INFLUENCE OF DIFFERENT ACID ANIONS ON THE RHEOLOGY AND AGGREGATION BEHAVIOUR OF TEMPO-OXIDISED CELLULOSE NANOFIBRIL AQUEOUS SUSPENSIONS

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ABSTRACT

In the present work, the changes in the rheological properties and aggregation behaviour of TEMPO CNF aqueous suspensions were studied, varying systematically the pH of the suspensions (by the addition of acids with different anions). CNF aggregation was studied by rheometry, dynamic light scattering, zeta potential and optical microscopy. At neutral pH conditions, for mass fractions higher than 0.35% strong gels are formed and the gel point is ca. 0.18%. On the other hand, aggregation is improved at acidic pH values, due to lower charge density of the fibrils and consequent weak repulsion, leading to an increase of the suspension viscosity, as well as to higher apparent yield stress values. However, distinct rheological behaviours were presented by CNF suspensions as different acids were applied. It was found that phosphate ions resulted in significant aggregation, leading to the formation of particles of larger size and very strong gels, at pH 2.3; on the other hand, the presence of acetate ions resulted in lower aggregation, lower particle size and weaker gels, at the same pH value.

Keywords: Aggregation, Hofmeister series, Hydrogels, Protonation, Rheological properties.

INTRODUCTION

Cellulose nanofibrils (CNF) are nanosized cellulose fibres with a high aspect ratio, usually ranging from 5 to 20 nm in thickness and up to 2 μm in length. These nanomaterials are crystalline, and due to the crystallinity and high aspect ratio, CNF suspensions are strong hydrogels, with high elasticity at a relatively low concentration. Thus, CNF suspensions appear as an interesting rheology modifier to be applied in cosmetics, paints, food, as a mineral suspending agent, among other applications [1]. Alternatively, CNF suspensions can be dried to form stiff and strong films, with low density and thermal expansion coefficient, becoming these materials an excellent choice for food packaging or printed electronics, thus replacing common plastic in some applications [2].

CNF’s are obtained from wood pulp or non-woody resources, using appropriate chemical/ enzymatic pre-treatments followed by mechanical treatment. The chemical treatment used to prepare TEMPO-oxidised CNF (sodium hypochlorite in the presence of catalytic amounts of TEMPO radical) introduces negative charges along the cellulose fibrils, which lead to high fibrillation yields and highly viscous suspensions.

The viscosity and the aggregation of TEMPO-oxidised cellulose nanofibrils (CNF) in the suspensions can be tuned by changing some conditions such as concentration, pH, ionic strength or addition of cosolutes. Thus, the rheology of the CNF suspensions can be controlled by changing the aggregation of the cellulose fibrils; however, it is also possible to take advantage of fibrils aggregation to improve the dewatering process, which for charged cellulose nanofibrils is a very time and energy-consuming process, and compromises the use of this kind of CNF in industrial applications [3].

The present work deals with the study of the rheological and aggregation behaviour of suspensions of TEMPO CNF, depending on the CNF concentration and suspension pH, being the latter effect evaluated by addition of different acids (acetic, lactic, citric and phosphoric).
EXPERIMENTAL

Chemicals

Acetic acid (ACS Reag. Ph. Eur., >99.9 %), lactic acid (AnalaR NORMAPUR, >89.2 % in aqueous solution), phosphoric acid (USP-NF, Ph. Eur., 85 % in aqueous solution) and citric acid (> 99.5 %) were obtained from VWR International and used without any further purification.

Cellulose nanofibrils preparation and characterization

Cellulose nanofibrils were produced from an industrial never dried bleached Eucalyptus globulus kraft pulp, following a previously described procedure [4]. Cellulose fibres were firstly refined at 4000 revs., in a PFI lab refiner, followed by oxidation with NaClO (7 mmol of NaClO per g of dry pulp) in the presence of TEMPO radical and NaBr, being washed (at the end of the oxidation step) with distilled water until the conductivity of the effluent reaches a value close to the one of distilled water. Finally, the fibres were mechanically treated in a high-pressure homogenizer (GEA Niro Soavi, model Panther NS3006 L), applying two passages (500 bar and 400 bar, respectively). The yield of fibrillation, carboxyl content, degree of substitution and degree of polymerization were determined for the TEMPO CNF produced.

Cellulose nanofibrils suspensions preparation

Suspensions of TEMPO CNF containing different concentrations were prepared by dilution of the original suspension of nanofibrils (0.77 wt%), by weighing the desired amount of suspension and adding the required mass of distilled water. The samples were kept under stirring for 30 min to ensure good dispersion of the fibrils. After dispersion, the pH of the suspensions was adjusted to the desired value using the different acids, and the samples were left to reach equilibrium during 30 min under agitation before pH measurement.

Rheology and aggregation studies of CNF suspensions

A controlled stress rheometer (Haake, Model RS1, Germany) was used for the rheological studies. All the measurements were performed at constant temperature (25 °C), being the temperature-controlled by a water recirculation bath (Haake Phoenix II, Germany). The measuring setup used a cone-plate geometry (C60/1) for the rotational tests and a plate-plate geometry (PP20Ti) for the oscillatory tests. Flow curves were obtained in controlled stress mode applying shear stresses ranging between 1.0 and 50.0 Pa. The power-law parameters, fitted using the Ostwald-de Waele model, were obtained using the Haake RheoWin 4.20.005 software (Haake, Germany). The phase angle, storage modulus (G’) and loss modulus (G”) were accessed by performing amplitude sweep experiments from 1.0 to 100.0 Pa, at 1 Hz. The changes in the structure of fibrils suspensions are given by the oscillatory stress dependence of the phase angle (δ), which describes the phase lag between the viscous and elastic components of the complex modulus, where:

\[
\tan \delta = \frac{G''}{G'}
\]

Values of δ above 45° indicate that tan δ > 1 and G” > G’ (predominantly viscous behaviour) while values of δ below 45° indicate that G’ > G” (predominantly elastic behaviour) and δ=45° indicates the phase transition (G”= G’) [1].

Besides rheometry, samples were also studied by polarized light microscopy. An Olympus BH-2 KPA microscope (Olympus Optical Co., Ltd, Japan) equipped with a high-resolution CCD colour camera (Olympus ColorView III) was used for that purpose. Cellulose nanofibrils samples with a consistency of 0.09 % at different pH values were kept between coverslips, illuminated with linearly polarized light and observed through a crossed polarizer. Images were captured and analysed using the analySIS software (Soft Imaging System GmbH).

The particle size of the suspensions in the different pH conditions was studied through dynamic light scattering (DLS) measurements using a Zetasizer NanoZS equipment (ZN 3500, Malvern Instruments, UK), with a 532 nm laser, and a backscatter angle detection of 173°, at 25 °C. The concentration of the suspensions used was lower than the estimated overlap concentration, to avoid extensive
interactions among fibrils. Thus, CNF suspensions with a concentration of 0.05 wt% were centrifuged at 4000 rpm for 10 min, previously to pH adjustment and size measurements to remove large particles in suspension. The suspensions were then gently transferred to a glass cuvette and checked for the presence of bubbles. The average particle size was determined, based in six repetitions, using the Zetasizer Nano software (version 7.11). The data were analysed according to the non-negative least-squares (NNLS) algorithm. Additionally, the zeta potential of the suspensions was carried out in the same equipment and with the same software, by electrophoretic light scattering, based in six repetitions to each sample.

RESULTS AND DISCUSSION

Cellulose nanofibrils suspensions typically behave as polymeric solutions, forming an entangled network above a critical concentration, being that network destroyed by increasing shear forces, leading to viscosity decrease, shear-thinning behaviour. Figure 1 shows the flow curves obtained for TEMPO-oxidised CNF for different fibrils concentrations.

As the CNF concentration increases, the shear viscosity also increases. The lowest concentrated suspension, 0.09 wt%, never formed an entangled network, and thus no shear thinning was observed. Contrary, the suspensions with a mass fraction higher than 0.18 % presented high viscosities at low shear stress values, due to the presence of the entangled network, and a shear-thinning region due to the destruction of the entangled network, for higher shear stress values. Therefore, it is possible to conclude that for the present CNF suspensions the overlap concentration is between 0.09 and 0.18 wt%.

Figure 2 shows the changes in the phase angle, obtained from oscillatory sweep tests performed on nanofibrils suspensions, for different fibrils mass fractions. The suspension containing 0.09 wt% of CNF presented a liquid-like behaviour, i.e., a phase angle higher than 45°, in the entire range studied. At mass fractions of 0.18 % and 0.35%, a phase transition was observed, from solid-like to liquid-like behaviour with the increase in the applied stress; it was also observed a delay in the transition, for higher stress values, as the concentration increases. For higher fibrils concentrations, the solid-like behaviour was observed for the stress range studied, demonstrating a strong fibrils network formed at 0.77wt% CNF.
Besides, aggregation also plays a major role in the suspension rheology behaviour. Aggregation of negatively charged CNF can be promoted by reducing the surface charge density (by protonation of carboxyl groups [5]) or by charge screening (salt addition). Figure 3 (top) depicts the flow curves obtained for 0.35% TEMPO CNF suspensions at pH 6.9 and pH of 2.3, with the pH adjusted with different acids. It is possible to observe an increase in the viscosity of the suspensions as the pH is decreased. At pH 2.3, the suspensions presented the highest apparent viscosity values, ca. 200,000 Pa.s, except when acetic acid was used to adjust the pH, where a decrease in the viscosity is observed with the shear stress increment. For the CNF samples at pH 6.9 and pH 2.3, adjusted with acetic acid, it was also possible to observe the yield stress point, i.e the shear stress necessary to be applied to the sample before it starts to flow due to the disruption of the network. Also, it is possible to conclude that the yield stress value was shifted to values higher than 100 Pa for the suspensions adjusted with lactic, citric and phosphoric acid, contrary to the suspension adjusted with acetic acid, Figure 3 top.
The yield stress point can also be obtained from the oscillatory amplitude sweep tests, Figure 3 bottom. The results obtained from the amplitude sweep tests agree with the rotational tests. For the suspension of CNF at pH 6.9, a yield stress point of ca. 15 Pa is obtained by both the methodologies. At pH 4.4, tendentially, a small shift to higher stresses was observed for the CNF suspensions, and at pH 2.3 only the suspension adjusted with acetic acid present a transition from solid-like to liquid-like behaviour, i.e., a yield stress point, in the studied range (1 – 100 Pa).

From the rotational tests (Figure 3 top) it was also possible to obtain the power-law parameters, by application of the Ostwald–de Waele model (τ = K × γ^n), where τ is the shear stress, K is the consistency coefficient, γ is the shear rate and n is the flow behaviour index. Table 1 summarizes the obtained results.

### Table 1 – Power law parameters for TEMPO CNF suspensions (0.35 %) at pH 2.3, adjusted with distinct acids.

<table>
<thead>
<tr>
<th>Acid type</th>
<th>K (Pa s^n)</th>
<th>n</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic</td>
<td>8.72 × 10^4</td>
<td>0.2622</td>
<td>0.980</td>
</tr>
<tr>
<td>Lactic</td>
<td>4.25 × 10^5</td>
<td>0.9263</td>
<td>0.990</td>
</tr>
<tr>
<td>Citric</td>
<td>6.96 × 10^5</td>
<td>0.9532</td>
<td>0.988</td>
</tr>
<tr>
<td>Phosphoric</td>
<td>3.59 × 10^5</td>
<td>0.9188</td>
<td>0.986</td>
</tr>
</tbody>
</table>

The fitting parameters and the correlation coefficients (R) were obtained using the Haake RheoWin 4.20.005 software.

An n value equal to unity indicates a Newtonian fluid; conversely, non-Newtonian fluids are expressed by n values smaller than 1, indicating a pseudoplastic (or shear thinning) behaviour, whereas n higher than 1, indicates a dilatant (or shear-thickening) behaviour. As can be seen, at pH 2.3, the suspension adjusted with acetic acid behave differently compared with the other three suspensions; lower consistency and flow indexes were obtained when compared with the suspensions adjusted with the other acids. Although not constant, the viscosity of the suspension adjusted with lactic, citric and phosphoric acid was not largely affected by the applied shear stress, in the studied range (n is approximately 1), contrary to the viscosity of the suspension adjusted with acetic acid, which is more affected by the stress applied. The differences observed can be explained by the differences in the aggregation behaviour, induced by the differentiated interaction of the acid’s anions with the fibrils, which can significantly change the aggregation extension and consequently the rheological properties of the suspensions. Aggregated fibrils can act to reinforce the formed network leading to a viscosity increment due to particle size growth, Figure 4.

Figure 4 shows images obtained by optical microscopy, under polarised light, the particle size obtained by dynamic light scattering and the zeta potential value obtained through electrophoretic mobility. At pH 6.9, the suspension containing 0.09 % (mass fraction) of CNF, does not present large aggregates, as can be seen by microscopy and by DLS (particle size of 160 nm). As the pH is decreased to 2.3, the aggregation of fibrils is noticed leading to the appearance of very large bundles of fibrils (several hundred microns), being the growth more pronounced when phosphoric acid is used (particle size > than 2 µm). Also, some fibres of cellulose appeared in the images being probably trapped by the growth of the aggregates (arrows indicate some of these cellulose fibres). The microscopic images obtained for the sample of CNF with acetic acid presented a clearer image compared to the other acids, indicating the presence of fewer fibril aggregates and of lower size.

Particle size results are in good agreement with the ones reported by Sato et al., who studied the charging and aggregation behaviour of CNF in aqueous solutions as a function of pH [6]. Authors investigated the aggregation behaviour at different ionic strengths as a function of pH (adjusted with HCl) and found a significant particle size increase for pH values below 4, more pronounced at higher ionic strengths, due to the extensive charge screening as a result of high salt concentrations in solution. The zeta potential results (Figure 4) show a large reduction in zeta potential as pH is decreased, being the larger drop observed for pH values below the pKa of carboxylic groups (ca. 4.8 [7]), i.e.,
at pH 2.3. At pH 2.3, all the cellulose fibrils presented a very low zeta potential due to almost full protonation of the carboxylic groups. Mautner et al. reported for TEMPO CNF an isoelectric point at ca. pH 1.5 [8]. However, the value obtained in the present study for the suspension adjusted with phosphoric acid was ca. pH 2.3. Being expected an identical protonation to a specific pH value, independent of the acid used, the differences in particle size and zeta potential can be explained by differences in the electrical double layer extension [6], according to the acid used.

To clarify the effects behind the different behaviours it is important to look to the partition coefficients of the used acids. Phosphoric acid is highly water-soluble and thus the partition coefficient is not available in the literature, being, however, this acid more hydrophilic than the other three used; on the other hand, the Log P values range from -0.31 (at 20 °C) for acetic acid, until -1.65 (20 °C) for citric acid, being -0.62 for lactic acid [1]. Thus, it is possible to rationalize the aggregation/disaggregation of cellulose nanofibrils by salting-in/salting-out effects (Hofmeister series), induced by the acid anions used. Acetate ions, due to their lower water solubility, are expected to have a higher interaction with virtually neutral fibrils (carboxylic groups are almost fully protonated at pH 2.3) than ions like phosphate, due to the high water solubility and consequently poor affinity with CNF surfaces. The presence of acetate anions close to fibrils neutral surfaces can stabilize the particles and reduce aggregation (salting-out effect less pronounced), but this behaviour is not expected for phosphate anions (higher salting-out effect). The salting-in and salting-out effects are very well described for interactions of cations and anions with proteins [9] and similar trends were observed for interactions with non-ionic polymers and other biopolymers [10].

**Figure 4** – Polarized light microscopy images of suspensions containing 0.09 % TEMPO CNF, at 25 °C. a) pH=6.9; b) at pH 2.3 (acetic acid); c) at pH=2.3 (citric acid); d) at pH=2.3 (phosphoric acid). Particle size is the average hydrodynamic diameter measured by dynamic light scattering.
CONCLUSIONS

In the present work the effects of different acid anions on the rheology and aggregation behaviour of TEMPO cellulose nanofibrils suspensions, with an estimated gel point of ca. 0.18 % (at pH 6.9), were explored. For concentrations above 0.18 %, the suspensions presented a solid-like behaviour, being the gel strength enlarged as the fibrils concentration increases, due to the increment in physical entanglements and reinforcement of the three-dimensional network. Besides entanglements, fibrils aggregation also plays a major role in the rheology of the suspensions. As the pH of the suspensions was decreased, and consequently the carboxylic groups were protonated, the viscosity of the suspensions increased, due to the fibrils aggregation, driven by the decrease in charge repulsion among fibrils. Additionally, the acid anion used to adjust the pH of the suspensions was found to play an important role in fibrils aggregation, and consequently on the rheology of the suspensions. Acetate ions led to a lower aggregation of TEMPO CNF fibrils when compared to phosphate, lactate or citrate ions. The phosphate anions resulted in an extensive aggregation of fibrils (at pH 2.3), and as a consequence, the CNF suspensions adjusted with phosphoric acid formed stronger gels. These distinct behaviours could be explained by differences in the interactions of the acid anions with virtually neutral fibrils, following the Hofmeister series. Therefore, the use of different acids can be used to control the rheology of the suspensions and can be also useful to improve the dewatering of negatively charged CNF suspensions, being phosphoric acid the most promising compound for this task.

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