APPLICATION OF FINITE VISCOELASTIC THEORY
TO THE DEFORMATION OF RUBBERLIKE MATERIALS
I. UNIAXIAL STRESS RELAXATION DATA

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I. Introduction

Since the formulation of the theories of viscoelasticity by Maxwell (1867) and Voigt (1889), there has been an exhausting development and reformulation by a large number of theoreticians in order to establish realistic constitutive equations for linear viscoelastic materials. Those linear theories which are valid only for small deformations are based on a superposition principle so that the constitutive equation can be written as a linear differential equation of nth order in time derivatives of strain and mth order in time derivatives of stress. For integral representation of the constitutive equation, Boltzmann (1874) and Volterra (1930) suggested a linear theory of viscoelasticity which is based on the assumption that the stress at the present time (at the time of measurement) is a function of the entire previous history of strain. Materials which are characterized by this postulate are usually called materials with hereditary characteristics or materials with memory. Such linear theories, when extended to the non-linear range of deformation gradients, generally violate the principle of objectivity, which states that the constitutive equation is invariant to the simultaneous rotation of the body and reference system.

In recent years the constitutive equations for finite viscoelastic materials have been formulated by various authors. In most of these formulations the following assumptions were usually made: i) the material is isotropic and simple (a simple material is one for which the stress terms depend only on one past time, and only on the first derivatives of the deformation tensor), ii) the motion is slow in the recent past time. In addition the principle of material objectivity was imposed.

More recently Coleman and Noll (1) developed constitutive equations for a material possessing continuous memory of its past history expressed in the form of integral equations with the physical assumption that the memory of a simple material fades in time.

When one postulates the viscoelastic behavior of a material by an integral representation with the principle of material objectivity imposed, the kernel of such an integral usually consists of four isotropic tensor functions, each of which can be represented by three
scalar functions (or relaxation functions) of the invariants of the deformation tensor and of time. Thus it may not be an easy task to determine the nature of such relaxation functions by any simple experimental program; however, as we shall see later five of twelve such functions must vanish in order that the constitutive equation be also valid in the limiting ranges of long and short times, where the material behaves elastically. This reduces greatly the aforementioned difficulty in determining such functions. Furthermore, by stress relaxation tests at different constant stretch ratios one can easily determine those functions with time as an argument and the invariants of the deformation tensor as constant parameters.

In this report the constitutive equation for finite viscoelastic materials will be postulated as the sum of equilibrium terms and integral terms which describe the viscoelastic behavior of the materials and vanish when the equilibrium state is reached or when the materials have always been at rest. It is also our purpose i) to show how the twelve relaxation functions are reduced to two independent ones in the case that the material has Mooney-Rivlin elastic behavior and that all the relaxation functions depend only on time, ii) to display the mechanics of evaluating the two non-zero relaxation functions from data obtained from uniaxial stress relaxation tests.
Notation

\( \chi^i \) : material coordinates

\( \chi^i \) : spatial coordinates \( \chi^i(t) = \chi^i \)

\( \mathbf{Z}^i \) : rectangular material coordinates

\( \mathbf{z}^i \) : rectangular spatial coordinates

\( G_{KL}(\chi^i) = \delta_{mn} \frac{\partial \mathbf{Z}^M}{\partial \chi^k} \frac{\partial \mathbf{Z}^N}{\partial \chi^l} \)

\( g_{KL}(\chi^i) = \delta_{mn} \frac{\partial \mathbf{z}^m}{\partial \chi^k} \frac{\partial \mathbf{z}^n}{\partial \chi^l} \)

\( C_{KL}(\chi^i, t) = g_{KL} \frac{\partial \mathbf{z}^k}{\partial \chi^i} \frac{\partial \mathbf{z}^l}{\partial \chi^i} \) \quad \text{Right Cauchy-Green Deformation Tensor}

\( B_{kl} = (C^{-1})^{kl} = G_{KL} \frac{\partial \mathbf{z}^k}{\partial \chi^i} \frac{\partial \mathbf{z}^l}{\partial \chi^i} \) \quad \text{Left Cauchy-Green Deformation Tensor}

\( C_{kl} = G_{KL} \frac{\partial \chi^k}{\partial \chi^i} \frac{\partial \chi^l}{\partial \chi^i} \)

\( \mathcal{C}_{kl, \tau} = \delta_{rs} \frac{\partial \chi^k(t)}{\partial \chi^r(t)} \frac{\partial \chi^l(t)}{\partial \chi^r(t)} \) \quad \text{relative deformation tensor}

\( t \) : present time

\( \tau \) : past time

\( s = t - \tau \) : past time relative to present time

\( \tilde{\tau} \) : true stress tensor referred to \( \chi \)-system
II. Constitutive Equations of Finite Viscoelasticity

Assuming that the material is isotropic and simple, and that the motion in which the deformation relative to the present time \( t \) is small at the recent past (the deformation relative to the present time may be finite at all past times), and by using the principle of material objectivity one can postulate the constitutive equation for finite viscoelastic materials as the sum of equilibrium terms and terms which vanish when the equilibrium state is reached or when the materials have always been at rest, namely:

\[
\dot{\sigma} = b_0 \mathbb{I} + b_1 \mathbb{E} + b_2 \mathbb{E}^2 + \int_0^\infty \phi_1(s, \mathbb{E}) \left[ \sigma(t-s) - \mathbb{I} \right] ds + \int_0^\infty \phi_2(s, \mathbb{E}) \left[ \sigma_t(t-s) - \mathbb{I} \right] ds + \int_0^\infty \phi_3(s, \mathbb{E}) \left[ \sigma_{tt}(t-s) - \mathbb{I} \right] ds
\]

\[
+ \mathbb{E} \text{Tr} \int_0^\infty \phi_4(s, \mathbb{E}) \left[ \sigma_t(t-s) - \mathbb{I} \right] ds + \mathbb{E} \text{Tr} \int_0^\infty \phi_5(s, \mathbb{E}) \left[ \sigma_{tt}(t-s) - \mathbb{I} \right] ds
\]

\[
(1)
\]

* The dot in equation (1) denotes differentiation with respect to \( s \) keeping the deformation fixed.
where

\[ b_0 = \frac{2}{\sqrt{I_B}} \left[ I_B \frac{\partial W}{\partial I_B} + I_B \frac{\partial W}{\partial \Pi_B} \right] \]  
\[ b_1 = \frac{2}{\sqrt{I_B}} \frac{\partial W}{\partial \Pi_B} \]  
\[ b_2 = -2\sqrt{I_B} \frac{\partial W}{\partial \Pi_B} \]  
\[ I_B = \text{Tr} \, \mathcal{B} \]  
\[ \Pi_B = \frac{1}{2} \left[ (\text{Tr} \, \mathcal{B})^2 - \text{Tr} \, \mathcal{B}^2 \right] \]  
\[ \Pi_B = \det \, \mathcal{B} \]  

\( W \) is the strain energy function at the equilibrium state (no time dependence), and \( \phi_i(s, \mathcal{B}) \) are isotropic tensor functions of \( \mathcal{B} \) and have the expansions

\[ \phi_i(s, \mathcal{B}) = \phi_i(0, \mathcal{B}) + \phi_i(t-z) \mathcal{B} + \phi_i(t-z) \mathcal{B}^\top \]  

in which \( \phi_i(t-z) \) are scalar functions of \( I_B, \Pi_B, \Pi_B \).

The theory based on (1) is usually called finite viscoelasticity and is applicable to a motion in which the deformation relative to the present time (at time of measurement) is small at the recent past only (the deformation relative to the present time may be finite at all past times).

Integrating equation (1) by parts, making use of relations

\[ \zeta(t) = I \]  
\[ \zeta(t-s) = 0, \quad t \leq s < \infty \]  
\[ \phi_i(\infty, \mathcal{B}) = 0 \]  

and replacing \( s \) by \( t-z \) we have

\[ \frac{\partial}{\partial \beta} \xi = \alpha \dot{\zeta} \mathcal{B} + \beta \mathcal{B} \frac{\partial}{\partial \beta} \bar{\mathcal{B}} + \gamma \mathcal{B} \frac{\partial}{\partial \beta} \mathcal{B} + \delta \mathcal{B} \frac{\partial}{\partial \beta} \mathcal{B}^\top \]  

\[ \mathcal{B}^\top \left[ I_B \mathcal{B}^\top + \Pi_B \mathcal{B} + \Pi_B \mathcal{B}^\top - \Pi_B \mathcal{B} \right] = 0 \]
which, after the application of relation (8), becomes

\[ \dot{t} = b_0 I + b_1 \varepsilon + b_2 \varepsilon^{-1} + \int_0^t \phi_i(t-z, \varepsilon) \dot{\varepsilon}_i(z) dz + \int_0^t \phi_i(t-z, \varepsilon) \dot{\varepsilon}_i(z) dz + \frac{\varepsilon}{\varepsilon} \int_0^t \phi_i(t-z, \varepsilon) \dot{\varepsilon}_i(z) dz \]

(12)

Thus the viscoelastic behavior of the materials is determined by the twelve relaxation functions \( \phi_{ij}(t-z) \). As we shall see later some of them must vanish in order that the constitutive equation also holds for elastic behavior at \( t=0 \) (glassy behavior).

Replacing \( \dot{\varepsilon}_i(z) dz \) by \( d\varepsilon_i(z) \), multiplying proper metric tensor \( q^{ij} (= \delta^{ij}) \) to the integral terms to secure symmetry of the stress tensor, equation (13) can be written in indicial notation in Cartesian coordinates, as

\[ \dot{t} = b_0 I + b_1 \varepsilon + b_2 \varepsilon^{-1} + \int_0^t \phi_i(t-z, \varepsilon) \dot{\varepsilon}_i(z) dz + \int_0^t \phi_i(t-z, \varepsilon) \dot{\varepsilon}_i(z) dz + \frac{\varepsilon}{\varepsilon} \int_0^t \phi_i(t-z, \varepsilon) \dot{\varepsilon}_i(z) dz \]

(13)
\[
\left[ \sum_\phi \left( z^{\pm w} \sum_\delta \delta \left( z^{-1} \right)^{2,\phi} \right) \right] + \\
\sum_\phi \left( z^{\pm w} \sum_\delta \delta \left( z^{-1} \right)^{2,\phi} \right) + \\
\sum_\phi \left( z^{\pm w} \sum_\delta \delta \left( z^{-1} \right)^{2,\phi} \right) + \\
\sum_\phi \left( z^{\pm w} \sum_\delta \delta \left( z^{-1} \right)^{2,\phi} \right) + \\
\sum_\phi \left( z^{\pm w} \sum_\delta \delta \left( z^{-1} \right)^{2,\phi} \right) + \\
\sum_\phi \left( z^{\pm w} \sum_\delta \delta \left( z^{-1} \right)^{2,\phi} \right) + \\
\sum_\phi \left( z^{\pm w} \sum_\delta \delta \left( z^{-1} \right)^{2,\phi} \right) + \\
\sum_\phi \left( z^{\pm w} \sum_\delta \delta \left( z^{-1} \right)^{2,\phi} \right) + \\
f_i \left( z^{-1} \right)^{2,\phi} + f_i \left( z^{-1} \right)^{2,\phi} = f_i \left( z^{-1} \right)^{2,\phi}
\]
III. Homogeneous Stress Fields

Let us now consider special application of equation (14) to homogeneous stress fields (also homogeneous stretch fields since the material is isotropic) for which, in Cartesian coordinates

\[
\begin{pmatrix} \varepsilon_1 \varepsilon_k \end{pmatrix} = \frac{\partial \mathbf{x}}{\partial \mathbf{x}^k} = \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{pmatrix}
\]  
(15)

\[
\mathbf{B} = \mathbf{K} \varepsilon \mathbf{x}_L = \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{pmatrix}
\]  
(16)

\[
\mathbf{B}^{-1} = \mathbf{K} \mathbf{x}_L \mathbf{K}^{-1} = \begin{pmatrix} \frac{1}{\lambda_1} & 0 & 0 \\ 0 & \frac{1}{\lambda_2} & 0 \\ 0 & 0 & \frac{1}{\lambda_3} \end{pmatrix}
\]  
(17)

\[
\mathbf{C}(t) = \mathbf{K} \mathbf{x}(t) \mathbf{x}^T(t) = \begin{pmatrix} \frac{\lambda_1^2(t)}{\lambda_1^2} & 0 & 0 \\ 0 & \frac{\lambda_2^2(t)}{\lambda_2^2} & 0 \\ 0 & 0 & \frac{\lambda_3^2(t)}{\lambda_3^2} \end{pmatrix}
\]  
(18)

where \( \lambda_i = \lambda_i(t) \)  

Then the constitutive equation (14) becomes

\[
\sigma_{ij} = t_{ii} = b_0 + b_1 \lambda_i + \frac{b_2}{\lambda_i^2}
\]  
(19)

A. Stress Relaxation Deformations

Let us now consider the stress relaxation deformations which are subclasses of homogeneous stress fields.

Suppose at \( t = 0 \) the stretch ratio \( \lambda_i(z) \) has a jump from \( \lambda_i(0) = 1 \) to \( \lambda_i(0^+) \) and is kept constant over the entire range of time so that

\[
\lambda_i(0^+) = \lambda_i(z) = \lambda_i(t) = \lambda_i, \quad z \geq 0^+ \quad (21)
\]

Then the constitutive equation (20) is reduced to the form

\[
t^{ii} = \frac{\sigma^i}{\sqrt{\mathbf{II}_B}} = \left[ b_0 + 2\phi(t) - 2\varphi(t) + \phi(t)\left(\frac{\mathbf{II}_B}{\mathbf{III}_B} - 3\right) + \phi(t)(\mathbf{I}_B - 3) + \frac{1}{\lambda_i^2}\left(\frac{\mathbf{II}_B}{\mathbf{III}_B} - 3\right)
\right]
\]

\[
+ \left[ b_1 + 2\phi(t) - \phi(t) + \phi(t)\left(\frac{\mathbf{II}_B}{\mathbf{III}_B} - 3\right) + \phi(t)(\mathbf{I}_B - 3) + \phi(t)\left(\frac{\mathbf{II}_B}{\mathbf{III}_B} - 3\right)
\right]
\]

\[
+ \left[ b_2 - 2\phi(t) + 2\phi(t) - \phi(t) + \phi(t)\left(\frac{\mathbf{II}_B}{\mathbf{III}_B} - 3\right) + \phi(t)(\mathbf{I}_B - 3) + \phi(t)\left(\frac{\mathbf{II}_B}{\mathbf{III}_B} - 3\right)
\right]
\]

Equation (22) must also hold true for short time elastic behavior (glassy behavior) at \( t = 0 \), and since for elastic case there can not be a term of \( 1/\lambda_i^2 \) in the constitutive equation it is required that

\[
\phi(t) = 0 \quad (23)
\]

For incompressible case ( \( \mathbf{III}_B = 1 \) ) we have

\[
b_0 = \frac{2}{\sqrt{\mathbf{III}_B}}\left(\mathbf{II}_B \mathbf{W}_2 + \mathbf{III}_B \mathbf{W}_3\right) = \bar{K}
\]

\[
b_1 = 2 \mathbf{W}_1
\]

\[
b_2 = -2 \mathbf{W}_2
\]
where

\[ \mathcal{W}_1 = \frac{\partial W}{\partial I_B} \quad , \quad \mathcal{W}_2 = \frac{\partial W}{\partial II_B} \]  

(27)

and \( \overline{K} \) is a function of coordinates. From the elastic constitutive equation

\[ t^{ij} = 2\left[ \mathcal{W}_1 B^{ij} - \mathcal{W}_2 (B^{-1})^{ij} \right] + \overline{K} \delta^{ij} \]  

(28)

\( \overline{K} \), for hydrostatic stress field \( (t^{ij} = -p \delta^{ij}) \) can be written as

\[ \overline{K} = -p - 2(\mathcal{W}_1^* - \mathcal{W}_2^*) \]  

(29)

where

\[ \mathcal{W}_1^* = \frac{\partial W}{\partial I_B} \begin{vmatrix} I_B = 3 \\ I_B = 3 \end{vmatrix} , \quad \mathcal{W}_2^* = \frac{\partial W}{\partial II_B} \begin{vmatrix} I_B = 3 \\ II_B = 3 \end{vmatrix} \]  

(30)

Thus the constitutive equation (22) can be written in the form:

\[ t^{ii} + p = \sigma^{ii} \lambda_i + p = \left[ 2(\mathcal{W}_2^* - \mathcal{W}_1^*) + 2\phi(t) - 2\phi(t) - \phi(t)(I_B - 3) + \phi(t)(I_B - 3) \right] \]  

\[ + \phi(t)(I_B - 3)^2 + 2 I_B \]  

\[ + \left[ 2\mathcal{W}_1 + 2\phi(t) - \phi(t)(I_B - 3) + 3(\mathcal{W}_1^* - \mathcal{W}_2^*) \right] \frac{1}{\lambda^2_i} \]  

(31)

The quantities inside the first bracket of equation (31) can not be functions of invariants for the elastic case and in the case that \( \phi(t) \) and \( \phi(t)^* \) are functions only of time we must have

\[ \phi(t) = 0, \quad \phi(t)^* = 0 \]  

(32)

* In the case \( \phi_0(t) \) and \( \phi_1(t) \) are also functions of invariants as well as of time, we must have \( \phi_0(t) = 0, \quad \phi_1(t) = 0 \), since the quantities inside the first bracket cannot be functions of invariants.
Then equation (31) becomes

\[ \sigma(t) \lambda + p = 2 \left( (W^*_2 - W^*_i) + \phi(t) - \phi(t) \right) \]

\[ + 2 \left[ 2 W_1^2 + 2 \phi(t) - \phi(t)(I_2 - 3) + \phi(t)(I_2 - 3) + \phi(t)(I_2 - I_2^2 + 2 I_2) \right] \lambda_i^2 \]

\[ - \left[ 2 W_2^2 + 2 \phi(t) + \phi(t)(I_2 - 3) - \phi(t)(I_2 - 3) - \phi(t)(I_2 - I_2^2 + 2 I_2) \right] \frac{1}{\lambda_j^2} \]  

(33)

and the principal stress difference between \( i \) and \( j \) directions takes on the form

\[ \frac{\sigma(t) \lambda - \sigma(t) \lambda_j}{\lambda_i^2 - \lambda_j^2} = \left[ 2 W_1^2 + 2 \phi(t) - \phi(t)(I_2 - 3) + \phi(t)(I_2 - 3) \right. \]

\[ + \phi(t)(I_2 - I_2^2 + 2 I_2) \]

\[ \left. - \phi(t)(I_2 - I_2^2 + 2 I_2) \right] \frac{1}{\lambda_i^2 \lambda_j^2} \]  

(34)

Thus the mechanical behavior of a viscoelastic material is characterized by the two scalar invariant functions, \( W_i \), \( W_2 \), and the eight relaxation functions \( \phi_i(t) \left[ \phi_j(t), \phi_j(t) \right] \) may be functions of invariants as well as of time. \( W_i \) and \( W_2 \) can be determined either from equilibrium data of an interrupted stress-stretch test or from long time data of stress relaxation tests at different stretch levels. While \( \phi_i(t) \) can not be easily determined in a simple experimental program, however, for a particular case for which \( W_i \) and \( W_2 \) are constants and \( \phi_i(t) \) are functions only of time \( \phi_i(t) \) and \( \phi_i(t) \) can be determined from Mooney-Rivlin plot of stress relaxation tests at different stretch ratios. The rest of \( \phi_i(t) \) must vanish since equation (34) must also hold for elastic case (glassy behavior) at \( t = 0 \). This will be shown in an uniaxial stress field.

Uniaxial Stress Relaxation. - Let the relaxation stress and stretch ratio in longitudinal direction (\( i = 1 \)) be denoted by \( \sigma_{uni}(t) \) and \( \lambda \), while those in lateral directions (\( i = 2, 3 \)) by \( \sigma_{lat}(t) \) \( [ \lambda ] = 0 \) and \( \lambda_{lat} \), then for incompressible case (\( \lambda \lambda_{lat}^2 = 1 \)) the principal stress difference takes on the form
\[
\frac{\sigma'_{\text{uni}}(t)}{\lambda - \frac{1}{\lambda^2}} = \left[ 2W_i + 2\phi(t) - \phi_3(t)(\Pi_8 - 3) + \phi_3(t)(I_8 - 3) + \phi_2(t)(\Pi_8 - \Pi_8^2 + 2I_8) \right]
+ \left[ 2W_2 + 2\phi(t) + \phi_4(t)(\Pi_8 - 3) - \phi_4(t)(I_8 - 3) - \phi_4(t)(\Pi_8 - \Pi_8^2 + 2I_8) \right] \frac{1}{\lambda}
\]

Assuming \( W_i \) and \( W_2 \) are constants (Mooney-Rivlin materials) and express the invariants in terms of \( \lambda \) we have

\[
\frac{\sigma'_{\text{uni}}(t)}{\lambda - \frac{1}{\lambda^2}} = \left[ 2W_i + 2\phi(t) + 3\phi_3(t) - 3\phi_3(t) + 2\phi_3(t) - 2\phi_4(t) \right]
+ \left[ 2W_2 + 2\phi(t) - 2\phi(t) + 2\phi_3(t) - 3\phi_4(t) + 3\phi_4(t) \right] \frac{1}{\lambda}
- \left[ \phi_3(t) - \phi_4(t) + 2\phi_4(t) \right] \frac{1}{\lambda^2}
+ \left[ \phi(t) - \phi_3(t) - \phi_4(t) - \phi_4(t) \right] \lambda
+ \left[ \phi(t) - \phi_3(t) - \phi_4(t) \right] \lambda^2
\]

where \( \phi_{ij}(t) \) are functions of time only. Since \( W_i = \text{constant} \), \( W_2 = \text{constant} \), the equation for principal stress difference does not contain those terms with some power of \( \lambda \) other than \( \lambda^0 \) and \( 1/\lambda \) it is required that the coefficient of such terms must vanish, i.e.,

\[
\phi_3(t) - \phi_4(t) + 2\phi_4(t) = 0
\]

\[
\phi_4(t) - \phi_4(t) = 0
\]

\[
\phi_3(t) = 0
\]

\[
\phi_4(t) = 0
\]
\[ 2\phi_{30}(t) - 2\phi_{32}(t) + \phi_{41}(t) - 2\phi_{42}(t) = 0 \]  
\[ \phi_{31}(t) - 2\phi_{32}(t) = 0 \]

from which results

\[ \phi_{30}(t) = \phi_{31}(t) = \phi_{32}(t) = \phi_{40}(t) = \phi_{41}(t) = \phi_{42}(t) = 0 \]

Hence equation (36) is simplified to:

\[ \frac{\sigma_{uni}(t)}{\lambda - \frac{1}{\lambda^2}} = 2\left[ W_1 + \phi_{11}(t) \right] + 2\left[ W_2 + \phi_{10}(t) \right] \frac{1}{\lambda} \]

Thus from Mooney-Rivlin plot one can easily obtain \( \phi_{10}(t) \) and \( \phi_{11}(t) \)
IV. Uniaxial Stress Relaxation Test

Styrene-Butadiene rubber* was used to provide relaxation data. A specimen of circular ring type (outside diameter = 1-5/16"), was cut out from a sheet of thickness 1/8" by means of a rotary cutter. The deviation of the stress field from a uniaxial one due to the bending of the ring (which causes more errors at small extensions than at large extensions) was eliminated by applying two metal pieces of semi-circular shape on the outer surface of both ends of the ring so as to bend the ring in such a way that its gauge section stayed straight (see figure 1).

The test was run in the Instron machine at a constant temperature of -25°F which was controlled by means of a temperature control chamber. The reason why this temperature was chosen is because at this temperature the material used evinces the largest relaxation and thus makes it easy to find the nature of the relaxation functions. In other words, at this temperature those curves in a Mooney-Rivlin plot** (see figure 2) corresponding to different instances of time during stress relaxation do not lie too close so that one can easily evaluate the relaxation functions from this plot.

One hour relaxation was run at different extension ratios. The upper limit of the extension ratio for this test was \( \lambda = 3 \), since the maximum travel range of the Instron cross-head was limited because of the attachment of the temperature control chamber to the Instron. For each extension, instead of using the same ring, an un-prestressed new ring was used. This eliminated the process and time to be spent for recovery of the same specimen.

The travel range of the cross-head of the Instron for certain desired extension ratios was set by the Instron dial gauge whose reading was obtained from the curve of the extension ratio of the ring vs. dial gauge reading. The specimen was stretched to the desired extension ratio at a speed of 20 in./min. and then underwent stress relaxation.

Figure 2 shows how the Mooney-Rivlin plot varies with time up

* The base polymer was S-1502-S of Shell Chemical Company, Torrance, California and vulcanization was by means of dicumyl peroxide only.

** The plot of non-linear shear modulus, \( \mu_{un} \equiv \frac{\sigma_{uni}}{\lambda - \frac{1}{\lambda^2}} \) against \( \frac{1}{\lambda} \).
to one hour, and the following table shows the change with time the
combined relaxation functions \(2\left[w_i + \phi_i(t)\right], 2\left[w_2 + \phi_l(t)\right]\) and the
non-linear shear modulus \(\mu_n(t)\).

<table>
<thead>
<tr>
<th>t(min)</th>
<th>(2\left[w_i + \phi_i(t)\right]) psi</th>
<th>(2\left[w_2 + \phi_l(t)\right]) psi</th>
<th>(\mu_n(t)) psi</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/4</td>
<td>13.0</td>
<td>112.0</td>
<td>125</td>
</tr>
<tr>
<td>1/2</td>
<td>9.8</td>
<td>107.2</td>
<td>117</td>
</tr>
<tr>
<td>1</td>
<td>7.0</td>
<td>103.0</td>
<td>110</td>
</tr>
<tr>
<td>2</td>
<td>5.0</td>
<td>97.0</td>
<td>102</td>
</tr>
<tr>
<td>5</td>
<td>3.2</td>
<td>88.8</td>
<td>92</td>
</tr>
<tr>
<td>10</td>
<td>2.3</td>
<td>82.7</td>
<td>85</td>
</tr>
<tr>
<td>20</td>
<td>1.6</td>
<td>72.4</td>
<td>74</td>
</tr>
<tr>
<td>60</td>
<td>1.0</td>
<td>68.0</td>
<td>69</td>
</tr>
</tbody>
</table>

Figure 3 shows the log-log plots of \(2\left[w_i + \phi_i(t)\right], 2\left[w_2 + \phi_l(t)\right]\) against time. The straightness of the three curves indicates that the
above three quantities vary with the power of \(t\) in the following way:

\[
\begin{align*}
w_i + \phi_i(t) &= 2.35 t^{-0.46885} \\
w_2 + \phi_l(t) &= 72.5 t^{-0.8629} \\
\mu_n(t) &= 167 t^{-0.1046}
\end{align*}
\]

It is noticed that \(w_i + \phi_i(t)\) changes with time faster than \(w_2 + \phi_l(t)\) and \(\mu_n(t)\). Roughly speaking, \(w_i + \phi_i(t)\) is inversely proportional to
the square root of \(t\), whereas \(w_2 + \phi_l(t)\) and \(\mu_n(t)\) vary inversely with
1/10 the power of \(t\).

After the functional forms of \(\phi_i(t), \phi_l(t)\) are known, one can integrate equation (20) by replacing \(t\) by \(\frac{\lambda - 1}{R}\) (\(R = \) constant) for a
constant strain rate tension in any homogeneous stress fields (incom-
pressibility is assumed), which can be used for prediction of the data for
a constant strain rate tension. This will be presented in a subsequent
report.
REFERENCES


Fig. 1. Ring Type Specimen for Uniaxial Stress Relaxation Test.
Fig. 2: Uniaxial Stress Relaxation of SBR for Various Stretch Ratios: Mooney-Rivlin Plot.
Fig. 3. Uniaxial Stress Relaxation of SBR: Time-Dependence of Nonlinear Shear Moduli.

\[ 2[w_i + \phi_i(t)] \]

\( (\text{psi}) \)

\[ \mu_{nn}(t) \]

\( (\text{psi}) \)

\[ 2[w_2 + \phi_2(t)] \]

\( (\text{psi}) \)

\begin{align*}
W_i + \phi_i(t) &= 2.35 t \\
W_2 + \phi_2(t) &= 72.5 t \\
\mu_{nn}(t) &= 167 t
\end{align*}

\( t \ (\text{sec.}) \)