

Rubber Elasticity on Chemical Relaxation

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Synopsis

The applicability of the formula $f(t) = n(t)RT(\alpha - \alpha^{-2})$ suggested by Tobolsky as the basis of chemorheology has been discussed. In this expression, $f(t)$ is the stress after t hours, $n(t)$ is the crosslinking density (mole/cc) after t hours, R is the gas constant, T is the absolute temperature, and α is the extension ratio. We have discussed the applicability of this formula, in another words, whether the degraded stress $f(t)$ calculated from this formula would be consistent with the initial stress $f_i(0)$ of other polymer if the degraded crosslinking density values $n(t)$ are equal to those of $n_i(0)$, the initial density values $n(0)$ of other polymer. Natural rubber vulcanizates and SBR vulcanizates were used as samples in these experiments. Assuming $n(t) = \sigma(t)n(0)$, $\alpha(t) = 1$, the applicability of the above formula was recognized from our experimental results.

INTRODUCTION

It is well known that eq. (1), the expression for the tensile stress to deform a rubber to an extension ratio α , was derived in somewhat different ways by Kuhn,¹ Wall,² James and Guth,³ Treloar,⁴ and Flory and Rehner⁵:

$$f(0) = n(0)RT(\alpha - \alpha^{-2}) \quad (1)$$

where $f(0)$, $n(0)$, R , and T are, respectively, the initial tensile stress, the initial crosslinking density, the gas constant, and absolute temperature.

From a chemorheological point of view, however, Tobolsky and others considered that the initial crosslinking density $n(0)$ would change to $n(t)$ after the degradation of crosslinked polymer and then eq. (2) would be applicable:

$$f(t) = n(t)RT(\alpha - \alpha^{-2}). \quad (2)$$

Equation (2) is regarded as the basis of other derived equations in chemorheological studies.

To make matters clearer, the ideal network of crosslinked polymer expressed by eq. (1) may be shown in Figure 1 (a) and the network structure of the cleft degradation expressed by eq. (2) is indicated by Figure 1(b).

In previous papers,⁶ it was shown that when the crosslinking density $n(0)$ (named as $n_s(0)$ hereafter since it is obtained by a swelling method) obtained by using the swelling formula (3) induced by Flory and Rehner⁷ is

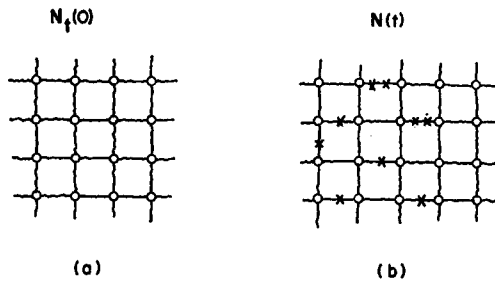


Fig. 1. Structure of ideal network $n_i(0)$ and degraded network $n(t)$.

compared with $n(0)$ (named as $n_M(0)$ hereafter since it is obtained by a mechanical method) obtained by eq. (1), $n_M(0)$ is always larger than $n_S(0)$:

$$n_S(0) = -\frac{\ln(1 - v_2) + v_2 + \mu v_2^2}{V(v_2^{1/2} - v_2/2)} \quad (3)$$

where v_2 , V , and μ are the volume fraction of rubber, the molar volume of solvent, and the coefficient of interaction between rubber and solvent, respectively.

Such being the case, we performed the following experiments to investigate the appropriateness of eq. (2), the degree of consistence between the values of $n_M(0)$ and $n_S(0)$, and its reasons.

EXPERIMENTAL

To distinguish between the ideal and degraded crosslinking densities after t hours, let $n_i(0)$ represent the former and $n(t)$ the latter. (Here, $n_i(0)$ means the ideal crosslink density of one sample which is equal to $n(t)$, the degraded crosslinking density of another sample.)

The values of $n_i(0)$ and $n(t)$ become $n_{M,i}(0)$ and $n_M(t)$, respectively, when measured by the mechanical method. It is clear that to find out whether the value of $n_{M,i}(0)$ will be equal to that of $n_M(t)$ when $n_i(0) = n(t)$, the validity of eq. (2) must be investigated.

For experiments, we used three kinds of different crosslinking density of SBR and natural rubber (NR). In the case of SBR which we cured with dicumyl peroxide, the crosslinking densities were $n_{M,i}(0) = 3.59 \times 10^{-4}$ mole/cc, 2.22×10^{-4} mole/cc, and 1.25×10^{-4} mole/cc. For these SBR samples, using chemical stress relaxation at 100°C in air by continuous and intermittent methods and plotting the results, $\log\{f(t)/f(0)\}$ (logarithmic relative stress) versus time was obtained (Fig. 2).

Results and Discussion

Now, let us compare both the values of $n_M(t)$, which is the degraded crosslinking density of cured SBR sample by chemical relaxation, and of $n_{M,i}(0)$, which is the ideal crosslinking density without degradation, with that of

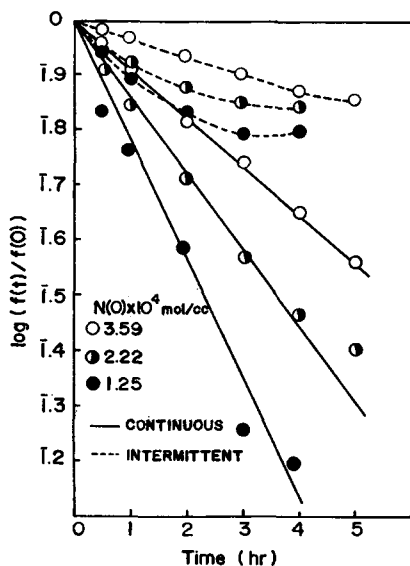


Fig. 2. Stress relaxation curves (100°C , $\alpha = 1.3$) of SBR vulcanizates.

$n_s(t)$, which is the real crosslinking density measured by swelling methods for the respective sample, as shown in Figure 3. (In Figure 3, the symbols \odot , \ominus , \bullet represent the three samples having ideal crosslinking densities.) Since the samples of $n_M(t)$ and $n_{M,t}(0)$ correspond to their respective $n_s(t)$ values and are considered to be ideal, it must be that $n_M(t) = n_{M,t}(0) = n_s(t)$. That is, it must entirely overlap the slope of unity of the straight line drawn from the zero point of the lower right corner of the graph in Figure 3. But, as can be seen in Figure 3 the slope of this line is less than unity. The three points \odot , \ominus , and \bullet on the line (solid line) correspond to the points of $n_{M,t}(0)$ equal to 3.59×10^{-4} , 2.22×10^{-4} , and 1.25×10^{-4} mole/cc, respectively. When these three samples are degraded by oxidation at 100°C in air, the degraded crosslinking density $n_M(t)$ obtained from the results of Figure 2 at each time t will overlap the broken line having almost the same slope shown by three broken lines in graph where the resultant values from the \odot , \ominus , and \bullet signs will be expressed by points \circ , \circ , and \bullet , respectively.

Though these crosslinking densities $n_M(t)$ of the degraded samples were the values obtained by eq. (2) and showed the residual effective crosslinking densities after degradation, the $n_s(t)$ values measured by swelling methods based on eq. (3) were the sum of the residual crosslinkings and those newly produced by that time.

The points obtained by plotting values of $n_s(t)$ and $n_M(t)$ of each sample measured by intermittent means become points \square , \square , and \square , respectively. And, as expected, these points, will overlap all the lines (solid line) drawn from the zero origin is as obviously shown by the figure. That is, points \square , \square , and \square , indicating true $n_M(t)$, and the three points \odot , \ominus , and \bullet ,

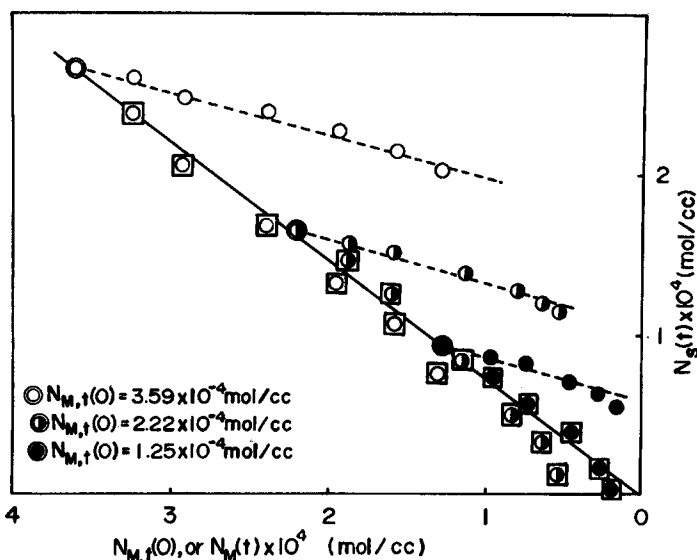


Fig. 3. Relation between $n_{M,t}(0)$ or $n_M(t)$ and $n_S(t)$ for SBR vulcanizates.

indicating $n_{M,t}(0)$ on the solid line, are together on the same line. Needless to say, the interval between two corresponding points \circ and \square of the two lines means newly produced crosslinking, and so on, because the points on the broken like were measured by continuous means.

It is obvious that this was the result, which would explain the validity of eq. (2) of our previous expectancy. From Figure 3, it was seen that $n_M(t)$ is equal to $n_{M,t}(0)$.

The result for natural rubbers using the same peroxide vulcanizates is shown in Figure 4. The figure was obtained by plotting $\log\{f(t)/f(0)\}$ versus t for the three natural rubber samples having crosslinking densities of $n(0) = 1.45 \times 10^{-4}$, 1.10×10^{-4} , and 1.02×10^{-4} mole/cc, using continuous together with intermittent stress relaxation methods at 120°C in air.

Figure 5 shows the results of comparison of the three samples of \circ , \bullet , and \bullet which are $n_M(t)$ the degraded crosslinking densities at t hours, and that of \circ , \bullet , and \bullet which are $n_{M,t}(0)$, the undegraded crosslinking densities against $n_S(t)$ which are the crosslinking densities by the swelling method for the equivalent samples. As previously mentioned, points \circ , \bullet , and \bullet , chemically relaxed from \circ , \bullet , and \bullet , overlap on the respective broken line.

This was obviously due to the effect of newly produced crosslinking when measuring stress by the continuous method. The corrected results were points \square , \square , and \square . Also, in this case, as shown in the figure, three corrected points shown by $n_M(t)$ kept in line with points \circ , \bullet , and \bullet , denoted by the ideal network densities $n_{M,t}(0)$.

From the above mentioned, as in the case of SBR, $n_M(t) = n_{M,t}(0)$ exists in the case for natural rubbers, too.

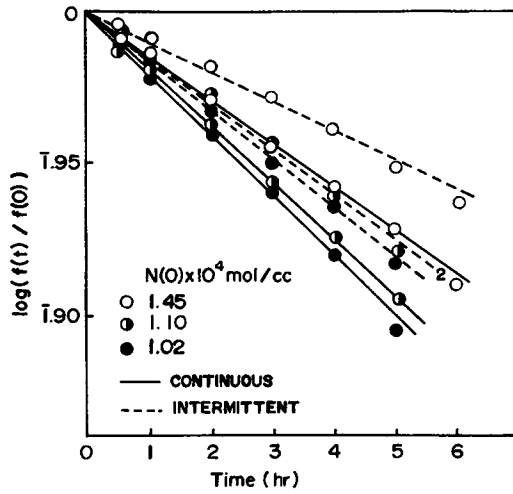


Fig. 4. Stress relaxation curves (120°C, $\alpha = 1.2$) of NR vulcanizates.

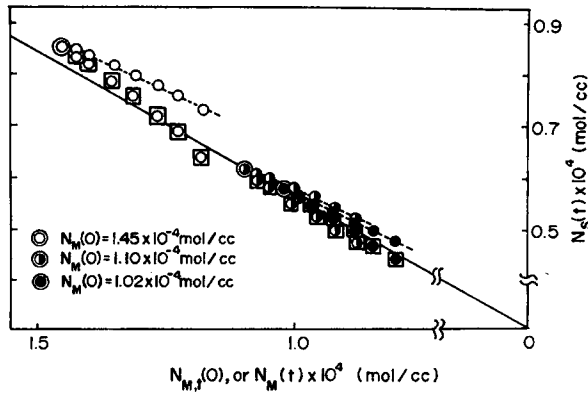


Fig. 5. Relation between $n_{M,i}(O)$ or $n_M(t)$ and $n_S(t)$ for NR vulcanizates.

The results obtained above can be restated using a quantitative expression. First, assume $n_M(t) \neq n_{M,i}(0)$ and consider the general equation

$$n_M(t) = \sigma(t) \cdot n_{M,i}(0). \tag{4}$$

By the way, when the number of moles of cleavages per cc is denoted by $q(t)$, the next equation was found by Tobolsky^{8,9}

$$q(t) = -n(0) \ln[n(t)/n(0)]. \tag{5}$$

In discussing the validity of eq. (2), in eq. (6), which correspond to eq. (5), the values of $q(t)$ are considered as apparent values (they are denoted $q_{app}(t)$):

$$q_{app}(t) = -n_{M,0}(0) \ln[n_M(t)/n_{M,0}(0)]. \tag{6}$$

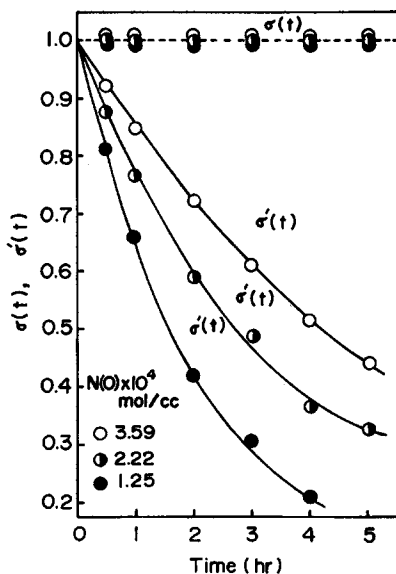


Fig. 6. Relation between $\sigma(t)$, $\sigma'(t)$, and time for SBR vulcanizates.

On the other hand, the intrinsic values $q_{\text{real}}(t)$ are expressed by the following two equations from the above reasons:

$$q_{\text{real}}(t) = -n_{M,0}(0) \ln [n_{M,t}(0)/n_{M,0}(0)] \quad (7)$$

Equation (7) is based on the following swelling method:

$$q'_{\text{real}}(t) = -n_S(0) \ln [n_S(t)/n_S(0)]. \quad (8)$$

From eqs. (4), (6), and (7), eq. (9) can be calculated:

$$\begin{aligned} q_{\text{app}}(t) &= -n_{M,0}(0) \ln \sigma(t) - n_{M,0}(0) \ln \{n_{M,t}(0)/n_{M,0}(0)\} \\ &= -n_{M,0}(0) \ln \sigma(t) + q_{\text{real}}(t). \end{aligned} \quad (9)$$

From eq. (9),

$$\sigma(t) = \exp \left\{ \frac{q_{\text{real}}(t) - q_{\text{app}}(t)}{n_{M,0}(0)} \right\} \quad (10)$$

In eq. (10), using $q'_{\text{real}}(t)$ of eq. (8) instead of $q_{\text{real}}(t)$, we obtain eq. (11):

$$\sigma'(t) = \exp \left\{ \frac{q'_{\text{real}}(t) - q_{\text{app}}(t)}{n_{M,0}(0)} \right\}. \quad (11)$$

In studying the relation between time and $\sigma(t)$ values on the oxidative degradation process in air at 100°C, for the previous three SBR samples, Figure 6 can be obtained. In Figure 6, the relation between $\sigma(t)$ and t would show the straight line of $\sigma(t) = 1$ independent of the elapsed time through the samples. So long as the relation of $n_M(t) = n_{M,t}(0)$ is substantiated by the previous experiments, it is a reasonable result. But the relation of $\sigma'(t)$ and t , as seen in the figure, shows a descending curve along elapsed t . This is owing to values of $n_S(t)$ and not of $n_M(t)$ for $q'_{\text{real}}(t)$, and, as previously mentioned, $n_M(t) > n_S(t)$.

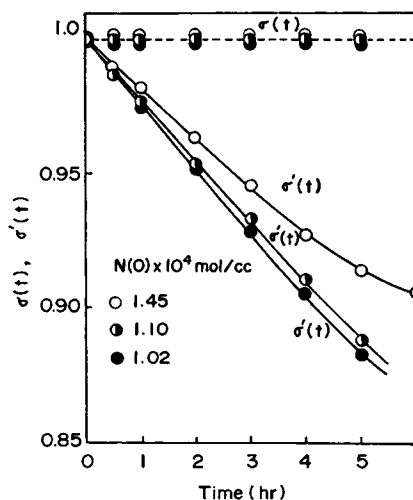


Fig. 7. Relation between $\sigma(t)$, $\sigma'(t)$, and time for natural rubber vulcanizates.

It is considered that the contribution of entanglement and strong semi-primary bonds, which will be extinguished to some extent by $n_s(t)$ of the swelling method and by $n_M(t)$ obtained by mechanical measurement, still exist.

In the case of cured natural rubbers, with the same step, plotting the relation $\sigma(t)$ and t , Figure 7 can be obtained. As in Figure 6, $\sigma(t) = 1$ independent upon t ; $\sigma(t)$ shows a parallel line with the abscissa and $\sigma'(t)$ shows a descending curve, for reasons that can be considered quite the same as with cured SBR.

Some problems remain unsolved for the experimental results obtained regarding eq. (11) and the data showing the relation between $\sigma'(t)$ and time in Figures 6 and 7, though a few papers have appeared recently.^{10,11}

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Received February 17, 1972

Revised April 6, 1972