

# Effect of Network Heterogeneities on the Physical Properties of Nitrile Rubbers Cured with Dicumyl Peroxide

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**ABSTRACT:** The scope of this study is to continue our earlier studies on the peroxide curing of diene elastomers. The effect of peroxide content and temperature on the curing and mechanical properties of NBR and H-NBR rubbers with different acrylonitrile content was evaluated. Experimental evidence indicates that saturated rubbers behave as expected whereas in unsaturated nitrile rubbers abstraction of allylic hydrogen and addition to the double bonds can act as mechanism of crosslinking,

the weight of each mechanism is dependent of DCP content and curing temperature. The addition mechanism produces densely crosslinked zones or clusters, generating a heterogeneous network with effect on the vulcanizate properties. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 3377–3382, 2007

**Key words:** crosslinking; networks; vulcanization; nitrile rubber; physical properties

## INTRODUCTION

Crosslinking is a process of forming a three-dimensional network from a linear polymer by a chemical or physical method. Often, this process involves the utilization of sulfur or sulfur compounds. However, the crosslinking of rubbers with organic peroxides is of considerable and practical interest. Compared with sulfur vulcanization, crosslinking by peroxides is a relatively simple process, with physical properties such as high modulus, low compression set and, of course, heat aging properties superior to sulfur cure systems. On the other hand, the peroxide crosslinking has many disadvantages, such as low tensile and tear strength, and flex resistance, which have restricted their use in diene rubbers.

Peroxide interacts with polymers in a variety of ways, depending on the polymer nature, type and concentration of peroxide, reaction temperature and substances that might be present, such as antioxidants. The peroxide reaction presents several competing mechanisms, and the physical properties of vulcanized compounds will depend on the balance between these often opposite reactions.

The mechanism of peroxide crosslinking has been the subject of important reviews.<sup>1–6</sup> The reaction consists basically of three steps. First, the homolytic decomposition of the peroxide molecule to produce two radical fragments takes place.<sup>7</sup> These radicals then

remove hydrogen atoms from the polymer forming a polymer radical. This process is called hydrogen abstraction. Finally, two polymer radicals combine to form a covalent crosslink. But also, the peroxide radicals can add to a double bond present in unsaturated rubbers, a process called *addition*. In this case, the result is that the initial peroxide radical is covalently bonded to the carbon and the radical is transferred to the other carbon atom that forms the double bond. This new radical has the capacity to react with other double bonds.

In practice, and apart from other reactions that give rise to crosslinks such as chains scission, radical transfer, and  $\beta$  cleavage of the oxyradical, the peroxide radicals can basically react in both ways by addition and abstraction with a diene rubber. Both ways involve the formation of bonds between polymer chains, but give rise to important differences in the properties of the final vulcanizates.

Many unsaturated rubbers, such as natural rubber (NR), styrene–butadiene rubber (SBR), butadiene rubber (BR), and acrylonitrile–butadiene-rubber (NBR), contain a varying degree of unsaturation in the polymer backbone or in pendant positions. Peroxide radical could potentially react by addition to a double bond or by abstraction of an allylic hydrogen, and both mechanisms occur concurrently in the vulcanization of unsaturated elastomers.<sup>8–10</sup> The balance of both reaction types is influenced by polymer structure, peroxide type and concentration, and reaction temperature. The number of moles of crosslink that can be formed from a mole of peroxide is called peroxide efficiency. In the abstraction reaction, 1 mole of peroxide can only form 1 mole of crosslink, with an efficiency of 1. In an addition

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TABLE I  
NBR Compounds Formulations (phr)

	N1	N2	N3	N4	N5	N6	N7	N8	N9	N10
Nipol DN 401	100	100	100	100	100	–	–	–	–	–
Nipol DN 003	–	–	–	–	–	100	100	100	100	100
DCP	1.0	1.5	2.0	2.5	3.0	1.0	1.5	2.0	0.5	0.0

mechanism, the peroxide efficiency can be much higher because a single radical can produce the formation of several bonds. The radical peroxide can attach to a double bond followed by transfer of the radical to another chain, generating a new crosslink, but on the other hand, this addition reaction could initiate the polymerization between adjacent double bonds, on different chains, generating small but densely crosslinked polymer cluster.<sup>9</sup> The presence of such heterogeneities in the crosslinked network, with regions densely crosslinked and regions weakly crosslinked, are of great importance on the mechanical stress–strain behavior.<sup>10</sup>

In SBR, BR, and NBR elastomers, the efficiency of peroxide has been observed to be higher than 1. On the other hand, the peroxide efficiency in NBR depends on acrylic nitrile group content, presumably because of the electron-withdrawing nitrile group.

In this work, the crosslinking of two NBR and two hydrogenated acrylonitrile–butadiene rubbers (H-NBR), with low and high nitrile content, is studied. The peroxide concentration and temperature effects on the crosslinking efficiency and the physical properties of its vulcanizates are also reported. The physical properties of NBR vulcanizates that present both mechanism active, and therefore present a heterogeneous network, are compared with those obtained with saturated hydrogenated acrylonitrile–butadiene rubber (H-NBR), which does not present the addition mechanism, and therefore does not form heterogeneities in the network. This different behavior between these two types of rubbers allows us to evaluate the effect of the presence of heterogeneities in the network on the mechanical properties of rubber vulcanizates.

## EXPERIMENTAL

### Materials

Dicumyl peroxide of laboratory grade (DCP) was obtained from Merck and recrystallized from methanol and water before use.

The NBR used were Nipol DN 401 and Nipol DN 003, cold-polymerized materials containing bound acrylonitrile 18 and 50% by weight, respectively. The hydrogenated acrylonitrile–butadiene rubbers used was Zeptol 0020 and Zeptol 4310, containing bound acrylonitrile 18% and 49% by weight, respectively. Both rubbers types were manufactured by Zeon Corp., Tokyo, Japan.

### Compounding and curing

The rubber composites were prepared in a two-roll rubber mill (fraction ratio 1 : 1.4). Measurements of degree of curing were conducted in a Monsanto Moving Die Rheometer, Model MDR 2000E, (Alpha Technologies, Wiltshire, UK) The rheograms were obtained at 1.66 Hz and  $\pm 0.5^\circ$  deformation. All samples were cured in a thermofluid press at their respective optimum cure times ( $t_{97}$  of the rheograms).

### Physical testing

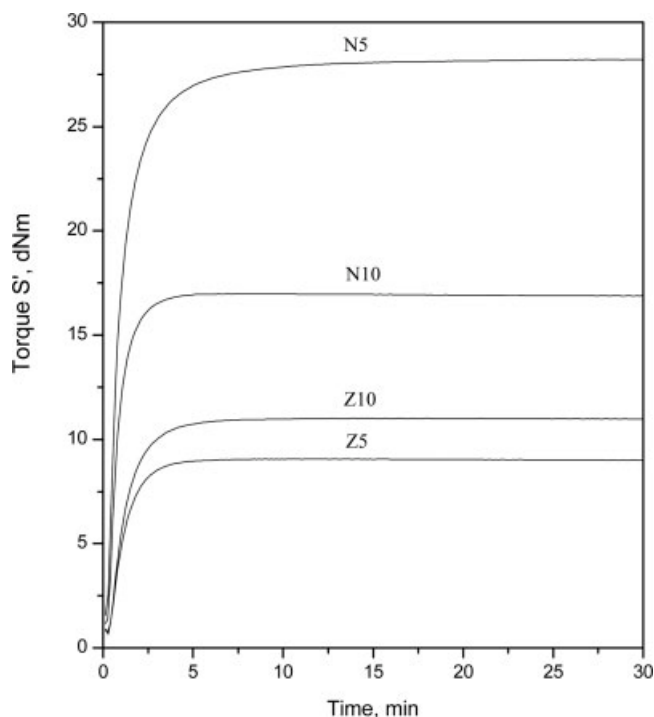
Tensile strength tests were performed a room temperature on an Instron 4301 universal testing machine (Instron, Buckinghamshire, UK), with a grip separation speed of 50 cm/min. The test samples were cut out from the vulcanized sheets using a microtensile dumbbell-type die (ISO 34, method C). All tensile results reported are the average values of five tests.

### Determination of crosslink density

Equilibrium swelling in benzene was used to determine the crosslink density of the different compounds cured at 170°C. Test samples were placed in reagent grade benzene and allowed to reach equilibrium swelling at 30°C (~ 3 days). The samples were blotted with tissue paper and immediately weighed, followed in a vacuum oven for 24 h at 60°C to completely remove the solvent, and reweighed. The  $V_r$  value (volume fraction of polymer in the swollen sample) was calculated and

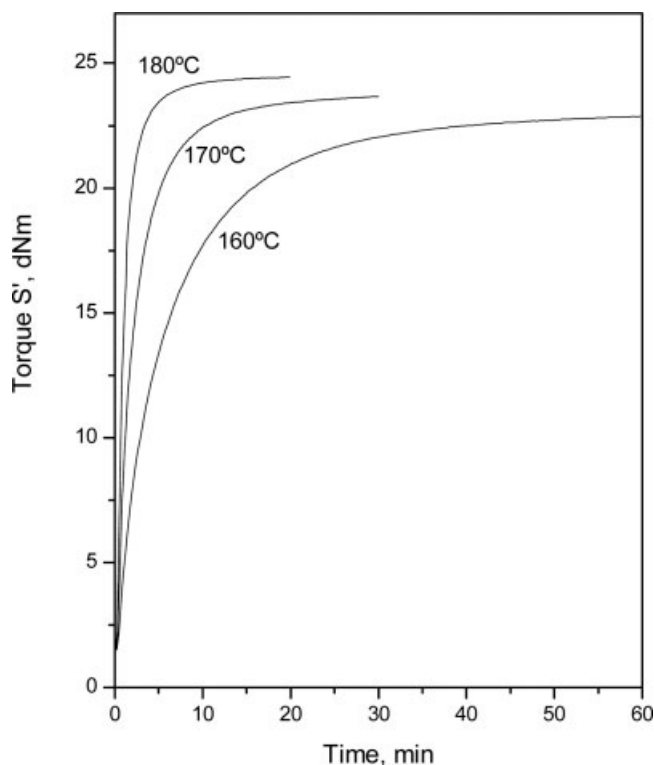
TABLE II  
H-NBR Compounds Formulations (phr)

	Z1	Z2	Z3	Z4	Z5	Z6	Z7	Z8	Z9	Z10
Zetpol 4310	100	100	100	100	100	–	–	–	–	–
Zetpol 0020	–	–	–	–	–	100	100	100	100	100
DCP	1.0	1.5	2.0	2.5	3.0	1.0	1.5	2.0	2.5	3.0



**Figure 1** Rheograms of compounds N5, N10, Z5 and Z10 cured at 180°C.

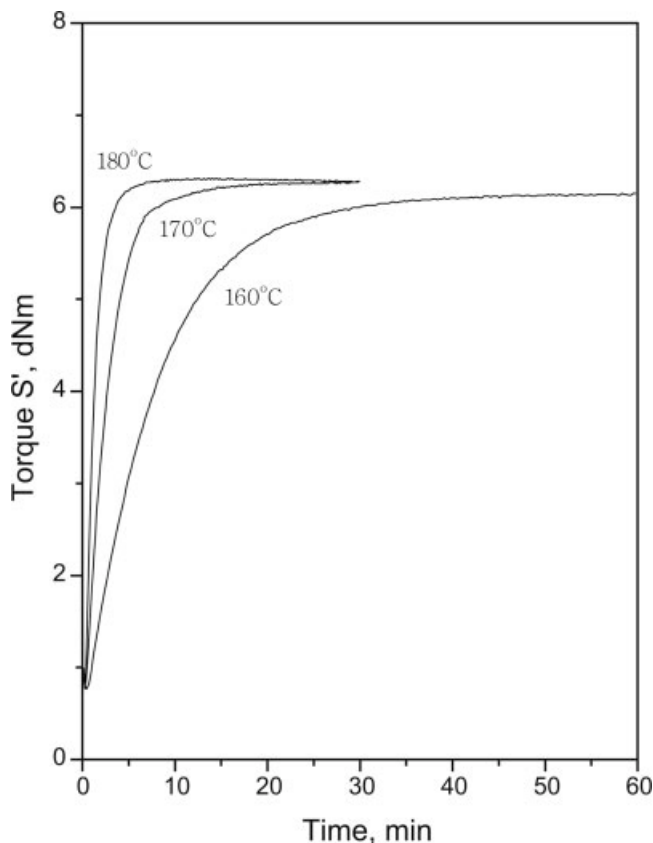
the crosslink density of the cured compounds was obtained by using the equation reported by Flory and Rehner.<sup>11</sup>



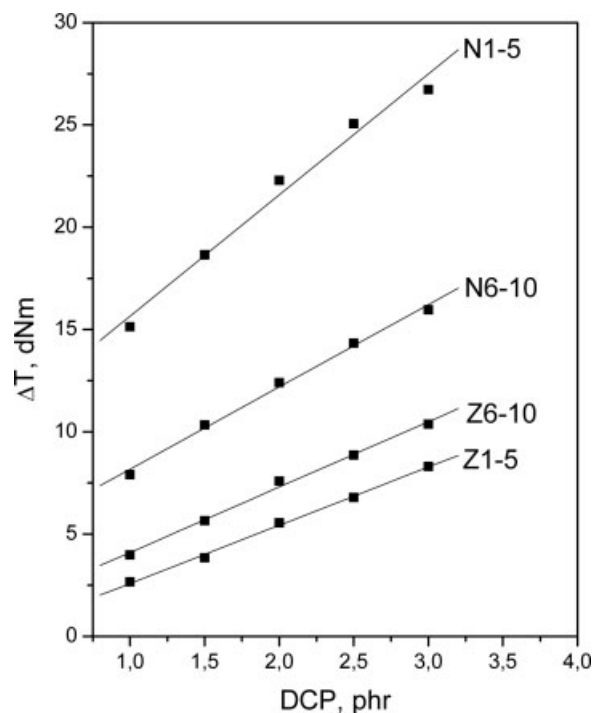
**Figure 2** Rheograms of compound N3 cured at different temperatures.

## RESULTS AND DISCUSSION

The formulations for the compounds based in NBR and H-NBR are given in Tables I and II. The crosslinking process was measured with an oscillating rheometer. Figure 1 shows the rheograms  $S'$  (elastic modulus) of compounds N5 and N10, and Z5 and Z10 cured at 180°C. These rheograms present the typical curves that would be expected for a compound crosslinked with dicumyl peroxide. The system is essentially nonreverting, and the chemical induction period is very short. The compound prepared with NBR with elevated content in unsaturation, N5, presents a very high torque increment  $\Delta T$  ( $\Delta T = T_{\max} - T_{\min}$ , where the  $T_{\max}$  and  $T_{\min}$  were the maximum and minimum torque, respectively) that corresponds to a compound with elevated crosslink density. This elevated value of  $\Delta T$  led us to think that the peroxide radical, apart from reacting via of the abstraction mechanism, can also react via addition to double bonds increasing the crosslink density. This new macroradical presents the ability to react again with other double bonds or with another radical in a termination reaction. When this addition reaction occurs, a cluster will be formed with effects on the properties of the vulcanizates. For N10, a compound prepared with a NBR with high content in acrylonitrile, the addition reaction to double bonds is more dif-



**Figure 3** Rheograms of compound Z3 cured at different temperatures.



**Figure 4** Torque increment as a function of the amount of the curing agent, vulcanized at 180°C, for the different compounds.

difficult because of the electron withdrawing nitrile groups. On the other hand, the torque maximum prepared with the saturated nitrile rubbers, Z5 and Z10, are much smaller with respect to the two unsaturated rubbers. The absence of unsaturation in these two compounds only permits the crosslinking via the abstraction mechanism, with a lesser crosslink density.

The rheograms of compound N3 cured at 160, 170, and 180°C are shown in Figure 2. The maximum torque increases with the cure temperature. The addition reaction requires a favorable orientation of the double bonds to be attacked by the polymer radical and thus it can be favored by raising the temperature to enhance molecular mobility. On the other hand, the rheograms of the compound prepared with totally saturated rub-

ber, compound Z3, cured at the same temperatures, present similar crosslink density for the three temperatures, as shown in Figure 3. Therefore, in this totally saturated rubber, the torque increment depends only on dicumyl peroxide concentration and not on the vulcanization temperature.

The variation of the torque increment,  $\Delta T$ , versus DCP content for the four series of compounds cured at 180°C is represented in Figure 4. A linear relationship can be approximated to the experimental points for the four series. The compounds prepared with saturated rubber present almost parallel lines. The difference in torque increment between the series prepared with saturated rubber can be explained as due to the increment of concentration of dicumyl peroxide with respect to the fraction of hydrogenated butadiene content that exists between both H-NBRs. Also, the higher content of acrylonitrile on Z6-10 compounds will produce harder vulcanizates with higher modulus, which will also be reflected on the torque level reached. The compounds prepared with unsaturated rubbers also show a linear behavior but with higher slopes, especially for the compounds N1-5 based on Nipol DN 401, the grade presenting higher content in unsaturation. These high values can be attributed to the "polymerization" of double bonds of close polymer chains. This reaction would be favored by temperature and DCP concentration.<sup>7</sup> As already reasoned in the Z series compounds, the N6-10 compounds, with higher acrylonitrile content, would be expected to reach higher torque values than the N1-5 compounds. However, the latter reach far higher torque. For these compounds, we think that the addition mechanism is favored by the higher concentration of butadiene units, producing higher crosslink density. This explains also the measured slopes, because due to the temperature dependence on the addition mechanism, the higher weight of this mechanism produces higher slopes.

The cure data and physical properties of all the compounds cured at 170°C are given in Table III and IV. The curing times for the series of compounds N1-5, with rubber containing 81% of butadiene, are longer

**TABLE III**  
Cure Parameters and Physical Properties for NBR Compounds Cured at 170°C

	$t_{97}$ (min)	$T_{max}$ (dNm)	$\Delta T$ (dNm)	Modulus 300 (MPa)	Tensile strength (MPa)	Elongation at break (%)	Hardness, Shore A	Crosslink density, $\nu$ ( $10^5$ ) (mol/g)
N1	13.6	15.8	14.4	—	3.7	130	54.2	10.21
N2	13.7	20.7	19.1	—	3.5	90	57.1	12.74
N3	13.6	23.7	22	—	3.3	70	59.5	19.32
N4	13.6	26.9	25.3	—	2	45	63	22.28
N5	13.6	28	26.5	—	1.6	40	65.7	24.54
N6	9.2	9.2	8.2	2.2	14.3	700	49.4	4.66
N7	7.9	12	10.8	3.3	17.6	620	50	6.13
N8	7.6	14	12.9	4.2	19	520	51.2	7.73
N9	7.5	14.3	13.2	5.2	16	450	51.5	11.82
N10	7.1	16.9	15.9	8.6	10.6	330	53	14.79



TABLE IV  
Cure Parameters and Physical Properties for H-NBR Compounds Cured at 170°C

	$t_{97}$ (min)	$T_{\max}$ (dNm)	$\Delta T$ (dNm)	Modulus 300 (MPa)	Tensile strength (MPa)	Elongation at break (%)	Hardness, Shore A	Crosslink density $\nu$ ( $10^5$ ) (mol/g)
Z1	12	3.5	2.7	1.8	12.2	750	35.2	0.69
Z2	11	4.8	4	1.9	14.8	650	37.6	1.76
Z3	10.5	6.5	5.7	2.5	7.6	530	40.6	3.52
Z4	10	7.3	6.5	2.8	5.4	400	42.4	4.45
Z5	10	8.8	7.8	3	4.1	310	44	5.7
Z6	15.5	4.9	4.2	1.1	19.6	800	48.7	1.86
Z7	14	6.6	6	1.2	20.3	720	50.4	3.07
Z8	13	8.4	7.7	1.5	26.6	670	51.4	5.21
Z9	12.3	9.7	9	1.6	25	650	51.5	6.19
Z10	12	11	10.3	1.9	23.5	600	52.3	7.35

than those presented for the series compounds N6-10, prepared with rubber with a butadiene content of 50%. The tensile strength and elongation at break of N1-5 series are very low, and although they present higher Shore hardness values, as corresponding to compounds with elevated crosslink density. The values are even higher than for compounds with elevated content in acrylonitrile, series N6-10 and Z6-10, despite it is very well-known that, when the acrylonitrile content is increased in the nitrile rubber, compounds with high hardness are obtained.

The tensile strength values for the series of compounds N6-10, cured at 170°C for their optimum cure time and with increase in the peroxide concentration, are much higher than those corresponding to the series N1-5. This behavior can be explained by the fact that we are in presence of a uniform network, a material with homogeneous crosslink distribution, which is cured fundamentally through the hydrogen abstraction mechanism. The shore A hardness increases also with peroxide concentration, an indication of the increase in crosslink density of the vulcanizates.

The physical properties for the series prepared with saturated nitrilic rubbers, cured at 170°C, increase with peroxide proportions. The moduli at 300% increase with peroxide concentration. In both series, the tensile strength passes through a maximum and then decreases with peroxide content. The elongation at break diminishes with peroxide concentration. The shore A hardness values increase proportionally to dicumyl peroxide proportion. In this totally hydrogenated acry-

lonitrile-butadiene rubbers, the crosslinking is possible only through the hydrogen abstraction mechanism, without the formation of inhomogeneities in the network, which are generated when double bonds exist in the polymer and addition mechanism takes place.

The physical properties obtained on the dicumyl peroxide crosslinked NBR and H-NBR elastomers provide evidence that the peroxide radical can act through abstraction and addition mechanisms in case of unsaturated rubbers, with formation of over-crosslinked domains (or clusters), while the hydrogenated rubbers can only be crosslinked via abstraction mechanism. In the latter, the crosslinks must be uniformly distributed in the material. Figure 5 shows a heterogeneous network model, presenting zones with high crosslinking density. In this complex topology, the network chains will bear different forces when the material is continuously deformed, magnifying chain forces locally. This is the start of molecular fracture, a precursor to crack formation: the chain breaking quickly and transfers the load to surrounding chains, which in turn become overloaded and break. When the molecular fracture is initiated, surrounding chains break quickly. The over crosslinked region (cluster) will experience the highest forces and a network strand will reach a critical force and break. Some chains in this cluster surpass the critical stress levels and their rupture is focalized in such a way that an anticipated material rupture is induced. This can explain the significantly lower tensile strength of NBR compound with elevated unsaturation.

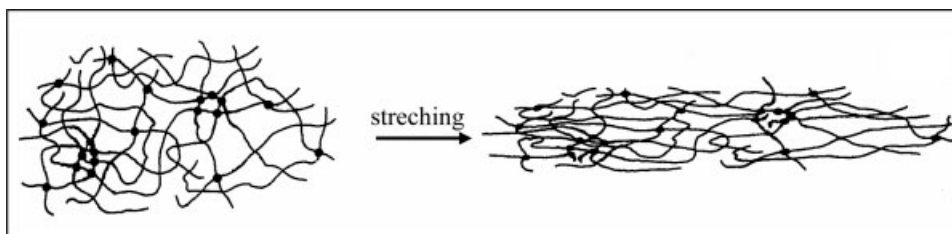


Figure 5 Model of heterogeneous network. The circles represent junctions. The picture present cluster before deformation and chain breaking in the deformed clusters.

## CONCLUSIONS

Several saturated and unsaturated nitrile rubbers were crosslinked with DCP in different conditions and their tensile properties evaluated.

Torque values reach higher values for unsaturated rubbers than for saturated rubbers. For saturated rubbers, torque increases with acrylonitrile content, whereas for the unsaturated compounds, the higher value is for lower acrylonitrile content. For both rubber types, an increase in DCP content leads to an increase in torque, but whereas for saturated rubber, the increase is temperature independent, for unsaturated rubber, torque value increases with temperature increment, and this increase being more pronounced for the low acrylonitrile content grade.

This behavior is explained on the basis of two possible crosslinking mechanisms, abstraction and addition. In saturated rubbers, only abstraction can take place, whereas in unsaturated rubbers addition to chain double bonds is also important, especially at higher double bond content and higher temperature, increasing the crosslink density.

Tensile stress-strain measurements fit this picture. Properties are lower and hardness higher for unsaturated rubbers, compared to their saturated counterparts, especially for the grade with lower acrylonitrile

content. Based on the proposed mechanism, it is supposed that the crosslinking generated by addition produces highly crosslinked local areas that trigger early failure.

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