Arch. Mech., **52**, 3, pp. 443–479, Warszawa 2000

Application of a constitutive equation for softening, yield and permanent deformation to finite plane simple shear

H. E. HUNTLEY [1], A. S. WINEMAN [2], K. R. RAJAGOPAL [3]

[1] *Department of Mechanical Engineering*
The University of Michigan–Dearborn
Dearbon, MI 48128, USA

[2] *Department of Mechanical Engineering and Applied Mechanics*
The University of Michigan
Ann Arbor, MI 48109, USA

[3] *Department of Mechanical Engineering*
Texas A and M University
College Station, TX 77843, USA

The finite homogeneous simple shear deformation of an incompressible material is considered. The response is modeled with a constitutive equation that reflects a continuous process of microstructural transformation as the deformation increases beyond a threshold value. The original and transformed portions of the material are both taken to respond as incompressible elastic solids. It is shown that the transformation can lead to softening of the response with increasing deformation and to a local maximum in the shear stress-shear strain curve. The existence of permanent deformation after release of the shearing traction is demonstrated. It is confirmed that a process of increasing deformation followed by decreasing deformation to the point of zero shear traction is a dissipative cycle. A special case is then considered in which both the original and transformed materials are assumed to respond as neo-Hookean solids. The critical volume fraction of transforming material at which the shear stress-shear strain curve loses monotonicity is found analytically. Representations are obtained for the dependence of the residual shear deformation on the fraction of transforming material; on the ratio of moduli of the original and transformed materials; and on the maximum shear reached before unloading.

1. Introduction

Considerable attention has been focused on the modeling of stress softening, yield and permanent set in polymeric materials. A constitutive equation was recently proposed by Wineman and Rajagopal [23] that assumes a continuous process of microstructural *conversion* as deformation increases beyond a threshold value. This conversion process entails the rupture of a stress-bearing *microstructural unit*, such as a chain molecule, a crosslink or an entanglement. Upon rupture, the microstructural unit cannot bear any stress. It is possible that a new microstructure forms in place of the original one, with a new unstressed reference configuration.

Several analytical and numerical studies have been conducted using the constitutive relation proposed by WINEMAN and RAJAGOPAL [23]. The constitutive equation has been applied to study the inflation of a circular membrane (WINEMAN and HUNTLEY [22]); the radial deformation of hollow spheres (HUNTLEY, WINEMAN and RAJAGOPAL [5, 7]); and the circumferential shear of a hollow cylinder (HUNTLEY, WINEMAN and RAJAGOPAL [6]). RAJAGOPAL and SRINIVASA [13, 14] have considerably generalized the model to describe the twinning of metals, traditional plasticity and solid-to-solid phase transition. HUNTLEY [3] has used the equation to model the Mullins effect and permanent deformation in vulcanized rubbers. HUNTLEY and WALDRON [4] have compared experimental results for polycarbonate from G'SELL and GOPEZ [1] with the response predicted by the constitutive theory suggested by WINEMAN and RAJAGOPAL [23] for finite plane simple shear. Agreement with measured pre-yield and post-yield response was excellent; a stress peak and subsequent drop was also predicted that conformed well to expectations of the events associated with yield.

In the present work, plane simple shear is studied within the context of the framework suggested by WINEMAN and RAJAGOPAL [23].

2. Constitutive equation

Consider a sample of material undergoing a homogeneous deformation described by $\mathbf{x} = \mathbf{x}(\mathbf{X}, t)$, where $\mathbf{x}$ is the current position of a particle located at $\mathbf{X}$ in the undeformed reference configuration, when $t = 0$. The deformation gradient associated with this mapping is $\mathbf{F} = \partial\mathbf{x}/\partial\mathbf{X}$ and the left Cauchy-Green tensor is given by $\mathbf{B} = \mathbf{F}\mathbf{F}^T$. Assume that there is a range of deformation for which the material behaves as an isotropic, incompressible, nonlinear Green elastic solid. It is well known (e.g., SPENCER [20]) that the Cauchy stress $\mathbf{T}$ for this material takes the form

$$\mathbf{T} = -p\mathbf{I} + 2[W_1^{(1)}\mathbf{B} - W_2^{(1)}\mathbf{B}^{-1}], \tag{2.1}$$

where $-p\mathbf{I}$ is an indeterminate part of the stress due to the constraint of incompressibility. It will be convenient to denote the extra stress by $\mathcal{T} = \mathbf{T} + p\mathbf{I}$. The strain energy per unit volume is $W^{(1)}(I_1, I_2)$, with $I_1 = \mathrm{tr}(\mathbf{B})$ and $I_2 = \mathrm{tr}(\mathbf{B}^{-1})$, the first two invariants of $\mathbf{B}$. Also, $W_1^{(1)} = \partial W^{(1)}/\partial I_1$ and $W_2^{(1)} = \partial W^{(1)}/\partial I_2$.

An activation criterion determines when the original material network begins to undergo microstructural change and form new networks. This criterion is taken to be expressed as a function of the deformation gradient $\mathbf{F}$ which vanishes when microstructural change begins. Material frame indifference, isotropy and incompressibility imply that the activation criterion can be expressed in terms of the invariants of $\mathbf{B}$: $A(I_1, I_2) = 0$.

In general, a proper, fully three-dimensional loading condition has to be considered. Here, however, only a restricted special deformation is considered. For such a deformation, the terms *increasing deformation* and *decreasing deformation* are meaningful, as there is a one-to-one relationship between the measure of the deformation and the scalar parameter s which is introduced below.

Transformation of the original microstructural network is assumed to be continuous with increasing deformation. Introduce a scalar deformation state parameter s whose value is determined by the extent of deformation. It is assumed that it can be expressed in terms of the stretch invariants: $s = s(I_1, I_2)$. The value of s increases as deformation increases. No unique definition of the term "increasing deformation" is proposed here. Instead, as in the previous applications of this constitutive equation (WINEMAN and RAJAGOPAL [23]; HUNTLEY [2, 3]; WINEMAN and HUNTLEY [22]; HUNTLEY, WINEMAN and RAJAGOPAL [5, 6, 7]; HUNTLEY and WALDRON [4]), an appropriate form of s is selected for the deformation process under consideration. Recasting the activation criterion in terms of the state parameter gives $A(I_1, I_2) = s(I_1, I_2) - s_a$. Microstructural conversion is initiated when the state parameter s first reaches the conversion-activation value s_a.

For $s < s_a$, no conversion has yet occurred; thus all material is original and the total stress is given by (2.1). At the current deformation state s, with $s \geq s_a$, stress in the remaining original material is also a function of the current deformation gradient $\mathbf{F}$.

Introduce the scalar-valued conversion rate function $a(s)$. As increasing deformation causes the state parameter to increase beyond $s = s_a$, the conversion rate function determines the amount of network transformation induced by additional deformation. The conversion rate function may have any form respecting the constraints $a(s) = 0$, $s < s_a$ and $a(s) \geq 0$, $s \geq s_a$. The function $a(s)$ must remain non-negative in order that an increase in the parameter s always be associated with additional microstructural change. It is assumed that a is a continuous function of s.

Consider a value of the deformation state parameter $\hat{s} \geq s_a$. It is assumed that a network is formed at this value of the deformation state parameter. Its reference configuration is the configuration of the original material at state $\hat{s}$. It is assumed to be an unstressed configuration for the newly formed network. The subsequent stress in such a material network is a function of the subsequent deformation of the network relative to this unstressed configuration. Define the relative deformation gradient for the material formed at state $\hat{s}$ as $\hat{\mathbf{F}} = \partial \mathbf{x} / \partial \hat{\mathbf{x}}$, where $\hat{\mathbf{x}}$

is the position of the particle in the configuration corresponding to deformation state $\hat{s}$. This gradient compares the neighborhood of a particle in the configuration at state s with the configuration of the new network when it was formed at state $\hat{s}$. The associated left Cauchy-Green tensor is given by $\hat{\mathbf{B}} = \hat{\mathbf{F}}\hat{\mathbf{F}}^T$.

Let it be assumed that the material network formed at state $\hat{s}$ is elastic, isotropic and incompressible. The extra Cauchy stress at state s in a network formed at the deformation state $\hat{s}$ then becomes

$$\mathcal{T}^{(2)} = 2\left[W_1^{(2)}\hat{\mathbf{B}} - W_2^{(2)}\hat{\mathbf{B}}^{-1}\right]. \tag{2.2}$$

Here $W^{(2)} = W^{(2)}(\hat{I}_1, \hat{I}_2)$ is the strain energy density of the material formed at state $\hat{s}$ and subsequently deformed to the state s, while $\hat{I}_1$ and $\hat{I}_2$ are the appropriate invariants of $\hat{\mathbf{B}}$. The strain energy density functions $W^{(1)}$ and $W^{(2)}$ may each be of any form. It is assumed that the single function $W^{(2)}$ governs the strain energy density in each newly formed network. The material defined by (2.1) and (2.2) and having multiple reference configurations is not a simple material in the sense of NOLL [10] (see RAJAGOPAL [12]).

Total current stress in the material is taken as the superposition of the contribution from the remaining material of the original network and the contributions from all network formed at deformation states $\hat{s} \in [s_a, s]$. During a process of increasing deformation the total current stress is given by

$$\mathbf{T} = -p\mathbf{I} + b(s)\mathcal{T}^{(1)} + \int_{s_a}^{s} a(\hat{s})\mathcal{T}^{(2)}d\hat{s}. \tag{2.3}$$

The function $b(s)$ is the volume fraction of the original network material remaining at state s, with $b(s) = 1$, $s \leq s_a$, and $b(s) \in [0,1]$, $s \geq s_a$. The volume fraction $b(s)$ decreases as s increases. The stress $\mathcal{T}^{(1)}$, found from (2.1), is the current stress in the remaining original material. The quantity $a(\hat{s})d\hat{s}$ may be interpreted as the volume fraction of original material that ruptures and reforms as the deformation state increases from $\hat{s}$ to $\hat{s} + d\hat{s}$. The stress $\mathcal{T}^{(2)}$, given by (2.2), is the stress in that portion of newly formed material. With (2.1) and (2.2), Eq. (2.3) can be written in the form

$$\mathbf{T} = -p\mathbf{I} + 2b(s)\left[W_1^{(1)}\mathbf{B} - W_2^{(1)}\mathbf{B}^{-1}\right] + 2\int_{s_a}^{s} a(\hat{s})\left[W_1^{(2)}\hat{\mathbf{B}} - W_2^{(2)}\hat{\mathbf{B}}^{-1}\right]d\hat{s}. \tag{2.4}$$

Equations (2.3) and (2.4) are constitutive equations for incompressible materials and respect the requirements of frame indifference.

Assume that the material has undergone a process of deformation whereby s has increased monotonically, and that the deformation is subsequently reduced, so that s decreases monotonically. Two assumptions are made concerning the process of decreasing the parameter s: (a) there is no further conversion of the original material; (b) there is no reversal of microstructural transformation. These assumptions are made partly for analytical convenience. It may also be said, however, that any more complicated theory governing the reduction of deformation will only be useful when more information concerning real material behavior is available to guide its formulation.

The above requirements imply that $a(s) = 0$ as the parameter s is reduced. Thus the upper limit of the integral in (2.3) becomes fixed at $s = s^*$, the maximum value of the state parameter reached. The volume fraction of remaining original material undergoes no further change, so that $b(s) = b(s^*)$ as the parameter s is reduced. The stress during a reduction from $s = s^*$ then has the form

$$\mathbf{T} = -p\mathbf{I} + b(s^*)\mathcal{T}^{(1)} + \int_{s_a}^{s^*} a(\hat{s})\mathcal{T}^{(2)} d\hat{s}, \tag{2.5}$$

where $\mathcal{T}^{(1)}$ is found from (2.1) and $\mathcal{T}^{(2)}$ is given by (2.2). Equation (2.5) can be written with (2.1) and (2.2) as

$$\mathbf{T} = -p\mathbf{I} + 2b(s^*)\left[W_1^{(1)}\mathbf{B} - W_2^{(1)}\mathbf{B}^{-1}\right] + 2\int_{s_a}^{s^*} a(\hat{s})\left[W_1^{(2)}\hat{\mathbf{B}} - W_2^{(2)}\hat{\mathbf{B}}^{-1}\right] d\hat{s}. \tag{2.6}$$

Equations (2.1), (2.4) and (2.6) represent the complete set of constitutive equations for all deformation processes.

Unhatted kinematic quantities, such as quantities, such as $\mathbf{F}$, $\mathbf{B}$, I_1 and I_2, are referred to as "current" and compare the configuration at the current deformation state s with the initial reference configuration. Kinematic quantities bearing the hat notation ($\hat{}$), such as $\hat{\mathbf{F}}$, $\hat{\mathbf{B}}$, $\hat{I}_1$ and $\hat{I}_2$, are called "relative" quantities. They represent comparison of the configuration at the current state s with the configuration as state $\hat{s}$.

The superscript $(\ )^{(1)}$ appearing in stress quantities such as $\mathcal{T}^{(1)}$ indicates that the stress is in the material with the original microstructure. Such stresses are functions of the current left Cauchy-Green tensor $\mathbf{B}$. The superscript $(\ )^{(2)}$ appearing, for example, in $\mathcal{T}^{(2)}$ indicates stress in a material network formed at the deformation state $\hat{s}$. These stresses are functions of the relative left Cauchy-Green tensor $\hat{\mathbf{B}}$. Unsuperscribed stresses, such as $\mathbf{T}$, are total stresses following the superposition given by (2.3) of stresses in the original and newly formed networks. They are thus functions of the current tensor $\mathbf{B}$ and of the relative tensors $\hat{\mathbf{B}}$ relating the current configuration to each state $\hat{s} \in [s_a, s]$ during increasing s. For a process of increasing deformation, unsuperscribed stresses also depend explicity on the current value of the deformation state parameter s, which appears as the upper limit of integration and as the argument of $b(s)$. During reversal of deformation, unsuperscribed stresses depend explicity on s^*.

The function $W^{(1)}$ denotes the Helmholtz strain energy density in the material with the original network; it is a function of the current stretch invariants I_1 and I_2. The function $W^{(2)}$ is the strain energy density in the material of a subsequently formed network and is a function of the relative invariants $\hat{I}_1$ and $\hat{I}_2$.

Non-dimensionalized quantities bear the tilde notation $\sim$, as $\tilde{\mathbf{T}}$.

For purposes of notational simplicity, none of the functional dependences mentioned above is indicated explicitly when kinematic or stress quantities are written.

3. Formulation

3.1. Kinematics of deformation

Consider a particle of an isotropic, incompressible material undergoing simple shear. The material is subjected to the shearing and normal tractions necessary to induce the isochoric mapping

$$
\begin{aligned}
x_1 &= X_1, \\
x_2 &= X_2 + kX_1, \\
x_3 &= X_3.
\end{aligned} \tag{3.1}
$$

Here, $x_i (i = 1, 2, 3)$ is the current position of the particle located at $X_j (j = 1, 2, 3)$ in the initial reference configuration, and k is the measure of the current amount of shear deformation relative to the reference configuration. It serves as the deformation control parameter. The current deformation gradient is found from (3.1) to be

$$
\mathbf{F}(k) = \begin{bmatrix} 1 & 0 & 0 \\ k & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}. \tag{3.2}
$$

The current left Cauchy-Green tensor is given by

$$
\mathbf{B}(k) = \mathbf{F}(k)\mathbf{F}^T(k) = \begin{bmatrix} 1 & k & 0 \\ k & 1+k^2 & 0 \\ 0 & 0 & 1 \end{bmatrix}. \tag{3.3}
$$

Its inverse is found to be

$$\mathbf{B}^{-1}(k) = \begin{bmatrix} 1+k^2 & -k & 0 \\ -k & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}. \tag{3.4}$$

The invariants of the left Cauchy-Green tensor are

$$I_1(k) = I_2(k) = 3 + k^2. \tag{3.5}$$

3.1.1. State parameter s. In order to evaluate the Cauchy stress tensor $\mathbf{T}$, specific forms will have to be chosen for the deformation state parameter $s(I_1, I_2)$, the conversion rate function $a(s)$ and the volume fraction of original material remaining $b(s)$. The only requirement yet imposed on $s(I_1, I_2)$ has been that it increase monotonically as the deformation increases. In general, $s(I_1, I_2)$ may be represented by any surface above or below the $I_1 - I_2$ plane which displays such monotonicity. It is not the intent of the present work to propose a form for $s(I_1, I_2)$ which would be valid over the entire $I_1 - I_2$ domain. Indeed, the development of such a form would first require the definition of a loading condition similar to that used in plasticity (see RAJAGOPAL and SRINIVASA [15, 16]). This definition is not needed for the present work, as the loading is a simple shear and s increases monotonically with the shear; thus no general definition will be proposed.

As the shear k increases monotonically from $k = 0$, I_1 and I_2, given by (3.5), increase monotonically from the undeformed state $I_1 = I_2 = 3$ along a path defined parametrically by (3.5). The associated point in the $I_1 - I_2$ plane associated with the current shear of the particle moves outward along the straight line $I_1 = I_2$. Thus in the specific case of simple shear, any choice for $s(I_1, I_2)$ which increases monotonically along the line $I_1 = I_2$ is valid. The deformation state parameter may thus be written as a monotonically increasing function of the current shear, $s = s(k)$.

3.2. Increasing deformation

3.2.1. $s < s_a$. For $s < s_a$, no microstructural transformation has yet occurred. The Cauchy stress tensor $\mathbf{T}$ in all the original material can thus be determined from (2.1), (3.3) and (3.4) as

$$\mathbf{T} = -p\mathbf{I} + 2\left\{ W_1^{(1)} \begin{bmatrix} 1 & k & 0 \\ k & 1+k^2 & 0 \\ 0 & 0 & 1 \end{bmatrix} - W_2^{(1)} \begin{bmatrix} 1+k^2 & -k & 0 \\ -k & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \right\}, \tag{3.6}$$

where p is an indeterminate scalar.

3.2.2. $s \geq s_a$. Let k_a denote the shear when $s = s_a$, i.e., $s_a = s(k_a)$. Consider the shear deformation to $\hat{k} > k_a$, which corresponds to state $\hat{s}$ by the relation $\hat{s} = s(\hat{k})$. Let the deformation gradient at state $\hat{s}$ be denoted by $\mathbf{F}(\hat{k})$. Subsequent deformation to the state $s > \hat{s}$ introduces the relative deformation gradient $\hat{\mathbf{F}}(k)$. The relative deformation gradient $\hat{\mathbf{F}}(k)$ of a network formed at state $\hat{s}$ relates its current configuration at state s to its new reference configuration at state $\hat{s}$. It is formed as $\hat{\mathbf{F}}(k) = \partial\mathbf{x}/\partial\hat{\mathbf{x}}$ or $\hat{F}_{ij}(k) = \partial x_i/\partial\hat{x}_j$. Here $\mathbf{x} = (x_i)$ is the current position vector of the particle, corresponding to the deformation state s; $\hat{\mathbf{x}} = (\hat{x}_j)$ is the new reference position vector of the particle, corresponding to state $\hat{s}$. The relative deformation gradient can be constructed as

$$\hat{F}_{ij}(k) = (\partial x_i/\partial X_k)(\partial X_k/\partial\hat{x}_j) \tag{3.7}$$

or

$$\hat{\mathbf{F}}(k) = \mathbf{F}(k)\mathbf{F}^{-1}(\hat{k}). \tag{3.8}$$

From (3.2) one can find

$$\mathbf{F}^{-1}(\hat{k}) = \begin{bmatrix} 1 & 0 & 0 \\ -\hat{k} & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}. \tag{3.9}$$

Equations (3.2), (3.7) and (3.9) then give the relative deformation gradient as

$$\hat{\mathbf{F}}(k) = \begin{bmatrix} 1 & 0 & 0 \\ k-\hat{k} & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}. \tag{3.10}$$

It should be noted that the quantity $(k-\hat{k})$ is the current shear deformation of a network formed at the state $\hat{s}$. The relative left Cauchy-Green tensor $\hat{\mathbf{B}}(k)$ and its inverse become

$$\hat{\mathbf{B}}(k) = \hat{\mathbf{F}}(k)\hat{\mathbf{F}}^T(k) = \begin{bmatrix} 1 & k-\hat{k} & 0 \\ k-\hat{k} & 1+(k-\hat{k})^2 & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{3.11}$$

and

$$\hat{\mathbf{B}}^{-1}(k) = \begin{bmatrix} 1+(k-\hat{k})^2 & \hat{k}-k & 0 \\ \hat{k}-k & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}. \tag{3.12}$$

The invariants of the relative left Cauchy-Green tensor are

$$\hat{I}_1 = \hat{I}_2 = 3 + (k - \hat{k})^2. \tag{3.13}$$

The current extra stress $\mathcal{T}^{(2)}(k-\hat{k})$ in a network element formed at the state of deformation $\hat{s}$ is determined from (2.2), (3.11) and (3.12) as

$$\frac{\mathcal{T}^{(2)}(k-\hat{k})}{2} = W_1^{(2)} \begin{bmatrix} 1 & k-\hat{k} & 0 \\ k-\hat{k} & 1+(k-\hat{k})^2 & 0 \\ 0 & 0 & 1 \end{bmatrix} - W_2^{(2)} \begin{bmatrix} 1+(k-\hat{k})^2 & \hat{k}-k & 0 \\ \hat{k}-k & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}. \tag{3.14}$$

At all states of deformation, the extra stress $\mathcal{T}^{(2)}(k-\hat{k})$ in any remaining original material follows (3.14). From (2.3), (3.6) and (3.14), the total stress during a process of increasing s is found to be

$$\mathbf{T} = -p\mathbf{I} + 2b(s)\left\{ W_1^{(1)} \begin{bmatrix} 1 & k & 0 \\ k & 1+k^2 & 0 \\ 0 & 0 & 1 \end{bmatrix} - W_2^{(1)} \begin{bmatrix} 1+k^2 & -k & 0 \\ -k & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \right\} + 2\int_{s_a}^{s} a(\hat{s}) \left\{ W_1^{(2)} \begin{bmatrix} 1 & k-\hat{k} & 0 \\ k-\hat{k} & 1+(k-\hat{k})^2 & 0 \\ 0 & 0 & 1 \end{bmatrix} - W_2^{(2)} \begin{bmatrix} 1+(k-\hat{k})^2 & \hat{k}-k & 0 \\ \hat{k}-k & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \right\} d\hat{s}. \tag{3.15}$$

3.2.3. Universal relation. The stress tensor $\mathbf{T}$ in (3.15) reveals a distinction between the present constitutive model for materials undergoing microstructural change and models for purely elastic isotropic materials. Discussions can be found in WINEMAN and GANDHI [21] and RAJAGOPAL and WINEMAN [17] of universal relations for isotropic elastic materials. For materials subjected to simple shear deformation, one of these relations reduces to that of RIVLIN [19]:

$$T_{22} - T_{11} = kT_{12}. \tag{3.16}$$

Upon substitution of the appropriate stress components from (3.15) and simplification, the equality (3.16) is seen not to hold: in general,

$$\int_{s_a}^{s} a(\hat{s})(W_1^{(2)} + W_2^{(2)})(k-\hat{k})^2 d\hat{s} \neq k \int_{s_a}^{s} a(\hat{s})(W_1^{(2)} + W_2^{(2)})(k-\hat{k}) d\hat{s}. \tag{3.17}$$

Since the behavior described by the constitutive Eq. (2.3) is not purely elastic, it may be said in general that the applicability of universal relations from elasticity cannot be guaranteed. Indeed, as can be seen from (3.17), such assurance cannot be given even if the constituent extra stresses $\mathcal{T}^{(1)}(k)$ and $\mathcal{T}^{(2)}(k-\hat{k})$ are themselves purely elastic.

3.2.4. Shear stress. Consider the current shear stress $T_{12}(k)$ as the shear deformation increases. It is given by (3.15) as

$$\frac{T_{12}(k)}{2} = b(s)(W_1^{(1)} + W_2^{(1)})k + \int_{s_a}^{s} a(\hat{s})(W_1^{(2)} + W_2^{(2)})(k-\hat{k}) d\hat{s}. \tag{3.18}$$

Note that

$$W_i^{(1)} = W_i^{(1)}(I_1(k), I_2(k)) \qquad (i = 1, 2). \tag{3.19}$$

On using (3.5), this becomes

$$W_i^{(1)} = W_i^{(1)}(3 + k^2, 3 + k^2). \tag{3.20}$$

For simplicity of notation, introduce the quantity

$$\mu^{(1)} = \mu^{(1)}(k^2) = W_1^{(1)}(k^2) + W_2^{(1)}(k^2). \tag{3.21}$$

Similarly,

$$W_i^{(2)} = W_i^{(2)}(\hat{I}_1(k), \hat{I}_2(k)) \tag{3.22}$$

becomes

$$(3.23) \qquad W_i^{(2)} = W_i^{(2)}(3 + (k - \hat{k})^2, 3 + (k - \hat{k})^2),$$

where the relative invariants are as given by (3.13). Introduce the notation

$$(3.24) \qquad \mu^{(2)} = \mu^{(2)}((k - \hat{k})^2) = W_1^{(2)}((k - \hat{k})^2) + W_2^{(2)}((k - \hat{k})^2).$$

Here, $\mu^{(1)}$ is the deformation-dependent shear modulus of the original material, while $\mu^{(2)}$ is the deformation-dependent shear modulus of the material of all subsequently formed networks. It is assumed that these moduli are strictly positive:

$$(3.25) \qquad \mu^{(1)} > 0; \qquad \mu^{(2)} > 0.$$

With the change of notation, (3.18) simplifies to

$$(3.26) \qquad \frac{T_{12}(k)}{2} = b(s)\mu^{(1)}k + \int\limits_{s_a}^{s} a(\hat{s})\mu^{(2)}(k - \hat{k})d\hat{s}.$$

The first term on the right-hand side of (3.26) represents the contribution to the total shear stress of the remaining material of the original network, while the second term is the contribution of all networks formed as the deformation increases. The change of notation given by (3.21) and (3.24) can also be applied to (3.26) to write

$$(3.27) \qquad T_{12}^{(1)}(k) = 2\mu^{(1)}k$$

and

$$(3.28) \qquad T_{12}^{(2)}(k - \hat{k}) = 2\mu^{(2)}(k - \hat{k}).$$

The shear stress in each constituent material is thus an odd function of its shear deformation.

3.3. Monotonicity of response

It is of interest to know whether there are conditions under which the shear response is non-monotonic. The monotonicity of the shear stresss-shear deformaton relation may be studied by inspection of the derivative of the shear stress with respect to the shear deformation. From (3.26), the current shear stress can be written as

$$(3.29) \qquad T_{12}(k) = b(s)T_{12}^{(1)}(k) + \int\limits_{s_a}^{s} a(\hat{s})T_{12}^{(2)}(k - \hat{k})d\hat{s}.$$

Differentiating the total shear stress (3.29) with respect to the current shear k gives

$$\frac{dT_{12}}{dk} = b(s)\frac{dT_{12}^{(1)}(k)}{dk} + \frac{db(s)}{dk}T_{12}^{(1)}(k) + \int_{s_a}^{s} a(\hat{s})\frac{dT_{12}^{(2)}(k-\hat{k})}{dk}d\hat{s}. \tag{3.30}$$

Note that the derivative of the integral in (3.29) with respect to its upper limit vanishes, as it is found from (3.28) that $T_{12}^{(2)}(k-\hat{k}) = 0$ when evaluated at $k = \hat{k}$.

The current volume fraction $b(s)$ of material composed of the original microstructural network is a positive number: the requirement that $b(s) \in [0,1]$ has been stated above. Recall also the requirement that $a(s) > 0$. The moduli $\mu^{(1)}$ and $\mu^{(2)}$ are assumed to be strictly positive, as stated in (3.25). The shear k is taken to be positive, as the material is sheared in the positive sense during loading. The quantity $k - \hat{k}$ must also be positive, as increasing deformation implies that the current shear k is greater than all previous values $\hat{k}$. It can then be seen from (3.27), (3.28) and (3.29) that the shear stresses $T_{12}^{(1)}(k)$ and $T_{12}^{(2)}(k-\hat{k})$ are positive.

It is the aim of the present work to isolate the effects of the microstructural conversion phenomenon from those of any constitutive assumptions implicit in the strain energy functions $W^{(1)}$ and $W^{(2)}$. Toward that end, let us confine attention to a certain class of strain energy density functions. Assume that the shear stress response is monotonic in the shear deformation, both for the original network and for the subsequently formed networks; that is,

$$\frac{dT_{12}^{(1)}(k)}{dk} > 0; \qquad \frac{dT^{(2)}(x)}{dx} > 0 \quad (x = k - \hat{k}). \tag{3.31}$$

Note that the argument of $T_{12}^{(2)}(x)$ is $x = k - \hat{k}$, the shear relative to the reference configuration at deformation state s. However, positiveness of the derivative with respect to this argument implies that the term $dT_{12}^{(2)}(k-\hat{k})/dk$ from (3.30) is also strictly positive.

The constitutive theory of microstructural change assumes that the volume fraction of original remaining network material decreases with increasing deformation:

$$\frac{db(s)}{dk} < 0. \tag{3.32}$$

It follows that

$$T_{12}^{(1)}(k)\frac{db(s)}{dk} < 0. \tag{3.33}$$

If the magnitude of this term becomes great enough to outweigh the positive terms in (3.30), then $dT_{12}/dk < 0$ and a local maximum in the shear stress-shear strain curve develops. Thus it can be seen from (3.30) that the process of network scission and healing introduces the possibility of a loss of monotonicity in the total stress response. Equations (3.29) and (3.30) indicate that a combination of factors could lead to this result: a state of relatively high current shear k; relatively great stiffness of the original network material; and rapid scission of the original material.

3.4. Reversal of deformation

For $s < s_a$, the extra stress is as found from (3.6) and assumes the same value for a given value of k whether shear deformation is increasing or decreasing. Thus when shear has been reversed to $k = 0$, all components of the total stress are returned to zero by appropriate choice of p.

Now consider a process of decreasing shear deformation after the state parameter has reached a value $s^* \geq s_a$. The expressions for $\mathcal{T}^{(1)}(k)$ in (3.6) and $\mathcal{T}^{(2)}(k - \hat{k})$ in (3.14) are still valid during reduction of the current shear from a state of maximum deformation s^*. From (2.5), (3.6) and (3.14), the stress tensor during this process then takes the form

$$
\begin{aligned}
\mathbf{T}(k) = -p\mathbf{I} + 2b(s^*)\Bigg\{ & W_1^{(1)} \begin{bmatrix} 1 & k & 0 \\ k & 1+k^2 & 0 \\ 0 & 0 & 1 \end{bmatrix} \\
& - W_2^{(1)} \begin{bmatrix} 1+k^2 & -k & 0 \\ -k & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \Bigg\} \\
& + 2\int_{s_a}^{s^*} a(\hat{s}) \Bigg\{ W_1^{(2)} \begin{bmatrix} 1 & k-\hat{k} & 0 \\ k-\hat{k} & 1+(k-\hat{k})^2 & 0 \\ 0 & 0 & 1 \end{bmatrix} \\
& - W_2^{(2)} \begin{bmatrix} 1+(k-\hat{k})^2 & \hat{k}-k & 0 \\ \hat{k}-k & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \Bigg\} d\hat{s}.
\end{aligned} \tag{3.34}
$$

Consider the shear stress $T_{12}(k)$ associated with current shear deformation k during reduction of deformation:

$$
\frac{T_{12}(k)}{2} = b(s^*)\mu^{(1)}k + \int_{s_a}^{s^*} a(\hat{s})\mu^{(2)}(k - \hat{k})d\hat{s}. \tag{3.35}
$$

This can be rewritten as

$$\text{(3.36)} \qquad \frac{T_{12}(k)}{2} = \left[b(s^*)\mu^{(1)} + \int\limits_{s_a}^{s^*} a(\hat{s})\mu^{(2)} d\hat{s} \right] k - \int\limits_{s_a}^{s^*} a(\hat{s})\mu^{(2)} \hat{k} d\hat{s}.$$

The first term on the right-hand side of (3.36) represents the contribution to the total stress of the volume fraction $b(s^*)$ of original material remaining at state s^*. The second term is due to stresses in networks that were formed at states $\hat{s}$ during the loading process, $s \in [s_a, s^*]$. Both of these contributions to the current stress show a direct dependence on the current shear k. The final term on the right-hand side of (3.36) is also due to stresses in newly formed networks. However, the only effect that the current shear deformation can have on this term is through the evaluation of the shear modulus $\mu^{(2)}$ at the relative strain invariants $\hat{I}_1(k - \hat{k})$ and $\hat{I}_2(k - \hat{k})$. Even so, one may assume positiveness of the shear modulus at all levels of decreasing deformation. Assume further that the shear modulus is bounded. The conversion rate $a(s)$ has been defined as a non-negative function. The quantity $\hat{k}$ represents the amount of shear corresponding to deformation state $\hat{s} \in [s_a, s^*]$. Since any level of shear $\hat{k}$ is induced by a positive shearing load, it also is positive. Therefore,

$$\text{(3.37)} \qquad \int\limits_{s_a}^{s^*} a(\hat{s})\mu^{(2)} \hat{k} d\hat{s} > 0.$$

This inequality will be useful in the following discussion of the residual state.

3.5. Residual state

3.5.1. Normal tractions. Assume that a material sample, portions of which have undergone microstructural conversion during a process of increasing shear, is returned to its original reference configuration $k = 0$. Then (3.36) and (3.37) imply that negative shearing strains and stresses exist in those portions of the material which formed new networks as the deformation was increased. From (3.36) and (3.37), it is seen that a negative shearing traction whose absolute value is $2 \int\limits_{s_a}^{s^*} a(\hat{s})\mu^{(2)} \hat{k} d\hat{s}$, is necessary to maintain the specimen in the state $k = 0$. Similarly, it can be found from (3.34) that normal tractions $T_{11}(k)$ and $T_{22}(k)$ are also required when the material is returned to its initial configuration. The extra portions of these normal tractions when $k = 0$ are

$$
\begin{aligned}
\mathcal{T}_{11}(0) &= 2b(s^*)(W_1^{(1)} - W_2^{(1)}) + 2\int_{s_a}^{s^*} a(\hat{s})[W_1^{(2)} - W_2^{(2)}(1+\hat{k}^2)]d\hat{s} \\
\mathcal{T}_{22}(0) &= 2b(s^*)(W_1^{(1)} - W_2^{(1)}) + 2\int_{s_a}^{s^*} a(\hat{s})[W_1^{(2)}(1+\hat{k}^2) - W_2^{(2)}]d\hat{s}.
\end{aligned} \tag{3.38}
$$

3.5.2. Permanent set. Conversely, suppose now that the external shear traction is released, so that $T_{12}(k) = 0$. Equations (3.36) and (3.37) imply a residual positive shear deformation $k^{\rm res}$ of the specimen which satisfies

$$
k^{\rm res} = \frac{\displaystyle\int_{s_a}^{s^*} a(\hat{s})\mu^{(2)}\hat{k}d\hat{s}}{b(s^*)\mu^{(1)} + \displaystyle\int_{s_a}^{s^*} a(\hat{s})\mu^{(2)}d\hat{s}} > 0. \tag{3.39}
$$

The original material network is in a state of residual positive shear with respect to the original reference configuration, while material networks formed at deformation states $\hat{s}$ during loading are in various states of residual negative or positive shear with respect to the reference configurations when they were formed. The positive shear stresses in the original material are balanced by negative shear stresses in the subsequently formed material, so that the total shear stress is zero.

3.6. Work done

It is not the purpose of the present work to place the constitutive Eqs. (2.3) and (2.5) within a complete and general thermodynamic framework. It seems reasonable, nonetheless, to expect that the net work done on a specimen be greater than or equal to zero for a mechanical cycle of deformations. Positive net work done indicates a dissipative process. It should be confirmed that the constitutive equations for materials undergoing microstructural change conform to this requirement.

Due to the nature of the simple shear deformation, the only stress that does work is the shearing stress $T_{12}(k)$. Define $T_{12}^{\rm inc}(k)$, given by (3.27) for $k < k_a$ or by (3.26) for $k \geq k_a$, as the shear stress during a process of increasing deformation; $T_{12}^{\rm dec}(k)$, given by (3.35), is defined as the shear stress during a process of decreasing deformation. It will be taken as a sufficient condition for positiveness of the net work done that the shear stress $T_{12}^{\text{dec}}(k)$ as deformation is reversed be less than the corresponding value of $T_{12}^{\text{inc}}(k)$ as deformation increases. This must hold for all values of $k \in [0, k^*]$, where k^* is the level of shear corresponding to deformation state s^*.

For $k \in [0, k_a]$, the difference between $T_{12}^{\text{inc}}(k)$ and $T_{12}^{\text{dec}}(k)$ is formed from (3.27) and (3.35) as

$$\frac{T_{12}^{\text{inc}}(k) - T_{12}^{\text{dec}}(k)}{2} = [1 - b(s^*)]\mu^{(1)}k - \int_{s_a}^{s^*} a(\hat{s})\mu^{(2)}(k - \hat{k})d\hat{s}. \tag{3.40}$$

With $s^* > s_a$, it is known that $1 - b(s^*) > 0$. Strict positiveness of the deformation-dependent shear moduli $\mu^{(1)}$ and $\mu^{(2)}$ has been established in (3.25). All values of $\hat{k}$ in the integral in (3.40) satisfy $\hat{k} > k_a$; thus the term $k - \hat{k} < 0$. It follows that $T_{12}^{\text{inc}}(k) - T_{12}^{\text{dec}}(k) > 0$ for $k \in [0, k_a]$.

For $k \in [k_a, k^*]$, the difference between the two expressions for the shear stress can be formed from (3.26) and (3.35) as

$$\frac{T_{12}^{\text{inc}}(k) - T_{12}^{\text{dec}}(k)}{2} = [b(s) - b(s^*)]\mu^{(1)}k - \int_{s}^{s^*} a(\hat{s})\mu^{(2)}(k - \hat{k})d\hat{s}. \tag{3.41}$$

Since s^* describes the state of maximum deformation reached during the deformation cycle, any current state s satisfies $s < s^*$. Furthermore, any value of the deformation state parameter $\hat{s}$ in the integral in (3.41) satisfies $s < \hat{s}$. The corresponding values of shear give $k - \hat{k} < 0$. It is known that $\mu^{(1)}$ and $\mu^{(2)}$ are positive. Thus $\int_{s}^{s^*} a(\hat{s})\mu^{(2)}(k - \hat{k})d\hat{s} < 0$. The volume fraction of remaining original material $b(s)$ is assumed to decrease monotonically as s increases, so $b(s) - b(s^*) > 0$ and $[b(s) - b(s^*)]\mu^{(1)}k > 0$. It then follows from (3.41) that $T_{12}^{\text{inc}}(k) - T_{12}^{\text{dec}}(k) > 0$ for $k \in [k_a, k^*]$.

The preceding discussion shows that the stress-shear curve for reversal of the shear deformation lies below the curve for increasing shear for all $k \in [0, k^*]$. Thus the cycle of increasing simple shear followed by reduction of shear is a dissipative process when the constitutive equation for microstructural change is employed. This result holds for any valid strain energy density functions $W^{(1)}$ and $W^{(2)}$.

4. Example – Neo-Hookean structure before and after conversion

Let it be assumed that both the original material and the material that is newly formed as deformation increases beyond s_a, are neo-Hookean. Then

$$W^{(1)}(I_1, I_2) = c^{(1)}(I_1 - 3); \qquad W^{(2)}(\hat{I}_1, \hat{I}_2) = c^{(2)}(\hat{I}_1 - 3), \tag{4.1}$$

where $c^{(1)}$ and $c^{(2)}$ are constants. To highlight the role of these constants as moduli in shear, let the notation $\mu^{(1)} = c^{(1)}$ and $\mu^{(2)} = c^{(2)}$ be adopted. It should be emphasized that the restriction to neo-Hookean network response is not at all necessary. Both original and subsequently formed materials are taken as neo-Hookean in order to demonstrate as well as possible the effects of the conversion phenomenon itself on overall mechanical response. To assume differing forms of response in the constituent material networks would lead to mathematical complexity which would cloud this investigation. However, for reasons which are discussed below, the possibility is admitted that the original and newly formed materials have different moduli in shear, that is, that $\mu^{(1)}$ and $\mu^{(2)}$ may not be equal.

4.1. Increasing deformation

4.1.1. $s < s_a$. At levels of deformation satisfying $s < s_a$, no material network has undergone conversion. Thus overall material response is given by that of the original material. From (3.6) and (4.1), the current Cauchy stress for $s < s_a$ is determined as

$$\mathbf{T}^{(1)} = -p\mathbf{I} + 2\mu^{(1)} \begin{bmatrix} 1 & k & 0 \\ k & 1+k^2 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \tag{4.2}$$

where p is an indeterminate scalar. The shear stress component when $s < s_a$ is seen from (4.2) to be

$$T_{12}(k) = T_{12}^{(1)}(k) = 2\mu^{(1)}k. \tag{4.3}$$

4.1.2. $s \geq s_a$. The stress in a material network formed at the deformation state $s \geq s_a$ depends on the current response of the remaining original material and on that of all newly formed networks. From (3.15) and (4.1) the current total Cauchy stress as deformation increases on $s \geq s_a$ is found to be

$$\mathbf{T} = -p\mathbf{I} + 2b(s)\mu^{(1)} \begin{bmatrix} 1 & k & 0 \\ k & 1+k^2 & 0 \\ 0 & 0 & 1 \end{bmatrix} + 2\mu^{(2)} \int\limits_{s_a}^{s} a(\hat{s}) \begin{bmatrix} 1 & k-\hat{k} & 0 \\ k-\hat{k} & 1+(k-\hat{k})^2 & 0 \\ 0 & 0 & 1 \end{bmatrix} d\hat{s}. \tag{4.4}$$

The current shear stress $T_{12}(k)$ is thus

$$\frac{T_{12}(k)}{2} = b(s)\mu^{(1)}k + \mu^{(2)} \int_{s_a}^{s} a(\hat{s})(k - \hat{k})d\hat{s}. \tag{4.5}$$

4.2. State parameter s

It has been stated that any choice for the deformation state parameter $s(k)$ which increases monotonically with k is valid. In a regime of positive current shear $k > 0$, the simplest function which satisfies this requirement is $s = k$. The present work is not concerned with the possible justification of any more complicated form. Therefore, let $s = k$ for the study of simple shear, so that the underformed state is represented by $s = k = 0$.

The forms for $a(s)$ and $b(s)$ discussed below have been introduced by RAJAGOPAL and WINEMAN [18]. The only restriction on the conversion rate function $a(s)$ has been stated in Sec. 2 and is repeated here for convenience:

$$a(s) = 0, \qquad s < s_a; \qquad a(s) \geq 0, \qquad s \geq s_a. \tag{4.6}$$

As in the case of the state parameter $s(I_1, I_2)$, $a(s)$ is chosen as a simple function which satisfies the requirements imposed. Let $s = s_c > s_a$ denote the value of the deformation state parameter at which microstructural transformation is completed. It is assumed that no further conversion occurs as s increases beyond s_c, regardless of the nature of the associated deformation. The maximum deformation must be finite, so s is assumed to vary on the finite domain $s \in [s_a, s_c]$. In examples studied in this work, deformations for values of $s > s_c$ are not considered. Let $a(s)$ be given as the quadratic polynominal

$$a(s) = \begin{cases} 0, & s < s_a \\ \alpha(s - s_a)(s - s_c), & s \in [s_a, s_c] \\ 0, & s > s_c \end{cases} \tag{4.7}$$

where α is a constant. A typical form of $a(s)$ is shown by the dotted line in Fig. 1.

Let C represent the total volume fraction of new network that has been formed when the conversion process is complete:

$$C = \int_{s_a}^{s_c} a(\hat{s})d\hat{s}. \tag{4.8}$$

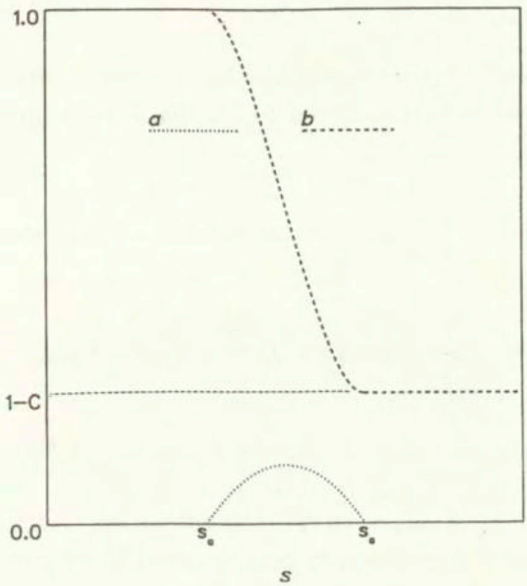

FIG. 1. Typical forms of conversion rate function and volume fraction of original material *versus* deformation state parameter.

It is emphasized that C represents the volume fraction of converted material when the deformation state reaches $s = s_c$. For any other value of $s \in [s_a, s_c]$, the current fraction of converted material is less than C. It follows from (4.7) and (4.8) that

$$\alpha = \frac{-6C}{(s_c - s_a)^3}. \tag{4.9}$$

A simple expression for the volume fraction $b(s)$ of material remaining in the original network can be formed in terms of the above quantities. First impose the restriction $C \le 1$. Assume now that each original material network which undergoes scission is replaced by exactly one new network, in effect, that "conservation of network junctions" holds. This implies that

$$b(s) = 1 - \int_{s_a}^{s} a(\hat{s})d\hat{s}. \tag{4.10}$$

From (4.7), (4.8) and (4.10), it can be seen that $b(s) = 1 - C$ for $s > s_c$. A typical form of $b(s)$ is shown by the dashed line in Fig. 1. The form (4.10) and the assumptions which underlie it are not necessary. The analysis that is carried out here can be easily redone when (4.10) does not hold.

With the substitution $s = k$, (4.7) through (4.10) can be rewritten to give expressions for $a(k)$, C, α and $b(k)$ in terms of k, $k_a = s_a$ and $k_c = s_c$.

4.3. Shear stress-shear relations

Let the shear stress be non-dimensionalized through division by the modulus $\mu^{(1)}$ of the original material. From (4.3), the dimensionless shear stress for $k < k_a$ is

$$\tilde{T}_{12}(k) = \tilde{T}_{12}^{(1)}(k) = 2k. \tag{4.11}$$

When the current level of deformation satisfies $k \geq k_a$, the non-dimensional shear stress is found from (4.5) to be

$$\tilde{T}_{12}(k) = 2b(s)k + 2\tilde{\mu} \int_{s_a}^{s} a(\hat{s})(k - \hat{k})d\hat{s}. \tag{4.12}$$

Here $\tilde{\mu} = \mu^{(2)}/\mu^{(1)}$ is the ratio of the shear moduli of the newly formed and original materials.

For all of the results in this example, the activation criterion is considered to be satisfied when $k_a = 0.5$; conversion is considered to be complete at $k_c = 2.65$. These values are selected solely to facilitate demonstration of the effects implied by the constitutive equation over what is assumed to be a reasonable range of simple shear deformation for highly elastic materials.

Figure 2 shows plots of the shear stress $\tilde{T}_{12}$ *versus* current shear k for various values of C. The solid line corresponds to a standard neo-Hookean model with no microstructural transformation ($C = 0.0$), while the curves lying below it show the results for varying values of the conversion fraction C. Here $\tilde{\mu} = 1.0$ is assumed. All of the plots coincide for $k < k_a$. It can be seen from Fig. 2 that the microstructural transformation which begins when $k = k_a$ induces a softening of the overall mechanical response of the material for all shear deformations $k > k_a$. Moreover, this softening becomes more pronounced as C increases. When $C = 1.0$, a loss of monotonicity of response is evident. This effect is discussed in greater detail below.

Figure 3 shows plots of $\tilde{T}_{12}$ *versus* k at various values of the conversion fraction C when $\tilde{\mu} = 2.0$. These results demonstrate the effect of the conversion process when the shear modulus of the newly formed material networks is greater than that of the original material. The plots display a softening effect similar to that observed in Fig. 2. As was the case above for $\tilde{\mu} = 1.0$, overall response becomes softer with increasing C. However, it is clear from Figs. 2 and 3 that the total loss of stiffness in shear is not as great in the case of $\tilde{\mu} = 2.0$. The higher modulus of the newly formed material leads to higher stress $\tilde{T}_{12}^{(2)}(k - \tilde{k})$ in material formed at state $\hat{s} = \hat{k}$ than is the case when $\tilde{\mu} = 1.0$. This effect tends to counteract the relaxation of stress in the material element which occurs when it undergoes scission and healing at state $\hat{k}$. Hence the total stress $\tilde{T}_{12}(k)$ remains higher for $k > k_a$ when $\tilde{\mu} = 2.0$. Response remains monotonic for all values of C.

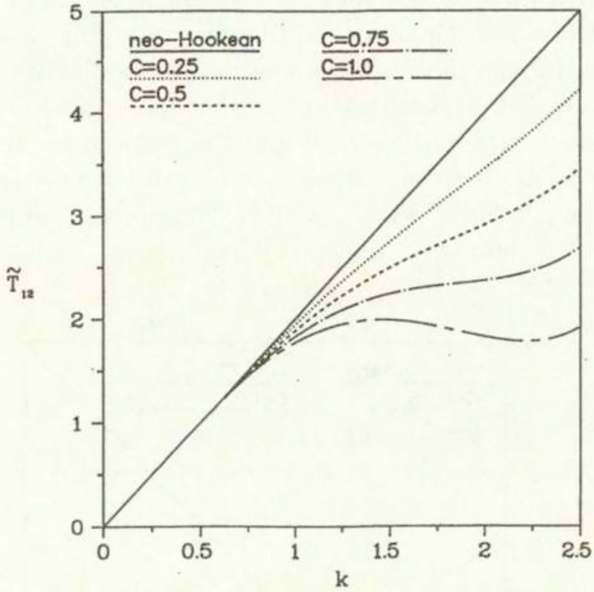

FIG. 2. Shear stress *versus* shear deformation as deformation increases for various conversion fractions, with $\tilde{\mu} = 1.0$, $k_a = 0.5$ and $k_c = 2.65$.

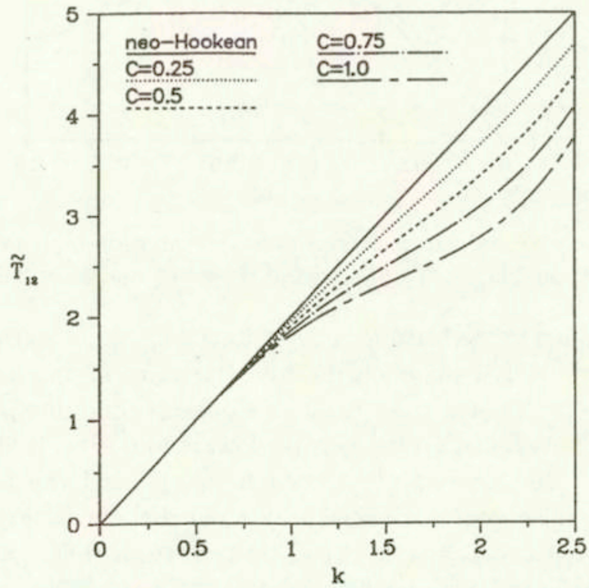

FIG. 3. Shear stress *versus* shear deformation as deformation increases for various conversion fractions, with $\tilde{\mu} = 2.0$, $k_a = 0.5$ and $k_c = 2.65$.

Figure 4 repeats the set of shear stress-shear plots with $\tilde{\mu} = 0.5$. The modulus of newly formed networks is now lower than that of the original network. The general form of the response is similar to that shown in Figs. 2 and 3. As may be anticipated, the reduced stiffness of the material formed at state $\hat{k}$ slows the regeneration of the stress that is released when that material undergoes conversion. Thus both the conversion process itself and the reduced modulus of the newly formed material contribute to the softening of overall response for $k > k_a$. As can be seen from a comparison of Figs. 2 and 4, the reduction of overall stiffness is greater when $\tilde{\mu} = 0.5$ than when $\tilde{\mu} = 1.0$. Furthermore, the loss of monotonicity occurs at a lower value of C for $\tilde{\mu} = 0.5$.

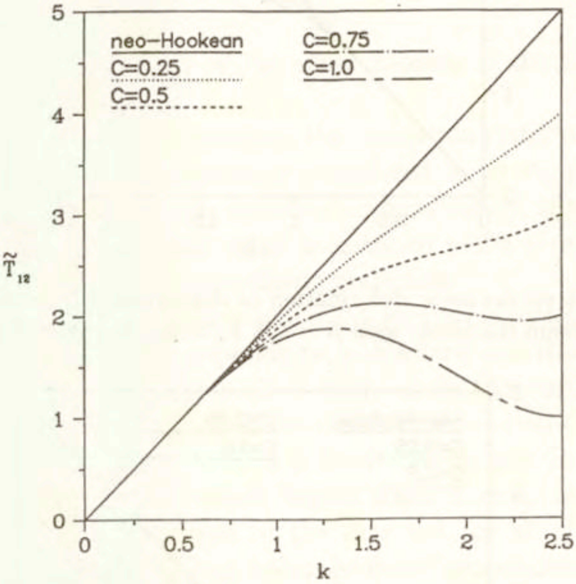

FIG. 4. Shear stress *versus* shear deformation as deformation increases for various conversion fractions, with $\tilde{\mu} = 0.5$, $k_a = 0.5$ and $k_c = 2.65$.

Figures 2 through 4, with values of $\tilde{\mu} \in [0.5, 2.0]$, show softening of response due to the conversion phenomenon. While the tangent modulus for $C = 1.0$ and $\tilde{\mu} = 2.0$ appears greater than the neo-Hookean modulus $\mu^{(1)}$ near $k = 2.5$ (Fig. 3), the secant modulus alvays remains lower than $\mu^{(1)}$. It should be pointed out, however, that the scission of original networks and the formation of new networks in their place does not necessarily have this effect. Figure 5 shows $\tilde{T}_{12}$ *versus* k for $C = 1.0$ and $\tilde{\mu} = 4.0$. It can be seen from this figure that response first softens after the initiation of conversion, as $\tilde{T}_{12}(k)$ is lower than the corresponding stress for the purely neo-Hookean material. As conversion proceeds, though, a hardening behavior becomes apparent, with the shear stress becoming greater than that for the neo-Hookean case. For k near k_a, the rupture of original networks entails release of the stress in those networks, which accounts for the early softening. As the deformation of subsequently formed networks relative to their new reference configurations increases at larger k, the much higher modulus $\mu^{(2)}$ of the new networks ultimately causes the effective stiffness of the material to be greater than in the neo-Hookean case. The assumption of $\tilde{\mu} \gg 1$ in the present constitutive equation may have application to the strain-dependent crystallization of polymers. PETERLIN [11] has studied this phenomenon; additional work has been done by NEGAHBAN [8] and NEGAHBAN and WINEMAN [9]. Henceforth, examples presented in this work will consider only cases of conversion-softening, whereby the secant modulus of the material is reduced by the conversion process.

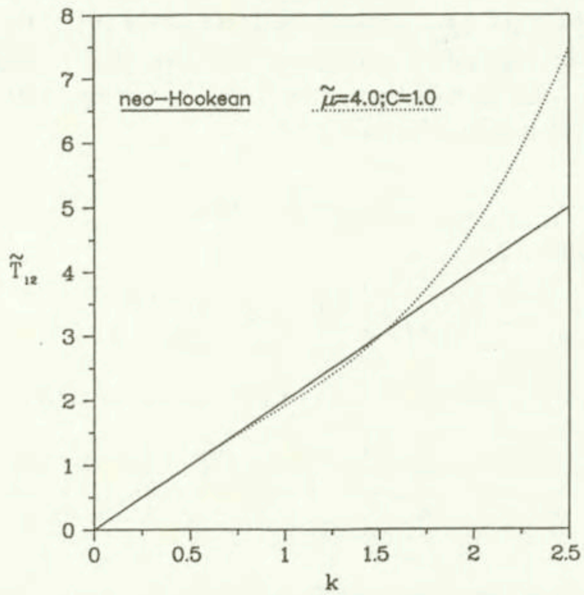

FIG. 5. Shear stress *versus* shear deformation as deformation increases for $\tilde{\mu} = 4.0$, with $C = 1.0$, $k_a = 0.5$ and $k_c = 2.65$.

4.4. Monotonicity of response

The plots of $\tilde{T}_{12}$ *versus* k for $C = 0.25$, $C = 0.5$ and $C = 0.75$ in Fig. 2 all display monotonic response. However, the curve for $C = 1.0$ clearly exhibits a local maximum. It may be assumed that a local maximum first appears at some value of $C \in (0.75, 1.0)$. That the rapid scission of original material networks could lead to such a loss of monotonicity has been discussed above. This situation arises if the negative quantity db/dk achieves a sufficiently great magnitude for some value of k. Since $db/dk = -a$ by (4.10), monotonicity may be lost if a

becomes large enough. When k_a and k_c are held fixed, (4.7) and (4.9) indicate that the fraction of total conversion C acts as a scaling factor of the conversion rate function a for any chosen value of $k \in [k_a, k_c]$. When the conversion fraction reaches a critical value $C = C^{cr}$, a becomes large enough to produce a point of inflection in the stress-shear curve. A value satisfying $C > C^{cr}$ then leads to a local maximum of T_{12} in k.

In order to study the conditions which cause the $\tilde{T}^{12} - k$ relation to become non-monotonic, consider the derivative of the shear stress (4.12) with respect to the shear k for $k \in [k_a, k_c]$:

$$\frac{d\tilde{T}_{12}}{dk} = 2[(1-\tilde{\mu})b(k) + \tilde{\mu} - ka(k)]. \tag{4.13}$$

Here a has the form of (4.7) and b the form of (4.10). To see more clearly the influence of the parameter C on the derivative (4.13), recall from (4.7) the definition of a for $k \in [k_a, k_c]$. The constant α is given by (4.9). When k_a and k_c are prescribed, $a(k)$ can be written as

$$a(k) = Ch_1(k), \tag{4.14}$$

where $h_1(k)$ is defined as

$$h_1(k) = -6\frac{(k-k_a)(k-k_c)}{(k_c-k_a)^3}. \tag{4.15}$$

With the use of (4.14) and (4.15), Eq. (4.13) can be written in the form

$$\frac{d\tilde{T}_{12}}{dk} = 2C\left[(\tilde{\mu}-1)\int\limits_{k_a}^{k} h_1(\hat{k})d\hat{k} - kh_1(k)\right] + 2. \tag{4.16}$$

Equation (4.16) shows that $d\tilde{T}_{12}/dk$ depends on the conversion fraction C and the ratio of moduli $\tilde{\mu}$. Monotonicity is lost if $d\tilde{T}_{12}/dk < 0$ for some $k \in [k_a, k_c]$. Therefore, monotonicity of response depends on both the extent of microstructural transformation and the relation of the material properties $\mu^{(1)}$ and $\mu^{(2)}$.

In determining C^{cr} for different values of $\tilde{\mu}$, it will be convenient to examine three distinct ranges of $\tilde{\mu}$.

First let $\tilde{\mu} = 1$. Equation (4.16) then gives

$$\frac{d\tilde{T}_{12}}{dk} = 2[1 - Ckh_1(k)]. \tag{4.17}$$

The condition for the shear stress-shear deformation curve to have a negative slope for $k \in [k_a, k_c]$ becomes

$$1 - Ckh_1(k) < 0. \tag{4.18}$$

It can be seen from (4.15) that $h_1(k) > 0$ for $k \in (k_a, k_c)$. Thus the condition (4.18) can be written as

$$C > \frac{1}{kh_1(k)}. \tag{4.19}$$

Recall additionally the restriction $C \leq 1$, which has been imposed above.

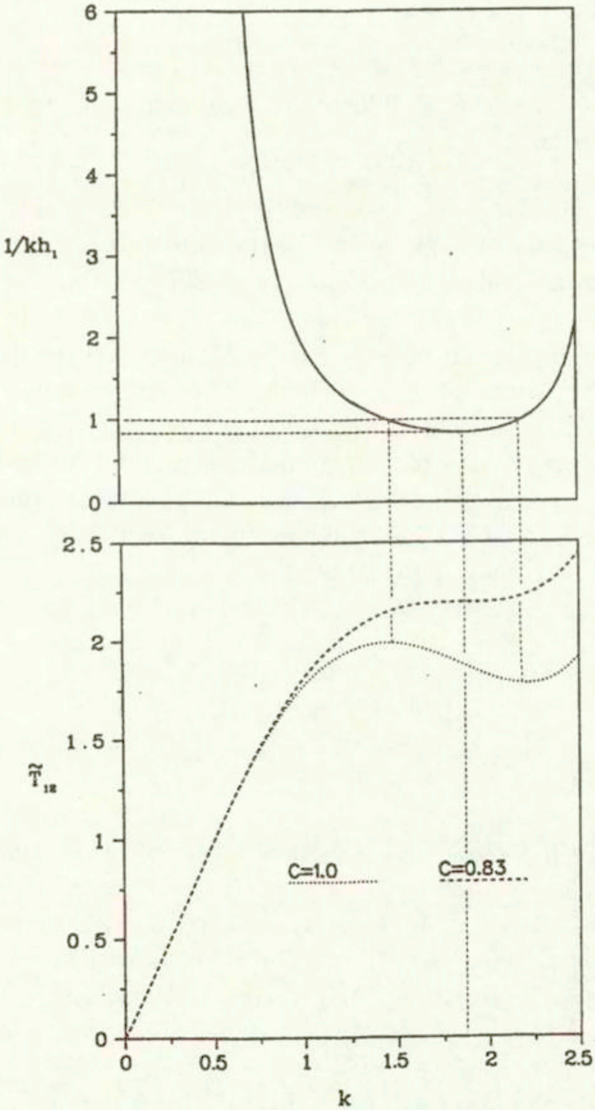

FIG. 6. Shear stress *versus* shear deformation as deformation increases for various conversion fractions and $1/kh_1$ vs. shear deformation, with $\tilde{\mu} = 1.0$, $k_a = 0.5$ and $k_c = 2.65$.

As an illustration of the condition (4.19), Fig. 6 shows $1/kh_1$ *versus* k and $\tilde{T}_{12}$ *versus* k. The quantity $1/kh_1$ is plotted only on the domain $k \in [0.7, 2.5]$; $\tilde{T}_{12}$ is represented by the dotted line for $C = 1.0$ and by the dashed line for $C = 0.83$. It can be seen that the domain on which (4.19) holds corresponds to the domain on which $d\tilde{T}_{12}/dk < 0$ when $C = 1.0$.

Given k_a and k_c and with $\tilde{\mu} = 1.0$, the critical value of C at which a point of inflection in the stress-shear curve first emerges can be found from (4.19) as

$$C^{\text{cr}} = \frac{1}{k^{\text{cr}} h_1(k^{\text{cr}})}, \tag{4.20}$$

where k^{cr} is the value of k at which the local minimum in $1/kh_1$ occurs. It satisfies the condition

$$\frac{d[1/k^{\text{cr}} h_1(k^{\text{cr}})]}{dk} = 0. \tag{4.21}$$

Owing to the simplicity of $h_1(k)$ in (4.15), the numerator of the derivative (4.21) is a quadratic polynomial in k^{cr}. Equation (4.20) can thus be solved in closed form for k^{cr}. With $\tilde{\mu} = 1.0$, this value is found to be $k^{\text{cr}} \approx 1.86$. Equation (4.20) then gives $C^{\text{cr}} \approx 0.83$. It can be seen from the figure that the derivative $d\tilde{T}_{12}/dk$ vanishes at $k = k^{\text{cr}}$ when $C = C^{\text{cr}} = 0.83$. The critical values C^{cr} and k^{cr} are indicated by light dashed lines on the $1/kh_1 - k$ curve of Fig. 6.

For values of $\tilde{\mu} \neq 1.0$, a cubic polynomial arises and a closed-form solution for k^{cr} is not possible. Let $\tilde{\mu} < 1$. It is assumed that there exist values of k at which $d\tilde{T}_{12}/dk = 0$. The critical value of the conversion fraction at which $d\tilde{T}_{12}/dk = 0$ first emerges is found from (4.16) to be

$$C^{\text{cr}} = \frac{1}{k^{\text{cr}} h_1(k^{\text{cr}}) + (1 - \tilde{\mu}) \int\limits_{k_a}^{k^{\text{cr}}} h_1(\hat{k}) d\hat{k}}. \tag{4.22}$$

Since the term $(1 - \tilde{\mu}) \int\limits_{k_a}^{k} h_1(\hat{k}) d\hat{k} > 0$, comparison of (4.20) and (4.22) indicates that C^{cr} is smaller when $\tilde{\mu} < 1.0$ than when $\tilde{\mu} = 1.0$. Less conversion is required to cause the shear stress-shear deformation relation to lose monotonicity if the newly formed networks are softer than the original material.

Consider now the case $\tilde{\mu} > 1$. If $\tilde{\mu}$ is sufficiently large, it can be seen from (4.16) that the positive term $(\tilde{\mu} - 1) \int\limits_{k_a}^{k} h_1(\hat{k}) d\hat{k}$ may dominate, with the result that $d\tilde{T}_{12}/dk > 0$ for any conversion fraction C. On the other hand, if $\tilde{\mu}$ is near unity, a negative slope may be expected somewhere on $k \in [k_a, k_c]$. The existence of a local maximum, then, depends on $\tilde{\mu}$.

Figure 7 shows the shear stress-shear curves produced for $C = 0.75$ when the ratio of shear moduli has the values $\tilde{\mu} = 2.0$, $\tilde{\mu} = 1.0$ and $\tilde{\mu} = 0.5$. It can be seen from the figure that decreasing the shear modulus of the newly formed material relative to the modulus of the original material leads to softer overall response for $k > k_a$. It has been indicated that high stiffness of the original material relative to that of the newly formed networks could lead to a loss of monotonicity. This situation corresponds to low values of $\tilde{\mu}$. While the curves for $\tilde{\mu} = 2.0$ and $\tilde{\mu} = 1.0$ show monotonic response, a local maximum is evident in the stress-shear graph when $\tilde{\mu} = 0.5$. It may be assumed that this loss of monotonicity first occurs at some critical value $\tilde{\mu}^{\mathrm{cr}} \in (0.5, 1.0)$. At $\tilde{\mu} = \tilde{\mu}^{\mathrm{cr}}$, there is a value of $k > k_a$ at which the generation of stress in the relatively soft newly formed material is exactly matched by the relaxation of stress due to the conversion process.

When k_a, k_c and C are prescibed, an analysis analogous to that used to find C^{cr} in (4.13) through (4.22) can be performed to find $\tilde{\mu}^{\mathrm{cr}}$. Equation (4.13) can be rewritten as

$$\frac{d\tilde{T}_{12}}{dk} = 2\{b(k) - ka(k) + \tilde{\mu}[1 - b(k)]\}. \tag{4.23}$$

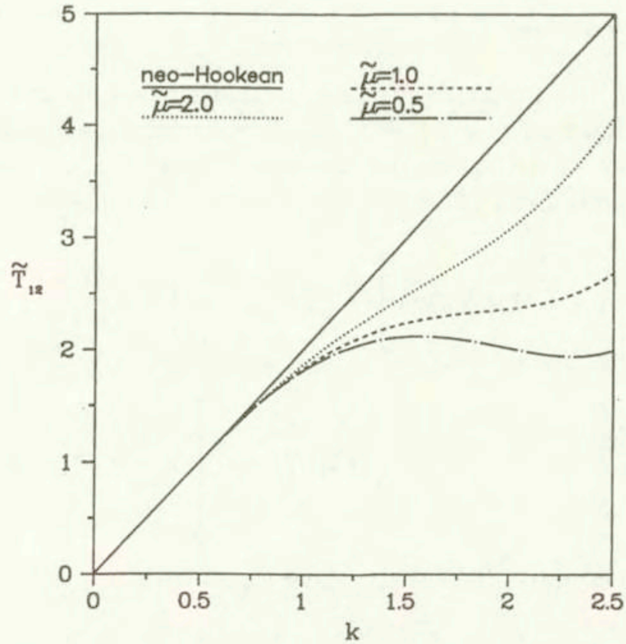

FIG. 7. Shear stress *versus* shear deformation as deformation increases for various shear modulus ratios, with $C = 0.75$, $k_a = 0.5$ and $k_c = 2.65$.

The condition for the stress-shear curve to have a negative slope becomes

$$b(k) - ka(k) + \tilde{\mu}[1 - b(k)] < 0, \tag{4.24}$$

or, since $1 - b > 0$,

$$\frac{ka(k) - b(k)}{1 - b(k)} > \tilde{\mu}. \tag{4.25}$$

For convenience, let

$$h_2(k) = \frac{ka(k) - b(k)}{1 - b(k)}, \tag{4.26}$$

so that (4.25) becomes

$$h_2(k) > \tilde{\mu}. \tag{4.27}$$

The critical value of $\tilde{\mu}$ at which monotonicity of the stress-shear relation is first lost, is given by $h_2(k^{\mathrm{cr}}) = \tilde{\mu}^{\mathrm{cr}}$. The critical shear k^{cr} is found as a solution of $dh_2(k^{\mathrm{cr}})/dk = 0$. For $\tilde{\mu} < \tilde{\mu}^{\mathrm{cr}}$, the release of stress due to network conversion dominates and there is a range of values of $k > k_a$ over which $d\tilde{T}_{12}/dk < 0$. When $a(k)$ has the form of (4.7) and $b(k)$ that of (4.10), $dh_2(k^{\mathrm{cr}})/dk = 0$ cannot be solved for k^{cr} in closed form. A numerical solution is not carried out here.

4.5. Reversal of deformation

Assume that deformation is reversed, so that current shear k decreases after reaching a maximum value k^*. If $k^* < k_a$, the Cauchy stress given by (4.2) holds during the process of decreasing deformation. When $k^* > k_a$, the current stress is formed from (2.5) and (4.4) as

$$\tilde{\mathbf{T}}(k) = -\tilde{p}\mathbf{I} + 2b(k^*)\begin{bmatrix} 1 & k & 0 \\ k & 1+k^2 & 0 \\ 0 & 0 & 1 \end{bmatrix} + 2\tilde{\mu}\int_{k_a}^{k^*} a(\hat{k})\begin{bmatrix} 1 & k-\hat{k} & 0 \\ k-\hat{k} & 1+(k-\hat{k})^2 & 0 \\ 0 & 0 & 1 \end{bmatrix} d\hat{k}. \tag{4.28}$$

In non-dimensional form, the current shear stress is then

$$\tilde{T}_{12}(k) = 2\left[b(k^*)k + \tilde{\mu}\int_{k_a}^{k^*} a(\hat{k})(k-\hat{k})d\hat{k}\right]. \tag{4.29}$$

Equations (4.28) and (4.29) hold regardless of the forms used for $a(k)$ and $b(k)$. The present theory of microstructural transformation assumes that no further conversion occurs during the reversal of deformation. Thus the shear stress in each material network is directly proportional to the shear deformation of the network relative to the state at which it is formed. For the original material, that deformation is the current shear k; in a newly formed element, it is given by $k - \hat{k}$. The roles of these two deformation measures can be seen from (4.28).

It is useful to rewrite (4.29) in the form

$$\tilde{T}_{12}(k) = 2\left\{\left[b(k^*) + \tilde{\mu}\int_{k_a}^{k^*} a(\hat{k})d\hat{k}\right]k - \tilde{\mu}\int_{k_a}^{k^*} a(\hat{k})\hat{k}d\hat{k}\right\}. \tag{4.30}$$

From (4.30), it is clear that there is a straight-line relation between the shear stress $\tilde{T}_{12}$ and the current shear k during reversal of deformation. Making use of the specific forms for $a(k)$ and $b(k)$ proposed in (4.7) and (4.10), Eq. (4.30) can be written as

$$\tilde{T}_{12}(k) = 2\left\{[(1-\tilde{\mu})b(k^*) + \tilde{\mu}]k - \tilde{\mu}\int_{k_a}^{k^*} a(\hat{k})\hat{k}d\hat{k}\right\}. \tag{4.31}$$

It is evident from (4.30) that the slope of the $\tilde{T}_{12} - k$ curve as k decreases depends on the material parameter $\tilde{\mu}$. It can be shown from (4.7), (4.9) and (4.10) that the fraction of original material $b(k^*)$ decreases as C increases; thus the slope of the shear stress-shear deformation curve also depends on C.

Inspection of (4.31) reveals that the slope increases with C when $\tilde{\mu} > 1.0$. A greater value of C means that as deformation increases, a larger volume fraction of material undergoes conversion to newly formed networks with shear modulus $\tilde{\mu}^{(2)} > \tilde{\mu}^{(1)}$. Thus the effective stiffness $\tilde{T}_{12}/k$ increases. The slope of $\tilde{T}_{12}$ *versus* k decreases for larger C when $\tilde{\mu} < 1.0$. As the fraction of conversion C is increased, more original material converts to new networks with modulus $\mu^{(2)} < \mu^{(1)}$. The effective material stiffness decreases and with it the slope of the shear stress-shear deformation curve for decreasing deformation. For $\tilde{\mu} = 1.0$, (4.31) reduces to

$$\tilde{T}_{12}(k) = 2\left[k - \int_{k_a}^{k^*} a(\hat{k})\hat{k}d\hat{k}\right]. \tag{4.32}$$

The slope of the stress-shear curve during reversal of deformation is thus independent of the conversion fraction C when the moduli of original and newly formed networks are equal.

Figure 8 replicates the plots from Fig. 2 of the dimensionless shear stress $\tilde{T}_{12}$ *versus* k for different values of the conversion fraction C, with $\tilde{\mu} = 1.0$. Figure 8 also plots $\tilde{T}_{12}$ *versus* k for the various values of C as deformation is reversed from $k^* = 2.0$ to the residual shear state denoted by k^{res}, where total current shear stress $\tilde{T}_{12} = 0$. Let this process of deformation increasing to $k = k^*$ and subsequently decreasing to $k = k^{\mathrm{res}}$ be referred to as the deformation cycle. The straight-line relation between $\tilde{T}_{12}$ and k during reversal of deformation is evident from the figure. It can also be seen that, for $\tilde{\mu} = 1.0$, the slope of this line is unaffected by C.

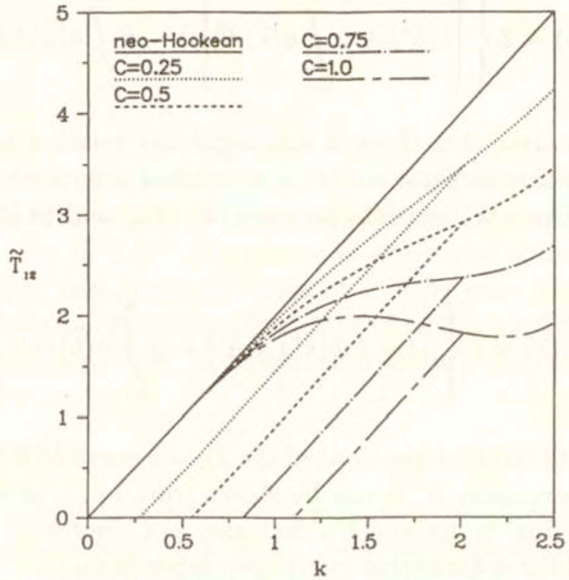

FIG. 8. Shear stress *versus* shear deformation as deformation increases and subsequently decreases for various conversion fractions, with $\tilde{\mu} = 1.0$, $k_a = 0.5$ and $k_c = 2.65$.

Figure 9 shows $\tilde{T}_{12}$ *versus* k at various values of C for the same deformation cycle when $\tilde{\mu} = 2.0$. It can be seen from the figure that the shear stress-shear curve for decreasing deformation is still a straight line, but that the slope is now steeper when the conversion fraction is greater.

Figure 10 shows the shear stress $\tilde{T}_{12}$ *versus* k for the deformation cycle, with various C and with $\tilde{\mu} = 0.5$. Here the slope of the $\tilde{T}_{12} - k$ lines for reversal of deformation is seen to decrease as the conversion fraction C is increased.

4.6. Permanent set

When $k^* < k_a$, all response is elastic and there is no residual deformation when the net external shear traction is returned to zero. Setting $\tilde{T}_{12} = 0$ in (4.30) gives the residual shear deformation for $k^* \geq k_a$ as

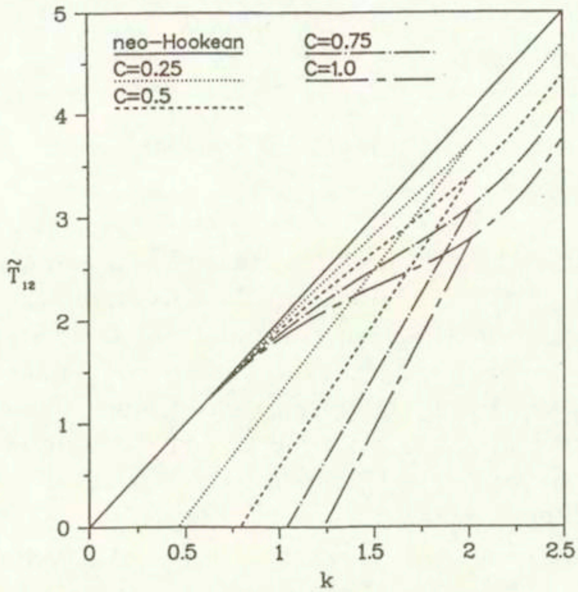

FIG. 9. Shear stress *versus* shear deformation as deformation increases and subsequently decreases for various conversion fractions, with $\tilde{\mu} = 2.0$, $k_a = 0.5$ and $k_c = 2.65$.

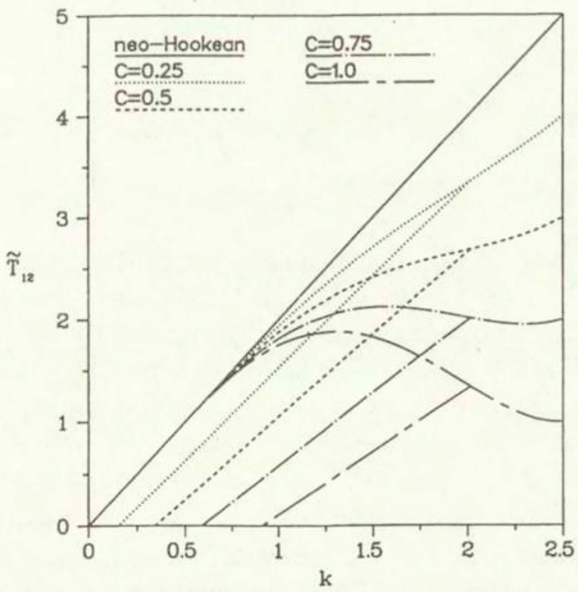

FIG. 10. Shear stress *versus* shear deformation as deformation increases and subsequently decreases for various conversion fractions, with $\tilde{\mu} = 0.5$, $k_a = 0.5$ and $k_c = 2.65$.

$$k^{\text{res}} = \frac{\tilde{\mu} \int\limits_{k_a}^{k^*} a(\hat{k})\hat{k}d\hat{k}}{b(k^*) + \tilde{\mu} \int\limits_{k_a}^{k^*} a(\hat{k})d\hat{k}}. \tag{4.33}$$

Equation (4.33) holds for all admissible forms of $a(k)$ and $b(k)$. Now consider the specific forms given by (4.7) and (4.10). It is known that with k_a and k_c specified, the only parameter affecting $a(k)$ and $b(k)$ at a prescibed value of k is the fraction of conversion C. Thus it can be seen from (4.33) that the residual shear deformation k^{res} depends on three coupled factors: the conversion fraction C; the ratio of original and new moduli $\tilde{\mu}$; and the state of maximum shear k^* reached before reversal of deformation. The partial derivatives of k^{res} with respect to each of these quantities are studied below.

Let $a(k)$ in (4.33) be given by (4.14). The partial derivative of k^{res} with respect to C is found from (4.33) to be

$$\frac{\partial k^{\text{res}}}{\partial C} = \frac{\tilde{\mu} \int\limits_{k_a}^{k^*} h_1(\hat{k})\hat{k}d\hat{k}}{\left[1 + C(\tilde{\mu} - 1) \int\limits_{k_a}^{k^*} h_1(\hat{k})d\hat{k}\right]^2}, \tag{4.34}$$

where $h_1(k)$ is given by (4.15). The inequality $\partial k^{\text{res}}/\partial C > 0$ holds for all admissible values of $\tilde{\mu}$ and for all $k^* \in [k_a, k_c]$. Thus k^{res} increases with C. Greater values of C imply that larger fractions of the original material have undergone conversion and adopted as their reference configurations the states of shear $k \in [k_a, k^*]$. As deformation is reversed from $k = k^*$, an increasing amount of the converted material is sheared in the negative sense relative to its reference configuration, with $k - \hat{k} < 0$. If $k < k_a$ is reached, all converted material elements are in states of negative shear. The negative shear stress $\tilde{T}_{12}^{(2)}(k - \hat{k}) = 2\tilde{\mu}(k - \hat{k})$ associated with the relative deformation of the network formed at state $\hat{k}$ tends to reduce the total positive shear stress $\tilde{T}_{12}(k)$ as current shear k is reduced. Thus the condition $\tilde{T}_{12}(k) = 0$ is satisfied at a higher value of residual shear k^{res}.

The partial derivative of the residual shear k^{res} with respect to $\tilde{\mu}$ is found from (4.32) as

$$(4.35)\qquad \frac{\partial k^{\text{res}}}{\partial \tilde{\mu}} = \frac{b(k^*)\displaystyle\int_{k_a}^{k^*} a(\hat{k})\hat{k}d\hat{k}}{\left[b(k^*) + \tilde{\mu}\displaystyle\int_{k_a}^{k^*} a(\hat{k})d\hat{k}\right]^2}.$$

Inspection of (4.35) reveals that $\partial k^{\text{res}}/\partial\tilde{\mu} > 0$. As in the case of increasing C, the physical reason is the more rapid generation of negative shear stress $\tilde{T}_{12}^{(2)}(k-\hat{k})$ in the converted material as current shear k is reduced from k^*. In the case of increasing $\tilde{\mu}$, however, $\tilde{T}_{12}^{(2)}(k-\hat{k})$ is greater in each newly formed network due to greater stiffness of the newly formed material relative to the original material. Thus $\tilde{T}_{12}(k) = 0$ is satisfied at a larger k^{res} as $\tilde{\mu}$ increases.

Differentiation of k^{res}, given by (4.33), with respect to the maximum shear k^* gives

$$(4.36)\qquad \frac{\partial k^{\text{res}}}{\partial k^*} = \frac{\tilde{\mu}(k^*)\left[k^* + (\tilde{\mu}-1)\displaystyle\int_{k_a}^{k^*} a(\hat{k})(k^*-\hat{k})d\hat{k}\right]}{\left[1 + (\tilde{\mu}-1)\displaystyle\int_{k_a}^{k^*} a(\hat{k})d\hat{k}\right]^2}.$$

In the integrand in the numerator of (4.36), the term $k^* - \hat{k} > 0$, as $k^* > \hat{k}$ for all $\hat{k} \in [k_a, k^*]$. The term $\tilde{\mu} - 1$ may be either positive or negative, depending on the value of $\tilde{\mu}$. All other terms in (4.36) can be shown to be positive. It is thus possible that $\partial k^{\text{res}}/\partial k^* < 0$ for some k^* if $\tilde{\mu}$ is sufficiently small. The larger the value of $k^* \in [k_a, k_c]$, the more total conversion occurs for a given C during the process of increasing deformation. For sufficiently large $\tilde{\mu}$, this causes the condition $\tilde{T}_{12}(k^{\text{res}}) = 0$ to be satisfied at a larger k^{res} as shear is reduced from k^* and hence causes $\partial k^{\text{res}}/\partial k^* > 0$.

The variation of the residual shear k^{res} with each of the three parameters discussed above is presented in Figs. 11 through 14. For all of the figures, shear deformation has been reversed from a maximum of $k^* = 2.0$. Figure 11 shows plots of k^{res} *versus* C for various values of $\tilde{\mu}$. It is evident from the figure that k^{res} increases monotonically with C for all $C \in [0.0, 1.0]$, as given by (4.34). While $\tilde{\mu}$ clearly influences the results shown in Fig. 11, the general trend of increasing residual shear resulting from increasing total microstructural conversion holds for all values of $\tilde{\mu}$ shown.

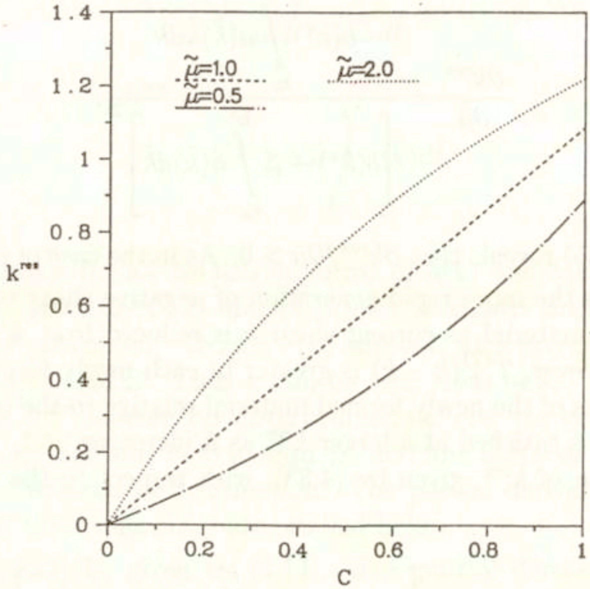

FIG. 11. Residual shear deformation *versus* conversion fraction for various shear modulus ratios, with $k^* = 2.0$, $k_a = 0.5$ and $k_c = 2.65$.

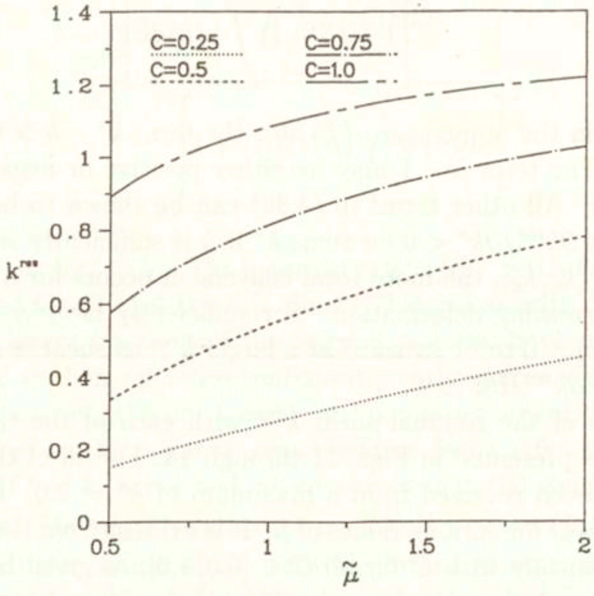

FIG. 12. Residual shear deformation *versus* shear modulus ratio for various conversion fractions, with $k^* = 2.0$, $k_a = 0.5$ and $k_c = 2.65$.

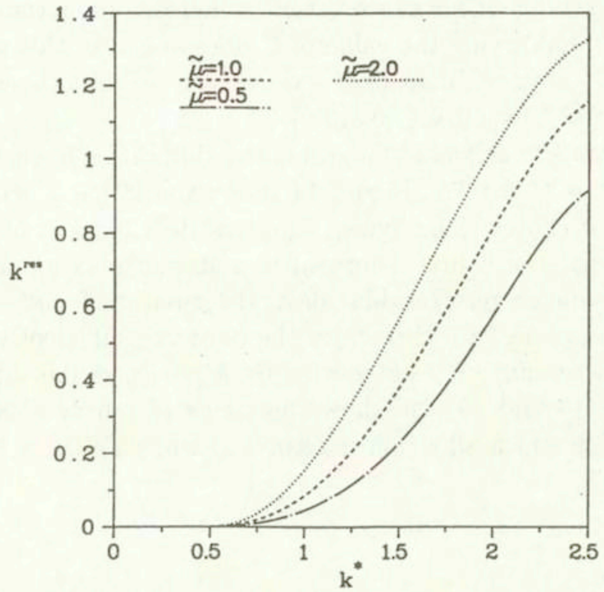

FIG. 13. Redidual shear deformation *versus* maximum shear deformation for various shear modulus ratios, with $C = 0.75$, $k_a = 0.5$ and $k_c = 2.65$.

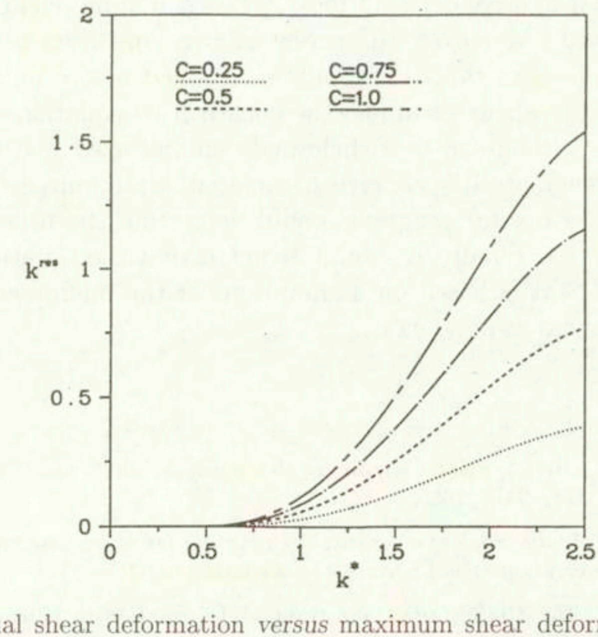

FIG. 14. Residual shear deformation *versus* maximum shear deformation for various conversion fractions, with $\tilde{\mu} = 1.0$, $k_a = 0.5$ and $k_c = 2.65$; when $k^* < k_a$, $k^{\mathrm{res}} = 0.0$.

Figure 12 shows k^{res} *versus* $\tilde{\mu}$ for different values of C. At all values of C considered, the residual shear can be seen to increase monotonically with $\tilde{\mu}$, as indicated by (4.35). Varying the value of C does not alter this general trend, as seen in the figure: greater values of C serve largely to shift the entire relation to a higher range of k^{res} for all $\tilde{\mu} \in [0.5, 2.0]$.

Figure 13 plots k^{res} *versus* k^* for various moduli ratios $\tilde{\mu}$ when the conversion fraction is taken as $C = 0.75$. Figure 14 shows the $k^{\text{res}} - k^*$ curves for various C when $\tilde{\mu} = 1.0$ is chosen. The figures show the development of greater residual shear when the material is first deformed to a greater maximum shear k^*. They also show the region of zero residual shear deformation for $k^* < k_a$. It is thus apparent that the values of $\tilde{\mu}$ chosen for the plots are sufficiently large to ensure monotonically increasing $k^{\text{res}} - k^*$ curves on $k^* \in [k_a = 0.5, 2.5]$. It should be noted that Figs. 13 and 14 also show the range of purely elastic deformation $k \in [0, k_a = 0.5]$ on which all strain is recovered when $\tilde{T}_{12}(k) = 0$.

5. Conclusion

The constitutive equation proposed by Wineman and Rajagopal [23] for materials undergoing microstructural change has proven to be successful in describing qualitatively some of the important responses exhibited by polymeric materials subjected to large deformations. Stress softening, yield and permanent set are all predicted. Moreover, the extent of permanent set is seen to depend on the maximum level of shear deformation attained before unloading. As evidenced by the neo-Hookean example, the constitutive equation can predict this complex response without an overwhelmingly complicated mathematical structure. Relatively few material-property parameters are required, indicating hope that practical experimental programs could determine the necessary constants for a specific material. Finally, it should be noted that the equation is not purely phenomenological, but is based on assumptions of the micromechanics of finite deformation processes in polymers.

References

1. C. G'Sell and J. Gopez, *Plastic banding in glassy polycarbonate under plane simple shear*, J. Mat. Sci., **20**, 3462–3478, 1985.
2. H. E. Huntley, *Applications of a constitutive equation for microstructural change in polymers*, Ph. D. dissertation, The University of Michigan, 1992.
3. H. E. Huntley, *The Mullins effect and residual deformation in uniaxial extension*, submitted for publication 1999.
4. H. E. Huntley and W. K. Waldron Jr., *A two-microstructure constitutive model for polycarbonate in finite plane simple shear*, submitted for publication 1999.

5. H. E. HUNTLEY, A. S. WINEMAN and K. R. RAJAGOPAL, *Chemorheological relaxation, residual stress and permanent set arising in radial deformation of elastomeric hollow spheres*, Math. Mech. Solids, **1**, 3, 267–299, 1996.

6. H. E. HUNTLEY, A. S. WINEMAN and K. R. RAJAGOPAL, *Stress softening, strain localization and permanent set in the circumferential shear of an incompressible elastomeric cylinder*, IMA J. App. Math., **59**, 309–338, 1997.

7. H. E. HUNTLEY, A. S. WINEMAN and K. R. RAJAGOPAL, *Load maximum behavior in the inflation of hollow spheres of incompressible material with strain-dependent damage*, Quart. Appl. Math. [in press].

8. M. NEGAHBAN, *Material symmetry and the evolution of anisotropies in first gradient theories of nonlinear material behavior; Inelasticity; polymer crystallization*, Ph. D. dissertation, The University of Michigan 1998.

9. M. NEGAHBAN and A. S. WINEMAN, *Modeling the mechanical response of a material undergoing continuous isothermal crystallization*, Int. J. Eng. Sci., 1992.

10. W. NOLL, *A mathematical theory of the mechanical behavior of continuous media*, Arch. Rat. Mech. Anal., **2**, 197–226, 1958.

11. A. PETERLIN, *Crystallization from a strained melt or solution*, Polym. Eng. Sci., **16**, 126–137, 1976.

12. K. R. RAJAGOPAL, *On constitutive relations and material modelling in continuum mechanics*, Report 6, Institute for Applied and Computational Mechanics, The University of Pittsburgh 1995.

13. K. R. RAJAGOPAL and A. R. SRINIVASA, *On the inelastic behavior of solids, Part I: Twinning*, Int J. Plast., **11**, 653–678, 1995.

14. K. R. RAJAGOPAL and A. R. SRINIVASA, *Inelastic behavior of materials, Part II: Energetics associated with discontinuous twinning*, Int J. Plast., **13**, 1–35, 1997.

15. K. R. RAJAGOPAL and A. R. SRINIVASA, *Mechanics of the inelastic behavior of materials, Part* I, Int J. Plast., **14**, 945–967, 1998.

16. K. R. RAJAGOPAL and A. R. SRINIVASA, *Mechanics of the inelastic behavior of materials, Part* II, Int. J. Plast., **14**, 968–995, 1998.

17. K. R. RAJAGOPAL and A. S. WINEMAN, *New universal relations for nonlinear isotropic elastic materials*, J. Elast., **17**, 75–83, 1987.

18. K. R. RAJAGOPAL and A. S. WINEMAN, *A constitutive equation for nonlinear solids which undergo deformation-induced microstructural changes*, In. J. Plast., **8**, 385–395, 1992.

19. R. S. RIVLIN, *Large elastic deformations of isotropic materials, VI Further results in theory of torsion, shear and flexure*, Phil. Trans. Royal Soc., **A 242**, 173–195, London 1949.

20. A. J. M. SPENCER, *Continuum mechanics*, Longman Mathematical Texts, New York 1980.

21. A. S. WINEMAN and M. GANDHI, *On local and global universal relations in elasticity*, J. Elast., **14**, 97–102, 1984.

22. A. S. WINEMAN and H. E. HUNTLEY, *Numerical simulation of the effect of damage-induced softening on the inflation of a circular rubber membrane*, Int. J. Solids Structures, **31**, 23, 3295–3313, 1994.

23. A. S. WINEMAN and K. R. RAJAGOPAL, *On a constitutive theory for materials undergoing microstructural changes*, Arch. Mech., **42**, 1, 53–75, 1990.

Received November 05, 1999; new version March 23, 2000.