Large Deformation Study of Temperature-Sensitive Hydrogel

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Abstract When the elastomer submerged in aqueous solution, temperature-sensitive hydrogels undergo a phase transition at a particular temperature, i.e. the volume of hydrogels changes with temperature discontinuously. In this paper, the inhomogeneous large deformation of temperature-sensitive hydrogels has been studied. Based on the monophasic gel inhomogeneous field theory, the governing equations and conditions of equilibrium for temperature-sensitive hydrogel have been derived. Furthermore, the free-energy function and derived constitutive equations for temperature-sensitive hydrogel are implemented using Finite Element Method. As an example, a uniaxially constrained-swelling hydrogels with cubic initial shape is studied. The simulating results are in reasonable agreement with available experimental data and analytical solutions. By analyzing the factors affecting the phase transition temperature of hydrogel, we suggest one possible chemical mechanism for the swelling behavior of temperature-sensitive gel during the phase transition process. Also we demonstrate the application of the proposed approach in the analysis of the complex phenomenon, such as to explain the deformation of implant in skin reconstruction. We hope this approach can explain various complex phenomena and provide a useful tool for further theoretical and experimental studies.

Keywords FEM, Inhomogeneous deformation, Phase transition temperature, Swelling behavior, Temperature-sensitive hydrogel,

1. Introduction

Long and flexible polymers chains can chemically crosslink to a three-dimensional network by covalent bonds. When the rubber-like material is submerged into an aqueous solvent, the network imbibes the solvent and swells, resulting in an elastomer gel. Great attention has been drawn to these polymeric gels due to their large and reversible deformation variation to many stimuli, including pH values[1, 2], forces[3], ionic concentration[4], temperature[5], electrical field[6, 7], and magnetic field, etc. For example, a temperature-sensitive hydrogel PNIPAM based on poly-(N-isopropyl-acrylamide) which exhibits the volume phase transition, has been investigated in the past years and the temperature-sensitive hydrogel has been developed for numerous applications[8-11], such as actuator[12], sensor[13, 14], switching device[15]. Furthermore, the temperature sensitive gels can be developed as drug delivery systems in the human body, where the gel releases a drug at a particular location in the body in response to the change of temperature.

The stimuli responsive behaviors of hydrogel have also motivated a large number of theoretical and numerical studies. Based on the statistical-mechanical hydrogel model developed by Flory and Rehner, Suo group proposed a gel theory coupling the two phase's deformation into a single phase[16]. Following this approach, Hong et al. implemented the finite element method (FEM) on polymeric gel theory by coding a UHYPER subroutine in the commercial software ABAQUS[17]. Meanwhile Marcombe et al. and Cai and Suo developed FEM for pH-sensitive gel[2] and temperature-sensitive gel[5], respectively. To perform the transient analysis of large deformation, Zhang et al. formulated FEM of mass transport in gel microfluidic valves, using fluid-structure

interaction (FSI)[18]. Liu et al. studied the buckling phenomena of gels[19, 20]. Toh et al. developed a dynamic FEM for inhomogeneous deformation[21, 22].

In this paper, we adopt Suo's monophasic model for temperature-sensitive hydrogel[5], which regard the interaction parameter as a function of temperature and concentration, and then a specific material model is employed in the finite element implementation by providing a user subroutine to analyze the deformation of the PNIPAM hydrogel. This implementation enables us to analyze diverse phenomena of temperature-sensitive gel including large deformation, contact, bifurcation, buckling of hydrogel, etc.

2. Gel theory for temperature-sensitive gel

When a dry polymer network is immersed in a solvent, e.g. water, the solvent molecules enter the polymer network and result in swelling. We define the initial state as the reference state X_K and the deformed state as the current state x_i. The state of deformation is characterized by the deformation gradient F_{iK}, defined by the mapping from the reference coordinates to the current coordinates,

$$F_{iK} = \frac{\partial x_i(X)}{\partial X_K}, \tag{1}$$

Using statistical theories and simplified network models, a free energy expression can be formulated. A free energy expression for the temperature-sensitive gel includes two parts (i) the stretching of the network W_s and (ii) the mixing energy of the polymer and the solvent W_m.

$$W = W_s + W_m = \frac{1}{2}NkT[F_{ik}F_{ik} - 3 - 2\log(det\mathbf{F}) + kT[Clog\frac{\upsilon C}{1+\upsilon C} + \frac{\chi C}{1+\upsilon C}] \tag{2}$$

where N is the number of polymer chains per unit dry volume, kT is the temperature in terms of energy, ν is the volume per water molecule, $\mathbf{F}$ is the deformation gradient relative to the dry network, C is the nominal concentration of solvent water molecule and χ is a dimensionless measure of the strength of pairwise interactions between species. This parameter χ is used to fit experimental data in the following form:

$$\chi(T, \phi) = \chi_0 + \chi_1\phi \tag{3}$$

$$\chi_0 = A_0 + B_0T, \chi_1 = A_1 + B_1T \tag{4}$$

Hong et al. assume that these individual long polymers and solvent molecules are incompressible[17]. The condition of molecular incompressibility can be expressed as following:

$$\phi = \frac{1}{1+\upsilon C} = \frac{1}{det(\boldsymbol{F})} \tag{5}$$

ϕ is the volume fraction of the polymer in the hydrogel. The values of A_0, B_0, A_1 and B_1 will be different for different types of temperature-sensitive hydrogel. Afroze et al. [23] provided the values of these parameters for a particular polymer: poly(N-isopropylacrylamide) (PNIPAM) as:

$$A_0 = -12.947, B_0 = 0.04496, A_1 = 17.92, B_1 = -0.0569 \tag{6}$$

To fully define the material in the subroutine, we adopt the above properties of PNIPAM gels in the examples presented herein.

The free energy is written in the form of $W = W(\mathbf{F}, T, C)$. Since the chemical potential must be a constant at the equilibrium state, we introduce another free-energy function $\widehat{W}$ with $\mathbf{F}$, μ and T as independent parameters via Legendre transform.

$$\widehat{W}(\mathbf{F}, T, \mu) = W - \mu C \tag{7}$$

$$\widehat{W}(\boldsymbol{F},T,\mu)=\frac{1}{2}NkT\left[J^{\frac{2}{3}}\bar{I}_1-3-2\,log(J)\right]+ \frac{KT}{v}\left[(J-1)\log\left(\frac{J-1}{J}\right)+(J-1)*\left(\frac{\chi_0}{J}+\frac{\chi_1}{J^2}\right)\right]-\frac{\mu}{v}(J-1) \quad (8)$$

Define the nominal stress as,

$$s_{iK}=\frac{\partial\widetilde{W}}{\partial F_{iK}}=NkT(F_{ik}-H_{ik})+J\left[log\left(\frac{J-1}{J}\right)+\frac{1}{J}+\frac{\chi_0-\chi_1}{J^2}+\frac{2\chi_1}{J^3}\right]H_{ik}-\frac{\mu}{v}JH_{ik} \quad (9)$$

where **H** is the transpose of the inverse of the deformation gradient **F**. This equation of state relates the nominal stress to the deformation gradient when the gel is hold at a constant chemical potential and constant temperature. The finite element modeling of large deformation process of temperature-sensitive gel is possible by utilizing currently gel monophasic theory and properties of PNIPAM.

3. Phase transition

Phase transition phenomena have been observed and studied by many researchers. The phase transition temperature is referred to as the temperature of the coexistent state, at which a sharp volume transition can be observed. Since gel's swelling process can be referred as a hydrated reaction, we assume that the gel may have two different phases before and after phase transition temperature, which imply two different hydrated quantities of hydrogel. In our previous work[24], we inferred variation of temperature leads to different hydrated quantities of hydrogel and thus the volume of gel changes significantly. When gel reaches the phase transition temperature, the free energy density function $W(\mathbf{F},\mu,T)$ has two local minima of equal value. Specifically, if the chemical potential is kept at a certain constant value μ_0, at a particular temperature T^*-the so called phase transition temperature, the two local minima of the free energy density function $W(\mathbf{F},\mu,T)$ would occur at two different deformation gradients $\mathbf{F_1}$ and $\mathbf{F_2}$, i.e.,

$$W(\mathbf{F_1},\mu_0,T^*)=W(\mathbf{F_2},\mu_0,T^*) \quad (10)$$

4. Numerical examples and discussions

4.1. Uniaxially constrained-swelling hydrogels

In our previous work[24], we investigated a PNIPAM hydrogel cube, which immersed in water ($\mu=0$) at certain temperature and allowed to frees welling. Now we adopt 8-node brick elements to model the uniaxial constrained swelling hydrogel. In the modeling, a hydrogel bar is first submerged in water and reaches an isotropic swelling stretch λ_0, and then the gel bar is stretched in longitudinal directions with fixed length. The stress in the transverse directions vanish, so that (9) gives

$$\frac{Nv}{{\lambda_2}^2\lambda_1}(\lambda_2^2-1)+\ln\left(1-\frac{1}{{\lambda_2}^2\lambda_1}\right)+\frac{1}{{\lambda_2}^2\lambda_1}+\left(\frac{\chi_0-\chi_1}{\lambda_2^4\lambda_1^2}+\frac{2\chi_1}{\lambda_2^6\lambda_1^3}\right)-\frac{\mu_0}{kT}=0 \quad (11)$$

$J=\frac{V}{V_0}={\lambda_2}^2\lambda_1$; for water $\mu_0=0$. Using the material model, we can also obtain the volume-temperature curve numerically by FEM. Since the value for Nv was not given in the report Suzuki et al. [25], we have to vary the value of the parameter Nv to fit the experiment data. The symbol k is the Boltzmann constant, and T_0 = 300K, $kT_0\approx 4.14\times10^{-21}J$. It's clearly shown in Figure 1 that when the level of longitudinal stress is different, volume changes sharply but the phase transition temperature alters just mildly.

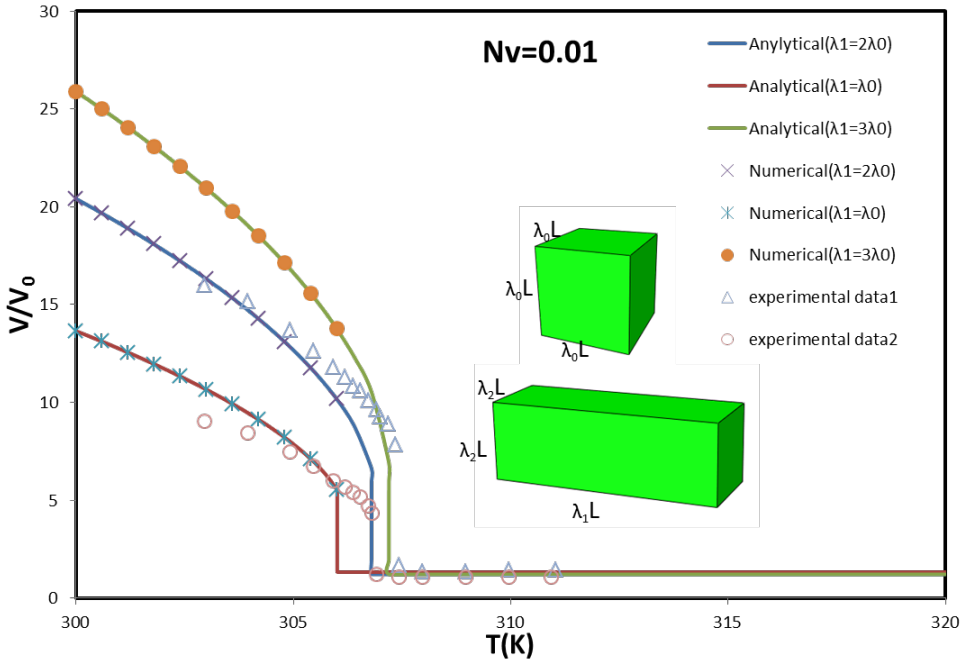
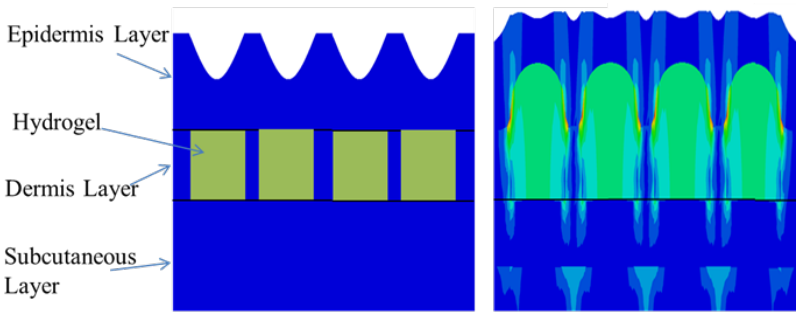


Figure 1. The volumes of uniaxially constrained-swelling hydrogels as functions of temperature. The solid curves are calculated for hydrogels of three levels of longitudinal stretches. The solid curves are obtained analytically for the free swelling of hydrogel at the three values of crosslink density. The marks on the curves are the corresponding numerical predictions. The triangle and circle symbols are experimental data for the corresponding longitudinal stretches taken from Suzuki et al[25].

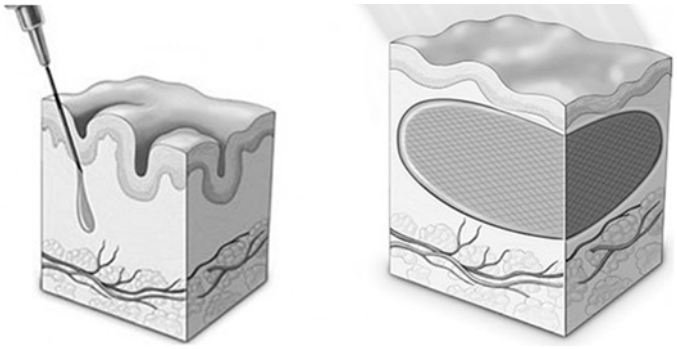
4.2. Simulation of the reconstructed skin

When aged or damaged, the skins of human beings can easily result in winkles or scars. Hillel et al. developed a biosynthetic soft gel replacement that can be injected and swelling in situ with stimuli[26], whereby the swelling of soft fillers of skin reduces or eliminates the skin wrinkles. In this study, we try to model the skin reconstruction procedure and explain how the soft fillers works in skin repair by using temperature-sensitive hydrogel deformation. It is assumed that the skin implant could be modeled as a temperature-sensitive gel material, in which temperature-sensitive hydrogel is injected into the dermis layer. Furthermore, by modulating the parameters of temperature-sensitive hydrogel, we can control the repair process.

As the temperature changes, the injected temperature-sensitive gel will swell. This corresponds to the deformation of soft fillers in the skin repair process. Fig. 2 (a) shows the initial stage which injected implant gel has not been deformed. The deformation pattern of the skin under reconstruction at deformed stage is illustrated in Fig. 2 (b). From Fig. 2 (b), it can be observed that the skin wrinkles can be eliminated. To better understand the skin repair process, the schematic diagrams of reconstructed skin procedure which is taken from Hillel et al.[26] are also shown in the Fig. 2 (c) and (d).



(a) (b)



(c) (d)

Figure 2. After the temperature-sensitive gel is injected into beneath of skin, the wrinkled skin can be eliminated. (a) The pattern of the repaired skin at initial stage; (b) the pattern of the repaired skin at deformed stage. (c) and (d) the schematic of the reconstructed skin taken from Hillel et al[26].

Conclusion

This paper focuses on large deformation of temperature-sensitive hydrogels in equilibrium with a solvent and mechanical load at varying temperature. Adopting a specific free energy density function and obtained constitutive equation, we have developed a finite element method for equilibrium analysis of temperature-sensitive hydrogels and implemented the theory via a user-defined subroutine in ABAQUS. From the simulated results, we demonstrate the potential applications of the proposed approach in the analysis of the complex phenomenon, such as how to explain the deformation of implant in skin reconstruction. We hope that this work can explain various complex phenomena in nature and can provide a useful tool for the future theoretical and experimental studies on temperature-sensitive hydrogel.

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