

Analysis of Variation of Molecular Parameters of Natural Rubber during Vulcanization in Conformational Tube Model. II. Influence of Sulfur/Accelerator Ratio

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ABSTRACT: A natural rubber (NR) with a conventional sulfur cure system and a ratio of sulfur/accelerator (Ω) equal to 3 was investigated. The network structure of the NR during vulcanization was analyzed using a model of rubber elasticity based on the tube concept, which was applied to the treatment of the stress–strain measurements. The influence of cure time and temperature on the chemical crosslinks density was analyzed. The values were compared with those obtained by means of an equilibrium volume swelling measurement. The differences between samples of NR cured with $\Omega = 3$ and 1.5 were analyzed. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2747–2755, 1999

Key words: tube model; crosslink density; swelling; natural rubber vulcanizates

INTRODUCTION

The studies of systems of vulcanization of elastomers by sulfur dominate various investigations.^{1–3} It is known that the 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 adding 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, composition and accelerator type, time and temperature of cure, and the accelerator/sulfur ratio.^{3,4}

There are several methods to estimate the crosslink density. Swelling by an organic solvent is one of the methods for characterizing elastomeric networks.^{5–8} This process gives quantitative information about the crosslink density and its composition (mono-, di-, and polysulfide crosslinks). Stress–strain measurement is another indirect method for determining the crosslink density.^{9,10} The analysis of uniaxial stress–strain data of unfilled and filled polymer networks in the frame of the conformational tube model allows a proper separation of the crosslink and constraint contributions to the mechanical behavior and gives a reliable determination of the crosslink densities.^{9–12}

This work deals with the structures of natural rubber (NR) vulcanizates with an accelerator/sulfur ratio of $\Omega = 3$ in its composition at different cure levels achieved at two different tempera-

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tures and times of cure. The chemical crosslinks in the network are determined by means of stress–strain and equilibrium volume swelling measurements. The stress–strain data are analyzed using the tube approach developed by Heinrich et al.⁹ Also, the change in the molecular parameters of the model with the degree of cure are obtained. Swelling measurements are performed and these results are used to determine the density of active crosslinks. These results are compared with those reported in a previous article¹¹ on NR vulcanized at different conditions of cure and a conventional cure system in which the ratio of the sulfur/accelerator was 1.5.

THEORETICAL

The tube model for crosslink networks assumes that, because of the topological constraints, the motion of the chain is essentially confined in a tubelike region made of the surrounding polymers. Heinrich et al.^{9,10} 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

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

with

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

where σ_M is the Mooney stress; λ is the expansion ratio ($1 + \epsilon$); β describes the relaxation of the deformed tube in the deformed state to an undeformed tube corresponding to the equilibrium state¹⁰; and G_c and G_n represent the crosslink and the constraint contributions of the modulus, respectively. They are connected to the molecular parameters by¹⁰

$$G_c = AkT \left\{ v_c - \frac{2\rho N_A}{(\phi - 2)M_n} \right\} \quad (3)$$

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

with

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

where n_{st} is the segment number density, l_{st} is the length of the statistical segment, d_o is the fluctuation range of a chain segment; c is the network chain density; M_n , ρ , and ϕ are the number average molecular weight of the primary chains, the polymer density, and the functionality of the crosslinks, respectively; N_A , k , and T are the Avogadro number, the Boltzmann constant, and the absolute temperature, respectively; and A is a microstructure factor that 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 as¹⁰

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

with

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

The parameter α allows the connection of the modulus G_n with the plateau modulus G_N^o of the uncrosslinked bulk polymer. The relationship was proposed^{9,12} as

$$\alpha = 3.04 \left(\frac{G_N^o}{G_n} \right)^{1/2} \quad (8)$$

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

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

and the fluctuation range of the chain segment d_o as

$$d_o = 0.8(0.5\alpha\beta)^{1/2} \left(\frac{kT l_{st}}{G_n} \right)^{1/4} \quad (10)$$

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

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

Table I Compound Formulation

Ingredient	$\Omega = 3$ (phr)	$\Omega = 1.5^a$ (phr)
SMR-20	100.0	100.0
Zinc oxide	5.0	5.0
Stearic acid	2.0	2.0
Antioxidant	1.0	1.0
TBBS	0.5	1.0
Sulfur	1.5	1.5

^a The formulation used by Mazocca et al.¹¹ is also shown.

We can introduce the network chain molecular mass, M_{ct} , as the molecular mass between two crosslinks connected by a polymer chain defined as¹³

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

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

On the other hand, the molecular weight of the network chain between chemical crosslinks for a phantom network, M_{cs} , is expressed by^{6,8}

$$M_{cs} = - \frac{\rho(1 - 2/\phi)V_1 v_{2C}^{2/3} v_{2m}^{1/3}}{\ln(1 - v_{2m}) + \chi v_{2m}^2 + v_{2m}} \quad (13)$$

where ρ is the density of the network chain, v_{2m} is the volume fraction of the polymer at the equilibrium (maximum) degree of swelling, V_1 is the molar volume of the solvent; the parameter v_{2C} is defined by the ratio v_d/v_o where v_d is the volume of the dry network and v_o represents the total volume of the polymer; and χ is an interaction parameter between the polymer and the swelling agent.⁸

EXPERIMENTAL

Preparation and Characterization of Materials

The material used in the present study was an unfilled NR gum mix with the formulation given in Table I. In this table the formulation used in a previous paper is also shown.¹¹ The number average molecular weight of the elastomer was 174750 g/mol as determined by gel permeation chromatography with a density (ρ) of 0.956 g/mL.

This polymer corresponds to the same raw material used in a previous study.¹¹

The gum mix was prepared in a laboratory mill, and after this it was characterized at 414 and 433 K by means of the torque curves in a Monsanto MDR2000 rheometer. From these curves the time to achieve certain degrees of cure, t_δ , was obtained by considering the following relationship that represents the cure degree¹⁴ (δ):

$$\delta = \frac{\tau - \tau_o}{\tau_{\max} - \tau_o} 100 \quad (14)$$

where τ_{\max} and τ_o are maximum and minimum torque, respectively, and τ is the torque at the t_δ time.

Various samples were cured at different t_δ at 414 (sample C) and 433 K (sample D). Vulcanized samples were supplied as $150 \times 150 \times 2$ mm sheets. These specimens were cooled rapidly in ice and water at the end of the curing cycle. In Table II the cure conditions (time and temperature) and the sol fraction (ω_s) of each sample are given.

The dynamic plateau modulus $G_N^o = 0.508$ MPa was measured using an automated torsion pendulum at room temperature and 60 Torr in an argon atmosphere.

To evaluate the heat of reaction of each sample produced during vulcanization, differential scanning calorimetry tests were performed with a Mettler TA10 with a DSC20 cell. Samples (15–25 mg) were encapsulated in aluminum holders under nitrogen and scanned at 10 K/min from 303 to 573 K. The overall heat of reaction, Q_o , and the heat of reaction up to time t , $Q(t)$, were measured on cured and uncured samples. Then the conversion at time t , $\gamma(t) = (Q_o - Q(t))/Q_o$, was calculated and their values are given in Table II.

Table II Cure Conditions of Samples

Sample	Temp. of Cure (K)	Cure Time (min)	ω_s	γ
C1	414	26	6.51	0.3
C2	414	34	5.14	0.73
C3	414	45	5.07	0.75
C4	414	90	5.06	1
D1	433	5	5.74	0.26
D2	433	8	4.11	0.65
D3	433	10	4.10	0.76
D4	433	20	4.23	1

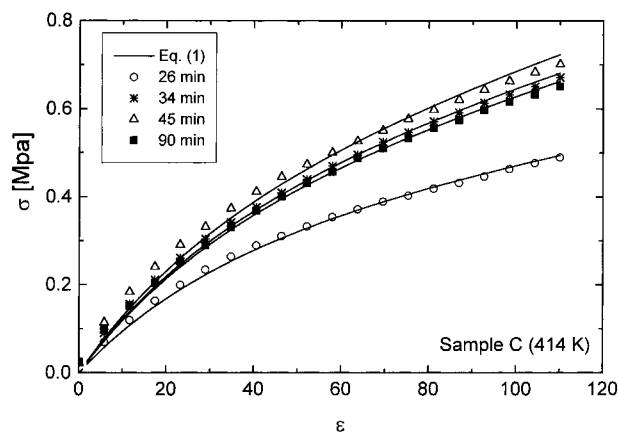


Figure 1 Stress–strain data and fit curves according to eq. (1) for samples cured at 414 K at different times.

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 $\dot{\epsilon} = 6 \times 10^{-4} \text{ s}^{-1}$. A load cell of 50 N was used to obtain good sensitivity. Strain was measured by means of a large deformation extensometer (Instron XL) with a 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 the stress of the three tests was less than 0.015 MPa and for the strain it was insignificant.

Swelling Tests

The swelling of a rubber compound is frequently used for the determination of the crosslink density. The density of chemical crosslinks was determined using the method described by Cunneen and Russell.¹⁵ The experiment consists of completely immersing a sample in solvent and waiting until swelling equilibrium occurs. The total weight was determined as 0.0001 g for all the samples, then the total number of crosslinks was determined after weighing the samples. The solvent used was *n*-decane ($\rho_{\text{dec}} = 0.73 \text{ g/mol}$).

RESULTS AND DISCUSSION

Determination of Network Parameters by Stress–Strain Measurements

A plot of σ – ϵ for the NR gum mix at different times of cure at 414 and 433 K is given in Figures

1 and 2, respectively. These figures show the experimental data and the fit curves according to eq. (1), considering $\beta = 1$. The network parameters G_c and G_n were obtained by the fit of the experimental data, and the values obtained are given in Table III. The error in the determination of G_n and G_c was less than $3 \times 10^{-4} \text{ MPa}$. The value of G_n remained approximately constant for all the samples. Mean values of 0.19 ± 0.05 and $0.20 \pm 0.05 \text{ MPa}$ were found for samples C and D, respectively.

Using eq. (8) with G_N^o and G_n , the values of α were estimated for the different samples and they are given in Table III.

Information about the network structure can be extracted by means of G_c and G_n . The n_{st} and d_o follow from G_n according to eqs. (9) and (10), respectively. Because n_{st} depends on the Kuhn's statistical segment length, l_{st} , it was extracted from the literature.¹⁶ For NR the $l_{\text{st}} = 0.88 \text{ nm}$, then $n_{\text{st}} = 4.06 \text{ nm}^{-3}$ and mean values of d_o of 2.61 and 2.54 nm were found for samples C and D, respectively. Considering the molecular mass of the statistical segment as $M_{\text{st}} = \rho N_A / n_{\text{st}}$, a value of 141.6 g/mol was obtained.

The molecular parameters relative to the crosslinks (M_{ct} and v_c) were estimated using the values of G_c . From eq. (3) and considering the case of a four functional network, it is possible to calculate the value of the network chain density, v_c , and, according to eq. (12), the value of the network chain molecular mass, M_{ct} . Because in these equations the microstructure factor A is involved, then M_{ct} , v_c , and A must be iteratively determined using eqs. (6) and (7). The procedure to calculate v_c is the following:

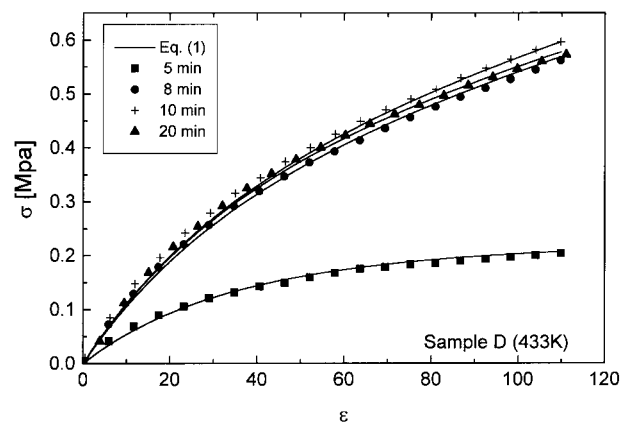


Figure 2 Stress–strain data and fit curves according to eq. (1) for samples cured at 433 K at different times.

Table III Variation of Molecular Parameters of Tube Model with Degree of Cure

Sample	t (min)	G_c (MPa)	G_n (MPa)	α	d_o (nm)	M_{co} (g/mol)	v_c (nm ⁻³)	R_c (nm)	A
C1	26	0.170	0.190	4.97	2.62	9974	0.058	6.76	0.76
C2	34	0.270	0.190	4.97	2.62	5621	0.102	5.23	0.66
C3	45	0.290	0.195	4.90	2.59	5166	0.111	5.03	0.65
C4	90	0.260	0.190	4.97	2.62	5910	0.097	5.35	0.67
D1	5	0.012	0.199	4.84	2.56	90727	0.006	15.1	0.94
D2	8	0.220	0.195	4.90	2.59	7854	0.073	6.14	0.73
D3	10	0.220	0.200	4.84	2.56	7475	0.077	6.00	0.73
D4	20	0.200	0.220	4.61	2.44	8624	0.066	6.41	0.74

t , Cure time.

1. Assuming the v_c value first, calculate M_{ct} using $\rho N_A/v_c$.
2. Solve eq. (12) and calculate R_c from eq. (11).
3. Calculate the A value using eqs. (6) and (7).
4. Obtain a new v_c value with the A value and eq. (3).
5. With the new v_c one can iteratively recalculate up to the converged value.

Note that in eq. (7) d_o 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.¹⁰

The end to end distance of a network chain, R_c , is presented in Table III for both samples according to eq. (11). From the results of R_c it can be observed that $l_{st} < d_o < R_c$ for each cure level analyzed. This kind of behavior was reported by different authors^{9,11–13} in their studies of several elastomers.

Effects of Increase of Sulfur/Accelerator Ratio

Walter and Helt⁴ pointed out that the formation of unstable crosslinks during curing can be controlled by the use of more efficient curing systems. To obtain a more stable crosslink density, the curative levels must be increased by following three basic methods: increase the sulfur, increase the accelerator, or increase both. Compared with previous research in our group¹¹ when a similar NR compound with a ratio of $\Omega = 1.5$ was used, in this work we decreased the level of accelerator while maintaining a constant sulfur level in order to obtain $\Omega = 3$.

To analyze the performance of the two compounds in the stress–strain behavior, the param-

eters obtained using the tube approach are discussed below.

From the values of G_n in Table III it is evident that the level of constraints in the material does not depend on the cure level (time and temperature) and the system cure. Obviously, the parameters associated with the constraints, n_{st} and M_{st} , remain as constants in both cases. If we compare the stress–strain curves (Figs. 1, 2) we observe that in the overcure samples a high reversion effect in the tensile properties takes place. This behavior can be attributed to some effect associated with the nature and density of the crosslinks. These findings agree with those previously reported.¹¹

Figures 3 and 4 show the variation in G_c with the degree of cure for both ratios of sulfur/accelerator at 414 and 433 K, respectively. The results

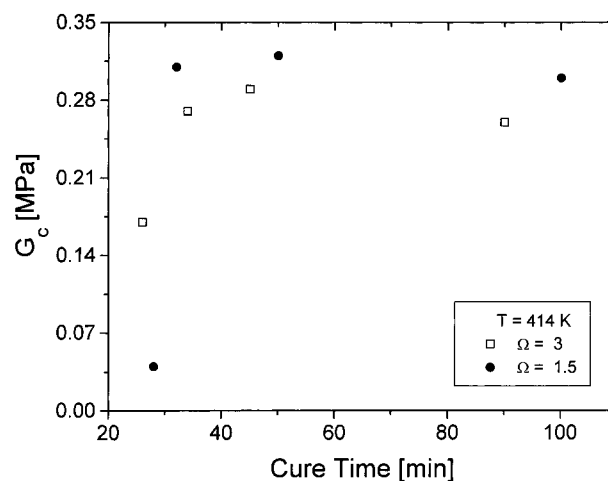


Figure 3 The effect of the time of cure and the ratio of the sulfur/accelerator (Ω) on the modulus contribution of the crosslink, G_c , at 414 K.

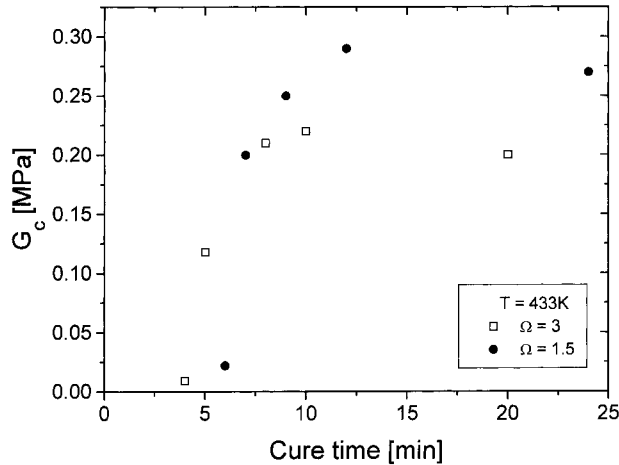


Figure 4 The effect of the time of cure and the ratio of the sulfur/accelerator (Ω) on the modulus contribution of the crosslink, G_c , at 433 K.

show that the cure affects the values obtained for all samples and the increase in the concentration of accelerator in the compound implies high values of G_c . The growth in the cure temperature amplifies the difference between the values of G_c at different Ω levels, which can be deduced by comparing Figures 3 and 4.

The crosslink density is also modified by the ratio of the sulfur/accelerator as shown in Figures 5 and 6 where the v_c decreases when the ratio of

the sulfur/accelerator increases. It is interesting to note that as the cure temperature increases, although the amount of sulfur remains constant, the efficiency of vulcanization falls and this effect is larger when the time of cure is longer. Walker and Helt⁴ reported similar results in NR cured at 414 and 453 K but with another accelerator N-cyclohexylbenzothiazole-2-sulphenamide (CBS). In that research they found that essentially monosulfidic crosslinks were obtained.

We are interested in analyzing the evolution of the network chain density following the contribution of crosslink formation and degradation. If we consider that there are no chemical crosslinks at the onset of the cure reaction, v_c could be fit as a function of the cure time t using the model in which crosslinking and degradation are assumed to be a first-order reaction,^{17,18}

$$v_c = C\{\exp[-\psi_1(t - t_o)] - \exp[-\psi_2(t - t_o)]\} \quad (15)$$

where ψ_1 and ψ_2 are associated with the rate constants of crosslinking and degradation, respectively, and t_o is an induction time.

It is clear from Figures 5 and 6 that the model provides a good fit to the data of v_c for both cure temperatures and Ω values. These plots also give the adjustments of v_c obtained for the present data given in a previous study¹¹ for a similar NR gum with $\Omega = 1.5$.

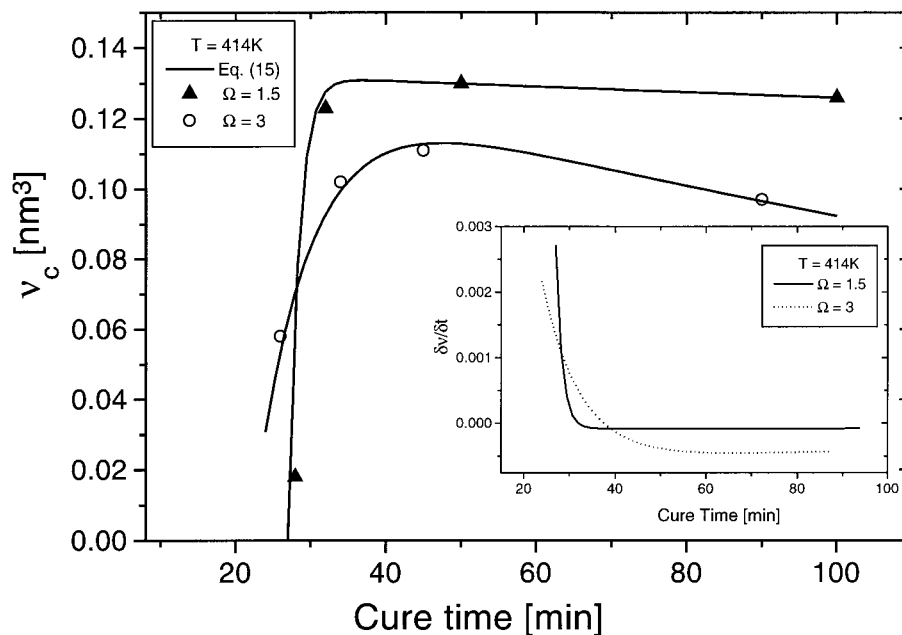


Figure 5 A comparison between the calculated crosslink densities v_c and the fit curves using eq. (15) and (inset) $\delta v_c / \delta t$ for samples vulcanized at 431 K at two Ω s.

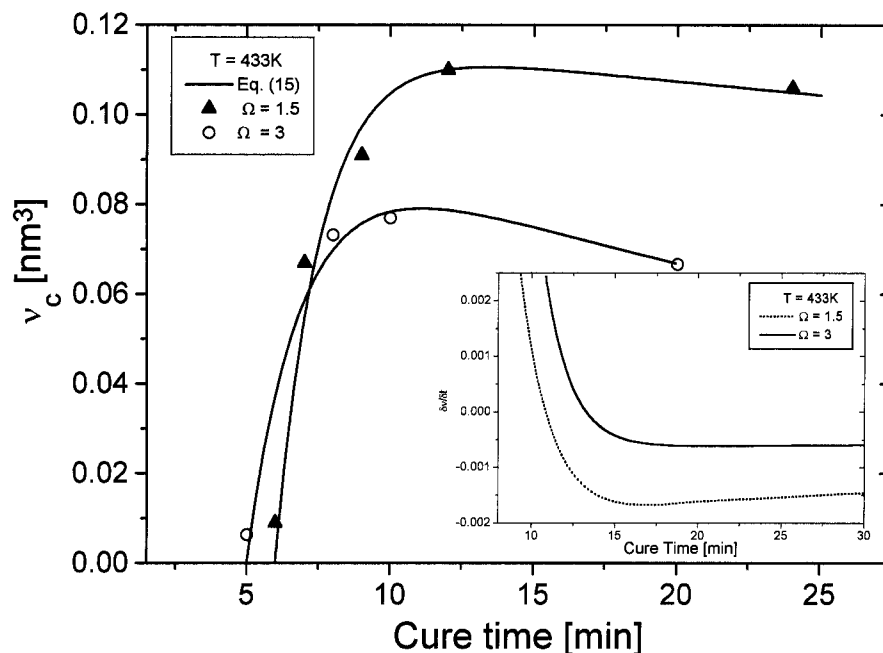


Figure 6 A comparison between the calculated crosslink densities v_c and the fit curves using eq. (15) and (inset) $\delta v_c / \delta t$ for samples vulcanized at 433 K at two Ω s.

The parameters C , ψ_1 , and ψ_2 are reported in Table IV for each level of cure temperature and sulfur/accelerator ratio.

The insets in Figures 5 and 6 illustrate the $\delta v_c / \delta t$ corresponding to each analyzed case. Note from Table IV that the rate of crosslinking increases with the temperature of cure and at higher values of Ω .

It is apparent for $\delta v_c / \delta t$ that the rate of degradation, once the maximum of v_c is attained, is higher in the case of $\Omega = 3$ at 414 and 433 K.

Our recipes are in accord with the conventional vulcanization (CV) system in which more polysulfidic crosslinks and more sulfur combined with rubber chains to form sulfur rings along the rubber molecular chain are present.¹⁹ When increasing the concentration of the accelerator in the recipe, going from a CV system to an efficient vulcanization (semi EV or EV), the desulfuration

of polysulfide crosslinks is very rapid and there is little crosslink elimination or main chain modification.³ In this last case the crosslinks are shorter than those formed in compounds with the CV system and this should give the best retention of crosslink density as cure temperature increases, forming a more stable network structure.

Although in this work we are comparing two NR gum mixes with two cure systems in the CV region, we observed that the recipe with higher accelerator concentration ($\Omega = 1.5$) gives a more stable structure for the overcure samples at both cure temperatures analyzed.

Determination of Chemical Crosslink Density by Swelling Test

The density of the chemical crosslinks was estimated from swelling for all samples. The values

Table IV Variation of Parameters of Eq. (15) with Temperature of Cure and Ω

Ω	C (nm^{-3})		Ψ_1 (min^{-1})		Ψ_2 (min^{-1})	
	414 K	433 K	414 K	433 K	414 K	433 K
1.5	0.1318	0.1165	0.00062	0.00579	0.71735	0.63954
3	0.1310	0.0958	0.00448	0.02403	0.13966	0.53508

Table V Molecular Weight of Network Chain Obtained by Analysis of Stress–Strain Data (M_{ct}) and Swelling Measurement (M_{cs})

Sample	Cure Time (min)	M_{ct} (g/mol)	M_{cs} (g/mol)
C1	26	8369	8009
C2	34	5010	4791
C3	45	4630	4708
C4	90	5255	5048
D1	5	41954	38600
D2	8	6910	5810
D3	10	6604	5340
D4	12	7517	5921

obtained for M_{cs} using eq. (13) are given in Table V. For these estimations a value of $\chi = 0.43$ for NR was used¹⁵ and v_{2C} was considered to be equal to 1.

With the goal of comparing the results obtained for the mechanical and swelling methods, the density of elastically active crosslink, μ_c , was calculated. In a four functional network assumed in the present case, μ_c is related to the density of all the network chains, v_o , by²⁰

$$v_o = 2\mu_c + v_n \quad (16)$$

where v_n is the density of the primary chain prior to vulcanization. The v_o and v_n can both be transformed to molecular weights by $v_o = \rho/M_C$ and $v_n = \rho/M_n$. Then μ_c is defined by

$$\mu_c = \frac{\rho}{2} \left(\frac{1}{M_C} - \frac{1}{M_n} \right) \quad (17)$$

where M_C is the network chain molecular mass.

If we replace M_C by M_{ct} in eq. (17), we obtain the density of elastically active crosslinks calculated from the stress–strain measurements, μ_{ct} .

On the other hand, if we use the value of M_{cs} , we obtain the density of elastically active crosslinks calculated from swelling measurements, μ_{cs} .

In Figure 7 μ_{ct} is plotted against μ_{cs} . In this figure the values obtained from samples of NR gum mixes with¹¹ $\Omega = 1.5$ and those calculated in this work were included. The data can be fit by a linear regression with a slope of 0.92 ± 0.05 and a regression coefficient (R^2) of 0.96. This fact points out that there is a good correspondence between the values obtained by swelling and

those calculated from the stress–strain data in the frame of the configurational tube model.

CONCLUSIONS

This work presents the changes in the network parameters of NR vulcanizates at two sulfur/accelerator ratios, Ω .

Relevant parameters (the network chain molecular mass and the network chain density) were evaluated using the tube model that takes into account the restrictions of conformation of polymer network chains. This model was applied to uniaxial stress–strain data at different cure conditions. Our results show that if the ratio of the sulfur/accelerator is decreased in the compound formulation by a change in the accelerator concentration, the network chain density will increase at both curing temperatures analyzed.

We verified that there is a dependence of the rate of crosslinking (ψ_1) and degradation (ψ_2) on Ω . In fact, ψ_1 is higher at higher levels of Ω . Moreover, the compound with lower Ω presents a more stable structure under overcure.

We also compared the results of the chemical crosslinks obtained by means of the mechanical analysis with that of the swelling measurements. There was a good correspondence in this value at 414 K. However, the test performed at 433 K showed a small difference with higher values of μ obtained in the mechanical analysis.

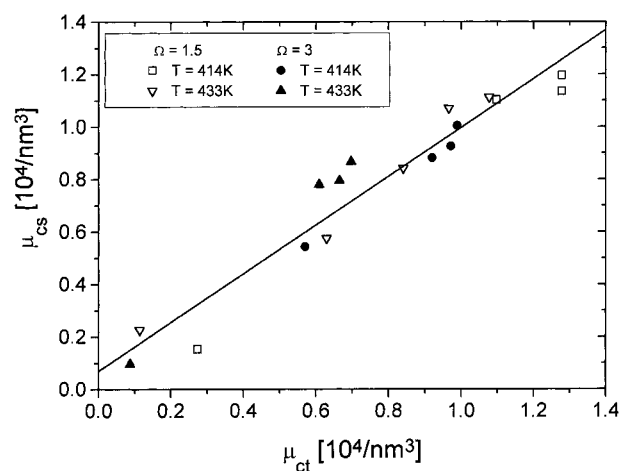


Figure 7 The density of elastically active crosslinks obtained from the analysis of stress–strain data μ_{ct} versus those calculated from swelling measurements μ_{cs} for $\Omega = 1.5$ and 3.

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REFERENCES

1. Chough, S.; Chang, D. *J Appl Polym Sci* 1996, 61, 449.
2. Loo, T. *Polymer* 1974, 15, 357.
3. Doyle, G. M.; Humphereys, R. E.; Russell, R. M. *Rubber Chem Technol* 1972, 15, 1051.
4. Walker, L. A.; Helt, W. F. *Rubber Chem Technol* 1986, 59, 285.
5. Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953; p 120.
6. Queslel, J. P.; Mark, J. E. *J Chem Phys* 1985, 82, 3449.
7. Queslel, J. P.; Mark, J. E. *Adv Polym Sci* 1985, 71, 229.
8. Mark, J. E.; Erman, B. *Rubberlike Elasticity: A Molecular Primer*; Wiley: New York, 1988; p 51.
9. Heinrich, G.; Straube, E.; Helmig, G. *Adv Polym Sci* 1988, 85, 33.
10. Straube, E.; Heinrich, G. *Kautsch Gummi Kunst* 1991, 44, 734.
11. Marzocca, A. J.; Cervený, S.; Raimondo, R. B. *J Appl Polym Sci* 1997, 66, 1085.
12. Heinrich, G.; Vilgis, T. A. *Macromolecules* 1993, 26, 1109.
13. Marzocca, J. A. *J Appl Polym Sci* 1995, 58, 1839.
14. Hill, D. A. *Heat Transfer & Vulcanization of Rubbers*; Elsevier: London, 1971; p 98.
15. Cunneen, J. I.; Russell R. M., *Rubber Chem Technol* 1970, 43, 1215.
16. Aharoni, S. *Macromolecules* 1986, 19, 426.
17. Scheele, W. *Rubber Chem Technol* 1961, 34, 1306.
18. Jurkowski, B.; Kubis, J. *Kautsch Gummi Kunst* 1985, 38, 515.
19. Coran, A. Y. In *Science and Technology of Rubber*, 2nd ed.; Mark, J. E.; Erman, B.; Eirich, F. R., Eds.; Academic: San Diego, CA, 1994; p 339.
20. Gronski, W.; Hoffmann, V.; Simon, G.; Wutzler, A.; Straube, E. *Rubber Chem Technol* 1991, 65, 63.