An Analysis of the Influence of the Accelerator/Sulfur Ratio in the Cure Reaction and the Uniaxial Stress–Strain Behavior of SBR

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ABSTRACT: Vulcanized styrene butadiene rubber (SBR) with different cure systems was prepared and analyzed by using the model of rubber elasticity based on the tube concept, applied to the treatment of the stress–strain measurements. Samples with several ratio accelerators to sulfur, Λ, between 0.22 and 3.0 cured at 433 K were studied. The network chain density and the crosslink density of the samples were evaluated. By means of normalized rheometer curves, the kinetics of cure of these samples were evaluated by considering the model of isothermal curing proposed by Kamal and Sourour. In this frame, the parameters of the kinetics model were obtained. A correlation between the order of the kinetic equation, n, and the network chain density of the cure samples was established. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 2601–2609, 2004

Key words: tube model; crosslink density; cure reaction; SBR vulcanizates

INTRODUCTION

The studies of the influence of crosslink structures in rubber vulcanized by using sulfur have been developed for several decades. It is known that rubbers are vulcanized at different conditions and with diverse chemicals to achieve an optimum balance of their mechanical properties.

Although vulcanization takes place by heat and pressure in the presence of sulfur, the process is relatively slow. A faster process can be achieved by using the addition of small amounts of chemicals known as accelerators. The quantity and kind of crosslinks formed during vulcanization are determined by the relative amounts of accelerator and sulfur used in the cure. Crosslink density is an important factor that affects the physical properties of the vulcanized elastomer network. The crosslink density of a compound depends mainly on the polymer, cure system, accelerator type, time and temperature of cure, and the sulfur/accelerator ratio.

In recent years, we have focused our research on the analysis of uniaxial stress–strain data of vulcanized rubbers in the frame of the conformational tube model.[1–4] Stress–strain measurements proved to be an indirect method for determining the crosslink density.[1–6] The analysis of uniaxial stress–strain data of unfilled and filled polymer network, in the frame of the conformational tube model, allows a proper separation of crosslink and constraint contribution to the mechanical behavior and gives a reliable determination of the crosslink densities.[1–6] The tube model assumes that, because of the topological constraints (e.g., entanglements), the motion of the molecular chain is essentially confined in a tubelike region made of surrounding polymers.[7,8]

This technique was used to analyze the effect of the cure conditions in oil extended styrene butadiene rubber (SBR 1712)[4] and natural rubber (NR).[5,6] In the last elastomer, two levels of sulfur/accelerator ratio in the compound were investigated and a very good correlation was found between the crosslink densities calculated by using the tube model and swelling techniques.[6] Stress–strain data of a blend of carbon black filled SBR/BR were also analyzed within the tube model to obtain the contribution of crosslinks and entanglements to the shear modulus.[9]

The present work deals with the structures of SBR vulcanizates with different ratios of accelerator/sulfur in its composition. Two types of studies were performed in these samples. By means of rheometric analysis, the cure reaction was evaluated by using the model proposed by Kamal and Sourour[10] and the kinetic parameters are obtained. On the other side, the chemical crosslinks in the network are determined by means of stress–strain measurements and are ana-

lyzed by using the tube approach developed by Heinrich et al.[1] Also, the change in the molecular parameters of the model with the composition of the curative ratio is obtained.

Finally, an experimental relation between the density of network chains and the order parameter of the kinetic equation is proposed.

THEORY

The tube model for crosslink networks assumes that due to the topological constraints, the motion of the chain is essentially confined in a tube-like region made of the surrounding polymers. Heinrich et al.[1,2] presented a relationship between stress, σ, and strain, ϵ, based on a tube model considering moderately crosslinked rubbers.

In this model, the reduced stress is expressed as

$$\sigma_M = \frac{\sigma}{(\lambda - \lambda^{-2})} = G_c + G_n f(\lambda) \tag{1}$$

with

$$f(\lambda) = 2 \frac{\lambda^{0.5\beta} - \lambda^{-\beta}}{\beta(\lambda^2 - \lambda^{-1})} \tag{2}$$

where σ_M is called the Mooney stress, λ is the expansion ratio $(1 + \epsilon)$, and β describes the relaxation of the deformed tube in the deformed state to an undeformed tube corresponding to the equilibrium state.[3] The parameter β ranges between 0 and 1. Values of β close to 0 indicate that the elastic properties in the network, prepared by end-linking reaction, are very sensitive to the completeness of the reaction.[1,11] At the other end, $\beta \approx 1$ was found to be relevant for almost complete converted unswollen well-connected networks made from long primary and crosslinked chains.[11] This is the case of sulfur crosslinked natural rubber.[5,6]

G_c and G_n represent the crosslink and the constraint contributions of the modulus, respectively, and G_c is connected to the molecular parameters by[3]

$$G_c = Akt \left\{ \nu_c - \frac{2\rho N_A}{(\phi - 2)M_n} \right\} \tag{3}$$

M_n, ρ, and ϕ are the number-average molecular weight of the primary chains, the polymer density, and the functionality of the crosslinks, and N_A, k, and T are the Avogadros's number, the Boltzmann's constant, and the absolute temperature, respectively.

The entanglements junctions confine the diffusion of a chain molecule within a tortuous path acting as a transient "crosslink," restricting the slippage of chains during deformation under applied stress.[12] In terms of the molecular parameters, G_n is expressed by

$$G_n = \frac{kT}{4\sqrt{6}} \beta^2 n_{st} \left(\frac{l_{st}}{d_0}\right)^2 \tag{4}$$

with

$$\frac{d_0}{l_{st}} = \alpha(n_{st}l_{st}^3)^{-1/2} \tag{5}$$

where n_{st} is the segment number density, l_{st} the length of the statistical segment, d_0 is the fluctuation range of a chain segment, and ν_c is the network chain density. The direct observation of the corresponding length scale, d_0, confirms the existence of the tube. These observations were reported by Richter et al.[13,14] by using neutron-spin-echo method for the analysis of dynamics of melts.

In eq. (3), A is a microstructure factor which depends on the ratio between the fluctuation range of a crosslink, d_c, and the end-to-end distance, R_c, of a network chain. A is defined as[3]

$$A = 1 - \frac{2}{\phi}\left[1 - \frac{2K\exp(K^2)}{\sqrt{\pi}\,\text{erf}(K)}\right] \tag{6}$$

with

$$K = \left(\frac{3\phi}{2}\right)^{1/2}\frac{d_c}{R_c} \tag{7}$$

The parameter α allows the connection of the modulus G_n with the plateau modulus G_N^0 of the uncrosslinked bulk polymer. The relationship is proposed[1,4] as

$$\alpha = 3.04 \frac{G_N^{0\ 1/2}}{G_n} \tag{8}$$

By using eqs. (4), (5), and (6), it is easy to obtain

$$n_{st} = 1.56\left(\frac{G_n}{l_{st}^3}\right)^{1/2}\left(\frac{2\alpha}{\beta}\right) = \left(\frac{4.74}{0.5\beta}\right)\left(\frac{G_N^0}{l_{st}^3 kT}\right)^{1/2} \tag{9}$$

and also the fluctuation range of the chain segment, d_0, as

$$d_0 = 0.8(0.5\alpha\beta)^{1/2}\left(\frac{kTl_{st}}{G_n}\right)^{1/4} \tag{10}$$

The end-to-end distance of a network chain, R_c, is expressed by

$$R_c = l_{st}\left(\frac{M_{ct}}{M_{st}}\right)^{1/2} \tag{11}$$

TABLE I
Compound Formulations (in phr), Density, Sol Fraction ω_s, and $t_{100\%}$ (MDR2000, 433 K)

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 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
Sulfur (S)	0.9	1.2	1.8	3.6	5.4	1.2	1.2
Λ (accelerator/S ratio)	1.33	1.00	0.66	0.33	0.22	1.5	3.0
$t_{100\%}$ (min)	33.7	30.9	28.3	22.3	22.1	27.0	26.9
ω_s	0.0971	0.0905	0.0892	0.0774	0.0694	0.0947	0.1143
Density (g/cm^3)	0.980	0.986	0.988	0.998	1.003	0.999	0.989

We can introduce the network chain molecular mass, M_{ct}, as the molecular mass between two crosslinks connected by a polymer chain defined as[15]

$$M_{ct} = \frac{(1 - \omega_s)M_{co}}{\left(1 + \dfrac{2M_{co}}{M_n}\right)} \quad (12)$$

where $M_{co} = \rho N_a/\nu_c$, ω_s is the sol fraction of the sample, and ν_c is obtained as a result of eq. (3).

EXPERIMENTAL PROCEDURES

Preparation and characterization of materials

The material used in the present study was unfilled styrene butadiene rubber (SBR 1502). Several formulations were prepared and they are given Table I. The average molecular weight of the elastomer was M_n = 176,000 g/mol determined by GPC, with a density ρ = 0.935 g/cm^3.

The gum mix was prepared in a laboratory mill, and it was characterized at 433 K by means of the torque curves in a Monsanto MDR2000 rheometer. From these curves, the time to achieve the maximum torque, $t_{100\%}$, was calculated.

The sample sheets of 150 × 150 × 2 mm were vulcanized 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, the $t_{100\%}$ values, and the sol fraction, ω_s, of each cured compound are given in Table I.

Vulcanization systems are normally classified in three major groups: conventional (CV), semiefficient (semi-EV), and efficient (EV) based on the level of sulfur and the value of the ratio accelerator to sulfur, Λ, in the recipe.[16,17] Following our compound formulation (Table I) and based on the Λ values, samples 1, 2, 3, and 6 correspond to the semi-EV group; samples 4 and 5 correspond to a CV system, and sample 7 is in the range of an EV system.

Stress–strain measurements

ASTM D412 samples for tensile tests were cut from the cured sheets. Stress–strain curves were measured with an Instron 4201 at room temperature at a deformation rate of $\dot{\epsilon} = 6 \times 10^{-4}$ s^{-1}. A load cell of $50N$ was used to obtain good sensitivity. Strain was measured by means of a large deformation extensometer (Instron XL) with 20 mm gauge length. A PC controlled the tests with software made in Basic language. The stress–strain curves were obtained for the three different samples of a given sheet and the average curve was calculated. The standard deviation in stress of the three tests was less than 0.015 MPa, whereas for the strain it was insignificant.

Dynamic mechanical measurements

To obtain the parameter α by means of eq. (8), it is necessary to evaluate the plateau modulus G_N^0 of the uncrosslinked bulk polymer. This was made by using a Rheometrics DMA IV in the traction mode in the frequency range between 0.01 and 150 Hz. Measurements were performed by using the isothermal mode at 293, 253, and 243 K. This mode is useful for measuring the storage modulus (E'), loss modulus E'', and loss tangent (tan δ). The plateau shear modulus is obtained from the plateau modulus E_N^0 by considering that $G = E/2(1 + \nu)$ with the Poisson modulus $\nu \approx 0.49$ for rubbers. The value of E_N^0 is equal to the storage modulus E' at the frequency where tan δ is at a minimum in the plateau zone[12,18] (i.e., $E_N^0 = [E']_{\text{tan }\delta \to \text{minimum}}$). The dynamic moduli as function of the angular frequency ω can be observed in Figure 1. At the minimum of tan δ, $E' = E_N^0 \approx 3.062$ MPa, then $G_N^0 \approx 1.027$ MPa.

RESULTS AND DISCUSSION

Normally, the cure level of a rubber compound is evaluated by means of the heat of reaction of the samples by using a differential scanning calorimetry (DSC). The cure level is defined as the ratio of the
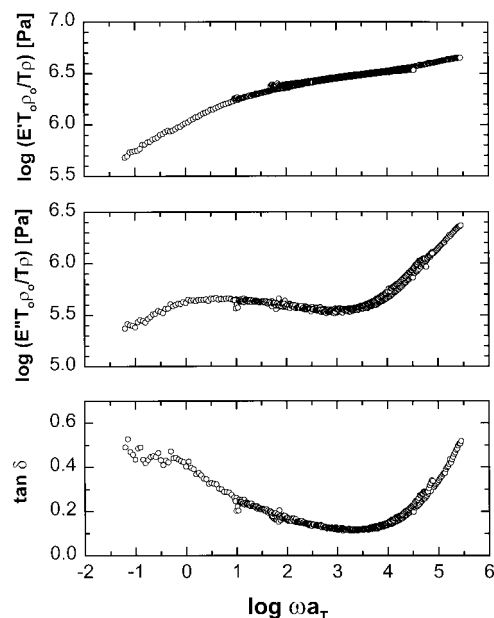
Figure 1 Master curves of SBR at 293 K. (a) Storage modulus, E'. (b) Loss modulus, E''. (c) Loss tangent, tan δ.

exothermic heat up to the experimental time, t, to the total heat reaction.

An indirect approach of evaluating the cure level of rubber compounds is through the rheometer torque curves. The rheometer responds only to the presence of elastically active crosslinks. In the case of the DSC curves, besides the elastically active crosslinking, the total of all enthalpic reactions are detected (pendant groups, cyclic sulfides, etc.).

The maximum torque of the rheometer curves is one of the most sensitive parameters to the crosslinks density. In Table II, the changes in the maximum torque M_h and the difference $(M_h - M_l)$, where M_l is the minimum torque, are given for all the samples prepared. The retractive force to resist a deformation is proportional to the number of network-supporting polymer chains per unit of elastomer and the higher number of junctures increases the number of supporting chains. Therefore, it is expected that M_h will increase at higher values of the network chain density.

This behavior is observed when increasing the sulfur content (samples 1 to 5 in Table II) and it is associated with a higher number of elastically active crosslinks.

If the level of sulfur in the formulation is constant and the accelerator (TBBS) increases, a higher value in the maximum torque is also observed (samples 2, 6, and 7 in Table II).

Normalized rheometer curves are shown in Figures 2 and 3 for the samples used in this research. In a recent article,[9] we analyzed rheometer curves of blends by using a model for isothermal curing[10,19] in which the state of cure (θ) is expressed by

$$\theta = \frac{\{k(t - t_0)\}^n}{1 + \{k(t - t_0)\}^n} \tag{13}$$

where k is the rate constant for the vulcanization, n is the order of the kinetic equation, t_0 is an induction time, and t is the reaction time. From the rheometer data, it can be stated that

$$\theta = \frac{M_h - M_t}{M_h - M_l} \tag{14}$$

with M_t the torque at time t. By using eqs. (13) and (14), the rheometer data of the samples were fitted with excellent agreement. Figures 2 and 3 show a comparison of the calculated and measured data pointing out the applicability of the concept. The obtained parameters for Eq. (13), k, n, and t_0, are given in Table II for each sample together with M_h and M_l. When analyzing the variation of n with the ratio of accelerator to sulfur, Λ, two behaviors were observed. If the amount of accelerator keeps constant in the recipe, n increases as the sulfur amount increases. On the other hand, if the amount of sulfur is the same and the amount of accelerator increases, the value of n increases too (Fig. 4).

To obtain the variation of the total density of crosslinks, the stress–strain curves of the samples were analyzed in the frame of the tube model.

A plot of $\sigma - \epsilon$ for the SBR gum mix cured at 433 K is given in Figures 5 and 6. These figures show the

TABLE II
Kinetic Parameters for the Different Samples According to Eq. (13)

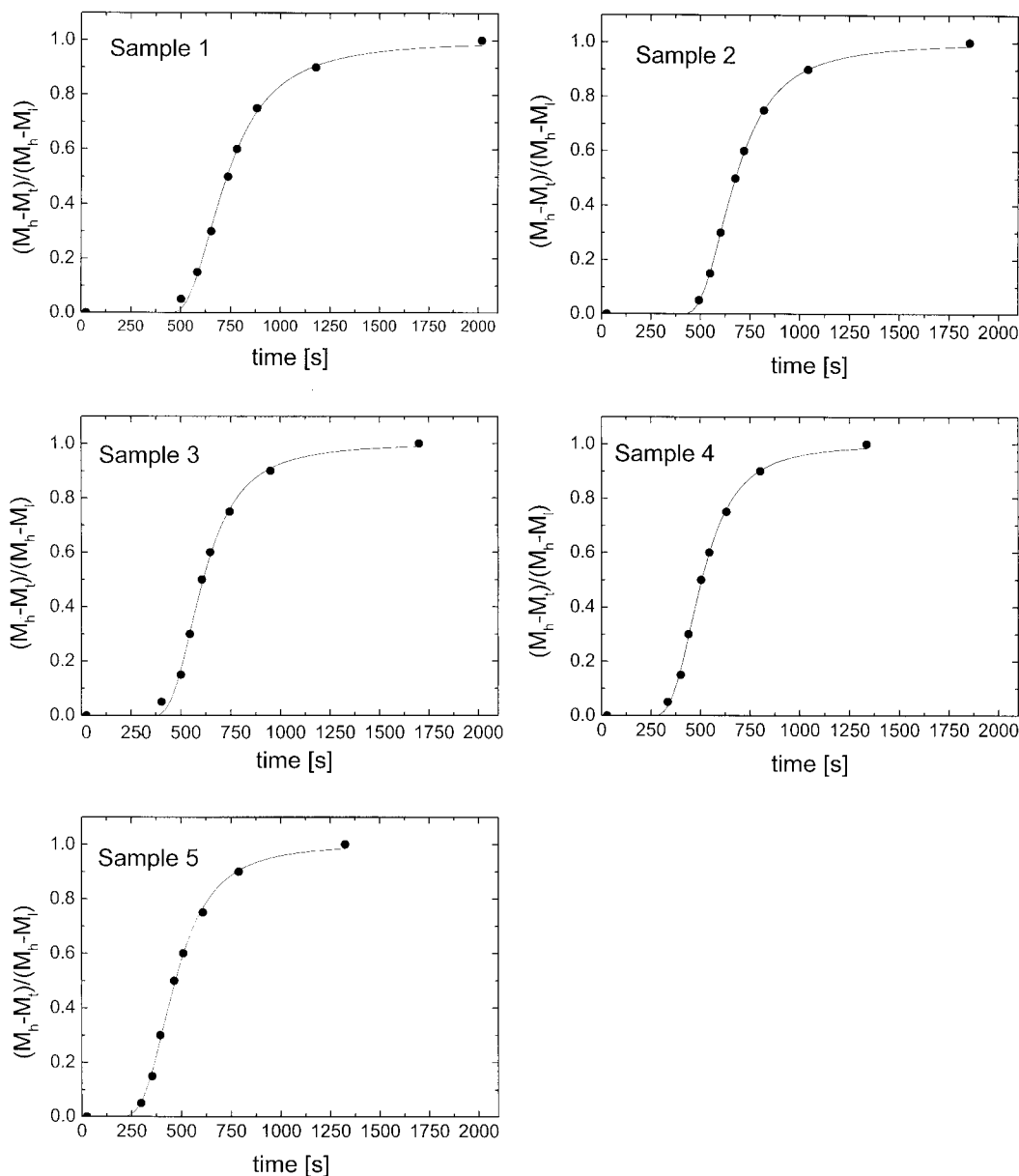| Sample	n	Rate constant k (s^{-1}) (10^3)	Induction time t_0 (s)	M_l (Nm)	M_h (Nm)	$M_h - M_l$ (Nm)
1	2.32	3.70	459	0.077	0.687	0.610
2	2.49	3.90	419	0.076	0.809	0.737
3	2.65	4.08	365	0.076	1.020	0.945
4	2.84	4.02	257	0.073	1.412	1.339
5	2.95	3.59	192	0.073	1.747	1.673
6	3.25	3.60	355	0.077	0.896	0.785
7	3.50	3.40	338	0.071	1.069	0.998

Figure 2 Normalized rheometer curves fitted to eq. (14) for SBR at 433 K: ●, experimental data; —, eq. (13). TBBS 1.2 phr, sulfur variable.

experimental data and the fit curves according to eq. (1). The overall error (χ^2) was less than 10^{-4}. The model parameters β, G_c, and G_n are given in Table III. The error in the determination of G_c and G_n was less than 1×10^{-3} MPa. The value of G_n remains approximately constant for all the samples with a mean value of (0.442 $\pm$ 0.018) MPa. The parameter β depends on the amount of sol fraction, solvent, and network defects and serves as an indicator of the completeness of the crosslink reaction. It can be observed in Table III that $0.9 \leq \beta \leq 1.0$ and these values are in the same range that we measured in sulfur crosslinked natural rubbers.[6]

By using eq. (8) with G_N^0 and G_n, the values of α were estimated for the different samples and they are

given in Table III. This parameter remains approximately constant with a value of 4.62 $\pm$ 0.09. A theoretical value of $\alpha \approx 8.5$ was reported in the case of melts.[20] However, for crosslinked rubbers, values in the range of $4 < \alpha < 5.8$ were reported.[1,4-6]

By means of G_c, G_n, and β, information about the network structure can be extracted. n_{st} and d_0 follow from G_n according to eqs. (9) and (10), respectively, and they are shown in Table III. Because n_{st} depends on the Kuhn's statistical segment length, l_{st}, it was extracted from literature. For SBR,[18] $l_{st} = 1.06$ nm; then average values of $n_{st} = 4.51$ nm^{-3} and $d_0 = (2.12 \pm 0.06)$ nm were calculated. This last value is in the range of the one obtained in other elastomers.[4-6] Considering the molecular mass of the statistical segment
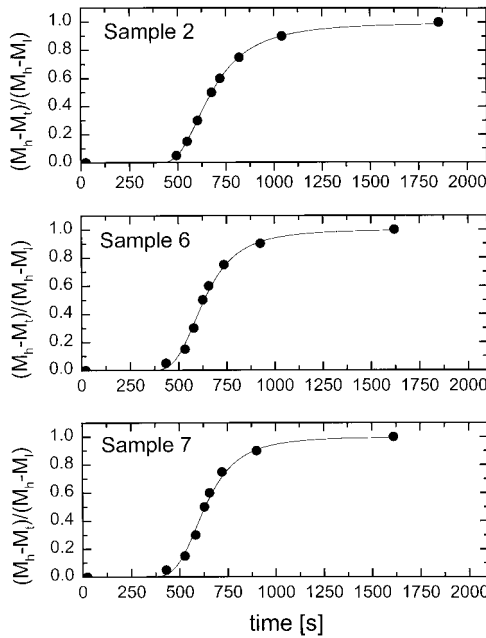
Figure 3 Normalized rheometer curves fitted to eq. (14) for SBR at 433 K: ●, experimental data; —, eq. (13). TBBS variable, sulfur 1.2 phr.

as $M_{st} = \rho N_A / n_{st}$, an average value of 125 g/mol was obtained. This value is close to the one calculated in another article.[4]

By using the values of G_c, the molecular parameters relative to crosslinks, M_{ct} and ν_c, were estimated. From eq. (3), and considering the case of a four-functional network, it is possible to calculate the value of the network chain density, ν_c, and, according to eq. (12), the value of network chain molecular mass, M_{ct}. Because in these equations the microstructure factor A is

involved, then M_{ct}, ν_c, and itself must be determined iteratively by using eqs. (6) and (7). The procedure to calculate ν_c is as follows:

1. Assuming first ν_c value, calculate M_{ct} by using $\rho N_A / \nu_c$.
2. Solve eq. (12) and calculate R_c from eq. (11).
3. Using eqs. (7) and (6), calculate A value.
4. With A value and eq. (3), obtain a new ν_c value.
5. With new ν_c, recalculate iteratively up to the value converged.

In eq. (7), it must be noted that d_0 is used instead of d_c. This implies that the additional constraints acting on a crosslink are approximately equal to constraints acting on a chain segment.[2]

According to eq. (11), the end-to-end distance of a network chain, R_c, is presented in Table III for both samples. From the results of R_c, it can be observed that $l_{st} < d_0 < R_c$ for each cure level analyzed. This kind of behavior was reported in other studies of elastomers.[1,3–6]

The network chain density ν_c is modified by the ratio accelerator to sulfur as can be appreciated from Figure 7(a).

In a four-functional network assumed in the present case, the density of elastically active crosslink μ_c is related to the density of all network chains, ν_o, by[21]

$$\nu_0 = 2\mu_c + \nu_n \tag{15}$$

where ν_n is the density of the primary chain prior to vulcanization. Both ν_0 and ν_n can be transformed by
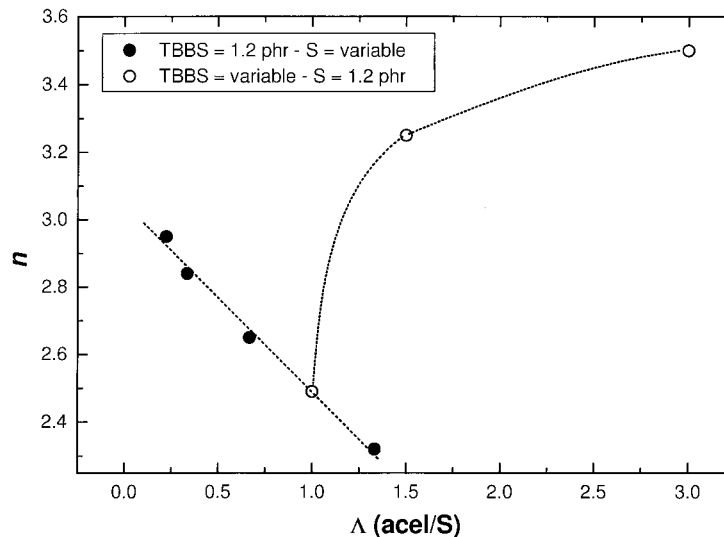

Figure 4 Variation of the reaction order n with the ratio accelerator to sulfur Λ in the analyzed SBR samples. Dotted lines are given only for showing the tendency.
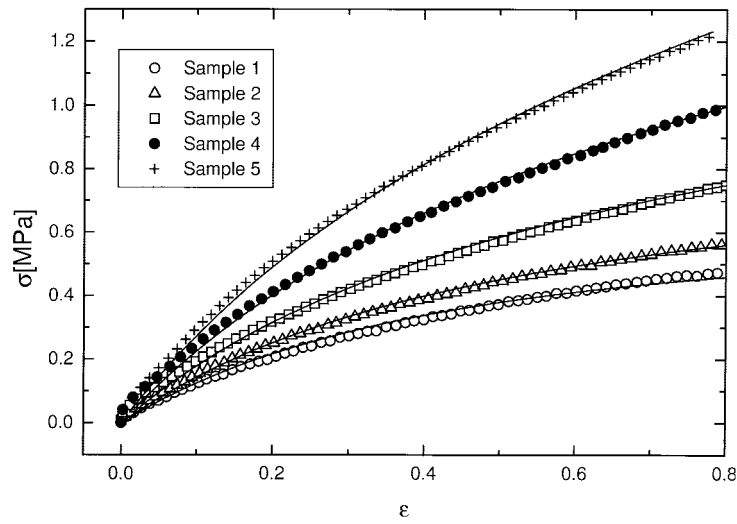
Figure 5 Stress–strain data and fit curves using eq. (1) of samples of SBR gum with 1.2 phr of accelerator and different sulfur content cured at 433 K.

using the molecular weights by $\nu_0 = \rho/M_{ct}$ and $\nu_n = \rho/M_n$. Then μ_c is defined by

$$\mu_c = \frac{\rho}{2}\left(\frac{1}{M_{ct}} - \frac{1}{M_n}\right) \tag{16}$$

In Figure 7(b), μ_c is plotted against Λ.

It is interesting to note the similar form of Figures 4 and 7(a, b). To our knowledge, there is no mention in literature that establishes a relationship between the reaction order of the vulcanization kinetic with the network chain density. However, if our data are observed carefully, an experimental relation between n and ν_c will be discovered. Typical results are shown in

Figure 8. It was found that substantially linear relations were obtained when log ν_c was plotted against log n. Then, experimentally, the results could be represented by

$$\log \nu_c = C + D \log n \tag{17}$$

where C and D are constants.

In Figure 8, two curves are shown: depending on the samples they have equal amounts of sulfur or accelerator in their individual recipes. It must be noticed that these findings were found for statistically crosslinked networks from long primary chains, as is the case of sulfur crosslinked rubbers, in which $\beta \approx 1$.[1]
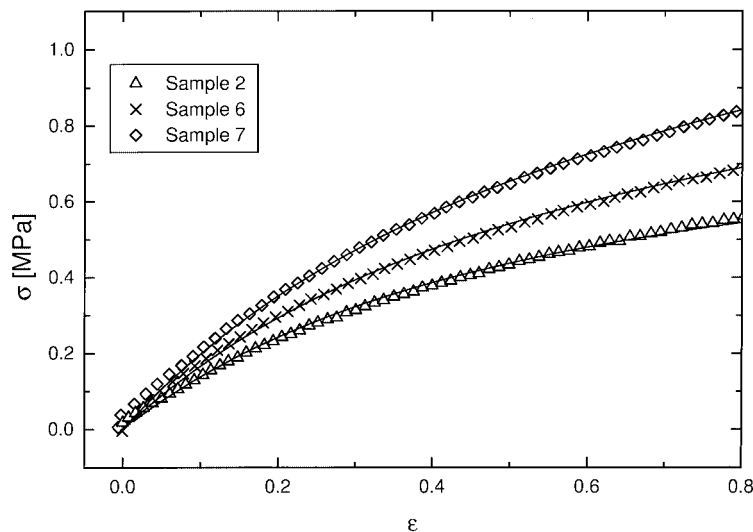

Figure 6 Stress–strain data and fit curves using eq. (1) of samples of SBR gum with 1.2 phr of sulfur and different accelerator content cured at 433 K.

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TABLE III
Variation of Molecular Parameters of Tube Model for the Samples

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Sample	β	G_c (MPa)	G_n (MPa)	α	n_{st} (nm^{-3})	M_{st} (g/mol)
1	0.90	0.052	0.432	4.69	4.86	116
2	0.90	0.121	0.433	4.68	4.86	116
3	1.00	0.251	0.430	4.70	4.37	129
4	1.00	0.406	0.448	4.60	4.37	129
5	1.00	0.562	0.470	4.49	4.37	129
6	1.00	0.217	0.420	4.75	4.37	129
7	1.00	0.294	0.462	4.53	4.37	129

Sample	d_0 (nm)	M_{co} (g/mol)	M_{ct} (g/mol)	ν_c (nm^{-3})	R_c (nm)	A
1	2.0660	34281	22275	0.016	14.69	0.962
2	2.064	16124	12394	0.035	10.96	0.933
3	2.183	7452	6258	0.075	7.38	0.848
4	2.139	4310	3791	0.131	5.75	0.779
5	2.088	2902	2615	0.194	4.77	0.721
6	2.209	8693	7140	0.065	7.82	0.862
7	2.106	6290	5200	0.089	6.73	0.833

The above preliminary results, although limited to the case of networks with $\beta \approx 1$, show that the total network chain density in the fully cured samples is related to the order parameter of the kinetic equation. Additional investigations should be performed if our results were to be extended to networks with $\beta \ll 1$ (for example, networks prepared by an end-linking reaction).[1]

The correlation $n - \nu_c$ presented in this work could be evaluated in future research not only in elastomers with different cure systems but also in cured filled compounds. This tool opens the possibility of obtaining more precise information on the behavior of rubber compounds starting from the use of widely accepted experimental methods.

CONCLUSION

This study shows that the model of Kamal and Sourour can be applied successfully to evaluate the reaction kinetics of SBR cured at 433 K by using torque curves obtained by means of an oscillating disk rheometer. It was shown that the reaction order, n, changes with the accelerator to sulfur ratio (Λ) in the compound. Keeping constant the accelerator fraction in the compound, n increases at higher levels of sulfur. Also, if the fraction of sulfur remains constant, an increase in the amount of accelerator produces higher values of n.

Uniaxial stress–strain curves of SBR cured samples with different values of Λ were predicted correctly by using the model of rubber elasticity based on the tube concept. In this frame, the variation of the density of elastically active crosslinks and the network chain density with Λ were evaluated.

Finally, an empirical relationship that links the reaction order with the density of network chains were settled down. We consider that it is a new area to explore in future research.
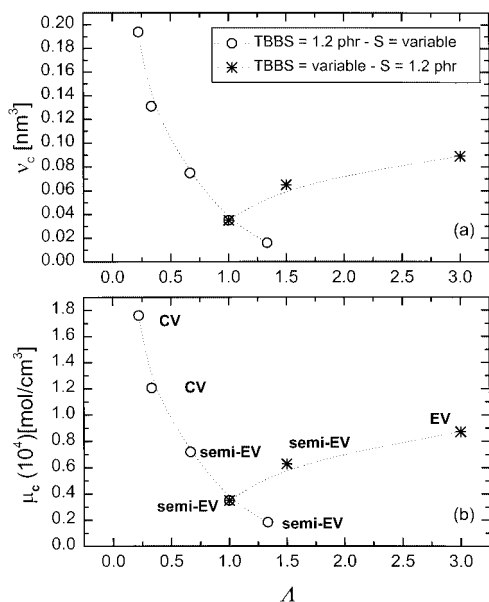

Figure 7 (a) Variation of the network chain density, ν_c, with the accelerator/sulfur ratio, Λ, for the different analyzed samples. (b) Variation of the crosslink density, μ_c, with the accelerator/sulfur ratio Λ for the different analyzed samples.
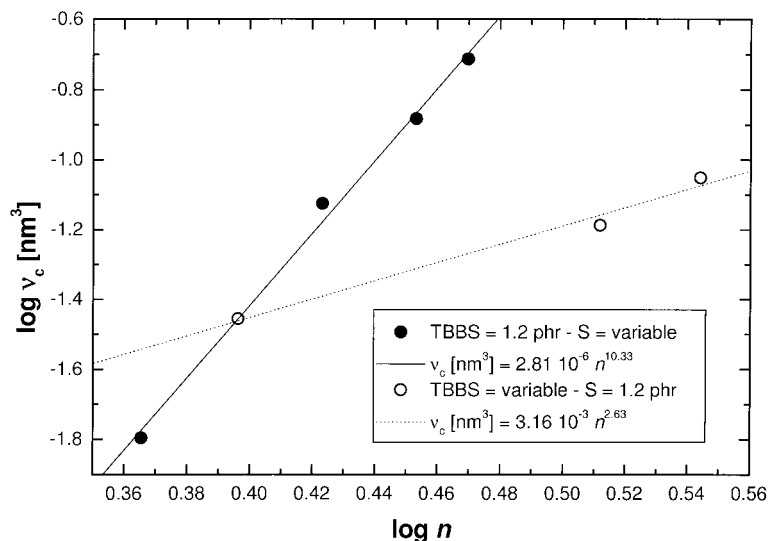
Figure 8 Correlation between the order of the kinetic equation n and the network chain density, ν_c.

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