

Crosslinking of Unfilled Carboxylated Nitrile Rubber with Different Systems: Influence on Properties

L. Ibarra, A. Rodríguez, I. Mora-Barrantes

Instituto de Ciencia y Tecnología de Polímeros (CSIC), c/Juan de la Cierva 3, 28006 Madrid, Spain

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ABSTRACT: The presence of two functional groups, nitrile and carboxyl, in carboxylated nitrile rubber allows it to be crosslinked with different agents. In this study, we examined the influence of different crosslinking agents on the properties of unfilled carboxylated nitrile rubber. Significant differences were found when different crosslinking agents were used, as shown in the vulcanization curves, especially in the variation of the viscous component with the reaction time. The reaction rate was highest when organic peroxide was used, and it was lowest when metallic peroxide or copper sulfate was used. When the crosslinking agents led to the formation of ionic bonds (metallic oxide and metallic peroxide), the carboxylic groups —COOH had a greater participation in the crosslinking. However, when copper sulfate was used, coordination bonds were formed, and the main contribution was due to the nitrile groups.

Tensile strength, tear strength, and abrasion properties were superior when the crosslinking systems used led to the formation of ionic bonds. On the contrary, the compression set was optimum when covalent bonds were formed. Copper sulfate behaved as an intermediate between the two previous situations. The mechanodynamic response of the compounds also depended on the crosslinking agent used. The correlation between crosslink density by swelling in dichloromethane, maximum damping temperature by dynamic measurements, and glass-transition temperature by differential scanning calorimetry had to be explained in terms of the crosslink type. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2197–2205, 2008

Key words: crosslinking; elastomers; mechanical properties

INTRODUCTION

In the structure of the carboxylated nitrile rubber (XNBR), as well as unsaturation and nitrile groups, carboxylic groups are present in a proportion of 7 wt %. This fact allows the crosslinking of the elastomer chains by means of several agents: conventional agents, such as sulfur and accelerators, bivalent metallic oxides, organic and metallic peroxides, and so on.

Depending on the system used for the crosslinking reaction, the bonds between the elastomeric chains will have different characteristics. Hence, conventional crosslinking with sulfur and accelerators leads to covalent sulfidic bonds; with metallic oxides, a reaction between the carboxylic group and the metallic ion takes place, which leads to the formation of the corresponding salt. These ionic bonds tend to associate and form an independent microphase, which is immersed in the elastomeric matrix. When metallic peroxides are used as an alternative to metallic oxides, covalent and ionic unions between the chains are formed. The former are due to the peroxide radi-

cal, whereas the latter are formed through the metallic oxide generated.¹

Our research group has been working on ionic elastomers based on XNBR crosslinked with different metallic oxides in different proportions.^{2,3} These materials show an excellent mechanical response and can be also recycled up to three times and still maintain their properties. However, because the ionic bonds have low bond energy, they are thermally unstable, and they show poor properties at high temperatures. For this reason, alternative noncovalent crosslinks are crucial for the optimum preparation of these materials.

Coordination bonds, which are the highest energy noncovalent bonds, have been used in supramacromolecular systems as a way to synthesize or crosslink polymers.⁴ Many interactions between metallic ions and ligands are stable and reversible and have high selectivity, even at high temperatures.⁵ In these cases, the majority of coordination polymers were synthesized in dilute solutions, and the methods used are not useful for crosslinking elastomers.

Recently,⁶ the crosslinking by *in situ* coordination between butadiene–acrylonitrile rubber and anhydrous copper sulfate(II) was reported. In this method, crosslinks are formed during rubber processing instead of in solution. On the basis of this article, the crosslinking between XNBR and anhydrous copper sulfate (CuSO₄) by means of coordination bonds was

Correspondence to: L. Ibarra (libarra@ictp.csic.es).

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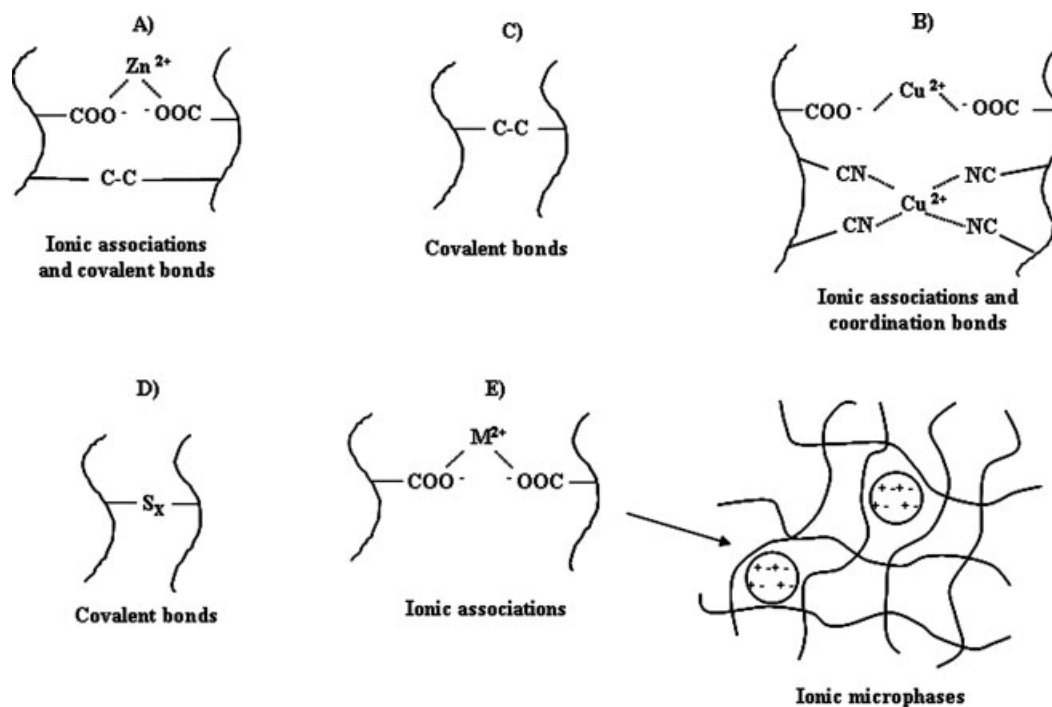


Figure 1 Possible crosslinks in XNBR as a function of the crosslinking agent: (A) ZnO_2 , (B) CuSO_4 , (C) organic peroxide, (D) sulfur/accelerators, and (E) metallic oxides.

obtained in our laboratory. Therefore, crosslinking by coordination bonds seems to be a novel alternative. Figure 1 shows the possible crosslinks in XNBR as a function of the crosslinking agent used.

The crosslinking reaction and its kinetics depend on the crosslinking agent used. In XNBR, there are different active functional groups: nitrile groups ($-\text{CN}$), carboxylic groups ($-\text{COOH}$), and double bonds. These groups can participate in the crosslinking reaction or be affected by it. Furthermore, the formation of crosslinks affects the mobility of the polymeric chains; logically, this influence depends on the system used.

In this study, we examined the influence of different agents on the crosslinking of XNBR, focusing on specific aspects: vulcanization kinetics and mechano-dynamic properties, which provide a deeper interpretation of the influence of the crosslinking system in terms of chain mobility.

EXPERIMENTAL

A XNBR, Krynac 7.40, was used and was supplied by Lanxess (Leverkusen, Germany). This grade contained 27 wt % acrylonitrile and 7 wt % carboxylic groups, and it had a Mooney viscosity of 40 MU.

The crosslinking agents used were as follows.

Conventional sulfur/accelerator systems (sulfur/*N*-cyclohexyl-2-benzothiazyl sulfonamide and sulfur/tetramethylthiuram disulfide) were used, from

which zinc oxide (ZnO) was deliberately excluded. The proportions added were typical of semiefficient vulcanization systems.

The metallic oxide used was magnesium oxide (MgO ; Elastomag 170 Special), which was supplied by Akrochem (Akron, OH). The MgO proportion used represented an excess over the amount needed to saturate the existing carboxylic groups.⁷

Rubber-grade stearic acid was used.

The metallic peroxide used was zinc peroxide (ZnO_2 ; Struktol ZP 1014) with a specific weight of 2.3 g/cm^3 , a 50 wt % concentration of the active compounds ZnO and ZnO_2 (29%), a 30 wt % concentration of inorganic dispersing agents, and a 20 wt % concentration of the organic dispersing agent; it was supplied by Schill-Seilacher (Hamburg, Germany) as a slightly gray powder that could be easily incorporated during rubber processing into the two-roller mixer. With respect to the Struktol ZP 1014 composition, the amount of the active crosslinking agent agreed with the proportion used for MgO .

Anhydrous copper sulfate(II), supplied by Fluka (Buchs SG, Switzerland), was also used as a crosslinking agent in the proportion used by Chifei et al.⁶

Dicumyl peroxide (98% purity), supplied by Sigma-Aldrich (Química S.A., Madrid, Spain), was also used as a crosslinking agent. The level of organic peroxide was typical for rubber vulcanization. Table I shows the recipes used.

The compounds were prepared on a Gumix (Barcelona, Spain) laboratory two-roll mill with a cylin-

TABLE I
Recipes with Different Crosslinking Agents

| | C-1 | C-2 | C-3 | C-4 | C-5 |
|-------------------|-----|-----|-----|-----|-----|
| XNBR 7.40 | 100 | 100 | 100 | 100 | 100 |
| Stearic acid | 1 | 3 | 3 | — | — |
| TMTD accelerator | 1 | — | — | — | — |
| CBS accelerator | 3 | — | — | — | — |
| Sulfur | 1 | — | — | — | — |
| MgO | — | 4.3 | — | — | — |
| Struktol ZP1014 | — | — | 8 | — | — |
| CuSO ₄ | — | — | — | 5 | — |
| Dicumyl peroxide | — | — | — | — | 2 |

CBS = *N*-cyclohexyl-2-benzothiazyl sulfonamide; TMTD = tetramethylthiuram disulfide.

der diameter of 15 cm and a length of 30 cm; the friction ratio between the cylinders was 1 : 1.5. The cylinders were refrigerated by the circulation of cold water through them during blending.

The vulcanization curves were obtained in a Monsanto (Wiltshire, UK) MDR rheometer 2000 E, with an oscillation arc of 0.5° at a temperature of 160°C. The vulcanization reaction was carried out in a hydraulic press, which was electrically heated at the vulcanization temperature, for the time corresponding to the cure time for 95% of conversion, as calculated from rheometric curves.

The physical properties of the compounds were measured according to national standards. Shore A hardness was determined on cylindrical samples with an automatic Bareiss (Oberdischingen, Germany) durometer, according to standard UNE EN ISO 868. Tensile tests were performed in an Instron (Barcelona, Spain) model 4301 dynamometer equipped with a video camera to measure deformations at a strain rate of 500 mm/min on type 1 dumbbell samples, according to standard UNE 53510. Five specimens were tested for each sample.

Tearing tests were carried out on angular-type samples, without notch, according to standard UNE 53516 part 1, at the same strain rate used for the tensile tests. Five specimens were also tested for each sample.

Dynamic mechanical measurements were carried out in a Rheometric Scientific (TA Instruments, Piscataway, NJ) DMTA V dynamic mechanical thermal analyzer under norm ISO 6721 in the tensile mode at frequencies of 5, 10, 15, and 20 Hz. The temperature was varied from 80 to 200°C at a rate of 1.5 K/min. Each specimen for the dynamic mechanical experiments was cut into a rectangular strip with approximate dimensions of 30 × 6 × 2 mm³.

Dynamic mechanical properties at variable strain were measured in a Metravib (Limonest, France) viscoanalyzer, model RAC 815 A, at a vibration frequency of 15 Hz in a strain range of 1–500 μm.

Infrared spectra were recorded on a PerkinElmer (Norwalk, CT) Spectrum One spectrophotometer

with the attenuated total reflectance technique with a resolution of 4 cm⁻¹. Ten spectra were recorded for each sample. The intensity of the bands was measured by means of OMNIC software (Thermo Scientific, Waltham, MA).

The determination of the glass-transition temperature by means of differential scanning calorimetry (DSC) was carried out in a Mettler Toledo (Posilfach, Switzerland) DSC 822E at a heating rate of 10°C/min in a temperature range between -80 and 320°C in a nitrogen flow at a rate of 10 mL/min. The glass-transition temperature was measured at the midpoint.

The direct estimation of crosslink density by solvent swelling in equilibrium in was not possible in this case because the value of the parameter of the polymer-solvent interaction corresponding to the system used (XNBR rubber and methylene dichloride at room temperature) was unknown. However, V_r could be determined and was defined as the fraction in the volume of rubber swollen in equilibrium:⁸

$$V_r = \frac{(D - FT)\rho_r^{-1}}{(D - FT)\rho_r^{-1} + A_0\rho_s^{-1}}$$

where T is the initial weight of sample; D is the dry sample weight after swelling; ρ_r and ρ_s are the densities of the polymer and the solvent, respectively; F is the fraction in weight of the insoluble ingredients in the mixture; and A_0 is the weight of the absorbed solvent.

From this expression, the crosslink density was determined in terms of V_r in the corresponding vulcanized compounds.

RESULTS AND DISCUSSION

Crosslinking reaction

Vulcanization curves

Figure 2(A,B) shows the variation of the normalized elastic component (S') and viscous component (S'') of the torque with time, respectively. The curves were obtained in the MDR rheometer at a temperature of 160°C. Table II shows the rheometric parameters obtained from the curves for the different crosslinking agents.

Independent of the crosslinking agent used, the variation of S' with time followed the same trend in all samples: a rapid growth with reaction time. In the case of sulfur, MgO, and organic peroxide vulcanization, a plateau was reached. However, with ZnO₂ and CuSO₄, the plateau was not achieved during the reaction time analyzed.

The variation of S'' with time showed a completely different behavior, as shown in Figure 2(B). There

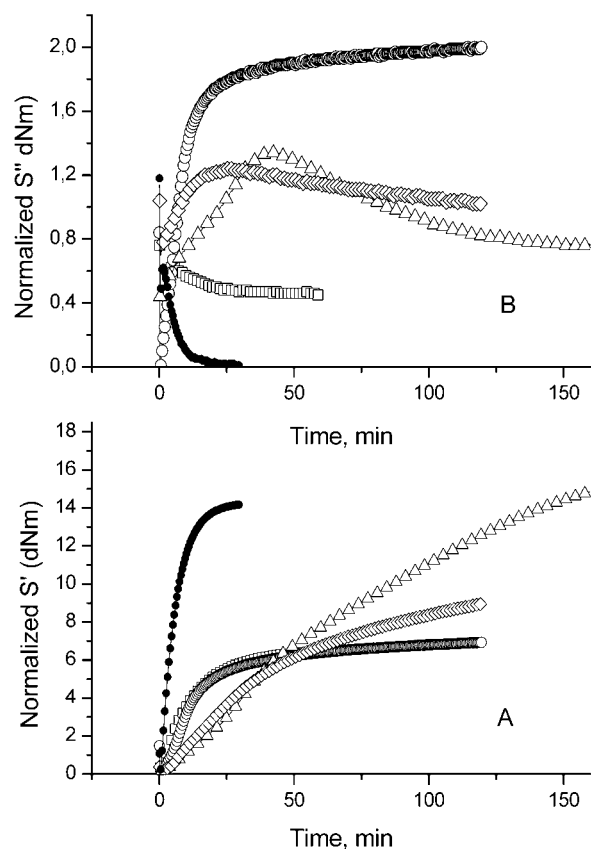


Figure 2 Normalized vulcanization curves of (\square) sulfur, (\circ) MgO, (\triangle) ZnO₂, (\diamond) CuSO₄, and (\bullet) dicumyl peroxide: (A) S' and (B) S'' .

were two extreme behaviors: on one hand, the curve corresponding to the crosslinking with dicumyl peroxide, which led to covalent bonds between the chains by means of a radical mechanism, decreased with vulcanization time until it reached a plateau. On the other hand, the curve corresponding to the crosslinking with the MgO, which formed ionic bonds,³ showed a similar behavior relative to that observed in the evolution of S' [Fig. 2(A)] with time: S'' increased until it reached a plateau.

When dicumyl peroxide was used, the decrease in S'' was attributed to the formation of covalent bonds, which increased the compound's elasticity and raised

S' with a consequent decrease in S'' . In the compound crosslinked with MgO, ionic bonds formed, which were unstable at high temperatures and increased S' . However, the formation of ionic cluster-type associations led to a remarkable increase in S'' .

The variation of S'' during the crosslinking reaction in the compound with the sulfur/accelerators system showed an initial increase due to the links formed between the sulfurate intermediates with the molecular chains, which restricted the mobility of the chains. Afterward, the behavior was similar to that observed in the reaction with the organic peroxide.

The S'' behavior observed when ZnO₂ and CuSO₄ were used was more complex. Previous studies in which Struktol ZP 1014 was used¹ showed that two reactions took place: first, the formation of ionic bonds, due to the presence of the ZnO in the product, and second, the peroxide decomposition followed by the formation of covalent bonds. This latter reaction was due to the presence of peroxide radicals, obtained by thermal decomposition of ZnO₂. This reaction mechanism would explain the shape of the S'' curve: a region of increase, as a consequence of the ionic bonds formation, followed by a region of decrease, which corresponded to the formation of covalent bonds. Therefore, the physical properties of the materials crosslinked with this agent depended on both the reaction time and temperature, as was demonstrated in a previous study.⁷

The curve for the reaction with CuSO₄ showed similarities to that obtained for ZnO₂: an initial increase in S'' , followed by a decreasing region, with a smoother slope than in the previous case. The explanation for this behavior is similar to that for ZnO₂; the presence of the Cu²⁺ ion must have favored the formation of the corresponding salt with the carboxylated groups present in the elastomeric chains, whereas in the nitrile groups (—CN), coordination bonds were formed,⁶ which were equivalent, in terms of mechanical performance at vulcanization temperatures, to covalent bonds.

The global crosslinking reaction rate is shown in Table II as the cure rate index. From the calculated values, it must be pointed out that a faster reaction

TABLE II
Rheometric Parameters from the Vulcanization Curves at 160 °C

| | C-1 | C-2 | C-3 | C-4 | C-5 |
|------------------------------|--------|-------------|------------------|-------------------|------------------|
| Cure system | Sulfur | Metal oxide | ZnO ₂ | CuSO ₄ | Organic peroxide |
| Maximum torque (dN m) | 7.02 | 7.7 | 17.11 | 9.57 | 14.76 |
| Minimum torque (dN m) | 0.54 | 0.76 | 0.33 | 0.61 | 0.57 |
| Change in S' (dN m) | 6.48 | 6.94 | 16.78 | 8.96 | 14.19 |
| Scorch time (min) | 4.75 | 7.15 | 17.35 | 13.92 | 1.39 |
| Time to 90% conversion (min) | 29.81 | 50.44 | 166.3 | 90.57 | 13.43 |
| Time to 95% conversion (min) | 38.35 | 75 | 182 | 104 | 18 |
| Cure rate index ^a | 3.99 | 2.23 | 0.67 | 1.30 | 8.30 |

^a Cure rate index = 100/(Time to 90% conversion – Scorch time).

TABLE III
Average Absorbance Values of the 966-cm^{-1} Band and Relative Absorbance with Respect to the 966-cm^{-1} Band of Cured and Uncured Compounds

| System | 966 cm^{-1} | | 2238 cm^{-1} | | 1699 cm^{-1} | |
|-------------------|----------------------|-------|-----------------------|-------|-----------------------|-------|
| | Uncured | Cured | Uncured | Cured | Uncured | Cured |
| Raw XNBR | 1.18 | — | 0.086 | — | 0.227 | — |
| Sulfur | 1.19 | 1.17 | 0.088 | 0.085 | 0.221 | 0.178 |
| MgO | 1.17 | 1.17 | 0.089 | 0.081 | 0.281 | 0.039 |
| ZnO ₂ | 1.18 | 1.18 | — | 0.079 | — | 0.029 |
| CuSO ₄ | 1.18 | 1.19 | 0.083 | 0.069 | 0.227 | 0.189 |
| Dicumyl peroxide | 1.18 | 1.17 | 0.087 | 0.088 | 0.248 | 0.209 |

was achieved when the organic peroxide was used. On the contrary, when Struktol ZP1014 was used, a slower, more complex reaction was observed.

Fourier transform infrared/attenuated total reflectance (FTIR-ATR) spectroscopy

Infrared spectra of the compounds were obtained for both raw and vulcanized compounds. Special attention was paid to the spectral regions of the —COOH and —CN groups to establish the existence of variations between the raw and the crosslinked states. Ten spectra were recorded for each sample to measure the absorbance amplitude of the more characteristics bands, assigned as follows:

2920 cm^{-1} : $\text{—CH}_2\text{—}$ asymmetric stretching vibration.

2238 cm^{-1} : $\text{—C}\equiv\text{N}$ stretching vibration.

1699 cm^{-1} : —C=O stretching vibration.

966 cm^{-1} : —C—H— out-of-plane deformation associated with —HC=CH— in the trans configuration.

The C—H deformation band associated with trans double bonds (966 cm^{-1}) was supposed to be invariable, as could be deduced from the average absorbance values of the different samples, shown in Table III. With respect to this band, the relative absorbance values of the bands at 1699 and 2238 cm^{-1} were calculated. The mean value obtained is shown in Table III. In Figure 3(a,b), the variation of the relative absorbance is shown in a diagram of maxima and minima.

With regard to the band at 1699 cm^{-1} [Fig. 3(a)], related to the —COOH group, we deduced that when the crosslinking system used was sulfur/accelerators, the relative absorbance values were below the lower limit of the average value obtained for uncrosslinked compounds. This was probably due to some kind of reaction with derivatives of the accelerators used. In the same way as the stearic acid participated in the formation of active complexes that start up the crosslinking reaction, the carboxylic

groups present in the polymers chains took part in the formation of these sulfurate complexes.

In a similar way, when anhydrous CuSO_4 was used as a crosslinking agent, the carboxylic groups participated to a small extent because the decrease observed in the relative absorbance was not significant. It was not surprising that the bivalent Cu^{2+} ion could form the corresponding salt with the carboxylic group. The FTIR-ATR spectrum showed a band at 1663 cm^{-1} , probably due to the corresponding copper salt (Fig. 4).

In the compound crosslinked with the organic peroxide, the values for the relative absorbance of the

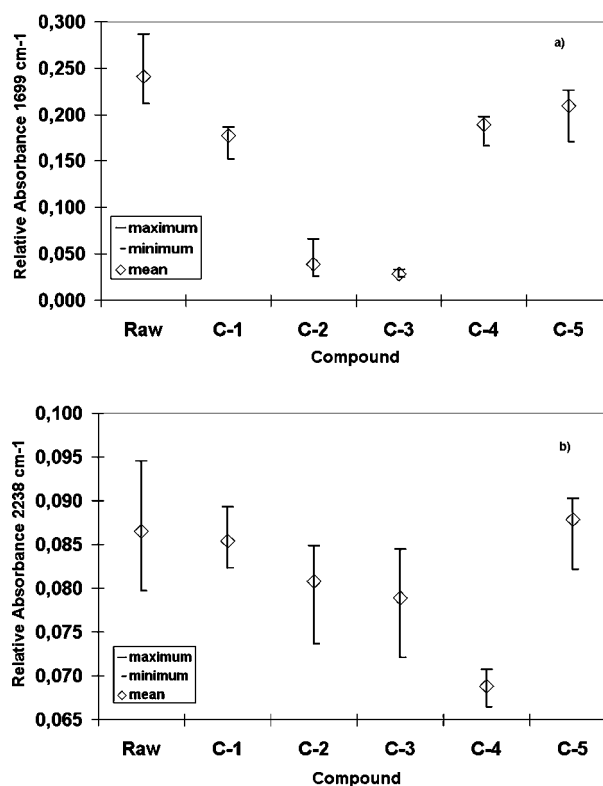


Figure 3 Maximum–minimum diagrams of the relative absorbance with respect to the 966-cm^{-1} band of cured samples: (a) 1699-cm^{-1} band and (b) 2238-cm^{-1} band.

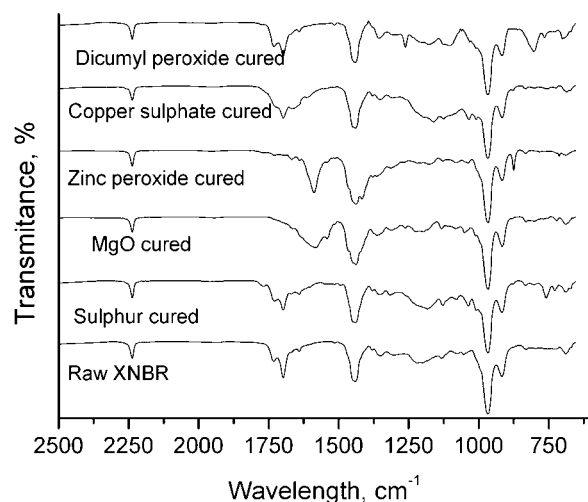


Figure 4 FTIR-ATR spectra of vulcanizates with different crosslinking systems.

band at 1699 cm^{-1} were on the same order of magnitude as those obtained for the uncured material.

In the cases where crosslinking agents based on metallic oxide and peroxide were used, the disappearance of the carboxylic groups was almost complete; no sharp band was observed in the spectrum.

Regarding to the band associated with the cyano group at 2238 cm^{-1} [Fig. 3(b)], when covalent bonds were formed, as occurred in the crosslinking with sulfur or peroxide, the values observed were similar to those obtained in raw compounds: in this case, nitrile groups did not participate in the reaction.

In the reactions where ionic bonds, that is, MgO, or ionic and covalent bonds, that is, ZnO_2 , were formed, the average values and the upper limits were within the interval obtained for raw materials, which indicated once again the inactivity of the nitrile groups during the crosslinking reaction.

Finally, when CuSO_4 was used to crosslink the elastomer by means of coordination bonds, a decrease in the values of the absorbance ratio took place. This drop of approximately 13.5% clearly indicated the participation of the nitrile groups during the reaction.

Influence of the crosslinking agents on the final properties of the materials

Dynamic mechanical properties

The dynamic mechanical properties were measured at variable strain amplitude and temperature.

Variable double strain amplitude (DSA). It is well known that in a filled vulcanized rubber the modulus is dependent on (1) the crosslink density of the rubber matrix, (2) the hydrodynamic effect caused by the filler, (3) the filler-rubber interactions, and (4) the filler-filler interactions.^{9,10} According to Payne and Whittaker,¹⁰ in unfilled vulcanized compounds,

the modulus should remain constant with the strain amplitude.

Figure 5 shows the variation of the storage modulus (E') with the amplitude in terms of DSA. The E' values and their variation with the strain depended on the crosslinking agent used.

Indeed, the lowest values of modulus were obtained for the pure XNBR, where no significant variations were observed during the strain amplitude ranges analyzed.

The curves obtained for the compounds crosslinked with sulfur or dicumyl peroxide, which led to covalent bonds, showed values significantly superior to those obtained for the pure gum due to the formation of a three-dimensional network. However, in the strain range studied, the modulus did not show any variation. This behavior was as expected for unfilled crosslinked rubbers.

The highest modulus values were observed in the compounds vulcanized with ZnO_2 and MgO. As has been previously demonstrated,¹¹ ZnO_2 led to covalent and ionic bonds. The ionic bonds formed ionic associations or clusters, which behaved as an ionic microphase separated from the elastomeric matrix. These clusters acted as reinforcing sites of the elastomer. In the case of MgO, only ionic bonds were formed, which had the same peculiarities as the ones mentioned previously. Therefore, the increase in modulus values was due to both crosslinks and ionic associations, which behaved as fillers and thus improved the reinforcement.

In this case, the decrease in modulus at high strains could be explained by the breaking of the ionic associations, similar to that which occurs in filler-filler interactions.

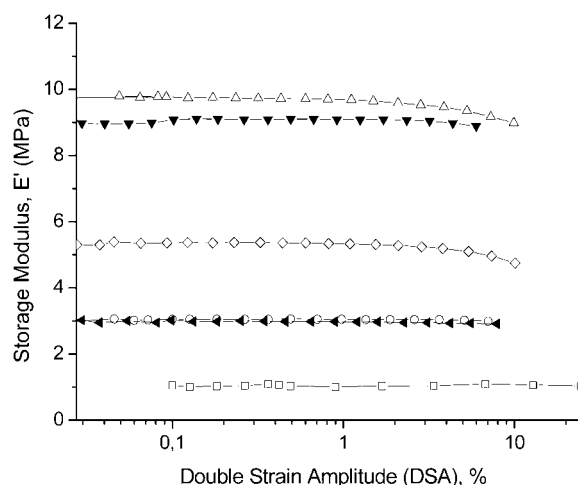


Figure 5 E' (MPa) as a function of DSA with an oscillation frequency of 11 Hz at room temperature: (\square) raw XNBR, (\circ) sulfur-cured compound, (\triangle) MgO-cured compound, (\blacktriangledown) ZnO_2 -cured compound, (\diamond) CuSO_4 -cured compound, and (\blacktriangleleft) dicumyl peroxide cured compound.

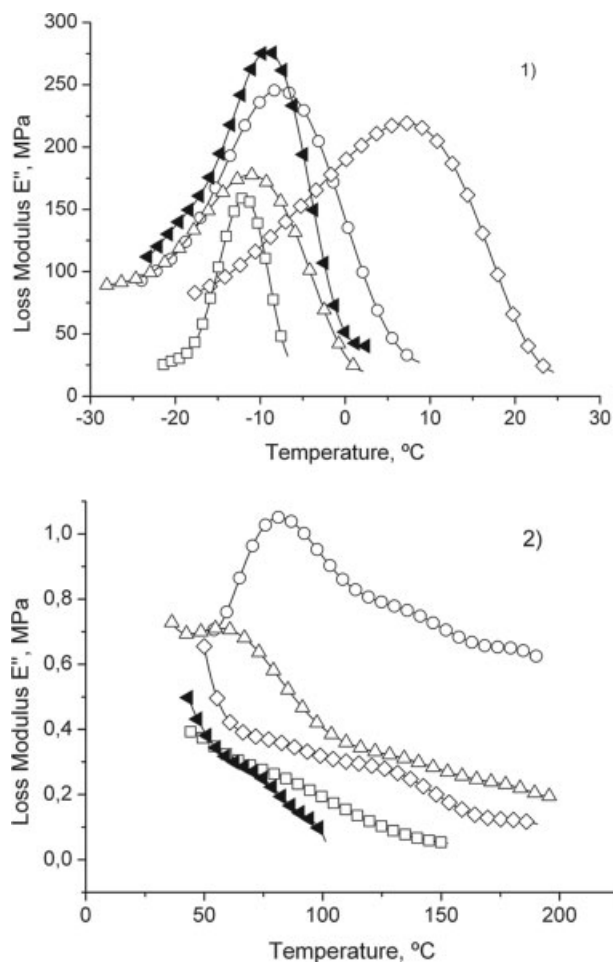


Figure 6 E'' (MPa) (1) at low temperatures and (2) at high temperatures with an oscillation frequency of 5 Hz: (□) sulfur-cured compound, (○) MgO-cured compound, (△) ZnO₂-cured compound, (◇) CuSO₄-cured compound, and (◄) dicumyl peroxide cured compound.

An intermediate situation was observed in XNBR compounds crosslinked with anhydrous CuSO₄. Recent work¹² has stated that the Cu²⁺ ion leads to coordination bonds with the nitrile (—CN) groups present in the nitrile rubber. As has been demonstrated,¹³ in XNBR, not only coordination bonds are formed but also ionic links between Cu²⁺ and the carboxylic groups (—COOH) of the elastomeric chains. Moreover, the unreacted CuSO₄ can behave as a filler in the vulcanized compound. Therefore, the observed increment in E' values relative to systems crosslinked with sulfur and organic peroxide could have been due to both crosslinks and the presence of the CuSO₄ filler. Once the strain amplitude was close to 100%, a decrease in the modulus took place: this fact can be explained by means of either ionic bonds or the rupture of CuSO₄ filler agglomerates.

Variable frequency and temperature. Figure 6(1,2) shows the variation of loss modulus (E'') with tem-

perature at a vibration frequency of 5 Hz. At low temperatures [Fig. 6(1)], all compounds showed maxima at different temperatures.

The temperature in which the maximum was observed could be considered a measure of the glass-transition temperature of the elastomeric matrix, as obtained by mechanodynamic measurements. The differences found were not only in the positions of the maxima but also in the peak width and length. As high temperatures [Fig. 6(2)], the maxima observed were due to the ionic transition that took place in compounds crosslinked with ZnO₂ or MgO, as expected. These maxima confirmed the existence of ionic associations in these vulcanized samples, which behaved as independent microphases inside the rubber matrix, and the transitions observed were characteristic of ionic elastomers.

In the compound crosslinked with CuSO₄, this transition was also expected because ionic links were also formed. However, due to the lower amount of ionic bonds and their dilution by coordination bonds between the nitrile group and the Cu²⁺ ion present in the elastomer network, the ionic transition was not observed. Nevertheless, if one observes Figure 6(2) carefully, a slight recovery in E'' can be seen between 100 and 150°C, which could be attributed the formation of these ionic bonds, as previously mentioned.

Table IV shows the values obtained for both transitions together with those obtained by DSC and crosslink densities in terms of V_r , as calculated by swelling measurements in dichloromethane. From the DSC measurements, a correspondence between the glass-transition temperature and crosslink density in terms of V_r existed: an increase in crosslink density was associated with a higher glass-transition temperature.

In the case of the glass-transition temperature obtained by dynamic measurements, the correspondence must be explained in terms of the type of links. In fact the displacement observed in the transi-

TABLE IV
Transition Temperatures from DSC and Dynamic Mechanical Measurements

| Crosslinking agent | From DSC | | From E'' | | V_r^a |
|--------------------|----------|-------|------------|-------|---------|
| | T_g | T_i | T_g | T_i | |
| None (pure XNBR) | -23.02 | — | — | — | — |
| Sulfur | -19.2 | — | -12.0 | — | 0.128 |
| MgO | -21.7 | 78.13 | -7.8 | 82.27 | 0.100 |
| ZnO ₂ | -22.0 | 65.46 | -11.1 | 64.17 | 0.069 |
| CuSO ₄ | -12.2 | — | 5.3 | — | 0.205 |
| Dicumyl peroxide | -18.9 | — | -9.4 | — | 0.172 |

T_g = glass-transition temperature; T_i = ionic-transition temperature.

^a By swelling in dichloromethane measurements.

TABLE V
Physical Properties of the Compounds Cured with Different Systems

| | Sulfur | MgO | ZnO ₂ | CuSO ₄ | Dicumyl peroxide |
|--|--------|-------|------------------|-------------------|------------------|
| Shore A hardness | 38 | 70 | 62 | 43 | 41 |
| Stress at 100% strain (MPa) | 1.02 | 4.11 | 3.1 | 1.25 | 1.11 |
| Stress at 300% strain (MPa) | 2.20 | 8.86 | 7.6 | 2.92 | 2.3 |
| Tensile strength (MPa) | 4.2 | 56.15 | 23 | 7.53 | 3.1 |
| Elongation at break (%) | 480.5 | 800 | 530 | 1220 | 329 |
| Tear strength (kN/m) | 12.85 | 44.4 | 30.11 | 18.45 | 17.86 |
| Abrasion loss (mm ³) | 79.66 | 62.8 | 42 | 80.57 | 356.51 |
| Compression set at room temperature and 72 h | 12.5 | 97 | 50 | 19.75 | 6.23 |

tion at low temperatures was a function of two aspects: on the one hand, the crosslink density of the vulcanized compound and, on the other, the presence or absence of ionic associations. When these associations do not exist, as occurs in crosslinking with sulfur and organic peroxide, the higher crosslink density in the latter produces a greater immobilization of the elastomeric chains, with a corresponding increase in the glass-transition temperature.

The presence of ionic associations immersed in the polymeric matrix also produces the immobilization of the chains, specially when the test is carried out under mechanodynamic solicitation. Therefore, the increase in the glass-transition temperature, measured as the maximum of E'' , did not correspond with the low crosslink density values observed.

When the crosslinking was done with CuSO₄, not only were coordination bonds between nitrile groups and Cu formed, but also the formation of copper salts with the carboxylic groups of the elastomer took place, and this did not lead to a separated ionic microphase. Furthermore, the crosslink density value was higher than the values obtained for the samples crosslinked with sulfur and organic peroxide, and consequently, the glass-transition temperature of the compounds vulcanized with CuSO₄ was higher. The differences observed in the glass-transition temperature were more significant under dynamic mechanical tests.

Physical properties

Table V shows the physical properties of the XNBR compounds crosslinked with different systems. The systems that led to the formation of ionic bonds, MgO and ZnO₂, gave superior final properties compared to those obtained for the other systems, except for the compression set response. However, the difference between these two systems was very significant. ZnO₂ formed not only ionic bonds but also covalent links between the elastomeric chains. These covalent bonds were responsible for the improve-

ment in material elasticity, which thus reduced its compression set. These compounds showed better tensile strength, tear strength, and abrasion resistance due to the presence of the ionic associations, which behaved as reinforcing sites. For the same reason, these were the compounds with the highest Shore A hardness.

The crosslink systems that led to covalent bonds, that is, sulfur and dicumyl peroxide, produced materials with a better compression set response. The highest values were achieved with the organic peroxide, which formed high-energy —C—C— links between the chains. In these systems, the strength properties were poor due to the absence of fillers.

Surprisingly, the tensile and tear strength values obtained for the compound crosslinked by CuSO₄ were superior to those obtained with sulfur or organic peroxide. They showed a low compression set and acceptable abrasion resistance, probably due to the presence of unreacted CuSO₄, which acted as a filler.

CONCLUSIONS

According to the results obtained in this study, the following conclusions can be drawn:

- The curve obtained for the variation of S'' (dN m) with time defined the bond type obtained for each crosslinking agent. When covalent bonds were formed, a descendant curve was obtained from the start of the reaction. During the formation of ionic bonds (MgO), the curve increased until it reached a plateau. When the system led to the formation of two types of links, ionic and covalent (ZnO) or ionic and coordination (CuSO₄), the curves showed an increasing period and a maximum, followed by a decrease in the modulus.
- Nitrile (—CN) and carboxylic (—COOH) groups participated in a different way during the crosslinking process, which depended on the crosslink agent used. In fact, —CN participated pref-

entially during the crosslinking reaction with CuSO_4 , whereas carboxylic groups participated in the reaction with metallic oxide and peroxide and, to a lesser extent, with CuSO_4 .

- Unfilled ionic compounds showed superior tensile, tear, and abrasion properties than the other systems. Compounds with covalent bonds showed a better compression set response but lower physical properties. The sample with CuSO_4 showed intermediate properties. Non-ionic compounds required the addition of filler to obtain good physical properties.
- The vulcanization systems used significantly influenced the dynamic response of the compounds: the variation of E' with the strain amplitude showed that in ionic compounds, ionic associations behaved as reinforcing sites. Unfilled samples with covalent bonds showed the lowest modulus values, whereas the compound with CuSO_4 gave intermediate values.

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