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Inhomogeneous large deformation study of temperature-sensitive hydrogel

Zhiwei Ding [a], Zishun Liu [b,*], Jianying Hu [b], Somsak Swaddiwudhipong [c], Zhengzhi Yang [a]

[a] Engineering Science Programme, National University of Singapore, Singapore 117576, Singapore
[b] Int. Center for Applied Mechanics, State Key Laboratory for Strength and Vibration of Mechanical Structure, Xi'an Jiaotong University, Xi'an 710049, China
[c] Dept. of Civil and Environmental Engineering, National University of Singapore, Singapore 117576, Singapore

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ABSTRACT

In this paper, inhomogeneous deformation of a temperature-sensitive hydrogel has been studied and analyzed under arbitrary geometric and boundary conditions. We present the governing equations and equilibrium conditions of an isothermal process based on the monophase gel field theory of hydrogel via a variational approach. We have adopted and implemented an explicit form of energy for temperature-sensitive hydrogel in a three-dimensional finite element method (FEM) using a user-supply subroutine in ABAQUS. For verification purpose, a few numerical results obtained by the proposed approach are compared with existing experimental data and analytical solutions. They are all in good agreement. We also provide several examples to show the possible applications of the proposed method to explain various complex phenomena, including the bifurcation, buckling of membrane, buckling of thin film on compliant substrate and the opening and closure of flowers.

1. Introduction

Flexible long-chained polymers can form a three-dimensional network by crosslinking through covalent bond. When the elastomer is submerged into a solvent, the network imbibes the solvent and swells, resulting in an elastomer gel. Determined by the functional group along the polymer chain, the deformation of the hydrogel can be affected by many stimuli including ionic concentration (Tanaka et al., 1980), temperature (Otake et al., 1990), forces (Doi, 2009), pH values (Marcombe et al., 2010) and electrical field (Osada and Gong, 1998; Shiga, 1997). Such stimuli-responsive gels have become a good material choice in diverse applications. For example, the capability of large and reversible deformation makes gel an attractive candidate material for sensors (Beebe et al., 2000; Westbrook and Qi, 2008), actuators (Carpi et al., 2009) and microvalves (Richter et al., 2004), whereas the biocompatibility and softness assure promising applications in the area of bioengineering, drug delivery devices (Dong et al., 2006; Peppas et al., 2006; Wichterle and Lim, 1960) and tissue engineering (Lee and Mooney, 2001).

The diverse applications and the complex material behavior observed in experiments (Guvendiren et al., 2009; Kuhn et al., 1950; Matsuo and Tanaka, 1992; Mora and Boudaoud, 2006; Southern and Thomas, 1965; Sultan and Boudaoud, 2008; Tanaka and Sigehuzi, 1994; Tanaka et al., 1987; Tirumala et al., 2005; Trujillo et al., 2008; Yang et al., 2010; Zhang et al., 2008) have motivated a large number of theoretical and numerical studies on hydrogel. The theoretical study dated back to more than a century ago. Gibbs (1878) proposed a thermodynamic theory of mobile molecules in an elastic solid. Biot (1941) derived the governing equations for the mass transport in a porous medium using thermodynamic theory and Darcy's law. Flory and Rehner (1943) developed a statistical-mechanical model for hydrogel. Baek and Srinivasa (2004) introduced a model of slow diffusion into a swelling solid undergoing large deformation. Dolbow et al. (2004) formulated a continuum model for chemically induced volume transition in hydrogel. Hui and Muralidharan (2005) did a comparison of the theories of Biot, Tanaka and Hocker, and Benedek. Other subsequent contributions include those work (An et al., 2010; Baek and Pence, 2011; Cai and Suo, 2011; Cai and Suo, 2012; Chester and Anand, 2010; Doi, 2009; Hong et al., 2009; Hong et al., 2010; Hong et al., 2008; Li et al., 2007; Marcombe et al., 2010; Zhang et al., 2012). Another group of researchers adopted the numerical approach to study the behavior of gels. Birgersson et al. (2008) studied a transient analysis of temperature sensitive gels using COMSOL MULTIPHYSICS. Hong et al. (2009) and Kang and Huang (2010) have developed FEM for gels in equilibrium while Marcombe et al. (2010) implemented FEM for pH-sensitive hydrogel under mechanical constraint. Zhang et al. (2009) formulated FEM for transient analysis of concurrent large deformation and mass transport in gels. Park et al. (2012) developed a dynamic FEM for inhomogeneous deformation and electromechanical instability for elastomer transducers. Recently, Cai and Suo (2011) modified the Flory–Rehner model for neutral gel by adopting the interaction parameter as a function of

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* Corresponding author. Tel.: +86 15209208735; fax: +86 2982668087.
E-mail addresses: zishunliu@mail.xjtu.edu.cn, zishunliu@nus.edu.sg (Z. Liu).

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temperature and concentration, and then used the model to analyze the deformation of the poly-(N-isopropylacrylamide) hydrogel. With a specific material model, such a theory enables analysis for the deformation of temperature-responsive hydrogel under different geometric and mechanic constraints.

In the current paper, we seek to fulfill three objectives. First, we construct a general theory of temperature-responsive hydrogel undergoing inhomogeneous deformation using a variational approach (Hong et al., 2009; Kang and Huang, 2010). A set of governing equations coupled the mechanical and chemical equilibrium is presented explicitly. Second, a specific material model is employed in finite element implementation by providing a user defined subroutine in the commercial software ABAQUS. This implementation enables us to analyze diverse phenomena including large deformation, contact, bifurcation, buckling of hydrogel, etc. Finally, we present several examples and compare the proposed simulation results with experimental data and analytical solutions. Hopefully, our model and subroutine were able to provide a powerful tool for other researchers to study the complex phenomena involving gels and the examples provided could give certain illuminating insights for further study.

The plan of this paper is as follows. In Section 2, we elaborate on the governing equations and equilibrium conditions for a gel undergoing inhomogeneous deformation under arbitrary geometric and boundary conditions. Section 3 describes the explicit free energy function using the Flory–Huggins theory while a finite element method for numerical simulation of the temperature-responsive hydrogel is developed, implemented and elaborated in Section 4. After introducing the definition of phase transition in Section 5, analytical and numerical solutions for homogeneous deformation are compared in Section 6. In Section 7, we apply the proposed model to explain the complex phenomena observed in the experiment such as bifurcation, buckling of swelling gel opening and closure of flower and buckling of thin film. This is followed by the concluding remarks in the last section.

2. A thermodynamic model of hydrogel

In this paper, we focus our discussion on FEM implementation for temperature sensitive hydrogel. We present the mono-phase gel theory which is developed by Suo's group (Hong et al., 2008) and elaborated more rationally by Kang and Huang (2010). Since the free energy function form in Kang and Huang's paper is more general, we adopt Kang and Huang's form instead of that of Hong et al. (2009) and follow the latter's approach to present the mono-phase gel theory in this section.

2.1. Governing equation

Consider a hydrogel body (current state) of volume Ω enclosed by a surface Γ, subject to a body force b_i and surface traction t_i. When the hydrogel is immersed in a solvent of chemical potential $\tilde{\mu}$, the solvent molecule can enter or leave polymeric gel across the surface Γ. In addition, the surface Γ may be mechanically constrained or chemically isolated from the solvent. To study the gel deformation, consider an infinitesimal process. In a short time δt, the displacement field in the reference coordinate is denoted by $\delta\mathbf{x}(\mathbf{X})$, and the work done δH by the environment is,

$$\delta H = \int_{\Omega} b_i \delta x_i dV + \oint_{\Gamma} t_i \delta x_i dS - \oint_{\Gamma} \tilde{\mu} n_k \delta i_k dS \tag{1}$$

where δi_k is the molecular flux density defined as the number of solvent molecules across per unit area of a surface element with the surface normal in the x_k direction, n_k is the kth component of the unit normal vector on the surface and the product $-n_k \delta i_k$ gives the number of solvent molecules entering the gel across unit area surface. We have adopted the dummy sum notation but ignored the injection of solvent molecules by source or distributed pump that was previously included in the theory by Hong et al. (2008) as we consider the whole domain of the hydrogel and the molecules can enter the hydrogel only through the boundary. The governing equations for the hydrogel are briefly described in this section (Hong et al., 2008; Kang and Huang, 2010). Let U denote the free energy of the whole hydrogel, and $w(\mathbf{x})$ be the free energy density. In an infinitesimal process, the variation of the whole energy of the hydrogel is,

$$\delta U = \delta\left(\int_{\Omega} w dV\right) \tag{2}$$

In addition, the mass conservation of the water molecule requires that

$$\delta\left(\int_{\Omega} c dV\right) = -\oint_{\Gamma} n_k \delta i_k dS \tag{3}$$

where c is the concentration of the solvent molecule in the hydrogel. Eq. (3) implies that the mass change of the molecules inside the gel is due solely to the molecular movement of the gel through its boundary. This is valid since we have assumed that there is no distributed pump or source inside the gel.

It is normally convenient to work in the reference coordinates. The hydrogel has a fixed volume Ω_0 and surface Γ_0 in reference coordinates, X. As shown in Fig. 1, the deformation gradient tensor $\mathbf{F}$, mapping the reference coordinates to the current coordinates, x, is defined as,

$$F_{ik} = \frac{\partial x_i(X)}{\partial X_k} \tag{4}$$

The differential volume and differential surface area at the current state are related to those in the reference state by

$$dV = J dV_0 \tag{5}$$

$$n_i dS = A_{iL} N_L dS_0 \tag{6}$$

where N_L is the Lth component of the unit normal on the surface at the reference state and $J = det(\mathbf{F})$ and $A_{iL} = \frac{1}{2} e_{ijk} e_{LMN} F_{jM} F_{kN}$

Then the nominal quantities can be defined as follows: the nominal body force $\mathbf{B}$: $B_i dV_0 = b_i dV$; the nominal surface traction $\mathbf{T}$: $T_i dS_0 = t_i dS$; the nominal molecular flux density I: $N_K \delta I_K dS_0 = n_k \delta i_k dS$; the nominal free energy density W: $W dV_0 = w dV$; and the nominal molecular concentration C: $C dV_0 = c dV$. Thus, Eqs. (1)–(3) can be rewritten in terms of the nominal quantities respectively as:

$$\delta H = \oint_{\Omega_0} B_i \delta x_i dV_0 + \oint_{\Gamma_0} T_i \delta x_i dS_0 - \oint_{\Gamma_0} \tilde{\mu} N_K \delta I_K dS_0 \tag{7}$$

$$\delta U = \int_{\Omega_0} \delta W dV_0 \tag{8}$$

$$\int_{\Omega_0} \delta C dV_0 = -\oint_{\Gamma_0} N_K \delta I_K dS_0 \tag{9}$$

Thermodynamic process requires that the free energy of the whole system must decrease or remain the same. Thus for the system con-

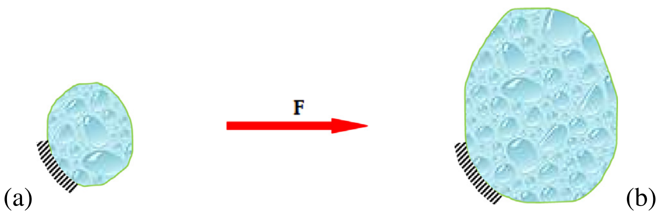

Fig. 1. Schematic illustration of (a) the reference state and (b) the equilibrium state of hydrogel.