Mechano-optical behavior of loosely crosslinked double-network hydrogels: Modeling and real-time birefringence measurement during uniaxial extension

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ABSTRACT

Real-time uniaxial strain-induced birefringence in loosely crosslinked double-network (DN) hydrogels synthesized from acrylamide (AAm) and N,N-dimethyl(acrylamide) (DMA) was measured. Tensile tests were performed at different extension rates from quasi-static conditions to very rapid tests followed by a holding for relaxation. Both DN hydrogels exhibited negative birefringence whose absolute value increased with extension and remained constant during relaxation. DN hydrogel synthesized from AAm displayed a linear stress optical (birefringence − true stress) behavior, however, a nonlinear trend was observed for the DN gel synthesized from DMA. A simple photoelastic model was developed based on the mechanical behavior of the gels using Fung elastic potential and Brewster's stress-optical law, and the model was compared with the experimental data.

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1. Introduction

Hydrogels are hydrophilic polymeric networks that absorb large amounts of water, but the network structure that is formed by chemical or physical crosslinks is insoluble [1]. Hydrogels are similar to biological tissues and this makes them attractive candidates for various applications in bioengineering [2]. The optical properties of hydrogels become important when they are used in ophthalmology, especially for contact lenses [3]. For example, with a birefringent hydrogel, it is possible to make multifocal contact lenses [4,5]. Apart from practical purposes, the measurement of optical properties such as birefringence can provide a deeper understanding of the orientation of polymer chains and development of optical anisotropy within a material during deformation. The first study of strain-induced birefringence of hydrogels was reported by Hrouz and Ilavský [6] who measured the birefringence of a loosely crosslinked polyacrylamide gel in a mixture of acetone and water for very small elongation, less than 20%. Geissler et al. [7] reported birefringence development during polymerization of polyacrylamide gels, which they termed *spontaneous birefringence*. They concluded that the birefringence was the result of the development of strain during the gelation process.

In order to study strain-induced birefringence in hydrogels under finite deformations, the hydrogel must be strong enough to be stretched to high stretch ratios. Conventional chemically cross-linked hydrogels are usually mechanically weak and break at relatively low extensions. Although there are various strategies to synthesize tough hydrogels [8], few studies considered or measured strain-induced birefringence of hydrogels in finite tensile deformation. Murata and Haraguchi [9] measured birefringence in nanocomposite hydrogels synthesized from N-isopropyl acrylamide under finite deformations. They observed a reversion in birefringence data of nanocomposite hydrogels in uniaxial deformation. Wu et al. [10] synthesized a robust optically anisotropic hydrogel by combining an anisotropic, physically cross-linked network of semirigid poly(2,2′-disulfonyl-4,4′-benzidine tereph-thalamide) (PBDT) and a chemically cross-linked network of poly-acrylamide (PAAm) based on the double-network concept developed by Gong et al. [11]. They measured the birefringence of PBDT/PAAm gels by a polarizing optical microscope after elongating

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the hydrogel samples to a certain strain using a vernier caliper, and observed reversion in the birefringence data. Recently, Shikinaka et al. [12] measured birefringence in extended hydrogels synthesized from acrylamide and imogolite nanotubes. They found that by increasing the concentration of nanotubes a reversion is observed in birefringence data. In all those investigations, however, the birefringence was measured off-line, after the hydrogel was deformed, which raises the question of the effects of polymer relaxation during the time between the stretching and the birefringent measurement. Real-time measurements eliminate that problem and provide a clearer understanding of the variation of birefringence during deformation. *In situ* mechano-optical measurements allow one to directly measure the birefringent behavior over the entire deformation history, in contrast to off-line measurements that can realistically access only discrete strains. Similarly, the measurement of birefringence at very low stretch ratio and low stress, which is of crucial importance for calculating the stress-optical coefficient − especially for non-linear deformation, is a daunting challenge for off-line measurements, but easily achievable with real-time experiments. In effect, since in off-line measurements there is no way to measure the load applied on the sample, it is not possible to see the variation of birefringence as a function of stress which is crucial in measuring the stress-optical coefficient.

This paper reports the first real-time birefringence measurements of chemically crosslinked hydrogels under finite tensile deformation. Specifically, the development of strain-induced birefringence is reported for two double-network (DN) hydrogels, one synthesized from acrylamide (AAm) and the other from *N,N*-dimethyl(acrylamide) (DMA). In order to perform birefringence measurements during finite deformations, the hydrogel must be tough enough to sustain the load. Recently, Shams Es-haghi and Weiss [13] developed a method to fabricate tough chemically crosslinked hydrogels from multiple neutral networks. This method will be used to make tough DN hydrogels from AAm and DMA. The stress-optical coefficient is independent of network topology, such as crosslink density, but it is sensitive to the chemical structure of the network, which affects the mean refractive index of the material [14]. Thus, with the two DN hydrogels that were used in this research, it was possible to determine the effect of the chemical structure on the development of strain-induced birefringence.

2. Experimental section

2.1. Materials

Acrylamide (AAm) and *N,N′*-methylenebis(acrylamide) (MBAA) were purchased from Sigma-Aldrich Chemical Co. and used as received. *N,N*-dimethyl(acrylamide) (DMA) was obtained from Sigma-Aldrich Chemical Co. and was vacuum distilled prior to use. A photoinitiator, 2-oxoglutaric acid (OXGA), was obtained from Fluka Chemical Co. and used as received.

2.2. Synthesis of double networks

DN hydrogels were synthesized by a two-step sequential free-radical polymerization [13]. The first network was prepared by adding OXGA and MBAA to a 4 M solution of AAm in deionized (DI) water. The monomer solution was injected into a glass mold made of two parallel glass slides, which was then exposed for 20 min to 365 nm ultraviolet (UV) light (15 mW/cm^2), see Scheme 1. The resulting single-network (SN) hydrogel was then immersed into the same reaction mixture until an equilibrium swelling was achieved. The AAm-swollen SN gel was then placed between two

parallel glass slides and exposed for 20 min to 365 nm ultraviolet (UV) light (15 mW/cm^2) to produce a AAm-DN hydrogel, Scheme 1. DMA-DN hydrogels were synthesized with the same procedure, Scheme 2.

Any unreacted monomer was removed by immersing the DN hydrogels in DI water, which was replaced a number of times with fresh water. Each individual network is described by the name of the monomer used, followed by four numbers in parenthesis that indicate 1) the molar concentration of monomer in DI water, 2) the mol% of photoinitiator with respect to monomer, 3) the mol% of crosslinking agent with respect to monomer and 4) UV dose used for the reaction (i.e., intensity × time of exposure). Thus, DMA(4,0.1,0.01,18) corresponds to the polymerization of a 4 M DMA solution using 0.1 mol% OXGA, 0.01 mol% MBAA and a UV dose of 18 J/cm^2. Table 1 summarizes the recipes used to synthesize the DN hydrogels in this study.

2.3. Mechano-optical measurements

A real-time mechano-optical measurement platform equipped with a CCD camera was used to study the deformation behavior of the DN hydrogels. Details of the equipment are discussed elsewhere [15]. In short, a rectangular specimen was clamped to clamps attached to two crossheads of the uniaxial stretching machine. Both top and bottom crossheads of this custom-made machine move in opposite directions during stretching, which allows the center of the specimen to remain stationary during extension. The analysis of the mechanical behavior assumed that the material was incompressible and the deformation was isotropic in the non-stretching directions. Thus,

$$D_0 W_0 L_0 = D_t W_t L_t, \tag{1}$$

$$\frac{W_t}{W_0} = \frac{D_t}{D_0}, \tag{2}$$

where D, W and L are the thickness, width and length of the specimen and the subscripts 0 and t denote the initial and instantaneous values, i.e., at time = 0 and time = t, respectively. The width of the center cross-sectional area was measured in real-time by a laser micrometer, and the true stress, σ_T, engineering strain, ε_e, and Hencky (true) strain, ε_H, were calculated by

$$\sigma_T = \frac{F_t}{W_t D_t} = \frac{F_t}{\left[D_0 \left(\frac{W_t^2}{W_0} \right) \right]}, \tag{3}$$

$$\varepsilon_e = \frac{L_t - L_0}{L_0} = \left(\frac{W_0}{W_t} \right)^2 - 1, \tag{4}$$

$$\varepsilon_H = Ln\left(\frac{L_t}{L_0} \right) = Ln\left[\left(\frac{W_0}{W_t} \right)^2 \right], \tag{5}$$

where F_t is the instantaneous force at time = t. A visible wavelength light source (λ = 546 nm) was used to measure the optical retardation (Γ) at the center of the specimen cross-section. The in-plane birefringence (Δn_{12}) was calculated by

$$\Delta n_{12} = \frac{\Gamma}{D_t} = \frac{\Gamma}{\left(\frac{W_t D_0}{W_0} \right)}. \tag{6}$$

The DN hydrogel specimens were stretched at room