



Dialdehyde cellulose microfibrils generated from wood pulp by milling-induced periodate oxidation

Juho Sirviö^a, Henrikki Liimatainen^b, Jouko Niinimäki^b, Osmo Hormi^{a,*}

^a Department of Chemistry, University of Oulu, P.O. Box 3000, FI-90014, Finland

^b Fibre and Particle Engineering Laboratory, University of Oulu, P.O. Box 4300, FI-90014, Finland

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ABSTRACT

An investigation was made into functionalized cellulose microfibrils produced from wood chemical pulp with a new method that combines both mechanical and chemical modifications. Dialdehyde cellulose (DAC) microfibrils were obtained by reactive milling, i.e. simultaneous cellulose pulp micronization with a wet stirred media mill and oxidation by sodium periodate. Milling significantly enhanced the pulp reactivity towards the periodate oxidation by reducing crystallinity and increasing the specific surface area of cellulose. DAC microfibrils with a high aspect ratio and aldehyde content of 0.26 mmol/g were obtained already after the first 15 min of milling. This new way to simultaneously modify cellulose material mechanically and chemically offers an effective route to produce highly functionalized cellulose microfibrils within short reaction times and with mild conditions. High temperature and use of metal salt as cellulose activator further enhanced the efficiency of oxidation during milling.

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1. Introduction

Cellulose is one of the most potential raw material to replace current oil-based and non-renewable products and for developing novel biomass-based materials. In particular, cellulose micro- and nanofibers, which cover a variety of particles from microfibrils and microfibrils to nano-sized whiskers, are considered to be amongst the most promising materials for this purpose (Pääkkö et al., 2007). The main efforts regarding these minuscule cellulose materials have focused on the generation of particles having optimized strength properties for use as reinforcing agents of composites (Alemdar & Sain, 2008; Deepa et al., 2011) and films (Spence, Venditti, Habibi, Rojas, & Pawlek, 2010), but also other novel and promising applications have been presented including papermaking additives, thickening agents for food and cosmetic products, and various medical applications (Dinand, Chanzy, & Vignon, 1999; Klemm et al., 2006; Turbak, Snyder, & Sandberg, 1983).

The feasibility of these cellulose particles for various applications can be further improved by various chemical derivatizations such as esterification (Berlioz, Molina-Boisseau, Nishiyama, & Heux, 2009) and silylation resulting in functionalized micro- and nanofibers (Andresen, Johansson, Tanem, & Stenius, 2006). In addition, oxidation offers one effective route to modify cellulose chemically. Many oxidants are capable of oxidizing cellulose, such as nitrogen oxides, but the most of them possess a lack of selectivity

(Kaverzneva, Ivanov, Salova, & Kisev, 1955; Kaverzneva & Salova, 1959). Amongst the few specific oxidation agents are 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) (da Silve Perez, Montanari, & Vignon, 2003) and periodic acid and its salts which show high selectivity towards specific hydroxyl groups of cellulose. Furthermore, these oxidation treatments have also been found to promote the disintegration of cellulose fibers into its constituent particles, i.e. microfibrils (Saito, Nishiyama, Putaux, Vignon, & Isogai, 2006).

Periodate is able to oxidize vicinal hydroxyl groups of cellulose at positions 2 and 3 to aldehyde groups, simultaneously breaking the corresponding carbon–carbon bond of the glucopyranose ring in order to obtain 2,3-dialdehyde cellulose (DAC). The aldehyde groups of DAC in turn have high reactivity towards further modification such as Schiff base reaction (Wu & Kuga, 2006), cationization (Van Brussel-Verraest, Besemer, Thiewes, & Verwilligen, 2003) and further oxidation to 2,3-dicarboxylic acid cellulose (DCC) (Kim & Kuga, 2001). Both DAC and its derivatives possess a great potential in high-end applications such as medical materials (Weber et al., 2010) and biodegradable composites (Hou, Liu, Liu, Duan, & Bai, 2008).

The low reactivity of cellulose is one of the key-problems in periodate oxidation reaction (Kim, Kuga, Wada, Okano, & Kondo, 2000). Cellulose has a high-ordered intra- and inter-molecular hydrogen bond network. Due to this dense hydrogen bonding, the availability of reactive free hydroxyl groups is restricted, which also results in poor solubility of the native cellulose. In addition, the hydrogen bond network causes the cellulose to adopt a highly crystalline structure, which further reduces cellulose solubility and reactivity. Thus, efficient methods to loosen the rigid hydrogen bonded

* Corresponding author. Tel.: +358 8 553 1631; fax: +358 8 553 1593.
E-mail address: osmo.hormi@oulu.fi (O. Hormi).

cellulose network and reduction of high crystallinity are required to promote the periodate reaction. However, there is a scarcity of publications that deals with this topic.

We have earlier shown that both chemical and mechanical activations can be used to increase the reactivity of cellulose pulp fibers in the periodate oxidation reaction. The use of metal salts and high temperature (>55 °C) during the oxidation reaction was found to result in increased aldehyde contents (Sirviö, Hyvakkö, Liimatainen, Niinimäki, & Hormi, 2011). This allows use of moderately low amount of toxic oxidant, which leads to more environmentally friendly production of DAC. Furthermore, our preliminary study suggested that simultaneous oxidation and micronization of cellulose may result in DAC particles with higher aldehyde content than the corresponding non-milled oxidations (Liimatainen, Sirviö, Haapala, Hormi, & Niinimäki, 2011). The aim of the current study was to investigate in detail simultaneous cellulose pulp fiber periodate oxidation and milling in DAC microfibrer generation. The focus here was on the analyses of the chemical conditions of oxidation and characterization of produced DAC microfibrers.

2. Experimental

2.1. Materials

Bleached birch (*Betula verrucosa*) commercial chemical wood pulp obtained in dry sheets was used as a cellulose raw material in milling-induced oxidation after disintegration in deionized water. The cellulose, xylan and glucomannan contents of the pulp were 74.8%, 23.6% and 1.1%, respectively, as determined by high performance anion exchange chromatography (HPAEC-PAD), according to a similar procedure as presented by Zuluaga et al. (2009). Lignin (TAPPI-T Method 222 om-02) and the extractive contents (SCAN-CM 49:03 standard) of the pulp were 0.4% and 0.08%. The Canadian Standard Freeness (CSF) and Schopper-Riegler (SR) values of the pulp, which reflect the water removal efficiency of the pulp, were 493 ml and 15.5, respectively, as measured according to TAPPI Method 227 om-99 and the EN ISO 5267-1:2000 standard. The average (length-weighted) length and width of the pulp fibers, as determined with a Metso FiberLab image analyzer, were 0.90 mm and 19.0 μm, respectively. The fines content given by the L&W STFI Fibermaster analyzer, was 3.4% and the zeta potential measured with a Müttek SZP-06 device in deionized water was −125 mV.

All the chemicals used for oxidation (NaIO₄, LiCl and CaCl₂) and product analysis (NH₂OH·HCl, CH₃COOH and CH₃COONa·2H₂O) were obtained as p.a. grade chemicals from Sigma–Aldrich and used without further purification. An acetate buffer solution used in the aldehyde content analysis (an oxime reaction) was made by charging a 2.0 dm³ volumetric flask with 27.4 g of sodium acetate trihydrate and adding 15 ml of a glacial acetic acid to the flask and diluting the resulting mixture to 2.0 dm³ with deionized water. Deionized water was used throughout the work.

2.2. Milling-induced periodate oxidation of wood pulp to dialdehyde cellulose microfibrers

Reactive milling, i.e. simultaneous oxidation and micronization of wood pulp fibers, was conducted with a horizontal agitated laboratory pearl mill (Hosokawa Alpine AHM 90). The mill consisted of a polyurethane-covered milling chamber (1.1 dm³) that was filled with ceramic grinding pearls and equipped with a water cooling jacket, a stirrer with six perforated discs and a slotted screen allowing the milled sample to pass through while retaining the pearls in the chamber. A schematic illustration of the operational principle of the mill can be found in Kwade (1999). The experiments were con-

ducted in batch mode by milling 4 g of oven-dry disintegrated pulp at a constant stirrer speed of 2000 rpm at room temperature (20 °C) using yttrium oxide (Y₂O₃), stabilized zirconia (ZrO₂) pearls with a diameter of 0.4–0.6 mm and filling volumes of 0.70 dm³. The oxidation agent (NaIO₄, 3.83 mmol/g of pulp) was dosed directly into the milling chamber at the beginning of each experiment. After milling the samples were centrifuged and washed with deionized water to remove any oxidation agents from the sample. As references, samples milled in similar conditions, but without oxidation, were also prepared.

Metal salt (LiCl and CaCl₂ used as activators) assisted reactive millings of cellulose were performed in the same manner as NaIO₄ experiments, but adding a desired amount of salt with NaIO₄ to the milling chamber at the beginning of experiment. Metal salt/AGU molar ratio of 7 was used.

Reference periodate oxidations were performed in a beaker (non-milled conditions) in a similar way as reported previously (Sirviö et al., 2011).

2.3. Determination of the dialdehyde content of the oxidized samples

The dialdehyde content of the oxidized celluloses was determined by an oxime reaction (Hou et al., 2008; Kim, Wada, & Kuga, 2004). The aldehyde groups of the sample (dry weight 0.1 g) were converted to oximes at pH 4.5 (0.1 M acetate buffer) at room temperature using hydroxylamine hydrochloride (1.39 g) after which the nitrogen content of the freeze-dried sample was measured with an elemental analyzer (PerkinElmer CHNS/O 2400 Series II). The amount of aldehyde groups was obtained directly from the measured nitrogen content.

2.4. Field emission scanning electron microscopy (FESEM)

FESEM (Zeiss ULTRA plus) images were taken from the freeze-dried and sputter coated (Pd) sample drops placed on a glass microscope slide. The accelerating voltage during imaging was 5 kV.

2.5. Particle size measurement

The average particle sizes of the dialdehyde microfibrers were determined with a laser diffractometer (Beckman Coulter LS 13 320) using a measuring range of 0.04–2000 μm. A surfactant (Sokolan CP 5, BASF) and ultrasonification (Fritsch Laborette 17) were used to disperse the particles before the measurement.

2.6. BET specific surface area measurement

The specific surface areas were measured using the Brunauer–Emmett–Teller (BET) method based on N₂ adsorption. The determinations were carried out from freeze-dried samples with a Micromeritics ASAP 2020 analyzer.

2.7. Degree of polymerization (DP) measurement

The average degree of polymerization (DP) of cellulose in the milled samples (without oxidation) was evaluated from the limiting viscosity, measured in cupriethylenediamine (CED) solution according to the ISO 5351 standard. The limiting viscosity values were converted to DP using Eq. (1) by da Silva Perez and van Heiningen (2002).

$$DP = \left(\frac{(1.65[\eta] - 116H)}{C} \right)^{1.111} \quad (1)$$

where $[\eta]$ is the limiting viscosity, C is the mass fraction of cellulose and H is the mass fraction of hemicelluloses. This calculation makes

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