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Anisotropic optical film embedded with cellulose nanowhisker

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ABSTRACT

We investigated anisotropic optical behaviors of composite films embedded with CNWs. To control the orientation of CNWs, elongation was applied to the composite film. Morphological and mechanical analyses of the specimens were carried out to examine the influence of the applied extension. The CNWs were found to be aligned in the elongated direction, yielding remarkable anisotropic microstructure and optical properties. As the applied elongation and CNW loading increased, the resulting degree of polarization and birefringence increased due to increased interactions between the embedded particles. This study suggests a way to prepare an anisotropic optical component with nanoparticles of which the microstructures, such as orientation and filler content, can be controlled.

1. Introduction

Cellulose is a fascinating renewable and abundant natural material offering manifold advantages in production cost, physical and chemical properties, and production security (Brahmakumar, Pavithran, & Pillai, 2005; Dumanli et al., 2014b; Iwatake, Nogi, & Yano, 2008; Jacob & Thomas, 2008; Jang, Jeong, Oh, Youn, & Song, 2012; Siro & Plackett, 2010). Recently, cellulose-based nanomaterials, including cellulose nanowhisker (CNW) and microfibrillated cellulose (MFC), have attracted growing interest for engineering advanced functional materials in many applications, such as structural, optical, biomedical, and energy areas (Cranston & Gray, 2006; Li, Wu, Song, Qing, & Wu, 2015b; Lin & Dufresne, 2014). In particular, CNWs possess compelling features, such as high specific modulus, low thermal expansion coefficient, unique morphology, high aspect ratio, optical transparency, negative anisotropic diamagnetic susceptibility, biocompatibility, and inherent sustainability (Dumanli et al., 2014a; Lagerwall et al., 2014; Wicklein et al., 2015). Furthermore, this natural nanoparticle can allow the manifestation of structural colors based on photonic crystal structures of biological matter and open a bio-inspired route for developing new multifunctional material systems. They can be incorporated into a wide range of polymers due to their relatively flexible surface chemistry (Goffin, Habibi, Raquez, & Dubois, 2012; Pan, Hamad, & Straus, 2010; Ten, Bahr, Li, Jiang, & Wolcott, 2012). CNWs are generally prepared through sulfuric acid hydrolysis from various plant products (e.g., wood, hemp, sisal, cotton, and ramie), sea animals, and bacteria (Kim, Kang, & Song, 2013; Li et al., 2010; Nakagaito & Yano, 2008; Shafiei-Sabet, Hamad, & Hatzikiriakos, 2013).

A CNW suspension with lyotropic liquid crystals can be used to prepare a film with optical chirality, due to the D-glucose building blocks of CNWs. Rod-like CNWs spontaneously produce left-handed chiral nematic structure (or cholesteric structure) at a critical concentration according to Onsager (Eichhorn, 2011). The cholesteric structure encompasses stacked planes of nematic CNWs aligned along a director with the orientation twisted from one plane to the next in an anticlockwise fashion (Kelly, Giese, Shopsowitz, Hamad, & MacLachlan, 2014). Also, the chiral nematic structure, the pitch of which is of the order of the wavelength of visible light, is capable of reflecting left-handed circularly polarized light, in general, across the near-IR and visible spectrum (Kelly, Shopsowitz, Ahn, Hamad, & MacLachlan, 2012). These attractive optical features enable applications such as security papers and chiral templates because they cannot be reproduced by photocopying (Pan, Hamad, & Straus, 2010). On the other hand, circular dichroism (CD), referring to the difference in absorption of left and right circularly polarized lights, and polarized microscopy measurements are used to examine chiral nematic structures embodied in the material (Shopsowitz, Qi, Hamad, & Maclachlan, 2010).

Controlling the orientation of CNWs is essential for designing and manufacturing novel nanoparticle-embedded composites with desirable optical and mechanical characteristics. For example, unlike isotropic spherical nanoparticles, the helical self-assembly characteristics of CNWs allows a material to have more complex internal structure with chirality and more enhanced mechanical properties. When a particle is subjected to an external field, it can be orientated relying on the applied field direction. For

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this, shear force (Ebeling et al., 1999; Li et al., 2015a), electric (Bordel, Putaux, & Heux, 2006), and magnetic fields (Kvien & Oksman, 2007; Sugiyama, Chanzy, & Maret, 1992) have been used. CNWs tend to align along an applied shear force and electric field direction but orient in a direction perpendicular to a magnetic field direction due to their negative diamagnetic anisotropy. Compared with the physical behavior of helically oriented CNWs, that of unidirectionally aligned CNWs under external fields still remains poorly understood and needs to be investigated in a more systematic manner.

In this study, elongation was used to unidirectionally align CNWs in a water soluble polymer, polyvinyl alcohol (PVA). We investigated the effects of applied elongation and concentration of CNWs on the mechanical and optical properties of CNW composite films. To our knowledge, this is the first report applying elongation to orient CNWs unidirectionally in a polymer and exploring the resulting degree of polarization and birefringence to look into the possibility of using the material as an optical element. As well as the influence of the draw ratio, we exploited the effect of the CNW concentration on the physical properties of the films.

2. Experimental

2.1. Materials and preparation of cellulose nanowhisker

Microcrystalline cellulose (MCC) power was obtained from Acros Organics; the average particle diameter was 50 μm. Sulfuric acid and filter paper with a pore size of 400 nm were purchased from Ducksan Chemical (Korea) and Whatman (USA), respectively. To isolate cellulose nanowhisker (CNW), acid hydrolysis of MCC was carried out with a sulfuric acid of 64 wt% at 45 °C for 2 h. The CNW suspension was sonicated in an ice bath and centrifuged. The supernatant was removed, followed by the addition of water. The suspension was diluted several times until an appropriate pH of the suspension was reached. When the suspension was stabilized, the supernatant was filtered and freeze-dried. The PVA used in this study had a molecular weight of 85,000–124,000 and a melting temperature of 200 °C. CNW/PVA suspension was cast and dried on a petri dish. To align CNWs in the polymer matrix, the CNWs/PVA films were extended. Different draw ratios were considered. Here, the draw ratio means the ratio of the length of the undrawn film to that of the drawn film.

2.2. Morphological characterization

The size of CNW was characterized using a Nano DS particle size analyzer (Cilas, France), which uses dynamic light scattering and static light scattering in a single optical system. Red and blue light wavelengths were employed, and the size distribution of CNW was determined based on the Mie scattering theory. Transmission electron microscope (TEM) measurement was carried out using JEM-200CX (JEOL). For the observation of CNWs, a droplet of the CNW suspension was deposited on a 200-mesh TEM grid, and carbon-coated. The applied voltage was 200 kV. The ImageJ software was used to measure the dimensions of the CNW. The cross-section of specimens was observed morphologically using scanning electron microscopy (JEOL, JSM-5410LV). Before the observation, all the specimens were coated with platinum using an ion sputter coater (JEOL, JFC-1100E).

2.3. Mechanical and optical characterization

Mechanical properties such as tensile strength, Young's modulus, and elongation at break were evaluated using a universal testing machine (UTM, Instron 3365) according to ASTM D638. Dumbbell-shaped film specimens with a thickness of 0.2 μm were prepared and the elongation rate was 5 mm/min.

A polarized optical microscope (Leitz-orthoplan, Leica) was used to obtain photomicrographs of CNW suspensions. The transmittance of the samples was measured at a wavelength in the range of 250–1000 nm using a UV–visible spectrometer (Lambda 1050, Perkin-Elmer). The degree of polarization (DP), a measure of the extent to which the light is polarized, was computed as follows:

$$\mathrm{DP}\,(\%) = \frac{T_{\max} - T_{\min}}{T_{\max} + T_{\min}} \times 100$$

where, $T_{\max}$ and $T_{\min}$ are the maximum and minimum transmittances of light. X-ray diffraction experiments of the CNW/PVA films were carried out using D/MAX-2500 (Rigaku) at 40 kV and 45 mA with Cu Kα radiation (wavelength = 0.154 nm) in the 2θ range of 0–40° with a step interval of 0.02°.(Yang et al., 2013) The birefringence of PVA film was measured with a Leitz orthoplan polarizing microscope (Leica, Germany). Retardation of PVA films was determined with a B-type Berek compensator. The thickness of samples was 30–75 μm. The birefringence was calculated using the following equation:

$$\Gamma = \Delta n \times d$$

where, Γ is the retardation, Δn is the birefringence, and d is the sample thickness. Circular dichroism (CD) experiments were conducted using a Jasco J-815 Spectropolarimer. Samples were scanned at 20 nm/min with a step resolution of 0.2 and 1 nm bandwidth. The light source was a xenon lamp covering the spectral range of 170–850 nm.

3. Results and discussion

Morphological characteristics of the CNW suspension are demonstrated in Fig. 1. Fig. 1a presents a photograph of the CNW suspension. Birefringence is materialized in the CNW suspension when CNWs act as a liquid crystal material with a stable and homogeneous dispersion. The birefringence pattern between two crossed polarizers is presented in Fig. 1b. The anisotropy leads to a birefringent glassy-like state with iridescent domains. The polarized optical microscopy image of the suspension is displayed in Fig. 1c. The concentration of CNWs was 0.5 wt%. The CNW suspension exhibits liquid crystalline behavior above a critical concentration, consistent with Onsager's theory for rigid rod-like particles (Onsager, 1949). As the concentration of CNWs increases, the suspension state changes from an isotropic phase with a random arrangement of CNWs, a chiral nematic phase, and a gel (Edgar & Gray, 2002). The CNW suspension encompasses anisotropic domains with the chiral nematic phase.

Fig. 2a shows the TEM image of CNWs. The size distribution of CNWs is presented in Fig. 2b. The isolated CNWs have an average length of 440 nm and diameter of 45 nm, giving an average aspect ratio of around 10.

Fig. 3 demonstrates the polarized optical microscopic images of CNW/PVA films. Similar to the birefringence images of the CNW suspension, interference colors were observed in the films. When the plane polarized light passes through CNWs with different refractive indices in their longitudinal and transverse directions in the polarized light microscopy, it is split into slow and fast lights in the CNW film, thereby generating a phase difference in the lights. When the lights pass through the rear polarizer, they interfere destructively or constructively, according to the phase difference induced by the birefringent CNW (Ross et al., 1997).

Fig. 4a–c exhibit the mechanical results of the CNW films: tensile strength, Young's modulus, and elongation at break as a function of the CNW content. Unlike conventional filler-reinforced