Supplemental Materials

S.1. Constrained Reactive Solid Mixtures

Each mixture constituent is denoted by the superscript γ. We may assume that one of these constituents represents the strong molecular bonds, which do not break in this model, whereas the remaining constituents represent weak molecular bonds. The position of a material point of γ in its reference configuration is denoted by $\mathbf{X}^\gamma$ and the motion of that material point is $\mathbf{x} = \boldsymbol{\chi}^\gamma\left(\mathbf{X}^\gamma, t\right)$. The corresponding velocity is $\mathbf{v}^\gamma = \partial \boldsymbol{\chi}^\gamma / \partial t$ and the deformation gradient is $\mathbf{F}^\gamma = \partial \boldsymbol{\chi}^\gamma / \partial \mathbf{X}^\gamma$. In a constrained mixture, all the constituents move together, implying that $\mathbf{v}^\gamma = \mathbf{v} \; \forall \gamma$, where we have adopted the reference configuration of one of these constituents as the master reference configuration $\mathbf{X}$. Though the velocities $\mathbf{v}^\gamma$ are all the same, the deformation gradients $\mathbf{F}^\gamma$ may be distinct.

The apparent density of γ (mass of γ per volume of the mixture in the current configuration) is denoted by ρ^γ. The axiom of mass balance for constituent γ may be written as

$$\frac{\partial \rho_r^\gamma\left(\mathbf{X}^\gamma, t\right)}{\partial t} = \hat{\rho}_r^\gamma\left(\mathbf{X}^\gamma, t\right) \tag{S.1}$$

where $\rho_r^\gamma = J \rho^\gamma$ is the referential apparent density of γ (mass of γ per volume of the mixture in the master reference configuration $\mathbf{X}$), $\hat{\rho}_r^\gamma = J \hat{\rho}^\gamma$ where $\hat{\rho}^\gamma$ is the mass density supply to γ from reactions with all other constituents, and $J = \det \mathbf{F}$ where $\mathbf{F}$ is the deformation gradient relative to the master reference configuration (Ateshian and Ricken, 2010). A constitutive relation is needed to describe $\hat{\rho}_r^\gamma$ for specific reactive processes. According to the axiom of mass balance for the mixture, the mixture mass supply is zero,

$$\sum_\gamma \hat{\rho}_r^\gamma = 0 \tag{S.2}$$

If each constituent is assumed to be intrinsically incompressible, and there are no pores in the mixture (i.e., the mixture of solids is saturated), then $J^\gamma = \det \mathbf{F}^\gamma = 1$ for all γ and the solid mixture is also incompressible. Both compressible and incompressible mixtures are included in this treatment.

We now adopt the constitutive assumption that the state variables for these constrained reactive mixtures are $(\theta, \mathbf{F}^\gamma, \rho_r^\gamma)$, where θ is the absolute temperature and γ spans all the solid constituents. These constitutive assumptions imply isothermal conditions and no dissipation via the rate of deformation (i.e., no rate-type viscoelasticity). Under this constitutive assumption, and according to Coleman and Noll (1963), the Clausius-Duhem inequality prescribes the following form for the Cauchy stress of a compressible mixture,

$$\mathbf{T} = \frac{1}{J} \sum_\gamma \frac{\partial \Psi_r}{\partial \mathbf{F}^\gamma} \cdot \left(\mathbf{F}^\gamma\right)^T \tag{S.3}$$

leaving the residual dissipation inequality

$$\sum_\gamma \hat{\rho}_r^\gamma \mu^\gamma \leq 0 \tag{S.4}$$

where Ψ_r is the mixture free energy density (free energy per volume of the mixture in the master reference configuration $\mathbf{X}$) and

$$\mu^\gamma = \frac{\partial \Psi_r}{\partial \rho_r^\gamma} \tag{S.5}$$

is the chemical potential of constituent γ (Tinoco et al., 1995; Ateshian and Ricken, 2010). For incompressible mixtures, the corresponding mixture stress is

$$\mathbf{T} = -p\mathbf{I} + \sum_\gamma \frac{\partial \Psi_r}{\partial \mathbf{F}^\gamma} \cdot \left(\mathbf{F}^\gamma\right)^T \tag{S.6}$$

and the residual dissipation inequality is given by

$$\sum_\gamma \hat{\rho}_r^\gamma \bar{\mu}^\gamma \leq 0 \tag{S.7}$$

where $\bar{\mu}^\gamma = \mu^\gamma + p/\rho_T^\gamma$ is the mechano-chemical potential of γ, ρ_T^γ is its true density (mass of γ per volume of γ, which is invariant for intrinsically incompressible constituents), and the pressure p arises from the incompressibility constraint.

In the treatment below, the mixture is assumed to include strong bonds and weak bonds. By definition, strong bonds do not break or reform, thus their mass density supplies $\hat{\rho}_r^\gamma$ are always zero and their corresponding referential mass densities ρ_r^γ remain constant. Therefore, there is no further need to distinguish individual strong bonds γ. For weak bonds, which break and reform, the constituent $\gamma = u$ corresponds to the bond generation that reforms at time u. In particular, the mass supply $\hat{\rho}_r^v$ of the latest generation v, which corresponds to bonds reforming in an unloaded configuration, can be obtained from the net rate at which bonds from all previous generations u are breaking, $\hat{\rho}_r^v = -\sum_{u<v} \hat{\rho}_r^u$.

In a constrained mixture, the deformation gradients of weak bonds $\mathbf{F}^u$ are not independent of each other, since for any other constituent v,

$$\mathbf{F}^v = \frac{\partial \mathbf{x}}{\partial \mathbf{X}^v} = \frac{\partial \mathbf{x}}{\partial \mathbf{X}^u} \cdot \frac{\partial \mathbf{X}^u}{\partial \mathbf{X}^v} = \mathbf{F}^u \cdot \mathbf{F}^{uv} \qquad \text{(S.8)}$$

where $\mathbf{F}^{uv} = \partial \mathbf{X}^u / \partial \mathbf{X}^v$ is invariant by definition. As reported earlier (Ateshian and Ricken, 2010), these constraints imply that the state of stress in each mixture constituent u remains indeterminate, though the mixture state of stress is determinate and given by Eq.(S.3) or Eq.(S.6).

S.2. Bond Reaction

In the master reference configuration $\mathbf{X}$ of the mixture, all the weak bonds are unloaded and intact. Upon loading, these loaded bonds progressively break over time; when they break, they immediately reform into unloaded bonds. Newly formed bonds may break and reform again when subjected to loading. Bonds formed at time u have a reference configuration that coincides with the current configuration of the mixture at time u, thus $\mathbf{X}^u = \boldsymbol{\chi}(\mathbf{X}, u)$, where $\boldsymbol{\chi}$ refers to the motion of the master constituent (e.g., the strong bonds). The relation between $\mathbf{F}^u$ and $\mathbf{F}$ is given in Eq.(1). Weak bonds u do not exist prior to time u, and $\mathbf{F}^u(\mathbf{X}, t)$ represents the deformation gradient of those bonds for all times $t \geq u$. Evidently, $\mathbf{F}^u(\mathbf{X}, u) = \mathbf{I}$, since the proposed model assumes that weak bonds are unloaded at the time they are reformed. (We use $\mathbf{F} = \mathbf{I}$ as shorthand for indicating a strain-free state, even though technically $\mathbf{F}$ is more generally a rotation tensor under strain-free conditions.)

The reaction whereby bonds that were originally formed in generation u break and reform into new unloaded bonds of a subsequent generation v may be written as

$$\mathcal{E}^u \to \mathcal{E}^v \qquad \text{(S.9)}$$

where $\mathcal{E}^\gamma$ denotes the $\gamma-$generation weak bond. This reaction is triggered by the loading of $u-$generation bonds at time v, therefore the kinetics of this reaction must depend on the state of strain (section S.6). The reaction of Eq.(S.9) describes the breaking and reforming of one weak bond species; when multiple bond species exist in a mixture, a similar reaction may describe their breakage, under the assumption that the breaking of one bond species has no influence on the breaking of other species. (More complex frameworks may be constructed by assuming that various bond species interact.)

S.3. Bond Free Energy

In mixture theory, the free energy density of a mixture is evaluated as the sum of the free energy densities of its constituents. Consider that the sum of the free energy densities of all strong bond species is given by $\Psi_r^e(\theta, \mathbf{F})$ and that of all weak molecular bonds of a single species b is $\Psi_r^b(\theta, \mathbf{F}^\gamma, \rho_r^\gamma)$, so that the total mixture free energy density is

$$\Psi_r(\theta, \mathbf{F}, \rho_r^\gamma) = \Psi_r^e(\theta, \mathbf{F}) + \Psi_r^b(\theta, \mathbf{F}^\gamma, \rho_r^\gamma) \qquad \text{(S.10)}$$

The constitutive assumption in this statement is that the free energy Ψ_r^e of strong bonds is independent of the evolving concentration ρ_r^γ of weak bonds. This assumption is adopted for its simplicity, and may be relaxed in a more general framework. To evaluate Ψ_r^b from the sum of free energy densities of all weak bonds in this species, we also adopt the constitutive assumption that the specific free energy (free energy per mass) of each bond generation $\gamma = u$ is given by $\psi^b(\theta, \mathbf{F}^u)$, with the functional form of ψ^b remaining the same for all bond generations u. This dependence of ψ^b on the deformation $\mathbf{F}^u$ should have the usual form of a specific strain energy function: ψ^b should be zero in the absence of strain, and positive for any non-zero strain state, to reflect the physics of energy storage in a bond. Restricting the state variables of ψ^b to θ and $\mathbf{F}^u$ (i.e., excluding ρ_r^γ) is a further simplifying constitutive assumption, implying that the specific free energy of a bond species is independent of the concentration of any generation of that species (or any other bond species in the mixture).

By definition, for each weak bond generation $\gamma = u$, the free energy density of that generation is $\rho_r^u \psi^b(\theta, \mathbf{F}^u)$, thus $\Psi_r^b = \sum_u \rho_r^u \psi^b(\theta, \mathbf{F}^u)$. For convenience, let $\rho_0^b = \sum_u \rho_r^u$ represent the total referential density of weak bonds from species b (where ρ_0^b is a constant), and let $\Psi_0^b = \rho_0^b \psi^b$, then

$$\Psi_r^b = \sum_u \rho_r^u \psi^b(\theta, \mathbf{F}^u) = \sum_u w^u \Psi_0^b(\theta, \mathbf{F}^u) \qquad \text{(S.11)}$$

where w^u is the current mass fraction of bonds from the $u-$generation,

$$w^u = \rho_r^u / \rho_0^b \tag{S.12}$$

Non-dimensional mass fractions w^u are more convenient variables than bond densities ρ_r^u for the purpose of tracking the free energy contribution of each generation, since explicit knowledge of ρ_0^b is not required. Thus, the mass balance relations in Eqs.(S.1) & (S.2) may be rewritten in the form of Eqs.(7) & (8), where

$$\hat{w}^u = \hat{\rho}_r^u / \rho_0^b \tag{S.13}$$

Substituting Eq.(S.11) into Eq.(S.10) produces Eq.(2), which results in the expressions for the stress given in Eqs.(3)-(6). Any desired constitutive relation may be selected for Ψ_r^e and Ψ_0^b, with no obligatory relation between these two functions. For example, if specific weak bond species are insensitive to certain strain invariants, Ψ_0^b may be independent of those, even though Ψ_r^e may depend on them.

It follows from Eqs.(S.5) & (S.10)-(S.11) that the chemical potential of the $\gamma-$generation of a bond species is simply

$$\mu^\gamma = \psi^b \left(\theta, \mathbf{F}^\gamma\right) \tag{S.14}$$

This equivalence between chemical potential and specific free energy occurs because of the simplifying constitutive assumption that ψ^b is not a function of ρ_r^γ. (In physical chemistry of solutions, this same assumption produces *ideal* solutions (Tinoco et al., 1995; Ateshian, 2007); we may thus describe this bond mixture model as an ideal mixture.) Substituting this relation into the residual dissipation inequality in Eq.(S.4), making use of Eqs.(S.2) & (S.13), recognizing that $\hat{\rho}_r^\gamma = 0$ for strong bonds, and recalling that the bond free energy of the youngest forming generation v is zero, $\psi^b \left(\theta, \mathbf{F}^v = \mathbf{I}\right) = 0$, produces

$$\sum_{u<v} \hat{w}^u \psi^b \left(\theta, \mathbf{F}^u\right) \leq 0 \tag{S.15}$$

This relation implies that the net free energy from all breaking bonds must be decreasing at all times. By construction (for stability), the bond specific free energy $\psi^b \left(\theta, \mathbf{F}^\gamma\right)$ is always positive. Therefore, to satisfy the Clausius-Duhem inequality for arbitrary deformation histories $\mathbf{F}^u(t)$, it is necessary and sufficient to let $\hat{w}^u \leq 0$ for all $u < v$ (i.e., for all breaking bond generations).

For incompressible mixtures, the equivalent relation for the stress stems from Eq.(S.6),

$$\mathbf{T}\left(\theta, \mathbf{F}^\gamma, \rho_r^\gamma\right) = -p\mathbf{I} + \mathbf{T}^e\left(\theta, \mathbf{F}^s\right) + \sum_\gamma w^\gamma \mathbf{T}^b\left(\theta, \mathbf{F}^\gamma\right) \tag{S.16}$$

where the functional forms for $\mathbf{T}^e$ and $\mathbf{T}^b$ are also given in Eqs.(5)-(6), with $J = 1$. The dissipation inequality of Eq.(S.7) similarly reduces to Eq.(S.15), by recognizing that ρ_T^γ appearing in the expression for $\bar{\mu}^\gamma$ is the same for all bond generations of a given bond species, and making use of Eq.(S.2) to show that $\sum_\gamma \hat{\rho}_r^\gamma \bar{\mu}^\gamma = \sum_\gamma \hat{\rho}_r^\gamma \mu^\gamma$.

The relation of Eq.(S.11) now shows that the bond free energy density Ψ_r^b reduces to zero when the deformation remains constant for a sufficiently long time, since w^u's of all but the youngest generation $(u < v)$ reduce to zero over time; though w^v of the youngest generation increases to unity, the corresponding $\Psi_0^b\left(\theta, \mathbf{F}^v\right)$ of that generation is equal to zero by definition, since $\mathbf{F}^v = \mathbf{I}$. Therefore, the mixture free energy Ψ_r reduces to the elastic free energy Ψ_r^e of the polymer species under a sustained constant deformation. Conversely, upon instantaneous application of a deformation relative to this steady-state condition, we find that $\Psi_r = \Psi_r^e + \Psi_0^b$, since $w^u = 0$ for $u < v$, $w^v = 1$ and $\mathbf{F}^v \neq \mathbf{I}$ at that instant. Thus, $\Psi_r^e + \Psi_0^b$ is the maximum strain energy density that can be stored in the mixture under instantaneous deformation.

S.4. Differentiation

When the free energy density Ψ_0^b is expressed as a function of $\mathbf{F}^u(t) = \mathbf{F}(t) \cdot \mathbf{F}^{-1}(u)$, differentiating it with respect to $\mathbf{F}$ produces the chain rule

$$\frac{\partial \Psi_0^b}{\partial \mathbf{F}} = \frac{\partial \Psi_0^b}{\partial \mathbf{F}^u} : \frac{\partial \mathbf{F}^u}{\partial \mathbf{F}} \tag{S.17}$$

Since

$$\frac{\partial \mathbf{F}^u}{\partial \mathbf{F}} = \mathbf{I} \underline{\otimes} \mathbf{F}^{-T}(u) \tag{S.18}$$

it follows that

$$\frac{\partial \Psi_0^b}{\partial \mathbf{F}} = \frac{\partial \Psi_0^b}{\partial \mathbf{F}^u} \cdot \mathbf{F}^{-T}(u) \tag{S.19}$$

Therefore, the Cauchy stress is

$$\mathbf{T}^b\left(\theta, \mathbf{F}^u\right) = J^{-1} \frac{\partial \Psi_0^b}{\partial \mathbf{F}} \cdot \mathbf{F}^T = J^{-1} \frac{\partial \Psi_0^b}{\partial \mathbf{F}^u} \cdot \left(\mathbf{F}^u\right)^T \tag{S.20}$$

and the second Piola-Kirchhoff stress is

$$\begin{aligned}\mathbf{S}^b\left(\theta,\mathbf{F}^u\right) &= \mathbf{F}^{-1}\cdot\frac{\partial\Psi_0^b}{\partial\mathbf{F}} \\ &= \mathbf{F}^{-1}\left(u\right)\cdot\left(\mathbf{F}^u\right)^{-1}\cdot\frac{\partial\Psi_0^b}{\partial\mathbf{F}^u}\cdot\mathbf{F}^{-T}\left(u\right)\end{aligned} \tag{S.21}$$

When the free energy density Ψ_0^b is expressed as a function of $\mathbf{C}^u = \left(\mathbf{F}^u\right)^T\cdot\mathbf{F}^u$, then

$$\frac{\partial\Psi_0^b}{\partial\mathbf{F}^u} = 2\mathbf{F}^u\cdot\frac{\partial\Psi_0^b}{\partial\mathbf{C}^u} \tag{S.22}$$

so that

$$\mathbf{T}^b\left(\theta,\mathbf{F}^u\right) = J^{-1}\mathbf{F}^u\cdot 2\frac{\partial\Psi_0^b}{\partial\mathbf{C}^u}\cdot\left(\mathbf{F}^u\right)^T \tag{S.23}$$

and

$$\mathbf{S}^b\left(\theta,\mathbf{F}^u\right) = \mathbf{F}^{-1}\left(u\right)\cdot 2\frac{\partial\Psi_0^b}{\partial\mathbf{C}^u}\cdot\mathbf{F}^{-T}\left(u\right) \tag{S.24}$$

Evidently, the expressions for the Cauchy stress, Eqs.(S.20) & (S.23), are more compact than those for the 2nd Piola-Kirchhoff stress, Eqs.(S.21) & (S.24), when evaluating these quantities as a function of the relative deformation gradient $\mathbf{F}^u$ or relative right Cauchy-Green tensor $\mathbf{C}^u$.

The expression for reactive quasilinear viscoelasticity in Eq.(18) may be rewritten in terms of the second Piola-Kirchhoff stress as

$$\begin{aligned}\mathbf{S}\left[\mathbf{F}\left(t\right)\right] &= \mathbf{S}^e\left[\mathbf{F}\left(t\right)\right] + g\left(t\right)\mathbf{S}^b\left[\mathbf{F}\left(t\right)\right] \\ &\quad - \int_{0^+}^{t}\dot{g}\left(t-u\right)\mathbf{S}^b\left[\mathbf{F}^u\left(t\right)\right]du\end{aligned} \tag{S.25}$$

where $\mathbf{S}^b\left[\mathbf{F}^u\left(t\right)\right]$ is given in Eq.(S.21) or Eq.(S.24).

S.5. Step Deformation

Consider a reactive viscoelastic material which is at rest for all $t \leq 0$, and subjected to a step deformation where $\mathbf{F}\left(\mathbf{X},t\right) = H\left(t\right)\mathbf{F}_0\left(\mathbf{X}\right)$. For this deformation history there are only two weak bond generations, $u = -\infty$ (the generation initially at rest) and $v = 0^+$ (the latest generation, formed starting at the time of loading), with $\mathbf{F}^u\left(\mathbf{X},t\right) = H\left(t\right)\mathbf{F}_0\left(\mathbf{X}\right)$ and $\mathbf{F}^v\left(\mathbf{X},t\right) = \mathbf{I}$. Substituting these expressions into Eq.(4) and recognizing that $\mathbf{T}^b\left[\mathbf{I}\right] = \mathbf{0}$ produces

$$\mathbf{T} = H\left(t\right)\left(\mathbf{T}^e\left[\mathbf{F}_0\right] + w^u\left(\mathbf{X},t\right)\mathbf{T}^b\left[\mathbf{F}_0\right]\right) \tag{S.26}$$

The mass fraction w^u of breaking bonds is obtained by solving Eq.(7) subject to the initial condition $w^u\left(0^+\right) = 1$ (all weak bonds are initially intact). Similarly, the mass fraction w^v of reforming bonds is solved with the initial condition $w^v\left(0^+\right) = 0$ (no weak bonds have started reforming immediately upon loading). Thus, $w^u\left(0^+\right) + w^v\left(0^+\right) = 1$; combining this initial condition with the mass balance for the mixture, Eq.(S.2), produces

$$w^u\left(t\right) + w^v\left(t\right) = 1\,,\quad t > 0 \tag{S.27}$$

Under this step loading configuration it follows that $w^u\left(t\to\infty\right) = 0$ as $w^v\left(t\to\infty\right) = 1$, when the reaction of Eq.(S.9) terminates. Therefore, according to this result and Eq.(S.26), the bond mass fraction $w^u\left(t\right)$ is equivalent to the reduced relaxation function $g\left(t\right)$ in response to this step deformation, with $\mathbf{T}\left(t\right) = \mathbf{T}^e\left[\mathbf{F}_0\right] + g\left(t\right)\mathbf{T}_b\left[\mathbf{F}_0\right]$ for $t > 0$. Specifically, the stress rises initially to $\mathbf{T}\left(0^+\right) = \mathbf{T}^e\left[\mathbf{F}_0\right] + \mathbf{T}^b\left[\mathbf{F}_0\right]$ and eventually relaxes to $\mathbf{T}\left(t\to\infty\right) = \mathbf{T}^e\left[\mathbf{F}_0\right]$.

In the classical quasilinear viscoelasticity framework, a step deformation with $\mathbf{F}\left(\mathbf{X},t\right) = H\left(t\right)\mathbf{F}_0\left(\mathbf{X}\right)$ produces $\mathbf{S}^b\left[\mathbf{F}\left(u\right)\right] = H\left(u\right)\mathbf{S}^b\left[\mathbf{F}_0\right]$. Substituting this expression into Eq.(25) and performing the integration produces $\mathbf{S}\left(t\right) = \mathbf{S}^e\left[\mathbf{F}_0\right] + g\left(t\right)\mathbf{S}^b\left[\mathbf{F}_0\right]$ for $t > 0$. Using Eq.(26), the corresponding Cauchy stress is $\mathbf{T}\left(t\right) = \mathbf{T}^e\left[\mathbf{F}_0\right] + g\left(t\right)\mathbf{T}^b\left[\mathbf{F}_0\right]$, which is identical to the expression from reactive quasilinear viscoelasticity. Therefore, in the special case of a prescribed step deformation, the two frameworks produce the same response. This equivalence does not hold under general conditions.

S.6. Effect of Strain on Breaking of Bonds

At any time $t \geq u$, there may be multiple bond generations γ of a bond species that are breaking ($\gamma < u$) while the $u-$generation is forming in its reference configuration (Figure 1). The $u-$generation bonds may start to break at time $v > u$ if $\mathbf{F}^u\left(v\right)$ produces a strain whose nature is constitutively assumed to cause breakage of that bond species. For example, it may be assumed that only distortional strains cause a specific bond species to break, whereas another bond species may break only in response to dilatational strains.

Criscione et al. (2000) proposed an invariant basis for natural (or Hencky) strain ($\boldsymbol{\eta} = \ln\mathbf{V}$ in the spatial frame, where $\mathbf{V}$ is the left stretch tensor), where the first invariant, $K_1 = \operatorname{tr}\boldsymbol{\eta} = \ln J$, measures only the amount of dilatation; and the second invariant, $K_2 = |\mathrm{dev}\,\boldsymbol{\eta}|$, measures only the amount of distortion. For a bond species that breaks only when subjected to distortional strain, the forming $u-$generation will start to break at time v only if $K_2^u\left(v\right) > 0$, where K_2^u is the value of the K_2 invariant evaluated from $\mathbf{F}^u$. Thus, K_2^u measures the distortional strain of $u-$generation bonds relative to their reference configuration. However, if $K_2^u\left(v\right) = 0$, the $u-$generation will continue to form at time v. Therefore, the value of $K_2^u\left(t\right)$ at any time $t > u$ may serve as the trigger for switching the $u-$generation from a forming to a breaking generation.

Similarly, if a different bond species breaks and reforms only in response to dilatational strain, we may choose $|K_1^u\left(v\right)| > 0$ as the trigger for this switch. More generally, $|K_1^u\left(v\right)| + K_2^u\left(v\right) > 0$ would trigger the breaking of a bond species that responds indiscriminately to any mode of strain.

Once a generation u starts breaking at $t \geq v$, the rate at which the breakage progresses may depend on the magnitude of the strain evaluated from suitable strain invariants derived from $\mathbf{F}^u\left(v\right)$. For example, for bond species that break in response to distortional strain, it may be reasonable to model the reduced relaxation function as a function of $K_2^u\left(v\right)$, such as

$$g\left(\theta, \mathbf{F}^u\left(v\right); \mathbf{X}, t - v\right) = \left(1 + \frac{t - v}{\tau\left(K_2^u\left(v\right)\right)}\right)^{-\beta} \tag{S.28}$$

where $\tau\left(K_2^u\right)$ represents a strain-dependent characteristic relaxation time that varies as a function of the value of $K_2^u\left(v\right)$. A constitutive relation for $\tau\left(K_2^u\right)$ may be given by

$$\tau\left(K_2^u\right) = \tau_0 + \tau_1\left(K_2^u\right)^{\alpha} \tag{S.29}$$

where τ_0 and τ_1 are material constants with units of time and α is a non-dimensional exponent. In principle, the exponent β in Eq.(S.28) may also be a function of $K_2^u\left(v\right)$.

As shown in these equations, for nonlinear viscoelasticity the function g may vary with the magnitude of strain invariants. More generally, any other strain invariants may be used to determine the response of g, including strain invariants under specific material symmetries, to account for anisotropic viscoelasticity as indicated below (section S.8).

S.7. Standard Linear Solid

Consider a one-dimensional analysis under infinitesimal strains, where the strong and weak bonds behave as linear elastic materials with strain energy densities given by $\Psi_r^e\left[\varepsilon\right] = \frac{1}{2}E^e\varepsilon^2$ and $\Psi_0^b\left[\varepsilon\right] = \frac{1}{2}E^b\varepsilon^2$. The resulting stresses are given by $T^e\left[\varepsilon\right] = E^e\varepsilon$ and $T^b\left[\varepsilon\right] = E^b\varepsilon$. Here, E^e and E^b represent Young's moduli of the strong and weak bonds, respectively. Consider that the reduced relaxation function is exponential, as given in Eq.(13).

For a stress-relaxation problem, let $\varepsilon\left(t\right) = \varepsilon_0 H\left[t\right]$. Then, according to Eqs.(19) & (21), the strain energy density of this standard linear viscoelastic solid is

$$\Psi_r\left(t\right) = \frac{1}{2}E^e\left(1 + \beta e^{-t/\tau}\right)\varepsilon_0^2 H\left[t\right] \tag{S.30}$$

and the corresponding stress response is

$$T\left(t\right) = E^e\left(1 + \beta e^{-t/\tau}\right)\varepsilon_0 H\left(t\right)\ . \tag{S.31}$$

where $\beta = E^b/E^e$.

For a creep problem, let $T\left(t\right) = T_0 H\left(t\right)$, where T_0 is the applied stress, in which case $\varepsilon\left(t\right)$ must be obtained from Eq.(21), such that

$$\frac{T_0}{E^e}H\left(t\right) = \left(1 + \beta\right)\varepsilon\left(t\right) - \frac{\beta}{\tau}\int_{0^+}^{t} e^{-\left(t-u\right)/\tau}\varepsilon\left(u\right)du \tag{S.32}$$

The solution to this equation is

$$\varepsilon\left(t\right) = \frac{1}{1 + \beta}\left[1 + \beta\left(1 - e^{-\frac{1}{1+\beta}\frac{t}{\tau}}\right)\right]\frac{T_0}{E^e}H\left(t\right) \tag{S.33}$$

This solution may be used to evaluate the strain energy density under creep using Eq.(19). The resulting expression is too lengthy to present here; but as an example, in the limit as $\beta \to 1$, this expression reduces to

$$\Psi_r\left(t\right) = \frac{T_0^2}{8E^e}e^{-t/\tau}\left[\frac{t}{\tau} + 2\left(1 - 2e^{t/2\tau} + 2e^{t/\tau}\right)\right] \tag{S.34}$$

The solutions of Eqs.(S.31) & (S.33) are equivalent to the corresponding responses of a standard linear solid, where E^b represents the stiffness of the spring in series with the dashpot, and E^e is the stiffness of the parallel spring. Representative plots of the temporal evolution of the strain energy density for the standard linear solid in stress-relaxation and creep are presented in Figure 5.

S.8. Anisotropic Viscoelasticity

Free energy densities of strong and weak bonds are functions of multiple strain invariants, whose number depends on material symmetry (three for isotropy, five for transverse isotropy, etc.) Functions of these invariants may be combined in any number of ways and it is straightforward to prescribe different relaxation functions for each combination.

For example, a compressible isotropic elastic solid may have a strain energy density given by

$$\Psi_r\left(\theta,\mathbf{F}\right)=\frac{\kappa}{2}K_1^2+\mu K_2^2 \tag{S.35}$$

where μ and κ are material constants that respectively represent the shear and bulk moduli in the limit of infinitesimal strains, and K_1 and K_2 represent two of the strain invariants of the natural strain tensor (Criscione et al., 2000) (also see section S.6). Similarly, a fiber bundle oriented along the unit vector $\mathbf{n}$ in its reference configuration may be modeled by the strain energy density function

$$\Psi_r\left(\theta,\mathbf{F}\right)=H\left(I_n-1\right)\frac{1}{2}\xi\left(I_n-1\right)^2 \tag{S.36}$$

where ξ is a material constant representing the fiber modulus, $I_n=\mathbf{n}\cdot\mathbf{C}\cdot\mathbf{n}$ is the square of the stretch along $\mathbf{n}$, $\mathbf{C}=\mathbf{F}^T\cdot\mathbf{F}$ is the right Cauchy-Green tensor, and the unit step function $H\left(I_n-1\right)$ imposes that the fiber only sustains tension.

For this viscoelastic solid, it may be proposed that there are three weak bond species entering into Eq.(22), with $\Psi_0^b=\kappa K_1^2/2$ for the first, $\Psi_0^b=\mu K_2^2$ for the second, and Ψ_0^b given by the expression of Eq.(S.36) for the third. Each of these bond species has a distinct reduced relaxation function $g_b\left(\theta,\mathbf{F};\mathbf{X},t\right)$ that may optionally depend only on the strain invariant that enters each of the corresponding Ψ_0^b. The functional form of the strain energy density Ψ_r^e of strong bonds (the elastic response) need not use the same combinations of strain invariants as those of the weak bonds. This example illustrates how anisotropic viscoelasticity may be introduced in a simple manner by incorporating multiple weak bond species that depend on different subsets of strain invariants, each species having distinct bond kinetics.

S.9. Continuous Relaxation Spectrum

For the reactive quasilinear viscoelasticity framework of Eqs.(17) & (18), the application of Eq.(22) for modeling multiple bonds produces

$$\begin{aligned}\Psi_r\left[\mathbf{F}\left(t\right)\right]&=\Psi_r^e\left[\mathbf{F}\left(t\right)\right]+\sum_b g_b\left(t\right)\Psi_0^b\left[\mathbf{F}\left(t\right)\right]\\&-\sum_b\int_{0^+}^t\dot{g}_b\left(t-u\right)\Psi_0^b\left[\mathbf{F}^u\left(t\right)\right]du\end{aligned} \tag{S.37}$$

A continuous relaxation spectrum may be constructed from Eq.(S.37) by assuming that Ψ_0^b has the same functional form for all the weak bond species, all of which have reduced relaxation functions $g_b\left(t\right)=g\left(\tau_b;t\right)$ whose relaxation times τ_b vary continuously from τ_1 to τ_2. In that case, the summations over b in Eq.(S.37) may be converted into suitable integrals,

$$\begin{aligned}&\Psi_r\left[\mathbf{F}\left(t\right)\right]=\\&\Psi_r^e\left[\mathbf{F}\left(t\right)\right]+\frac{1}{g_0}\int_{\tau_1}^{\tau_2}g\left(\tau_b;t\right)d\tau_b\,\Psi_0^b\left[\mathbf{F}\left(t\right)\right]\\&-\frac{1}{g_0}\int_{0^+}^t\left(\int_{\tau_1}^{\tau_2}\dot{g}\left(\tau_b;t-u\right)\,d\tau_b\right)\Psi_0^b\left[\mathbf{F}^u\left(t\right)\right]du\end{aligned} \tag{S.38}$$

where the scale factor

$$g_0=\int_{\tau_1}^{\tau_2}g\left(\tau_b;0\right)d\tau_b \tag{S.39}$$

has been introduced to maintain the convention that Ψ_0^b represents the weak bond free energy density when all weak bonds are intact. For example, if the reduced relaxation function g is exponential as given in Eq.(13), the resulting integrals over τ_b produce

$$\begin{aligned}\int_{\tau_1}^{\tau_2}g\left(\tau_b;t\right)d\tau_b&=\tau_2e^{-t/\tau_2}-\tau_1e^{-t/\tau_1}\\&+t\left[Ei\left(-\frac{t}{\tau_1}\right)-Ei\left(-\frac{t}{\tau_2}\right)\right]\end{aligned} \tag{S.40}$$

with $g_0=\tau_2-\tau_1$, and

$$\int_{\tau_1}^{\tau_2}\dot{g}\left(\tau_b;t-u\right)\,d\tau_b=Ei\left(-\frac{t-u}{\tau_1}\right)-Ei\left(-\frac{t-u}{\tau_2}\right) \tag{S.41}$$

where $Ei\left(\cdot\right)$ represents the exponential integral function.

S.10. Reactive Versus Classical

This section provides several illustrative comparisons of the responses achieved when using

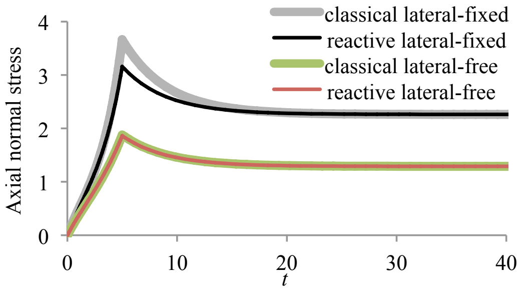

Figure S.1: Comparison of reactive and classical quasilinear viscoelasticity frameworks in uniaxial tensile stress-relaxation, with fixed or free lateral boundaries. The axial stretch ratio at the end of the ramp is 2.

the exponential reduced relaxation function g of Eq.(13) in the reactive quasilinear framework, Eq.(18), versus the classical quasilinear framework, Eq.(25), in the range of very large deformations. All calculations were performed using the FEBio open-source finite element software (Maas et al., 2012)(www.febio.org), where the reactive viscoelasticity framework has been implemented using the discrete forms of Eqs.(2) & (4). In all cases, the strong and weak bonds are modeled using the nonlinear isotropic elastic constitutive model of Holmes and Mow (1990), whose strain energy density is given by

$$\Psi_r = c\left(e^Q - 1\right)/2 \tag{S.42}$$

where

$$Q = \beta \frac{I_2 - 3 - 2\nu\left(I_1 - 3\right)}{2\left(1-\nu\right)} - \beta \ln\left(J^2\right) \tag{S.43}$$

and

$$c = \frac{1-\nu}{\left(\nu+1\right)\left(1-2\nu\right)} \frac{E}{\beta} \tag{S.44}$$

In the limit of infinitesimal strains, E represents Young's modulus and ν is Poisson's ratio; β is a nonlinear parameter that controls the exponential response in Eq(S.42); I_1 and I_2 are the first and second invariants of $\mathbf{C}$, respectively. In all the examples illustrated here, these properties were set to $E = 1$, $\nu = 0.3$ and $\beta = 0.5$ for both strong and weak bonds, and $\tau\left(\theta\right) = 4$ for the function g.

In the first example (Figure S.1), a uniaxial tensile stress-relaxation response is analyzed under a ramp-and-hold deformation profile. The ramp time is 5 and the axial stretch ratio at the end of the ramp is 2. Responses are examined when the lateral boundaries are either free or fixed. Inspite of the large deformation, the lateral-free responses are nearly identical between the reactive and classical frameworks. However, when lateral boundaries are fixed, the reactive model shows a lower peak stress.

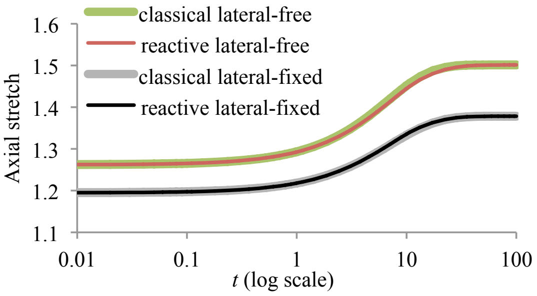

Figure S.2: Comparison of reactive and classical quasilinear viscoelasticity frameworks in uniaxial tensile creep, with fixed or free lateral boundaries. The prescribed axial stress is equal to 1.

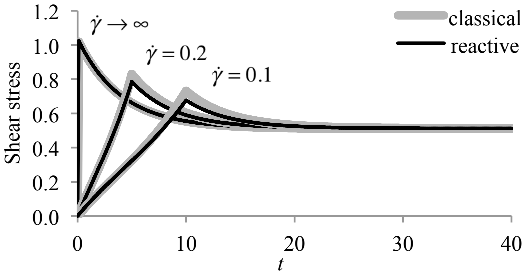

Figure S.3: Comparison of reactive and classical quasilinear viscoelasticity frameworks in simple shear stress-relaxation at different shear rates $\dot{\gamma}$. The Lagrangian shear strain at the end of the ramp is $E_{xy} = 0.5$. The graph displays the shear stress component T_{xy}.

In the second example (Figure S.2), a uniaxial tensile creep response is examined under a prescribed step tensile traction of 1. Similarly to the previous example, the analysis includes the cases of free and fixed lateral boundaries. In both cases of lateral boundary conditions, the creep responses of the reactive and classical models are very similar, though not identical.

In the final example (Figure S.3), the material is subjected to simple shear at a constant shear rate $\dot{\gamma}$ to achieve a Lagrangian shear strain $E_{xy} = 0.5$, then allowed to relax in this sheared configuration. The resulting shear stress T_{xy} is plotted in the figure, showing that the reactive and classical frameworks produce identical outcomes for instantaneous shearing ($\dot{\gamma} \to \infty$), but the reactive framework produces lower peak stresses than the classical framework with decreasing shear rates.

In summary, the responses under the classical and reactive viscoelasticity frameworks may differ depending on the loading rates and boundary conditions. These differences, when they occur, only become apparent at larger strains, since the two frameworks agree exactly in the limit of infinitesimal strains when the reduced relaxation function is exponential.