



Uniaxial and plane orientations of clay platelets in nanocomposite gels with different compositions during stretching and recovery



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ARTICLE INFO

Article history:

Received 7 November 2016

Received in revised form

6 December 2016

Accepted 9 December 2016

Available online 21 December 2016

Keywords:

Optical anisotropy

Birefringence

Nanocomposite gels

Clays

Plane orientation

ABSTRACT

Changes in the birefringence (Δn_{NC}) of nanocomposite (NC) gels upon stretching and recovery were investigated for gels comprising a poly(*N*-isopropylacrylamide)–clay network structure. Irrespective of the composition of the NC gels, a change in the birefringence appeared upon stretching; Δn_{NC} varied greatly depending on the clay and water contents (C_{clay} and C_{w} , respectively) of the gels and the stretching ratio. The NC gels with low C_{clay} gave rise to unique Δn_{NC} vs. strain curves with a maximum Δn_{NC} . For samples with higher C_{clay} , the variation of Δn_{NC} s observed in the edge- and through-directions, which is attributed to plane-orientation of the clay platelets, increased with increasing C_{clay} . This was confirmed by scanning electron microscopy observation, and the percentage plane-orientation was evaluated from the Δn_{NC} data. On recovery of the strain, the plane-oriented clay platelets underwent minimal reversion to the original state, although most of the PNIPA chains reverted to the random conformation. The effects of C_{w} on the Δn_{NC} –strain curves were also clarified.

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1. Introduction

Optical anisotropy analysis is one of the most effective means of characterizing the structure of materials, such as minerals, layered materials, liquid crystals, polymers, and composites [1–5]. In polymer science, numerous studies have been conducted on various types of polymeric materials, such as polymer crystals with lamellar or extended structures [6,7], liquid crystal polymers with mesogenic groups in the main-chain and/or side-chains [8,9], liquid crystal elastomers [10,11], polymer solutions [12–14], fibers [15], films [16–18], and nanocomposites [13,19], to reveal their crystalline nature, super-structures, and changes in their structure and properties under external stimuli. However, there are only a few reports on polymer hydrogels consisting of three-dimensional polymer networks with water filling the interstitial space of the network, because these hydrogels are normally amorphous (optically isotropic) and are also incapable of extensive stretching. Thus far in this field, optical anisotropy analysis has only been performed for polymeric hydrogels containing mesogenic groups [12,20,21] or for those oriented by a flow-gelation process [22], an electric field

[21,23], and an inclusion of graphene oxide [24].

Nanocomposite hydrogels (NC gels) have been prepared in situ by free radical polymerization of monomers (acrylamide derivatives; e.g., *N*-isopropylacrylamide) in the presence of exfoliated inorganic clay in aqueous media [25,26]. Due to the unique organic (polymer)–inorganic (clay) network structures [27,28], the NC gels exhibit extraordinary mechanical properties, including a high stretching ratio and high strength, as well as high transparency and well-defined thermoresponsive properties [29,30]. In particular, extremely high toughness (e.g., tensile strength ~1 MPa) and total control of the coil-to-globule transition of the polymer chains has been achieved for NC gels with clay content higher than the critical value [31,32]. A number of new functions such as self-healing behavior, ultra-high surface hydrophobicity, contractive force generation, cell harvesting, and large and rapid swelling/deswelling behaviors have been realized with NC gels [33].

In a previous communication [34], we reported changes in the optical anisotropy of NC gels with relatively low clay content upon stretching. In the present paper, we report changes in the optical anisotropy of NC gels with different compositions upon uniaxial stretching in more detail, focusing on differences in the birefringence observed in the edge- and through-direction; the effects of the clay and water contents and changes in the birefringence on the strain recovery are also studied in order to evaluate the orientation

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and relaxation properties of the clay and PNIPA chains during the deformation process.

2. Experimental

2.1. Materials

N-Isopropylacrylamide (NIPA), provided by Kohjin Co., Japan, was purified by recrystallization from a toluene/*n*-hexane mixture (1/200 w/w) and dried under vacuum at 40 °C. Other reagents were purchased from Wako Pure Chemical Industries, Japan, and used without further purification. The water used for all experiments was ultrapure water (18 M Ω) supplied by a Puric-Mx system (Organo Co., Japan). Dissolved oxygen in the ultrapure water was removed by bubbling with nitrogen gas for more than 3 h prior to use. As the inorganic clay, the synthetic hectorite “Laponite XLG” (Rockwood, Ltd., UK; [Mg_{5.34}Li_{0.66}Si₈O₂₀(OH)₄]Na_{0.66}; layer size = ca. 30 nm diameter \times 1 nm thickness, cation exchange capacity = 104 mequiv/100 g) was used after washing with ethanol and freeze-drying. Here, we used the molar mass of Laponite XLG: 762 g mol⁻¹. Potassium persulfate (KPS) and *N,N,N',N'*-tetramethylethylenediamine (TEMED) were used as the initiator and the catalyst, respectively.

2.2. Synthesis of NC gels

The sample codes for the NC gels are defined in terms of the concentration of clay (C_{clay}) in the initial reaction solution. For example, “NC n gel” refers to an NC gel prepared using an aqueous solution with 1 M NIPA and n mol% of clay (which equals $0.76 \times n$ wt% based on the formula Mg_{5.34}Li_{0.66}Si₈O₂₀(OH)₄). The clay concentration ($C_{\text{clay}} = n \times 10^{-2}$ mol L⁻¹H₂O) was varied in the range of $n = 2$ –23, while the monomer concentration was fixed at 1 M for all samples. The procedure for synthesis of the NC gels with low ($n < 10$) and high ($n \geq 10$) clay concentrations are the same as those reported previously [31]. As a typical example, to prepare a NC n gel film, a transparent aqueous solution consisting of water (30 g), inorganic clay ($0.229 \times n$ g), NIPA (3.39 g), catalyst (TEMED, 24 μ L), and initiator (KPS, 0.03 g) was poured into a laboratory-made film apparatus (150 mm \times 50 mm \times 2 mm thickness) under an atmosphere of nitrogen gas and kept in a water bath at 20 °C for 20 h to allow in-situ, free-radical polymerization. For the lightly chemically crosslinked PNIPA hydrogels, the same solutions with very small amounts of *N,N'*-methylenebis(acrylamide) (BIS) (0.05 mol% of monomer), instead of clay, were used. NC n and PNIPA gels with different water contents were prepared by slow drying at room temperature or by allowing the gels to swell in water at 20 °C. The water content (C_w) is defined as follows: $C_w (\%) = 100 \times W_{\text{H}_2\text{O}}/W_{\text{gel}}$, where W_{gel} and $W_{\text{H}_2\text{O}}$ are the weights of the gel and the water in the gel, respectively.

2.3. Measurements

2.3.1. Optical anisotropy (birefringence)

NC gels with dimensions of 70 \times 4 \times 2 (mm) were stretched uniaxially to a predetermined length under the following conditions: 25 °C, gauge length = 30 mm, cross-head speed = 100 mm min⁻¹. The thickness and width of the stretched gels were monitored by using a microscope equipped with a digital camera system (DXM1200C, Nikon). The stretched gels were fixed on a frame in order to measure the optical anisotropy of the gels at 25 °C and 90–100% relative humidity (to avoid drying). The retardation (I) of the NC gels at different strains was determined using a polarizing microscope (Nikon, Eclipse LV100 Pol) equipped with

two compensators (Senarmont and Berek) in conjunction with crossed polarizers. The birefringence is given by: $\Delta n \equiv n_{\parallel} - n_{\perp} = I/d$, where n_{\parallel} and n_{\perp} are the refractive indices parallel and perpendicular to the direction of uniaxial stretching, respectively; d is the gel thickness corrected for the drawing ratio. The refractive indices of the as-prepared NC gel films were measured by using an Abbe refractometer (2T, Atago Co., Japan) at 25 °C.

2.3.2. Scanning electron microscopy (SEM)

The NC20 gel film was stretched to 600% and dried at ambient temperature for one day with the ends fixed. The film was then calcined by heating to 650 °C (3 °C \cdot min⁻¹), and kept at 650 °C for 60 min in air. A calcined sample of the as-prepared NC5 gel film was also prepared by drying the gel with the ends free, followed by calcination under the same conditions used for the NC20 gel. The samples were coated with platinum (ca. 5 nm thickness) before the observations. Scanning electron microscope (SEM) observations were conducted by using a FE-SEM S-8000 (Hitachi Co., Japan) instrument at an accelerating voltage of 20 kV.

2.3.3. Tensile mechanical properties

Tensile mechanical tests were conducted in the same manner as described in the former section (2.3.1) using a Shimadzu Autograph AGS-H system. In the recovery measurements, the residual strains (%), $(L(t) - L_0) \times 100/L_0$, were 20% for NC5, 100% for NC10, and 200% for NC20, where $L(t)$ is the sample length at t min (=1 min) after releasing the stress, and L_0 is the initial sample length (30 mm).

2.3.4. Viscosity

The reaction solutions (without initiator) were subjected to viscosity measurements using a vibro-viscometer (frequency = 30 Hz, Model-SV10, A&D Company, Japan) at 20 °C.

3. Results and discussion

3.1. Birefringence of NC gel films

The NC n gels with different C_{clay} ($n = 2$ –23) were all obtained as transparent films with high mechanical properties. The optical transmittance, refractive index, and tensile mechanical properties (tensile strength, and elongation at break) and the gel compositions are summarized in Table 1. Visual observation with a polarizing microscope using cross nicols revealed that the NC n gels with $n < 10$ and $n \geq 10$ were optically isotropic and anisotropic, respectively, as shown for the typical NC5 and NC15 gels in the inset in Fig. 1a. This is consistent with the results reported in the previous paper [35]. That is, NC gels with C_{clay} higher than the critical value ($C_{\text{clay}}^* = 10 \times 10^{-2}$ mol L⁻¹H₂O; $n = 10$) exhibit optical anisotropy due to the spontaneous liquid crystal-like packing of the clay platelets due to steric hindrance. Above C_{clay}^* , random arrangement of the clay platelets is restricted in the network because the average inter-

Table 1

Compositions, transmittance, refractive indices, and tensile mechanical properties of as-prepared NC n gel films and viscosity of corresponding reaction solutions (without initiator).

NC n gel	NC2	NC5	NC10	NC15	NC20	NC23
Composition (wt%)						
Clay: $W_{\text{clay}}/W_{\text{dry}}$	11.5	25.6	38.9	48.1	56.5	60.8
Water: $W_{\text{water}}/W_{\text{gel}}$	88.9	86.5	84.1	80.8	79	77.6
Refractive index (-)	1.355	1.356	1.358	1.363	1.366	1.368
Transmittance (%)	91	92	93	91	90	90
Tensile strength (KPa)	45	110	423	835	990	1062
Elongation at break (%)	1265	1005	968	1024	915	920
Viscosity (mPa \cdot s)	1	3	9511	52420	119260	>120000

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