Rheological Properties of Jute-Based Cellulose Nanofibers under Different Ionic Conditions

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> Cellulose nanofibers (CNF) were produced by 2,2,6,6tetramethylpiperidinyl-1-oxyl (TEMPO) oxidation and mechanical shearing of jute pulp. The cross section dimension of CNFs was determined by small-angle neuron scattering (SANS), yielding a width of about 5 nm and thickness of about 1.5 nm, which were further confirmed by transmission electron microscopy (TEM). The effect of NaCl concentration on the rheological properties of the jute-based CNF as a function of concentration was investigated. The viscosity of CNF suspensions was found to increase by addition of the monovalent NaCl, which exhibited a critical concentration behavior. However, the critical concentration value was highly dependent on the CNF concentration. The effect of the cation valency on the rheological properties was also investigated. It was found that both viscosity and stiffness of the CNF gel increased with increasing the valency of the cation.

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Introduction

The production and characterization of cellulose nanofibers (CNF) are currently in the focus of materials research community due to the combination of several exciting properties (1) together with the ability of producing new nanomaterial from a variety of sustainable resources (2-4). CNF has already been employed in several applications, and it continues to find ways into new applications (5-8). In the context of nanocellulose, cellulose microfibrils can be considered as the smallest constituents of the cellulose fiber, where CNF is an aggregate of cellulose microfibrils. The fiber length in CNF can reach several hundred nanometers to microns; whilst the characteristic cross-sectional sizes are only about few to few tens of nanometers (9). The wide size range of CNF is mainly due to the versatile routes for the production of material, which combines a variety of chemical and mechanical (shearing) processes. Examples of the chemical processes include, enzymatic hydrolysis (10), carboxymethylation (11), periodate oxidation, phosphorylation (12), cationization (13) and TEMPO oxidation (14). And examples of mechanical shearing processes are ball milling, refining, cryo-crushing, high pressure homogenization and sonication.

TEMPO-based CNF is one of the most studied systems by cellulose research community. This is due the ability of this method to produce CNF with relatively narrow size-distribution without excessive mechanical shearing (equals high energy cost); the ease of study of the system is hence understood. However, there are also several drawbacks with the process, among others the severe lowering of the degree of polymerization of the nanofibers and the need to recover the costly TEMPO radical are highlighted.

The TEMPO oxidized CNF contains a negatively charged surface, due to the C6 conversion of the hydroxyl groups into carboxyl groups. Highly charged systems are prone to changes in the ambient ionic strength, and highly charged CNFs are no exception. Jowkarderis and van de Ven (15) investigated the effect of monovalent (and divalent) inorganic salts on a highly charged (and highly diluted) TEMPO-based system (charge density 0.7 mmol/g). The authors found the intrinsic viscosity to decrease with increasing the ionic strength of the system, as long as $\kappa d \leq 1$ (where κ denotes the inverse Debye length of the system and d denotes the diameter of the fibers). However, at higher salt concentrations ($\kappa d > 1$) an upturn in the viscosity property of the system was observed, which was related to the flocculation of the nanofibers. Tanaka et al. (16) found that the addition of a small amount of NaCl (0.5 mmol/L) to 0.1 % (w/w) TEMPO-based CNF (charge density ≈ 1.5 mmol/g) decreased the relative viscosity of the system. However, an increase in turbidity property was observed when the NaCl concentration was increased; which could be attributed to the aggregation of CNFs. Fukuzumi et al. (17) investigated the impact of NaCl addition on the viscosity of a 0.1 % (w/w) TEMPO-based CNF (charge density ≈ 1.5 mmol/g). The authors first observed 3 orders of magnitude of increase in the shear viscosity of the system ([NaCl] =10 mmol/L to 100 mmol/L), before the viscosity decreased upon the continuous addition of the salt ([NaCl] = 200 mmol/L to 400 mmol/L), which was related to phase separation of CNF suspension. In this context, the contributions of Naderi and Lindström (18, 19) are of interest, in which the addition of NaCl (1 mmol/L

to 10 mmol/L) to 1 % (w/w) carboxymethylated CNF suspensions (charge density ≈ 0.6 mmol/g) were found to lower the viscosities of the systems.

It is imperative to point out that the above cited observations have been obtained through the study of highly diluted CNF suspension in a fixed concentration range. It could be argued that the observation may not apply in conditions where more concentrated CNF systems are studied

The current study aims at elucidating the impact of CNF concentration in varying ionic strength conditions. In the investigations, the non-wood based CNFs were extracted from jute using the TEMPO oxidation method. Another stated ambition of this study is to investigate the impact of the valency of the cation on the rheological properties.

Experimental Section

Materials

Raw jute fibers were purchased from Toptrans Bangladesh Ltd. (Bangladesh). The carbohydrate and lignin composition in these samples were first determined in Innventia AB, Stockholm, Sweden. The results indicated the contents of cellulose, hemicellulose and lignin in the chosen jute fiber were 51.2 wt%, 10.7 wt% and 17.8 wt% respectively. 2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO) was purchased from Acros. Sodium chlorite (NaClO₂, A.C.S. reagent), Sodium bromide (NaBr, A.C.S. reagent), acetic acid, sodium acetate, uranyl acetate, hydrochloric acid (36.5 wt%), sodium chloride, magnesium chloride and aluminium chloride were obtained from Sigma-Aldrich. Sodium hypochlorite (NaClO, solution, 12 wt%) was purchased from Spectrum and sodium hydroxide (NaOH) was bought from Fisher Scientific Company. De-ionized water was used throughout the study.

Pretreatment of Jute Pulp Prior to TEMPO-Oxidation

The jute fibers were first soaked in 1 mol/L NaOH aqueous solution for 24 hours under continuous stirring. After washing with water, the fibers were immersed in 1% (w/v) NaClO₂ buffer solution (acetic acid and sodium acetate buffer solution, pH 5) and heated at 70 °C for 2 hours under continuous stirring. The procedure was repeated until the color of fibers became white. Subsequently, the recovered samples were washed several times with water. The bleached jute pulp was stored in fridge for further use.

TEMPO Oxidation

The bleached jute fibers (10 g) were first suspended in water (960 ml). Afterwards, NaBr (1 g) and TEMPO (0.2 g) were added. The reaction started with addition of 75 g of NaClO solution at room temperature; the slurry was stirred continuously for 24 h. During the reaction, the pH value of the suspension was kept between 10 and 10.3 through the addition of 1M NaOH. After 24 h, the reaction was terminated by quenching with 10 ml ethanol. The oxidized cellulose slurry was dialyzed against deionized water until the conductivity was less than 5

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 μ S. Conductometric studies (based on the method of Habibi et al. (20)) revealed a charge density of about 1.5 mmol/g.

The TEMPO-oxidized pulp was subsequently delaminated at 0.6 wt% by a homogenizer (Cole Parmer, VCX-400) for 3 min with an output power of 320 W (3). The suspension was diluted at room temperature into different concentration ranging from 0.01wt% to 0.6wt%. In the dilution process, the different suspensions were sonicated, as described above, to achieve homogeneous suspensions.

Preparation of CNFs in Different Ionic Strength Conditions

The ionic strengths of CNFs were adjusted by addition of minute amounts of 1 mol/L NaCl, MgCl₂ and AlCl₃ to the suspensions under stirring, the change of overall concentration of the CNFs was hence considered negligible. The CNF suspensions with different ions and ionic strength were further sonicated for 10 min at an output power of 100 W.

Transmission Electron Microscopy (TEM) Measurements

The morphology of CNFs was investigated by a TEM (FEI Bio TwinG2) instrument, equipped with an AMT digital camera. The operating voltage was 120 kV. A drop of 0.01 wt% CNF suspension (diluted by using a sonicator at output power of 100 W for 10 min) was deposited onto a carbon-film-coated copper grid, and was allowed to equilibrate for 2 min (3). After that, the excess suspension was removed by using a filter paper. To stain the sample, a drop of 2 wt% uranyl acetate aqueous solution was deposited onto the grid and was allowed to equilibrate for 30 s. The excess liquid was carefully removed by filter paper, and the grid was left to dry in ambient environment, before TEM measurements.

Fourier Transform Infrared (FTIR) Spectroscopy and Solid-State CP-MASS ¹³C NMR Measurements

Raw jute fibers, bleached jute fibers and freeze-dried TEMPO oxidized cellulose nanofibers were characterized by Fourier transform infrared (FTIR) spectroscopy and solid-state ¹³C NMR. The FTIR spectra were recorded using Thermo Nicolet iS10 FTIR spectrometer with a resolution of 1 cm⁻¹ over the range of 4000 to 500 cm⁻¹ (*3*). Solid-state 13C NMR spectra were obtained from Bruker 600 MHz wide-bore solid-state NMR spectrometer with cross-polarization magic angle sample spinning (*3*). The spinning speed was 12 kHz, pulse delay was 5 s and contact time was 1 ms.

Degree of Oxidation Measurement

Degree of oxidation was determined using the conductometric titration method (20). Specifically, 0.1 M hydrochloric acid solution was added to 300 g of a 0.1 wt% CNF suspension until the pH reached 2.5. Under continuous stirring, the suspension was titrated with 0.1 M NaOH solution until the pH reached about 10. During titration, the conductivity was monitored using a conductivity meter.

Small-Angle Neutron Scattering (SANS)

SANS experiments were performed at the NG7-30m beamline in NIST Center for Neutron Research (NCNR), National Institute of Standards and Technology (NIST). Three instrumental configurations, with sample-to-detector distances (SDD) being 1 m, 4 m and 13 m, respectively, were employed to obtain the scattering data with a q range from ~0.003 to ~0.5 Å⁻¹ ($q = (2/\lambda)\sin(\theta/2)$, with λ being the neutron wavelength, and θ being the scattering angle). The neutron wavelength was 6 Å, with a wavelength spread of ~ 13 %. The neutron beam size was 12.7 mm. Demountable titanium cells with quartz windows were used to hold the samples. CNF was dispersed in D₂O by repeatedly washing and centrifuging TEMPO oxidized slurry using D_2O for three times, followed by ultrasonic homogenizing for 3 min. Scattering data from empty cell and cell filled with D_2O were also measured for background subtraction purposes. Data reduction involving 2D image averaging, correction for sample absorption. and background subtraction was carried out using the IGOR macro software developed by Kline (21).

Rheological Measurements

Rheological measurements were performed using a Kinexus stress controlled rotational rheometer (Malvern Instruments, UK) together with the software rSpace (Malvern Instruments, UK) (3). A standard (ISO 3219/DIN 53019) metal concentric cylinder (bob and cup) geometry having serrated surfaces were used (to minimize slippage effects) to characterize CNF suspensions $\geq 0.2\%$ (w/w). The height and distance between the serrations were 300 μ m and 1000 μ m, respectively. The diameter and length of the bob were 25 and 37.5 mm, respectively. The diameter and wall height of the cup were 27.5 and 62.5 mm, respectively. The investigation of CNF suspensions (< 0.2 % w/w) was conducted by a metal concentric cylinder geometry with smooth surfaces. The diameter and length of the bob were 25 and 37.5 mm, respectively. The diameter and height of the smooth cup were the same as the serrated equivalent. A working gap of 9.15 mm was employed in the measurements. The set experimental temperature was 25 °C and the samples were covered with a protective hood during the measurements.

The CNF samples were sheared at 100 s^{-1} for 1 min in the measuring chamber, as a means to even out the heterogeneities, and then were left to equilibrate for 2 min before conducting the real measurements. The controlled shear rate measurements were conducted in the range of 0.1 to 100 s⁻¹. The thixotropic

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properties of the CNF suspension were studied by first decreasing the shear rate to 0.1 s⁻¹ and then subsequently increasing it to 100 s⁻¹. The evolution of the shear viscosity was followed for 100 s. Oscillatory frequency sweep measurements were studied from 0.1 to 100 Hz. The strain in the experiment was set to 1%, which was inside the linear viscoelastic region determined by the amplitude sweep experiments at a frequency of 1 Hz. The strain range was set from 0.1 % to 100 % to investigate the strain dependence at a frequency of 1 Hz.

Results and Discussion

Structure, Morphology, and Property Characterization of Cellulose Nanofibers

Figure 1 shows a typical TEM image of CNF prepared from the 0.6% (w/w) TEMPO oxidized jute fiber suspension. The average width of the nanofibers could be estimated, which was found to be approximately 5 nm. However, the length of the nanofibers is difficult to quantify due to the entangled state of CNF and the imaging limit. The cross-section of these fibers have been shown to be ribbon like (22). Unfortunately, the average thickness of the nanofibers could not be estimated by TEM.



Figure 1. TEM image of a CNF that was produced by the homogenization of 0.6% (w/w) TEMPO oxidized jute pulp.

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The cross-sectional dimensions of CNF in the dispersion state were investigated by SANS measurements, where the scattered profiles were fitted by the ribbon model (22, 23). This model assumes that CNFs are infinitely long (the aspect ratio is larger than 100), which is reasonable based on typical results of the fiber length being sub-microns and the fiber cross-section dimension of a few nanometers. In the ribbon model, the cross-section is assumed to be rectangle-shaped, due to the nature of crystal habit from the crystallographic packing of cellulose chains in an unit cell (24). By considering the polydispersity in both width and thickness of the cross-section, the analytical form of 1D scattering intensity can be given by Eq. 1 (16).

$$\frac{I(q)}{c} = \frac{2\pi}{q^3} \{1 - \operatorname{Re}[(1 + \frac{iq\sigma_a^2}{a_0})^{-(a_0/\sigma_a)^2}]\}(b_0^2 + \sigma_b^2) \times {}_3F_2(\frac{1}{2}, 1 + \frac{b_0^2}{2\sigma_b^2}, \frac{3}{2} + \frac{b_0^2}{\sigma_b^2}; \frac{3}{2}, 2; -\frac{q^2\sigma_b^4}{b_0^2})$$
(1)

where I(q) is the scattered intensity, a_0 and b_0 are mean values of thickness and width of the cross-section, respectively; and σ_a and σ_b are the corresponding standard of deviation, ${}_{3}F_2$ is a hypergeometric function (details can be found elsewhere (22)).



Figure 2. SANS profiles of CNF suspension prepared at 0.6 wt% and then concentrated or diluted to different CNF concentrations (0.1 wt%, 0.2 wt%, 0.4 wt%, 1.0 wt%). The lines denote the fitting of the curves using the ribbon model in Eq. 1.

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CNF concentration	Debye length (nm)	a ₀ (nm)	b ₀ (nm)	σ _a (nm)	σ_b (nm)
0.1 wt%	7.7	1.5	5.4	0.20	1.5
0.2 wt%	5.5	1.8	5.4	0.02	1.5
0.4 wt%	3.9	1.4	5.4	0.5	1.5
1.0 wt%	2.5	N/A	N/A	N/A	N/A

Table 1. Cross-sectional dimensions and corresponding standard deviationsof CNF particles fitted by the ribbon model (Eq. 1). The Debye lengthof the systems was estimated by regarding the charged nanofibers andcorresponding counterions as a monovalent salt.

Figure 2 illustrates the SANS profiles and the fit results (solid lines) using the ribbon model (Eq. 1) of CNF suspensions at different concentrations: 0.1 wt%, 0.2 wt%, 0.4 wt% and 1.0 wt%. The SANS intensity profile is governed by a form factor and a structure factor. The contribution of the structure factor is minimal in dilute solution, but its effect increases with increasing concentration. In Figure 2, it is seen that the scattered intensities from CNF suspensions at concentration below 0.4 wt% can be well described by the ribbon model, yielding consistent cross-section dimensions with $a_0 \approx 1.5$ nm and $b_0 \approx 5$ nm (the best fitted values of a_0 and b_0 derived from curves of lower concentration suspensions are summarized in Table 1). Furthermore, the width value b₀ was found to match that determined by TEM (Figure 1). However, the scattering curve from the higher concentration suspension (i.e., 1.0 wt%) could not be fitted by the ribbon model, which only consider the form factor. This indicates that the role of the structure factor became dominant. The scattering curve of the 1.0 wt% CNF suspension revealed a small scattering bump at ~0.01 Å⁻¹ (indicated by an arrow in Figure 2), which could be due to the inter-fiber interference.

The chemical structure change in jute fibers during TEMPO oxidation was characterized using the FTIR spectrum and solid-state ¹³C NMR techniques. Representative FTIR and solid-state NMR spectra from jute fiber raw materials, bleached jute fibers and freeze-dried TEMPO oxidized jute cellulose nanofibers are shown in Figure 3. It is seen that the FTIR spectra for bleached jute fibers and jute fiber raw materials (Figure 3a) are about very similar. However, TEMPO oxidation leads to the appearance of a peak at 1605 cm⁻¹, which is due to the stretching vibrations mode of carboxylate groups from the oxidation of hydroxyl groups at the C6 position of the cellulose chain.

More insightful information were revealed in the NMR spectra of these three samples. In Figure 3b, the peak at 56 ppm and a series of small ones positioned between 110 and 155 ppm in the spectrum of jute raw materials were attributed to the lignin composition (25). They disappeared after delignification processing (NaOH washing, see Experimental section). The pectin and hemicellulose compositions were also removed in delignification process, as indicated by the decrease of intensities of the peak at 62 ppm (26) and those between 81 and

82 ppm (27) in the spectrum of bleached jute cellulose pulp. Compared to the spectrum of bleached jute fibers, an intense peak at 175 ppm appeared after the TEMPO oxidation treatment, which can be assigned to the carboxylate group (COO-). In the same time, the intensities of peaks at both 63 ppm and 66 ppm corresponding to the C6 position decreased. However, the intensities of the C1 (105 ppm) and C4 (81 to 92 ppm) peaks remained unchanged. The comparative NMR spectra confirmed that only the hydroxyl groups at the C6 position were oxidized into carboxylate groups.



Figure 3. Comparison of FTIR (a) and solid-state NMR (b) spectra from jute fiber raw materials, bleached jute fibers and freeze-dried TEMPO oxidized cellulose nanofibers.

The titration curve for the determination of the degree of oxidation (DO) of the resulting CNF is shown in Figure 4, where the DO was calculated using the following equation:

$$DO = \frac{162g \cdot mol^{-1} \times 0.1M \times (V_2 - V_1) \times 10^{-3}}{300g \times 0.1wt\%} = 24.3\%$$
(2)

In Eq. 2, the value 162 is the molecular weight of the glucose unit, V_1 and V_2 are the volumes of NaOH solution at the two inflection points of the curve. In Figure 4, $V_1 - V_2$ is found to be 4.5 ml and the application of Eq. (2) leads to the DO value of around 24.3%, corresponding to a charge density of about 1.5 mmol/g. In this context, it is noted that zeta potential studies on a 0.05 wt% CNF suspension revealed a value of -55 mV, confirming the existence of high repulsion interactions between the charged CNF particles in the suspension.



Figure 4. Conductometric curve for TEMPO oxidized cellulose nanofibers.

Rheological Behavior of CNF Suspensions with Different Ionic Strengths

The evolution of shear viscosity as a function of shear rate for CNF suspensions at various concentrations is shown in Figure 5. At CNF concentrations below 0.1 wt%, Newtonian fluidic behavior was observed. At higher CNF concentrations, the viscosity curves display the characteristic shear thinning, which could be attributed to the alignment and/or disentanglement of charged CNF particles. The rheological data suggests the existence of a critical concentration at $\sim 0.2\%$ (w/w) that is associated with the threshold value beyond which a network formation occurs. To elucidate this point clearly, viscosities of CNF suspensions at different concentrations were measured at a steady shear rate of 100 s^{-1} , where the results are illustrated in Figure 6a. In this double logarithmic plot of the viscosity-concentration relationship, a sharp transition point (or the critical concentration) is found at ≈ 0.2 % (w/w) due to the slopes change. This critical concentration is of the same order of value as that reported for a TEMPO-oxidized CNF system having similar charge density by Tanaka et al. (16) From the structure perspective, the critical concentration is associated with the formation of a CNF network. That is above the critical concentration, CNFs entangle and form a network structure, resulting in a significant increase in viscosity. In Figure 6a, a slope of ≈ 2.3 is seen when the suspension concentration exceeds the critical value. This is in good agreement with the results reported by several other groups previously (28-30).



Figure 5. Steady shear viscosity versus shear rate in CNF suspension at various concentrations.

Figure 6b-d shows the influence of adding monovalent salt (NaCl) in the rheological behavior of CNF suspensions at three different concentrations: 0.05%, 0.2%, and 0.6% (w/w). These concentrations were selected to cover three different regimes: well below (0.05%), in the vicinity (0.2%) and well above (0.6%) the critical concentration of CNF, where the network formation can occur without the presence of salt. It is interesting to note that the incorporation of NaCl can effectively increase the viscosity of CNF suspension. This can be explained by the effect of screening to reduce the electrostatic repulsion forces between nanofibers, which also results in the network formation of CNFs. However, the critical NaCl concentration that leads to the increase of viscosity is different from that of the critical CNF concentration. It is found that at 0.05% (w/w) CNF concentration, the viscosity starts to take off at [NaC1] = 30 mmol/L; but at 0.2% and 0.6% (w/w) CNF, the critical [NaCl] value drop to about 10 and 3 mmol/L, respectively. In other words, the critical NaCl concentration decreases with the increasing CNF concentration. This behavior can be rationalized by the consideration of interfiber distance. That is the reduction of inter-fiber distance occurs not only due to the increase in number of nanofibers at higher CNF concentrations, but also the increase in amount of counterions that suppresses the electrostatic repulsion forces between the nanofibers. Consequently, the effect of adding counterions in CNF suspension is similar to that of increasing CNF concentration in promoting the network formation, where the critical NaCl concentration is lower in CNF suspensions of higher concentrations.



Figure 6. (a) The shear viscosity measured at 100 s⁻¹ as a function of CNF concentration. Impact of the NaCl contents in CNF suspensions with different concentrations (b) 0.05 wt%, (c) 0.2 wt% and (d) 0.6 wt%.

The effect of counterions in a charged colloidal system, such as CNF suspension, can be understood in a quantitative manner by the concept of Debye length (κ^{-1}) using the following formula:

$$\kappa^{-1} = \left(\frac{\varepsilon \varepsilon_0 k_B T}{e^2 N_A \sum_i z_i^2 M_i}\right)^{1/2}$$
(3)

where ε is the dielectric constant of the system, ε_0 is the permittivity of the free space (vacuum), k_B is the Boltzmann constant, T is the temperature, e is the electron charge (C), N_A is the Avagadro's constant, z_i is the charge number of species i, and M_i is the molar concentration of that species (mol/L). If we assumed the charged nanofibers particle behaves as a monovalent salt, the Debye lengths of the CNF suspensions at different concentrations could be estimated and the results are listed in Table 1. It is seen that the Debye length decreases with the increase in CNF concentration. At 0.2 wt% CNF concentration (around the critical concentration), the calculated Debye length was found to be very similar to the b_0 value (the width) of the CNF particle determined by SANS.

More insight into the network formation was obtained by further analyzing the SANS curves in Figure 2. Figure 7 illustrates the Lorentz-corrected SANS curves (Iq^2) of CNF suspensions at 4 different concentrations. It is found that the shape of the curve changes from a diffuse profile without the scattering maximum to a pronounced scattering peak at the concentration of 1.0 wt%. This behavior clearly indicates the formation of a microstructure due to the decrease in inter-fiber distance, where the structure factor becomes significant and cannot be ignored.



Figure 7. Lorentz-corrected intensity (Iq^2) plot of the systems in Figure 2.

The effect of the cation valency on the rheological behavior of the CNF suspension was also investigated. The visual evidence of the salt effect on the gelation behavior of a 0.6 wt% CNF suspension using salts with different valency (Na⁺, Mg²⁺, Al³⁺) is shown in Figure 8. It is seen that the control sample without salt is visually homogenous and fluidic (Figure 8a). Addition of different salts (NaCl, MgCl₂ and AlCl₃) at 40 mmol/L can all induce gelation (Figure 8b-d). However, the degree of gelation seems to be different. With the increase in valency, the CNF suspension becomes more inhomogeneous (see the comparison of two samples in Petri dishes shown in Figure 8b and 8d). Similar gelation behavior induced by different ions has also been observed in sulfuric acid hydrolyzed cellulose nanocrystals (CNCs) aqueous systems (31). In this study, we attribute the gelation behavior of CNF suspension induced by cations to the reduction in Debye length and the stronger screening of electrostatic repulsion between the CNF particles. The combined effects make van der Waals forces and interfibrillar hydrogen bonding interactions two dominant forces, favoring the CNF association.



Figure 8. The visual appearance of salt 0.6 wt% CNF after incorporation of different salts: (a) no salt, (b) 40 mmol/L NaCl, (c) 40 mmol/L MgCl₂, (d) 40 mmol/L AlCl₃.

It is noted that the Debye length of the systems can be kept constant, thus eliminating the effect of Debye length, by using varying amounts of the different cations. The shear viscosities of CNF gels with different amounts and types of cations, having the same Debye length, are shown in Figure 9. The viscosity of the CNF suspension is still seen to increase with the increase in the cation valency. Since the Debye length is the same in these suspensions, the observed difference can be attributed to the formation of cross-links, where the cation acts as a cross-linking agent. It is thus clear that the cross-linking ability increases with the valency of the cation.

In Figure 9, the appearance of the four viscosity curves (pure CNF suspension and three gels, induced by Na⁺, Mg²⁺, Al³⁺) is different. While the viscosity curve of the salt-free system displays a smooth shear thinning behavior, the appearances of the salt containing curves are much more complex even though the general shear thinning behavior is preserved. This may be due to the inhomogeneity of the salt containing systems, since the dispersion the salt ions becomes increasingly more difficult as the viscosity of the system increases. In addition to the inhomogeneity caused by the problem of ion dispersion, the destabilization of CNF suspension induced by cations should also be considered.



Figure 9. Shear viscosity of 0.6 wt% CNF gel with various ions as a function of shear rate and their recovery behavior.

The understanding of the thixotropic behavior in CNF suspensions is important for many applications, from coating of dense thin films to fabrication of porous membranes. The thixotropic behavior in different CNF gel systems has been clearly displayed in Figure 9, where the viscosity of the system can rapidly recover upon the cessation of shear. Similar observations have been made in other CNF systems before (19). It was also noted that the relaxation time of the gel generally decreases with increasing valency (i.e., ion charge number) due to the formation of a stronger cross-linked network. However, the recovery of the sheared Al⁺³ induced CNF gel was found to behave differently than those in three other CNF gels. In specific, the viscosity in Al⁺³ induced CNF gel reached a maximum immediately when shear stopped, then it decreased gradually. In contrast, all other gels exhibited a rapid initial increase and then a slow rise with time. The Al⁺³ induced CNF gel clearly showed a more elastic behavior due to the stronger network formation, which was further verified by the oscillatory rheological measurement. Figure 10 shows the effect of the cation charge number on the storage modulus (G') and loss modulus (G") of the gel during dynamic frequency sweep. For salt-free CNF suspension, the G' is larger than G" at low frequency, while G' decreases and becomes below G" at high frequency. The change from solid-like elastic behavior to liquid-like viscous behavior is due to the breaking of the network structure under high shear rate. For ion induced gels, the G' is always larger than G" over the entire range of oscillatory frequencies (from 0.1 to 100 Hz). In addition, both elastic and viscous contributions to the gel rigidity increase with the increase of cation charge number in the order of Na⁺<Mg²⁺<Al³⁺. More intuitive, the complex modulus ($G^* = G' + iG''$), which characterizes the rigidity of a gel, also increases dramatically with the increase of valency. The moduli results from the frequency sweep measurement of different CNF gels at a frequency of 1 Hz are listed in Table 2, which clearly confirms our argument.



Figure 10. Dynamic frequency sweeps for 0.6 wt% pure CNF suspension (squares), 0.6 wt% CNF gel with 40 mmol/L NaCl (equilateral triangle), 13 mmol/L MgCl₂ (inverted triangle) and 6.7 mmol/L AlCl₃ (diamond). The variations in the storage modulus (G') and loss modulus (G'') are shown with closed and open symbols respectively. The dynamic frequency sweeps were performed at 1% strain.



Figure 11. Dynamic strain sweeps of 0.6 wt% pure CNF suspension (squares), 0.6 wt% CNF gel with 40 mmol/L NaCl (equilateral triangle), 13 mmol/L MgCl₂ (inverted triangle) and 6.7 mmol/L AlCl₃ (diamond). The variations in the storage modulus (G') and loss modulus (G") are shown with closed and open symbols respectively. The frequency was fixed at 1 Hz.

The oscillatory strain sweep results of different CNF gels are shown in Figure 11. The normal crossover behavior of G' and G" at high strain was observed in all three metal ion-induced gels, except for the salt free gel. The crossover strain is found to shift to a lower value with the increase in ion charge number, again indicative of a denser and stronger network system. The modulus values obtained at a strain of 0.2 % are also listed in Table 2. Again, the results indicate the enhanced elasticity of CNF gels with the increasing valency of cation.

Table 2. Dynamic rheological properties of CNF gels. Results obtained from the frequency sweep measurement (modulus recorded at a frequency of 1 Hz) and the strain sweep measurement (modulus recorded at a strain of 0.2 %). G', G" and G* represent storage modulus, loss modulus and complex modulus respectively.

Samples –	Frequency sweep (1Hz)			Strain sweep (0.2%)		
	G' (Pa)	G" (Pa)	G* (Pa)	G' (Pa)	G" (Pa)	G* (Pa)
Pure CNF gel	2.5	1.0	2.7	1.2	0.6	1.3
CNF-NaCl	118.3	8.4	118.6	128.6	10.3	129.0
CNF- MgCl ₂	1350	144.9	1357.8	1481	126.7	1486.4
CNF-AlCl ₃	3690	686.8	3753.4	4081	601.7	4125.1

Conclusions

Cellulose nanofibers (CNF) were prepared by the combination of TEMPO-mediated oxidation and mechanical disintegration processes of jute pulp. The dispersed CNF fibrous nanoparticles possessed a ribbon like cross-section with a mean width of about 5 nm and mean thickness of about 1.5 nm, as determined by SANS and confirmed by TEM. The shear viscosity of the CNF suspension was found to be dependent on CNF concentration, added salt ion concentration, and valency of salt ion. With NaCl, it was noted that the critical salt concentration also inversely correlated with the CNF concentration – the critical NaCl concentration decreased with increasing CNF concentration. This behavior could be rationalized by the reduction in interfibrillar distance between CNF particles due to the lowering of electrostatic repulsion forces by increasing the amount of counterions. The viscosity (from the steady state shear measurement) and moduli (from oscillatory dynamic measurement) of the ion-induced CNF gel all increased with the increase in valency of ion (or charge number). Hence, the Al³⁺ ion is the most effective crosslinking agent for CNF suspension, resulting in the most rigid gel.

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