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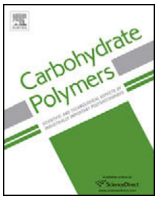

Rheological properties of nanocrystalline cellulose suspensions

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ABSTRACT

Rheological behavior, including linear and nonlinear, as well as transient rheology of nanocrystalline cellulose (NCC) suspensions was studied in this work. Two kinds of polymer solutions, aqueous poly(vinyl alcohol) (PVA) with flexible chain structure and aqueous carboxymethyl cellulose (CMC) with semi-rigid chain structure, were used as the suspension media to further explore the role that the interactions among NCC and polymers played during shear flow. The results reveal that NCC has lower values of percolation threshold in the PVA solution than in the CMC one during small amplitude oscillatory shear (SAOS) flow because the flexible PVA chain has higher adsorbed level onto NCC particles than the negatively charged semi-rigid CMC chain, which is further confirmed by the Fourier transformed infrared (FT-IR) spectroscopy tests. As a result, the NCC suspension shows a weak strain overshoot in PVA solution during large amplitude oscillatory shear (LAOS) flow, which cannot be seen on the one in CMC solution. During startup shear flow, both of these two suspensions show evident stress overshoot behavior with the strain-scaling characteristics, indicating the formation of ordered long-term structure of rod-like NCC particles with self-similarity during flow. However, NCC suspension have far stronger stress overshoot response in CMC solution relative to the one in PVA solution. A possible synergy mechanism between NCC and CMC chain is hence proposed.

1. Introduction

As typical biomass with a wide variety of applications, cellulose has attracted much attention in recent years because of sharply increasing demand for renewability and sustainability. In particular, considerable effort has been devoted over the past decades to the study of nanocrystalline cellulose (NCC), because this kind of nanomaterial has high surface area, low density and good mechanical strength, with availability, biodegradable and non-toxic nature (Habibi, Lucia, & Rojas, 2010). Nowadays NCC has gained many successful applications in both the industrial and daily use fields, such as drug delivery excipients, reinforcements in polymer composites and adhesives, as well as personal care products, e.g. hair conditioners and shampoos (Brinchi, Cotana, Fortunati, & Kenny, 2013).

To those applications, especially to the drug carriers and the electronic fields, the rheology of NCC suspensions is very important. Therefore, the rheological properties, especially the linear flow behavior and steady shear response of the NCC suspension systems in water and in polymer solutions, have been explored up to now (Brinchi et al., 2013). In general, the negatively charged NCC particles can form stable aqueous dispersions because of the electrostatic repulsion among individual NCCs (Bercea & Navard 2000; Lasseuguette, Roux, & Nishiyama, 2008; Liu, Chen, Yue, Chen, & Wu, 2011). In this case, the rheological responses of aqueous NCC suspensions are mainly dominated by the short-range structural aspects of rod-shaped NCC particles such as aspect ratio and surface properties, and also by their long-range structure such as orientation state of particles and hydrodynamic particle–particle interactions, which is closely related to the concentration and surface charge of NCC particles (Puisto, Illa, Mohtaschemi, & Alava, 2012; Shafiei-Sabet, Hamad, & Hatzikiriakos, 2012; Noroozia, Grecova, & Shafiei-Sabet, 2014; Derakhshandeh, Petekidis, Shafiei-Sabet, Hamad, & Hatzikiriakos, 2013; Jin et al., 2015; Lenfant, Heuzey, van de Ven, & Carreau, 2015; Lu, Hemraz, Khalili, & Boluk, 2014).

In polymer solutions, the situation becomes much more complicated. The dispersion stability of NCC particles is affected by both adsorbed and non-adsorbed polymers (Boluk, Zhao, & Incani, 2012). In this kind of suspensions, polymer chain can cause two types of steric interactions among NCC particles: either bridging by adsorption of polymer chain on NCC particle surface

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or depletion by non-adsorbing polymers, both resulting in the enhanced stress response and system elasticity (El Kissi et al., 2008; Gomez Martinez, Stading, & Hermansson, 2013; Mihranyan, 2013). Besides, it is expectable that the surface charge of polymers should also have large influence on the colloidal stability and rheological response of NCC suspensions, which is supposed to be very similar with the case of the suspensions containing spherulitic or platelet-like particles (Sjoberg, Bergstrom, Larsson, & Sjostrom, 1999). However, for the NCC suspension in polymer solutions, no literature report can be found on this issue.

Moreover, the reported rheological studies on the NCC suspension systems in water or in polymer solutions mainly focus on the linear flow behavior, or the steady shear responses. The former is limited in a quite narrow stress or strain region, which is far less than the engineering levels; and the latter can merely give the final stress or strain levels, and cannot reveal the transient response that is closely related to the structure evolution during shear flow. Therefore, in this work, both the nonlinear and transient rheology of NCC suspensions were studied deeply, together with the linear dynamic rheology. Two kinds of polymer solutions, electrically neutral aqueous poly(vinyl alcohol) with flexible chain structure and negatively charged aqueous carboxymethyl cellulose with semi-rigid chain structure, were used as the suspension media to further explore the role that the NCC-polymer interactions played during flow. The main objective of this work is to make a full and deep study on the flow behavior of NCC suspension in polymer solutions, and to provide useful information on the applications of NCC suspension systems.

2. Experiment

2.1. Materials

Poly(vinyl alcohol) (PVA1788) used in this work is a commercial product of Aladdin Industrial Co. Ltd. (P.R. China) with the molecular weight of 44.05×10^3 g mol^{-1} (polydispersity index (PDI = 2.25)) and the density of 1.3×10^3 kg m^{-3}. Its degree of alcoholysis (DA) is about 87.0–89.0% (mol mol^{-1}). Carboxymethyl cellulose (CMC) with the molecular weight of 260.24×10^3 g mol^{-1} (PDI = 1.37) and the density of 1.6×10^3 kg m^{-3} was also purchased from Aladdin Industrial Co. Ltd., which has a viscosity of 600–1000 mPa s for the solution with concentration of 2 wt% at 25 °C. Its charge density is about −15.82 mc m^{-2}. The microcrystalline cellulose (MCC) used for the preparation of NCC was purchased from Sinopharm Chemical Reagent Co. Ltd. (P. R. China), with the degree of polymerization (DP) of 210–240. The average length and diameter of MCC are 20–100 μm and 10–20 μm, respectively.

2.2. Preparation of NCC and its suspensions

NCC aqueous suspensions (deionized water was used) were prepared according to the procedure reported in the previous work (Bai, James, & Li, 2009; Chen et al., 2015). TEM image of as-obtained NCC particles is shown in Fig. 1. Their average diameter and length are about 20 nm and 300 nm, respectively. The PVA or CMC was then dissolved in the aqueous NCC suspensions, with stirring at moderate level at 30 °C for 12 h, followed by the 12 h rest for defoaming. Because CMC is hard to be fully dissolved in water at the higher concentration level (>1 wt%), its concentration is fixed as 1 wt% in the suspension system. The PVA concentration is determined as 10 wt% because at this concentration the PVA solution has the same viscosity level as the CMC solution (Fig. S1 of the Supplementary information), which favors rheological property comparison of two kinds of NCC suspensions. The NCC loadings vary from 0.1 to 3.0 wt%. The film samples casted from suspensions are characterized using atomic force microscope and the results are shown in Fig. S2 of the Supplementary information (the bumps or dark parts on the force images are part of the NCC particles embedded by polymer matrix because NCC has higher modulus than polymer matrix (Xu et al., 2016)).

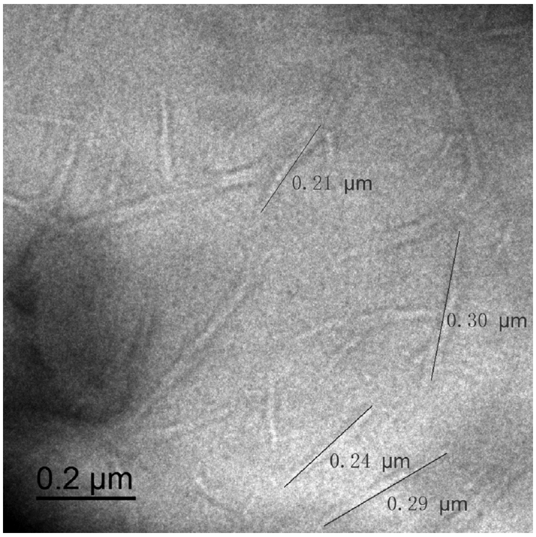

Fig. 1. TEM image of NCC particles with the scale bar of 0.2 μm.

2.3. Morphological characterizations

The dispersion of NCC in the cast film of PVA and CMC was detected using atomic force microscope (AFM). An Icon AFM (Bruker Co. Ltd, Santa Barbara, USA) was operated in the quantitative nanomechanical mapping mode (QNM). Silicon AFM probes were used (tip radius < 8 nm, force constant 40 N m^{-1}, resonance frequency 300 kHz) to acquire images in air at room temperature. Line scan rates were set as lower at 256 lines per frame with a scanning rate of 1 Hz. Image processing was performed with the NanoScope Analysis software.

2.4. Structure characterizations

Fourier transformed infrared spectroscopy (FT-IR) was used to identify the possible interactions between NCC particles and polymers. Infrared absorption spectra were recorded in the wavelength region of 4000–600 cm^{-1} using a Bruker IFS66/S FT-IR spectrophotometer (Germany). All the FT-IR spectra were obtained by repeating 64 scans at room temperature with the resolution of 2 cm^{-1}. The hydrodynamic radius of NCC in water and in the polymer solutions was determined by a ZEN360 dynamic light scattering apparatus (DLS, Malvern Co. Ltd., United Kingdom) at 25 °C. The scattering angle and operating wavelength were 90° and 632 nm, respectively. The zeta potential (ζ) (also measured by DLS apparatus) was calculated from the velocity of the particles under a given electrical current. Its values were obtained along with the DLS tests.

2.5. Rheological measurements

The rheological tests were performed on a rotational rheometer (HAAKE RS600, Thermo Electron Co., USA) equipped with a parallel plate geometry (60 mm diameter plates). The samples were hold at 10–20 °C for 3 min in the parallel plate fixture to eliminate residual thermal and stress histories, and then experienced various kinds of shear flows (the water is volatile and therefore, a lower temperature range, 10–20 °C, was chosen for rheological tests). During