Estimation by Mechanical Analysis of the Molecular Parameters of SBR Vulcanizates at Different Cure Conditions

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SYNOPSIS

The changes in the network structure of SBR-1712 during vulcanization were analyzed by means of a study of the stress–strain behavior at uniaxial extension at room temperature. In order to obtain different degrees of crosslinking, samples were cured at 414 K and 433 K at several times and were characterized by a rheometer. The conformational tube model was applied for the treatment of the stress–strain measurements of vulcanized samples. This theory allows the separation of crosslink and constraint contributions to the stress–strain behavior and relevant network parameters can be estimated. In this article the change with the temperature and time of cure of the average molecular mass of the mobile network chains, the crosslink density, the microscopic lateral tube dimension, and the root-mean-square end-to-end distance of the network chain are evaluated. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

In the last few years a new theory based on a tube model for rubber elasticity was developed.[1,2] This model takes into account local restrictions, as entanglements, of conformations of polymer network chains. It is known that in dense rubbers the chains are restricted in their movements because they cannot pass through each other. This constraint can be considered as confining each chain's movement inside a tube-like region and is an effective picture for considering entanglement effects in systems without crosslinks.[3] In the case of polymer networks, permanent crosslinks introduce additional restrictions, and the chain is localized within the tube because the crosslinks prevent infinite movement in the longitudinal direction.

Heinrich and Straube[4] modeled the polymer chains by a central line configuration (mean configuration) independent of time and a mean field interaction, keeping the chain configurations close to the mean configuration.

Recently, stress–strain data of a set of vulcanized SBR and NR samples were analyzed using mean field tube models for the determination of network parameters.[5-7] This theory allows the separation of crosslinks and constraint contributions to stress–strain behavior and an acceptable determination of crosslink densities. Matzen and Straube[5] applied the tube model for the treatment of stress–strain data on SBR-1500 vulcanizates with different sulfur/accelerator ratios to consider different crosslink levels.

In this theoretical frame, a complementary model was developed to analyze the stress–strain behavior of filled elastomers,[8] and carbon black-loaded SBR rubbers and polybutadiene rubbers were investigated.[9,10]

In this article, stress–strain data of unfilled SBR-1712 are presented at moderate strains and at different cure levels. Samples were prepared at two levels of temperature and at several cure times to achieve different crosslink levels. Data were analyzed using the tube approach considered by Hein-

rich et al.[2] In this scheme, the separation of crosslink and constraint contributions and their dependence on the cure level were evaluated. The crosslink densities and the network chain of molecular masses were also obtained. In other research,[5-7] this model was applied to obtain the molecular parameters of some completely cured elastomers. The objective of this work is to show the applicability of the model in partially vulcanized samples and to analyze the changes in the molecular parameters of the theory with the degree of cure.

THEORY

Following the model developed by Heinrich et al.[2] to explain the elastic deformation of crosslinked rubbers, the stress–strain relationship for uniaxial deformations of an incompressible sample can be written as

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

with

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

where λ is the expansion ratio, σ the nominal tension, and σ_M is called the Mooney stress. G_c is associated with the crosslink contribution and G_n with the constraint contribution. These entities are related to molecular parameters as[6]

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

$$G_n = \frac{kT}{6^{1/2}} (\beta\mu)^2 n_{st}(l_{st}/d_0)^2 \tag{4}$$

with

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

where n_{st} is the segment number density, l_{st} is the length of the statistical segment, M_n the number average molecular weight of the primary chains, ρ the polymer density, ϕ the functionality, ν_c the network chain density, d_0 the fluctuation range of the chain segment, N_A the Avogadro's number, k the Boltzmann's constant, and T the absolute temperature. A, β and μ are dimensionless parameters whose meaning will be discussed below.

The parameter μ describes different constraint mechanisms. For example, in the case of high crosslink density of small coil interpenetration $\mu = -0.25$, and in the melt case, where the effect of constraints is more important than the crosslink contributions, $\mu = 0.33$. In the case of moderately crosslinked rubbers, the value of $\mu = 0.5$ was considered.[2,5,6]

β is an empirical parameter that considers the relation of the deformed tube in the deformed state to an undeformed tube corresponding to the equilibrium state.[6,8] This parameter depends on network preparation and can be considered as an index of the completeness of the crosslinking reaction too. The value of $\beta = 1$ can be used for an almost dry network made from long primary chains and with a considerable level of crosslinking which implies that $M_n \gg M_c$, where M_c is the number average molecular weight of a network chain.[2]

The parameter A is a microstructure factor that depends on the fluctuation range of a crosslink (d_c) and the end-to-end distance of a network chain (R_c). This factor was evaluated by Kastner[11] within the theory of restricted junction fluctuations as

$$A = 1 - \frac{2}{\phi}\left\{ 1 - \frac{2K\exp(K^2)}{\pi^{1/2}erf(K)} \right\} \tag{6}$$

with

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

where it is taking into account that the constraints acting on crosslinks are stronger than the constraints acting on segments of the network chains distant from the crosslinks.

According to literature,[2,8] the modulus G_n is proportional to the plateau modulus G_N^0 of the uncrosslinked bulk polymer. The relationship between these entities was proposed as

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

Therefore, from the stress–strain data and the plateau modulus, α can be obtained.

EXPERIMENTAL

The material used in this study was an unfilled SBR compound. Compound formulation is given in Table I. The components were mixed in a laboratory mill.

The molecular weight of the compound was measured with GPC and a value of $M_n = 102,400$ g/mol was obtained.

Table I Compound Formulation

Ingredient	% in Weight
SBR-1712	89.3
Zinc oxide	3.0
Stearic acid	1.9
Antioxidant	0.8
Paraffin	1.6
Processing aid	1.3
TBBS	0.7
TMTD	0.2
Sulfur	1.2

The vulcanized samples were cured at 414 K (samples A) and 433 K (samples B). Samples A were cured at five different times: 7.5, 30, 37, 46, and 92 min, and samples B at four times: 3.0, 11.5, 15, and 30 min. Samples were supplied as sheets 150 × 150 × 2 mm.

Table II shows the values of sol fraction, ω, and the cure level estimated according to rheometer curves[12] for each sample. The compound density was 0.966 g/cm^3.

ASTM D412 samples for tensile test were cut from cured sheets. Stress-strain measurements were performed with an Instron 4201 at room temperature at a deformation rate of 6 × 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 three different samples of a given sheet and the averages of the three data points were calculated.

According to literature,[5] dynamic contributions were reduced using low deformation rates during tensile tests. To evaluate this contribution, stress relaxation measurements were performed following an expansion ratio of λ = 2.0.

Dynamic plateau modulus of unvulcanized samples, G_N^0, was evaluated using an automated torsion pendulum.[13] We obtained $G_N^0 \sim$ 0.59 MPa at room temperature.

RESULTS AND DISCUSSION

Figures 1 and 2 show the stress-strain data together with the fit curves according to eq. (1) for samples A and samples B, respectively. In this case, we have considered β = 1 and μ = 0.5, and it can be appreciated that there is very good agreement between experimental data and the theoretical approach.

The values of G_c and G_n can be obtained from the linear regression for the generalized Mooney plots σ_M vs. $f(\lambda)$. The corresponding values to each sample are listed in Table III and from Figures 3 and 4, it can be observed that G_c increases at a higher degree of cure for samples A, although this behavior is different on samples B where a maximum is obtained. This fact can be due to overcure of the specimen after some time of vulcanization.

The constraint contribution remains approximately constant within the evaluated time of cure. The same constancy was found by Straube and Heinrich in their studies on SBR 1500 vulcanizates at different concentration of crosslinking agent.[6]

Using eq. (8) with G_n and G_N^0 the values of α were estimated for the different samples and are given in

Table II Sample Cure Data

Sample	Cure Time (min)	Cure Degree	w_s
A1	7.5	0.500	0.3477
A2	30.0	0.939	0.3261
A3	37.4	0.968	0.3293
A4	46.0	0.983	0.3311
A5	92.0	1.000^a	0.3280
B1	3.0	0.500	0.3443
B2	11.5	0.948	0.3290
B3	15.0	0.983	0.3262
B4	30.0	1.000^b	0.3220

^{a} In this case, the sample was cured 30 min over the time of 100% of cure.

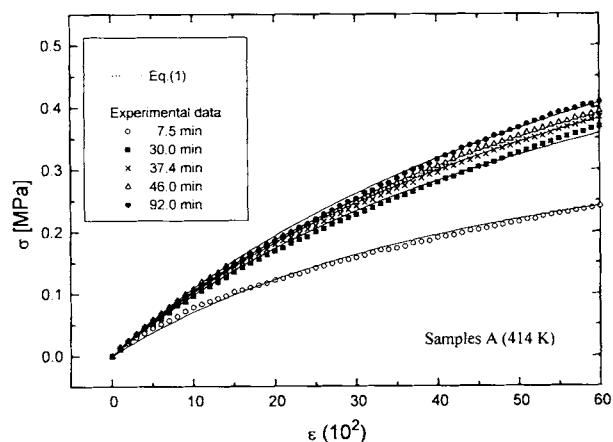^{b} In this case, the sample was cured 12 min over the time of 100% of cure.

Figure 1 Stress-strain data and fit curves using eqs. (1) and (2) of samples cured at 414 K at different times ($\varepsilon = \lambda - 1$).
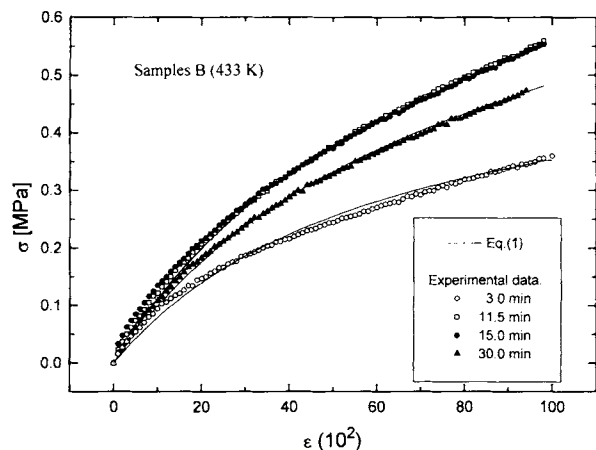
Figure 2 Stress–strain data and fit curves using eqs. (1) and (2) of samples cured at 433 K at different times ($\varepsilon = \lambda - 1$).

Table III. These values are associated with the ratio of lateral tube dimensions in the melt and in the corresponding network $\delta = d_0^{melt}/d_0^{netw}$.[2] In fact, it is easy to show[2,8] that $\delta = 8.44/\alpha$, and these values are given in Table III. Our values indicate that the tube diameter of the crosslink network is smaller than in the case of the uncured sample. This behavior was previously noted in other elastomers and was ascribed to the fact that crosslinks give additional contributions to the constraining potential.[8]

Inserting eq. (5) into eq. (4) and using eq. (8) results the value of n_{st}

$$n_{st} = 1.56(G_n/l_{st}^3 kT)^{1/2}(\alpha/\beta\mu)$$

$$= (4.74/\beta\mu)(G_N^0/l_{st}^3 kT)^{1/2} \quad (9)$$

and then replacing in eq. (5)

$$d_0 = 0.8(\alpha\beta\mu)^{1/2} (kTl_{st}/G_n)^{1/4} \quad (10)$$

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

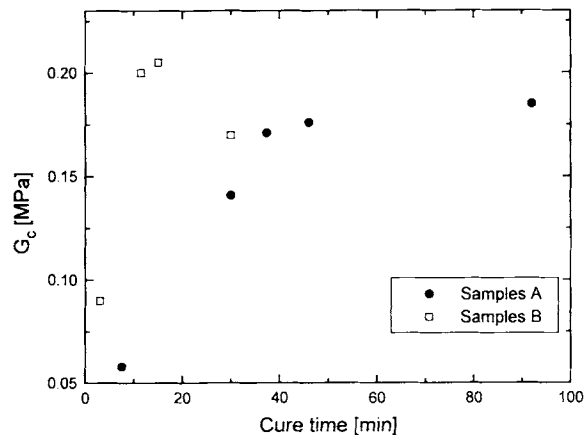| Sample	Cure Time (min)	G_c (MPa)	G_n (MPa)	α	δ	d_0 (nm)
A1	7.5	0.058	0.215	5.04	1.68	2.69
A2	30.0	0.141	0.235	4.82	1.75	2.57
A3	37.4	0.171	0.220	4.98	1.70	2.66
A4	46.0	0.176	0.223	4.94	1.71	2.64
A5	92.0	0.185	0.230	4.87	1.73	2.59
B1	3.0	0.090	0.215	5.04	1.68	2.69
B2	11.5	0.200	0.225	4.92	1.72	2.63
B3	15.0	0.205	0.218	5.00	1.69	2.67
B4	30.0	0.170	0.206	5.14	1.64	2.75

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

To evaluate n_{st} and d_0, it is necessary to know the value of Kuhn's statistical segment length, which is not completely specified in literature in the case of styrene butadiene copolymer networks. In fact, there is not agreement between different sources in literature, as shown in Table IV. Once n_{st} is known, the average number of statistical units within a cube length l_{st} can be calculated as $n = n_{st} l_{st}^3$, and the molecular mass of a statistical segment, M_{st}, is given by $M_{st} = \rho N_A/n_{st}$. Considering a molecular mass of the monomeric unit $M_{mon} = 65.5$ g/mol,[15] the number of monomer units within a statistical segment is $z = M_{st}/M_{mon}$. All the parameters mentioned above are listed in Table IV, evaluated for different l_{st} according to cited references. We note that M_{st} follows naturally once l_{st} is fixed and n_{st} is evaluated from eq. (9).

In Table III, the values of d_0 obtained using eq. (10) and considering $l_{st} = 1.09$ nm[14] are also given.
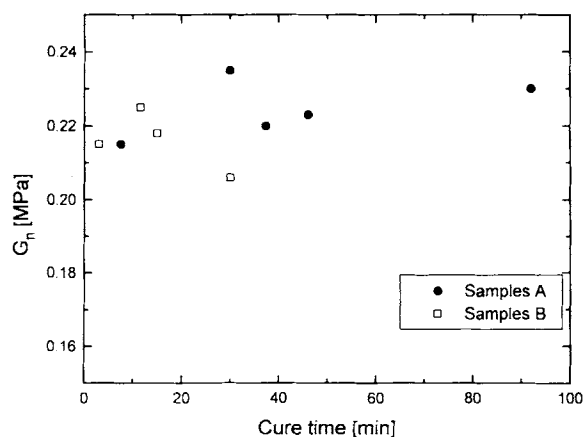

Figure 4 Variation of the modulus contribution of constraints, G_n, with the temperature and time of cure.

Table IV   Values of Molecular Parameters of SBR According to Different References

l_{st} (nm)	n_{st} (nm^3)	M_{st} (g/mol)	n	z	Ref.
1.09	3.31	176	3.94	2.7	14
0.90	4.23	137	3.08	2.0	5
0.67	6.59	88	1.98	1.3	15

In both groups of samples A and B, d_0 is higher than the statistical length segment of the polymer. This fact was observed in experiences with other elastomers, too.[10] The variation of d_0 with the degree of cure is not important, though it seems to increase in samples B.

The dependence of d_0 with the increase of crosslink density is not clear and further work is needed to establish this behavior. A mean value of 2.63 ± 0.05 nm and 2.68 ± 0.05 nm was found for samples A and B, respectively. The tube diameter estimate yields the mean number of statistical segments N_e between two successive entanglements in the mobile polymer phase $N_e = (d_0/l_{st})^2$.[8] Using our results, we obtain $N_e = 6$.

Following Matzen and Straube,[5] the number average molecular weight of network chain, M_c, is estimated from G_c and ν_c in eq. (3) according to

$$M_c = \frac{(1 - \omega)M_{co}}{\left(1 + \dfrac{2M_{co}}{M_n}\right)} \tag{11}$$

with

$$M_{co} = \rho N_A/\nu_c \tag{12}$$

Using eq. (3) and eq. (12), it is easy to obtain

$$\frac{G_c M_n}{\rho N_A kT} = A\left(\frac{M_n}{M_{co}} - 1\right) \tag{13}$$

If we fixed an arbitrary starting value of A, M_{co} would be obtained from eq. (13) and M_c would be evaluated from eq. (11). The end-to-end distance of a network chain, R_c is expressed by

$$R_c = l_{st}(M_c/M_{st})^{1/2} \tag{14}$$

and using it in eqs. (6) and (7), a new value of A is established as new starting value in eq. (13) and the process continues until convergence. It must be noted that in eq. (7) d_0 is used instead of d_c. This

fact implies that additional constraints acting on a crosslink are approximately equal to constraints acting on a chain segment.[6]

The change in R_c, ν_c, and M_c with the degree of cure is shown in Figures 5, 6, and 7, respectively. From the results of R_c in Figure 5, it can be obtained that $l_{st} < d_0 < R_c$ for each cure level analyzed. This fact is in accordance with the predictions mentioned in literature.[2,8,16,17]

The decrease of R_c with the time of cure is related to the increase of G_c, which is a result of the creation of new crosslinks during vulcanization.

Samples cured at different temperatures but with the same cure levels according to rheometer analysis, presented higher values of ν_c at higher vulcanization temperature.

If we consider that there are no chemical crosslinks at the onset of the cure reaction, ν_c could be fitted to a function of the time cure, t, as

$$\nu_c = A_0\{1 - \exp(-\psi_0 t)\} \exp(-\psi_1 t) \tag{15}$$

or

$$\nu_c = A_0\{\exp(-\psi_1 t) - \exp(-\psi_2 t)\} \tag{16}$$

where $\psi_2 = \psi_1 + \psi_0$.

Equation (16) is a function in which crosslinking and degradation are assumed to be of first order. ψ_1 and ψ_2 are the rate constants of crosslinking and degradation.[18,19]

In Table V, the values of A_0, ψ_1, and ψ_2 are given for each level of vulcanization temperature. It can be appreciated that for samples A the rate of degradation is negligible. In Figure 6(a) and (b), the eq.
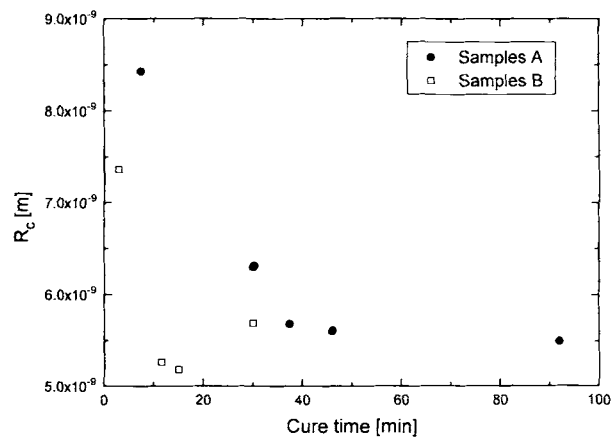
Figure 5   Effect of the temperatures and times of cure on the root-mean-square end-to-end distance of the mobile network chain, R_c.

Figure 7 Variation of the network chain molecular masses, M_c, with the temperature and time of cure.
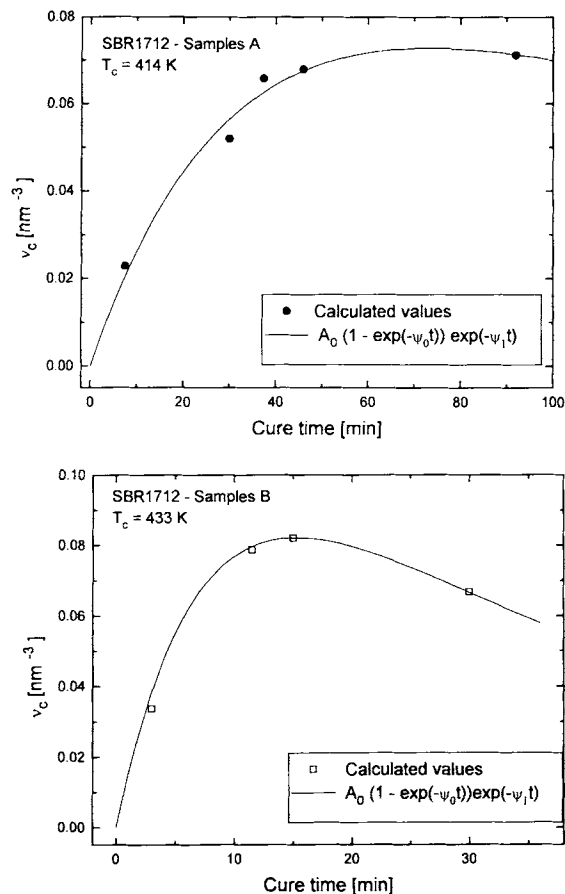

Figure 6 Comparison between the calculated crosslink densities, v_c, and the fit curve using eq. (15). (a) Samples vulcanized at 414 K. (b) Samples vulcanized at 433 K.

samples A, M_c decreases with the time of cure reaching an equilibrium value. This fact confirms that the degradation of crosslinks is not important in samples overcured at 414 K for the times considered in this research. However, an increase in the value of M_c was obtained for the overcured sample at 433 K, showing that the degradation in this case is considerable.

(16) is shown together with data obtained from the previous analysis for both vulcanization temperatures. Fair agreement between them was observed.

Gronski et al.[7] compared the crosslink densities of sulfur and peroxide-cure NR vulcanizates, obtained by ^{13}C-NMR and that derived from G_c using the tube approach. The agreement of v_c between the two methods was not completely satisfactory, but it was attributed to complications arising from non-equilibrium effects in the stress–strain curves. However, in the case of SBR and BR vulcanizates, good agreement was obtained between M_c measured from mechanical analysis and ^{1}H-NMR relaxation.[20,21]

Our experiences show that the expected increase in the crosslink density with the degree of cure of the sample is observed and, in the case of sample B4, the decrease of v_c is attributed to chain scission due to overcure.

The molecular mass of an intercrosslink chain, M_c, was evaluated for all the samples (Fig. 7). For
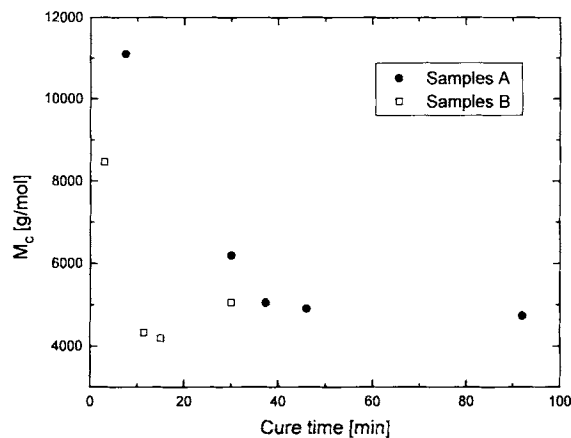
CONCLUSIONS

The theory of rubber elasticity based in the tube model, which takes account local restrictions of conformations of polymer network chains, was used to explain the stress–strain measurements obtained for SBR-1712 at room temperature and moderate strains. In this research, the crosslink level was changed using different times and temperatures of cure.

The application of the mean field-like tube model to stress–strain measurements yields the characteristic length scales of R_c and d_0 and the relation $l_{st} < d_0 < R_c$ was also found.

The variation of the model parameters, G_n, G_c, M_c, R_c, and d_0 were estimated with the time and temperature of vulcanization, and it was possible to

Table V Parameters of Eq. (15) that Fit the Variation of v_c with the Cure Time

T (K)	A_0 (nm^{-3})	ψ_0 (min^{-1})	ψ_1 (min^{-1})
414	0.1189	0.02614	0.00452
433	0.1558	0.10380	0.02683

obtain the crosslink density at each cure level. The value of the parameter α was also evaluated and does not depend on the degree of crosslinking.

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