



Rheological characterization of microfibrillated cellulose suspensions after freezing

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ABSTRACT

This work aims to investigate the rheological properties of microfibrillated cellulose (MFC) suspensions. The effect of some experimental parameters, such as cellulose concentration, temperature, ionic strength and pH has been studied. For that purpose, suspensions of microfibrillated cellulose have been prepared by strong mechanical treatments of a purified sugar-beet pulp cellulose-based residue in aqueous medium. Cellulose suspensions at different concentrations (from 0.25 to 3 w/w%) have been found to display a viscoelastic solid-like behaviour, even for the lowest concentration tested. The storage modulus at 0.1 rad s^{-1} increased strongly upon increasing concentration from 0.25 to 3 w/w%, following a power law with an exponent of 2.58. All suspensions exhibited a shear-thinning behaviour. It was also found that viscoelastic properties of the suspensions of cellulose are not affected by temperature or by varying pH from 4.5 to 9 while the G' and G'' moduli increased as salt concentration of the suspensions increased. This reinforcement of the viscoelastic properties by increasing ionic strength can be related to a screening of the electrostatic repulsions between the microfibrils, due to the presence of uronic acid groups, enhancing the fiber–fiber interactions. Mechanical treatment did not affect cellulose crystallinity. The effect of freezing was investigated as an alternative way to the most conventional cellulose preparation that consists to freeze-dry the suspensions for their conservation. It was shown that freezing preserved the rheological properties of the suspensions, contrary to freeze drying.

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1. Introduction

Cellulose is a natural polymer available in large amount on earth. It has been estimated that globally between 10^{10} and 10^{11} tons of cellulose are synthesized each year (Hon, 1994). This biopolymer is biosynthesized by higher plants, by a wide variety of bacteria, algae and fungi and by some animals (tunicates for instance) (Atalla, 1999; Horii, 2000; Salmon & Hudson, 1997). It is the less expensive biopolymer and it is totally biodegradable, recyclable and renewable. In recent years there has been increasing concern for the preservation of environment and sustainability of resources. These are the main reasons leading to the growing interest of cellulose-based products for applications in which synthetic polymers have traditionally been prime materials.

Cellulose is a linear homobiopolymer consisting of glucan chains with repeating β -(1 \rightarrow 4)-D-glucopyranose units (Kirk & Othmer, 1967). These chains form parallel nanoscale bundles, the microfibrils, which again aggregate to form cellulose fibers. According to literature (Maréchal & Chanzy, 2000), native cellulose, the so-called cellulose I, has intrachain and interchain hydrogen bonds which are, respectively, responsible for the stiffness and the sheet-like nature of cellulose (Kondo, 2005). A specific feature

of cellulose-based compounds is the high density of hydroxyl groups which provides the hydrophilic nature of these materials, making them good candidates for hydrogels (Liang, Zhang, Li, & Xu, 2007). Depending on their biological origin, the microfibril dimensions range from about 2 to 20 nm in diameter and can rise up to several tens of microns in length (Chanzy, 1990). Native cellulose contains disordered and ordered domains, which can be considered as amorphous and crystalline regions, respectively (Rowland & Roberts, 1972). It may be classified as a semicrystalline fibrillar material. Because of the stable structure of their crystalline regions, microfibrils display high mechanical properties along the longitudinal direction (Page & El-Hosseiny, 1983; Sakurada, Nukushina, & Ito, 1962). Cellulose nanofibers can be considered as functional materials, because they are individualized, continuous, with a constant thickness and a high crystallinity. Due to these unique characteristics, numerous studies have been conducted on cellulose nanofibers to investigate the preparation of separated fibrils or aggregates of fibrils. However, the preparation of aqueous homogeneous cellulose suspensions is very difficult. Several routes have been described in literature. For example, original methods described the delamination of pulp fibers by using a high-pressure homogenizer in which the pulp fibers are submitted to shearing forces (Herrick, Casebier, Hamilton, & Sandberg, 1983; Turbak, Snyder, & Sandberg, 1983). During the treatment, the cell wall structure consisting of nanofibers in a multi-layered structure is

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broken down by the shearing forces generated by the high pressure, and then nano-sized fibers are separated from the pulp fibers. Cellulose suspensions resulting from high pressure treatments are called microfibrillated cellulose (MFC). Other processes reported the use of a microfluidizer or a grinder for mechanical fibrillation (Taniguchi & Okamura, 1998). Wood pulp, cotton, tunicin and bacterial cellulose are separated into nanofibers by a combination of oxidation by 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) radical and simple mechanical treatment using a waring blender (Saito, Nishiyama, Putaux, Vignon, & Isogai, 2006). Recently, mild enzymatic hydrolysis has been introduced and combined with mechanical shearing and a high-pressure homogenization, leading to a controlled cellulose delamination down to nanoscale and a network of long and highly entangled cellulose I elements (Pääkkö et al., 2007). The grinding treatment in an undried state after the removal of the non-cellulosic polysaccharides has also shown to be effective to obtain cellulose nanofibers with a uniform width of approximately 15 nm (Abe, Iwamoto, & Yano, 2007).

Microfibrillated cellulose was intended to be used in products such as foods, cosmetics, and medical products (Herrick et al., 1983). Applications in paper coatings or other coating compositions have also been proposed (Turbak et al., 1983). Use of cellulosic nanofibers as a reinforcing phase in nanocomposite films has also been studied (Chanzy, Rotzinger, & Smith, 1987). Therefore, research has been focused on the rheological properties of different types of cellulose suspensions from a variety of sources (bacterial cellulose, algal cellulose, cotton, tunicate cellulose, wood pulp, sugar beet primary cell wall cellulose), as cellulose whiskers (Azizi Samir, Alloin, & Dufresne, 2005; Bercea & Navard, 2000; Ebeling et al., 1999; Orts, Godbout, Marchessault, & Revol, 1998), cellulose microcrystalline hydrogels (Mihiranyan, Edsman, & Stromme, 2007; Rudraraju & Wyandt, 2005; Tatsumi, 2007; Tatsumi, Ishioka, & Matsumoto, 1999, 2002), and MFC suspensions (Dinand, Chanzy, & Vignon, 1996, 1999; Lowys, Desbrieres, & Rinaudo, 2001; Pääkkö et al., 2007; Tatsumi, 2007; Tatsumi et al., 1999, 2002; Togrul & Arslan, 2003; Wågberg et al., 2008).

In many cases, cellulose suspensions have been used directly after preparation (Dinand, Chanzy, & Vignon, 1997; Dinand et al., 1996; Dinand et al., 1999; Tatsumi, 2007; Tatsumi et al., 1999; Tatsumi et al., 2002; Wågberg et al., 2008) because they are difficult to be preserved. For economic and practical reasons, it would be judicious to find a way of conservation of this cellulosic material. As for other biopolymers (starch, pectin, etc.), it would be interesting to have the microfibrillated cellulose in the dried form to facilitate their storage and carriage. Unfortunately, upon drying, an increase in the degree of cross-linking between microfibrils due to additional hydrogen bonds is observed, which can not be broken during rewetting (Minor, 1994; Weise, 1998). Therefore, the initial swelling properties are not restored after fiber rewetting and beating. The microfibrils are said to be “hornified” (Jayme, 1942). Therefore, redispersion of microfibrillated cellulose in water, after drying, does not allow the recovery of the rheological properties of the initial suspension (Lowys et al., 2001). In particular, freeze-drying which is the method of conservation usually employed involves an important loss of the rheological properties (Lowys, 1999). However, to prevent or reverse this phenomenon, water-soluble polymeric additives such as hemicelluloses, sodium carboxymethylcellulose, sodium polyacrylate or cationic polycrylamide derivative have been added to cellulose suspensions before drying (Centola & Borruo, 1967; Kohnke & Gatenholm, 2007; Lowys et al., 2001; Rebuzzi & Evtuguin, 2006) but this procedure is either too costly to be practical or create other problems (i.e. unpractical for the commodity recycled paper). To find a process of conservation easily applicable to the industrial scale and affecting little the rheological properties of the cellulose suspensions remains still a challenge.

In this work, the rheological properties of sugar beet microfibrillated cellulose have been studied, depending on different experimental parameters, such as cellulose concentration, temperature, pH or ionic strength. The effect of freezing, as an alternative method to freeze-drying to store cellulose suspensions, has also been investigated.

2. Materials and methods

2.1. Materials

A batch of dried sugar-beet pulp (11% of water content) was obtained from S.I.D.E.S.U.P society (45, Engenville – France) and was used as a source of cellulose. The different steps of the extraction process (Fig. 1) of cellulose from sugar-beet pulp were carried out at large scale following the procedure described by Heux, Dinand, and Vignon (1999) slightly modified by decreasing heating time and the nature of the acid. To remove other polysaccharides, the sugar-beet pulp was dispersed in 0.1N HNO₃ (15 kg of pulp in 252 L) for 30 min at 85 °C and filtered through two sieves with a diameter of 400 µm and 160 µm. The filtrate was centrifuged at 5500 g using a Westfalia separator (type SA14 06-076) to recover the products passed through the sieves. This acidic extraction was carried out three times. The residual product was washed abundantly with deionized water and subjected to an alkaline extraction (0.5N NaOH, 127.5 L for 30 min at 80 °C). This operation

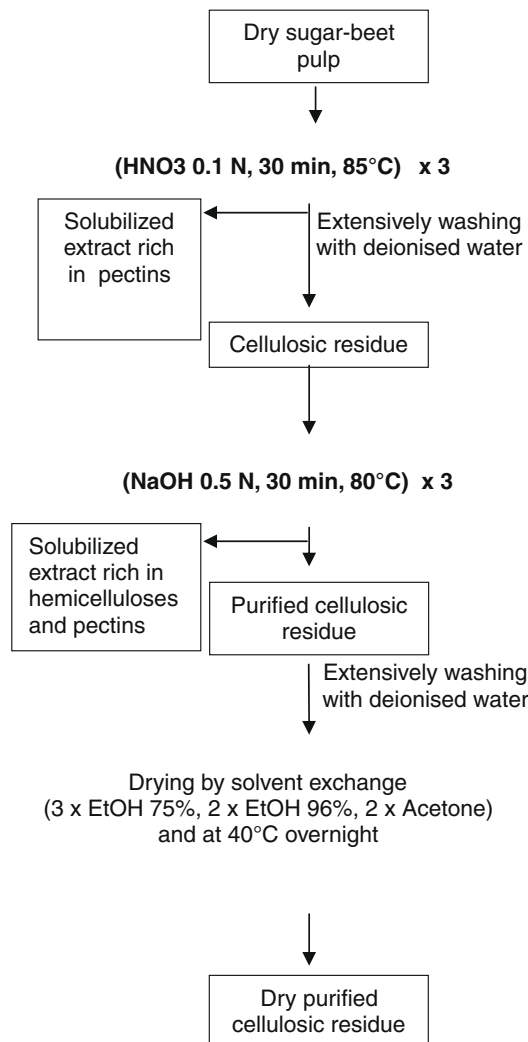


Fig. 1. Extraction process of cellulose residue from sugar-beet pulp.

was performed three times. The final residue was washed abundantly with deionized water, dried by solvent exchange (ethanol, acetone) and left overnight at 40 °C. At the end of the process, 2.3 kg of dry purified cellulosic residue was obtained, leading to an extraction yield close to 15%.

2.2. Preparation of cellulose microfibrils

The cellulose residue, at 2 w/w% concentration in deionized water was left overnight at 4 °C under gentle magnetic stirring and then dispersed by mechanical stirring using a Polytron (Typ X 40/34, Ystral GMBH, Dottingen, Germany) at 30,000 rpm for 20 min. After dilution of the initial suspension to the concentration of 1.6 w/w%, the sample was sonicated using a high intensity ultrasonic processor (Sonicator Ultrasonic, Sonics and Materials Inc., Danbury, USA; Power 500 W, frequency 20 kHz) with a plate tip of 13 mm diameter, during 4 min by share of approximately 250 mL. The sonicated suspension was diluted to 1 w/w% and heated at 65 °C for 20 min. The sample was immediately homogenized by 10 passes (five passes at 300 bars and five other passes from 380 to 400 bars) through a Rannie two-stages Homogenizer (Rannie Homogenizer, typ LAB 16/50; pressure 50–400 bars). The ultrasound dispersion was performed to promote cellulose fibers delamination and avoid blocking of the constriction chambers of the homogenizer. Sodium azide (0.02%) was added to the cellulose suspension to prevent from bacteria contamination. Most of the delaminated suspension (1 w/w%, pH ~ 8) was deep-frozen (–20 °C). Around 1 L was kept at 4 °C during few days for characterization in a fresh state, and another volume was freeze-dried.

2.3. Chemical characterization

Individual neutral sugars were analysed as their alditol acetate derivatives by gas–liquid chromatography (Blakeney, Harris, Henry, & Stone, 1983) after hydrolysis by 2N H₂SO₄ at 100 °C for 2 h. The cellulose residue was first prehydrolysed in 72 w/v% H₂SO₄ for 3 h at 25 °C. Inositol was used as an internal standard. The uronic acid (as galacturonic acid) content of the cellulose residue was determined colorimetrically by the automated m-hydroxybiphenyl method (Thibault, 1979). Proteins were measured in the residue colorimetrically by a modified Berthelot method after classical Kjeldahl samples mineralization. Ash was determined by incineration overnight in a muffle furnace at 550 °C.

2.4. Observation by TEM (transmission electron microscopy)

A drop of each diluted (0.001 w/w%) aqueous fresh dispersion was first placed on a carbon-coated TEM copper grid (Quantifoil, Germany) and let for air-drying. The sample was then negatively stained with uranyl acetate (Merck, Germany). To this aim, the sample-coated TEM grid was successively placed on a drop of an aqueous solution of uranyl acetate (2 w/w%) and on a drop of distilled water. The grid was then air-dried before introducing them in the electron microscope. The samples were viewed using a JEOL JEM-1230 TEM operating at 80 kV.

2.5. Wide angle X-ray scattering (WAXS)

X-ray diffraction was carried out on freeze-dried samples of cellulose (before and after mechanical treatment). Approximately 20 mg of sample was sealed between two tape foils to prevent any significant change in water content during the measurement. Diffraction diagrams were monitored by recording X-ray diffraction diagrams every 10 min on a Bruker D8 Discover diffractometer. The X-ray radiation Cu K α_1 (λ = 1.5405 Å), produced in a sealed tube at 40 kV and 40 mA, was selected and parallelized using a Göbel mir-

ror parallel optics system and collimated to produce a 500 μ m beam diameter. The X-ray diffraction data were collected using a two-dimensional GADDS detector. Acquisition time was 600 s. The degree of crystallinity was determined by the method initially developed for cellulose (Wakelin, Virgin, & Crystal, 1959).

2.6. Samples preparation

The frozen samples were left overnight after defrosting at 4 °C under gentle magnetic stirring, and sonicated as described above. Samples were then concentrated (from 1 w/w% to 4.31 w/w%) by osmotic compression against dextran solution (18 w/w%; M_w = 100,000 g mol^{–1}). The suspension concentration was determined by measuring the dry weight residue. After dilution of the initial suspension to the desired concentration, in the range 0.25–3 w/w%, and fixing pH to 6.8 with 0.1M and 0.01M HCl, the samples were dispersed with a high intensity mixer (Polytron PT 45/80, Kinematica, Switzerland) at 20,000 rpm for 5 min. Freeze-dried samples were dispersed in water to reach a concentration of 1 w/w%, sonicated and dispersed in the same way than defrosted suspensions.

To investigate the influence of ionic strength on the rheological properties of cellulose suspensions, salt solutions were added to obtain concentrations ranging from 0.05 to 0.1M NaCl and 0.05 to 0.1M CaCl₂, for a cellulose concentration of 0.50 w/w%. The pH was adjusted at 6.8 for each suspension. To investigate the influence of pH, a 1 w/w% cellulose suspension was adjusted at pH 4.5, 6.8 and 9, with 0.5M HCl or 0.1M NaOH. All the samples were then redispersed with the high intensity mixer (Polytron PT 45/80, Kinematica, Switzerland) as above.

2.7. Rheological characterization

Rheological measurements were carried out using an ARES (TA Instruments) controlled strain rheometer equipped with a 40 mm Teflon plate-and-plate geometry and a Peltier temperature controller. The gap was fixed at 1 mm. Samples were covered with paraffin oil to prevent evaporation during measurements.

Before measurements, the samples were heated at 80 °C for 30 min and poured at 80 °C on the rheometer. A first mechanical spectrum (G' and G'' as a function of angular frequency) was obtained at 80 °C in the range of 100–0.1 rad s^{–1}. Then, a temperature sweep test (1 °C/min) was performed from 80 °C down to 20 °C, then from 20 °C up to 80 °C and back to 20 °C, at an angular frequency of 1 rad s^{–1}, in order to evaluate the temperature dependence. This was followed by a mechanical spectrum at 20 °C in the range of 100–0.1 rad s^{–1}. In all experiments, the measurements were performed at a 0.7% strain, which was in the linear viscoelasticity domain.

At the end of the viscoelastic measurements, flow measurements were performed at 20 °C. First, the thixotropic behaviour has been estimated by programming a shear rate cycle between 0 and 100 s^{–1} for 2 \times 2 min to detect an eventual hysteresis. Then apparent viscosity was monitored by decreasing the shear rate from 100 to 0.01 s^{–1} to describe the flow behaviour. Each measurement was performed in triplicate (n = 3).

3. Results and discussion

3.1. Chemical characterization of the cellulosic residue

Chemical composition of the cellulose residue from sugar-beet pulp is presented in Table 1. It can be noted that the sum of all components does not reach 100%. This can be explained by the limited accessibility of glucosidic bonds in the glucan chains of cellulose to the acid used for prehydrolysis and hydrolysis. Cellulose is

Table 1
Chemical composition of cellulose residue from sugar-beet pulp.

	(% Dry weight)
<i>Neutral sugars</i>	
Glucose	80.33 ± 1.61
Xylose	3.93 ± 0.08
Mannose	1.75 ± 0.07
Galactose	0.72 ± 0.05
Arabinose	0.50 ± 0.07
Rhamnose	0
Fucose	0
<i>Galacturonic acid</i>	1.20 ± 0.10
<i>Proteins</i>	1.35 ± 0.07
<i>Ash</i>	3.61 ± 0.04

then not totally hydrolysed, leading to an under-estimated glucose content. However, increasing the time of hydrolysis time presents the risk of non-cellulosic components damage. Besides glucose, the main neutral sugar in the residue, the other neutral sugars were arabinose, xylose, mannose and galactose, in a much lower amount. This confirms that the major polysaccharide present in this residue is cellulose. This composition is rather similar to previous results (Dinand et al., 1996; Zykwiniska, Ralet, Garnier, & Thibault, 2005). The low amount of galacturonic acid (1.2%) and of the other neutral sugars indicates, respectively, low pectin and low hemicellulose contents. These surface encrustants of cellulose fibers have been suggested to be responsible for the unusual stability of the suspensions of dispersed cellulose microfibrils in water (Dinand et al., 1999). For instance, the residual galacturonic acid content yields a negative surface charge of cellulose fibers (Ribitsch, Stana-Kleinschek, & Jeler, 1996). A low protein content (1.35%) was detected, owing to the persistence of residual proteins into the sugar-beet pulp. The ash content was ~3.6% in agreement with previously reported values (Lowys, 1999). This relatively high content of ash in the cellulose residue can be explained by the presence of a high ash content in sugar-beet pulps which is usually ~10% (Bertin, Rouau, & Thibault, 1988; Michel, Thibault, Barry, & de Baynast, 1988; Ralet, Thibault, Hallaert, Vandamme, & Van Loo, 1990), due to persistence of soil particles after the industrial process.

3.2. Effect of mechanical treatment on cellulose crystallinity

Diffraction diagrams obtained prior and after the mechanical treatment are shown in Fig. 2. The diffraction diagram recorded from dried cellulose after applying the entire delamination process is very close to the one of the non-treated cellulose. The calculated degree of crystallinity was of 13% and 11% respectively before and after treatment. This observation suggests that the mechanical treatment, consisting of sonication and passing several times through a Rannie two-stages Homogenizer, does not affect cellulose crystallinity. Heux et al. (1999) showed an increase of the crystallinity index of sugar-beet pulp cellulose determined by solid-state NMR, from 32% to 38%, before and after mechanical treatment. In comparison to these values, ours are relatively low, in agreement with those obtained also by NMR by Pääkkö et al. (2007) who determined a degree of crystallinity in the range of 8–12% for microfibrillated cellulose from bleached sulfite softwood cellulose pulp.

3.3. Transmission electron microscopy (TEM) characterization of cellulose suspensions

TEM micrographs of native cellulose and fresh cellulose microfibrils obtained by extensive mechanical shearing are showed in

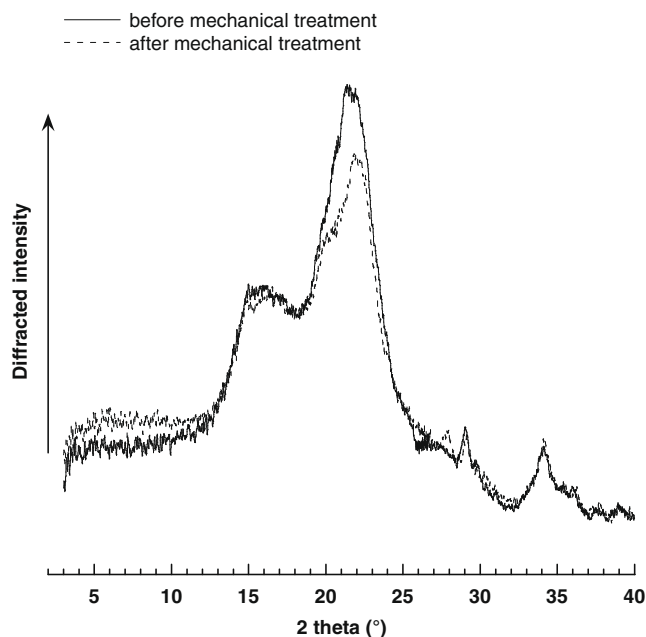


Fig. 2. X-ray diffraction diagrams obtained prior and after the drastic mechanical treatment of cellulose.

Fig. 3. Before treatments (Fig. 3a and b), native cellulose appeared as bundles or clusters of cellulose fibers. After treatments (Fig. 3c and d), cellulose appears as more or less delaminated and entangled microfibrils. A random dispersion of small and lengthened isolated microfibrils (with a diameter of 2–15 nm and a length of up to 10 µm) and of bundles of variable numbers of microfibrils is noticed. This observation is typical of dispersed parenchymal cellulose (Dinand et al., 1999; Goussé, Chanzy, Cerrada, & Fleury, 2004). From these micrographs, it is clear that the mechanical shearing induced extensive delamination of cellulose fibers. A practical result was that the homogenized suspensions did not sediment nor flocculate anymore.

The micrographs obtained from the defrosted cellulose suspensions (Fig. 3e and f) revealed globally the same network structure as that described for the delaminated cellulose suspensions before freezing (Fig. 3c and d). Less material is seen because of the concentration of the initial suspension (0.5 w/w% instead 1 w/w%). However, this does not affect microfibril dimensions. These observations show that freezing does not change the structural organization of cellulose suspensions.

3.4. Rheological characterization of cellulose suspensions

3.4.1. Influence of freezing on the rheological behaviour

The dynamic viscoelasticity of 0.5 and 1 w/w% of cellulose suspensions obtained after delamination is shown in Fig. 4. The mechanical spectra at 20 °C showed the storage modulus G' to be higher than the loss modulus G'' within all the angular frequency range. G' and G'' were only slightly dependent of the angular frequency, evidencing a gel-like behaviour. Mechanical spectra obtained for defrosted suspension showed the same shape and were almost superimposed with those of the fresh suspension. In contrast, mechanical spectra obtained for suspensions prepared from freeze-dried microfibrils were shifted to lower values throughout the all pulsation range, even if the same shape was observed (results not shown).

The values of the storage modulus and of $\tan \delta$ for all the systems are reported in Table 2. The constant value obtained for $\tan \delta$ (~0.1) clearly evidences that the systems are all structured in the

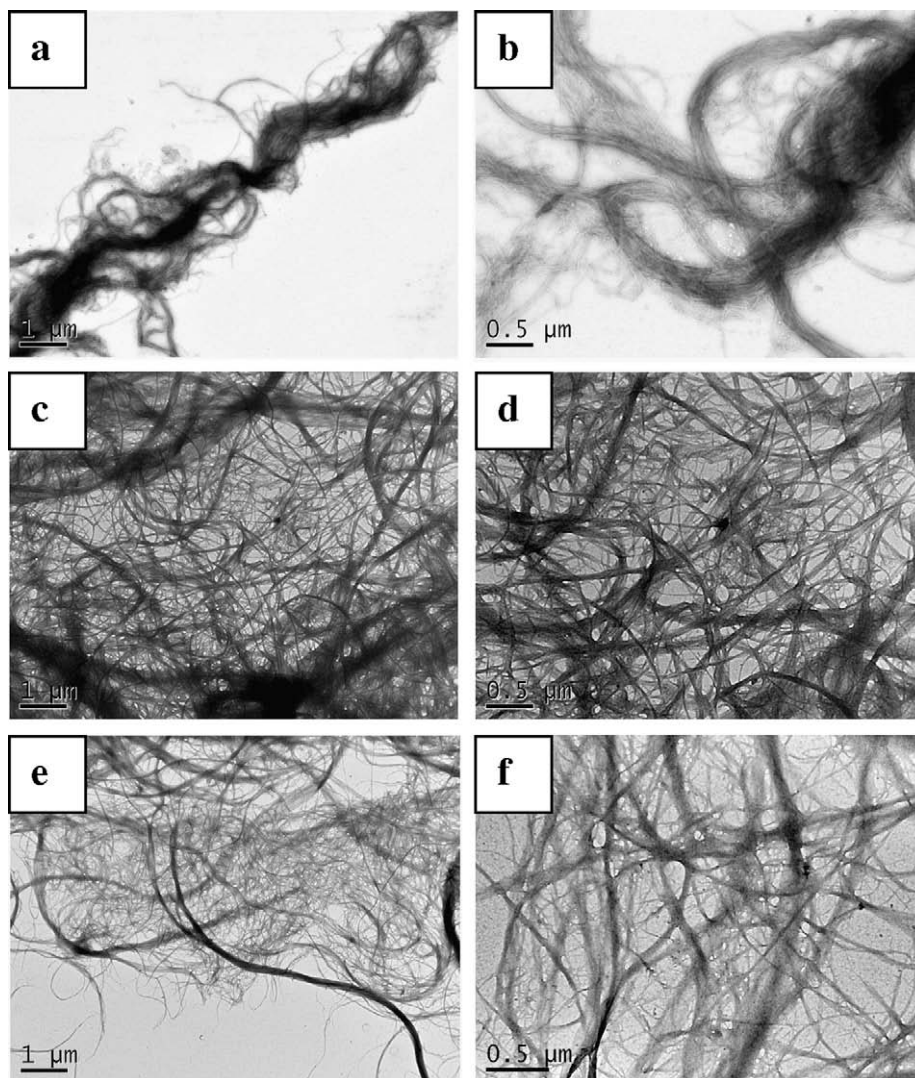


Fig. 3. TEM micrographs of cellulose fibers. (a and b) Native cellulose after extraction (1 w/w%); (c and d) delaminated cellulose suspensions before freezing (1 w/w%); (e and f) defrosted cellulose suspensions (0.5 w/w%). The samples are observed after dilution (1000 times). Scale bar: 1 μm (a, c and e); 0.5 μm (b, d and f).

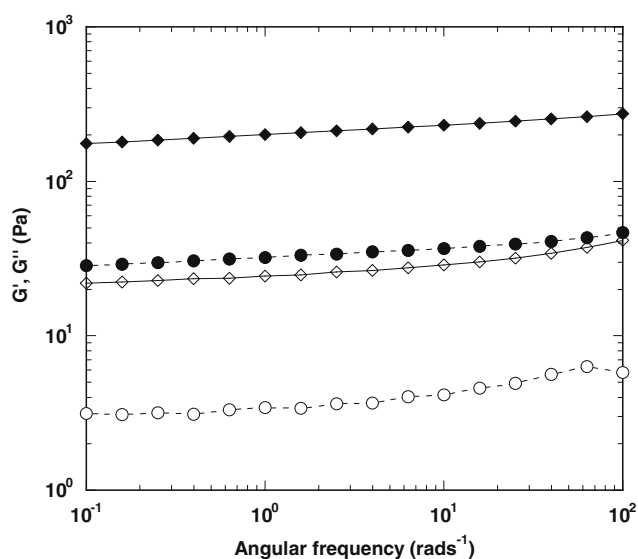


Fig. 4. Mechanical spectra of fresh cellulose suspensions at 0.50 w/w% (dashed lines with ●, ○) and 1 w/w% (line with ◆, ◇) at 20 °C and 0.7% strain amplitude. G' , filled symbols; G'' , empty symbols.

Table 2

Values of G' and $\tan \delta$ obtained from the mechanical spectra at 20 °C and 0.1 rad s^{-1} for fresh and defrosted cellulose suspensions and for suspensions prepared from freeze-dried microfibrils, at cellulose concentrations of 0.50 and 1 w/w%.

Samples	Cellulose concentrations			
	0.5 w/w%		1 w/w%	
	G' (Pa)	$\tan \delta$	G' (Pa)	$\tan \delta$
Fresh suspensions	29	0.11	176	0.12
Defrosted suspensions	30	0.11	170	0.12
Freeze-dried suspensions	13	0.11	50	0.12

same way. Freeze-drying clearly leads to an important loss of the viscoelastic properties, as already shown by Lowys (1999), which is not the case when applying a freezing treatment to the initial suspension.

Flow behaviour curves displayed a shear-thinning behaviour for all the suspensions, with flow curves very close to each other for initial and defrosted suspension. In contrast, apparent viscosity values were lower for suspensions prepared from freeze-dried microfibrils (results not shown).

All these observations evidence that there is a significant change of the rheological properties due to freeze-drying, because

of a strong aggregation of the dispersed microfibrils via hydrogen bonds (Minor, 1994; Weise, 1998). On the contrary, initial rheological properties and ultrastructure (Fig. 3) were recovered after both ultrasound dispersion and mechanical treatment of the defrosted suspensions, showing that freezing the microfibrils in aqueous medium prevents from strong aggregation. This appears to be more efficient than freeze-drying for the storage of cellulose suspensions.

3.4.2. Viscoelastic properties at 20 °C as a function of concentration

Similar mechanical spectra as in Fig. 4 have been obtained for defrosted cellulose aqueous suspensions at concentrations ranging from 0.25 to 3 w/w% (results not shown). The storage moduli, G' , and the loss moduli, G'' , increased with the concentration. The storage modulus at 0.1 rad s⁻¹ varied from ~8 to >4000 Pa when the concentration increased from 0.25 to 3 w/w%. The loss tangent value ($\tan \delta$), (G''/G') ratio, was of the order of 0.1 for all the concentrations investigated. This means that, whatever the concentration (0.25–3 w/w%), the medium is structured in the same way, leading to gel-like structure.

Interestingly, the values of the moduli, G' and G'' , are relatively high in comparison to those obtained for microcrystalline cellulose hydrogels (for example, G' of around 1 and 10 Pa, respectively, at concentrations of 1% and 2% w/w) (Rudraraju & Wyandt, 2005). Similarly, 1 w/w% of the present suspensions leads to $G' > 10^2$ Pa as obtained earlier for fresh sugar beet MFC suspensions (Lowys et al., 2001). These pronounced viscoelastic properties can be related to the morphology of microfibrils, which are very long, as seen in TEM observations, leading to a rigid entangled fiber network. The negative charge carried by the microfibrils, due to residual galacturonic acid, allows the fibers to electrostatically repulse each other, increasing the organization and the stability of the system.

In Fig. 5, the storage modulus G' at 6.28 rad s⁻¹ is plotted as a function of cellulose fiber concentration. The present results are compared to the ones reported by Pääkkö et al. (2007). In the present case, the storage modulus at 6.28 rad s⁻¹ increased from 9 to >5000 Pa upon increasing the concentration from 0.25 to 3 w/w%. The relation between G' and cellulose concentration (C) can be expressed as a simple power equation: $G' = 235.5C^{2.58}$.

As can be seen in Fig. 5, there is no major difference between the present experimental data and the ones reported by Pääkkö

et al. (2007) even if the power-law they obtained for fresh soft-wood MFC suspensions at concentrations ranging from 0.5 to 5.9 w/w% was about 3. In contrast, Tatsumi et al. (2002) reported much lower values for MFC suspensions from purified wood pulp. The G' values at 0.01 rad s⁻¹ for 0.3 w/w% was ~0.3 Pa and ~55 Pa at 3 w/w%. However, the exponent value was of 2.25 that is slightly lower than the one from our experiments. Surprisingly enough, the exponent value of 2.25 is close to that theoretically required for polymer gels (de Gennes, 1979). However, as cellulose is not an aqueous soluble polymer, polymer gel theory is questionable for this type of system.

From the experimental data reported by Pääkkö et al. (2007) and Hill (2008) attempted to describe the concentration dependence of G' on a theoretical basis starting from the fact that a change in slope was experienced as the concentration increased. Then, the exponent value from microfibrillar cellulose gels appears to depend essentially on the fiber mass fraction. In addition, Tatsumi et al. (2002) showed that in the relation $G' = kC^\alpha$, the exponent value remains constant over a wide range of fiber length and diameters, in the contrary of the k factor, which changes according to the types of fibers. The authors conclude that the parameters k and α , reflect, respectively, the individual fiber characteristics and the structural property of the whole suspension. From these observations, we may state that the exponent value of 2.58 obtained in the present aqueous MFC suspension reflect the rigid network structure of the system.

3.4.3. Influence of temperature on the rheological properties

Temperature sweep experiments were performed in order to evaluate the temperature dependence of defrosted cellulose suspensions after redispersion. G' and G'' variations under heating and cooling processes were measured for cellulose suspensions at various concentrations from 0.25 to 3 w/w%. From 20 to 50 °C, the moduli showed no dependence on temperature, and they decreased very slightly with further increase of temperature from 50 to 80 °C, the G''/G' ratio remaining constant (results not shown). By cooling the suspensions from 80 to 20 °C, a total recovery of the properties was evidenced indicating the entire thermo-reversibility of the suspensions. This was confirmed by the superimposition of mechanical spectra obtained at 20 °C for all cellulose concentrations before and after the temperature sweep experiments (results not shown), showing that a temperature treatment does not affect the organization of the defrosted sugar beet MFC suspensions. This very slight dependence of G' and G'' upon temperature has also been reported in the case of wood fresh cellulose suspensions, in the range 20–80 °C (Pääkkö et al., 2007). The same behaviour was observed on sugar-beet pulps fresh cellulose suspensions, between 25 and 60 °C (Lowys et al., 2001). The known stability of the viscoelastic properties of fresh cellulose suspensions with temperature appears then to be not affected by using freezing as a method of conservation.

3.4.4. Flow behaviour at 20 °C

For all the investigated concentrations, an hysteresis loop was seen, the up curve being above the down curve between 0 and 100 s⁻¹ (results not shown). This fact means that the aqueous cellulose suspension display a thixotropic flow behaviour. Moreover, it appeared that the thixotropic character was more pronounced when cellulose concentrations increased.

The second cycle showed that the up and down curves were superimposed, showing that the structure has been partially disturbed by shearing, leading to an equilibrium state.

The equilibrium flow curves, $\eta_a(\dot{\gamma})$ and $\tau(\dot{\gamma})$, in logarithmic scales, of defrosted cellulose suspensions at various concentrations from 0.25 to 3 w/w% are shown in Fig. 6. All suspensions exhibited a shear-thinning behaviour with a large decrease of apparent

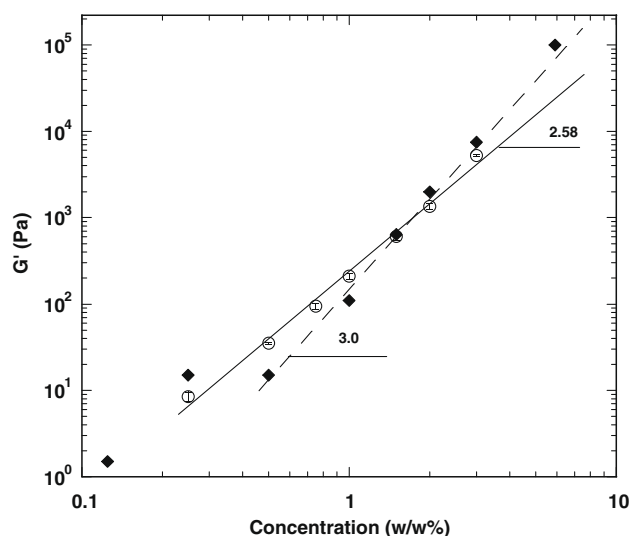


Fig. 5. Storage modulus G' as a function of concentration at 20 °C and at an angular frequency of 6.28 rad s⁻¹: present data (○); data (◆) reported by Pääkkö et al. (2007).

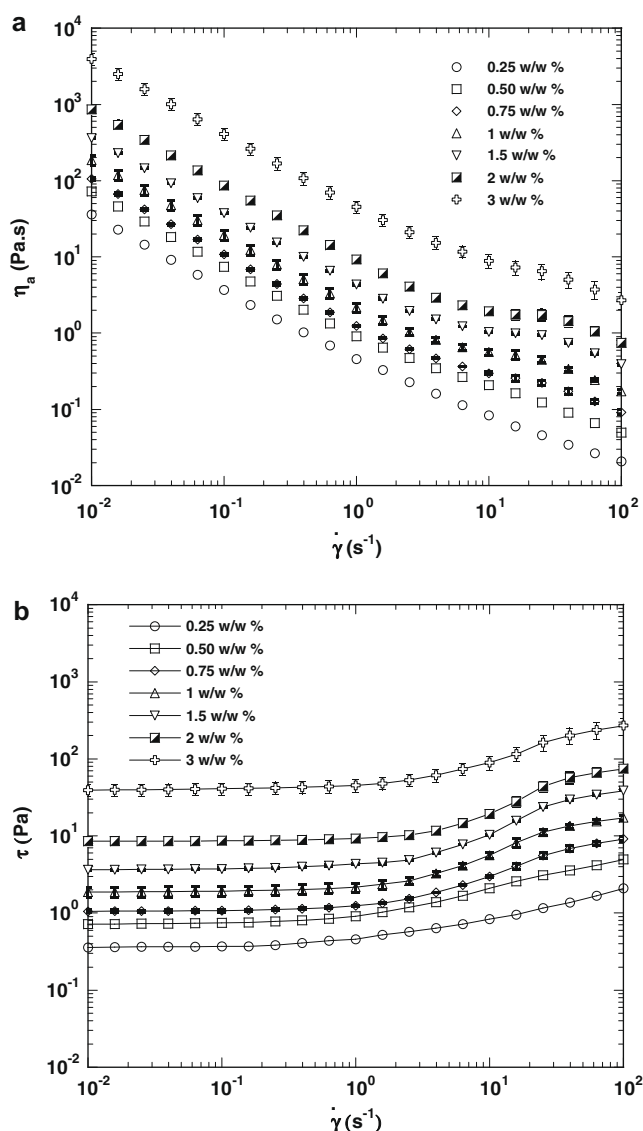


Fig. 6. Flow curves of cellulose suspensions at different concentrations. (a) apparent viscosity as a function of shear rate; (b) shear stress as a function of shear rate. Measurement temperature: 20 °C.

viscosity with increasing shear rate (Fig. 6a). For concentrations higher than 0.50 w/w%, the suspensions showed a noticeable plateau region between 15 and 40 s^{-1} which coincided with an inflection point clearly evidenced in the $\tau(\dot{\gamma})$ curve (Fig. 6b). The apparent viscosity increased as the cellulose concentration increased as did the storage modulus as described above. It is noteworthy that the apparent viscosity was much higher than for cellulose whiskers. For example, it was of ~ 4000 Pa s, at a shear rate of $10^{-2} s^{-1}$ at 3 w/w% for the present MFC suspensions to be compared to 100 Pa s for cellulose whiskers (Bercea & Navard, 2000).

From Fig. 6b, it is clear that MFC suspensions displayed a yield stress indicating that below this value there is no real macroscopic flow into the system. The yield stress increased from ~ 0.4 Pa for the most diluted suspension (0.25 w/w%) to ~ 40 Pa for the most concentrated one (3 w/w%). This varied as $C^{1.81}$, this exponent being quite close to the one obtained by Tatsumi et al. (2002), who showed that the yield stress varied as C^2 for fresh various type of cellulose suspensions.

In addition, the noticeable plateau region observed in the flow curves has been noticed earlier in the flow curves of pulp fiber sus-

pensions (Chen, Tatsumi, & Matsumoto, 2002). The authors suggested that some structures consisting of individual fibers were formed inside the suspensions within this range of shear rate and that the suspensions did not uniformly flow. The phenomenon we observed may explain our own observations.

Moreover, the fact that the suspensions exhibit a yield stress in flow can be related to the solid-like character of the suspension.

3.5. Influence of the addition of salt (NaCl or $CaCl_2$) and pH

Fig. 7 shows the viscoelastic behaviour ($G'(\omega)$ and $G''(\omega)$) for defrosted cellulose suspensions at a concentration of 0.50 w/w% in 0.05 and 0.1M NaCl (Fig. 7a) and $CaCl_2$ (Fig. 7b). G' and G'' increased when NaCl concentration increased from 0 to 0.1M (Fig. 7a). In absence of added salt, the storage modulus was about 30 Pa at 0.1 $rad s^{-1}$, whereas in 0.05 and 0.1M NaCl, it increased to 55 and 67 Pa, respectively. In $CaCl_2$, the increase was larger (82 Pa) in 0.05M $CaCl_2$ but no further change was observed by increasing

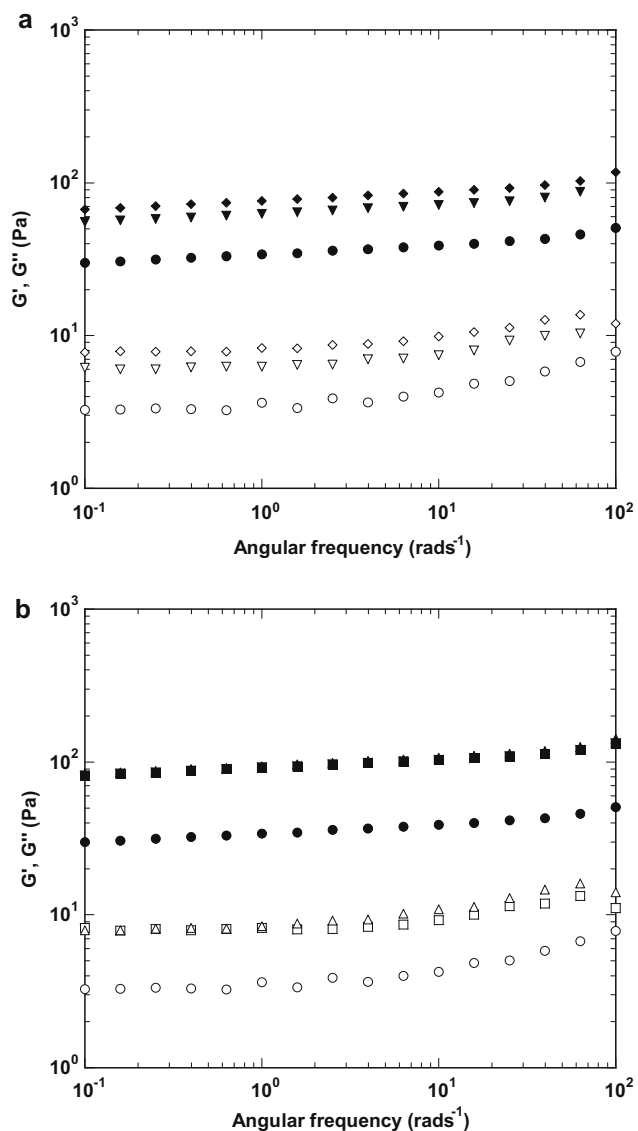


Fig. 7. Storage and loss moduli as a function of angular frequency for 0.50 w/w% of cellulose suspensions at various concentrations of salts. In deionised water (\bullet , \circ); (a) NaCl: 0.05 M (\blacktriangledown , \triangle); 0.1M (\blacklozenge , \lozenge); (b) $CaCl_2$: 0.05 M (\blacksquare , \square); 0.1M (\blacktriangle , \triangle). Measurement temperature: 20 °C; strain amplitude, 0.7%. G' , filled symbols; G'' , empty symbols.

the concentration at 0.1M (84 Pa) (Fig. 7b). Similar phenomena have been observed in the case of NaCl at different concentrations for fresh cellulose suspension (Lowys et al., 2001; Tatsumi et al., 1999). The reinforcement of the viscoelastic properties by increasing the ionic strength can be related to a screening of the electrostatic repulsions between the microfibrils, due to the presence of uronic acid groups, enhancing the fiber–fiber interactions. The higher moduli obtained in presence of calcium can be explained by the higher valency of Ca^{2+} ions, leading to a better screening of the charge. Even if the possibility of calcium chelating between two uronic groups of different chains can not be ruled out, it has to be noticed that the shapes of the mechanical spectra in NaCl and CaCl_2 are identical, evidencing the same type of global organization of the MFC pseudo-gels as also indicated by the $\tan \delta$ value which is of the same order (0.1) whatever the salt used.

The effect of salts on the flow properties for a defrosted dispersion at 0.5 w/w% is illustrated in Figs. 8 and 9. It can be observed that the addition of NaCl increased the apparent viscosity as well

as the yield stress of the suspensions, this effect been slightly more pronounced at low shear rate values (Fig. 8a and b). In the presence of CaCl_2 , the same effect was observed with a slightly higher apparent viscosity and yield stress (Fig. 9a and b). The plateau and the inflection point, slightly visible at high shear rates in water, were not seen anymore when salt was added, meaning that electrostatic screening hindered the formation of particular structure under shear.

Regarding the effect of pH, the viscoelastic properties of 1 w/w% sugar beet MFC suspension were totally unaffected when varying the pH from 4.5 to 9, the three mechanical spectra been superimposed (results not shown). This is in contradiction with the results obtained by Pääkkö et al. (2007) who observed a decrease of the viscosity of a 0.25 w/w% suspension of cellulose when pH increased from 2 to 10. However, the concentration was lower and it is possible to think that addition of ions for pH setting influences more the behaviour of a diluted dispersion than in our experiments.

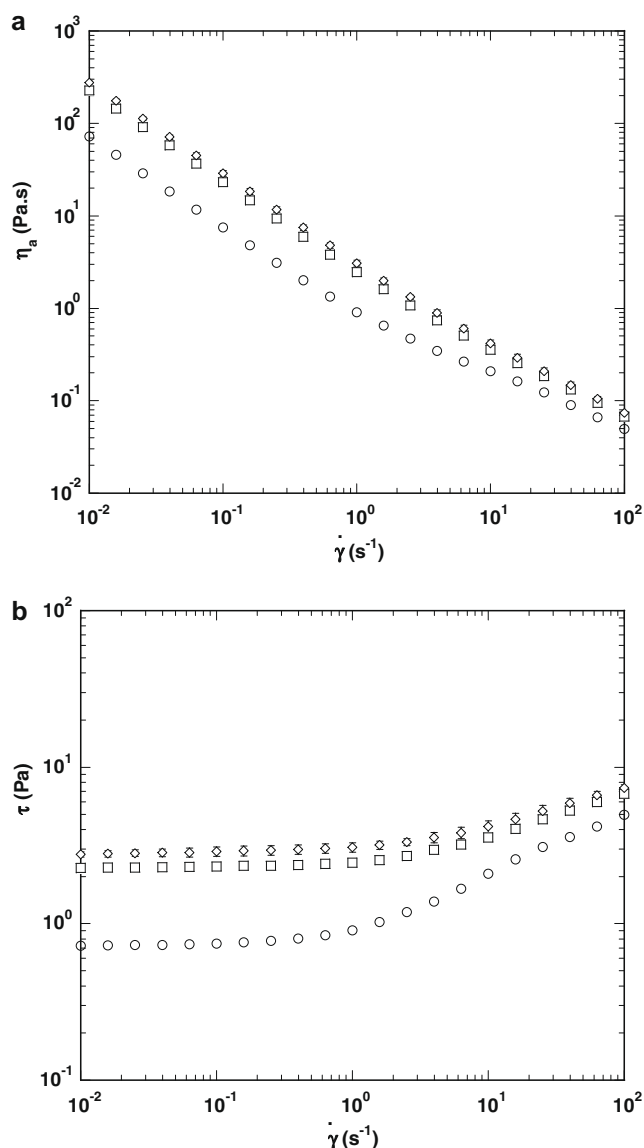


Fig. 8. Influence of NaCl on the flow behaviour of 0.50 w/w% cellulose suspensions at various concentrations of salts. (a) apparent viscosity as a function of shear rate; (b) shear stress as a function of shear rate. In deionised water without salt (○); 0.05 M (□); 0.1 M (◇). Measurement temperature: 20 °C.

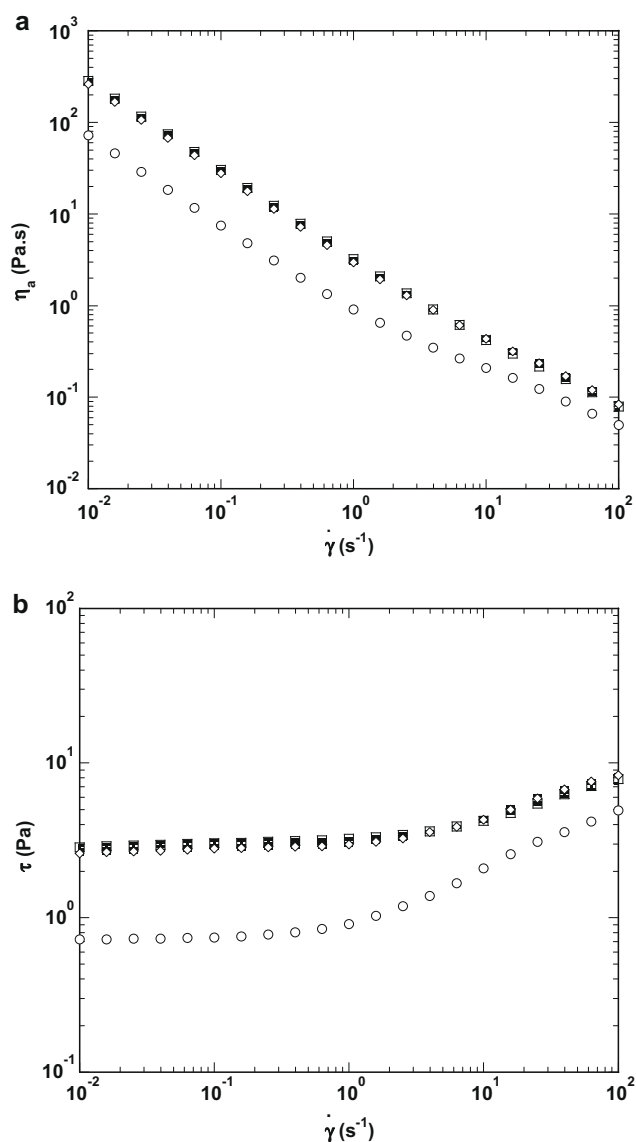


Fig. 9. Influence of CaCl_2 on the flow behaviour of 0.50 w/w% cellulose suspensions at various concentrations of salts. (a) apparent viscosity as a function of shear rate; (b) shear stress as a function of shear rate. In deionised water without salt (○); 0.05 M (□); 0.1 M (◇). Measurement temperature: 20 °C.

4. Conclusion

Cellulose suspensions from sugar-beet pulp display outstanding rheological properties with solid-like viscoelastic behaviour and a shear-thinning flow behaviour.

The known shear-thinning behaviour of fresh MFC suspensions (Dinand et al., 1996; Lowys et al., 2001; Pääkkö et al., 2007) observed for the aqueous frozen cellulose suspensions, means that they can be considered as a classical pseudoplastic material like cellulose whiskers (Azizi Samir et al., 2005; Bercea & Navard, 2000; Ebeling et al., 1999; Orts et al., 1998), or microcrystalline cellulose hydrogels (Mihiranyan et al., 2007; Rudraraju & Wyandt, 2005).

Freezing did not significantly affect the rheological properties of the suspensions. This appears to be an efficient way of its conservation although the product is not obtained in a dried state as most of the biopolymers. On the other hand, the mechanical treatment, consisting of sonication and passing several times through a Rannie two-stages homogenizer, did not affect cellulose crystallinity. It was also found that an increase in the ionic strength or in cellulose concentration reinforce the viscoelastic properties of MFC suspensions. Addition of ions reinforced the viscoelastic properties, while these properties were not affected neither by temperature treatment nor by pH.

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