

Analysis of the Variation of Molecular Parameters of NR During Vulcanization in the Frame of the Conformational Tube Model

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ABSTRACT: The network structure of natural rubber (NR) achieved during vulcanization was analyzed using the model of rubber elasticity based on the tube concept, applied to the treatment of the stress–strain measurements. This theory allows the separation of constraint and crosslink contributions. Also, network parameters can be calculated. The crosslink level of the material was changed using different times and temperatures of cure. The change in the molecular parameters of the model with the degree of cure was estimated. The present research is useful for the precise determination of the chemical crosslink density of the NR network. The values were compared with those obtained by means of equilibrium volume swelling measurement. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1085–1092, 1997

Key words: tube model; crosslink density; swelling; NR vulcanizates

INTRODUCTION

In recent years a new theory based on the tube model for rubber elasticity has been developed.^{1,2} The tube model assumes that, due to the topological constraints (e.g., entanglements), the motion of the molecular chain is essentially confined in a tubelike region made of surrounding polymers.^{3,4} This theory has been used to analyze stress–strain data of natural rubber (NR) and styrene–butadiene rubber (SBR).^{1,2,5}

Gronsky et al.⁶ compared the density of elastically active crosslinks in NR vulcanizates obtained by means of two experimental methods:

¹³C-NMR and uniaxial stress–strain data in the frame of the tube model.¹ Straube et al.^{2,7} studied the dependence of the parameters of the tube model on sulfur contents of cure SBR-1500. Recently, Marzocca analyzed the variation of these parameters with the time of cure of SBR-1712 at two curing temperatures.⁵

Swelling by an organic solvent is one of the methods used to characterize elastomeric networks. In this process, the polymer is mixed with a solvent of low molecular weight. As a result of swelling phenomena, the polymer–solvent system presents a change in the Gibbs free energy. The statistical treatment of the process of swelling has been analyzed by several authors.^{8–12} Queslel and Mark⁹ proposed a relationship between swelling and the degree of crosslinking for a randomly crosslinked polymer network.

In the present work, uniaxial stress–strain data at room temperature of unfilled NR vulcanized at different cure levels were measured. Sam-

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ples were prepared at two temperatures and at several cure times to achieve different crosslink levels. Data were analyzed using the tube approach developed by Heinrich et al.¹ The change in the molecular parameters of the model with the degree of cure was obtained. The crosslink density, the molecular mass of the network chain, and the density of elastically active crosslinks were attained. Also, swelling measurements were performed and these results were used to determine the density of elastically active crosslinks. Finally, both estimations of crosslink density were compared.

THEORY

For the case of moderately crosslinked rubbers, Heinrich et al.^{1,2} presented a relationship between stress, σ , and strain, ε , based on a tube model. In this model, the constitutive equation of an uniaxial deformation of an incompressible sample has the form

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

with

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

where σ_M is called the Mooney stress, λ is the expansion ratio ($1 + \varepsilon$), and β describes the relaxation of the deformed tube in the deformed state to an undeformed tube corresponding to the equilibrium state.²

G_n and G_c represent the crosslink contribution and the constraint contribution of the shear modulus, respectively. They are connected with the molecular parameters by²

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

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

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, and d_o is the fluctuation range of a chain segment normally associated with the tube diameter. ν_c is the network chain density.

M_n , ρ , and ϕ represent the number-average molecular weight of the primary chains, the polymer density, and the functionality of crosslinks, respectively.

N_A , k , and T are the Avogadro's number, the Boltzmann's constant, and the absolute temperature as usual.

A is a microstructure factor that depends on the ratio between the fluctuation range d_c of a crosslink and the end-to-end distance R_c of a network chain. A is defined by Kastner¹³ as

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

with

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

According to Heinrich et al.,^{1,2} eq. (6) takes into account the fact that the constraints acting on a crosslink are stronger than the constraints acting on segments of network chain distant from crosslink.

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 was proposed^{1,14} as

$$\alpha = 3.04 \left(\frac{G_N^0}{G_n} \right)^{1/2} \quad (8)$$

Using eqs. (4), (5), and (6), n_{st} can be obtained as

$$n_{st} = 1.56 \left(\frac{G_n}{l_{st}^3} \right)^{1/2} \left(\frac{2\alpha}{\beta} \right) = \left(\frac{9.5}{\beta} \right) \left(\frac{G_N^0}{l_{st}^3 kT} \right)^{1/2} \quad (9)$$

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

$$d_o = 0.57 (\alpha\beta)^{1/2} \left(\frac{kT l_{st}}{G_n} \right)^{1/4} \quad (10)$$

We can introduce the network chain molecular

Table I Compound Formulation

Ingredient	Weight (%)
SMR-20	90.4
Zinc Oxide	4.5
Stearic Acid	1.8
Antioxidant	0.9
<i>N-t</i> -Butylbenzothiazole-2-sulfenamide (TBBS)	0.9
Sulphur	1.3

mass as the molecular mass between two crosslinks connected by a polymer chain. M_{ct} can be estimated as⁵

$$M_{ct} = \frac{(1 - \omega_s)M_{co}}{\left(1 + \frac{2M_{co}}{M_n}\right)} \quad (11)$$

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 PROCEDURE

Materials

The polymer used in this investigation was unfilled NR. The molecular weight was $M_n = 174,750$ g/mol determined by GPC and the density was $\rho = 0.956$ g/cm³.

Natural gum mix, with the compound formulation given in Table I, was prepared in a laboratory mixer.

The unvulcanized NR gum mix was characterized by the value of the dynamic plateau modulus G_N^0 measured with an automated torsion pendulum at 60 Torr in argon atmosphere.¹⁵ $G_N^0 = 0.508$ MPa and was obtained at room temperature.

Samples were cured in a steam-heated press at 414 K (sample A) and 433 K (sample B). Sample A was cured at four different times: 28, 32, 50, and 100 min, and sample B at five times: 6, 7, 9, 12, and 24 min. Vulcanized samples were supplied as sheets $150 \times 150 \times 2$ mm. Molds were cooled rapidly in ice and water at the end of the curing cycle. Table II shows the cure conditions (time, temperature) and the sol fraction, ω_s of each sample.

To evaluate the heat of reaction of each sample, differential scanning calorimetry (DSC) 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 K 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, $\gamma(t) = (Q_o - Q(t))/Q_o$, was calculated and their values are given in Table II.

Mechanical Tests

ASTM D412 (die C) samples for tensile tests were cut from the cured sheets. Stress–strain measurements were carried out with an INSTRON 4201 at room temperature at a deformation rate of $\dot{\epsilon} = 6 \times 10^{-4}$ s⁻¹. Force was measured with a load cell of 50 N to obtain good sensitivity. Strain was measured by means of a large deformation extensometer (INSTRON XL) with 20-mm gauge length. The tests were controlled by a PC with software made in Basic language. The stress–strain curves were obtained for the three probes 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, and it was insignificant for the strain.

Swelling Tests

The concentration of chemical crosslinks in the network was determined by measuring swelling in *n*-decane using the method described in the article by Cunnen and Russell.¹⁶ The samples used were the same as those in the case of stress–strain measurement. First, the total weight was determined for all the samples to 0.0001 g. Samples were swelled in *n*-decane ($\rho_{dec} = 0.73$ g/mol, molar volume $V_1 = 194.9$ mL/mol) and the change in total volume of the samples was used to determine the total number of crosslinks.

RESULTS AND DISCUSSION

Determination of Molecular Parameters by Analysis of Stress–Strain Data

Figures 1 and 2 show the stress–strain data obtained for NR gum mix at different times of cure at 414 and 433 K, respectively. In both cases, the data points are given together with the fit curves obtained using eq. (1). The overall error (χ^2) was less than 10^{-4} .

Table II Cure Conditions of Samples

Sample	Cure Temperature (K)	Cure Time (min)	ω_s	γ
A1	413	28	3.75	0.4
A2	413	32	4.84	0.6
A3	413	50	4.54	0.89
A4	413	100	5.15	1
B1	433	6	6.53	0.25
B2	433	7	6.64	0.45
B3	433	9	6.3	0.61
B4	433	12	5.49	0.7
B5	433	24	5.15	1

For the evaluation of the network parameters, first G_n and G_c were determined by a least squares fit of a σ_M versus $f(\lambda)$ starting with $\beta = 1$. With G_n and G_c , β was recalculated. The values obtained for each sample are shown in Table III and Figures 3 and 4. The error in the G_n and G_c parameters was less than 1×10^{-3} MPa and 0.01 in the value of β . The crosslink contribution, G_c , increases until a maximum value is reached, while the constraint contribution, G_n , does not seem to have a definite tendency. Similar behavior was found by others in SBR copolymers.^{2,5,7}

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. Mean values of 5.39 ± 0.30 and 5.02 ± 0.28 were obtained for sample A and B, respectively.

From the values of G_c and G_n , information on the parameters of the network structure can be extracted. For the estimation of the parameters associated with constraint it is necessary to know

the value of the Kuhn's statistical segment length, l_{st} , for natural rubber. This value was taken from literature¹⁷ being $l_{st} = 0.88$ nm. Using eqs. (9) and (10), the value of n_{st} and d_o was obtained.

If n_{st} is known, it will be possible to evaluate the molecular mass of the statistical segment, M_{st} , by $M_{st} = \rho N_A/n_{st}$. Then it is easy to obtain $n_{st} = 4.06 \text{ nm}^{-3}$ and $M_{st} = 141.6$ g/mol.

The variation of the tube diameter, d_o , with the time of cure is observed in Table III. In both samples it seems that, at low cure level, where only a few sulphidic bridges are present, the value of d_o is higher. Once the systems begin to crosslink, there is a slump in the value of d_o , and at higher crosslink levels the tube diameter increases. As Doi and Edwards⁴ point out, the tube diameter is determined by local conditions of the polymer network. As a result of this work, we believe that once the crosslinking appears, the network chains become shorter and more aligned upon stretching. In this case, the conformational

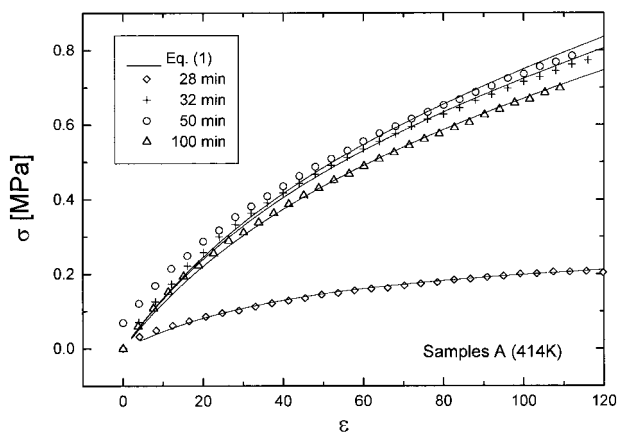
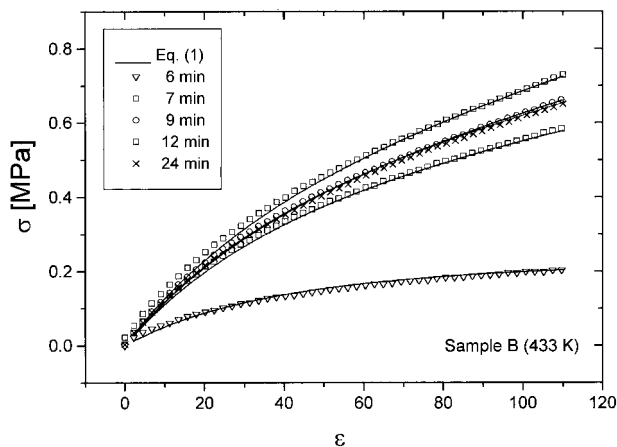
**Figure 1** Stress-strain data and fit curves using eq. (1) of samples cured at 414 K at different times.**Figure 2** Stress-strain data and fit curves using eq. (1) of samples cured at 433 K at different times.

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

Sample	t^a (min)	G_c (MPa)	G_n (MPa)	β	α	d_o (nm)	M_{co} (g/mol)	ν_c (nm ⁻³)	R_c (nm)	A
A1	28	0.04	0.14	0.99	5.81	3.07	40030	0.018	12	0.88
A2	32	0.31	0.18	1.00	5.10	2.70	4578	0.125	4.75	0.62
A3	50	0.32	0.17	1.00	5.25	2.77	4294	0.130	4.62	0.59
A4	100	0.30	0.16	1.00	5.41	2.86	4560	0.126	4.74	0.59
B1	6	0.022	0.17	0.99	5.25	2.77	62160	0.009	13.6	0.92
B2	7	0.20	0.22	1.00	4.62	2.44	8565	0.067	6.30	0.76
B3	9	0.25	0.20	1.00	4.84	2.56	6309	0.091	5.48	0.69
B4	12	0.29	0.18	1.00	5.11	2.70	4816	0.110	4.86	0.63
B5	24	0.27	0.17	1.00	5.27	2.78	5393	0.106	5.13	0.64

^a Time of cure.

constraints are less effective and a light increase in d_o is expected.

Using the values of G_c , the molecular parameters relative to crosslinks, M_{ct} , ν_c , and R_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. (11), also 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 using eqs. (6) and (7). In eq. (7), it must be noted that 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.² On the other hand, the end-to-end distance of a network chain, R_c , is expressed by

$$R_c = l_{st} \left(\frac{M_{ct}}{M_{st}} \right)^{1/2} \quad (12)$$

In Figure 5, the influence of the vulcanization temperature and time on ν_c is shown. It can be observed that as the curing temperature increases, the density of the network chain decreases. This behavior is characteristic of a conventional cure system (CV) such as the formulation used in our samples where the ratio sulfur/accelerator is greater than 1. Similar behavior was reported in SBR vulcanizates with a CV system also.⁵

If we compare the stress–strain curves (Figs. 1 and 2) at similar cure levels and in the overcure samples, a reduction in the tensile properties appears at higher temperatures of cure. A first inter-

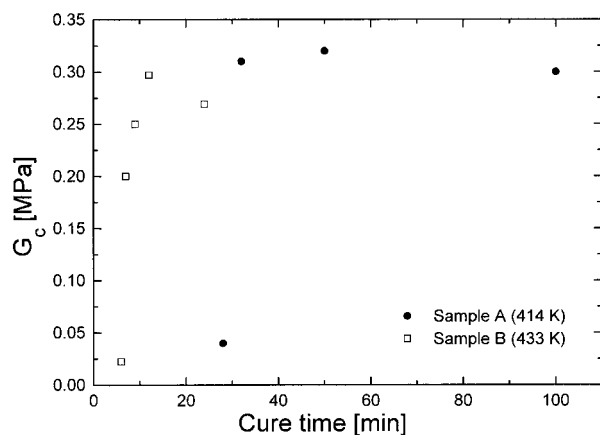


Figure 3 Variation of the modulus contribution of crosslink, G_c , with the time and temperature of cure.

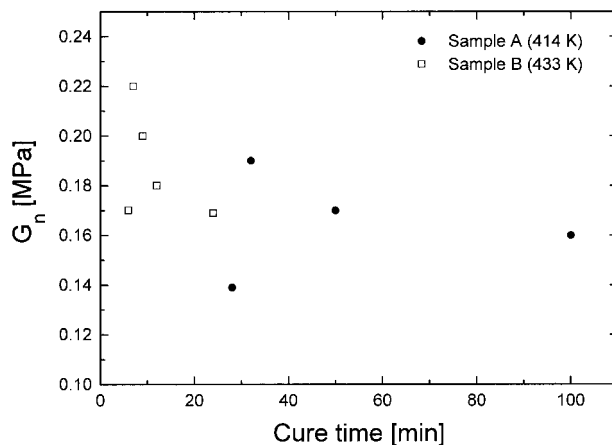


Figure 4 Variation of the modulus contribution of constraints, G_n , with the time and temperature of cure.

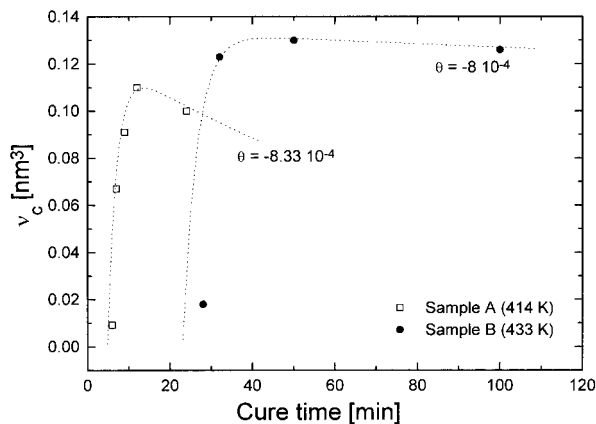


Figure 5 Variation of the network chain density, ν_c , with the time and temperature of cure. The rate of reversion, θ , is given in for each curve.

pretation would lead us to two possible causes for this behavior: the degradation in the polymer backbone because of chain scission or some effect associated with the nature and density of the crosslink.¹⁸ The first mechanism is less probable because, according to Loo's investigation,¹⁹ there is no chain scission during vulcanization between 413 and 473 K.

Loo¹⁹ reported similar results for vulcanized NR gum at different temperatures. In that article, he noticed a substantial fall in the maximum density of chemical crosslinks and an increase in the rate of reversion, once the optimum crosslink is attained, as the cure temperature is raised. In Figure 5 we can see that the rate of reversion, $\theta = \partial\nu_c/\partial t$, increases substantially with the temperature of cure for periods of time longer than the maximum in ν_c . According to Loo's research,¹⁹ the conversion of poly and disulphidic bridges to monosulphidic ones is accelerated at temperatures of 433 K and above, and this affects the mechanical properties of the material. Based on that article, we consider in our experiences that the reduction in the network chain density with the vulcanization temperature is due to a drop in the number of polysulphidic and disulphidic crosslinks.

The behavior of the average molecular mass of the network chain, M_{ct} (Table IV), was the same in samples A and B. M_{ct} decreases with the time of cure until a minimum is obtained but it does not reach an equilibrium value. This fact shows that degradation due to the time of cure is considerable.

Table III shows the variation in R_c with the time of cure for both samples. 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^{1,5,14} on their studies on several elastomers.

The variation of the microstructure factor A [eq. (6)] with the degree of cure is given in Table III for both group of samples. This parameter decreases at higher cure levels reaching an asymptotic value. Straube and Heinrich² reported similar values in SBR-1500 vulcanizates. In that research they found that A was lower with higher amounts of crosslinking achieved with different concentrations of accelerator.

Determination of Crosslink Density by Swelling Test

As previously mentioned, swelling for all samples was measured. The molecular weight of the network chain between chemical crosslinks for a phantom network, M_{cs} , is expressed by^{9,12}

$$M_{cs} = - \frac{\rho(1 - 2/\phi)V_1v_{2C}^{2/3}v_{2m}^{1/3}}{\ln(1 - v_{2m}) + \chi v_{2m}^2 + v_{2m}} \quad (13)$$

where ρ is the density of the network chain, v_{2m} the volume fraction of polymer at equilibrium (maximum) degree of swelling, and V_1 molar volume of 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 polymer. χ is an interaction parameter between the polymer and the swelling agent.¹² According to literature,¹⁶ a value of $\chi = 0.43$ can be used for NR and v_{2C} can be considered equal to 1.

Table IV Molecular Weight of the Network Chain Obtained from Analysis of Stress-Strain Data, M_{ct} , and Measurement by Swelling, M_{cs}

Sample	Cure Time (min)	M_{ct} (g/mol)	M_{cs} (g/mol)
A1	28	26425	15919
A2	32	4140	4140
A3	50	3907	3662
A4	100	4111	3665
B1	6	33948	18798
B2	7	7283	7929
B3	9	5513	5489
B4	12	4331	4194
B5	24	4817	4354

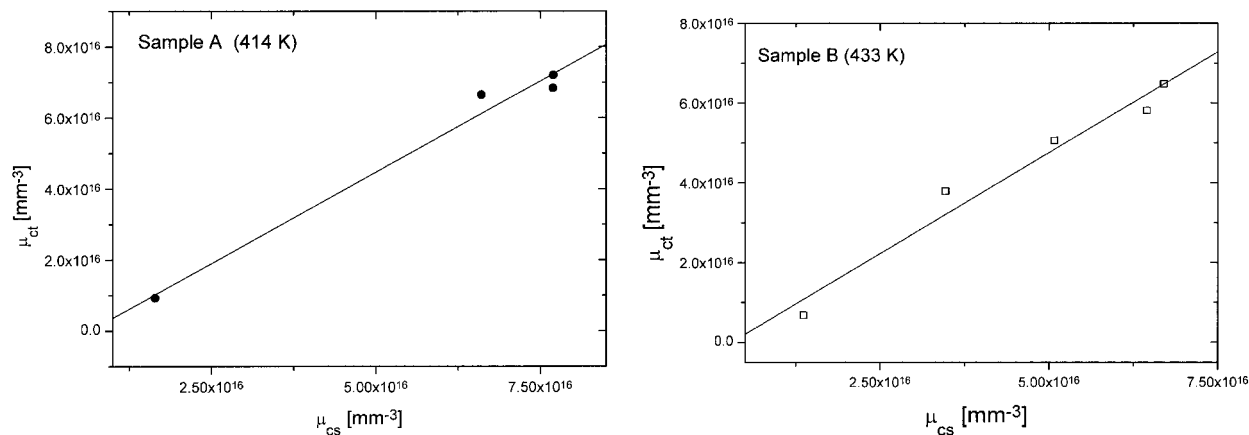


Figure 6 Density of elastically active crosslinks obtained from analysis of stress–strain data, μ_{ct} versus the calculated for swelling measurements, μ_{cs} . (a) Cure temperature = 414 K; (b) cure temperature = 443 K.

Using eq. (13), M_{cs} was evaluated for all the samples and these values are given in Table IV.

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 network chains, ν_o , by⁶

$$\nu_o = 2\mu_c + \nu_n \quad (14)$$

where $\nu_n = N_A\rho/M_n$ and is the density of the primary chain prior to vulcanization. Both ν_o and ν_n can be transformed to molecular weights by $\nu_o = N_A\rho/M_C$ and $N_A\rho/M_n$. Then μ_c is defined by

$$\mu_c = 0.5N_A\rho\left(\frac{1}{M_C} - \frac{1}{M_n}\right) \quad (15)$$

where M_C is the network chain molecular mass.

If we replace M_C by M_{ct} in eq. (15), 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 6(a,b), μ_{ct} is plotted against μ_{cs} for samples A and B. It is obvious that a linear relationship can be established for these cases. The data were fitted by a linear function where slope is 1.02 ± 0.09 (regression coefficient $r = 0.991$) for the sample A and 1.04 ± 0.07 ($r = 0.983$) for the sample B.

In the article by Gronsky et al.,⁶ the crosslink

density determined by ¹³C- and ¹H-NMR does not have a good correspondence with that obtained from uniaxial stress–strain data analyzed within the tube model. However, Simon et al.²⁰ obtained good correlation between the crosslink density determined by ¹H-NMR and that of the mechanical analysis for SBR vulcanized. In that work, the strain rate applied to the samples in the tensile tests was in the range of $1 \times 10^{-2} \text{ s}^{-1}$, two orders higher than the strain rate used in our measurements. At higher strain rates, the stress relaxation effects are more important and the parameters, obtained when the experimental data are fit to eq. (1), are different from the calculated ones at lower strain rate. This fact increases the value of G_c and G_n and the evaluated crosslink density.

CONCLUSION

The present study shows that the theory of rubber elasticity based on the tube model that considers local restriction on conformation of polymer network chains can be used to explain stress–strain data of NR cured at different conditions. One of the advantages of using this model is that it allows the separation between the contribution of the entanglements and crosslinks to the elastic modulus. In this way, the variation of the molecular parameters associated with the model with the cure level were estimated.

A moderate change in the value of the tube diameter was obtained during the vulcanization process of the samples analyzed in this article.

The analysis of the density of the network chain

shows a significant rate of reversion once the optimum crosslink is attained when the cure temperature is increased, and this effect could be associated to the nature of crosslinks present in the compound. There was good agreement between the density of elastically active crosslinks determined by equilibrium volume swelling measurements and by means of the stress-strain data.

We can conclude that the predictions of the theory of rubber elasticity based on the tube model can be used as a method to estimate the density of elastically active crosslink, when the strain rate applied to the samples in the mechanical test is less than 10^{-3} s^{-1} .

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