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Rheological behavior of cellulose nanowhisker suspension under magnetic field

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ABSTRACT

We investigated the influence of a magnetic field on the rheology of cellulose nanowhisker (CNW) suspension. The morphology of CNWs was analyzed by using polarized optical microscopy (POM) and transmission electron microscopy (TEM). The findings show that the application of the magnetic field leads to an increase in shear viscosity and viscoelastic properties such as the storage and loss moduli. A mesoscale constitutive model was adopted to provide better understanding of the effect of particle concentration on the orientation of CNWs. As the concentration increases, the steric interaction between particles becomes significant and the effect of the applied magnetic field on the internal structure of the CNW suspension was reduced. In addition, the size distribution of CNWs was characterized using a light scattering method.

1. Introduction

Recently, one of the main issues in advanced material engineering is the need to reduce the environmental footprint (Abdul Khalil, Bhat, & Ireana Yusra, 2012; Lu, Askeland, & Drzal, 2008; Souza Lima & Borsali, 2004; Wood, Coles, Maggs, Meredith, & Kirwan, 2011). This leads to an exponential growth of the interest in natural materials (Casetta & Bertini, 2007; Karus & Kaup, 2002; Lee & Song, 2013; Oksman, Skrifvars, & Selin, 2003). In particular, cellulose is an attractive renewable and abundant natural resource able to meet this strong demand, offering a number of advantages in production cost and physical and chemical properties (Brahmakumar, Pavithran, & Pillai, 2005; Iwatake, Nogi, & Yano, 2008; Jacob & Thomas, 2008; Jang, Jeong, Oh, Youn, & Song, 2012; Siro & Plackett, 2010).

Cellulose nanowhisker (CNW) (or nanocrystalline cellulose (NCC)) is a defect free rodlike nanoparticle, which is generally harvested via sulfuric acid hydrolysis and centrifugation from various plants (e.g., wood, hemp, sisal, cotton, and ramie), sea animals, and bacteria (Kim, Kang, & Song, 2013; Li et al., 2010; Shafiei-Sabet, Hamad, & Hatzikiriakos, 2013). Since CNWs are strongly competitive in terms of mechanical properties (including high specific modulus, high stiffness, low thermal expansion coefficient, unique morphology, and high aspect ratio), and their inherent sustainability, they can be incorporated into a wide range of polymers (Goffin, Habibi, Raquez, & Dubois, 2012; Ten, Bahr, Li, Jiang, & Wolcott, 2012). Colloidal aqueous suspensions of NCC develop three different phase structures, from isotropic, chiral nematic ordered structure to gel as the concentration of CNWs increases. Depending on the size, surface charge, polydispersity, and ionic strength of CNWs, the phase–phase transition and the characteristics of the suspension phase change. For the chiral nematic ordered structure, the cholestric pitch determining the optical properties of the CNW suspension and film is determined from the concentration, flow field, electric and magnetic field, and temperature (Bercea & Navard, 2000; Kimura & Kimura, 2008; Shopsowitz, Qi, Hamad, & MacLachlan, 2010).

Regarding the rheological behavior of the CNW suspension, it has been reported that the chiral nematic ordered suspension above a first critical concentration shows a so-called three-region viscosity behavior similar to a typical liquid crystal polymer solution. On the other hand, isotropic suspension at a low concentration and gel suspensions above a second critical concentration exhibit a single shear thinning behavior similar to a conventional polymer solution. Rheology, a powerful tool used to examine the internal structure of complex fluids, can provide valuable information such as size, dispersion, concentration, interaction, and surface properties in the CNW suspension (Lu, Hemraz, Khalili, & Boluk, 2014; Shafiei-Sabet et al., 2012; Wu et al., 2014).

When a particle is subjected to a magnetic field, it can be rotated depending on the applied field direction and its magnetic feature. Since CNWs have negative, anisotropic diamagnetic susceptibility,

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CNWs are likely to align in a direction perpendicular to the magnetic field direction (Kvien & Oksman, 2007; Sugiyama, Chanzy, & Maret, 1992). During processes such as casting, extension, and spinning, the orientation control of CNWs make it possible to tailor the structure and final properties (Bordel, Putaux, & Heux, 2006; Ebeling et al., 1999). In this sense, a magnetic field is a useful means of manipulating the orientation of CNWs in a liquid state. However, the shear stress has thus far been employed as the main driving force to control the orientation of CNWs in the suspension using a rheometer, and the resulting rheological properties have been studied. Therefore, the effect of the magnetic field on the orientation of CNWs needs to be understood in a more systematic fashion (Chen, Yu, Liu, Chen, Wang, & Quyang, 2013; Pullawan, Wilkinson, & Eichhorn, 2012; Urena-Benavides, Ao, Davis, & Kitchens, 2011).

In the current study, the relationship between the magnetic field and rheological behavior of CNW suspension was investigated. We analyzed morphologies of CNWs prepared through sulfuric acid hydrolysis using polarized optical microscopy (POM) and transmission electron microscopy (TEM). The size distribution of CNWs was characterized using a light scattering method.

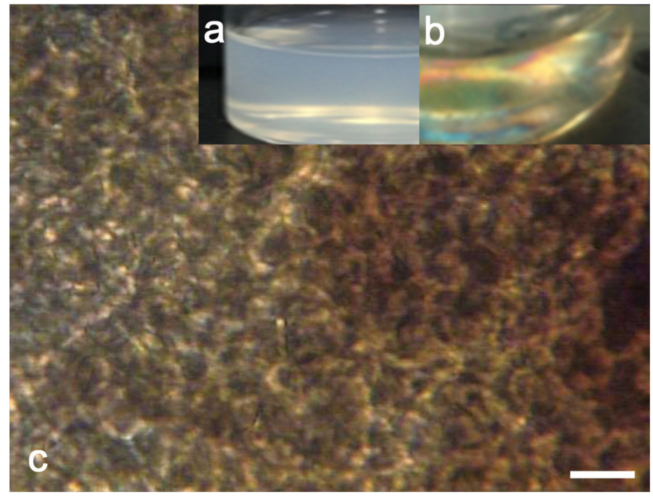

Fig. 1. Morphological observation of CNW suspension: (a) photograph, (b) polarized light image, and (c) polarized optical microscopy image. The scale bar indicates 40 μm.

2. Experimental

2.1. Materials

Microcrystalline cellulose powder (MCC) with an average diameter of 50 μm was purchased from Acros Organics. Sulfuric acid and filter paper with a pore size of 400 nm were supplied by Ducksan Chemical (Korea) and Whatman (USA), respectively.

2.2. Preparation of cellulose nanowhisker

Acid hydrolysis of MCC was conducted with 64 wt% sulfuric acid at 45 °C for 2 h in order to isolate the cellulose nanowhisker (CNW). The hydrolysis reaction was terminated by adding cold distilled water. The CNW suspension was sonicated in an ice bath and centrifuged. The resulting supernatant was removed, and water was then added. The suspension was diluted several times through a similar process to reach an appropriate pH of the suspension. When the suspension was stabilized, the supernatant was filtered and freeze-dried.

2.3. Size 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. Water was used a dispersion liquid, and CNWs of 0.1 wt% were suspended in the liquid. Red light wavelength and blue light wavelength were employed, and the size distribution of CNW was obtained based on the Mie scattering theory.

2.4. Morphological characterization

Transmission electron microscope (TEM) measurement was carried out using JEM-200CX (JEOL). For the observation of CNW, a droplet of the CNW suspension was deposited on a 200-mesh TEM grid and then carbon-coated. The applied voltage was 200 kV. The commercial software, ImageJ, was adopted to measure the dimensions of CNW.

A polarized optical microscope (Leitz-orthoplan, Leica) was employed to obtain photomicrographs of the CNW suspension.

2.5. Rheological characterization

Magnetorheological features of the CNW suspension were analyzed using a parallel plate rheometer (MCR 302, Anton Paar) equipped with an electromagnet kit which can generate a magnetic field perpendicular to the shear flow direction. The apparent viscosity was measured with varying shear rate ranging from 0.01 to 100 s^{-1} under the magnetic field. In this experiment, the intensity of the magnetic field ranged from 0 to 1 T. The tests were carried out after removing the previous shear stress history. The time-dependent viscosity was measured in the range of 0–1000 s with a constant shear rate of 0.1 s^{-1}. In the oscillatory shear mode, dynamic viscoelastic properties, including the storage modulus, loss modulus, tangent delta, and complex viscosity, were obtained while applying an angular frequency sweep of 0.01–100 rad s^{-1}. The applied strain amplitude was 0.5–1% during the oscillatory shear test. To prevent the evaporation of specimens, silicone oil was placed on the periphery of the specimen along with an evaporation blocker. Prior to the measurement, the suspension was sonicated for 10 min for the better dispersion of CNWs. All rheological measurements were conducted at 25 °C unless otherwise mentioned.

2.6. Theory

To understand these rheological behaviors more profoundly, we adopted the theoretical model proposed by Bhandar and Wiest (2003). They proposed a mesoscale constitutive model where acicular magnetic particles were regarded as rigid dumbells dispersed in a solvent. It was assumed through a single-particle mean field approach that only one particle could represent the average behavior of dispersed particles orienting along external fields. In the model, Brownian motion, anisotropic hydrodynamic drag, a steric force (i.e., the Maier–Saupe potential), and a mean field magnetic

Table 1
Flow behavior index of the power law model.

Sample	Magnetic field	n
0.1 wt%	0.0	0.1337
	0.5	0.068
	1.0	−0.002
0.5 wt%	0.0	−0.036
	0.5	−0.05
	1.0	−0.036