# Stress Relaxation in Rubbers Containing Reinforced Fillers*

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## Synopsis

Stress relaxation in rubber stocks containing various fillers was measured at room temperature, and an empirical equation found for relating decrease in tension, $f_t$, over a period of time from 0.1 sec. to 6 months, namely:

$$f_t = f_{1.0}t^{-n}$$

where $f_{1.0}$ is force after 1 min. of relaxation, $n$ is the relaxation rate of material (by definition) and $t$ is time in minutes. Raw rubbers were examined under compression, and cured rubbers were tested under tension. In both cured and raw butadiene rubbers, stress relaxation was found to be a viscous-controlled process. In raw rubbers, reinforcing carbon blacks decrease the rate of relaxation, while in cured rubbers the effect of carbon black is very small. However, in swollen (to $V_R = 0.25$), cured rubbers, the rate of relaxation increases with increasing carbon black loading, indicating a slippage and/or breakage of some carbon black–polymer attachments.

## INTRODUCTION

When viscoelastic materials are deformed to a given degree, the stresses set up gradually decrease with time. This is the phenomenon of stress relaxation; it can constitute a major disadvantage of rubber springs in engineering applications. Stress relaxation may be related to other time-dependent phenomena like creep and hysteresis,[1] since all of these effects depend on realignment of molecular network under stress. The speed of orientation of molecular chains in the direction of applied force is obviously controlled by frictional resistance to flow between the chains and length of these chains. In a crosslinked polymer network it further depends on breakage or slippage of linkages constituting such a network.

The following kinds of linkages should be considered: (1) simple polymer–polymer covalent crosslinks; (2) effective crosslinks due to polymer entanglements; (3) covalent filler–polymer linkages; (4) effective filler–polymer linkages resulting from polar and van der Waals forces.

Under our experimental conditions, stress relaxation is not influenced by factors (1) and (3) above, since chemical scission of chains occurs only to a negligible extent within the temperature range employed. It may further

be assumed that the number of effective crosslinks due to polymer entanglements, factor (2) above, remains the same in a filled or an unfilled elastomer crosslinked to the same degree. It was hoped, therefore, to learn more about factor (4) i.e., effective filler–polymer linkages resulting from polar forces by use of stress relaxation techniques and hence gain a further understanding of the reinforcing action of fillers.

## GENERAL STRESS–TIME RELATIONSHIP

In one of the earliest studies of viscoelastic deformations, Nutting[2] postulated that an empirical equation of the form

$$\sigma = \epsilon^{\beta} \psi t^{-n} \tag{1}$$

(where $\epsilon$ = strain, $\sigma$ = stress, $t$ = time, and $\psi$, $\beta$, and $n$ are material constants) is applicable to a large number of polymeric systems. The Nutting equation was subsequently applied by Buchdahl and Nielsen[3] to other polymers such as plasticized poly(vinyl chloride), styrene–butadiene rubber, and polystyrene. They have shown that constant $n$ in eq. (1) is closely related to the damping coefficient, $\delta$, as obtained from dynamic-mechanical measurements, and the temperature dependence of $n$ and $\delta$ are about the same.

Stress relaxation in pure SBR rubbers was further examined by Landel and Stedny,[4] who proposed that Ferry's method of reduced variables may be extended to large deformations by defining a strain-reduced modulus, $E^{*}(t) = E(t) f(\alpha)$, where $f(\alpha)$ is obtained from the Martin-Roth-Stiehler equation.[5] These authors also found a linear relationship between log $E(t)$ and log $(t)$ over a range of temperatures from 25 to 55°C. Tobolsky and Takahashi[6] observed a similar relationship for materials in the rubbery state, but at very short times (or very low temperatures) the modulus increased more rapidly with decrease in time than eq. (1) would predict.

Nichols, Kienle, and Clifton[7] studied stress relaxation in pure elastomers under compression, and postulated that the over-all relaxation may be broken into two components represented by $(f_0 - f_{10})$ and $(f_{10})$, where $(f_t)$ is force after $t$ minutes. Their treatment of data, however, was found not to be applicable to carbon black-filled stocks.

In the present work we found that all rubbers at room temperature obeyed an empirical equation of the form

$$f_t = f_{1.0} t^{-n} \tag{2}$$

where $f_t$ is force at time $t$ (in minutes), $f_{1.0}$ is force after 1 min. of relaxation, and $n$ is the relaxation rate of the material (by definition). This equation is in general agreement with findings of most previous workers.[2,3,4,6] It can easily be shown that the constant $n$ in eq. (2) is equal to $(df/f)/\log (t)$, i.e., percentage decrease in force per unit log cycle of time, and corresponds to the definition of the rate of stress relaxation utilized by Gent.[1]

## EXPERIMENTAL

### Raw Rubbers

Test samples were prepared by milling filler and rubber on a two-roll mill (rolls maintained at 30°C.), and subsequently molding cylinders, 0.75 in. diameter and 0.50 in. high, at 145°C. for 30 min. The unvulcanized material was cooled to room temperature, removed from the mold, and relaxed overnight. All compression measurements were performed by using an Instron machine, the crosshead was adjusted to travel at 0.5 cm./min. during the compression cycle and to stop at 30% compression (as calculated from the original thickness of test specimens). The tests were normally run at 24°C.

Bound rubber measurements were performed on molded specimens by using a standard procedure.[8] Intrinsic viscosity measurements were made at 30°C. on solutions of unbound polymer in benzene by using an Ubbelohde dilution viscometer.

### Vulcanized Rubbers

Ring samples having an outside diameter of 4.19 cm. and an inside diameter of 3.56 cm. were punched out of regular tensile sheets approximately 0.25 cm. thick. Each sample was placed between two freely rotating $1/4$-in. diameter steel rods and extended to the desired length on the Instron
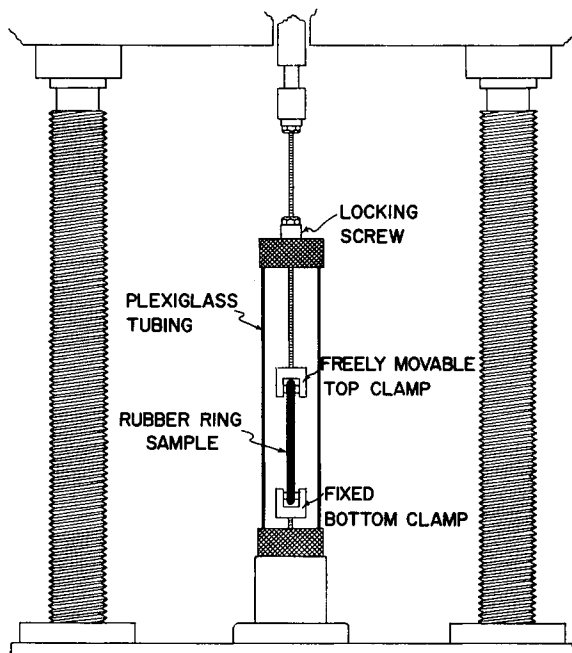


Fig. 1. Diagram of the relaxation cell.

machine at a crosshead speed of 10 cm./min.   The top, movable, clamp could then be fixed to hold the sample at that elongation by use of a simple screw arrangement (Fig. 1), and the whole relaxation cell could be removed from the Instron machine without disturbing the sample.   The residual stress in the sample could then be measured at any desired time interval by simply inserting the relaxation cell back into the Instron machine and moving the crosshead downward (at 0.05 cm./min.) until the top clamp became fully released from the locking screw.   It has been found that a complete release was obtained within 0.02 cm. of crosshead travel, i.e., after imposing a negligibly small additional extension on the tested specimen.

Unless otherwise stated, all relaxation experiments were done at 75% elongation at room temperature.   All samples were cured for 60 min. at 155°C. and contained 0.4 phr Di-cup R (95% pure dicumyl peroxide manufactured by Hercules Powder Co.).

All swollen samples were prepared by placing cut ring samples in contact with a weighed amount of solvent (decahydronaphthalene) in a closed container for a period of 3 days.   At the end of this time the samples were uniformly swollen and ready for testing.

## General

Butadiene rubber (Cis-4, Phillips Petroleum Co.) was selected for this study because it does not degrade as much as some other rubbers (e.g., SBR-1500) and has a relatively sharp molecular weight distribution.[9] Some experiments were also performed on peroxide-cured SBR-1500 styrene–butadiene rubber.   All stocks contained only rubber, filler, peroxide (if any), and Antioxidant 2246 (Cyanamid Co.); no plasticizers, softeners, or oils were included.   All the carbon blacks investigated were commercially available products of Cabot Corporation, except for a series of experimental blacks which were heat-treated at different temperatures.

## RESULTS AND DISCUSSION

### Raw Rubbers

In a preliminary study it was found that the rates of stress relaxation (under compression) could be accurately represented by eq. (2) above.

A plot of log $(f_t)$ versus log $(t)$ gave a straight line over four decades of time (0.1–4000 min.) in SBR and BR compounds.   In view of the above, the experimental procedure was subsequently simplified to recording the residual force at 0.4 $(f_{0.4})$ and 10.0 $(f_{10})$ min. after the crosshead had been stopped.   The logarithmic exponent $n$ could then be readily calculated and was found to be independent of the speed at which samples were compressed.   Although the values of $f_{0.4}$ and $f_{10}$ varied from sample to sample, the value of exponent $n$ was reproducible to within ±2%.   Earlier workers[7] used the values at the peak, $f_0$; however, this is a function of crosshead speed and temperature, since some molecules will relax partially while the sample is being compressed.

In styrene–butadiene rubbers (SBR-1500), the rate of stress relaxation was closely related to the percentage bound rubber for a number of compounds varying in carbon black loading (Table I), while $f_{1.0}$ values were proportional to Mooney viscosity values. Intrinsic viscosity of unbound polymer was found to decrease markedly with increased loading and/or activity of carbon black. Polymer degradation produced an additional variable in SBR compounds, since the rate of relaxation would be expected to increase with a decrease in molecular weight of polymer.

The effect of surface "activity" of fillers was investigated by incorporating into SBR-1500 50 phr of ISAF black (Vulcan 6) heat-treated at various temperatures in the range of 500–2700°C., since it is known that such treatment removed the active groups from the surface of carbon black particles without changing their structure.[10] It may be observed that relaxation rate increased as the surface activity of the black was reduced (i.e., lower bound rubber, Table II), although the Mooney viscosity value remained nearly constant.

TABLE I
Influence of Carbon Black Loading (ISAF Vulcan 6) on Rate of Relaxation of Raw SBR-1500 (under Compression to 70%)

| Carbon black loading, phr | Bound rubber, % | $[\eta]$ (benzene, 30°C.) | Mooney viscosity (MS at 100°C.) | $f_{1.0}$, kg. | $10^2 \times n$ | $\Delta E$, kcal./ mole |
|---|---|---|---|---|---|---|
| 0 | — | 1.80 | 28 | 2.6 | 26 | 18 |
| 5 | — | 1.98 | 33 | 3.1 | 26 | 18 |
| 20 | — | 1.64 | 41 | 4.3 | 24 | — |
| 35 | 24.3 | — | 50 | 5.9 | 24 | 18 |
| 50 | 32.5 | 1.10 | 62 | 9.9 | 21 | 17, 15 |
| 80 | 49.4 | 1.00 | — | 64.0 | 9 | 18 |

TABLE II
Effect of Carbon Black Heat Treatment on Stress Relaxation (under Compression to 70%) of Raw SBR-1500 Compounds

| 50 phr ISAF carbon black; treated at temp., °C. | Bound rubber, % | $[\eta]$ (benzene, 30°C.) | Mooney viscosity (MS at 100°C.) | $f_{1.0}$, kg. | $10^2 \times n$ | $\Delta E$, kcal./ mole |
|---|---|---|---|---|---|---|
| Pure gum | — | 1.80 | 28 | 2.6 | 26 | 18 |
| Control | 33.0 | 1.10 | 59 | 11.4 | 18 | 17, 15 |
| 800 | 30.1 | 1.18 | 61 | 10.1 | 21 | 15 |
| 1200 | 27.7 | 1.39 | 62 | 8.6 | 23 | 15 |
| 1500 | 10.4 | 1.71 | 61 | 7.3 | 24 | — |
| 2700 | 8.5 | 1.52 | 58 | 7.5 | 26 | 16 |

The value of the constant $f_{1.0}$ (force after 1 min.) represents the combined effect of viscous and elastic components, but it is a short-term response. As such, it relates well with other measurements of "viscosity" which usually are performed within relatively short time intervals and, therefore, cannot differentiate between the entanglement-network (elastic) response and long time (viscous) response of the chain. In actual fact, a good relationship between Mooney viscosity and $f_{1.0}$ values for BR and SBR polymers was observed. A large increase in $f_{1.0}$ values with carbon black loading reflects rapidly increasing viscosity of the compounded stock, since at carbon black concentrations above 70–80 phr the viscous flow must include destruction of the bound polymer layer.

In order to learn more about the processes responsible for observed stress relaxation, selected samples were run at various temperatures in the range from −9 to 80°C. and stress relaxation curves were plotted for the first 10 min. after crossheads were stopped. The data so obtained were then transposed to a standard temperature (24°C.) by using Leaderman's superposition principle. Smooth master curves were then drawn and compared with actual experimental points obtained in separate, continuous experiments run for periods up to 3 days. An excellent agreement between calculated and observed curves was obtained, confirming the validity of the superposition principle in the present application. This technique assumes that the effect of temperature on viscoelastic properties is to multiply (or divide) the time scale by a constant factor at each temperature, that is the activation energy does not change. Under such circumstances it is possible to calculate the activation energy for the relaxation process from the shift required on log $(t)$ axis.[11]

A number of such experiments was performed on compounds with and without fillers (Tables I and II). Activation energies for the relaxation process were found to be 16 ± 2 kcal./mole in all instances, i.e., identical within the experimental error. Since activation energy for a viscoelastic process would be expected to be 15–25 kcal./mole at this temperature range, it might be concluded that the observed relaxation process is controlled by the molecular friction as well as by stiffening action of chain entanglements.[11] At the first application of compressive force, the entanglements act like crosslinks, hence the short time response of the material should closely approximate the response of crosslinked polymer network. Such entanglements are, however, highly mobile, allowing the molecular chains to rearrange and flow under applied force.

In an attempt to rationalize the present results, it is suggested that the rubber shell around each filler particle contributes an additional number of entanglements (or effective crosslinks) in the polymer network, thereby increasing the elastic (short time) response. The number of such additional entanglements will obviously depend on the surface activity of the filler, proportional approximately to the bound rubber content when such filler is incorporated into an elastomer. At higher loadings of carbon black, some weak van der Waals linkages between filler particles and poly-

mer molecules may also be broken as a result of applied stress. A fairly good relationship was actually observed between the relaxation rate (constant $n$) and percentage bound rubber in all the BR and SBR compounds investigated here.

## Vulcanized Rubbers

A typical relaxation curve of Cis-4 pure gum is shown in Figure 2. A straight-line log–log relationship is observed over a period of time from 0.2 min. to 6 months (i.e., five decades of time).
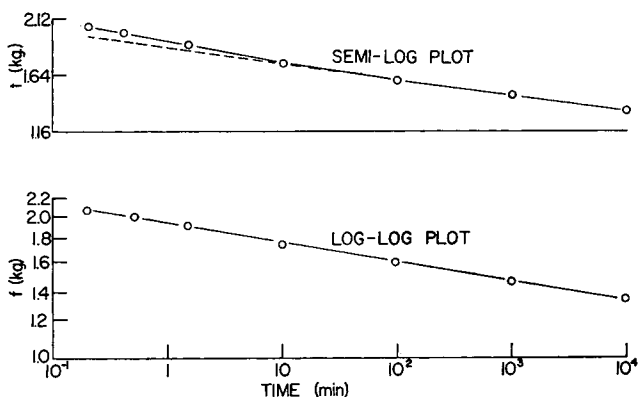


Fig. 2. Stress relaxation at 100% elongation for Cis-4 pure gum.

The rate of stress relaxation in pure gum stocks was found to decrease (Table III) significantly, and the value of $f_{1.0}$ was found to increase with increased crosslink density (achieved by increasing concentration of dicumyl peroxide at constant conditions of cure: 60 min. at 155°C.). A similar trend of results was observed in rubbers swollen to constant $V_R = 0.25$.

These results may easily be explained in terms of kinetic theory of rubber elasticity which predicts that equilibrium modulus is proportional to the number of "active chains" or crosslinks. The value of $f_{1.0}$ is closely related to the equilibrium modulus. Rate of relaxation in raw rubbers

TABLE III
Stress Relaxation of Pure Gum (Cis-4) Compounds at 75% Elongation

| Samples[a] | Nonswollen | | Swollen to $V_R = 0.25$ | |
|---|---|---|---|---|
| | $f_{1.0}$, kg./cm.$^2$ | $10^2 \times n$ | $f_{1.0}$, kg./cm.$^2$ | $10^2 \times n$ |
| 0.2 phr Di-cup R | 2.6 | 62 | 0.6 | 1.7 |
| 0.4 phr Di-cup R | 4.5 | 29 | 3.4 | 0.7 |
| 1.0 phr Di-cup R | 7.4 | 11 | — | — |

[a] Cured for 60 min. at 155°C.

has already been shown to be related to: the frictional resistance of molecules to flow, and the number of mobile entanglements. The number of mobile entanglements[12] and the final extensibility of molecular chains are, however, decreased appreciably as crosslinks are introduced, and this is responsible for the decrease in the relaxation rate. In Table IV it is shown that the rate of relaxation in filled and pure gum stocks is not significantly influenced by the moderate degree (75–250%) of sample elongation in BR and SBR rubbers, hence it does not depend on the retractive force of molecular chains. This is substantially in agreement with findings of Gent.[13]

TABLE IV

Relaxation Rates of Nonswollen Samples at 75% and 250% Elongation[a]

| ISAF carbon black 50 phr, treated at temp., °C. | At 75% elongation | | At 250% elongation | |
|---|---|---|---|---|
| | $f_{1.0}$, kg./cm.$^2$ | $10^2 \times n_{75}$ | $f_{1.0}$, kg./cm.$^2$ | $10^2 \times n_{250}$ |
| In Cis-4 | | | | |
| Pure gum | 4.5 | 2.9 | 7.1 | 1.9 |
| Control | 8.1 | 4.0 | 21.2 | 3.6 |
| 500 | 8.7 | 3.6 | 23.2 | 3.4 |
| 800 | 8.2 | 3.9 | 21.4 | 3.8 |
| 1100 | 8.3 | 3.3 | 20.5 | 3.1 |
| 1500 | 7.1 | 3.3 | 10.6 | 3.0 |
| 2700 | 5.3 | 3.8 | 11.2 | 3.6 |
| In SBR-1500 | | | | |
| Pure gum | 2.4 | 8.6 | 4.3 | 6.7 |
| Control | 5.9 | | 16.2 | 5.9 |
| 2700 | 3.7 | 9.2 | 9.4 | 7.0 |

[a] Samples containing 0.4 phr Di-cup R, cured for 60 min. at 155°C.

The effect of carbon black loading on the relaxation rates of SBR and Cis-4 compounds is shown in Table V. In unswollen Cis-4 compounds there is no large change in the constant $n$ with carbon black loading, although in swollen samples (to $V_R = 0.25$) a very large increase in the rate of relaxation occurs as the carbon black loading is increased. Using the technique described earlier, energies of activation for cured Cis-4 rubbers were calculated at a temperature range from $-20$ to $40°C$. For pure gum and filled (50 phr ISAF carbon black) stocks the values were 14.5 and 15.5 kcal./mole, respectively, i.e., identical within experimental error and the same as found for raw rubbers. This clearly indicates that in the unswollen sample the relaxation rate due to carbon black–polymer interaction is masked by viscous flow of polymer. In unswollen SBR stocks the rate of relaxation increases appreciably with carbon black loading; however, this is due to breakdown in the original molecular weight of the polymer matrix and hence a larger correction due to "free ends"[14] present in the polymer network which leads to higher rates of relaxation.

TABLE V
Effect of Carbon Black (Vulcan 6H) Loading on Rates of Relaxation at 75% Elongation[a]

| Carbon black loading, phr | Nonswollen | | Swollen to $V_R = 0.25$ | |
|---|---|---|---|---|
| | $f_{1.0}$, kg./cm.$^2$ | $10^2 \times n$ | $f_{1.0}$, kg./cm.$^2$ | $10^2 \times n$ |
| | | In Cis-4 | | |
| 0 | 4.5 | 2.9 | 3.4 | 0.7 |
| 30 | 6.2 | 3.7 | 3.9 | 1.2 |
| 50 | 8.2 | 4.0 | 6.1 | 1.7 |
| 80 | 33.0 | 4.0 | — | — |
| | | In SBR-1500 | | |
| 30 | 3.6 | 9.1 | 1.9 | 2.2 |
| 50 | 4.2 | 10.3 | — | — |
| 80 | 13.4 | 16.2 | — | — |

[a] Samples containing 0.4 phr Di-cup R, cured for 60 min. at 155°C.

The value of $f_{1.0}$ (in both swollen and unswollen samples) increases significantly with increased carbon black loading. In unswollen samples a particularly large increase is found on increasing Vulcan 6 loading from 50 to 80 phr, and it is closely similar to the phenomenon observed in uncured compounds.

The influence of carbon black activity on the relaxation rates in Cis-4 compounds is illustrated in Table VI. In unswollen compounds we find no influence of carbon black, and the relaxation mechanism is controlled by the viscous flow of polymer molecules. The picture becomes radically changed, however, when we examine the relaxation rates of the same compounds swollen to constant $V_R = 0.25$.

We note that in swollen compounds the relaxation rate decreases as the activity of carbon black decreases (i.e., as the temperature of thermal treatment is increased), until a compound containing fully graphitized carbon black (treated at 2700°C.) shows the same relaxation rate as pure

TABLE VI
Effect of Carbon Black Activity on Relaxation Rates
of Cis-4 Rubbers at 75% Elongation[a]

| 50 phr ISAF black, treated at temp., °C. | Nonswollen | | Swollen to $V_R = 0.25$ | |
|---|---|---|---|---|
| | $f_{1.0}$, kg./cm.$^2$ | $10^2 \times n$ | $f_{1.0}$, kg./cm.$^2$ | $10^2 \times n$ |
| Pure gum | 4.5 | 2.9 | 3.4 | 0.7 |
| — | 8.1 | 4.0 | 6.4 | 1.7 |
| 800 | 7.8 | 3.6 | 6.8 | 1.9 |
| 1200 | 7.1 | 3.3 | 5.1 | 1.2 |
| 1500 | 5.3 | 3.8 | 3.1 | 1.0 |
| 2700 | 5.7 | 3.4 | 3.0 | 0.8 |

[a] Samples containing 0.4 phr Di-cup R, cured for 60 min. at 155°C.

TABLE VII

Relaxation Rates of Swollen (to $V_R = 0.25$) Cis-4 Rubbers at 30% and 75% Elongation[a]

| ISAF carbon black treatment at temp., °C. | At 30% elongation | | At 75% elongation | |
|---|---|---|---|---|
| | $f_{1.0}$, kg./cm.² | $10^2 \times n$ | $f_{1.0}$, kg./cm.² | $10^2 \times n$ |
| Pure gum | 2.2 | 0.6 | 3.4 | 0.7 |
| Control | 2.3 | 1.5 | 6.4 | 1.7 |
| 800 | 2.4 | 1.7 | 6.8 | 1.9 |
| 1200 | 2.1 | 1.2 | 5.1 | 1.2 |
| 1500 | 1.2 | 0.8 | 3.1 | 1.0 |
| 2700 | 1.2 | 0.8 | 3.0 | 0.8 |

[a] Samples contain 0.4 phr Di-cup R and 50 phr Vulcan 6, cured for 61 min. at 155°C.

gum stock. The modulus values, $f_{1.0}$ follow approximately the same order. No significant difference between relaxation rates of swollen samples extended to 30% and 75% elongation was observed (Table VII) The value of modulus, $f_{1.0}$, increased in both swollen and nonswollen samples as sample elongation was increased.

In order to test the hypothesis that in cured nonswollen samples the rate of relaxation is controlled by a viscous process, Cis-4 stocks containing 50 phr Vulcan 6, graphitized Vulcan 6, and pure gum were prepared. From these compounds two sets of samples containing respectively 25, 50, and 66% solvent (decalin) were prepared. One set of swollen samples was left uncured and the viscosities were measured by using the Mooney viscometer (large rotor) at room temperature. The other set of samples was first cured under standard conditions (0.4 phr Di-cup R, cured
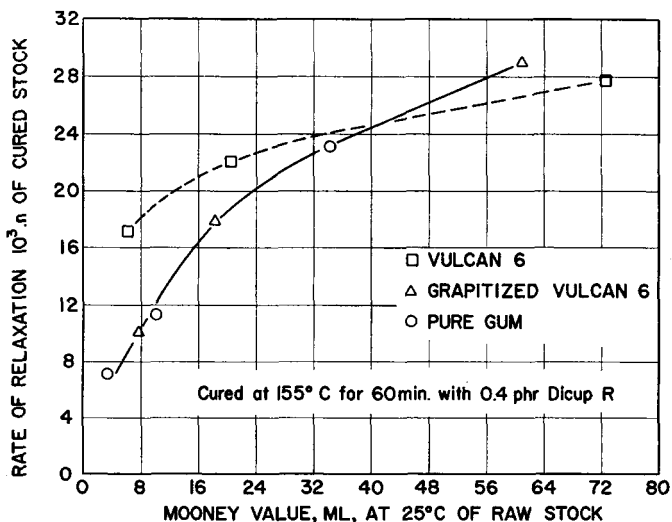


Fig. 3. Influence of polymer viscosity on stress relaxation of Cis-4 rubbers at 75% elongation.

for 60 min. at 155°C.), then swollen to the required degree, and the rate of relaxation measured at 75% elongation. In Figure 3, a plot of relaxation rates versus Mooney viscosity values (at 25°C.) is shown, and a number of interesting conclusions may be reached.

(1) There is no difference between the behavior of pure gum stocks and those containing graphitized Vulcan 6. The relaxation rate of these stocks approaches zero as their viscosity is decreased.

(2) There is very little difference between the behavior of unswollen gum stocks and those containing Vulcan 6; however, this difference increases as the viscosity of the compounds is decreased. As the viscosity of Vulcan 6 stocks is decreased (by swelling), the plot approaches a positive intercept on the rate of relaxation axis. This extrapolated intercept obviously reflects the contribution of carbon black to the relaxation process.

(3) The values for relaxation rates obtained on stocks swollen to $V_R = 0.25$ (75% solvent on pure gum basis) closely approximate the extrapolated intercept of the plot of the rate of relaxation versus the Mooney viscosity.

The rate of relaxation in both swollen and nonswollen compounds, with or without carbon black, markedly increases with a decrease in crosslink density (Table VIII).

Observed relaxation rates for pure gum and carbon black-loaded vulcanizates indicate that most of the molecular relaxation in pure gum stocks occurred at times much shorter than those measured on the Instron machine.

In order to examine the response of rubber samples at very short times, some experiments were run at a crosshead speed of 15,000 cm./sec. by use of a high-speed tensile tester (Plas-Tech Corp.). This permitted an extension of the time scale by another three decades (i.e., 0.1 sec. to 6 months). However, even at these times the experimentally observed stress relaxation (Fig. 4) of both swollen and nonswollen samples obeyed the log–log relationship postulated earlier [eq. (2)]. Due to experimental difficulties,

TABLE VIII
Relaxation Rates of Cis-4 Compounds Cured to Different Crosslink Densities

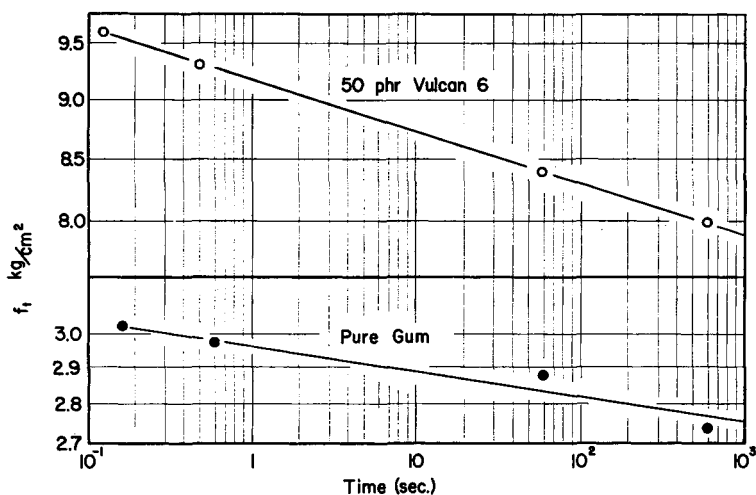| 50 phr ISAF carbon black, treated at temp., °C. | 0.2 phr Di-cup R | | 0.4 phr Di-cup R | | 1.0 phr Di-cup R | |
|---|---|---|---|---|---|---|
| | $f_{1.0}$, kg./cm.$^2$ | $10^2 \times n$ | $f_{1.0}$, kg./cm.$^2$ | $10^2 \times n$ | $f_{1.0}$, kg./cm.$^2$ | $10^2 \times n$ |
| Nonswollen | | | | | | |
| Pure gum | 2.4 | 6.2 | 4.5 | 2.9 | 7.4 | 1.1 |
| Control | 6.0 | 5.3 | 8.1 | 4.0 | 17.6 | 1.9 |
| 800 | 4.6 | 6.3 | 8.2 | 3.9 | 15.8 | 1.7 |
| 2700 | — | — | 5.7 | 3.4 | 10.3 | 1.6 |
| Swollen | | | | | | |
| Pure gum | 0.5 | 1.7 | 3.4 | 0.7 | — | — |
| Control | 4.6 | 2.7 | 6.4 | 1.7 | 22.6 | 1.2 |
| 2700 | 0.8 | 2.1 | 2.9 | 0.8 | 10.5 | 0.4 |

Fig. 4. Stress relaxation of cured swollen Cis-4 rubbers, tested by using a high-speed tensile tester.

the reproducibility of these runs was not as good as of those obtained at lower speeds. It is concluded therefore that in pure gum vulcanizates the major part of relaxation occurs at times much shorter than those examined here, i.e., less than 0.1 sec.

## White Fillers

The effect of various white fillers on stress relaxation in raw and lightly vulcanized, swollen stocks is shown in Table IX. As has already been observed with various carbon blacks, the relaxation rate of raw stocks decreases while the relaxation rate of cured, swollen, rubbers increases with increase in reinforcing properties of the filler. All fillers have been used at the same volume loading and, for the sake of completeness, the data for ISAF black (Vulcan 6) at the same loading and a pure gum stock has been added.

TABLE IX
Relaxation Rates of Raw and Cured Cis-4 Compounds
Containing Various White Fillers at the Same Volume Fraction Loading

| Filler | Filler loading, phr | Raw Rubber under 30% Compression | | Cured, swollen rubber under 70% Extension[a] | |
|---|---|---|---|---|---|
| | | $f_{1.0}$, kg. | $10^2 \times n$ | $f_{1.0}$, kg. | $10^2 \times n$ |
| None | — | 0.6 | 33 | 3.4 | 0.7 |
| Atomite | 74.4 | 0.9 | 36 | 2.5 | 0.9 |
| Super Multifex | 74.4 | 1.3 | 32 | 3.6 | 1.2 |
| Hi-Sil 233 | 52.5 | 3.4 | 25 | 9.1 | 1.4 |
| Vulcan 6 | 50.0 | 8.4 | 16 | 6.1 | 1.7 |

[a] Cured with 0.4 phr Di-cup R for 60 min. at 155°C.

## SUMMARY

The present study has shown that reinforcing fillers influence the stress relaxation by two separate mechanisms. In raw rubbers stress relaxation is a viscous-controlled process, and its rate decreases in the presence of reinforcing fillers, probably caused by a decrease in the apparent viscosity of the medium. At the other extreme, in lightly cured swollen rubbers, reinforcing fillers increase the rate of relaxation, and this increase is related to the modulus, $f_{1.0}$, value, i.e., the reinforcing potential of the filler.

In lightly cured, nonswollen rubbers the rate of relaxation is only slightly increased on addition of reinforcing fillers and the change is nearly of the same magnitude as experimental error. The rate of relaxation in both swollen and nonswollen stocks is very sensitive to the degree of crosslinking; it increases with a decrease in crosslink density.

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## Résumé

On a mesuré à température normale la relaxation de tension dans des blocs de caoutchouc contenant divers remplissages et on a trouvé une équation empirique qui décrit la diminution de la tension, $f_t$, pendant une péridde de temps comprise entre 0.1 sec. et 6 mois, soit $f_t = f_{1.0}t^{-n}$ où $f_{1.0}$ est la force après 1 min. de relaxation, $n$ la vitesse de relaxation du matériau (par définition) et $t$ le temps en minutes. On a examiné le comportment des caoutchoucs bruts à la compression et des caoutchoucs traités à la tension. On a trouvé que la relaxation de tension était un processus contrôlé par la viscosité et cela aussi bien dans les polymères du butadiène bruts que traités. Dans les caoutchoucs bruts, une augmentation de la teneur en noir de carbone diminue la vitesse de relaxation, tandis que l'effet du noir de carbone est très petit dans les caoutchoucs traités. Cependant, dans les caoutchoucs traités et gonflés (jusqu'à $V_R =$

0.25), la vitesse de relaxation augmente avec la charge en noir de carbone, ce qui indique un glissement et/ou une scission de certains liens entre le polymère et le noir de carbone.

## Zusammenfassung

Die Spannungsrelaxation in Kautschukproben mit verschiedenen Füllstoffen wurde bei Raumtemperatur gemessen und eine empirische Gleichung für den Spannungsabfall $f_t$ über eine Zeitdauer von 0.1 sec bis 6 Monaten $f_t = f_{1.0}t^{-n}$ gefunden, wo $f_{1.0}$ die Kraft nach 1 min Relaxationsdauer, $n$ die Relaxationsgeschwindigkeit des Materials (definitionsgemäss) und $t$ die Zeit in Minuten ist. Rohe Kautschukproben wurden unter Kompression und vulkanisierter Kautschuk unter Zug getestet. Sowohl bei vulkanisierten als auch bei unvulkanisierten Kautschukproben erwies sich die Spannungsrelaxation als ein viskositätskontrollierter Prozess. Bei Rohkautschuk setzen verstärkende Russe die Relaxationsgeschwindigkeit herab, während bei vulkanisiertem Kautschuk der Einfluss von Russ sehr klein ist. Bei gequollenem (auf $V_R = 0.25$) vulkanisiertem Kautschuk nimmt jedoch die Realaxationsgeschwindigkeit mit steigender Russfüllung zu, was für ein Schlüpfen oder einen Bruch einiger Bindungsstellen zwischen Russ und Polymeren spricht.