



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 → 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 (Mihriyan, 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 polyacrylamide derivative have been added to cellulose suspensions before drying (Centola & Borruso, 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

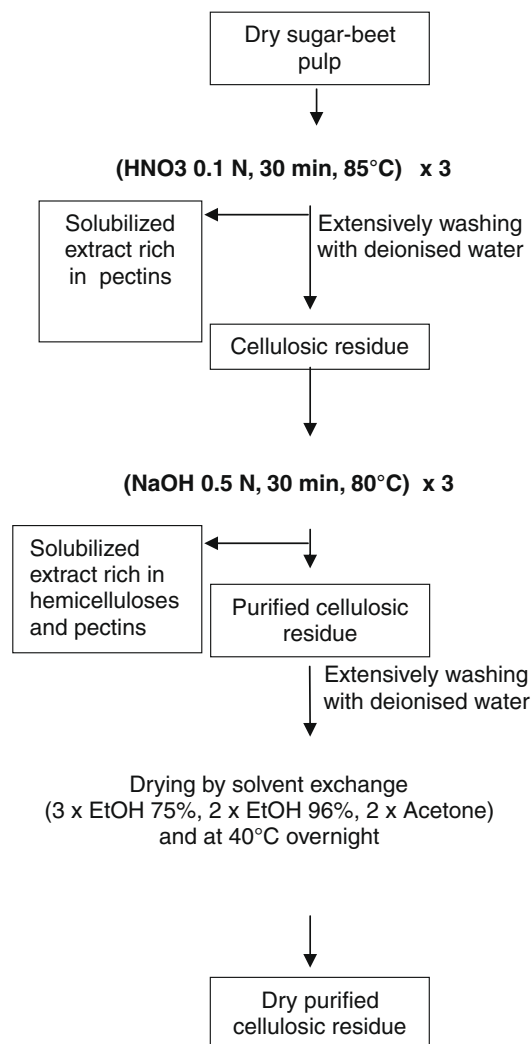


Fig. 1. Extraction process of cellulose residue from sugar-beet pulp.

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