Effect of Different Cross-Linking Systems on Properties of Highly Saturated Nitrile Rubber Compounds

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SYNOPSIS

The peroxide curing of highly saturated nitrile rubber was analyzed. Reactions such as chain scission occurred that account for the drop in physical properties. The results are compared with an alternative cross-linking that is currently being assessed. With a new curing agent the chain-scission reaction was not present and the properties of the compounds were improved. Finally, an estimation of the free volume of the materials tested was attempted by using the WLF equation. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Hydrogenated nitrilic rubbers (HNBR) are the result of selective hydrogenation of the respective acrylonitrile butadiene copolymer (NBR).[1-4]

With an increasing degree of hydrogenation, resistance against heat, ozone, and organic fluids improve notably. Behavior at low temperatures measured in terms of elasticity preservation, also increases with polymer saturation.

The blending and transformation capacity of HNBR, due to the polyethylene portion in the polymeric chain, shows a similar behavior to that of NBR, from which it derives. By the same token HNBR can be cross-linked by the same agents as NBR by means of peroxides or sulfur-accelerator systems.

For polymers hydrogenated above 95%, the peroxide system proves to be the most appropriate cross-linking agent, whereas sulfur accelerator is the system of choice for polymers with lower degrees of hydrogenation, generally with a saturation level of 90%.

The use of radicals in elastomer curing, apart from the cross-linking process, may trigger other reactions without giving rise cross-links, such as chain scission, radical destruction by bimolecular disproportionation, etc., with the result that the efficiency potential of cross-linking with peroxides is lessened.

In this work three highly saturated nitrile rubbers with 0.1, 2.1, and 4.7 mol % "insaturation," respectively, were cured with dicumyl peroxide (DCP) with the purpose of determining peroxide efficiency of the cross-link reaction. The performance data obtained are then compared to those of an alternative cross-linking system being assessed in our laboratory for the curing of saturated and slightly insaturated polymers. This system exploited the different reaction capacity from the azide function. The reactive used is benzene 1,3 disulphonyl azide (BSA).[5]

EXPERIMENTAL

Materials

The elastomers used were Tornac A, B, and C with an insaturation of 0.1, 2.1, and 4.7 mol %, respectively (manufactured by Bayer–Polysar) with an acrylonitrile content of 39 mol %. DCP, 97%, was supplied by Merck. The BSA was prepared by reacting 1,3 benzene dichloro-sulfonyl with sodium azide[4]:

BSA
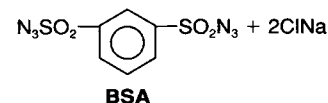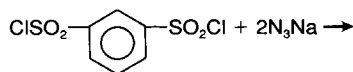
Compounding and Curing

The rubber composites were prepared in a two-roll rubber mill (friction ratio 1 : 1.4). Optimum curing times of the samples were measured with a Monsanto rheometer, model MDR 2000E. The physical properties were determined according to national standards using compounds cured at their respective optimum times ($t_{c,97}$ of the rheograms) at 160°C in a thermofluid-heated press.

The experimental apparent degree of cross-linking was determined by means of the polymer volume fraction in the swollen network, V_r. As the vulcanizates under study are filled with carbon black, the volume fractions of swollen rubber are calculated assuming simple additivity of the different portions, in conformity with the following formula:

$$V_r = (D - FT)\delta_r^{-1}/[(D - FT)\delta_r^{-1} + A\delta_s^{-1}]$$

where T expresses the weight of the test specimen; D the unswollen weight; F the weight fraction of insoluble components in the sample; A the weight of the adsorbed solvent; and δ_r and δ_s represent the rubber and solvent densities, respectively.

As the carbon black presents strong physical and chemical adsorptions, filler addition may change the cross-linking density in the polymer matrix. However, as the filler portions are always the same, the differences in cross-link density can be attributed exclusively to the curing system.

Dynamic Mechanical Measurements

Viscoelastic dynamic measurements were conducted by means of tensile compression on strips of 4 × 2 × 10 mm cut from the network sheets, with a Metravib Viscoelasticimeter at frequencies of 5, 7, 10, 15, 50, and 100 Hz. The dynamic deformation was 15 μm. The samples were heated, not in the continuous mode, but in stages in the range of −90–25°C.

RESULTS

The range of the cross-linking reaction over time was measured on a Monsanto rheometer. The induction time t_i and the curing rate constant k were determined following Scheele's method.[5] The appropriate function describing the cross-linking reaction is an exponential function of the type:

$$M_t - M_{min} = (M_{max} - M_{min})(1 - e^{-k(t - t_i)})$$

where M_{max}, M_{min}, and M_t are the torque maximum,

minimum, and at time t, respectively. The vulcanization curves of Tornac A with 3 phr of BSA in the presence of 45 phr of carbon black type N 330 (HAF), at different temperatures are shown in Figure 1. The curing reaction adjusts to a first-order kinetics. Table I compiles the induction times, rate constants, and the activation energy. As can be observed, both induction times and rate constants increase with polymer insaturation. However, the activation energy of the curing reaction decreases with saturation increase.

In order to compare the cross-linking capacity of BSA to that of DCP, the volume fractions V_r in the cross-linked and swollen samples were measured. The molar ratio of the cross-linking agents is the same, varying only the degree of polymer insaturation. In Table II the formulations of the different composites are listed.

V_r variation as a function of polymer insaturation for the BSA and DCP cross-linked compounds is shown in Figure 2. As expected, the chain density of the BSA cross-linked compound does not vary with the insaturation of the rubber. For the DCP samples, however, cross-link density increases proportionate to polymer insaturation. The reaction efficiency improves with the content of double bonds in the rubber. The most saturated polymer, when cross-linked with DCP shows a lower V_r value than the respective BSA sample. However, the molar concentration of both cured agents is the same.

The physical properties of the different HNBR composites filled with 45 phr carbon black and cured with BSA and DCP are compiled in Table III. The optimum curing times for the BSA samples drop significantly with increasing degree of insaturation. In contrast, in DCP curing the optimum time does not vary with the polymer insaturation.
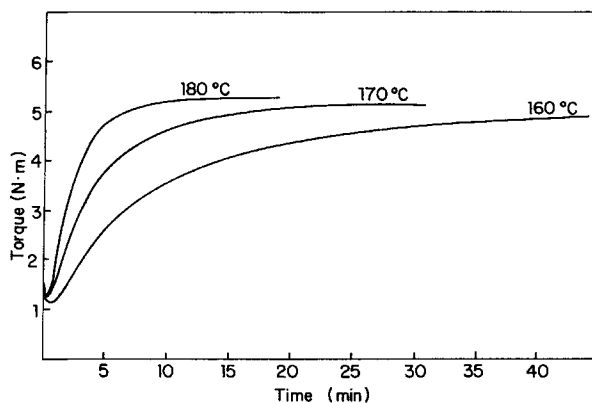
Figure 1 Curve-rheometer of Tornac A compound cured at different temperatures with 3 phr of BSA.

Table I Kinetic Parameters of HNBR Cured with BSA

Temperatures (°C)	Sample					
	TA/1		TB/1		TC/1	
	t_1 (min)	k (min^{-1})	t_1 (min)	k (min^{-1})	t_1 (min)	k (min^{-1})
160	1.64	0.0831	1.4	0.1461	2.4	0.2633
170	1.20	0.1994	1.68	0.2920	1.83	0.4789
180	0.79	0.4538	1.13	0.6002	1.46	0.7357
E_a (kJ/mol)	138.37		115.19		83.89	

Formulations in Table II.

As regard the mechanical properties, the most saturated polymer (Tornac A), when cross-linked with BSA, presents higher tensile strengths and moduli values than when it is cured with DCP. The difference between the two cross-linking agents is less spectacular in the more unsaturated polymers, although the moduli and elongation are higher for the BSA samples.

When subjected to accelerated thermal ageing at 150°C for 7 days, all the experimental compounds show a similar behavior, with a high degree of property retention, independent of the cross-linking agent.

Finally a dynamic mechanical study was conducted with the most saturated rubber (Tornac A), both with BSA and DCP vulcanizates. As expected, the active fillers adsorb the polymer with the consequential reduction in the molecular mobility of the polymer. In our case, the nature and volume of the filler are the same for both composites, and hence the changes observed in network elasticity are exclusively attributable to the effect of the cross-linking agent. The changes brought about in the polymer (molecular weight, cross-link densities, etc.) during the curing process have an immediate impact on the glass-transition temperature, T_g, of the composite.

Table IV compiles the values of E_a, the apparent activation energy necessary to activate segmental movements in the network during the relaxation process. This E_a is obtained from the position of the maximum loss peak (tan δ_{max}) at different frequencies. In addition, Table IV shows the T_gs of the two networks at 5 Hz, as well as the volume fractions of the swollen rubber, V_r, which were used to represent the cross-link density of the cured compounds.

The standardized plots of the elastic modulus E' against frequency were used to calculate the free volume fraction (Fig. 3). The constants C_1 and C_2 of the Williams–Laudel–Ferry (WFL) equation allow the calculation of the free volume of the network. Following the free volume theory and taking into account the temperature-dependence of the parameter, C_1 and C_2 are defined in the expressions[6]:

$$C_1 = B/2.303 f_g \quad \text{and} \quad C_2 = f_g/a_r$$

where B is an empirical constant whose value approaches 1; f_g stands for free volume at glass transition; and a_r is the thermal expansion coefficient above T_g. The value of a_r of the vulcanizates was determined by means of thermal mechanical analysis (TMA). Replacing C_1 and C_2 in the WLF equa-

Table II Rubber Vulcanizates Formulations (phr)

	Sample					
	TA/1	TA/2	TB/1	TB/2	TC/1	TC/2
Polymer	100	100	100	100	100	100
Carbon black[a]	45	45	45	45	45	45
Maglite D[b]	5	5	5	5	5	5
BSA	3	—	3	—	3	—
DCP	—	2.81	—	2.81	—	2.81

[a] N-330.
[b] MgO.
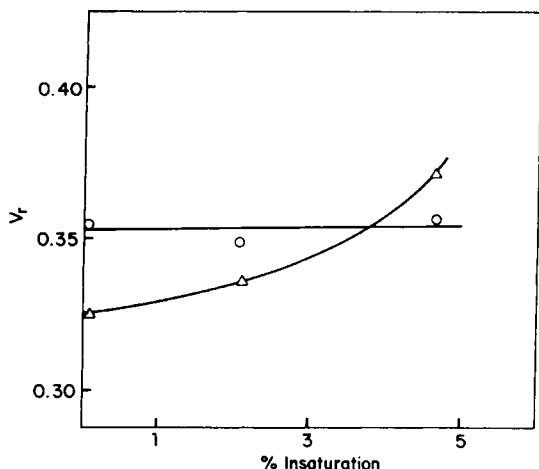
Figure 2 The volume fraction of polymer at maximum degree of swelling (V_r) as a function of polymer insaturation, for (O) BSA and (△) DCP cured compounds.

tion for their respective expressions, the equation can be rewritten as:

$$-1/2.303 f_g[(T - T_g)/\log \alpha_T]$$

$$= f_g/a_r + a_r(T - T_g)$$

which now allows the calculation of the free volume f_g, whose values are listed in Table IV.
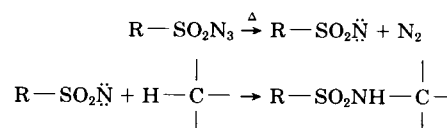
DISCUSSION

The BSA cross-link, based on the most favorable mechanisms at least for saturated polymers, occurs when the nitrene generated during the thermal or photomechanical decomposition of an azide group
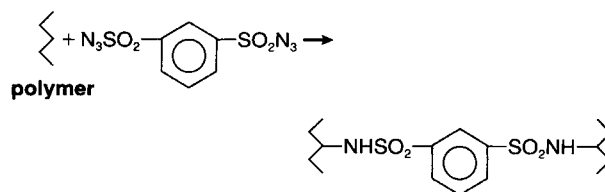
Table IV   Various Properties of Tornac A Vulcanizates

Cure Agent	E_a (kJ/mol)	T_g (°C)	V_r	f_g
BSA	198	−5.5	0.3553	0.0178
DCP	170	−11.3	0.3241	0.0249

E_a, activation energy; T_g, glass-transition temperature; V_r, volume fraction swollen of rubber; f_g, free volume fraction.

extracts one hydrogen from the polymer and is then linked to it.

$$R-SO_2N_3 \xrightarrow{\Delta} R-SO_2\ddot{N} + N_2$$

$$R-SO_2\ddot{N} + H-\overset{|}{\underset{|}{C}}- \rightarrow R-SO_2NH-\overset{|}{\underset{|}{C}}-$$

and in our case with BSA.

These thermolysis reactions of sulfonyl azide are adjusted to first-order plots, generally to 90% reaction. The decisive step in the reaction rate is the loss of a nitrogen molecule to form the active species nitrene, which reacts with substrate or undergoes intersystem crossing forming a triplet nitrene.[7-11]

$$R-SO_2\ddot{N} \rightarrow R-SO_2\ddot{N}\cdot$$
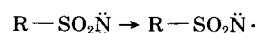
The majority of nitrene singlets undergo *insertion*

Table III   Physical Properties of Compounds Based on HNBR Cured with BSA and DCP

	Sample					
	TA/1	TA/2	TB/1	TB/2	TC/1	TC/2
Cure time, min at 160°C	27.0	19.5	17.5	21.0	11.2	20.0
Tensile strength, MPA	30.0	25.7	30.1	29.1	29.1	29.5
100% modulus, MPa	5.1	3.4	4.4	3.5	4.3	4.5
300% modulus, MPA	27.8	18.1	25.9	21.8	19.9	—
Elongation at break, %	330	455	390	357	337	307
Tear strength, N (d.Delft)	57.7	65.8	53.5	53.4	61.3	39.8
Hardness, shore A	68	65	66	67	67	69
Properties change after 7 days ageing at 150°C						
Tensile strength, % ret.	97	88	97	84	100	83
100% modulus, % ret.	228	252	347	293	447	320
Elongation at break, % ret.	70	78	54	85	47	62
Hardness, shore A	74	74	76	74	79	78
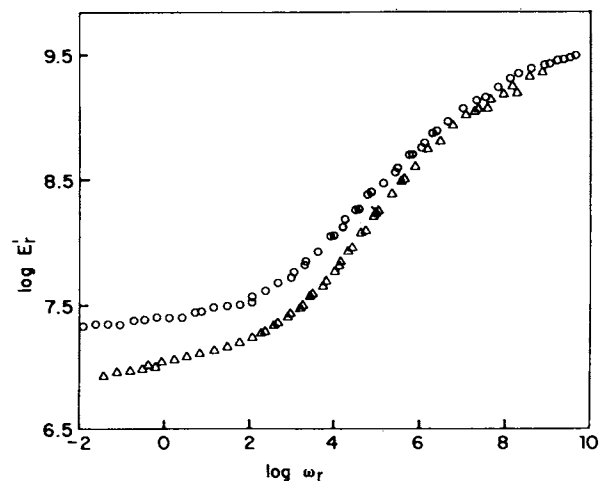
Figure 3 Master curves for the elastic modulus against frequency. Tornac A cured with (○) 3 phr of BSA and (△) 2.81 phr of DCP.

into $C\!-\!H$ bonds, preserving their configuration, whereas the nitrene triplets preferably give rise to hydrogen *abstraction* reactions from the chain forming radicals.

$$R\!-\!SO_2\ddot{N}\cdot + H\!-\!\overset{|}{C}\!-\! \rightarrow \!-\!\overset{|}{\dot{C}}\!-\! + R\!-\!SO_2\dot{N}H$$
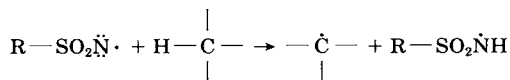
The order of singlet stability of the three nitrenes would be sulphonyl > formyl > aryl. Sulphonyl nitrenes generate a relatively small number of hydrogen abstractions and their reactivity adjusts to the order tertiary carbons > secondary carbons > primary carbons.[7]

With the thermal decomposition of the peroxide the cross-linking process is initiated. The radical fragments participate in hydrogen abstraction forming a radical in the polymeric chain. Neutralization between two polymeric radicals generates the cross-link. In principle the decomposition of one DCP molecule can be assumed to generate one cross-link in the polymer.

BSA is supposed to display a similar behavior (on condition that the triplet route is not implemented in a significant way): for each BSA molecule a cross-link is formed in the polymer.

According to the kinetic parameters in Table I, the curing process with BSA is favored by the degree of insaturation of the three rubbers. The rate constant increases and the process activation energy decreases when the elastomer possesses a major number of double bonds in the polymeric chain. The allylic hydrogens (which possess a higher reactivity) increase in number and their extraction by means

of the nitrene is likewise favored, as proven by the shortening of optimum curing time (Table III).

The apparent cross-linking density, as indicated by the volume of the swollen polymer V_r, is shown in Figure 2 for the two cross-linking systems and the three polymers. The BSA-cured networks, which maintain the diazide concentration constant, present similar V_r values, the degree of polymer insaturation thus having no effect. In contrast, in the DCP vulcanizates the number of the elastically effective cross-links is directly related to the degree of polymer insaturation. The more saturated rubber presents a V_r that is notably lower than that obtained for the respective BSA vulcanizate that suggests that the degree of efficiency of the DCP cross-linking reaction is lower than that obtained with BSA. Other possible reactions are assumed to take place, such as scission, cyclization, etc., which reduce the performance level of the cross-linking reaction. In the DCP cross-linked compounds V_r increases as a function of polymer insaturation. The efficiency of the peroxide in the cross-linking reaction is conditioned by the degree of insaturation.

Therefore the compound prepared with the most insaturated polymer, Tornac C, present a higher V_r value than when cross-linked with BSA. This enhanced efficiency of the peroxide may be attributed to that apart from the cross-links formed between the polymeric radicals generated by means of hydrogen alkyl abstraction; the peroxide radical itself may also react with the vinyl hydrogen, which subsequently initiates a polymerization reaction with adjacent double bonds.[12-14] These networks do not possess uniformly distributed cross-links and, when subjected to stress, they account for the relevant decrease in strength at low strain (moduli), as well as for a significant loss in tear strength.

When examining the data compiled in Table IV, both cross-linking systems have a strong impact on the T_g, of the Tornac A compounds. The compounds cross-linked with BSA present a T_g shifted toward higher temperatures, as appropriate for a more densely cross-linked network. However the temperature differential existing between the networks prepared with BSA and DCP cannot be accounted for solely by the difference between the cross-linking densities of both networks. Moreover this phenomenon could be explained by scission reaction during the DCP-curing process, which gives rise to a greater number of chain terminals, which accounts for imperfect packing around the ends of the molecules. This phenomenon implies increments in the free volume of the system, which suppose a drop of the T_g of the polymer. The value of f_g, which is higher

in the DCP cross-linked network as compared to the BSA values, may serve to support this hypothesis.

The behavior of highly saturated nitrile elastomers cured with DCP in applications that require good response in compression relaxation or set is not supposed to be satisfactory due to the chain ends deriving from the scission reactions that occur during the cross-linking process. This aspect is being further pursued.

REFERENCES

1. K. Hashimoto and Y. Todani, in *Handbook of Elastomers*, A. Bhowmick and H. Stephens, Eds., Marcel Dekker, New York, 1988, Chap. 24.
2. S. Hayashi, H. Sakakida, M. Oyama, and T. Nakagawa, *Rubber Chem. Technol.*, **64**, 534 (1991).
3. K. Hashimoto, Y. Todani, M. Oyame, and N. Watanabe, Paper No. 5 at the Meeting of the Rubber Division of the American Chemical Society, Cleveland, OH, 1985.
4. J. L. de Benito, L. Ibarra, and L. González, *Kautsch. Gummi Kunstsf.*, **43**, 146 (1990); **43**, 607 (1990).
5. W. Scheele, *Rubber Chem. Technol.*, **34**, 1306 (1961).
6. J. D. Ferry, in *Viscoelastic Properties of Polymers*, John Wiley & Sons, New York, 1980.
7. D. S. Breslow, M. F. Sloan, N. R. Newburg, and W. B. Renfrow, *J. Am. Chem. Soc.*, **91**, 2273 (1969).
8. D. S. Breslow, T. J. Prosser, A. F. Marcantonio, and C. A. Genge, *J. Am. Chem. Soc.*, **89**, 2384 (1967).
9. M. Apple, R. Huisgen, *Chem. Ber.*, **92**, 2961 (1961).
10. P. A. S. Smith and J. H. Hall, *J. Am. Chem. Soc.*, **84**, 480 (1962).
11. P. Walker and W. A. Waters, *J. Am. Chem. Soc.*, 1632 (1962).
12. H. F. Mark, *Rubber Chem. Technol.*, **61**, G73 (1983).
13. B. M. E. Van der Hoff, *Appl. Polym. Symp.*, **7**, 21 (1968).
14. B. M. E. Van der Hoff, *Ind. Eng. Prod. Res. Dev.*, **2**, 273 (1960).