

# Influence of Physical Relaxation on Chemical Stress-Relaxation of Natural Rubber Vulcanizates

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## Synopsis

Networks were prepared in the swollen and dry states to investigate the influence of physical relaxation on chemical stress-relaxation. The stress-relaxation behavior of solution-cured samples was different significantly from that of the samples crosslinked conventionally. The same result was also observed in the number of chain scission for both kinds of samples. On the other hand, the number of chain scission estimated by using the swelling method for samples crosslinked conventionally was in good agreement with that by the chemical stress-relaxation for solution-cured samples. It was found that there is little or no influence of the physical relaxation caused by entanglements, and no effect of dangling chains arising from scission in the equilibrium swelling. The relative change of network chain density determined by means of the swelling method was also consistent with that by sol fraction determination. These results indicate that the swelling method can be used as a measure of a degree of degradation on chemorheology. Taking into account the influence of physical relaxation on chemical stress-relaxation, a new relationship between the relative stress decay and the relative network chain density was experimentally proposed.

## INTRODUCTION

Chemorheology affords some useful information on degradation of rubber vulcanizates.<sup>1</sup> For example, the number of chain scission and its mechanism during aging can easily be estimated by chemorheological treatment. Tobolsky<sup>2</sup> used chemical stress-relaxation technique for the discrimination of the scission mechanism. For this purpose, he proposed that the number of chain scission can be evaluated directly from the value of relative stress determined during chemical stress-relaxation. In a previous paper,<sup>3</sup> however, it was found that the physical relaxation caused by entanglements affects significantly on chemical stress-relaxation.

The purpose of this paper is to explore the quantity of chain scission of rubber vulcanizates having different amounts of trapped entanglements and to investigate the influence of physical relaxation on chemical stress-relaxation in more detail. Networks were prepared in the swollen state in order to obtain topologies simpler than those prepared by conventional vulcanization. Then, the quantity of chain scission for networks prepared in the swollen and dry states was evaluated by means of chemical stress-relaxation. The degree of degradation for both kinds of networks was also determined by the degree of equilibrium swelling and by sol fraction determination of degraded networks. By comparing the chemical stress-relaxation of both networks with

the degree of degradation, the influence of physical relaxation on chemical stress-relaxation was discussed.

### EXPERIMENTAL

The material used in the present study was natural rubber (NR; pale crepe No. 1). Dicumyl peroxide was used as a crosslinking agent. Two kinds of samples were prepared; One was crosslinked in the swollen state (SC), and the other was crosslinked conventionally (DC), as described previously.<sup>3</sup> All samples were extracted with acetone at 318 K for 48 h and dried *in vacuo*. Preparation of these two types of samples are summarized in Table I.

Sol fraction and network chain density were determined as follows. Aged network strips were immersed in benzene at room temperature for 48 h. After the complete dissolution of soluble part, the gel was deswollen in methanol and dried *in vacuo*, and then the sol fraction was calculated from the weight loss of the strip. In order to determine the equilibrium degree of swelling on each of the network strips, the dried strips were immersed again in toluene for 24 h at 303 K. The network chain density  $n_{sw}$  was evaluated from the equilibrium degree of swelling by using the Flory-Rehner equation.<sup>4</sup> The value of interaction parameter between the polymer and solvent is 0.43.

The measurement of chemical stress-relaxation was carried out in air at various temperatures. The apparatus used is described in Ref. 5. The samples were about 5 mm wide, 30 mm long, and 0.5 mm thick.

The equilibrium stress-strain modulus of samples were determined in the following way. The samples were swollen to equilibrium in toluene at room temperature. The swollen samples were mounted between two clamps in the apparatus described previously,<sup>5</sup> and the stress-strain measurements were carried out in a glass tube filled with the toluene. For each samples, five or six elongations were measured. After changing elongations, ca. 1 h was allowed to obtain the equilibrium stress. From the Mooney-Rivlin type analysis of these data, the equilibrium stress-strain modulus was evaluated.

TABLE I  
Preparation of Samples Crosslinked in the Dry and Swollen States

Sample	$\Phi^a$	DCP <sup>b</sup> (phr) <sup>c</sup>	Curing time (min)	$10 \times n_{sw}^d$ (mol dm <sup>-3</sup> )
SC-1	0.1	2	120	0.11
SC-2	0.1	3	120	0.18
SC-3	0.1	5	120	0.37
DC-1	1.0	2	8	0.19
DC-2	1.0	2	10	0.22
DC-3	1.0	2	15	0.39
DC-4	1.0	3	20	0.58

<sup>a</sup>Volume fraction of rubber present during crosslinking.

<sup>b</sup>Dicumyl peroxide.

<sup>c</sup>Parts per hundred rubber.

<sup>d</sup>Network chain density determined by using the swelling method.

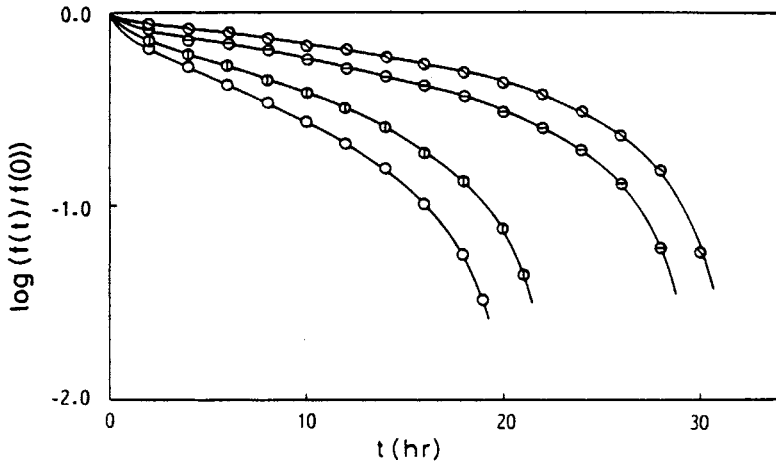


Fig. 1. Chemical stress-relaxation curves for DC-samples at 383 K in air: DC-1 (O), DC-2 (⊕), DC-3 (⊖), DC-4 (⊗). The extension ratio  $\alpha$  is 1.2.

### RESULTS AND DISCUSSION

The chemical stress-relaxation curves for DC samples degraded in air at 383 K are shown in Figure 1. The logarithm of relative stress,  $\log[f(t)/f(0)]$ , of the DC samples decreases with time, and the relaxation rate becomes slower with increasing the network chain density. The logarithm of relative stress decreases rapidly at the short times of degradation for the samples DC-1 and DC-2, whereas such a stress decay is not observed for the samples DC-3 and DC-4.

Figure 2 shows the chemical stress-relaxation curves for SC samples degraded in air at 383 K. For the SC samples, the logarithm of relative stress

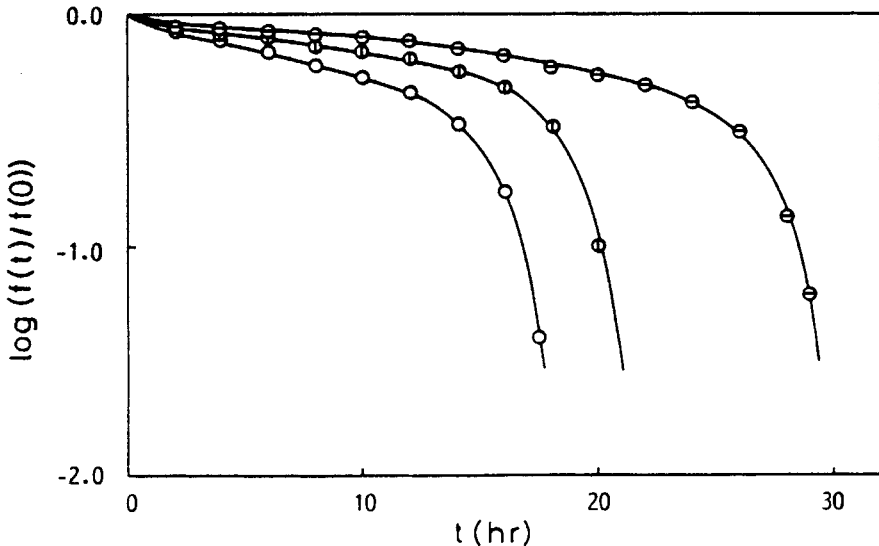


Fig. 2. Chemical stress-relaxation curves for SC-samples at 383 K in air: SC-1 (O), SC-2 (⊕), SC-3 (⊖). The extension ratio  $\alpha$  is 1.2.

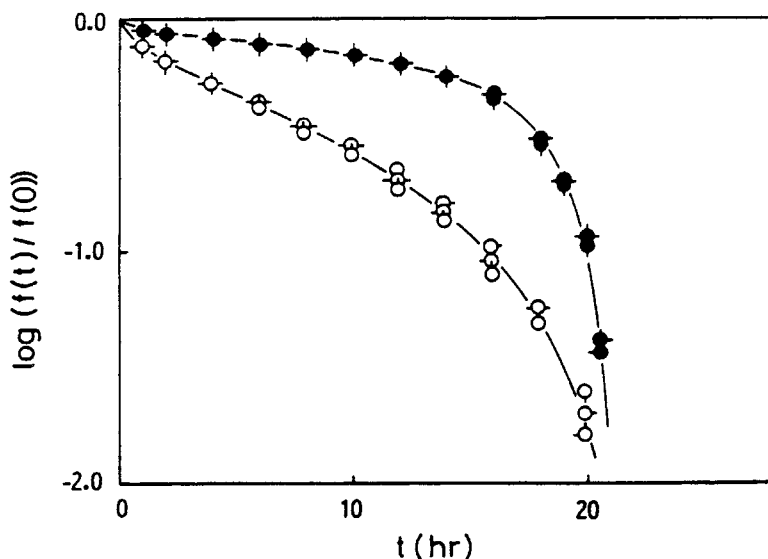


Fig. 3. Effect of the extension ratio on the chemical stress-relaxation behavior for DC and SC samples. Measurements were carried out at 383 K in air. The open and filled circles indicate the DC and SC samples, respectively. The extension ratio: pip up, 1.2; right, 1.5; down, 2.0; left 2.5.

does not decrease rapidly at the short times of aging even in the case of the sample SC-1 having a low network chain density, and differs significantly from that of the DC samples over the whole range of time.

Since the SC samples have a quite different chain conformation compared with that of the DC samples, it is necessary to investigate the effect of extension ratio on stress relaxation behavior for both networks. Figure 3 shows the effect of extension ratio on chemical stress-relaxation for SC and DC samples. From the results of Figure 3, it is apparent that such effects are not found in the elongation region of about 1.2–3. On the other hand, it was reported that the strain-induced crystallization of natural rubber vulcanizates affects on chemical stress-relaxation behavior.<sup>1</sup> On chemorheology, therefore, the extension ratio has been limited within relatively low elongations (ca. 200%) in order to avoid the strain-induced crystallization. In the present investigation, all measurements were carried out at the extension ratio,  $\alpha = 1.2$ .

The number  $q_m(t)$  of chain scission that have occurred up to time  $t$  in each network was investigated to study quantitatively the difference in chemical stress-relaxation behavior for both networks, as shown in Figures 1 and 2. The relation between the number  $q_m(t)$  of chain scission and the relative stress decay has been proposed by Tobolsky et al.,<sup>6</sup> which is given by

$$q_m(t) = -n(0) \ln[f(t)/f(0)] \quad (1)$$

where  $f(t)$  is the stress at time  $t$  measured in a sample maintained at fixed extension,  $f(0)$  is the initial stress, and  $n(0)$  is the initial network chain density of rubber sample.

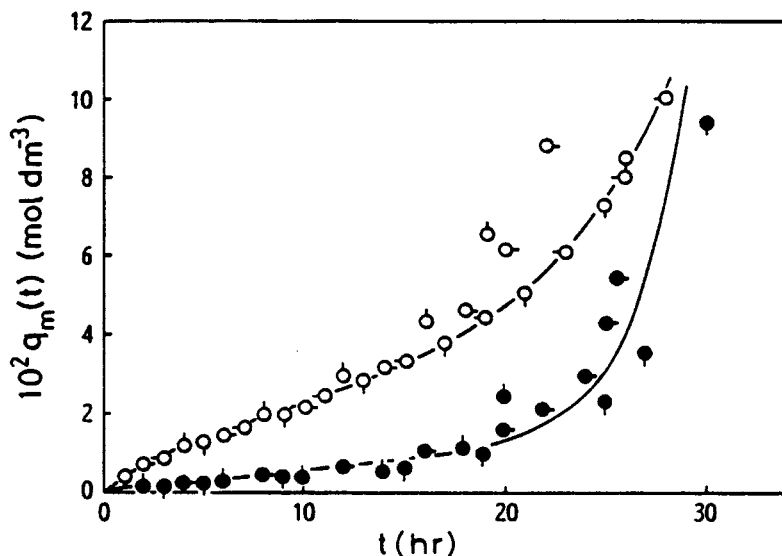


Fig. 4. Number of scission,  $q_m(t)$ , determined by means of chemical stress-relaxation for DC and SC samples: DC-1 (O), DC-2 (○), DC-3 (◊), DC-4 (◌), and SC-1 (●), SC-2 (●), SC-3 (●).

Figure 4 shows the number  $q_m(t)$  of chain scission during degradation for DC and SC samples. The  $q_m(t)$  of both samples is independent of the initial network chain density within experimental errors. According to Tobolsky's theory,<sup>2</sup> a fundamental distinction can be made between those cases where the chain scission occurs specially at the network crosslinks and those cases where the chain scission occurs at random along the main chains: If chain scission were to occur at network junction only, the quantity  $q_m(t)$  would be proportional to the concentration of crosslinks. If, on the other hand, chain scission were to occur at random along the main chains, the quantity  $q_m(t)$  would be essentially independent of the number of crosslinks, and therefore  $q_m(t)$  would be independent of  $n(0)$  in a series of rubbers that have different network chain densities. From the result of Figure 3, thus, one can easily suppose that the chain scission occurs at random along the main chains for DC and SC samples. On the other hand, a significant difference in  $q_m(t)$  between DC and SC samples is shown in Figure 3. As mentioned in the previous paper,<sup>3</sup> the SC sample has an entanglement density less than the DC sample because the network crosslinked in the solution state, and hence the chemical stress-relaxation observed during aging is affected by the different amounts of entanglements in each network. Therefore, this influence of entanglements is directly reflected in the  $q_m(t)$  of both networks.

The quantity  $q_m(t)$  has frequently been evaluated in terms of the change of number-average molecular weight during aging in noncrosslinked rubber,<sup>1,7,8</sup> and the relation is expressed as the following equation:

$$q_m(t) = d \left[ 1/M_n(t) - 1/M_n(0) \right] \quad (2)$$

where  $d$  is the rubber density,  $M_n(0)$  is the initial number-average molecular weight, and  $M_n(t)$  is the number-average molecular weight at time  $t$ .

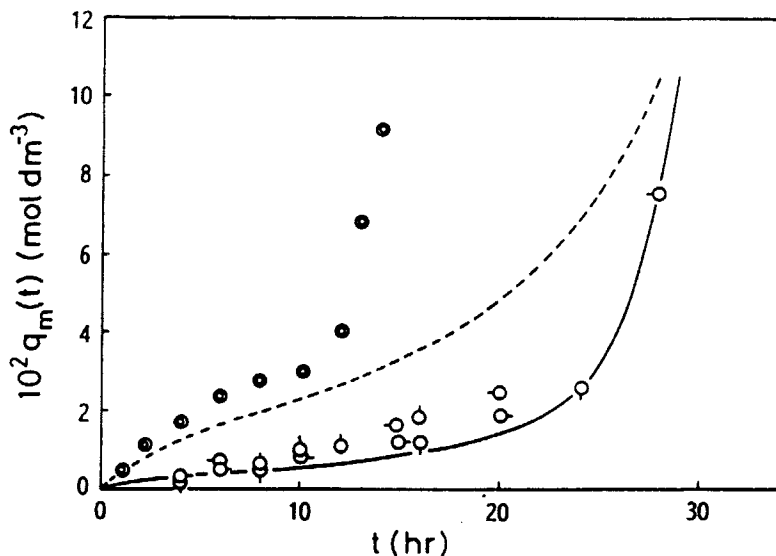


Fig. 5. Number of scission,  $q_m(t)$ , determined by means of degradation of noncrosslinked NR (Q1: ●), chemical stress-relaxation of DC-sample (Q2: ---), and/or SC-sample (Q3: —), and the swelling method of DC-samples (Q4: tagged open circles; symbols are the same as those in Figure 3). Each sample was degraded at 383 K in air for a given interval of aging.

The  $q_m(t)$  evaluated from the several different methods is shown in Figure 5. The  $q_m(t)$  of noncrosslinked rubber calculated from eq. (2) (Q1) is in almost agreement with that of DC samples determined by means of chemical stress-relaxation (Q2) at the short times of aging. However, an enormous deviation of Q1 from Q2 is observed at the later stage of degradation.

There is still a great question that the method Q1 is desirable in comparison with the  $q_m(t)$  of crosslinked rubber. We have, therefore, attempted to evaluate the  $q_m(t)$  by substituting the relative change of network chain density determined by the swelling method,  $n_{sw}(t)/n_{sw}(0)$ , into the relative stress decay,  $f(t)/f(0)$  in eq. (1):

$$q_m(t) = -n(0) \ln[n_{sw}(t)/n_{sw}(0)] \quad (3)$$

where  $n_{sw}(0)$  and  $n_{sw}(t)$  are the network chain density of sample at time zero and  $t$ , respectively. The quantity  $q_m(t)$  of DC samples calculated from eq. (3) (Q4) is in good agreement with that of SC samples determined by means of chemical stress-relaxation (Q3) over the whole range of degradation time. For the method Q4, it is not necessary to consider the influence of the physical relaxation caused by entanglements in the  $q_m(t)$ , as well as in case of Q3.

Degraded networks have very large numbers of dangling chains arising from chain scissions compared with that of undegraded samples. For both kinds of networks, it is very difficult to obtain the information on the number of such dangling chains and their effects on elastic properties in networks. On the other hand, eq. (3) is based on the assumption that dangling chains do not affect the equilibrium swelling state.<sup>9-11</sup> In order for this assumption to be valid, it is necessary to make sure that the relation between the equilibrium elastic modulus on swelling state and the degree of swelling for degraded networks is consistent with that of undegraded networks.

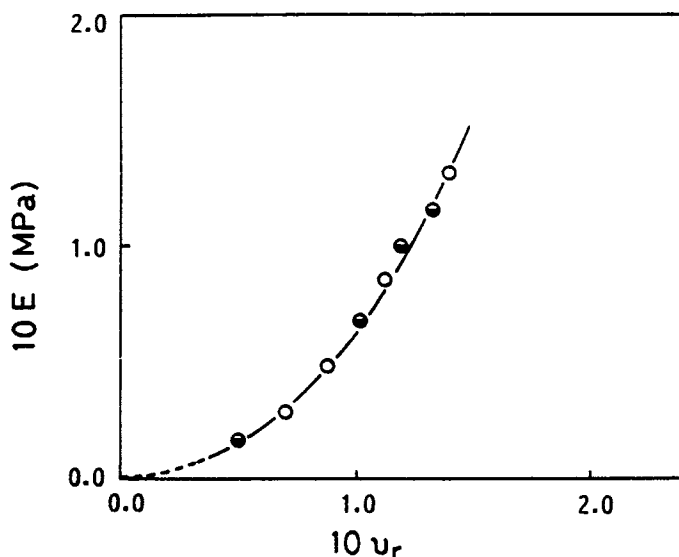


Fig. 6. Dependence of the equilibrium modulus  $E$  on the degree of swelling  $\nu_r$  for DC-samples:  $\circ$ ; undegraded sample,  $\ominus$ ; sample degraded at 383 K in air. The equilibrium modulus  $E$  was measured in the swollen state.

The plots of equilibrium elastic modulus  $E$ , calculated from the results of stress-strain behavior of swollen samples, vs. the degree of swelling,  $\nu_r$ , for degraded and undegraded DC samples are shown in Figure 6. The result of degraded sample is quite consistent with that of undegraded sample. Thus, it is evident that eq. (3) can be applied to evaluate the quantity  $q_m(t)$ .

The measurement of sol fraction was also employed for the investigation of the chain scission mechanism of rubber vulcanizates by Horikx.<sup>12</sup> He applied Charlesby's theory<sup>13</sup> of gelation to the oxidative degradation of network chains. According to the Horikx's theory, the relation between the relative network chain density and sol fraction at an arbitrary stage of aging was derived as follows for the case where the chain scission occurs at random along the main chain:

$$\nu_e(t)/\nu_e(0) = [1 - s(t)^{1/2}]^2 / [1 - s(0)^{1/2}]^2 \quad (4)$$

where  $\nu_e(0)$  and  $\nu_e(t)$  are the network chain density at time zero and  $t$ , and  $s(0)$  and  $s(t)$  are the sol fractions of sample at time zero and  $t$ , respectively. Comparison of the relative change of network chain density, that is, a degree of degradation by measuring the degree of swelling and sol fraction with that by chemical stress relaxation behavior for the samples DC-1 and SC-2 degraded at 383 K in air, is shown in Figure 7(a). The value of  $\log[n_{sw}(t)/n_{sw}(0)]$  is in good agreement with that of  $\log[\nu_e(t)/\nu_e(0)]$  for the samples DC-1 and SC-2. Furthermore, both values are consistent with that of  $\log[f(t)/f(0)]$  for the sample SC-2 having almost the same network chain density of the sample DC-1. For the samples DC-3 and SC-3, the same results were obtained as shown in Figure 7(b). From these results, it has become apparent that the thermooxidation degradation of both samples have progressed similarly, and

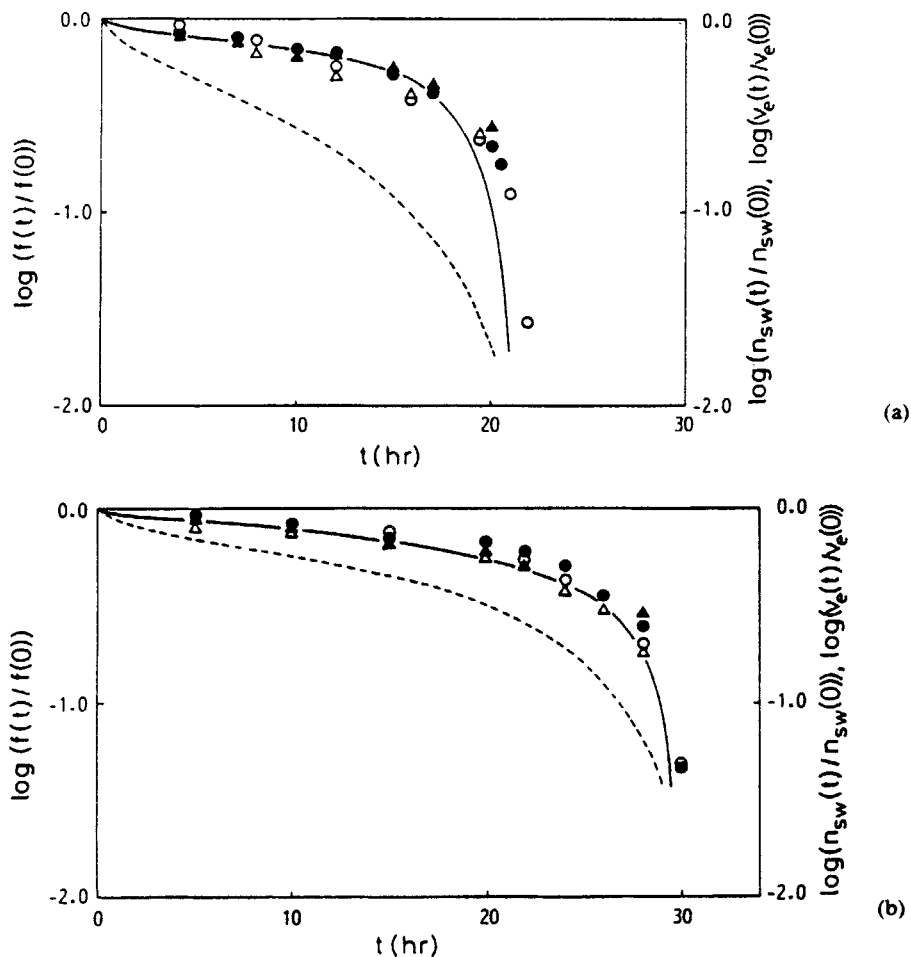


Fig. 7. (a) Comparison of the degree of degradation with the chemical stress-relaxation curves for sample DC-1 (---) and SC-2 (—). The degree of degradation was determined by measuring the degree of equilibrium swelling (open and filled triangles) and sol fractions (open and filled circles). The experimental data for DC-samples were represented as open circles and triangles, and for SC-samples were filled circles and triangles.

Fig. 7. (b) Comparison of the degree of degradation with the chemical stress-relaxation curves for sample DC-3 and SC-3. Symbols are the same as those in Figure 7(a).

that the chemical stress-relaxation for SC samples corresponds well to the scission of network chains during degradation. In Figures 7(a) and (b), the degree of physical relaxation, which is represented as the difference between the relative stress decay and the relative degree of degradation for DC samples, decreases with increasing the initial network chain density. As mentioned in the previously study,<sup>3</sup> these differences are due to the influence of the physical relaxation caused by disentanglement of trapped entanglements during aging.

From the above experimental data, it is easily assumed that the physical relaxation is closely related to the portion of trapped entanglements in network and the initial network chain density. In order to investigate these relations in more detail, the degree of physical relaxation on chemical stress-relaxation was determined as described below.



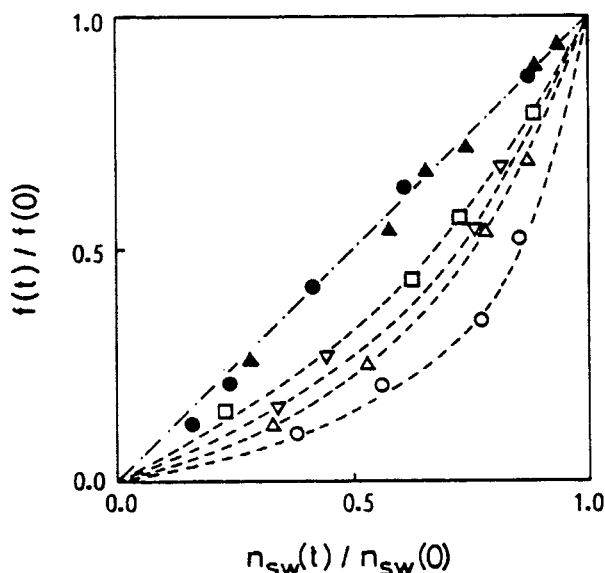


Fig. 8. Relation between the relative stress decay and the relative change of network chain density for SC and DC samples at 383 K in air: DC-1 (O), DC-2 ( $\Delta$ ), DC-3 ( $\nabla$ ), DC-4 ( $\square$ ), and SC-1 ( $\bullet$ ), SC-2 ( $\blacktriangle$ ). The network chain density was determined by using the swelling method.

The plots of  $f(t)/f(0)$  and  $n_{sw}(t)/n_{sw}(0)$  for DC and SC samples are shown in Figure 8. For SC samples, values of  $f(t)/f(0)$  are in good agreement with those of  $n_{sw}(t)/n_{sw}(0)$  and are independent of the initial network chain density of samples. Thus, the relationship can be expressed as follows:

$$f(t)/f(0) = n_{sw}(t)/n_{sw}(0) \quad (5)$$

For DC samples, on the contrary, values of  $f(t)/f(0)$  do not agree with those of  $n_{sw}(t)/n_{sw}(0)$  and are greatly dependent on  $n_{sw}(0)$ .

The reciprocal plots of  $f(t)/f(0)$  vs.  $n_{sw}(t)/n_{sw}(0)$  give linear relations for DC samples as shown in Figure 9, and hence the following equation can be easily derived:

$$f(t)/f(0) = \{A[n_{sw}(0)/n_{sw}(t) - 1] + 1\}^{-1} (A \geq 1) \quad (6)$$

where  $A$  (slope) is a constant representing the degree of physical relaxation in chemical stress-relaxation. The dependence of values of  $A$  for temperature and the initial network chain density is shown in Figure 10. The value of  $A$  decreases linearly with increasing  $n_{sw}(0)$  except for lower degrees of crosslinking, where its value increases abruptly. On the other hand, the value of  $A$  hardly depends on temperature. This can be interpreted in terms of the amounts of trapped entanglements in networks. At the lower degrees of crosslinking, there is a lot of portion of trapped entanglements in networks compared with that of the chemical crosslinks. As the degree of crosslinking increases, on the contrary, the portion of chemical crosslinks is predominant in networks so that the influence of the physical relaxation diminishes. This result is in qualitative agreement with a previous study of the contribution of trapped entanglements to the total concentration of effective network chains.<sup>14</sup>

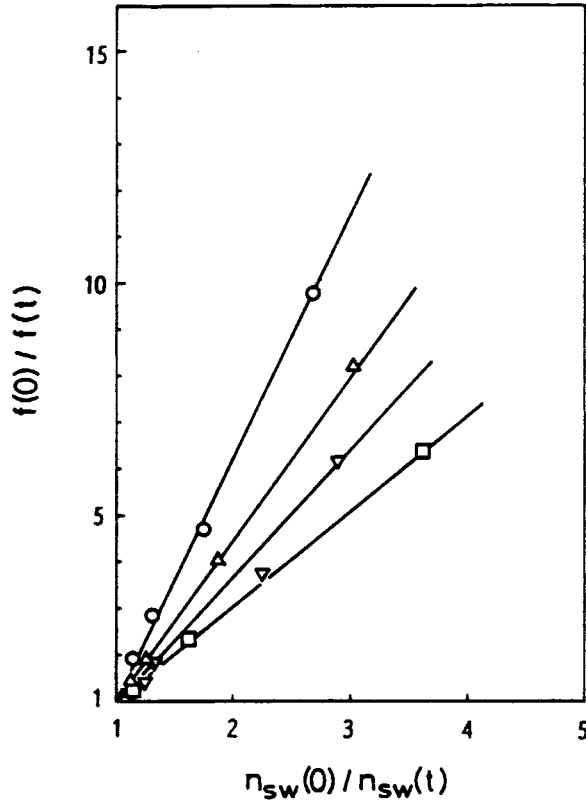


Fig. 9. Plots of the reciprocal values of the relative stress decay vs. the reciprocal values of the relative changes of the network chain density for DC-samples degraded at 383 K in air. Symbols are the same as those in Figure 8.

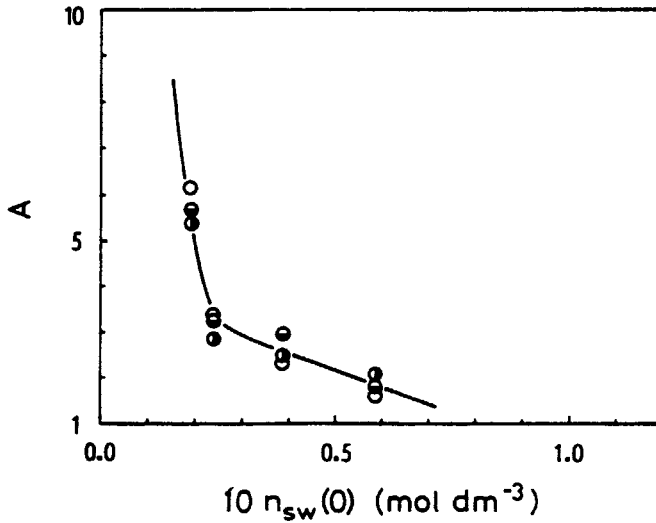


Fig. 10. Dependence of  $A$  on the initial network chain density  $n_{sw}(0)$  for DC-sample degraded at various temperatures in air: 373 K ( $\circ$ ), 383 K ( $\ominus$ ), 393 K ( $\odot$ ). " $A$ " represents the degree of a physical relaxation in chemical stress-relaxation.

## CONCLUSIONS

The number  $q_m(t)$  of chain scission estimated by the swelling method is in good agreement with that of determined by a chemical stress-relaxation technique for SC samples. At the present stage, it is reasonable to consider that this alternative method is the most effective approach for the following reasons:

(1) There is little or no influence of physical relaxation caused by entanglements in the equilibrium swelling.

(2) The effect of dangling chains arising from scission on swelling equilibrium is negligible.

The degree of degradation determined by the equilibrium swelling and sol fraction method was compared with the results of a chemical stress-relaxation for DC and SC samples. From these results, it has become apparent that the chemical stress-relaxation for SC samples corresponds well to the scission of network chains during aging, whereas, for DC samples, the influence of physical relaxation should be taken into consideration. Consequently, a new relationship between the relative stress decay and the relative change of network chain density for DC samples was experimentally proposed.

## References

1. A. V. Tobolsky, *Properties and Structure of Polymer*, Wiley, New York, 1960.
2. A. V. Tobolsky, *J. Appl. Phys.*, **27**, 673 (1956).
3. K. D. Suh, H. Oikawa, and K. Murakami, *Rubber. Chem. Technol.*, **59**, 541 (1986).
4. P. J. Flory, *J. Chem. Phys.*, **18**, 108 (1950).
5. S. Tamura and K. Murakami, *J. Appl. Polym. Sci.*, **16**, 1149 (1972).
6. A. V. Tobolsky, D. J. Metz, and R. B. Mesrobian, *J. Am. Chem. Soc.*, **72**, 1142 (1950).
7. S. Tamura and K. Murakami, *J. Appl. Polym. Sci.*, **16**, 1149 (1972).
8. H. Oikawa and K. Murakami, *J. Polym. Sci., Polym. Lett. Ed.*, **19**, 283 (1981).
9. A. L. Andrady, M. A. Llorente, M. A. Sharaf, R. R. Rahalkar, and J. E. Mark, *J. Appl. Polym. Sci.*, **28**, 1829 (1983).
10. J. Bastide, C. Picot, and S. Candau, *J. Polym. Sci., Polym. Phys. Ed.*, **17**, 1441 (1979).
11. J. Bastide, C. Picot, and S. Candau, *J. Macromol. Sci., Phys.*, **13**, 13 (1981).
12. M. M. Horikx, *J. Polym. Sci.*, **19**, 445 (1956).
13. A. Charlesby, *J. Polym. Sci.*, **11**, 513 (1953).
14. N. R. Langley and K. E. Polmanteer, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 1023 (1974).

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