Dicumyl Peroxide Cross-Linking of Nitrile Rubbers with Different Content in Acrylonitrile

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ABSTRACT: The scope of this article is the study of peroxide curing of two nitrile rubbers with low and high nitrile content. The peroxide efficiency can be much higher than one, and the polymer structure determines the mechanism of cross-linking. In the rubber with low nitrile content, the peroxide radical may give rise to a polymerization reaction between adjacent double bonds generating a heterogeneous network with a negative effect on the vulcanizate properties. On the contrary, in the nitrile rubber with high nitrile content, this negative effect it is not present or is present to a lesser extent, and their vulcanizates show good physical properties. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 1–5, 2005

Key words: rubber; cross-linking density; mechanical properties

INTRODUCTION

The cross-linking of rubber with organic peroxide is of considerable and practical interest. The peroxides produce vulcanizates with physical properties such as high modulus, high hardness, and low compression set and, of course, their heat aging properties are far superior to sulfur cure systems. On the other hand, the peroxide systems have disadvantages, the vulcanizates present low tensile and tear strengths, a slower rate of cure, and lack of delayed action during cure. These factors have drastically restricted their use in diene rubbers.

Peroxides interact with polymers in a variety of ways. The effect that a peroxide has on the cross-linking reaction depends on the polymer nature, type, and concentration of peroxide, reaction temperature, and reactivity of other components that might be present (i.e., antioxidants). The peroxide reaction consists of several competing mechanisms, and the properties of the final cure state will depend on the balance between these often opposite reactions.

The mechanism of peroxide vulcanization has been the subject of important reviews.[1–5] The cross-linking reaction involves the homolytic decomposition of the peroxide molecule to produce two radical fragments.[6] Next, these radicals remove hydrogen atoms from the polymer forming a polymer radical in what is called the *hydrogen abstraction* reaction. Also, these peroxide radicals could add to a double bond present in unsaturated rubbers and generate a polymer radical. Finally, two polymer radicals combine to form a covalent cross-link. Although nominally this reaction is relatively simple, the reaction usually is quite complex due to numerous side reactions that can occur. Some of these reactions may increase the cross-link, making the peroxide radical more efficient. Thus, the generated macroradical can react with an unsaturated rubber chain by addition to a double bond. This would lead to a new macroradical with the ability to react again with other double bonds or with another radical in a termination reaction.

Basically, the peroxide radicals could react in both ways by *addition* and *abstraction*, with a diene rubber. Both ways involve the formation of bonds between polymer chains, but there are important differences in the effect that each one could have on the properties of the final vulcanizates.

Many unsaturated rubbers such as natural rubber (NR), styrene-butadiene rubber (SBR), polybutadiene rubber (BR), and butadiene-acrilo-nitrile rubber (NBR) contain a varying degree of unsaturation in the polymer backbone or in pendant positions.[1] A peroxide radical potentially could react by addition to a double bond or by abstraction of an allylic hydrogen. The number of moles of cross-links that can be formed from a mole of peroxide is called peroxide efficiency. In the abstraction reaction, 1 mol of peroxide can form only 1 mol of cross-link; therefore, the peroxide efficiency is 1. In an addition mechanism, the peroxide efficiency can be much higher because one radical can produce the formation of several bonds. Because several cross-links induced by the addition reaction attach several chains, these interchain bonds could form

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a cluster that should have an impact on the properties of the vulcanizates.[2,3] In SBR and *cis*-BR elastomers, efficiency of peroxide has been observed to be ≥10.[1] This high peroxide efficiency suggests that for these polymer structures, there is competition between the hydrogen abstraction and addition reactions.[7] On the contrary, the peroxide efficiency in nitrile rubber has been reported to be one that indicates that abstraction is predominant,[1] presumably because of the electron-withdrawing nitrile group.

In this work, we studied the efficiency of dicumyl peroxide in the cross-link of two NBR rubbers with low and high nitrile content. The number of cross-links formed was obtained from equilibrium swelling measurements. In addition, this article reports on the peroxide concentration and the temperature effects on the cross-linking efficiency and the physical properties of its vulcanizates.

EXPERIMENTAL

Materials

The bis(α,α-dimethyl benzyl) peroxide (DCP), laboratory grade, was obtained from Merck (Darmstadt, Germany) and recrystallized from methanol and water before use. The nitrile rubbers were Krynac 1965 and Krynac 5075 (Bayer AG, Leverkusem, Germany), the cold polymerized type, containing 81 and 50% butadiene, respectively.

Blending and curing

The master batches were compounded on a two-roll mill at a temperature of 40–50°C. Measurements of the degree of curing were conducted in a Monsanto moving die rheometer, model MDR 2000 E (Alpha Technologies, Wilshire, U.K.), and in a rubber process analyzer (RPA 2000; Alpha Technologies). All samples for physical testing were cured in a thermofluid press at their respective optimum cure times.

Physical testing

Tensile strength tests were performed at room temperature, according to the International Organization for Standardization (ISO 37), in an Instron tensile tester, model 4361 (Instron Ltd., Buckinghamshire, U.K.), with a grip separation speed of 50 cm/min. The test samples were cut out from vulcanizate sheets using a microtensile dumbbell-type die. All tensile results reported are the average values of five tests.

Determination of cross-link density

The volume fraction of rubber in the swollen network of the vulcanizates V_r, was determined by means of

TABLE I
Compounds Formulations (phr)

Compounds	1	2	3	4	5	6
Krynac 1965	100	100	100	—	—	—
Krynac 5075	—	—	—	100	100	100
DCP	1.0	1.5	2.0	1.0	1.5	2.0

equilibrium swelling in toluene, laboratory grade (Merck), at 30°C. The equilibrium swelling ratio was used to calculate the cross-link density, applying the Flory-Rehner equation.[8]

Infrared spectra

A Fourier transform infrared (FTIR) spectrophotometer Model Spectrum One (Perkin-Elmer Instruments, Norwalk, CT), with a universal attenuated total reflection (ATR) sampling accessory, was used to record the spectra of cured samples. Resolution was 4 cm^{-1} and the spectra were the average of four scans.

DMTA measurements

Viscoelastic dynamic measurements were conducted on a strip cut from the vulcanizate sheets, using a Metravib Viscoelasticimeter, model Mark 03 (Metravib RDS, Limonest, France), at a frequency of 5 Hz. The samples were heated stepwise, covering a range from −60 to 60°C.

RESULTS AND DISCUSSION

The formulations for the compounds are given in Table I. The cross-linking process was measured with an oscillating rheometer. The rheograms of compounds 3 and 6 at 140, 150, 160, and 170°C are shown in Figure 1. The torque increment (ΔT) is a quantitative assessment of the cross-link density of a vulcanizate, and, as such, it is an effective means for measuring the effect of an additive on the cure efficiency.

Maximum torque of compound 3 increases with the cure temperature, whereas, compound 6 practically is not affected by the cure temperature. Note that torque maxima for compound 3 are very high with respect to compound 6 with a lesser butadiene content.

These elevated values of ΔT for compound 3 led us to believe that the peroxide radical, apart for reacting with the diene rubber via the abstraction mechanism, also can initiate the addition reaction to double bonds, giving an important increase in cross-link density. When these interchain bonds occur, they will form a cluster that will impact on the properties of the vulcanizates.

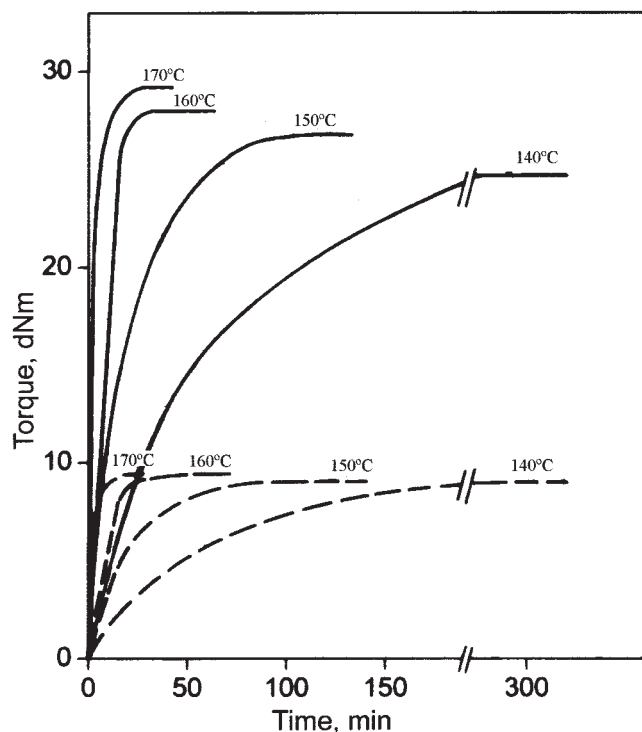Figure 2 shows the ΔT for all compounds at different temperatures and dicumyl peroxide concentra-

Figure 1 Rheograms of compounds 3 (—) and 6 (—)cured at different temperatures at 0.5° arc and 100 cpm.

tions. The Krynac 5075 compounds show that torque increment depends only on dicumyl peroxide concentration and not on the cure temperature, whereas for Krynac 1975, the rubber with a higher content in butadiene, ΔT depends on both temperature and peroxide concentration.

The peroxide radical is in the presence of an environment rich in allylic hydrogen. The addition reaction requires a favorable orientation of the double bond to be attacked by the macroradical and it can be boosted by raising the temperature to enhance molecular mobility and, hence, the probability to induce the reaction.

These much elevated values of ΔT for compound 3 led us to suppose that cracks could develop in the rheometer die under more elevated shear deformation. For this reason, we resorted to a rubber process analyser (RPA 2000) to study the cure state at a strain amplitude of 5° (arc angle), which corresponds to 70% of shear deformation. Figure 3 shows the rheograms for compounds 3 and 6 cured at 170°C at a strain amplitude of 5°. In the vulcanization of compound 3, S'' starts to grow when S' is still increasing, and therefore the peroxide is not consumed completely yet. Finally, when S' surpasses the maximum, it starts a decrease that we attribute to the sample subjected to high deformation, cracking within the rheometer chamber, with the correspondent decrease in elastic modulus S' and an increase in loss modulus S''. Effectively, the material extracted from the rheometer
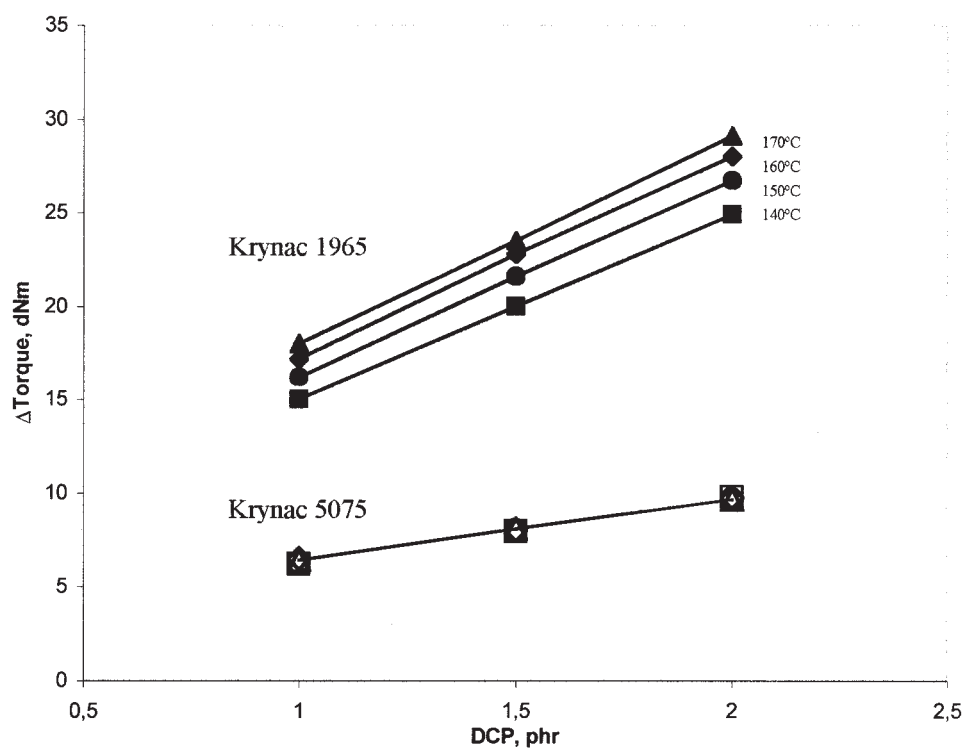

Figure 2 Torque increment as a function of the amount of curing agent at different temperatures.
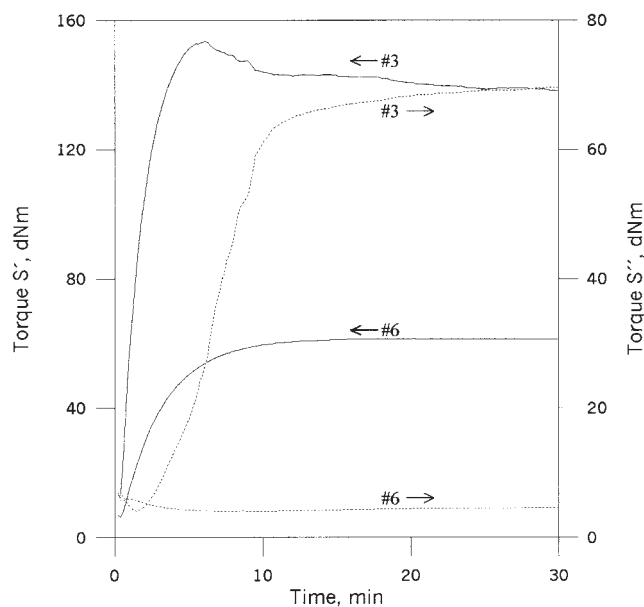
Figure 3 Rheograms of compounds 3 and 6 cured at 170°C at 5° arc and 100 cpm.

Figure 4 IR spectra of Krynac 1965, compound 3, uncured and cured at 170°C.

chamber is very stiff and brittle and crushes in the grooves while it is in the chamber.[9] On the other hand, compound 6 presents the usual behavior and elastic modulus S' increases with the cross-link reaction, reaching a plateau, and the loss modulus S″ decreases reaching a plateau also.

Table II shows the variation in cross-link density for the compounds cured at 140 and 160°C for their optimum times. Compound 3 presents very high values of cross-link density compared with the theoretical values. Increasing cure temperature also increases cross-linking degree. These high values can be attributed to the "polymerization" of double bonds of the polymer. On the other hand, compound 6 presents a cross-link density a little higher than the theoretical value, accounting for some entanglement and minor addition reaction contributions. Presumably, the addition reac-

TABLE II
Network Chain Density the Using Swelling Method

Compounds	Theoretical network density[a] (mol/cm^3, $\times 10^5$)	Network density by the swelling method (mol/cm^3, $\times 10^5$)	
		140°C	160°C
1	3.4	21.2	24.2
2	5.1	35.2	38.2
3	6.8	45.0	48.8
4	3.7	6.4	6.5
5	5.5	12.2	12.4
6	7.4	15.8	15.5

[a] One cross-link formed per one DCP molecule.

tion is difficult in this rubber with a higher content in the electron-withdrawing nitrile group.

The greater efficiency of peroxide could be caused by the polymerization reaction, and this fact could be appropriately checked by means of IR spectroscopy. Figure 4 shows the IR spectra of compound 3 cured at 170°C with 2 parts of dicumyl peroxide. The spectra only take up the frequency range between 1200 and 600 cm^{-1}, where bands at 966, 728, and 911 cm^{-1} appear, corresponding to the out-of-plane deformation γ (=C-H) *trans*, γ (=C-H) *cis*, and ω (=CH$_2$) *vinyl*, respectively. The rubber Krynac 1965 shows a decrease in *cis* and *vinyl* bands, the *trans* band remaining unmodified. On the contrary, compound 6 cured at 170°C presents an IR spectrum similar to it (uncured), without changes in the unsaturation bands.

The physical properties of compounds cured at 170°C for their optimum cure times are given in Table III. The Shore A hardness, for compounds 1, 2, and 3, increases with the peroxide concentration, which is an indication of the elevated cross-link density of the vulcanizates. At the same time, the tensile strengths are very low. This spectacular drop can be again explained by the fact that during cross-linking with peroxide the macroradicals react with the diene rubber also by producing the addition of the double bonds. This mechanism would give rise to a relatively small volume of densely cross-linked polymer ("cluster").

TABLE III
Physical Properties of the Compounds Cured at 160°C and Their Optimum Cure Times t_{97}.

Compound	1	2	3	4	5	6
Shore A hardeness	56.0	58.5	62.0	55.0	55.5	57.5
Stress at 300% (MPa)	—	—	—	2.9	3.4	3.9
Tensile strength (MPa)	2.0	1.6	1.7	14.6	18.0	19.5
Elongation at break (%)	90	60	45	700	630	550

Obviously, when a heterogeneous network is subjected to strain, the nonuniform stress distribution may induce anticipated material rupture. In contrast to this, compounds 4, 5, and 6 present very high tensile strength values, and the Shore A hardness values are much lower, an indication of a network with minor cross-link density. We think that this response corresponds to a uniform network, a material with homogeneous cross-link distribution that is cured fundamentally through the hydrogen abstraction mechanism.

The variation of tan δ with the temperature for different compounds cured at 160°C at their optimum cure times is shown in Figure 5. The peak maximum corresponds to the T_g of the cross-linked rubber and its value for the compound is shifted to higher temperatures when the cross-link density increases, producing a lower molecular mobility. For the compounds prepared with Krynac 1965, which incorporate 80% of butadiene, the T_g shifting toward higher temperatures is very important and may be attributed to the formation of more densely cross-linked networks because of the "polymerization" of rubber double bonds. On the contrary, for the compounds prepared with Krynac 5075, which incorporate 50% of butadiene, the T_g shift toward higher temperatures is negligible and the samples show practically overlapping graphs, which suggest that they are compounds with similar networks. In this case, we assume the predominant cross-linking mechanism to be abstraction, which implies that the dicumyl peroxide efficiency is close to unity.

CONCLUSIONS

A very different curing behavior has been found in two NBR rubbers differing in butadiene content. The curing of the high butadiene NBR rubber depends not only on peroxide content but also on cure temperature, and the maximum torque reached in the rheometer is far superior to that reached by the low butadiene NBR rubber.

In addition, when shear deformation is substantially increased, the high butadiene NBR rubber develops cracks in the rheometer chamber, and S'' follows an unusual trend.

The differences in peroxide curing for these NBR rubbers are explained by an addition mechanism or "polymerization" between the double bond of adjacent rubber chains taking place at the high butadiene rubber and is supported by the decrease in double bond bands measured by FTIR and the noticeable increase in T_g measured by DMTA.

"Polymerization" of double bonds produces areas of high cross-link density or clusters that induce early failure, as it can be seen by the dramatic drop in physical properties for the high butadiene NBR rubber with respect to the low butadiene NBR rubber.

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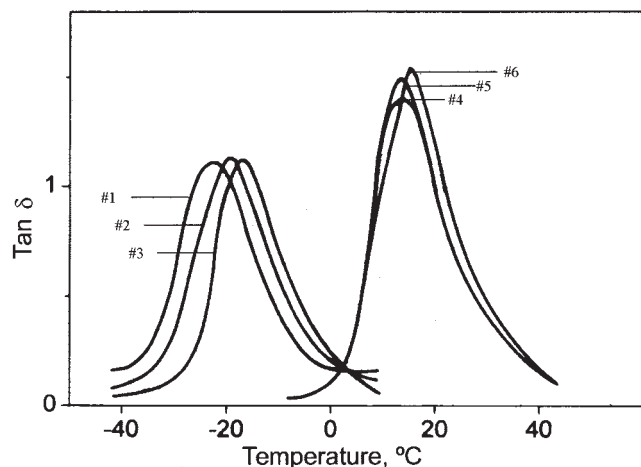9. González, L.; Rodríguez, A.; del Campo, A.; Marcos-Fernández, A. Polym Int 2004, 53, 1426.

Figure 5 Loss tangent versus temperature for all compounds cured at 170°C for their optimum cure time.