

Chemorheological Treatment of Crosslinked EPDM. II

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Synopsis

Stress relaxation mechanisms were investigated on three kinds of ethylene-propylene terpolymers (EPDM), differing only in the structure of the crosslinkage, in both nitrogen and air at 160°C. The crosslinking site in these polymers consists of a carbon-carbon bond, a polysulfide linkage, and a carbon-carbon bond and a polysulfide linkage, respectively. Stress relaxation in air for peroxide-cured EPDM was based on the oxidative scission of the main chain. Analysis of the stress relaxation data of sulfur-cured EPDM in nitrogen indicated the presence of stable mono- and disulfide linkages and that the main relaxation process resulted from an interchange reaction between polysulfide linkages. In air, in addition to the interchange reaction, oxidative cleavage of mono- and disulfide linkages occurred. Further, the stress relaxation for peroxide-sulfur-cured EPDM polymers containing various amount of sulfur was observed in air and nitrogen and was discussed in the connection with highly crosslinked polymers.

INTRODUCTION

In a previous paper,¹ we investigated the stress relaxation mechanisms on three kinds of ethylene-propylene terpolymers (EPDM) differing only in the structure of the crosslinkage, at 109°C in both air and nitrogen. At this temperature, the EPDM main chain is stable to oxidative scission. Therefore, the stress relaxation of these polymers could clarify the structural characteristics of the crosslinkage. However, it was found that the oxidative scission of the EPDM main chain occurred at a higher temperature, i.e., at 160°C, and that the stress relaxations differed from those of the previous paper.¹

In this paper, stress relaxation mechanisms are investigated on three crosslinking systems of EPDM polymer in both air and nitrogen at 160°C. These are dicumyl peroxide-cured, accelerated-sulfur-cured, and dicumyl peroxide-sulfur-cured EPDM.

EXPERIMENTAL

Ethylene-propylene terpolymer (EPDM, Royalene 301, Sumitomo Chemical Industry Ltd.) was cold milled with the curing ingredients as described in Table I, which also shows curing conditions. Sheets (about 0.5 mm) of the milled polymer were pressed under 200 kg/cm² at the curing

TABLE I
Preparation of Cured EPDM Polymers

	Sample 1	Sample 2	Sample 3
Rubber	100	100	100
Sulfur		2	various
Zinc oxide		5	
Stearic acid		2	
Tetramethylthiuram disulfide (TT)		1	
Mercaptobenzothiazole (MBT)		0.5	
Dicumyl peroxide (DCP)	2		2
Curing time, min ^a	20	13	various

^a Curing temperature, 150°C.

temperature. Three kinds of EPDM polymer (1, 2, and 3), differing only in the structure of the crosslinkage, were prepared. It is evident that the crosslinking site in these samples consist of a carbon-carbon bond, a polysulfide linkage ($-\text{S}_x-$), and a carbon-carbon bond and a polysulfide linkage in the mix for samples 1, 2, and 3, respectively. All the samples were extracted with acetone for 72 hr and dried in vacuo. The stress relaxation apparatus used here was made in our laboratory, and its mechanism was a usual strain-gauge system. The initial network chain density $n(0)$ was estimated by the stress-strain measurement based on the statistical theory of rubber-like elasticity. The extension ratio α was about 1.2.

RESULTS AND DISCUSSION

Stress Relaxation of Dicumyl Peroxide-Cured EPDM (Sample 1)

The continuous stress relaxation of three no. 1 samples having different initial network chain density $n(0)$ was measured in both air and nitrogen at 160°C. These stress relaxation curves (relative stress, $f(t)/f(0)$ versus time, $\log t$) are shown in Figure 1. It can be seen that in both air and nitrogen, relative stress decreases sharply with increasing $n(0)$. When we consider the chemical structure, it can be assumed that sample 1 is ther-

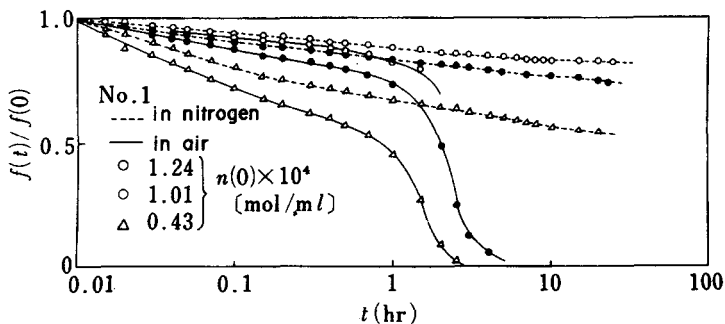


Fig. 1. Continuous stress relaxation curves of dicumyl peroxide-cured EPDM (sample 1) in air and nitrogen at 160°C.

mally stable in nitrogen at 160°C. Therefore it seems very reasonable to consider that the relaxation mechanism of sample 1 in nitrogen is due to physical relaxation. The figure indicates a typical case of oxygen-induced cleavage of the main chain.

Also, intermittent stress measurements on sample 1 in air at 160°C were approximately in agreement with continuous stress relaxation. This indicates that for this substance scission occurs with practically no crosslinking reaction.

The Stress Relaxation of Sulfur-Cured EPDM (Sample 2)

Figure 2 shows the continuous stress relaxation curves of sample 2 in air and nitrogen at 160°C. From this figure, we can see that the relaxation curves in both air and nitrogen are represented by a curve independent of $n(0)$, and also independent of the atmosphere in the initial stage. This result is interesting, for it differs not only with the behavior of stress relaxation of sample 1 (Fig. 1), but also with that of sample 2 at 109°C described in the previous paper,¹ where the stress decay at 109°C was dependent on $n(0)$ and decreased with increasing $n(0)$ in both air and nitrogen.

Next, we discuss the mechanism of chemical relaxation of sample 2 at 160°C. From the difference in relaxation rates in nitrogen for peroxide and sulfur-cured polymers of approximately the same crosslink density at 160°C, the chemical stress relaxation was obtained, and this is shown in Figure 3. This curve was analyzed by the procedure of Tobolsky and Murakami² to give the three straight lines also indicated in Figure 3. The uppermost straight line becomes parallel to the abscissa. This retention of stress seems to be based on thermally stable mono- and disulfide crosslinks. The other two straight lines are identified by the interchange reaction of polysulfide crosslinkages, as described in part I.¹ The above description (Fig. 3) can be expressed by

$$f(t)/f(0) = A \cdot e^{-k_1 t} + B \cdot e^{-k_2 t} + \text{constant}. \quad (1)$$

The relaxation in air on the long-time side in Figure 2, which is approximately independent of $n(0)$, can be explained by the well-known Tobolsky

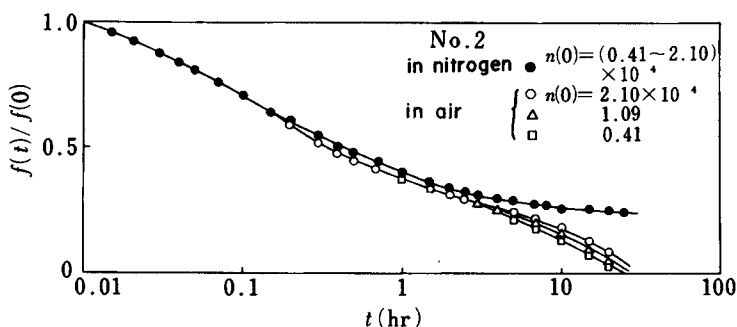


Fig. 2. Continuous stress relaxation curves of sulfur-cured EPDM (sample 2) in air and nitrogen at 160°C.

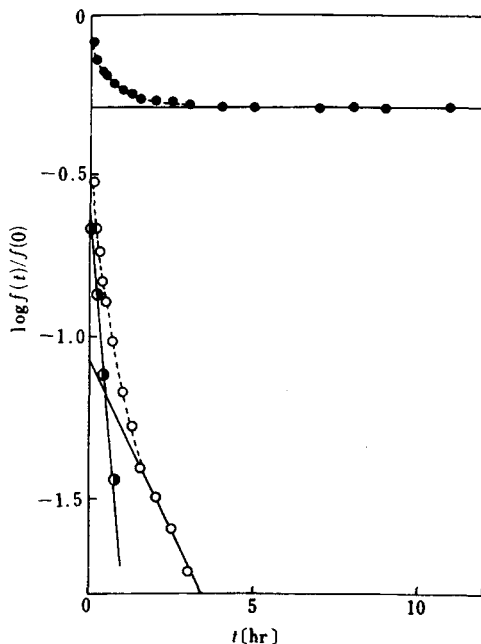


Fig. 3. $\log f(t)/f(0)$ vs. time t of sample 2 in nitrogen at 160°C .

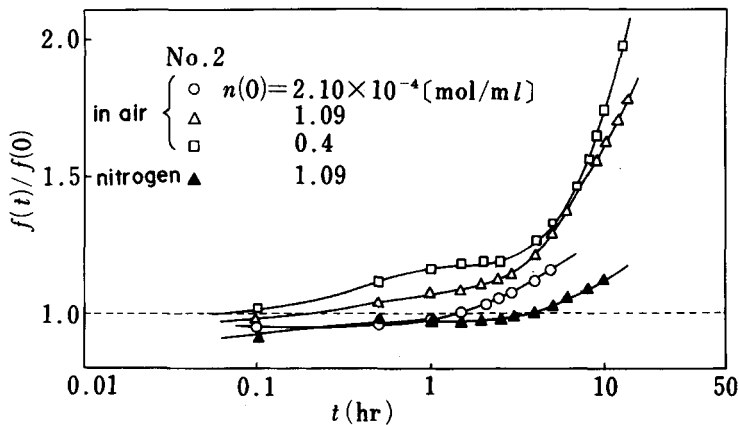


Fig. 4. Intermittent stress measurement of sample 2 in air at 160°C .

theory.³ Accordingly, in the case of scission at the crosslink site, $f(t)/f(0)$ is independent of $n(0)$. Therefore, this relaxation suggests the existence of oxidative cleavage of mono- and disulfide linkages.

Next, intermittent stress measurements of sample 2 were undertaken in air at 160°C . These relaxation curves are shown in Figure 4. In the initial stage, the relative stress $f(t)/f(0)$ increases with decreasing $n(0)$. This is related to the interchange reaction of polysulfide linkages. That is, when the initial density $n(0)$ is changed by the curing time only, it can be

expected from the thermostability of crosslinkages that the number of polysulfide linkages will be decreased with curing time. Therefore, the increase in $f(t)/f(0)$ in the initial stage in Figure 4 suggests an increase in crosslinks due to interchange reactions of polysulfide linkages. The rapid increase of stress on the long-time side seems to be an increase in effective network chains due to oxidative crosslinking. This may be due to a presence of unsaturated termonomer, i.e., cyclopentadiene, containing in EPDM polymer.

Stress Relaxation of Dicumyl Peroxide-Sulfur-Cured EPDM (Sample 3)

We investigated how the stress relaxation of sulfur-containing samples (sample 3) changes with sulfur content. Crosslinked polymers were prepared with 0 (sample 1), 0.1, 0.25, 0.5, 0.7, 1.0, 2.0, and 3.0 phr of sulfur and 2.0 parts of dicumyl peroxide. These samples, with a nearly equal value of $n(0)$, that is, $n(0) \approx 1.05 \times 10^{-4}$ mole/ml, were prepared by change in curing time. We assume that the crosslinks of these polymers consist of carbon-carbon bonds and mono-, di-, and polysulfide linkages. Figure 5 shows the relaxation curves of sample 3 in nitrogen at 160°C. It can be seen from this figure that, as the sulfur level is increased to 0.7 phr, the relaxation rate also gradually increases. However, the rate of stress relaxation of samples containing 0.7 phr sulfur or more is almost independent of sulfur content. This can be explained as follows. Since the relaxation experiments have been carried out in nitrogen, it is considered from the previous results that carbon-carbon bonds and mono- and disulfide linkages are thermally stable at this temperature. Therefore, it is concluded that the stress relaxation in Figure 5 is due to an interchange reaction of polysulfide crosslinks and a physical flow of the polymer chain. Hence Figure 5 indicates that polysulfide crosslinks, which are thermally labile linkages, are increased with increasing sulfur content up to 0.7 phr and become constant in the samples containing sulfur of 0.7 phr or more.

Dunn⁴ recently has carried out chemical relaxation in respect of dicumyl peroxide-cured ethylene-propylene copolymers containing various levels of sulfur in the mix under approximately similar conditions as ours. The

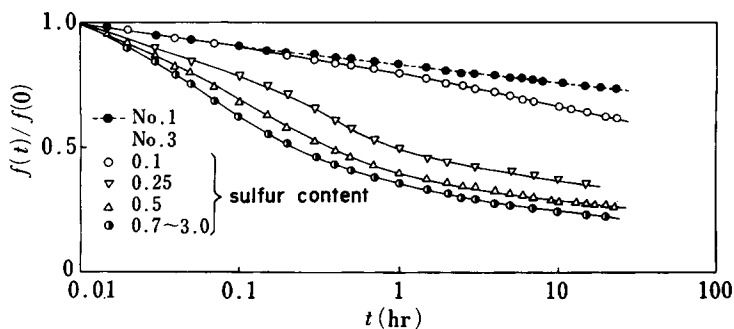


Fig. 5. Continuous stress relaxation of dicumyl peroxide-cured EPDM containing various levels of sulfur (sample 3) in nitrogen at 160°C.

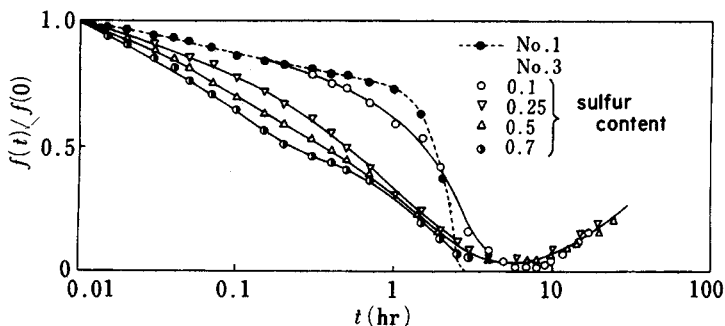


Fig. 6. Continuous stress relaxation curves of sample 3 containing up to 0.7 parts of sulfur in air at 160°C.

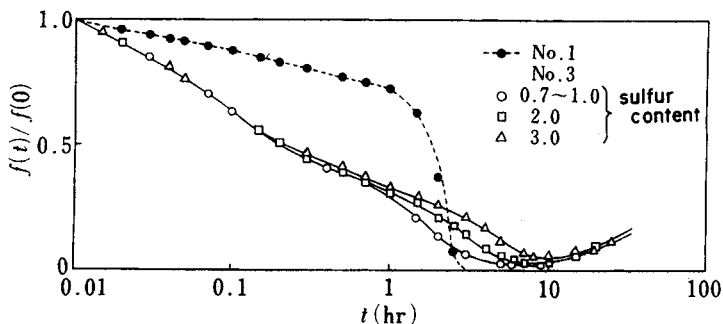


Fig. 7. Continuous stress relaxation curves of sample 3 containing 0.7 parts sulfur or more in air at 160°C.

experimental results he obtained, however, are different from ours. His paper has described that in these polymers, polysulfidic crosslinks are present only at sulfur levels in excess of 0.5 parts, that is, the relaxation of samples under vacuum up to 0.5 parts of sulfur is very slow and that of samples containing sulfur levels in excess of 0.5 phr increases with sulfur content. This can be attributed to the difference in chemical structure between EPDM and EPR. As EPDM polymer incorporates an unsaturated monomer, polysulfide crosslinks are likely to be formed in this polymer. On the other hand, as EPR polymer has no double bond, polysulfide crosslinks are difficult to be formed.

Next, we carried out stress relaxation measurements in air at 160°C on sample 3. The experimental results are shown in Figures 6 and 7. The figures indicate that the initial relaxation of samples containing up to 0.7 parts of sulfur increases with increasing sulfur content and that of samples containing 0.7 phr sulfur or more is independent of sulfur content and is also in agreement with the initial relaxation in nitrogen. As described above (Fig. 5), this also can be related to the number of polysulfide crosslinks. It is interesting that on the long-time side in Figure 7, the rate of relaxation of samples containing 0.7 phr sulfur or more is decreased with increasing sulfur content.

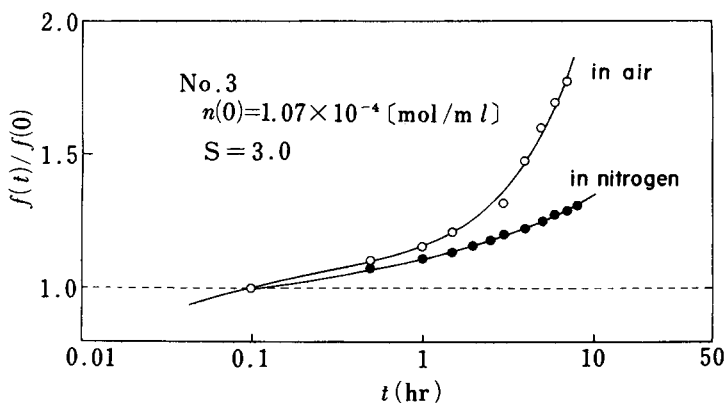


Fig. 8. Intermittent stress measurement of sample 3 in air and nitrogen at 160°C.

We cannot give an explanation of this experimental behavior. It may be related to the crosslinking structure; the difference between the number of carbon-carbon crosslinks; and the mono-, di-, and polysulfide crosslinks in these polymers. What is further interesting in Figures 6 and 7 is that the relative stress $f(t)/f(0)$ in the end-time region goes up gradually with time, independent of sulfur content.

Figure 8 shows intermittent stress measurements in air and nitrogen of sample 3 containing 3.0 phr sulfur. The rapid increase in relative stress on the long-time side represents the increase in effective network chains based on oxidative crosslinking as described above. The results of other no. 3 samples of various sulfur contents also are similar to that of Figure 8. The increase in relative stress of sample 3 was usually larger than that of sample 2. Considering Figure 8, the increase in $f(t)/f(0)$ in the end-time region in Figures 6 and 7 is explained as follows: Under these experimental conditions, sample 3 on the long-time side becomes a highly crosslinked polymer. Therefore, the assumption proposed by Tobolsky⁵ does not necessarily apply in this case, and only few of the newly produced networks seem to contribute to the stress as effective chains. Actually, Murakami et al.⁶ have observed that continuous stress relaxation curves for highly crosslinked polymers do not show the decay curves, but go up higher.

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Received March 2, 1972

Revised May 24, 1972