Intermittent Stress Relaxation and Thermal Aging of Vulcanized Rubber

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Thermal aging at a high temperature was investigated in relation to the network concentration in vulcanized rubber. Intermittent stress relaxation of vulcanized rubber was studied using a Geer oven under conditions similar to those of the aging test. It was found that sulphur-zinc oxide mixed rubber had a slow rate of crosslinking and a fast relaxation and tetramethyl thiuram disulphide (TMTD)-zinc oxide mixed rubber had a fast rate of crosslinking and a slow relaxation. The equation for the change in network concentration with time was derived from the results.

VULCANIZED rubber deteriorates with constant use and prolonged storage; it becomes sticky, or its surface cracks because of gradual hardening. Its physical properties become generally poorer. This is known as aging and its extent can be determined by, for example, the decrease in tensile strength; the decrease in elongation at the breaking modulus; the increase in hardness; and changes in the stress-strain curve.

Tobolsky[1] *et al* have indicated the relationships between the intermittent and continuous stress relaxation and the network concentration in rubber. In this study, thermal aging at a high temperature was investigated and related to the network concentration of the vulcanized rubber. The network concentration bears a simple relationship to the modulus (i.e. the stress which gives a certain stretch) and therefore a change in network concentration can be determined by measuring the change in modulus with time for intermittent stress relaxation. The intermittent stress relaxation experiments on vulcanized rubber were carried out under conditions similar to those of the aging test in a Geer oven.

Following on from our previous work[2], the intermittent stress relaxation experiments were carried out, above 100°C, on tetramethyl thiuram disulfide (TMTD) mixed rubber; sulphur mixed rubber; and sulphur-zinc oxide mixed rubber; and from these results the equation for the change in network concentration with time was derived.

EXPERIMENTAL

We used the same apparatus as in our previous work[2] for our studies on intermittent stress relaxation and carried out the experiments in the following way. The upper and lower ends of a sample of vulcanized rubber ($2 \times 5 \times 70$ mm) were fixed on a vertical holder in a constant temperature air bath, taking care that the sample was free from strain, and we gave the sample an instantaneous stretch (20%) at certain time intervals. The force required for stretching, namely 20% modulus (S), was measured and the relationship between the ratio of the modulus to its initial value S, and the period of heating, was studied. The temperature was above 130°C in all

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cases. Measurement of intermittent stress relaxation was carried out by measuring the variation in the stress (20% modulus) with time. The sample is put back to a stress-free condition immediately after the measurement of the stress (modulus).

The samples used were a TMTD, sulphur, and zinc oxide mixed rubber (referred to as TSZ from now on) with a high cure rate; a TMTD and zinc oxide mixed rubber (TZ) with a medium cure rate; and a sulphur-zinc oxide mixed rubber (SZ) with a low cure rate

The first two rubbers (TSZ and TZ) showed maximum tensile strengths at vulcanizing periods of 3 min and 20 min, respectively, and a vulcanizing temperature of 141°C [276×10^3 N/m^2 (40 lbf/in^2) steam pressure]. The sample SZ, however, did not show a maximum tensile strength even after a 3 h period of vulcanization (*Figure 1*).

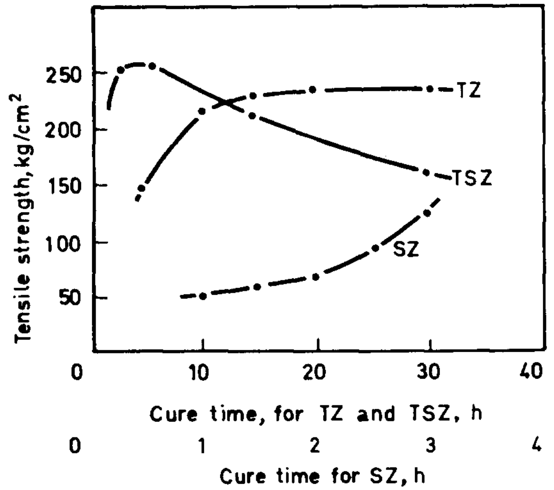

Figure 1—Tensile strength and cure time for TSZ (TMTD, S, ZnO mixed rubber), TZ (TMTD, ZnO mixed rubber) and SZ (S, ZnO mixed rubber)
[Cure temperature: 141°C, 276×10^3 N/m^2 (40 lbf/in^2)]

RESULTS AND DISCUSSION

We have determined the aging of vulcanized rubber mainly by measuring its tensile strength. Usually a maximum tensile strength is reached on vulcanization and excessive vulcanization decreases the tensile strength. This leads us to suppose that a high network concentration hinders orientation of the molecules (and hence crystallization) during stretching, and therefore causes a decrease in the tensile strength[3]. However, this explanation does not apply in all the cases; for example, a lowering of the modulus sometimes occurs with prolonged vulcanization. As we have noted before[2], breakdown of the molecule must also be considered.

Where rubber elasticity exists, the network concentration and the modulus are related to each other in a simple way. Softening of vulcanized rubber corresponds to a decrease, and hardening to an increase in the network concentration. From the theory of rubber elasticity, the modulus is proportional to the network concentration,

$$S = \nu\, kT(\alpha - 1/\alpha^2) \tag{1}$$

where α, the extension ratio (L/L_0) is small.

As the stretching at the time of the observation is constant in intermittent stress relaxation:

$$\nu_t/\nu_0 = S/S_0 \tag{2}$$

and ν_t can be obtained from the modulus S at a time t.

The increase in network concentration is mainly due to crosslink formation and the decrease due to the cleavage of chain units by oxygen, ozone, heat, etc.[4]. Cleavage at the bridge point is also thought to be involved[5]. These reactions of rubber may be written as follows:

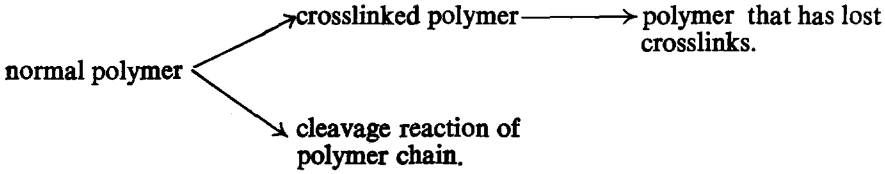

Figure 2 shows the differences in the intermittent stress relaxation curves at 130°C due to the differences in mixing. TMTD vulcanized rubber (TZ) had a long relaxation period, especially when the vulcanization period was short so that unreacted sites were left for further crosslinking.

The sulphur mixed rubbed had a slow rate of crosslinking and a fast relaxation. *Figure 3* shows the dependence of the intermittent relaxation of the sulphur mixed rubber on the degree of vulcanization, and from this

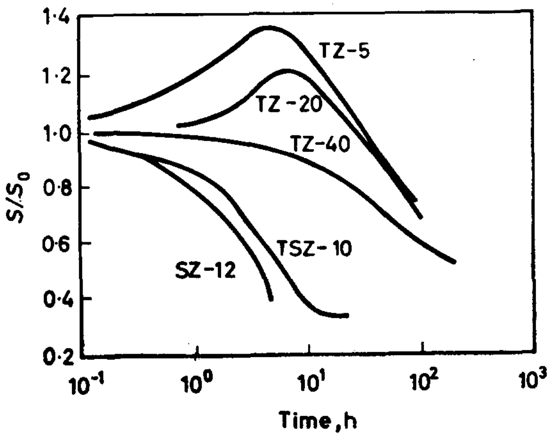

Figure 2—Intermittent stress relaxation curves at 130°C for vulcanized rubber. Cure times of TZ-5, TZ-20, TZ-40, TSZ-10 and SZ-12 were 5, 20, 40, 10 min and 12 h, respectively

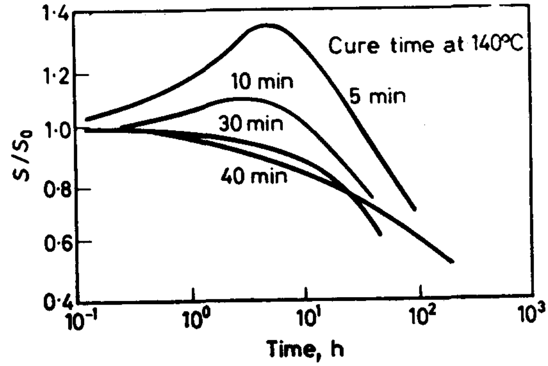

Figure 3—Dependence of intermittent stress relaxation curves at 130°C on cure times of sample TZ

we can determine the effect of the crosslink-formation reaction on the relaxation.

Figure 4 shows the dependence of the intermittent stress relaxation on temperature. Assuming that the number of sites for crosslink formation (double bonds or methylene groups of rubber) is much greater than the initial concentration of the crosslink-forming reagent and that the change in concentration of the sites can be neglected, the rate of formation of crosslinks can be represented by the following first order equation[6]

$$-\mathrm{d}a/\mathrm{d}t=k_1a \tag{3}$$

where a is the concentration of crosslink-forming reagent and k_1 is the rate constant for crosslinking.

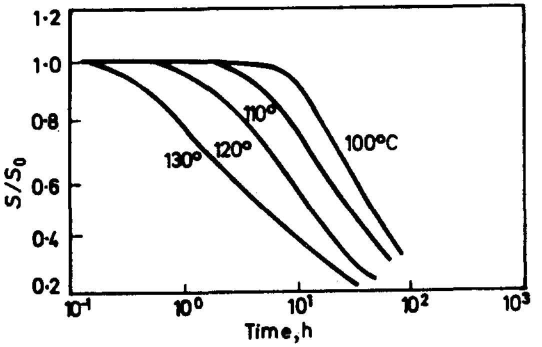

Figure 4—Dependence of intermittent stress relaxation on temperature for sample SZ-12

On integration,

$$a=a_0\mathrm{e}^{-k_1t} \tag{4}$$

where α_0 is the initial concentration of crosslink-forming reagent.

If we assume that the rate of formation of crosslinks is proportional to the concentration of the crosslink-forming reagent (a) and the rate of their cleavage is proportional to the number of crosslinks[7], the change in the number of crosslinks can be written as follows:

$$d\nu / dt = k_1 a - k_2 \tag{5}$$

where ν is number of crosslinks present, ν_0 is the initial concentration of crosslinks and k_2 is the rate constant for the cleavage of crosslinks, which is equal to the rate of disappearance of the network.

From equations (3) and (5)

$$-d\nu / da = 1 - k_2 \nu / k_1 a \tag{6}$$

is obtained and its integration gives equation (7).

$$-\frac{k_1 - k_2}{k_1} \ln \frac{a}{a_0} = \ln \frac{1 + (k_1 + k_2)/k_1 \times \nu / a}{1 + (k_1 - k_2)/k_1 \times \nu_0 / a_0} \tag{7}$$

Equation (7) can be rewritten as follows

$$\nu = \frac{k_1 a}{k_1 - k_2} \times \left[\left\{ 1 + \frac{(k_1 - k_2)}{k_1} \times \frac{\nu_0}{a_0} \right\} \left(\frac{a}{a_0} \right)^{\frac{-(k_1 k_2)}{k_1}} - 1 \right] \tag{8}$$

From equations (4) and (8),

$$\nu = \frac{k_1 a_0}{k_1 - k_2} \times \left[\left(1 + \frac{k_1 - k_2}{k_2} \times \frac{\nu_0}{a_0} \right) e^{-k_2 t} - e^{-k_1 t} \right] \tag{9}$$

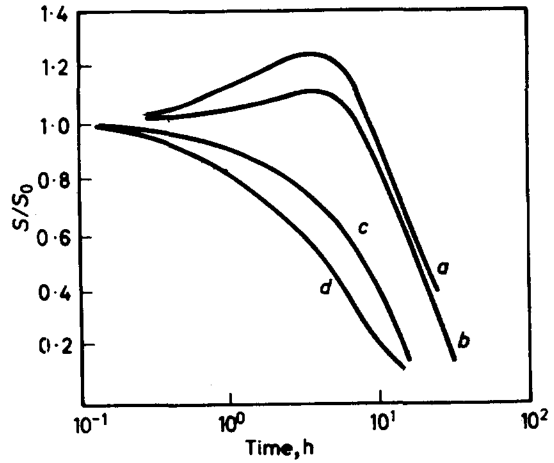

Figure 5—Theoretical curves of S/S_0 *vs.* time from equation (10) or (11) in the case of the extent of vulcanization is constant n=1. Curve (a) $k_1=0{\cdot}3$, $k_2=0{\cdot}1$; (b) $k_1=0{\cdot}2$, $k_2=0{\cdot}1$; (c) $k_1=0{\cdot}1$, $k_2=0{\cdot}2$; (d) $k_1=0{\cdot}1$, $k_2=0{\cdot}3$

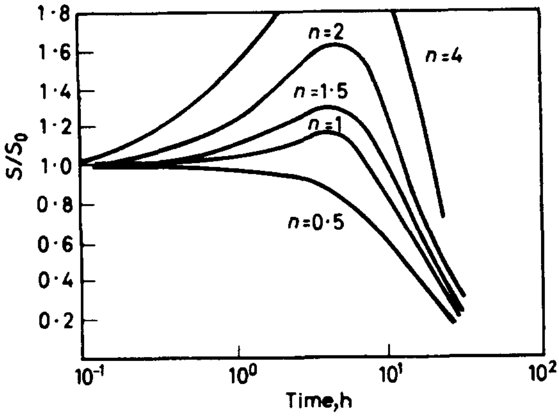

Figure 6—Theoretical curves of S/S_0 *vs.* time from equation (10) or (11) in the case of the rate of change in network in constant, $k_1=0{\cdot}2$, $k_2=0{\cdot}1$

is obtained, which can be rewritten as follows,

$$\frac{\nu}{\nu_0}=\frac{k_1}{k_1-k_2}\times\frac{a_0}{\nu_0}\left(e^{-k_2t}-e^{-k_1t}\right)+e^{-k_2t} \tag{10}$$

$$\nu/\nu_0=S/S_0=(mn+1)e^{-k_2t}-mne^{-k_1t} \tag{11}$$

where $m=k_1/(k_1+k_2)$ and $n=a_0/\nu_0$.

Therefore, the change in the modulus and the network concentration of vulcanized rubber with time can be formulated in terms of k_1, k_2 and m, which are related to the extent of vulcanization. *Figure 5* shows the S/S_0 *vs.* time curve for the case where the extent of the vulcanization was constant and k_1 and k_2 were varied and *Figure 6* shows the S/S_0 *vs.* time curve for which the rate of change of the network was constant and the extent of vulcanization was changed. From the above facts, it was found that the intermittent stress relaxation results could be explained by equation (11).

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