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Viscoelasticity using reactive constrained solid mixtures

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ABSTRACT

This study presents a framework for viscoelasticity where the free energy density depends on the stored energy of intact strong and weak bonds, where weak bonds break and reform in response to loading. The stress is evaluated by differentiating the free energy density with respect to the deformation gradient, similar to the conventional approach for hyperelasticity. The breaking and reformation of weak bonds is treated as a reaction governed by the axiom of mass balance, where the constitutive relation for the mass supply governs the bond kinetics. The evolving mass contents of these weak bonds serve as observable state variables. Weak bonds reform in an energy-free and stress-free state, therefore their reference configuration is given by the current configuration at the time of their reformation. A principal advantage of this formulation is the availability of a strain energy density function that depends only on observable state variables, also allowing for a separation of the contributions of strong and weak bonds. The Clausius–Duhem inequality is satisfied by requiring that the net free energy from all breaking bonds must be decreasing at all times. In the limit of infinitesimal strains, linear stress–strain responses and first-order kinetics for breaking and reforming of weak bonds, the reactive framework reduces exactly to classical linear viscoelasticity. For large strains, the reactive and classical quasilinear viscoelasticity theories produce different equations, though responses to standard loading configurations behave similarly. This formulation complements existing tools for modeling the nonlinear viscoelastic response of biological soft tissues under large deformations.

1. Introduction

Many biological soft tissues exhibit viscoelastic responses (Fung, 1981), often with relaxation times that depend on the strain magnitude, suggesting a nonlinear viscoelastic behavior (Provenzano et al., 2001; Park and Ateshian, 2006; Duenwald et al., 2009). Though nonlinear viscoelasticity frameworks such as that of Schapery (1969) are used in biomechanics (Provenzano et al., 2002; Duenwald et al., 2010), they have not been adopted widely possibly because existing formulations remain complex. Nonlinear elasticity formulations broadly follow the elegant framework of Coleman and Noll (1963), where the stress response is derived from a free energy potential expressed as a function of the deformation gradient. However, that simplicity has not yet emerged in formulations of viscoelasticity.

Viscoelasticity is a macroscopic manifestation of the dissipation of energy in a loaded continuum. Microscopically, in long chain polymeric materials such as biological soft tissues, the mechanisms causing loss of free energy are typically related to breakage and reforming of weak molecular bonds under loading. Historically, formulations of viscoelasticity have relied on the introduction of internal variables to account for the relaxation mechanism characteristic of viscoelasticity, as first proposed by Green and Tobolsky (1946) for polymer solutions, and subsequently extended by Lubliner (1985) for isotropic solids and by Simo (1987) for anisotropic solids.

Internal state variables, also known as hidden variables, are non-observable by definition. Coleman and Gurtin (1967) provided a formalism for the thermodynamics of continua that employ internal state variables, which influence the free energy and are governed by differential equations involving the state of strain. Holzapfel and Simo (1996) and Holzapfel (1996) explicitly appealed to the formalism of Coleman and Gurtin (1967) in their modeling of solids with linear viscoelasticity.

Other authors, such as Fung (1981) and Puso and Weiss (1998), directly adopted the Boltzmann superposition principle for linear viscoelasticity with nonlinear elastic behavior. Fung (1981) described this type of material response as quasilinear viscoelasticity. These equivalent approaches have become the common standard for modeling viscoelastic tissues in the field of biomechanics.

An alternative approach to this traditional framework has been proposed by Wineman (2009), based on the concept of elastomer scission and cross-linking introduced by Tobolsky (1960), and using the framework of microstructural changes presented by

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Wineman and Rajagopal (1990) and Rajagopal and Wineman (1992).

The main objective of this study is to demonstrate that a complete framework for nonlinear viscoelasticity may be formulated using only observable state variables, where the stress is derived from a free energy potential using the traditional approach of Coleman and Noll (1963). This objective is achieved by reformulating Green and Tobolsky (1946)'s bond-breaking-and-reforming concept in the context of constrained reactive multigenerational solid mixtures (Ateshian, 2007; Ateshian and Ricken, 2010), where bonds are treated as mixture constituents whose breakage and reforming into new bonds is modeled as a reaction governed by the axiom of mass balance.

Permanent strong bonds are responsible for the elastic response and reacting weak molecular bonds that repeatedly break and reform are responsible for the viscous response. Consistent with concepts introduced by Green and Tobolsky (1946) and Tobolsky (1960), and reprised by Wineman (2009), this approach assumes that weak molecular bonds can only sustain their loaded configuration temporarily, eventually breaking and immediately reforming into a new unloaded configuration that coincides with the current configuration of the mixture. Multiple generations of breaking and reforming bonds may exist simultaneously, each with its own reference configuration.

2. Reactive viscoelasticity

2.1. General formulation

The detailed formulation of the reactive mixture viscoelasticity framework is presented in Section S.1 of the Supplemental materials. The key finding from this formulation is that the strain energy density Ψ_r of a viscoelastic solid is dependent on the free energy stored in strong bonds that are permanent (in the absence of damage), and in weak bonds that break and reform in response to the loading. Strong bonds provide the elastic response and weak bonds are responsible for the viscous response.

In the master reference configuration $\mathbf{X}$ of the viscoelastic solid, all bonds are unloaded and intact. Upon loading, weak loaded bonds progressively break over time; when they break, they immediately reform into unloaded weak bonds (Section S.2). Newly formed weak bonds may break and reform again when subjected to further loading. Bonds formed at time $t=u$ have a reference configuration $\mathbf{X}^u$ that coincides with the current configuration of the material at time u, thus $\mathbf{X}^u = \chi(\mathbf{X},u)$, where $\chi(\mathbf{X},t)$ denotes the motion of the solid relative to the master configuration $\mathbf{X}$, which also corresponds to the motion of the strong bonds. Weak bonds that (re)form at time u are described as u-generation bonds.

Different weak bond species may coexist in a viscoelastic solid, which may break and reform at different rates, or in response to different forms of loading. For example, some bonds may only break and reform in response to distortional strain, whereas others may respond to dilatational strain. These distinctions become important in the context of formulating a general viscoelasticity theory as addressed below. However, for simplicity, we start by assuming that there is only one species of weak bonds. All weak bonds can break and reform at any time t; let $w^u(\mathbf{X},t)$ represent the current mass fraction of total weak bonds from this species that were (re)formed at u. By definition, w^u is bounded $(0 \le w^u \le 1)$ and its value is zero for $t \le u$. The bond mass fraction w^u represents an observable (i.e., non-hidden) state variable in this formulation, whose temporal evolution is governed by the axiom of mass balance.

Let the free energy density of strong bonds be denoted by $\Psi_r^e(\theta,\mathbf{F})$, where θ is the absolute temperature and $\mathbf{F} = \partial\chi/\partial\mathbf{X}$ is the deformation gradient of the solid. Similarly, let the free energy density of weak bonds formed at u be denoted by $w^u\Psi_0^b(\theta,\mathbf{F}^u)$, where Ψ_0^b is the free energy density of this weak bond species when all its bonds are intact (Section S.3), and $\mathbf{F}^u = \partial\chi/\partial\mathbf{X}^u$ is the deformation gradient relative to the reference configuration $\mathbf{X}^u$. These two deformation gradients are related by

$$\mathbf{F}(\mathbf{X},t) = \mathbf{F}^u(\mathbf{X},t)\cdot\mathbf{F}(\mathbf{X},u) \tag{1}$$

where $\mathbf{F}(\mathbf{X},u) = \partial\mathbf{X}^u/\partial\mathbf{X}$ is time-invariant. $\mathbf{F}^u(\mathbf{X},t)$ is equivalent to Truesdell and Noll (1992)'s relative deformation gradient $\mathbf{F}_{(u)}(\mathbf{X},t)$. When bond generations occur at discrete times u (i.e., if the strain changes stepwise at discrete time points), the net free energy density of the viscoelastic solid is given by

$$\Psi_r(\theta,\mathbf{F},w^\gamma) = \Psi_r^e(\theta,\mathbf{F}) + \sum_u w^u \Psi_0^b(\theta,\mathbf{F}^u) \tag{2}$$

where w^γ refers generically to all w^u's and the summation is taken over all discrete generations u; all state variables in this expression (i.e., θ, $\mathbf{F}$ or $\mathbf{F}^u$, and w^u) are evaluated at $(\mathbf{X},t)$. In the treatment below, the following notational simplification is adopted: for state variables v, we may use the simplified notation $v(t) \equiv v(\mathbf{X},t)$. For functions of state f, we may use the simplified notations $f(v) \equiv f(v;\mathbf{X},t)$ and $f[v(t)] \equiv f(v;\mathbf{X},t)$ when the time variable must be explicit.

For self-consistency in the summation of Eq. (2), the free energy density Ψ_0^b represents free energy per volume in the reference configuration $\mathbf{X}$. The corresponding expression for the Cauchy stress $\mathbf{T}$ of the viscoelastic solid is derived from this expression using the standard hyperelasticity relation, as shown from the theory of constrained solid mixtures (Ateshian and Ricken, 2010)

$$\mathbf{T}(\theta,\mathbf{F},w^\gamma) = \frac{1}{J}\frac{\partial\Psi_r(\theta,\mathbf{F},w^\gamma)}{\partial\mathbf{F}}\cdot\mathbf{F}^T \tag{3}$$

Substituting Eq. (2) into Eq. (3), employing the relation of Eq. (1) and recognizes that w^u's are state variables independent of the deformation gradient produces

$$\mathbf{T}(\theta,\mathbf{F},w^\gamma) = \mathbf{T}^e(\theta,\mathbf{F}) + \sum_u w^u\mathbf{T}^b(\theta,\mathbf{F}^u) \tag{4}$$

Here, $\mathbf{T}^e(\theta,\mathbf{F})$ is the Cauchy stress resulting from strong bonds

$$\mathbf{T}^e(\theta,\mathbf{F}) = \frac{1}{J}\frac{\partial\Psi_r^e(\theta,\mathbf{F})}{\partial\mathbf{F}}\cdot\mathbf{F}^T \tag{5}$$

where $J = \det\mathbf{F}$, and $\mathbf{T}^b(\theta,\mathbf{F}^u)$ is the Cauchy stress of fully intact weak bonds

$$\mathbf{T}^b(\theta,\mathbf{F}^u) = \frac{1}{J}\frac{\partial\Psi_0^b(\theta,\mathbf{F}^u)}{\partial\mathbf{F}^u}\cdot(\mathbf{F}^u)^T \tag{6}$$

Details of the differentiation are presented in Section S.4.

2.2. Bond kinetics

The time evolution of the bond mass fraction w^u is governed by the kinetics of bond breaking and reforming (Section S.2), constrained by the axiom of mass balance for each bond generation

$$\partial w^u/\partial t = \hat{w}^u \tag{7}$$

where $\hat{w}^u$ is the bond mass fraction supply to generation u from all other generations (Section S.3). Since $\hat{w}^u$ is a function of state, its functional form must be provided by a constitutive model that describes the rate of bond reforming and breaking in response to loading. In general, $\hat{w}^u$ is a function of all the state variables $(\theta,\mathbf{F},w^\gamma)$ in this framework. According to the axiom of mass balance for the mixture, there can be no net change in total bond mass from this species

$$\sum_u \hat{w}^u = 0 \tag{8}$$

Combining Eqs. (7) and (8), integrating the resulting expression and making use of the initial condition when there is only a single