About the Activation Energies of the Main and Secondary Relaxations in Cured Styrene Butadiene Rubber

Ada Ghilarducci,[1] Horacio Salva,[1] Angel J. Marzocca[2]

[1]Centro Atómico Bariloche, Comisión Nacional de Energía Atómica, Instituto Balseiro, CC 439, Bariloche, RN8400, Argentina
[2]Universidad de Buenos Aires, Facultad de Ciencias Exactas y Naturales, Dpto. Física, Laboratorio de Polímeros y Materiales Compuestos, Pabellón 1, Buenos Aires C1428EGA, Argentina

ABSTRACT: This article studies the influence of the network structure on the activation energies of the α and β relaxations in vulcanized styrene butadiene rubber, SBR. A cure system based on sulphur and TBBS (N-t-butyl-2-benzothiazole sulfenamide) was used in the formulation of several compounds cured at 433 K. The activation energies were evaluated from internal friction (loss tangent) data of the compounds using an automated subresonant forced pendulum in a wide frequency range and between 80 K and 273 K. The internal friction data of the samples reveal two transitions, α and β, characterized by the temperatures T_α and T_β, due to the glass transition and the phenyl group rotation of the copolymer, respectively. Although T_α increases at higher crosslink density, it shows also a dependence with the amount of polysulphide and monosulphide linkages present in the samples. The highest activation energy for this process is obtained for the samples with high crosslink density and 30% of monosulphides in this structure. In the case of the β-relaxation, there is a pronounced change in the activation energy between the uncured and the cured samples. The type of structure formed during vulcanization has an important effect in the activation energy of the segmental mode-process. In the case of the β-process, the *cis-trans* isomerization that takes place during vulcanization in the butadiene part of the SBR, might be the cause of conformational changes in the surrounding of the phenyl rings that affect the energy barrier associated to the phenyl rotation. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 2361–2367, 2009

Key words: styrene butadiene rubber; crosslinks; α-relaxation; β-relaxation; activation energy

INTRODUCTION

One of the most widely used synthetic rubbers is the copolymer styrene butadiene rubber (SBR). This polymer is mainly used as a cured material in industrial applications as compounds in tyres, membranes, wires, and cables.[1] In the majority of these applications, SBR compounds are vulcanized using sulphur and accelerator as cure system.

Although vulcanization takes place by heat and pressure in presence of sulphur, the process is relatively slow. The inclusion of small amounts of chemicals known as accelerators in the compound formulation makes the vulcanization process faster.

In previous works of our research group, we focused our attention on the study of vulcanized SBR, using the system of cure with sulphur and TBBS (N-t-butyl-2-benzothiazole sulfenamide) as accelerator.[2–6] Various accelerator complexes are formed during the induction time in the cure process and in the case of sulfenamides, such as TBBS, there is a long scorch delay in comparison with other commercial accelerators.[7]

Sulphur crosslinking produces elastically active linkages in the macromolecular structure of the polymer. In the case of SBR, these linkages are polysulphides, disulphides, and monoslphides, depending mainly of the sulphur/accelerator ratio and the cure conditions, i.e., time and temperature.[5,6,8,9] During the vulcanization process, cyclic linkages that only give intramolecular bonds and pendant groups are also formed. It is known that the longer the bridge links in $C-S_x-C$, i.e., larger values of x (being x number of sulphur atoms joining the chains), the easier it is for individual chains to move when the polymer is subjected to any external stress.

An early work of Bartenev and Zelenev[10] was published analyzing SBR by mechanical and electrical spectroscopy in the region from 83 to 300 K. Some of the authors of the present work[11] studied

TABLE I
Compound Formulations (in phr), $t_{100\%}$, Crosslink Density μ_c, and Percentage of Crosslink Types in Each Cured Sample (433 K, $t_{100\%}$)

	Sample						
	1	2	3	4	5	6	7
SBR 1502	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2
Antioxidant	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Accelerator (TBBS)	1.2	1.2	1.2	1.2	1.2	1.8	3.6
Sulphur (S)	0.9	1.2	1.8	3.6	5.4	1.2	1.2
$t_{100\%}$ [min]	33.7	30.9	28.3	22.3	22.1	27.0	26.9
μ_c (10^{-5}) [mol/cm^3][6]	2.0	3.7	7.7	12.9	18.8	6.7	9.3
Polysulphides [%][6]	26.2	50.8	55.0	43.1	39.3	57.2	34.0
Disulphides [%][6]	49.4	34.3	26.7	32.3	30.9	26.7	23.4
Monosulphides [%][6]	24.4	14.9	18.3	24.7	29.8	16.1	42.6

the dynamic mechanical behaviour of a carbon black filled compound of SBR, measured in the frequency range from 0.001 Hz to 10 Hz and between 80 and 300 K. The internal friction data revealed two transitions, α and β, characterized by the temperatures T_α and T_β. Both processes showed Arrhenius behaviour and the activation energies were calculated for each one.

The present work continues our research in SBR vulcanizates with the system sulphur/TBBS. In a recent article,[6] samples prepared with different amounts of sulphur and TBBS in the formulations and cured subsequently at 433 K, showed different network structures due to the different proportions of mono, di, and polysulphides linkages obtained in the compounds. In the present article, measurements of internal friction in those samples were made over a wide range of temperatures and frequencies. The influence of the network structure in the α and β relaxation is analyzed through the amount and type of crosslinks present in compound structure,

EXPERIMENTAL

Materials

In this research it was used unfilled SBR, 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 of the elastomer was M_n = 176 kg/mol determined by GPC, with a density ρ = 935 kg/m^3. To obtain different network structures, seven formulations based on the system of cure sulphur/TBBS were prepared and they are given in Table I. The cured samples can be grouped in two classes: one with 1.2 phr of TBBS and vari-

able sulphur in their compositions and the second one with 1.2 phr of sulphur and variable TBBS.

The compounds were prepared in a laboratory mill and characterized at 433 K by means of the torque curves in an Alpha MDR2000 rheometer (for more details see Ref. 3) and the times to achieve the maximum torque, $t_{100\%}$, was calculated in each sample and are given in Table I.

Sample sheets of 150 $\times$ 150 $\times$ 2 mm were cured at 433 K at a time equal to $t_{100\%}$, in order to guarantee that the vulcanization reaction was completed. These specimens were rapidly cooled in an ice-water bath at the end of the curing cycle. For the dynamic mechanical test, samples of dimension 60 $\times$ 4 $\times$ 2 mm were from the cured sheets cut with a die.

In previous articles,[6] the total crosslink density μ_c of each cured samples and the type of crosslinks were calculated from swelling tests in toluene. This information is also given in Table I.

Dynamic mechanical test

The internal friction (loss tangent or tan δ) of the samples was measured in a He atmosphere at 0.2 Torr, with an automated subresonant forced pendulum.[12] The principle of measurement is based on the relationship between stress, σ, and strain, ε. Considering a sinusoidal stress applied to the system, the strain will also be sinusoidal though lagging behind the stress by a phase angle, ϕ. The loss tangent is the tangent of this angle, that is tan δ = tan $(\phi(\omega))$, where ω is the angular frequency.

The strain amplitude was maintained constant at a value of 5 $\times$ 10^{-5} during the test. This low value guarantees the linear viscoelastic behaviour.

Three types of evaluations were made. First, tan δ was measured at a constant frequency of 1 Hz with a temperature ramp of 0.25 K/min in the range of 80 to 273 K. Second, isothermal measurements were
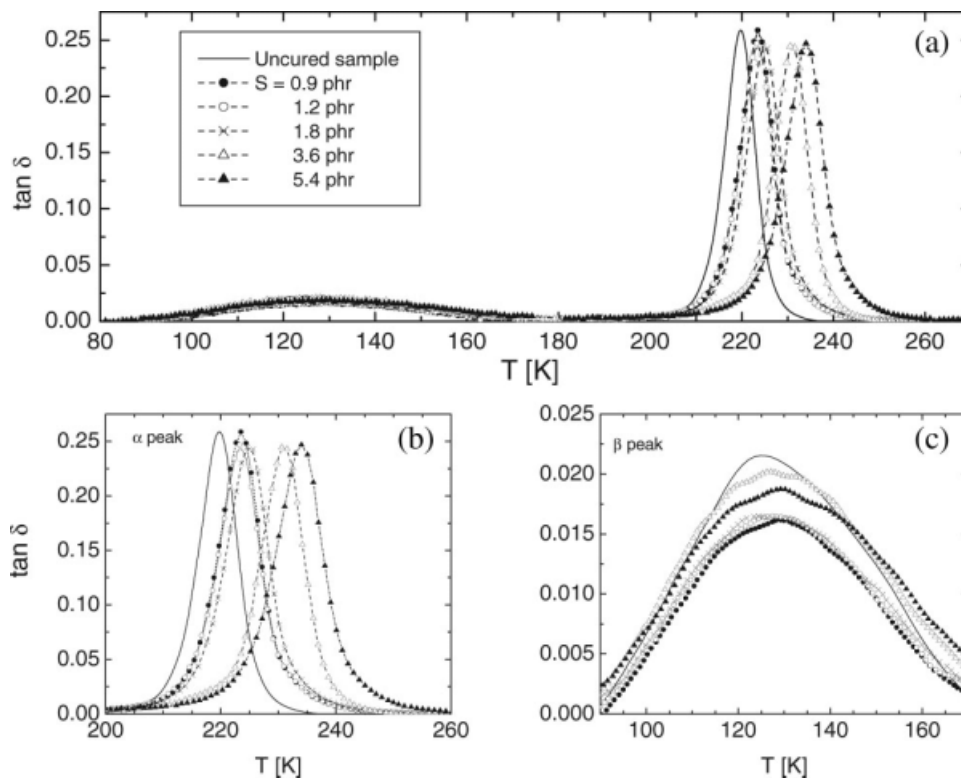
Figure 1 a) Plot of tan δ vs. temperature for SBR-1502 at 1 Hz. Samples with TBBS = 1.2 phr, S = variable. Uncured sample is also included. b) Detail of the α-relaxation zone. c) Detail of the β-relaxation zone. The error in tan δ is ± 0.5% and ± 0.1 K in temperature.

made for a frequency range of 0.001 Hz to 30 Hz for temperatures between 220 and 240 K. Finally, tan δ was evaluated within a temperature range of 80 at 160 K at a frequency between 0.025 Hz and 30 Hz.

As it is usual in a sub-resonant pendulum, the experimental data of tan δ vs. temperature were analyzed assuming a background exponential of loss tangent using the following formulae[11,12]

$$\tan \delta = a_0 + \frac{a_1}{T} \exp\left(-\frac{H_B}{kT}\right) \quad (1)$$

where a_0 and a_1 are the adjusting constants, H_B is the activation energy of the background, k the Boltzmann constant, and T the absolute temperature. This background was subtracted for all data of loss tangent vs. temperature.

RESULTS AND DISCUSSION

Figure 1 shows the plot of tan δ for SBR-1502 as a function of the temperature at 1 Hz for the uncured sample and those cured samples with 1.2 phr of TBBS and different amount of sulphur in their compositions. In this figure, the background was subtracted using the relationship given in eq. (1) with $\Delta H_B = 0.71$ kcal/mol. In all the curves, it is possible to see two peaks of tan δ. One is associated with the

main relaxation α related to the glass transition temperature of the compound, T_α, and the second to the secondary relaxation β around 125 K. This secondary transition is in correspondence to those reported in other works[10,11] in SBR-1502. As it is expected the glass transition temperatures is higher at higher crosslink density in the cured sample.

Figure 2 shows the plot of tan δ, as a function of the temperature at 1 Hz, for the uncured sample and those cured samples with 1.2 phr of sulphur and different amount of TBBS in their compositions. The same behaviour with the crosslink density is observed for the T_α.

The influence of the network structure on the glass transition temperature is summarised in Figure 3(a,b). The increase in the total crosslink density, μ_c, due to the amount of sulphur or accelerator in the compound formulation, produces an increase in the value of T_α as it can be observed in Figure 3(a). However, it is interesting to notice that T_α changes with the types of linkages formed during vulcanization. Figure 3(b) shows that the maximum value of T_α is obtained with a network structure of around 40% polysulphides linkages and 30% monosulphide linkages.

For several of the samples prepared in this research, isothermal tests of tan δ, as function of the test frequency were made around the maximum of the α peak, between 220 and 240 K. As an example
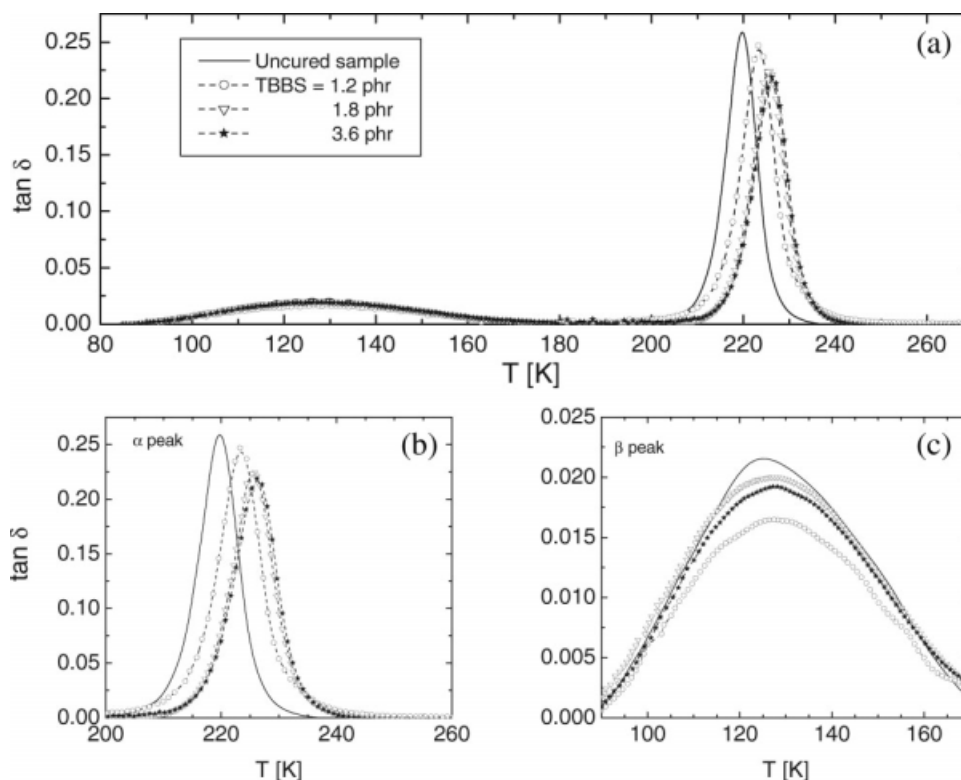
Figure 2 a) Plot of tan δ vs. temperature for SBR-1502 at 1 Hz. Samples with S = 1.2 phr, TBBS = variable. Uncured sample is also included. b) Detail of the α-relaxation zone. c) Detail of the β-relaxation zone. The error in tan δ is ±0.5% and ±0.1 K in temperature.

Figure 4(a,b) show the tan δ experimental curves for sample 1 and sample 5 as a function of the test frequency at constant temperature. The plots, made on a logarithmic scale, show a broad peak of tan δ, for each temperature.

The curves in Figure 4 indicate that tan δ is dependent on frequency. The main effect of the increase in frequency is the shift of the curve to the right (i.e., to higher temperatures). Based on the curves of Figure 4, it can be defined a characteristic time as $\tau_\alpha = 1/(2\pi\nu_\alpha)$ where ν_α is the frequency of the corresponding maximum tan δ at each tested temperature.

In literature, the α relaxation in polymers is analyzed by means of several models. Among these we can mention the free volume theory,[13] the Adams-Gibbs theory,[14,15] the coupling mode theory,[16] the coupling model[17,18] and atomistic simulations[19] among others. The Adam-Gibbs theory gives the theoretical basis of the Vogel-Fulcher-Tamman (VFT) equation[20–22] that it is generally accepted as a good description of the relaxation time with temperature

$$\tau_\alpha = A \exp\left[\frac{B}{T - T_V}\right]$$

where A is a hypothetical relaxation time at infinite temperature, B is a fitted parameter that is sometimes related to an apparent activation energy, and

T_V is the Vogel temperature that is often considered as a temperature, that is reached upon quasi-static cooling, at which chain segments become immobile.

Considering the values of ν_α obtained for each sample and their corresponding temperatures, the plot of Figure 5 is obtained in logarithmic scale in frequency. It is evident that an Arrhenius-type relationship can be used for comparison purposes, then

$$\ln \nu_\alpha = \ln \nu_o - \Delta H_\alpha/kT \qquad (2)$$

In this case, ΔH_α is the apparent activation energy of the process, k the Boltzmann constant, T the absolute temperature at the peak, and ν_o a pre-exponential factor. As it is observed, there is an excellent agreement between the experimental data and eq. (2). Then, the activation energy ΔH_α is calculated from the slope of the straight line for each sample and the values are given in Table II. The difference in the apparent activation energy between the uncured and cured samples is around 15 kcal/mol indicating the influence of the crosslink presence in the compounds.

Figure 6 show, as contour plots, how the activation energy ΔH_α associated to the α relaxation change with the crosslink density and the fraction of monosulphides linkages in the structure. A decrease in the activation energy is obtained with a higher
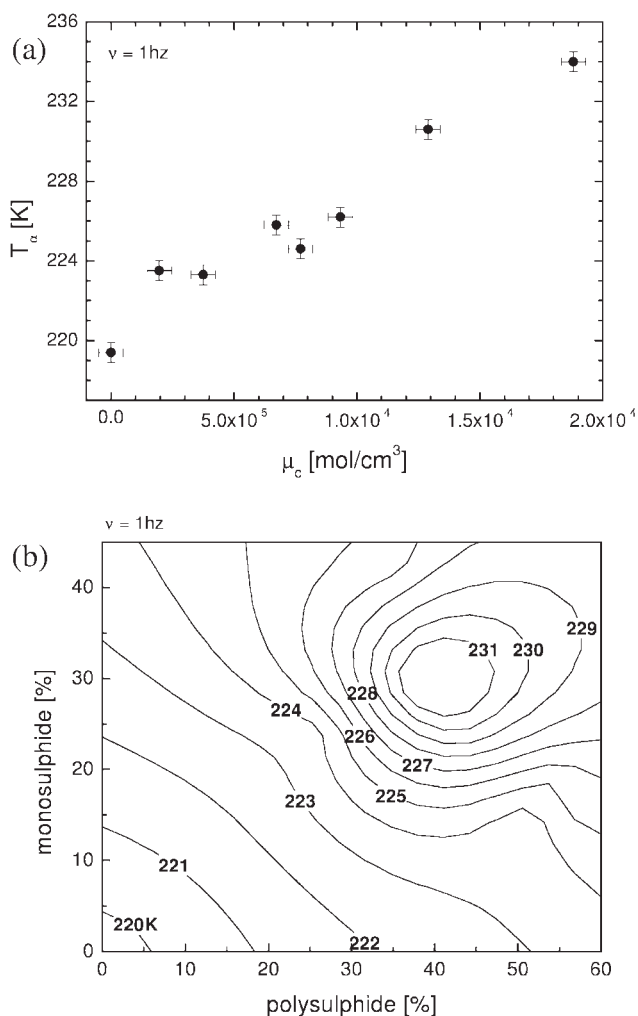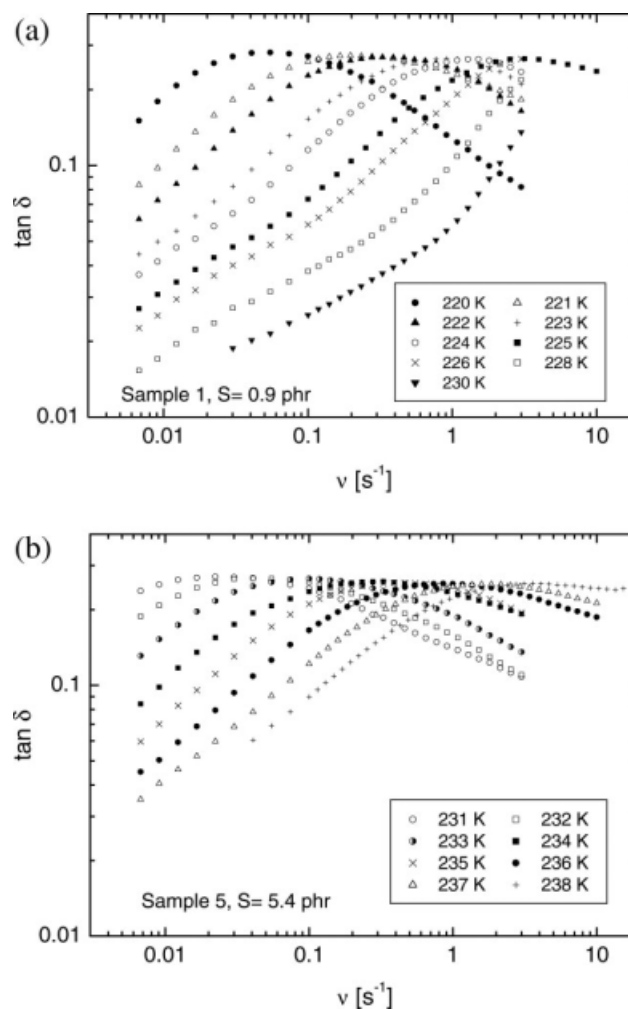
Figure 3 a) Dependence of the glass transition temperature, T_α, with the total crosslink density μ_c. b) Contour plot of the glass transition temperature, T_α, as function of the percentage of polysulphide and monosulphide linkages in the cured compound.

Figure 4 $\tan\delta$ of cured SBR-1502 plotted against the frequency for several temperatures in the α-relaxation range a) Sample 1, S = 0.9 phr and TBBS = 1.2 phr, b) Sample 5, S = 5.4 phr and TBBS = 1.2 phr. The error in $\tan\delta$ is $\pm$ 0.5% and $\pm$ 0.1% in frequency.

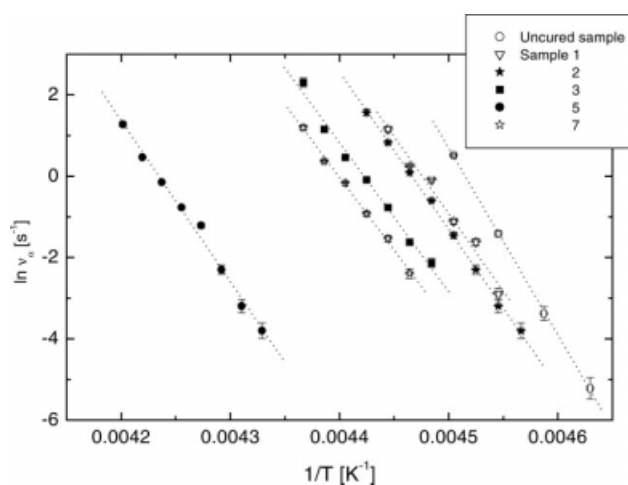proportion of monosulphide crosslinks in the cured sample.

In our measurements of $\tan\delta$ as function of temperature at 1 Hz (Figs. 1 and 2), we found a secondary transition around 125 K for all the samples analyzed. To calculate the activation energy of the process, we carried out measurements of $\tan\delta$ at several frequencies in the range of temperatures between 80 K and 180 K. The measurements were performed in the uncured sample and samples 3, 4, 5, 6, and 7.

Figure 7 (a,b) show the β-relaxation in the uncured sample and sample 3 as an example. It can be observed that with the increase of the test frequency, T_β, the temperature at which the maximum of β-peak appears, is shifted toward higher values.

Because the plot of $\ln\nu$ against reciprocal absolute temperature ($1/T_\beta$) at the peak position is linearly accurate (Fig. 8), we may express the temperature dependence of ν in the Arrhenius form of the type:

Figure 5 The Arrhenius plot. The slopes are related to the activation energy of the α-peak for each compound.

TABLE II
Values of the Apparent Activation Energy ΔH_α for the α-Relaxation Process and ΔH_β for the β-Relaxation Process

| Sample	μ_c (10^{-5}) [mol/cm^3]^6	ΔH_α [kcal/mol]	ΔH_β [kcal/mol]
Uncured	–	91.7 ± 1.3	14.5 ± 1.2
1	2.0	75.6 ± 2.1	–
2	3.7	77.0 ± 1.2	–
3	7.7	72.7 ± 2.1	10.0 ± 0.5
4	12.9	–	10.1 ± 1.2
5	18.8	78.9 ± 2.3	–
6	6.7	–	10.0 ± 0.2
7	9.3	71.1 ± 1.8	10.6 ± 0.2

$$\ln \nu = \ln \nu_1 - \Delta H_\beta / kT_\beta \qquad (3)$$

where ν_1 is the pre-exponential term. Therefore for the β-relaxation, the activation energy ΔH_β is obtained from the slope of the lines in Figure 8. The obtained values are given in Table II and it is clear the difference in the activation energy between the uncured sample and the cured ones.

Considering only the cured samples, there is no evidence of the influence of the crosslink level in the ΔH_β values. In a previous article, we obtained activation energy of 10.3 kcal/mol for a cured SBR compound filled with carbon black.[11] In the present investigation, the value of ΔH_β corresponding to unfilled cured SBR compound is similar to that one.

The β-relaxation in SBR is associated to the phenyl group rotation[11] due to the presence of styrene in the copolymer. Studies of the energy activation due to phenyl group rotation in polystyrene are in the range between 10 and 20 kcal/mol.[23–27]
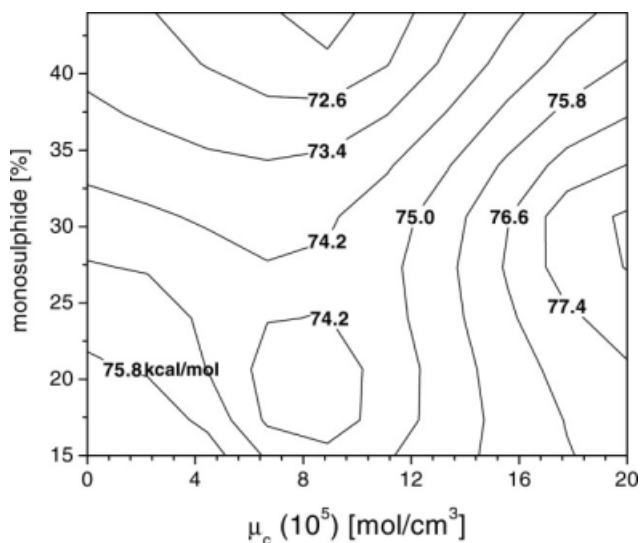
Figure 6 Contour plot of the activation energy for the α-relaxation, ΔH_α, as function of the total crosslink density and the percentage of monosulphide linkages in the compound.
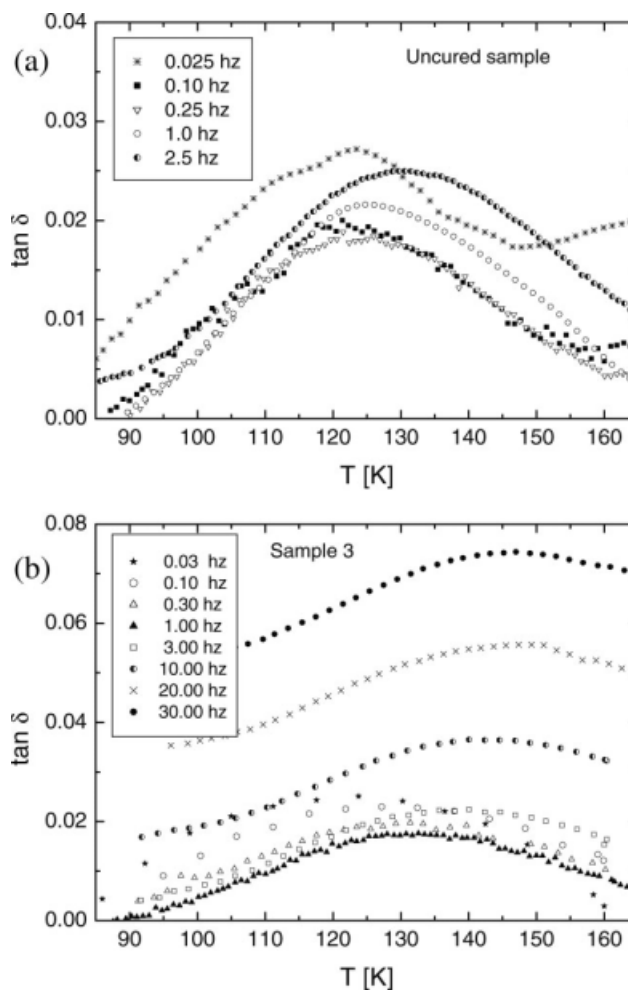
Figure 7 Plot of tan δ vs. temperature for the β-relaxation at various frequencies. a) Uncured sample, b) Sample 3, S = 1.8 phr and TBBS = 1.2 phr. The error in tan δ is ± 0.5% and ± 0.1% in frequency.

Molecular mechanics studies of phenyl ring flip motion in single chains of polystyrene indicates that the transition is due to a cooperative movement of
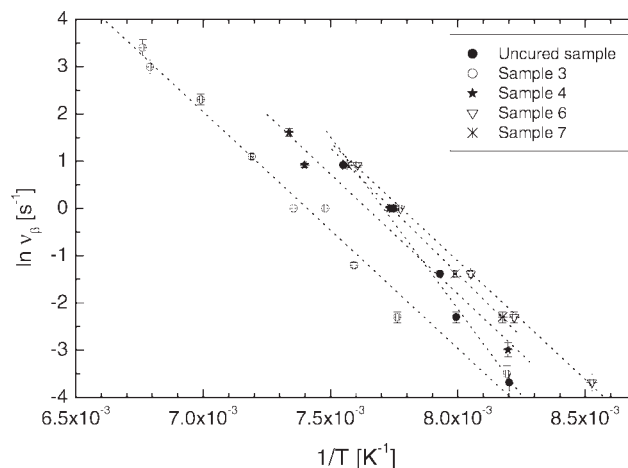
Figure 8 The Arrhenius plot. The slopes are related to the activation energy of the β-peak for each compound.

the phenyl ring at the chain backbone.[27] The ring flip transition in polystyrene is defined as a 180° rotation of the phenyl group around the carbon-carbon bond connecting it to the backbone of the polymer chain. The resistance to the phenyl group rotation depends on the conformation of the polymer backbone.[25–27]

It is known that both high *cis* 1,4-polybutadiene and high *trans* 1,4-polybutadiene isomerise with heat in presence of elemental sulphur.[28] As it was mention previously, the chemical structure of butadiene in the used SBR consists of 55% trans-1,4, 9.5% cis-1,4, and 12% 1,2-butadiene. Pellicioli et al.,[9] studying the network structure of sulphur cured SBR by solid state ^{13}C NMR, found out *cis-trans* isomerization during the vulcanisation process. This fact implies that the local conformations of the butadienes in SBR changes undergoing the uncured to the cured state. In this scenario it is expected some changes in the value of the activation energy ΔH_β of the transition process. Then the change in the activation energy of the β-relaxation from the uncured to the cure state might be associated to the *cis-trans* isomerisation. However, additional work must be done to stress this assertion.

CONCLUSIONS

Uncured and cured SBR compounds with different network structure were analyzed by means of dynamic mechanical tests in temperature range between 80 and 273 K. The crosslink density and the types of crosslinks in each compound depends on the sulphur/accelerator ratio in the formulation.

Loss tangent plots show two transitions. The main relaxation, α-relaxation, associated with the glass transition temperature has activation energy ΔH_α that depends on the total crosslink density and the types of linkages in network. At higher crosslink densities ΔH_α increases. In the range of low crosslink densities the amount of monosulphides linkages in the network structure changes the activation energy of the process.

The second relaxation in the glassy region of the SBR compound is associated to the rotation of phenyl group in the styrene of the SBR copolymer, with activation energy ΔH_β near to 10 kcal/mol. There was not difference in ΔH_β due to the crosslink density of the cured compounds but it is interesting to notice a difference with the value for the uncured sample. The *cis-trans* isomerization that takes place during vulcanization in the butadiene part of the SBR, might be the cause of conformational changes in the surrounding of the phenyl rings that affect the energy barrier associated to the phenyl rotation.

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