Modeling the response of double-network gels with sacrificial junctions under swelling

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A B S T R A C T

Constitutive equations are derived for the time- and rate-dependent response of double-network gels under three-dimensional deformation with finite strains accompanied by swelling. The polymer network of a gel involves permanent and transient components. Chains in the permanent network are bridged by covalent cross-links, while chains in the transient network are connected by temporary junctions that break and restore under loading. The model is applied to the analysis of tensile cyclic tests and relaxation tests on fully swollen specimens and constrained water uptake tests on as-prepared samples. Good agreement is demonstrated between experimental data and results of simulation.

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1. Introduction

Hydrogels are three-dimensional networks of hydrophilic chains bridged by chemical and physical cross-links, hydrogen bonds, van der Waals interactions, and crystallite associations (Van Vlierberghe et al., 2011). The mechanical response of gels subjected to swelling has recently become a focus of attention as these materials demonstrate potential for a wide range of smart applications including biomedical devices, drug delivery carriers, scaffolds for tissue engineering, filters and membranes for selective diffusion, sensors, and soft actuators (Stuart et al., 2010; Koetting et al., 2015).

A drawback of covalently cross-linked gels is that they are relatively weak (the elastic modulus of 100 kPa) and brittle (the fracture energy of 1 J/m^2). Their mechanical properties can be enhanced significantly (elastic modulus of 10 MPa, fracture energy of 10^3 J/m^2) by formation of a sacrificial network where physical cross-links break and restore under deformation (Chen et al., 2015; Neal et al., 2015). Design and preparation of double-network gels (with a permanent network formed by chemical cross-links and a transient network bridged by temporary junctions) with high stiffness, strength, toughness, and fatigue resistance have attracted noticeable attention in the past few years (Chen et al., 2016a). Several mechanisms are proposed to create reversible sacrificial bonds: (i) ionic interactions [ionic cross-linking of bound charges in polyelectrolyte gels by multivalent ions (Sun et al., 2012; Wang et al., 2015) and formation of polyion complexes between fixed ions in polyam-

pholyte gels (Sun et al., 2013; Luo et al., 2016)], (ii) hydrophobic association (Jiang et al., 2010; Li et al., 2012; Zhang et al., 2015), (iii) supramolecular interaction based on coordination bonds (Tang et al., 2016) and association of host-guest pairs (Nakahata et al., 2016).

Unlike covalently cross-linked gels whose mechanical response is elastic, the response of gels with sacrificial cross-links is time- and rate-dependent. The viscoelastic behavior of physically cross-linked gels is observed in relaxation tests as a substantial decay in stress with time (Mayumi et al., 2013; Xin et al., 2015; Zhang et al., 2015; Sun et al., 2016). Their viscoplastic behavior is demonstrated in tensile tests as a strong increase in stress with strain rate (Mayumi et al., 2013; Xin et al., 2015) and in cyclic tests where a pronounced difference is observed between the loading and unloading paths of a stress–strain diagram (Sun et al., 2012; 2013; Xin et al., 2015; Zhang et al., 2015; Chen et al., 2016b). The viscoelasto-plastic response is observed in self-recovery tests which reveal that the stress–strain diagram of a virgin gel specimen coincides with that of the sample subjected to cyclic loading followed by recovery (Sun et al., 2012; 2013; Lin et al., 2015; Zhang et al., 2015; Tang et al., 2016).

The growing interest to viscoelasticity of double-network gels is driven, in particular, by their biomedical applications as scaffolds for migration, proliferation, and differentiation of mesenchymal stem cells. Recent observations demonstrate that stress relaxation in a gel scaffold plays the key role in regulation of adherent cell behavior (Chaudhuri et al., 2016).

The viscoelastic response of gels with sacrificial cross-links is conventionally described within the concept of transient polymer networks with temporary junctions that break and rearrange at
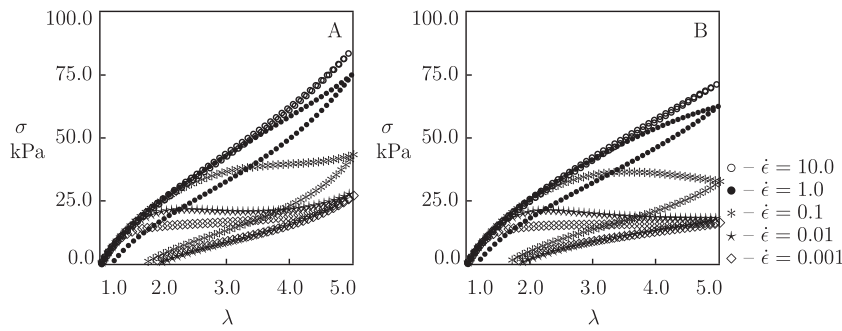
Fig. 1. Stress σ versus elongation ratio λ. Symbols: results of simulation for cyclic tests with $\lambda_{max} = 5.0$ and various strain rates $\dot{\epsilon}$ s^{-1}. A: $K = 100.0$. B: $K = \infty$.

random times being driven by thermal fluctuations (Green and To-bolsky, 1946; Tanaka and Edwards, 1992). To reach quantitative agreement with observations, the initial variant of this theory was refined in Drozdov (1998), where (i) a distribution of temporary junctions with various activation energies was introduced (to predict non-exponential relaxation diagrams) and (ii) the rate of rearrangement was linked with mechanical factors (to account for the effect of strain on the kinetics of relaxation).

The concept of transient networks was first applied to the analysis of self-recovery of gels in Hui and Long (2012). Several variants of this theory were recently developed and validated by comparison with observations (Long et al., 2014; Guo et al., 2016; Meng et al., 2016). To ensure agreement with experimental data, the rate of restoration of temporary junctions was presumed to be non-exponential (Long et al., 2014; Guo et al., 2016) and to depend on some measure of current strain (Meng et al., 2016).

A shortcoming of the conventional theory of transient networks is that it implies that the fully swollen state of a gel is independent of concentration of temporary junctions (under water uptake, stresses in chains bridged by physical cross-links relax totally due to the rearrangement process whose characteristic time is substantially lower than the characteristic time for diffusion of water). This conclusion contradicts, however, experimental data in water uptake tests that show a pronounced decay in equilibrium degree of swelling with concentration of physical cross-links (Jiang et al., 2010; Zhang et al., 2015).

The objective of this study is to develop constitutive equations for the mechanical response of a double-network gel under an arbitrary three-dimensional deformation accompanied by swelling that (i) demonstrate agreement with observations in relaxation tests and cyclic tests on fully swollen samples and (ii) describe adequately the kinetics of water uptake. The model is grounded on the concept of transient networks with mechanically-induced rearrangement of chains.

For definiteness, we consider a gel whose polymer chains are bridged by permanent junctions formed due to chemical cross-linking and temporary junctions created due to association of hydrophobic segments. The network is treated as a combination of two networks with permanent and temporary junctions. Permanent junctions remain unchanged under loading, while a temporary junction can break when shear stress in the network exceeds its strength. The rate of breakage is proportional to the excess shear stress. Immediately after rupture, each temporary junction restores, but the reference (stress-free) state of strands linked by this junction differs from the initial state of the network. The transient network is presumed to be strongly inhomogeneous (Webber et al., 2007; Xin et al., 2014), and its heterogeneity is characterized by distribution of temporary junctions with various shear strengths.

The exposition is organized as follows. Constitutive equations for the mechanical response of a double-network gel subjected to

swelling are derived in Section 2 by means of the free energy imbalance inequality. The governing relations are applied to the analysis of tensile relaxation tests and cyclic tests on swollen samples in Section 3. The kinetics of constrained swelling of a thin gel layer attached to a rigid substrate is studied in Section 4. Concluding remarks are formulated in Section 5. To clarify the exposition, long formulas are collected in Appendix.

2. Constitutive model

A gel is treated as a two-phase medium composed of solid (a polymer network) and fluid (water) constituents. The solid and fluid phases are modeled as immiscible (mass exchange between the phases is disregarded) inter-penetrating continua (any elementary volume contains both phases). The polymer network is composed of two components. The first (permanent) network is formed by chains bridged by covalent cross-links. The other (transient) network is formed by chains connected by temporary junctions rearranging with time. Interaction between the networks is disregarded (Huang et al., 2007). For schematic representation of the structure of double-network gels, the reader is referred to Fig. 1 in Peak et al. (2013).

2.1. Kinematic relations

Macro-deformation of a gel coincides with deformation of its permanent network (the affinity hypothesis). For definiteness, the initial configuration of the gel is chosen to coincide with that of an undeformed dry specimen. Transformation of the initial configuration into the actual configuration at time t is described by the deformation gradient $\mathbf{F}(t, \mathbf{X})$, where $\mathbf{X}$ stands for Lagrangian coordinates. To simplify the notation, arguments of functions are dropped when this does not lead to confusion.

Denote by C concentration of water molecules (number of molecules per unit volume in the initial state). According to the molecular incompressibility condition,

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

where v stands for the characteristic volume of water molecule. Eq. (1) states that volume deformation of a gel is driven by changes in concentration of water only. Concentration of water molecules per unit volume in the actual configuration reads

$$c = \frac{C}{J}. \tag{2}$$

Volume fractions of water molecules and polymer network are given by

$$\phi_w = \frac{Cv}{1 + Cv}, \qquad \phi_n = \frac{1}{1 + Cv}. \tag{3}$$

Denote by N_1 concentration of junctions in the permanent network (the number of chemical cross-links between strands per unit