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Constitutive modeling for polymer hydrogels: A new perspective and applications to anisotropic hydrogels in free swelling

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ABSTRACT

The paper presents a modified theoretical framework for isotropic and anisotropic deformation of hydrogels in both steady and transient states. By applying the kinematic constraint between the mechanical and chemical fields in the second law of thermodynamics, a unified constitutive equation could be obtained, which is capable to describe the isotropic or anisotropic deformation of hydrogels at the same time. Also, the diffusion equation for solvent molecules is modified based on the constraint and the Lagrange multiplier used to force the constraint is avoided being introduced in the free energy function. The theoretical framework is specialized to describe the steady swelling behaviors of anisotropic hydrogels and the corresponding solution properties for the equations of free swelling are discussed. The anisotropic-swelling behaviors for several kinds of configurations are investigated, including hydrogel blocks and a cylindrical tube with one or two families of reinforced fibers. We find that the swelling of anisotropic hydrogels shows rich behaviors even for the simple configurations in free states, such as selective expansion/shrinkage and anomalous residual stress. An agreement between the results obtained by the constitutive equations and experiments for the transversally isotropic swelling demonstrates the effectiveness of the constitutive model.

1. Introduction

Hydrogels are three-dimensional (3D) crosslinked polymeric networks filled with water. Such kinds of materials have great potential as ingredients to reconstruct soft biological tissues due to biocompatibility, large-strain reversible deformability and smart responsiveness to various chemical or physical stimuli (e.g., temperature, PH, salt concentration, electric field, etc.). To achieve this goal, one of important issues, except for high toughness, stiffness and strength, is to introduce anisotropic mechanical properties into hydrogels, which could be widely observed in soft biological tissues of the real world, such as the ice plant capsule (Harrington et al., 2011), the jellyfish mesogloea (Zhu et al., 2012) and human organs (e.g., muscle, cartilage, tendon, vessel, skin, etc.) (Zhu et al., 2013; Gong, 2014).

Though hydrogels have been the focus of researches in the past several decades, the preparation techniques for artificial anisotropic gels were achieved in the recent years. One choice is to reinforce the traditional single-network hydrogels in specific directions with specific materials, such as inorganic clay (Haraguchi et al., 2005), woven rough knitted fabrics (Young et al., 1998), cellulose nano-fibers (Osorio-Madrazo et al., 2012). The reinforced phase plays roles in producing the anisotropic mechanical property and improving the toughness and strength of the material. The synthesized hydrogels show a broad range of mechanical properties that could mimic the toughness and anisotropy of biological tissues, such as porcine heart valves (Mohammadi, 2011) and aorta and heart valve leaflets (Millon and Wan, 2006). Other techniques are also proved to be efficient to generate similar anisotropic microstructures, such as a combination of chemical crosslinks and patterned photocrosslinks within a single-crosslinked hydrogel (Zawko et al., 2009) and template polymerization (Shigekura et al., 2005).

Generating aligned porous microstructures using the directional freezing-thawing (DFT) technique is another common approach to prepare anisotropic hydrogels (Zhu et al., 2013). The DFT technique could be combined with other experimental techniques, such as radiation-induced polymerization and crosslinking (Chen et al., 2012), redox polymerization (Zhu et al., 2013), frozen UV initiated polymerization (Barrow and Zhang, 2013), etc., to fabricate

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anisotropic hydrogels in specific conditions. The synthesized gels have long and wide aligned channels in the direction parallel to the freezing direction and pores in the perpendicular direction. Such well-patterned microstructures could be observed in both dry and swollen states and give rise to the macroscopically anisotropic deformation in response to chemical swelling and mechanical loadings in comparison with conventional synthetic hydrogels. In addition, a control of the diffusion direction of ions in the preparation process could also lead to centimeter-scale anisotropic hydrogels with self-assembled aligned fibrous bundles (Yang et al., 2008; Wu et al., 2011).

The mechanical strain can also play a key role in producing the material anisotropy in the process of preparation or even on service. For example, the isotropic double-network hydrogel would be transformed to be anisotropic in swelling deformation when the internal damages happen along specific directions after the applied strain reaches a critical value (Nakajima et al., 2013). In the preparation process, aligned lamellar bilayers of self-assembled dodecyl glyceryl itaconate could be introduced by applying shear-flow to the precursor solution (Haque et al., 2010). Also, controlled tension or compression loads applied to the samples for a specified time could achieve the anisotropy in hydrogels and the synthesized hydrogels can be used as tissue expander or cardiovascular tissues (Millon et al., 2006; Swan et al., 2011).

In a word, anisotropy in hydrogels can be well achieved and controlled using various techniques. Though unique microstructures could be found in different kinds of hydrogels, they show similar anisotropic mechanical properties, for which, it is meaningful to develop a unified model that could describe such kind of behaviors.

We should also note that, in the last century, big progresses concerning theories and computations for the coupled fluid permeation and finite deformation in swelling hydrogels have been achieved, from basic theoretical explorations (Gibbs, 1978; Biot, 1941; Flory, 1942; Hong et al., 2008; Duda et al., 2010; Chester and Anand, 2010; Drozdov, 2013; Doi, 2009; Bouklas and Huang, 2012) to numerical procedures (Hong et al., 2009; Lucantonio et al., 2013; Li et al., 2014; Chester et al., 2015; Liu et al., 2015; Bouklas et al., 2015), from some kinds of specific problems (Birgersson et al., 2008; Zhao et al., 2008; Deng and Pence, 2010) to general engineering applications (Liu et al., 2010; Baek and Pence, 2011; Chester and Anand, 2011; Toh et al., 2014), to mention a few. However, to the authors' knowledge, most related works so far are limited to the isotropic cases, in which the stretches in all directions are equal in the free-swelling state. The constitutive framework that is able to characterize the anisotropic behaviors of hydrogels obviously falls behind the preparation techniques and applications as mentioned above. Recently, we noted that Nardinocchi et al. developed a constitutive formulation for anisotropic swelling of thin gel sheets with one family of stiff fibers (Nardinocchi et al., 2015), which was based on the constitutive framework proposed in Hong et al. (Hong et al., 2008). However, more general cases, such as hydrogels with two families of stiff fibers and the solution properties, are still needed to be investigated.

In the current contribution, we first introduce the traditional theory for hydrogel swelling from a new perspective, in which, the condition of incompressibility of solvent molecules is treated in a different way. Based on the thermodynamical inequality and the volumetric constraint arising from the incompressibility of solvent molecules, a unified constitutive equation which is able to describe both isotropic and anisotropic deformation of hydrogels under chemical swelling and mechanical loading is derived. The two independent equations in previous constitutive framework (Hong et al., 2008; Chester and Anand, 2010) that characterize the deformations induced by mechanical stress and chemical swelling, respectively, are incorporated into a unified one which can be extended from the isotropic cases to anisotropic cases straightforwardly. Also, the diffusion equation describing the fluid migration in hydrogels is modified by introducing the kinematic constraint, which provides a new perspective to solve the coupled equations for transient swelling of hydrogels, especially from the numerical aspect.

Based on the developed constitutive framework, general constitutive equations considering the anisotropy with one or two preferred directions are introduced. To investigate the deformation features, anisotropic hydrogels in free-swelling states are considered with various configurations of fibers. A quantitative comparison between the data obtained from the constitutive equations and the experiment (Haque et al., 2010) is also made to verify the availability of the model. Some intriguing swelling behaviors are noticed and explained, such as the selective expansion/shrinkage in the cases with two families of non-orthogonal fibers and the anomalous residual stress arising in the fiber-reinforced cylindrical tube.

The paper is organized as follows. In Section 2, the kinematic description, the balance equations and the constitutive equations to describe the coupled solvent diffusion and finite deformation in hydrogels are introduced. The general constitutive equations for anisotropic hydrogels are deduced and the specific forms with respect to one or two families of fibers in the free-swelling cases are also discussed in detail. In Section 3, the physical regulation of the free swelling of anisotropic hydrogels is investigated and summarized for various configurations of fibers and hydrogel geometries. Finally, conclusions are made in Section 4.

2. A continuum theory for transient swelling of hydrogels

2.1. Kinematics

Considering a continuous undeformed hydrogel described by a set of material points $\mathbf{X}$, we refer to such kind a point set as a reference configuration $\mathscr{B}_{\mathrm{R}}$. The position of the points $\mathbf{X}$ at time t can be represented as

$$\mathbf{x} = \boldsymbol{\varphi}(\mathbf{X}, t) \tag{1}$$

where $\boldsymbol{\varphi}$ is a one-to-one mapping from $\mathscr{B}_{\mathrm{R}}$ to $\mathscr{B}$, $\boldsymbol{\varphi} : \mathscr{B}_{\mathrm{R}} \to \mathscr{B}$, with $\mathscr{B}$ denoting a current configuration occupied by points $\mathbf{x}$. The deformation gradient tensor is defined as $\mathbf{F} = \partial\boldsymbol{\varphi}/\partial\mathbf{X} = \mathrm{Grad}\boldsymbol{\varphi}$, where $\mathrm{Grad}(\cdot) = \partial(\cdot)/\partial\mathbf{X}$ denotes the material gradient operation with respect to $\mathbf{X}$. Then, the Jacobian is $J = \det\mathbf{F}$ which satisfies $\mathrm{d}v = J\mathrm{d}v_{\mathrm{R}}$ with $\mathrm{d}v_{\mathrm{R}}$ and $\mathrm{d}v$ denoting the volume element in $\mathscr{B}_{\mathrm{R}}$ and $\mathscr{B}$, respectively. The Green strain is defined as follows

$$\mathbf{E} = \frac{1}{2}\left(\mathbf{F}^{\mathrm{T}}\mathbf{F} - \mathbf{1}\right) = \frac{1}{2}(\mathbf{C} - \mathbf{1}) \tag{2}$$

where $\mathbf{C} = \mathbf{F}^{\mathrm{T}}\mathbf{F}$ is the right Cauchy-Green tensor and $\mathbf{1}$ denotes the identity tensor. We can see that $\mathbf{E}$ vanishes when the material is unstrained. The velocity gradient tensor defined with respect to $\mathscr{B}$ follows

$$\mathbf{l} = \frac{\partial\mathbf{v}}{\partial\mathbf{x}} = \mathrm{grad}\,\mathbf{v} = \dot{\mathbf{F}}\mathbf{F}^{-1} = \mathbf{d} + \boldsymbol{\omega} \tag{3}$$

where $\mathrm{grad}(\cdot)$ represents gradient operator in $\mathscr{B}$, the stretching $\mathbf{d}$ and the spin $\boldsymbol{\omega}$ are the symmetric and antisymmetric parts of $\mathbf{l}$, respectively,

$$\mathbf{d} = \mathrm{sym}\,\mathbf{l} = \frac{1}{2}\left(\mathbf{l} + \mathbf{l}^{\mathrm{T}}\right),\ \boldsymbol{\omega} = \mathrm{asym}\,\mathbf{l} = \frac{1}{2}\left(\mathbf{l} - \mathbf{l}^{\mathrm{T}}\right) \tag{4}$$