

The Determination of Network Chain Density and the Chemical Stress Relaxation of Crosslinked Polymers

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Synopsis

Both initial network chain densities $n_M(0)$ and $n_S(0)$ of dicumyl peroxide-cured natural rubbers were determined from the tensile stress and swelling method, respectively. The difference between $n_M(0)$ and $n_S(0)$ was usually constant, independent of the magnitude of network chain density. That is, it was found that the number of entanglement network chains in the crosslinked natural rubber was usually constant, independent of network chain density. The entanglement network chain density $n_{II}(0)$ was 0.7×10^{-4} mole/cc. This led to the supposition that the molecular weight between entanglement points (M_e) would be about 9000. Although this value is far from exact, it does not differ too greatly from the value found for noncrosslinked natural rubber. Next, in order to calculate the number of main-chain scission of crosslinked polymers from their chemical stress relaxation, we proposed our modification of Tobolsky's equation. Using our equation, it was found that the scission of dicumyl peroxide-cured natural rubber occurred in the main chain only. Furthermore, this value agreed with the one obtained from the oxidation of toluene solution of noncrosslinked rubber under the same conditions.

INTRODUCTION

The chemorheological treatment of crosslinked polymers is based on the statistical theory of rubber-like elasticity that the modulus of a crosslinked polymer network is proportional to the density of chains, where a chain is the portion of a molecule between successive crosslinks.

But from the detailed study for the practical crosslinked rubber, it appears to be necessary to consider the effects of chain entanglements and network flaws due to free ends. Tobolsky¹ and Mullins et al.² have investigated these effects for rubber-like elasticity. Mullins has reported the measurement of the numbers of chemically crosslinked chains and entanglement network chains of crosslinked natural rubber at relatively low degrees of crosslinking.

In this study, which extends to high degrees of crosslinking, we investigated the effect of entanglement network chains in crosslinked natural rubbers. Furthermore, we discuss the chemorheology of the crosslinked natural rubber by considering the entanglement network chains.

EXPERIMENTAL

Preparation of Crosslinked Rubbers

Natural rubbers (NR RSS No. 1) were cold milled with the curing ingredient dicumyl peroxide as described in Table I. Table I also shows time, temperature, and methods of curing. Thin sheets (about 0.5 mm) of the milled polymer were pressed under 200 kg/cm² at the curing temperature. All the samples were extracted with hot acetone during 72 hr and dried in vacuo.

TABLE I
Preparation and Characterization of Crosslinked Natural Rubber

Sample number	DCP	Curing time, ^a min	$n_M(0)$, mole/ml $\times 10^{-4}$	$n_S(0)$ mole/ml $\times 10^{-4}$	$n_{SM}(0)$, mole/ml $\times 10^{-4}$
1	2.0	10	0.66	0.25	0.14
2	2.0	20	1.10	0.44	0.23
3	2.0	30	1.25	0.68	0.36
4	2.0	40	1.48	0.83	0.52
5	3.0	30	2.22	0.97	0.68
6	3.0	65	2.35	0.78	1.02
7	3.0	80	2.46	1.60	1.10
8	5.0	20	1.96	1.28	0.81
9	5.0	30	2.72	1.85	1.55
10	5.0	40	2.89	2.40	1.56
11	5.0	45	3.15	2.20	1.88
12	10.0	30	5.13	3.01	4.16
13	10.0	40	5.53	5.06	4.23
14	10.0	50		5.51	
15	10.0	90	7.83		5.71
16	10.0	120	8.50		
17	10.0	210	8.34		8.45

^a Curing temperature, 150°C.

Determination of Crosslinked Network Chain Density

The three densities of network chains of rubbers, $n_M(0)$, $n_{SM}(0)$ and $n_S(0)$, were estimated as follows. $n_M(0)$ was determined by the stress-strain measurement based on the statistical theory of rubber-like elasticity² at 30°C in nitrogen. The extension ratio α was approximately 1.08–1.20. In this range of α -values, the estimate of $n_M(0)$ was not independent of the strain. $n_{SM}(0)$ was determined by the stress-strain measurement of swollen rubber.⁴ After being swollen in xylene for 72 hr at 30°C, this was estimated at $\alpha = 1.08$ –1.20. Lastly, $n_S(0)$ was estimated from swelling measurements using the Flory-Huggins equation. Selected pieces of the vulcanizate were accurately weighed and swollen in benzene at 30°C.

Measurement of Stress Relaxation

The stress relaxation apparatus used here was made by T. Kusano and K. Murakami in our laboratory; its mechanism is the usual strain-gauge

system. Experiments were carried out in air at 109°C. The extension ratio α used here is about 1.2. The stress relaxation results are plotted as $f(t)/f(0)$ against $\log t$, where $f(0)$ is the initial stress and $f(t)$ is the stress at time t .

RESULTS AND DISCUSSION

Effect of Chain Entanglements

In Table I, $n_M(0)$, $n_S(0)$, and $n_{SM}(0)$ of various crosslinked natural rubbers were tabulated. It was found that values of $n_M(0)$ were usually larger than those of $n_S(0)$ or $n_{SM}(0)$. The statistical theory of rubber-like elasticity states that tensile stress needed to stretch a rubber is proportional to the number of network chains in unit volume. It was further shown that a correction was necessary to account for loose chain ends in the rubber. This correction is given by Flory.⁵ In the present paper, still another correction, that is, effect of chain entanglements, is discussed. The entanglements which become trapped on crosslinking will act in many respects as if they were true chemical crosslinks. Therefore, $n_M(0)$ includes a portion of chain entanglements. On the other hand, $n_S(0)$ and $n_{SM}(0)$ will indicate the number of chemically crosslinked chains, because it is considered that such chain entanglements do not affect the estimation of the network chain density in the swollen rubber. Therefore, the result in Table I is predicted sufficiently. The relations of $n_S(0)$ versus $n_M(0)$ and $n_{SM}(0)$ versus $n_M(0)$ are shown in Figure 1. This figure indicates that either should be a straight line of slope equal to unity for the overall range of $n(0)$ without very low degrees of crosslinking. $n_S(0)$ and $n_{SM}(0)$ measures the same parameter, but the relation of $n_S(0)$ versus $n_M(0)$ is not consistent with the relation of $n_{SM}(0)$ versus $n_M(0)$. This presumably can be attributed to the differences in swelling solvent and experimental method. This suggests that the number of effective chain entanglements is constant, independent of network chain density $n(0)$ at high degrees of crosslinking. Therefore,

$$n_M(0) = n_I(0) + n_{II}(0) = n_I(0) + \text{constant} \quad (1)$$

where $n_I(0)$ is $n_S(0)$ or $n_{SM}(0)$ represented chemical network chain density and $n_{II}(0)$ is the number of effective chain entanglements. This result is consistent with the work of Mullins.² Mullins' data were obtained on natural rubber at low degrees of crosslinking. Our result indicates that eq. (1) also applies to high degrees of crosslinking. Since the intercept of the straight lines of unit slope is $n_{II}(0)$ according to eq. (1), from Figure 1 it is evident that $n_{II}(0) \approx (0.7-1.0) \times 10^{-4}$ (mole/ml). This leads to the supposition that the molecular weight between entanglement points (M_e) will be about 9,000-12,000. This also agrees with Mullins' data and does not differ too greatly from the value found on noncrosslinked natural rubber. However, we are not sure if such a relation (eq. (1)) between $n_M(0)$ and $n_S(0)$ or $n_{SM}(0)$ applies at higher degrees of crosslinking. Actually, from the recent study on SBR,⁶ IR, and CR⁷ cured by dicumyl peroxide, we

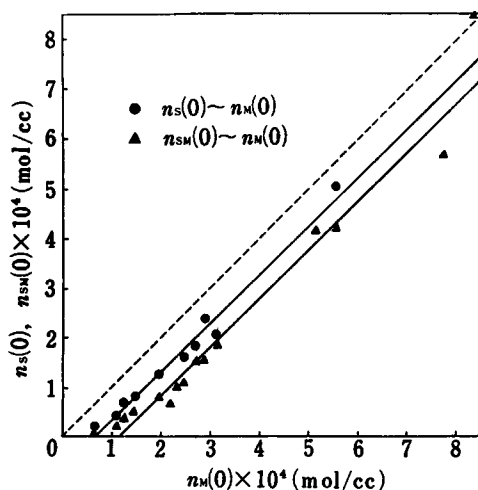


Fig. 1. Relation of $n_S(0)$ vs. $n_M(0)$ and $n_{SM}(0)$ vs. $n_M(0)$.

found that the region of $n_M(0) < n_S(0)$ is presented at very high degrees of crosslinking. These results cannot be explained by considering the chain entanglements described above. This is a large subject of prospective study.

Chemorheological Treatment of Dicumyl Peroxide-Cured Natural Rubber

On the basis of the discussion in the preceding section, we investigated the chemorheology of crosslinked natural rubber. The stress relaxation of crosslinked natural rubber was measured at 109°C in air. These stress relaxation curves (relative stress $f(t)/f(0)$ versus $\log t$) are shown in Figure 2. Tobolsky⁸ suggested that $f(t)/f(0)$ was equal to $n(t)/n(0)$, where $n(t)$ is the number of network chains per unit volume at time t . Furthermore, assuming that chain scission occurs randomly throughout the rubber network, he derived that the number of scissions $q_M(t)$ (mole/ml) was represented by the following equation:

$$q_M(t) = -n_M(0) \ln f(t)/f(0) = -n_M(0) \ln n_M(t)/n_M(0). \quad (2)$$

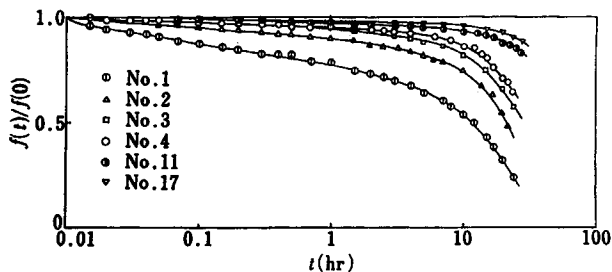


Fig. 2. Stress relaxation curves of crosslinked natural rubbers at 109°C in air.

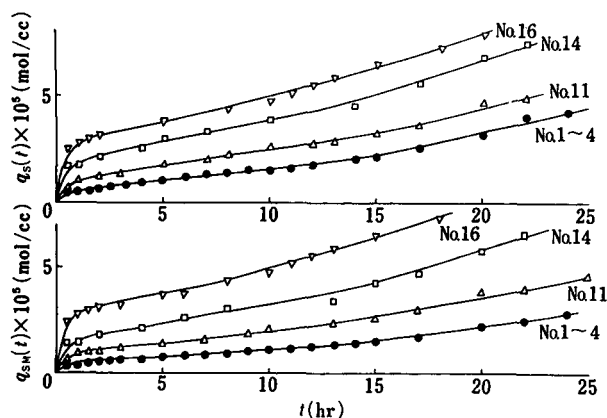


Fig. 3. Relation of $q_S(t)$ vs. t and $q_{SM}(t)$ vs. t for various samples.

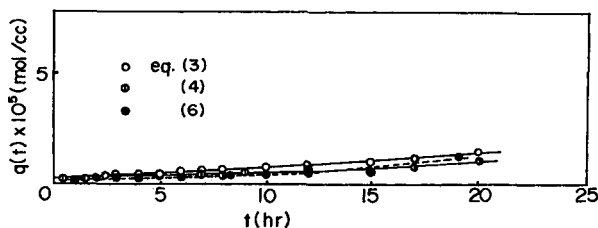


Fig. 4. $q(t)$ vs. t curves estimated by eqs. (3), (4), and (6).

If in this rubber scission occurred only at the links of the network chains, the relationship of $q_M(t)$ versus t must be represented by a curve independent of $n_M(0)$. But our result shows that $q_M(t)$ decreases with $n_M(0)$. So, considering the effect of chain entanglements as described in the previous section, we propose eqs. (3) and (4) as modifications of eq. (2). These equations give the number of real main chain scissions, because the chain entanglements have been removed:

$$q_S(t) = -n_S(0) \ln n_S(t)/n_S(0) \quad (3)$$

$$q_{SM}(t) = -n_{SM}(0) \ln n_{SM}(t)/n_{SM}(0). \quad (4)$$

The relation of $q_S(t)$ versus t and $q_{SM}(t)$ versus t is shown in Figure 3. In the small range of $n_S(0)$ or $n_{SM}(0)$ (samples 1 to 4), this relation is represented by a curve, that is, scission of dicumyl peroxide-cured natural rubber occurs at the main chain. At large values of $n(0)$, this relation deviates from the curve, and it is shown that the greater $n_S(0)$ or $n_{SM}(0)$, the greater the $q_m(t)$. This phenomenon cannot be explained in the present paper since we have not yet investigated it.

Next, scission in noncrosslinked rubber was followed by intrinsic viscosity determination of toluene-rubber solution oxidized at 109°C. The relationship between $[\eta]$ and molecular weight \bar{M}_n is given by eq. (5):

$$[\eta] = 5.00 \times 10^{-4} \bar{M}_n^{0.67}. \quad (5)$$

The quantity $q_m(t)$ was determined by

$$q_m(t) = d[1/\bar{M}_n(t) - 1/\bar{M}_n(0)] \quad (6)$$

where d is the natural rubber density, $\bar{M}_n(0)$ the initial number-average molecular weight, and $\bar{M}_n(t)$ is the number-average molecular weight at later times.

Lastly, the various quantities $q(t)$ estimated by eqs. (3), (4), and (6) are shown in Figure 4. These curves are approximately consistent with one another. Consequently, it was found that from chemorheological treatment, the number of main chain scission could be quantitatively obtained by using the above equations proposed by us.

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