The Effect of Crosslinking Type on the Physical Properties of Carboxylated Acrylonitrile Butadiene Elastomers

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ABSTRACT: Vulcanization of carboxylated nitrile rubber (XNBR) with different vulcanizing agents (i.e., zinc peroxide, sulphur, and a zinc peroxide–sulphur mixed system) was studied. Properties of the vulcanized compounds depend on the type of crosslinking produced (i.e., ionic or covalent) rather than the crosslinking density. Ionic crosslinks gave rise to greater stress relaxation, relaxation rates, and a greater generation of heat. In the relaxation spectra, tan δ versus temperature, two transitions appeared. Those occurring at the lower temperature corresponded to the polymer T_g, while the transition occurring at the higher temperature was associated with ionic structures. The properties of the vulcanized compounds with ionic crosslinks decreased drastically after treatment with ammonia, which acts as a plasticizer of the ionic aggregates formed. The effect of ammonia disappeared on expansion in solvent, which resulted in the recovery of the original crosslinks, producing a value of v_r—volume fraction of swollen rubber in equilibrium—close to the original value and the reappearance of the ionic transition. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 927–933, 1999

Key words: carboxylated nitrile rubber; ionic crosslinking; mechanical, dynamic, and stress relaxation properties

INTRODUCTION

Crosslinking of carboxylated nitrile rubbers can be achieved both by conventional systems, based on the use of sulphur accelerators, or by using metallic oxides, preferentially zinc oxide.[1] One drawback of crosslinking with zinc oxide is that the compounds produced have a very short scorch time and, although these show good properties, this vulcanization system cannot be used in practice. This problem can be resolved using vulcanization agents such as metal peroxides, either in the master batch with the elastomer or in special preparations.[2]

During the molding process of carboxylated nitrile rubber (XNBR), a carboxylic acid salt is formed in the presence of zinc oxide that gives rise to the production of an ionic elastomer or an ionomer[3] with greatly improved physical properties.[4,5] The crosslinks produced with both the oxide and the peroxide are ionic in contrast to those produced in the vulcanization with sulphur accelerators, which are covalent. To know more about the nature of the ionomeric phases the effect of plasticizers on their physical properties were studied.[6–8] 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.

The aim of the present work is to study the properties of vulcanized compounds with both kinds of crosslinking agents in relation to the different types of bonding that they generate. To do this, a special commercial mixture of zinc peroxide was used, and the properties obtained with

Table I   Formulation of Compounds

	A	B	C
XNBR Krynac 7.4	100	100	100
Stearic acid	1	1	1
TMTD accelerator	1	—	1
CBS accelerator	3	—	3
Sulphur	1	—	1
Zn Peroxide	—	4	4

a mixed vulcanization system based on zinc peroxides and sulphur accelerators were studied, which would logically give rise to ionic and covalent crosslinks. Mechanical, viscoelastic, and stress relaxation properties are analyzed in this work because they are representative of and distinguish between both types of bonding. Also, the properties of the vulcanized compounds were studied after treatment with ammonia, which acts as an ionic plasticizer.[9]

EXPERIMENTAL

The formulations used are recorded in Table I. The elastomer used was a carboxylated nitrile rubber, Krynac 7.4, with an acrylonitrile content of 27% and 7.4 mol % of carboxylic groups. The zinc peroxide used was Strutkol ZP1014, of specific weight 2.3 and a ZnO_2 content of 29%, supplied by Schill-Seilacher as a light gray powder, which incorporated perfectly into the mixer.

All mixtures were prepared in a laboratory 12-inch long, two-roll mix at a friction ratio of 1 : 1.2. Cylinders were constantly cooled with cold water.

The crosslinking density was measured from the volume fraction of rubber swollen in equilibrium (V_r), using benzene as a solvent and immersed for 6 days at room temperature.

The mechanical properties and the stress relaxation in traction were measured in an Instron dynamometer, model 4301, equipped with a video system to determine the deformation, and at a stretching rate of 500 mm/min. For the tensile tests, dumbbell test pieces were used, 4 mm wide in their straight section. To measure the stress relaxation, test pieces 6 mm wide and 2 mm thick were used; an initial deformation of 100% was applied and a relaxation time of 60 min.

Viscoelastic properties were measured with an RAC 80 Metravib viscoanalyzer based on the principle of nonresonant forced vibrations that permit one to work in a frequency interval between 5 and 1000 Hz at temperatures between -120 and 300°C, and with a dynamic deformation of up to 500 μm, associated or not with static deformation.

Treatment with ammonia involved exposure of vulcanized compounds for 24 h in an ammonia saturated steam (30% aqueous solution) in a desiccator.

RESULTS AND DISCUSSION

Crosslink Density

The direct estimation of crosslink density by swelling in a solvent to equilibrium was not possible in this case because the value of the polymer–solvent interaction parameter corresponding to the system used, XNBR rubber and benzene at room temperature, was unknown. However, V_r can be determined, and is defined as the fraction of the volume of rubber swollen in equilibrium given by the expression

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

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

From this expression, crosslinking density was qualitatively estimated in terms of V_r in the corresponding vulcanized compounds. The results show that there was a greater crosslink density in the compounds vulcanized with zinc peroxide (0.26) than in those vulcanized by sulphur accelerators (0.25), and gave a maximum value with the mixed crosslinking system (0.29). Similarly, after treatment with ammonia there was almost no change in the crosslink densities; 0.26, 0.27, and 0.29, respectively. This can be explained by the fact that the effect of ammonia as an ionic plasticizer is lost when the vulcanized compound is swollen by adding solvent, which leads to recovery of the structures that generate crosslinks resulting in a return to the same density.

In principle, one would also expect these compounds to have similar physical properties because they have similar crosslink densities.

Table II Mechanical Properties of Vulcanizates Before and After Ammonia Treatment

Before Ammonia Treatment			
	A	B	C
Stress at 100% strain, MPa	1.7	2.0	1.8
Stress at 300% strain, MPa	2.7	4.5	4.5
Stress at 500% strain, MPa	3.6	9.6	16.1
Tensile strength, MPa	3.9	11.6	19.6
Elongation at break, %	559	552	512
Tear strength, n	10.6	29	25.7
After Ammonia Treatment			
Stress at 100% strain, MPa	1.2	1.4	1.6
Stress at 300% strain, MPa	2.7	2.5	4.5
Tensile strength, MPa	4.1	6.1	5.4
Elongation at break, %	415	409	313

Mechanical Properties

Table II shows the mechanical properties of the vulcanized compounds. From these results the best balance of properties was obtained with vulcanization that produced ionic structures (B and C), and especially with the mixture that combined the two vulcanization systems. This is because of the existence of a rigid microphase that acts as a reinforcing agent. Vulcanization by sulphur accelerators gave poor results. On the other hand, differences in the properties cannot be explained by differences in crosslink densities measured by V_r, although they do seem to depend on the kind of crosslinking produced, with ionic crosslinks generating better mechanical properties.

The highest values of tensile strength were attributed to the possibility of stress-induced changes of the metallic carboxylate bonds because the energy for these changes is lower than that required for complete separation of the charge of two pairs of ions, according to the mechanism proposed by Chakraborty et al.[10] Likewise, higher values of the properties were obtained with a mixed peroxide/sulphur system rather than with peroxide alone, especially tensile strength and stresses at large deformations (500%). These properties can, therefore, be described as being more attributable to ionic than to covalent bonds.

Similarly, in Table II the results obtained after treatment with ammonia are recorded. When vulcanization was done using sulphur, there was no change in the properties. When zinc peroxide was used, there was a reduction in the stress at large deformations and in the tensile strength. When vulcanization was done using the mixed system, there was only a reduction in the tensile strength. Hence, dissolution of the physical crosslinks, produced by ionic aggregates, by the action of ammonia causes this reduction in the properties, especially in the tensile strength. However, covalent crosslinks remain unchanged, and as a consequence, the values of stress at high deformations when vulcanization was carried out using the mixed system were maintained.

Finally, once again it is confirmed that mechanical properties of vulcanized compounds are influenced more by the type of crosslinking than by its density of crosslinking.

Stress Relaxation

In accordance with the equation derived by Cotten and Boonstra[11]

$$\log f_1 = \log f_0 - n \log t \qquad (2)$$

where f is the stress at time t, f_0 the stress after 1 min of relaxation, and n the relaxation rate of the material. The graphical representation of $\log f/f_0$ versus $\log t$ is shown in Figure 1. The rate of relaxation, n, was determined from the slope and is recorded in Table III, together with the maximum value of stress for an initial deformation of 100%, before and after treatment with ammonia. Both are greater for vulcanized compounds with ionic crosslinks (samples B and C). However, the curves show a greater decrease in stress in vulcanized compounds for crosslink densities of the same order, which can be explained by the fact that metal peroxide produces crosslinks with a significantly lower energy than those formed by covalent bonds.

Relaxation of the vulcanized compound with the ZnO_2/sulphur mixture was fitted to two straight lines of different slope. The first corresponds to relaxation of ionic crosslinks, and the second to the slower relaxation of covalent crosslinks. The stress relaxation of the vulcanized compounds was intermediate, and was controlled by both kinds of crosslinks, producing first of all relaxation of the lower energy bonds.

After treatment with ammonia as a consequence of dissolving the ionic aggregates, the values of maximum stress and relaxation rate decreased, and in the compound vulcanized by a mixed system, had a similar value to the one

Figure 1   Relaxation stress rate: (□) sample A; (△) sample B); (◇) sample C; (▲) sample B after ammonia treatment; (◆) sample C after ammonia treatment.

vulcanised using sulphur. Similarly, relaxation was smaller after treatment with ammonia.

Dynamic Properties

The dynamic properties E', E'' and tan δ were measured at several deformations, frequencies, and temperatures. Variation of the storage modulus, E', was linear over the entire interval of deformations studied, which is logical taking into account that there are pure rubber compounds.[12]

Table III   Maximum Stress and Stress Relaxation Rate Before and After Ammonia Treatment

	A	B	C
Stress, MPa	0.95	2.6	2.7
n (*10^2)	4	13	11 and 7
Stress after, MPa	1.1	1.2	1.6
n (*10^2) after	6	10	7

Logically, vulcanization with ZnO_2, which produces ionic crosslinks, generated more rigid structures with a higher modulus than those value obtained with crosslinks with the sulphur/accelerator. The crosslinked compound obtained with the mixed system with both kinds of structure presented an intermediate storage modulus.

If the material is treated with ammonia, which produces a loss in the rigidity originated by ionic aggregates, there is a decrease in the storage modulus.

Figure 2 shows the hysteresis, or loss of energy transferred into heat in relation to the amplitude of deformation before and after treatment with ammonia. The compound vulcanized by the sulphur accelerator produced the least heat, whereas the compounds with ionic crosslinks generated more heat. This, in addition to the greater stress relaxation observed, coincides with the findings of Gent,[13] who reported a direct relation between stress relaxation and hysteresis. Nevertheless, this relation does not exist after treatment with

Figure 2   Energy loss as a function of strain amplitude. Symbols as in Figure 1.

ammonia because the compound produced by vulcanization with peroxide, which presents a relaxation slower and less pronounced than that recorded prior to treatment, is the one that generates the most heat.

Figure 3 represents the change in loss factor, tan δ, as a function of temperature for an oscillation frequency of 5 Hz and a constant dynamic deformation equal to 0.012% before and after treatment with ammonia. Before treatment, those vulcanizates with ionic crosslinks presented two transitions, whereas that corresponding to sulphur only presented one, the transition taking place at the lower temperature corresponding to the glass transition of the polymer. The transition at the higher temperature is attributed to the harder phase that arises from the ionic clusters or conglomerates.[14]

The morphological structure of the ionomers is based on the multiple cluster model,[15] in which the mobility of the polymer chains is restricted around the aggregates of the ionic salts giving rise to a hard phase. Clusters can be formed by association of multiplets. This association is favored by electrostatic interactions between the multiplets, and is opposed by the retractile elastic forces of the chain skeleton. Therefore, immobility of the polymer chains would result in a higher glass transition in vulcanized compounds with ionic structures. Indeed, Table IV shows the temperatures corresponding to the transitions observed at a vibration frequency of 5 Hz, calculated from the peaks of the tan δ versus temperature curves, together with the apparent activation energy of the relaxation process, determined from the maximum damping temperatures at several frequencies.

From the values in the table it can be deduced that the temperature of maximum damping is higher in ionic vulcanized compounds. However, the activation energies of the relaxation process do not significantly change, indicating that the relaxation taking place is the same, in this case also in the glass transition of the polymer.

Regarding the transition due to ionic structures at greater crosslinking density, it took place

Figure 3   Loss factor tan δ as a function of the temperature. Vibration frequency, 5 Hz; dynamic strain 0.012%. ($\square$) sample A; ($\triangle$) sample B; ($\diamond$) sample C; ($\blacktriangle$) sample B after ammonia treatment; ($\blacklozenge$) sample C after ammonia treatment.

at higher temperatures, and there was no significant change in activation energy.

It is believed that treatment with ammonia can form a coordinated bond with the zinc ions of zinc carboxylate salts[16,17] or can solvate the carboxylic ions,[18,19] which results in a decrease in the electrostatic interaction of the multiplets, inhibiting cluster formation. In accordance, the transition at high temperatures disappeared and the values of the physical properties decreased after treatment with ammonia. Indeed, in Figure 3 there was no transition in the region in which these were observed before the treatment, either in the sample vulcanized with peroxide (mixture B) or in the

Table IV   Maximum Damping Temperatures at Low- and High-Temperature Transitions, at a Vibration Frequency of 5 Hz, and Apparent Activation Energy (kcal/mol), Before and After Ammonia Treatment

	Before Ammonia Treatment				After Treatment	
	Low Temperature		High Temperature		Low Temperature	
Sample	T (°C)	kcal/mol	T (°C)	kcal/mol	T (°C)	kcal/mol
A	-10.7	58.9	—	—	-9.1	55.4
B	-6.7	57.6	68.7	19.6	-8.5	52.3
C	-7.5	56.8	71.5	24.4	-5.7	57.8

mixed system (mixture C). Regarding the glass transition temperature, it is shifted to lower values in the vulcanized compounds with ionic crosslinks. This occurs as a consequence of the disappearance of the restriction of chain mobility, mentioned above, with practically no change in the activation energy of the relaxation process. However, in the compound vulcanized with sulphur or with a mixed system there was a slight displacement of T_g to higher values, also without energy changes, as reflected in Table IV.

It has been mentioned previously that when the crosslink density is measured in terms of V_r, after treatment with ammonia the values obtained are close to the original ones. This has been attributed to regeneration of the ionic structures by expansion in the solvent followed by drying. When the dynamic properties of a vulcanized compound undergoing these treatment processes were determined, a new ionic transition was found to occur.

CONCLUSIONS

The properties of vulcanized XNBR depend more on the kind of crosslink formed, which varies according to the vulcanization agent, than on the crosslink density obtained.

Treatment with ammonia results in the disappearance of ionic aggregates, which decreases mechanical properties and increases heat generation and results in the disappearance of the transition at high temperature. Nevertheless, maintenance of the crosslink density after treatment with ammonia could be explained by the presence of the solvent that produces expansion and breakage of the coordinated bonds between ammonia and the zinc ions or solvates them with carboxylic ions recovering the original zinc–carboxylate crosslinks and regenerat-

ing ionic structures that produce the so-called ionic transition.

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