



Mechanical behavior of temperature-sensitive gels under equilibrium and transient swelling

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ABSTRACT

Water uptake by a thermo-responsive gel is strongly affected by temperature: the gel swells below its volume phase transition temperature T_c and shrinks above T_c . Observations reveal two types of equilibrium swelling diagrams: discontinuous (with degree of swelling Q falling abruptly at T_c) and continuous (with Q decreasing smoothly with temperature). A constitutive model is developed for the mechanical behavior of a temperature-sensitive gel subjected to swelling that accounts for changes in its structure (phase separation) at T_c . Adjustable parameters are found by fitting experimental data in equilibrium swelling tests, transient deswelling–reswelling tests, and tensile-compressive tests on poly(N , N -diethylacrylamide) gel with a continuous equilibrium swelling curve and poly(N – n -propylacrylamide) gel with a discontinuous diagram. Numerical simulation demonstrates qualitatively different responses of gels with discontinuous and continuous swelling diagrams.

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1. Introduction

Hydrogels are three-dimensional networks of hydrophilic chains bridged by chemical and physical cross-links. Thermo-responsive (TR) gels form a special class of hydrogels whose equilibrium water uptake is strongly affected by temperature. TR gels swell noticeably at temperatures below their volume phase transition temperature T_c and shrink above T_c . Equilibrium and transient swelling of TR gels has recently attracted substantial attention due to a wide range of potential applications of these materials as micro- and nano-carriers for targeted drug delivery and release (Bergueiro & Calderon, 2015), biodegradable scaffolds for cell growth and tissue regeneration (Kim et al., 2015), thermo-regulated catalytic systems (Hapiot, Manuel, & Monflier, 2013), transducers, sensors (Deligkaris, Tadele, Olthuis, & van den Berg, 2010) and thermal actuators (Deng, Rohn, & Gerlach, 2016) for microfluidic (Hilber, 2016; Klatt et al., 2012) and small-scale robotic devices (Hines, Petersen, Lum, & Sitti, 2017).

A strong decay in equilibrium degree of swelling of a TR gel in the vicinity of its critical temperature T_c is conventionally explained by changes in the effective hydrophilicity of chains containing hydrophilic and hydrophobic segments (Aseyev, Tenhu, & Winnik, 2011; Halperin, Kroger, & Winnik, 2015). Below T_c , each hydrophobic segment is surrounded by a cage-like structure formed by water molecules bridged by hydrogen bonds. When temperature grows, clustered water molecules are destabilized by thermal fluctuations. Breakage of cages formed by water molecules induces association of hydrophobic segments and formation of aggregates from which water molecules are expelled. Above T_c , most cages are broken, and the structure of a TR gel becomes inhomogeneous (Kurzbaach, Junk, & Hinderberger, 2013): it consists of a number of deswollen

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hydrophobic aggregates bridged by hydrophilic segments and separated by nano-channels in which water molecules are located.

Experimental and theoretical studies on water uptake by TR gels were initiated by Hirokawa and Tanaka (1984), Matsuo and Tanaka (1988) and Li and Tanaka (1990). A constitutive framework for the analysis of water transport and elastic behavior of TR gels under three-dimensional deformations with finite strain was developed in Ji, Mourad, Fried, and Dolbow (2005), Birgersson, Li, and Wu (2008), Chester and Anand (2011), Cai and Suo (2011), Ding, Liu, Hu, Swaddiwudhipong, and Yang (2013), Toh, Ng, Hu, and Liu (2014) and Ding, Toh, Hu, Liu, and Ng (2016). These studies are grounded on the Flory–Rehner theory, where the Flory–Huggins (FH) parameter χ is replaced with an “effective” coefficient χ treated as a function of temperature T and volume fraction of the polymer network ϕ_n (Kojima & Tanaka, 2010; Quesada-Perez, Maroto-Centeno, Forcada, & Hidalgo-Alvarez, 2011). Another approach, where changes in equilibrium degree of swelling with temperature were described within the Landau theory of phase transition, was suggested in Drozdov (2014a, 2015).

A shortcoming of the concept of effective FH parameter is that it disregards formation of hydrophobic aggregates serving as physical junctions between chains. As a result, this theory cannot predict a strong (ten-fold) increase in the elastic moduli induced by the growth of concentration of physical bonds above T_c (Guo, Sanson, Marcellan, & Hourdet, 2016; Hinkley, Morgret, & Gehrke, 2004; Shibayama, Morimoto, & Nomura, 1994), see also Figs. 6–8 below. To describe temperature-induced changes in elastic moduli, a polymer network in a TR gel is thought of as a superposition of two networks. The first is formed by covalently cross-linked chains, while the other is developed when temperature exceeds T_c and extra physical junctions (hydrophobic aggregates) arise between chains due to phase separation.

The objective of this work is three-fold: (i) to derive constitutive equations for the elastic response of and diffusion of solvent through TR gels that account for formation of hydrophobic aggregates above T_c , (ii) to determine adjustable parameters in the governing relations by fitting observations in equilibrium water uptake tests, uniaxial tensile tests, and transient deswelling–reswelling tests, and (iii) to apply the model to the analysis of stresses developed in T -jump experiments on thin disks made of temperature-sensitive gels.

In a T -jump test, a gel sample equilibrated in a water bath with some initial temperature T_0 is transferred into another bath with temperature T , and degree of swelling Q is measured as a function of time t elapsed after changes in temperature (Shibayama & Nagai, 1999). Parameter Q decreases with t when $T_0 < T$ (deswelling) and grows with t when $T_0 > T$ (reswelling).

Poly(*N*-isopropylacrylamide) (NIPA) gel is conventionally used in experimental investigation of TR gels. Observations on this gel reveal two types of equilibrium swelling diagrams (Okajima, Harada, Nishio, & Hirotsu, 2002): (i) discontinuous (with a pronounced decay in degree of swelling Q at the critical temperature T_c), and (ii) continuous (with Q decreasing smoothly with temperature T). Changes in chemical structure of NIPA gels (an increase in molar fractions of monomers and cross-linker) induce transformation of discontinuous diagrams into continuous curves.

To realize how smoothness of an equilibrium swelling curve correlates with stresses developed in a TR gel under transient water uptake, this study focuses on the analysis of observations on two alkyl-substituted acrylamide gels (Bae, Okano, & Kim, 1990) that show discontinuous (poly(*N* – *n*-propylacrylamide) (NnPA) gel) and continuous (poly(*N*, *N*-diethylacrylamide) (DEAM) gel) swelling diagrams independently of their composition, provided that molar fractions of monomers and cross-linker are changed in reasonable intervals.

The novelty of this study consists in the following. (I) It is revealed that the difference between discontinuous and continuous equilibrium swelling curves can be associated with evolution of the FH parameter χ above the volume phase transition temperature T_c . This quantity remains constant at $T > T_c$ for TR gels with discontinuous swelling diagrams (which implies that all hydrophobic segments released from their cages form aggregates serving as physical junctions) and grows with temperature for TR gels with continuous swelling curves (this growth of hydrophobicity of the network reflects an increase in concentration of hydrophobic segments not associated into aggregates). (II) It is demonstrated that the growth of χ above T_c induces drastic changes in the distribution of water molecules in a TR gel subjected to a T -jump test. Under appropriate conditions, a gel specimen is split into water-poor and water-rich domains separated by a sharp interface moving inside the sample. This process is accompanied by a pronounced growth of stresses that can lead to breakage of hydrophobic aggregates and cause instabilities in a gel sample.

The exposition is organized as follows. A model for the mechanical response of and water diffusion through a TR gel is reported in Section 2. Equilibrium unconstrained water uptake is analyzed in Section 3. Evolution of elastic moduli with temperature is discussed in Section 4. Water transport through a thin free-standing disk is studied in Section 5. Section 6 focuses on the analysis of observations on NnPA and DEAM gels. Concluding remarks are formulated in Section 7. Derivation of the governing equations is presented in Appendices A to D.

2. Constitutive model

A gel is treated as a two-phase medium composed of solid (polymer network) and fluid (water) constituents.

2.1. Kinematic relations

The initial configuration of a gel coincides with that of an undeformed dry specimen at some temperature $T_{in} < T_c$. With reference to the affinity hypothesis, we suppose that macro-deformation of a gel coincides with deformation of its polymer

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