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Viscoelastic characteristics of all cellulose suspension and nanocomposite

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ABSTRACT

We prepared cellulose nanocrystal (CNC)/carboxymethyl cellulose (CMC) suspensions and nanocomposites and carried out rheological analysis of the all-cellulose samples. Morphological observation of the prepared CNCs was conducted using transmission electron microscopy (TEM) and atomic force microscopy (AFM). The electrokinetic characteristic of the CNCs was evaluated from zeta potential measurement. A simple shear test, an oscillatory shear test, and dynamic mechanical analysis (DMA) were carried out, and their results were compared. The findings revealed that the greater shear-thinning behavior and more solid-like rheological behavior were observed with an increase in the content of CNCs embedded in both the suspensions and nanocomposites. In addition, the viscoelastic properties acquired in different experimental modes (i.e., shear and extension) were compared from a rheological perspective.

1. Introduction

Today, natural substances such as cellulose, silk, and protein are attracting a great deal of attention as advanced engineering materials in order to minimize the environmental damage caused by the production of manmade materials. In particular, cellulose, a promising renewable and sustainable natural material, has many advantages, including low cost, good chemical and physical properties, sustainability, and low environmental load (Clasen and Kulicke, 2001; Kim, Kang & Song, 2013; Motta, Fambri & Migliaresi, 2002; Park, Park & Ruckenstein, 2001; Sehaqui et al., 2012). Thus far, much effort has been made to prepare and apply nanosized cellulosic fillers in various applications (Raquez et al., 2012; Shafiei-Sabet, Hamad & Hatzikiriakos, 2012; Yang et al., 2013). Nanofibrillated cellulose (NFC) can be disintegrated from the plant cell wall of cellulose. In general, NFC of 1–2 micron meters in length and a diameter of around 10 nm has been adopted as a substrate and a reinforcing filler for electrical and mechanical applications, respectively (Abdul Khalil, Bhat & Ireana Yusra, 2012; Lu, Wang & Drzal, 2008; Sehaqui et al., 2012). NFC can be harvested using hydrodynamic mechanical forces with a homogenizer, a microfluidizer, or a sonicator. On the other hand, cellulose nanocrystals (CNCs) are prepared through sulfuric acid hydrolysis. The dimensions of CNCs are tens of nanometers in diameter and hundreds of nanometers in length depending on the preparation condition. CNCs exhibit promising physical properties such as high modulus, high stiffness, low thermal expansion coefficient, unique morphology, and high aspect ratio and demonstrate excellent chemical properties such as inert and chemical stability (Kvien & Oksman, 2007; Pullawan, Wilkinson & Eichhorn, 2012) For this reason, CNCs show considerable potential for use as an effective reinforcing agent in polymer matrices. The chemical treatment with sulfuric acid allows the esterification of hydroxyl groups on the surface, leading to an electrically negative characteristic of CNCs after the reaction. Consequently, electrical double layers are generated on the CNC surface when being dispersed in aqueous solution.

While CNCs have been extensively investigated for a wide range of application areas such as composites, optics, electronics, cosmetics, etc., the rheological behavior of the CNC suspension is not fully understood (Kim & Song, 2015a). In particular, the rheological characteristics of CNCs, when they interact with other matters suspended in a solution, have not been explored in a systematic manner. Basically, since the suspension is a rheologically complex fluid, it is not easy to analyze and comprehend its rheological behavior. Rheology can act as a powerful tool to examine the internal structure of complex fluids, and offer valuable information such as size, dispersion, concentration, and surface properties in the CNC suspension (Lu, Hemraz, Khalili & Boluk, 2014; Shafiei-Sabet, Hamad & Hatzikiriakos, 2012; Vallejos, Peresin & Rojas, 2012; Wu et al., 2014).

Carboxymethyl cellulose (CMC), a cellulose derivative, is currently being used in various applications such as petroleum drilling,

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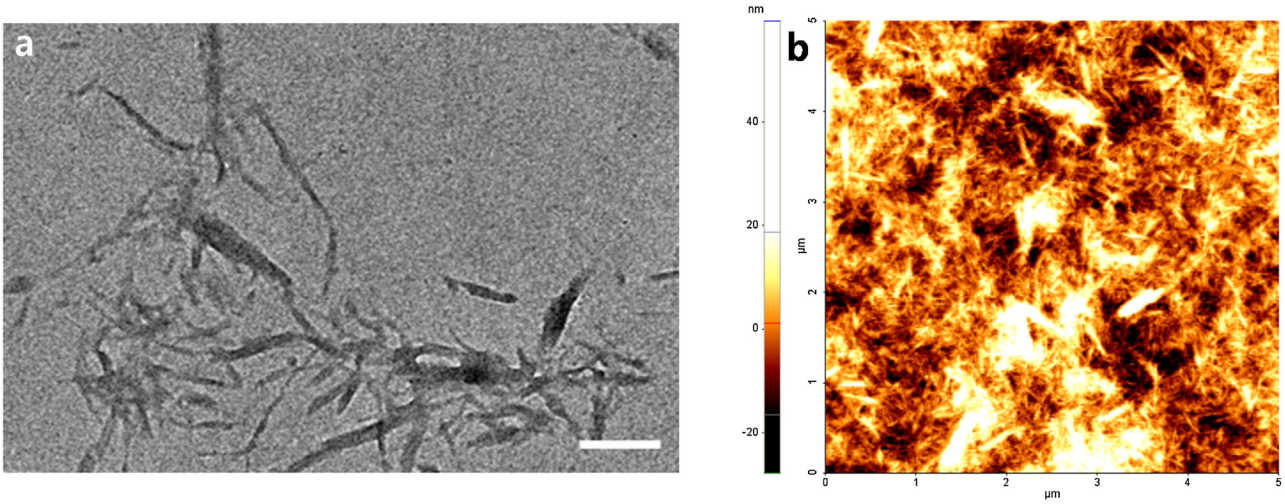

Fig. 1. (a) transmission electron microscopy (TEM) and (b) atomic force microscopy (AFM) image of CNCs. The scale bar indicates 200 nm.

cosmetics, pharmaceutics, films, and coating agent, since it has superior physcochemical properties such as good binding, thickening, and stabilizing (Benchabane & Bekkour, 2008). Interestingly, CMC is likely to act as a good additive together with CNC due to the similarity of its chemical structure. Even if a great deal of experimental and theoretical studies on the rheological (or viscoelastic) behavior of CMCs have been reported, self-reinforced or all-cellulose materials have not been sufficiently addressed in material science and engineering (Gindl & Keckes, 2006).

In this study, we investigated the viscoelastic behaviors of all-cellulose suspensions and nanocomposites. Assuming that CNC and CMC inherently interact well with each other, they were adopted as additives in the aqueous suspension. We conducted morphological analysis including transmission electron microscopy (TEM) and atomic force microscopy (AFM), rheological analysis including steady shear and oscillatory shear tests, and dynamic mechanical analysis. In addition, Fourier transform infrared (FT-IR) spectrum and differential scanning calorimetry (DSC) experiments were carried out.

2. Experimental

2.1. Sample preparation

Carboxymethyl cellulose sodium (CMC) and microcrystalline cellulose (MCC) were bought from TCI (Japan) and Acros Organics, respectively. The particle size of MCC was 50 μm in diameter. Sulfuric acid and filter paper with a pore size of 700 nm were purchased from Ducksan Chemical (Korea) and Hyundai Micro (Korea), respectively. MCC was hydrolyzed with 64 wt% sulfuric acid at 45 °C for 2 h to harvest the CNCs. The prepared CNC suspension was sonicated in an ice bath, followed by centrifuging. Thereafter, the supernatant was eliminated, and additional water was supplied. Prior to reaching a proper pH for the suspension, it was rinsed several times. When the suspension was stabilized, the supernatant was filtered and freeze-dried.

The CMC was dissolved in DI water, while stirring, on a hot plate at 70 °C for 4 h. The content of CMC was 2 wt%, and its degree of polymerization was 1050. The CNCs were then added to the suspension. For the fabrication of CNC/CMC films, the complex suspension was cast and dried on a petri dish.

2.2. Measurements

To evaluate the stability of the CNC suspension, the electrokinetic characteristic, the zeta potential implying the potential difference between a bulk fluid and a fluid layer attached to the suspended particle, was analyzed using Zetasizer Nano ZSP (Malvern). Transmission electron microscopy (TEM) analysis was performed with JEM-2100F HR (FE-TEM, JEOL). The dried CNCs on a 200-mesh TEM grid were carbon-coated, and then 200 kV was applied for the measurement. Additional morphological analysis was carried out using atomic force microscopy (AFM). A droplet of the aqueous CNC suspension was deposited on a Si wafer for the test.

Rheological properties of the CNC/CMC suspension were evaluated using a rheometer (MCR 302, Anton Paar) equipped with a cup and bob fixture. The steady shear viscosity was measured in the shear rate range of from 0.01 to 1000 s^{-1}. Prior to the test, the previous shear stress history was removed. In the oscillatory shear mode, dynamic viscoelastic properties, including the storage modulus, loss modulus, and complex viscosity, were measured applying an angular frequency sweep of 0.1–100 rad s^{-1} . The applied strain was 0.1% during the oscillatory shear test. All rheological measurements were conducted at 30 °C unless otherwise stated. In addition, dynamic mechanical analysis (DMA) for the CNC/CMC film was conducted using a universal extensional fixture UXF kit (Anton Paar). Two different experimental conditions were considered. First, angular frequencies of 1–30 rad s^{-1} were swept at a constant temperature of 30 °C. Second, a temperature sweep of 60 °C to 150 °C was applied at a constant frequency of 1 Hz. The measurement chamber was purged with N_2 during heating. The Fourier transform infrared (FT-IR) spectra of the samples were recorded using FT-IR spectrometer (Nicolet 6700, Thermo Scientific). A KBr-pellet method was adopted, and the scan range was 4000–400 cm^{-1}. The thermal characteristics of the specimens were investigated using differential scanning calorimetry (DSC, Q2000 system, TA Instruments). The specimens for the DSC experiments were scanned from 30 °C to 250 °C at 10 °C/min.

3. Results and discussion

It is known that anionic sulfuric ester groups introduced onto the surface of the CNCs via sulfuric acid hydrolysis result in a stable dispersion in water (Kim & Song, 2015b). The stability of CNCs suspended in water can be evaluated with help of the zeta poten-