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Relaxation Processes in Vulcanized Rubber. I. Relation among Stress Relaxation, Creep, Recovery, and Hysteresis

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I. INTRODUCTION

When vulcanized rubbers are deformed, 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. The same delayed response appears in other circumstances: (*1*) When a constant stress is imposed, the resulting deformation increases continuously; this is known as *creep*, or drift. (*2*) When the stress is eventually removed, the unstrained state is not attained immediately; the deformation that remains is known as *set;* it gradually decreases. The deformation that is recovered, i.e., the amount of *recovery*, correspondingly increases with time. (*3*) Under small, sinusoidally varying stresses, the deformation lags behind the stress by a constant (phase) angle, whose tangent d affords a measure of *hysteresis*.

These are different manifestations of what is presumably a single relaxation process. The relation between them constitutes an initial problem, which forms the subject of the present investigation. The different relaxation processes which can occur in vulcanized rubbers at normal temperatures will be described in a subsequent publication (Part II).[1]

Previous workers[2–5] have remarked on the difference between the relative amount of tensile stress relaxation which takes place in a given time interval and the relative amount of tensile creep in the same interval. They have attributed the disparity to the nonlinear nature of the stress–strain relationship in extension. Experimental verification of this appreciation and quantitative measurements of its importance have been lacking, however. Also, the relation between either of these relaxation phenomena and the corresponding recovery from a prior deformation does not appear to have been considered previously.

In Section II, below, a simple theoretical treatment is advanced to relate the stress relaxation at a constant deformation, the creep under a constant load, and the recovery from a previous deformation. In later sections experimental measurements of creep and recovery are described for varied deformations, with different load–deformation relationships, and the results are compared with the theoretical predictions. Finally, measurements of hysteresis are described and compared with values calculated from the observed relaxation rates.

The experimental measurements were carried out at a temperature of 23 ± 2°C. The relaxation of stress was determined by measuring the residual force in the test piece at intervals of time ranging from 10^{-1} to 10^4 min. after imposing a constant deformation. Creep and recovery measurements were made at similar intervals after applying or removing a constant load. The experimental arrangements did not allow measurements to be made in shorter times than 10^{-1} min., while the imposition and removal of load or deformation occupied a second or two, so that time intervals of this order would be correspondingly ill defined.

Vulcanized rubbers are substantially elastic in behavior at normal temperatures, and the observed changes in deformation or in stress are relatively small over the entire experimental time range. It is therefore possible to consider without serious ambiguity that measurements taken soon after applying the load are quasi-equilibrium values. In the present work, the deformation after 1 min. under load has been used in this way, i.e., to characterize the elastic properties of the vulcanizate.

II. RELATIONSHIP AMONG STRESS RELAXATION, CREEP, AND RECOVERY

Relations are derived below, between the *rates* of stress relaxation, creep, and recovery. The corresponding *amounts* that take place in a given time interval are considered subsequently.

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The rate of creep C may be defined as:

$$C = (1/e)(\partial e/\partial t)_\sigma \quad (1)$$

where e is the deformation at a time t after the stress is imposed, and σ is the (constant) applied stress. The rate of stress relaxation, S, at a constant deformation is defined similarly:

$$S = -(1/\sigma)(\partial \sigma/\partial t)_e$$

When the respective deformations (and stresses) are equal, the two rates are related as follows:

$$C = AS \quad (2)$$

where:

$$A = (\sigma/e)(\partial e/\partial \sigma)_t$$

The rate of recovery R from an imposed deformation of amount e_0 may be defined by replacing e in eq. (1) by $e - e_0$. As the present measurements deal only with the final stages of recovery, when the remaining deformation e is much smaller than e_0, R is given to a good approximation by

$$R = -(1/e_0)(\partial e/\partial t)_{\sigma=0}$$

R is related to the corresponding rate of stress relaxation S', i.e., that which occurs after a forced return to the undeformed state from a prior deformation of amount e_0. The relation is analogous to eq. (2) and takes the form

$$R = BS' \quad (3)$$

where:

$$B = (\sigma_0/e_0)(\partial e/\partial \sigma)_{t,\, \sigma=0}$$

σ_0 is the stress corresponding to the deformation e_0.

The rate S' is not necessarily equal to the rate of stress relaxation S under the original deformation e_0. Indeed, relaxation processes can be envisaged in which this would not be the case, as, for example, when the original relaxation is due to permanent structural changes taking place in the deformed material. "Symmetrical" relaxation processes may also be imagined, however, in which S' and S would be substantially equal. The later stages of relaxation of a Maxwell element, consisting of a spring and dashpot in series, or of an array of such elements, would be of this type. As described below, the relaxation of vulcanized rubber appears to be symmetrical in this sense over a wide deformation range, and the rates S' and S are found to be effectively equal.

The quantities A and B are properties of the relation between stress (or load) and deformation at constant time. When this is linear, i.e., for Hookean elastic behavior, A and B both take the value unity and the rates of creep and recovery become numerically identical with the rates of stress relaxation. But when the load–deformation relation is nonlinear, as it is for vulcanized rubber in simple extension, for example, the values of A and B may differ considerably, both from unity and from each other, which will lead to considerable differences in the rates of creep, stress relaxation, and recovery.

The following load–deformation relation in simple extension has been found to apply accurately to vulcanized rubbers subjected to extensions of less than about 200%.[6,7]

$$P = 2a_0(C_1 + C_2/\lambda)(\lambda - 1/\lambda^2) \quad (4)$$

$\lambda (= 1 + e)$ is the extension ratio measured at a constant time interval after the load P is imposed, a_0 is the unstrained cross-sectional area, and C_1 and C_2 are elastic constants of the rubber, the ratio $T = C_2/C_1$ lying generally within the range 0.5 to 1.0.[6,7]

The quantities A and B may be readily calculated from eq. (4):

$$A = \frac{\lambda(\lambda^2 + \lambda + 1)(\lambda + T)}{\lambda^4 + 2\lambda + 3T} \quad (5)$$

and:

$$B = \frac{(\lambda^2 + \lambda + 1)(\lambda + T)}{3\lambda^3(1 + T)} \quad (6)$$

Values of A and B may also be calculated for any other form of load–deformation relationship. When the load P is proportional to a numerical power of the corresponding deflection e, i.e.,

$$P = ke^n$$

where k and n are constants, then the quantity A takes the particularly simple form $1/n$, and is independent of the degree of deformation. In this case, therefore, the rate of creep is 1 nth of the rate of stress relaxation at any deformation.

The total changes in the deformation, stress, or recovered deformation are relatively small in the experimental time range. The values of A and B at any deformation may therefore be considered invariant with time, to a first approximation, and the relations between the instantaneous rates of the relaxation processes, given in eqs. (2) and (3), will also apply to the total amounts observed in a given time interval.

Also, the relations derived above, between the rates of different relaxation processes (and the corresponding amounts, when these are small) do not depend upon the particular scale adopted for the measurement of time. The quantity t may therefore be replaced by any monotonically increasing function of time. As described below, a convenient choice for vulcanized rubbers is the logarithmic function, i.e., the replacement of t by $\log t$ in eq. (1).

III. EXPERIMENTAL EXAMINATION OF STRESS RELAXATION, CREEP, AND RECOVERY

Time Dependence

A typical creep experiment in simple extension is shown in Figure 1, where the measurements of extension under a constant load are represented by open circles. Over the time range given, the deformation is found to increase in proportion with the logarithm of the time under load, as has been remarked previously in connection with vulcanized rubbers and other materials.[8–13] The exact form of the time dependence is not further considered, although it may be noted that the observed linearity with log time must fail to hold both for very short and for very long times. At short times, the characteristic viscoelastic flow curve,[14] corresponding to the transition from a glasslike to a rubberlike state, would be expected, while at long times an equilibrium deformation must be approached for cross-linked rubbers, in the absence of structural failure.

However, an accurately linear dependence is found to obtain over several decades of time, so

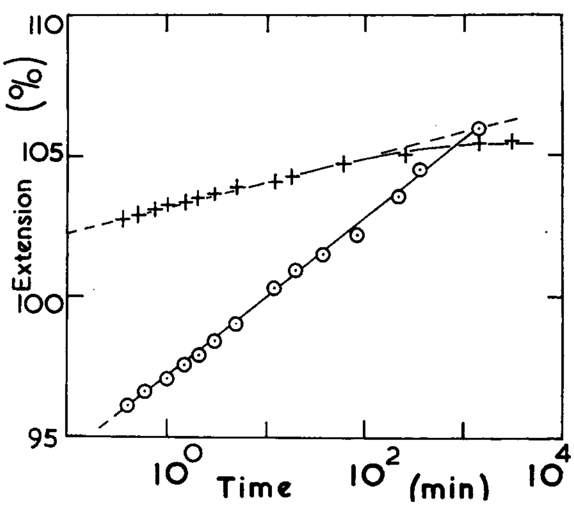

Fig. 1. Extension (⊙) and retraction (+) relations for vulcanizate C. The abscissa denotes time after applying and removing the load, respectively.

that a convenient quantity for describing the rate of creep over the experimental range is given by its slope, i.e., by replacing t by $\log t$ in eq. (1). The value obtained is quite small for natural rubber vulcanizates: of the order of a few per cent of the deformation per decade in time.

Extent of Recovery

The recovered deformation is also shown in Figure 1. The amount of deformation recovered, represented by crosses, is plotted against time after removal of the load. A linear dependence is again observed until, after times comparable to the total time under load, when almost all the original deformation has been recovered, the recovery becomes increasingly slow and appears to cease. A small "permanent" set remains, of the order of 0.5% of the total deformation, but it seems probable that some part of this, if not all, would have been recovered after much longer times.

The recovered deformation after short times is clearly much larger than the deformation that had occurred after the same period under load. The subsequent rate of recovery, given by the slope of the linear recovery relation of Figure 1, is correspondingly lower than the rate of creep (this behavior is discussed in a later section).

Creep Under Repeated and Interrupted Loading

A test piece of a natural rubber vulcanizate C was subjected to a series of loading cycles in simple shear. The load was imposed for 40 min., the course of the creep process being followed during this period, and then the load was removed and the test piece allowed to recover for 24 hr. The test was then repeated. Altogether, four successive creep experiments were carried out in this way.

The measured deflections from the original unstrained state are plotted in Figure 2. It is clear that the four curves are virtually identical, within the experimental error. It appears, therefore, that the rubber is not permanently affected by the prolonged deformation, and the relaxation process is accurately reproducible.

In another experiment, a test piece of vulcanizate B was subjected to a tensile load, which was removed after 5 min., for a few seconds, and then replaced. This was repeated every five minutes, so that in the complete experiment, occupying some 3 hr., the load was removed and replaced about thirty times. The deformation was measured toward the end of each 5 min. period, to allow any transitory effect due to the brief relaxation to disappear. The

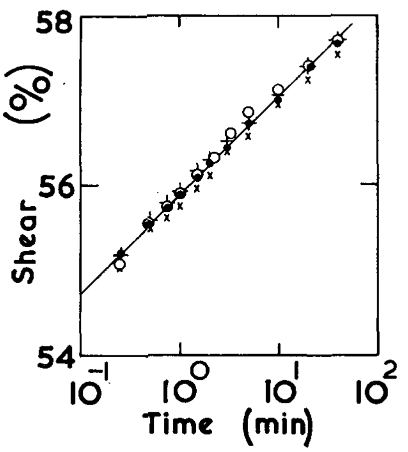

Fig. 2. Deformation relations for vulcanizate C under a repeated simple shear load: (○, ●, +, ×) first, second, third, and fourth loading, respectively.

resulting creep curve is shown in Figure 3, the interrupted portion being represented by a broken line.

For comparison, the creep curve is also shown in Figure 3 for a similar test piece having the same tensile stress imposed without interruption. The two relations are seen to be closely similar. The process of applying the load does not appear to influence the amount or rate of creep.

These observations suggest that the present relaxation mechanism is a physical one, not involving permanent changes in the vulcanizate structure. It probably reflects the final stages of the attainment of equilibrium in the crosslinked network, by a slow rearrangement of molecular chains or aggregates.

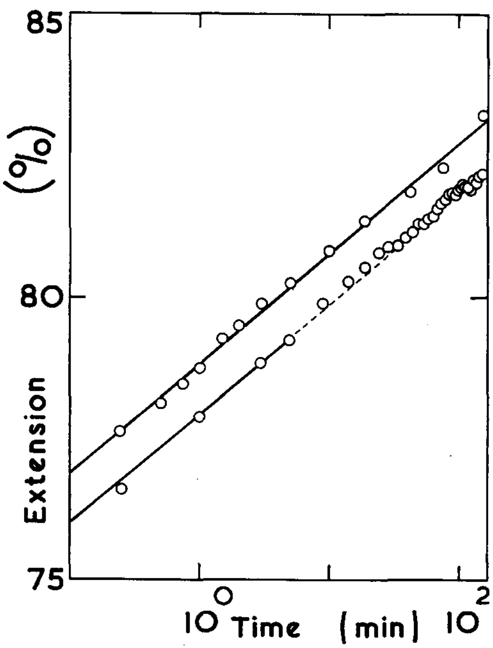

Fig. 3. Creep in simple extension of vulcanizate A under a steady load (full line) and an interrupted load (broken line).

Comparison of Rates of Creep, Recovery, and Stress Relaxation in Simple Extension

In Figure 4 the rates of creep and recovery are plotted as a fraction of the extension after 1 min., against the same quantity. As the applied stress and, hence, the extension after 1 min., increases, the rate of creep increases by a factor of about 2 while the rate of recovery decreases by a similar factor, so that at extensions of the order of 100% the former is about four times greater than the latter. This disparity is clearly evident in Figure 1, where a typical creep and recovery experiment at moderate deformations is portrayed.

The stress relaxation at a constant extension was also found to follow a linear dependence upon log time, but in this case the rate was found to be virtually independent of the imposed deformation. The experimentally determined values are represented by filled-in circles in Figure 4; they average 1.75% per decade for the present vulcanizate (C).

Values of the rate of creep were calculated by means of eq. (2), using the values of A obtained from eq. (5) and the constant value found for the rate of stress relaxation S, namely, 1.75% per

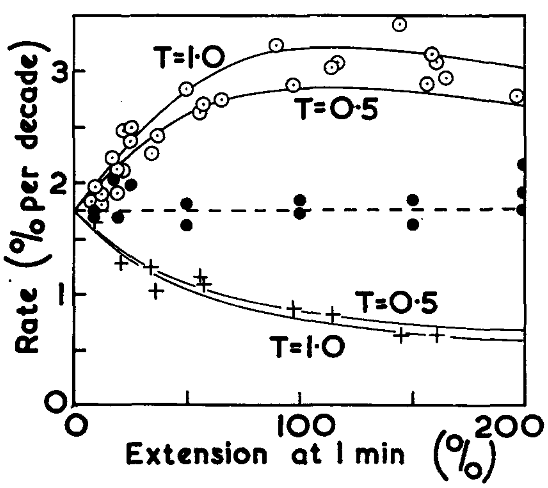

Fig. 4. Rates of creep (⊙), stress relation (●) and recovery (+) for vulcanizate C at various extensions. The full curves represent calculated relations for two values of $T = C_2/C_1$, namely, 0.5 and 1.0, the rate of stress relaxation assumed to be invariant with extension, as represented by the broken line.

decade. The resulting relations for two extreme values of T, the ratio of the elastic constants C_1 and C_2, are represented by the upper full curves of Figure 4. The calculated relations are, clearly, not particularly sensitive to the exact value chosen for T, and are seen to describe the experimentally measured creep rates with considerable success. It appears, therefore, that the observed variations in the rate of creep are due primarily to the nonlinear nature of the stress–strain relation in simple extension, the rate S of stress relaxation being substantially independent of the amount of deformation over the present range.

If the same value is assumed for the rate S' of stress relaxation after a forced return to the undeformed state, values of the rate of recovery may be calculated similarly, by means of eqs. (3) and (6). Relations calculated in this way are represented by the lower full curves of Figure 4, and are seen to describe accurately the measured rates of recovery. Thus, the observed variations in the rate of recovery may also be attributed to the nonlinear nature of the stress–strain relation, and the rate S of stress relaxation is apparently independent of both the amount and the direction of the deformation. It may thus be considered a more fundamental measure of the relaxation process.

Experiments in Simple Shear

The stress–strain relationship for vulcanized rubbers in simple shear is substantially linear for shear displacements of up to about 80% of the test piece thickness.[15] The creep rate C and recovery rate R would therefore be expected to be independent of the degree of deformation in this range, to be similar in magnitude, and to be numerically equal to the rate of stress relaxation.

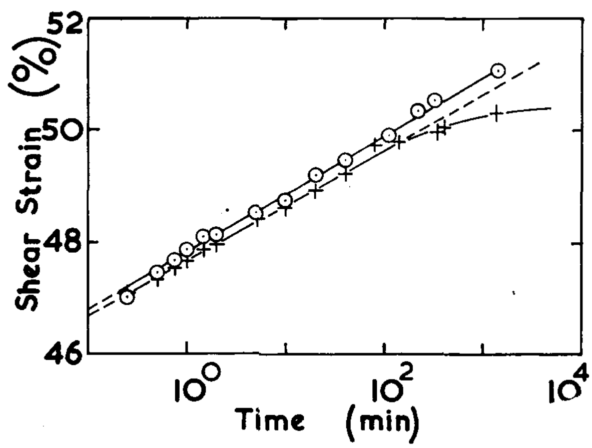

Fig. 5. Deformation (⊙) and retraction (+) relations for vulcanizate C in simple shear. The abscissa denotes time after applying and removing the load, respectively.

A typical creep and recovery experiment in simple shear is shown in Figure 5. The two processes are seen to be indeed closely similar, and from a number of such measurements a value of 2.0% per decade was obtained for the average rate.

This value is higher than the rate of stress relaxation found previously for this vulcanizate, namely, 1.75% per decade, but the difference is small. It is attributed to the inherent irreproducibility of vulcanizate properties in repeated preparations.

Experiments with Other Types of Deformation

A vulcanizate H of a butadiene–styrene copolymer (75:25, Polysar S) was employed in the following experiments, since it exhibited a much greater relaxation rate than did the natural rubber vulcanizates, and the experimental accuracy was correspondingly higher. The creep rates were determined under three types of deformation:

(*1*) A thin strip of the vulcanizate of rectangular cross section of sides 3.6 and 1.8 mm., and length 10 cm., was examined in simple extension, by using two values of tensile stress. From the extensions after 1 min. under load, values of the quantities A and B were calculated by means of eqs. (5) and (6), a value for T of 1.0 being assumed. The measured rates of creep and recovery are given in the fourth column of Table I, and the values of the rate of stress relaxation calculated from them with the aid of the corresponding values of A or B are listed in

TABLE I

Rate of Stress Relaxation S, Calculated from Creep Measurements under Varied Deformations

Deformation	Load, g.	Deflection e after 1 min., cm.	$\frac{1}{e}\left(\frac{\partial e}{\partial t}\right)_\sigma$, %/dec.	S, calc. from $\frac{1}{e}\left(\frac{\partial e}{\partial t}\right)_\sigma$ %/dec.
1 Simple extension:				
(a) Creep	100	1.72	18.4	14.7
	200	4.67	22.0	13.9
(b) Recovery	100	1.79	12.0	15.1
	200	5.02	9.1	15.2
2 Indentation	100	0.0605	10.0	15.0
	200	0.0974	10.1	15.2
	400	0.1655	10.8	16.2
3 Sidewise deflection of a clamped strip	10	1.20	4.78	14.3
	20	1.52	4.78	14.3
	40	1.91	5.05	15.2

the final column. They are seen to be closely similar, averaging 14.7% per decade.

(*2*) A cylindrical block of the same vulcanizate, about 2.5 cm. in diameter and 0.8 cm. in thickness, was subjected to indentation by a rigid spherical indentor 0.244 cm. in diameter. The block rested on a rigid plane and the indentor was suspended immediately above the center of its upper surface by means of a soft helical spring. Weights were then added to the indentor and the resulting indentation was observed through a microscope. The deflection was found to increase in proportion to the logarithm of the time under load, as before. The rates of increase for three values of the applied load are given in the fourth column of Table I. They are seen to be approximately equal, averaging 10.3% per decade.

The relation between the applied load P and the resulting indentation e for small indentations by a rigid spherical indentor is of the form:[16]

$$P = ke^{3/2}$$

where k is a constant containing the value of Young's modulus for the rubber. Hence, as discussed in Section II, the stress relaxation rate will be given by $^3/_2$ times the creep rate. We conclude, therefore, that the stress relaxation rate for this vulcanizate is about 15.5% per decade, and largely independent of the degree of deformation. This value is in good agreement with that deduced from the former experiment.

(*3*) A thin strip of the same vulcanizate, of the same dimensions as in experiment *1*, was suspended horizontally between two rigid clamps so that it was straight and unstretched. Weights were then applied by means of a light saddle to the center of the strip and the resulting vertical deflection was observed by means of a microscope. The deflection again was found to increase in proportion to the logarithm of the time under load; the rates of increase are given in the fourth column of Table I for three values of the applied load. Again they are substantially equal, and average 4.87% per decade.

In this case the relation between the applied load P and the corresponding deflection e is of the form:[17]

$$P = ke^3$$

The rate of stress relaxation is therefore deduced to be about 14.6% per decade, and independent of the degree of deformation. This is in good agreement with the conclusions of the preceding two experiments.

Thus, rates of creep which vary between 5 and 22% per decade, depending upon the type and amount of deformation, are, in fact, in accord with a substantially constant rate of stress relaxation. The good quantitative agreement provides strong support for the treatment developed in Section II.

IV. RELATION BETWEEN RATE OF STRESS RELAXATION AND HYSTERESIS

Kuhn, Künzle, and Preissman[18] have shown that both the linear dependence of stress relaxation or creep upon the logarithm of time, and the observed constancy of the components of the complex dynamic modulus over a wide range of deformation frequencies, are described by a hyperbolic distribution of relaxation times. In this way they obtained a relation between the rate of creep (or stress relaxation) and the hysteresis d, i.e., the ratio n''/n' of the imaginary and real components of the complex dynamic modulus. It may be put in the approximate form:

$$S = 2(\ln 10)d/\pi \tag{7}$$

a relation which has also been obtained by Dunell and Tobolsky,[19] and may be derived directly by Fourier analysis if n' and n'' are assumed to be independent of the deformation frequency.

Kuhn and Künzle[20] measured the hysteresis under slow deformation cycles and the rate of creep under a steady load for one sample of vulcanized rubber, and found good agreement with the predictions of eq. (7). Apart from these measurements, only those reported by Dunell and Tobolsky[19] are known to the author; they found approximate agreement for a large number of diverse materials.

Measurements of the rates of creep and recovery were obtained for a number of rubber vulcanizates in the course of the present work. It was considered of interest to measure hysteresis for the same materials also, and to compare the experimentally obtained values with those calculated from the rates of stress relaxation by means of eq. (7).

The average rates of stress relaxation, S, calculated from the measured creep and recovery rates in simple extension by using eqs. (2) and (3), are given in Table II for all the vulcanizates examined. The values of d calculated from them are also given in the table, together with experimentally determined values for two widely different frequencies of deformation. Good agreement is seen to obtain with the values determined at the lower frequency, the largest discrepancy being less than 20%. With this imprecision, which is comparable to the experimental error, the observed hysteresis clearly may be attributed to the same viscoelastic mechanism as is the stress relaxation. It seems likely that some part of the discrepancies found previously[19] may be due to the fact that the hysteresis measurements were carried out at deformation frequencies that did not correspond to the times under load used in the relaxation experiments. The measured hysteresis is not altogether independent of the frequency of deformation, as a comparison of the last two columns of Table II shows.

TABLE II
Hysteresis d and Rate of Stress Relaxation S

Vulcanizate	S, %/dec.	d(%), calc. from S	d(%), meas.: At 10^{-3} c.p.s.	d(%), meas.: At 10^{-1} c.p.s.
A (natural rubber)	0.98	0.67	0.65	0.45
B ,,	1.40	0.95	0.85	0.83
C ,,	1.74	1.18	1.35	2.25
D ,,	1.76	1.20	1.15	1.45
E ,,	2.74	1.86	2.15	2.35
F ,,	6.15	4.20	3.6	6.3
G (butadiene–styrene copolymer)	9.60	6.55	5.6	10.5

V. DISCUSSION

Related Observations

The experiments have revealed considerable differences in the amounts of creep, recovery, and stress relaxation in the same time interval, for different types of deformation. The differences have been shown to arise solely from nonlinear elastic behavior, and good quantitative agreement has been obtained on the assumption that the rate of stress relaxation is invariant with amount or type of deformation. A number of different observations may be accounted for by these conclusions.

Cooper[9] has reported that the rates of creep in vulcanized rubbers are higher in simple extension, and lower in compression, than in simple shear. These findings are in accord with the treatment given in Section II, if the rate of stress relaxation is assumed constant. Kohlrausch,[21] in a series of experiments with a stretched rubber thread, observed deviations from "congruency" at the larger extensions, the amount of recovery that took place a short time after removing the load being greater than the corresponding deflection after the same period under load. This effect was observed in the present work (see Fig. 1, for example), and arises directly from the nonlinear elastic behavior in extension, as Kohlrausch himself surmized.

Scott Blair and Burnett,[22] in experiments on a renneted milk gel, observed the opposite effect. They found the recovery to be considerably smaller a short time after unloading than was the deflection at a similar time after imposing the load. However, the material they used is described as showing "strain stiffening," which might be understood as an increasing stiffness as the deformation increases. This form of nonlinearity is the opposite of that shown by rubber in tension, so that a reversal of effect would not be unexpected.

Amount of Set

Permanent set appears to be extremely small in the rubbers examined, the recovery being substantially complete after a period of recovery equal to that for which the load or deformation was maintained. After a smaller interval t, an amount of set e_t would be observed, equal to the recovery which has still to take place. To a first approximation, therefore, if linear recovery with log time is assumed to hold to completion,

$$e_t = R \log t_1/t$$

where t_1 is the time for which the load or deformation was imposed. Quite large values of "set" may thus be obtained for rubbers that would eventually recover completely.

The British Standards method of test for compression set,[23] and that specified by the American Society for Testing Materials,[24] both involve a measure which is made a comparatively short time after releasing the testpiece from a compressive deformation maintained for many hours. In the British Standards test, for example, a recovery period of 10 min. is recommended, after release from a compressive deformation imposed for 24 hr. The amount of set expected would therefore be

$$e_t = 2.16\,R$$

From the imposed compression (of 25%) a value of B may be calculated by means of eq. (6), on the assumption that the material obeys eq. (4) in compression. The values obtained vary from 1.37 to 1.60 as the ratio T of the elastic constants varies from 0 to 1. The measured set is therefore about $3S$, where S is the rate of stress relaxation. In fact, the test affords a relatively sensitive means of measuring the relaxation rate for rubbers capable of complete recovery.

Conclusions

The experiments have confirmed previous observations that the creep of vulcanized rubbers at normal temperatures is approximately proportional to the logarithm of the time under load, in the range 10^{-1} to 10^4 min. However, the rate has been found to vary considerably, with both the magnitude of the load and the type of deformation imposed. This has been shown to arise from nonlinearity of the load–deformation relationships. Good agreement has been obtained between the measured rates and those calculated from a simple theoretical treatment, when the rate of stress relaxation is assumed invariant with amount or type of deformation.

On removal of the load at the conclusion of a creep experiment, almost complete recovery occurs after a time equal to that for which the original deformation was maintained. The rate of return to the undeformed state varies with the amount and type of the original deformation, but the measured rates are again found to be in good agreement with those calculated on the assumption that the corresponding rate of stress relaxation is independent of the amount or type of deformation and equal to that deduced from the creep measurements.

In this case, the appropriate stress is that generated by a forced return to the undeformed state. Since the relaxation rate deduced for it is equal to that governing the creep process, the relaxation process can be described as "symmetrical," i.e., it follows an identical time dependence whether the deformation is imposed or removed.

Symmetry in this sense is not a general property of relaxing systems. It would not be shown in relaxation due to deterioration of the vulcanizate structure, for example, or by a model Maxwell element, except in the final stages of relaxation. However, the present experiments are concerned with the later stages of relaxation only, and the symmetrical nature of the relaxation would not be unexpected for an array of Maxwell elements in these circumstances. Such an array has been successfully employed to represent the viscoelastic behavior of rubbers in the transition from a glassy to a rubbery state.

It appears, therefore, that the present process is a physical one, consisting of the final stages of the attainment of equilibrium in the crosslinked network, probably by the slow rearrangement of molecular chains or aggregates. The process has been shown to be recoverable and reproducible, as this understanding would require.

The rate of stress relaxation under moderate deformations has been confirmed, by direct measurement, to be substantially independent of the amount of deformation. It may thus be considered a more fundamental measure of the process.

Values of hysteresis for a number of vulcanizates have been shown to be in satisfactory accord with those calculated from the relaxation rates. It appears, therefore, that the same relaxation process is concerned in the phenomena of creep, recovery, stress relaxation, and hysteresis.

APPENDIX

The following mix formulations and vulcanization conditions were employed in preparing the test pieces. The amount of each ingredient is given in parts by weight.

	A	B	C	E	F	G
Natural rubber (smoked sheet)	100	100	100	100	100	—
Butadiene–styrene copolymer (75:25, Polysar S)	—	—	—	—	—	100
Zinc oxide	5	5	5	5	5	5
Stearic acid	1	1	1	1	0.5	1
CBS	1.5	0.75	—	—	—	0.8
MBT	—	—	0.75	—	0.3	—
TMT	—	—	—	3	—	—
Sulfur	4	2.5	3	—	1.5	2
Phenyl-β-naphthylamine	1	1	1	1	1	1
Vulcanization time, min. at 140°C.	20	30	45	50	40	50

CBS = N-cyclohexyl benzthiazyl sulfenamide. MBT = mercaptobenzthiazole. TMT = tetramethylthiuram disulfide. D was prepared as E and extracted for 24 hr. with hot acetone, after vulcanization. H was identical with G except for a shorter vulcanization period, of 40 min.

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Synopsis

An experimental study is described of stress relaxation, creep, recovery, and hysteresis in vulcanized rubbers under moderate deformations. The measurements indicate that the rate of stress relaxation is substantially independent of the amount or type of deformation for moderate deformations, and is simply related to the hysteresis. The rates of creep and recovery are found to be in good agreement with values calculated from the form of the load–deformation relationship and the (constant) value of the relaxation rate.

Résumé

Une étude expérimentale du relâchement de tension, du fluage, de la récupération et de l'hystérèse dans les caoutchoucs vulcanisés sous des déformations modérées est décrite. Les mesures indiquent que la vitesse de relâchement de tension est essentiellement indépendante du taux ou du type de déformation pour des déformations modérées et se trouve en relation simple avec l'hystérèse. On a trouvé que les vitesses de fluage et de récupération s'accordent bien avec les valeurs calculées à partir de la forme de la relation charge-déformation et de la valeur (constante) de la vitesse de relâchement.

Zusammenfassung

Es wird eine experimentelle Untersuchung der Druckrelaxation, des Fliessens, der Spannungsrückbildung und Hysterese an vulkanisierten Kautschukarten unter mässigen Deformationen beschrieben. Die Messungen zeigen, dass die Geschwindigkeit der Druckrelaxation im wesentlichen vom Betrag und Typ der Deformation bei mässigen Deformationen unabhängig ist und in einfachem Zusammenhang mit der Hysterese steht. Weiters wurde gefunden, dass die Fleiss- und Rückbildungsgeschwindigkeiten mit den aus der Form der Beziehung zwischen Belastung und Deformation und aus dem (konstanten) Wert der Relaxationsgeschwindigkeit berechneten Werten gut übereinstimmen.

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