

Analysis of Network Structure Formed in Styrene–Butadiene Rubber Cured with Sulfur/TBBS System

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Received 1 May 2006; accepted 5 August 2006

DOI 10.1002/app.25264

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Several styrene–butadiene rubber (SBR) compounds were prepared with different cure systems based on sulfur and TBBS (*N*-*t*-butyl-2-benzothiazole sulfenamide), varying the amount of sulfur and accelerator between 0.5 and 2.5 phr in the formulation. Torque curves, measured with a moving die rheometer at temperatures at 433 K, were used to characterize the vulcanization. The time to achieve the maximum torque, $t_{100\%}$, was evaluated for each sample, and this time was set to vulcanize sheets at 433 K. The

density and type of elastically active crosslinks of each cured sample were evaluated by means of swelling measurements and were related to the vulcanizing system. Finally, the rheometer data were analyzed considering the network structure formed during vulcanization. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1105–1112, 2007

Key words: styrene–butadiene rubber; vulcanization; crosslink types

INTRODUCTION

The mechanical properties of the cured rubber compounds are strongly influenced mainly by elastomer type, the cure system, and the process conditions.¹

In the case of rubber compounds prepared with a cure system based on sulfur and accelerator, the relative quantity of these components in the compound formulation has a strong influence in the kind and density of generated crosslinks during the cure process,² with important consequences on the physical properties of the cured material. The compounds used in sulfur vulcanization are normally classified in three systems based on the accelerator/sulfur ratio (Λ). Usually, the conventional system (CV) is considered for Λ of 0.1–0.6, semiefficient system (semi-EV) for values 0.7–2.5, and an efficient system (EV) for values in the range 2.5–12.²

In previous research works, we focused our attention on the study of vulcanized styrene–butadiene rubber (SBR) using the system of cure sulfur/TBBS (*N*-*t*-butyl-2-benzothiazole sulfenamide). TBBS is a general purpose primary accelerator that combines a fast cure with good scorch safety. We analyzed the influence of the degree of cure and the amount of sulfur in the composition in the free volume of the vulcanized polymer, using positron annihilation

spectroscopy and dynamic mechanical tests.^{3,4} We also studied the kinetic of cure of samples with different amounts of sulfur and accelerator by means of normalized rheometer curves.^{5,6} An empirical relationship that links the reaction order with the density of network chains was settled down.⁵

The precise interaction of the accelerator and sulfur during vulcanization has not been clearly elucidated. Various accelerator complexes are formed during the induction time, and in the case of sulfenamides, as TBBS, there is a long scorch delay if we compare them with other commercial accelerators.⁷

Layer^{8,9} analyzed the role of sulfur and accelerator in the crosslinks formed during the cure process. He concludes that sulfur is related to the overall amount of reaction, while the accelerator determines the length of sulfur chains.

By means of solid-state ¹³C-NMR, Pelliccioli et al.¹⁰ analyzed the structural changes that occur during the vulcanization of SBR samples, using the cure system sulfur and CBS as accelerator. Comparing two systems with a constant amount of sulfur, the assigned monosulfidic peak in the resonance diagram increases with the decreasing S/CBS ratio.

The present work continues our research in SBR vulcanizes with the system sulfur/TBBS. The crosslink densities and the kind of crosslinks formed during curing at 433 K were measured, by means of swelling techniques, in a wide range of compositions varying the amount of sulfur and accelerator. The influences of the compound composition in the rheometer torque curves at 433 K were analyzed.

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Contract grant sponsor: University of Buenos Aires.

TABLE I
Compound Formulations (phr)

Sample no.	SBR 1502	Zinc oxide	Stearic acid	Antioxidant	Accelerator (TBBS)	Sulfur (S)	Λ (accelerator/S ratio)	Density (g/cm ³)	f
1	100	5	2	1.2	2.5	0.5	5	0.972	0.047
2					2	1	2	0.971	0.047
3					1.5	1.5	1	0.972	0.047
4					1	2	0.5	0.972	0.047
5					0.5	2.5	0.2	0.977	0.048
6					0.5	0.5	1	0.965	0.049
7					1	1	1	0.973	0.048
8					2	2	1	0.982	0.047
9					2.5	2.5	1	0.993	0.047
10					1.5	0.5	3	0.972	0.047
11					0.5	1.5	0.33	0.969	0.048
12					2.5	1.5	1.66	0.987	0.047
13					1.5	2.5	0.6	0.988	0.047

The relation accelerator/sulfur, Λ , density, and ash content (f) of samples cured at 433 K are also included. The variation is ± 0.001 g/cm³ in density and ± 0.001 in f .

EXPERIMENTAL

Samples preparation

The material used in the present study was unfilled styrene-butadiene rubber SBR-1502 that contains 23.5% bound styrene, i.e., a molecular proportion in

the chains of one styrene to about six or seven butadienes. The chemical structure of butadiene in the SBR copolymer consists of 55% *trans*-1,4, 9.5% *cis*-1,4 and 12% 1,2-butadiene.

The average molecular weight (M_n) of the elastomer was 92,800 g/mol determined by GPC, with a

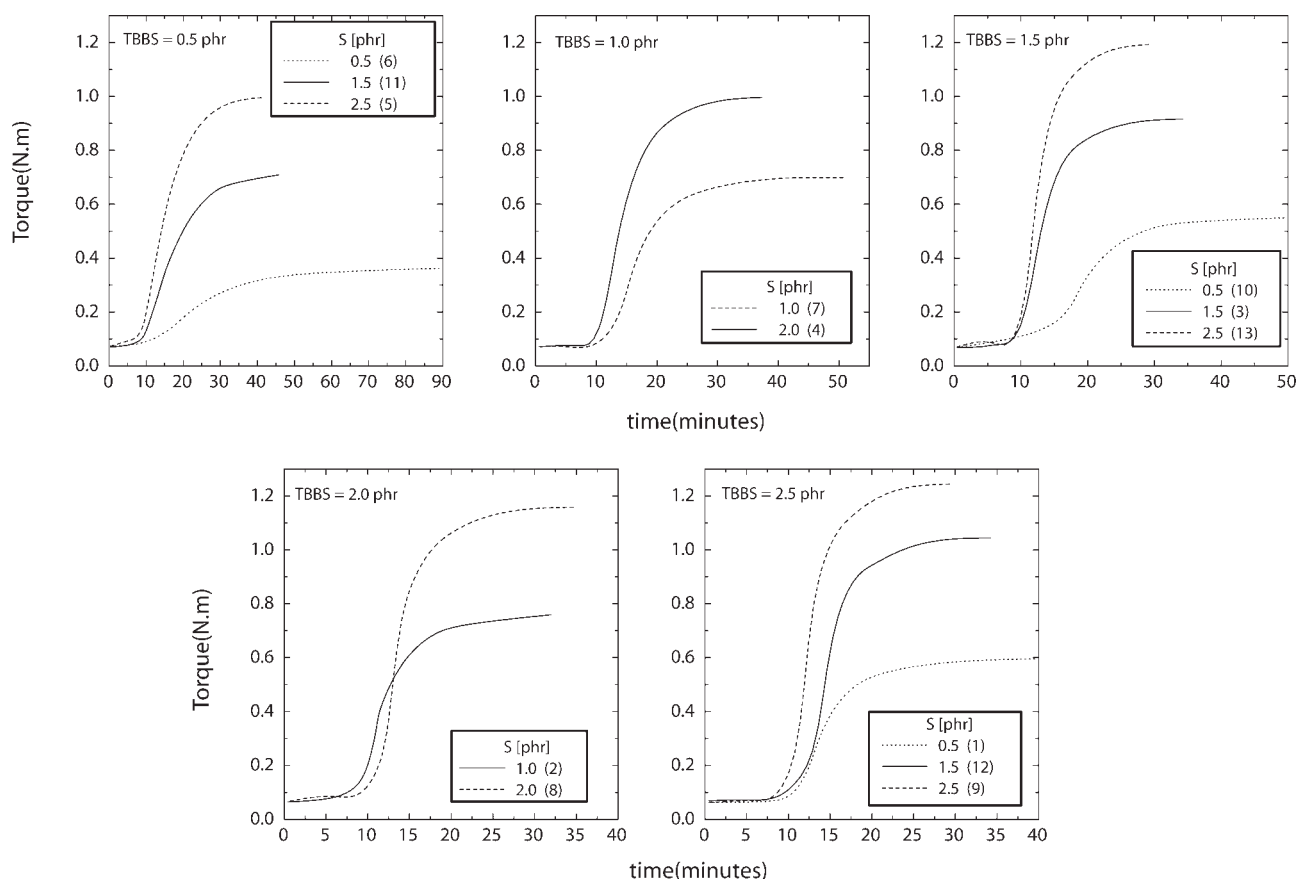


Figure 1 Torque curves of SBR compounds at 433 K, as a function of the time for all the studied samples. The sample number is indicated in each plot between parentheses. The variation of the torque values is < 0.003 N m.

TABLE II
Values of τ_l , τ_h , and $\Delta\tau$ (in N m) Obtained from the Rheometer Curves for All the Samples Tested at 433 K

Sample no.	τ_l	τ_h	$\Delta\tau$	$t_{100\%}$ (min)
1	0.063	0.595	0.532	39.5
2	0.065	0.759	0.694	31.9
3	0.069	0.916	0.847	34.2
4	0.071	0.997	0.926	37.3
5	0.073	0.995	0.922	41.5
6	0.074	0.363	0.289	89.9
7	0.072	0.699	0.627	51.2
8	0.068	1.158	1.09	34.9
9	0.063	1.244	1.181	29.4
10	0.069	0.56	0.491	53.1
11	0.071	0.71	0.639	45.8
12	0.069	1.044	0.975	34.2
13	0.07	1.192	1.122	29.2

The variation of the torque values is < 0.003 N m. The value of $t_{100\%}$ is also given.

density $\rho = 0.935$ g/cm³. To obtain different network structures, 13 formulations based on the system of cure sulfur/TBBS (*N-t*-butyl-2-benzothiazole sulfenamide) were prepared. The recipes, in parts per hundred of rubber (phr), are given in Table I where the accelerator/sulfur ratio, Λ , is also given. The gum mixes were prepared in a laboratory mill of 150 mm \times 250 mm, with a friction ratio of 1.4 and a 2 mm gap (give a final sample thickness of about 5 mm). The temperature of the mill cylinders was 323 K.

The gum mixes were characterized at 433 K by means of the torque curves in a Monsanto MDR2000 rheometer. These curves are shown in Figure 1. From each of these curves, some characteristic parameters as the torque minimum, τ_l , and the torque maximum, τ_h , were obtained. The time taken to achieve the maximum torque, $t_{100\%}$ was calculated too. These values are given in Table II.

Sample sheets of 150 \times 150 \times 2 mm³ were vulcanized in a press at 433 K up to time $t_{100\%}$. This fact guarantees that all the vulcanization reaction took place. These specimens were cooled rapidly in ice and water at the end of the curing cycle. The measured densities of these samples are given in Table I. As it is expected, the density increases with the total amount of sulfur and accelerator in the recipe.

Swelling tests

Swelling of rubber compounds is frequently used for the determination of the crosslink density. The molecular weight of the network chain between chemical crosslinks for a phantom network, M_{cs} , is expressed by the Flory–Rehner relationship^{11,12}

$$M_{cs} = \frac{-\rho(1 - 2/\phi)V_1v_{2m}^{1/3}}{\ln(1 - v_{2m}) + \chi v_{2m}^2 + v_{2m}} \quad (1)$$

where ρ is the polymer density, ϕ the functionality of the crosslinks, v_{2m} the volume fraction of polymer at equilibrium (maximum) degree of swelling, and V_1 the molar volume of solvent. χ is an interaction parameter between the polymer and the swelling agent.¹³

Four disks of each cured compound were cut with a die of 16 mm diameter. One disk of each cured compound was used for calculating the weight fraction of ash content (f), using ASTM D296-90. These values are given in Table I. The other three disks of each cured compound were previously weighted and then were allowed to stand 24 h in pyridine. They were continuously extracted for 16 h in acetone in a Soxhlet apparatus (following ASTM D296-90). After extraction, the samples were dried at 333 K until constant weight was obtained in the samples.

The three groups of extracted disks were used for estimating the total crosslink density (Group 1), (di + monosulfidic) crosslink density (Group 2) and the monosulfidic crosslink density (Group 3) respectively, of each cured sample.

Samples of Group 2 were preswollen in *n*-hexane for 16 h at room temperature, followed by a treatment with piperidine (0.4M) and propane-2-thiol (0.4M) in *n*-hexane. After standing the samples 2 h in this solution, the polysulfidic crosslinks are cleaved.^{14–17} After this, the specimens were dried at 323 K until constant weight.

Samples of Group 3 were treated with a probe solution of *n*-hexanethiol (7 mL) and piperidine (86 mL) at room temperature during 48 h. This treatment cleaves all the disulfidic and polysulfidic crosslinks and was used in researches in both natural and synthetic rubbers.^{14,16,17}

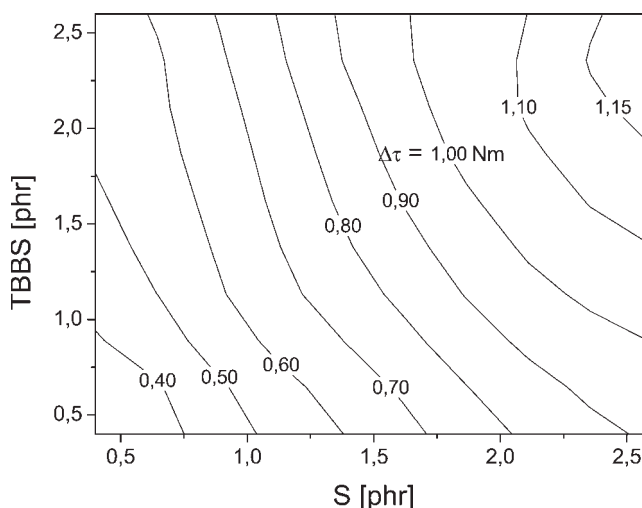


Figure 2 Variation of $\Delta\tau$ with the amount of sulfur and accelerator TBBS in the sample, measured with rheometer test at 433 K.

TABLE III
Values of $1/2M_{cs}$, Obtained from Swelling Measurements, Using Eq. (1)
for All the Samples Cured at 433 K

Sample no.	S (phr)	TBBS (phr)	$1/2M_{cs}$ (g/mol 10^{-5})			
			Total	Polysulfidic	Disulfidic	Monosulfidic
1	0.5	2.5	2.86	0.47	1.48	0.91
2	1.0	2.0	4.09	1.07	1.75	1.27
3	1.5	1.5	5.05	1.15	2.32	1.59
4	2.0	1.0	5.24	1.07	2.55	1.62
5	2.5	0.5	5.54	0.79	2.41	2.34
6	0.5	0.5	0.68	0.00	0.41	0.27
7	1.0	1.0	2.89	0.47	1.76	0.65
8	2.0	2.0	7.38	1.28	3.81	2.30
9	2.5	2.5	9.33	2.39	4.17	2.77
10	0.5	1.5	2.31	0.42	1.37	0.52
11	1.5	0.5	2.79	0.35	0.92	1.51
12	1.5	2.5	6.60	0.78	2.42	3.40
13	2.5	1.5	7.62	1.35	4.50	1.78

Then, the v_{2m} values were obtained for the samples of the three groups by swelling in toluene ($\rho_{\text{tol}} = 0.8669 \text{ g/cm}^3$, $V_1 = 106.29 \text{ mL/mol}$).¹⁸ First, the total weight of each sample was determined to 0.0001 g. The samples were immersed completely in toluene and swelling equilibrium occurred approximately in 48 h. Then, the swollen samples were surface dried with filter paper and quickly weighted. The volume fraction of rubber, v_{2m} , was obtained using the following equation:

$$v_{2m} = \frac{W_d(1-f)/\rho}{[W_d(1-f)/\rho + (W_s - W_d)/\rho_s]} \quad (2)$$

where W_d is the weight of the sample after swelling and drying, W_s the weight of the swollen sample, and ρ_s the density of the solvent. Then using the

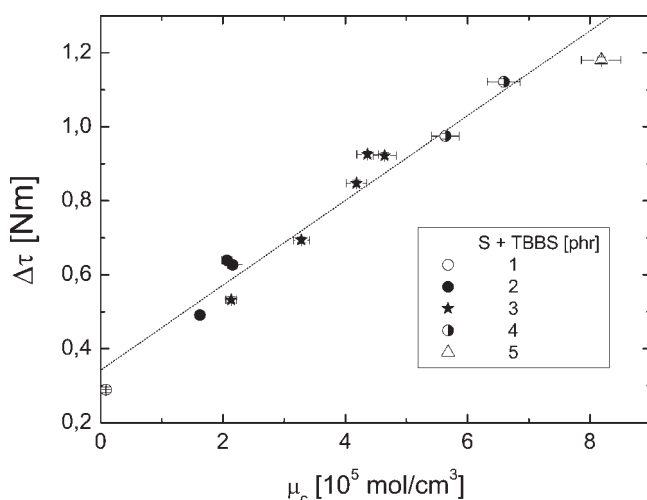


Figure 3 Relation between $\Delta\tau$ and the total crosslink density μ_c , for SBR cured at 433 K.

results of eq. (2) in eq. (1) the value of M_{cs} can be obtained. The polymer–solvent interaction parameter χ for the system SBR-toluene used was 0.446.¹⁹ The deviation for M_{cs} was 3%.

The density of polysulfidic crosslinks was calculated from the difference between the total crosslinks density (Group 1) and (di + monosulfidic) crosslink density (Group 2). Finally, the disulfide crosslink density was obtained from the difference between the (di + monosulfidic) crosslink density (Group 2) and monosulfidic crosslink densities (Group 3).

RESULTS AND DISCUSSION

An indirect approach of evaluating the cure level of rubber compounds is through the rheometer torque

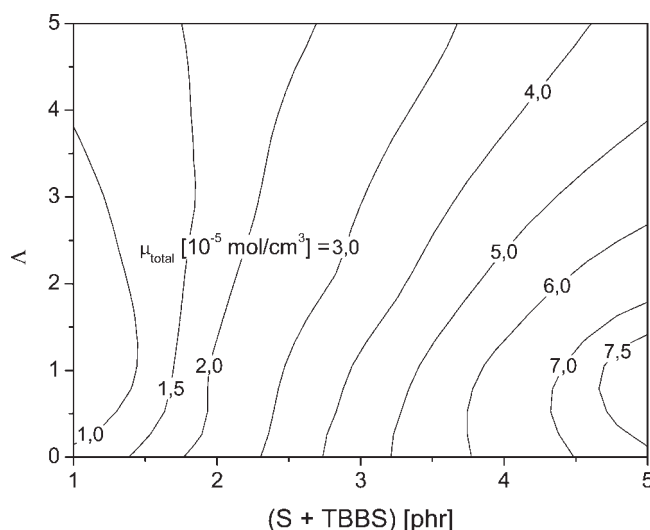


Figure 4 Contour plot of the total crosslink density μ_c as a function of the total sulfur plus accelerator TBBS and the relation accelerator/sulfur, Λ , in the compound.

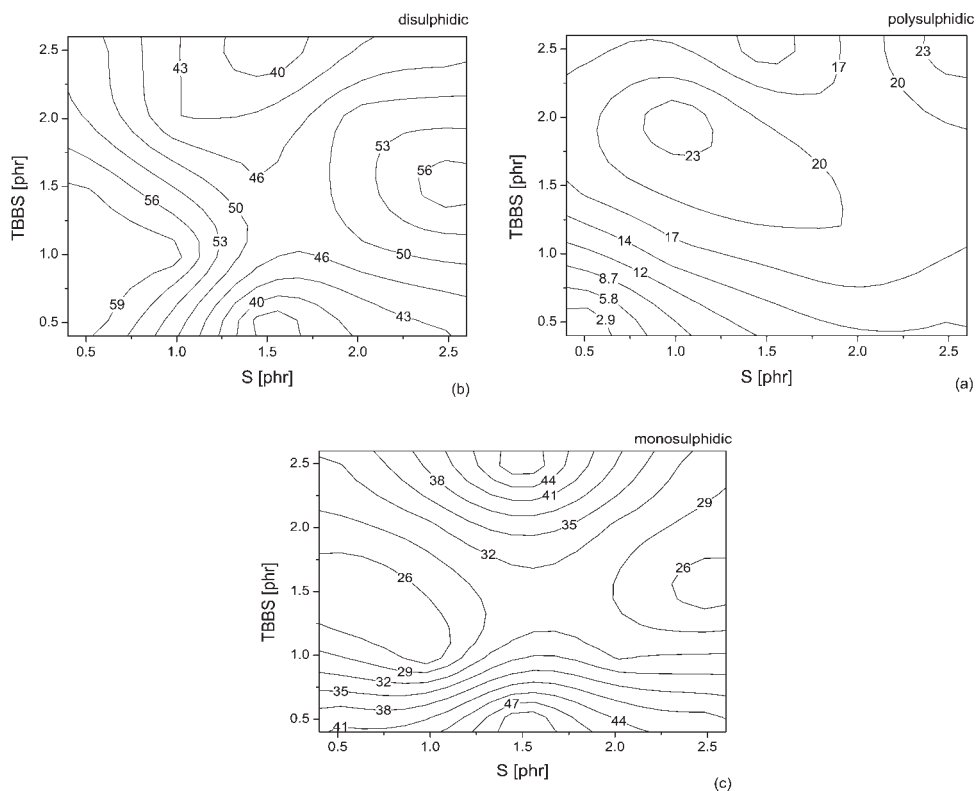


Figure 5 Contour plots showing the percentage of the different types of crosslinks present in SBR compounds cured at 433 K, as a function of the sulfur and TBBS in the compound composition. (a) Polysulfides; (b) disulfides; (c) monosulfides.

curves. The rheometer responds only to the presence of elastically active crosslinks. It is expected that τ_h will increase at higher values of the network chain density.⁹ On the other hand, if the effects of the viscosity in the interpretation of the rheometer test results want to be minimized, usually the entity $\Delta\tau = (\tau_h - \tau_l)$, named effective torque, is used for analyzing the experimental data. Figure 2 shows the influence of the composition in the behavior of $\Delta\tau$ at 433 K. It follows that there is a tendency to increase this value when both the amount of sulfur and the accelerator (TBBS) are higher.

To evaluate the effect of the amount of sulfur and TBBS in $\Delta\tau$, a multiple regression can be fitted to the measured values obtaining

$$\Delta\tau(\text{Nm}) = 0.106 + 0.323 S(\text{phr}) + 0.136 \text{TBBS}(\text{phr})$$

with a value of $R^2 = 0.964$. It is clear that the contribution of the sulfur to $\Delta\tau$ is higher than that of the accelerator.

The parameter $\nu_{cs} = 1/2M_{cs}$ is defined as the moles of effective elastic strands per unit volume, where the molecular weight between crosslinks, M_{cs} , is measured using eq. (1). The values $1/2M_{cs}$ for the total, polysulfide, disulfide, and monosulfide crosslinks are given in Table III for the different samples analyzed considering a functionality $\phi = 4$.

Indeed, the crosslink density in a 4-functional network is defined by²⁰

$$\mu_c = \frac{\rho}{2} \left[\frac{1}{M_{cs}} - \frac{1}{M_n} \right] \quad (3)$$

From eq. (3) and Table III, the total crosslink density was evaluated for each sample.

Figure 3 shows the expected linear relationship between $\Delta\tau$ and μ_c , considering the total crosslink density for all the cure compounds. The total amount of SBR and TBBS corresponding to each sample analyzed is also included in Figure 3. It is clear that both the value of $\Delta\tau$ and the crosslink density increase with the total amount of S and TBBS in the compound. The influence of the accelerator/sulfur ratio, Λ , with the crosslink density is observed in Figure 4 as contour plot, considering also the amount of sulfur and accelerator in the composition of the cured samples. From this information, the crosslink density increases in the condition of high (S + TBBS) content and low Λ values.

From Table III, it is easy to estimate the proportion of the different types of crosslinks present in each cured compound. Figure 5(a–c) show, as contour plots, how these quantities change with the amount of sulfur and accelerator in each compound composition.

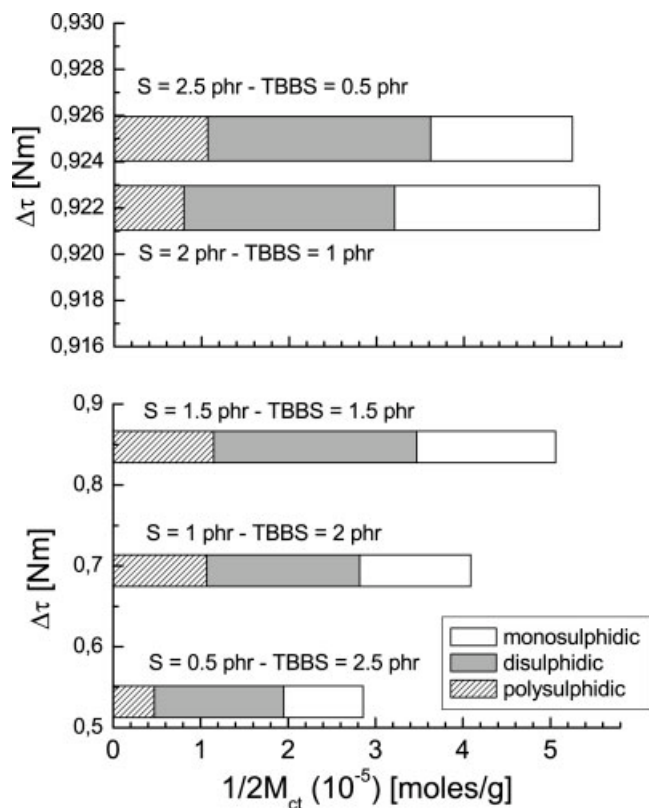


Figure 6 Variation of $\Delta\tau$ with $1/2M_{cs}$ showing the contribution of each crosslink type, in cases of samples with S + TBBS = 3 phr in the formulation.

It is interesting to observe how the crosslink distribution affects the rheometer values in several cases. First, we analyze the behavior of $\Delta\tau$ in samples with S + TBBS = 3 phr in their formulations as it is shown in Figure 6. The concentrations of mono and disulfidic linkages are high comparing to the polysulfidic linkages in all the samples. There is a composition with TBBS (1.5 phr)/S (1.5 phr), which maximizes the amount of polysulfidic crosslinks in the sample. As long as monosulfidic crosslinks are concerned, a different situation was observed: there was a significant increase at higher amounts of sulfur (i.e., low amounts of TBBS) in the samples. In the case of cured natural rubber (NR), it is accepted that polysulfidic bonds predominate with CV systems at relatively high sulfur levels, whereas EV systems produce mainly monosulfidic and disulfidic crosslinks with high values of Λ .²¹ Our results in cured SBR, given in Figure 6, do not indicate a predominant presence of polysulfidic linkages in the CV system (samples 1 and 2) as in NR vulcanizates.

Figure 7(a) shows the influence of the accelerator TBBS in $\Delta\tau$ and the different linkages formed during the vulcanization at 433 K in samples with 0.5 phr of sulfur in their composition. Increasing the value of Λ , i.e., going from a semi-EV to EV system, there is

an increase in the amount of all the types of crosslinks analyzed. It must be mentioned that the sample 6, TBBS (0.5 phr)/S (0.5 phr), was the only one with no polysulfidic linkages. On the other hand, Figure 7(b) shows samples with 2.5 phr of sulfur in their composition in which, when increasing the amount of accelerator, they are CV or semi-EV systems. The relative amount of polysulfidic linkages is higher at higher values of Λ , with a decrease in the relative amount of monosulfidic linkages contribution. This fact can also be observed in Figure 5.

Figure 8(a,b) show the behavior $\Delta\tau$ in samples with the same amount of TBBS in their formulations. In the case with TBBS = 0.5 phr, the increase in the ratio Λ produces a decrease of the polysulfidic crosslinks. The same effect is observed when TBBS = 2.5 phr, if the formulation goes to EV system, less polysulfidic linkages are formed at $t_{100\%}$.

Other interesting situation is deduced from Figure 9 in which samples with the same accelerator/sulfur ratio ($\Lambda = 1$) are considered. As it is expected, $\Delta\tau$ increases if the amount of total crosslinks, represented by $1/2M_{cs}$, increases too. However, the proportion of different kind of crosslinks in the samples is not the same. When increasing the quantity

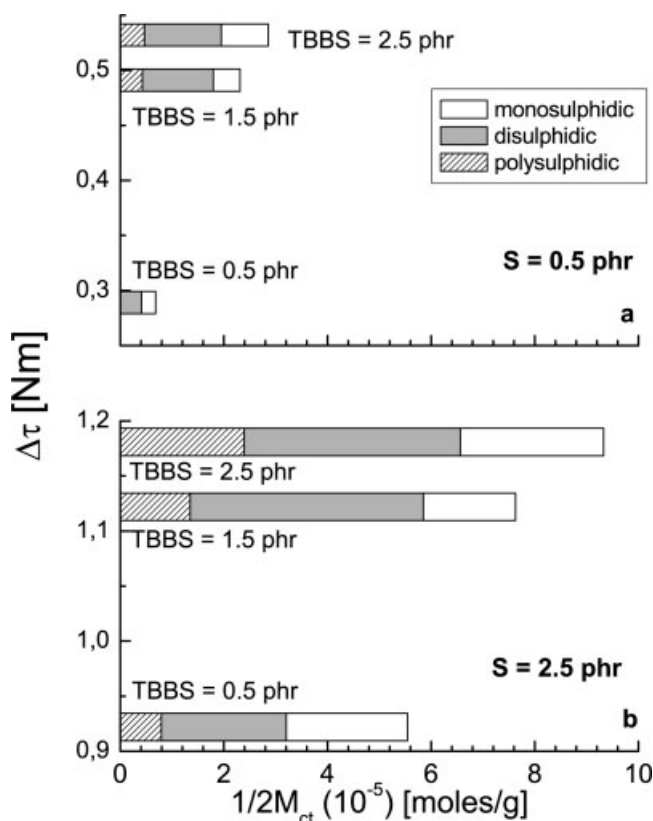


Figure 7 Variation of $\Delta\tau$ with $1/2M_{cs}$ showing the contribution of each crosslink type, in cases with constant sulfur concentration in the formulation: (a) S = 0.5 phr; (b) S = 2.5 phr.

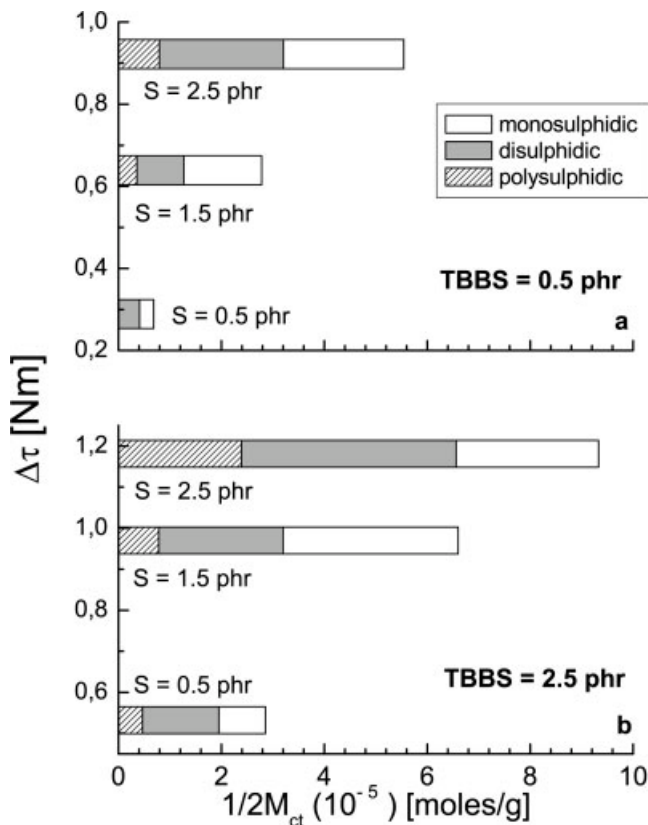


Figure 8 Variation of $\Delta\tau$ with $1/2M_{cs}$ showing the contribution of each crosslink type, in cases with constant accelerator concentration in the formulation: (a) TBBS = 0.5 phr; (b) TBBS = 2.5 phr.

(S + TBBS) in the sample formulation, it is observed that more polysulphidic linkages begin to appear with a decrease in the disulphidic linkages. For S + TBBS > 2 phr, the percentage of monosulphidic linkages remains unaffected.

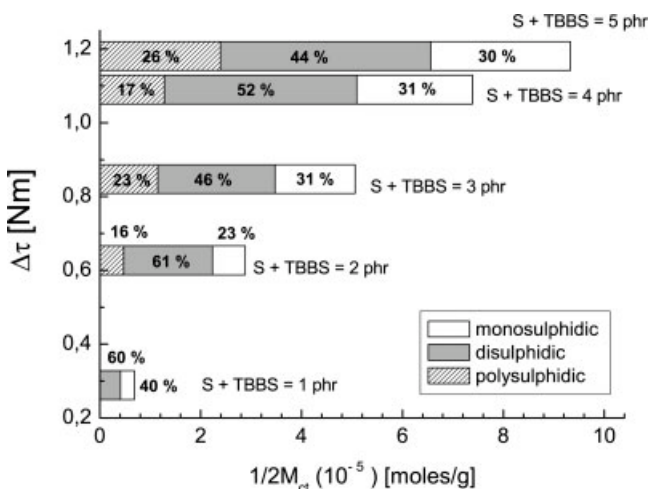


Figure 9 Variation of $\Delta\tau$ with $1/2M_{cs}$ showing the contribution of each crosslink type, for samples with $\Lambda = 1$ in the formulation.

TABLE IV
Experimental ($\Delta\tau$) and Calculated ($\Delta\tau_{cal}$) Values of Effective Torque, Obtained from Eq. (4), for All the Samples Tested at 433 K (the difference between the two values (δ) is also included)

Sample no.	$\Delta\tau$ (N m)	$\Delta\tau_{cal}$ (N m)	δ (%)
1	0.532	0.588	10.5
2	0.694	0.686	1.2
3	0.847	0.804	5.1
4	0.925	0.836	9.6
5	0.922	0.893	3.1
6	0.289	0.353	22.2
7	0.627	0.595	5.1
8	1.090	1.094	0.3
9	1.181	1.233	4.4
10	0.491	0.525	6.9
11	0.639	0.579	9.3
12	0.975	1.020	4.6
13	1.122	1.128	0.5

Where applicable, response equations of the type

$$\Delta\tau_{cal} = C + ax_1 + bx_2 + cx_3 \quad (4)$$

are fitted to the data using regression analysis. We can use this equation to evaluate numerically the influence of the type of crosslink in the rheometer response at 433 K. In this case, it is considered $x_1 = 1/2M_{cs}$ (polysulphidic), $x_2 = 1/2M_{cs}$ (disulphidic), $x_3 = 1/2M_{cs}$ (monosulphidic), and the corresponding values for each sample are given in Table III. The adjustment of eq. (4) to the experimental data was performed with a multiple regression program provided by Origin 6.0 software (Microcal). The correlation coefficient was $R^2 = 0.978$ with parameters $C = 0.265$ N m, $a = 3135$ N m mol/g, $b = 13,561$ N m mol/g, and $c = 11,825$ N m mol/g. The experimental values of $\Delta\tau$ are given in Table IV together with and the calculated ones with eq. (4).

Upon observation of Table IV, an acceptable correlation is perceived between the experimental values and those of the eq. (4). The higher deviation between the empirical eq. (4) and the experimental values of $\Delta\tau$ appears for samples corresponding to the composition with lower level of sulfur and accelerator. This composition is that one with lower total crosslink density, i.e., the large strand length between crosslinks. The crosslink process traps in the dynamic entanglements present in the uncrosslinked melt, and these trapped entanglements dominate the modulus.²² We suspect that the contribution of the trapped entanglements is hidden in the term C of eq. (4), which is very complex to elucidate and it is out of the scope of the present research.

CONCLUSIONS

This research was focused on the effect of the network structure in cured SBR samples, at 433 K and

at time $t_{100\%}$, on the effective torque behavior, measured with a moving die rheometer.

Based on the results obtained in this research, the following points can be mentioned.

1. In SBR vulcanizates with the system sulfur/TBBS, with composition between $0.5 \text{ phr} \leq S \leq 2.5 \text{ phr}$ and $0.5 \text{ phr} \leq \text{TBBS} \leq 2.5 \text{ phr}$, the presence of polysulfidic crosslinks in the network structure is minority comparing with the disulfidic and monosulfidic linkages.
2. The maximum response of rheometer torque curves is obtained at higher amount of TBBS and sulfur in the SBR compound. A linear relationship can be stated relating $\Delta\tau$ with the amount of TBBS and sulfur in each analyzed sample. The total crosslink density is governed by the total sulfur plus accelerator, and increases at lower values of Λ .
3. In the special case of equal amounts (in phr) of TBBS and sulfur in the samples, i.e., $\Lambda = 1$, the percentage of polysulfidic crosslinks in the cure compound decrease at lower amount of both substances.
4. At first order, an empirical linear relationship was stated between $\Delta\tau$ and the moles of effective elastic strands per unit volume, $1/2M_{cs}$, of each type, i.e., polysulfidic, disulfidic, and monosulfidic.

The authors thank FATE SAICI (Argentina) for the cooperation in the development of this research. This work was supported by the University of Buenos Aires (Investigation Project X808).

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