Stress Softening in Carbon Black-Reinforced Vulcanizates.   Strain Rate and Temperature Effects

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Synopsis

Stress softening of carbon black-reinforced butadiene–styrene rubber was studied as a function of the rate and temperature of the original tensile deformation.   To a good approximation, stress softening depends on the product of the extension rate and a temperature function which is analytically well represented by the familiar Williams-Landel-Ferry relationship.   When the elongation of the original deformation is also varied, a good correlation is obtained between stress softening and the maximum stress attained in the original extension, irrespective of the particular combination of strain, strain rate and temperature used to achieve this stress.   Variables which tend to increase the stiffness of the vulcanizate, such as increased degree of crosslinking or carbon black chain structure, also increase stress softening; dilution by plasticizers decreases it.   Prestressing at high strain rates and low temperatures affects the stress–strain curve of the softened vulcanizates beyond the elongation of the original extension.   Connections are established between stress softening and viscoelastic and failure behavior.   The evidence presented favors the contribution of several mechanisms to the general phenomenon of stress softening.   These are thixotropy of transient filler structures, network chain rupture, and breakage of "permanent" filler structure.   The latter appears to be most important at high strain rates, low temperatures, and with highly reticulated "structure" blacks.

INTRODUCTION

When a strip of a filler-reinforced rubber vulcanizate is extended to a given elongation, returned to zero strain, and subsequently extended again, it will appear softened; the new stress–strain curve will lie below the original curve.   This well known phenomenon, frequently referred to as the "Mullins effect" or "Mullins softening,"[1-3] has been the subject of many publications and is believed by some authors to be of great importance in the mechanism of filler reinforcement of elastomers.

Some workers have treated this effect as an essentially static phenomenon in which the degree of softening depends on the elongation of the prestretch.[3-5]   However, viewed as a form of thixotropy, it should be governed by rate effects as well.   Indeed, the original work of Mullins clearly suggests[2] connections between stress softening of vulcanizates and thixotropic effects in uncured rubbers.   The present paper describes the results of a

detailed investigation of stress softening* in carbon black-filled styrene–butadiene rubber (SBR) as a function of temperature and strain rate of the original deformation. It will be shown that stress softening is strongly rate-dependent and has profound effects on the viscoelastic and failure behavior of filler-reinforced rubbers.

EXPERIMENTAL

Vulcanizates were prepared with Philprene 1500 (Phillips Petroleum Company), a general purpose butadiene–styrene "cold" rubber (SBR) of 46–58 Mooney viscosity. The stocks were compounded either in a Banbury mixer or on a two-roll mill. The carbon blacks used were high abrasion furnace blacks (Philblack 0) of normal, high (HS) and low (LS) structure. The structure property was assessed by the standard oil absorption test which is a measure of reticulation of the carbon black particles (Table I).

TABLE I

Black	Nitrogen surface area, m.²/g.	Mean particle diameter, A.	Oil absorption, cc./g.	pH
HAF-HS	80	260	0.67	8.4
HAF	80	280	1.24	8.2
HAF-LS	77	280	0.98	7.3

The compounding recipes are shown in Table II. The compounds were cured into slabs of approximately 1.8 mm. thickness. Vulcanization time was 30 min. at 153°C.

Ring specimens were used for both constant rate of strain and stress-relaxation measurements. These specimens, 2.48 cm. inside diameter and 2.74 cm. outside diameter, were cut from cured slabs with a double blade cutter mounted in a drill press. An Instron table model tester (Instron Engineering Co., Quincy, Mass.) was used to obtain stress–strain data at strain rates of 0.0414 and 0.414 sec.$^{-1}$, and a Plastechon high speed tester (Plas-Tech Equipment Co., Natick, Mass.) was used for rates of 4.1, 41, and 310 sec.$^{-1}$. Stress-relaxation data for vulcanizates A and D were recorded on the Plastechon with the ram stop set at 300% elongation. After allowing 10 min. for attainment of temperature equilibrium, the specimens were extended at a rate of 100 sec.$^{-1}$, and stress was recorded in the time interval between 0.1 and 1000 sec.

Stress softening for each vulcanizate was measured by the following procedure.

* It should be made clear at this point that the term "stress softening" is used in this paper to denote only irreversible softening, measured after substantially complete elastic recovery. On the other hand, the term "Mullins effect" is often taken to apply to softening measured shortly after prestressing, in which case it will include a contribution due to incomplete recovery.

TABLE II
Compounding Recipes (Cure 30 min. at 153°C.)

	A	B	C	D	E	F	G	H
Philprene 1500	100	100	100	100	100	100	100	100
HAF Black	—	50	50	50	50	80	—	—
HAF, LS black	—	—	—	—	—	—	50	—
HAF, HS black	—	—	—	—	—	—	—	50
Philrich 5	10	—	—	10	30	60	—	—
Zinc oxide	3	3	3	3	3	3	3	3
Stearic acid	1	1	1	1	1	1	1	1
Flexamine	1	1	1	1	1	1	1	1
Sulfur	1.75	1.75	1.3	1.75	1.75	2.6	1.75	1.75
Santocure	1.3	1.2	1.2	1.3	1.2	1.8	1.2	1.2
v_r,[a]	0.392	0.434	0.410	0.422	0.386	0.407	0.434	0.447

[a] Inverse swelling ratio in n-heptane, 30°C.

The stress–strain curve of the vulcanizate was recorded to rupture at 25°C. and 0.0414 sec.$^{-1}$ strain rate.

Separate specimens were softened by extending them to the chosen elongation at various strain rates and temperatures. They were then returned to zero strain, allowed to relax 6 days in n-heptane vapor, and dried at room temperature *in vacuo*. Their stress–strain curves were then determined as above.

Areas under the stress–strain curves of the original and softened samples were measured graphically up to the breaking elongation of the unsoftened specimen. Stress-softened specimens usually had higher breaking elongations than unsoftened specimens.

Per cent stress softening was calculated as

$$\left[1 - \int_0^{\epsilon_b} \sigma d\epsilon / \int_0^{\epsilon_b} \sigma_0 d\epsilon \right] \times 100$$

where σ_0 and σ are the tensile stresses at strain ϵ of the original and softened vulcanizate, respectively, and ϵ_b is the ultimate elongation of the original sample.

Permanent set of softened vulcanizates was reduced to 3% or less by swelling and deswelling in n-heptane vapor. Stress–strain curves of unsoftened vulcanizates were unaffected by swelling and deswelling.

Electrical resistivities were measured with a d.c. Wheatstone bridge using a dynamic condenser preamplifier as a detector driving a servo system to balance the bridge.[6] Leads to the bridge were attached to pieces of aluminum foil covering the enlarged sections of double paddle-shaped specimens which were clamped to the Instron. Resistivity was thus measured for stretched or unstreched samples in the direction of stretch. End sections of the specimens were painted with a silver paint to insure good electrical contact, and the jaws of the Instron clamps were covered with 15 mil thick plastic insulating tape to insulate the specimen from the Instron. One of the jaws was also insulated from the Instron by a 1-in. thick reinforced Synthane insulator.

RESULTS AND DISCUSSION

Variables Affecting Stress Softening

Figure 1 shows a typical set of stress–strain curves illustrating the stress-softening effect. All curves were obtained at 25°C. and a strain rate of 0.0414 sec.$^{-1}$; they differ only in the rate and temperature at which the vulcanizate was prestretched. These curves demonstrate an important point. After mild conditions of prestretch the stress–strain curve tends to rejoin the original curve once the elongation of the prestretch is exceeded. This has been considered characteristic of the stress-softening effect by previous investigators.[2,4] The results of Figure 1 shows that this is not true when the prestressing conditions are severe; the entire stress–strain curve is affected by prestretching to elongations well below the point of rupture.
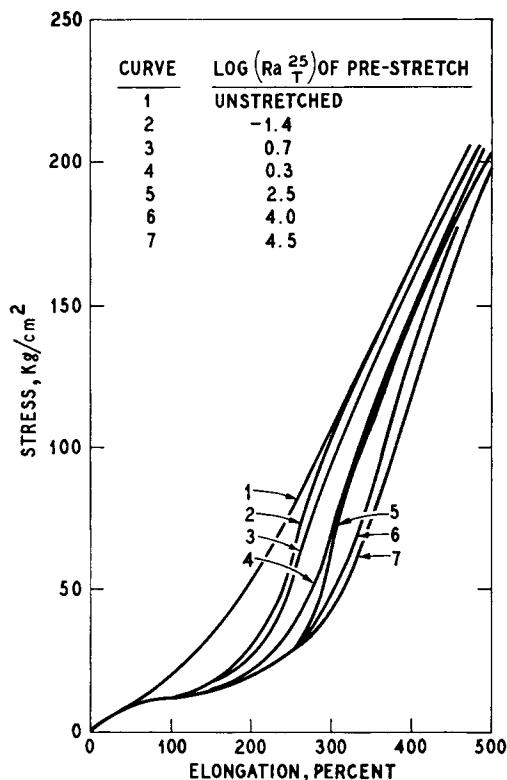
Fig. 1. Stress–strain curves as a function of stress softening for vulcanizate C. Curves were recorded at 25°C. and $R = 0.041$ sec.$^{-1}$ after prestretch to 250% elongation at reduced strain rate ($Ra_T{}^{25}$) and recovery in toluene vapor.

For quantitative comparisons it is convenient to define stress softening as the per cent reduction in the work expended to extend the sample to the ultimate elongation of the original unsoftened vulcanizate. This quantity is readily obtained as the reduction in area under the stress-strain curve.

Since both extension rate and temperature of the prestretch affect the degree of stress softening, one is led to test the applicability of rate–temperature equivalence. Accordingly, stress softening should be a function of the product of the extension rate R and a temperature-dependent function a_T. An appropriate form of a_T is given by the Williams-Landel-Ferry[7] equation

$$\log a_T = -8.86(T - T_s)/(101.6 + T - T_s)$$

where T_s is a reference temperature, usually about 50°C. above the glass transition temperature.   Smith[8] and others have shown the applicability of the WLF equation to the viscoelastic and failure properties of unfilled SBR with $T_s = -10°C$.   In Figure 2 we have plotted stress softening versus $\log Ra_T{}^{25}$ for three different vulcanizates, wherein
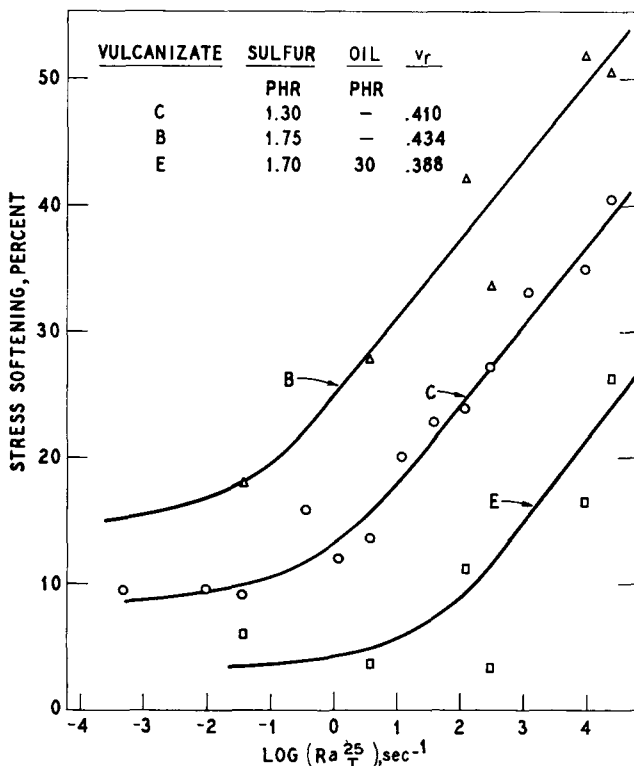
$$\log a_T{}^{25} \equiv \log a_T - \log a_{25}$$

Fig. 2. Stress softening as a function of reduced strain rate for HAF vulcanizates. Softening determined at 25°C. and $R = 0.041$ sec.$^{-1}$ after prestretch to 250% elongation at reduced strain rate.

thus reducing all data to 25°C.   The success of the reduction is apparent. The data indicate that stress softening is more severe in tighter networks and tends to be less in oil-extended vulcanizates.

Figure 3 shows similar plots for three carbon blacks of similar particle size, but differing in the amount of carbon black "chain structure."   These data indicate that high structure blacks give rise to particularly severe stress-softening effects.   This observation has already been made by others.[3,5]

Figure 4 illustrates the dependence of stress softening on the elongation of the original extension.   These results have been replotted in Figure 5 to suggest that to a fair approximation stress softening of a vulcanizate is simply a function of the maximum stress (based on the actual cross section) attained during prestretch, regardless of the particular combination of temperature, strain rate, and strain employed to realized this stress.   The emergence of stress as the critical variable also explains qualitatively the behavior described in Figures 2 and 3: crosslinking and high degree of reticulation in the carbon black lead to increased stiffness of vulcanizates, while dilution with a plasticizer has the opposite effect.   The extent of softening follows the same trends.
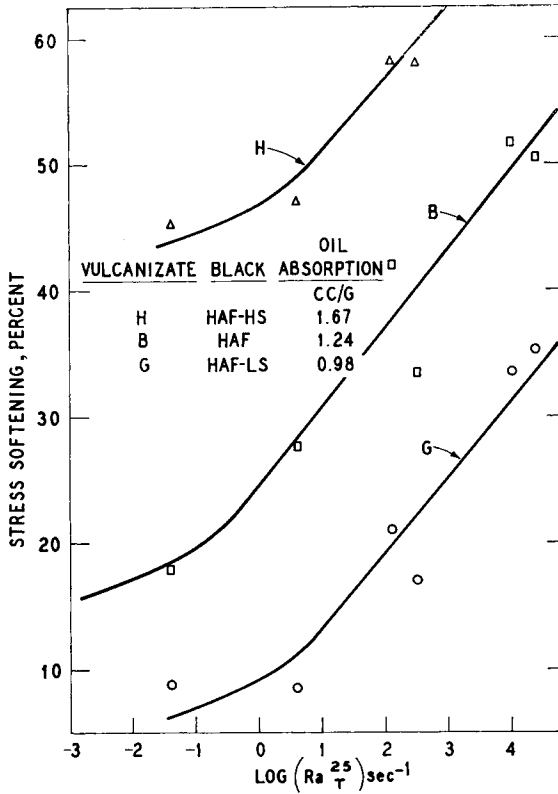
Fig. 3. Stress softening as a function of carbon black structure. Softening determined at 25°C. and $R = 0.041$ sec.$^{-1}$ after prestretch to 250% elongation at reduced strain rate.
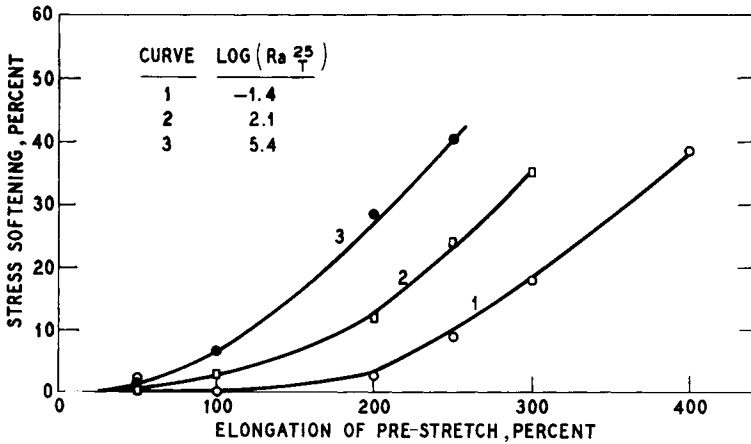

Fig. 4. Stress softening as a function of prestretch elongation for vulcanizate C. Softening determined at 25°C. and $R = 0.041$ sec.$^{-1}$ after prestretch at reduced strain rate.
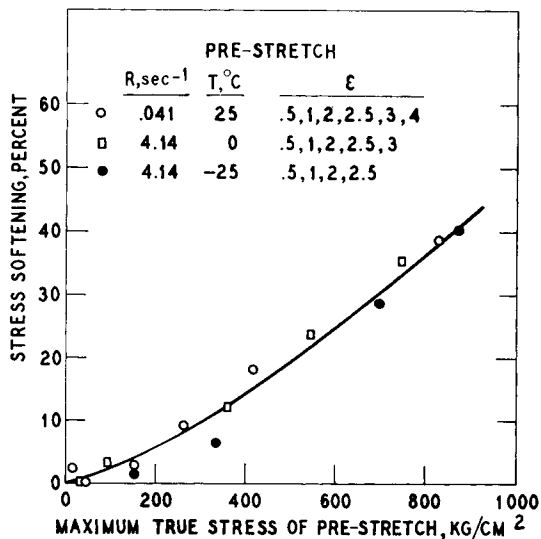
Fig. 5. Stress softening as a function of maximum true tensile stress attained on prestretch. Softening determined at 25°C. and $R = 0.041$ sec.$^{-1}$ after prestretch at reduced strain rate.

Changes Induced in the Polymer Network

It is widely accepted that stress softening involves the breakage of polymer–filler or polymer–polymer bonds in network chains attached to the filler surface.[4,9] To ascertain the extent of bond breakage in the network, inverse swelling ratios, v_r, in n-heptane were obtained for several vulcanizates after prestressing under various conditions. Figure 6 shows the results of vulcanizate C prestressed to 250% elongation at varying temperature and strain rate. Calculations based on the Flory-Rehner theory of swelling[10] indicate that the change in network chain density of a gum vulcanizate corresponding to the maximum change in v_r observed here would be of the order of 15%. The stress-softening effects are much larger (Fig. 2). Thus it appears that if the effect is to be ascribed entirely to broken network chains, these must carry a disproportionately high share of the load. This is in agreement with theoretical considerations by F. Bueche[4] regarding the effect of the distribution of network chain lengths in filled vulcanizates on stress softening. Uncertainties in the application of network theories to filled rubbers make a closer analysis of this effect of doubtful value.

In vulcanizates filled with nonreinforcing fillers, extension is accompanied by volume expansion[11] due to pulling away of polymer from the filler. If stress softening in carbon black-filled vulcanizates is caused by polymer–filler bond rupture, high-speed extension may result in measurable volume expansion caused by more extensive bond rupture and vacuole formation around filler particles. To investigate this possibility, volume expansion was measured for a SBR vulcanizate filled with 50 phr of HAF black and stretched to 300% elongation (Table III).
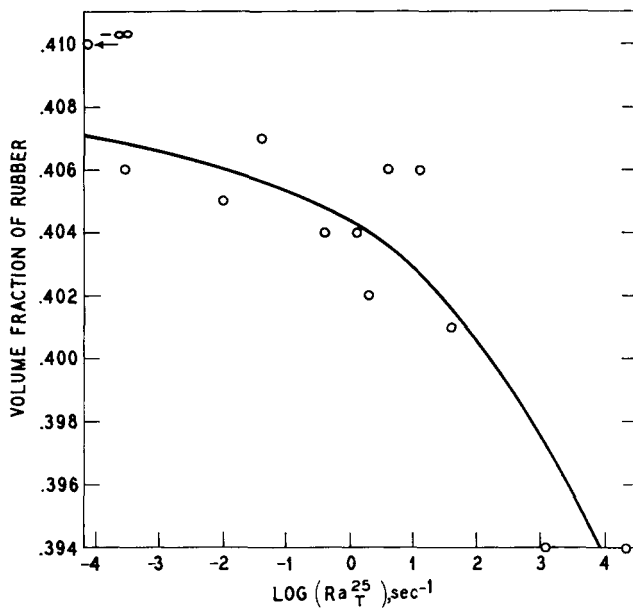
Fig. 6. Equilibrium swelling of vulcanizate C in n-heptane after prestretching to 250% elongation at reduced strain rate.

The volume expansion at 25°C. and 1 sec.$^{-1}$ extension rate was 1.9%, in good agreement with similar data of Mullins and Tobin.[12] While volume expansion was increased by increasing speed or reducing temperature of extension, the effect was gradual. There was no sharp increase in volume expansion, even at 0°C. This seems to indicate that vacuoles formed around zinc oxide particles as proposed by Mullins[12] are mainly responsible for the volume increase at high speed and low temperature. Recent electron microscope studies by Hess[13] indicate that vacuole formation around carbon black particles is inappreciable at elongations below 300%. In any case, while vacuoles might explain the increased swelling of stress-softened vulcanizates, they apparently cannot account for the very large changes in stiffness.

Effect of Carbon Black Chain Structure

As shown in Figure 3, stress softening is strongly dependent on carbon black structure. Since chainlike aggregates stiffen the rubber more than

TABLE III
Volume Expansion of HAF-Filled SBR Vulcanizate Extended to 300%

Extension rate, sec.$^{-1}$	Temperature, °C.	$Ra_T{}^{25}$	Volume expansion, %
1	25	1	1.9
100	25	100	3.0
100	0	3160	3.5

TABLE IV
Comparison of Changes in Swelling and Stress Softening for
Vulcanizates Containing Carbon Blacks of Different Structure

Black	Structure	Maximum stress softening, %	Maximum change in v_r accompanying stress softening
HAF	Low	35	$0.434 \rightarrow 0.420$
	Normal	52	$0.435 \rightarrow 0.424$
	High	58	$0.447 \rightarrow 0.434$

spherical particles and softening is a function of the stresses built up in the network, one might expect larger changes in v_r to accompany the high degree of stress softening observed with high structure blacks.   This is not found to be the case (Table IV).   The data therefore suggest the possibility of the structure being partially destroyed during deformation of the rubber, a mechanism also considered by Brennan and associates.[5]

Electrical conductivity measurements shed some light on the situation. Figure 7 shows the relative changes in room temperature electrical resistivity observed on stretching a strip of rubber to different strains (ϵ). All data were obtained by raising the elongation at a low strain rate (0.017 sec.$^{-1}$) in increments of $\Delta\epsilon = 0.5$ and holding the strip at each strain for 10 minutes.   The curves shown represent the results of this experiment for (1) the sample as cured, (2) the same sample prestretched at a strain rate of
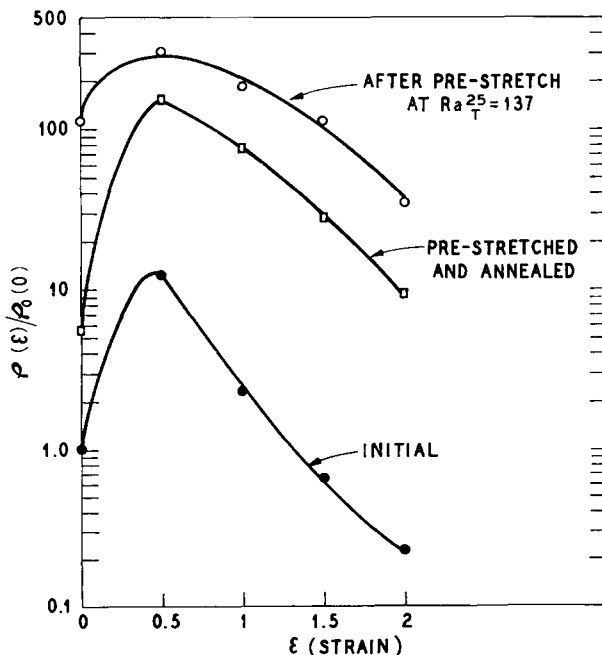

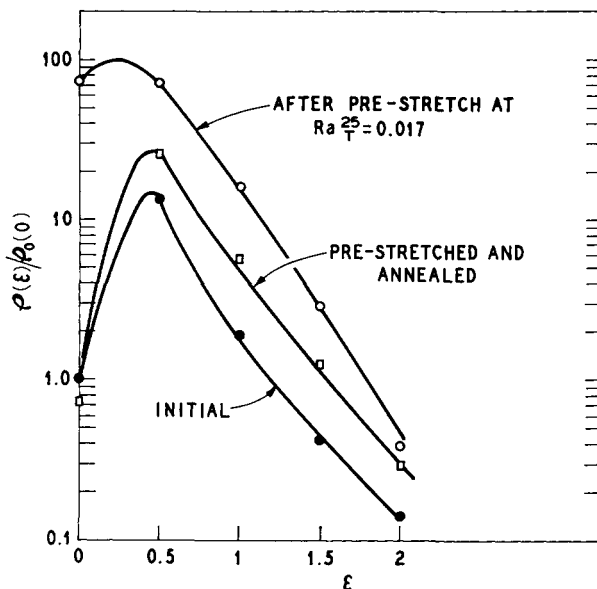Fig. 7. Change in electrical resistivity due to stretching of vulcanizate B at high strain rate.

Fig. 8. Change in electrical resistivity due to stretching of vulcanizate B under less severe conditions of prestretch than Fig. 7.

41.7 sec.$^{-1}$ at $-22°C$. and allowed to recover by the vapor swelling technique, and (*3*) the same sample annealed at 100°C. for 16 hr. Figure 8 shows the result of a similar sequence of tests in which the prestretch was at a low strain rate (0.017 sec.$^{-1}$) and at 25°C.

These results show that even a mild prestretch causes a large increase in electrical resistivity measured at zero strain. Annealing restores the original value of this resistivity. This result is in agreement with the results of Wack et al.[14] After a severe prestretch the increase in resistivity is larger, particularly at the higher elongations, and little of this change is recoverable by annealing. This behavior suggests two mechanisms for the resistivity changes induced by stretching: a disruption of the carbon black network formed by interparticle contacts, which is largely reversible, and a more profound irreversible change caused by breaking of strong reticulate carbon black aggregates. The latter requires prestretching under severe conditions and will contribute substantially to stress softening. These ideas are in complete accord with conclusions based on rheological, dielectric, and conductimetric studies of carbon black dispersions.[15]

Stress Relaxation

The processes believed responsible for the stress-softening effect, i.e., breakage of highly strained network chains and disruption of black structure, are undoubtedly not instantaneous. If a strip of filled rubber is extended rapidly to a high elongation and held there, the early part of the stress-relaxation curve should, therefore, exhibit unusually rapid relaxation
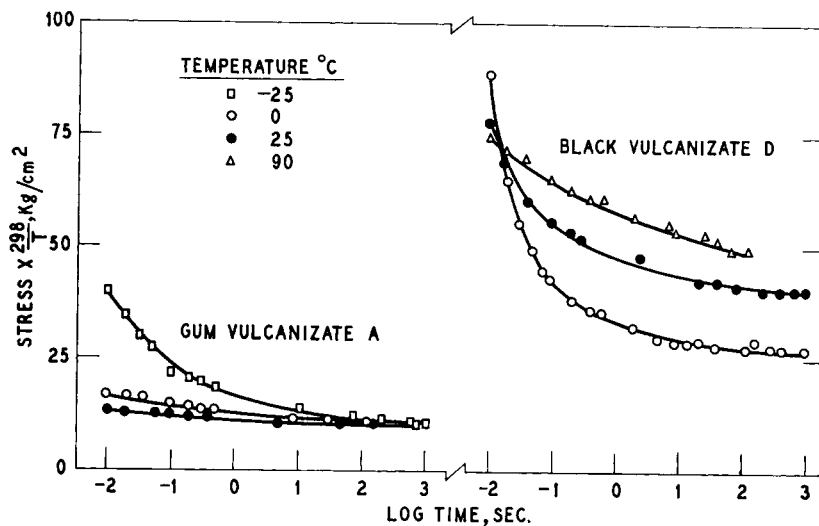
Fig. 9. Stress relaxation of Philprene 1500 gum and black vulcanizates. Specimens extended to 300% elongation at $R = 100$ sec.$^{-1}$.
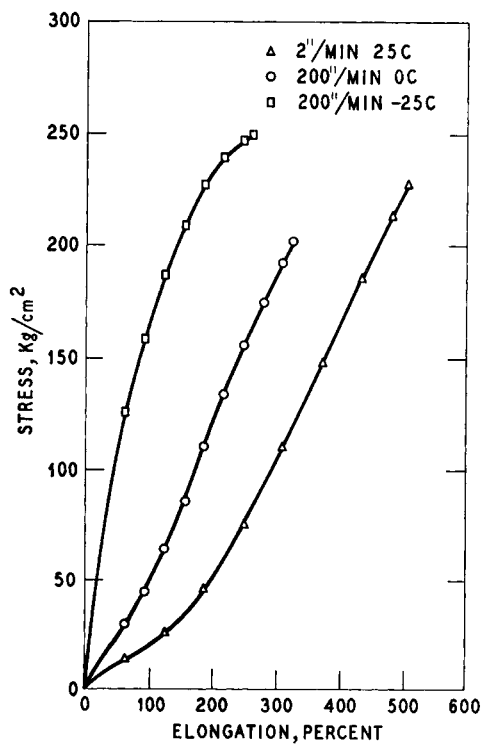

Fig. 10. Stress–strain curve as a function of strain rate and temperature for vulcanizate C.
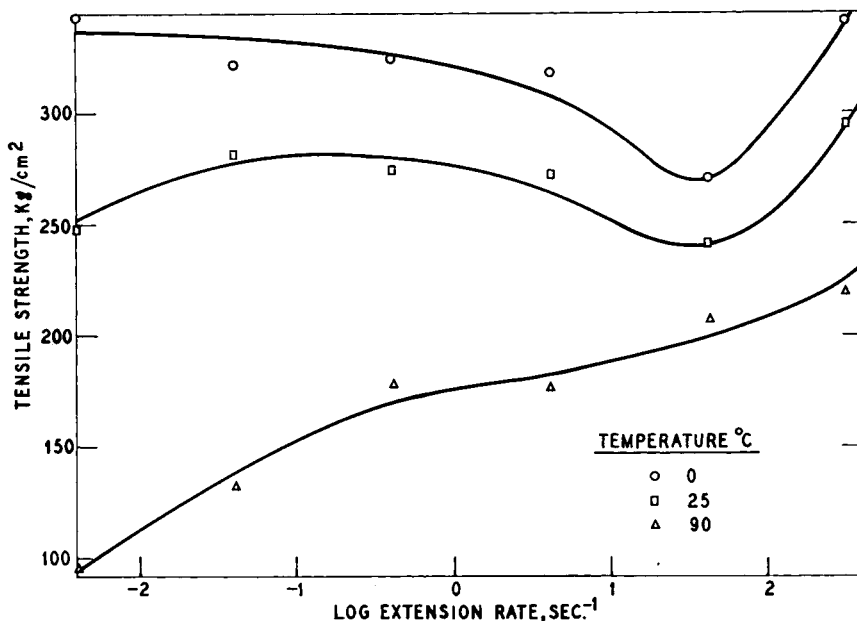
Fig. 11. Tensile strength as a function of extention rate for vulcanizate C.

as these effects are superimposed on normal viscoelastic relaxation. This leads to an apparent anomaly in the stress relaxation of filled stocks: when stress relaxation is measured at different temperatures following rapid extension, the most rapid relaxation is observed at the lowest temperature (Fig. 9). This is diametrically opposite to the behavior of unfilled rubbers. Because of stress-softening effects, the entire stress-relaxation curve of a filled rubber depends strongly on the rate and temperature at which the sample is extended to the elongation of the relaxation experiment.

Stress–Strain Curves

The observation that prestretching under sufficiently severe conditions of a vulcanizate to a given elongation will affect the shape of the stress–strain curve even beyond this elongation means that stress-softening must also influence the original stress–strain curve. The stress at higher elongations is affected by changes occurring in the vulcanizate at lower extensions. This effect is observed in an inflection toward the strain axis[16,17] at high elongations in stress–strain curves obtained at high strain rates and low temperatures (Fig. 10). At the highest elongations this effect is probably augmented by extensive failure of the rubber–filler bond leading to vacuole formation.[13]

Ultimate Properties

It has been shown that in unfilled vulcanizates the rate–temperature relationships governing failure phenomena (e.g., tensile strength) are the

same as those for viscoelastic properties.[8]   Thus the tensile strength of a gum vulcanizate increases with rate of strain and decreases with temperature in the same manner as the modulus.   In filled vulcanizates this simple relationship must be disturbed by stress-softening effects.   One would expect these to be most obvious at high strain rates and low temperatures, a prediction which is fully confirmed by experiment.   Figure 11 shows tensile strength as a function of strain rate at three temperatures for a SBR vulcanizate reinforced with HAF black.   While the behavior at 90°C. appears more or less normal, i.e., tensile strength rises with strain rate, the data at 0°C. show a region in which tensile strength decreases with rate giving rise to both a maximum and a minimum.   At 25°C. the behavior is
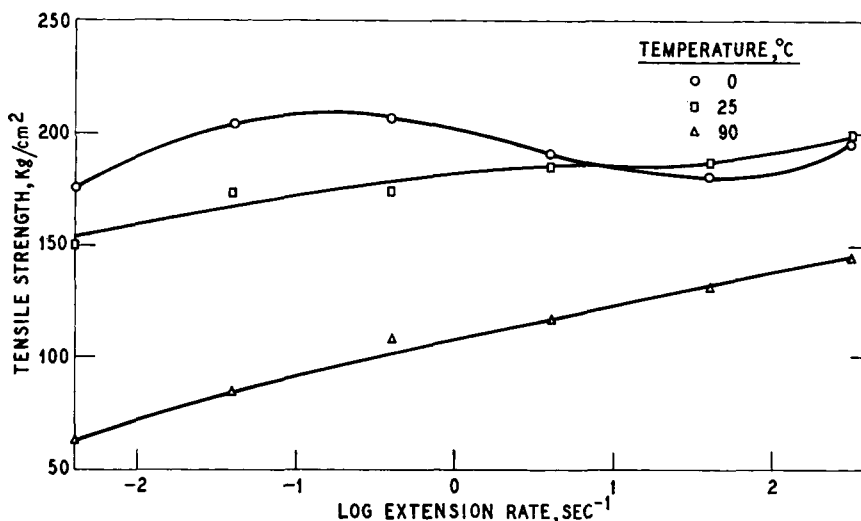

Fig. 12. Tensile strength as a function of extension rate for vulcanizate F.

intermediate.   This behavior, which has been reported previously but given different interpretations,[16,18] is quite general and has been confirmed with several different carbon blacks and rubbers.

Additional evidence for the identification of the minimum in the tensile strength–strain rate relation with stress softening has been obtained from the study of oil-extended rubbers.   These show both diminished stress softening (Fig. 2) and less tendency toward maxima and minima in tensile strength as strain rate is varied (Fig. 12).

It is well known that maxima and minima with strain rate also exist in the characteristic tearing energy of some reinforced rubbers.[19]   The minima likewise tend to occur at low temperatures and high tearing rates.[20]   Since tensile failure is undoubtedly related to tearing, a connection between the present results and their interpretation on one hand, and behavior in tearing on the other seems most likely.

CONCLUSIONS

The results of this study indicate that stress softening in filled vulcanized rubbers is due to three distinct causes.

(1) Thixotropy involving transient carbon black structures as visualized originally by Mullins and observed in the studies of Payne[21] is an effect which is essentially reversible. Because of the high strains employed and precautions taken to insure complete recovery, this mechanism probably did not contribute appreciably to the observations described in this paper.

(2) Rupture of network chains connecting filler particles[3,4] is an irreversible effect and would be expected to depend on the temperature and rate of prestressing.

(3) Disruption of the "permanent structure" of the carbon black is irreversible and strongly rate- and temperature-dependent. It does not appear to have been clearly recognized in previous studies of stress softening.

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Résumé

On a étudié le ramollissement à l'étirement de caoutchoucs styrène–butadiène renforcés par du noir de carbone en fonction de la vitesse et de la température de la déforma-

tion de tension de départ. En bonne approximation, le ramollissement à l'étirement dépend du produit de la vitesse d'extension et d'une fonction de la température qui est bien représentée analytiquement par la relation familière de Williams, Landel et Ferry. Lorsque l'élongation de la déformation originale est également variée, une bonne corrélation est obtenu entre le ramollissement à l'étirement et la tension maximum atteinte de l'extension originale, indépendamment d'une combinaison particulière de la tension, de la vitesse de tension et de la température utilisée pour effectuer cette tension. Les variables qui tendent à accroître la rigidité des vulcanisats tels que des degrés croissants de pontage ou une structure de la chaîne due au noir de carbone, accroissent également ce ramollissement à l'étirement; par contre, la dilution par des plastifiants la décroît. Une tension appliquée préalablement à vitesse de tension élevée et basse température, affecte la courbe tension–élongation des vulcanisats moux au delà de l'élongation de la tension originale. Des connections sont établies entre le ramollissement à l'étirement et le comportement viscoélastique et la brisure. Il semble donc qu'il y ait de nombreaux mécanismes qui contribuent au phénomène général de ramollissement à l'étirement. Ceux-ci sont la thixotropie, la structure de la charge, la rupture de la chaîne en réseau et la rupture de la structure de la chaîne permanente. Cette dernière semble être la plus importante aux vitesses de tension élevées, aux basses températures et dans les noirs de structure hautement réticulée.

Zusammenfassung

Die Spannungserweichung von russverstärktem Butadien–Styrolkautschuk wurde als Funktion der Geschwindigkeit und der Temperatur der ursprünglichen Spannungsverformung untersucht. In guter Näherung hängt die Spannungserweichung von Produkt der Dehnungsgeschwindigkeit und einer Temperatur funktion ab, welche analytisch gut durch die bekannte Williams-Landel-Ferry-Beziehung wiedergegeben werden kann. Wenn auch die Elongation der ursprünglichen Deformation variiert wird, wird eine gute Korrelation zwischen Spannungserweichung und der bei der ursprünglichen Dehnung erreichten Maximalspannung erhalten, ungeachtet der zur Erreichung dieser Spannung verwendeten besonderen Kombination von Verformung, Verformungsgeschwindigkeit und Temperatur. Variable, welche die Steifigkeit des Vulkanisats erhöhen, wie erhöhter Vernetzungsgrad oder Russkettenstruktur, erhöhen auch die Spannungserweichung, während eine Verdünnung durch Weichmacher diese herabsetzt. Eine Vorspannung bei hoher Verformungsgeschwindigkeit und niedriger Temperatur beeinflusst die Spannungs-Dehnungskurve der erweichten Vulkanisate über die Elongation der ursprünglichen Dehnung hinaus. Zusammenhänge zwischen Spannungserweichung sowie viskoelastischem und Bruchverhalten werden festgestellt. Die vorgelegten Ergebnisse sprechen für den Beitrag mehrer Mechanismen zum allgemeinen Phänomen der Spannungserweichung Dazu gehören die Thixotropie der Übergangsstrukturen des Füllstoffs, der Bruch von Netzwerkketten und die Zerstörung "permanenter" Füllstoffstrukturen. Letztere scheint am wichtigsten bei hoher Verformungsgeschwindigkeit, niedrigen Temperaturen und bei hochvernetzten "Struktur"-Russen zu sein.