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

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ABSTRACT

An investigation was made into functionalized cellulose microfibers produced from wood chemical pulp with a new method that combines both mechanical and chemical modifications. Dialdehyde cellulose (DAC) microfibers 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 microfibers 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 microfibers 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.

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 microfibers 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, & Verwillingen, 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 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

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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 (Sirvio, Hyvakko, Liimatainen, Niinimaki, & 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 microfiber generation. The focus here was on the analyses of the chemical conditions of oxidation and characterization of produced DAC microfibers.

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 Mütek SZP-06 device in deionized water was −125 mV.

All the chemicals used for oxidation ($NaIO_4$, LiCl and $CaCl_2$) and product analysis ($NH_2OH{\cdot}HCl$, CH_3COOH and $CH_3COONa{\cdot}2H_2O$) 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 dm^3 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 dm^3 with deionized water. Deionized water was used throughout the work.

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

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 dm^3) 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 conducted 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 (Y_2O_3), stabilized zirconia (ZrO_2) pearls with a diameter of 0.4–0.6 mm and filling volumes of 0.70 dm^3. The oxidation agent ($NaIO_4$, 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 $CaCl_2$ used as activators) assisted reactive millings of cellulose were performed in the same manner as $NaIO_4$ experiments, but adding a desired amount of salt with $NaIO_4$ 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 (Sirvio 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 microfibers 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 N_2 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 Silve Perez and van Heiningen (2002).

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

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

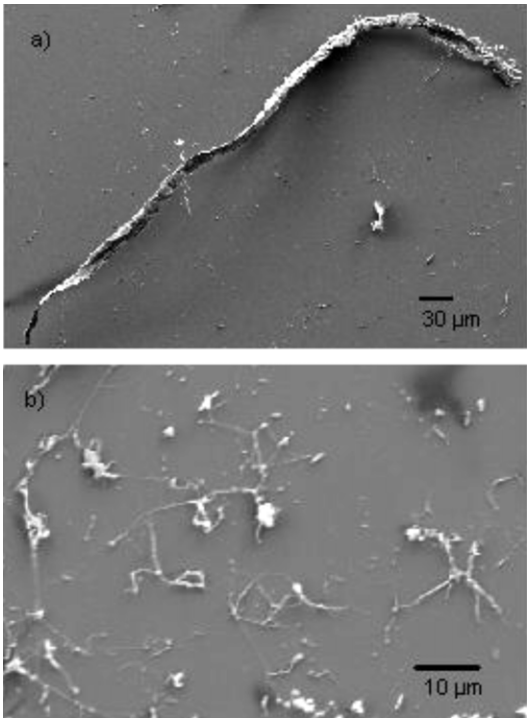

Fig. 1. FESEM micrographs of (a) original chemical wood pulp fiber, and (b) dialdehyde cellulose microfibers after 60 min of simultaneous milling and oxidation of pulp (oxidation agents: $NaIO_4 + CaCl_2$, 20 °C).

a correction for the contribution of hemicelluloses to the limiting viscosity number and DP of cellulose, assuming that the average DP of hemicelluloses is 140.

2.8. X-ray diffractometry

The crystallinity of the cellulose after oxidation and milling was analyzed by wide angle X-ray diffractometry (WAXD). Measurements were conducted with a Siemens D5000 diffractometer using Cu Kα radiation (λ = 0.1542 nm). Samples were prepared by pressing tablets with a thickness of 1 mm from freeze-dried microfibers. Scans were taken over a 2θ (Bragg angle) range from 5° to 50° at a scanning speed of 0.02°/s using a step time of 1 s. The degree of crystallinity in terms of the crystallinity index (CrI) was calculated from the peak intensity of the main crystalline plane (0 0 2) diffraction (I_{002}) of 2θ at 22.8° and the peak intensity of 2θ at 18.0° associated to the amorphous fraction of cellulose (I_{am}), according to Eq. (2) (Segal, Creely, Martin, & Conrad, 1959).

$$\mathrm{CrI} = \left(\frac{I_{0\,02} - I_{am}}{I_{002}}\right) \cdot 100\% \quad (2)$$

2.9. FTIR spectroscopy

FTIR spectra of the DAC and oxime derivate of DAC were recorded using a Bruker FTIR spectrometer. The sample of DAC was prepared by weighing out 2 mg of oven dried product from the suspension having pH of 6.5 and pressing it into a pellet with 200 mg of KBr. The sample of oxime derivate of DAC was prepared by weighing out 2 mg of product and pressing it into a pellet with 200 mg of KBr.

3. Results and discussion

3.1. Characteristics of dialdehyde cellulose microfibers

Simultaneous periodate oxidation and wet stirred media milling was used to convert the wood cellulose pulp to dialdehyde cellulose. Pulp fibers were subjected to a large number of stress events and high stress intensity during pearl milling by the stirring function of the grinding media, which collided randomly with the pulp material. The original hypothesis was that this mechanochemical modification of wood pulp would create new cellulose surfaces, a loose cellulose crystal structure and disintegrate the hierarchical structure of fibers resulting in increased reactivity of cellulose, which is hindered by the rigid hydrogen bond network of cellulose.

The morphology of samples obtained by milling-induced oxidation was studied using FESEM. Typical FESEM micrographs of the original pulp fiber and sample obtained by milling-induced oxidation are shown in Fig. 1. FESEM micrographs show that milling completely disintegrated the fiber structure and produced fibrillar particles with a length from 10 to 50 μm and diameters ranging from a few hundreds of nanometers to 1 μm depending on the conditions used. According to the definition given by Chakraborty, Sain, and Kortschot (2006), these cellulose fibrils can be treated as microfibers, having a diameter between 0.1 and 1 μm, and a minimum length of 5–50 μm. It was found that microfibers generated by milling-induced oxidation were thinner and they had more even size distribution than the microfibers milled without oxidation. FESEM images of microfibers generated with same method but without oxidation are shown in Liimatainen et al. (2011). This effect suggests that periodate oxidation promotes the micronization of fibers into its constituent particles.

The frayed surface structure of the DAC microfibers is probably related to the attachment of minuscule particles to the surfaces during sample pretreatment, use of dried cellulose pulp (Iwamoto, Abe, & Yano, 2008), and the disintegration mechanism of wet stirred media milling. In stirred media mills, comminution is based mainly

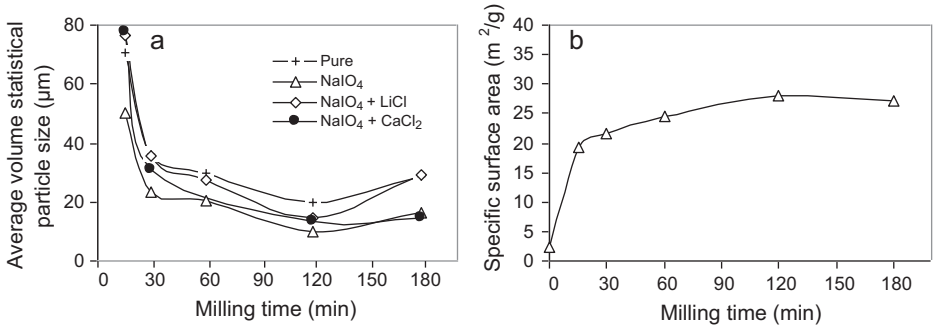

Fig. 2. (a) Average volume statistical particle sizes of milled cellulose (pure), and milled and oxidized dialdehyde cellulose samples ($NaIO_4$, $NaIO_4 + LiCl$ and $NaIO_4 + CaCl_2$) and (b) BET specific surface area of milled cellulose pulp (without oxidation, 20 °C).

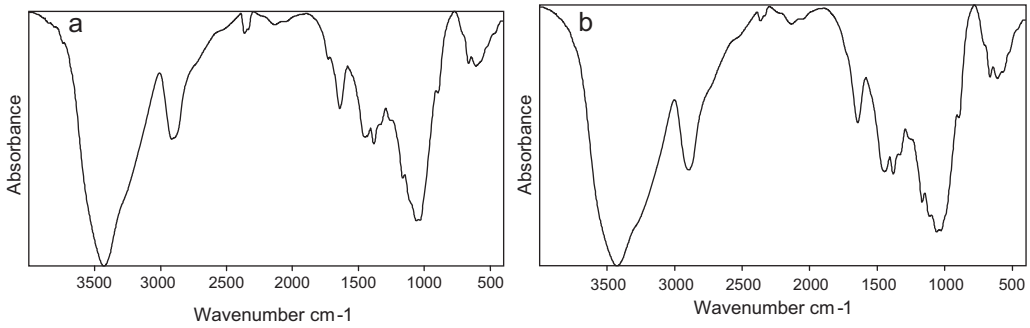

Fig. 3. FTIR spectra of (a) DAC (2 h oxidation with $NaIO_4$) after oven drying it from the suspension having pH of 6.5 and (b) oxime derivate of DAC.

on the continuous impact and attrition effects of grinding media that cause local stresses and can result in a frayed surface structure. For example, comminution in dry disintegration methods is in many cases caused by abrasion and the cutting effects of tangential forces, resulting in the tearing of smoother fibrillar particles from the matrix.

The average volume statistical particle sizes, in terms of the equivalent sphere diameter of microfibers measured by a laser diffractometer, are presented in Fig. 2a. The results show that microfibers possessing a size about 50–80 μm were already obtained from the original fibers (average fiber length 0.90 mm) after 15 min of milling. The size reduction progressed very rapidly during the first 30 min of milling after which the disintegration was slower. After 120 min of milling, the particle size started to increase, which is due to the aggregation of microfibers that was likely promoted by the hydrogen bonding between the free hydroxyl groups of cellulose surfaces formed during milling.

The particle size results as well as FESEM images clearly show that the periodate oxidation promoted micronization of pulp as the size of reference pulp that was milled without oxidants was larger than samples from the milling-induced oxidation. Previously Saito et al. (2006) reported that the oxidation of primary hydroxyls of cellulose to anionic carboxylates by TEMPO facilitated fibrillation of wood fibers to nanofibers due to increased repulsion between cellulose chains. Basically, periodate oxidation could also convert aldehydes partially to anionic carboxylate groups, which would then promote micronization of fibers. To study the presence of carboxylates, we measured IR-spectra from the oxidized sample (2 h oxidation with $NaIO_4$) after oven drying it from the suspension having pH of 6.5 (pK_a values of dicarboxycellulose are 3.7 and 4.8 (Kim & Kuga, 2001)). However, the spectrum showed typical characteristics of DAC without indication of anionic carboxylate peaks at 1600 cm^{-1} (Varma & Chavan, 1995) (Fig. 3). We measured spectrum also after converting aldehydes to corresponding oximes to avoid the overlapping of aldehyde and carboxylate signals, but the carboxylate peak at 1730 cm^{-1} (Varma & Chavan, 1995) was still lacking. In addition, polyelectrolyte titration using poly(dimethyldiallylammonium)chloride (polyDACMAC) as cationic polymer showed that periodate oxidation did not increase the charge of micronized samples. Actually, the charge of reference sample produced by milling without oxidation was significantly higher than that of corresponding oxidized sample (67 vs. 15 μeq/g). This was likely due to the dissolution of hemicelluloses by the oxidation, which was also supported by reduced yield of samples after milling-induced periodate. Thus, the promoting effect of periodate oxidation on fiber micronization was probably related to the weakening of hydrogen bonding network of cellulose due to the conversion of hydroxyl groups to aldehydes. Especially, the intermolecular hydrogen bonds between carbons 3 and 6 are lost when the hydroxyls are converted to aldehydes. This effect eases the fracture of fibers.

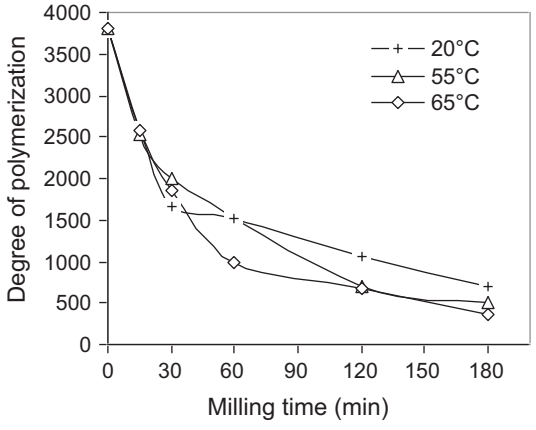

Fig. 4. Degree of polymerization of cellulose samples milled without oxidation at various temperatures.

Fig. 2b shows the specific surface area of microfibers (without oxidation) measured by the BET method. The surface area of original fibers increased substantially from the initial value of 2.2 m^2/g to 20–27 m^2/g depending on the conditions applied during micronization. These values are comparable with those reported earlier by Pääkkö et al. (2008) for cellulose nanofiber aerogels. It can be assumed that the surface area of oxidized microfibers was also close to these values since their particle sizes were in the same range.

The DPs of the cellulose were measured only from the microfibers that were generated without oxidation, because dialdehyde cellulose degrades in cupriethylenediamine (CED) solution used in the DP analysis (Calvini, Conio, Lorenzoni, & Pedemonte, 2004). Consequently, these values imply the influence of mechanical stress of milling on DP of cellulose. Besides this phenomenon, periodate probably breaks the cellulose chains to some extent despite its selectivity resulting in a further decrease in DP. The results show that the DP decreased asymptotically as a function of milling time, as shown in Fig. 4. The decrease in DP was moderately sharp during the first 30 min, since the original DP of about 3800 fell to 1600–2000, depending on the milling temperature.

The crystal structure of microfibers was evaluated by WAXD (Fig. 5). The X-ray diffractograms present typical peaks of cellulose I with a significant reduction in crystalline ordering caused by milling and periodate oxidation (Fig. 5a). The main 2θ diffractions were close to 14.5°, 16.0° and 22.8°, which are associated with crystalline planes of 1 0 1, 1 0 $\bar{1}$ and 0 0 2. The calculated crystalline indices (CrI) exhibited similar behavior to the particle sizes and surface areas, i.e. a rapid change was achieved during the first 30 min of milling, after which the decrease in CrI was slower. A clear effect of periodate oxidation on crystallinity reduction can be seen as the CrI of oxidized microfibers was notably smaller than with microfibers generated without oxidation. This is con-

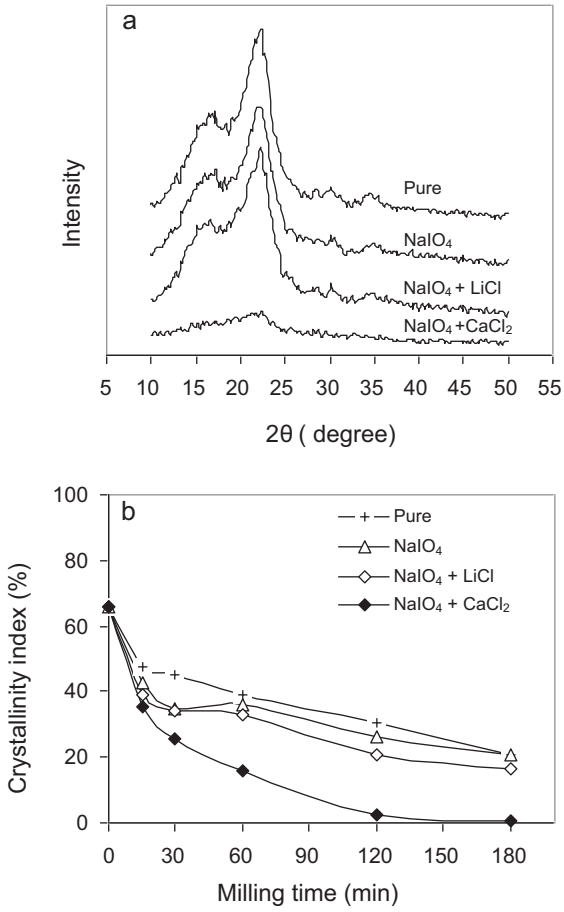

Fig. 5. WAXD analysis of samples: (a) diffractograms of milled (60 min) cellulose (pure) and dialdehyde cellulose microfibers after milling (60 min) and oxidation ($NaIO_4$, $NaIO_4$ + LiCl and $NaIO_4 + CaCl_2$) at 20 °C and (b) calculated crystallinity indices.

sistent with the previous results by Varma, Chavan, Rajmohanan, and Ganapathy (1997). Furthermore, $CaCl_2$ used as an activator in the oxidation seemed to dramatically promote the decrease in crystallinity. For example, after 120 min of milling practically all of the crystalline cellulose was removed. The reason for this phenomenon is unclear and should be clarified in more detail in future.

3.2. Aldehyde content of microfibers

Table 1 shows the dialdehyde content of cellulose after milling-induced oxidation and after oxidation in reference conditions (non-milled samples) at different temperatures and reaction times. The results clearly show that the milling increased the aldehyde content at room temperature (20 °C) significantly. For example, the aldehyde content was more than three times higher after 15 min in the milled oxidation compared to the corresponding non-milled oxidation. The maximum oxidation level obtained after 3 h was 7% of cellulose AGUs.

At higher temperatures, the aldehyde content was also significantly improved by milling-induced oxidation compared to corresponding non-milled oxidations, but not as dramatically as at room temperature. The improvements obtained by milling were in the range of 11–41%. Up to 15% cellulose AGUs were oxidized to corresponding dialdehyde units after 3 h at 55 °C.

With long reaction times (>0.5 h) at 65 °C, milling-induced oxidations resulted in a smaller content of aldehyde than the corresponding non-milled oxidations. This phenomenon is probably

Table 1
Aldehyde content of DAC produced by reactive milling oxidations and non-milled reference oxidations.

Temperature (°C)	Reaction time (h)	Aldehyde content (mmol/g)	
		Non-milled	Milled
RT	0.25	0.09	0.26
	0.5	0.11	0.43
	1	0.26	0.65
	3	0.43	0.88
55	0.25	0.36	0.51
	0.5	0.61	0.71
	1	0.95	1.16
	2	1.31	1.86
	3	1.68	1.90
65	0.25	0.43	0.80
	0.5	0.71	0.78
	1	1.26	1.05
	2	1.86	1.80
	3	2.20	1.87

due to the uneven distribution of heat along the milling chamber and the formation of temperature peaks inside the mill, which causes the periodate to decompose. This was also supported by the color change in the reaction solution. Decomposition lowers the reaction efficiency and may also lead to undesirable side reactions. The aggregation of micronized cellulose particles may also reduce the aldehyde content in long reaction times, as the free hydroxyl groups of the cellulose surface formed during milling are hydrogen-bonded, making them less available to the periodate.

One of the main reasons for the promoting effect of milling on cellulose reactivity is most likely the notable decrease in the crystallinity of cellulose during micronization, as seen in Fig. 5. Previous studies of Kim et al. (2000) show that crystallinity has a high impact on the accessibility of cellulose materials in the periodate oxidation reaction. In addition, milling efficiently decreases the average particle size and increases the specific surface area of the cellulose due to which the amount of free hydroxyl groups on cellulose surface is increased. This is supported by the fact that both the particle size (Fig. 2a) and surface area (Fig. 2b) changed rapidly during the first 30 min when the aldehyde content also showed the fastest increase compared to the corresponding non-milled oxidation. The decrease in DP can have further promoting effect on oxidation effectivity (El Meligy, El Rafei, & Abu-Zied, 2005).

Our previous studies have shown that metal salts, such as $CaCl_2$ and LiCl, can promote the cellulose oxidation reaction by disturbing the hydrogen bond network between cellulose molecules (Sirvio et al., 2011). Ca^{2+} and Li^+ ions are known to interact with cellulose hydroxyl groups (Brendler, Fischer, & Leipner, 2002; Fischer, Leipner, Thummler, Brendler, & Peters, 2003) which lead to partial break down of hydrogen bond network of cellulose. This results in better reactivity of cellulose.

Therefore, we also conducted milling-induced periodate oxidations using $CaCl_2$ and LiCl as activators. Table 2 shows the aldehyde content from the metal salt assisted periodate oxidations with and without milling. A significant promoting effect of metal salts on the aldehyde content was observed. Furthermore, milling-induced oxidation resulted in a clearly higher aldehyde content than non-milled reactions except when long reaction times (>2 h) and high temperatures were used. This is probably related to the decomposition of periodate by the metal salts at high temperatures, which we have reported previously. In general, the $CaCl_2$ assisted oxidation gives DAC with higher aldehyde content than corresponding LiCl assisted reactions. The maximum aldehyde content that was achieved in the milling-induced metal salt assisted reactions was about 16% of cellulose AGUs.

Table 2
Aldehyde content of DAC produced by milled and non-milled metal salt assisted oxidations.

Temperature (°C)	Reaction time (h)	Aldehyde content (mmol/g)			
		Non-milled with LiCl	Milled with LiCl	Non-milled with $CaCl_2$	Milled with $CaCl_2$
RT	0.25	0.12	0.42	0.21	0.58
	0.50	0.26	0.64	0.26	0.91
	1	0.36	0.83	0.36	1.24
	3	0.80	1.17	0.77	1.84
55	0.25	0.61	0.74	0.71	0.84
	0.5	0.81	1.06	0.99	1.38
	1	1.22	1.56	1.39	2.04
	2	1.59	1.73	1.64	2.09
	3	2.18	1.92	2.11	2.03
65	0.25	0.74	1.15	0.86	0.82
	0.5	0.98	1.37	1.30	1.61
	1	1.66	2.00	1.81	2.07
	2	2.28	1.44	2.66	1.64
	3	2.87	1.58	2.67	1.64

4. Conclusion

Highly functionalized DAC microfibers were effectively produced by wet stirred media reactive milling, i.e. simultaneous micronization and periodate oxidation of cellulose wood pulp in a pearl mill. Reactive milling notably improved pulp reactivity towards oxidation and resulted in dialdehyde microfibers with a high aspect ratio. The high reactivity of cellulose in the milling-induced oxidations was attributed to the accessibility of free hydroxyl groups due to reduction of cellulose crystallinity, decreases in DP, and the increase in specific surface area of cellulose pulp due to particle size reduction. High temperature and the use of metal salts can further promoted oxidation reaction.

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