THEORETICAL AND EXPERIMENTAL STUDIES OF THE VISCOELASTIC BEHAVIOR OF SOFT POLYMERS

Thesis by

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To my parents and my wife

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ABSTRACT

The first order approximation of the theory of the so-called simple material describes the viscoelastic behavior of soft polymers in large deformations with twelve time-dependent material functions and three material constants, all functions of the three invariants of the deformation tensor. Restricting consideration to deformations in which time shift invariance is preserved, a series of models was developed which describe the time dependence of the stress through the Boltzmann superposition integral incorporating into it a suitable nonlinear measure of strain. The theory was developed in its most general three-dimensional form. Its predictions for homogeneous deformations were tested in a series of experiments on an uncrosslinked styrene-butadiene copolymer.

For the prediction of the viscoelastic behavior of soft polymers the simplest form of the theory requires only one time function, the relaxation modulus. In addition, it requires a strain parameter which is a characteristic material constant. The dependence of this parameter on temperature and other material and experimental variables was examined on hand of estimates from published data as well as from the experimental results reported here.

Sensitive tests in which small (theoretically infinitesimal) deformations were superposed on a finite stretch, allowed a distinction to be made between the two simplest forms of the theory which, in principle, should apply to solidlike and to liquidlike behavior, respectively. Although uncrosslinked styrene-butadiene copolymer behaves in many respects like a liquid, it showed unprecedented excellent agreement with the predictions of the solid model at room temperature. It was concluded that under this condition the liquidlike character of the copolymer is not strong enough to satisfy the special requirements of the liquid model.

The new theory allows specific predictions to be made concerning the contribution of internal energy to the restoring force in rubberlike materials. It represents an advance over former theories in that it permits the contribution to be obtained on uncrosslinked as well as on crosslinked soft polymers. Literature data were reviewed and examined in the light of the theory.

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INTRODUCTION

Every engineer at one time or another in his career has to deal with problems related to the deformation of materials. Frequently he is asked to predict or to interpret the response of a material under different excitation conditions. A mathematical model for the response of the material is indispensable for such an assignment. The fundamental tool is mechanics.

The task of mechanics is to link the deformation of a body and the forces applied to it in such a way as to yield good models for the behavior of the material. For sufficiently smooth fields the application of the conservation laws for force (or torque) and energy lead to the familiar *field equations*. In addition, *initial* and/or *boundary conditions* have to be specified. Even with these two pieces of information it is generally not possible to determine the response of the material adequately. Experience has shown that different materials generally behave differently when subjected to the same excitation conditions. Therefore, further restrictions must be introduced before the deformation of a continuum can be determined. Ever since the days of Euler and Cauchy, phenomenological theories of the mechanical behavior have rested on the *constitutive equation* which spells out the relation between the kinematic and dynamic variables.

There are basically two ways to develop a constitutive equation: the phenomenological approach and the molecular (or structural) approach. The former falls into the realm of continuum mechanics. The latter is based on statistical mechanics, molecular hydrodynamics, etc. In the last two decades mathematics research in the field of continuum mechanics has made profound progress(1-9). The efforts of mathematicians have clarified a number of basic concepts such as the definition of various solids and liquids, and also set guide lines for formulating constitutive equations. For the polymer scientist or engineer rational mechanics provides a logical way of proposing constitutive equations and it rationalizes the treatment of the observed mechanical behavior of polymers.

On the other hand, there has been a renaissance of thermodynamics and statistical mechanics during the last twenty years. In particular, the theory of irreversible processes has advanced at an ever increasing rate(10). A general theory of non-equilibrium systems has been developed by van Hoeve and Prigogine(11); a new theory of the linear response of systems to an external perturbation has been developed by Kubo(12-14); the methods of quantum field theory have been introduced successfully into statistical mechanics(14,15). Although these advances are still far from allowing the complete description of general physical systems, answers for some special problems have been obtained.

Continuum mechanics may provide an adequate phenomenological description of observed behavior. Statistical mechanics, on the other hand, may help to establish a reasonable model which incorporates the molecular characteristics of the material into the constitutive equations. Such a model allows correlation of mechanical with other properties (e.g. electrical, optical, etc.), lends physical meaning to the parameters in the phenomenological equations, and supplies a physical picture to predict new phenomena. Therefore, linking the statistical mechanical with the continuum mechanical approach is imperative for accelerating our understanding to the rheological properties of polymers.

Over the past thirty years, there have been significant advances in the field of deformation of polymers. To some extent, however, these advances have suffered from fragmentation among efforts directed towards experiment, phenomenological theory, molecular theory, and engineering applications. Attempts at integration of difference viewpoints should produce cross-fertilization. What the field appears to need most today is probably best expressed by Sir Francis Bacon(16): "The mere rationalists are like spiders who spin a wonderful but flimsy web out of their own bodies; the mere empiricists are like ants who collect raw materials without selection and store them up without modification. True and fruitful science must combine rationalism with empiricism, and be like the bee who gathers materials from every flower and then works them up by her own activities into honey".

The subject of this thesis is the theoretical and experimental investigation of a new approach to the phenomenological description of the viscoelastic behavior of soft (rubberlike) materials in moderately large deformations. For the purposes of this thesis, moderately large deformations are those in which time shift invariance is preserved as explained in Chapter 1. In this chapter the concept of incorporating a generalized strain measure into the Boltzmann superposition integral is introduced and some experimental confirmation is given. In Chapter 2 the rigorous mathematical theory is presented, and two specific three-dimensional constitutive equations are proposed, and are compared with other constitutive models. In Chapter 3 the two models are tested on hand of our own as well as literature data on uncrosslinked soft polymers in uniaxial deformation under different loading histories. Finally, in Chapter 4 the application of the theory to thermoelastic measurements of the internal energy contribution to the restoring force of viscoelastic materials is disucssed.

The format of this thesis consists of a series of self-contained papers. Chapter 1 has now been accepted for publication in the Proceedings of the National Academy of Sciences. Chapter 2 will be submitted to Rheologica Acta. Chapter 3 is slated for submission to the Journal of Polymer Science, and Chapter 4 will be submitted to Macromolecules.

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CHAPTER 1

THE TIME DEPENDENT RESPONSE OF SOFT POLYMERS IN MODERATELY LARGE DEFORMATIONS

ABSTRACT

A new theory successfully describes the time-dependent mechanical behavior of soft incompressible isotropic polymers in moderately large deformations. The theory is based on the introduction of a generalized measure of strain into the Boltzmann superposition integral.

In a polymeric material the ratio of stress at time t to that at an arbitrary reference time t_r in a stress relaxation experiment is usually independent of strain. For stress relaxation in simple tension this behavior was observed by Tobolsky and Andrews (1) on styrene-butadiene rubber rubber (SBR), by Guth et al. (2) on natural rubber (NR), and by us on 1,4-polybutadiene (PBD). Chasset and Thirion (3) studied the stress relaxation behavior of NR and SBR specimens which were prepared with different crosslinking agents. They concluded that the observation holds generally for various network structures. The same behavior was also seen in carbon black and starch xanthide reinforced SBR by Bagley and Dixon (4).

Similar observations have been made in other deformation fields. Our own unpublished data as well as the data of Bergen (5) on carbon black filled SBR and on PVC samples containing various amounts of plasticizer, the data of Gent (6) on SBR, of Valanis and Landel (7) on silica filled poly(dimethyl siloxane) rubber, and by Kawabata (8) on NR and SBR all indicate that the phenomenon is not restricted to simple tension.

This behavior suggests that a constitutive equation containing only a single integral might be more appropriate for the description of time-dependent mechanical properties than one containing multiple integrals. Indeed, several one-dimensional modified Boltzmann integrals have been proposed (e.g. 2,9-12). These attempts can be divided into two classes. One generalizes the integral by replacing the true stress by an experimentally determined function of the tensile stress (12,13). The other replaces the infinitesimal strain of the classical Boltzmann integral by replacing the true stress by an experimentally determined function of the tensile stress (12,13). The other replaces the infinitesimal strain of the classical Boltzmann integral by a finite strain measure such as the Cauchy or Green strain (9,11,13). Leaderman (14) concluded from multiple step creep and creep recovery experiments that the first approach is inadequate. *Hence, it is ruled out from our considerations.*

The observations we have cited strongly intimate that the non-linear mechanical response of soft (i.e. rubberlike) materials results from strain non-linearity while time shift invariance is essentially preserved (i.e. the normalized modulus density on relaxation time remains unchanged), at least in moderately large deformations. The term "moderately large" will be made more precise further on.

To introduce our formalism we first consider the purely elastic deformation of an incompressible isotropic soft material. We write our constitutive equation as

$$t^{k}{}_{\ell} = -p\delta^{k}{}_{\ell} + 2Gb^{k}{}_{\ell} \qquad [1]$$

where $t^{k}{}_{\ell}$ is the (mixed) Cauchy stress tensor, p is an arbitrary hydrostatic pressure, $\delta^{k}{}_{\ell}$ is the Kronecker delta, G is the shear modulus, and

$$b^{k}{}_{\ell} = (\bar{c}^{1k}{}_{\ell} - \delta^{k}{}_{\ell})/2 \qquad [2]$$

is a (mixed) strain tensor defined in terms of Finger's deformation tensor whose contravariant form is

$$\overset{-1}{c}{}^{k\ell} = G^{KL} x^{k}{}_{,K} x^{\ell}{}_{,L} \tag{3}$$

In Eq. 3 the $\{x^k\}$ are the spatial (deformed) coordinates, the comma denotes partial differentiation with respect to the material (undeformed) coordinates $\{X^K\}$, and G_{KL} is the metric tensor of the material system.

Rotation to principal axes yields

$$t_{\alpha} = \nu^{\alpha}{}_{k}\, t^{k}{}_{\ell}\, \nu^{\ell}{}_{\alpha} \qquad \text{(no summation on } \alpha) \qquad [4]$$

and

$$\overset{-1}{c}{}_{\alpha} = n^{\alpha}{}_{k}\, \overset{-1}{c}{}^{k}{}_{\ell}\, n^{\ell}{}_{\alpha} \qquad \text{(no summation on } \alpha) \qquad [5]$$

where $\alpha=1,2,3$, and the $\{\nu^k\}$ and $\{n^k\}$ are the eigenvectors of the stress tensor and the deformation tensor, respectively. For purely elastic isotropic materials, these eigenvectors are identical. Substituting Eqs. 4, 5, and 2 into 1 gives

$$t_{\alpha} = -\,p + 2Gb_{\alpha} \qquad [6]$$

where

$$b_{\alpha} = (\overset{-1}{c}{}_{\alpha} - 1)/2 = (\lambda_{\alpha}{}^{2} - 1)/2 \qquad [7]$$

In Eqs. 4 through 7 the $\{t_\alpha\}$, $\{b_\alpha\}$, and $\{\overset{-1}{c}{}_\alpha\}$ are the principal components of the respective tensors, and the $\{\lambda_\alpha\}$ are the principal stretch ratios. We note that $b_\alpha = E_\alpha$ where the $\{E_\alpha\}$ are the principal components of the Lagrangean strain tensor, and that $t_\alpha = \bar{\sigma}_\alpha$ where the $\{\bar{\sigma}_\alpha\}$ are the true stress components. This establishes the connection with the notation we have used in preceding publications (19-21). The principal components (i.e. the eigenvalues) of the two tensors, $b^k{}_\ell$ and $E^K{}_L$, are identical. We have replaced $E^K{}_L$ by a strain tensor in spatial coordinates for convenience in extending the treatment to viscoelastic behavior.

To generalize the strain measure, Eq. 7, we now write

$$\underline{b}_\alpha = (\underline{c}_\alpha^{-1\ n/2} - 1)/n = (\lambda_\alpha^n - 1)/n \qquad [8]$$

where the underscore distinguishes the generalized tensor components from the classical ones. We prefer $\underline{b}_\alpha$ because the strain exponent, n, will then be positive definite for a rubberlike material. We note that n, a material parameter, has nothing to do with the eigenvectors, n^k.

The idea of a generalized measure of strain is not new. Its earlier history has been reviewed by Truesdell and Toupin (15). Some new measures were proposed by Karni and Reiner (16). Seth (17, 18) applied it to transition field problems such as elastic-plastic transitions, creep, boundary layers, and shocks. Blatz, Sharda, and Tschoegl (19-21) and Ogden (22) independently adopted the idea of a generalized strain measure to predict equilibrium stress-strain relations for crosslinked SBR and NR samples under various modes of deformation. The agreement between the predictions of their theories and the experimental results was unprecedentedly good.

We now adapt the idea to the problem of time-dependent (viscoelastic) deformations by introducing our generalized strain, Eq. 8, into the Boltzmann superposition integral. We obtain

$$\bar{\sigma}_{\alpha}(t) = -p + 2\int_{0}^{t} G(t-u)\frac{d\underline{b}_{\alpha}(u)}{du}du \qquad [9]$$

where t is the present time, u is the past time, and G(t) is the shear relaxation modulus in small (theoretically infinitesimal) deformation. Excluding the glassy and upper transition regions of the viscoelastic response from consideration, we may replace 3G(t) by E(t) where the latter is the tensile small deformation relaxation modulus. Introducing, in addition, the second of Eqs. 8 into Eq. 9 we obtain

$$\bar{\sigma}_{\alpha}(t) = -p + (2/3n)\int_{0}^{t} E(t-u)\frac{d\lambda^{n}_{\alpha}(u)}{du}du \qquad [10]$$

Eq. 10 is limited to moderately large deformations for both theoretical and experimental reasons to be discussed elsewhere. Under a moderately large deformation we understand one which requires only the first term of the elastic potential functions of Blatz, Sharda, and Tschoegl and of Ogden for the description of their mechanical response in purely elastic deformations. In our present notation this single term potential function becomes

$$W = (2G/n)\ I_{\underline{b}} \qquad [11]$$

where $I_{\underline{b}}$ is the first invariant of the generalized strain tensor $\underline{b}^k{}_\ell$. Typically, in a moderately large deformation of an unfilled crosslinked rubber the stretch ratio would not exceed about 2.5 in simple tension.

Equation 10 is neither the only admissible form nor is it the most general one. Other admissible forms and their relations with mechanical models will be discussed in a separate paper. The equation reduces to the classical Boltzmann superposition integral for infinitesimal deformations, and it reduces to the stress-strain relations given by Blatz, Sharda and Tschoegl (20) in purely elastic deformations. In particular, the response to a step function of strain in simple tension becomes

$$\bar{\sigma}(t) = (2/3n)(\lambda^n-\lambda^{-n/2})E(t) \tag{12}$$

We note that this relation is true for all times, and, hence, also for a specific isochronal time.

The only material information needed to apply Eq. 10 is a relaxation function and the strain exponent n. The relaxation function can be constructed, utilizing the time-temperature superposition principle, by conducting stress relaxation tests at different temperatures in small deformations. The exponent n can be found, using non-linear least squares fitting, from isochronal stress-strain relations cross-plotted from stress relaxation measurements in simple tension at different values of strain in moderately large deformations. The exponent n, its variation with temperature, crosslink density, nature of material, etc., will be discussed in another forthcoming publication.

As an example, we show here the application of Eq. 10 to constant rate of strain experiments. The experiments were made on specimens of dicumyl peroxide cured SBR 1502 having a 100 minute tensile modulus of 7.55 bar at 23°C. The specimens were slightly swollen (about 1.5%) in silicone oil. The reasons for this are irrelevant to the present discussion and will be presented elsewhere. The strain exponent, n, was 1.22 for this sample at 23°C.

For constant rate of strain, $\dot{\varepsilon}$, Eq. 10 specializes to

$$\bar{\sigma}(t) = (2\dot{\varepsilon}/3)\int_{0}^{t} E(t-u)[\lambda^{n-1}(u) + 0.5\lambda^{-n/2-1}(u)]du \qquad [13]$$

where $\lambda(u) = 1 + \dot{\varepsilon}u$. Fig. 1 shows data at four strain rates. The filled circles and the lines represent the experimental data and the theoretical predictions, respectively. Fig. 2 embodies the results of an experiment in which the specimen was first extended at the indicated rate of strain to a predetermined strain, left to relax ($\dot{\varepsilon}$=0), and then brought back to zero stress at a different strain rate 10 minutes after the first stretch was begun (t_r).

We have examined numerous literature data as well as our own. In all cases the agreement between theory and experiment was within experimental error. We have extended our treatment to uncrosslinked materials with similarly good results. These studies will be presented in a series of papers now in preparation.

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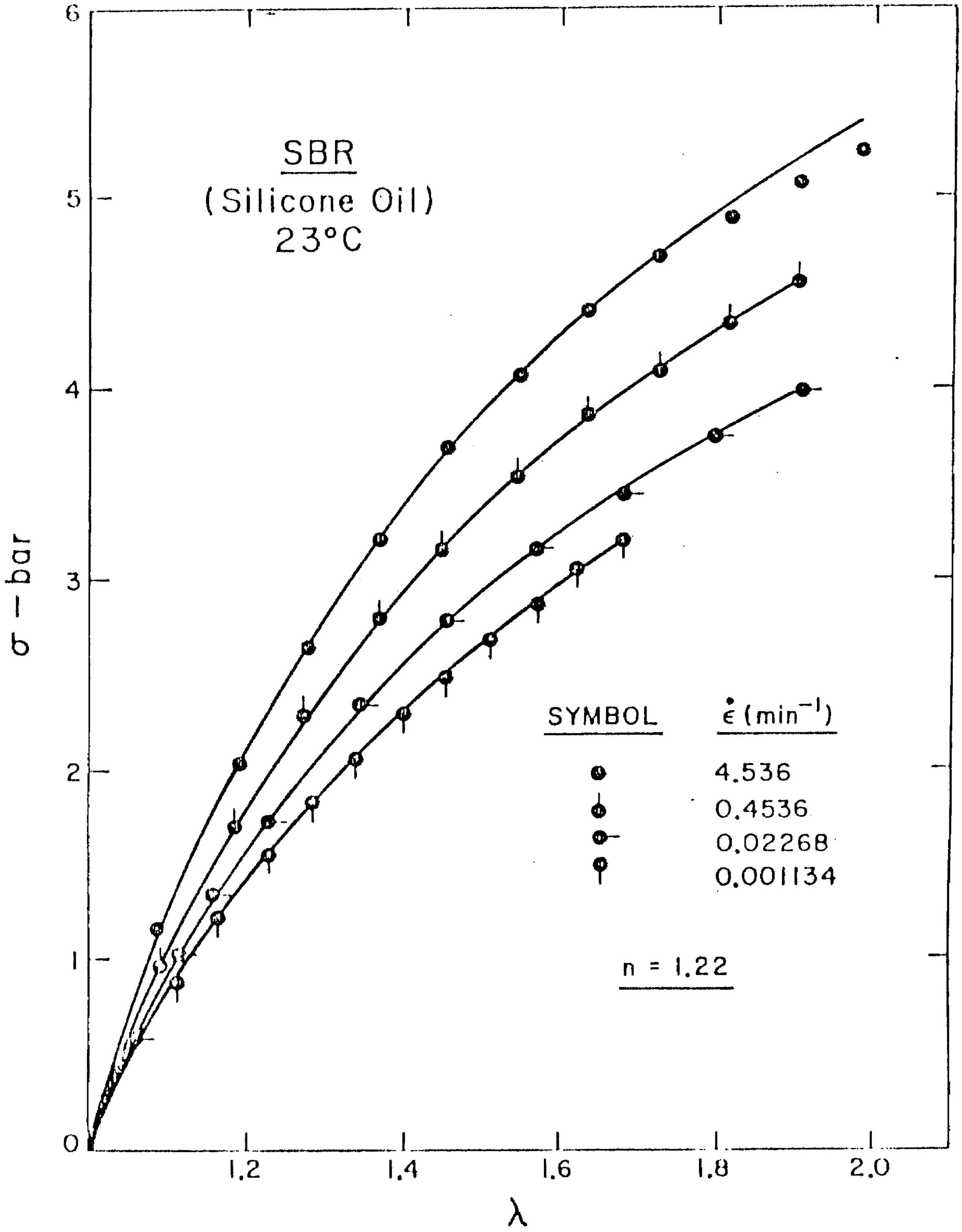

Figure 1. Stress-strain curves on styrene-butadiene rubber at different rates of extension fitted by Eq. 13.

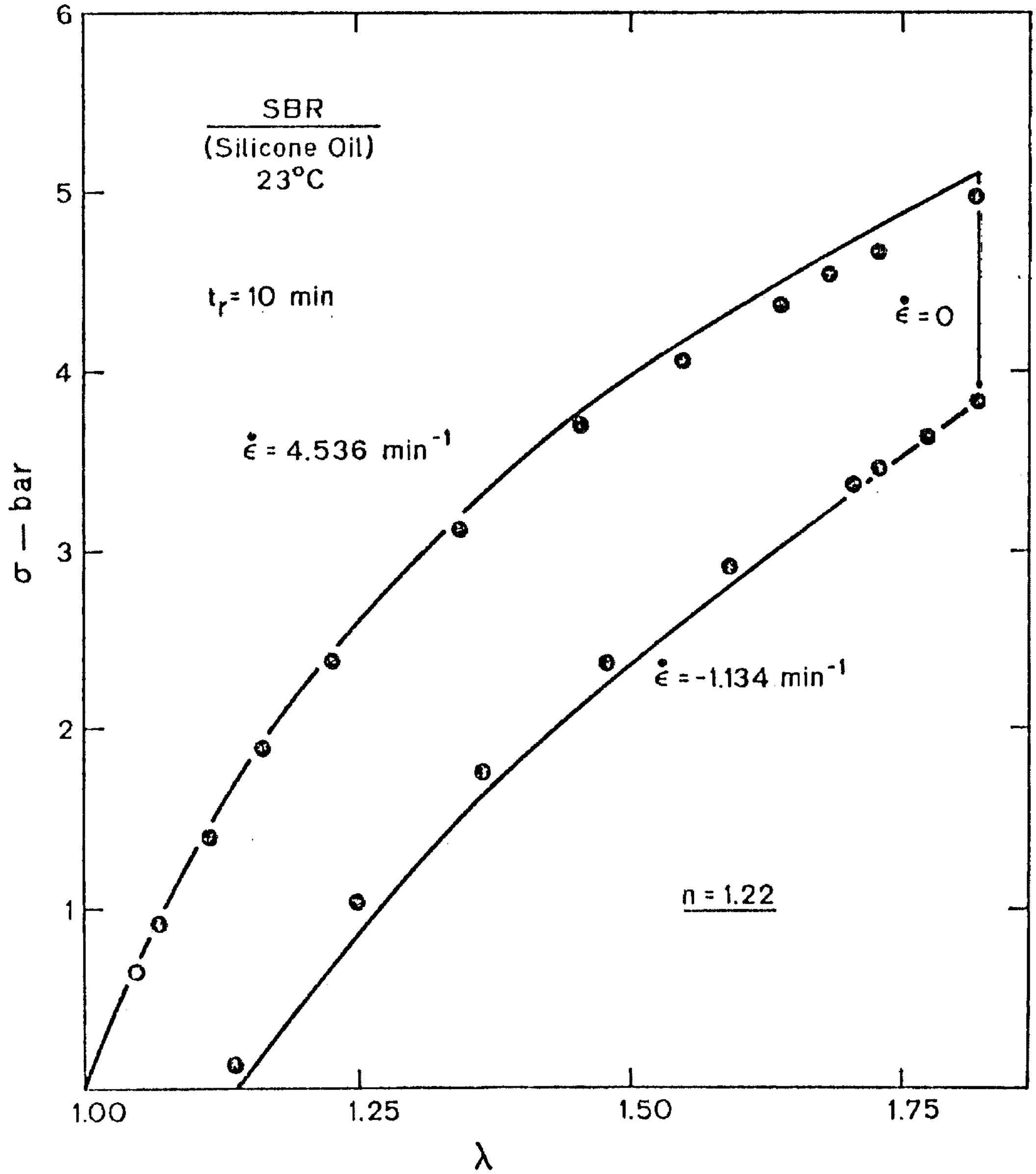

Figure 2. Response to a trapezoidal strain excitation fitted by Eq. 13.

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CHAPTER 2

ON THE VISCOELASTIC THEORIES OF LARGE DEFORMATIONS

1. Introduction

A key aim of research in polymer rheology is to obtain, for specific materials, a three dimensional constitutive equation which accounts for the observed mechanical properties. Despite a great deal of progress, it appears that the search for constitutive equations which give realistic descriptions of the viscoelastic behavior of polymeric materials and is mathematically simple enough for use in engineering applications, is far from concluded (1,2,3,4). In this paper we propose a linear integral theory which is based on the introduction of a generalized measure of strain into the Boltzmann superposition integral. A special version of the theory was formulated in terms of the principal directions and was experimentally verified in an earlier publication (5). Further experimental evidence (6,7) and the range of applicability of the theory (8,9,10) will be presented elsewhere.

The theory assumes that the viscoelastic behavior of a material is represented by its relaxation spectrum and that the spectrum remains unchanged in moderately large deformations. In other words, in such deformations the nonlinear viscoelastic behavior results solely from (time-independent) stress-strain nonlinearity. While time shift invariance is preserved. The stress-strain nonlinearity can be properly accounted for by choosing an appropriate strain measure.

In the following discussion we shall use tensor component notation only in a subordinate way. A tensor field is logically distinct from its components in a given coordinate system just as a function is logically distinct from its value at a point. As pointed out by Lodge (11), working with the tensors themselves instead of their components not only facilitates manipulation but also enhances the understanding of the underlying processes.

We generally use Truesdell's notation (1). However, the rank of a tensor will be denoted by the number of bars underlining its symbol. For a second rank tensor $\underline{\underline{A}}$, we shall denote the transpose by $\underline{\underline{A}}^T$, and the inverse, when it exists, by $\underline{\underline{A}}^{-1}$. The identity or unit tensor is written $\underline{\underline{I}}$. We shall write $\underline{\underline{A}}^2$ for the second rank tensor $\underline{\underline{A}}\cdot\underline{\underline{A}}$, with a similar convention for products of higher integral order. We denote the trace of a tensor $\underline{\underline{A}}$ by $\mathrm{tr}\underline{\underline{A}}$. The symbol $\underline{\underline{Q}}$ will be used only for orthogonal tensors. We denote the matrix formed from the mixed components of a tensor by a wavy underscore.

2. Fundamental Kinematics

Consider a material point or particle ξ of a body $\mathcal{B}$. Suppose that ξ occupies the position $\underline{X}$ when $\mathcal{B}$ is in a reference configuration. Let ξ occupy the instantaneous position $\tilde{\underline{x}}$ at the time u. Then the motion of $\mathcal{B}$ may be written in the form

$$\tilde{\underline{x}} = \tilde{\underline{x}}(\underline{X},u) \qquad [2.1]$$

Thus the instantaneous location $\tilde{\underline{x}}$ may be represented as a function of the reference location $\underline{X}$ and of the past time u.

The gradient $\underline{\underline{F}}(u)$ of $\tilde{\underline{x}}(\underline{X},u)$ with respect to $\underline{X}$ becomes

$$\underline{\underline{F}}(u) = \nabla\tilde{\underline{x}}(\underline{X},u) \qquad [2.2]$$

where ∇ is the del operator. $\underline{\underline{F}}(u)$, a second rank tensor, is called the deformation gradient tensor at the material point ξ at time u.

By the theorem of polar decomposition (1), $\underline{\underline{F}}$ can be split into a symmetric positive definite *stretch tensor* and an orthogonal *rotation tensor*. Thus

$$\underline{\underline{F}}(u) = \underline{\underline{R}}(u)\cdot\underline{\underline{U}}(u) = \underline{\underline{V}}(u)\cdot\underline{\underline{R}}(u) \qquad [2.3]$$

where

$$\underline{\underline{R}}(u)\cdot\underline{\underline{U}}(u) = \underline{\underline{V}}(u)\cdot\underline{\underline{R}}(u) \qquad [2.4]$$

$\underline{\underline{U}}$ and $\underline{\underline{V}}$ are the right and left stretch tensors, respectively.

In general, the calculation of the components of $\underline{\underline{U}}$ and $\underline{\underline{V}}$ is involved and it is preferable to introduce the *deformation tensors*

$$\underline{\underline{C}} = \underline{\underline{U}}^2 = \underline{\underline{F}}^T\cdot\underline{\underline{F}} \qquad [2.5]$$

$$\underline{\underline{B}} = \underline{\underline{V}}^2 = \underline{\underline{F}}\cdot\underline{\underline{F}}^T \qquad [2.6]$$

which are called the right Cauchy-Green (or Green tensor), and the left Cauchy-Green (or Finger) tensor, respectively. $\underline{\underline{C}}$ and $\underline{\underline{B}}$ are related by

$$\underline{\underline{R}}(u)\cdot\underline{\underline{C}}(u) = \underline{\underline{B}}(u)\cdot\underline{\underline{R}}(u) \qquad [2.7]$$

Next, let us denote the position occupied by the material point ξ at time t (the present time) as $\underline{x}$. Then

$$\underline{x} = \underline{x}(\underline{X},t) \qquad [2.8]$$

which, in the applications we are considering here, possesses a unique inverse so that

$$\underline{X} = \underline{X}(\underline{x},t) \qquad [2.9]$$

Therefore, we may write

$$\tilde{\underline{x}} = \tilde{\underline{x}}_t(\underline{x},u) \qquad [2.10]$$

which should be compared with eq. [2.1]. Eq. [2.10] gives the instantaneous location $\tilde{\underline{x}}$ as a function of the past time u and the present location, i.e. the location at the present time t. Hence, we can define the deformation gradient tensor at time u relative to the configuration at time t as

$$\underline{\underline{F}}_t(u) = \underline{\underline{F}}(u)\cdot\underline{\underline{F}}^{-1}(t) = \nabla_{\underline{x}}\tilde{\underline{x}}_t(\underline{x},u) \qquad [2.11]$$

where the subscript on ∇ emphasizes the independent variable of differentiation. Similarly, we define the right Cauchy-Green and left Cauchy-Green tensors, respectively, at time u relative to the configuration at time t, by

$$\underline{\underline{C}}_t(u) = \underline{\underline{U}}_t^{\,2}(u) = \underline{\underline{F}}_t^{T}(u)\cdot\underline{\underline{F}}_t(u) \qquad [2.12]$$

$$\underline{\underline{B}}_t(u) = \underline{\underline{V}}_t^{\,2}(u) = \underline{\underline{F}}_t(u)\cdot\underline{\underline{F}}_t^{\,T}(u) \qquad [2.13]$$

It follows from their definitions that both the right and left Cauchy-Green tensors are symmetric and are positive definite. Furthermore,

$$\underline{\underline{F}}_t(t) = \underline{\underline{U}}_t(t) = \underline{\underline{V}}_t(t) = \underline{\underline{R}}_t(t) = \underline{\underline{C}}_t(t) = \underline{\underline{B}}_t(t) = \underline{\underline{I}} \qquad [2.14]$$

We also have

$$\underline{\underline{F}}_u(t) = \underline{\underline{F}}(t)\cdot\underline{\underline{F}}^{-1}(u) = \nabla_{\tilde{\underline{x}}}\,\underline{x}_u(\tilde{\underline{x}},t) \qquad [2.15]$$

where $\underline{x}_u(\tilde{\underline{x}},t)$ denotes the present location as a function of the instantaneous location and the present time. Thus

$$\underline{\underline{C}}_t(u) = \underline{\underline{B}}_u^{-1}(t) \qquad [2.16]$$

when $\underline{\underline{B}}_u^{-1}(t)$ is the inverse Finger tensor at the present time t relative to the past time u.

Any constitutive equation must satisfy the principle of material frame indifference. This is a mathematical statement of the requirement that the response of a material be invariant under a rotation of reference frame. A reference frame is an object with respect to which the motion is observed. There is a fundamental difference between reference frames and coordinate systems. Tensors of any rank are, by definition, invariant to a change of coordinates within a given frame of reference. They are, however, not necessarily invariant under a change of the reference frame. A vector $\underline{r}$ and a second rank tensor $\underline{\underline{T}}$ are called frame-indifferent if they are related in two frames of reference by

$$\underline{r}^{*} = \underline{\underline{Q}}(t)\cdot\underline{r} \qquad [2.17]$$

and

$$\underline{\underline{T}}^{*} = \underline{\underline{Q}}(t)\cdot\underline{\underline{T}}\cdot\underline{\underline{Q}}^{T}(t) \qquad [2.18]$$

In eqs. [2.17] and [2.18] the asterisks denotes the new frame and $\underline{\underline{Q}}$ (t) represents a time-dependent relative rotation of the two frames. It can be shown that $\underline{\underline{F}}_t(u)$, $\underline{\underline{U}}(u)$, $\underline{\underline{V}}_t(u)$, $\underline{\underline{C}}(u)$, $\underline{\underline{B}}_t(u)$ are not frame-indifferent, and $\underline{\underline{V}}(u)$, $\underline{\underline{U}}_t(u)$, $\underline{\underline{B}}(u)$, $\underline{\underline{C}}_t(u)$ are frame-indifferent (12).

We note that the velocity field

$$\underline{v}(\underline{x},t) = - \left.\frac{\partial \underline{x}_t(\underline{\tilde{x}},u)}{\partial u}\right|_{u=t} \qquad [2.19]$$

is not frame-indifferent. We define a velocity gradient tensor

$$\underline{\underline{G}}(t) = \nabla_{\underline{x}}\underline{v}(\underline{x},t) = \underline{\underline{d}}(t) + \underline{\underline{\omega}}(t) \qquad [2.20]$$

where $\underline{\underline{d}}(t)$ is a symmetric second rank tensor called the stretching tensor and $\underline{\underline{\omega}}(t)$ is an antisymmetric tensor called the vorticity (or spin) tensor. The tensor $\underline{\underline{d}}(t)$ is frame indifferent but the tensor $\underline{\underline{\omega}}(t)$ is not.

The velocity gradient tensor is related to the deformation gradient tensor at time u relative to the configuration at time t by

$$\underline{\underline{G}}(t) = \left.\frac{d}{du}\,\underline{\underline{F}}_t(u)\right|_{u=t} \qquad [2.21]$$

By eq. [2.3a]

$$\underline{\underline{G}}(t) = \dot{\underline{\underline{U}}}_t(t) + \dot{\underline{\underline{R}}}_t(t) \qquad [2.22]$$

where

$$\dot{\underline{\underline{U}}}_t(t) = \frac{d}{du}\underline{\underline{U}}_t(u)\Big|_{u=t} = \underline{\underline{d}}(t) \qquad [2.23]$$

and

$$\dot{\underline{\underline{R}}}_t(t) = \frac{d}{du}\underline{\underline{R}}_t(u)\Big|_{u=t} = \underline{\underline{\omega}}(t) \qquad [2.24]$$

by equating the symmetric and antisymmetric tensors. It further follows from eq. [2.12b] that

$$\frac{d}{du}\underline{\underline{C}}_t(u)\Big|_{u=t} = 2\underline{\underline{d}}(t) \qquad [2.25]$$

because $\underline{\underline{\omega}}(t)$, being antisymmetric, cancels in the differentiation.

3. Constitutive Equations for Materials with Fading Memory.

Mathematical theories of constitutive equations for materials with memory have been formulated in recent years by several authors (1,2, 13-20). In general, all these theories start from the principles of determinism, local action and material frame indifference (1), and can be classified into two categories. In constitutive equations belonging to the first category (17-20), the stress tensor and its time derivatives are related to various kinematic quantities such as gradients of deformation, velocities, and higher order accelerations. These are usually called rate theories and emerge from Oldroyd's original work (18). Couching constitutive equations in terms of derivatives makes it impossible to compute the stress tensor for all but the simplest kinematics except by perturbation methods or by seeking numerical solutions, since one must solve six simultaneous equations (21). Furthermore, some constitutive equations of this type suffer from an apparent instability above a critical shear rate in superposed simple or sinusoidal shearing and are therefore unsuitable for the description of polymeric behavior (22). Hence, we will not discuss them here.

In constitutive equations belonging to the second category, the stress tensor is functionally related to the entire history of deformation (1). An important special case is the constitutive equation for the so-called simple material in which the stress at a particle is determined by the cumulative history of the deformation gradient at that particle (1, 15, 23). Mathematically, it has the form

$$\underline{\underline{\sigma}}(t) = \underset{u=\infty}{\overset{u=t}{\underline{\underline{\mathcal{F}}}}} \, [\underline{\underline{F}}(u)] \qquad [3.1]$$

where $\underline{\underline{\sigma}}(t)$ is the Cauchy stress and $\underline{\underline{\mathcal{F}}}$, is a tensor-valued functional which depends on the material coordinates $\underline{X}$ and the present time t.

The application of the principle of material frame indifference leads to

$$\underline{\underline{Q}}(t)\cdot\underline{\underline{\sigma}}(t)\cdot\underline{\underline{Q}}^{T}(t) = \underset{u=-\infty}{\overset{u=t}{\underline{\underline{F}}}} [\underline{\underline{Q}}(u)\cdot\underline{\underline{F}}(u)] \qquad [3.2]$$

which imposes restrictions on the constitutive functional and its arguments. For example, one reduced form (1) of eq. [3.1] is

$$\underline{\underline{\sigma}}(t) = \underline{\underline{R}}(t)\cdot \underset{u=-\infty}{\overset{u=t}{\underline{\underline{F}}}} [\underline{\underline{U}}(u)]\cdot\underline{\underline{R}}^{T}(t) \qquad [3.3]$$

For an isotropic material, it can be shown (1) that

$$\underline{\underline{\sigma}}(t) = \underset{u=-\infty}{\overset{u=t}{\underline{\underline{F}}}} [\underline{\underline{V}}(u)] \equiv \underset{u=-\infty}{\overset{u=t}{\underline{\underline{G}}}} [\underline{\underline{B}}(u)] \qquad [3.4]$$

The functional $\underline{\underline{G}}$ will in general depend on the configuration which is taken as reference in computing the deformation gradient. Some materials such as crosslinked elastomers and crystals possess certain special configurations which, when taken as reference configurations, will simplify the form of $\underline{\underline{G}}$.

Eq. [3.3] states that for a simple material the dependence of the stress tensor on the rotation tensor $\underline{\underline{R}}$ is explicitly known but the dependence on the stretch tensor $\underline{\underline{U}}$ is arbitrary. From the results of one stretching history it is not possible to predict the results of other stretching histories in general. Furthermore, the entire history of the body can never be completely specified. Hence, a theory of this type is still too general for the experimentalist to design experiments from which the rheological properties of the material can be deduced.

We need to define a norm which provides a precise measure of the distance between two deformation histories. With this as a basis we can define the continuity and smoothness of functionals. With the further assumption that the stress functional is continuous, the functional can be expanded in terms of a series of multiple integrals. This expansion is similar to the Taylor expansion of an analytic function into an infinite series. There are various representations of the functional $\underset{=}{G}$ in terms of series of multiple integrals. Here, we will briefly discuss the two most referenced ones, the Green-Rivlin (13) and the Coleman-Noll (14) representations which will be denoted by G-R and C-N, respectively, from now on. In both theories the concept that deformations that occurred in the distant past should have less significance in determining the present stress than those that occurred in the recent past is used to define the distance between two deformation histories. Therefore, these theories are frequently referred to as theories for materials with fading memory.

Based on this principle of fading memory, Coleman and Noll (14) defined a Fréchet differential of the stress functional. By assuming that the functional is Fréchet differentiable n times about the zero history they obtained n successive approximations. This is basically a generalization of the Weierstrass theorem which states that a continuous function may always be approximated by a polynomial. Furthermore, they also proved that the Boltzmann superposition integral constitutes the limit of infinitesimal deformation. They also pointed out that any given stretch history $\underline{\underline{U}}(t)$ may be regarded as arising from the superposition of an additional stretch on some arbitrarily chosen state of steady stretch $\underline{\underline{U}}_o$. In particular, we may take $\underline{\underline{U}}_o$ to be $\underline{\underline{U}}(t)$, and rewrite eq. [3.4] as

$$\underline{\underline{\sigma}}(t) = \underline{\underline{W}}[\underline{\underline{B}}(t)] + \underset{u=-\infty}{\overset{t}{\mathcal{G}}} [\underline{\underline{D}}(u;t);\underline{\underline{B}}(t)] \qquad [3.5]$$

where

$$\underline{\underline{D}}(u;t) \equiv [\underline{\underline{C}}_t(u)-\underline{\underline{I}}]/2 \qquad [3.6]$$

and the conditions

$$\underline{\underline{D}}(t;t) = 0 \qquad [3.7]$$

and

$$\underset{u=-\infty}{\overset{t}{\underline{\underline{\mathcal{G}}}}} [\underline{\underline{0}};\underline{\underline{B}}(t)] = 0 \qquad [3.8]$$

apply. In eq. [3.5], $\underline{\underline{W}}$ represents the equilibrium response of the material, $\underline{\underline{D}}$ depends parametrically on t and the functional $\underline{\underline{\mathcal{G}}}$ depends parametrically on $\underline{\underline{B}}(t)$.

For isotropic materials, Coleman and Noll prove that, under the restriction of slow motions, the rheological properties can be approximated by a first order Fréchet differential which can in turn be expressed by three material functions of the strain invariants and twelve relaxation functions which are also functions of the strain invariants. Mathematically, it has the form (24)

$$
\begin{aligned}
\underline{\underline{\sigma}}(t) = {}& {}^{0}\phi_{0}\,\underline{\underline{I}} + {}^{1}\phi_{0}\,\underline{\underline{B}} + {}^{2}\phi_{0}\,\underline{\underline{B}}^{2} \\
& + \int_{-\infty}^{t} \{ [{}^{0}\phi_{1}(t-u)\underline{\underline{I}} + {}^{1}\phi_{1}(t-u)\underline{\underline{B}} + {}^{2}\phi_{2}\underline{\underline{B}}^{2}]\cdot\dot{\underline{\underline{C}}}_{t}(u) \\
& + \dot{\underline{\underline{C}}}_{t}(u)\cdot[{}^{0}\phi_{1}(t-u)\underline{\underline{I}} + {}^{1}\phi_{1}(t-u)\underline{\underline{B}} + {}^{2}\phi_{1}(t-u)\underline{\underline{B}}^{2}] \\
& + \underline{\underline{I}}\,\mathrm{tr}[\dot{\underline{\underline{C}}}_{t}(u)\cdot({}^{0}\phi_{2}(t-u)\underline{\underline{I}} + {}^{1}\phi_{2}(t-u)\underline{\underline{B}} + {}^{2}\phi_{2}(t-u)\underline{\underline{B}}^{2})] \\
& + \underline{\underline{B}}\,\mathrm{tr}[\dot{\underline{\underline{C}}}_{t}(u)\cdot({}^{0}\phi_{3}(t-u)\underline{\underline{I}} + {}^{1}\phi_{3}(t-u)\underline{\underline{B}} + {}^{2}\phi_{3}(t-u)\underline{\underline{B}}^{2})] \\
& + \underline{\underline{B}}^{2}\mathrm{tr}[\dot{\underline{\underline{C}}}_{t}(u)\cdot({}^{0}\phi_{4}(t-u)\underline{\underline{I}} + {}^{1}\phi_{4}(t-u)\underline{\underline{B}} + {}^{2}\phi_{4}(t-u)\underline{\underline{B}}^{2})]\}\,du
\end{aligned}
\qquad [3.9]
$$

where

$$\dot{\underline{\underline{C}}}_{t}(u) \equiv \frac{d}{du}\,\underline{\underline{C}}_{t}(u), \qquad [3.10]$$

and

$$\underline{\underline{B}} \equiv \underline{\underline{B}}(t), \qquad [3.11]$$

${}^{0}\phi_{0}$, ${}^{1}\phi_{0}$, ${}^{2}\phi_{0}$ are functions of the three invariants of $\underline{\underline{B}}$, and ${}^{i}\phi_{j}(t)$, where i=1,2,3 and j=1,2,3,4, are twelve relaxation functions of time and of the three invariants of $\underline{\underline{B}}$, such that

$$\lim_{t\to\infty} {}^{i}\phi_{j}(t) = 0 \qquad [3.12]$$

For an incompressible material, the number of material functions can be further reduced to nine relaxation functions and two material functions of the invariants (14). It is evident that the determination of all these eleven functions experimentally is not only a formidable but an impossible task. If we cannot deal effectively with the simplest case of an isotropic incompressible material, should we even mention more complicated cases? Therefore, the C-N theory suffers from its own generality and offers little practical usefulness.

The Green-Rivlin expansion of eq. [3.1] in a series of multiple integrals leads to a slightly more useful expression. Since it involves higher order tensors, it is more convenient to use the indicial notation. In rectangular Cartesian coordinates the G-R constitutive equation for an anisotropic incompressible material can be expressed as

$$\sigma_{ij}(t) \equiv F_{iI}(t)\; S_{IJ}(t)\; F_{jJ}(t) \qquad [3.13]$$

and

$$S_{IJ}(t) = \underset{u=-\infty}{\overset{t}{\mathcal{K}_{IJ}}} [E_{AB}(u)] \tag{3.14}$$

where $S_{IJ}(t)$ is the Piola stress tensor at time t, and $E_{AB}(u)$ is the Green strain tensor defined by

$$E_{AB}(u) = [C_{AB}(u) - \delta_{AB}]/2 \tag{3.15}$$

By assuming that the strain histories are continuous and that the material has fading memory, the strain histories can be expanded into Fourier series. With the further assumption that the functionals $\underline{\underline{K}}$ are continuous, $\underline{\underline{S}}$ may be regarded as a continuous function of the coefficients of the Fourier series. From Weierstrass's Theorem, it follows that $\underline{\underline{S}}$ can be approximated as closely as desired by a polynomial in the Fourier coefficients. Hence we write

$$S_{IJ}(t) = \sum_{n=1}^{\infty} \int_{-\infty}^{t} \cdots \int_{-\infty}^{t} Q_{IJA_1B_1\ldots A_nB_n}(t-u_1, t-u_2 \ldots . t-u_n) \times E_{A_1B_1}(u_1) \ldots . E_{A_nB_n}(u_n)\, du_1 \ldots . du_n \tag{3.16}$$

It is straightforward to show that eqs. [3.13] and [3.16] satisfy the principle of material frame indifference. Eq. [3.16] can be separated into two parts as follows

$$S_{IJ}(t) = \sum_{n=1}^{\infty} N_{IJA_1B_1\ldots A_nB_n} E_{A_1B_1}(t)\ldots E_{A_nB_n}(t)$$

$$+\sum_{n=1}^{\infty}\int_{-\infty}^{t}\ldots\int_{-\infty}^{t} M_{IJA_1B_1\ldots A_nB_n}(t-u_1, t-u_2\ldots t-u_n)E_{A_1B_1}(u_1)\ldots E_{A_nB_n}(u_n) \qquad [3.17]$$

where $N_{IJA_1B_1\ldots A_nB_n}$ is a tensor of rank 2(n+1) which represents the instantaneous elastic response of the material and the $M_{IJA_1B_1\ldots A_nB_n}$ are commonly referred to as the memory functions.

Equation [3.17] can be converted to the following equation by integration by parts if $\dot{\underline{\underline{E}}}(u)$ is continuous. The equation is

$$S_{IJ}(t) = \sum_{n=1}^{\infty}\int_{-\infty}^{t}\ldots\int_{-\infty}^{t} G_{IJA_1B_1\ldots A_nB_n}(t-u_1, t-u_2\ldots t-u_n) \times$$

$$\dot{E}_{A_1B_1}(u_1)\ldots\dot{E}_{A_nB_n}(u_n)\, du_1\ldots du_n \qquad [3.18]$$

where the dot indicates the time derivative and the $G_{IJA_1B_1\ldots A_nB_n}$'s are the relaxation moduli. Equation [3.18] can also be developed by the technique leading to eq. [3.16] and assuming that S_{IJ} is a function of the strain rate histories. Since strain rate histories are less smooth than strain histories for a given deformation history, eq. [3.18] may converge more slowly than eq. [3.16]. Therefore, for a given order of approximation, these two representations may not be exactly the same.

Parallel to eq. [3.13] an inverse theory can be written formally as

$$E_{AB}(t) = \underset{u=-\infty}{\overset{t}{\mathcal{D}}}_{AB}[S_{IJ}(u)] = \underset{u=-\infty}{\overset{t}{\mathcal{D}}}_{AB}[F^{-1}_{Ii}(u)\ \sigma_{ik}(u)\ F^{-1}_{kJ}(u)] \qquad [3.19]$$

Hence, the stress history involves not only the Cauchy stress tensor but also the deformation gradient. Because the stress in not entirely separated from the kinematic quantities in the constitutive equation, eq. [3.19] is more complicated than [3.13]. Furthermore, as pointed out by Rivlin (17), this type of equation will lead to the difficulty that the relatively complicated equations of compatibility must be used for the reduced Cauchy strain in place of the three equations of motion when boundary value problems are considered. There are six compatibility equations because there are only three independent variable functions in eq. [3.13]. These are the displacement components. In eq. [3.19] there are six independent variable functions, the components of the Piola stress tensor.

Green and Rivlin (13) show that in the simple case of an initially isotropic material there are two kernels in the first order approximation, six kernels in the second order approximation, and twelve kernels in the third order approximation. Pipkin (24) shows that for incompressible materials, only four independent stress-relaxation moduli are involved in the third order theory.

Green and Rivlin's approach has been applied to describe the creep behavior of some plastics (25-27), plastic filaments (28,29) and polyurethane (30). In uniaxial creep or creep recovery, the third order approximation provides a satisfactory description for experimental results on oriented polypropylene monofilament (28) and plasticized

PVC (25). However, when we wish to apply the theory to more general cases, such as three dimensional loading or multiple loading, and want to predict stress relaxation and constant rate of strain experiments from creep data, some shortcomings of the theory become evident.

The determination of the kernel functions of the G-R theory involves a great deal of experimental work. For the simple third order approximation theory, the determination of the twelve relaxation functions requires more than 100 tests (26). This is quite impractical for industrial characterization purposes. Even if all the kernel functions have been determined, usually the predictions are not very satisfactory. Findley and his coworkers (26,27,29) have applied the third order approximation theory to two-dimensional loading tests. Their results indicate that the agreement between the predictions and the experimental results is not very good. In certain cases a modified superposition principle yields better results (30).

Furthermore, the multiple integral theory generally fails to predict the unloading part of the response to a triangular strain excitation (2).

Another disadvantage of using the G-R theory with a finite order of approximation in describing the mechanical response of real materials was pointed out by Brereton et al. (29). Whereas stress relaxation and creep experiments have equal status, the representations of the two constitutive equations (eq. [3.13] and eq. [3.19]) in general do not. For example, the stress may perhaps be adequately described by a polynomial in the strain with terms no higher than the third order, but we usually would not obtain a tolerable description for strain as a polynomial in stress, even by extending the expansion to terms of much higher order.

Rivlin (15) pointed out that it is not generally true that the percentage error in the first order approximation becomes arbitrarily small as the size of the strain history decreases even though the absolute deviation can be made arbitrarily small. Brereton (29) and Pipkin (24) also realized that the accuracy of eqs. [3.16] and [3.18] cannot in general be improved merely by adding higher order integrals. The kernel functions in the lower order terms must be altered as the order of approximation increases if improved accuracy is to be obtained.

We conclude from the above discussion that the C-N and G-R theories, although they are quite general in the mathematical sense, do not furnish convenient ways to characterize real materials. Their shortcomings are three: first, they are too complicated to have popular uses; second, the convergence rate is usually too slow; third, there are some materials, e.g. solid propellants (31), which do not fall into the category of materials with fading memory.

Next, we wish to say a few words about the Coleman-Noll theory of the simple fluid (19). The term fluid, as it is usually used, does not have a precise definition. A fluid, unlike a solid, does not possess a preferred configuration or natural state which, when taken as the reference configuration, will yield a constitutive equation of a particularly simple form. Hence Coleman and Noll defined a fluid as a substance with the property that every configuration is an undistorted configuration. Therefore, taking the current configuration as the reference configuration, they specialized the theory of the simple material to the theory of the simple fluid which has the form

$$\underline{\underline{\sigma}}(t) = \underset{u=-\infty}{\overset{t}{\underline{\underline{L}}}} [\underline{\underline{C}}_t(u);\rho(t)] \qquad [3.20]$$

where $\rho(t)$ is the density of the fluid at time t. It follows from the theory of the simple fluid that every simple fluid is isotropic and that a simple fluid cannot support a shearing stress indefinitely without flowing. With the further assumption that the fluid is incompressible, eq. [3.20] can be reduced to

$$\underline{\underline{\sigma}}(t) = -p\underline{\underline{I}} + \underset{u=-\infty}{\overset{t}{L}} [\underline{\underline{C}}_t(u)] \qquad [3.21]$$

Coleman and Noll also proved that the perfect fluid, the Newtonian fluid and the Rivlin-Ericksen fluid (17) are all particular cases of the simple fluid if, in case of the Newtonian fluid, discontinuous changes in the velocity gradient are disallowed (15).

The simple fluid theory can be approximated by the retarded-history expansion approach proposed by Coleman and Noll (19), or by the approach advocated by Pipkin (24). The latter is similar to the G-R integral expansion method. Coleman and Noll show that normal stress effects are present already in the second order approximation but that a third order approximation is needed to describe non-Newtonian behavior. The third order theory has been tested experimentally, but the results are not very encouraging (22). It appears that this kind of expansion also suffers from a slow convergence rate. However, for some particular classes of flows the general theory of the simple fluid can offer certain predictions which are useful for material characterization purposes.

4. Some Special Nonlinear Viscoelastic Theories

There are basically two ways to construct a constitutive equation. The axiomatic approach is based on a few general assumptions whose logical consequences are developed. Because of its generality the results obtained within the framework of the theory may have a wide validity. However, precisely because of its generality very few problems can be solved within this general frame without more specific assumptions. Some constitutive theories belonging to this category are the C-N theory, the G-R theory, Coleman and Noll's simple liquid theory (19), Farris's theory of the material with permanent memory (31), etc.

In the other approach one may formulate, without violating the conditions to which a constitutive equation is subject, some theories more useful to the experimentalist by focussing on some particular class of materials. One may then reduce the number of material parameters to a manageable number by adding assumptions which seem reasonable on the basis of experience. Schapery's theory derived from irreversible thermodynamics (32-35), and Kinder and Sternstein's path-dependent theory (36) are examples of theories belonging to this category. We are interested in soft polymeric materials, i.e. polymeric materials at temperatures above their glass transition temperature. Special constitutive equations for these materials have been developed by Lianis (37), and by Bernstein, Kearsley and Zapas (BKZ theory) (38, 39).

Lianis's theory is an approximate form of the C-N theory and contains four time-dependent but strain-independent relaxation functions and three equilibrium constants. Four assumptions were introduced in Lianis's theory. First, the material is considered to be incompressible; second, the relaxation functions of the C-N theory are assumed to be independent of the strain invariants. Third, the long time behavior of the material is assumed to satisfy the equation

$$\underline{\underline{\sigma}} = - P\underline{\underline{I}} + [C_{10} + C_{20} (I_1-3) + C_{01} I_1]\underline{\underline{B}} - C_{01}(\underline{\underline{B}}^2) \qquad [4.1]$$

where P is an arbitrary hydrostatic pressure, I_1 is the trace of Finger's tensor, and C_{10}, C_{20}, and C_{01} are material constants. Eq. [4.1] is similar in form to the constitutive equation of the incompressible hyperelastic material with the strain energy density function

$$W = C_{10}(I_1-3) + C_{20}(I_1-3)^2 + C_{01}(I_2-3) \qquad [4.2]$$

often referred to as Signorini's potential (38). In eq. [4.2] I_2 is the second invariant of Finger's tensor. Fourth, Lianis further assumed that the elastic response at short times can be expressed by an equation similar to [4.1] but with different material constants. With this assumption, he reduced eq. [3.9] to

$$\begin{aligned}\underline{\underline{\sigma}}(t) = &- P(t)\ \underline{\underline{I}} + [C_{10} + C_{20}(I_1-3) + C_{01}I_1]\ \underline{\underline{B}} - C_{01}\underline{\underline{B}}^2 \\ &+ \int_{-\infty}^{t} \phi_1(t-u)\ \dot{\underline{\underline{C}}}_t(u)\ du + \underline{\underline{B}}\cdot\int_{-\infty}^{t} \phi_2(t-u)\ \dot{\underline{\underline{C}}}_t(u)\ du \\ &+ \left[\int_{-\infty}^{t} \phi_2(t-u)\ \dot{\underline{\underline{C}}}_t(u)\ du\right]\cdot \underline{\underline{B}} + \underline{\underline{B}}^2\cdot\int_{-\infty}^{t} \phi_3(t-u)\ \dot{\underline{\underline{C}}}_t(u)\ du \\ &+ \left[\int_{-\infty}^{t} \phi_3(t-u)\ \dot{\underline{\underline{C}}}_t(u)\ du\right]\cdot\underline{\underline{B}}^2 + \underline{\underline{B}}\int_{-\infty}^{t} \phi_4(t-u)\ \dot{I}_1(u)\ du\end{aligned} \qquad [4.3]$$

where the four $\phi_i(t-u)$'s are relaxation functions which are independent of the strain invariants.

The applicability of this constitutive equation has been well investigated by Lianis and his associates on several materials and in different loading conditions (40-43). The deviations of the predictions from the experimental data were clearly shown in the cases of constant stretch rate unloading curves (40), superposition of a small sinusoidal oscillation on a finite strain (41), and combined tension-torsion (43). These deviations can result either from the inadequacy of eq. [4.1] or from the assumed independence of the relaxation functions on the invariants. We believe the former to be more likely. Tschoegl (44) has shown that eq. [4.1] does not generally represent the equilibrium stress-strain behavior of soft polymeric materials since it is only one of many three-term equations which will fit a given set of data. These equations can be derived from appropriate functions of the Taylor expansion of the strain energy density function in terms of

I_1 and I_2. Unpublished results of Tschoegl show that these equations are not constitutive equations because data obtained on the same material in different deformation fields cannot be fitted with the same constants. This is a consequence of the slow convergence of the expansion.

In recent years many specialized constitutive equations for polymer solutions and polymer melts have been proposed. Most of these contain single integrals and have the form

$$\underline{\underline{\sigma}} = - P \underline{\underline{I}} + \int_{-\infty}^{t} \{M_1(t-u)\ \underline{\underline{C}}_t^{-1}(u) - M_2(t-u)\ \underline{\underline{C}}_t(u)\}\ du \qquad [4.4]$$

where the memory functions M_1 and M_2 depend, in general, on some invariants of the deformation history. The memory functions can be classified into three categories: (A) They are functions of the invariants of $\underline{\underline{d}}(u)$ (4,45-51); (B) They are functions of some time average of $\underline{\underline{d}}(u)$ from $\underline{\underline{d}}(u)$ to $\underline{\underline{d}}(t)$ (3,49); (C) They are functions of the invariants of $\underline{\underline{C}}_t(u)$ (39, 52-55). Depending on the way in which the memory functions are expressed in terms of these invariants, special theories were proposed in each category.

Most of these theories qualitatively describe the viscosity, the normal stresses, and the response in small amplitude oscillatory experiments of polymeric liquids. However, literature data on stress growth at the start of shearing flow, stress relaxation after cessation of steady flow (3,4,56,67), finite amplitude sinusoidal simple shearing (58), and stress versus strain hysteresis loop (59) show deviations from the predictions of some models in category (A). Furthermore, the experimental results of Simmons (60) and of Tanner and Williams (61) indicate that the dynamic viscosities measured by superposing in-line and transverse small-amplitude oscillations on steady simple shearing are independent of the base rate of shear at ultrasonic frequencies. Bernstein and Huilgol (62) recently showed that this experimental fact contradicts the predictions of the Bird-Carreau model (50) and M-OWFS model (51).

These failures did not answer the question whether they were due to inadequacy of these special models or of all models belonging to category (A). Several attempts were made to tackle this problem (62-66). The procedures used by van Es and Christensen (64) and by Sakai et al. (65) provide ways to check the basic hypothesis that the memory functions are functions of $\underline{\underline{d}}(u)$, without the need to determine the memory functions themselves. Application of these procedures to standard materials indicate the inadequacy of the basic hypothesis. The validity of the constitutive equations of category (A) and (B) was discussed most clearly by Marrucci and Astarita (66). They pointed out that the constitutive models of categories (A) and (B) reduce to linear viscoelastic behavior in the limit of very small deformation rates. By contrast, the general theory of the simple fluid predicts linear viscoelastic behavior in the limit of very small deformations. Hence the constitutive theories of category (A) and (B) do not belong to the general frame of the simple fluid. Which theories are more appropriate must be decided on the basis of experimental data.

Philippoff's data on polyisobutylene solutions (67) in small amplitude oscillatory motion at different frequencies and different maximum shear rates show deviation from linear viscoelastic behavior at constant deformation rather than constant deformation rate. This provides unequivocal evidence of the inadequacy of the theories based on deformation-rate dependent memory functions [categories (A) and (B)].

As pointed out by Astarita and Marrucci (68), if coupling effects resulting from deformations occurring at different times are excluded, eq. [3.21] can be rewritten as

$$\underline{\underline{\sigma}}(t) = -P\underline{\underline{I}} + \int_{-\infty}^{t} \{M_1[t-u,\ I_1(t,u),\ I_2(t,u)]\underline{\underline{C}}_t(u) - M_2[t-u,\ I_1(t,u),\ I_2(t,u)]\underline{\underline{C}}_t^{-1}(u)\}\, du \qquad [4.5]$$

where I_1 and I_2 are the first and second invariants of $\underline{\underline{C}}_t(u)$. Therefore, the models in category (3) are all special cases of the simple fluid. Among these models, we discuss in more detail the so called BKZ theory of the incompressible elastic fluid (39,40). Borrowing the idea of an elastic potential from the theory of finite elasticity, Bernstein, Kearsley, and Zapas write the memory functions in eq. [4.5] as

$$M_1 = \frac{\partial U}{\partial I_1} = U_{I_1}[I_1(t,u),\ I_2(t,u),t-u]$$

$$M_2 = \frac{\partial U}{\partial I_2} = U_{I_2}[I_1(t,u),\ I_2(t,u),t-u] \qquad [4.6]$$

where U is a time-dependent potential function. If U_{I_1} and U_{I_2} are delta functions located at u=0, eqs. [4.5] and [4.6] reduce to the Mooney-Rivlin equation. The physical features of the BKZ theory are: (1) the configuration of the body at any past time u can be considered as a stress-free configuration; (2) the transition from a configuration at the past time u to the configuration at the present time t (i.e. the deformation) will generate a stress; (3) the stress is elastic in origin, i.e. it can be derived from a potential function; (4) the potential depends not only on the configurations at the past time u and the present time t, but also on the elapsed time t-u; (5) the stress at the present time t is the sum of all the contributions from u<t.

The BKZ model has been applied to uncrosslinked amorphous polymers (39,69), crosslinked rubbers (39,70), polymer melts, and polymer solutions (4,60,61,62,71). The data seem to be roughly in agreement with the theory. However, Zapas's recent data (72) on stress growth at various rates of shear for a polyisobutylene solution clearly show that the BKZ model fails at high shear strains. Yen and

McIntire (73) assume that in simple shear eq. [4.5] can be simplified to

$$\tau = \int_{-\infty}^{t} M(t-u)F(\gamma)\, du \qquad [4.7]$$

where τ is the shear stress, M(t-u) is a memory function depending on the elapsed time, $F(\gamma)$ is a function of the shear strain γ which is defined as the product of the rate of shear $\dot{\gamma}$ and the elapsed time t-u. They calculated $F(\gamma)$ for Ashare's data on a polystyrene solution (74) and Chen's data (2) on a polyethylene melt in steady-state shearing flow. They found that $F(\gamma)$ does not possess a unique value at high shear rates and that $F(\gamma)$ calculated from viscosity data was different from $F(\gamma)$ calculated from normal stress data. The predictions of stress growth from $F(\gamma)$ calculated from steady state shearing flow did not agree with the experimental data. They attributed the discrepancies partly to the inadequacy of the BKZ fluid model at high shear rates and partly to data scatter. We feel that part of the deviation may also be due to the fact that they assumed a strain and strain rate independent relaxation spectrum.

Changes in the relaxation spectrum as functions of strain and strain rate may arise from orientation and disentanglement of the molecules in the shearing flow. Therefore, one must be careful in applying the BKZ model with parameters determined in steady shearing flow to predict behavior in transient response.

The claim that a liquid theory such as the BKZ theory is more suitable (39) than a solid theory for crosslinked polymers which have a well-defined stress-free state is something that needs further checking. In its most general form given by eq. [4.5] the BKZ theory does not assume a specific potential function. However, in most practical applications a specific potential must be assumed. The use of the Signorini potential, eq. [4.1], has been tested by Lianis and his associates on both crosslinked and uncrosslinked polymers (41,42). Large discrepancies were found between the theory's predictions and the experimental results. From Goldberg and Lianis's data (41) as well as our own data (7) obtained by superposing small deformations on a finite stretch it appears that a simpler constitutive equation can be obtained if the stress-free state is taken as a reference state (7).

In summary, in spite of more than thirty years of research, there is still no simple, accurate constitutive equation which can adequately describe the finite viscoelastic behavior of polymers. The key to the successful formulation of a useable constitutive equation which can adequately describe the finite viscoelastic behavior of polymers appears to be the incorporation of characteristic features of particular classes of materials into the general theory. The characteristic features may be deduced from experimental observations or from theoretical considerations. In the next sections we introduce a generalized linear theory for soft viscoelastic polymeric solids and liquids in moderately large deformations. We define a moderately large deformation as one in which the relaxation spectrum is not altered by the deformation. The theory is a special case of the theory of the incompressible simple material and is based on the concept of a generalized measure of strain.

5. The Generalized Strain Measure

A material body subjected to a deformation assumes a new configuration. It is convenient to define a measure of the deviation of this configuration from a suitably chosen reference configuration. Any measure will serve which determines the directions of the principal axes of the deformation and the magnitude of the deformation in these directions. Such a measure is called *strain*. We recognize it as being essentially a measure of the difference in distance between two material particles in different configurations. Thus, it is completely independent of the coordinate system in which one wished to describe it and is therefore a tensor.

Conceptually, a deformation and, hence, a strain, is probably most easily described by a body coordinate system (11,23). The changes in the metric tensor of such a system adequately describe the deformation and can therefore be used to define a measure of strain. However, when solving boundary value problems, all variables and, therefore, the equations linking them, must be referred to a space coordinate system external to, and independent of, the body. It is generally convenient to adopt one system (the spatial or Lagrangean system) for the undeformed configuration and another (the material or Eulerian system) for the deformed configuration. The deformation can then be viewed as a transformation of coordinates from one system to the other. Which one is chosen as the reference system is, in principal, immaterial.

In practice, one or the other of the dual approaches may have advantages. The simplest and most widely used strain measures in the theory of finite elasticity is Green's strain tensor

$$\underline{\underline{E}}_G = (\underline{\underline{C}}-\underline{\underline{I}})/2 \qquad [5.1]$$

which is defined in terms of the undeformed or Lagrangean coordinates, and Almansi's strain tensor

$$\underline{\underline{e}}_A = (\underline{\underline{I}}-\underline{\underline{c}})/2 \qquad [5.2]$$

which is defined in terms of the deformed or Eulerian coordinates. In eq. [5.2] $\underline{\underline{c}}$ is Cauchy's deformation tensor which is the inverse of Finger's tensor, B. For infinitesimal deformations $\underline{\underline{E}}_G$ and $\underline{\underline{e}}_A$ reduce to Cauchy's strain measure

$$\underline{\underline{E}}_c = (\underline{\underline{F}}+\underline{\underline{F}}^T)/2 - \underline{\underline{I}} \qquad [5.3]$$

and to Swainger's strain measure

$$\underline{\underline{e}}_s = \underline{\underline{I}} - (\underline{\underline{F}}+\underline{\underline{F}}^T)/2 \qquad [5.4]$$

respectively.

These strains are based on considering $(ds)^2 - (dS)^2$, where dS and ds are the elemental undeformed and deformed length between two particles, as the measure of deformation (16). Instead of the length, we may, however, consider the elemental area defined by the cross product of two vectors connecting a material point to two others. As a result of the deformation the magnitude of the vectors and the angle between them changes. Hence, the undeformed elemental area dA is transformed into the deformed elemental area da and the difference between the squares of the elemental areas, $(dA)^2 - (da)^2$, may serve as a measure of the deformation (16). On this basis we define two more measures of strain. We call

$$\underline{\underline{e}}_F = (III_c \underline{\underline{c}}^{-1} - \underline{\underline{I}})/2 \qquad [5.5]$$

Finger's strain tensor which is defined in terms of the Eulerian coordinates. In eq. [5.5] III_c is the determinant of $\underline{\underline{c}}$. We also have

$$\underline{\underline{E}}_P = (\underline{\underline{I}} - III_C \underline{\underline{C}}^{-1})/2 \qquad [5.6]$$

which we call Piola's strain tensor. C^{-1} is Piola's deformation tensor and III_C is the determinant of C. $\underline{\underline{E}}_P$ is defined in terms of the Lagrangean coordinates. For an incompressible body we have

$$\underline{\underline{e}}_F = (\underline{\underline{c}}^{-1} - \underline{\underline{I}})/2 \qquad [5.7]$$

and

$$\underline{\underline{E}}_P = (\underline{\underline{I}}-\underline{\underline{C}}^{-1})/2 \qquad [5.8]$$

For infinitesimal deformations $\underline{\underline{e}}_F$ and $\underline{\underline{E}}_P$ reduce to $\underline{\underline{e}}_S$ and $\underline{\underline{E}}_C$ respectively.

$\underline{\underline{C}}$ and $\underline{\underline{c}}^{-1}$ are symmetric and their matrices can therefore be diagonalized by orthogonal transformations. We have

$$\underset{\sim}{C} = \underset{\sim}{N}\underset{\sim}{\Lambda}^2\underset{\sim}{N}^T \qquad [5.9]$$

and

$$\underset{\sim}{c}^{-1} = \underset{\sim}{n}\underset{\sim}{\Lambda}^2\underset{\sim}{n}^T \qquad [5.10]$$

where $\underset{\sim}{C}$ and $\underset{\sim}{c}^{-1}$ are the matrices of the mixed components of the tensors $\underline{\underline{C}}$ and $\underline{\underline{c}}^{-1}$, $\underset{\sim}{N}$ and $\underset{\sim}{n}$ are the matrices formed from the eigenvectors of $\underset{\sim}{C}$ and $\underset{\sim}{c}^{-1}$, $\underset{\sim}{N}^T$ and $\underset{\sim}{n}^T$ are their transposes, and $\underset{\sim}{\Lambda}$ is the matrix of the eigenvalues of $\underset{\sim}{C}$ which are identical with those of $\underset{\sim}{c}^{-1}$. We define $\underset{\sim}{\Lambda} = \mathrm{diag}(\lambda_1,\lambda_2,\lambda_3)$ where the λ's are the stretch ratios in the principal directions. We also have

$$\underset{\sim}{F} = \underset{\sim}{n}\underset{\sim}{\Lambda}\underset{\sim}{N}^T \qquad [5.11]$$

which relates $\underset{\sim}{\Lambda}$ to the matrix of the deformation gradient tensor, and

$$\underset{\sim}{n} = \underset{\sim}{R}\underset{\sim}{N} \qquad [5.12]$$

which establishes the connection between the two eigenvector matrices.

We list, without proof, the conditions which a strain measure must satisfy to be acceptable as: (1) it must exclude rigid body rotations; (2) it must vanish identically when the deformation gradient tensor is a unit tensor; (3) it must be a second rank isotropic tensor function of $\underline{\underline{C}}$ or $\underline{\underline{c}}^{-1}$; and (4) any of its principal values should be positive if the corresponding stretch ratio is greater than unity. In addition, (5) for an incompressible material it must reduce to Cauchy's or Swainger's measure when the deformation is infinitesimal.

$\underline{\underline{E}}_G$, $\underline{\underline{e}}_A$, $\underline{\underline{e}}_F$, and $\underline{\underline{E}}_P$ are not the only possible strain tensors. We may define a *generalized* Lagrangean strain tensor

$$\underset{\sim}{E}_{GL} = \underset{\sim}{N}\underset{\sim}{\Phi}_{GL}(\underset{\sim}{\Lambda})\underset{\sim}{N}^T \qquad [5.13]$$

and a *generalized* Eulerian strain tensor

$$\underset{\sim}{e}_{GE} = \underset{\sim}{n}\underset{\sim}{\Phi}_{GE}(\underset{\sim}{\Lambda})\underset{\sim}{n}^T \qquad [5.14]$$

The generalized strain functions $\underset{\sim}{\Phi}_{GL}(\underset{\sim}{\Lambda})$ and $\underset{\sim}{\Phi}_{GE}(\underset{\sim}{\Lambda})$ are matrix functions of $\underset{\sim}{\Lambda}$ and are chosen so that they satisfy the condition

$$\underset{\sim}{\Phi}(\underset{\sim}{I}) \equiv \underset{\sim}{0} \qquad [5.15]$$

where $\underset{\sim}{0}$ is the null matrix.

The idea of a generalized strain measure is not new. Its earlier history has been reviewed by Truesdell and Toupin (75), and some new measures were proposed by Karni and Reiner (76). A particular form of the generalized measure of strain may be obtained by letting

$$\Phi_\alpha(\lambda_\alpha) = (\lambda_\alpha^n - 1)/n \qquad \alpha = 1,2,3 \qquad [5.16]$$

where n is a strain parameter which we allow to be any real number and which has nothing to do with the eigenvector matrix $\underset{\sim}{n}$. Substitution of eq. [5.16] into eq. [5.14] yields

$$\underset{\sim}{e}_{Fn} = \underset{\sim}{n}\left(\frac{\underset{\sim}{\Lambda}^n - \underset{\sim}{I}}{n}\right)\underset{\sim}{n}^T \qquad [5.17]$$

where $\underset{\sim}{e}_{Fn}$ is the matrix of the Finger strain tensor based on the n-measure of strain. In tensor notation

$$\underset{=}{e}_{Fn} = (\underset{=}{B}^{n/2} - \underset{=}{I})/n \qquad [5.18]$$

For the n-measure based Green strain tensor we have analogously

$$\underset{\sim}{E}_{Gn} = \underset{\sim}{N}\left(\frac{\underset{\sim}{\Lambda}^n - \underset{\sim}{I}}{n}\right)\underset{\sim}{N}^T \qquad [5.19]$$

and

$$\underline{\underline{E}}_{Gn} = (\underline{\underline{C}}^{n/2}-\underline{\underline{I}})/n \qquad [5.20]$$

The n-measure of strain has been applied by Seth to transition field problems (78). Hsu (79) used it to describe creep in metals. Blatz, Chu, and Wayland (80), and Chu and Blatz (81) applied it to animal tissues and rubberlike materials. Ogden (82), and independently, Blatz, Sharda, and Tschoegl (83,84,85) further developed its use for the description of the elastic large deformation behavior of rubberlike materials. Chang and Blatz (86,87) discussed its application to the prediction of the elastic response of rubberlike materials in small deformations superposed on a finite homogeneous elastic deformation. Recently, Chang, Bloch, and Tschoegl (5) extended its use to viscoelastic behavior.

The choice of a particular strain measure to simplify the constitutive equation is similar to the selection of a particular coordinate system to deal with a given geometry or, equivalently, to the selection of a particular set of base vectors to simplify a mathematical representation. In most cases the choice is between equally acceptable alternatives and is therefore a matter of taste, convenience, or economy, rather than one of principle. Because of its unorthodox nature some comments are in order, however, concerning the n-measure of strain.

The strain parameter n is a material parameter and must be determined by experiment. It is generally not an integer. Its magnitude and dependence on temperature and other variables have been studied by us for a styrene-butadiene rubber (5-9). We have also assembled a series of estimates, based mostly on published data, of its magnitude and temperature dependence for other polymeric materials. Its dependence on molecular parameters is unclear at present. In connection with rubberlike material we have discussed it elsewhere (9) in the light of the Gaussian statistical theory (88) for which n=2.

Objections to its use can be countered by the practical argument that it is simple, economical, and highly successful and is thus perfectly acceptable for applications in rubber engineering. We do not believe, however, that there are any convincing arguments against it on theoretical grounds. There appear to be two main objections: (1) that it makes the strain measure a material as well as a kinematic variable; and (2) that it is of fractional power. Traditionally, strain is indeed defined as a purely kinematic variable. However, there is nothing wrong on phenomenological grounds in letting the strain measure become a material property. This simply means that the measure of strain with which the description of the mechanical properties of a given material can be cast in the simplest form, is a property of the material.

With respect to its non-integral nature we point to the well known thermodynamic relation connecting the volume, V, of a gas to its pressure, P. This relation is

$$P = cV^{-\gamma} \qquad [5.21]$$

where γ is non-integral. For an ideal gas, γ can be given a precise physical meaning (89) as C_P/C_V where C_P and C_V are the heat capacities at constant pressure and constant volume, respectively. For a monatomic ideal gas the molecular kinetic theory gives γ=1.4.

With respect to the n-measure of strain, $n \neq 2$ means that the definition of deformation in terms of the square of the elemental length $(ds)^2$ cannot be expressed by a quadratic form, i.e. we must admit a form more general than

$$(ds)^2 = d\underline{x} \cdot d\underline{x} \qquad [5.22]$$

This is tantamount to saying that the deformation cannot be described in Euclidean space. While such a statement is certainly unorthodox, there is no *a priori* reason to reject it out of hand. In fact, it would be the continuum mechanical corollary of the finding that the (suitably averaged) end-to-end distance of entangled chains in *not* of the classical (90) form

$$\langle r^2 \rangle = \beta m l^2 \qquad [5.23]$$

where $\langle r^2 \rangle$ is the mean square end-to-end distance, β is a factor depending mainly on chain geometry, m is the number of links, and l is the link length. At this time we offer this merely as a basis for speculation.

6. The Generalized Linear Viscoelastic Theory

In a polymeric material the ratio of stress (or strain) at time t to that at an arbitrary reference time t_r in a stress relaxation experiment (or a creep experiment) is independent of strain (or stress). For stress relaxation in simple tension this behavior was observed by Tobolsky and Andrews (91) on a crosslinked styrene-butadiene rubber (SBR), and by Guth et al. (92) on natural rubber (NR). Chasset and Thirion (93) studied the stress relaxation behavior of NR and SBR specimens which were prepared with different crosslinking agents. They concluded that the observation holds generally for various network structures. Uncrosslinked polymers show similar behavior. Experiments on uncrosslinked polymers have been conducted by us on SBR and on 1,4-polybutadiene (PBD) (6), by Djiauw and Gent (94) on SBR, polyisobutylene (PIB), and polyisoprene. The same phenomenon was also observed in carbon black and starch xanthide reinforced crosslinked SBR by Bagley and Dixon (95), in carbon black reinforced cured and uncured SBR by us (10), and in carbon black reinforced uncured SBR and uncured polyiosprene by Djiauw and Gent (94).

Similar observations have been made in other deformation fields. Our own data (10) as well as the data of Bergen (96) on carbon black filled SBR and on PVC samples containing various amounts of plasticizer, the data of Gent (97) on SBR, of Valanis and Landel (98) on silica filled poly(dimethyl siloxane) rubber, and by Kawabata (99) on NR and SBR all indicate that the phenomenon is not restricted to simple tension.

The phenomenon is not confined to relaxation behavior. Leaderman (100) studied it in the creep behavior of plasticized poly(vinyl chloride) (PVC). Work on the creep behavior of other polymers, in which the same phenomenon was noticed, has been reviewed by Staverman (101).

This remarkable observation strongly suggests that constitutive equations of the multiple integral type (see Section 3) can be simplified to single integral equations if one is willing to restrict oneself to deformations in which time shift invariance is preserved i.e. in which the relaxation or retardation spectra do not change with the magnitude of the deformation. Indeed, if time shift invariance is preserved, the observed nonlinearities are reduced to stress-strain nonlinearities and the Boltzmann superposition integrals of the linear theory remain valid with respect to time-dependent behavior. They can, presumably, be modified to account for stress-strain nonlinearity. Several one-dimensional modified Boltzmann superposition integrals have in fact been proposed (27,100-103). These can be grouped into two categories. One generalizes the integral by replacing the true stress by an experimentally determined function of the tensile stress (27,102). The other replaces the infinitesimal strain measure of the classical integral by some finite strain measure (101,103, 103) such as $(\lambda^2-1)/2$. Leaderman (25) concluded from multiple step creep and creep recovery experiments that the first approach is inadequate. Furthermore, as discussed in Section 3, it introduces some inconvenience in solving boundary value problems. Hence, we omit it from our considerations here.

Our aim is the development of a three-dimensional constitutive equation based on a generalized measure of strain such as those discussed in Section 5. A similar, but one-dimensional approach has been used by Fung (104) for describing the viscoelastic behavior of soft biological tissues.

As our generalized measure of strain we adopt the n-measure we discussed in Section 5. To develop our equation, we start from the stress-strain relations for homogeneous deformations in elastic equilibrium as derived from the single-term BST potential (83,84)

$$\bar{\sigma}_\alpha = -P + (2G/n)(\lambda_\alpha^{\,n}-1) \qquad \alpha=1,2,3 \qquad [6.1]$$

where G is the shear modulus. Extending these relations to shift invariant time-dependent behavior, we write

$$\bar{\sigma}_\alpha(t) = -P + (2/n)\int^{t} G(t-u)\,\frac{d\lambda_\alpha^{\,n}(u)}{du}\,du \qquad [6.2]$$

Eq. [6.2] represent the predictions of what we have elsewhere (5,6) called the (simple) *solid model* (denoted as model S), for orthogonal deformations, i.e. in a deformation in which the orientation of the principal directions remains unchanged.

To prepare for the next step, we first cast Eq. [6.2] in the mathematically equivalent redundant form

$$\bar{\sigma}_\alpha(t) = -P + (1/n)\int_0^t G(t-u)\ \{\lambda_\alpha^{\ n}(t)\ \frac{d}{du}\left[\frac{\lambda_\alpha^{\ n}(u)}{\lambda_\alpha^{\ n}(t)}\right] + \frac{d}{du}\left[\frac{\lambda_\alpha^{\ n}(u)}{\lambda_\alpha^{\ n}(t)}\right]\lambda_\alpha^{\ n}(t)\}\ du \qquad [6.3]$$

where, in keeping with the C-N theory (cf eq. [3.5]) of the simple material, we have taken the configuration at the present time, t, as the reference configuration in the differential. To extend Eq. [6.3] to the case of a general deformation we make the substitution

$$\lambda_\alpha^{\ n}(t) \longrightarrow \underline{\underline{B}}^{n/2}(t) \qquad [6.4]$$

(cf. Eqs. [5.17] and [5.18]) where $\underline{\underline{B}}(t)$ is Finger's tensor at the present time, t, and

$$\frac{d}{du}\left[\frac{\lambda_\alpha^{\ n}(u)}{\lambda_\alpha^{\ n}(t)}\right] \longrightarrow \frac{d}{du}\,\underline{\underline{C}}_t^{\ n/2}(u) \qquad [6.5]$$

where $\underline{\underline{C}}_t(u)$ is Green's tensor at the past time, u, referred to the present time, t. We chose $\underline{\underline{B}}(t)$ in substitution [6.4] but $\underline{\underline{C}}_t(u)$ in [6.5] to ensure that the relations to be derived be frame indifferent. This will be shown explicity later on. We obtain

$$\underline{\underline{\sigma}}(t) = -P\underline{\underline{I}} + (1/n)\int_{-\infty}^{t} G(t-u)\,[\underline{\underline{B}}^{n/2}(t) \cdot \frac{d}{du}\,\underline{\underline{C}}_t^{\;n/2}(u)$$

$$+ \frac{d}{du}\,\underline{\underline{C}}_t^{\;n/2}(u) \cdot \underline{\underline{B}}^{n/2}(t)]\; du \qquad [6.6]$$

We note that the term in brackets is a symmetric tensor. We wrote eq [6.3] as the average of two equal terms to facilitate the transition to the general case. Eq. [6.6] represents the predictions of our model S for the general deformation of a simple solid.

From eq. [6.6] we may derive an equation for a simple liquid. The predictions of a liquid model cannot depend on the original configurations at u=0 because, as discussed in Section 3, a liquid does not possess a natural reference state. Hence we must have

$$\underline{\underline{B}}(t) = \underline{\underline{I}} \qquad [6.7]$$

and substitution into eq. [6.6] leads to

$$\underline{\underline{\sigma}}(t) = -PI - (2/n)\int_{-\infty}^{t} G(t-u)\,\frac{d}{du}\,\underline{\underline{C}}_t^{-n/2}(u)\; du \qquad [6.8]$$

Eq. [6.8] represents the predictions of what we have called elsewhere (6.7) the (simple) *liquid model* (denoted as model L) for the case of a general deformation. We note that the deformation tensor in eq. [6.8] is Piola's tensor. We have made the change from Green's to Piola's tensor (which entails the change in sign in front of the integral) to ensure positive values of n. As a consequence of eq. [6.7], n would assume negative values if data were fitted to the form of eq. [6.8] with Green's tensor.

For homogeneous deformations (6,7) eq. [6.8] becomes

$$\bar{\sigma}_{\alpha}(t) = -p-(2/n)\int_{-\infty}^{t} G(t-u) \frac{d}{du}\left[\frac{\lambda_{\alpha}^{n}(t)}{\lambda_{\alpha}^{n}(u)}\right] du \qquad [6.9]$$

We note that eqs. [6.3], [6.6], [6.8], and [6.9] reduce to eq. [6.1] for a purely elastic material, as they should.

For a Newtonian (purely viscous) material

$$G(t-u) = \eta\delta(t-u) \qquad [6.10]$$

where η is the constant (Newtonian) viscosity and $\delta(t)$ is the delta function. Substitution into eq. [6.8] yields

$$\bar{\underline{\underline{\sigma}}}(t) = -P\underline{\underline{I}} - (2\eta/n) \lim_{u\to t} \frac{d}{du} \underline{\underline{C}}_{t}^{-n/2}(u) \qquad [6.11]$$

But, by eq. [7.34] of the next section

$$\lim_{u\to t} \frac{d}{du} \underline{\underline{C}}_{t}^{-n/2}(u) = -n\underline{\underline{d}}(t) \qquad [6.12]$$

where $\underline{\underline{d}}(t)$ is the stretching tensor at the present time, t. Combining eqs. [6.11] and [6.12] and dropping the now unnecessary explicit reference to the present time, t, gives

$$\underline{\underline{\sigma}} = -P\underline{\underline{I}} + 2\eta\underline{\underline{d}} \qquad [6.13]$$

which is the equation for a Newtonian fluid.

Eqs. [6.6] and [6.8] can also be written in terms of memory functions

$$M(t-u) = -\frac{dG(t-u)}{du} \qquad [6.14]$$

This leads to

$$\bar{\underline{\underline{\sigma}}}(t) = -P\underline{\underline{I}} + 2G_e\,\underline{\underline{e}}_{Fn} +$$

$$(1/n)\int_{-\infty}^{t} M(t-n)\,[\underline{\underline{B}}^{n/2}(t) \cdot \frac{d}{du}\,\underline{\underline{C}}_t^{\,n/2}(u) \qquad [6.15]$$

$$+ \frac{d}{du}\,\underline{\underline{C}}_t^{\,n/2}(u) \cdot \underline{\underline{B}}^{n/2}(t)]\,du$$

for model S and to

$$\bar{\underline{\underline{\sigma}}}(t) = -P\underline{\underline{I}} + 2G_e\,\underline{\underline{e}}_{Fn} - (2/n)\int_{-\infty}^{t} M(t-u)\,\underline{\underline{C}}_t^{\,-n/2}(u)\,du \qquad [6.16]$$

for model L. In eqs. [6.15] and [6.16] G_e is the equilibrium shear modulus. When either model is applied to a liquid, we set $G_e=0$.

Several of the foregoing equations contain the n/2-power of $\underline{\underline{C}}_t(u)$, $\underline{\underline{C}}_t{}^{-1}(u)$, and $\underline{\underline{B}}(t)$. The former are obtained from

$$\underset{\sim}{C}^{n/2}{}_{t}(u) = \underset{\sim}{N}_{t}(u)\underset{\sim}{\Lambda}_{t}{}^{n}(u)\ \underset{\sim}{N}^{T}{}_{t}(u) \qquad [6.17]$$

and

$$\underset{\sim}{C}^{-n/2}_{t}(u) = \underset{\sim}{N}_{t}(u)\underset{\sim}{\Lambda}_{t}{}^{-n}(u)\ \underset{\sim}{N}^{T}{}_{t}(u) \qquad [6.18]$$

where $\underset{\sim}{\Lambda}_t^{2}(u)$ and $\underset{\sim}{\Lambda}_t^{-2}(u)$ are the diagonal matrices of the eigenvalues of $\underset{\sim}{C}_t(u)$ and $\underset{\sim}{C}_t{}^{-1}(u)$, respectively, and $\underset{\sim}{N}_t(u)$ is the matrix formed from the eigenvectors of $\underset{\sim}{C}_t(u)$ or $\underset{\sim}{C}_t{}^{-1}(u)$. The n/2-power of $\underline{\underline{B}}(t)$ is obtained from

$$\underset{\sim}{B}^{n/2}(t) = \underset{\sim}{n}(t)\underset{\sim}{\Lambda}^{n}(t)\underset{\sim}{n}^{T}(t) \qquad [6.19]$$

where $\overset{2}{\underset{\sim}{\Lambda}}(t)$ is the matrix of the eigenvalues of $\underset{\sim}{B}(t)$, and $\underset{\sim}{n}(t)$ is the matrix of its eigenvectors.

We show next that both models satisfy the principle of material frame indifference. Let us denote all tensors by their mixed component matrices and denote those referring to the rotational frame by a superscript *. Then the equation for model S becomes

$$\bar{\underline{\underline{\sigma}}}^*(t) = -P\,\underline{\underline{I}} + (1/n)\int_{-\infty}^{t} G(t-u)\,\Big[\underline{\underline{B}}^{*n/2}(t)\cdot\frac{d}{du}\underline{\underline{C}}_t^{*n/2}(u) + \frac{d}{du}\underline{\underline{C}}_t^{*n/2}(u)\cdot\underline{\underline{B}}^{*n/2}(t)\Big]\,du \qquad [6.20]$$

in the rotational frame. But, from the discussion in Section 2 we have

$$\underline{\underline{\sigma}}^*(t) = \underline{\underline{Q}}(t)\cdot\underline{\underline{\sigma}}(t)\cdot\underline{\underline{Q}}^T(t) \qquad [6.21]$$

and

$$\underline{\underline{B}}^*(t) = \underline{\underline{Q}}(t)\cdot\underline{\underline{B}}(t)\cdot\underline{\underline{Q}}^T(t) \qquad [6.22]$$

and

$$\underline{\underline{C}}_t^*(u) = \underline{\underline{Q}}(t)\cdot\underline{\underline{C}}_t(u)\cdot\underline{\underline{Q}}^T(t) \qquad [6.23]$$

It follows from eq. [6.19] and [6.22], and from eq. [6.17] and [6.23], respectively, that

$$\underset{\sim}{n}^{*}(t) = \underset{\sim}{Q}(t)\underset{\sim}{n}(t) \qquad [6.24]$$

and

$$\underset{\sim}{N}_t{}^{*}(u) = \underset{\sim}{Q}(t)\underset{\sim}{N}_t(u) \qquad [6.25]$$

Thus, we have

$$\underline{\underline{B}}^{*n/2}(t) = \underline{\underline{Q}}(t)\cdot\underline{\underline{B}}^{n/2}(t)\cdot\underline{\underline{Q}}^{T}(t) \qquad [6.26]$$

and

$$\underline{\underline{C}}_t{}^{*n/2}(u) = \underline{\underline{Q}}(t)\cdot\underline{\underline{C}}_t^{n/2}(u)\cdot\underline{\underline{Q}}^{T}(t) \qquad [6.27]$$

Making the appropriate substitutions we see that eq. [6.20] is satisfied and, hence, model S obeys the principle of material frame indifference. An entirely similar derivation proves the frame indifference of model L.

Models S and L have the following characteristics: 1) They represent three-dimensional constitutive equations for an incompressible and initially isotropic material; 2) They satisfy the principle of material frame indifference; 3) They form subclasses of the simple material; 4) They reduce to the BST equation if the material is elastic; 5) Model L reduces to the Newtonian fluid if $G(t) = \eta\delta(t)$; 6) Model L predicts the first and the second normal stress effects; 7) In the application of these models the only material information required is the relaxation function, G(t), and the strain parameters n. Their determination as well as the application of the models to crosslinked and uncrosslinked SBR have been discussed elsewhere (6,7).

Models S and L are neither the only admissible forms nor are they the most general forms. Models S and L can be further generalized if we replace $\underset{\sim}{B}^{n/2}(t)$ and $\underset{\sim}{C}_t^{n/2}(u)$ according to

$$\underset{\sim}{B}^{n/2}(t) \longrightarrow \underset{\sim}{n}(t)\ \ \underset{\sim}{\Phi}_1[\underset{\sim}{\Lambda}(t)]\ \ \underset{\sim}{n}^T(t) \qquad [6.28]$$

and

$$\underset{\sim}{C}_t^{\,n/2}(u) \longrightarrow \underset{\sim}{N}_t(u)\ \ \underset{\sim}{\Phi}_2[\underset{\sim}{\Lambda}_t(u)]\ \ \underset{\sim}{N}_t^T(u) \qquad [6.29]$$

and $C_t^{-n/2}(u)$ according to

$$\underset{\sim}{C}_t^{-n/2}(u) \longrightarrow \underset{\sim}{N}_t(u)\ \ \underset{\sim}{\Phi}_3[\underset{\sim}{\Lambda}_t(u)]\ \ \underset{\sim}{N}_t^T(u) \qquad [6.30]$$

where the $\underline{\underline{\Phi}}_i[\underline{\underline{\Lambda}}(t)]$ are isotropic tensor functions of $\underline{\underline{\Lambda}}(t)$. Since the latter is diagonal, so are the former. We call the models obtained in this way (10) the *generalized solid model* (model GS) and the *generalized liquid model* (model GL), respectively.

As an example of another admissible form we briefly mention the solid model represented by

$$\underline{\underline{S}}(t) = -P\underline{\underline{I}} + (2/n) \int_{-\infty}^{t} G(t-u) \frac{d}{du} \underline{\underline{C}}^{n/2-2}(u)\, du \qquad [6.31]$$

in which $\underline{\underline{S}}(t)$ is Piola's stress tensor. This model is similar in form to model L. However, the time-dependent Green's tensor is referred to the original configuration.

7. The Differential Form of the Generalized Linear Theory

With the preservation of time shift invariance, the generalized linear integral models proposed in the last section can be recast in terms of linear differential operators with constant coefficients. In this section, we illustrate this process by defining a new differential operator and then using it to convert eq. (6.5) into a tensor differential equation. Hence, we link the integral equation representation (105) to the representation by mechanical models which, in turn, can be linked to some of the molecular models of the spring-and-bead type (105,106). The differential operator representation requires derivatives of the stress and strain tensors.

Historically, the first three-dimensional rate theory was proposed by Zaremba (107) in 1903. He realized that the generalization of even a simple Maxwell model to three dimensions is not a trivial matter. As mentioned in Section 3, a constitutive equation must satisfy the principle of material frame indifference. The central problem involved in rate theories is that the time derivatives of tensors are not necessarily frame indifferent. For example, for a stressed body performing a rigid body rotation, neither the partial derivative, $\partial\sigma_{ij}/\partial t$, nor the material derivative, $D\sigma_{ij}/Dt$, of the stress vanishes identically. Therefore it is necessary to define rate derivatives of stress, and similarly, strain, which obey the principle of material frame indifference.

The properties of a material are independent of the choice of a particular derivative which, like the choice of a measure of strain, is a matter of convenience although subject to certain necessary conditions. There are infinitely many such derivatives among which we mention the convective derivative (18,20) and the corotational derivative (or Jaumann derivative) (107,108).

The corotational derivative of a second rank tensor $\underline{\underline{T}}$ is defined as (1)

$$\overset{\circ}{\underline{\underline{T}}} \equiv \frac{d}{du}\left[\underline{\underline{R}}_t^{T}(u)\cdot\underline{\underline{T}}(u)\cdot\underline{\underline{R}}_t(u)\right]\Big|_{u=t} \qquad [7.1]$$

$$= \dot{\underline{\underline{T}}} + \underline{\underline{\omega}}^{T}\cdot\underline{\underline{T}} + \underline{\underline{T}}\cdot\underline{\underline{\omega}} \qquad [7.2]$$

where $\dot{\underline{\underline{T}}}$ is the material derivative of $\underline{\underline{T}}$ with respect to t and $\underline{\underline{\omega}}$ is the vorticity tensor.

Given a convective frame, i.e. a frame which deforms with the body, there are four frame-invariant derivatives according to whether we consider its covariant, contravariant, or mixed components. When these are referred to the laboratory frame, each yields a different tensor which we will denote by arrows placed over the symbol.

Corresponding to the covariant components of a second rank tensor, the convective derivative in the laboratory frame becomes

$$\overset{\downarrow}{\underline{\underline{T}}} \equiv \frac{d}{du}\left[\underline{\underline{F}}_t^{T}(u)\cdot\underline{\underline{T}}(u)\cdot\underline{\underline{F}}_t(u)\right]\Big|_{u=t} \qquad [7.3]$$

$$= \overset{o}{\underline{\underline{T}}} + \underline{\underline{d}}\cdot\underline{\underline{T}} + \underline{\underline{T}}\cdot\underline{\underline{d}} \qquad [7.4]$$

where $\overset{o}{\underline{\underline{T}}}$ is the carotational derivative defined above, and $\underline{\underline{d}}$ is the stretching tensor. Convective derivation of the contravariant components gives

$$\overset{\uparrow}{\underline{\underline{T}}} \equiv \frac{d}{du}\left[\underline{\underline{F}}_u(t)\cdot\underline{\underline{T}}(u)\cdot\underline{\underline{F}}_u^{\,T}(t)\right]\Big|_{u=t} \qquad [7.5]$$

$$= \overset{o}{\underline{\underline{T}}} - \underline{\underline{d}}\cdot\underline{\underline{T}}-\underline{\underline{T}}\cdot\underline{\underline{d}} \qquad [7.6]$$

Convective derivatives of the left and the right mixed components are defined as

$$\overset{\leftarrow}{\underline{\underline{T}}} \equiv \frac{d}{du}\left[\underline{\underline{F}}_u(t)\cdot\underline{\underline{T}}(u)\cdot\underline{\underline{F}}_t(u)\right]\Big|_{u=t} \qquad [7.7]$$

$$= \overset{o}{\underline{\underline{T}}} - \underline{\underline{d}}\cdot\underline{\underline{T}} + \underline{\underline{T}}\cdot\underline{\underline{d}} \qquad [7.8]$$

and

$$\overset{\rightarrow}{\underline{\underline{T}}} \equiv \frac{d}{du}\left[\underline{\underline{F}}_t^{\,T}(u)\cdot\underline{\underline{T}}(u)\cdot\underline{\underline{F}}^T(t)\right]\Big|_{u=t} \qquad [7.9]$$

$$= \overset{o}{\underline{\underline{T}}} + \underline{\underline{d}}\cdot\underline{\underline{T}} - \underline{\underline{T}}\cdot\underline{\underline{d}} \qquad [7.10]$$

respectively.

If $\underline{\underline{T}}$ is the unit (i.e. metric) tensor $\underline{\underline{I}}$, eqs. [7.4], [7.6], [7.8] and [7.10] reduce, respectively, to

$$\overset{\downarrow}{\underline{\underline{I}}} = 2\underline{\underline{d}} = \frac{d}{du}\,\underline{\underline{C}}_t(u)\Big|_{u=t} \qquad [7.11]$$

$$\overset{\uparrow}{\underline{\underline{I}}} = -2\underline{\underline{d}} = -\frac{d}{du}\,\underline{\underline{B}}_u(t)\Big|_{u=t} \qquad [7.12]$$

$$\overset{\leftarrow}{\underline{\underline{I}}} = \overset{\rightarrow}{\underline{\underline{I}}} = 0 \qquad [7.13]$$

Eq. [7.12] can also be written as

$$-\overset{\uparrow}{\underline{\underline{I}}} = \frac{d}{du}\,\underline{\underline{C}}_t^{-1}(u) \qquad [7.14]$$

We note that $\overset{\downarrow}{\underline{\underline{I}}}$ is the first Rivlin-Ericksen (17) tensor $\underline{\underline{A}}_1$, and $-\overset{\uparrow}{\underline{\underline{I}}}$ is the first White-Metzner (109) tensor, $\underline{\underline{D}}_1$. Higher order Rivlin-Ericksen and White-Metzner tensors can be generated by using eqs. [7.4] and [7.6] as recurrence relations.

For incompressible isotropic materials two constitutive equations were proposed (110-116). These are based on the convective derivatives of the covariant and contravariant components of the stress and the strain tensors. The equations are of the operator form and replace the operator equation of the infinitesimal theory of visocelastic behavior (105).

The first equation is

$$\sum_{i=0}^{i=n} p_i \overset{\downarrow i}{\underline{\underline{\sigma}}} + P\underline{\underline{I}} = \sum_{j=0}^{j=m} q_j \overset{\downarrow j}{\underline{\underline{A}}} \qquad [7.15]$$

and the second takes the form

$$\sum_{i=0}^{i=n} r_i \overset{\uparrow i}{\underline{\underline{\sigma}}} + P\underline{\underline{I}} = \sum_{j=0}^{j=m} s_j \overset{\uparrow j}{\underline{\underline{D}}} \qquad [7.16]$$

In eqs. [7.15] and [7.16] the symbols placed on the tensors denote convective derivation of order indicated, the zeroth order implying the quantity itself. P is an arbitrary isotropic pressure, the p, q, r, and s are material constants which are independent of time, stress, and strain, and $\underline{\underline{A}}$ and $\underline{\underline{D}}$ are the Rivlin-Ericksen and White-Metzner tensors, respectively.

To represent the mechanical behavior of real materials, the index m in eqs. [7.15] and [7.16] should be n for the representation of solids and n-1 for liquids (105).

Eq. [7.15] can be recast in integral form as

$$\underline{\underline{\sigma}}(t) = - P\underline{\underline{I}} + \int_{-\infty}^{t} G(t-u) \frac{d}{du} \underline{\underline{C}}_t(u) \, du \qquad [7.17]$$

After differentiating using eqs. [2.12] and [2.25] we have

$$\underline{\underline{\sigma}}(t) = -P\underline{\underline{I}} + 2\int_{-\infty}^{t} G(t-u)\ \underline{\underline{F}}_t^{\,T}(u)\cdot\underline{\underline{d}}(u)\cdot\underline{\underline{F}}_t(u)\ du \qquad [7.18]$$

In terms of the memory function M(t-u) eq. [7.18] becomes

$$\underline{\underline{\sigma}}(t) = -P\underline{\underline{I}} + 2\int_{-\infty}^{t} M(t-u)\ \underline{\underline{D}}(u;t)\ du \qquad [7.19]$$

which, by eq. [3.6], is

$$\underline{\underline{\sigma}}(t) = -P\underline{\underline{I}} + \int_{-\infty}^{t} M(t-u)\ \underline{\underline{C}}_t(u)\ du \qquad [7.20]$$

absorbing the constant term into $P\underline{\underline{I}}$.

Similarly, eq. [7.16] can be written as

$$\underline{\underline{\sigma}}(t) = -P\underline{\underline{I}} - \int_{-\infty}^{t} G(t-u)\ \frac{d}{du}\,\underline{\underline{C}}_t^{-1}(u)\ du \qquad [7.21]$$

$$= -P\underline{\underline{I}} + 2\int_{-\infty}^{t} G(t-u)\ \underline{\underline{F}}_u(t)\cdot\underline{\underline{d}}(u)\cdot\underline{\underline{F}}_u^{\,T}(t)\ du \qquad [7.22]$$

and

$$\underline{\underline{\sigma}}(t) = -P\underline{\underline{I}} + 2\int_{-\infty}^{t} M(t-u)\ \hat{\underline{\underline{D}}}[d;t]\ du \qquad [7.23]$$

where

$$\hat{\underline{\underline{D}}}(u,t) = [I - \underline{\underline{C}}_t^{-1}(u)]/2 \qquad [7.24]$$

Thus

$$\underline{\underline{\sigma}}(t) = -\ P\underline{\underline{I}} - 2\int_{-\infty}^{t} M(t-u)\ \underline{\underline{C}}_t^{-1}(u)\ du \qquad [7.25]$$

Equations [7.17] and [7.21] correspond to the special cases of n=-2 and n=2 of our model L, eq. [6.5]. These two models and their various forms given by eqs. [7.17] to [7.24] were proposed by several workers (110-116). Eq. [7.21] predicts the first normal stress effect but not the second. Conversely, eq. [7.17] predicts the second normal stress effect but not the first. Combinations of eqs. [7.20] and [7.24] have been proposed. Neither of these equations and combinations, however, can predict the shear gradient dependence of the viscosity.

Since both eqs. [7.17] and [7.21] are special cases of our eq. [6.5], it is natural to attempt to define an invariant differential operator which is similar but more general than those defined by eqs.

[7.3] and [7.5]. We shall call this new operator the generalized convective differential operator. We first express $\underline{\underline{C}}_t(u)$ in terms of its eigenvecotrs and eigenvalues of $\underset{\sim}{C}_t(u)$. We have

$$\underset{\sim}{C}_t(u) = \underset{\sim}{N}_t(u)\underset{\sim}{\Lambda}^2\underset{\sim}{N}_t^T(u) \qquad [7.26]$$

where

$$\underset{\sim}{\Lambda}^2 = \underset{\sim}{\Lambda}^2_t(u) \qquad [7.27]$$

and

$$\underset{\sim}{\Lambda}^2_t(u)\Big|_{u=t} = \underset{\sim}{I} \qquad [7.28]$$

Taking derivatives with respect to u, we obtain

$$\dot{\underset{\sim}{C}}_t(u) = \dot{\underset{\sim}{N}}_t(u)\underset{\sim}{\Lambda}^2\underset{\sim}{N}_t^T(u) + 2\underset{\sim}{N}_t(u)\underset{\sim}{\Lambda}\dot{\underset{\sim}{\Lambda}}\underset{\sim}{N}_t^T(u) \qquad [7.29]$$

$$+ \underset{\sim}{N}_t(u)\underset{\sim}{\Lambda}^2\dot{\underset{\sim}{N}}_t^T(u)$$

Since $\underset{\sim}{N}_t(u)$ is an orthonormal matrix, we have

$$\underset{\sim}{N}_t(u)\dot{\underset{\sim}{N}}_t(u) + \dot{\underset{\sim}{N}}_t(u)\underset{\sim}{N}_t^{T}(u) = 0 \qquad [7.30]$$

In particular, at u=t

$$\underset{\sim}{N}_t(t)\dot{\underset{\sim}{N}}_t^{T}(t) + \dot{\underset{\sim}{N}}_t(t)\underset{\sim}{N}_t^{T}(t) = 0 \qquad [7.31]$$

As discussed by Blatz and Chang (86), $\underset{\sim}{N}_t(t)$ does not have to be I.

Taking the limit of $\dot{\underset{\sim}{C}}_t(u)$ as u approaches t and then substituting eqs. [7.28] and [7.31] into the resulting equation, we obtain

$$\dot{\underset{\sim}{C}}_t(t) = 2\underset{\sim}{N}_t(t)\dot{\underset{\sim}{\Lambda}}(t;t)\underset{\sim}{N}_t^{T}(t) \qquad [7.32]$$

As shown in Section 2, by eq. [2.25]

$$\dot{\underset{\sim}{C}}_t(t) = 2\underset{\sim}{d}(t) \qquad [7.33]$$

Thus eq. [7.32] indicates that $\dot{\underset{\sim}{\Lambda}}(t;t)$ and $\underset{\sim}{N}_t(t)$ are the matrices of eigenvalues and eigenvectors of the stretching tensor. Similarly, we can show that

$$\left.\frac{2d\underset{\sim}{C}_t^{\,n/2}(u)}{ndu}\right|_{u=t} = 2\underset{\sim}{N}_t(t)\dot{\underset{\sim}{\Lambda}}(t;t)N_t^{\,T}(t) = 2\underset{\sim}{d}(t) \qquad [7.34]$$

which includes both eqs. [7.11] and [7.22] as special cases.

We next define the transpose of the (n/2)-power of the relative deformation gradient as

$$\underset{\sim}{F}_t^{\,T(n/2)}(u) = \underset{\sim}{N}_t(u)\underset{\sim}{\Lambda}^{n/2}\underset{\sim}{n}_t^{\,T}(u) \qquad [7.35]$$

where $n_t(u)$ is the matrix of eigenvectors of

$$\underset{\sim}{B}_t(u) = \underset{\sim}{F}_t(u)\underset{\sim}{F}_t^{\,T}(u) = \underset{\sim}{n}_t(u)\underset{\sim}{\Lambda}^2\underset{\sim}{n}_t^{\,T}(u) \qquad [7.36]$$

$N_t(u)$ and $n_t(u)$ are related by

$$\underset{\sim}{n}_t(u) = \underset{\sim}{R}_t(u)\underset{\sim}{N}_t(u) \qquad [7.37]$$

where $\underset{\sim}{R}_t(u)$ is the matrix of the mixed components of the rotational tensor of $\underline{\underline{F}}_t(u)$. Therefore,

$$\underset{\sim}{n}_t(t) = \underset{\sim}{N}_t(t) \qquad [7.38]$$

since $\underset{\sim}{R}_t(t) = \underset{\sim}{I}$.

Furthermore,

$$\dot{\underset{\sim}{N}}_t(u)\Big|_{u=t} = [\dot{\underset{\sim}{R}}_t(u)\underset{\sim}{N}_t(u) + \underset{\sim}{R}_t(u)\dot{\underset{\sim}{N}}_t(u)]\Big|_{u=t} \qquad [7.39]$$

$$= \dot{\underset{\sim}{R}}_t(t)\underset{\sim}{N}_t(t) + \dot{\underset{\sim}{N}}_t(t) \qquad [7.40]$$

which gives

$$\dot{\underset{\sim}{N}}_t(t) = \underset{\sim}{\omega}\underset{\sim}{N}_t(t) + \dot{\underset{\sim}{N}}_t(t) \qquad [7.41]$$

With eqs. [7.33], [7.37], [7.40] and [7.43] we derive

$$\frac{d}{du}\,\underset{\sim}{F}_t^{T(n/2)}(u)\Big|_{u=t} = 0.5\ n\underset{\sim}{d}(t) - \underset{\sim}{\omega}(t) \qquad [7.42]$$

Similarly

$$\frac{d}{du}\,\underset{\sim}{F}_t^{n/2}(u)\Big|_{u=t} = 0.5\ n\underset{\sim}{d}(t) + \underset{\approx}{\omega}(t) \qquad [7.43]$$

Furthermore,

$$\underset{\sim}{C}_t^{n/2}(u) = \underset{\sim}{F}_t^{T(n/2)}(u)\ \underset{\sim}{F}_t^{n/2}(u) \qquad [7.44]$$

so that

$$\frac{d}{du}\underset{\sim}{C}_t^{n/2}(u)\Big|_{u=t} = \frac{d}{du}\underset{\sim}{F}_t^{T(n/2)}(u)\Big|_{u=t} + \frac{d}{du}\underset{\sim}{F}_t^{n/2}(u)\Big|_{u=t} \qquad [7.45]$$

Eqs. [7.45] agrees with eq. [7.34]

We now define an nth power convective derivative of a tensor $\underline{\underline{T}}$ as

$$\overset{\Delta}{\underline{\underline{T}}} = \frac{d}{du}\left[\underline{\underline{F}}_t^{T(n/2)}(u)\cdot\underline{\underline{T}}(u)\cdot\underline{\underline{F}}_t^{n/2}(u)\right]\Big|_{u=t} \qquad [7.46]$$

$$= \overset{o}{\underline{\underline{T}}} + 0.5n(\underline{\underline{d}}\cdot\underline{\underline{T}} + \underline{\underline{T}}\cdot\underline{\underline{d}}) \qquad [7.47]$$

$\overset{\Delta}{\underline{\underline{T}}}$ is frame indifferent since $\overset{o}{\underline{\underline{T}}}$, $\underline{\underline{d}}$, and $\underline{\underline{T}}$ are also. We note that

$$\overset{\Delta}{\underline{\underline{T}}} = \overset{\uparrow}{\underline{\underline{T}}} \qquad (n = -2) \qquad [7.48]$$

and

$$\overset{\Delta}{\underline{\underline{T}}} = \overset{\downarrow}{\underline{\underline{T}}} \qquad (n = 2) \qquad [7.49]$$

Higher order derivatives can be generated by using eq. [7.47] as recurrence relation. As an example, the kth order nth power convective derivative of the unit (metric) tensor can be written as

$$\overset{\Delta k}{\underline{\underline{I}}} = \frac{d^k}{du^k} \underline{\underline{C}}_t^{\,n/2}(u)\Big|_{u=t} \qquad [7.50]$$

In principle, eq. [7.50] can be further generalized to the form

$$\overset{*}{\underline{\underline{T}}} = \overset{o}{\underline{\underline{T}}} + \underline{\underline{\Psi}}(\underline{\underline{d}})\cdot\underline{\underline{d}} + \underline{\underline{d}}\cdot\underline{\underline{\Psi}}(\underline{\underline{d}}) \qquad [7.51]$$

where $\underline{\underline{\Psi}}$ is an isotropic tensor function of $\underline{\underline{d}}$ and hence $\overset{*}{T}$ can be considered as a definition of the generalized convective differential operator. Thus, our model GL can be considered as a linear combination of higher order derivatives of the Cauchy stress tensor and the metric tensor defined in terms of the generalized convective differential operator. Similar conclusions apply to our model GS.

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CHAPTER 3

A STUDY OF THE VISCOELASTIC BEHAVIOR OF UNCROSSLINKED (GUM) RUBBERS IN MODERATELY LARGE DEFORMATIONS

INTRODUCTION

One of the central problems of polymer rheology is the establishment of a three dimensional rheological equation for viscoelastic materials which are capable of large deformations. Basically, there are two ways to approach the problem. One is to develop a mathematical constitutive theory based on only a few assumptions and aimed at rather broad classes of materials. There exist several such theories among which the most notable are the Green-Rivlin theory[1] and the Coleman-Noll[2] theory. Because of their generality, they are usually too complicated to be utilized by material scientists to characterize materials and by engineers to estimate the response of materials under service conditions.

The other alternative is to focus on a restricted class of materials and/or a restricted class of deformations without violating the principles to which a constitutive equation is subject such as the principles of determinism, local action, material frame indifference, and entropy. One may build into the constitutive equation some experimentally known facts and thus produce an equation that is useful to the applied scientist or the engineer. In an earlier article[3] a single integral constitutive theory for soft polymeric systems was proposed. Such systems include both crosslinked and uncrosslinked polymers in their low transition region and in their equilibrium or terminal region, respectively. For such systems, published data indicate that the effects of time and strain are separable in both uniaxial and multiaxial stress relaxation and/or creep tests[3]. The equilibrium stress-strain data for such systems are better represented by constitutive equations based on a generalized measure of strain[4,5]. The theory was developed by taking both of these facts into consideration.

Two particular models, S and L, resulted from specification of the forms of the strain measure[3]. We have discussed the application of these models to the behavior of crosslinked rubbers in another publication[6] in which we also presented a detailed derivation of the necessary equations for model S which we have called the *solid model*. These equations will only be summarized in this paper in which we derive the equations for model L, called the *liquid model*. We apply both models here to the behavior of uncrosslinked rubberlike polymers.

THEORY OF THE APPLICATION OF THE LIQUID MODEL

Our liquid model (model L of reference 3), designed for an isotropic incompressible elastic liquid, yields

$$\bar{\sigma}_\alpha(t) = -P - \frac{2}{3n}\int_{\infty}^{t} E(t-u)\,\frac{d}{du}\left[\frac{\lambda_\alpha(t)}{\lambda_\alpha(u)}\right]^n du \qquad (1)$$

as the equation for the principal true stress components in an orthogonal deformation, i.e. in a deformation in which the orientation of the principal directions remains unchanged. In eq. (1) $\bar{\sigma}_\alpha(t)$ is the principal true stress in the α-direction at the current time t, P is an unspecified hydrostatic pressure, n is the material constant characterizing the strain measure[4,5], E(t) is the small deformation tensile relaxation modulus, and $\lambda_\alpha(u)$ is the principal stretch ratio in the α-direction at the past time u. Eq. (1) is limited to isothermal deformations, although it can be modified to cover nonisothermal conditions. In an isothermal deformation (the case we are interested in) $\lambda_\alpha(u)$ is defined by

$$\lambda_\alpha(u) = L_\alpha(u,T)/L_{\alpha o}(T) \tag{2}$$

where $L_{\alpha o}(T)$ is the length of the specimen in the α-direction at zero stress at the test temperature T, and $L_\alpha(u,T)$ is the length of the specimen in the same direction at time u at the same temperature. Eliminating P we obtain the true stress in uniaxial tension as

$$\bar{\sigma}(t) = -\frac{2}{3n}\int_{-\infty}^{t} E(t-u)\,\frac{d}{du}\left[\left(\frac{\lambda(t)}{\lambda(u)}\right)^{n} - \left(\frac{\lambda(t)}{\lambda(u)}\right)^{-n/2}\right]du \tag{3}$$

If $\lambda(u)$ is continuous, we may use

$$\bar{\sigma}(t) = -\frac{2}{3}\int_{-\infty}^{t} E(t-u)\left[\left(\frac{\lambda(t)}{\lambda(u)}\right)^{n} + 0.5\left(\frac{\lambda(t)}{\lambda(u)}\right)^{-n/2}\right]\frac{d\ln\lambda(u)}{du}\,du \tag{4}$$

We now develop special forms of eqs. (3) or (4) for different strain histories in uniaxial tension. For the strain histories to be discussed, the lower limit of integration in eqs. (3) and (4) is zero because when $u < 0$, $\lambda(u)$ will be constant.

Ramp Function of Strain

We begin by considering the imposition of a constant rate of strain, i.e. a ramp function. The stretch ratio becomes

$$\lambda(u) = 1 + \dot{\varepsilon}u \qquad (5)$$

where $\dot{\varepsilon}$ is the rate of strain. Thus

$$d\lambda(u) = \dot{\varepsilon}du \qquad (6)$$

and eq. (4) yields

$$\bar{\sigma}(t) = \frac{2\dot{\varepsilon}}{3}\int_o^t \left[\left(\frac{1+\dot{\varepsilon}t}{1+\dot{\varepsilon}u}\right)^n + 0.5\left(\frac{1+\dot{\varepsilon}t}{1+\dot{\varepsilon}u}\right)^{-n/2}\right]\frac{E(t-u)}{1+\dot{\varepsilon}u}\,du \qquad (7)$$

The nominal stress results as

$$\sigma(t) = \bar{\sigma}(t)/(1+\dot{\varepsilon}t) \qquad (8)$$

Evaluation of the integral requires numerical integration.

Exponential Stretch Ratio

Let the excitation function be given by

$$\lambda(u) = \exp(ku) \qquad (9)$$

where k is a constant. Then

$$d\lambda(u) = k\ \exp(ku)du \qquad (10)$$

and substitution into eq. (4) yields

$$\bar{\sigma}(t) = (2k/3)\int_0^t E(t-u)\left\{\left[\frac{\exp(kt)}{\exp(ku)}\right]^n + 0.5\left[\frac{\exp(kt)}{\exp(ku)}\right]^{-n/2}\right\}\frac{du}{\exp(ku)} \tag{11}$$

Again, numerical integration is necessary to evaluate $\bar{\sigma}(t)$.

Ramp Followed by a Constant Strain

If the strain history consists of the imposition of a constant rate of strain to $t = t_1$ at which time the extension is held constant, we have

$$\lambda(u) = 1 + \dot{\varepsilon}uh(u) - \dot{\varepsilon}(u - t_1)h(u - t_1) \tag{12}$$

where h(u) is the unit step function. Then

$$d\lambda(u) = \dot{\varepsilon}[h(u) - h(u - t_1) + u\delta(u) - (u - t_1)\delta(u - t_1)]\ du \tag{13}$$

where $\delta(u)$ is the delta function. Inserting this into eq. (4) we see that the delta function terms contribute nothing so that we may write

$$d\lambda(u) = \begin{cases} \dot{\varepsilon}du & \text{for} \quad u < t_1 \\ 0 & \text{for} \quad u > t_1 \end{cases} \tag{14}$$

Consequently, for $t > t_1$

$$\bar{\sigma}(t) = \frac{2\dot{\varepsilon}}{3}\int_0^{t_1} E(t-u)\left[\left(\frac{1+\dot{\varepsilon}t_1}{1+\dot{\varepsilon}u}\right)^n + 0.5\left(\frac{1+\dot{\varepsilon}t_1}{1+\dot{\varepsilon}u}\right)^{-n/2}\right]\frac{1}{1+\dot{\varepsilon}u}\,du \qquad (15)$$

which differs from eq. (7) only in the upper limit of integration. We note that eq. (15) is not a convolution integral.

Step Function of Strain

For an excitation represented by a step function of strain we may write

$$\left(\frac{\lambda(t)}{\lambda(u)}\right)^n = \lambda_o^n + (1 - \lambda_o^n)h(u) \qquad (16)$$

where λ_o is the stretch ratio corresponding to the constant strain ε_o imposed at $t = 0$. Thus, when $u < 0$, $\lambda(u) = 1$ and we have $\lambda(t) = \lambda_o$ as it should because $\lambda(t)$ is the extension at the present time t. When $u > 0$, $\lambda(t)/\lambda(u)$ becomes 1 as required.

Substitution of eq. (16) into eq. (3) yields

$$\bar{\sigma}(t) = (2/3n)E(t)(\lambda_o^n - \lambda_o^{-n/2}) \qquad (17)$$

as the sought-for expression for the stress, the nominal stress being given by

$$\sigma(t) = (2/3n)E(t)[\lambda_o^{n-1} - \lambda_o^{-(n+2)/2}] \tag{18}$$

The liquid and solid models predict the same response to a step function of strain.

We note that it is not possible experimentally to impose a finite strain instantaneously. In practice a step function of strain is invariably a ramp followed by a step as discussed earlier. However, if t_1 is much smaller than the first time of interest, the "ramp transients" will have effectively decayed and the response will have become indistinguishable from the response elicited by the imposition of a true step function.

Two Step Functions of Strain

In double step stress relaxation the stretch ratio $\lambda(u)$ has the value 1 when $u<0$. At $u = 0$, $\lambda(u)$ is changed to some other value λ_I, and is held at λ_I until some time t_1. At time t_1 the value of $\lambda(u)$ is changed to λ_{II} at which it is kept constant up to the current time t. For this deformation history we can write

$$\frac{\lambda^n(t)}{\lambda^n(u)} = \lambda_{II}{}^n + \left(\frac{\lambda_{II}{}^n}{\lambda_I{}^n} - \lambda_{II}{}^n\right) h(u) + \left(1 - \frac{\lambda_{II}{}^n}{\lambda_I{}^n}\right) h(u-t_1) \tag{19}$$

and substitution into eq. (3) yields

$$\bar{\sigma}(t) = \frac{2}{3n} E(t) \left[\lambda_{II}{}^{n} - \lambda_{II}{}^{-n/2} - \left(\frac{\lambda_{II}}{\lambda_{I}}\right)^{n} + \left(\frac{\lambda_{II}}{\lambda_{I}}\right)^{-n/2} \right]$$

$$+ \frac{2}{3n} E(t-t_1) \left[\left(\frac{\lambda_{II}}{\lambda_{I}}\right)^{n} - \left(\frac{\lambda_{II}}{\lambda_{I}}\right)^{-n/2} \right] \tag{20}$$

Small Step Function Superposed on a Finite Step of Strain

We now consider a small deformation superposed on a moderately large one. Let the small strain superposed at t_r be given by $\varepsilon_s(t)$ and the large stretch ratio by λ_r. Further, assume that the stress due to the finite deformation has substantially relaxed when the small deformation is superimposed. Then

$$\lambda = \lambda_r + \varepsilon_s(t) \tag{21}$$

and we have

$$\lambda^n = \lambda_r^n + \lambda_r^{n-1}\, n\, \varepsilon_s(t) \tag{22}$$

because, by stipulation, $\varepsilon_s(t) \ll (\lambda_r - 1)$. Thus, for a superposed step function of small strain we have

$$\frac{\lambda^n(t)}{\lambda^n(u)} = \lambda_r^n + n\lambda_r^{n-1}\varepsilon_s(t) + \left[1 + \frac{n\varepsilon_s(t)}{\lambda_r} - \lambda_r^n - n\lambda_r^{n-1}\varepsilon_s(t)\right] h(u)$$

$$- n \frac{\varepsilon_s(t)}{\lambda_r} h(u-t_r) \tag{23}$$

Now, the incremental true stress at $t > t_r$ arising from the superposition of the small deformation at $t = t_r$ is

$$\Delta\bar{\sigma}(t-t_r) \equiv \bar{\sigma}(t) - \bar{\sigma}_r(t) \tag{24}$$

where $\bar{\sigma}(t)$ is obtained from eq. (3) using eq. (23), and $\bar{\sigma}_r(t)$ is obtained using eq. (17). Consequently,

$$\Delta\bar{\sigma}(t-t_r) = \frac{2}{3} E(t) \left(\lambda_r^n + 0.5\lambda_r^{-n/2}\right) \frac{\varepsilon_s(t)}{\lambda_r} - \frac{E(t)}{\lambda_r} \varepsilon_s(t)$$

$$\frac{1}{\lambda_r}\int_{t_r}^{t} E(t-u) \frac{d\varepsilon_s(u)}{du} du \tag{25}$$

If the superimposed infinitesimal deformation is a step function of strain, i.e. if

$$\varepsilon_s(u) = \varepsilon_s h(u-t_r) \tag{26}$$

then the superimposed relaxation modulus $E_s(t-t_r)$ obtained from the superposed strain is given by

$$E_s(t-t_r) = \frac{\Delta\bar{\sigma}(t-t_r)}{\varepsilon_s} = \frac{2E(t)}{3\lambda_r}\left(\lambda_r^n + 0.5\ \lambda_r^{-n/2}\right) - \frac{E(t)}{\lambda_r} + \frac{1}{\lambda_r}\ E(t-t_r) \tag{27}$$

Eq. (27) reduces to $E(t-t_r)$ if $\lambda_r = 1$.

Small Ramp Function Superposed on a Finite Step Function of Strain

For strain history we have

$$\varepsilon_s(u) = \dot{\varepsilon}(u-t_r)h(u-t_r) \tag{28}$$

Eq. (25) becomes

$$F_s(t-t_r) = \frac{\Delta\bar{\sigma}(t-t_r)}{\dot{\varepsilon}(t-t_r)}$$

$$= \frac{2E(t)}{3\lambda_r}\left(\lambda_r^n + 0.5\ \lambda_r^{-n/2}\right) - \frac{E(t)}{\lambda_r} + \frac{1}{\lambda_r}\ F(t-t_r) \tag{29}$$

where

$$F(t) = \frac{1}{\dot{\varepsilon}t}\int_0^t E(t-u)\ du \tag{30}$$

Small Sinusoidal Oscillations Superposed on a Finite Step Function of Strain

We have

$$\varepsilon_s(u) = \varepsilon_s \exp[j\omega(u-t_r)]h(u-t_r) \tag{31}$$

Substituting in eq. (25) we obtain

$$\begin{aligned}\frac{\Delta\bar{\sigma}(t-t_r)}{\varepsilon_s} &= \frac{E(t)}{3\lambda_r}\left[2\lambda_r{}^n + \lambda_r^{-n/2} - 3 \exp j\omega(t-t_r)\right] \\ &+ \frac{j\omega}{\lambda_r}\int_{t_r}^{t} E(t-u)\exp j\omega(u-t_r)\, du\end{aligned} \tag{32}$$

The steady state solution is obtained as

$$E_s'(\omega) = E(t)[2\lambda_r{}^n + \lambda_r^{-n/2}-3]/3\lambda_r + E'(\omega)/\lambda_r \tag{33a}$$

$$E_s''(\omega) = E''(\omega)/\lambda_r \tag{33b}$$

where $E'(\omega)$ and $E''(\omega)$ are the real and imaginary components of the complex tensile modulus.

THEORY OF THE APPLICATION OF THE SOLID MODEL

We summarize for convenience the corresponding equations for our solid model (model S of reference 3) which we derived elsewhere[6]. For a ramp function of strain

$$\bar{\sigma}(t) = (2\dot{\varepsilon}/3)\int_0^t E(t-u)\left[(1+\dot{\varepsilon}u)^{n-1} + 0.5\ (1+\dot{\varepsilon}u)^{-(n+2)/2}\right] du \tag{34}$$

For an exponential stretch ratio

$$\bar{\sigma}(t) = (2k/3)\int_0^t E(t-u)\ \exp(ku)\left[\left(\ \exp(ku)\right)^{n-1} + 0.5\ \left(\ \exp(ku)\right)^{-(n+2)/2}\right] du \tag{35}$$

For a ramp function of strain followed by a step function of strain

$$\bar{\sigma}(t) = (2\dot{\varepsilon}/3)\int_0^{t_1} E(t-u)\left[(1+\dot{\varepsilon}u)^{n-1} + 0.5\ (1+\dot{\varepsilon}u)^{-(n+2)/2}\right] du \tag{36}$$

For a step function of strain

$$\bar{\sigma}_r(t) = (2/3n)\ E(t)\left[\lambda_o^n - \lambda_o^{-n/2}\right] \tag{37}$$

For a step function of strain followed by another step of strain

$$\bar{\sigma}(t) = (2/3n)\left\{E(t)\left(\lambda_1^{n}-\lambda_I^{-n/2}\right) + E(t-t_r)\left(\lambda_{II}^{-n/2}-\lambda_I^{n}+\lambda_I^{-n/2}\right)\right\} \qquad (38)$$

For a superposition of a small step function of strain on a finite step of strain

$$E_s(t-t_r) = f(\lambda_r)E(t-t_r) \qquad (39)$$

where

$$f(\lambda_r) = (2/3)\left[\lambda_r^{n-1} + 0.5\ \lambda_r^{-(n+2)/2}\right] \qquad (40)$$

For a small ramp superposed on a finite strain

$$F_s(t-t_r) = f(\lambda_r)F(t-t_r) \qquad (41)$$

For a small sinusoidal oscillation superposed on a finite strain

$$E_s'(\omega) = f(\lambda_r)E'(\omega) \qquad (42a)$$

$$E_s''(\omega) = f(\lambda_r)E''(\omega) \qquad (42b)$$

MATERIALS

The work described in this paper was carried out on a styrene-butadiene copolymer, Phillips® SBR 1502.

Sample Preparation

Samples were prepared according to the following recipe:

SBR 1502	100 parts
N-phenyl-2-naphtyl amine (antioxidant)	1 part

The ingredients were cold-milled on a two-roll laboratory mill. The milled material was placed in 15.2 x 15.2 x 0.2 cm (6 x 6 x 0.08 inch) molds and heated for fifteen minutes at about 1750 bar (25000 psi) pressure at a temperature of about 116°C (240°F).

The gel fraction of the samples never exceeded 0.1%. The weight average molecular weight was 170000 as determined by intrinsic viscosity measurements in toluene at 30°C[7].

Two samples (molded sheets) of polybutadiene (PBD) were supplied by Phillips Petroleum Company. The information supplied by the company on these samples is given below:

Sample	A	B	
Solprene 235	100	100	parts
Zinc stearate	0.2	0.4	parts
Resin	0.133	0.266	parts
Sulfur	0.10	0.20	parts
Santocure	0.08	0.16	parts

This compounding recipe was intended to produce very slightly crosslinked materials. However, they were found to be soluble in toluene. Hence, they were not crosslinked but are likely to contain branched structures.

Specimen Preparation

All experiments were made on tab bonded strip specimens. The strips were cut from the molded sheets using a knife-edged mill blade. U-shaped phosphorus bronze tabs were glued to the ends using a poly(cyano acrylate) adhesive (Devcon Corp. Zip Grip 10®).

The specimens had dimensions of about 12 x 0.5 x 0.2 cm. To minimize end effects, the area of contact between the strips and the tabs (i.e. the bonded area) was kept as small as possible. The length of overlap on each side at both ends of the strips was about 1.5 mm.

The exact width and length of the specimens were measured with a travelling microscope. Thicknesses were determined with a micrometer. When not in use, the specimens were kept in a refrigerator at 0°C.

EXPERIMENTAL METHODS

Experiments were made in uniaxial tension on a Model TTB Instron Testing machine fitted with a Missimers temperature control chamber. Special baffles were installed to reduce the effect of the air currents which tended to shake the specimen, thus superposing random oscillations on the force recorded. The temperature was monitored through a thermocouple placed close to the specimen. The temperature could be controlled to about ±0.1°C in the operative range from -20 to 23°C.

The range of crosshead speeds covered the entire operative range of the instrument from about 0.00508 to 50.8 cm (0.002 to 20 inches) per minute. No appreciable heat built up in the specimen even at the highest crosshead speed over the short time interval required. Careful experiments[8] showed that strains calculated from cathetometer readings of bench marks placed on specimens agreed with those calculated from the recorded trace of force against time.

To increase the precision of the measurements, most of the work reported in detail was made on a single specimen. Ample time (never less than five times the previous duration of the experiment) was allowed between experiments so that the sample would relax completely. During these recovery periods the specimen was removed from the grips. To decrease the recovery time between experiments, each series of experiments was carefully planned and tests requiring smaller deformations were made before those in which larger deformations were applied. The length of the optimum recovery times was established in a series of tests not reported here[8]. The dimensions were redetermined after each experiment.

Upon installation, the specimen was first attached to the upper grip so that it would hang by its own weight (about 1.5 g). The force registering on the load cell was then balanced to zero, and the specimen was connected to the lower grip. Since this operation normally introduced some stress in the specimen, the crosshead was now adjusted until the force reading again returned to zero, and the specimen was rested for at least thirty minutes. Bending or buckling of the specimen was minimized by proper alignment. This problem is discussed in detail elsewhere[8].

Because the moduli of our materials were high enough, the error resulting from creep under the specimens own weight is negligible. In principle, specimens of uncrosslinked materials of low modulus should be immersed in an inert solvent of matching density.

RESULTS

The two models which we have discussed earlier assume that the ratio of stress at time t to that at an arbitrary reference time t_r in a stress relaxation experiment is independent of strain. We therefore first looked at the experimental evidence in support of this assumption. We reviewed published data (mainly on crosslinked materials) elsewhere[3,9]. We now present data on our uncrosslinked SBR at 23°C. In Fig. 1 we plotted the engineering stress as a function of time in logarithmic coordinates in stress relaxation experiments obtained at different levels of the constant stretch ratio ranging from 1.004 to 1.852. In such a plot the curves must be parallel if our assumption is justified. The broken lines in Fig. 1 indicate the response to the ramp excitation ($t<t_1$) which preceeds the constant strain in a stress relaxation experiment. Ramp transient behavior had effectively decayed away for times longer than 10 t_1 where t_1 is the time required to impose the final strain. The solid curves are all parallel, thus confirming our basic assumption that the distribution of relaxation times is not affected by the level of strain. At the highest elongation the specimen would break after about 30 minutes at the test temperature. Since all experiments were to be made on the same specimen we generally stopped taking data 10 minutes after starting the deformation. At the lower elongations the upper limit was set essentially by our ability to read the force precisely. At lower temperatures the time-to-break at a given elongation increases and we were able to confirm our assumption over four decades of time. These data are not shown.

Our PBD samples gave similar results (not shown) indicating that our assumption is valid for uncrosslinked linear materials and highly branched ones as well as crosslinked systems.

Our next task was the determination of the small deformation tensile relaxation modulus, E(t), at the reference temperature, 23°C. This was accomplished by the standard procedure, using time-temperature superposition to widen the experimental window. At each temperature several experiments were made using different ramp speeds to attain different final strains. The data for $t > 10t_1$ were averaged at each temperature. Stretch ratios were determined from the Instron record. This procedure is faster and more accurate than cathetometric determinations[8] if the ratio of free-to-bound area of the specimen is chosen to ensure a tolerable error (1%) in $(\lambda-1)$. In principle, the faster the ramp speed, the smaller the effect of ramp transients and, hence, the wider the experimental window at a given level of strain. However, the precision with which the stretch ratio can be obtained from the recorder chart decreases as the pulling rate increases.

The master curve is displayed in Fig. 2. The temperature dependence of the horizontal shift function, log a_T, is shown in the insert in Fig. 2. No vertical shifts were required[10]. Although numerical data may be used, it is more convenient to represent the relaxation modulus by an equation. The equation we adopted has the form

$$E(t) = E_o (t/\tau)^{-k_1} [1+(t/\tau)^{k_2}]^{-1} \qquad (43)$$

which the coefficients found by nonlinear least squares fitting are: E_o = 25.091 bar*, τ = 0.004461 minute, k_1 = 0.0422, and k_2 = 0.37716. This equation fitted the data within ± 2% over the time interval from $2x10^{-7}$ to 10^3 minutes.

The second piece of information which the theory requires is the strain parameter n. This was determined as detailed in our paper[6] on crosslinked SBR. A plot of the stress, σ_r, at the isochronal time t_r as function of λ_r is shown in Figs. 3 and 4. The data displayed in Fig. 3 were obtained at 23°C. The least squares fit gave n=0.4. The insert shows that the isochronal true stress-strain relation is linear at least up to 2% strain for two different isochronal times, t_r=1 and t_r=10 minutes. The points in Figs. 4 and 5 show data obtained on our SBR gum in the temperature range from -20 to 23°C at rates of strain spanning two decades of time. The curves represent the predictions of model L, eqs. (7) and (8), using n=0.4. The agreement is within ±2% and may be considered excellent.

Model S fitted the data within about the same error. Thus, these data do not allow us to distinguish between models S and L. We therefore turned to the more sensitive superposition test[6] and, in addition, endeavored to obtain data at longer times. This required experiments at lower temperatures. Data were obtained at -17°C superposing small ramps on a finite stretch. The best fit to the data were obtained with n=0.6. Figure 6 shows a plot of $F_s(t-t_r)$ against λ_r. The solid points represent experimental data and the solid lines give the predictions of eq. (29) for model L and of eqs. (41) and (40) for model S,

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*One bar equals 10^6dyne/cm^2 or 14.5 psi.

both for the isochronal time of 10 minutes. An additional datum point was obtained for an isochronal time of 300 minutes. For $\lambda_r = 1.790$ F(t-300) was 12·21 ± 0.5 bar. Using n=0.6, the liquid model gave 10.23 bar while the solid model predicted 11.98 bar. Thus the data clearly favor the solid model.

We believe that the value of n found in the superposition experiments (n=0.6) is the more accurate one because of the high sensitivity of the test. If we consider the predictions of the solid model for the step experiment [Eq. (17)] the primitive, then the predictions for the ramp experiment [Eq. (34)] may be considered in some sense as the integral, and the predictions of the ramp superposition experiment [Eq. (41)] may be thought of again in some sense as the derivative. Being thus essentially a differential test, the superposition test is the most sensitive one[11].

For this uncrosslinked material the parameter n appears to be independent of temperature. This is shown in Figs. 4 and 5 in which data ranging from -20 to + 23°C where fitted with the same n. We remark that n=0.6 gave an equally good fit within the experimental error with which the relaxation modulus, the temperature, and the temperature function, a_T, can be determined[8]. We estimate the uncertainty in n obtained from ramp test to be about ± 0.1. An example of the fit with n=0.6 is presented in Fig. 7 which shows data at -17°C. The insert indicates that, at this temperature, the isochronal true stress is linear with respect to the strain up to about 6%.

DISCUSSION

We address ourselves here to two groups of problems. We shall first consider the applicability of our models L and S to our own as well as published data. We then discuss the dependence of the strain parameter n on experimental variables.

Comparison of the Liquid and Solid Models

In an earlier publication[6] we have shown that our model S, based on the introduction of the n-measure of strain[4] into the Boltzmann superposition integral, successfully predicted the viscoelastic behavior of crosslinked soft (rubberlike) materials in tensile deformations in which the spectrum of relaxation times remains essentially undisturbed. In the preceeding section we adduced evidence based on experiments on an uncrosslinked SBR that model S is also successful in describing the viscoelastic behavior of uncrosslinked rubberlike materials (gums). We also found that the parameter n is smaller for the uncrosslinked SBR and that it appears to be independent of temperature over the range investigated (-20 to +23°C) in the uncrosslinked material although it showed a definite dependence on temperature[6] over essentially the same range in the crosslinked SBR.

In addition to presenting our own results, we again examine the data of others. The data points in Fig. 8 represent the response of an uncrosslinked polyisobutylene (PIB) to an exponential strtch ratio excitation as obtained by Goldberg, Bernstein, and Lianis[12]. The solid curves represent the predictions of our model L for n=0.6 both for the data at -5 and 20°C, using eq. (11). We determined n and the tensile relaxation modulus mastercurve by fitting the relaxation data given in their paper to eq. (17) at both temperatures and shifting the two isothermal segments into superposition. We note that we obtained the same value of the strain parameter, n=0.6, at both temperatures. Model S gave an identical fit with the same value of n. Thus, again, we were unable to decide between the two models.

Goldberg and Lianis[13] obtained data on a polyester-based polyurethane, B.F. Goodrich Estane® X100, using small sinusoidal oscillations superposed on a finite stretch. Estane X100 is uncrosslinked, although, as many polyurethanes, it behaves almost like a crosslinked material. The data were obtained for two values of λ_r over the frequency range from 0.01 to 0.25 Hz. Measurements were commenced at t_r=12 minutes. Now, according to model L,

$$\lambda_{r_1} E''_s(\omega)\Big|_{\lambda_{r_1}} = \lambda_{r_2} E''_s(\omega)\Big|_{\lambda_{r_2}} \tag{44}$$

and, since E(t) could certainly not have been zero over the period of measurement

$$\lambda_{r_1} E'_s(\omega)\Big|_{\lambda_{r_1}} \neq \lambda_{r_2} E'_s(\omega)\Big|_{\lambda_{r_2}} \tag{45}$$

by eqs. (33). On the other hand, according to model S we should have

$$\frac{\lambda_{r_1} E_s'(\omega)\Big|_{\lambda_{r_1}}}{\lambda_{r_2} E_s'(\omega)\Big|_{\lambda_{r_2}}} = \frac{\lambda_{r_1} E_s''(\omega)\Big|_{\lambda_{r_1}}}{\lambda_{r_2} E_s''(\omega)\Big|_{\lambda_{r_2}}} \tag{46}$$

We find that the data obey neither the equality (44) nor the inequality (45). The mean value over several frequencies of the expression on the left hand side of eq. (46) equals the mean value of the expression on the right within the experimental error. Essentially the same conclusion can be drawn[6] from Goldberg and Lianis's data[13] on a crosslinked SBR. The data for Estane X100 and the SBR are tabulated elsewhere[14]. We conclude that the superposition experiments of Goldberg and Lianis again favor model S over model L.

We point out that the failure of model L is not due to the particular form of the strain function, i.e. the n-measure of strain, which we have built into it. In the Appendix we consider a generalized liquid model constructed in terms of a general strain function $\Phi[\lambda(t)/\lambda(u)]$. From eq. (A 18) of the Appendix we obtain for superposed sinusoidal oscillations in the steady state

$$E_s'(\omega) = E(t)\phi(\lambda_r) + E'(\omega)/\lambda_r \tag{47}$$

and

$$E''_s(\omega) = E''(\omega)/\lambda_r \tag{48}$$

where

$$\phi(\lambda_r) = (2/3)\Phi'(\lambda_r) + (1/3)\lambda_r^{-3/2}\Phi'(\lambda_r^{-1/2}) - \lambda_r^{-1} \tag{49}$$

Thus, the generalized liquid model (model GL) also leads to the equality (44) and the inequality (45). For the case we have considered here, i.e. for small oscillations superposed on a finite stretch, the theory of Bernstein, Kearsley, and Zapas[15] also leads to eqs. (47) and (48), albeit with a different expression for $\phi(\lambda_r)$.

It follows from eqs. (47) and (48) or, more precisely, from (44) and (45) to which they lead, that liquid models in general cannot predict the results in superposition experiments in simple tension on both the uncrosslinked and crosslinked materials we have investigated here and in the previous publication[6]. We do not know at this time why models specifically developed for polymeric liquids fail when applied to uncrosslinked rubberlike materials. Most theories for polymer melts are also essentially liquid theories. We intend to examine the applicability of our model GL to polymer melts in a later publication. It is possible that our uncrosslinked SBR simply does not have enough liquidlike character at 23°C. Measurements at higher temperatures may allow us to decide this issue.

The Dependence of n on Experimental Variables

We have attempted to collect information on the strain parameter n for a number of different polymeric systems. This information is assembled in Table I. The five methods we used to obtain it are designated by capital letters in column four of the table. Method A represents n-values obtained from a least squares fit to near equilibrium stress-strain data. Method B is similar but is based on isochronal stress-strain relations. Method C refers to estimates obtained from the ratio of the Mooney-Rivlin constants, C_2/C_1, as explained below. Method D signifies n-values obtained from a least squares fit to isochronal $\sigma/(\lambda-\lambda^{-2})$ vs. $1/\lambda$ data crossplotted from constant strain rate experiments. Method E denotes n-values obtained from superposition tests using eq. (40). The entries in column 2 of the table indicate whether the material was crosslinked and whether one or more samples with differnt degrees of crosslinking were considered.

The constants C_1 and C_2 of the so-called Mooney-Rivlin equation

$$\sigma = 2(C_1 + C_2/\lambda)(\lambda-\lambda^{-2}) \tag{50}$$

have been obtained on many materials[27]. Our parameter n can be estimated from C_2/C_1. Figure 9 shows a plot of $\bar{\sigma}(n)/\bar{\sigma}(2)$, where

$$\bar{\sigma}(n) = (2G/n)(\lambda^n-\lambda^{-n/2}) \tag{51}$$

against λ^{-1}. Equation (51) is the equation of Blatz, Sharda, and Tschoegl (BST equation[4]). With n=2 Eq. (51) represents the stress-strain relation predicted by the Gaussian statistical theory of rubber elasticity. The open circles in Fig. 9 thus represent Mooney-Rivlin plots of a hypothetical material obeying the BST equation with n=1.64. From the slope and intercept of the straight lines representing the best fit to the circles one can calculate the corresponding constants C_1 and C_2. Figure 9 demonstrates the well known fact that these constants differ in tension and in compression, implying that the Mooney-Rivlin equation is not a constitutive equation. From a number of plots such as those shown in Fig. 9 we constructed the nomograms shown in Fig. 10. The ratio C_2/C_1 is much smaller in compression than in tension for a given value of n. This is a reflection of the common observation[28] that most rubberlike materials obey the statistical theory (n=2) more closely in compression than in tension.

We note that according to the BST equation Mooney-Rivlin plots should be linear within the normal experimental error in simple tension only in the range from about $\lambda^{-1} = 0.6$ to 0.9, depending on the value of n. In fact, the apparent linearity often extends down to lower values of λ^{-1} because the upswing reflecting the second term of the BST equation tends to compensate the downswing demanded by the first term alone.

Since C_1 and C_2 do not have the same value in simple tension and compression, they almost always give different values for the shear modulus $G=2(C_1+C_2)$. The nomogram presented in Fig. 11 in conjunction with that in Fig. 10 allows one to estimate G from C_1 and C_2.

The BST equation predicts a maximum in the Mooney-Rivlin plot at $\lambda^{-1}=1$ for n=2. If n<2, the maximum lies in the compression half, if n>2, it lies in the tension half of Fig. 9. At the origin we have

$$\left.\frac{d\sigma/(\lambda-\lambda^{-2})}{d\lambda^{-1}}\right|_{\lambda=1} = 0.5G(2-n) \tag{52}$$

Hence, n may be regarded as a measure of the derivation of the behavior of real materials from the predictions of the statistical theory. At very small values of λ the Mooney-Rivlin plot can show up these deviations with much greater sensitivity than a plot of either the stress or the true stress against the stretch ratio.

From the tabulation of n-values in Table I we infer that (1) n depends on temperature in crosslinked but not in uncrosslinked systems; (2) in uncrosslinked polymers n is usually smaller than in crosslinked ones and appears to show little variation with the nature of the polymer; (3) the value of n in uncrosslinked polymers is about 0.5; polyurethane is not really an exception because it is effectively crosslinked through domain formation; (4) in crosslinked systems n increases with the degree of crosslinking.

Since n can be related to C_2/C_1 through the nomogram presented in Fig. 9, certain inferences may be drawn concerning its dependence on variables which have been investigated in their relations to C_1 and C_2[27,29,30]. Thus, we expect that it would depend on the degree of swelling and on the nature of the swelling agent in the presence of specific interactions. We also expect it to depend on the nature of the crosslinking procedure, i.e. on the network topology. The latter effects include the presence or absence of a diluent and possible chain orientation during crosslinking.

We consider the Gaussian statistical theory an ideal limiting theory to which the behavior of real rubberlike materials may approach under certain conditions. Much further work is needed before these conditions can be clarified. However, we expect that n will approach 2 in swollen polymers as the degree of swelling increases[18,29] and that chain orientation and swelling during crosslinking may produce the same effect[29].

We conclude by remarking that one way to generate information to facilitate arriving at a molecular interpretation of n - if such an interpretation is possible - might be through observation of the role it plays in predicting the restoring force in crosslinked[10,31] and in uncrosslinked[10] rubberlike materials.

Appendix

We derive here a general equation for the response to a small (theoretically infinitesimal) deformation in simple tension superposed on a finite stretch. The equation is based on a model introduced elsewhere[3], which we have called generalized liquid model (model GL).

Model GL gives the principal components of the true stress as

$$\bar{\sigma}_\alpha(t) = -P - 2\int_{-\infty}^{t} G(t-u)\,\frac{d}{du}\left[\Phi\left(\frac{\lambda_\alpha(t)}{\lambda_\alpha(u)}\right)\right] du \tag{A1}$$

where α=1,2,3 denotes the principal directions, P is an arbitrary hydrostatic pressure, G(t) is the (small deformation) shear relaxation modulus, λ_α is the stretch ratio in the direction α, t is the present time, u is the past time, and Φ is a generalized strain function defined in such a way that

$$\Phi(1) \equiv 0 \tag{A2}$$

and

$$\Phi'(1) = \frac{d}{du}\left[\Phi\left(\frac{\lambda_\alpha(t)}{\lambda_\alpha(u)}\right)\right]\Bigg|_{\lambda_\alpha(t)/\lambda_\alpha(u) = 1} \equiv 1 \tag{A3}$$

Condition (A2) ensures that $\bar{\sigma}_\alpha(t) = -P$ in the absence of any deformation. Condition (A3) allows the liquid model to be applied to the behavior of materials possessing an equilibrium modulus by ensuring that the kernel function in eq. (A1) coincide with the accepted definition of the shear relaxation modulus.

Eliminating P, and considering that the material had been completely at rest before imposition of the finite stretch, Eq. (A1) becomes

$$\bar{\sigma}(t) = -\int_0^t G(t-u)\,\frac{d}{du}\left\{\Phi\left[\frac{\lambda(t)}{\lambda(u)}\right] - \Phi\left[\left[\frac{\lambda(t)}{\lambda(u)}\right]^{-1/2}\right]\right\} du \tag{A4}$$

in simple tension.

For the superposition, at time $t = t_r$, of a general tensile deformation on a finite step of strain with stretch ratio λ_r we have

$$\Phi\left[\frac{\lambda(t)}{\lambda(u)}\right] = \Phi\left[\lambda(t)\right] + \left\{\Phi\left[\frac{\lambda(t)}{\lambda_r}\right] - \Phi\left[\lambda(t)\right]\right\} h(u)$$
$$+ \left\{\Phi\left[\frac{\lambda(t)}{\lambda_s(u)}\right] - \Phi\left[\frac{\lambda(t)}{\lambda_r}\right]\right\} h(u-t_r) \tag{A5}$$

where λ_s is the stretch ratio after imposition of the superposed tensile deformation. Substitution of eq. (A5) into (A1) leads to

$$\bar{\sigma}(t) = -\,2G(t)\left\{\Phi\left[\frac{\lambda(t)}{\lambda_r}\right] - \Phi\left[\left[\frac{\lambda(t)}{\lambda_r}\right]^{-1/2}\right]\right.$$
$$\left. - \Phi\left[\lambda(t)\right] + \Phi\left[\left[\lambda(t)\right]^{-1/2}\right]\right\} \tag{A6}$$
$$-2\int_{t_r}^{t} G(t-u)\,\frac{d}{du}\left\{\Phi\left[\frac{\lambda(t)}{\lambda_s(u)}\right] - \Phi\left[\left[\frac{\lambda(t)}{\lambda_s(u)}\right]^{-1/2}\right]\right\} du$$

The true stress resulting from the superposed deformation alone becomes

$$\Delta\bar{\sigma}(t-t_r) = \bar{\sigma}(t) - \bar{\sigma}_r(t) \tag{A7}$$

where $\bar{\sigma}(t)$ is given by eq. (A6) and

$$\bar{\sigma}_r(t) = 2G(t)\left\{\Phi[\lambda_r] - \Phi[\lambda_r^{-1/2}]\right\} \tag{A8}$$

If the material is a liquid, i.e. has no equilibrium shear modulus, eq. (A7) reduces to

$$\Delta\bar{\sigma}(t-t_r) = -2\int_{t_r}^{t} G(t-u)\,\frac{d}{du}\left\{\Phi\left[\frac{\lambda(t)}{\lambda_s(u)}\right] - \Phi\left[\left[\frac{\lambda(t)}{\lambda_s(u)}\right]^{-1/2}\right]\right\} du \tag{A9}$$

as both t ant t_r approach infinity while $t-t_r$ remains finite because then $G(t) \to 0$. With the change of variables $t = t'+t_r$ and $u = u'+t_r$, i.e. shifting the reference point of the time scale from $t=0$ to $t=t_r$, we obtain

$$\bar{\sigma}(t') = -2\int_{0}^{t'} G(t'-u')\,\frac{d}{du'}\left\{\Phi\left[\frac{\lambda(t')}{\lambda_s(u')}\right] - \Phi\left[\left[\frac{\lambda(t')}{\lambda_s(u')}\right]^{-1/2}\right]\right\} du' \tag{A10}$$

where we define $\lambda(t')$ as $\lambda(t)/\lambda_r$ because the reference length has now become λ_r instead of unity. Equation (A10) has the same form as eq. (A4). This is a consequency of the fact that there is no preferred reference configuration for a liquid as pointed out by Coleman and Noll[2]. It is, of course, for this reason that we use the current deformation as the reference deformation for liquidlike behavior.

We now consider that the superposed deformation is small so that

$$\lambda_s(u) = \lambda_r + \varepsilon_s(u) \qquad \text{(A11)}$$

where $\varepsilon_s << (\lambda_r - 1)$. To substitute eq. (A11) into eq. (A7) we expand $\Phi[\lambda(t)/\lambda(u)]$ into a Taylor series around $\lambda(t)/\lambda(u) = 1$, keeping the first order term only. This is justified because $\lambda(t) = \lambda_r + \varepsilon_s(t)$ and so $\lambda(t)/\lambda_r$ is close to unity. Using eqs. (A2) and (A3) we obtain

$$\Phi[\lambda(t)/\lambda_r] \simeq \varepsilon_s(t)/\lambda_r \qquad \text{(A12)}$$

$$\Phi[[\lambda(t)/\lambda_r]^{-1/2}] \simeq -\varepsilon_s(t)/2\lambda_r \qquad \text{(A13)}$$

$$\Phi[\lambda(t)/\lambda_s(u)] \simeq [\varepsilon_s(t) - \varepsilon_s(u)]/\lambda_r \qquad \text{(A14)}$$

$$\Phi[[\lambda(t)/\lambda_s(u)]^{-1/2}] \simeq [\varepsilon_s(u) - \varepsilon_s(t)]/2\lambda_r \qquad \text{(A15)}$$

We also expand $\Phi[\lambda(t)]$ around λ_r to get

$$\Phi[\lambda(t)] = \Phi[\lambda_r] + \Phi'(\lambda_r)\varepsilon_s(t) \qquad \text{(A16)}$$

and

$$\Phi[[\lambda(t)]^{-1/2}] = \Phi[\lambda_r^{-1/2}] - 0.5\lambda^{-3/2}\Phi'[\lambda_r^{-1/2}]\varepsilon_s(t) \tag{A17}$$

Substituting eqs. (A12) through (A17) into eq. (A7) then yields

$$\begin{aligned}\Delta\bar{\sigma}(t-t_r) = {} & 2G(t)[\Phi'(\lambda_r) + 0.5\lambda_r^{-3/2}\Phi'(\lambda_r^{-1/2}) \\ & - 1.5\lambda_r^{-1}]\varepsilon_s(t) + 3\lambda_r^{-1}\int_{t_r}^{t} G(t-u)\,\frac{d\varepsilon_s(u)}{du}\,du\end{aligned} \tag{A18}$$

as the prediction of the generalized liquid model for the true stress arising from a superposed infinitesimal deformation.

Figure Captions

Figure 1 Engineering stress, $\sigma(t)$, as function of time t in logarithmic coordinates. Step response of uncrosslinked SBR at 23°C to strain at various stretch ratios.

Figure 2 Relaxation modulus master curve for uncrosslinked SBR at 23°C.

Figure 3 Engineering stress as function of stretch ratio at the isochronal time t_r=10 min. Uncrosslinked SBR at 23°C.

Figure 4 Engineering stress as function of stretch ratio. Response of uncrosslinked SBR at 23°C to ramp functions of strain at various rates of strain.

Figure 5 Engineering stress as function of stretch ratio. Response of uncrosslinked SBR at different temperatures to ramp functions of strain at various rates of strain.

Figure 6 Comparison of the predictions of the solid and the liquid models. $F_s(t-t_r)$ as function of the stretch ratio.

Figure 7 Engineering stress as function of stretch ratio at the isochronal time t_r=10 min. Uncrosslinked SBR at -17°C.

Figure 8 Response of polyisobutylene (PIB) to different experimental strain excitations as function of time. Data of Goldberg et al.[12].

Figure 9 Mooney stress as function of $1/\lambda$ predicted by BST theory with $n = 1.64$.

Figure 10 Nomogram for the estimation of n from C_2/C_1 in tension and in compression.

Figure 11 Nomogram for the estimation of $2(C_1+C_2)/G$ from n.

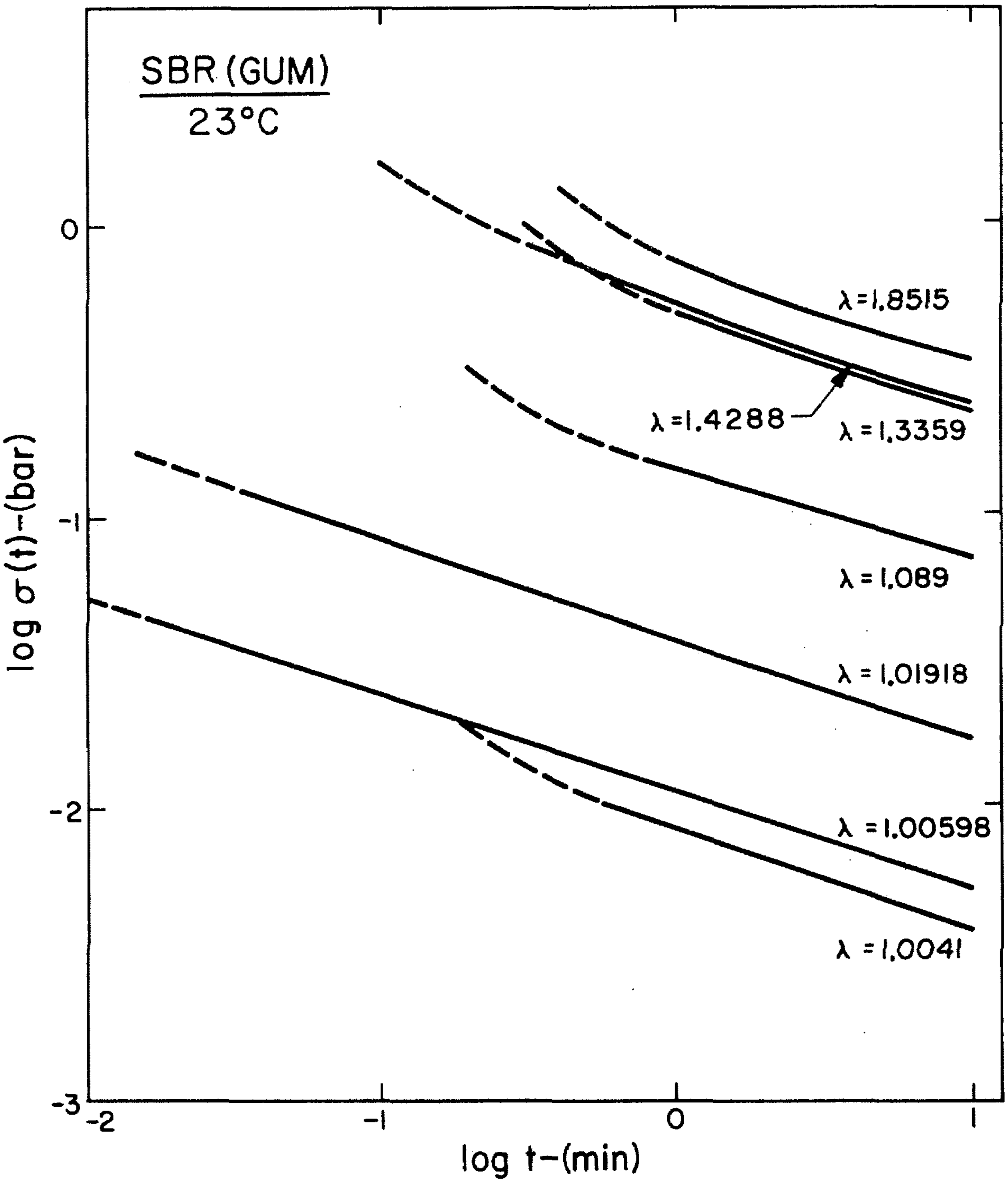

Figure 1 Engineering stress, σ(t), as function of time t in logarithmic coordinates. Step response of uncrosslinked SBR at 23°C to strain at various stretch ratios.

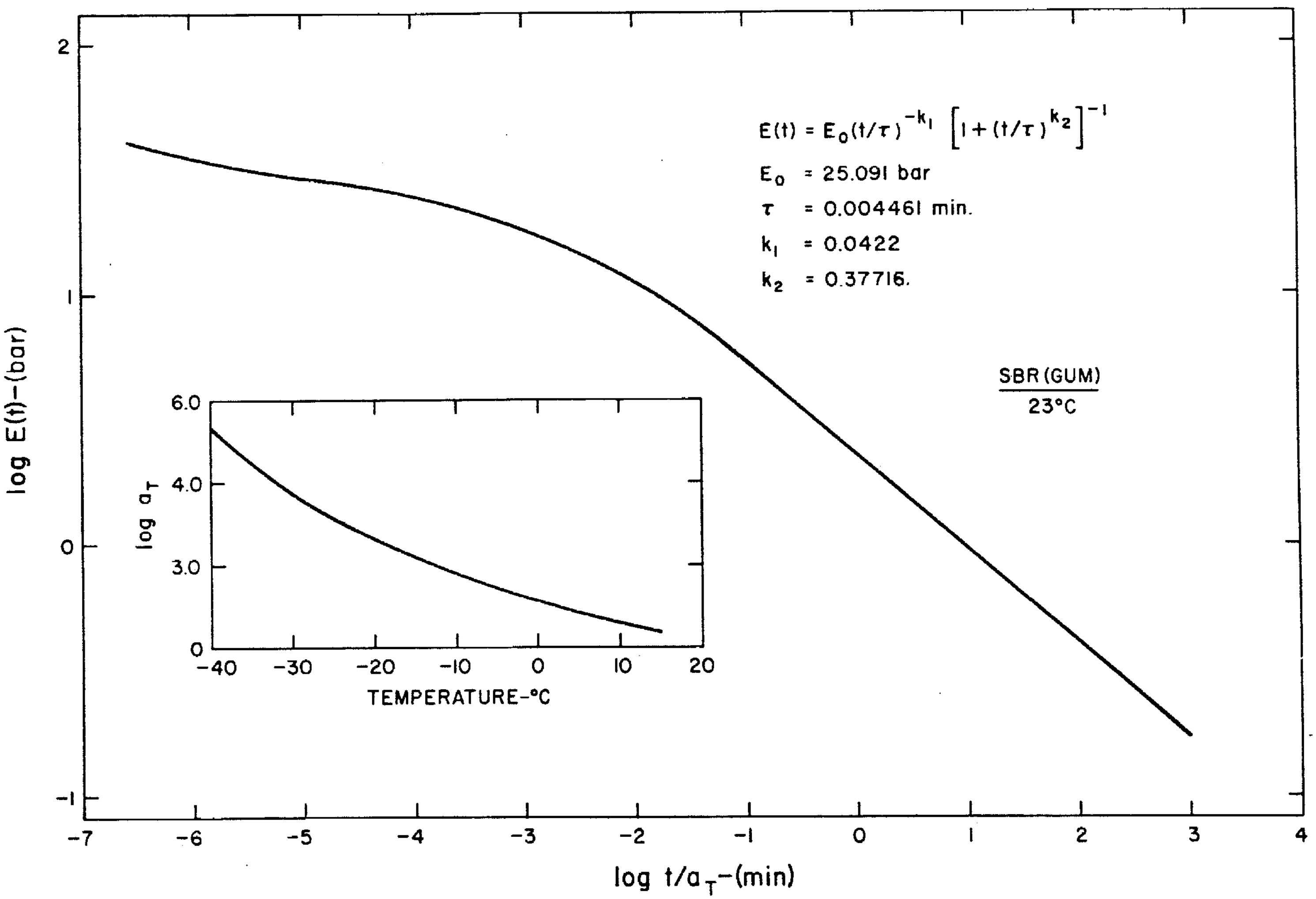

Figure 2 Relaxation modulus master curve for uncrosslinked SBR at 23°C.

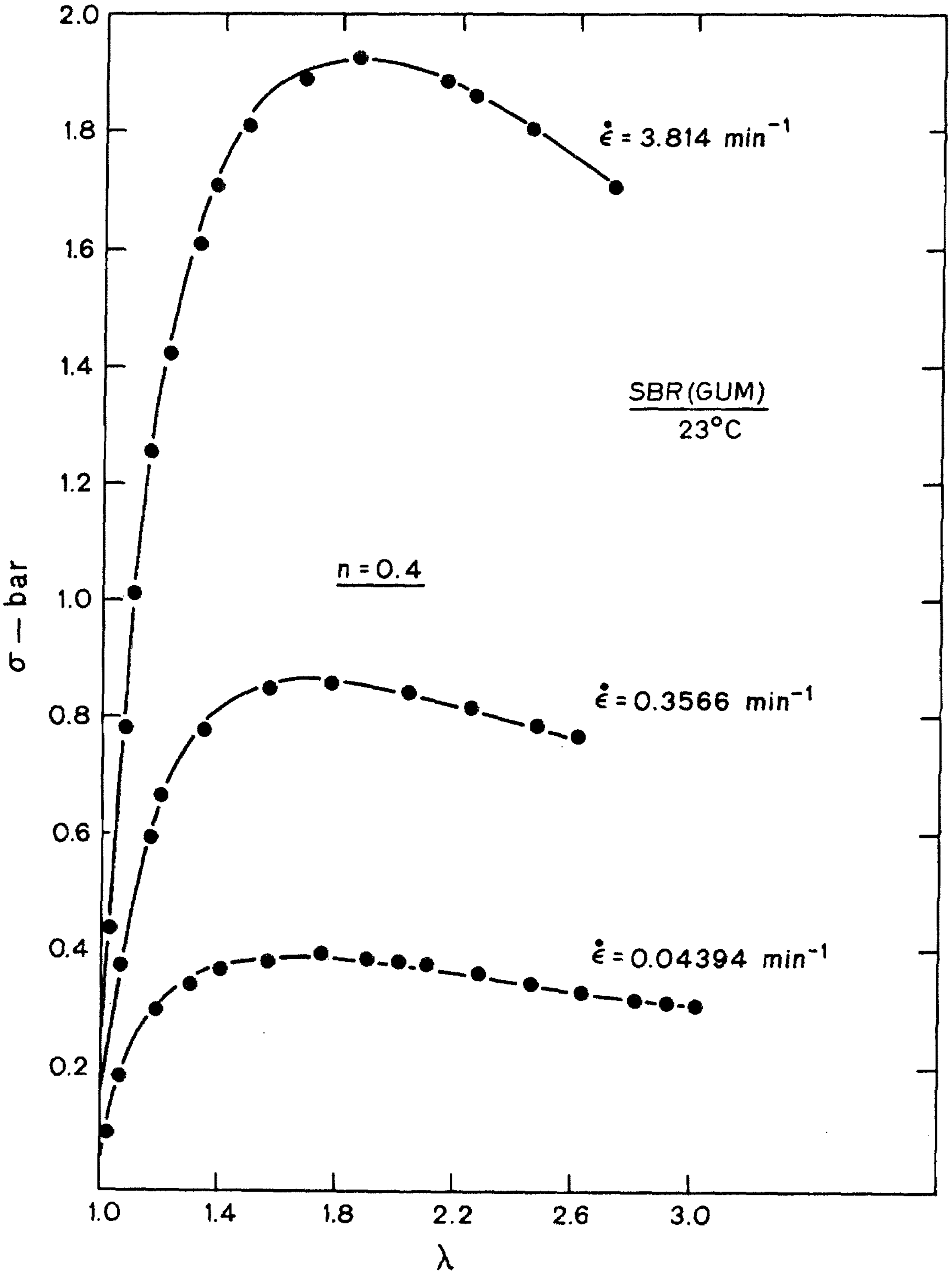

Figure 3 Engineering stress as function of stretch ratio at the isochronal time t_r=10 min. Uncrosslinked SBR at 23°C.

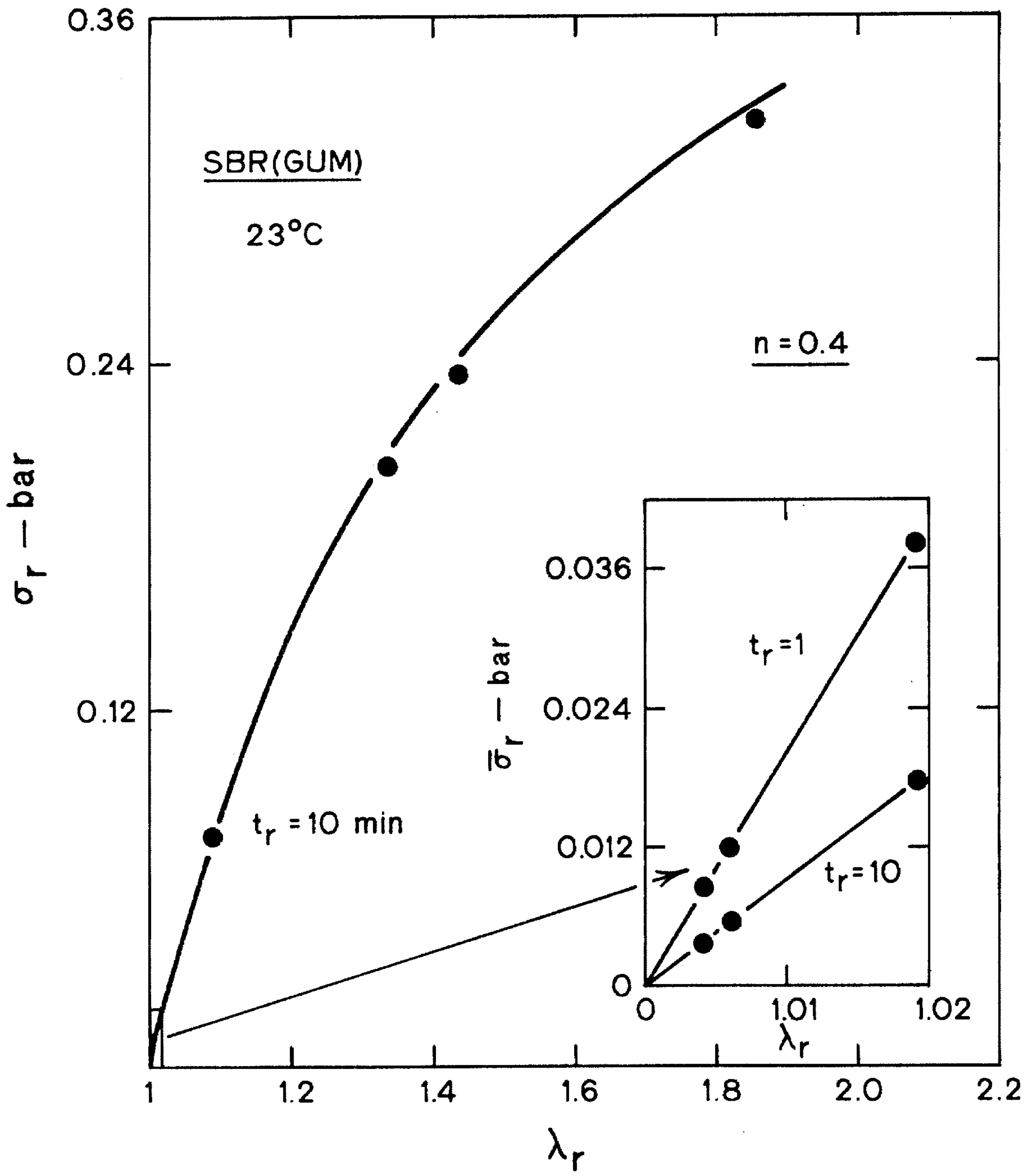

Figure 4 Engineering stress as function of stretch ratio. Response of uncrosslinked SBR at 23°C to ramp functions of strain at various rates of strain.

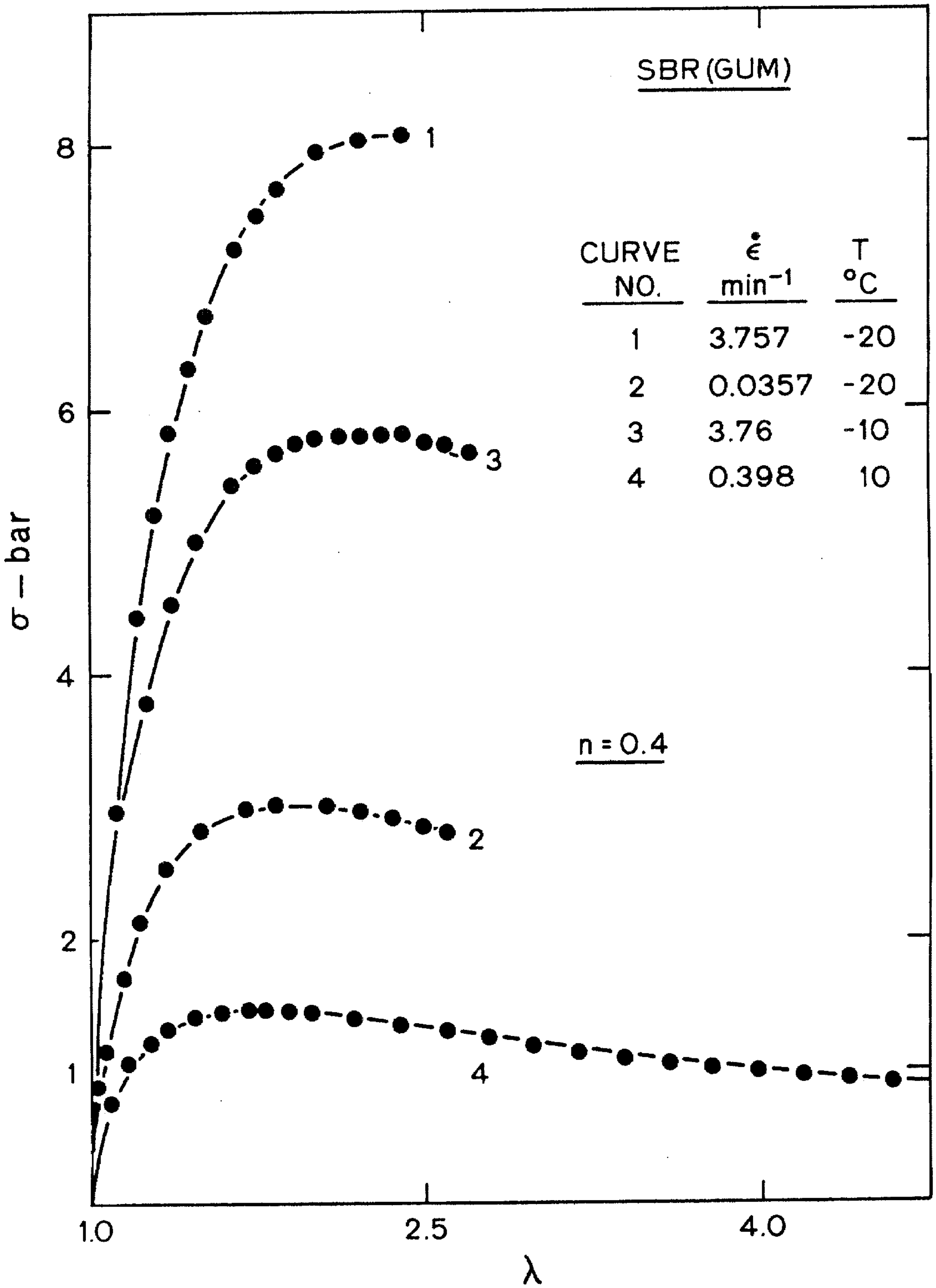

Figure 5 Engineering stress as function of stretch ratio. Response of uncrosslinked SBR at different temperatures to ramp functions of strain at various rates of strain.

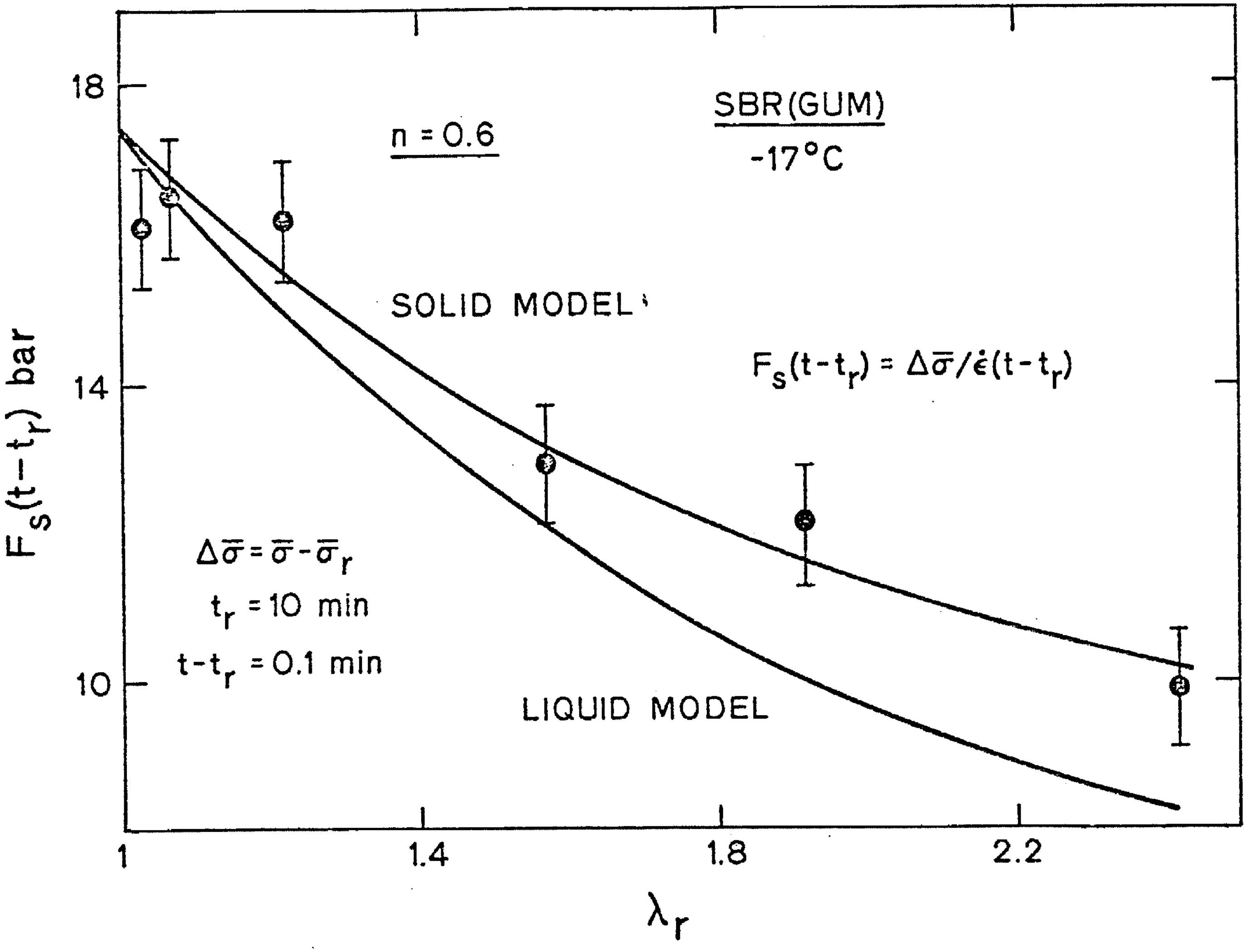

Figure 6 Comparison of the predictions of the solid and the liquid models. $F_s(t-t_r)$ as function of the stretch ratio.

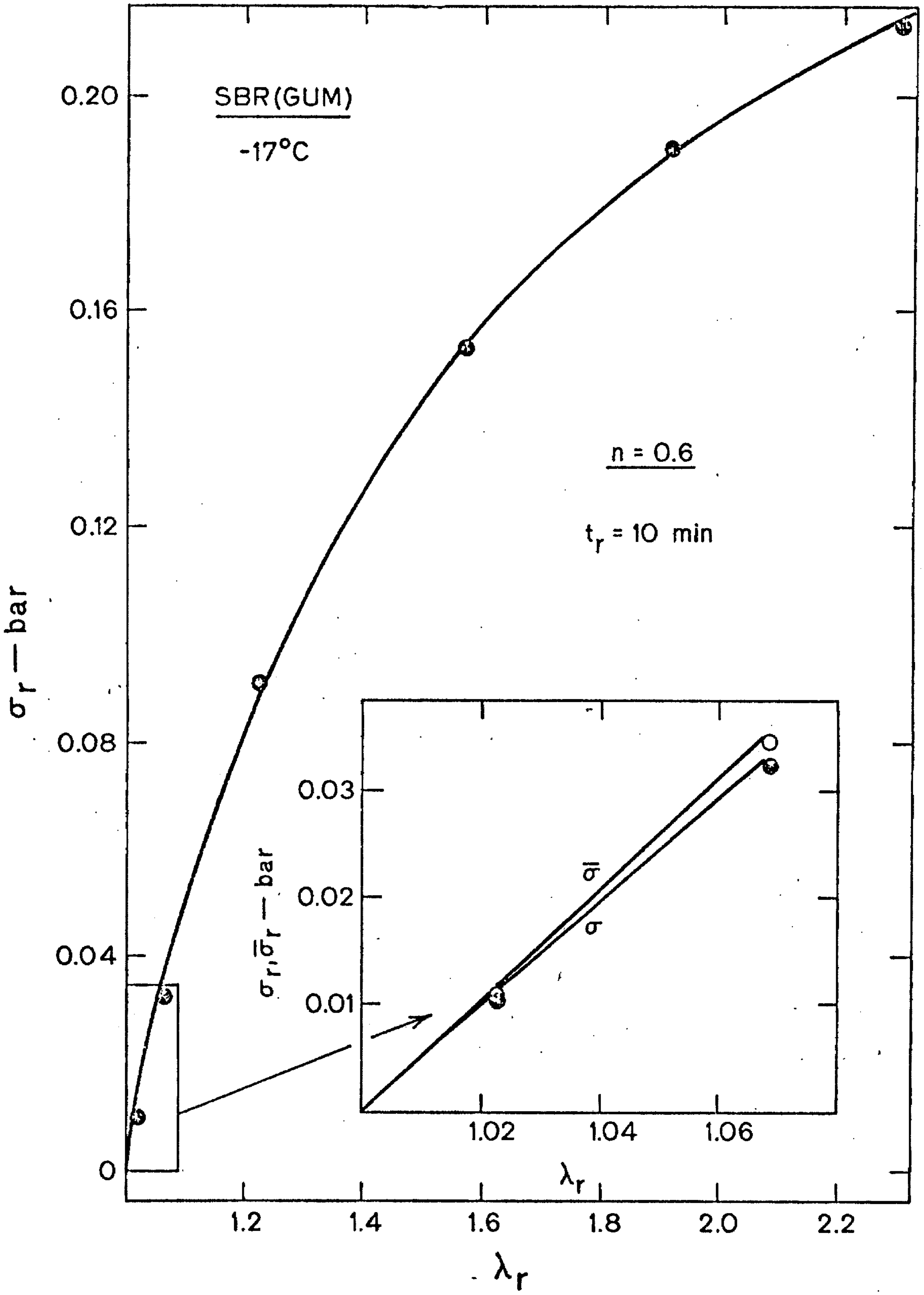

Figure 7 Engineering stress as function of stretch ratio at the isochronal time t_r=10 min. Uncrosslinked SBR at -17°C.

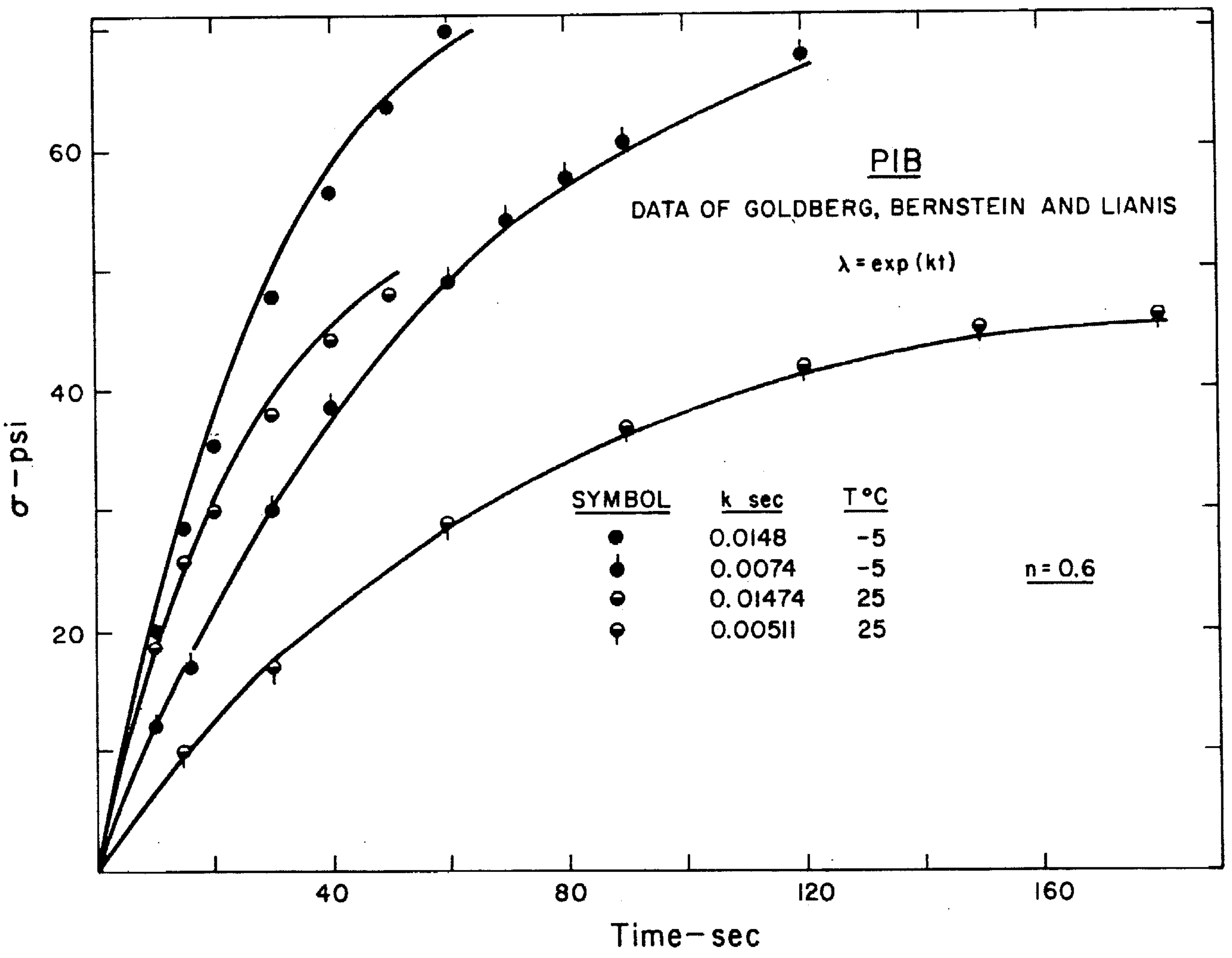

Figure 8 Response of polyisobutylene (PIB) to different experimental strain excitations as function of time. Data of Goldberg et al.[12]

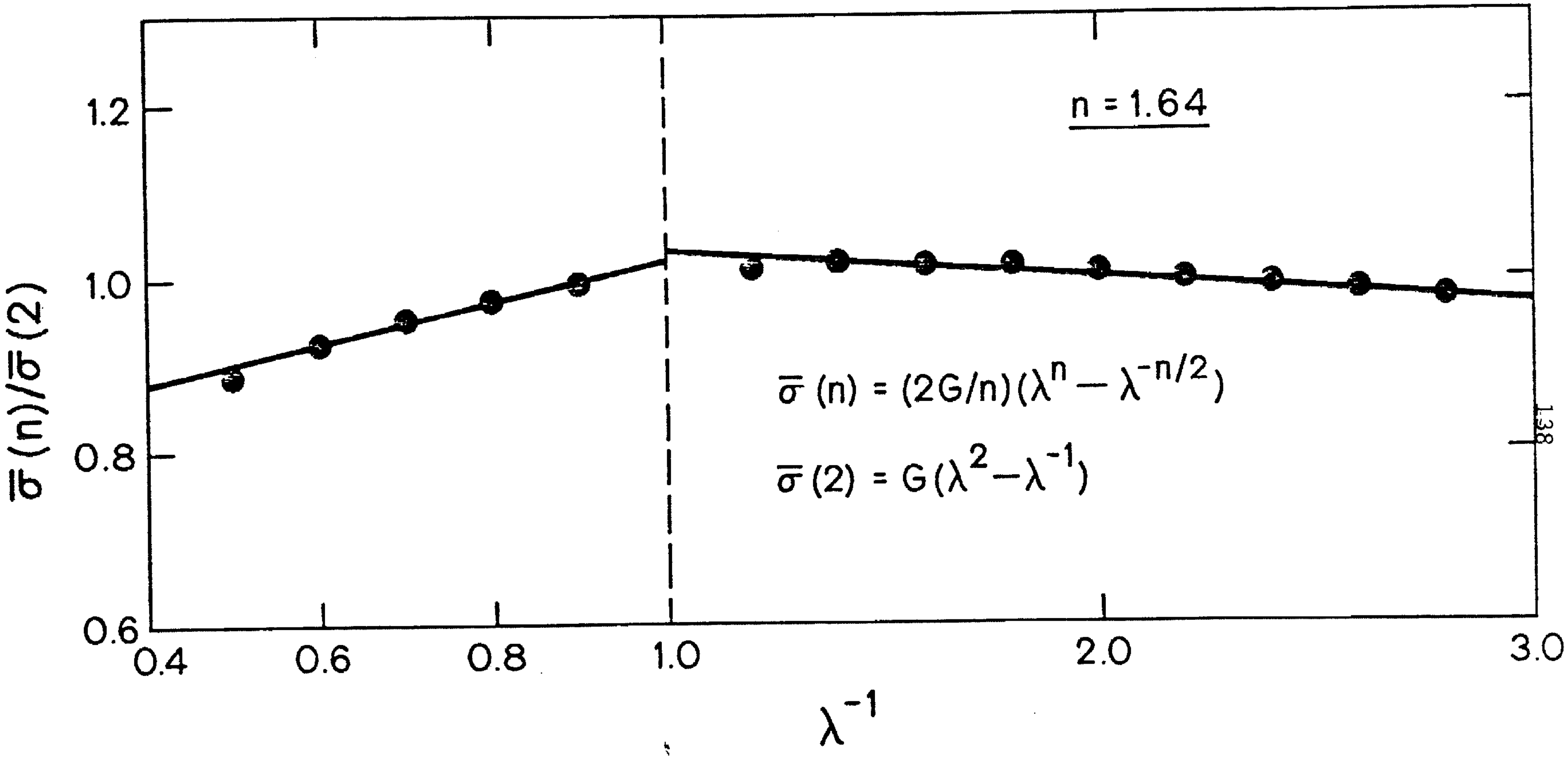

Figure 9 Mooney stress as function of 1/λ predicted by BST theory with n = 1.64.

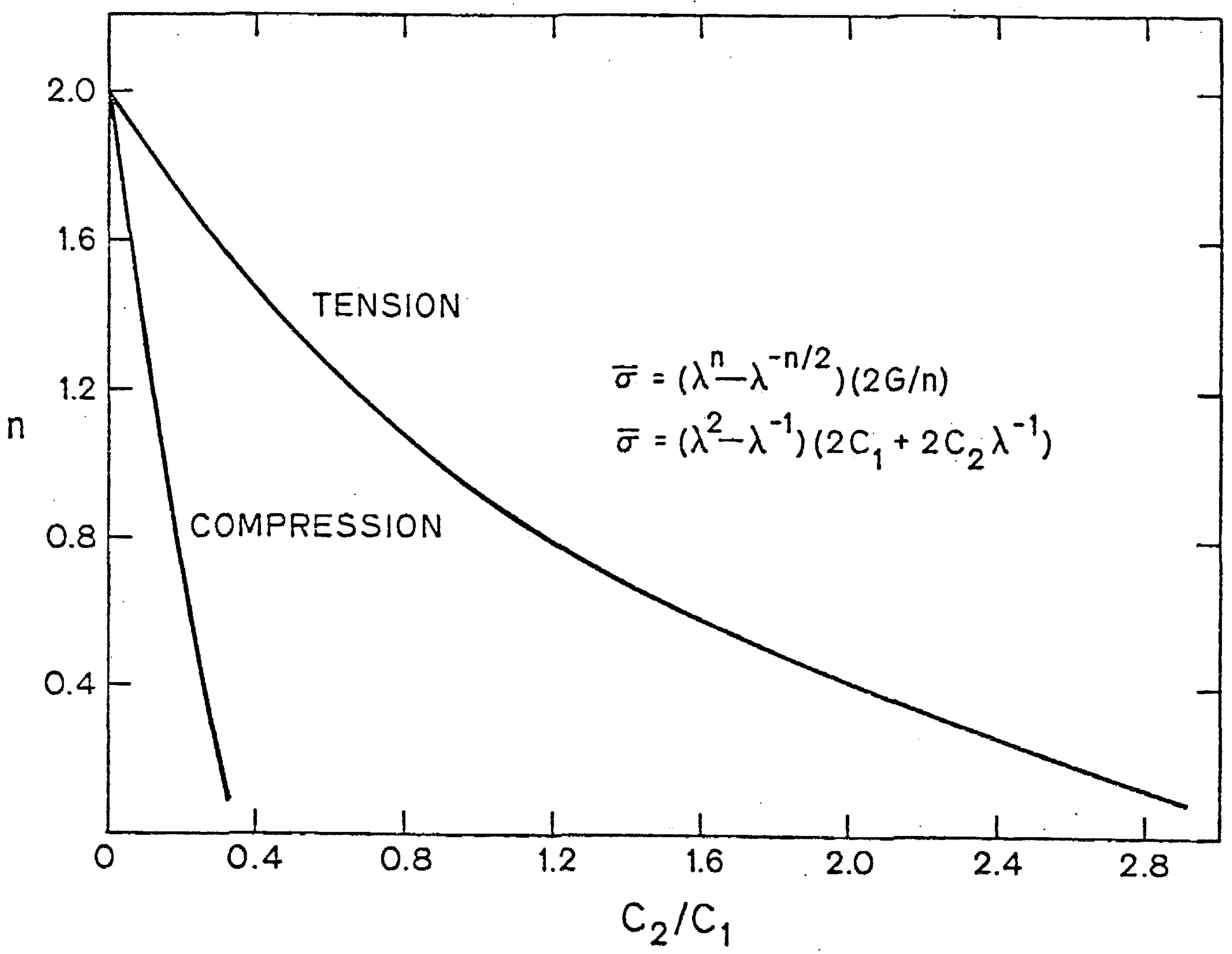

Figure 10 Nomogram for the estimation of n from C_2/C_1 in tension and in compression.

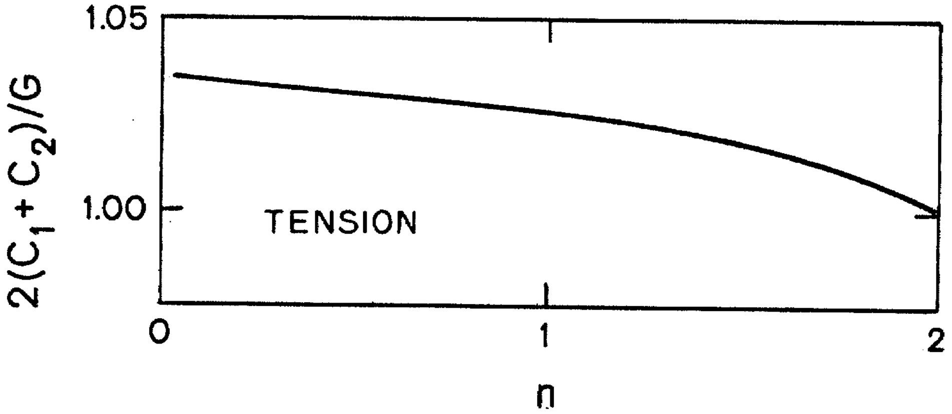

Figure 11 Nomogram for the estimation of $2(C_1+C_2)/G$ from n.

TABLE 1

The Parameter n for Various Polymers

Polymer	Crosslinked	T (°C)	n	Method	Ref.
Natural rubber	yes	10→70	1.64	A	16
	yes	25	1.64	A	17
	yes	0→60	1.64	A	4
	various	25	0.9→1.6	C	18
SBR	yes	25	1.34	A	19
	yes	-45→23	0.4→1.22	B,E	6
	yes	0	1.4	E	13
	yes	0	1.0	B	12
	various	26	1.0→1.5	C	20
	no	-20→23	0.6	B,E	This work
EPR (chlorinated)	yes	15	1.71	A	21
Polyethylene	yes	180	≃2.0	A	22
Polystyrene	yes	170	1.95	A	23
PIB (Vistanex B-140)	no	-50→25	0.5	B	15
PIB (Vistanex L-100)	no	25	0.5	B	24
	no	-5→25	0.6	B	12
Viton A-HV	two	-5→130	0.4→1.8	D	25
Butyl rubber	yes	-50	0.5	B	15
	yes	-20	1.71	D	26
	yes	-5	1.73	D	26
Polyurethane (Estane X-100)	no	-1	2.4	E	13

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Chapter IV

The Internal Energy Contribution to the Restoring Force in Viscoelastic Rubberlike Materials

I. Introduction

Elastomers can be stretched reversibly to remarkably high elongations because they consist of flexible crosslinked long chain molecules. The statistical theory of rubber elasticity[1-5] ascribes the restoring force in a deformed elastomer predominantly to the change in the configurational entropy of the chains which accompanies the deformation. Contributions from changes in internal energy are considered to play generally a subsidiary role. In natural rubber, the elastomer *par excellence*, internal energy changes contribute roughly one-fifth of the restoring force at elongations below about 200%. Experimentally, the magnitude of the internal energy contribution is commonly determined from measurements of the force-temperature coefficient. Such experiments are often referred to as thermoelastic studies because they assume that the elastomer under study behaves as a purely elastic body although elastomers, like all polymers, are viscoelastic. Thus, the measurements must be conducted at elastic equilibrium, i.e. in the completely relaxed state. In practice this situation can only be approached asymptotically.

Although the relaxation processes can be accelerated by increasing the temperature, this device is limited by the possibility of thermal degradation. Therefore, thermoelastic experiments are rarely, if ever, made under conditions in which all measurements can be considered to have been obtained sufficiently close to elastic equilibrium to render negligible the error resulting from residual viscoelastic relaxation. The magnitude of the error depends not only on the experimental conditions such as temperature, waiting period, stretch ratio, etc., but also on the nature of the elastomer. Thus, the error is small for natural rubber at 0°C but may not be so for another elastomer at the same temperature.

In a series of recent papers[6-10] we have presented a theory for the description of the viscoelastic behavior of rubberlike materials in moderately large deformations. This theory easily spans the range of deformations which are commonly employed in thermoelastic studies. It is based on the assumption that time shift invariance is preserved in moderate deformations of elastomers. In materials for which this assumption proves valid, the effects of strain and time are separable in the response to a step function of strain in simple tension, the most commonly used technique in thermoelastic measurements. In this paper we propose a method, based on this separability, which circumvents the difficulties inherent in attaining elastic near equilibrium by referring all measurements to a reduced isochronal time. We call isochronal time that time which refers the isothermal response of a polymer to the same state of relaxation. The concept of reduced isochronal time generalizes the (isothermal) isochronal time by applying to it the well known principle of time-temperature-pressure superposition. We have used isochronal time in several previous publications[8,9], in which we have denoted it by t_r. T.L. Smith[11,12] had earlier used a similar concept in reducing data obtained in ramp (constant rate of strain) experiments. We define the reduced isochronal time, t^*_r, by

$$t^*_r = t_r/a_{T,P} \tag{1}$$

where $a_{T,P}$ is the temperature and pressure function[13,14].

In the past, thermoelastic measurements were made only on crosslinked materials because of the impossibility of attaining elastic equilibrium in uncrosslinked polymers. The concept of reduced isochronal time removes this restriction. Hence, it becomes possible to examine changes in the internal energy contribution as a function of temperature as well as crosslink density. The concept of reduced isochronal time also permits extension of thermoelastic studies from the rubbery into the transition region as far as the theory allows. Examples are presented in this paper.

To illustrate the concepts introduced here we use Sharda and Tschoegl's strain energy density function for compressible materials[15,16] to represent the stress-strain relations of viscoelastic rubberlike materials at reduced isochronal time. The Sharda-Tschoegl function is an adaptation of the strain energy density function of Blatz, Sharda and Tschoegl[17] to compressible materials. Both functions are based on the concept that each material carries its own strain measure which, if properly chosen, will greatly simplify the form of the constitutive equation.

The strain measure was assumed to be independent of temperature by Blatz, Sharda, and Tschoegl[17]. However, our recent studies indicate[8,9] that the strain measure does depend on temperature although this dependence is relatively small in natural rubber. We show in this paper that a temperature dependent strain measure implies that the relative internal energy contribution to the total restoring force is not independent of the stretch ratio even at elongations below about 200%.

The prediction is in contradiction to the Gaussian statistical theory which implies that the internal energy is independent of the deformation. Careful examination of the literature data appears to support our view.

Simple tension is not the only, nor is it necessarily the most appropriate, mode of deformation for thermoelastic studies. Treloar[2] advocates the torsion-tension test. In simple tension our present theory is not applicable in the glassy region and in the upper transition region because it does not allow for volume relaxation. Such effects arising from volume dilatation in simple tension would be eliminated in shear[14,18], but the volume relaxation incident upon cooling a specimen to lower temperatures would still persist[18]. The closer the temperature is to the glass transition temperature, the more effects of volume relaxation will be.

Thermoelastic studies are undertaken to ascertain the range of conditions over which the molecular theories of the mechanical behavior of rubberlike materials is valid. The concepts which we present in this paper are intended to broaden the range of investigation with respect to time, temperature, and pressure.

II. Thermoelastic Theory

We now proceed to develop the required basic relations. From the thermodynamics of elastic deformation, we obtain for simple tension,

$$dU = TdS - PdV + fdL \tag{2}$$

and

$$dA = -SdT - PdV + fdL \tag{3}$$

where U is internal energy, T is the temperature, S is the entropy, P is the pressure, V is the volume, f is the tensile force, L is the length of the specimen, and A is the Helmholtz free energy.

From eq 1 we can derive[4]

$$\frac{f_u}{f} = \left.\frac{\partial U}{\partial L}\right|_{V,T} = 1 - \frac{T}{f}\left.\frac{\partial f}{\partial T}\right|_{V,L} \tag{4}$$

as the relative contribution to the force from the internal energy, U. Equation 4, being based solely on thermodynamics, is independent of any constitutive model.

A. Statistical Theory

In principle, eq 4 provides a criterion for checking the validity of the statistical theory of rubber elasticity. In its current form[19] this theory gives the restoring force in simple tension as

$$f = \nu kTA_o(\langle r\rangle^2{}_o/\langle r\rangle^2{}_f)(\lambda-\lambda^{-2}) \tag{5}$$

where ν is the number of effective chains in the network per unit undeformed volume, k is the Boltzmann constant, A_o is the undeformed cross-sectional area of the specimen, λ is the stretch ratio, $\langle r^2\rangle_o$ is the mean-square end-to-end distance of chains between crosslinks, and $\langle r^2\rangle_f$ is the same distance if the chains are freed of the constraint of the crosslinks. The temperature dependence of $\langle r^2\rangle_o$ is related to the thermal expansion of the sample but $\langle r^2 \rangle_f$ is characteristic of the chemical structure of the chains. From eq 2 one may derive[4]

$$\frac{f_u}{f} = T \frac{d\ln\langle r^2 \rangle_f}{dT} \tag{6}$$

which relates f_u to $\langle r^2 \rangle_f$. Equation 6 thus links thermoelastic studies to solution behavior and to the rotational isomeric state model of the behavior of chain molecules[5,20].

From eq 4 one may derive the equation of Flory, Ciferri, and Hoeve[21]

$$\frac{f_u}{f} = 1 - T \left.\frac{\partial \ln f}{\partial T}\right|_{P,L} - \frac{3\alpha_o T}{\lambda^3 - 1} \tag{7}$$

as well as the equation of Shen and Blatz[22]

$$\frac{f_u}{f} = 1 - T \frac{d\ln G}{dT} - \alpha_o T \tag{8}$$

where G is the shear modulus at atmospheric pressure, and α_o is the linear thermal expansion coefficient of the undeformed material. The last two equations allow determination of f_u/f at constant pressure by invoking the statistical theory as modified by Flory[19]. It can be shown that eq 7 is equivalent to eq 8. However, due to the presence of the term $(\lambda^3-1)^{-1}$ in eq 7, a small experimental error in the vicinity of $\lambda = 1$, which is experimentally unavoidable, will greatly affect the calculation of f_u/f. Eq 8 has the advantage of averaging out the experimental uncertainties over the whole region of strain before calculating the value of f_u/f. Equations 6 and 8 claim that f_u/f, i.e. the *relative* contribution of the internal energy to the restoring force, is independent of strain. This is a direct consequence of the assumption of the Gaussian statistical theory that the relative contribution by internal energy is to be accounted for by intrachain energy alone.

To prove the validity of the modified statistical theory, measurements based only on thermodynamic considerations and completely independent of structural models and constitutive equations are needed. Equation 4 is difficult to use experimentally because determination of the force-temperature coefficient at constant volume requires imposition of large hydrostatic pressures to counteract small changes in volume. Using the appropriate Maxwell relation[23], eq 4 can be recast as

$$\frac{f_u}{f} = 1 - T \left.\frac{\partial \ln f}{\partial T}\right|_{P,L} - T \frac{\beta_{P,L}}{\kappa_{T,L}} \left.\frac{\partial \ln f}{\partial P}\right|_{T,L} \qquad (9)$$

where

$$\beta_{P,L} = \frac{1}{V} \left.\frac{\partial V}{\partial T}\right|_{P,L} \qquad (10)$$

is the volumetric expansion coefficient at constant pressure and length, and

$$\kappa_{T,L} = -\frac{1}{V}\frac{\partial V}{\partial P}\bigg|_{T,L} \tag{11}$$

is the isothermal compressibility at constant length.

By determining the force-temperature coefficient, the force-pressure coefficient, the volumetric expansion coefficient and the isothermal compressibility at constant length, as required by eq 9 Allen et al.[24], and Sharda and Tschoegl[16] determined f_u/f for natural rubber at temperatures above 0°C.

Allen's data give values of f_u/f which are in good agreement with values obtained from thermoelastic data carried out at constant pressure and analyzed by eq 7. This agreement, and the fact that f_u/f does not show any significant dependence either on temperature or on strain, seems to give a satisfactory confirmation of the theory. Furthermore, the reported good agreement[4] among values of $d\ln\langle r^2\rangle_o dT$ obtained from thermoelastic measurements, those obtained from viscosity-temperature measurements on polymer solutions, and values calculated from the rotational isomeric state theory of chain configuration provides another indication of the essential success of the theory.

B. Phenomenological Theory

Sharda and Tschoegl[16] found good, but not complete, agreement between their data and the statistical theory. They introduced a strain energy density function[15] for compressible isotropic rubberlike materials and discussed their data in the light of a phenomenological theory based on this function. In this paper we propose a modification which takes into account the temperature dependence of the strain parameter n which, in their theory, characterizes the nonlinear stress-strain behavior.

Their strain energy density function has the form

$$W = J^{\gamma} \left\{\frac{2G}{n}\left[I_E - \frac{3(J^{n/3}-1)}{n}\right] + \frac{K}{k}\left[(J-1) + \frac{J^{1-k}-1}{k-1}\right]\right\} \tag{12}$$

where

$$I_E = \Sigma_{\alpha}\left(\lambda_{\alpha}^{n} - 1\right)/n \qquad \alpha=1,2,3 \tag{13}$$

and

$$J = V/V_o = \Pi_{\alpha}\lambda_{\alpha} \tag{14}$$

In eqs 12, 13, and 14, V and V_o are the deformed and undeformed volume, respectively, at the test temperature; V_o is taken to be at atmospheric pressure; n is the parameter of the generalized strain measure which characterizes[17] the stress-strain relation under moderately large deformations; the parameter γ, first introduced by Tobolsky and Shen[25,26], takes into account the dependence of the shear modulus on volume according to

$$G(J) = GJ^{\gamma} \tag{15}$$

where $G = G(1)$; K is the bulk modulus at atmospheric pressure defined by

$$K(P) = K + kP \tag{16}$$

where P is the gage pressure.

In eqs 13 and 14 the stretch ratio is given by

$$\lambda_\alpha = L_\alpha(T)/L_{\alpha o}(T) \tag{17}$$

where L_α and $L_{\alpha o}$ are the deformed and undeformed length of the specimen in the principal direction α, respectively, at the test temperature, T, and $L_{\alpha o}$ is at atmospheric pressure. The parameters n, γ, G, K, and k are independent of stress by definition, and hence are independent of hydrostatic pressure also.

By the application of the principle of virtual work, we have

$$\bar{\sigma}_\alpha = \frac{\lambda_\alpha}{J}\frac{\partial W}{\partial \lambda_\alpha} \tag{18}$$

where $\bar{\sigma}_\alpha$ is the true stress in the principal direction α. For the special case of simple tension and superimposed hydrostatic pressure, we have $\bar{\sigma}_1 = \bar{\sigma} - P$, $\bar{\sigma}_2 = \bar{\sigma}_3 = P$, and $\lambda_1 = \lambda$, $\lambda_2 = \lambda_3 = \sqrt{J/\lambda}$. Substituting these into eqs (12) and (18) yields

$$\bar{\sigma} = (2G/n)J^{\gamma-1}(\lambda^n - J^{n/2}/\lambda^{n/2}) = f\lambda/A_oJ \tag{19}$$

where f is the force and A_o is the cross-sectional area at test temperature T, at zero force, and at atmospheric pressure.

Equation 19 can be written as

$$f = A_o(T,P_o)E(T)J^{\gamma}\Psi[\lambda,n(T)] \tag{20}$$

where

$$\Psi[\lambda,n(T)] = (2/3n)(\lambda^n - J^{n/2}/\lambda^{n/2})/\lambda \tag{21}$$

We have assumed that E(T) = 3G(T) since the bulk modulus of a soft polymer is usually about four decades higher than its shear modulus. The function Ψ depends on temperature and crosslink density through the parameter n. The effect of pressure on the restoring force appears through its effect on J and λ at constant temperature. The parameter γ may also depend on temperature and crosslink density.

We now seek an expression for $(\partial \ln f/\partial T)_{V,L}$. Taking logarithms, eq 20 can be rewritten as

$$\begin{aligned} \ln f = {} & \ln(2/3n) + \ln E(T) + \ln A_o(T,P_o) + \gamma \ln J \\ & + \ln(\lambda^{3n/2} - J^{n/2}) - (n/2 + 1)\ln\lambda \end{aligned} \tag{22}$$

From the definitions of G, γ, and n we have

$$\left.\frac{\partial \ln G}{\partial T}\right|_{V,L} = \frac{d\ln G}{dT}$$

$$\left.\frac{\partial \gamma}{\partial T}\right|_{V,L} = \frac{d\gamma}{dT} = 0 \qquad (23)$$

$$\left.\frac{\partial n}{\partial T}\right|_{V,L} = \frac{dn}{dT}$$

where d/dT is the total differential. The assumption that $d\gamma/dT = 0$ is based on literature data[5]. Using eq 17

$$\left.\frac{\partial \ln\lambda}{\partial T}\right|_{V,L} = -\frac{1}{L_o(T)}\frac{dL_o(T)}{dT} \qquad (24)$$

because of the requirement of constant L(T). Equation 24 can be recast as

$$\left.\frac{\partial \ln\lambda}{\partial T}\right|_{V,L} = \frac{1}{L_o(T)}\left.\frac{\partial L_o(T)}{\partial T}\right|_{P} = -\alpha_o(T) \qquad (25)$$

since L_o is independent of pressure by our definition. The thermal expansion coefficient of the undeformed length is given by

$$\alpha_o = \beta_o/3 \qquad (26)$$

where β_o is the expansion coefficient of the undeformed (unstressed) volume. Further

$$\left.\frac{\partial \ln A_o}{\partial T}\right|_{V,L} = \frac{1}{A_o(T)} \left.\frac{\partial A_o(T)}{\partial T}\right|_{P} = 2\alpha_o(T) \qquad (27)$$

and

$$\left.\frac{\partial \ln J}{\partial T}\right|_{V,L} = - \frac{1}{V_o(T)} \left.\frac{\partial V_o(T)}{\partial T}\right| = - 3\alpha_o(T) \qquad (28)$$

$$\frac{\partial \ell n(\lambda^{3n/2}-J^{n/2})}{\partial T}_{V,L} =$$

$$\frac{1}{(\lambda^{3n/2}-J^{n/2})}\left[\frac{3n}{2}\lambda^{(3n-2)/2} \left.\frac{\partial \lambda}{\partial T}\right|_{V,L} - \frac{n}{2}\, J^{(n-2)/2} \left.\frac{\partial J}{\partial T}\right|_{V,L}\right] \qquad (29)$$

$$+ 0.5(3\lambda^{3n/2}\ell n\lambda - J^{n/2}\ell nJ) \left.\frac{\partial n}{\partial T}\right|_{V,L}$$

By substituting eqs 23, 25, 27, 28 and 29 into the derivative of 22 we obtain

$$\left.\frac{\partial \ell nf}{\partial T}\right|_{V,L} = \frac{d\ell nG}{dT} + \alpha_o(3-3\gamma-n) + \hat{q}(n,\lambda,J)\,\frac{dn}{dT} \qquad (30)$$

where

$$\hat{q}(n,\lambda,J) = \frac{1.5\lambda^{3n/2}\ell n\lambda - 0.5J^{n/2}\ell nJ}{\lambda^{3n/2}-J^{n/2}} - \frac{1}{n} - \frac{\ell n\lambda}{2} \qquad (31)$$

At atmospheric pressure J ≃ 1 and, therefore,

$$\hat{q}(n,\lambda,1) = \frac{1.5\lambda^{3n/2}\ell n\lambda}{\lambda^{3n/2}-1} - \frac{1}{n} - \frac{\ell n\lambda}{2} = q(n,\lambda) \tag{32}$$

The function $q(n,\lambda)$ is displayed in Figure 1 for $n=2, 1.64, 1.22$, and 0.4. We notice that

$$\lim_{\lambda\to 1} q(n,\lambda) = 0 \tag{33}$$

Substituting eq 30 into eq 4 we have

$$\frac{f_u}{f} = 1 - T\,\frac{d\ell nG}{dT} - \alpha_o T(3-n-3\gamma) - T\frac{dn}{dT}\,\hat{q}(n,\lambda,J) \tag{34}$$

We note that G must be determined strictly in accordance with the chosen definition of L_o as discussed in the Appendix. Failure to do so can lead to appreciable error in dG/dT. The same comment applies to eq 8 also. Equation 34 agrees with the corresponding equation of Sharda and Tschoegl[16] except for the last term on the right which arises because of the temperature dependence[8,9] of n. Sharda and Tschoegl had considered this to be zero. As will be shown later, this is a good assumption for natural rubber, the material with which they were concerned.

We now turn to the determination of the parameter γ. The procedure proposed by Sharda and Tschoegl[15,16] is based on the determination of the force-pressure coefficient $(\partial f/\partial P)_{T,L}$. Because n, G, γ, L_o, A_o, V_o are independent of pressure and so is λ at constant temperature and length, Sharda and Tschoegl derive

$$\left.\frac{\partial \ln f}{\partial P}\right|_{T,L} = \kappa_{T,L} \left[\frac{(n/2)J^{n/2}}{\lambda^{3n/2}-J^{n/2}} - \gamma\right] \qquad (35)$$

Another method is suggested further on (eq 41).

One of our aims in presenting this paper is to call attention to the temperature dependence of n. This dependence leads to the prediction that f_u/f depends on the degree of deformation, as indicated by eq 34. In contrast to our prediction, most current theories, such as the Gaussian statistical theory, the Shen-Blatz theory[22], etc., conclude that f_u/f is independent of deformation. Furthermore, it is also considered to be independent of the crosslink density. There is experimental evidence, however, that f_u/f may depend both on the stretch ratio[26-34] and on the degree of crosslinking[30]. The former discrepancy may be explained partly by recognizing that measurements at low values of λ are relatively unreliable because of difficulties in measuring the initial length[5,22]; however, other literature data[28-34] seem to indicate a clear dependence on λ even when the deformations are moderately large.

The work of Sharda and Tschoegl[16] had shown that the statistical theory needs modification in two respects: it is necessary to take into account the volume (pressure) dependence of the shear modulus, and it is necessary to modify the dependence of the force on the stretch ratio. The particular modifications used by Sharda and Tschoegl are not unique but simple and appear to be adequate.

III. Viscoelastic Theory

We now extend our thermoelastic treatment to viscoelastic materials.

To this end we make use of the concept of the separability of strain and time effects in the response to a step function of strain[6-9]. At the test temperature and pressure the restoring force in a material of crosslink density ν (which may be zero) can be written

$$f(t_r,\lambda_r,T,P;\nu) = A_o(T,P_o)\hat{E}(t_r,T,P;\nu)\psi(\lambda_r,T) \tag{36}$$

where $\hat{E}$ is the uniaxial relaxation modulus, ψ is a suitably formulated strain function which vanishes as $\lambda \to 1$, and $A_o(T,P_o)$ is the area measured at atmospheric pressure and at the test temperature T as required by our definition of the reference state in eq. 17.

A step function of strain requires an infinitely fast pulling rate during the imposition of the strain. In practice, it is approximated by a fast but finite pulling rate. Therefore, the true response to a step function of strain is achieved only after the initial ramp transients have died out. According to eq 36, curves of the responses to different strains as functions of time in logarithmic coordinates are parallel to each other. A typical example is shown in Fig. 2 which displays data on an uncrosslinked SBR at 23°C and at atmospheric pressure[9]. The engineering stress, σ, in Figure 2 is defined as f/A_o.

From Figure 2 we may take an isochronal cut at t_r and crossplot the engineering stress vs. λ_r as illustrated in Figure 3. From this crossplot we can separate the uniaxial relaxation modulus $\hat{E}(t_r,T,P;\nu)$ from $\psi(\lambda_r,T)$. For the class of materials we are now considering we may use the Sharda-Tschoegl potential function. Thus

$$\psi(\lambda_r,T) = \Psi[\lambda_r,n(T)] \tag{37}$$

When the experiments are conducted at atmospheric pressure, $J\simeq1$. The parameter n and $\hat{E}(t_r,T,P;\nu)$ can then be determined by nonlinear least squares fitting of data such as those displayed in Figure 3.

One may then conduct similar experiments at different temperatures, keeping the pressure constant. Therefore, n can be determined as a function of temperature. Simultaneously, one obtains segments of $\hat{E}(t_r,T;P_o,\nu)$ at various temperatures. In the next step one determines the relaxation modulus master curve at the reference temperature T_o and the pressure P_o. The horizontal shift factor a_T and the vertical shift factor $p(T;T_o)$ can be obtained from the $\hat{E}(t_r,T;P_o,\nu)$ segments by the standard procedure used for thermorheological simple materials[13,35]. We call $E(t_r^*;T_o,P_o,\nu)$ the master curve. It is defined by

$$\hat{E}(t_r,T;P_o,\nu) = p(T;T_o)E(t_r^*,a_T;T_o,P_o,\nu) \tag{38}$$

We then perform similar experiments at constant temperature but at various pressures and determine the horizontal shift factor a_P and the vertical shift factor $p(P;P_o)$. For piezorheologically[14] simple materials one must obtain the same master curve as that defined by eq 38. Thus we have

$$\hat{E}(t_r,P;T_o,\nu) = \tilde{p}(P;P_o)E(t_r^*,a_P;T_o,P_o,\nu) \tag{39}$$

Considering that both the constant temperature and the constant pressure experiments should yield the same master curve, and invoking[14] the free volume theory, allows us to combine eqs 38 and 39 to give

$$\hat{E}(t_r,T,P;\nu) = p(T;T_o)\tilde{p}(P;P_o)E(t_r^*,a_{T,P};T_o,P_o,\nu) \tag{40}$$

Obviously, this procedure of determining $a_{T,P}$, p and $\tilde{p}$ is to some extent arbitrary because of uncertainities in the experimental data. The precision of the procedure can be improved by conducting both constant temperature and constant pressure experiments[14].

It follows from eq 15 that

$$\tilde{p}(P;P_o) = G(J)/G(1) = J^\gamma \tag{41}$$

But $J \simeq 1+3\Delta L/L_o$. Hence, J can be obtained by monitoring the length for which the force is zero at various pressures, and γ can be obtained from experimental determinations of $\tilde{p}(P;P_o)$. Equation 41 is valid in shear. However, in the rubbery state, G = E/3 with excellent approximation. The volume ratio determined by the above procedure is not at constant reduced time t_r^*. However, the rate of volume relaxation is very fast in the materials we are interested in. Thus the error may be deemed negligible. By combining eq 36, 40 and 41 we obtain

$$f(t_r,\lambda_r,T,P;\nu) = A_o(T,P_o)E(t_r^*,a_{T,P};T_o,P_o,\nu)p(T;T_o)J^\gamma\Psi(\lambda_r,T) \tag{42}$$

According to eq 42 the dependence of the force on t_r for given T and P becomes a dependence on t_r^* referred to T_o and P_o. Hence, eq 42 expresses the fact that f_u/f is independent of time at the reduced isochronal time t_r^*. Equation 4 can thus be restated as

$$\left.\frac{f_u}{f}\right|_{t_r^*} = 1 - T \left.\frac{\partial \ell nf}{\partial T}\right|_{V,L,t_r^*} \tag{43}$$

The changes in force with temperature must be measured at constant volume and length, and at the same reduced time. As mentioned earlier, the constant volume condition is extremely difficult to meet. Hence, we have to use an equation similar to eq 9 to determine the relative internal energy contribution to the restoring force at constant reduced time experimentally. The equation has the form

$$\left.\frac{f_u}{f}\right|_{t_r^*} = 1 - T \left.\frac{\partial \ln f}{\partial T}\right|_{P,L,t_r^*} - T \frac{\beta_{P,L,t_r^*}}{\kappa_{T,L,t_r^*}} \left.\frac{\partial \ln f}{\partial P}\right|_{T,L,t_r^*} \tag{44}$$

where now the volumetric expansion coefficient and the isothermal compressibility are also measured at the reduced isochronal time t_r^*. To use eq 44 we thus require experimental values of $(\partial \ln f/\partial T)_{P,L,t_r^*}$, $(\partial \ln f/\partial P)_{T,L,t_r^*}$, and β_{P,L,t_r^*} and κ_{T,L,t_r^*}.

The determination of $\partial \ln f/\partial T$ and $\partial \ln f/\partial P$ is similar to that of the vertical shifts $p(T;T_o)$ and $\tilde{p}(P;P_o)$. The only difference is that for these partial derivatives we do not compare moduli but forces at constant length L. We can measure β and κ by monitoring the lateral dimensions, or the volume, in the experiments in which $\partial \ln f/\partial T$ and $\partial \ln f/\partial P$ are determined. Simultaneously, we also obtain the information necessary for the determination[15] of γ by the use of the reduced time form of eq 35. This can be used to check the accuracy of the determination of γ by eq 41.

Substituting eqs 37 and 42 into eq 43, we obtain

$$\left.\frac{f_u}{f}\right|_{t_r^*} = 1 - \frac{d\ln p(T;T_o)}{d\ln T} - \alpha_o T(3-n-3\gamma) - q(n,\lambda)T\,\frac{dn}{dT} \tag{45}$$

where α_o is thermal expansion coefficient at constant reduced isochronal time t_r^*. In theory this can be determined from

$$\alpha_o = \lim_{L\to L_o} \beta_{P_o,L,t_r^*} \tag{46}$$

We note that in the soft rubbery region β_{P,L,t_r^*} and κ_{T,L,t_r^*} will be nearly independent of t_r^*. This considerably simplifies their determination.

The values of $(f/f_u)_{t_r^*}$ predicted by eq 45 can be checked by comparison with the experimental values obtained from eq 44.

In thermoelastic measurements assuming near elastic equilibrium the force-temperature coefficient can be determined along any of several paths. The customary path is to change the temperature at several fixed lengths and to measure the resulting (equilibrium) force. If near elastic equilibrium is not attained, the requirement that one must work at constant reduced isochronal time, t_r^*, limits the choice of paths. The path usually followed in thermoelastic measurements is not convenient because of difficulties in defining the temperature history of the specimen and, hence, t_r^*. The procedure outlined in this section automatically leads to data at constant t_r^*.

Finally, we must consider the effect of crosslink density on the internal energy contribution. The statistical theory of rubber elasticity gives

$$G = \nu kT \langle r^2\rangle_o/\langle r^2\rangle_f = E_e/3 \tag{47}$$

where ν is deemed to be independent of temperature at constant volume. Both $\langle r^2\rangle_o$ and $\langle r^2\rangle_f$, however, are temperature dependent. For convenience, eq 47 can be generalized to

$$E_e = 3\zeta k\Theta(T;\zeta) \tag{48}$$

where ζ is a temperature independent parameter, and $\theta(T;\zeta)$ is an unspecified function of temperature. Equation 48 would also account, e.g., for a possible temperature dependence of temporary entanglements[13]. Substituting this into eq 45 we obtain

$$\frac{f_u}{f}\bigg|_{t^*_{r,\zeta}} = 1 - \frac{d\ln\Theta(T;\zeta)}{d\ln T} - \alpha_o T(3-n-3\gamma) - q(n,\lambda)\; T\frac{\partial n}{\partial T}\bigg|_\zeta \tag{49}$$

Equation 49 implies that the effect of changes in crosslink density will only manifest itself through changes in $d\Theta(T;\zeta)/dT$ and through possible changes in α_o, γ, n, and $\partial n/\partial T$.

IV. Discussion

We now proceed to consider published data on f_u/f in the light of the theory developed in the preceeding sections.

A. Natural Rubber (NR)

We begin with a discussion of NR data. It is known (see, e.g., reference 36) that the stress-strain relations predicted by the statistical theory are not well obeyed by NR. It is claimed[4], however that the behavior of this material closely conforms to the predictions of the statistical theory with respect to f_u/f. This claim is based primarily on the alleged independence, demanded by the theory, of f_u/f on the stretch ratio, swelling ratio, and crosslink density. We discuss these in turn.

Stretch Ratio. We consider primarily the data of Allen et al.[24] and those of Sharda and Tschoegl[16]. These represent the only attempts so far on any elastomer to determine f_u/f by using eq 3. From the experimental procedures followed it is clear that these data were obtained at near elastic equilibrium.

Allen and co-workers presented data for NR samples of various crosslink densities. The data obtained with their sample A with $M_c = 26{,}400$ can be fitted best by eq 34 in the form

$$f_u/f = 0.178 - 0.33\, q(1.15,\lambda) \tag{50}$$

We estimated the parameter n from the Mooney-Rivlin constants C_1 and C_2 supplied by Allen et al. using the nomograph presented elsewhere[9]. From eqs 50 and 34 we obtain $dn/dT \simeq 0.001/°C$. The plot is shown in Figure 4.

For their sample D with $M_c = 13{,}300$, the best fit is obtained by assuming $dn/dT = 0$. For some of their other samples dn/dT is negative.

Sharda and Tschoegl applied eq 34 to their data on natural rubber using $n = 1.64$ and assumed $dn/dT = 0$. The fit of their data can be improved, however, using eq 34 in the form

$$f_u/f = 0.26 - 0.116\ q(1.64,\lambda)$$

from which $dn/dT \simeq 0.0004/°\mathrm{C}$. This value is so small that it could not be obtained from near-equilibrium measurements in simple tension. Plots of f_u/f vs λ for the sample used by Sharda and Tschoegl are also shown in Fig. 4. We infer that for natural rubber dn/dT is small, and, consequently, f_u/f is sensibly independent of the stretch ratio.

Boyce and Treloar[37] determined M_u/M where M_u is the internal energy contribution to the restoring torsional couple M, by Treloar's[38] ingenious torsion-tension test. Data obtained in this test are independent of any constitutive assumption as are data based on eq 3. Their data on NR show a definite dependence on the angle of torsion, ϕ, equivalent to a dependence of f_u/f on λ. Boyce and Treloar[37] averaged over this dependence, considering it to be within the experimental error.

Roe and Krigbaum[39] and Tanaka et al.[40] estimated f_u/f from eq 7. This equation tests the statistical theory only inasmuch as the term $3\alpha_o T/(\lambda^3-1)$ is derived from eq 5. Nevertheless, their data show a slight but definite dependence of f_u/f on λ. Roe and Krigbaum[39] attempted to explain this through the dependence of the Mooney-Rivlin constants C_1 and C_2 on temperature. This is analogous to our attempt to explain the same observation through the temperature dependence of n. As pointed out elsewhere, the so-called Mooney-Rivlin equation is not a constitutive equation[9,41].

Swelling Ratio. The Gaussian statistical theory assumes that changes in the internal energy at constant volume arise solely from intramolecular interactions. This assumption may be tested by changing the intermolecular interactions in the network by swelling with inert solvents and observing whether f_u/f changes. In studies on NR swollen in n-decane[24] and in n-hexadecane[26] it was found that f_u/f was essentially independent of the degree of swelling, q, and of the solvent used.

According to our theory the degree of swelling should have an influence on f_u/f through the parameters dlnG/dlnT, n, dn/dT, and γ in eq 34. Shen[26] has shown that f_u/f changes very little with the degree of swelling from $q = 1.0$ to 1.5. Inferring[8,36] n again from the values of C_2/C_1, we deduce that n increases with q. Nothing is known at present about the effect of q on γ. We suspect that compensatory effects weaken the dependence of f_u/f on q. This is in accord with the findings of Allen et al.[24] that the effect of the swelling ratio on f_u/f is not a sensitive test of the statistical theory.

Crosslink Density. Equation 6 implies that f_u/f should be independent of crosslink density provided that the length of chains between crosslinks is large enough. By contrast, our theory again predicts a dependence of f_u/f on the crosslink density through $d\ln\Theta(T;\zeta)/d\ln T$, n, $\partial n/\partial T$, α_o, and γ.

The effect of increasing concentrations of dicumyl peroxide on the internal energy contribution in natural rubber was studied by Shen et al.[42] and Allen et al.[24]. Their data do not show any discernible change in f_u/f over most of the region they covered.

In Table I we assembled literature data on f_u/f for natural rubber. The second column contains the value of the equilibrium shear modulus which may be taken as a measure of crosslink densities. The fourth column contains the range of stretch ratios over which the f_u/f values were averaged to produce the entry in the first column. Columns 3, 5, and 7 are self-explanatory. In column six we listed the experimental method used to obtain f_u/f. The meaning of the symbols is as follows: A - simple tension at constant V and L; B - torsion-tension at constant P,L, and ϕ; C - simple tension at constant P and L; D - simple tension at constant P and T. The data assembled in Table I show considerable scatter. This is probably explained in part by the use of different samples, experimental methods, and conditions (e.g. temperatures, stretch ratios, etc.), and different equations for calculating f_u/f. They do not indicate a definite trend in f_u/f with crosslink density for natural rubber. However, the range of moduli and, hence, degrees of crosslinking which were covered in these studies is not extensive (1-6 bar). At lower or higher values of the modulus the situation may be different. Thus, Shen et al.[42] mentioned that their sample with the lowest crosslink density (0.5 phr dicumyl peroxide) exhibited an increase in the f_u/f value over that of the other samples. At higher crosslink densities than those covered in Table I we have no information on n, $\partial n/\partial T$, α_o, or γ. However, we do have values of dlnG/dlnT, the dominant term in eq 34, as a function G from the work of Wood[46]. These data are displayed in Figure 5. We infer from these data and eq. 34 that f_u/f should decrease with increasing crosslink density for moduli higher than about 7 bar. It has been shown by Katz and Tobolsky[47] that very highly crosslinked polymer networks show no glass transition, i.e. they are essentially polymeric glasses. It is known that dlnG/dlnT is negative for glasses. Hence we suspect that dlnG/dlnT would have become negative if Wood had used even higher concentration of dicumyl peroxide. Thus, we conjecture that f_u/f might show a minimum as a function of crosslink density.

Wood[48] found that dG/dT was constant with temperature and considered this a vindication of the Gaussian statistical theory. We point out that the Gaussian statistical theory does not require a constant dG/dT and a constant dG/dT does not imply Gaussian behavior. Differentiation of eq 47 gives

$$\frac{1}{G}\frac{dG}{dT} = \frac{1}{\nu}\frac{d\nu}{dT} + \frac{1}{T} + \frac{d\ln\langle r^2\rangle_o}{dT} - \frac{d\ln\langle r^2\rangle_f}{dT} \tag{52}$$

But $d\ln\nu/dT = -\,d\ln V_o/dT$ by the definition of ν, and $\langle r^2\rangle_o$ is proportional to the undeformed cross-sectional area at the test temperature. Hence $d\ln\langle r^2\rangle_o/dT = 2\alpha_o$ and

$$\frac{dG}{dT} = G\left[\frac{1}{T} - \alpha_o - \frac{d\ln\langle r^2\rangle_f}{dT}\right] \tag{53}$$

Thus dG/dT will not in general be independent of temperature, and its constancy cannot be considered a vindication of the Gaussian statistical theory.

B. Other Elastomers

Van der Hoff and Buckler[28] showed that f_u/f depends on the stretch ratio for a series of materials. These include *cis*-1,4-polybutadiene, poly(dimethyl siloxane), isoprene-acrylonitrile rubber, ethylene-propylene rubber, and polyisobutylene. Here we shall discuss primarily the effect of stretch ratio on f_u/f for some other elastomers. Few data are available on the effect of the degree of crosslinking.

Styrene-Butadiene Rubber (SBR). Van der Hoff and Buckler[28] calculated f_u/f for a crosslinked SBR from older data of Stearns and Johnson[49]. The plot of f_u/f vs λ is shown in Fig. 6 and indicates a strong dependence of the relative internal energy contribution to the restoring force in this material on the stretch ratio.

In another paper[8] we have presented data on the dependence of the equilibrium tensile modulus, E_e, and of n on the temperature for a crosslinked SBR. Figure 7 shows plots of f_u/f vs λ predicted from eq. 34 for this material at three temperatures. The values of n shown in Fig. 7 were taken from our earlier paper. We used $\alpha_o = 2.8 \times 10^{-4}$/°C as determined for their SBR sample by Cirlin et al.[50]. Since we do not know the value of γ for this material, we assume that $\gamma = 0$. The curve at 23°C lies between those at -10°C and -40°C. We have no explanation for this inversion at this time.

We have also studied an uncrosslinked (gum) SBR for which $n \approx 0.6$.

The temperature dependence of n and of G for this material is quite weak over the range studied, i.e. from -40 to 23°C. Thus f_u/f is virtually independent of λ. Using $\gamma = 0$, and $\alpha_o = 2.8 \times 10^{-4}/°C$, we obtained the unexpectedly high value of $f_u/f = 0.79$ at 30°C.

Viton A. Roe and Krigbaum[29] published f_u/f data on Viton A calculated from eq 7 instead of the strictly thermodynamic eqs. 3 or 9. Viton A is a copolymer of vinylidene fluoride and hexafluoropropylene. Equation 7, being based on the statistical theory, assumes n = 2 but Roe and Krigbaum's force-elongation data at T = 45°C are better represented by assuming n = 1.48. The best fit of their data in terms of our theory results as

$$f_u/f = -0.1 - 1.143\ q(1.48,\lambda) \qquad (54)$$

which gives $dn/dT \simeq 0.0036°C$. We could have recalculated the data according to the appropriate equations[16]. However, this would not have affected the conclusion that here, as in SBR, f_u/f depends on the stretch ratio.

Crosslinked Polystyrene. Orofino and Ciferri[33] presented data on polystyrene crosslinked with divinyl benzene. The best fit of their force-elongation data gives n = 1.95. The data are best represented by

$$f_u/fT = 7.85 \times 10^{-4} - 0.00266\ q(1.95,\lambda) \qquad (55)$$

Thus $dn/dT = 0.00266/°C$. Both the data and the fit are shown in Fig. 8

in which f_u/fT is plotted on the ordinate instead of f_u/f. The data again show a dependence on λ.

Crosslinked Polyethylene. Opschoor and Prins' data[30] on radiation crosslinked polyethylene show a clear dependence of f_u/f on the stretch ratio as shown in Fig. 9 in which again f_u/fT is plotted as function of λ for samples with different crosslink densities. Their force-elongation data indicate that $n \simeq 2.0$ for crosslinked polyethylene. The values of dn/dT range from 0.0025 to 0.0041.

A plot of $(f_u/f)\big|_{\lambda=1}$ against the γ-radiation dose is shown in Fig. 10. The curve shows a strong dependence of $(f_u/f)\big|_{\lambda=1}$ on crosslink density. At $\lambda=1$, $q(n,\lambda)$ is equal to zero and, hence, according to eq 49, the change in f_u/f due to the difference in crosslink density should arise from changes in $d\ln\theta(T;\zeta)/dT$, α_o, n, and γ. It appears that in polyethylene $d\ln\theta(T;\zeta)/dT$ depends on the crosslink density. This is consistend with Wood's data on natural rubber (see Figure 5).

C. Conclusions

In NR f_u/f data appear to agree with the predictions of the Gaussian statistical theory of rubber elasticity. However, one must bear in mind that swelling measurements do not afford a sensitive test, that there is a small but probably real dependence on the stretch ratio, and that there are indications that f_u/f may depend on the crosslink density outside of the range that has so far been investigated.

The picture is different if we consider other elastomers. A definite dependence on the stretch ratio appears to be discernible in a number of materials as discussed above. The conclusion that f_u/f is a function of the stretch ratio had been reached independently by various authors[28,30,39,51]. The evidence for a dependence on the degree of crosslinking is scantier because of the lack of experimental data. A clear dependence is shown, however, for crosslinked polyethylene.

Our phenomenological theory can account for the observed behavior. We conclude that NR may not be the best material for testing the statistical theory through measurements of f_u/f. In terms of our theory this arises primarily from the weak dependence of n on T in this material over the range of temperature and crosslink density over which it has been investigated. We note that the stress-strain behavior of NR does not conform well to the predictions of the statistical theory either. By contrast crosslinked polystyrene or polyethylene with values of n close to 2 in the rubbery region would conform closely to the statistical theory in their stress-strain relations according to our theory, but would, nevertheless, show dependence of f_u/f on λ and/or ν.

We have proposed a phenomenological theory which should allow extension of measurements of f_u/f to uncrosslinked materials. This raises interesting possibilities. E.g. in styrene-butadiene gum stock $n \simeq 0.6$ and $dn/dT \simeq 0$. Thus, in the light of our theory it should deviate strongly in its mechanical behavior from the equation

$$\sigma = G(\lambda - \lambda^{-2}) \tag{56}$$

but should show no dependence of f_u/f on λ.

Appendix

It is clearly important that the reference length L_o should be defined in a consistent manner in deriving a set of interrelated data. Failure to do so can lead to appreciable error in f_u/f.

Let us consider a specimen subjected to a uniaxial stretch λ at temperature T and atmospheric pressure. Since $J \simeq 1$, eq 19 takes the form

$$f = 2G\, A_o(T)[\lambda^n - (J/\lambda)^{n/2}]/n\lambda \tag{A1}$$

$A_o(T)$ is the undeformed cross-sectional area at the temperature T. In force-temperature measurements at constant length

$$\lambda = \lambda^*/\lambda_o = L(T)/L_o(T) \tag{A2}$$

where

$$\lambda^* = L(T)/L_o(T_o) \tag{A3}$$

and

$$\lambda_o = L_o(T)/L_o(T_o) \tag{A4}$$

$L(T)$, $L_o(T)$, and $L_o(T_o)$ are the deformed length of the specimen at temperature T, the undeformed length at the same temperature, and undeformed length at the reference temperature T_o, respectively. The stretch ratio arising from the linear thermal expansion of the specimen from $L_o(T_o)$ to $L_o(T)$ is λ_o and λ^* is the apparent stretch ratio referred to the undeformed length at T_o.

Let us denote the undeformed cross-sectional area at T_o as $A_o(T_o)$. We then have

$$A_o(T) = A_o(T_o)\lambda_o^{\,2} \tag{A5}$$

Substituting eqs A2 through A5 into A1 we obtain

$$f = 2G\ A_o(T_o)\lambda_o^{3-n}[\lambda^{*n}-(J_o/\lambda^*)^{n/2}]/n\lambda^* \tag{A6}$$

where

$$J_o = \frac{V(T)}{V_o(T_o)} = \lambda_o^{\,3}J \simeq \lambda_o^{\,3} \simeq 1 + 3\alpha_o(T-T_o) \tag{A7}$$

Equation A6 can be rewritten as

$$f = 2G^*A_o(T_o)\ [\lambda^{*n}-(J_o/\lambda^*)^{n/2}]/n\lambda^* \tag{A8}$$

where

$$G^* = G\ J_o^{\,1-n/3} \tag{A9}$$

G^* is an apparent shear modulus defined in terms of λ^* instead of λ. Therefore, a change of the reference length from $L_o(T)$ to $L_o(T_o)$ changes the modulus but does not change the value of n. Furthermore, if $J \neq 1$, the restoring force f does not reduce to 0 when $\lambda^* \rightarrow 1$. Differentiation of eq A9 with respect to temperature leads to

$$\frac{dG^*}{dT} = J_o^{\,1-n/3} \frac{dG}{dT} + G(3-n)\, \alpha_o\, J_o^{\,-n/3} - [(G/3)J_o^{\,1-n/3} \ln J_o] \frac{dn}{dT} \qquad \text{(A10)}$$

Equation A9 indicates that G^* does not differ too much from G. However, dG^*/dT is quite different from dG/dT.

We illustrate this on hand of data determined on natural rubber in our laboratory. With a reference temperature of 25°C and a test temperature of 60°C, G = 6.22 bar at the test temperature, n = 1.64, $\alpha_o = 2.30 \times 10^{-4}$/°C, dG/dT = 9.86×10^{-3} bar/°C, we find $G^* = 6.33$ bar and $dG^*/dT = 12.78 \times 10^{-3}$ bar/°C, assuming that dn/dT = 0. Thus f_u/f at 60°C calculated from dG^*/dT is 0.090 lower than that calculated from dG/dT. It is clear that application of eqs. 9 and 34 requires very high precision in the determination of G. Thus, Shen and Blatz[22] have noted that specimen end effects can have a significant influence on f_u/f. As shown elsewhere[52] the ratio of free to bonded area in the specimen should be at least 50:1.

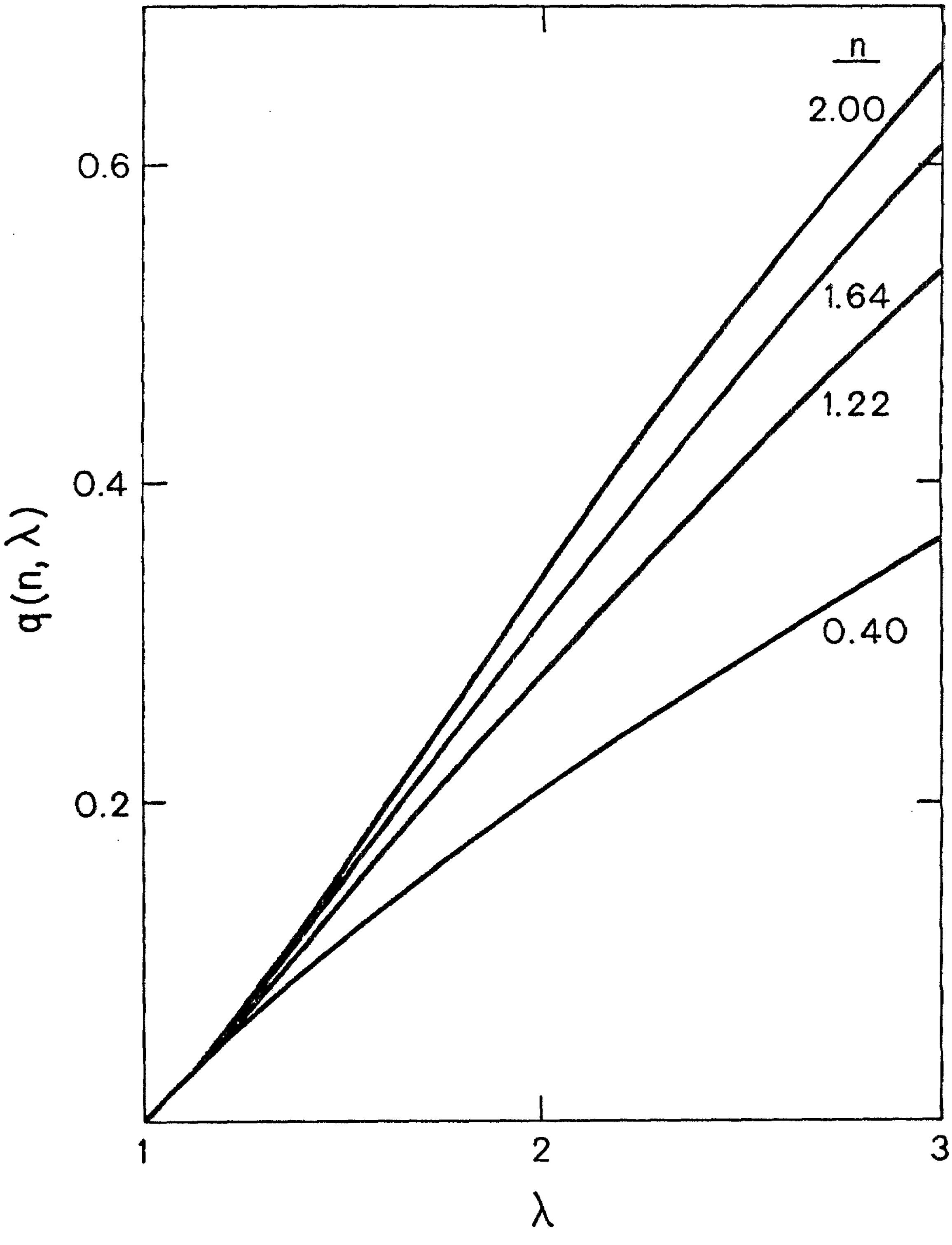

Figure 1 The function q(n,λ) for different values of n as function of λ.

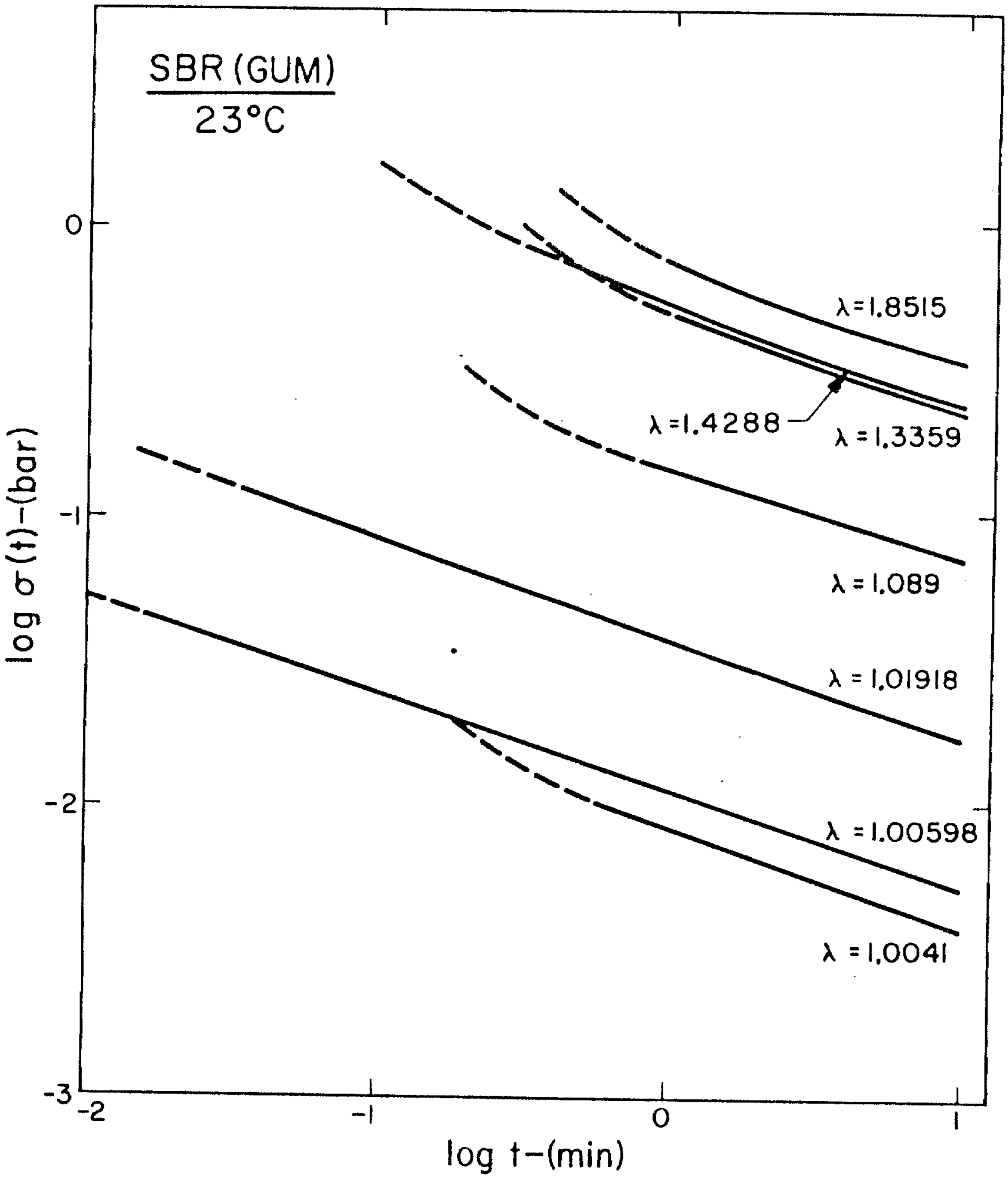

Figure 2 Engineering stress, σ(t), as function of time t in logarithmic coordinates. Step response of uncrosslinked SBR at 23°C.

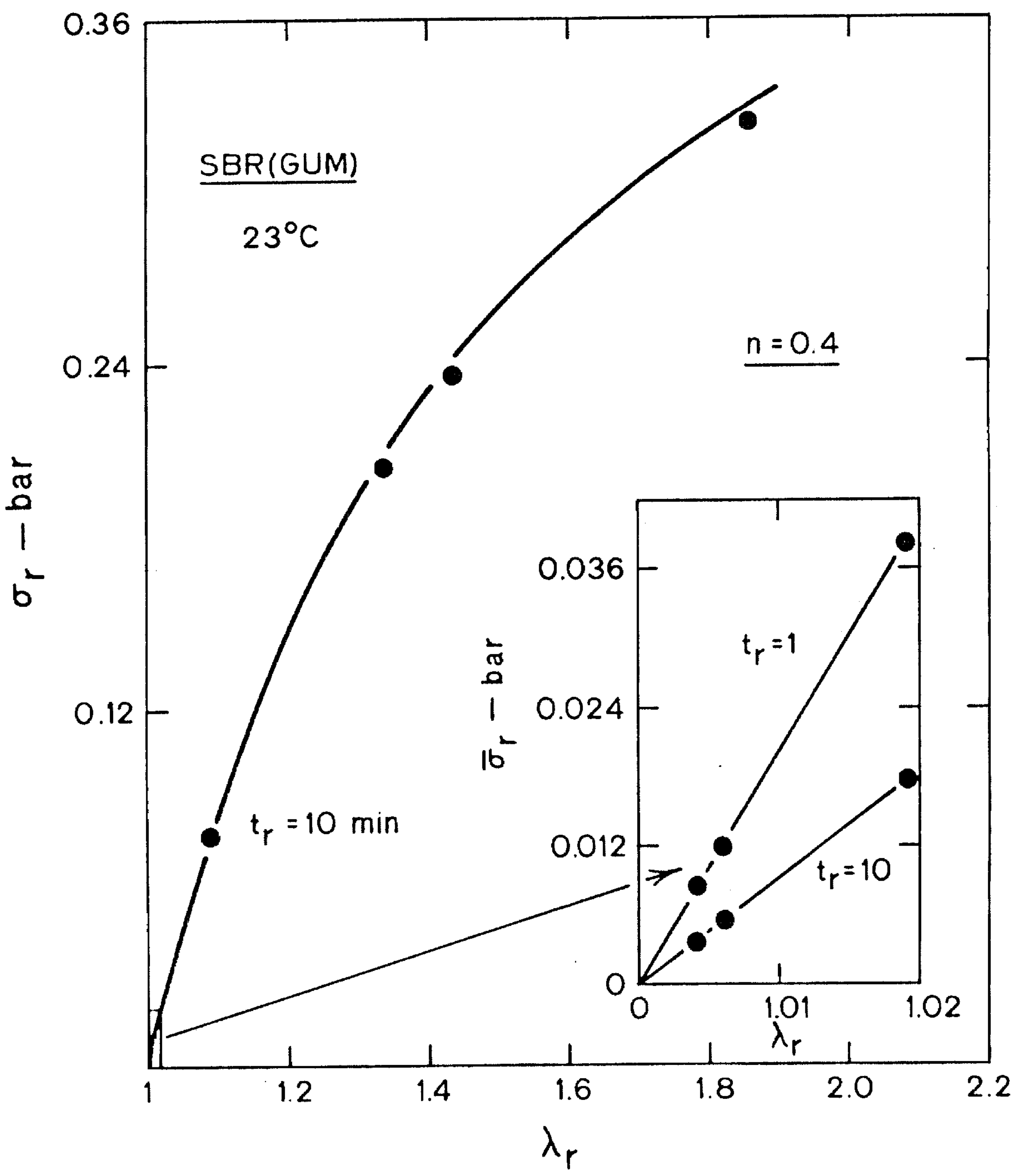

Figure 3 Stress as a function of stretch ratio at the isochronal time t_r = 10 min. Uncrosslinked SBR at 23°C.

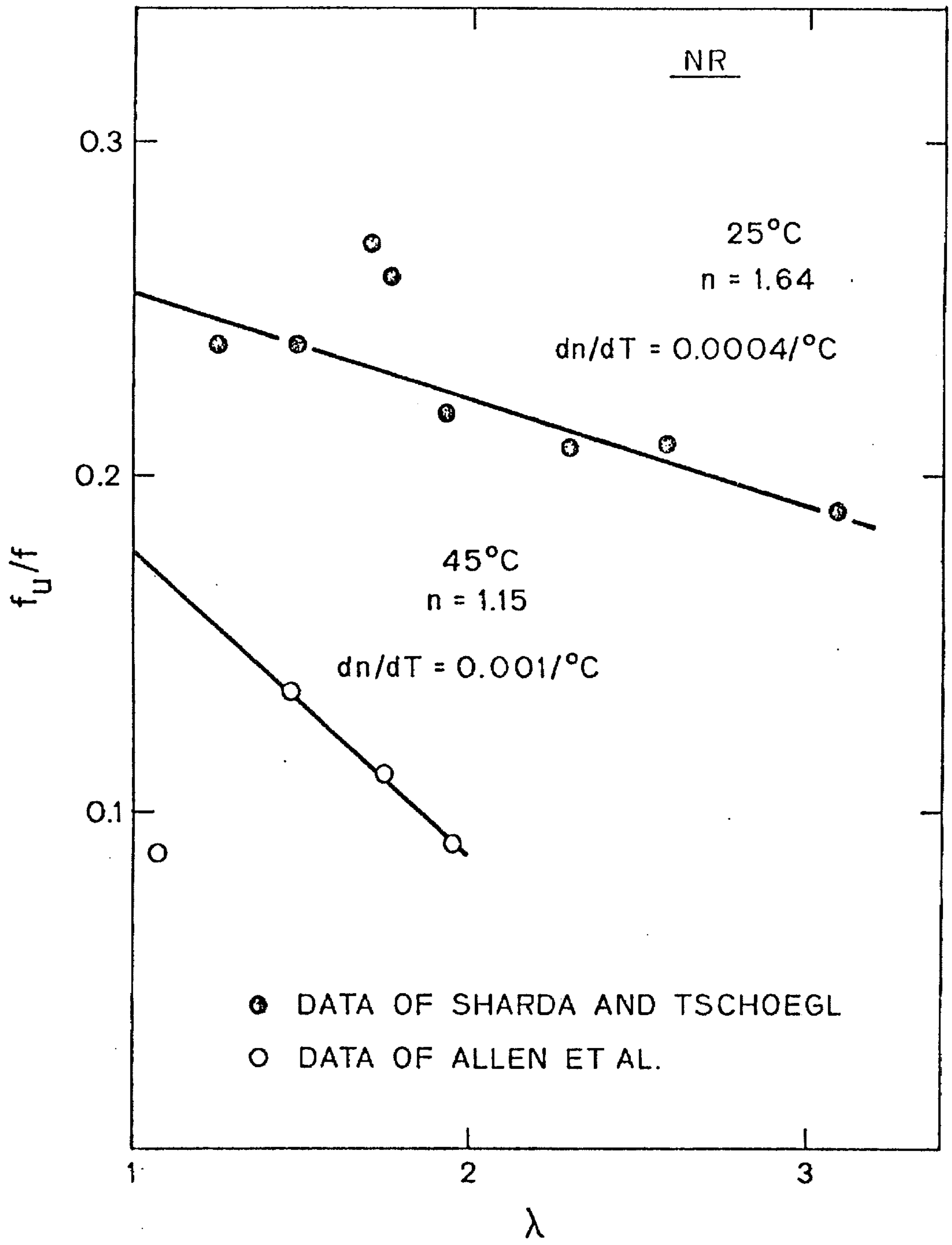

Figure 4 f_u/f as function of λ for natural rubber at 25 and 45°C, respectively. Data of Sharda and Tschoegl[16] and of Allen et al.[24].

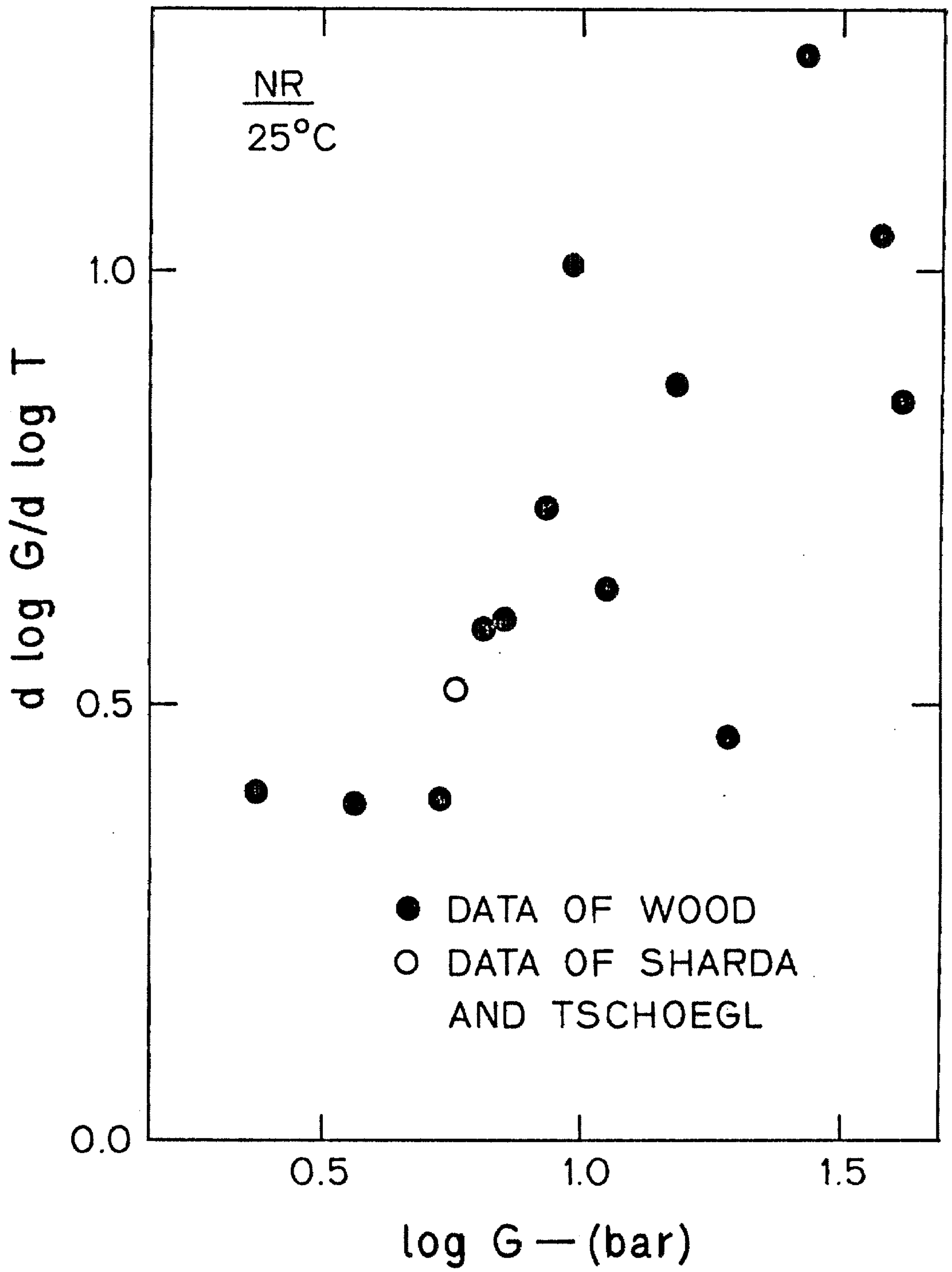

Figure 5 dlnG/dlnT as function of log G for natural rubber at 25°C. Data of Wood[46].

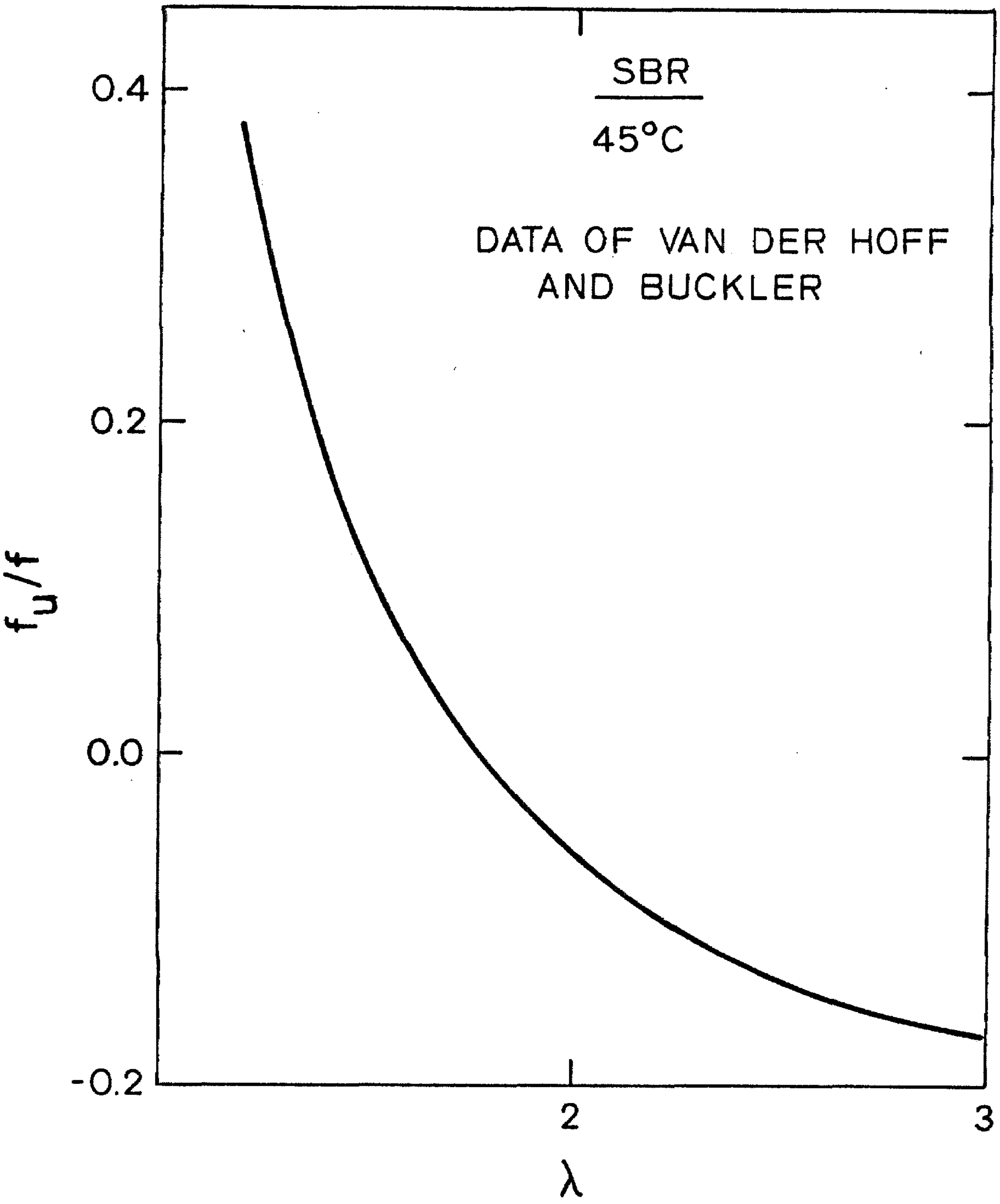

Figure 6 f_u/f as function of λ for SBR at 45°C. Data of Van der Hoff and Buckler[28].

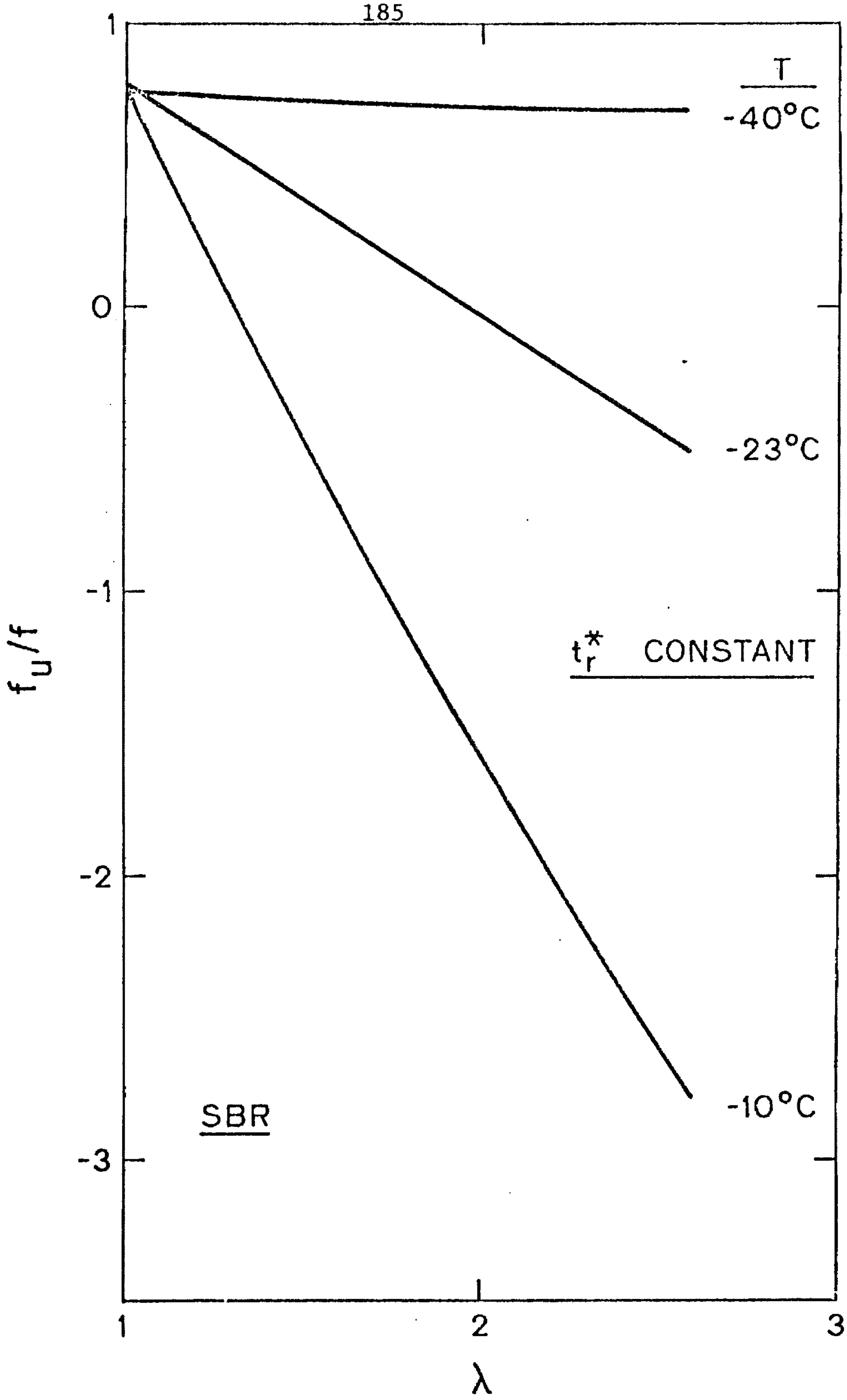

Figure 7 Predicted values of f_u/f as function of λ for SBR at constant isochronal reduced time, at -40, -23, and -10°C.

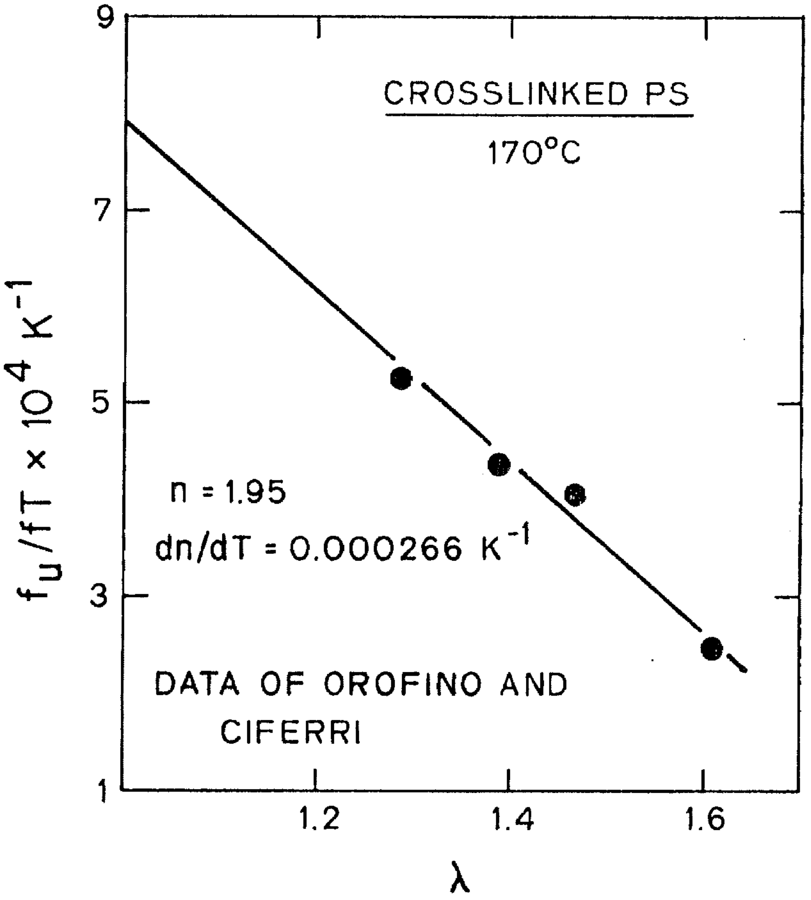

Figure 8 f_u/fT as function of λ for crosslinked polystyrene at 170°C. Data of Orofino and Ciferri[33].

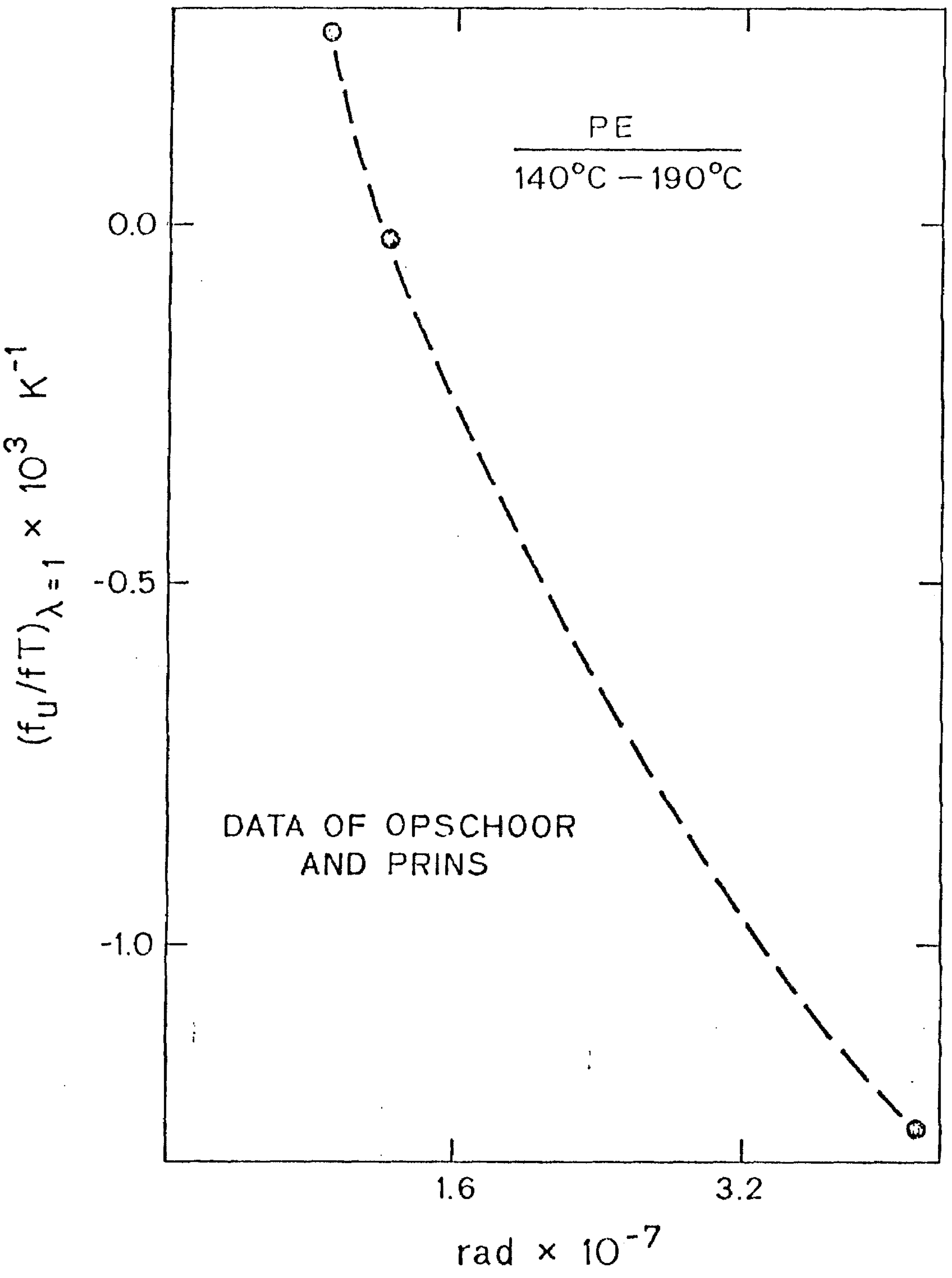

Figure 10 f_u/fT as function of the radiation dose for crosslinked polyethylene at 140°-190°C. Data of Opschoor and Prins[30].

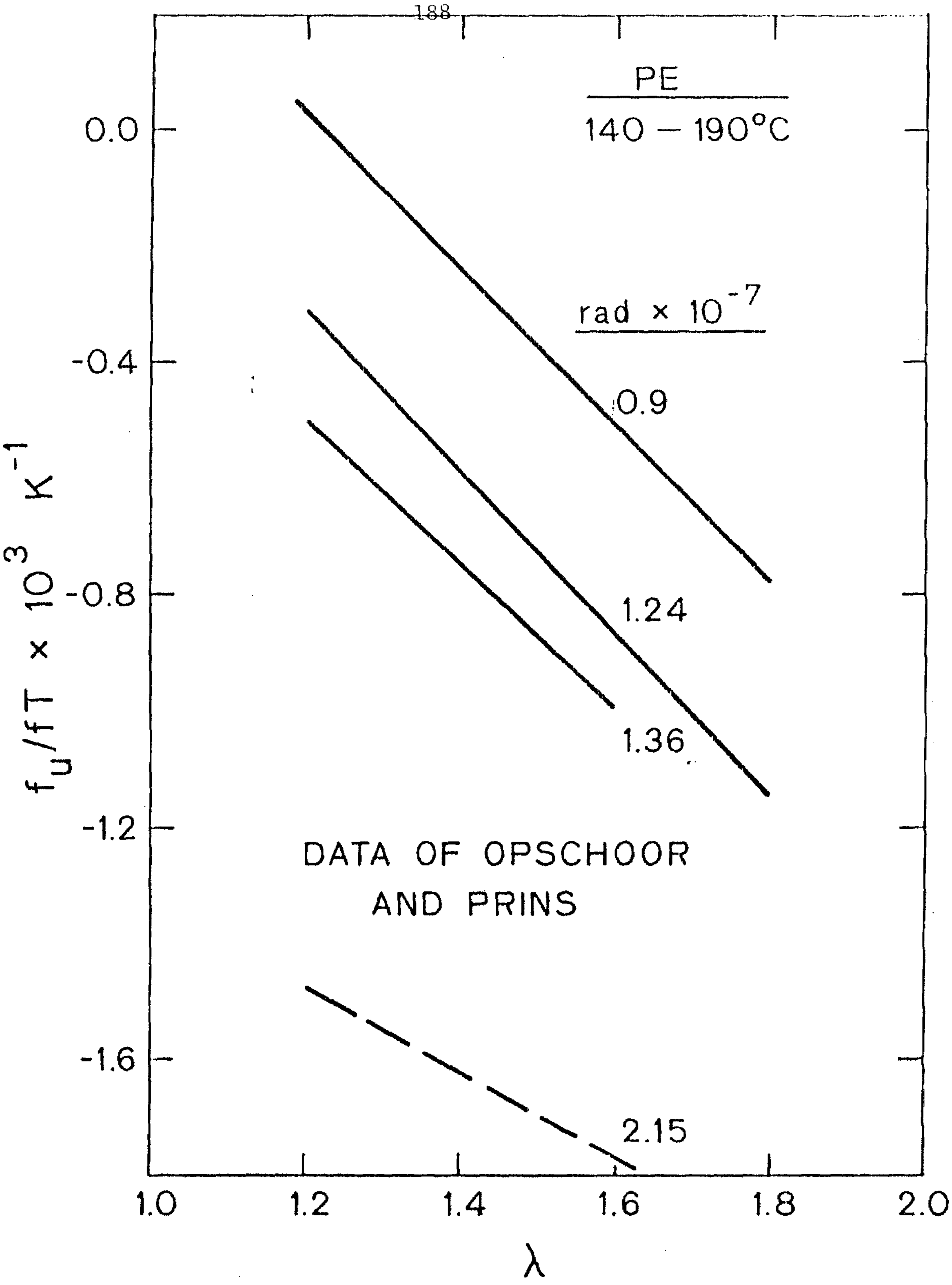

Figure 9 f_u/fT as function of λ for crosslinked polyethylene at 140-190°C. Data of Opschoor and Prins[30].

TABLE I

Values of Relative Internal Energy Contribution (f_u/f) to the Restoring Force in Natural Rubber

f_u/f	G(BAR)	T(°C)	λ	X link.	Expt.	Ref.
0.107	1.69[a]	30	1.08→1.948	DCP	A	24
0.145	2.69[a]	30	1.474→1.982	DCP	A	24
0.143	4.50[a]	30	1.180→1.902	DCP	A	24
0.120	2.64[a]	30	1.445→2.095	DCP	A	24
0.123	4.57[a]	30	1.130→1.484	DCP	A	24
0.23	5.87	25	>1.25	S	A	16
0.126	3.7	20	1.13→1.25	DCP	B	37
0.18	-	50	1.42→2.58	Rad	C	43
0.13	2.09	30	1.0→2.0	DCP	C[b]	22
0.33	2.10	30	1.0→2.0	DCP	C[c]	22
0.18	5.97	30	1.0→2.0	DCP	D	26
0.15	5.97	30	1.0→2.0	DCP	C	26
0.18	4.62	30	0.9→1.7	DCP	E	44
0.18	3.9[a]	30	>1.30	Rad	C	45
0.18	4.1[a]	30	>1.30	Rad	C	45
0.18	3.1[a]	30	>1.30	DCP	C	45
0.18	5.2[a]	30	>1.30	S	C	45
0.25	3.49[a]	45	1.3	Rad	C	39
0.11	3.49[a]	45	2.5	Rad	C	39
0.215	-	50	1.0275	S	C	40
0.068	-	50	2.76	S	C	40

[a] Obtained from the Mooney-Rivlin Constants C_1 and C_2.

[b] Butt jointed sample

[c] Sandwiched sample

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APPENDIX

TABLES FOR CHAPTER 3

Table I

Superposition of ramps on finite stretch

SBR 1502 Gum - 17°C $n = 0.6$

$t-t_r = 0.1$ min $R(t-t_r) = 17.54$ bar

I. $t_r = 10$ min $E(t_r) = 4.93$ bar

λ_r	1.0228	1.0685	1.229	1.572	1.915	2.424
$\dot{\varepsilon}$ min^{-1}	0.01141	0.0228	0.114	0.228	0.228	0.228
$R(t-t_r)$bar						
solid model	17.2	16.9	15.48	13.2	11.71	10.2
liquid model	17.18	16.5	15.08	12.07	9.83	8.23
experimental	16.1±.8	16±0.8	16.2±0.8	12.9±0.8	12.1±0.8	9.96 ±0.8

II. $t_r = 300$ min $E(t_r) = 3.425$ bar

$\lambda_r = 1.7904$

$\dot{\varepsilon} = 0.0394$ min^{-1}

$R(t-t_r)$bar	
Solid model	11.98
liquid model	10.226
experimental	12.21±0.5

*Estimated from the figures in reference 11

Table II Superimposed dynamic storage modulus (E_s') and loss modulus (E_s'') of SBR*

	SBR (o°C)					
	$\lambda_r E_s'$ (psi)					
f(HZ) λ_r	0.01	0.025	0.05	0.1	0.25	0.5
1.53	3.17-3.22	3.5-3.6	3.9-4.1	4.2-4.35	4.35-4.5	4.45-4.6
1.96	4.35-4.50	4.45-4.58	4.6-4.8	4.8-5.05	5.05-5.26	5.2-5.32
	$\lambda_r E_s''$ (psi)					
1.53	1.5	1.9-2.06	2.16-2.4	2.37-2.63	2.76-3.0	2.9-3.1
1.96	2.1	2.45-2.75	3.1-3.35	3.4-3.6	3.6-3.85	3.8-4.05

$\dfrac{(\lambda_r E_s')\big|_{\lambda_r = 1.96}}{(\lambda_r E_s')\big|_{\lambda_r = 1.53}}$: mean = 1.365, standard deviation = 0.11

$\dfrac{(\lambda_r E_s'')\big|_{\lambda_r = 1.96}}{(\lambda_r E_s'')\big|_{\lambda_r = 1.53}}$: mean = 1.271 - standard deviation = 0.07

*Estimated from the figures of reference 11.

TABLE III Superimposed dynamic storage modulus (E_s') and loss modulus (E_s'') of Estane x-100*

Estane x-100 (-1°C)					
		$E_s'\lambda_r$ (psi)			
λ_r \ f(HZ)	0.01	0.025	0.05	0.1	0.25
1.55	1.9	2.3-2.65	2.7-3	3.3-3.95	3.95-4.8
1.99	3.4	4.6-5.3	4.8-5.7	5.8-6.35	7-7.6
		$E_s''\lambda_r$ (psi)			
1.55	0.68-0.79	0.84-1.07	1.4-1.52	1.9-2.4	2.7-3.3
1.99	1-1.4	1.9-2.6	2-2.8	2.8-3.4	3.7-4.25

$$\frac{(E'\lambda_r)|_{\lambda_r = 1.99}}{(E'\lambda_r)|_{\lambda_r = 1.55}} : \text{ mean} = 1.81, \text{ standard deviation} = 0.266$$

$$\frac{(E''\lambda_r)|_{\lambda_r = 1.99}}{(E''\lambda_r)|_{\lambda_r = 1.55}} : \text{ mean} = 1.72, \text{ standard deviation} = 0.56$$