

# Time-dependent response of soft polymers in moderately large deformations

(viscoelasticity/strain measure/rubbers/elastomers)

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**ABSTRACT** We present a theory that 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, by Guth *et al.* (2) on natural rubber, and by us on 1,4-polybutadiene. Chasset and Thirion (3) studied the stress relaxation behavior of specimens of natural and styrene-butadiene rubbers that 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 styrene-butadiene rubber 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 Our own unpublished data as well as the data of Bergen (5) on carbon black filled styrene-butadiene rubber and on samples of poly(vinyl chloride) containing various amounts of plasticizer, the data of Gent (6) on styrene-butadiene rubber, of Valanis and Landel (7) on silica filled poly(dimethyl siloxane) rubber, and of Kawabata (8) on natural and styrene-butadiene rubbers, 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 a finite strain measure such as the Cauchy or Green strain (9, 11, 13). Leaderman *et al.* (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 nonlinear mechanical response of soft (i.e., rubberlike) materials results from strain nonlinearity, 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

$$t^k_l = -p\delta^k_l + 2Gb^k_l \quad [1]$$

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

$$b^k_l = (c^{-1k}_l - \delta^k_l)/2 \quad [2]$$

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

$$c^{-1kl} = G^{KL}x^k_{,K}x^l_{,L} \quad [3]$$

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

$$t_\alpha = \nu^\alpha_k t^k_l \nu'^l_\alpha \quad (\text{no summation on } \alpha) \quad [4]$$

and

$$c^{-1}_\alpha = n^\alpha_k c^{-1k}_l n'^l_\alpha \quad (\text{no summation on } \alpha) \quad [5]$$

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

$$t_\alpha = -p + 2Gb_\alpha \quad [6]$$

where

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

In Eqs. 4 through 7 the  $\{t_\alpha\}$ ,  $\{b_\alpha\}$ , and  $\{c^{-1}_\alpha\}$  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. The principal components (i.e., the eigenvalues) of the two tensors,  $b^k_l$  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

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

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,  $n^k$ .

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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 samples of natural and styrene-butadiene rubbers under various modes of deformation. The agreement between the predictions of their theories and the experimental results were 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

$$\bar{\sigma}_\alpha(t) = -p + 2 \int_0^t G(t-u) \frac{db_\alpha(u)}{du} du \quad [9]$$

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

$$\bar{\sigma}_\alpha(t) = -p + (2/3n) \int_0^t E(t-u) \frac{d\lambda_\alpha^n(u)}{du} du. \quad [10]$$

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

$$W = (2G/n)I_b \quad [11]$$

where  $I_b$  is the first invariant of the generalized strain tensor  $b^i_j$ . Typically, in a moderately large deformation of an unfilled crosslinked rubber the stretch ratio would not exceed about 2.5 in simple tension.

Eq. 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

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

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 nonlinear least squares fitting, from isochronal stress-strain relations crossplotted from stress relaxation measurements in simple tension at different values of strain in moderately large deformations. The expo-

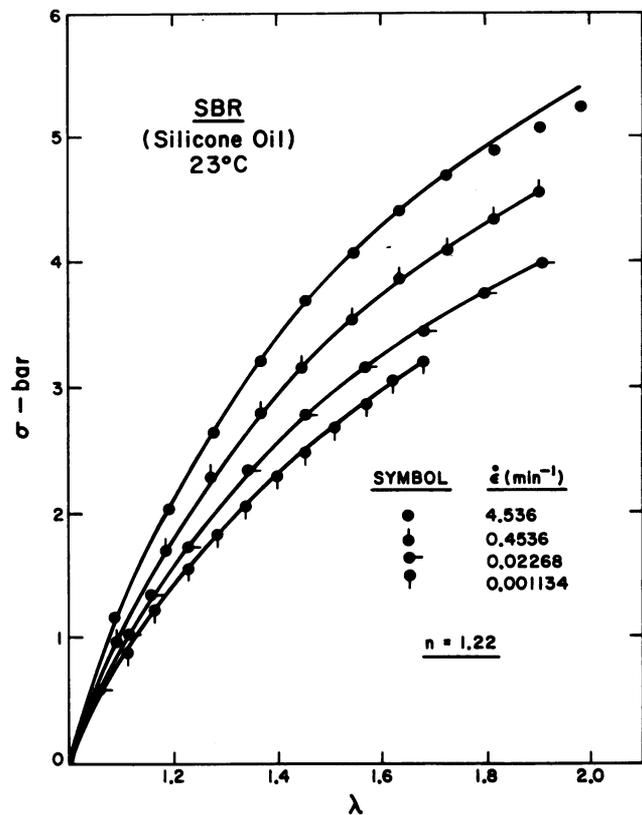


FIG. 1. Stress-strain curves on styrene-butadiene rubber (SBR) at different rates of extension fitted by Eq. 13.

nent  $n$ , 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

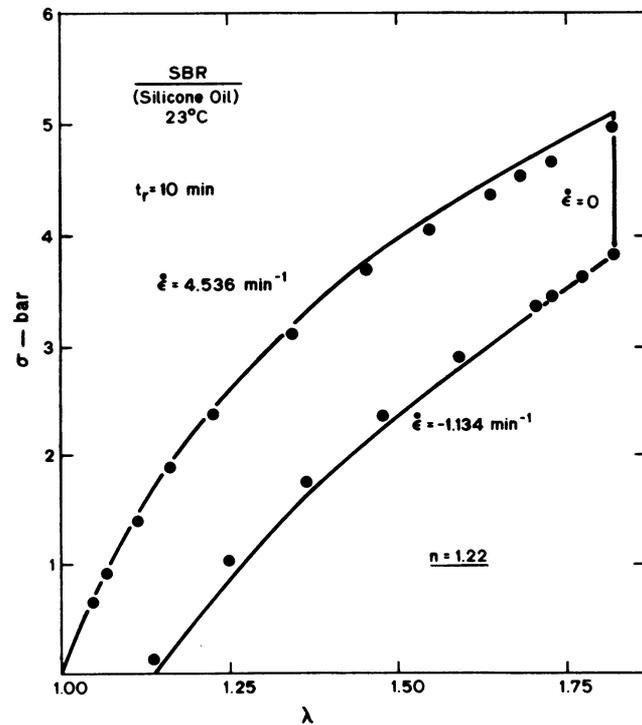


FIG. 2. Response to a trapezoidal strain excitation fitted by Eq. 13. SBR, styrene-butadiene rubber.

constant rate of strain experiments. The experiments were made on specimens of dicumyl peroxide cured styrene-butadiene rubber 1502 having a 100 min tensile modulus of 7.55 bar ( $7.55 \times 10^5$  pascal) at 23°. 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°.

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

$$\bar{\sigma}(t) = (2\dot{\epsilon}/3) \int_0^t E(t-u) [\lambda^{n-1}(u) + 0.5\lambda^{-n/2-1}(u)] du \quad [13]$$

where  $\lambda(u) = 1 + \dot{\epsilon}u$ . 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 ( $\dot{\epsilon} = 0$ ), 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 published 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.

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