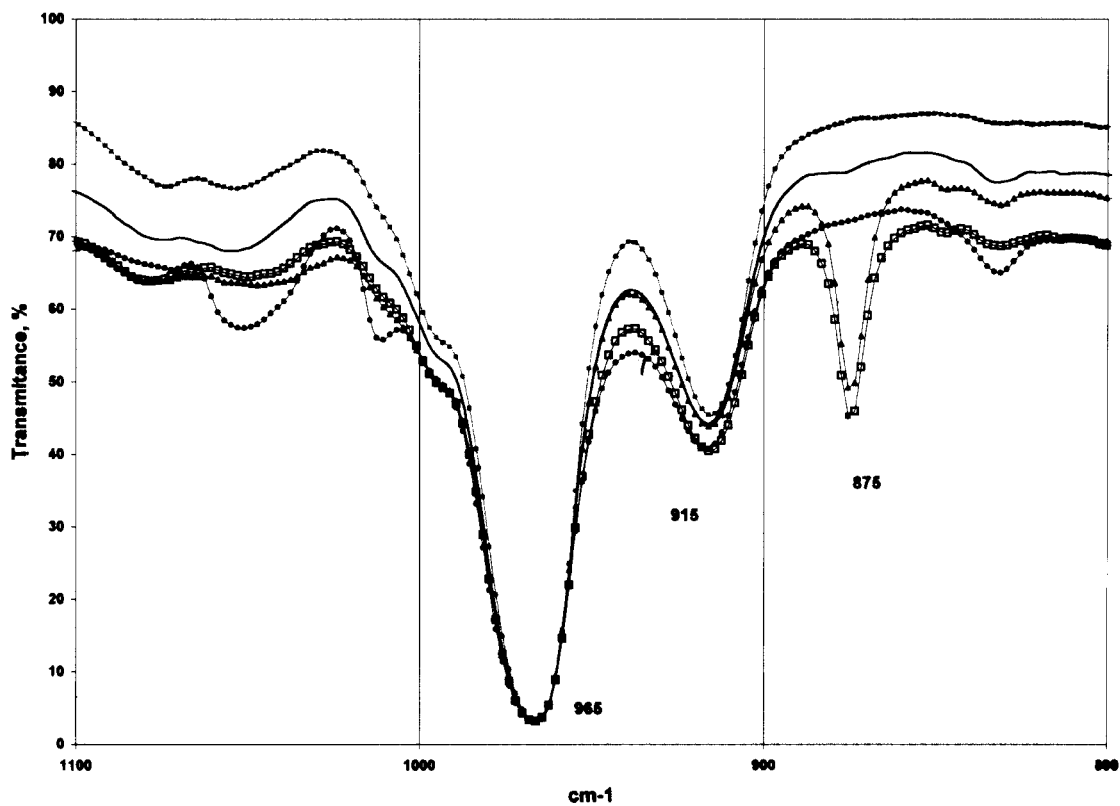
### Vulcanization Curves

Figures 1 and 2 show the changes in elastic,  $S'$ , and viscous,  $S''$ , components of the torque with time, respectively, obtained with the Rheometer Monsanto MDR 2000E. The elastic component of the torque increases with vulcanization time. Likewise, at the same time a higher value of torque is reached with increasing carboxyl group content in the elastomer matrix. Therefore, both parameters, time and  $-\text{COOH}$  content, determine the degree of vulcanization or the crosslinking of the material. In any case, the curves do not reach a plateau, i.e., a zone parallel to the abscissa, except in the case of low carboxyl group content in which they approximate a plateau. In the same figures,  $S'$  and  $S''$  curves for a NBR/Styruktol ZP1014 compound cured at  $150^\circ\text{C}$ , are displayed.

The increase in viscous component with time,  $S''$  (Fig. 2), is characteristic of vulcanizations that



(a)



(b)

**Figure 3** ATR spectra of the: (■) NBR; (●) XNBR; (—) raw sample C-4; (□) uncured sample C-4; (△) cured sample C-4 at 45'/150°C. (a) Region 1300–1800  $\text{cm}^{-1}$ ; (b) region 800–1100  $\text{cm}^{-1}$ .

**Table II** Relative Absorbances ( $I/I_{2920} \text{ cm}^{-1}$ )

Sample	1730	1698	1660	1640	1540	960	915		
a) Uncrosslinked samples									
C-1	0.01	0.00	0.06	0.13	0.30	3.57	0.67		
C-2	0.04	0.04	0.08	0.11	0.25	3.71	0.66		
C-3	0.07	0.12	0.10	0.15	0.28	3.77	0.66		
C-4	0.12	0.25	0.09	0.12	0.29	3.45	0.62		
C-5	0.14	0.31	0.08	0.09	0.24	3.66	0.62		
C-6	0.18	0.38	0.09	0.10	0.26	3.70	0.63		
Sample	1730	1698	1660	1640	1590	1540	1418	966	916
b) Crosslinked at 150°C/45 min									
C-1	0.01	0.00	0.09	0.15	0.00	0.41	0.00	3.09	0.53
C-2	0.01	0.00	0.09	0.13	0.27	0.19	0.00	3.89	0.67
C-3	0.03	0.01	0.11	0.16	0.38	0.16	0.00	3.81	0.64
C-4	0.02	0.01	0.13	0.17	0.54	0.16	1.06	3.76	0.62
C-5	0.03	0.03	0.10	0.12	0.63	0.27	1.12	3.55	0.58
C-6	0.02	0.02	0.10	0.11	0.66	0.35	1.07	3.03	0.47
c) Crosslinked at 150°C/90 min									
C-1	0.01	0.00	0.06	0.11	0.10	0.04	0.55	3.60	0.46
C-2	0.00	0.00	0.12	0.17	0.22	0.13	0.86	3.90	0.67
C-3	0.02	0.01	0.11	0.16	0.35	0.11	0.90	3.72	0.62
C-4	0.02	0.02	0.11	0.13	0.52	0.16	1.00	3.66	0.60
C-5	0.03	0.02	0.11	0.11	0.54	0.38	1.02	2.98	0.48
C-6	0.02	0.00	0.17	0.16	0.54	0.23	0.87	2.49	0.37

give rise to ionic bonds.<sup>8</sup> For low carboxyl group contents (up to C-4) the curves reach a plateau. At higher contents, the curves form a peak at around 45 min that shifts to longer times (approximately 60 min) with increasing COOH content. After the peak the curves drop again.

For NBR,  $S'$  variation stays practically unchanged, allowing us to state that, at 150°C, NBR does not crosslink with Struktol ZP1014. As a result of this, the changes taken place in the torque for compounds C-1 to C-6 should be a consequence of the XNBR crosslinking, with no contribution of the NBR part to the torque.

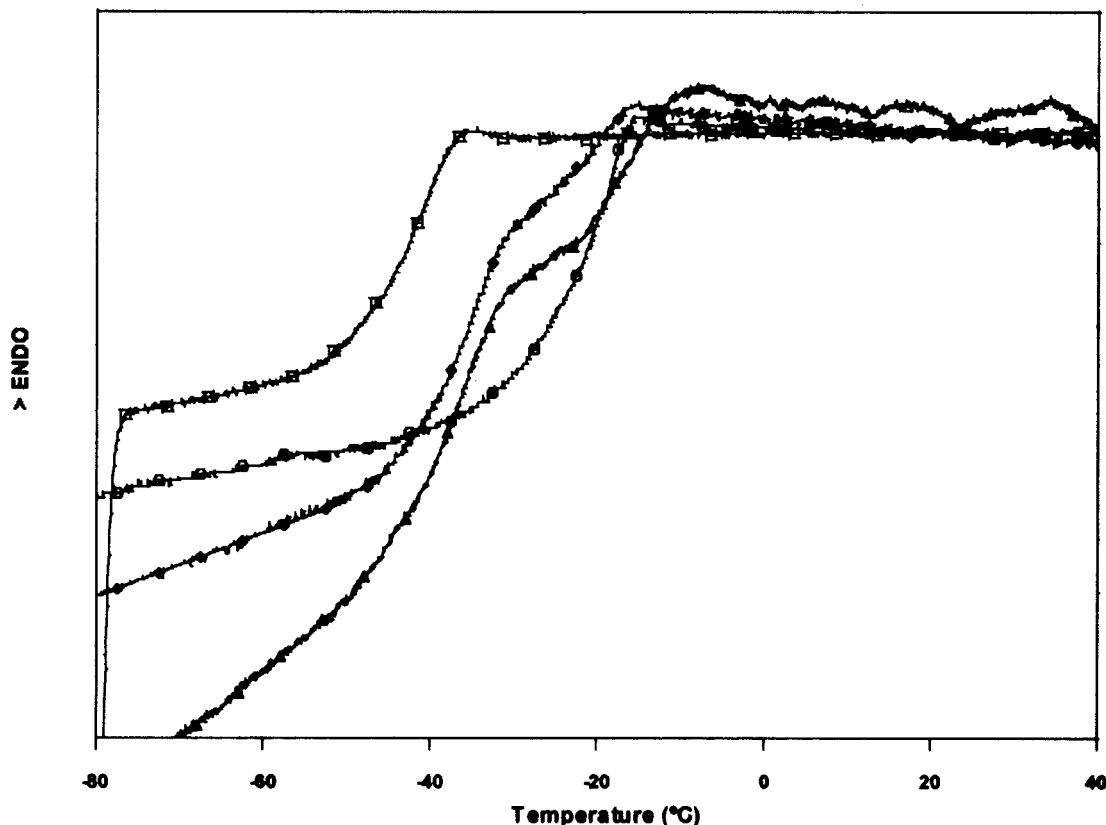
In addition, two vulcanization times have been tested—one when the curve  $S''$  reaches a plateau or peak, the second is 90 min for all the mixtures. In all cases, the vulcanization temperature remains at 150°C.

### ATR Spectra

Figures 3(a) and 3(b) show ATR spectra for sample C-4, taken as an example, in two different regions, 1300–1800  $\text{cm}^{-1}$  and 800–1100  $\text{cm}^{-1}$ , respectively. A virgin blend—only polymers—an uncrosslinked and crosslinked compound C-4

spectra are shown, together with spectra for pure NBR and XNBR. The most significant bands are highlighted. The main differences between them are found in the region 1300–1800  $\text{cm}^{-1}$ . These correspond to disappearance of the bands at 1700  $\text{cm}^{-1}$ , assigned to H-bonded —COOH, and at 1730  $\text{cm}^{-1}$ , assigned to the C=O of free carboxyl groups,<sup>9</sup> and appearance of the bands at 1590  $\text{cm}^{-1}$  and 1540  $\text{cm}^{-1}$ , attributed to the asymmetric stretching of the metal carboxylate ion.<sup>10</sup> Appearance of the doublet in this region results from the generation of different types of zinc carboxylated coordinated structures;<sup>11</sup> the band at 1590  $\text{cm}^{-1}$  is assigned to the tetrahedral structure of the zinc carboxylated ion, and the band at 1540  $\text{cm}^{-1}$  is due to the octahedral structure of the zinc carboxylated ion<sup>10,12</sup> or to a hexacoordinated zinc carboxylate multiplet.<sup>9</sup> Also, in the vulcanized sample, a intense shoulder at 1418  $\text{cm}^{-1}$  emerges. The same considerations also apply to the other samples.

In the range 800–1100  $\text{cm}^{-1}$ , no significant changes are observed except for the apparition of a peak at 875  $\text{cm}^{-1}$  corresponding to the Struktol ZP1014.



**Figure 4** DSC curves of: (□) pure NBR; (○) XNBR; (◇) unvulcanized C-3; (△) vulcanized C-3.

Table II lists the relative absorbances, ratioed to the band at  $2920\text{ cm}^{-1}$ , of the main bands showing variation. In the uncrosslinked samples, bands at  $1730$  and  $1700\text{ cm}^{-1}$  increase upon the XNBR proportion. These bands disappear in the vulcanized samples. The rest of the band remain practically unchanged with the proportion of XNBR.

For the crosslinked samples, Table II(b) and (c), in addition to the disappearance of the cited bands, two bands at  $1590$  y  $1540\text{ cm}^{-1}$  and a shoulder at  $1418\text{ cm}^{-1}$ , appear and develop, pointing to some kind of change in the chain skeleton due to crosslinking. Thus, the formation of some other type of bond, other than ionic, produced by peroxide decomposition, cannot be discarded. This point has been subjected to research and will be published.<sup>13</sup>

The band at  $1540\text{ cm}^{-1}$  is already present in the spectra of unvulcanized samples, indicating the formation of metallic salts even during the mixing process, evolving to other structures during the crosslinking process.

Bands at  $960$  and  $915\text{ cm}^{-1}$  are assigned to unsaturation present on the compound, as the weak bands at  $1660$  and  $1640\text{ cm}^{-1}$ . Relative absorbances do not change much from unvulcanized to vulcanized samples. Only in the compounds with the highest content of XNBR—C-5 and C-6—and at long vulcanization times, a significant reduction of the original values takes place.

#### DSC Analysis

The calorimetric curves for XNBR, NBR, and compound C-3 unvulcanized and vulcanized are shown in Figure 4. In the traces corresponding to sample C-3, two steps can be recognized, related to NBR and XNBR  $T_g$ , respectively, although slightly shifted to higher temperatures with respect to the pure polymers; this finding evidences the incompatibility of both polymers. The slight shift from the pure polymers in the unvulcanized sample can be due to the interaction between the polar groups of the polymer and the Struktol

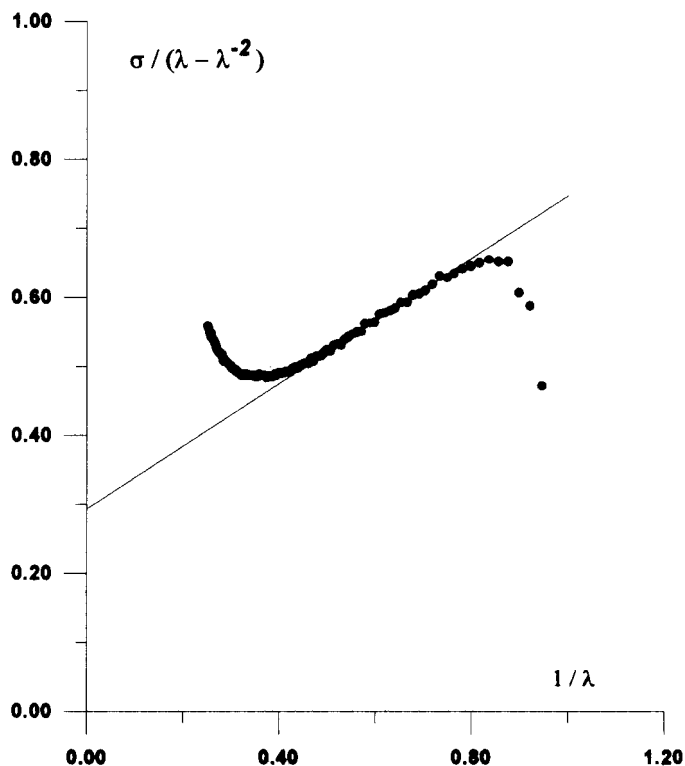


Figure 5 Mooney-Rivlin plot of sample C-6.

ZP1014. When the compound is vulcanized, the  $T_g$  corresponding to NBR does not change, as it should be if it does not intervene in crosslinking, whereas the  $T_g$  corresponding to XNBR shifts to higher values as a result of the crosslinks formed.

#### Crosslinking Density

Crosslinking densities were determined from stress-deformation measurements using the Mooney-Rivlin equation, which describes the general stress-deformation behavior and is represented by the expression

$$\sigma = 2C_1(\lambda - 1/\lambda^{-2}) + 2C_2(1 - 1/\lambda^3) \quad (1)$$

where  $C_1$  and  $C_2$  are constants,  $\sigma/(\lambda - \lambda^{-2})$  is the reduced stress, and  $\lambda$  is the extension or deformation ratio. In the diagram, that depicts reduced stress vs.  $1/\lambda$ , the experimental data fit a straight line in a wide interval of  $1/\lambda$ ,<sup>14</sup> as shown in Figure 5 for sample C-6, vulcanized at 150°C for 90 min.

In accordance with J.E. Mark,<sup>15</sup> from the reduced stress extrapolated to  $1/\lambda = 0$  it is possible to calculate the crosslinking density determined by  $\rho/M_c$ , where  $\rho$

Table III Crosslinking Density from Mooney-Rivlin Equation

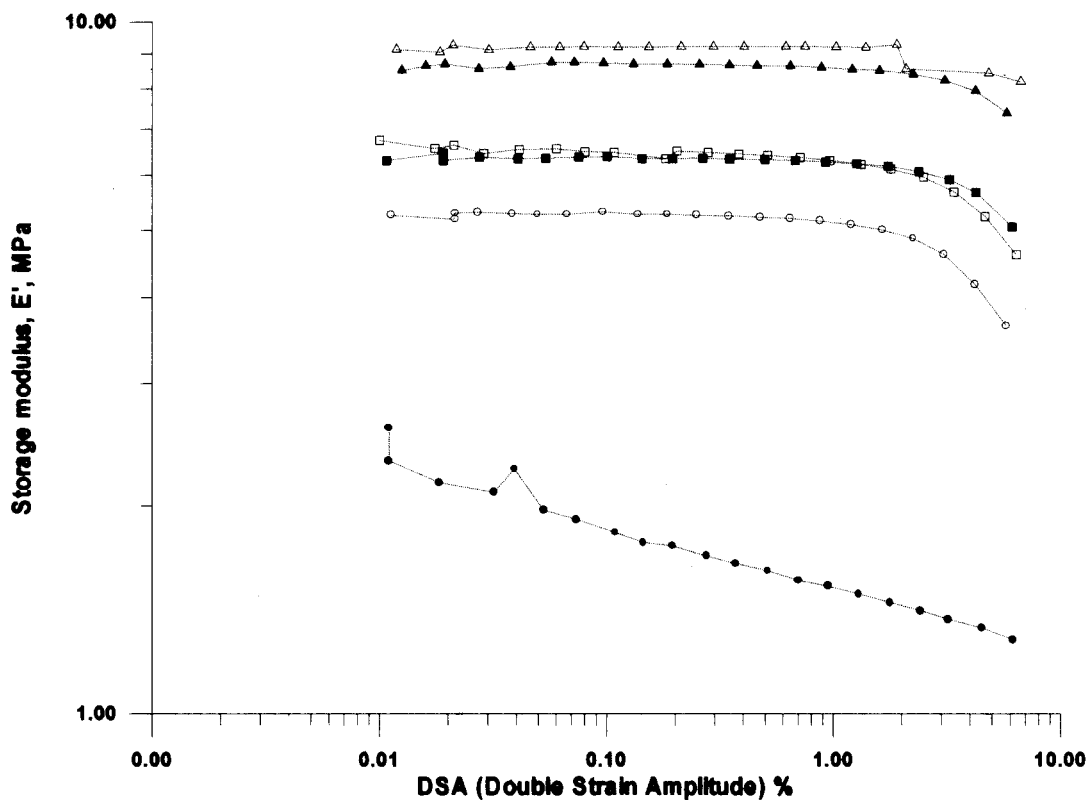
Sample	Vulcanization Time (min)	$\nu \cdot 10^5$ (mol/cc)	Vulcanization Time (min)	$\nu \cdot 10^5$ (mol/cc)
C-1	45	0.4	90	2.1
C-2	45	3.6	90	5.9
C-3	45	8.7	90	13.9
C-4	45	9.6	90	16.4
C-5	45	10.1	90	18.7
C-6	60	11.1	90	23.9

**Table IV Physical Properties**

	C-1	C-2	C-3	C-4	C-5	C-6
a) Vulcanization time: 45 min/150°C						
Shore A hardness	26	34	44	52	55	61
Stress at 100% strain, MPa	0.4	0.8	1.3	2.0	2.2	2.9
Stress at 300% strain, MPa	0.3	1.2	3.3	4.9	6.2	8.9
Stress at 500% strain, MPa	0.3	1.7	7.1	—	—	—
Tensile Strength, MPa	0.4	1.8	7.2	11.7	17.6	23.0
Elongation at break, %	1620	646	500	462	482	496
Tear strength, <i>N</i>	6.4	10.7	19.1	22.2	25.3	32.1
b) Vulcanization time: 90 min/150°C						
Shore A hardness	28	38	46	55	59	62
Stress at 100% strain, MPa	0.5	0.9	1.6	2.2	3.0	3.3
Stress at 300% strain, MPa	0.5	1.6	4.1	6.1	8.7	8.6
Stress at 500% strain, MPa	0.6	2.5	—	—	—	—
Tensile Strength, MPa	1.8	2.6	8.1	11.6	17.6	22.4
Elongation at break, %	1370	674	456	422	438	496
Tear Strength, <i>N</i>	10.8	13.9	22.6	25.4	31.5	34.3

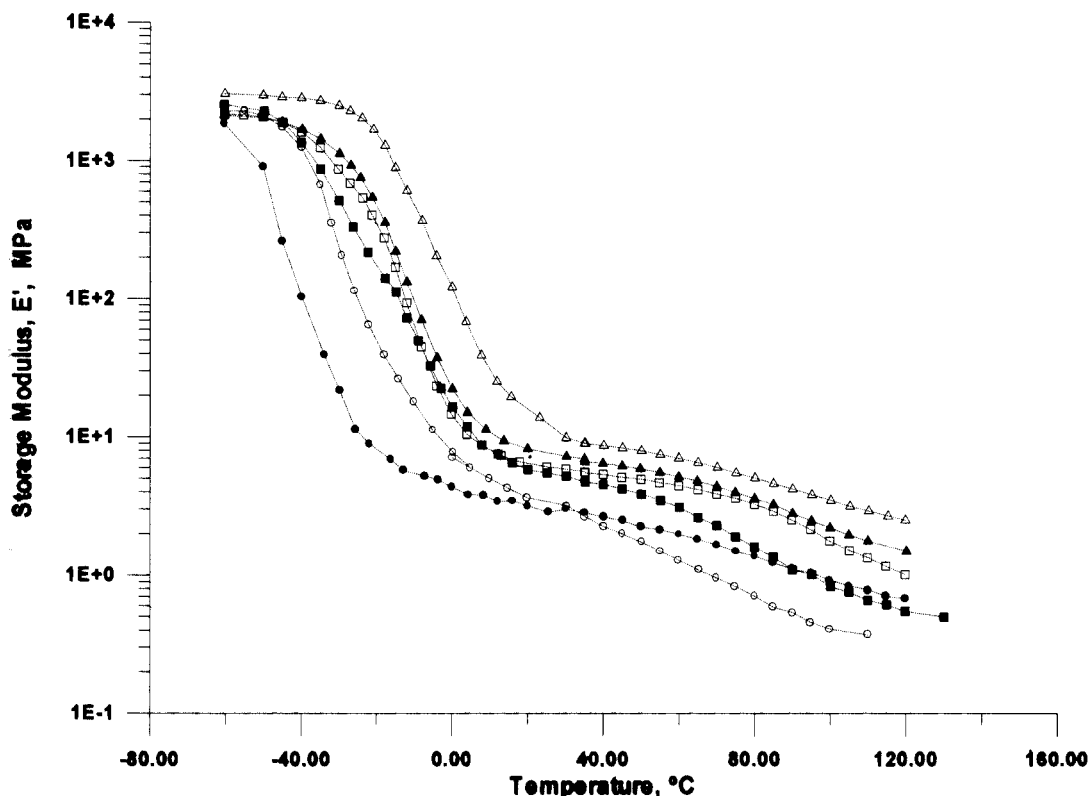
is the density of the polymer and  $M_c$  is the molecular weight of the polymer chains between sites of crosslinking, according to the expression

$$[\sigma/(\lambda - \lambda^{-2})]1/\lambda = 0 = \left(1 - \frac{2}{\Phi}\right) \frac{\rho PT}{M_c} \quad (2)$$



**Figure 6** Variation of storage modulus,  $E'$ , as a function of strain amplitude; (●) sample C-1; (○) sample C-2; (■) sample C-3; (□) sample C-4; (▲) sample C-5; (△) sample C-6. Oscillation frequency, 11 Hz. Room temperature.





**Figure 7** Variation of storage modulus,  $E'$ , as a function of temperature. Symbols as in Figure 6. Oscillation frequency 5 Hz. Dynamic strain 5  $\mu\text{m}$ .

where  $\Phi$  is the crosslinking functionality.

In this way, the crosslinking densities were determined for all the samples, and the values obtained are recorded in Table III.

As expected, the crosslinking density increases with the carboxyl group content and with vulcanization time, which explains why no plateau was formed in the vulcanization curves.

The amount of crosslinking agent, zinc peroxide/zinc oxide, is the same in all the mixtures, and in all cases this is sufficient to saturate all the acid groups, as demonstrated by the disappearance of the bands at 1698 and 1730  $\text{cm}^{-1}$  from the spectra in the crosslinked materials. If a crosslinking was produced by peroxide that gave rise to covalent bonds, the crosslinking densities would be more similar, or closer. The difference observed in the crosslinking densities suggests that this is not so.

In brief, the crosslinking density corresponds preferentially to ionic bonds as a function of the carboxyl group content in the elastomeric matrix and the vulcanization or reaction time, although some covalent bonding due to peroxide decomposition cannot be ruled out.

### Physical and Dynamic Properties

Table IV shows the tensile properties, Shore A hardness, and tear strength of the materials.

All the properties increase together with the rise in carboxyl group content in the elastomeric matrix and the crosslinking time. This means that the properties depend on the ionic crosslinks formed, as NBR contribution to the properties can be considered negligible, as shown by its rheometer curve, with no torque increment at the curing temperature.

The ionic structures act as reinforcing agents in the elastomeric matrix, and there is a sharp rise in these properties upon reaching a medium carboxyl group content (sample C-3), that corresponds approximately to the 50/50 XNBR/NBR mixture.

Figure 6 shows the change in storage modulus with the deformation rate in terms of DSA (Double Strain Amplitude). As the carboxyl group contents raise, the value of the modulus for the same deformation also increases as a consequence of the increased rigidity of the material due to the greater amount of ionic structures formed. With

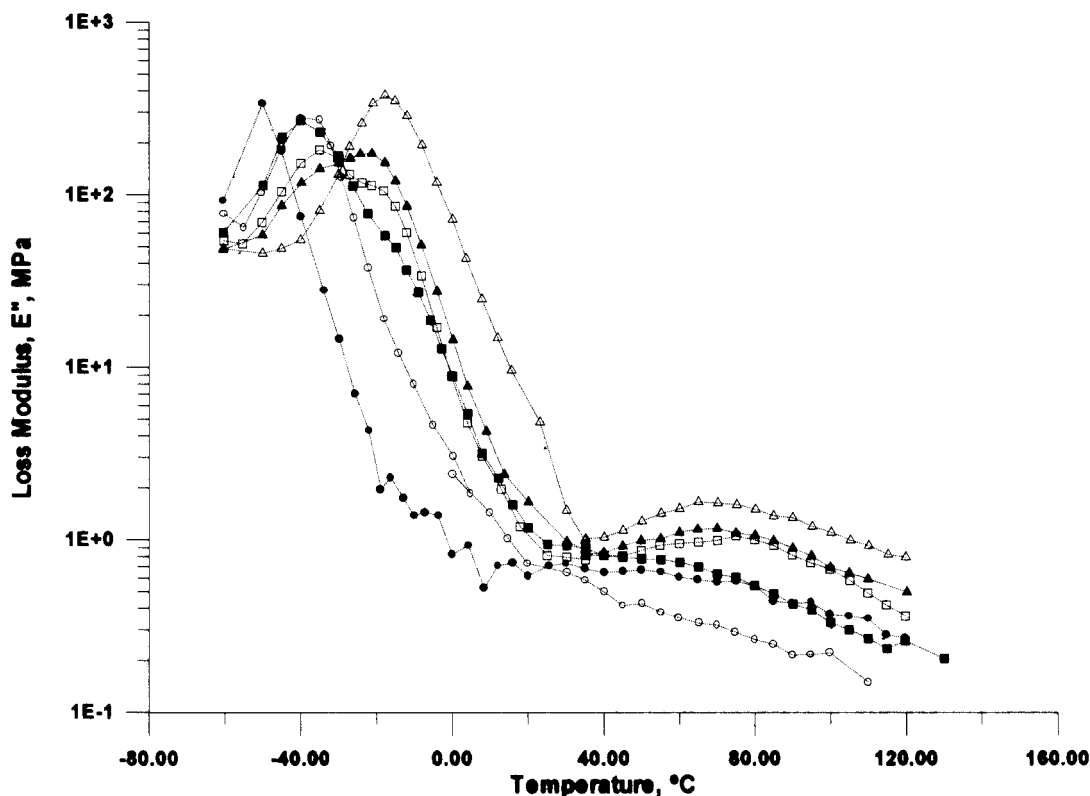


Figure 8 Variation of loss modulus as a function of temperature. Conditions and symbols as in Figure 7.

the exception of sample C-1, all the materials present a broad region in which there is a linear relationship between the modulus and the deformation. At higher deformations ( $\cong 2\%$ ), a drop occurs in the modulus, possibly related with the loss in resistance of the ionic associations, similar to that which occurs in conventional elastomers with reinforcing fillers.

Figure 7 shows the change in the storage modulus in the temperature interval  $-60$  to  $120^\circ\text{C}$ . Although the shape of the curve is similar for all the samples, there are differences among them, resulting from the different carboxyl group content.

Ionic materials are known to present two types of transitions<sup>16</sup>—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. In the diagram, these two transitions correspond to a drop in the modulus but, when increasing carboxyl group content, the one associated with the glass transition of the polymer is displaced to higher temperatures, whereas the one associated with ionic formations remains almost unaltered.

The shift in temperature of the glass transition to higher values can be observed more clearly in Figure 8, where the change in the loss modulus  $E''$  vs. time is depicted, and in which both transitions are represented by a peak. As can be seen from the diagram, the ionic transition begins to be visible in materials with a 50/50 XNBR/NBR content and coincides with the sudden increase in mechanical properties observed. Therefore, when these ionic associations are present to a significant degree there is an overall rise in the values of the properties that defines the reinforcing nature of ionic clusters in this type of material.

In relation to the glass transition of the polymer, there is a clear differentiation between samples C-1 and C-6, with a considerably higher value of the glass transition temperature in the latter, to be expected in a material rich in carboxyl groups. The intermediate samples, C-2–C-5, present two peaks in this region, due to the non-homogeneous nature of the NBR/XNBR mixture. The size of these peaks change in opposite directions as the XNBR content increases in the material. As already found by DSC, in samples C-2 to C-6, the maximum corresponding to NBR remains at the same temperature.

## CONCLUSIONS

In the light of the results described here the following deductions can be made:

1. At the experimental temperature used, 150°C, crosslinking of nonhomogeneous mixtures of NBR/XNBR with zinc peroxide takes place preferentially via the carboxyl groups present in the XNBR, without definitely ruling out some covalent crosslinking coming from peroxide decomposition.
2. In all the samples, the amount of crosslinking agent used is sufficient to saturate the carboxyl groups present.
3. Zinc salt formation starts in the mixing phase, as shown by infrared spectra, developing to other types of coordination structures of zinc when vulcanized.
4. The properties of the material are dependent on the carboxyl group content and the vulcanization time such that increases in both the content and vulcanization time lead to higher values in all the properties. NBR contribution to properties is practically negligible, as at vulcanization temperature, 150°C, no torque increase is produced. NBR acts as a diluent; the mixture NBR/XNBR is already immiscible before vulcanization, and after vulcanization remains as such.

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