

# Vulcanization Kinetic of Styrene–Butadiene Rubber by Sulfur/TBBS

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**ABSTRACT:** Torque curves, measured with a moving die rheometer at temperatures between 413 and 473 K, were used to characterize the vulcanization of styrene–butadiene rubber with different cure systems based on sulfur and TBBS (*N*-*t*-butyl-2-benzothiazole sulfenamide). Several compounds were prepared varying the amount of sulfur and accelerator between 0.5 and 2.5 phr in the formulation. By means of normalized torque curves, the kinetic of cure of these samples was evaluated considering the model of isothermal curing proposed by Kamal and Sourour. In this frame, the parameters of the kinetic model were obtained.

The effect of the amount of sulfur and accelerator in the compound on the kinetic parameters was investigated and a maximum of the rate parameter  $k$  for the compound with formulation with 1.0 phr of sulfur and 2.0 phr of accelerator was found. A marked decrease in the activation energy of the cure process of the elastomer was observed at higher levels of TBBS in the compound. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 35–41, 2006

**Key words:** styrene–butadiene rubber; vulcanization; cure reaction; kinetics; activation energy

## INTRODUCTION

The influence of crosslink structures in rubber vulcanized using sulfur has been studied during several decades. It is known that the mechanical properties of the cured rubber compounds are strongly influenced mainly by the cure system and the process conditions.<sup>1</sup>

Although vulcanization takes place by heat and pressure in presence of sulfur, the process is relatively slow. A faster process can be achieved 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 and the time, temperature, and pressure applied in the process. For many applications, the accelerator–sulfur vulcanization is the only rapid crosslinking technique, which can give the delayed action required for processing, shaping, and forming before the formation of the cured network.<sup>1</sup>

The main techniques used to study rubber vulcanization include chemical analysis, differential scanning calorimetry, oscillating disk rheometry (ODR), and moving die rheometry (MDR). The last two ones consider that the crosslinking density is proportional to

the stiffness of the rubber and the change of this mechanical property is measured during the isothermal curing of the sample. A test piece of rubber compound is contained in a sealed test cavity under positive pressure and maintained at a specified elevated temperature. In the case of ODR, a rotor is embedded in the test piece and is oscillated through small specified rotary amplitude. In the other side, MDR has an oscillating lower die that eliminates the need of a rotor giving a better data accuracy and thermal recovery. This action exerts a shear strain on the test piece and the torque (force) required to oscillate the disc (ODR) or the moving die (MDR) depends upon shear modulus of the rubber compound.

Several research works were done in the past to explain the complete kinetic, thermal, and rheological characterization of the vulcanization of rubber compounds. Ding and Leonov<sup>2</sup> proposed a kinetic approach based on a realistic model reaction scheme that considers the induction, curing, and overcured periods present during the vulcanization of rubber. The model prediction demonstrated a good agreement with isothermal rheometer data of oil extended SBR and NR compounds.<sup>2,3</sup> Ghosh et al.<sup>4</sup> developed a kinetic model using population balance methods considering the polysulfide nature of the crosslinks to explain the vulcanization of natural rubber with 2-(morpholinothio) benzothiazole as accelerator. On the other hand, the phenomenological approach is based on experimental observations. An Arrhenius relationship is frequently used to explain the induction time

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TABLE I  
Compound Formulations in Parts per Hundred of Rubber (phr)

Sample no.	SBR 1502	Zinc oxide	Stearic acid	Antioxidant	Accelerator (TBBS)	Sulfur (S)	$\Lambda$ (accelerator/S ratio)
1	100	5	2	1.2	2.5	0.5	5.00
2	100	5	2	1.2	2.0	1.0	2.00
3	100	5	2	1.2	1.5	1.5	1.00
4	100	5	2	1.2	1.0	2.0	0.50
5	100	5	2	1.2	0.5	2.5	0.20
6	100	5	2	1.2	0.5	0.5	1.00
7	100	5	2	1.2	1.0	1.0	1.00
8	100	5	2	1.2	2	2	1.00
9	100	5	2	1.2	2.5	2.5	1.00
10	100	5	2	1.2	1.5	0.5	3.00
11	100	5	2	1.2	0.5	1.5	0.33
12	100	5	2	1.2	2.5	1.5	1.66
13	100	5	2	1.2	1.5	2.5	0.60

and the application of the so-called general form of macrokinetics is employed for the curing periods.<sup>5-7</sup>

In our research group, we analyzed the influence stress-strain curves and dynamic-mechanical properties of SBR and NR compounds with different sulfur/accelerator ratio in their compositions.<sup>8-12</sup> An empirical relationship that links the reaction order with the density of network chains were settled down.<sup>10</sup>

The present work deals with the structures of SBR vulcanizates with different ratio accelerator/sulfur in their composition. Measurements of torque as function of time with a MDR in isothermal condition proved to be a successful tool to analyze the cure kinetics of elastomers.<sup>10,13</sup> By means of the rheometric analysis, the cure reaction is evaluated using the model proposed by Kamal and Sourour<sup>5</sup> and the kinetic parameters were obtained. In this study, we extend the application of the model to a broader range of concentrations of sulfur and accelerator in the SBR compound at different cure temperatures. Considering an Arrhenius dependence of the process rate with temperature, the dependence of the activation energy of the process with the main components of the cure system, i.e., sulfur and accelerator, is analyzed.

### THEORY

In recent articles,<sup>8,9,13</sup> we analyzed rheometer curves of rubber compounds using a model for isothermal curing<sup>5,6</sup> in which the state of cure ( $\theta$ ) is expressed by

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

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. This last equation responds to a macrokinetic model proposed by Kamal and Sourour<sup>5</sup> used to describe the evolution of the heat of reaction

during curing. The model assumes that the exothermic heat generated during isothermal cure is proportional to the reactions between sulfurating species and allylic hydrogens in the polymer system.

Equation (1) can be used for explaining the curing period of the accelerated sulfur vulcanization. It is not useful for the analysis of the process in the scorch delay or induction period. During this period, it is believed that the accelerator chemistry plays the main role in the vulcanization process. Following the curing period, a third period can be considered where the

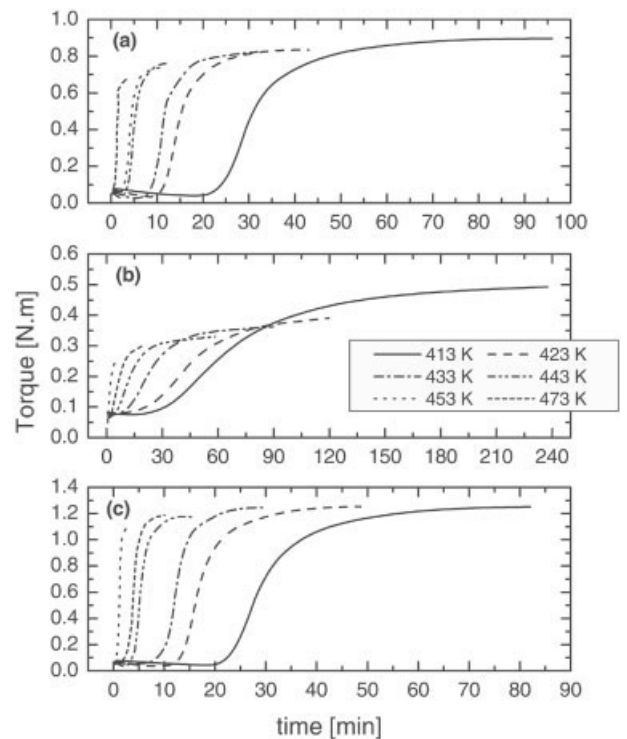


Figure 1 The torque curves as a function of the time and temperature: (a) sample 2, (b) sample 6, and (c) sample 9.

**TABLE II**  
**Values of  $M_l$  and  $M_h$  (Nm) Obtained from the**  
**Rheometer Curves for All the Samples at the Analyzed**  
**Temperatures**

Sample no	T (K)					
	413	423	433	443	453	473
1						
$M_l$	0.655	0.592	0.595	0.059	0.055	0.049
$M_h$	0.55	0.92	0.95	0.552	0.618	0.523
2						
$M_l$	0.079	0.071	0.066	0.059	0.055	0.049
$M_h$	0.817	0.763	0.759	0.702	0.686	0.630
3						
$M_l$	0.079	0.072	0.069	0.060	0.055	0.051
$M_h$	0.931	0.898	0.916	0.809	0.777	0.704
4						
$M_l$	0.086	0.077	0.071	0.063	0.056	0.053
$M_h$	1.078	1.016	0.996	0.917	0.848	0.771
5						
$M_l$	0.086	0.080	0.073	0.067	0.059	0.055
$M_h$	1.054	1.032	0.995	0.946	0.876	0.824
6						
$M_l$	0.080	0.080	0.073	0.064	0.060	0.050
$M_h$	0.493	0.391	0.363	0.330	0.301	0.253
7						
$M_l$	0.081	0.081	0.081	0.081	0.081	0.081
$M_h$	0.688	0.645	0.699	0.593	0.619	0.566
8						
$M_l$	0.080	0.070	0.068	0.059	0.055	0.052
$M_h$	1.140	1.096	1.158	1.046	1.065	0.987
9						
$M_l$	0.079	0.070	0.063	0.058	0.055	0.051
$M_h$	1.251	1.252	1.244	1.173	1.189	1.104
10						
$M_l$	0.085	0.072	0.069	0.062	0.059	0.055
$M_h$	0.601	0.578	0.560	0.526	0.562	0.613
11						
$M_l$	0.082	0.075	0.070	0.063	0.063	0.052
$M_h$	0.720	0.690	0.710	0.649	0.690	0.531
12						
$M_l$	0.082	0.077	0.069	0.063	0.055	0.049
$M_h$	1.104	1.077	1.044	1.033	0.984	0.895
13						
$M_l$	0.084	0.077	0.070	0.063	0.058	0.052
$M_h$	1.241	1.221	1.192	1.157	1.099	0.989

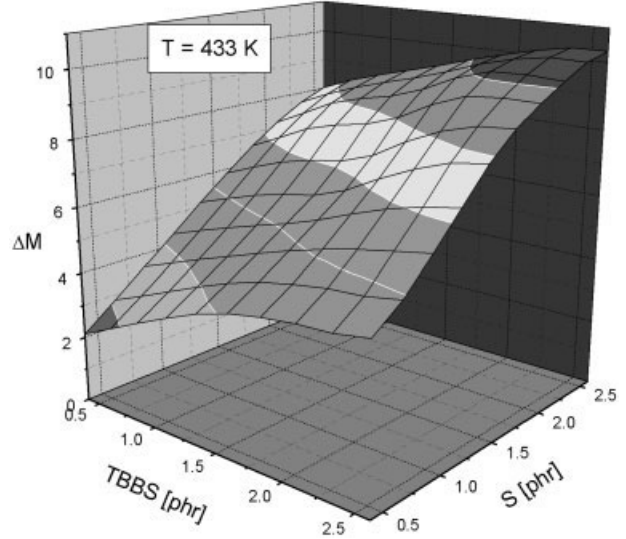
formed networks could maintain an equilibrium value, reversion, or increasing modulus depending on the characteristics of the rubber compound.<sup>2</sup>

The rate constant  $k$  is normally expressed by an Arrhenius-type temperature dependence

$$k = k_0 \exp(-E/RT) \quad (2)$$

where  $k_0$ ,  $E$ , and  $R$  are the pre-exponential constant, activation energy, and gas constant, respectively.  $T$  is the absolute temperature.

The use of the relationship expressed by eq. (1) to analyze torque rheometer data is due to the fact that the formation of elastically active crosslinks during isothermal curing is the cause of the changes in the



**Figure 2** Variation of  $\Delta M$  with the amount of sulfur and accelerator in the sample for the rheometer test at 433 K.

torque measurement needed to maintain the oscillating deformation in the sample.

Then, from the rheometer data, it can be stated that

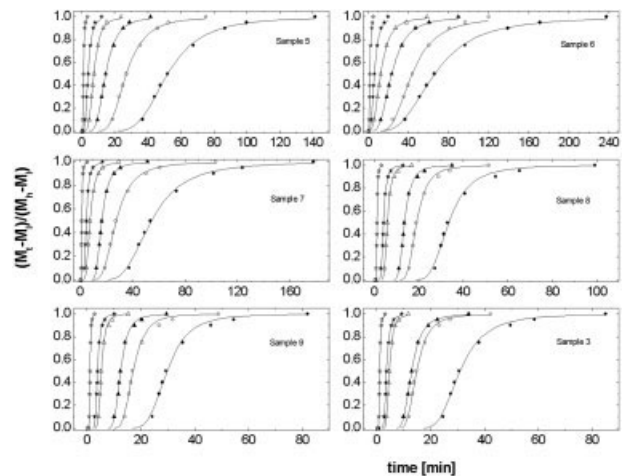
$$\theta = \frac{M_t - M_l}{M_h - M_l} \quad (3)$$

where  $M_h$  is the maximum torque,  $M_l$  is the minimum torque, and  $M_t$  is the torque at time  $t$ . Using eqs. (1) and (3) the rheometer data of the samples could be fitted and the kinetic parameters could be evaluated.

## EXPERIMENTAL

### Sample preparation

The material used in the present study was unfilled styrene-butadiene rubber (SBR) SBR-1502 that con-



**Figure 3** Comparison between torque-normalized curves (experimental data) and eq. (1).

**TABLE III**  
Kinetic Parameters Obtained Fitting the Experimental Data Normalized Torque Versus Time with of eq. (1)

Temperature (K)	$n$	$k$ (min <sup>-1</sup> )	$t_o$ (min)	$\chi^2$	$E$ (kJ/mol)
Sample 1					
413	2.65	0.062	22.8	0.44	78.6 ± 7.2
423	2.65	0.144	10.7	0.44	78.6 ± 7.2
433	2.65	0.188	8.8	0.44	78.6 ± 7.2
443	2.65	0.381	3.5	0.44	78.6 ± 7.2
453	2.65	0.384	3.3	0.44	78.6 ± 7.2
473	2.65	1.406	1.0	0.44	78.6 ± 7.2
Sample 2					
413	2.90	0.083	19.2	1.61	85.5 ± 5.9
423	2.90	0.172	9.3	1.61	85.5 ± 5.9
433	2.90	0.230	7.3	1.61	85.5 ± 5.9
443	2.90	0.486	2.9	1.61	85.5 ± 5.9
453	2.90	0.587	2.4	1.61	85.5 ± 5.9
473	2.90	2.268	0.8	1.61	85.5 ± 5.9
Sample 3					
413	3.11	0.069	16.6	0.43	83.7 ± 6.3
423	3.11	0.151	8.3	0.43	83.7 ± 6.3
433	3.11	0.174	7.2	0.43	83.7 ± 6.3
443	3.11	0.459	2.5	0.43	83.7 ± 6.3
453	3.11	0.566	1.9	0.43	83.7 ± 6.3
473	3.11	1.614	0.5	0.43	83.7 ± 6.3
Sample 4					
413	3.01	0.052	27.7	0.23	88.7 ± 2.7
423	3.01	0.089	14.0	0.23	88.7 ± 2.7
433	3.01	0.148	7.4	0.23	88.7 ± 2.7
443	3.01	0.262	2.9	0.23	88.7 ± 2.7
453	3.01	0.439	1.4	0.23	88.7 ± 2.7
473	3.01	1.399	0.4	0.23	88.7 ± 2.7
Sample 5					
413	3.10	0.031	19.6	0.19	97.0 ± 4.3
423	3.10	0.057	9.6	0.19	97.0 ± 4.3
433	3.10	0.097	4.3	0.19	97.0 ± 4.3
443	3.10	0.176	1.7	0.19	97.0 ± 4.3
453	3.10	0.297	0.5	0.19	97.0 ± 4.3
473	3.10	1.186	0.2	0.19	97.0 ± 4.3
Sample 6					
413	2.69	0.020	11.4	0.24	96.9 ± 5.9
423	2.69	0.031	11.8	0.24	96.9 ± 5.9
433	2.69	0.051	4.0	0.24	96.9 ± 5.9
443	2.69	0.085	0.6	0.24	96.9 ± 5.9
453	2.69	0.176	0.4	0.24	96.9 ± 5.9
473	2.69	0.674	0.2	0.24	96.9 ± 5.9
Sample 7					
413	2.86	0.028	19.1	0.34	99.6 ± 3.6
423	2.86	0.058	10.4	0.34	99.6 ± 3.6
433	2.86	0.129	8.9	0.34	99.6 ± 3.6
443	2.86	0.188	2.4	0.34	99.6 ± 3.6
453	2.86	0.343	1.9	0.34	99.6 ± 3.6
473	2.86	1.222	0.5	0.34	99.6 ± 3.6
Sample 8					
413	3.20	0.066	18.4	0.87	84.7 ± 3.8
423	3.20	0.131	11.4	0.87	84.7 ± 3.8
433	3.20	0.202	8.6	0.87	84.7 ± 3.8
443	3.20	0.368	3.1	0.87	84.7 ± 3.8
453	3.20	0.494	2.1	0.87	84.7 ± 3.8
473	3.20	1.691	0.6	0.87	84.7 ± 3.8

**TABLE III** *Continued*

Temperature (K)	$n$	$k$ (min <sup>-1</sup> )	$t_o$ (min)	$\chi^2$	$E$ (kJ/mol)
Sample 9					
413	3.50	0.073	15.8	0.84	83.6 ± 3.3
423	3.50	0.132	9.4	0.84	83.6 ± 3.3
433	3.50	0.204	7.6	0.84	83.6 ± 3.3
443	3.50	0.401	2.9	0.84	83.6 ± 3.3
453	3.50	0.531	2.1	0.84	83.6 ± 3.3
473	3.50	1.673	0.6	0.84	83.6 ± 3.3
Sample 10					
413	2.73	0.032	28.0	0.53	92.4 ± 3.7
423	2.73	0.064	14.4	0.53	92.4 ± 3.7
433	2.73	0.119	11.0	0.53	92.4 ± 3.7
443	2.73	0.209	4.1	0.53	92.4 ± 3.7
453	2.73	0.292	2.7	0.53	92.4 ± 3.7
473	2.73	1.083	0.4	0.53	92.4 ± 3.7
Sample 11					
413	2.77	0.023	15.0	0.42	98.9 ± 2.8
423	2.77	0.041	5.3	0.42	98.9 ± 2.8
433	2.77	0.097	5.6	0.42	98.9 ± 2.8
443	2.77	0.150	1.3	0.42	98.9 ± 2.8
453	2.77	0.293	1.0	0.42	98.9 ± 2.8
473	2.77	0.868	0.7	0.42	98.9 ± 2.8
Sample 12					
413	3.30	0.064	30.4	0.92	82.2 ± 2.8
423	3.30	0.114	17.0	0.92	82.2 ± 2.8
433	3.30	0.185	9.3	0.92	82.2 ± 2.8
443	3.30	0.290	4.7	0.92	82.2 ± 2.8
453	3.30	0.465	2.2	0.92	82.2 ± 2.8
473	3.30	1.425	0.6	0.92	82.2 ± 2.8
Sample 13					
413	3.37	0.065	25.1	0.25	86.7 ± 3.1
423	3.37	0.115	17.9	0.25	86.7 ± 3.1
433	3.37	0.191	7.2	0.25	86.7 ± 3.1
443	3.37	0.307	3.5	0.25	86.7 ± 3.1
453	3.37	0.526	1.6	0.25	86.7 ± 3.1
473	3.37	1.688	0.4	0.25	86.7 ± 3.1

tains 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  $M_n = 92,800$  g/mol determined by GPC, with a density 0.935 g/cm<sup>3</sup>. 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 ratio accelerator/sulfur,  $\Lambda$ , is also given. The gum mixes were prepared in a laboratory mill of 150 mm × 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.

### Rheometer tests

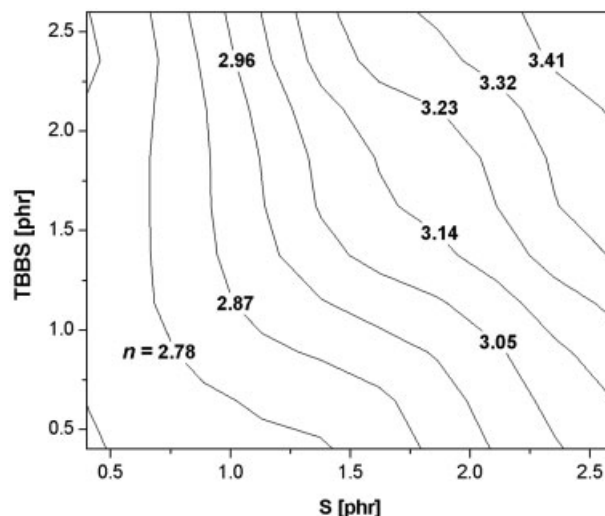
The gum mixes were characterized at 413, 423, 433, 443, 453, and 473 K by means of the torque curves in a Monsanto MDR2000 rheometer. As an example, some of these curves are shown in Figure 1. From each of these curves some characteristic parameters as the torque minimum  $M_l$  and the torque maximum  $M_h$  were obtained. These values are given in Table II at each tested temperature.

## RESULTS AND DISCUSSION

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.

The maximum torque of the rheometer curves is one of the most sensitive parameters to the crosslinks density. 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.<sup>9</sup> As it can be observed in Table II, the variation of the minimum torque with the composition of the sample is not so important related with the maximum torque at the same temperature. To avoid this effect, normally the difference  $\Delta M = (M_h - M_l)$  is used to analyze the experimental data. Figure 2 shows an example of the influence of the composition on the behavior  $\Delta M$  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. The same behavior was observed at the other test temperatures.

From the experimental data shown in Figure 1, the normalized curves of the rheometer tests were obtained using eq. (3). Then, these curves were fitted using eq. (1) for each test temperature. For this fitting, we have considered that the parameter associated with the reaction order ( $n$ ) does not vary with temperature. This assumption is used in several research works of vulcanization in literature.<sup>2,6,7</sup> Then, we assume that  $n$  could change with the compound formulation, i.e. the amount of sulfur and accelerator in each compound. Through nonlinear curve fitting routine provided by Origin 6.0 software (Microcal), we fit simultaneously to eq. (1) all the torque-normalized curves of the same compound at the six tested temperatures. Comparison between experimental and the theoretical approach is given in Figure 3 where we selected some examples. As it can be observed the agreement is very good. The parameters obtained for the kinetic eq. (1),  $k$ ,  $n$ , and  $t_o$  are given in Table III for each sample at each temperature. The goodness of fit is given in Table III by the values of  $\chi^2$ .



**Figure 4** Variation of  $n$  with the level of sulfur and accelerator (TBBS) in the compound.

The values for the parameter  $n$  are similar to those obtained in our previous research in this kind of compound.<sup>9</sup> In Figure 4, a contour graph of  $n$  can be appreciated showing the variation with the amount of sulfur and accelerator TBBS in the compound formulation. There is a tendency to increase the value of  $n$  with the quantity of sulfur and accelerator.

It is interesting to notice that the rate parameter  $k$  does not show a monotonous increase when increasing both the sulfur and accelerator content in the compound formulation. In fact, maximum value of  $k$  is observed for compositions close to 1.0 phr of sulfur and 2.0 phr of TBBS. This behavior is shown in Figure 5 where contour plots of  $k$  as function of the sulfur and accelerator content are given. A change is not observed in the shape of the plots with the cure temperature.

The variation of the rate parameter  $k$  was also analyzed as function of the temperature. Figure 6 shows this dependence in a semilog plot. For all the samples, a straight line can be fitted to the data. This implies that the eq. (2) represents in a good way the behavior of  $k$  with temperature and the slope of each linear fit is related to the activation energy of the cure process  $E$ . These values are also included in Table III for each analyzed compound and they are similar to those obtained in several research works in literature for the kinetic reaction of SBR with other cure systems.<sup>3,7</sup>

Figure 7 shows the dependence of the activation energy with the cure system used in each sample, i.e. the amount of sulfur and accelerator used in each composition. It is interesting to notice that  $E$  increases at lower amounts of accelerator in the compound and the variation of  $E$  with the sulfur content is less important in the range of studied formulations in this research. This fact stresses the idea that the change in

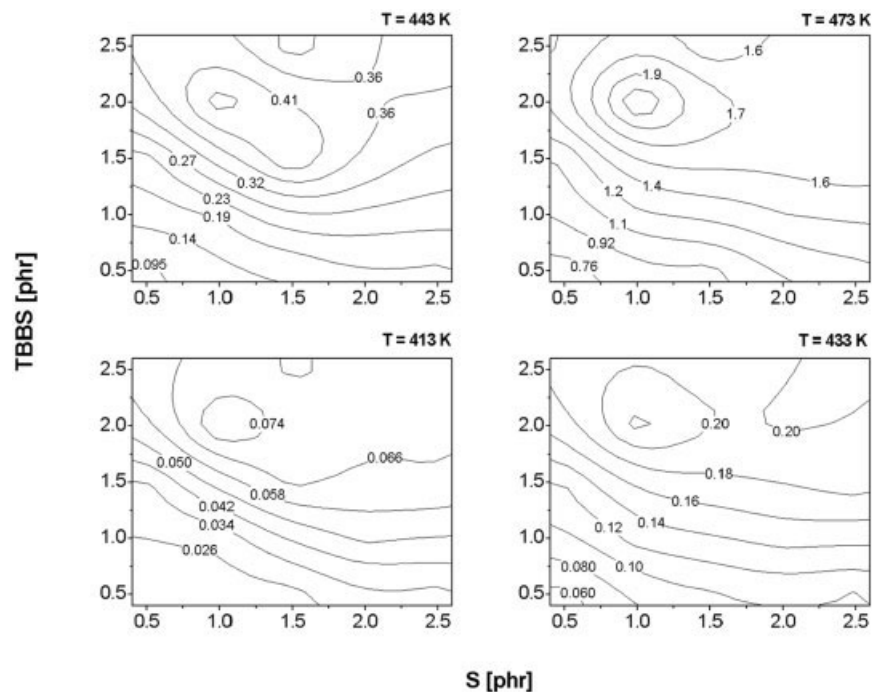


Figure 5 Contour plot of the rate parameter  $k$  ( $10^{-3}$ ) [ $\text{min}^{-1}$ ] at four different test temperatures.

the activation energy with the cure system is closely related to the network structure formed during vulcanization. The variation of the total crosslink density in SBR1502 increases with the sulfur content<sup>12,14–16</sup> keeping the same amount of accelerator in the compound. A closer view showed that poly-

sulfide, disulfide, and monosulfide crosslink densities also increase with the sulfur content, but the proportion of polysulfides in the sample with higher sulfur content is lower.<sup>12</sup> Preliminary results in the same polymer with 1.2 phr of sulfur in the compound showed that if the amount of TBBS is in-

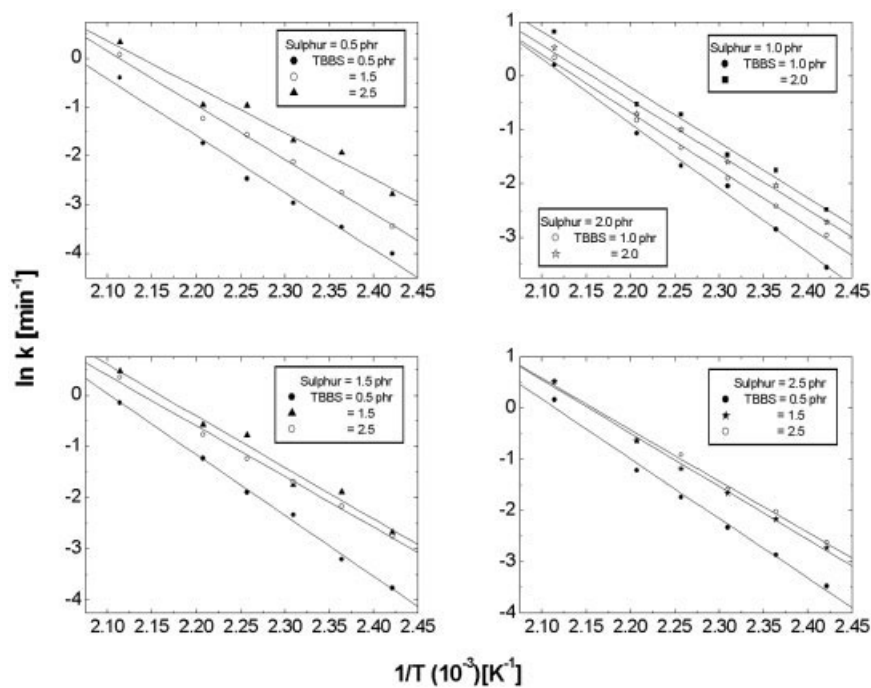


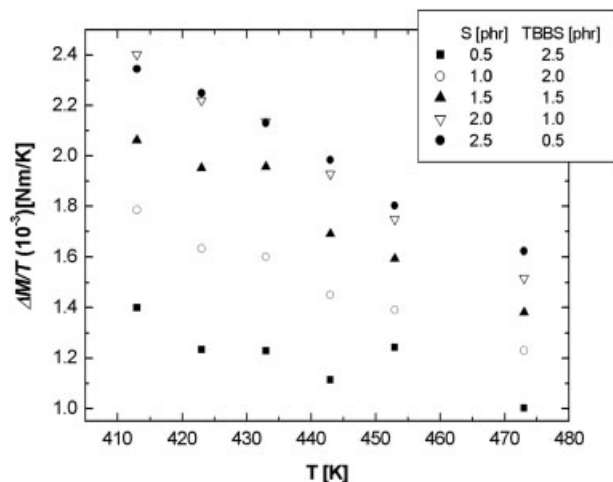
Figure 6 Variation of the rate constant  $k$  with temperature for all the compounds.

creased in the compound, the proportions of mono-sulfides crosslinks will increase.<sup>14</sup>

As it was previously mentioned, the MDR is based on the fact that the crosslinking density is proportional to the compound stiffness. The torque measured by the rheometer is directly related to the shear modulus, and following the rubber elasticity, the quantity  $\Delta M/T$  would be proportional to the crosslink density of the sample. As an example, Figure 8 shows the variation of  $\Delta M/T$  with the cure temperature for the five samples in which  $S + TBSS = 3$  phr. Although one observes (in each sample) a variation of this parameter with the cure temperature caused by a reduction of the crosslink density, the change with  $\Delta$  for the same cure conditions is more important, which implies differences in the network structure that would be correlated to the activation energies.

## CONCLUSIONS

1. Normalized torque curves obtained from data collected using a MDR were used to investigate the cure kinetic of SBR1502 in a broad range of compositions and cure temperatures. The kinetic model proposed by Kamal and Sourour<sup>5</sup> results a good tool for the analysis of these experimental data over the studied temperature range. This treatment offers a practical means for estimating the kinetic coefficients of the cure reaction.
2. It was found that the order parameter  $n$  increases both with sulfur and TBBS in the composition of the material. The kinetic parameter  $k$ , which controls the rate of cure, also depends on the composition, but shows a maximum value, at each cure temperature investigated, for concentrations of 1.0 phr of sulfur and 2.0 phr of TBBS.
3. Finally, the activation energy of vulcanization was evaluated and a contour map shows that it changes with the compound formulation. This fact can be a consequence of the difference in the types of network formed in each case.



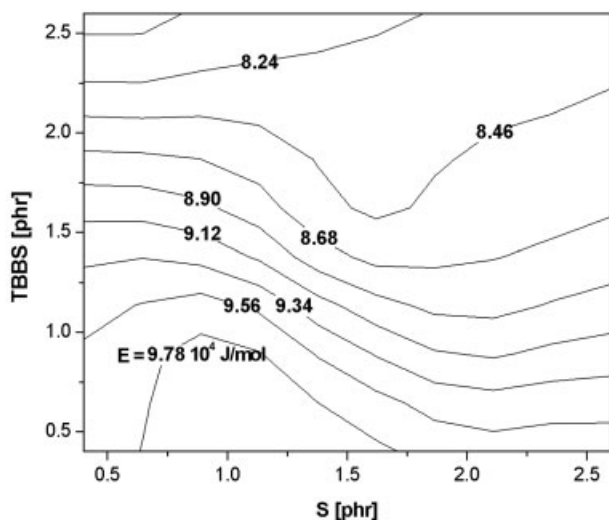
**Figure 8** Variation of  $\Delta M/T$  with the cure temperature  $T$  for samples with  $(S + TBBS) = 3$  phr in the formulation.

imum value, at each cure temperature investigated, for concentrations of 1.0 phr of sulfur and 2.0 phr of TBBS.

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**Figure 7** Contour map of the variation of the activation energy  $E$  with the level of sulfur and accelerator (TBBS) in the compound.