

Ionic Elastomers Based on Carboxylated Nitrile Rubber and Calcium Oxide

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ABSTRACT: The properties of carboxylated nitrile rubber crosslinked through ionic crosslinks with calcium oxide (CaO) have been studied at two reaction temperatures (100 and 150°C). These properties increase with the CaO content to reach an optimum level, after which they tend to drop again as the level of CaO increases further. The changes in the properties are directly proportional to the amount of

carboxylate formed. At any CaO content, a rise in the temperature and the corresponding reduction in the reaction time have a favorable effect on the properties. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 805–813, 2003

Key words: ionomers; ionic elastomers; properties

INTRODUCTION

Carboxylated nitrile rubber (XNBR) is an elastomer with carboxylic groups distributed along the hydrocarbon chain that can react with metal oxides, among other compounds,¹ to form carboxylic salts that constitute ionic crosslinks. These carboxylic salts tend to group together in multiplets or clusters,² which correspond to an ionic microphase immersed within a non-polar matrix that is responsible for the final properties of these materials.

The crosslinking of XNBR with sulfur,³ zinc peroxide,^{4,5} and a mixed system of sulfur and zinc peroxide⁶ has been studied in our laboratories. The former and latter vulcanizing systems give rise to conventional covalent bonds. The zinc peroxide produces both ionic and covalent bonds.⁷ The main goal of this work is to study the behavior of XNBR when crosslinking takes place only through ionic bonds with calcium oxide (CaO) as a crosslinking agent. This oxide is preferred to zinc oxide because of the vulcanization problems presented by the latter on account of its scorch characteristics.

EXPERIMENTAL

XNBR (Krynac 7.4) with a carboxylic group content of 7 wt % and a Mooney viscosity of 40, supplied by

Polysar (Barcelona, Spain), was used. CaO (rubber-grade) and stearic acid (rubber-grade) were also used. The recipes are given in Table I.

The compounds were prepared in a Gumix laboratory cylinder mixer (Barcelona, Spain), with rollers 15 cm in diameter and 30 cm long, cooled by circulating cold water during the mixing process and with a friction ratio of 1:1.15.

Vulcanization curves were obtained with a Monsanto MDR 2000E rheometer (Alpha Technologies, Swindon, UK) with an oscillation arch of 1° at different temperatures.

Vulcanization was carried out in a hydraulic press heated with a thermofluid. Two vulcanizations were performed: 120 min at 100°C and 45 min at 150°C.

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 53510.

Tearing tests were carried out on Delft-type samples in agreement with UNE 53516 part 2 at the same deformation rate used for the tensile tests. Five samples were tested in each case.

The dynamic properties were measured with a Metravig model RAC 815 A (Lyon, France) viscoanalyzer according to the principle of nonresonant forced vibrations at variable deformation and variable frequency at frequencies of 5, 8, 12, and 20 Hz within a temperature interval of -60 to 200°C.

The infrared (IR) spectra were obtained with a Nicolet model 520 Fourier transform infrared spectrophotometer (Perkin Elmer, Norwalk, CT) with the attenuated total reflectance (ATR) technique at a scanning speed of 4 cm s⁻¹ and at a resolution of 4 cm⁻¹.

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TABLE I
Recipe for Compounds (phr)

	CaO-2	CaO-4	CaO-5	CaO-6	CaO-8	CaO-10
XNBR 7.40	100	100	100	100	100	100
Stearic acid	3	3	3	3	3	3
CaO	2	4	5	6	8	10

RESULTS AND DISCUSSION

Vulcanization curves

Figure 1 shows the changes in the elastic component of the torque, S' , for the different compounds tested at 100°C. In all cases, the torque progressively increases with the vulcanization time, indicating that the vulcanization reaction is taking place. All the curves reach a plateau, and this implies that the reaction is finished. However, when the different compounds are compared, it can be seen that the torque value increases as the amount of the crosslinking agent increases until a content of about 5 or 6 phr. However, at greater concentrations of CaO, the torque decreases successively.

Figure 2 is equivalent to Figure 1 and shows the changes in S' in the same samples but at 150°C. Like the samples that were vulcanized at 100°C, the CaO-10 mixture achieves a smaller torque than CaO-8. However, and in contrast to those samples vulcanized at 100°C, the curve of CaO-8 at 150°C shows that, for longer periods of time, the maximum value of S' is greater than that reached by CaO-6. This suggests that

at these higher concentrations, the solubility of the metallic oxide in the elastomer is present in excess when vulcanization is carried out at 150°C.

With respect to the reaction rate, which is given by the slope of the curve before the plateau, maximum vulcanization rates have been recorded for CaO-6 vulcanized at both 100 and at 150°C. At greater concentrations of CaO, the reaction rate progressively decreases, and the slowest rate corresponds to the recipe with the greatest CaO content. Comparing both figures, we observe that at any crosslinking agent content, vulcanization takes place faster at 150°C than at 100°C and reaches a greater torque except for CaO-4, which is the stoichiometric mixture and which vulcanizes at 100°C. In this case, although the reaction is slower, the value of the torque is higher than at 150°C.

As can be observed from the curves, there is practically no induction period. The compounds begin to vulcanize almost immediately, and this is characteristic of crosslinking with metal oxides.

From these observations, the following deductions can be made:

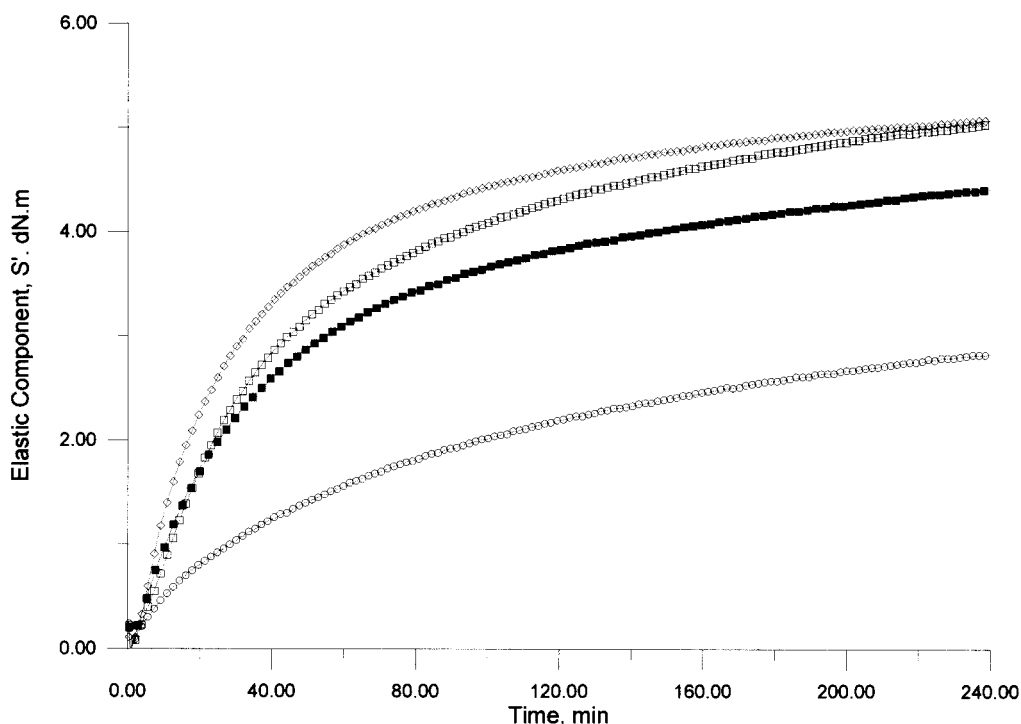


Figure 1 Vulcanization curves at 100°C: (□) CaO-4, (◇) CaO-6, (■) CaO-8, and (○) CaO-10.

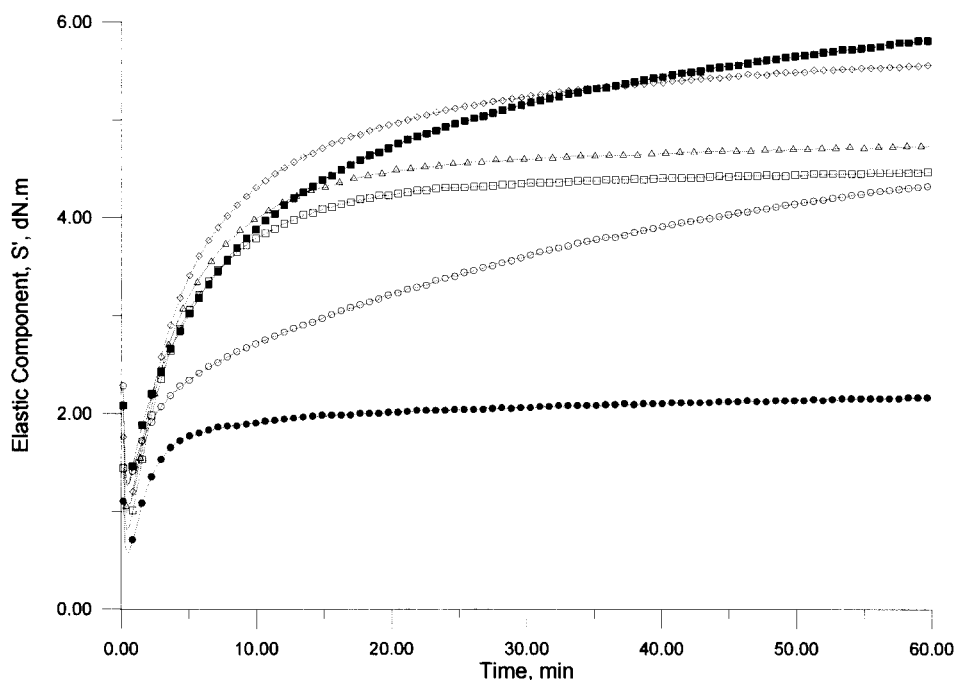


Figure 2 Vulcanization curves at 150°C: (●) CaO-2, (□) CaO-4, (△) CaO-5, (◇) CaO-6, (■) CaO-8, and (○) CaO-10.

1. When the stoichiometric mixture, CaO-4, is vulcanized, the vulcanization reaction is more favored at 100°C than at 150°C; that is, a larger torque is obtained at the lower temperature.
2. A compound with a small excess of the crosslinking agent (6 phr) reaches, at longer time periods, a similar torque at both 100 and 150°C. This torque exceeds that obtained with the stoichiometric mixture at both temperatures, especially at 150°C.
3. In the presence of a higher excess of the crosslinking agent (8 or 10 phr), the reaction is much more favored at a higher temperature (150°C) because both the maximum torque obtained and the reaction rate are much higher than the values that could be reached at 100°C. This can be attributed to the greater solubility of CaO in the elastomer at higher temperatures.

Therefore, in relation to the rheometric data, the optimum recipe for reasonably short vulcanization times at 150°C would contain around 6 or 8 phr CaO.

In an attempt to study the influence of temperature on the vulcanization process, we chose the CaO-5 sample, and curves have been plotted at several temperatures. Figure 3 shows that in all cases, the vulcanization rate increases as the temperature increases. However, the maximum torque decreases above 140°C.

To study the different properties, we chose two vulcanization times and temperatures for all the compounds: 120 min at 100°C and 45 min at 150°C.

Physical properties

According to the percentage of CaO, changes in the physical properties of the vulcanized samples have been observed, as shown in Table II. As deduced from the vulcanization curves, optimum properties are observed for sample CaO-6 vulcanized at both 100 C and 150°C. High values of the properties were obtained, especially for the sample vulcanized at the higher temperature, as can be expected from the formation of ionic crosslinks. The values of the strain at constant deformation, tensile strength, tear resistance, and hardness decrease as the CaO content in the compound increases further from CaO-6. CaO-10 presents the greatest drop in all the measured properties. However, following the trends of the rheometric curves, at the reaction times studied, the samples vulcanized at 150°C show higher values in their properties than those vulcanized at 100°C.

The large elongations at break that these elastomers exhibit can be attributed to the existence of ionic clusters that tend to relax when the material is subjected to a strain.⁸

Dynamic properties at various deformation amplitudes

Figure 4(a,b) shows the change in the storage modulus, E' , with the deformation amplitude expressed as the double-strain amplitude, in samples vulcanized at 100 and 150°C, respectively. Those vulcanized at 150°C present greater E' values than those vulcanized

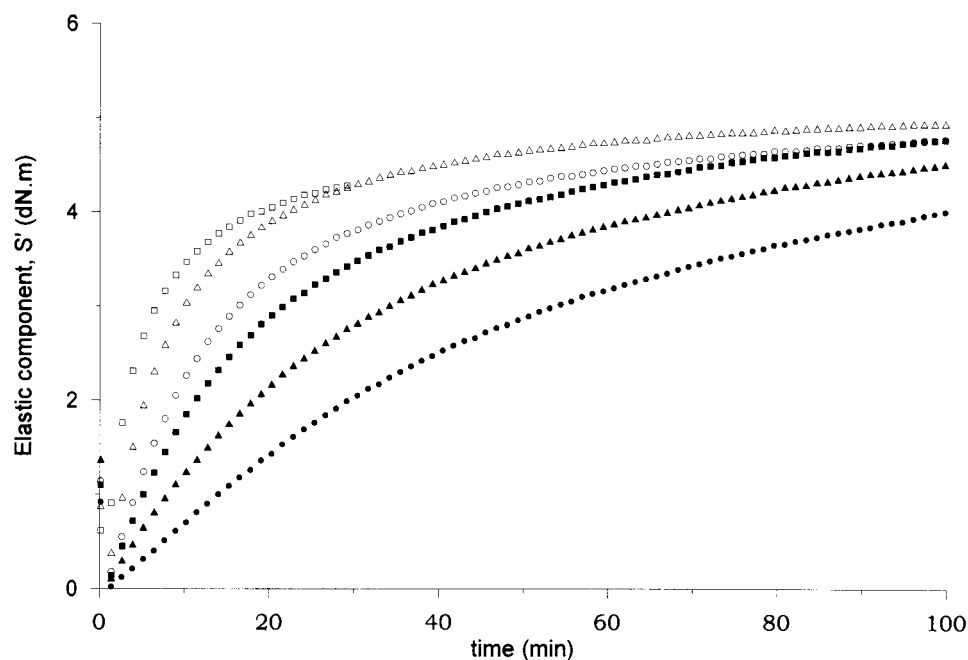


Figure 3 Vulcanization curves of CaO-5 at different temperatures: (●) 100, (▲) 110, (■) 120, (○) 130, (△) 140, and (□) 150°C.

at 100°C, as also observed in the mechanical properties. Here also, the CaO-10 sample shows the lowest values at both vulcanization temperatures.

In all cases, E' remains constant at deformations below 2% and begins to drop at higher deformations. This reduction is also typical of conventional rubbers with reinforcing fillers and can be interpreted in these compounds as the breakup or disruption of the ionic agglomerates formed.

Dynamic properties at various temperatures

Figure 5(a,b) shows the change in the loss factor, $\tan \delta$, as a function of the temperature of samples vulcanized at 100 and 150°C, respectively, for an oscillation frequency of 5 Hz. In all cases, two transitions appear. The first takes place at low temperatures (-12°C , ap-

proximately) and corresponds to the glass-transition temperature (T_g) of the elastomer; the second takes place at high temperatures and is called the ionic transition (T_i), during which the clusters or ionic associates begin to relax and weaken and the elastomer loses its rigidity.

When analyzing the curves in relation to the CaO contents in samples vulcanized at both 100 and 150°C, we observed that the maximum $\tan \delta$ value during the glass transition is greater in CaO-10 than in the other samples and that T_i begins at temperatures much lower than in the other samples, even up to 40 or 50°C lower. This agrees with the physical properties of the samples and implies that the microstructure of the ionic phase of sample CaO-10 is less stable than those of the other samples for both vulcanization temperatures. However, T_g is similar in all the samples.

TABLE II
Physical Properties of Cured Compounds

	CaO-4		CaO-5		CaO-6		CaO-8		CaO-10	
	100°C, 120 min	150°C, 45 min	100°C, 120 min	150°C, 45 min	100°C, 120 min	150°C, 45 min	100°C, 120 min	150°C, 45 min	100°C, 120 min	150°C, 45 min
Shore A hardness	72.2	75.1	66.9	72.1	74	78.4	65.4	77.8	56.4	68.1
Stress at 100% strain (MPa)	2.21	4.28	2.33	3.20	2.67	4.51	1.81	4.31	0.99	2.37
Stress at 300% strain (MPa)	3.92	8.4	4.22	6.10	4.92	10.09	3.03	9.28	1.26	4.05
Stress at 500% strain (MPa)	8.85	16.2	8.90	16.28	11.18	20.32	6.02	19.50	1.59	7.62
Tensile strength (MPa)	27.92	27.28	27.25	28.94	28.36	31.58	22.82	30.06	9.74	18.19
Elongation at break, (%)	675	600	656	649	680	680	720	610	1300	700
Tear strength (N)	39.65	51.59	45.5	50.4	41.81	56.61	34.39	53.41	15.99	31.28

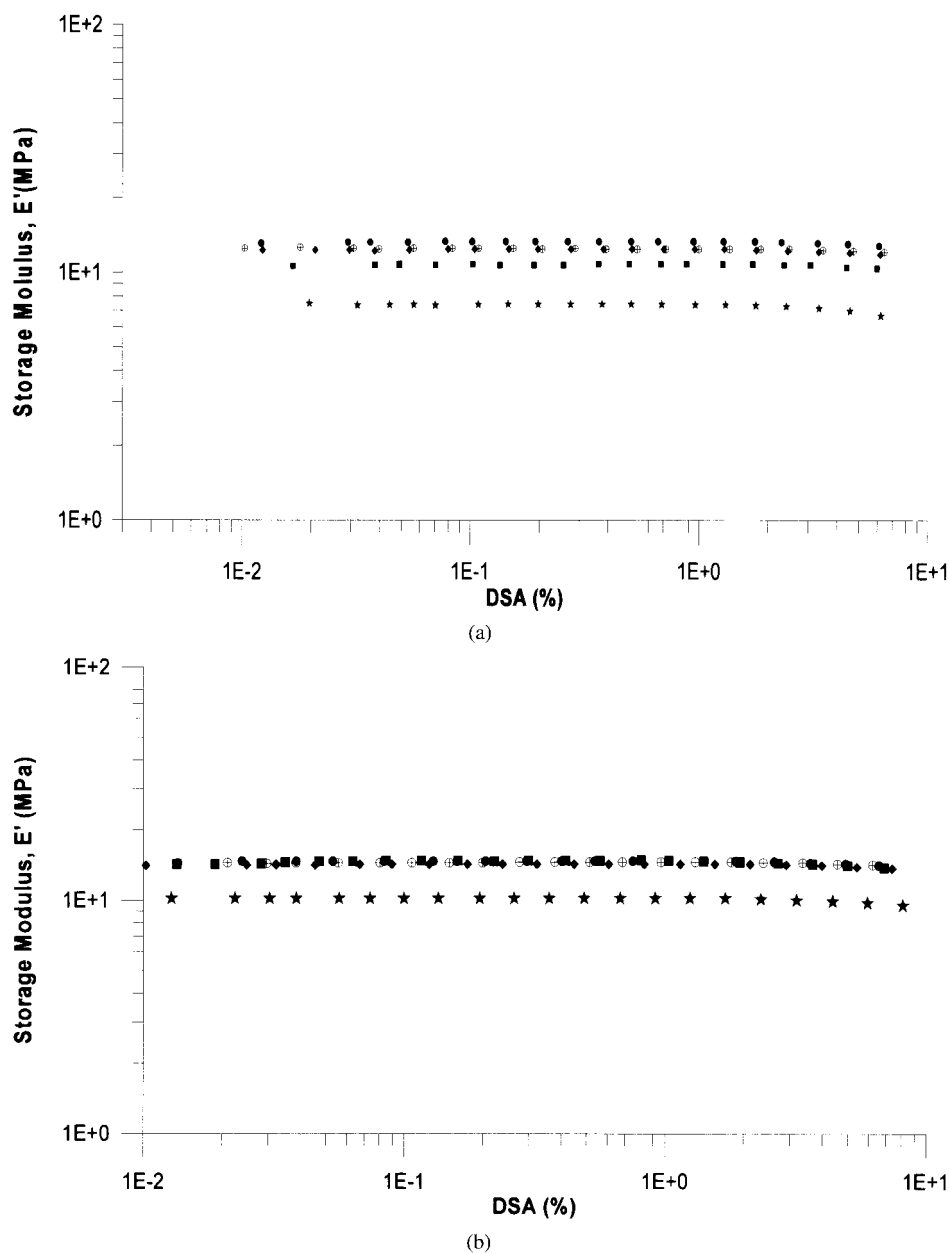


Figure 4 E' as a function of the double-strain amplitude of samples vulcanized at (a) 100 and (b) 150°C: (◆) CaO-4, (⊕) CaO-5, (●) CaO-6, (■) CaO-8, and (★) CaO-10.

IR analysis

The ATR spectra in the region of $1800\text{--}1300\text{ cm}^{-1}$ of the uncured CaO-6 sample and the samples vulcanized at 100 and 150°C are shown in Figure 6. The uncured sample shows two bands at 1698 and 1732 cm^{-1} , which disappear in the samples crosslinked at 100 and 150°C because of the chemical change from weak acid to ionic crosslink or salt formation. The first is attributed to a vibration in the tension mode characteristic of the carbonyl group of the acid in its dimer form. The second is due to an ester-type impurity formed during the polymerization process of the elastomer and is assigned to the tension mode of the

carbonyl group of the ester.⁹ All the samples vulcanized at both 100 and 150°C show a wide band at approximately 1545 cm^{-1} , which includes two peaks, one at 1578 cm^{-1} and the other at 1542 cm^{-1} . However, pure XNBR does not show these peaks. Papers in the literature^{10,11} attribute this doublet to the vibration of the metal carboxylate in the asymmetric tension mode, which is due to the calcium salt formed. Its height varies according to a pattern similar to some of the physical properties of these samples. This effect is illustrated in Figure 7, which shows the relationship that exists between the mechanical properties of samples at 100°C and the height of the band at 1545 cm^{-1} ,

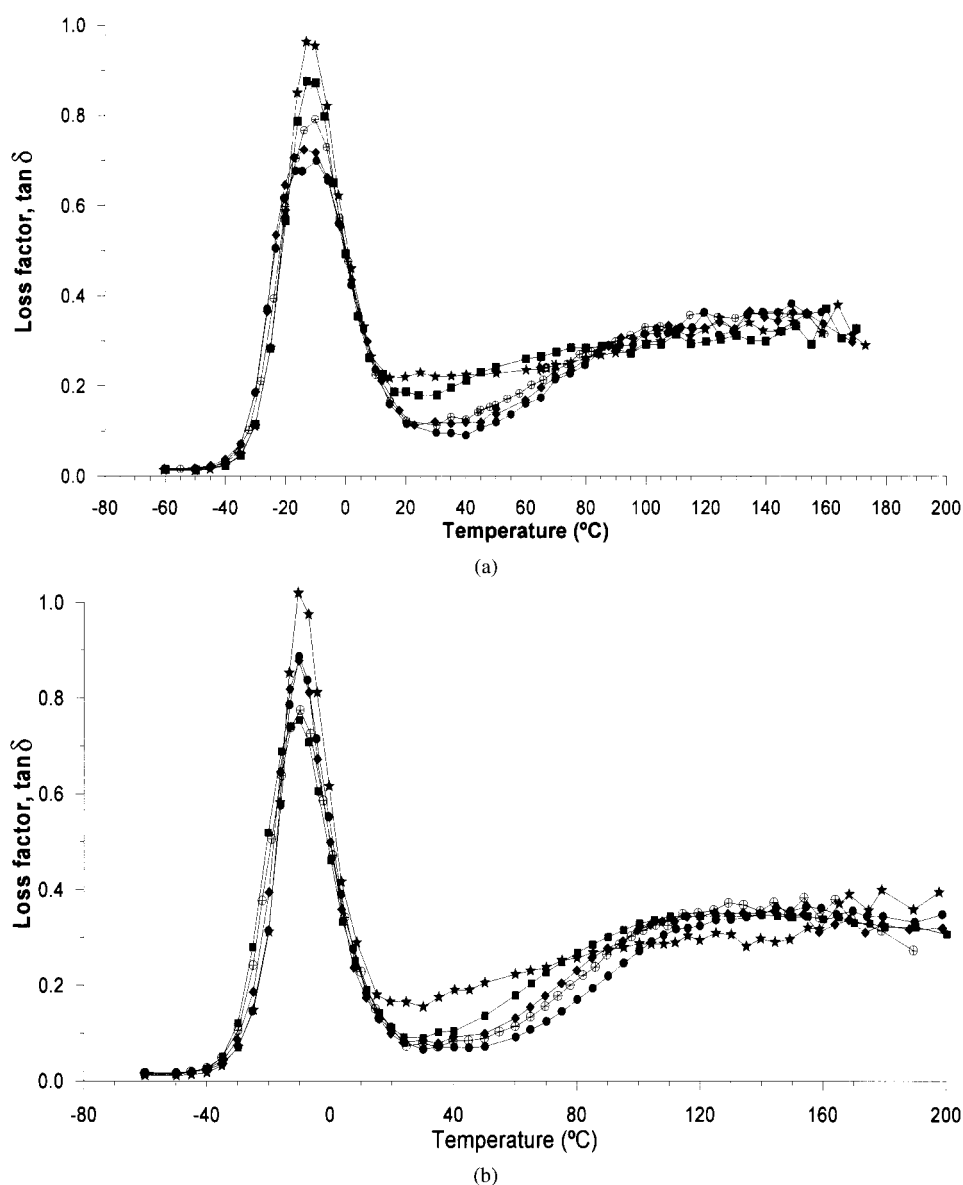


Figure 5 $\tan \delta$ as a function of temperature in samples crosslinked at (a) 100 and (b) 150 $^{\circ}\text{C}$: (\blacklozenge) CaO-4, (\oplus) CaO-5, (\bullet) CaO-6, (\blacksquare) CaO-8, and (\blackstar) CaO-10.

which is associated, as mentioned previously, with the formation of ionic bonds. This clearly shows that the tear resistance and tensile strength of these compounds have a linear relationship with the amount of salt formed, which is maximum in sample CaO-6.

In an attempt to compare the compounds according to their CaO contents, we have recorded in Table III the heights of the three most significant bands (1732, 1698, and 1545 cm^{-1}) obtained in all the spectra. These peaks have been normalized in relation to the 2920- cm^{-1} band, which is attributed to the vibration in the tension mode of the saturated C—H bond, which remains constant in the uncured and vulcanized samples. The height of the bands in the uncured samples does not depend on the amount of CaO present. Therefore, all the uncured samples have bands of sim-

ilar intensities. The heights of peaks at 1732 and 1698 cm^{-1} decrease to very low levels in the CaO-4 and CaO-6 samples (vulcanized at both 100 and 150 $^{\circ}\text{C}$), increase slightly for CaO-8 and CaO-10 (vulcanized at 150 $^{\circ}\text{C}$), and increase considerably for CaO-8 and CaO-10 (vulcanized at 100 $^{\circ}\text{C}$). The band that corresponds to salt formation grows at the expense of a reduction in the band attributed to carboxylic acids. From these results, it can be deduced that the crosslink density of the mixtures decreases when the concentration of the crosslinking agent exceeds 6 phr and that this causes the physical properties and the maximum torque of the vulcanization curve to decrease.

In an attempt to confirm the relationship existing between the rheometric curve and the ionic crosslinking, we chose the CaO-5 sample to assess the change

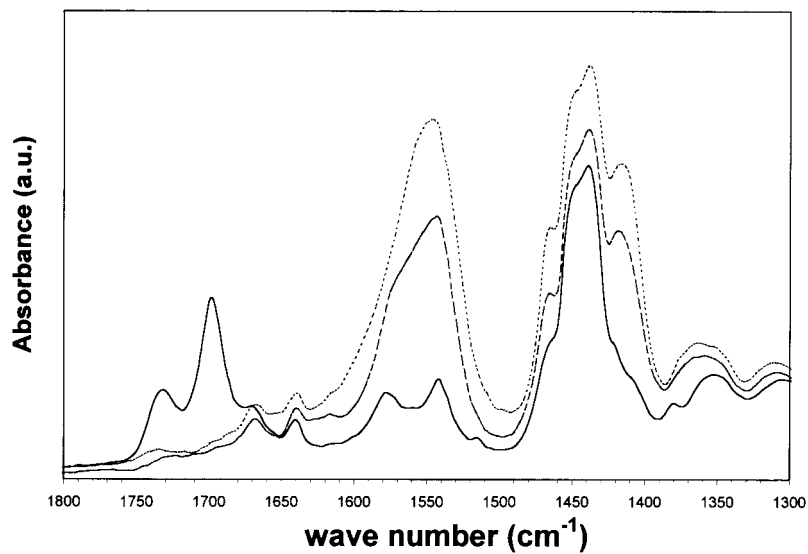


Figure 6 ATR spectra of CaO-6: (—) uncured sample, (---) sample crosslinked at 100°C for 120 min, and (···) sample crosslinked at 150°C for 45 min.

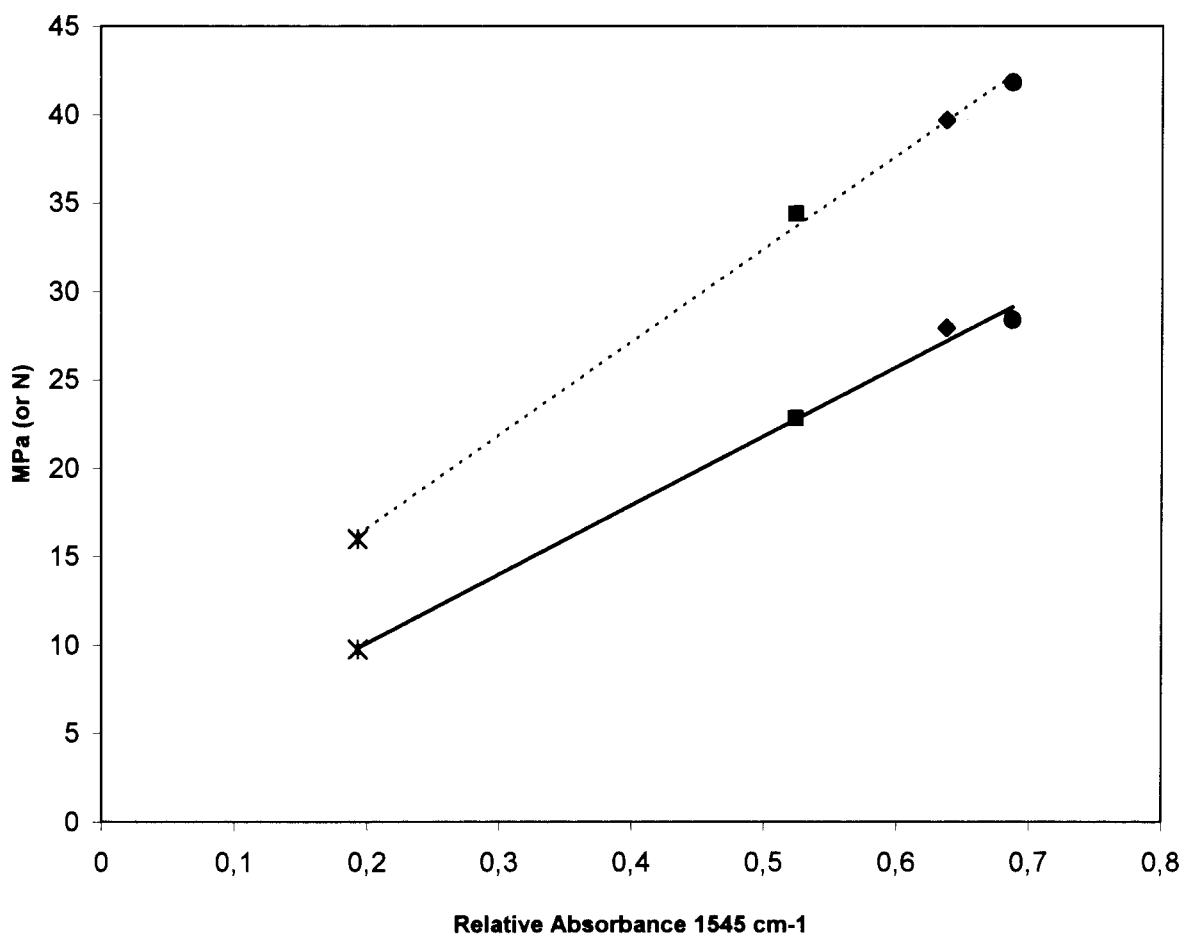


Figure 7 (—) Tensile strength (MPa) and (---) tear resistance (N) as a function of the relative absorbance at 1545 cm⁻¹ of vulcanizates at 100°C for 120 min: (◆) CaO-4, (●) CaO-6, (■) CaO-8, and (X) CaO-10.

TABLE III
Relative Height of Peaks (with Respect to 2920 cm^{-1})

		1732 cm^{-1}	1698 cm^{-1}	1545 cm^{-1}
Uncured	CaO-4	0.21	0.48	—
	CaO-6	0.19	0.43	—
	CaO-8	0.19	0.43	—
	CaO-10	0.19	0.45	—
	CaO-4	0.05	0.09	0.64
Cured at 100°C	CaO-6	0.03	0.05	0.69
	CaO-8	0.08	0.15	0.52
	CaO-10	0.20	0.28	0.19
	CaO-4	0.06	0.08	0.64
	CaO-6	0.03	0.04	0.74
Cured at 150°C	CaO-8	0.06	0.08	0.63
	CaO-10	0.08	0.10	0.54

in the band height characteristics as a function of the vulcanization time at 150°C. The results are shown in Figure 8, in which the height of the two largest bands (1698 and 1545 cm^{-1}) is shown in relation to the vulcanization time. After the first 5 min, the formation of calcium carboxylate is almost finished. Indeed, as mentioned previously, these compounds do not have an induction period, and small amounts of salt even begin to form in the uncured state. However, in this same period, the corresponding rheometric curve (see Fig. 2) has not even reached the 50% torque that it has at the plateau region. One explanation for this could be that after ionic crosslink formation has taken place, which corresponds to a very quick reaction that requires a low activation energy, there is a second phase of much longer duration that could be called the dif-

fusion phase into clusters. Here, there is a relaxation of the previously formed ionic crosslinks, which are highly favored at high temperatures in ionic elastomers, and they slide over one another, eliminating the tensions produced in the initial rapid reaction. This is made manifest by the progressive increase in the torque after the vulcanization reaction.

CONCLUSIONS

A slight excess of CaO over the stoichiometric value improves the properties of vulcanized samples independently of the chosen vulcanization temperature. This could be because a certain amount of Ca^{2+} ion reacts with water OH^- groups, giving rise to salt formation, as previously mentioned by Sato¹² for the reaction of XNBR with zinc oxide.

In the presence of even more excess crosslinking agent (8 or 10 phr), particles of CaO that have not reacted tend to agglomerate and constitute the weak points of the compound, responsible for reducing its properties.

Nevertheless, a high vulcanization temperature favors the final result. This probably occurs because, at a fast vulcanization rate, the temperature favors redistribution of the clusters formed, resulting in a change in their microstructure, alleviating tensions formed in the first stage, and, therefore, considerably improving the vulcanization obtained. An example of the opposite is given by the deformations obtained with sample CaO-10 vulcanized at 100 and 150°C: 1300 versus

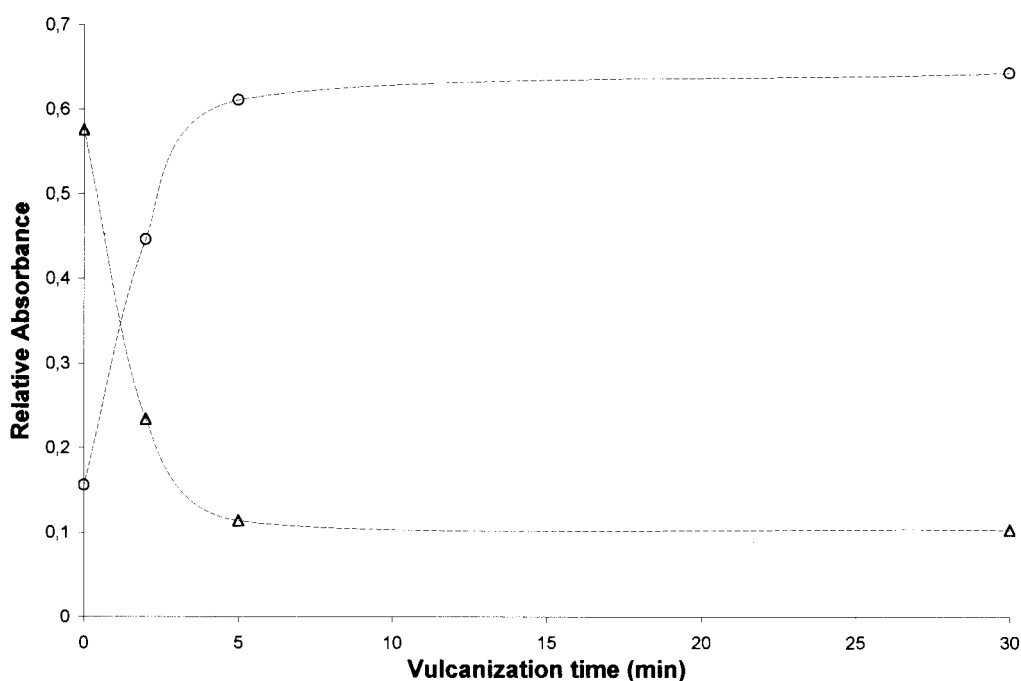


Figure 8 Relative IR absorption of some important bands: (Δ) 1698 and (\circ) 1545 cm^{-1} as a function of the vulcanization time in CaO-5 vulcanized at 150°C for 45 min.

700%, respectively, with tensile strengths of approximately 10 and 18 MPa, respectively. In the first case, the clusters formed in the first stage of the reaction have hardly any chance to diffuse because they are larger and more poorly distributed than at 150°C. This explains their greater extension (by relaxation of the clusters) and smaller resistance (due to a worse distribution).

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