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Rheology of semi-dilute suspensions of carboxylated cellulose nanofibrils

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ABSTRACT

Cellulose nanofibrils (CNF) in water make entangled networks and stiff gels, which have a number of promising applications. In this work, the rheology of semi-dilute TEMPO-mediated oxidized CNF hydrogels, and the effects of cationic polyacrylamide and calcium ions on their viscoelastic properties are investigated. The elastic modulus varies with CNF volume fraction with a power law exponent of 4.52. Creep–recovery results show that suspensions with higher mass fractions exert a higher resistance against deformation, and a higher degree of recovery. Low ionic strengths and polyelectrolyte concentrations increase the creep deformation because of screening the surface charge. Higher ionic strengths and polyelectrolyte concentrations lead to fibril aggregation, which stiffens the network structure, decreasing the creep deformation. However, the recovery response is not significantly affected by additives. The critical strain at the onset of non-linear viscoelasticity is independent of mass fraction in two different concentration regimes, with a transition at 0.35% w/w CNF.

1. Introduction

Increasing environmental concerns have led to efforts to increase the use of renewable and biodegradable materials in many industrial applications. Wood pulp is one of the major sources of raw materials for bioproducts.

Disintegration of wood fibers into cellulose nanofibrils (CNF) has recently attracted significant interest. Cellulose is a linear polysaccharide with a large number of hydroxyl groups. CNF consists of aligned extended molecules that are adhered together by hydrogen bonds. Due to their high aspect ratio and high degree of crystallinity, cellulose nanofibrils form stiff hydrogels with high elasticity. They have been recommended as rheology modifier for food, paint and cosmetics (Herrick, Casebier, Hamilton, & Sandberg, 1983; Turbak, Snyder, & Sandberg, 1983). CNF films and CNF coated papers have been suggested for packaging applications (Henriksson, Berglund, Isaksson, Lindström, & Nishino, 2008; Spence, Venditti, Rojas, Habibi, & Pawlak, 2010; Syverud & Stenius, 2009). CNF has been also proposed to be used in the production of functional materials such as nanocomposites (Lopez-Rubio et al., 2007; Nakagaito & Yano, 2005) and antimicrobial films (Andresen et al., 2007).

Since 1983, several methods have been developed for the preparation of cellulose nanofibrils. Fibril dimensions and the number of surface charges vary depending on the preparation method. CNF is mechanically produced by disintegration of wood fibers in a homogenizer under high shearing forces. The resulting nanofibrils are 5–20 nm in diameter and several micrometers in length (Herrick et al., 1983; Turbak et al., 1983). To avoid the high energy consumption for mechanical fibrillation of wood fibers, chemical pretreatment of wood pulp has been suggested. Chemical methods are mainly based on inducing strong electrostatic repulsions among the nanofibrils in water, by introducing negatively charged functional groups onto their surface. Nanofibrils can then be disintegrated by gentle mechanical treatments such as sonication.

It has been shown that mild enzymatic hydrolysis of softwood pulp decreases the homogenization energy, and produces high aspect ratio nanofibrils with high mechanical strength (Henriksson & Berglund, 2007; Paakko et al., 2007). Paakko et al. (2007) added monocomponent endoglucanase to the softwood pulp suspension and passed it through a homogenizer after refining. The achieved fibril diameter was 5–20 nm, providing strong aqueous gels with large elastic modulus, practical for reinforcing multicomponent mixtures. TEMPO-mediated oxidation with sodium hypochlorite followed by gentle mechanical sonication has been introduced as another preparation method, yielding cellulose nanofibrils with 3–4 nm diameter, several micrometer length, and a large

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number of surface charges in the form of COO^- groups (Isogai, Saito, & Fukuzumi, 2011; Saito, Nishiyama, Putaux, Vignon, & Isogai, 2006). Water dispersions of TEMPO-mediated oxidized CNF showed pseudo-plastic behavior, and a strongly consistency-dependent shear viscosity at concentrations >0.2% w/w (Lasseuguette, Roux, & Nishiyama, 2008; Saito, Kimura, Nishiyama, & Isogai, 2007).

Fibril dimensions and its charge density directly affect the suspension rheology. It has been reported that the elastic modulus of CNF suspensions produced by TEMPO-mediated oxidation of palm tree wood pulp is larger than previously reported by Paakko et al. (2007) for CNF prepared by enzymatic hydrolysis, in spite of the similar fibril dimensions (Benhamou, Dufresne, Magnin, Mortha, & Kaddami, 2014). The authors ascribe it to the higher charge density of their oxidized fibrils compared to the non-oxidized CNF.

The rheology of colloidal suspensions can be also affected by interparticle bridging (Abbas Zaman & Delorme, 2002; Otsubo, 1999; Swerin, 1998). This phenomenon is used in industry to control the product viscosity and stiffness. Bridging can be induced by addition of polyelectrolytes or multivalent ions. Oxidized cellulose nanofibrils are negatively charged, therefore cations such as Ca^{2+}, and polymers such as cationic polyacrylamide can flocculate them. Cationic polyacrylamide is widely used in papermaking as a retention aid (Hubbe, 2007; Vanerek, Alince, & van de Ven, 2000a, 2000b). Retention of fine particles necessitates their deposition on the fibers and fiber flocculation. Fine particles could be mineral fillers which are very small and might be lost during filtration in the papermaking process (van de Ven, 1984), or they could be fiber fines or hydrophobizers used for internal sizing (Hubbe, 2007). Paper machine conditions can significantly decrease the chemical efficiency of these agents if they are not retained in the sheet. Calcium ions are also present in papermaking suspensions, especially when calcium carbonate $CaCO_3$ is used in paper as a filler.

This paper aims to study the rheological behavior of TEMPO-mediated oxidized CNF hydrogels in the semi-dilute regime. We have studied the rheology of dilute CNF suspensions previously (Jowkarderis & van de Ven, 2014). Moreover, we investigate the effect of interfibrillar bridging on the mechanical strength of the suspensions using cationic polyacrylamide and $CaCl_2$ at various concentrations. Experimental results on the creep–recovery response, and the variations of the elastic modulus as a function of CNF volume fraction are compared to available theoretical models.

2. Experimental

2.1. Materials

A 0.67% w/w aqueous suspension of CNF produced by TEMPO-mediated oxidation of spruce wood pulp was received from Forest Products Laboratory (FPL) (Madison, WI, USA). The COONa density was reported as 0.65 mmol g^{-1} dry CNF. The dimensions of the nanofibrils were measured previously as ≈4.7 nm in diameter and ≈550 nm in length, and average aspect ratio $r \approx 110$ (Jowkarderis & van de Ven, 2014).

Due to the polydispersity in cellulose nanofibrils dimensions, it is not easy to directly determine the volume fraction of CNF suspensions. In this paper, the volume fraction is considered as $\phi \approx \phi_m/\rho_r$, where ϕ_m is the mass fraction and $\rho_r \approx 1.5$ is the relative density of cellulose (Hermans, Hermans, & Vermaas, 1945). CNF suspensions with mass fractions ϕ_m ranging from 0.1% to 0.67% w/w were prepared by addition of deionized water, corresponding to volume fractions ϕ in the range 7×10^{-4} to 4.5×10^{-3}, within the semi-dilute regime. Recall that semi-dilute suspensions are obtained when $r^{-2} < \phi < r^{-1}$ (Mewis & Wagner, 2012).

Polymer bridging was induced using cationic polyacrylamide (C-PAM) (PERCOL292), with mass average molecular weight ~5×10^6, and degree of substitution ~20%. A 5 g L^{-1} polymer solution was prepared by adding dry polymer beads to deionized water and subjecting it to magnetic stirring for 18 h. The solution was then used to make 0.3% w/w CNF suspensions with polymer concentrations in the range 10–200 mg g^{-1} dry CNF. Since the amount of polymer used in the suspension is very small, maximum ≈600 ppm, its effect on the viscosity of the suspending medium is negligible (less than 1%). $CaCl_2$, purchased from Sigma–Aldrich, was used for physical cross-linking of cellulose nanofibrils. A 1 M salt solution was added to 0.3% w/w CNF suspensions to make samples with salt concentrations ranging from 1×10^{-5} to 5×10^{-3}M.

All samples were tested the second day after preparation. All the measurements were performed at pH ≈6.9.

2.2. Rheometry

Rheology measurements were carried out using DHR (TA Instrument) and MCR 302 (Anton-Paar) rheometers. Parallel plates geometry (40 mm diameter) was used to study CNF suspensions with mass fractions $\phi_m \geq 0.3$ %. Consistent results were obtained for all suspensions using either sand blasted, roughened, or smooth surface plates. The gap was set to 1 mm. Changing the gap from 1 to 2 mm did not affect the results. Suspensions with $\phi_m < 0.3$ % were tested using double-wall concentric cylinders (internal gap: 0.41 mm, external gap: 0.47 mm, effective height: 40 mm).

The linear viscoelastic (LVE) region was determined at frequencies 0.5, 6.28 and 50 rad s^{-1}, over a strain range of 0.1–1000%. Subsequently, frequency sweep tests were conducted at 3% strain, which was within the linear region at all CNF volume fractions.

The creep tests were conducted at stress $\tau = 0.2$ Pa, for 10 min. The stress was then suddenly released and the recovery response was recorded for 10 min.

Solvent traps were used to prevent water evaporation in all the tests. The temperature was set to 25 °C. The samples were allowed to relax for 5 min before each measurement. All the tests were performed in triplicate with fresh samples, and their average is reported here.

3. Results and discussion

3.1. Elastic and viscous moduli

The elastic G' and viscous G'' moduli of TEMPO-mediated oxidized cellulose as a function of frequency are shown in Fig. 1, at various mass fractions. Our results are consistent with the data previously reported by Benhamou et al. (2014). G' and G'' increase with increasing ϕ_m, indicating the formation of stiffer networks. However, the G' and G'' values are more than one order of magnitude larger than the values obtained by Lasseuguette et al. (2008) at similar mass fractions. The reason can be incomplete disintegration of wood fibers in their system, after mechanical treatments. Non-disintegrated fibers do not form strong network structures, and their dispersions are weaker than suspensions of nanofibrils with equal consistency. The charge density of the oxidized CNF is not mentioned by the authors.

At $\phi_m > 0.3$ %, the elastic and viscous moduli are comparable to the observations of Paakko et al. (2007) for enzymatic hydrolyzed cellulose, and of Agoda-Tandjawa et al. (2010) for cellulose microfibrils prepared by strong mechanical treatments, with fibril dimensions larger than the oxidized fibrils used here. Therefore at high mass fractions, the higher surface charge compensates for the effect of smaller fibril dimensions. At $\phi_m \leq 0.3$ %, the increase of G' and G'' with frequency is noticeable, while Paakko et al. (2007)