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A multiscale model for anisotropic damage and hysteresis in biodegradable polymers

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Abstract. Predicting the mechanical response of biological soft materials requires an understanding of the complex phenomena characterizing their microscale. In this work, we use an existing versatile framework, based on assumptions on the statistical distribution of biolpolymers at the network scale, for extending our previous entropic constitutive model of Worm-Like Chains networks to different deformation classes. Furthermore, we include the effect of molecules topological constraints by introducing an energy term depending on the second invariant of the Green-Cauchy tensor. In this way we are able to qualitatively reproduce, with a limited set of physically meaningful constitutive parameters, a range of observed phenomena such as induced anisotropy, stress softening, hardening, Mullins effect, evolution of permanent stretches.

Introduction

In this work, we extend our previous micromechanical model [1] by accounting for a fully three-dimensional distribution of polymeric chains, taking care of damage and contour length variation depending on loading history. The analysis is inscribed in the framework of statistical mechanics. The constitutive Helmholtz free energy is considered to stem from two terms: a microscopic Worm Like Chain type and a macroscale topological one describing network constraints. This novel model is described by a set of five parameters: one for each component of the WLC and topological free energy, one that relates contour length to end-to-end molecules variations, and two describing refolding and unfolding during unloading and reloading, respectively [2]. In this way we are able to capture both irreversible damage, onset of residual stretches (Mullins effect), hysteresis and induced anisotropy. With the single chain characterization in hand, the three dimensional model is directly obtained via a numerical integration of the energy on the microsphere [3]. The micro-to-macro shift in scale relies on the classical affinity hypothesis commonly used in rubberlike elasticity. We show the versatility and effectiveness of the present framework in describing the aforementioned effects by means of a parametric study. The constitutive parameters have a clear physical interpretation, which allows predicting the range of parameters variation. We believe that the present model is useful in describing the mechanical response of biopolymers exhibiting damage and permanent deformations of interest in material design and biomedical applications.

Methods

In this section, first we model the behavior of a single filament, then we use this model for passing to the macroscopic scale via the microsphere approach [3] and an additional macroscopic additional term.

Macromolecule model. In the previous works [1, 4] about absorbable suture threads, we modified the Helmholtz free energy of [5] in order to account for residual stretches. Here we use the same free energy of the macromolecule and the entropic force

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$$\Psi(\lambda,\lambda_n)=\kappa\frac{(\lambda-\lambda_n)^2}{\lambda_c-\lambda},\quad f=\frac{\partial\Psi}{\partial\lambda}=\kappa\left[\left(\frac{\lambda_c-\lambda_n}{\lambda_c-\lambda}\right)^2-1\right] \tag{1}$$

In the formulas above, λ, λ_c and λ_n are the molecule stretch, contour stretch and natural stretch, respectively. The parameter κ accounts for temperature and number of free monomers. The natural and contour stretch are related as , based on well known statistical mechanics considerations such as e.g. in [6, 7], where λ_{co} is the initial contour stretch ($\lambda_{co}>1$). Observe that the natural stretch λ_n corresponds to a zero value of the force, thus the residual stretch λ_{res} is identified by the condition $\lambda=\lambda_n$. Simultaneously, the contour stretch λ_c is a limit stretch. Notice that the force tends to infinity as $\lambda\rightarrow\lambda_c$.

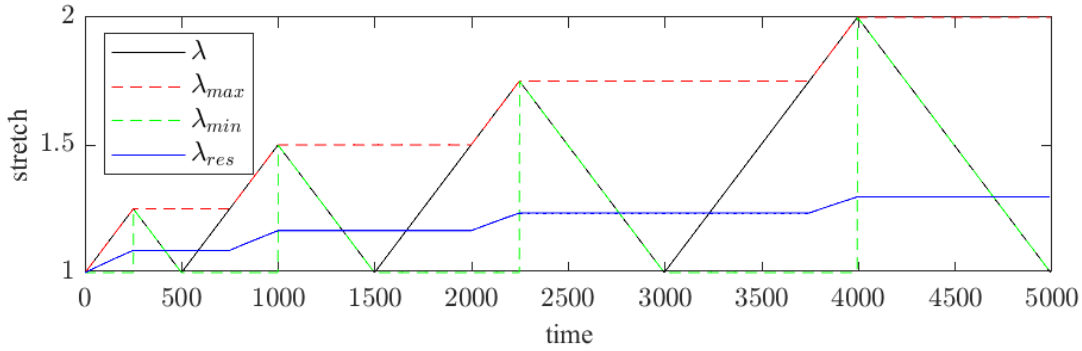

Figure 1: Evolution of the stretches under cyclic loading. The unloading parameter, describing partial refolding andthus residual stretches λ_{res} of copolymer domains is taken β_u = 0.2.

As in our previous work [4], in order to model folding and unfolding of the macromolecule under stretch, we assume the following phenomenological evolution law for the natural stretch

$$\lambda_n=\sqrt{\lambda_{max}}\left(\frac{\lambda}{\lambda_{max}}\right)^{-\beta_u+\beta_r\sqrt{\lambda-\lambda_{min}}}, \tag{2}$$

depending on the two constitutive parameters and . The former β_u describes the number of free monomers to crystallize during unloading, whereas the latter β_r models unfolding under reloading. Observe that, according to this evolution law, the maximum force exerted at the reach of λ_{max} on the primary path before unloading is exactly attained again at $\lambda=\lambda_{max}$ after reloading. In other words our model satisfies the so called Return Point Memory property [8]. Notice that the exponent term $\sqrt{\lambda-\lambda_{min}}$ is nonzero only in reloading as shown in Fig.1. Furthermore, (4) also identifies residual stretches. The filament force of Eq.(2) vanishes at $\lambda=\lambda_n$, thus the residual stretch must meet the condition $\lambda=\lambda_n=\lambda_{res}$ which returns the analytical dependency $\lambda_{res}=\lambda_{\max}^{\frac{1}{2}\frac{1-2\beta_u}{1-\beta_u}}$ of filament residual stretches and maximum historical load in the simple form of power law.

Macroscopic deformation. For a material point, the rate of work carried out by the first Piola-Kirchhoff stress Σ must equal the rate of change of free energy, , where the macroscopic deformation is described through the deformation gradient **F**. Entropic free energies terms like the one in Eq.(1) are usually able to describe the mechanics of polymers in solution. When the polymers are, as in solids, crosslinked in networks, additional energy terms are needed for considering self and mutual entanglement effects (see [9, 4]). Here we adopt a hybrid approach and, leaving untouched the microscopic energy, we add a topological energy term at the macroscopic level borrowing by solid mechanics (e.g. [10]). Denoting terms of microscopic and macroscopic origin with *m* and *M,* the stress tensor can be decomposed into

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$$\boldsymbol{\Sigma} = \boldsymbol{\Sigma}_m + \boldsymbol{\Sigma}_M = \frac{\partial \Psi_m}{\partial \mathbf{F}} + \frac{\partial \Psi_M}{\partial \mathbf{F}}. \tag{3}$$

Notice that the quasi-static assumption allows treating time as a unitless order parameter. We assume that the stretches are applied along the principal directions and, as usual, the solid is incompressible, i.e. det**F**=1. Therefore, by looking at Fig.2, we are able to describe uniaxial extension, equibiaxial extension and pure shear via a unique macrostretch variable Λ as follows (see [10]):

$$\mathbf{F}(\Lambda) = \begin{cases} \mathrm{diag}(\Lambda, \Lambda^{-\frac{1}{2}}, \Lambda^{-\frac{1}{2}}) & (\text{uniaxial}) \\ \mathrm{diag}(\Lambda, \Lambda, \Lambda^{-2}) & (\text{equibiaxial}) \\ \mathrm{diag}(\Lambda, 1, \Lambda^{-1}) & (\text{pure shear}) \end{cases} \tag{4}$$

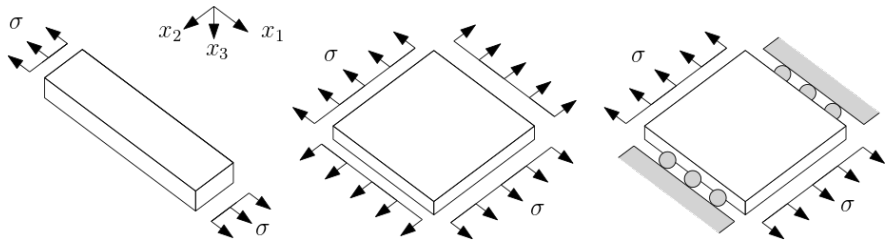

Figure 2: Deformation classes. From left to right: uniaxial extension, equibiaxial extension, pure shear.

In this way, one can find the components of $\boldsymbol{\Sigma}_m$ that contribute to the microscopic term work as

$$\sigma_m = \frac{1}{4\pi\delta} \int_{\text{sphere}} \frac{\partial \psi}{\partial \lambda} \frac{\mathrm{d}\lambda}{\mathrm{d}\Lambda} \, \mathrm{d}\Omega = \frac{1}{4\pi\delta} \int_{\text{sphere}} f(\lambda) \frac{\mathrm{d}\lambda}{\mathrm{d}\Lambda} \, \mathrm{d}\Omega. \tag{5}$$

with δ=1 for uniaxial extension and pure shear, δ=2 for equibiaxial extension. As in standard nonlinear elasticity [10], notice in Fig.2 that pure shear is obtained by imposed elongation in direction 1, zero displacement in direction 2 and free stretch, i.e. here resulting from incompressibility, across the thickness in direction 3. Moreover, assuming the classical affinity hypothesis, the stretch $\lambda(\Lambda, \mathbf{d}) = \|\mathbf{F}(\Lambda)\mathbf{d}\|$ of a filament oriented along the unit vector $\mathbf{d}=[d_1, d_2, d_3]$ and its derivative with respect to the independent stretch variable Λ have to be evaluated. A numerical quadrature rule for integrals of the kind Eq.(5) was discovered by [11] and successfully applied to polymer mechanics for the first time by [3]. This is the so-called microsphere approach. It is based on N quadrature orientations $\mathbf{d}_j$ such that, for a function v defined at the microscale, the macroscale counterpart can be computed as a simple weighted average. In order to consider the interaction between the network macromolecules we add a further term to the total energy, which enforces topological constraints. It has been repeatedly highlighted in literature that the second invariant I_2 of the right Cauchy-Green deformation tensor $\mathbf{C}=\mathbf{F}^T\mathbf{F}$, plays a crucial role in describing the energy, especially for large deformations of rubber-like and biological materials (e.g. see [12, 13] and references therein). Similarly as in the classical Mooney-Rivlin model of incompressible hyperelasticity, we assume that the energy depends linearly on I_2, which accounts for the square of the aerial deformation normal to the elongating fibers. Following the same thermodynamic reasoning as in Eq.6, we obtain

$$\sigma_M = \kappa C_2 \frac{\mathrm{d}I_2}{\mathrm{d}\Lambda}, \tag{5}$$

so that C2 is unitless.

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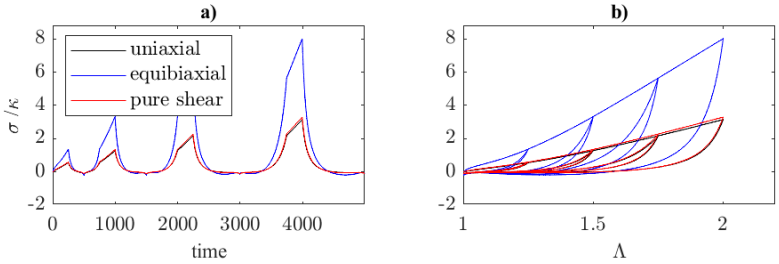

Figure 3: Mechanical response of the microscopic term. The material is cyclically tested inuniaxial extension,equibiaxial extension and pure shear. Material parameters: β_u=0.2, β_r=0.2, λ_{co}=1.1, C_2 = 0. a) Normalized stress vstime. b) Normalized stress vs macroscopic stretch.

Results and conclusions

In order to show the versatility of the present model, here we perform a parametric analysis which elucidates the role of the five parameters in capturing Mullins effect, internal hysteresis and permanent set in the three loading cases above considered. In Fig.3, we show the mechanical response in absence of the topological term. The material is cyclically tested in uniaxial extension, equibiaxial extension and pure shear.

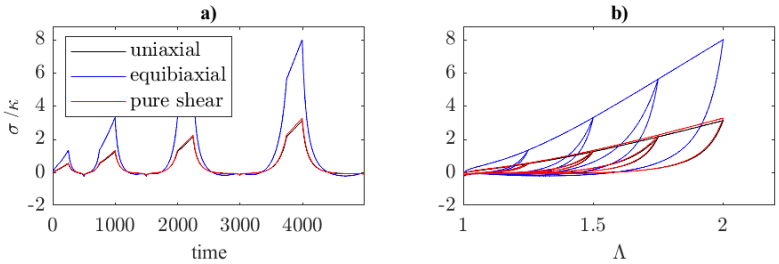

Figure 4: Mechanical response of the microscopic term. The material is cyclically tested inuniaxial extension,equibiaxial extension and pure shear. Material parameters: β_u=0.2, β_r=0.2, λ_{co}=1.1, C_2 = 0. a) Normalized stress vstime. b) Normalized stress vs macroscopic stretch.

In Fig.4 the effect of initial contour stretch is investigated. Looser chains, i.e. with a higher λ_{co}, show a lower response in terms of stresses for all loading scenarios.

The contribution of reversible folding is depicted in Fig.5. A higher unloading parameter β_u, i.e. a higher rate of refolding, causes lower stresses in unloading. A higher reloading parameter βr entails higher stresses in reloading. Finally, the contribution of the second invariant related macrostress is numerically analysed in Fig.6. Whereas the multiscale microsphere network predicts a very similar behavior for uniaxial extension and pure shear, the adding of a macrostress depending on the second invariant of the right Cauchy-Green deformation tensor allows the model to differentiate the two cases as measured in experiments such as in [14].

The main contribution of this work is a multiscale constitutive model which is able to predict, with only five physically motivated parameters, a wide range of phenomena and deformation classes.

Numerous biological materials are constituted by a network of stiff macromolecules, e.g.. collagen, immersed into a soft incompressible extracellular matrix (see [15,16]). This enables outstanding mechanical properties which, as in this work, can be explained via a multiscale approach. Future work will quantitatively investigate real biological materials by means of our novel two-scale energy function.

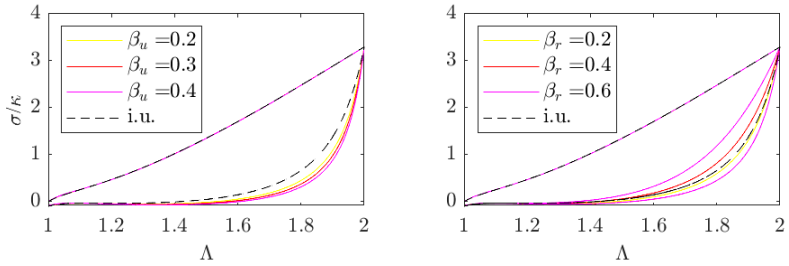

Figure 5: Effect of reversible folding. In dotted line the case of only irreversible unfolding,i.e. β_u and β_r are null and the only unfolding is along the primary path. Left-hand side)A higher unloading parameter β_u, i.e. a higher rate of refolding, causes lower stresses in unloading. Right-hand side) The lowest magenta curve is the common unloading stress forthe three cases. A higher reloading parameter βr entails higher stresses in reloading.

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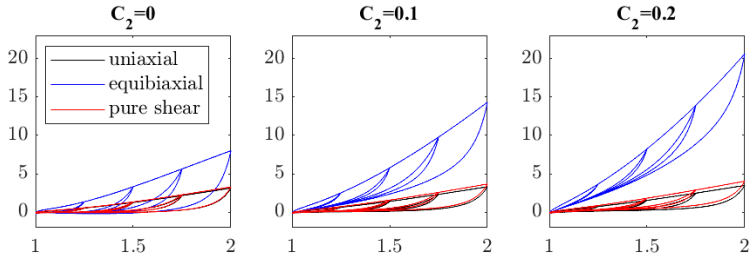

Figure 6: Effect of second invariant related macrostress. Whereas the multiscale microsphere network predicts a very similar behavior for uniaxial extension and pure shear, the adding of a macrostress depending on the second invariant of the right Cauchy-Green deformation tensor allows the model to differentiate the two as measured in published experiments.

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