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Mechanical response and equilibrium swelling of temperature-responsive gels

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ABSTRACT

A model is developed for the mechanical behavior of thermo-responsive gels that accounts for an increase in concentration of physical cross-links between chains driven by phase separation. Governing equations are derived for equilibrium water uptake under unconstrained and constrained swelling, as well as for the elastic response of swollen gels. These relations are applied to the analysis of swelling diagrams on NIPA, VCL, PEG, and NIPA-DMIAA gels. The ability of the model to predict the growth of elastic moduli above the volume phase transition temperature is confirmed by numerical simulation.

1. Introduction

Hydrogels are three-dimensional networks of polymer chains connected by chemical and physical cross-links. Temperature-sensitive gels form a special class of gels whose equilibrium water uptake is strongly affected by temperature. These gels swell noticeably being immersed into a water bath at temperatures T below their volume phase transition temperature T_c and shrink when temperature exceeds T_c. Equilibrium and transient response of temperature-sensitive gels has attracted substantial attention in the past decade due to a wide range of potential biomedical applications of this class of stimuli-responsive polymers [1,2].

An abrupt decay in equilibrium degree of swelling of a thermo-responsive gel at the critical temperature T_c is explained by changes in effective hydrophilicity of polymer chains containing hydrophilic and hydrophobic segments [3,4]. At temperatures below T_c, each hydrophobic segment is surrounded by a cage-like structure (clathrate) formed by water molecules bridged by hydrogen bonds. Due to thermal fluctuations, these structures become unstable when temperature grows. Breakage of cages formed by water molecules around hydrophobic segments induces their agglomeration and formation of aggregates from which water molecules are expelled. At $T > T_c$, most clathrates are broken, and the micro-structure of a thermo-responsive gel becomes inhomogeneous [5]. It consists of deswollen hydrophobic aggregates bridged by hydrophilic segments of chains and separated by a network of nano-channels in which water molecules are located. Transition from a homogeneous (below T_c) to an inhomogeneous (above T_c) micro-structure (separation of a gel into polymer-rich and polymer poor phases) has been studied by means of dynamic light scattering, nuclear magnetic resonance, small-angle neutron scattering, fluorescence spectroscopy, and infrared absorption spectroscopy [6,7].

Experimental and theoretical studies on water uptake by temperature-sensitive gels have been initiated about 40 years ago [8,9]. This subject has recently become a focus of attention [10–17] due to possible applications of thermo-responsive gels as micro- and nano-carriers for targeted drug delivery [18] and controllable three-dimensional scaffolds for growth and differentiation of stem cells [19].

Changes in equilibrium degree of swelling of thermo-responsive gels with temperature are conventionally described within the Flory-Rehner theory, where the Flory-Huggins parameter χ is replaced with an "effective" coefficient treated as a function of

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temperature T and volume fraction of polymer network $\phi_{\rm n}$ [8,9]. An increase in concentration of hydrophobic segments driven by thermally induced breakage of cages formed by water molecules around these segments is described by setting

$$\chi = \chi_0(T) + \chi_1(T)\phi_{\rm n} \tag{1}$$

and presuming the coefficients χ_0 and χ_1 to evolve linearly with T or T^{-1} [20]. An advantage of this concept is that it allows experimental swelling diagrams to be approximated by means of a model with a modest number of adjustable parameters. Its shortcoming is that this approach fails to predict evolution of mechanical properties with temperature, in particular near and above the volume phase transition temperature $T_{\rm c}$. This disadvantage can be explained by the fact that elastic moduli of a gel are proportional to the number of cross-links, whereas the conventional theory disregards the growth of physical junctions between chains induced by aggregation of hydrophobic segments under heating. It has recently been demonstrated that mechanical properties of thermo-responsive gels play the key role in their biomedical applications [21,22]. This implies the need in adequate modeling of the mechanical response of temperature-sensitive gels together with the kinetics of water uptake.

The objective of this study is twofold: (i) to derive a constitutive model for the mechanical behavior of thermo-responsive gels that takes into account formation of physical junctions induced by aggregation of hydrophobic segments and (ii) to determine adjustable parameters in the governing equations by fitting observations in unconstrained and constrained equilibrium swelling tests and mechanical tests on swollen samples at various temperatures.

The novelty of the proposed approach consists in treatment of the polymer network in a temperature-sensitive gel as a superposition of two networks: the first is formed under preparation when flexible chains are covalently cross-linked, while the other is developed when temperature exceeds $T_{\rm c}$ and extra physical junctions arise due to association of hydrophobic segments. These two networks have different reference (stress-free) states and different elastic moduli (the modulus of the first network is temperature-independent, while that of the other network grows with temperature due to an increase in concentration of hydrophobic aggregates).

For simplicity, hydrophobic aggregates are treated as permanent junctions, and their rearrangement (breakage and reformation) is neglected. This implies that the mechanical behavior of a thermo-responsive gel above $T_{\rm c}$ is treated as nonlinearly elastic, and the viscoelastic phenomena [23] are disregarded.

The exposition is organized as follows. Constitutive equations for a thermo-responsive gel under an arbitrary three-dimensional deformation with finite strains are developed in Section 2 by means of the free energy imbalance inequality. These relations are applied to study equilibrium water uptake in Section 3. Temperature-induced changes in elastic moduli are discussed in Section 4. Adjustable parameters in the governing equations are found by fitting experimental data in Section 5. Concluding remarks are formulated in Section 6.

2. Constitutive model

A gel is thought of as a two-phase medium composed of solid (polymer network) and fluid (water) constituents. The solid and fluid phases are modeled as immiscible (mass exchange between the phases is disregarded) interpenetrating continua (any elementary volume contains both phases).

2.1. Kinematic relations

The initial configuration of a gel coincides with that of an undeformed dry specimen at a fixed temperature $T_0 < T_{\rm c}$. Transformation of the initial configuration into the actual configuration at an arbitrary temperature T is described by the deformation gradient $\mathbf{F}$.

Denote by C concentration of water molecules (number of molecules per unit volume in the initial state). Disregarding thermally induced volume expansion, we adopt the molecular incompressibility condition in the form

$$\det \mathbf{F} = 1 + Cv, \tag{2}$$

where v stands for the characteristic volume of water molecule. Eq. (2) means that volume deformation of a gel is driven by changes in solvent content only.

Concentration of water molecules (per unit volume in the actual state) is given by $c = C/J$, where $J = \det \mathbf{F}$, and volume fractions of the polymer network $\phi_{\rm n}$ and solvent $\phi_{\rm s}$ are determined by

$$\phi_{\rm n} = \frac{1}{1+Cv}, \qquad \phi_{\rm s} = \frac{Cv}{1+Cv}. \tag{3}$$

The polymer network in a gel consists of two parts. The first network is formed under preparation when cross-linking polymerization of monomers of a pre-gel solution is performed. The other network is formed at temperatures T exceeding the volume phase transition temperature $T_{\rm c}$ due to association of hydrophobic segments whose aggregates serve as physical junctions between polymer chains. Adopting the affinity hypothesis, we suppose that macro-deformation of a gel coincides with macro-deformations of the networks.

The reference state of the covalently cross-linked network (where stresses in chain vanish) coincides with the as-prepared state of the gel. Transformation of the initial configuration into the reference configuration is described by a deformation gradient $\mathbf{f}_1$. For an isotropic polymer network, we set