

Microscopic Fracture of Cross - Linked Polymers

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Introduction

In the present study, we investigated the mechanism dealing with the reactivities of cross linkages in ethylene-propylene rubber (EPDM) containing nonconjugated diene compounds as the third component.

Materials and Experiments

Three kinds of crosslinked EPT (Nos. 1, 2, and 3) were prepared by using di-cumyl peroxide, accelerated sulfur and tetramethylthuram disulfide as the crosslinking agents, respectively. It is evident that the crosslinking site consists of a carbon-carbon bond, a polysulfide linkage ($-\hat{S}_x-$) and a monosulfide linkage ($-S-$) for types 1, 2, and 3, respectively. The samples were all extracted with acetone for 72 hr and dried in vacuo.

Results and Discussion

The stress relaxation of dicumyl peroxide-cured EPT (sample 1) was measured at 109°C in air, in nitrogen, and in air containing a proper amount of antioxidant. These stress relaxation curves showed almost the same slope in the three samples. The relaxation mechanism of the sample is due to a physical relaxation.

Also, the stress relaxation of type 1 samples having an initial chain density $n(0)$ of 0.53×10^{-4} and 1.45×10^{-4} mole/ml, samples 2 and 3 having $n(0)$ of 1.39×10^{-4} and 0.62 mole/ml, respectively, were measured in air at 109°C. The result is shown in Figure 1. Because these were obtained

under the same conditions, the superposed portions of the curves for samples 2 and 3 with that of sample 1 are considered to be due to a physical relaxation. From Figure 1 it was found that the stress decay due to a physical relaxation at the initial stages is independent of the kind of crosslink if the crosslinking density of these polymers is equivalent. Further, materials with different kinds of crosslinks and with identical initial densities $n(0)$ were prepared. In these materials, the crosslinks are C-C bond and polysulfide linkage ($-Sx-$), and $n(0)$ of the samples have the same density, 0.78×10^{-4} , 1.39×10^{-4} , and 2.26×10^{-4} mole/ml. From the stress relaxation curves of these samples it is clear that with a nearly equal value of $n(0)$, the physical relaxations in the initial stage are the same and they overlap, regardless of the kind of crosslink.

In order to discuss the mechanisms of the chemical relaxation in detail, the portions of the stress decay based upon physical flow were reduced from the original stress relaxation curves of EPT polymers; for samples cured with TT (sample 3, Figure 1) and with sulfur (sample 2, Figs. 1 and 2) and their pure chemical stress relaxation curves were replotted as $\log f(t)/f(0)$ versus time (Figs. 3 and 4).

In Figure 3, a fine straight line was obtained for sample 3. Because there still remained a curved portion of the plot in the short-time region for sample 2 as shown in the figure, we used our suggested procedure and repeated it until we obtained a straight line in the whole time scale region. The stress relaxation curve for sample 2 is divided into three fine straight lines.

In Figure 4, three straight lines having the same slope

in the long-time side region were obtained as shown.

The chemical stress relaxation curves of sample 2 at 109°C in both air and nitrogen are shown in Figure 5. From Figure 5, we may consider that in sample 2, in addition to the interchange reaction of the polysulfide linkages, an oxygen-induced cleavage of mono- and disulfide linkages in the air could explain this behavior.

Generally, scission occurs only at a crosslink in chains of the polymer network. If we represent the number of initial crosslinkages by $C(0)$, the number of scissions after time t by $q(t)$ and the proportionality constant by k , the following equation will be established.

$$dq(t)/dt = k\{C(0) - q(t)\} \tag{1}$$

On solving eq. (1), eq. (2) is obtained:

$$q(t) = C(0)(1 - e^{-kt}) \tag{2}$$

If $f(t)/f(0)$ is the relative stress and $n(0)$ the initial chain density and if scission occurs only at the crosslinks, then eq. (3) is valid:

$$f(t)/f(0) = 1 - \{2q(t)/n(0)\} \tag{3}$$

In an ideal network of chains, eq. (4) is obtained:

$$2C(0) = n(0) \tag{4}$$

Therefore eq. (5) is deduced:

$$f(t)/f(0) = e^{-kt} \tag{5}$$

On the other hand, from recent studies, it has been ascertained that the stress relaxation mechanism of crosslinked polymers which undergo an interchange reaction can be expressed by the sum of two exponential terms.

Now, in the case of the sulfur-cured EPT polymer (sample 2), it is assumed from the various experimental results described above that the crosslinking sites of this sample

consist of polysulfide, monosulfide, and disulfide linkages. We can deduce for sample 2, that two reactions occur simultaneously at the crosslinkage: typical interchange and cleavage. Therefore it is considered from the above reactions that the relationship between relative stress and time be expressed by eq. (6):

$$\frac{f(t)}{f(0)} = A e^{-k_1 t} + B e^{-k_2 t} + C e^{-k_3 t} \quad (6)$$

The first two terms in the right-hand side of eq. (6) are due to the mechanisms of typical interchange reaction and the third term refers to cleavage at the crosslinkage.

For question of why all the slopes of the first straight line in the sample 2 and the ones in the sample 3 equal independent of $n(0)$ may now be answered on the basis of eq. (5) or the third term in eq. (6). According to Tobolsky et al. in the case when scission occurs only at crosslinkage in the crosslinked polymer, it is recognized that the decay curves of $f(t)/f(0)$ versus time are identical and independent of the chain density $n(0)$. Therefore the value of k of eq. (5) or the third term in eq. (6) is usually a universal constant and is independent of $n(0)$.

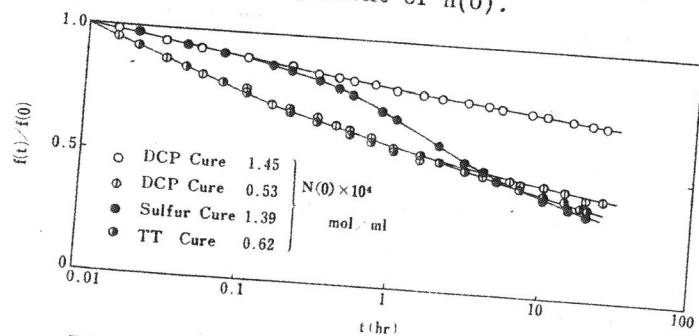


Fig. 1. Stress relaxation of samples 1, 2 (sulfur-cured EPT), and 3 (TT-cured EPT) in air at 109°C.

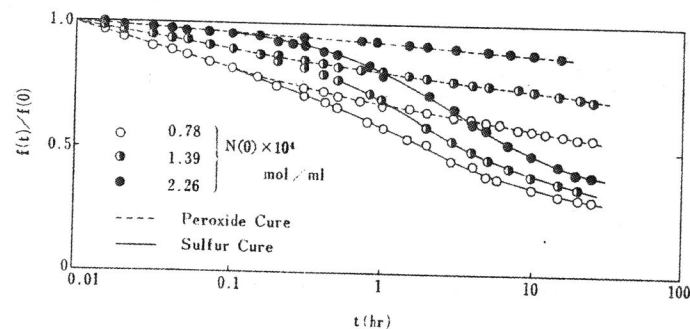


Fig. 2. Stress relaxation of three groups of samples 1 and 2 having the same value of $n(0)$ in air at 109°C.

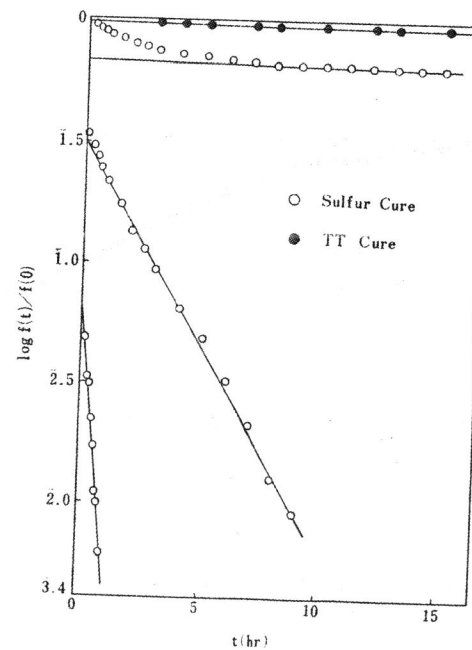


Fig. 3. Replot as $\log f(t)/f(0)$ versus time of two chemical stress relaxation curves.

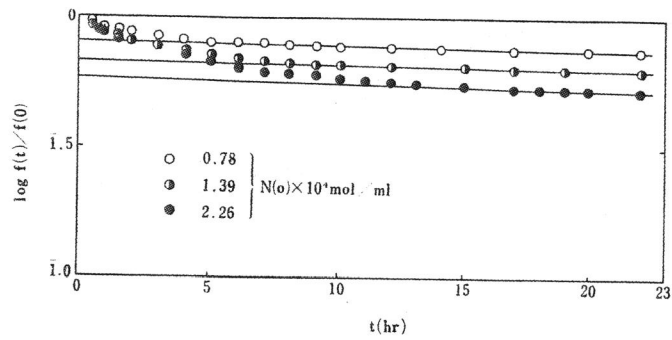


Fig. 4. Replot as $\log f(t)/f(0)$ versus time of three chemical stress relaxation curves.

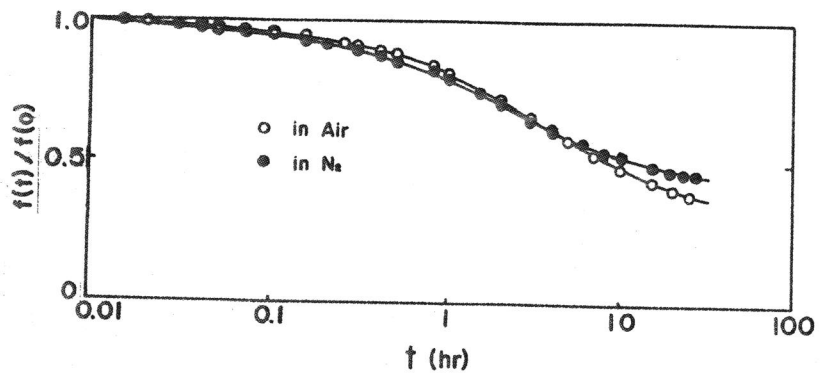


Fig. 5. Stress relaxation curves of sample 2 in air and under nitrogen at 109°C .