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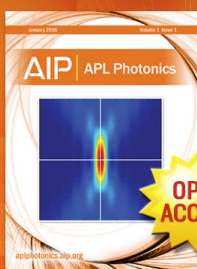Phys. Fluids A 1, 1133 (1989); 10.1063/1.857338

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Systems Manifesting Superposed Elastic and Viscous Behavior*

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Actual substances exhibit a very complicated behavior under mechanical stresses which cannot be described by classical elasticity theory nor by the classical theory of the hydrodynamics of viscous fluids. A general molecular theory describing the behavior of matter under stress is discussed and related to previous investigations and to experimental observations. Particular attention is devoted to rubberlike substances for which the classical theories are definitely inadequate. Experimental results on relaxation and creep of rubbers are interpreted in terms of modern structural concepts. It is found that these substances exhibit three regions of stress-temperature-time dependence. At intermediate temperatures there exists a region of relative stability in which the statistical-thermodynamic theory of rubber elasticity is valid. At elevated temperatures relaxation and creep are caused by chemical changes involving the rupture and formation of primary valence bonds. These chemical changes, which are responsible for the aging of rubber, can be isolated and studied by appropriate experimental techniques. At low temperatures relaxation and creep are caused by the slipping of secondary interchain bonds which are breaking and reforming in times comparable to experimental times of measurement. Theories are advanced to explain the observed stress-temperature-time behavior of rubbers over the entire temperature range studied.

THE theory of the mechanical behavior of deformable substances is divided into three parts. First there is the geometrical problem of defining the state of strain in a body. This problem has been solved in terms of the strain tensor for the case of small deformations. Secondly, there is the dynamical problem of defining the state of stress in a body and of extending Newton's laws of motion to derive equations of motion and equilibrium for non-rigid matter. Finally, it is necessary to postulate relationships between the components of the strain tensor and the components of the stress tensor. It is this aspect alone which relates to the specific nature of the substance involved. The classical theory of elasticity, which in certain ranges of deformation, temperature, and frequency applies very closely to the mechanical behavior of crystalline solids, is characterized by the assumption of Hooke's law which states that there is a linear relation between the components of stress and the components of strain. The classical theory of hydrodynamics, which applies very closely to the mechanical behavior of simple liquids and gases, is characterized by the assumption of Newton's viscosity law, which states that there is a linear relation between stress and rate of strain.

However, a very wide class of substances exhibits mechanical behavior in which elastic and viscous behavior are clearly superposed. Many of these substances, including rubbers, fibers, plastics, leathers, glasses, muscle tissue, and wood, are of great commercial or biological interest because of their complex mechanical behavior. The classical physicists, including illustrious men such as Maxwell and Boltzmann, were not unaware of the importance and theoretical interest attached to substances exhibiting superposed elastic and viscous behavior, and a classical theory for these phenomena was formulated.

Nearly a century ago Maxwell postulated an equation for one type of superposed elastic-viscous behavior, namely, the relaxation of stress in substances held at constant deformation, which phenomenon is particularly noticeable in substances such as pitch. The so-called Maxwell relaxation equation is:

$$\frac{ds}{dt} = \frac{1}{G}\frac{df}{dt} + \frac{1}{\eta}f, \qquad (1)$$

where ds/dt is the rate of strain, f is the stress, G an elastic modulus, and η a coefficient of vis-
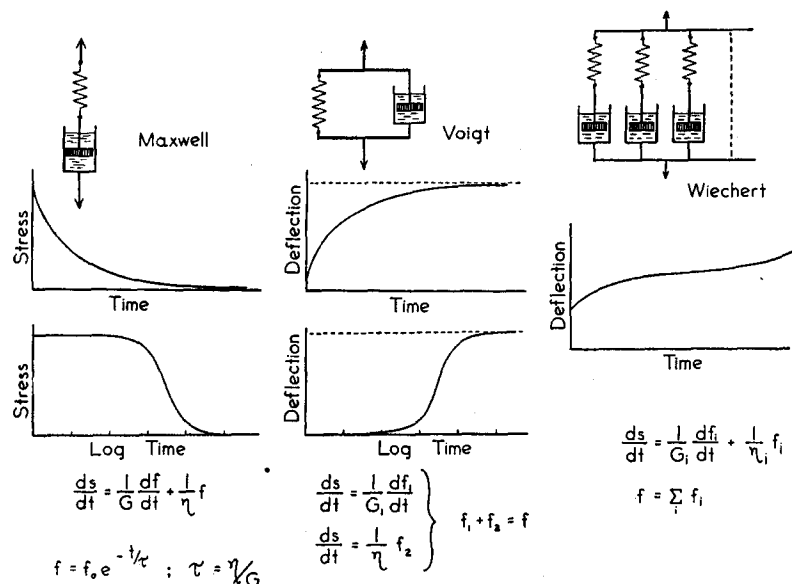
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FIG. 1. Mechanical models of matter.

cosity. This equation corresponds to a mechanical model consisting of a spring and dashpot in series which we shall henceforth call a Maxwell element. If the strain is held constant ($ds/dt=0$) then the decay of stress at constant strain can be found by integrating Eq. (1) giving

$$f=f_0e^{-t/\tau}; \quad \tau=\eta/G, \tag{2}$$

where f_0 is the initial stress (at time $t=0$) and τ, the relaxation time, is defined as above.

The mechanical model corresponding to Maxwell's relaxation equation and graphs of the stress decay function plotted against linear and against logarithmic time are shown in Fig. 1.

The Maxwell theory is incomplete because it fails entirely to account for the phenomenon of creep under constant stress (or constant load). This behavior of matter can be readily paralleled by a mechanical model first introduced by Voigt, in which an elastic element (spring) and viscous element (dashpot) are placed in parallel. This, of course, corresponds to a linear differential equation for each element as shown in Fig. 1, the stress dividing itself in each member in such a way that the rate of strain is the same in each. In Fig. 1 are shown the differential equations corresponding to the Voigt model, and the deflection vs. time curves obtained from these equations. The Voigt theory is also incomplete

because it does not account for relaxation of stress at constant elongation.

A theory that includes as special cases the results of the Maxwell and Voigt theories was proposed by Wiechert. The mechanical model suggested by Wiechert is simply a large number of Maxwell elements placed in parallel as shown in Fig. 1. Mathematically, this corresponds to a system of linear differential equations of the Maxwell type, the rate of strain appearing in each equation being the same throughout the system, and the partial stresses appearing in each equation each being an aliquot portion of the total stress. Each equation can be specified by a relaxation time, and in the general case an infinite number of Maxwell elements can be used by specifying a distribution of relaxation times.

It can be readily seen that this type of generalized theory can "explain" very complicated elastic-viscous behavior. However, the theory cannot be regarded as satisfactory without a sound molecular basis for interpreting the constants appearing in the equations in terms of the detailed structural theories of matter. Moreover, the assumptions concerning the linearity of the relations between stress and strain and stress and rate of strain need to be re-examined.

New interest in problems of general rheology

was awakened by the commercial development of synthetic rubbers, fibers, plastics, etc., whose physical properties could be controlled by various polymerization methods. This, together with new information and theories concerning the structure of polymeric materials, led to attempts to give specific meaning to the "springs" and "dashpots" of the classical theory in terms of the structural features of particular substances. Among the workers in this field were W. Kuhn, H. Mark, H. Leaderman, R. Simha, P. Kobeko, A. Lazurkin, J. D. Ferry, and many others. Simultaneously a deeper insight into the nature of molecular relaxation processes was achieved through the work of P. Debye, L. Prandtl, R. Becker, J. Frenkel, H. Eyring, R. Barrer, and other workers. Finally, in the field of rubberlike or high elasticity, a sound approach was provided by the work of H. Mark, K. H. Meyer, E. Guth, H. M. James, F. T. Wall, L. R. G. Treloar, and P. J. Flory.

It is impossible to detail the work of the various writers and workers in the field of elastic-viscous phenomena. Furthermore, inasmuch as the subject is still in a stage of rapid development, it is not possible to attain a proper perspective of the field as yet. For these reasons the following discussion will be restricted to work with which the authors have been directly connected: theoretical work of the senior author with Professor H. Eyring of Princeton University, and joint ex-
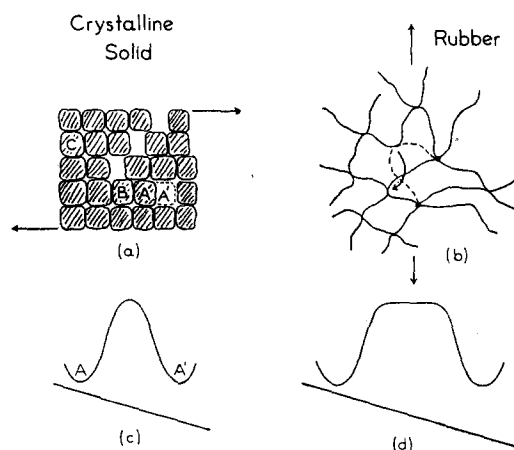

FIG. 2. Elastic-viscous processes.

perimental-theoretical researches of both authors with Dr. J. H. Dillon and Mr. I. B. Prettyman of the Firestone Tire and Rubber Company, and Mr. R. B. Mesrobian and Mr. T. E. Allen of Princeton. The work of other authors is referred to only as it contributes directly to the single viewpoint adopted here.

ELASTIC-VISCOUS PROCESSES

The molecular processes that give rise to macroscopic elastic-viscous phenomena depend on the particular structural features of each new class of substances studied, but there are nevertheless certain underlying similarities in the ele-

$$\frac{ds}{dt} = \frac{1}{m\lambda_i}\frac{d\phi}{dt} + \frac{\lambda}{\lambda_i}k'\left[\exp\left\{\frac{\alpha\phi\lambda}{kT}\right\} - \exp\left\{\frac{(1-\alpha)\phi\lambda}{kT}\right\}\right]$$

$$\frac{ds}{dt} = \frac{1}{m\lambda_i}\frac{d\phi}{dt} + \frac{\lambda}{\lambda_i}k'\,2\sinh\frac{\phi\lambda}{2kT}$$

$$\phi = \frac{f}{N} \qquad k' = \frac{kT}{h}e^{-\Delta F^*/kT}$$

$$\frac{ds}{dt} = \frac{1}{mN\lambda}\frac{df}{dt} + \frac{\lambda}{\lambda_i}k'\,2\sinh\frac{f\lambda}{2NkT}$$

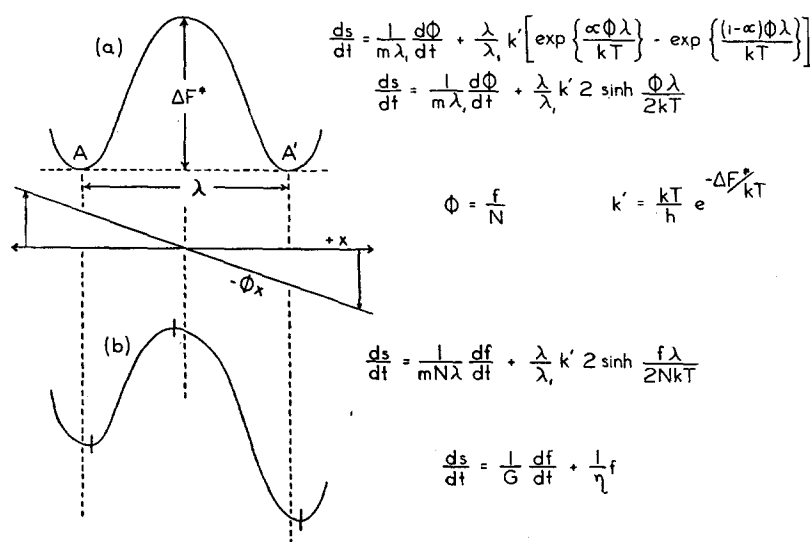$$\frac{ds}{dt} = \frac{1}{G}\frac{df}{dt} + \frac{1}{\eta}f$$

FIG. 3. Unit process of deformation.

mentary processes which are common to all condensed phases. It is necessary to idealize the situation and assume that in a body subjected to external stresses there exist certain regions of elementary molecular movements and readjustments to the stresses, that recur throughout the substance and are independent of the molecular movements in neighboring regions. We shall call the elementary process that occurs in such a region a "unit process of deformation," remembering that the motion of an atom, molecule, or group of atoms or molecules might be involved in this unit process. Figure 2 exemplifies the types of elastic-viscous processes that might occur in a crystalline solid and in substances such as rubber. Because of the external shearing stresses atom A in the crystal lattice might jump into the new position of equilibrium A', in addition to undergoing an immediate coherent change in the equilibrium distance to centers of neighboring atoms. It might also be that the unit process of deformation involves the two atoms A and B simultaneously moving to a new position of equilibrium. Not all unit deformation processes in the substance are alike. For example, in order for atom C, which is not near a defect, to jump to a new position of equilibrium, a large scale reorientation of neighboring atoms is necessary. Atom C will, however, move relative to other atoms because of the elastic shift of all lattice distances in the crystal under the action of the external shearing stress.

In Fig. 2 is also shown a typical unit process that occurs in polymeric networks such as rubber. Here too the external stress acts in two ways: It tends to uncoil elastically the portions of the molecular chains between network junctures, and at the same time it tends to cause a breaking and reforming in relaxed positions of the network junctures which are formed by secondary bonds between the chains.

For a quantitative formulation of the elastic-viscous behavior represented by a unit process of deformation, we imagine the atom or group of atoms involved in the unit process to be momentarily at rest and consider the free energy surface on which this atom or group of atoms moves. This free energy surface, shown in Fig. 2(c), arises, of course, from the interaction with neighboring atoms. At the instant under consideration the deformation unit is at equilibrium at point A

and therefore occupies a minimum position in a free energy well. At point A' another position of equilibrium is available and therefore point A' corresponds to another minimum in the free energy surface. Between A and A' the deformation unit must move through energetically unfavorable configurations which correspond to a free energy hill. The effect of stress is to subtract a linear potential gradient from the original free energy configuration.

UNIT PROCESS OF DEFORMATION

Consider a molecule at equilibrium in a potential well at point A next to a new equilibrium position at point A' (see Fig. 3). The potential curve will for mathematical simplicity first be assumed to be of the form

$$\frac{\Delta F^{\ddagger}}{2}\left(1 - \cos\frac{2\pi x}{\lambda}\right), \qquad (3)$$

so that $\Delta F^{\ddagger}$ will be the free energy of activation for movement from one equilibrium position to the next and λ will be the distance between successive equilibrium positions. The coordinate x will be taken in the direction in which the local force owing to the field of external stresses is acting. The effect of this force is to add a linear term $-\phi x$ to the potential surface in which the molecule moves, where ϕ is the local force and x is the distance. The new potential surface after addition of the stress gradient is shown in Fig. 3(b).

The rate of deformation is given by the sum of two terms: In the first place, the unit at A will, under the action of stress, shift its position in the free energy well to a new position of equilibrium at B. This shift will occur in phase with the stress, and will be the elastic component of the deformation. The amount of elastic shift is related to the curvature of the free energy well.

Secondly, there will be a jumping over the barrier from A to A' as well as in the opposite direction. The free energy of activation in the forward direction will be less than that in the backward direction as shown in Fig. 3(b). The resulting net rate of flow in the forward direction will also contribute to the rate of shearing.[1]

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[1] H. Eyring, J. Chem. Phys. **4**, 283 (1936).

In a previous publication[2] it was shown how the rate of strain resulting from the local force could be calculated exactly from the potential curve (3). The resulting expression is

$$\frac{ds}{dt} = \frac{\lambda^2}{2\pi^2 \lambda_1 \Delta F^{\ddagger}} \frac{d\phi}{dt} + \frac{\lambda^2 e^{-\Delta F^{\ddagger}/kT}}{\lambda_1 h} 2 \sinh \frac{\phi\lambda}{2kT}, \quad (4)$$

where ds/dt is the rate of strain, k is Boltzmann's constant, h is Planck's constant, and λ_1 is the root mean square distance between identical deformation units projected in a direction perpendicular to the plane over which the stress is considered.

For a more general free energy surface, which is, nevertheless, of the same general shape as shown in Fig. 3, the rate of strain is given by

$$\frac{ds}{dt} = \frac{1}{m\lambda_1} \frac{d\phi}{dt} + \frac{\lambda}{\lambda_1} k' 2 \sinh \frac{\phi\lambda}{2kT}, \quad (5)$$

where

$$k' = \frac{kT}{h} e^{-\Delta F^{\ddagger}/RT},$$
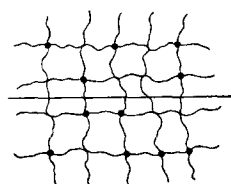
$$f = f_1 + f_2 + f_3$$

Primary Network Chains:

$$\frac{ds}{df} = \frac{1}{G_1} \frac{df_1}{dt} + n_1\lambda k' e^{f_1\lambda/2N_1kT}$$

Secondary network chains (interchain forces):

$$\frac{ds}{dt} = \frac{1}{G_2} \frac{df_2}{dt} + n_2\lambda k_2' 2 \sinh \frac{f_2\lambda}{2N_2kT}.$$

Segment motion (intra-chain forces):

$$\frac{ds}{dt} = \frac{1}{G_3} \frac{df_3}{dt} + \frac{1}{\eta_3} f_3.$$

FIG. 4. Mechanical behavior of polymers.

where m is the curvature of the potential barrier near the minimum. It is to be observed that m is the force constant describing the interaction between molecules. It is clear that the first term on the right in Eq. (5) represents an elastic deformation, while the second term is a term representing flow.

In actual substances the structural features are such that we can classify together a number of unit processes of deformation, calling these

[2] A. V. Tobolsky, R. E. Powell, and H. Eyring, *Frontiers of Chemistry: The Chemistry of Large Molecules* (Interscience Publishers, Inc., New York, 1943), Chapter V.

processes of type i. Let there be ν_i such processes per unit volume. In general we shall wish to consider the effect of stress across a given plane of the medium. The direction perpendicular to this plane will be taken as the Z direction, and the total stress localized on the ith type of units will be called f_i.

Let the root mean square value of the projected distance along the Z axis between neighboring regions where processes of type i are occurring be λ_{1i}. Then it will be assumed that the local force on each process of type i is given by

$$\phi = \frac{f_i}{N_i}, \quad \text{where} \quad N_i = \nu_i \lambda_{1i}. \quad (6)$$

This assumption is valid if the total stress on each of the ith type of deformation units is distributed uniformly among these units.

Having established the very general rheological equations for the unit process of deformation, it remains necessary to specify the manner in which the external stress divides between various units, and how the macroscopic rate of strain relates to the rate of strain for the deformation units. For this the reasonable assumption is made that the medium retains the identity of its microscopic features under stress or deformation; in other words, it is assumed that the stress divides itself among the deformation units in such a way that the rate of strain is the same for each and equal to the macroscopic rate of strain. This is equivalent to the basic assumption of the Wiechert model. The general elastic-viscous equations from Eqs. (5) and (6) are

$$\frac{ds}{dt} = \frac{1}{m_i\lambda_{1i}} \frac{d\phi_i}{dt} + \frac{\lambda}{\lambda_1} k' 2 \sinh \frac{\phi_i\lambda_i}{2kT} \quad (7)$$

$$i = 1, 2, 3 \cdots,$$

where

$$\phi_i = f_i/N_i; \quad f = \sum_i f_i,$$

and

$$k' = \frac{kT}{h} e^{-\Delta F^{\ddagger}/RT}.$$

The symbols have been defined in the previous section; the subscript i refers to the ith type of unit process of deformation.

The theory presented here is therefore similar to the Maxwell-Wiechert theory. The chief differ-
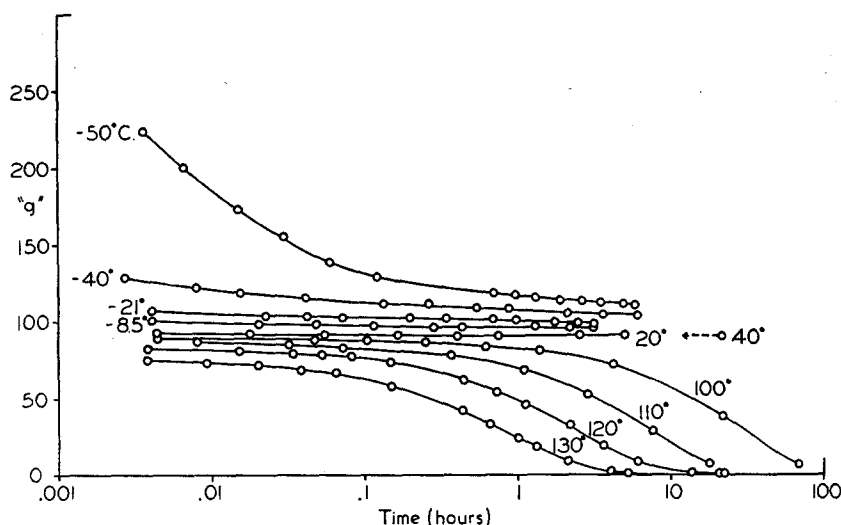
FIG. 5. "g" as a function of time for various temperatures; Hevea gum, 50 percent elongation.

ences lie in the fact that a non-linear flow term which becomes linear under the condition of small internal stress fields replaces the linear Newtonian flow term in Maxwell's equation, and the constants appearing in the equation are given specific molecular interpretation.

PHYSICAL PROPERTIES OF RUBBERLIKE MATERIALS

The general theory of superposed elastic-viscous behavior of matter presented in the previous sections must be supplemented by a detailed picture of the structural properties of the particular class of substances under consideration if useful application of the theory is to be made. In the remainder of this article we shall devote our discussion to polymeric materials in the rubbery state of aggregation—particularly natural and synthetic rubbers. These materials are characterized both by a long range and by a local structure. The long range structure is a polymeric network, the network junctures being composed of sparsely-occurring bonds between the coiled polymeric chains. These bonds may be primary cross links, or secondary interchain bonds such as dipole-dipole bonds or regions of local crystallinity. The portions of the network connecting contiguous network junctures are called network "chains." The local structure of the network is very similar to the local structure of liquids, the segments of the long chain molecules being in

continual, fairly rapid motion, moving from one equilibrium position to the next. It is desirable to construct a theory of the over-all physical properties based on molecular quantities such as the number of network junctures of a given type per unit volume, the strength of these cross-linking bonds, and the internal viscosity of the local liquid-like structure.[3]

To find the relations between rate of strain, stress, and rate of stress over a given plane direction in a deformed rubberlike material we imagine a planar cut passing through the material in that plane. This cut will pass through a large number of network chains, some of which are terminated by primary cross links and others by secondary cross links. Let us denote by N_1 the number of chains (henceforth called primary network chains) terminated by primary cross links per unit area of the planar cut, and let N_2 denote the number of chains (henceforth called secondary network chains) terminated by secondary cross links per unit area of the planar cut. In general there may be more than one type of secondary cross link so that classifying all secondary network chains together is a simplification. If s_1 and s_2 are the number of primary and of secondary network chains per unit volume, respectively, then n_1 and n_2, where

$$n_1 = s_1/N_1; \quad n_2 = s_2/N_2,$$

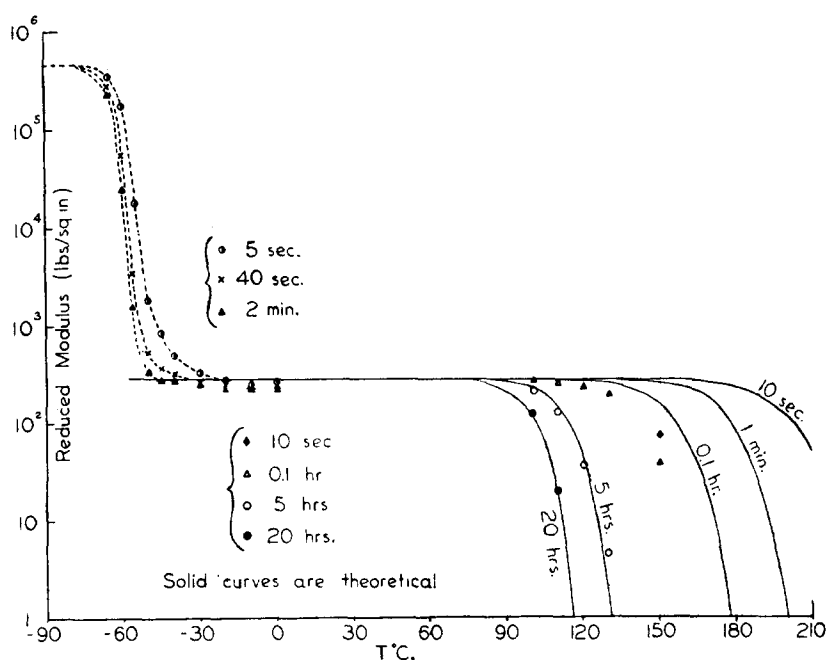[3] A. V. Tobolsky and H. Eyring, J. Chem. Phys. **11**, 125 (1943).

FIG. 6. Reduced modulus *vs.* temperature, Hevea gum.

are the reciprocal lengths between primary cross links and secondary cross links in the direction perpendicular to the planar cut.

The structural features described above are the deformation units in terms of which the elastic-viscous properties of these substances must be explained. The equations of motion for pure tension or pure shear for primary network chains and for secondary network chains in terms of the defined molecular quantities are shown in Fig. 4. The elastic term in these equations represents the uncoiling of network chains assuming that the terminal points (cross links) remain relatively fixed. The flow terms represent the contribution to the rate of deformation of rupturing processes at primary bonds along the chain which break the chains loose, and slipping processes occurring at the secondary cross bonds. The specific rate constants which appear in the equations of motion for primary network chains and for secondary network chains are defined by

$$k_1' = \frac{kT}{h} \exp\left(-\Delta F_1^{\ddagger}/RT\right);$$

$$k_2' = \frac{kT}{h} \exp\left(-\Delta F_2^{\ddagger}/RT\right);$$

where $\Delta F_1^{\ddagger}$ is the free energy of activation for the rupture of primary bonds, and $\Delta F_2^{\ddagger}$ is the free energy of activation for the breaking of secondary bonds. Generalization of these equations of motion to three-dimensional stresses and strains can be carried out readily.

A third type of unit process of deformation is included to account for the intra-chain motion of chain segments. These motions are such that the local environment of chain segments resembles the environment of molecules in the liquid state. This motion has a damping effect on the motion of the primary and secondary network chains as a whole, much as if a viscous liquid were pervading the network structure of the polymeric substance.

STATISTICAL THEORY OF ELASTICITY FOR RUBBER NETWORKS

The "high elasticity" of rubberlike substances is caused by the fact that under stress the "chains" between network junctures can uncoil.[4,5] In rubbers, for certain regions of temperature, the chains are very mobile, and as we shall see there

[4] F. T. Wall, J. Chem. Phys. **10**, 485 (1942).
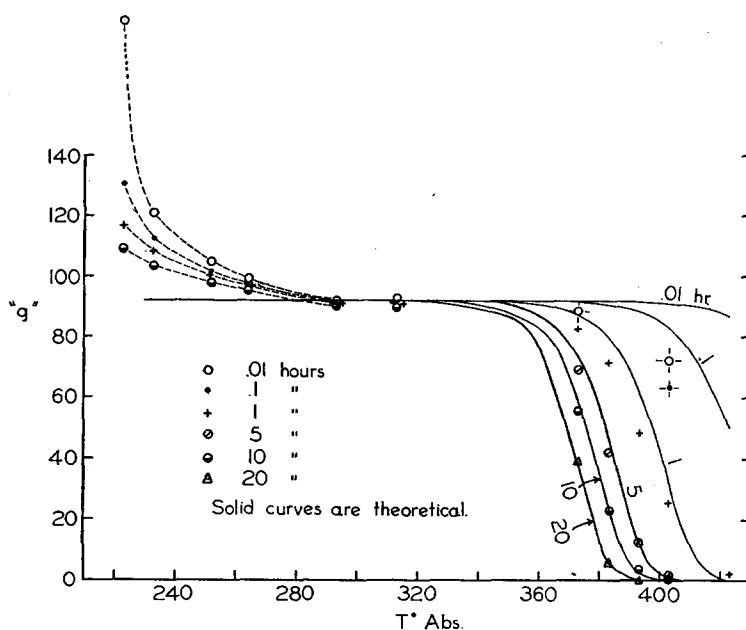[5] E. Guth and H. M. James, J. Chem. Phys. **11**, 455 (1943).

FIG. 7. "g" as a function of temperature for various times, Hevea gum.

is evidence that the internal energy of the network does not change as the network is stretched. The resistance to stretch is, therefore, caused by a decrease in entropy upon stretching, and this in turn is caused by the fact that the network chains can assume many more conformations in the unstretched state, where the distance between network junctures is small, than in the stretched state, where the distance between network junctures is larger.

From thermodynamics we can immediately derive the law

$$f = \left(\frac{\partial E}{\partial l}\right)_T - T\left(\frac{\partial S}{\partial l}\right)_T, \qquad (8)$$

where f is tension, l represents length, E is internal energy, S is entropy, and T is temperature. Inasmuch as the first term on the right-hand side of Eq. (8) is taken equal to zero, the equation of state can be derived if we can relate S to l. This is done by relating S to the probability P by Boltzmann's relation

$$S - S_0 = k \ln P/P_0, \qquad (9)$$

where P/P_0 represents the ratio of the probabilities (or ratio of total number of available configurations) for the stretched and unstretched networks.

The evaluation of the probabilities P and P_0 is accomplished by determining the number of ways that a coiling hydrocarbon chain can assume a projected length x between its ends along any direction in space. The stable configuration for successive bond directions is believed to be the staggered configuration. The meanderings of a hydrocarbon chain can be described as a continuous path on a diamond lattice, each path being equally likely if we neglect the effect of steric hindrance.

Suppose that the total number of carbon-carbon bonds in the chain is n, and the bond length divided by $\sqrt{3}$ is taken as the unit of length. The problem of the random walk on a diamond lattice turns out to be equivalent to the problem of finding the distribution in heads of a penny that is being tossed n times and has a $\frac{2}{3}$ probability of repeating its last flip.

The result of a rather lengthy calculation[2] is that the probability of a chain of n bonds having the projected length x along any direction in space is

$$p_n(x) = \frac{1}{2\sqrt{\pi n}} \exp\left(-x^2/4n\right). \qquad (10)$$

This formula can be directly applied to the the case where "ends" of the hydrocarbon chain
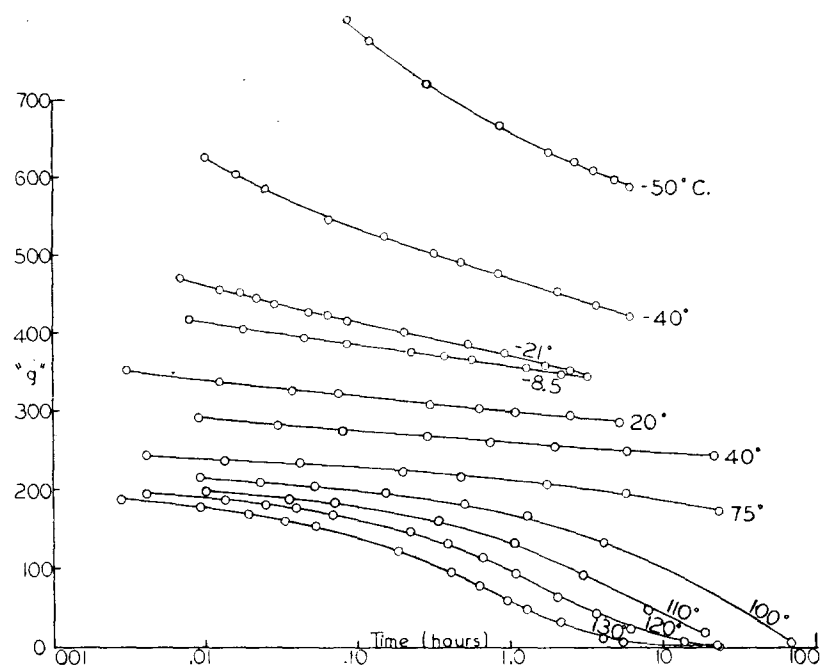
FIG. 8. "g" as a function of time for various temperatures, Hevea tread.

are successive juncture points in a polymer network. It is assumed that upon stretching there is a homogeneous change in the components of distance between successive network junctures throughout the rubber which is the same as the change in dimensions of the macroscopic sample. By averaging over all orientations and over all chains of the network, P/P_0 in Eq. (9) can be
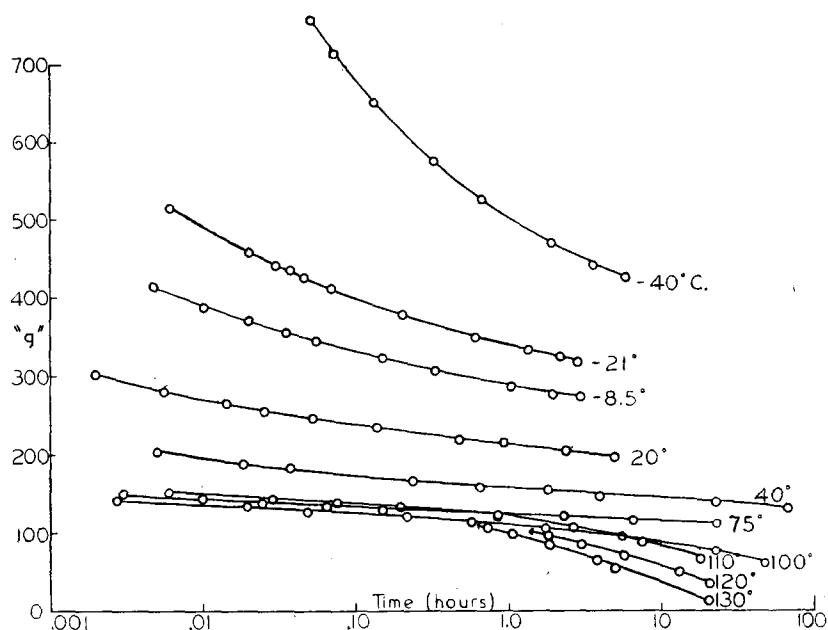

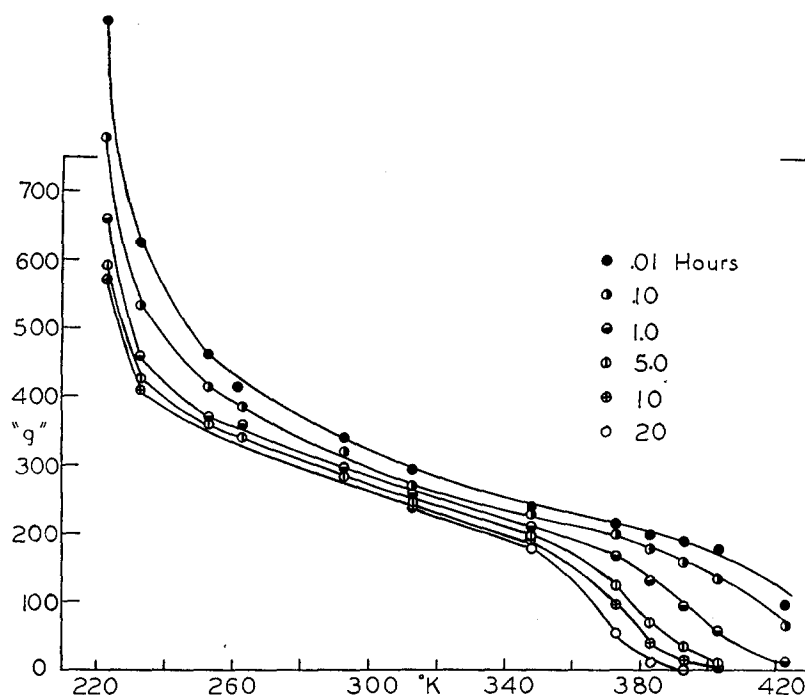FIG. 9. "g" as a function of time for various temperatures, GR-S tread.

FIG. 10. "g" as a function of temperature for various times, Hevea tread.

evaluated, and thereby the stress-strain curve at equilibrium can be derived.[4, 5] The result is:

$$f = skT\left\{\frac{l}{l_u} - \left(\frac{l_u}{l}\right)^2\right\}, \qquad (11)$$

where l_u represents unstretched length, l the equilibrium length at tension f, and s represents the number of network chains of all kinds per cc that remain unbroken and unrelaxed at the time of measurement.

The values of the elastic moduli G_1 and G_2 appearing in the equations of Fig. 4 can be expressed as follows from Eq. (11):

$$G_1 = 3s_1kT, \qquad (12)$$

$$G_2 = 3s_2kT, \qquad (13)$$

where s_1 and s_2 are as defined above: the number of primary network chains per cc and the number of secondary network chains per cc, respectively. G_3 appearing in Fig. 4 is an ordinary elastic modulus for crystalline substances (the modulus in the case that the temperature is sufficiently low for segment motion to be completely frozen). Usually G_1 has a magnitude of about 10^6-10^7

dynes/cm² for soft rubber, whereas G_3 is of the order of magnitude of 10^{11} dynes/cm².

We have presented above a theory based upon *a priori* considerations concerning stress-strain relationships and upon several assumptions regarding the structural characteristics of rubber-like polymers. In the succeeding sections we shall show how experimental results bear upon this theory, and also how these results suggest modifications and extensions of the theory.

STRESS-TEMPERATURE-TIME RELATIONS FOR NATURAL AND SYNTHETIC RUBBERS

An equation has been given in the previous section which relates the stress and the elongation of a rubber sample in terms of the concentration of network chains in the rubber and the temperature, as follows:

$$f = skT\left\{\frac{l}{l_u} - \left(\frac{l_u}{l}\right)^2\right\}, \qquad (14)$$

where f is the stress (calc. on original cross section), s is the number of network chains per cc of the rubber, k is Boltzmann's constant, T is the absolute temperature, l is the stretched
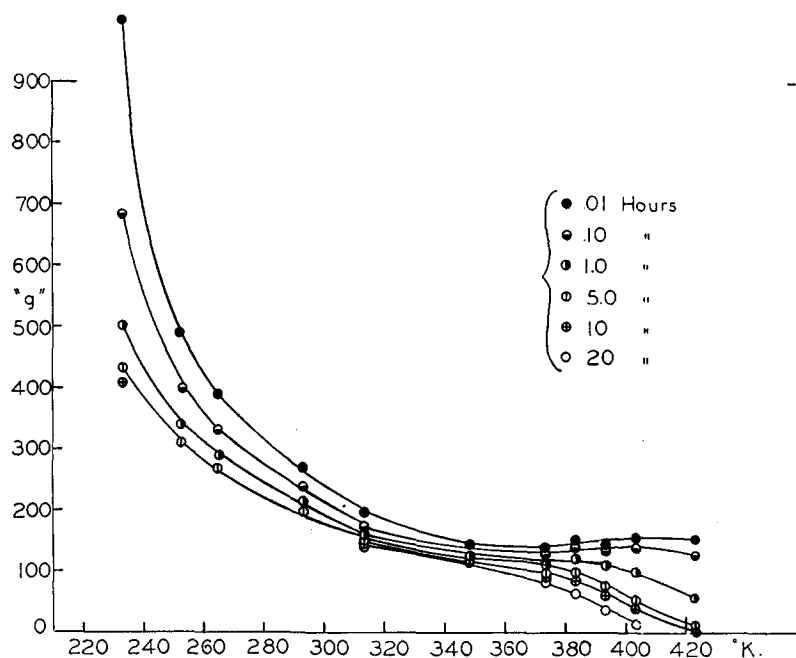
FIG. 11. "g" as a function of temperature for various times, GR-S tread.

length, and l_u is the unstretched length of the sample. Thus, according to this equation, any changes in the stress of a rubber sample held at constant temperature and constant elongation must be caused by changes in the number of network chains s per unit volume of the rubber that are effective in maintaining the stress. As can be seen from Eq. (14), changes in s can be measured in two ways: (1) one may keep the elongation l constant and measure the changes in f, or (2) one may keep f constant and measure the changes in l. The first method is referred to as "stress relaxation at constant elongation" and the second method as "tensile creep under constant load." Both types of measurement can be made in two different ways: First, one can keep the sample continuously elongated, or under load, as the case may be—this will be called the "continuous" method; or, one can elongate the sample or apply the load only momentarily when a measurement is taken, allowing the sample to remain unstretched at all other times—this will be called the "intermittent" method. Certain fundamental differences exist between the continuous and intermittent types of measurement, as will appear in the subsequent discussion.

Measurements of stress as a function of time

in rubber samples held at constant elongation ("continuous relaxation"), using a variety of different rubber types, and made over a wide range of temperatures,[6] have indicated that for both natural and synthetic rubbers three general temperature regions can be distinguished: (1) a low temperature region of rapid change of stress with time, (2) an intermediate temperature region in which there is practically no change in stress with time, (3) a high temperature region in which there is again a marked decay of stress with time.

The low temperature region is the region in which stiffening of the rubber is observed because of the stability of secondary bonds (van der Waals bonds) between network chains. The relaxation of stress occurring in this region has been postulated as owing to the relaxing of these secondary bonds in the network structure (such as dipole-dipole bonds, etc.) which are partially stable during experimental times (roughly from 10 sec. to 10 hours) in that temperature range, and thus are able to contribute to the stress. The secondary bonds supposedly break and then reform in new, unstressed positions (where they no longer con-

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[6] A. V. Tobolsky, I. B. Prettyman, and J. H. Dillon, J. App. Phys. 15, 380 (1944).
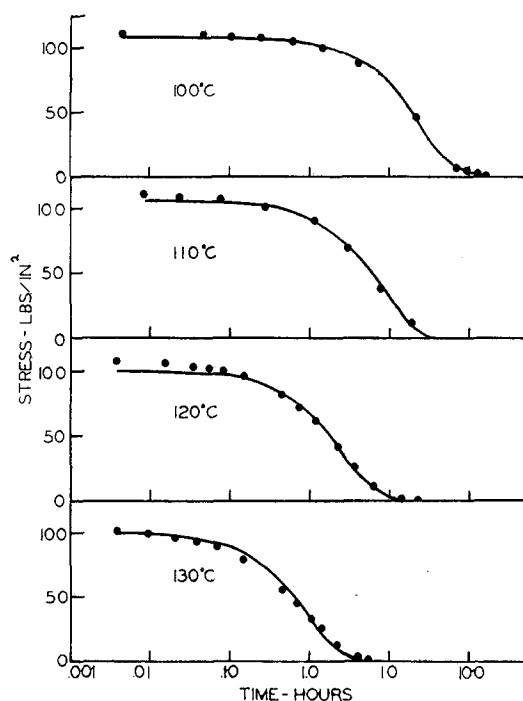
FIG. 12. Hevea gum stock; 50 percent elongation, theoretical curves, experimental points.

tribute to the stress) so that the changes occurring in the rubber during secondary bond relaxation are "reversible," and there is no permanent change in the rubber.

The high temperature region of instability of stress with time is that temperature region associated with "heat aging" phenomena—softening and hardening which permanently destroy the rubbery properties of the material. The relaxation of stress in this region is attributed to a definite chemical reaction which cuts chains by breaking primary valence bonds in the network structure; thus the changes in the rubber accompanying the relaxation of stress in this temperature region are not reversible, but cause a permanent deterioration of the network structure. This chemical scission reaction has been shown to require the presence of oxygen in order to occur, but only a slight amount of oxygen was found to be necessary.

In the intermediate temperature region secondary bonds are so unstable that they have all relaxed by the time the first stress reading can be taken, and the primary bond scission reaction is occurring so slowly that it produces no notice-

able effect during the experimental time. It is in this intermediate temperature region of relative thermodynamic stability that statistical and kinetic treatments of rubber elasticity, which do not take time effects into account, have their greatest validity.

If experiments could be carried out at low enough temperatures, one might expect to find a fourth temperature region—a very low temperature region where secondary bonds as well as primary bonds would be completely stable within experimental times, and therefore there would be no change in stress with time.

The first three temperature regions mentioned above can be seen in Fig. 5, where continuous relaxation data for Hevea gum over the temperature range $-50°$ to $+130°C$ are shown.* It will be noted that reduced stress, "g," has been plotted as the ordinate rather than the stress itself. The reason for this is that at a fixed elongation the stress is presumably proportional to the absolute temperature T as well as to the concentration of chains in the network s, as is seen from Eq. (14). Thus by eliminating the effect of temperature by "reducing" the stress values arbitrarily to 25°C (i.e., the stress f is multiplied by $298/T$ at each temperature T to give "g"), the stress values at different temperatures are then directly comparable in terms of s. There is considerable decay of stress observed in the low and high temperature data, whereas in an intermediate temperature range there is little change in stress with time. This is seen even more clearly in Fig. 6 where "reduced modulus" (modulus times $298/T$) at different fixed times is plotted against temperature. The ordinate could be changed to reduced stress simply by relabelling the ordinate scale (reduced modulus $= 2.985 \times$ reduced stress). The fact that the reduced modulus remains the same in this temperature range of stability means, of course, that the stress f is directly proportional to absolute temperature in this range. From this fact it can be proved thermodynamically that the assumption, made in all kinetic theories of rubber elasticity, that

the internal energy does not change when the rubber is stretched, is correct. Consider the thermodynamic relation

$$\left(\frac{\partial E}{\partial l}\right)_T = -T\left(\frac{\partial f}{\partial T}\right)_l + f. \qquad (15)$$

If f is directly proportional to T, then by substituting in Eq. (15) obviously $(\partial E/\partial l)_T$ is equal to zero.

The experimental data in this graph were obtained from two sources: The data at 0°C and below were obtained from what might be considered a modified form of continuous creep experiment which measures modulus as a function of time. The experimental method, which has been described elsewhere,[7] measures the bending of a horizontal bar sample, supported at the ends and with a weight applied in the center, as a function of time. These modulus data are undoubtedly not completely comparable with continuous relaxation data, although the 5-sec. modulus points should correspond at least roughly to the 5-sec. stress relaxation values. The modulus data were used here because they extend down to -65°C, where the effect of secondary bonds becomes very important in Hevea gum, and the modulus data give some idea of the magnitude of the secondary bond effect.[*] Dotted curves

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[7] J. W. Liska, Ind. Eng. Chem. **36**, 40 (1944).
[*] These data were kindly supplied us by Dr. J. W. Liska of the Firestone Physics Research Division, and have been more fully discussed by him at the June, 1944 meeting of the Division of High-Polymer Physics. We wish to thank Dr. Liska for extending this courtesy.

have been drawn through the experimental points and extrapolated to a maximum flat value toward which the points seem to be converging. This flat would be expected to extend all the way down to 0°K. In this very low temperature region (-273°C to about -75°C) the effect of secondary bonds is so predominant that, if the flat value is approximately correct, less than a tenth of one percent of the stress is to be attributed to primary bonds in the network, all the rest being caused by secondary bonds. In this temperature region the rubber is essentially a crystalline solid, showing no rubbery properties whatever.

The high temperature experimental points were taken from the stress relaxation curves of Fig. 5. The solid curves drawn to accompany the high temperature data were calculated theoretically from Eq. (16), which will be discussed later. It is seen that they agree excellently with the 5-hr. and 20-hr. experimental points. Figure 7, which is replotted entirely from the data of Fig. 5, shows essentially the same points of interest as Fig. 6.

The thing particularly to be noticed in these graphs is the clear separation between the three (possibly four) temperature regions which have been discussed particularly the intermediate temperature region of stability of stress (or modulus) with time, which is clearly set off from the low and high temperature regions of instability, and which extends from about -10°C to $+75$°C.

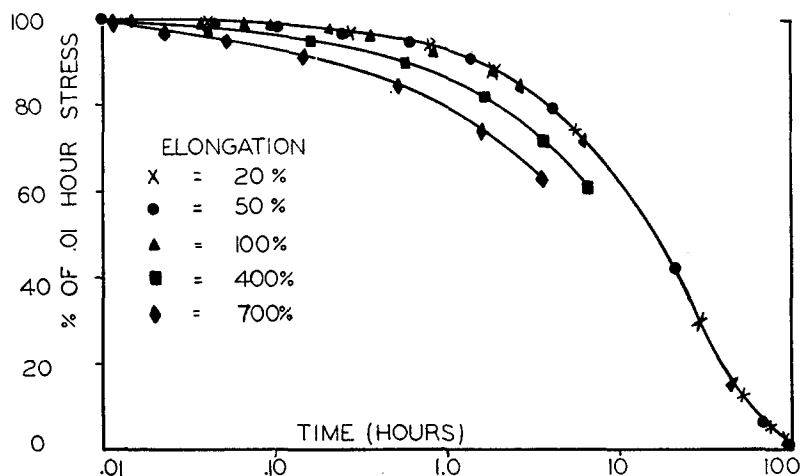In Figs. 8 and 9, stress relaxation data for

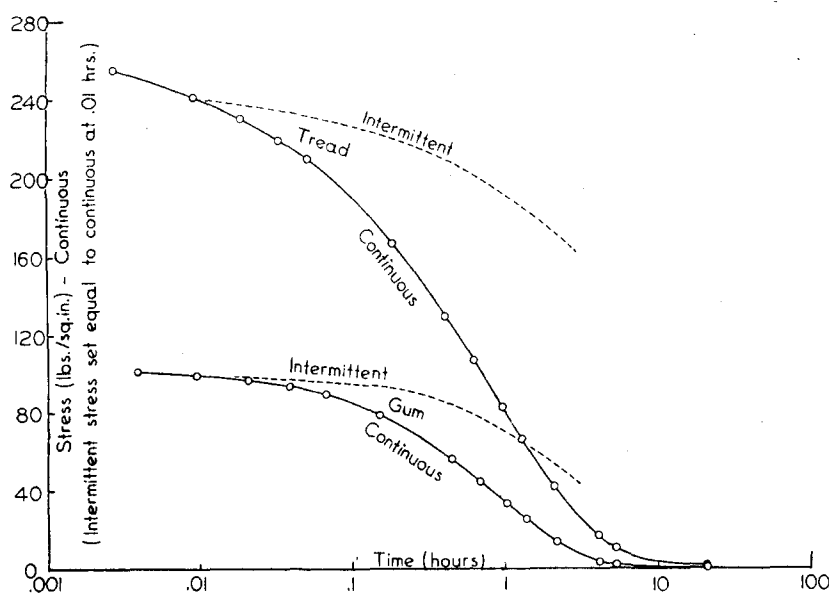FIG. 13. Effect of percent elongation on relaxation rate; Hevea gum—100°C.

FIG. 14. Continuous and intermittent stress relaxation; 50 percent
elongation; 130°C; Hevea stocks.

Hevea tread and GR-S tread are shown for the temperature range $-50°$ to $+130°C$ (the $-50°$ curve for GR-S tread is not shown because the "g" values are too high to appear on the graph). In Figs. 10 and 11 the data from Figs. 8 and 9 are replotted as "g" vs. temperature at different fixed times. The most striking thing to be noticed in these latter graphs is that in these rubber stocks the secondary bond relaxation region overlaps the primary bond relaxation region to a much greater extent than is the case for Hevea gum. There is no temperature region in which the stress does not change with time. However, one can distinguish a roughly defined region where the stress does not change greatly with time. This is the general rule rather than the exception; Hevea gum is unique among those rubbers studied in its wide, clearly defined temperature region of stress stability.

HIGH TEMPERATURE PRIMARY BOND PHENOMENA

The high temperature stress relaxation curves of Hevea gum are found to fit the simple unimolecular rate law:

$$f = f_0 e^{-k't}, \qquad (16)$$

where k' is of course the rate constant of the process, f is the stress at time t, and f_0 is the initial stress. The dependence of the relaxation rate on temperature is given by the equation

$$k' = \frac{kT}{h} e^{-\Delta F^{\ddagger}/RT} = \frac{kT}{h} e^{-\Delta H^{\ddagger}/RT} e^{\Delta S^{\ddagger}/R}, \qquad (17)$$

where k is Boltzmann's constant, T is absolute temperature, h is Planck's constant, R is the gas constant, $\Delta F^{\ddagger}$ is the free energy of activation, and $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ the heat and entropy of activation, respectively. It is found in fitting the experimental curves of Hevea gum that $\Delta F^{\ddagger} = 30.4$ kcal., and that the free energy of activation is entirely heat of activation, $\Delta S^{\ddagger}$ being equal to zero. The success with which experimental data can be fitted with Eqs. (16) and (17), taking $\Delta F^{\ddagger}$ equal to 30.4 kcal., is seen in Fig. 12, where experimental points and calculated curves are shown for Hevea gum at 100°, 110°, 120°, and 130°C.

Of all the various natural and synthetic rubbers studied, Hevea gum is the only rubber whose relaxation of stress curve follows the simple unimolecular decay law (16). Nevertheless, if the "relaxation rate constant" k' of these other rubbers at any temperature is taken as the reciprocal of the time at which $f/f_0 = e^{-1} = 1/e$ [as is properly true only of rubbers obeying
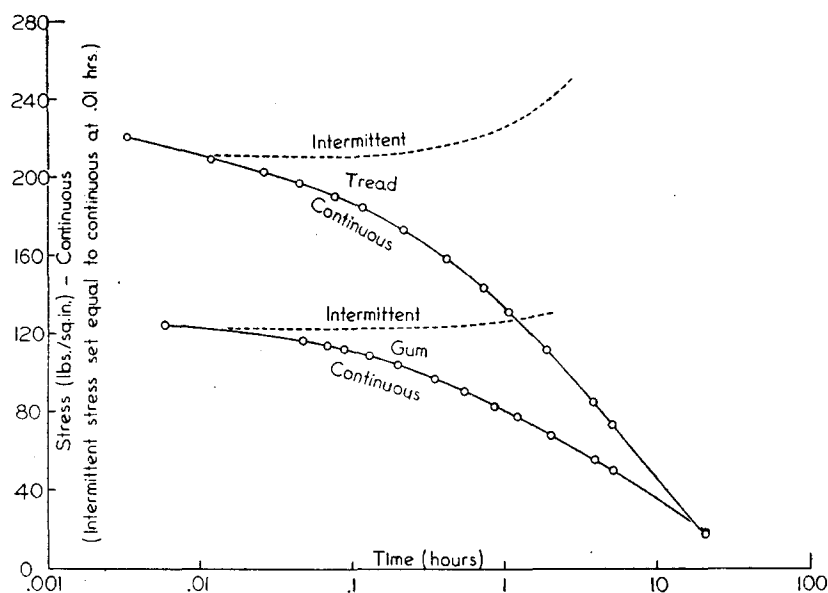
FIG. 15. Continuous and intermittent stress relaxation; 50 percent
elongation; 130°C; GR-S stocks.

Eq. (16)], it is found that the temperature dependence of the "rate" is given by Eq. (17), just as for Hevea gum. The values of $\Delta F^{\ddagger}$ obtained for these various rubbers all fall within the range 30.4 ± 2.0 kcal., with $\Delta S^{\ddagger}$ again equal to zero; and although these differences correspond to large practical differences in relaxation rates, the fact that $\Delta F^{\ddagger}$ is about the same in all cases suggests that the mechanism of relaxation is of the same type in all. As mentioned before, this high temperature relaxation mechanism has been shown to be a scission process occurring in the presence of oxygen. By carrying out the relaxation experiments in purified nitrogen (highly oxygen-free), the relaxation rates of both natural and synthetic rubbers could be reduced about 1000-fold. Also, in a continuous creep experiment on a natural rubber stock, carried out at 110°C in a vacuum of 10^{-5} mm of Hg, the creep rate was perhaps a thousand times less than that observed in air at the same temperature.

The effect of elongation on the relaxation rate is illustrated for Hevea gum in Fig. 13. It is seen that in the range of 20 percent to 100 percent elongation, the relaxation curves obtained are identical (the five curves have been set equal at 0.01 hr. to facilitate comparison), showing that elongation has no effect in this range. However, at 400 percent and 700 percent elongation, the rate of relaxation is seen to be increased, most so at 700 percent. A possible explanation for this is that at these very high elongations some of the molecular chains may have uncoiled to their maximum possible extent, and the valence angles of the carbon atoms in the chains are being strained, which makes it easier to break the chains.

The general shape of the relaxation curve is characteristic of the rubber being used. The curves of the other rubbers are in every case more spread out in a log time plot than the unimolecular relaxation curve of Hevea. By comparing the relaxation curves of various gum stocks with the curves of the corresponding tread stocks, one finds that the presence of carbon black in the vulcanizate has comparatively little effect on the relaxation rate. The main effect of the carbon black is to increase the magnitude of the stress (see Figs. 14 and 15). The relaxation rate can be definitely slowed down, however, by the addition of antioxidant to the vulcanizate, the difference in rates being perhaps a factor of three or four. On the other hand, changing from sulphur to non-sulphur cures does not markedly affect the relaxation curves.

After this brief discussion of the main characteristics of relaxation curves obtained by the "continuous" method (constant elongation), we
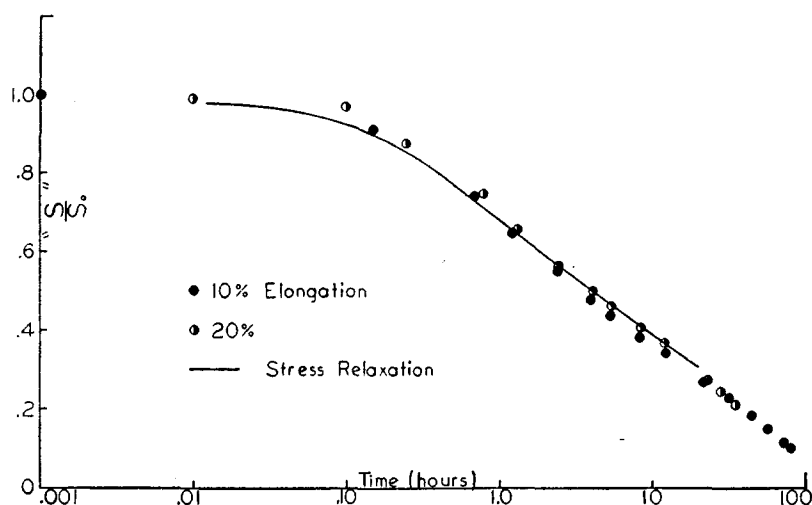
FIG. 16. Continuous creep; Butyl gum 120°C.

now turn to a consideration of "intermittent" relaxation curves. These intermittent stress relaxation measurements are really simply periodic measurements of the modulus of the sample, and the curve obtained could be called a "modulus vs. time" curve instead of an "intermittent stress relaxation" curve if one so desired. The thing immediately noticed in examining the intermittent relaxation curves is that the intermittent curve differs markedly from the continuous curve of the same rubber (see Figs. 14 and 15). In the continuous relaxation curves the stress always decreases continuously, and eventually reaches zero if the experiment is carried out for a long enough time. In the intermittent curves a remarkable variety of behavior is observed: The stress may decrease regularly, or increase regularly from the beginning; the stress may remain practically constant for a time, then begin to increase, or decrease; and in one case (Hevea at 100°C) the stress was observed to decrease initially, reach a minimum, and then increase. It is observed, in comparing the continuous and intermittent relaxation curves of any rubber, that the stress values of the intermittent curve are always greater than the stress values of the continuous curve; even when the continuous stress has decayed to zero, there is usually a sizable stress at that time in the intermittent curve. This accords with the observation that in those rubbers whose intermittent curve increases with time, when the stress has

decayed to zero in a sample held at constant elongation, the sample is actually found to be very hard, with an extremely large modulus. This might seem rather surprising, since from Eq. (14) one would expect that when the stress had decayed to zero, there would be no network chains s left in the rubber, and the rubber sample would be very soft with no elasticity remaining. An increase or decrease of stress in the intermittent curve corresponds to the hardening or softening which one observes in examining the rubber sample, since the experiment is simply a periodic measurement of the modulus.

Apparently the explanation of these various observations is that at high temperatures *two* reactions are occurring simultaneously in the rubber: one a scission or breaking of molecular chains, and the other a cross linking of chains. The two reactions are competing with each other, and the intermittent curve measures the *net* change in the number of network chains per cc of the rubber, resulting from the combined effect of both reactions. But apparently the new network chains formed by cross linking are always formed in relaxed, equilibrium configurations, so that their formation does not increase the stress of a sample being held at constant elongation. For this reason the continuous relaxation curve is completely unaffected by the cross-linking reaction, measuring only the cutting of those network chains supporting the stress (i.e., those chains originally present in the rubber). Thus

the continuous relaxation curve isolates the scission reaction, while the intermittent relaxation curve measures the net effect of both reactions. The intermittent relaxation curve indicates whether scission or cross linking is predominating in the rubber. The intermittent stress values constantly increase in GR-S, which indicates that cross linking predominates over scission in GR-S from the beginning. The intermittent curve of Butyl decreases rapidly after a period of slight decrease, indicating that scission predominates in Butyl. In Hevea the intermittent curve first decreases, then increases, which indicates that scission predominates initially, but is eventually overtaken by cross linking. These trends correspond exactly to the observations that GR-S hardens, Butyl softens, and Hevea first softens, then hardens in heat aging.

Continuous and intermittent creep measurements made at high temperatures are also to be interpreted in terms of the scission and cross linking of the rubber molecules.[8] Intermittent creep measurements are, like intermittent relaxation measurements, simply a periodic measurement of the modulus of the sample, made in an alternate way. Both intermittent creep and intermittent relaxation data give the same curve when they are plotted in an equivalent way, and, of course, measure the same quantity—the net

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[8] R. B. Mesrobian, R. D. Andrews, and A. V. Tobolsky, incorporated in Senior Thesis of Mr. R. B. Mesrobian, Princeton University (1944).

result of cross linking and scission. The most satisfactory way to plot relaxation and creep data in an equivalent way is to plot s/s_0 as the ordinate for both—the number of chains per cc of the rubber at time t divided by the number of chains per cc at zero time. Both types of data can be cast into this form by use of Eq. (14). At zero time we may write that

$$f_0 = s_0 kT \left\{ \frac{l_0}{l_u} - \left(\frac{l_u}{l_0} \right)^2 \right\}, \qquad (18)$$

where the zero subscripts indicate zero time. Correspondingly at time t:

$$f = skT \left\{ \frac{l}{l_u} - \left(\frac{l_u}{l} \right)^2 \right\}. \qquad (19)$$

To obtain s/s_0 we now divide (19) by (18), transpose all but s/s_0 to the other side, and cancel where possible. For stress relaxation, both continuous and intermittent, $l = l_0$ and so we obtain the simple expression

$$s/s_0 = f/f_0. \qquad (20)$$

The significance of s is not the same in the two cases, however: In the intermittent data s signifies the total number of network chains per cc of the rubber at time t; in the continuous data s is the number (per cc) of those network chains present in the rubber at zero time which still remain uncut at time t. The significance of s_0
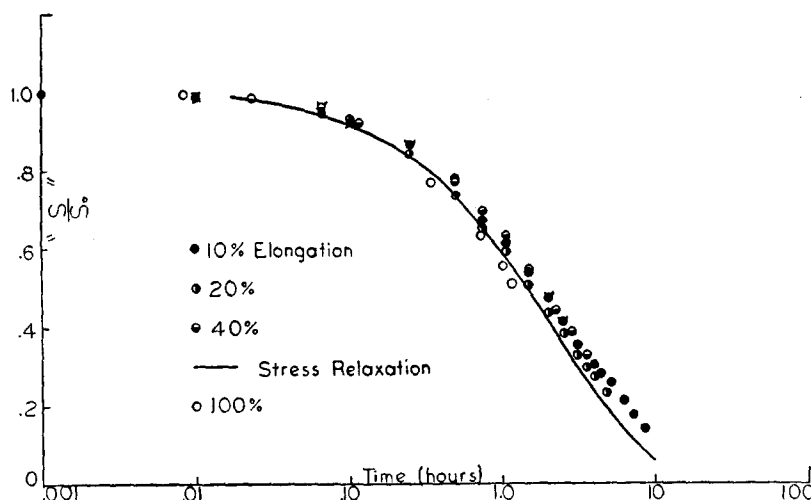

FIG. 17. Continuous creep; Hevea gum 120°C.

is the same for both: The total number of network chains per cc of the rubber at zero time.

For "creep under constant load," both continuous and intermittent, remembering that $f=f_0$, we obtain from Eqs. (18) and (19) the expression

$$s/s_0 = \left\{ \frac{l_0}{l_u} - \left(\frac{l_u}{l_0}\right)^2 \right\} \bigg/ \left\{ \frac{l}{l_u} - \left(\frac{l_u}{l}\right)^2 \right\}. \quad (21)$$

Here s/s_0 for intermittent creep has the same significance as for intermittent relaxation. In continuous creep, however, a complication enters. If only scission were taking place in the rubber the continuous creep curve would be identical with the continuous relaxation curve (in fact, all four types of curve would be identical). But cross linking is always taking place at the same time; and although the new chains are in unstressed, equilibrium configurations at the moment of formation, the elongation of the rubber is constantly increasing, and as soon as the elongation becomes greater than that at which any chain was formed, that chain begins to help support the load. The contribution of these new chains to the stress, however, is not as great as that of the chains originally present in the rubber; this is because the l_u of these chains is the elongation of the sample at which they were formed rather than the original unstretched length of the sample, and l/l_u for these chains at any particular l is therefore less than the l/l_u for

the original chains. Thus the cross linking has a retarding effect on the creep rate, and from the considerations given above we would expect the continuous creep curve to be slightly slower than the continuous relaxation curve, the divergence being greatest in those rubbers in which the cross-linking reaction is most marked. This is found experimentally to be the case. Continuous creep data for Butyl, Hevea, and GR-S are shown in Figs. 16 to 20. Since the continuous creep curve measures principally scission, but does reflect to some extent the cross linking going on at the same time, the ordinate is labelled "s/s_0," the quotation marks indicating that the continuous creep values are only pseudo values of the true s/s_0 as measured by continuous relaxation. The corresponding continuous relaxation curves are shown as solid lines. Continuous creep data at more than one initial elongation are generally shown, incidentally illustrating that the creep curves obtained are identical, within experimental error, from 20 percent to 100 percent initial elongation.

It will be seen that no noticeable deviation from the stress relaxation curve is observed in the continuous creep data of Butyl gum at 120°C (Fig. 16). The creep data of Hevea gum at 120°C are slightly slower than the relaxation curve (Fig. 17), but not to any great extent. In both of these rubbers scission is predominant (in the experimental time the rate of cross
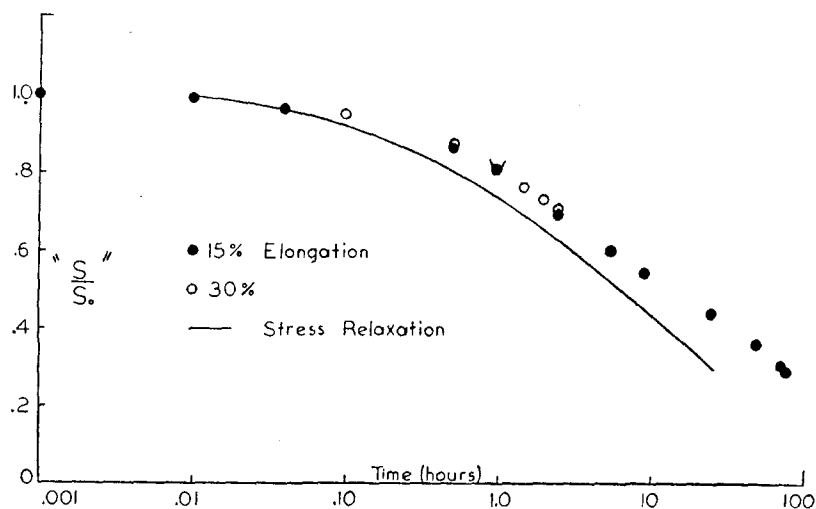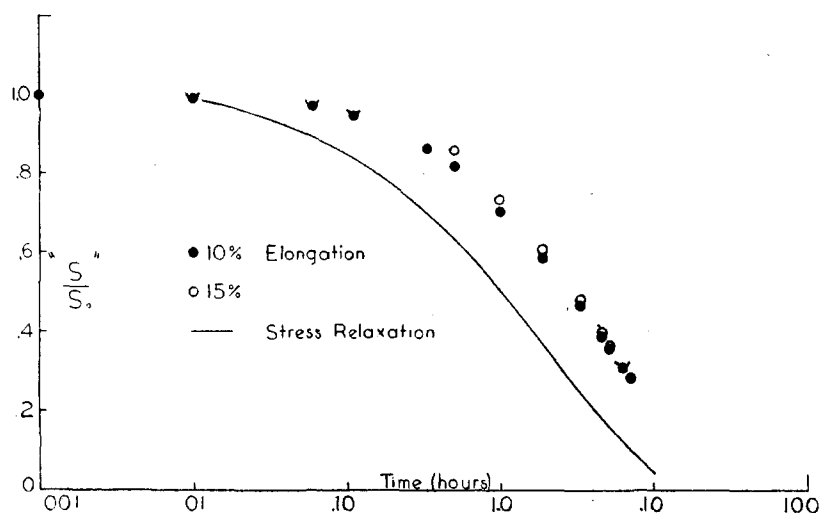

FIG. 18. Continuous creep; GR-S gum 120°C.

FIG. 19. Continuous creep Hevea tread 120°C.

linking has not overtaken the rate of scission in Hevea gum). In Fig. 18 continuous creep data at 120°C are shown for GR-S gum, in which cross linking predominates over scission, and which would therefore be expected to show a more marked effect. It is seen that the deviation of the creep data from the relaxation curve is significantly greater in GR-S gum than in Butyl and Hevea gums.

The effect of carbon black can be seen by comparing Hevea tread and GR-S tread (Figs. 19 and 20) with the corresponding gum stocks (Figs. 17 and 18). It is seen that the deviation is greater in the tread stock than in the gum stock in both cases; this is observed to be the general case. This would seem to indicate that cross linking occurs more rapidly in the tread stock than in the gum stock, though the rate of the scission reaction has been found to be about the same in both. This is confirmed by a comparison of the continuous and intermittent relaxation curves of gum and tread stocks in Figs. 14 and 15. The explanation of this fact is not clear at the present time. It has been suggested that the rubber molecules cling to the surface of the carbon black particles in tread stocks, thereby giving the rubber a higher modulus. It may be that the carbon black particles bring the chain molecules closer together in this way, and thus make cross linking easier, the effect being the opposite of that of swelling agents, which will be discussed in the following section.

This high temperature oxidative scission and cross linking do not manifest themselves only in continuous and intermittent relaxation and creep measurements. Another interesting manifestation is in the dissolution of vulcanizates. When pieces of vulcanizate are heated at fairly high temperatures in a good swelling liquid (such as toluene or xylene), in the presence of small amounts of oxygen, the vulcanizate eventually disintegrates and goes into solution. This is true even of GR-S, in which cross linking occurs more rapidly than scission when the rubber is heated in air at the same temperatures. The explanation of this phenomenon apparently is that when the solvent swells the rubber, the molecular chains of the network are pushed farther apart, making cross linking more difficult, while molecular scission remains as easy as before. Thus in swollen GR-S vulcanizate, scission apparently takes place more rapidly than cross linking and eventually is effective in completely disintegrating the network of the polymer. The breaking of the network is caused not by the swelling force of the solvent, but by the effect of swelling in changing the relative rates of cross linking and scission in the polymer. When solvents which are not good swelling agents (i.e., water, acetic anhydride, castor oil) are used under the same conditions, dissolution does not occur, and the cross-linking reaction actually hardens the GR-S vulcanizate.[9] The

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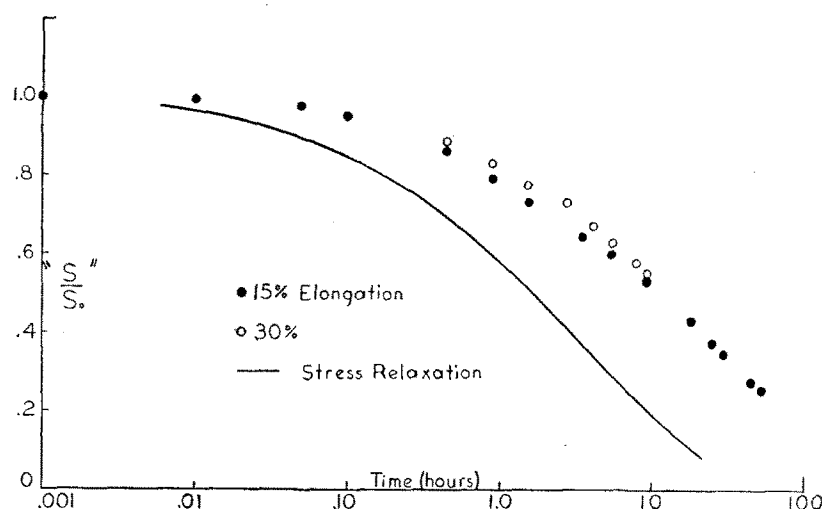[9] Unpublished experiments of M. Magat and A. V. Tobolsky.

FIG. 20. Continuous creep GR-S tread 130°C.

time required for dissolution is roughly the time required to relax fairly completely in a continuous relaxation test.

The measurement of high temperature cross linking and scission in raw polymer must be done with special methods. Stress relaxation and creep can of course only be used with vulcanizates. One method of attack is provided by the fact that the molecules of raw polymer can be divided into two groups on the basis of their solubility in a good rubber solvent (benzene or toluene, for example). There is an insoluble or "gel" fraction, consisting of the highly branched mole-

cules and three-dimensional networks; and a soluble or "sol" fraction consisting of the more linear, low molecular weight molecules. Oxidative cross linking and scission of the molecules cause changes in the character and relative proportions of the sol and gel fractions of the polymer, which can be followed by various methods.

Cross linking will increase the gel fraction and increase the "tightness" (concentration of network junctures per unit volume) of the gel. Scission will decrease the gel fraction and make the gel "looser." When pieces of raw polymer
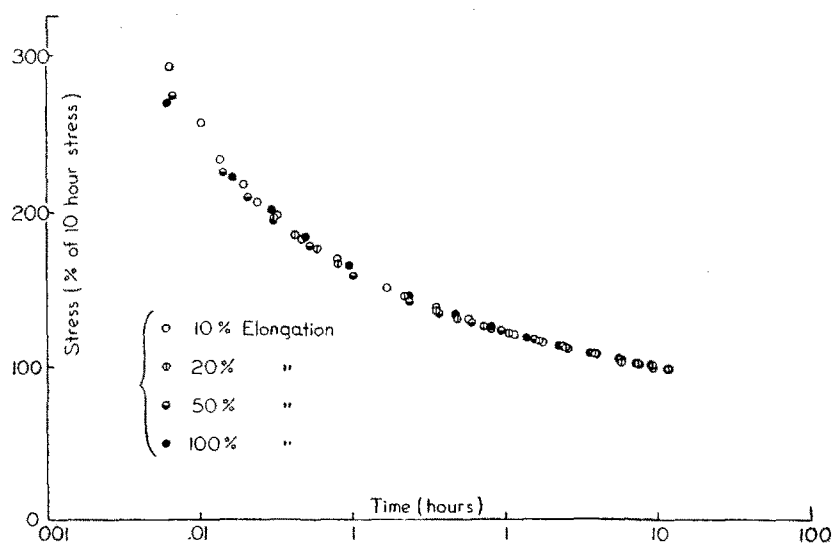

FIG. 21. Effect of elongation on low temperature stress relaxation, GR-S gum: −50°C.

are allowed to stand in benzene or toluene, the sol molecules go into solution, and the gel swells but does not dissolve. By weighing the swollen gel and measuring the concentration of the sol solution, the percent gel in the polymer can be calculated and also the "swelling index" of the gel (weight of swollen gel, rubber plus absorbed solution, divided by the weight of rubber in the gel), which should give a measure of the "tightness" of the gel. The average molecular weight of the sol molecules can be obtained by measuring the intrinsic viscosity of the sol solution. By making these measurements after various times of aging, the effects of cross linking and scission can be followed. Evaluating the softening and hardening of the raw polymer by hand test as aging progresses should provide a rough measure of the net effect of cross linking and scission, much as intermittent relaxation and creep measurements do. The rate of scission can be isolated almost completely by measuring the decrease in intrinsic viscosity of a rubber solution contained in a sealed viscosimeter. The solvent makes cross linking very difficult by keeping the molecules far apart, while the scission rate is unchanged; the action of the solvent is the same as described in the dissolution of vulcanizates, the effect being even greater here, however.

LOW TEMPERATURE SECONDARY BOND PHENOMENA

At low temperatures the secondary forces between chains and between portions of the same chain become sufficiently strong so that when the rubber is stretched many secondary interchain bonds do not relax during the stretching process and thus contribute to the measured initial stiffness of the rubber. These bonds will gradually relax, however, and reform in new positions which relieve the stress, so that if the rubber is maintained at constant elongation the stress will gradually decay until it approaches the equilibrium stress for that temperature as determined by the primary network (see Fig. 5).

Intermittent measurements of the stress required to attain a given elongation at low temperatures will give a constant value, provided that the rate of stretching is constant and that the rubber is undergoing no slow crystallization.

The effect of elongation on low temperature stress relaxation is shown in Fig. 21, where data for GR-S gum at $-50°C$ are shown for four different elongations: 10 percent, 20 percent, 50 percent, and 100 percent.* Percent of 10-hour stress is plotted as the ordinate, to make the data readily comparable. It appears that in this range of elongations the relaxation curve obtained is independent of the elongation. For the very short time measurements, the 10 percent data are slightly above the others, but during the course of the curves as a whole no regular variation with elongation is found.

The relaxation of stress in rubbers maintained

* These data were sent us through the courtesy of Mr. I. B. Prettyman of the Firestone Physics Research Division.
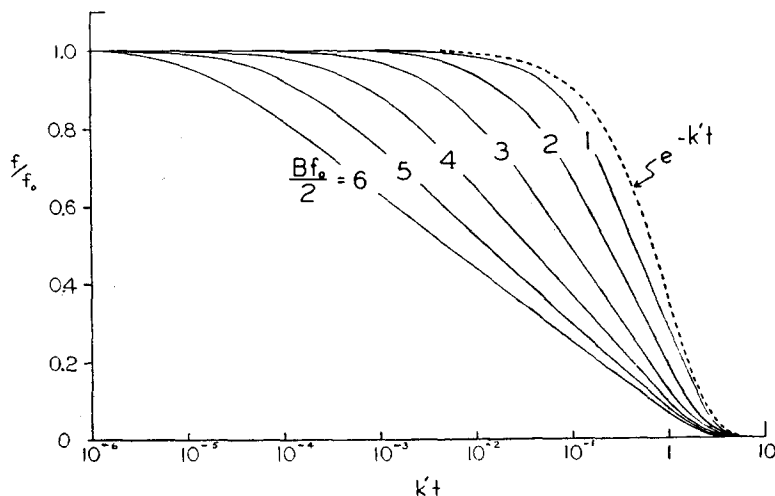

FIG. 22. Secondary bond relaxation (hyperbolic tangent decay).
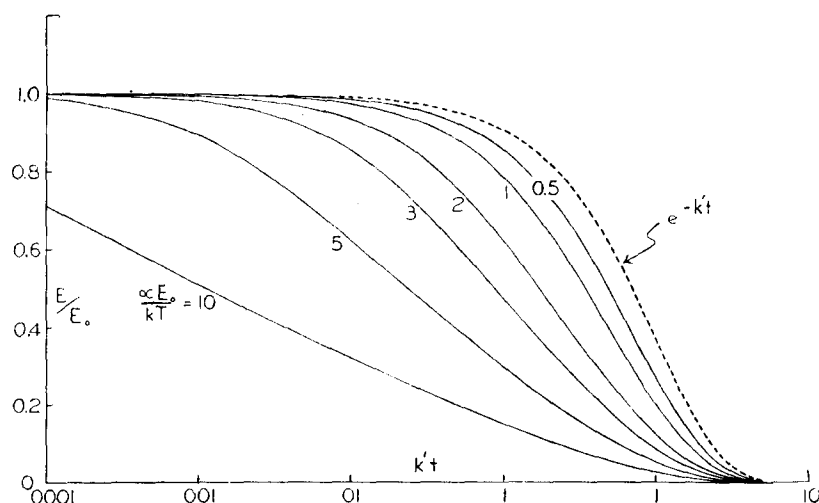
FIG. 23. Secondary bond relaxation (exponential integral decay).

at constant elongation at low temperatures does not follow the Maxwell decay law

$$f = f_0 e^{-t/\tau}, \tag{21}$$

where f is stress, t is time, $f_0 =$ stress at time $t = 0$, and $\tau =$ relaxation time. Equation (21) is obtained by integrating Maxwell's equation (1) when $ds/dt = 0$. The Wiechert generalization of Maxwell's decay law gives

$$f = \sum_i (f_i)_0 \exp(-t/\tau_i), \tag{22}$$

where we assume a number of relaxation times or in the limit, a distribution of relaxation times. This mathematical result corresponds to a distribution of bond strengths, the relaxation behavior of each type of bond being governed by a linear relaxation law of the Maxwell type. For this case $(f_i)_0$ is the contribution of the ith type of bond to the stress at zero time and τ_i is the relaxation time for the ith type of bond. Equation (22) has the advantage of explaining naturally the fact that the stress decay curves for different
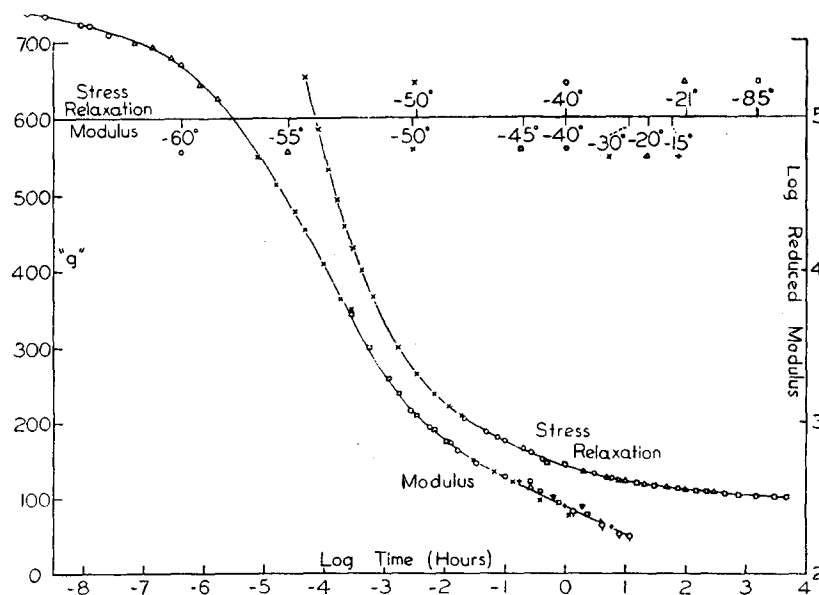

FIG. 24. Composite stress relaxation and composite low temperature modulus (GR-S gum).
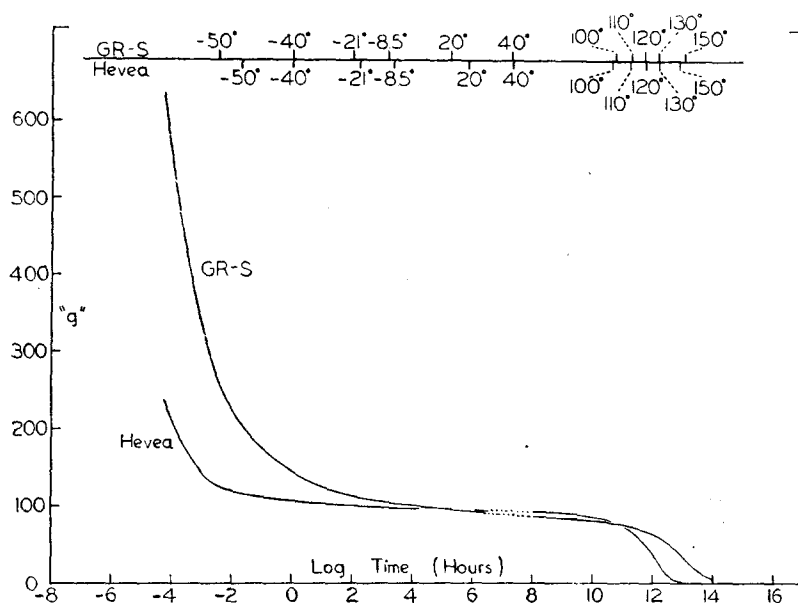
FIG. 25. Composite stress relaxation gum stocks.

elongations differ only by a scale factor (for elongations up to at least 100 percent) as discussed in the previous paragraph. This theory cannot be considered complete unless the actual distribution in relaxation times can be obtained from first principles. So far as agreement with experiment is concerned, any data can be fitted by a sufficiently complicated distribution of relaxation times.

Other possible relaxation laws exist, in particular the generalized Maxwell equation

$$\frac{ds}{dt} = \frac{1}{G}\frac{df}{dt} + n\lambda\frac{kT}{h}e^{-\Delta F\ddagger/RT}2\sinh\frac{f\lambda}{2NkT}. \quad (23)$$

This equation is non-linear and the various quantities appearing in it have been defined previously. It may be written in the simplified form

$$\frac{ds}{dt} = \frac{1}{G}\frac{df}{dt} + A\sinh Bf, \quad (24)$$

where

$$A = 2n\lambda\frac{kT}{h}e^{-\Delta F\ddagger/kT},$$

and

$$B = \frac{\lambda}{2NkT}.$$

Integrating Eq. (24) for the case that $ds/dt = 0$

the following expression is obtained:

$$\tanh\left(\frac{Bf}{2}\right) = \tanh\left(\frac{Bf_0}{2}\right)e^{-k't}, \quad (25)$$

where $k' = ABG$.

A graph of the hyperbolic tangent decay function is shown in Fig. 22, where f/f_0 is plotted against the logarithm of $k't$. The solid curves are the decay function for different values of $(Bf_0/2)$, and the dotted curve, included for comparison, is that of the simple first-order decay function

$$f = f_0 e^{-k't}. \quad (26)$$

In order to explain by this theory the experimental fact that relaxation curves at different elongations differ only by a scale factor, it is necessary that $(Bf_0/2)$ be equal to a constant. Any reason why this should be is not known at present.

As a final example of a decay law that we may derive from *a priori* reasoning let us consider the dissipation of "non-equilibrium" energy. For constant extension experiments we shall assume that the stress and the extra stress energy (beyond the equilibrium value as determined by the primary network) are both functions of the number of secondary bonds that are
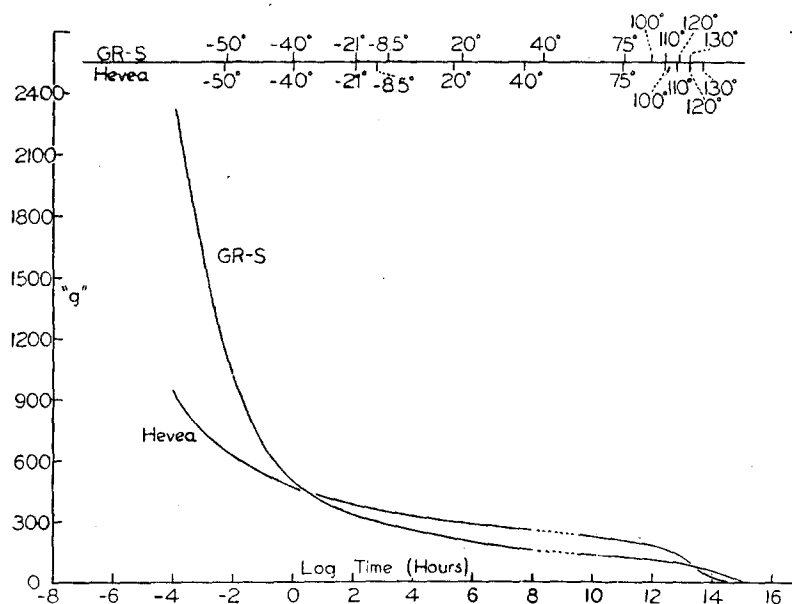
FIG. 26. Composite stress relaxation tread stocks.

holding in non-relaxed positions. In the unstretched state the interchain bonds form and reform in new relaxed positions without preference for either position. In the stretched state, however, the "extra" energy causes an asymmetry in the potential curve—in other words, there will be a net tendency for the bonds to move from stressed to relaxed positions with a concomitant dissipation of the excess stress energy. The equation derived from this picture is

$$-\frac{1}{E}\frac{dE}{dt}=k'[e^{\alpha E/kT}-e^{-(1-\alpha)E/kT}], \quad (27)$$

where k' is the specific rate constant associated with the forming and reforming of secondary interchain bonds in the unstretched state, and α is equal to $\frac{1}{2}$ for symmetrical barriers. The integrated form of Eq. (27) (exponential integral decay) obtained by neglecting the second term in the bracket on the right-hand side is shown in Fig. 23. The stress is presumed to be related to the energy by some factor of proportionality inasmuch as the material is held at constant extension.

It is apparent that sufficient experimental work is not yet available to make a complete test of any of the theories presented here or elsewhere, although some interesting work has been done in this direction.[10] One of the difficulties is that at any given temperature, measurements extending over very many cycles of logarithmic time must be made to obtain a complete picture of the stress decay process.

COMPOSITE RELAXATION OF STRESS CURVES

To overcome the difficulty of obtaining experimental results over very extended times, it was observed that relaxation data (plotted in the form of "g" versus log t) obtained at one temperature could be superposed upon data obtained at another temperature merely by a translation along the log time axis. The reason for this is obvious in the case of the decay law

$$\text{"}g\text{"}=\text{"}g\text{"}_0 e^{-k't}, \quad (28)$$

which is obeyed by Hevea gum at high temperatures. The fact that the low temperature data can also be superposed in this way indicates that the time-temperature dependence of g follows a law of the kind

$$-dg/dt=\phi(T)\psi(g). \quad (29)$$

How well low temperature data at different temperatures, either stress relaxation or modulus

[10] M. Mooney, W. E. Wolstenholme, and D. S. Villars, J. App. Phys. 15, 324 (1944).

(measured by the bending creep method of Dr. Liska), can be superposed by translation along the log time axis is shown in Fig. 24. Values of "g" and the logarithm of the reduced modulus are shown plotted against the log-time scale appropriate for −40°C. The origin of the log-time scale for each temperature is shown in the scale on top of the page. The one-hour value (log time equals zero) is marked for each temperature on this scale, and the log-time scale below can be used for each temperature merely by reference to the correct origin. The different types of points represent data at different temperatures.

By this method a single graph can be used to show the complete stress-temperature-time relations of a rubberlike substance. Figures 25 and 26 based on the same principle as Fig. 24 are complete "stress biographies" of the Hevea and GR-S gum and tread stocks studied. From these figures the complete stress-time-temperature behavior of these rubbers can be determined for times that would be impossible to attain experimentally. Even though "g," the reduced stress, is plotted only as 50 percent elongation data, the curves have greater generality because at different elongations these curves would be altered only by a scale factor in the ordinate.

It should be remembered that two processes are shown in these composite curves, primary and secondary bond relaxation, with very different activation energies, and therefore different temperature coefficients. For this reason it is to be expected that if the primary bond relaxation at two different temperatures is superposed, the secondary bond relaxation at the two temperatures will not be superposed in that position. Two composite curves are really needed, one for primary and the other for secondary bonds, with the time origin for each temperature marked on the log time abscissa of each. Then to obtain the complete relaxation curve at any tempera-ture, one would slide the first graph along the second until the two log time origins for that temperature coincided. Dotted lines are used to connect the primary and secondary regions of the composite curves in Figs. 25 and 26 to indicate this—that a single continuous relaxation curve, including both primary and secondary relaxation regions, is not universal for all temperatures, simply by choosing the appropriate point along the log time scale as origin. The reason that a single curve was obtained in the graphs shown here was merely the result of the fact that, in most of the superposition, one or the other of the two relaxation regions was being superposed.

The conclusions stated in this section of course depend on the validity of the superposition procedure. It seems fairly clear at the present time that the superposition procedure is truly applicable at high temperatures (i.e., for the primary bond relaxation region). The position of the origin on the log time scale for any temperature can be calculated by use of Eq. (17). At low temperatures the data used overlapped only to a small extent, so that it was very difficult to tell whether the curves at different temperatures really would superpose completely. Low temperature data over more extended times are needed to check this. For this reason the conclusions expressed here must be regarded as only tentative at the present time.

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