



Time-dependent mechanical properties of tough ionic-covalent hybrid hydrogels



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ABSTRACT

Hybrid gels featuring interpenetrating covalent and ionic crosslinked networks have recently been shown to exhibit both high toughness and recoverability of strain-induced network damage. The high toughness results from the energy dissipated as entropically strained network strands are released by the dissociation of ionic crosslinks. As in the so-called double network hydrogels, the toughening process is inherently linked to network damage. This damage, however, can be recovered to a large degree in hybrid gels due to the reformation of ionic associations when the gel is unloaded. The stability of the ionic network under load is here investigated and it is shown that these networks show large stress relaxation at constant strain, time dependent stress-strain behaviour and rate-dependent toughness. A double exponential model is invoked to mathematically describe the stress relaxation of the hybrid gels indicating at least two relaxation mechanisms. The rate-dependent toughness and the relaxation behaviour of the hybrid gels are attributed to the labile unzipping of the ionic crosslinks which is assumed to be load and time dependent.

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1. Introduction

The super water-absorbing capabilities and external-stimuli responsiveness of hydrogels are of interest for a wide range of biological and bio-mechanical applications, such as sensors, actuators, and replacement materials for human tissues [1–3]. Unfortunately, many proposed applications are not realized due to the poor mechanical properties of conventional covalently-crosslinked hydrogels. Enhancing the mechanical performance of hydrogels has thereby become a central challenge and several breakthroughs have been achieved including double network hydrogel (DN gel) [4], clay-polymer nano-composite hydrogel (NC gel) [5], and sliding hydrogel (SR gel) [6]. These novel hydrogels exhibit remarkably-improved mechanical strength and toughness compared with the conventional hydrogels [7].

Recently, in het Panhuis et al. [8] and Suo et al. [9] have independently reported an interpenetrating polymer network hydrogel based on a covalently crosslinked polyacrylamide (PAAm) and an ionically crosslinked biopolymer (gellan gum in the former study and alginate in the latter). Since the hydrogels combined two interpenetrating networks with different crosslinking types, they were referred to as “ionic-covalent entanglement” hydrogel (ICE) [8] or a “hybrid gel” [9]. Both hydrogel systems exhibit high toughness and recoverability in mechanical properties, which is a major advantage over other tough hydrogels that are permanently damaged during loading and unsuitable for applications where repeated loading and unloading is required.

When the network topologies of PAAm-alginate hybrid gel were optimized, the resulting hydrogel was found to be highly stretchable (extended to >20 times its original length), very tough (fracture energy reaches 9000 J/m²), and recoverable in mechanical properties. Mechanical hysteresis is a feature of these materials wherein the loading and unloading tensile curves are different. Importantly, it has been shown that a rest period after unloading allows the hybrid gels to recover and reloading follows closely the previous loading path. In contrast, the reloading curves in DN gels follow the previous unloading curve indicating the permanent

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nature of the damage occurring in these covalently crosslinked gels. The high toughness and mechanical recoverability of the hybrid gel system originates from the ionic crosslinks, where the guluronic units (also known as G group) on the alginate chains are associated by Ca^{2+} ions to form a zip-like junction described by a so-called “egg-box” model [10–13]. When a hybrid gel is subject to external force the crosslinks are “unzipped”, dissipating dissociation energy of the ionic bonds and entropic energy of the loaded network strands. High toughness of the hybrid gel is obtained when the alginate network is highly-crosslinked and the PAAm network is loosely-crosslinked [9,14–18], which mirrors the topologies known to maximize toughness in DN gels [19]. The ionic bonds that are pulled apart during the hybrid gel deformation are re-formed at zero-stress at a temperature-induced network recovery process to largely retrieve the mechanical properties of the virgin gel [9].

The unstable nature of the egg-box ionic crosslinks formed between the divalent cations and G groups on the alginate chains has been noted previously. In particular, a very large and rapid stress relaxation was reported in a Ca^{2+} ion crosslinked alginate single network. More than 90% of the initial stress relaxed when the ionic alginate gel was stretched and held at a set strain. The major mechanism accounting for the rapid stress relaxation was the unzipping of the ionic crosslinks. In many practical applications hydrogels are required to function under applied loads where stress relaxation and/or creep are undesirable. It is, therefore, important to determine the load stability and time-dependent mechanical properties of hybrid ionic/covalent tough gels.

The present study investigates the time-dependent behaviour of the ionic-covalent PAAm-alginate hybrid gel. We attempt to provide direct experimental evidence for the effect of the labile ionic crosslinks on the mechanical properties of the hybrid gel system over time. Rate-dependent toughness and stress relaxation tests were conducted on hybrid gel samples. We also characterize the mechanical strength and toughness of the hybrid gels prepared with various ionic and covalent crosslinker concentrations and swollen to equilibrium in water. Previous work studied the mechanical properties of the hybrid gels in the non-equilibrium, as-synthesized state.

2. Experimental

2.1. Materials

The monomer of the covalently-crosslinked network was acrylamide (AAM, 40 wt% aqueous solution; Sigma–Aldrich). Potassium persulfate (KPS; Sigma–Aldrich) and N,N'-methylenebisacrylamide (MBAA; Sigma–Aldrich) were used as radical initiator and crosslinking agent for the polymerization of PAAm gel, respectively. Sodium alginate from brown algae (Alg; Sigma–Aldrich) was used to prepare the ionically crosslinked network, and calcium chloride (CaCl_2 ; Sigma–Aldrich) was used as ionic crosslinker. All the chemical reagents were used as received. Deionized water was used in gel preparation.

2.2. Hydrogel preparation

2.2.1. Ionic-covalent PAAm-alginate hybrid gel

Two sets of sample gels were synthesized. In respective sets, the amount of MBAA or CaCl_2 was varied systematically while the concentration of other chemical reagents remained constant. In set 1, to prepare hybrid gels with different covalent crosslinking densities, 0.1 mol% KPS and various amounts of MBAA (0.01, 0.05, 0.1, and 0.5 mol%) were dissolved in 40 wt% aqueous AAM solution. The concentration of KPS and MBAA was with respect to the molar concentration of AAM. The alginate solution was made with

1.33 g alginate and 23 g deionized water. Two solutions were then blended and stirred for 2 h with final AAM and alginate concentrations at, respectively, 12 wt% and 4 wt%. The gel solution was next bubbled by nitrogen for 40 min and then degassed in a vacuum environment for 2 h to remove dissolved oxygen, and then injected into a glass reaction mould consisting of two glass plates separated by a 2 mm thick silicon spacer. The mould was placed in a 60 °C fanned oven for 6 h to finalize the polymerization. The resulting gels were called covalent PAAm-alginate gels until they were immersed in 2 wt% CaCl_2 solution for 5 days to ionically crosslink the alginate. In set 2, MBAA and KPS concentration was fixed at 0.05 and 0.1 mol% with respect to the molar concentration of AAM. All the gel preparation procedures were identical to set 1 until the covalent PAAm-alginate gels were obtained. Those gels were next immersed in CaCl_2 solutions of different concentrations (0.05, 0.1, 0.5, and 2 wt%) to produce hybrid gels with various ionic crosslinking densities. In the following text, for simplicity, the hybrid gel is referred to by its characteristic MBAA or Ca^{2+} concentration. For example, in set 1, the gel prepared with MBAA concentration at 0.05 mol% is referred to as 0.05 mol% gel. In set 2, if the gel was immersed in 2 wt% CaCl_2 solution, it was named as 2wt% gel. Before any mechanical test was conducted, the hybrid gels were soaked in deionized water for 7 days to reach the swelling equilibrium.

2.2.2. Covalent PAAm-alginate gel

The same procedure introduced above was applied to prepare covalent PAAm-alginate gel. The only difference was that the gel was not immersed in CaCl_2 solution, hence it was composed of non-ionically crosslinked alginate and covalently crosslinked PAAm network. In the present work, the covalent PAAm-alginate gel was prepared with identical chemical composition to the 0.05 mol% hybrid gel, and it was used in the as-synthesized state in the stress relaxation test, since soaking in water would cause the loss of the uncrosslinked alginate from the gel.

2.2.3. PAAm gel

PAAm single network gel was prepared with 40 wt% acrylamide solution containing 0.1 mol% KPS and 0.05 mol% MBAA with respect to the acrylamide. After the gel solution was bubbled with nitrogen, it was transferred into the same glass reaction mould used for hybrid gel synthesis. The mould was then placed in 60 °C fanned oven for 6 h to obtain PAAm single network gel. The as-synthesized PAAm gel was used directly in the stress relaxation test, since equilibrating in water would lead to excessive swelling of this loosely crosslinked gel.

2.3. Tensile and fracture energy test

All the mechanical measurements were carried out on an EZ-L mechanical tester (Shimadzu, Japan). Tensile tests were performed on dumbbell shaped samples with gauge length of 20 mm and width of 4 mm. Strain and strain rate were determined by crosshead displacement. Standard rubber elasticity theory was fitted to the initial extension ratio (λ) of stress (σ)-stretch curve to calculate shear modulus (μ) of each tested sample from Ref. [20]:

$$\sigma = \mu \left(\lambda - \frac{1}{\lambda^2} \right) \quad (1)$$

Fracture energy was obtained by the tearing test where the hybrid gel was cut into a rectangular shape (50 mm × 7.5 mm) with a 20 mm long initial notch. The thickness of each sample was measured using a digital calliper. The fracture energy of a sample gel was calculated as:

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