Int. J. Solids Structures, 1977, Vol. 13, pp. 771–781. Pergamon Press. Printed in Great Britain

VISCOELASTIC RESPONSE TO SMALL DEFORMATIONS SUPERPOSED ON A LARGE STRETCH

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(Received 10 February 1977)

Abstract—Viscoelastic stress-deformation relations for small dynamical deformations superposed on a large uniaxial stretch are derived for materials that are incompressible and initially isotropic. The equations incorporate the effects of relaxing pre-stress and strain-induced anisotropy. The stress relaxation moduli depend parametrically on the time since the material was stretched, as well as on the usual times of relaxation. Analysis of data to separate the two kinds of time dependence is discussed, and is illustrated with data for highly stretched natural rubber. The data show that the one-minute modulus increases rapidly as the age increases if the rubber is so highly stretched that crystallization can occur.

1. INTRODUCTION

The dynamic torsional modulus of a stretched rubber tube undergoing stress relaxation has been studied in some recent experimental work[1]. The equilibrium theory of large elastic deformations (Rivlin[2]) predicts that at a fixed stretch, the torsional modulus is directly proportional to the axial tension. This suggests that when stress relaxation is taking place in a viscoelastic material, the torsional modulus should decrease as the axial tension does. It was found[1] that this is the case at low and moderate stretches, but at stretches of the order of four or greater, the modulus increases as time progresses, even though the axial tension is simultaneously decreasing very rapidly. Both the rapid relaxation and the increasing torsional stiffness appear to be due to crystallization, which is known to take place in highly stretched natural rubber[3, 4].

In order to provide a general theoretical framework for the organization of data from such experiments, in the present paper we derive viscoelastic stress-deformation relations for small dynamic deformations superposed on a large uniaxial stretch. We restrict attention to materials that are incompressible and initially isotropic. The required relations can be obtained by a suitable specialization of the general equations for small deformations superposed on large that were derived by Pipkin and Rivlin[5]. However, the case considered here is so special that it is simpler and more informative to derive the equations from first principles, and we do this in Sections 2–4. We also rederive the appropriate self-consistency conditions[5], in Section 5.

We use these equations to discuss the effect of the axial tension on the stress relaxation moduli of the material, in Sections 5 and 6. With reference to the modulus that determines the torsional rigidity of a stretched specimen, we show that the shearing stress relaxes in direct proportion to the axial tension if the shearing is carried out at the same instant as the stretching, but in general not otherwise.

The relaxation moduli depend on two time variables, the times that have elapsed since the stretching and since the superposed small deformation. In Section 7 we discuss some simple examples that illustrate the significance of the two kinds of time dependence. According to the constitutive equations proposed by Bernstein, Kearsley, and Zapas[6] and by Lianis (see Goldberg and Lianis[7]), each modulus can be expressed as the sum of two functions of only one time variable each. In Section 8 we show how to analyze data to test this representation. We use experimentally determined data on natural rubber to show that while the representation in terms of two functions is acceptable at lower stretches, it is drastically inaccurate at stretches so high that crystallization is taking place. We conclude by discussing the probable nature of the moduli when crystallization is taking place, in Section 9.

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2. SMALL DISPLACEMENTS SUPERPOSED ON A FINITE STRETCH

We consider a rod or tube of arbitrary cross-section, composed of an isotropic incompressible, viscoelastic material. The rod is initially in thermodynamic equilibrium, under no stress except the ambient pressure. At time zero the rod is stretched to λ times its original length, and it is then subjected to a further small deformation with infinitesimal displacement field $\underline{u}(\underline{x}, t)$.

The tensile stress T required to maintain the large stretch depends on λ and on the time t that has elapsed since the stretching. In addition to this stress, there is an isotropic pressure p that is not related to the deformation, since the material is incompressible. Consequently, the stress before any small deformation is superimposed has the form

$$\sigma_{ij}^0 = -p\delta_{ij} + T\delta_{3i}\delta_{3j}. \tag{2.1}$$

We have taken the x_3-axis of a system of Cartesian coordinates to be along the axis of the rod.

The superposed small deformation requires an additional stress, S'_{ij}. The total stress then has the form

$$\sigma_{ij} = -p\delta_{ij} + T\delta_{3i}\delta_{3j} + S'_{ij}. \tag{2.2}$$

Because only the total stress can be measured, and because p is not directly determined by the deformation, S'_{ij} is not well-defined until some convention concerning its normal components has been established. Rather than using the usual convention that S'_{ij} be deviatoric, here it is more convenient to specify that

$$S'_{11} + S'_{22} = 0. \tag{2.3}$$

We suppose that the value of S'_{ij} at $\underline{x}$ and t is a continuous linear functional of the components $u_{i,j}$ of the displacement gradient at $\underline{x}$, at times up to t. S'_{ij} presumably may depend on λ and t as well. Then S'_{ij} has the form

$$S'_{ij}(t) = \int_{-\infty}^{t} c'_{ijkl}(\lambda, t; t-t')\,\mathrm{d}u_{k,l}(t'). \tag{2.4}$$

Thus, we assume that the usual stress-relaxation integral form of the consitutive equation for linear viscoelasticity theory is valid, but with relaxation moduli c'_{ijkl} that depend not only on the time lag $t-t'$ but also on the stretch λ and the time t that has elapsed since the stretching occurred. We usually abbreviate (2.4) by using the convolution notation

$$S'_{ij} = c'_{ijkl} * \mathrm{d}u_{k,l}. \tag{2.5}$$

3. EFFECTS OF STRAIN AND ROTATION

Because of the pre-stress T, the stress disturbance S'_{ij} depends on rotations as well as on strain components. The dependence on rotations can be determined explicitly.

Let us suppose that the stretched body is rotated slightly at time t_0, so that the displacement gradient history has the form

$$u_{i,j}(t) = \omega_{ij}H(t-t_0), \qquad \omega_{ji} = -\omega_{ij}. \tag{3.1}$$

Here $H(t)$ is the unit step function. This rotation can alter the existing state of stress σ_{ij}^0 only by rotating it by the same amount. Consequently, the stress after the infinitesimal rotation must be

$$\sigma_{ij} = (\delta_{ik} + \omega_{ik})(\delta_{jl} + \omega_{jl})\sigma_{kl}^0. \tag{3.2}$$

By using the expression for the pre-stress given in (2.1), and neglecting terms quadratic in the infinitesimal rotation, we find that the stress disturbance is

$$S'_{ij} = (\omega_{i3}\delta_{j3} + \omega_{j3}\delta_{i3})T(\lambda, t). \tag{3.3}$$

The stress disturbance given by the constitutive eqn (2.5) must agree with (3.3). By using (3.1) in (2.5) we obtain

$$S'_{ij} = c'_{ijkl}(\lambda, t; t - t_0)\omega_{kl}. \tag{3.4}$$

Thus, the right-hand members of (3.3) and (3.4) must be equal.

Now let $\omega_{ij}(t)$ be any history of rotation, and replace ω_{ij} in (3.3) and (3.4) by $d\omega_{ij}(t_0)$. Integration with respect to t_0 then yields

$$c'_{ijkl} * d\omega_{kl} = [\omega_{i3}(t)\delta_{j3} + \omega_{j3}(t)\delta_{i3}]T(\lambda, t). \tag{3.5}$$

For an arbitrary displacement gradient history, we introduce the usual decomposition into strain and rotation:

$$u_{i,j} = \epsilon_{ij} + \omega_{ij}. \tag{3.6}$$

We also introduce symmetrized moduli c_{ijkl}, defined by

$$2c_{ijkl} = c'_{ijkl} + c'_{ijlk}. \tag{3.7}$$

Then by using (3.6) and (3.7) in (2.5), and taking (3.5) into account, we obtain

$$S'_{ij} = (\omega_{i3}\delta_{j3} + \omega_{j3}\delta_{i3})T + S_{ij}, \tag{3.8}$$

where

$$S_{ij} = c_{ijkl} * d\epsilon_{kl}. \tag{3.9}$$

4. MATERIAL SYMMETRY AND INCOMPRESSIBILITY

Because the material is isotropic, any lack of symmetry in its response to a small superposed deformation is due to lack of symmetry in the initial large deformation. The uniaxial stretch introduces one preferred direction, which is along the x_3 axis. Then the relation (3.9) must have the form appropriate for transversely isotropic materials [8]. Except that multiplication is replaced by convolution, this is the same as the elastic stress-strain relation for a material with no strain-energy function (Sokolnikoff [9]). It is convenient to break the relation into three parts, and to introduce special notation for those moduli that are not identically zero:

$$\begin{aligned} S_{33} &= E * d\epsilon_{33} + E_1 * d\epsilon_{\alpha\alpha}, \\ S_{3\alpha} &= 2G * d\epsilon_{3\alpha}, \\ S_{\alpha\beta} &= 2G_1 * d\left(\epsilon_{\alpha\beta} - \frac{1}{2}\epsilon_{\gamma\gamma}\delta_{\alpha\beta}\right) + (C_1 * d\epsilon_{33} + C_2 * d\epsilon_{\gamma\gamma})\delta_{\alpha\beta}. \end{aligned} \tag{4.1}$$

Here Greek subscripts have the range 1, 2, and a repeated subscript implies summation over that range.

These relations apply to compressible materials as well as to incompressible materials. The three relaxation moduli E_1, C_1, and C_2 are redundant if the material is incompressible, as we assume it to be. For, since $\epsilon_{ii} = 0$, then $\epsilon_{\alpha\alpha} = -\epsilon_{33}$, and that the terms involving E_1 and C_2 can be omitted. In addition, the convention (2.3) implies that $S_{\alpha\alpha} = 0$; this is true for all strain histories only if $C_1 = 0$, given that $C_2 = 0$.

By collecting the results (3.8) and (4.1) in (2.2), we find that the stress-deformation relations for an incompressible material take the form

$$\sigma_{33} = -p + T + E * d\epsilon_{33},$$

$$\sigma_{3\alpha} = T\omega_{\alpha 3} + 2G * \mathrm{d}\epsilon_{\alpha 3},$$

$$\sigma_{\alpha\beta} = -p\delta_{\alpha\beta} + 2G_1 * \mathrm{d}\left(\epsilon_{\alpha\beta} - \frac{1}{2}\epsilon_{\gamma\gamma}\delta_{\alpha\beta}\right). \tag{4.2}$$

In this final form there are three independent stress-relaxation moduli, the tensile modulus E and two shear moduli, G and G_1. Each modulus is a function of λ, t, and $t - t'$, and the convolution is carried out with respect to t'. For example,

$$G * \mathrm{d}\epsilon_{\alpha 3} = \int_{-\infty}^{t} G(\lambda, t; t - t')\, \mathrm{d}\epsilon_{\alpha 3}(t'). \tag{4.3}$$

When $\lambda = 1$, so that the material is not stretched, the relations (4.2) must reduce to the usual constitutive equations of linear viscoelasticity theory, for isotropic, incompressible materials. If $G(t')$ is the shearing stress relaxation modulus for infinitesimal deformations of such a material, this requires that

$$G(1, t; t') = G_1(1, t; t') = (1/3)E(1, t; t') = G(t'). \tag{4.4}$$

In addition, consistency with the linear theory requires that T be related to G by

$$T(1, t) = 0, \qquad T'(1, t) = 3G(t). \tag{4.5}$$

Here T' is the derivative of T with respect to λ. Since $G(t)$ is known for many materials (see Ferry[10], for example), these relations provide some boundary values for the moduli G, G_1 and E.

5. SELF-CONSISTENCY CONDITIONS

The two moduli E and G are not entirely independent of the tensile stress relaxation function T. The relations among these functions are obtained by considering static uniaxial stretches with a stretch ratio slightly different from λ or with an axis slightly different from the x_3 axis. The stress for such deformations can be evaluated in two different ways, and the two results must agree.

We first consider a superposed small displacement history of the form

$$u_3 = \epsilon x_3 H(t), \qquad u_\alpha = -\frac{1}{2}\epsilon x_\alpha H(t). \tag{5.1}$$

This is a superposed axial extension ϵ, applied at the same time as the large stretch λ and held constant thereafter. Thus, the total deformation is a uniaxial stretch applied at time zero, with the stretch ratio $\lambda(1+\epsilon)$. It follows that the tensile stress must be $T(\lambda + \mathrm{d}\lambda, t)$, with $\mathrm{d}\lambda = \lambda\epsilon$, and thus the stress perturbation is $T'(\lambda, t)\lambda\epsilon$, where the prime denotes differentiation with respect to λ. On the other hand, the tensile stress perturbation found by using (5.1) in (4.2) is $E(\lambda, t; t)\epsilon$. Then consistency requires that

$$E(\lambda, t; t) = \lambda T'(\lambda, t). \tag{5.2}$$

In the remainder of this section we use a slightly more involved argument to show that the shearing stress relaxation modulus is related to the tensile stress by

$$G(\lambda, t; t) = \frac{1}{2}\frac{\lambda^3 + 1}{\lambda^3 - 1} T(\lambda, t). \tag{5.3}$$

This will be done by considering a large uniaxial stretch along a direction $\underset{\sim}{c}$ that differs slightly from the axial unit vector $\underset{\sim}{k}$:

$$\underset{\sim}{c} = \underset{\sim}{k} + \epsilon \underset{\sim}{i}. \tag{5.4}$$

(The base vectors for the coordinate system are denoted $\underset{\sim}{i}$, $\underset{\sim}{j}$, and $\underset{\sim}{k}$.) We observe that $\underset{\sim}{c}$ is a unit vector, to first order in ϵ.

In a stretch by the amount λ along the direction $\underset{\sim}{c}$, a particle initially at the place $\underset{\sim}{X}$ is moved to the place

$$\underset{\sim}{x}' = \lambda \underset{\sim}{c}(\underset{\sim}{c} \cdot \underset{\sim}{X}) + \lambda^{-1/2}[\underset{\sim}{X} - \underset{\sim}{c}(\underset{\sim}{c} \cdot \underset{\sim}{X})]. \tag{5.5}$$

If the stretching had been exactly along the x_3 direction, the particle would have come to the place

$$\underset{\sim}{x} = \lambda \underset{\sim}{k}(\underset{\sim}{k} \cdot \underset{\sim}{X}) + \lambda^{-1/2}[\underset{\sim}{X} - \underset{\sim}{k}(\underset{\sim}{k} \cdot \underset{\sim}{X})]. \tag{5.6}$$

The deformation (5.5) can be viewed as an axial stretch (5.6), plus a small displacement $\underset{\sim}{u} = \underset{\sim}{x}' - \underset{\sim}{x}$.

If we view the deformation directly as a large stretch along the direction $\underset{\sim}{c}$, we see that the stress must be

$$\begin{aligned}\sigma_{ij} &= -p\delta_{ij} + Tc_ic_j \\ &= -p\delta_{ij} + Tk_ik_j + Tk_i(c_j - k_j) + T(c_i - k_i)k_j.\end{aligned} \tag{5.7}$$

Here we have neglected terms quadratic in the small difference $\underset{\sim}{c} - \underset{\sim}{k}$.

We now evaluate the stress again, by using the constitutive eqn (4.2). By combining (5.4), (5.5) and (5.6), we find that

$$\underset{\sim}{x}' - \underset{\sim}{x} = (\lambda - \lambda^{-1/2})(\underset{\sim}{j}X_3 + \underset{\sim}{k}X_2)\epsilon. \tag{5.8}$$

With $X_2 = \lambda^{1/2}x_2$ and $X_3 = \lambda^{-1}x_3$ according to (5.6), (5.8) yields

$$\underset{\sim}{u} = (\lambda - \lambda^{-1/2})(\underset{\sim}{j}\lambda^{-1}x_3 + \underset{\sim}{k}\lambda^{1/2}x_2)\epsilon. \tag{5.9}$$

Hence,

$$u_{2,3} = (1 - \lambda^{-3/2})\epsilon \quad \text{and} \quad u_{3,2} = (\lambda^{3/2} - 1)\epsilon, \tag{5.10}$$

and all other components of the displacement gradient are equal to zero. By using these values in (4.2b), we find that

$$\sigma_{23}/\epsilon = \sigma_{32}/\epsilon = \frac{1}{2}T(\lambda, t)(2 - \lambda^{3/2} - \lambda^{-3/2}) + G(\lambda, t; t)(\lambda^{3/2} - \lambda^{-3/2}). \tag{5.11}$$

The corresponding value obtained from (5.7) is simply $T(\lambda, t)$. On setting this equal to the right-hand member of (5.11), we obtain the self-consistency condition (5.3).

6. QUASI-ELASTIC RESPONSE

If the response of the material is purely elastic, the tension T and the moduli in (4.2) are time-independent, and the convolutions there reduce to ordinary products. Relations of the same form as these elastic stress-deformation relations are obtained even for viscoelastic materials, provided that the disturbance $\underset{\sim}{u}$ is applied at a single instant t_s, say, and then held fixed. The convolutions again reduce to simple products, but the moduli depend on the times that have elapsed since the deformations. The resulting quasi-elastic equations are

$$\begin{aligned}\sigma_{33}(t) &= -p(t) + T(\lambda, t) + E(\lambda, t; t - t_s)u_{3,3}, \\ \sigma_{3\alpha}(t) &= \left[\frac{1}{2}T(\lambda, t) + G(\lambda, t; t - t_s)\right]u_{\alpha,3} + \left[-\frac{1}{2}T(\lambda, t) + G(\lambda, t; t - t_s)\right]u_{3,\alpha},\end{aligned} \tag{6.1}$$

and a similar equation for $\sigma_{\alpha\beta}$.

We note that the effective shear modulus for a shear $u_{\alpha,3}$ is larger than that for a shear $u_{3,\alpha}$ by an amount equal to the axial tension. Thus when stress relaxation is taking place, it is not possible for both of the effective moduli to be functions of $t-t_s$ alone. We also note that the theory does *not* imply that dependence on t, through T, affects only the modulus for a shear $u_{\alpha,3}$, although it leaves open the possibility that this might be the case.

If the small static disturbance is applied at time $t_s=0$, the relevant values of the moduli E and G can be expressed in terms of T by using the self-consistency conditions (5.2) and (5.3). In this case (6.1) becomes

$$\begin{aligned}\sigma_{33}(t)&=-p(t)+T(\lambda,t)+\lambda T'(\lambda,t)u_{3,3},\\ \sigma_{3\alpha}(t)&=T(\lambda,t)(\lambda^3u_{\alpha,3}+u_{3,\alpha})/(\lambda^3-1).\end{aligned} \tag{6.2}$$

In this case the shearing stress relaxation functions for shears $u_{\alpha,3}$ and $u_{3,\alpha}$ are both directly proportional to T, with known factors of proportionality. Because of this proportionality, Rivlin's[2] formula for torsional rigidity as an explicit function of T and λ remains valid during stress relaxation, provided that the twist is performed at the same time as the stretching and is held fixed thereafter. Goldberg and Lianis[7] have verified this experimentally. Indeed, Rivlin and Saunders'[11] experimental verification of the relation for equilibrium conditions presumably implies that the relation is valid during stress relaxation, because it is not likely that equilibrium conditions were actually achieved.

Stress relaxation in elastomers is roughly linear in the logarithm of the time that has elapsed since the deformation, so that the rate of relaxation is inversely proportional to the elapsed time. For this reason we should expect that when $t-t_s$ is small in comparison to t in (6.1), the main variation in stress that is observed should be due to the variation of $t-t_s$, with no great change in stress due to the variation of t, the "age" of the material. On the other hand, when t is much larger than t_s, so that t and $t-t_s$ are of the same order of magnitude, there should be little error in taking $t_s=0$ as an approximation and thus using the relations (6.2) even though the stretching and the superposed deformation did not occur simultaneously. Thus, suppose that a rod is held stretched until stress relaxation appears to have ceased; it is then twisted, and held twisted, until the twisting moment appears to have decreased to its equilibrium value. Under such circumstances, we should expect that the expression for the moment in terms of T and λ given by elasticity theory would be rather accurate, even though the material is not behaving elastically nor even satisfying (6.2b) exactly. We believe that this is the correct interpretation of the experiments of Rivlin and Saunders[11].

7. TIME-SEPARABLE MODULI

Because the moduli E, G and G_1 depend on two time variables, the experimental determination of these functions requires a large number of tests. It is useful to attempt to represent these functions in terms of functions of only a single time variable, both in order to reduce the required number of tests and in order to simplify the tabulation of results. In the following discussion we consider only G; it will be apparent that much of the discussion applies to E and G_1 as well.

The moduli can be determined, in principle, from a sufficiently large number of stress-relaxation tests, in which a small displacement step is applied at time t_s and held constant thereafter. To be specific, suppose that the stretched rod is sheared, so that $u_{2,3}$ has the form $\epsilon H(t-t_s)$ and all other components of the displacement gradient are zero. (Twisting gives histories locally of this form at each particle, with the x_2 direction interpreted as the azimuthal direction.) The shearing stress σ_{23} is measured. The modulus σ_{23}/ϵ is a function $R(\lambda,t_s;t')$ that depends on the amount of stretch, the time of the step, t_s, and the time t' that has elapsed since the step. Data can be taken nearly continuously in t', for each fixed set of values of λ and t_s. According to (6.1b), the measured response function R is related to T and G by

$$R(\lambda,t_s;t')=\frac{1}{2}T(\lambda,t_s+t')+G(\lambda,t_s+t';t'). \tag{7.1}$$

With simultaneous measurement of the axial tension T, this yields values of G.

Since it is the function R that is given most directly by the experimental results, it is simpler to rewrite the constitutive equation in terms of R rather than G. With the notation $u_{2,3}(t) = \epsilon(t)$ and $\sigma_{23}(t) = \sigma(t)$, the relation between these quantities has the form

$$\sigma(t) = \int_{-\infty}^{t} R(\lambda, t_s; t - t_s)\, \mathrm{d}\epsilon(t_s). \tag{7.2}$$

The self-consistency condition (5.3) implies that

$$R(\lambda, 0; t') = T(\lambda, t')/(1 - \lambda^{-3}). \tag{7.3}$$

Thus, the values of R for $t_s = 0$ can be obtained from the axial tension data rather than by actually applying a displacement step at time zero.

Let us consider three special forms of $R(\lambda, t_s; t')$, none of which is likely to be correct, in order to indicate the roles that the time variables play. First suppose that R does not depend on the aging parameter t_s. This means that the response to a superposed small deformation does not depend on the time that has elapsed between the initial large stretching and the time at which the displacement perturbation is applied. In this case R has the same form for any value of t_s that it has for $t_s = 0$, which is given by (7.3). For this non-aging response, the shearing response is known immediately when the axial tension has been measured.

Second, let us suppose that $R(\lambda, t_s; t')$ depends only on the total elapsed time $t = t_s + t'$. In this case (7.2) reduces to

$$\sigma(t) = R(\lambda, 0; t)\epsilon(t). \tag{7.4}$$

The response is quasi-elastic, not merely for a static strain but also for a variable strain. The modulus changes in time, but a strain change produces no viscoelastic aftereffect. The tensile stress rotation term in (4.2b) is a term of this kind. We note that the response function in (7.4) is given in terms of T by (7.3), so again in this case the shearing response is completely determined by the axial tension.

Third, let us suppose that R depends on t_s alone. In this case (7.2) takes the form

$$\sigma(t) = \int_{-\infty}^{t} R(\lambda, t_s; 0)\, \mathrm{d}\epsilon(t_s). \tag{7.5}$$

The material exhibits permanent memory in this case. The stress increment due to a given strain change depends on the time at which that change occurred, but this stress increment does not relax with the passage of time. The latter feature of this kind of time-dependence is intrinsically unreasonable.

Bernstein, Kearsley, and Zapas[6] and Lianis (see [7]) have proposed non-linear single-integral constitutive equations for large viscoelastic deformations, which are intended to be applicable to all strain histories, and not merely to small deformations superimposed on a large stretch. When these constitutive equations are applied to the type of deformation that we consider here, relations of the form (4.2) are obtained, with special forms for the moduli. Because of the additive-functional nature of these constitutive equations, the moduli split into sums of a function of t and a function of t', the two times that have elapsed since the two strain changes. The response function R then takes the form

$$R(\lambda, t_s; t') = A(\lambda, t') + B(\lambda, t_s + t'). \tag{7.6}$$

The first function, A, represents viscoelastic behavior of the non-aging type. The second, B, represents quasi-elastic response.

In order to test the relation (7.6), we propose a more general relation that includes (7.6) as a special case:

$$R(\lambda, t_s; t') = A(\lambda, t') + B(\lambda, t_s + t') + C(\lambda, t_s). \tag{7.7}$$

In Section 8 we show how to determine the functions A, B and C from measured values of R. If the function C is found to be zero, to within experimental error, we may have some confidence that the two-term decomposition (7.6) is valid. If C is found to be different from zero, then (7.6) is not correct, but this does not imply that (7.7) is correct. Further data, more than the minimum necessary to determine A, B and C, would be needed in order to test (7.7). We return to this point in Section 9, where we discuss the nature of R for highly stretched rubber in more detail.

8. ANALYSIS OF DATA

Given a function R that can be represented in the form (7.7), we wish to determine the functions A, B and C. Since λ enters the equation only as a parameter, in the present section we suppress λ from the notation.

The functions A, B and C are not uniquely determined by (7.7). For, if we add $a + bt'$ to A and $c + bt_s$ to C, while subtracting $a + c + bt$ from B, the total response R is unchanged. We can remove this indeterminacy by imposing some physically reasonable restrictions on A, B and C.

We believe that when it is possible to represent real data in the form (7.7) at all, it will be possible to do so with functions that approach finite limits as their time arguments approach infinity. We restrict attention to data for which this is the case. This removes the indeterminacy in the slopes of A, B and C. To set the levels of these functions, we specify that $A(\infty)=0$ and $C(0) = 0$.

Under these assumptions, from (7.7) we obtain the relations

$$A(t) = R(\infty, t) - R(\infty, \infty), \tag{8.1}$$

$$B(t) = R(0, t) - A(t), \tag{8.2}$$

and

$$C(t) = R(t, 0) - B(t) - A(0). \tag{8.3}$$

These relations suggest the manner in which A, B and C can be determined from R. The actual procedure is more complicated, since data cannot be acquired at zero or infinite values of the time arguments, except for values of $R(0, t)$.

The function R can be determined by measuring the torsional modulus of a stretched rod or tube. Min[12] has obtained values of the functions $R(0, t)$, $R(t_s, 1m)$ and $R(24h, t)$ for natural rubber by this method, and we use some of his data for illustration in the following discussion. Ideally, one might obtain all three functions for the same value of λ in tests over a period of two days. Axial tension measurements yield $R(0, t)$ through (7.3). Occasional small twists are used to measure the one-minute modulus ($R(t_s, 1m)$ at various times t_s. Finally, a twist applied after the specimen has been stretched for a day yields $R(24h, t)$. The latter function will replace $R(\infty, t)$, and $R(t_s, 1m)$ will replace $R(t_s, 0)$.

The analysis of data is illustrated in Tables 1, 2 and 3, which apply to values of λ nominally equal to 2.5, 3.2 and 4.2, respectively. The data for a particular value of λ were not all acquired

Table 1. ($\lambda = 2.5$)

	$t = 1m$	$t = 10m$	$t = 100m$	$t = 24h$
1. $R(2.505, 24h, t)$	26.71*	26.61	26.49	—
2. D_1	0.22	0.12	0	—
3. $R(2.5, 0, 24h + t)$	26.21	26.205	26.195	—
4. D_2	0.015	0.01	0	—
5. $A(t) - A(100m)$	0.21**	0.12	0	$-0.135E$
6. $R(2.5, 0, t)$	27.50	27.09	26.68	26.21
7. $B(t) + A(100m)$	27.29	26.97	26.68	26.34
8. $R(2.495, t - 1m, 1m)$	27.3	27.2	26.9	26.71*
9. $C(t - 1m) + A(1m) - A(100m)$	0.0	0.2	0.2	0.37
10. $C(t - 1m)$ raw	-0.2	0.0	0.0	0.16
11. $C(t - 1m)$ adjusted	0	0.2	0.2	0.37

Table 2. ($\lambda = 3.2$)

	$t = 1m$	$t = 10m$	$t = 100m$	$t = 24h$
1. $R(3.221, 24h, t)$	41.32*	41.14	40.93	—
2. D_1	0.39	0.21	0	—
3. $R(3.23, 0, 24h + t)$	39.51	39.50	39.44	—
4. D_2	0.07	0.06	0	—
5. $A(t) - A(100m)$	0.36**	0.18	0	$-0.20E$
6. $R(3.23, 0, t)$	43.65	42.65	41.65	39.51
7. $B(t) + A(100m)$	43.29	42.47	41.65	39.71
8. $R(3.236, t - 1m, 1m)$	43.9	43.7	43.3	41.32*
9. $C(t - 1m) + A(1m) - A(100m)$	0.6	1.2	1.65	1.61
10. $C(t - 1m)$ raw	0.24	0.84	1.29	1.25
11. $C(t - 1m)$ adjusted	0	0.6	1.05	1.01

Table 3. ($\lambda = 4.2$)

	$t = 1m$	$t = 10m$	$t = 100m$	$t = 24h$
1. $R(4.195, 24h, t)$	86.88*	84.67	81.94	—
2. D_1	4.94	2.73	0	—
3. $R(4.2, 0, 24h + t)$	47.15	47.13	46.95	—
4. D_2	0.20	0.18	0	—
5. $A(t) - A(100m)$	4.84**	2.64	0	$-3.06E$
6. $R(4.2, 0, t)$	64.35	58.01	52.57	47.15
7. $B(t) + A(100m)$	59.51	55.37	52.57	50.21
8. $R(4.222, t - 1m, 1m)$	$65E$	77.3	83.8	86.88*
9. $C(t - 1m) + A(1m) - A(100m)$	$5.5E$	21.9	31.2	36.67
10. $C(t - 1m)$ raw	$0.7E$	17.1	26.4	31.83
11. $C(t - 1m)$ adjusted	0	16	26	31

in a single run as described above, and for this reason the three functions R are at slightly different values of λ and slightly different temperatures. Indeed, the values shown for $R(0, t)$ were obtained by interpolation from data at other stretches. All modulus values are in bars.

The relation (8.1) is replaced by the operations shown in lines 1 to 5 of the tables. No absolute determination of $A(t)$ is possible since $R(\infty, \infty)$ cannot be known, but $A(t) - A(100m)$ can be determined with good accuracy. Line 1 of the table shows the values of $R(24h, t)$, and line 2 shows the difference D_1 defined by

$$D_1 = R(24h, t) - R(24h, 100m). \tag{8.4}$$

According to (7.7), this is equal to

$$D_1 = A(t) - A(100m) + [B(24h + t) - B(24h + 100m)]. \tag{8.5}$$

The terms involving B nearly cancel if B is changing relatively slowly after 24 hours. To estimate the change in B, in line 3 we show the values of $R(0, 24h + t)$ and in line 4, the difference D_2 defined by

$$D_2 = R(0, 24h + t) - R(0, 24h + 100m). \tag{8.6}$$

According to (7.7), this difference is equal to

$$D_2 = A(24h + t) - A(24h + 100m) + [B(24h + t) - B(24h + 100m)]. \tag{8.7}$$

If A and B are both monotonically decreasing, we can take the change in B to be half of D_2, with an error then equal to half of D_2 at most. Since D_2 is quite small, the resulting error in the determination of A is insignificant. By subtracting $D_2/2$ from line 2, we obtain line 5, which gives the approximate values of $A(t) - A(100m)$. The value at $t = 24h$ is then estimated by assuming that $A(t)$ is linear in $\log t$, with the same slope that it had between $t = 10m$ and $t = 100m$.

The determination of B is nearly the same as indicated by (8.2). Line 6 shows the values of $R(0, t)$. By subtracting line 5 from line 6, we obtain line 7, which is then equal to $B(t) + A(100m)$.

Lines 8 to 11 implement the analysis suggested by (8.3). Line 8 shows the values of $R(t - 1m, 1m)$. The value at $t = 24h$ is at a slightly different value of λ. This value, marked by an asterisk, is taken from line 1.

Line 9 is the difference between line 8 and line 7,

$$R(t - 1m, 1m) - B(t) - A(100m) = C(t - 1m) + [A(1m) - A(100m)]. \tag{8.8}$$

The difference in A values in the right-hand member is obtained from line 5, where the appropriate value is marked by a double asterisk. Subtracting this difference from line 9 yields line 10, which should be equal to $C(t - 1m)$.

Although $C(0) = 0$ by definition, the corresponding value in line 10 is not zero because the values of R from which it was computed are not all at the same value of λ and not all at exactly the same temperature. The computed value of $C(0)$ indicates the amount of error introduced by these discrepancies. This value is subtracted from all of the values in line 10 to obtain the adjusted values in line 11. In Table 1 the adjustment is the major part of the final values of $C(t)$, and so these values are doubtful. In Table 2 the adjustment is less important, and in Table 3 it is negligible in comparison to the computed values of C.

The preceding analysis shows how to determine A, B and C from three cross-sections of the function R, under the assumption that (7.7) is valid, but it does not prove that the assumption is correct. A fourth cross-section, such as $R(12h, t)$, would be needed in order to test the relation.

However, since (7.7) is more general than (7.6) and includes it as a special case, our analysis does show that (7.6) is not valid for highly stretched natural rubber. If it were, we would have found the function C to be zero to within experimental error. For the data at $\lambda = 2.5$ it might be argued that the computed values of C are attributable to error, but at $\lambda = 4.2$ the values of C contribute a major part of the modulus.

9. BEHAVIOR OF THE SHEAR MODULUS DURING CRYSTALLIZATION

The data for the two lower stretches, in Tables 1 and 2, are strikingly different from the data at the highest stretch, in Table 3. At the lower stretches the shearing stiffness appears to be mainly an effect of the axial tension in the stretched specimen. If the material is sheared 24 hr after it was stretched, the modulus (line 1) is only slightly larger than the resolved axial tension at that time (line 3), and it is lower than the modulus for a shear at time zero (line 6). The modulus clearly decreases as the axial tension does. The viscoelastic aftereffect that can be attributed to the *change* in strain is already quite small when one minute has elapsed since the shearing.

At the highest stretch (Table 3), the modulus for a shearing after 24 hr (line 1) is drastically higher than the resolved axial tension at that time (line 3). The difference is accentuated because the axial tension is relaxing much faster than it did at the lower stretches, but the difference would still be large even if this were not so, because the modulus for a shear after 24 hr is much higher than the modulus for a shear at time zero (line 6).

In the representation (7.7), the function B accounts for the contribution from the axial tension, and the viscoelastic aftereffect due to a change in strain is represented by the sum $A + C$. In the latter sum, C represents a growth in the stiffness of the material between the time at which it was stretched and the time at which it was sheared, and A represents the subsequent relaxation after shearing. The large qualitative difference between the data at low and high stretches is accounted for, in this representation, by rapid growth of the function C when the stretch is large.

Qualitative reasoning about molecular behavior suggests that the decomposition of the aftereffect into a sum $A + C$ is not correct, even though it is compatible with the limited data considered here. The effects that are observed at large stretches are presumably due to the formation of crystallites in the material, a process that is known to occur in highly stretched natural rubber [3, 4]. It is well known that crystallization relaxes the tension that produces it, or at least this is a natural corollary of the additional extension that occurs when crystallization takes place under constant stress. This accounts for the rapid decrease in $R(\lambda, 0;t)$ in Table 3.

The growth in the shearing stiffness of the material is not so well known or so easy to explain. Although the crystallites may be very stiff, they are also small and dispersed, and their stiffness cannot account for that of the gross material. In a shearing deformation the crystallites will merely rotate with no distortion, and their stiffness is irrelevant. It appears probable that the crystallites contribute to the stiffness of the material in the same way that the cross-links produced by vulcanization would do so. Cross-linking inhibits relative motion of molecules and thus retards stress relaxation.

The stress immediately after a change in strain may be orders of magnitude higher than it is only a short time later. In Tables 1 to 3, the earliest values are those recorded one minute after a change in strain. At the lower stretches, it appears that most of the stress increment has already relaxed during this minute, but at the highest stretch, the crystallites have retarded relaxation to such an extent that the stress remains at a high level after one minute.

The present limited data can be represented in terms of retarded relaxation just as well as in terms of the sum $A+C$; we have used the latter representation here because it leads to much simpler data analysis. We are pursuing further work to support the conjecture of retarded relaxation or to disprove it.

Acknowledgements—This work was supported by a grant from the Advanced Research Projects Agency to the Materials Research Laboratory at Brown University, and by the National Science Foundation under a Grant MCS76-08808. We gratefully acknowledge this support. We also wish to record our sincere thanks to Mrs. E. Fonseca for preparing the manuscript.

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