Carbohydrate Polymers 83 (2011) 2005–2010

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Characterization of highly accessible cellulose microfibers generated by wet stirred media milling

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ARTICLE INFO

Article history:
Received 9 September 2010
Received in revised form 28 October 2010
Accepted 1 November 2010
Available online 9 November 2010

Keywords:
Cellulose microfiber
Dialdehyde cellulose
Microfibril
Pulp
Reactive milling

ABSTRACT

In this work, highly accessible cellulose microfibers produced from kraft wood pulp by a novel method based on a single mechanical treatment with a wet stirred media mill were characterized. The high mechanical stress of milling resulted in the complete disintegration of the fiber cell wall and produced cellulose microfibers with a length of below 50 μm and diameter ranging from a few hundred nanometers to 1 μm after only 5 min of milling. The noticeable increase in BET (Brunauer, Emmett, Teller-method) surface area from the initial value of 2.2 m^2/g to 25–60 m^2/g and decrease in crystallinity index from 65% to 20–30% during milling (5–60 min) indicated that microfibers possessed a highly accessible surface area and a large number of amorphous sites. This was also supported by the significantly increased reactivity of the microfibers compared to the reference pulp in the periodate oxidation reaction of cellulose to dialdehyde cellulose.

1. Introduction

The ongoing global trend to promote the production and usage of sustainable and biodegradable materials from natural resources as well as the saturation of traditional cellulose pulp markets in Western Europe and the USA have increased interest towards novel, high-value cellulose-based products. Cellulose micro- and nanofibers, which cover a variety of particles from microfibers and microfibrils to nano-sized whiskers, are considered to be amongst the new components with the highest potential for this purpose. The feasibility of these minuscule cellulose components with a high aspect ratio and surface area is based on their unique mechanical and chemical properties such as superior strength (Chakraborty, Sain, & Kortschot, 2006), low density (Bledzki, Reihmane, & Gassan, 1996), high viscosity (Herrick, Casebier, Hamilton, & Sandberg, 1983; Turbak, Snyder, & Sandberg, 1983), and water retention capacity (Herrick et al., 1983). Combining these properties gives them improved performance in high-end applications when compared with cellulose fibers and many synthetic fiber materials.

So far, the main efforts regarding cellulose micro- and nanofibers have focused on the generation of particles with a highly crystalline structure having optimized strength properties for use as reinforcing agents of composite materials (Siró and Plackett, 2010). In addition, other novel and promising applications have been presented for elongated micronized cellulose and its derivatives. With these a more open and less ordered cellulose structure can be beneficial as strength is not the most critical property, but so far they have gained less attention. They include papermaking additives, thickening agents for food and cosmetic products, and various medical applications (Dinand, Chanzy, & Vignon, 1999; Klemm et al., 2006; Turbak et al. 1983). It is possible that these cellulose particles could also be used to replace microcrystalline cellulose in some applications.

Most of the methods presented for the production of intact and highly crystalline cellulose particles involve several processing steps including chemical (Bhattacharya, Germinario, & Winter, 2008; Dufresne, Cavaille, & Vignon, 1997) or enzymatic treatments (Henriksson, Henriksson, Berglund, & Lindström, 2007; Pääkkö et al., 2007). Hence, they are rarely suitable for large-scale commercial production. Furthermore, maintaining the intact crystalline structure of cellulose is not reasonable in all minuscule cellulose products. Consequently, novel and more straightforward processing methods are required to enhance the economy and energy efficiency of the production of nano- and micron-sized cellulose particles with high accessibility. Promising developments may be spurred on by existing comminuting technologies when the paradigm of strong cellulose structures can be overlooked, as is the case for many applications outside composite structure engineering.

Wet stirred media mills, which are able to comminute materials into smaller sizes than most dry mills (Lowrison, 1974), are widely

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doi:10.1016/j.carbpol.2010.11.007

used for the fine and ultrafine grinding of mineral and ceramic materials. A large number of stress events and high stress intensity are achieved in stirred media mills by the stirring function of the grinding media (e.g. pearls), which collide randomly with the processed material. Since the exploitation of these high capacity mills in commercial production is well known, their use in cellulose micronization is also very attractive. The feasibility of using wet stirred media mills is further increased by the possibility of chemically modifying the cellulose material during the milling process. However, until now, the application of stirred media mills in cellulose disintegration has been limited mainly to dry mills or their use for other purposes than cellulose micronization.

The aim of this paper was to characterize micronized cellulose particles produced by a novel method based on laboratory-scale wet stirred pearl milling of kraft wood pulp. In addition, the chemical accessibility of the micronized cellulose was evaluated by regioselective oxidation of microparticles to dialdehyde cellulose (DAC) during milling. Laser diffractometry, BET (Brunauer, Emmett, Teller-method) surface area determination, specific volume measurement, and field emission scanning electron microscopy (FESEM) were used to measure the size and morphology of the micronized samples. The mechanochemistry of the milled particles, i.e. the chemical properties of mechanically stressed cellulose, was evaluated in terms of the average degree of polymerization (DP), crystallinity index (CrI), and total anionic charge.

2. Materials and methods

2.1. Materials

Bleached birch (*Betula verrucosa*) commercial chemical wood pulp obtained in dry sheets was used as a raw material in cellulose micronization after disintegration in deionized water. The cellulose, xylan and glukomannan 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.

Sodium (meta)periodate (Sigma–Aldrich, p.a. grade) was used as an oxidation agent for the regioselective oxidation of cellulose to 2,3-dialdehyde cellulose during milling to characterize the reactivity and chemical accessibility of the micronized samples.

2.2. Pulp micronization with a wet stirred media mill

A horizontal agitated laboratory pearl mill (Hosokawa Alpine AHM 90) was used for wet micronization of pulp. 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 pearl mill can be found in Kwade (1999). The experiments were conducted in batch mode by milling 5 g of oven-dry disintegrated pulp at a constant stirrer speed of 3500 rpm at room temperature (25 °C). 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 and 0.94 dm^3 were used.

The chemical accessibility and reactivity of the micronized cellulose were evaluated by oxidizing cellulose to 2,3-dialdehyde cellulose during milling. The oxidation agent (2.7 mmol/g of pulp) was dosed directly into the milling chamber at the beginning of each experiment. In this instance, the volume of pearls used was 0.70 dm^3. After milling the samples were centrifuged and washed with deionized water to remove any oxidation agents from the sample. Reference samples were prepared by oxidizing untreated fibers in a stirred beaker at 25 °C.

2.3. Analyses of micronized celluloses

The average particle size of the milled pulp samples was determined with a laser diffractometer (Beckman Coulter LS 13 320) using a measuring range of 0.04–2000 μm.

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.

Analytical centrifugation (LUMiFuge, L.U.M. GmbH, Germany) was used to measure the specific volumes of the samples. The centrifuge measures light transmission at 800 nm over the plastic sample cuvettes simultaneously as a function of time and position and automatically determines the position of the solid–liquid interface during separation. The specific volumes were determined at several centrifugal forces (23, 52, 71, 118 and 145 G at a consistency of 0.15%) and the corresponding value at normal gravity (1 G) was obtained from this data by extrapolation.

FESEM (Zeiss ULTRA plus) images were taken from freeze-dried and sputter coated (Pd) sample drops placed on a glass microscope slide. The accelerating voltage during imaging was 5 kV. As pretreatment for the FESEM and particle size measurements a surfactant (Sokolan CP 5, BASF) and ultrasonification (Fritsch Laborette 17) were used to disperse the particles.

The average degree of polymerization (DP) of cellulose in the untreated and milled samples 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).

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

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

The crystallinity of the cellulose was analyzed by wide angle X-ray diffractometry (WAXD). Measurements were conducted with a Siemens D5000 diffractometer using Cu Kα radiation ($\lambda = 0.1542$ nm). Samples were prepared by drying a thin film of suspension on a glass microscope slide. 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 ($I_{0\,0\,2}$) 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).

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

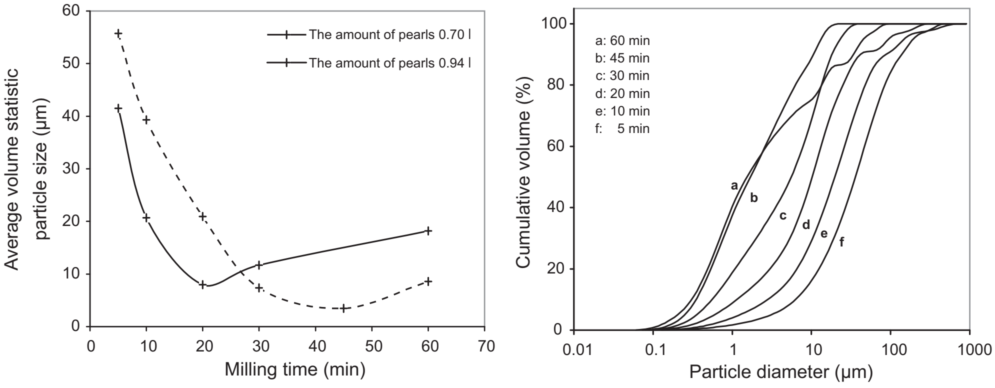

Fig. 1. Volumetric particle sizes of micronized cellulose: (a) mean values and (b) cumulative distributions (the amount of pearls used was 0.70 dm^3).

The total anionic charge of the samples was measured by the methylene blue adsorption method (Fardim et al., 2002) at pH 8.2. The method is based on the stoichiometric replacement of the counter ions of anionic groups by the cationic dye in a buffered media.

2.4. Determination of the dialdehyde content of the oxidized samples

The dialdehyde content of the oxidized celluloses was determined by an oxime reaction (Hou, Liu, Duan & Bai, 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 contents.

3. Results and discussion

3.1. Particle size of micronized cellulose

The mean and cumulative volume statistical particle sizes, in terms of the equivalent sphere diameter of micronized particles given by a laser diffractometer, are shown in Fig. 1. Micro-scale particles possessing a size of about 50 µm were already obtained from the original fibers (average fiber length 0.90 mm) after 5 min of milling. As shown in cumulative distributions, further milling increased the amount of sub-micron particles in particular. For instance, the amount of particles in this size range was about 50% after 45 min of milling. Consequently, the mean particle size decreased almost linearly as a function of milling time until a constant particle size of 5–15 µm was obtained after 30–45 min of milling. Presumably, this phenomenon of unchanging particle size after a certain milling time is due to the equilibrium between the competing processes of particle comminution and aggregation (Zhang, Liang, & Lu, 2007), which is promoted by the hydrogen bonding between the free hydroxyl groups of cellulose surfaces formed during milling. Therefore, dispersing agents which reduce particle aggregation could probably further decrease the particle size that can be achieved. The rate of particle size reduction was observed to be higher when the amount of pearls in the milling chamber was increased. This is likely to be associated with an increase in the collision frequency and the total number of stress events that occur.

3.2. Specific surface area and volume of micronized cellulose

The surface areas of the micronized samples and original pulp given by BET analysis are shown in Fig. 2. The surface area was observed to increase substantially from the original value of 2.2 m^2/g to 25–60 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. In fact, in our case, a similar method of aerogel preparation was used to dry the samples for BET analysis.

A novel method based on analytical centrifugation was used to measure the specific volumes of the micronized samples. Results with good repeatability were obtained by extrapolating specific volume values measured with various centrifugal forces to normal gravity. Specific volume decreased in a similar way to the mean particle size, showing a constant value after 20–45 min of milling (Fig. 3).

3.3. FESEM analysis of micronized cellulose

According to FESEM imaging, wet stirred media milling completely disintegrated the original fiber structure and produced micro-sized particles with a relatively high aspect ratio. Fig. 4 presents some typical images of the milled particles. It can be seen that milling resulted in a wide distribution of particles. The typical length of fibrillar particles, which were quite strongly entangled, was below 50 µm after only 5 min of milling, while the diameter ranged from a few hundreds of nanometers to 1 µm. As defined by Chakraborty et al. (2006), these fibrils can be treated as microfibers

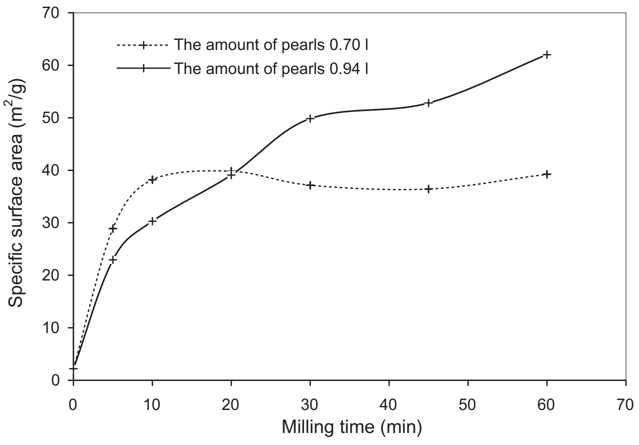

Fig. 2. Specific surface areas of micronized and untreated samples.

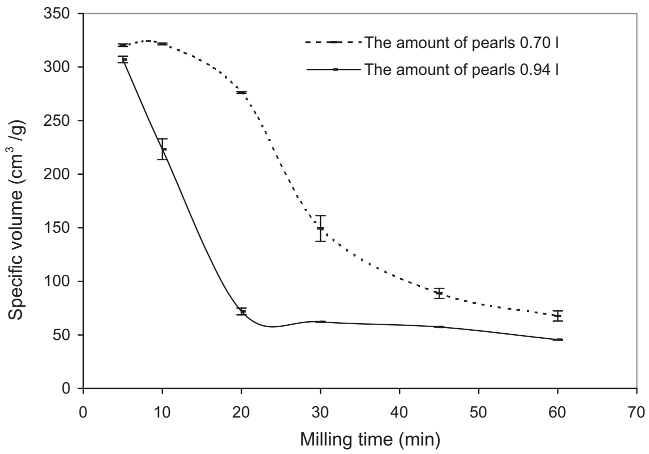

Fig. 3. Specific volumes of micronized samples.

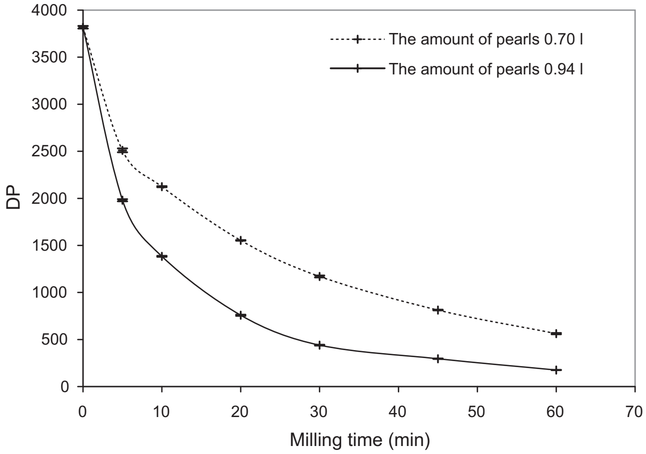

Fig. 5. Degree of polymerization of micronized and untreated pulp samples.

having a diameter between 0.1 and 1 μm and a minimum length of 5–50 μm. After 45 min of milling the aspect ratio of the particles decreased and the amount of sub-micron particles was significantly increased, as also seen in the cumulative particle size distributions (Fig. 1b). The particle length determined from the FESEM images was shown to be consistent with the values measured by laser diffractometry.

The microfibers produced by wet milling were found to have quite a frayed surface structure. This is probably related to the attachment of minuscule particles to the surfaces during sample pretreatment, use of dried pulp material and the disintegration mechanism of wet stirred media milling. In stirred media mills, comminution is based mainly 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.

3.4. Degree of polymerization, crystallinity index, and total anionic charge of the micronized cellulose

The influence of wet milling on the mechanochemistry of micronized particles was characterized in terms of the degree of polymerization, crystallinity index, and the total anionic charge of cellulose. Mechanical stress causes changes in both bond length and in the angles of hydrogen bonded rigid cellulose molecules while distorting the mutual packing of polymeric chains, which leads to a decrease in crystal ordering.

The DPs of the samples, calculated from the limiting viscosity values measured in cupriethylenediamine (CED) solution, decreased asymptotically as a function of milling time, as shown in Fig. 5. In contrast to the particle sizes, however, the equilibrium values of DP were not achieved within the milling time used. The decrease in DP was moderately sharp, since the original DP of about 3800 fell to a value of below 1000 after only 15 or 35 min of milling, depending on the amount of pearls used. Similar DP values were previously reported for kraft pulp microfibers generated by the combined treatment of intensive milling with a PFI refiner for 125,000 revolutions (about 85 min) and cryocrushing (Chakraborty et al., 2006).

The effect of wet milling on the crystal structure of cellulose measured by WAXD is shown in Fig. 6. The X-ray diffractograms present typical peaks of cellulose I with a significant reduction in crystalline ordering during milling (Fig. 6a). 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. No rearrangement of the cellulose structure into another crystalline form was observed, unlike ball milling, which has reportedly transformed cellulose I into cellulose II (Ago, Endo, & Hirotsu, 2004).

The crystallinity in terms of the crystalline index (CrI) decreased rapidly after 5 min of milling from its initial value of 65% to 20–30%, after which it remained almost constant at longer milling times. In previous investigations, a similar crystallinity level was achieved after 60 min of pan milling (Zhang, Liang, & Lu, 2007) and 330 min of ball milling (Quajai & Shanks, 2006) with pulp of similar initial crystallinity. This supports the assumption that wet stirred media milling can efficiently produce microfibers and particles with highly accessible amorphous sites.

The total charges of original fibers and milled samples measured by the methylene blue adsorption method from samples which were converted to sodium form are presented in Fig. 7. The anionic charge of the micronized samples decreased during milling, but a

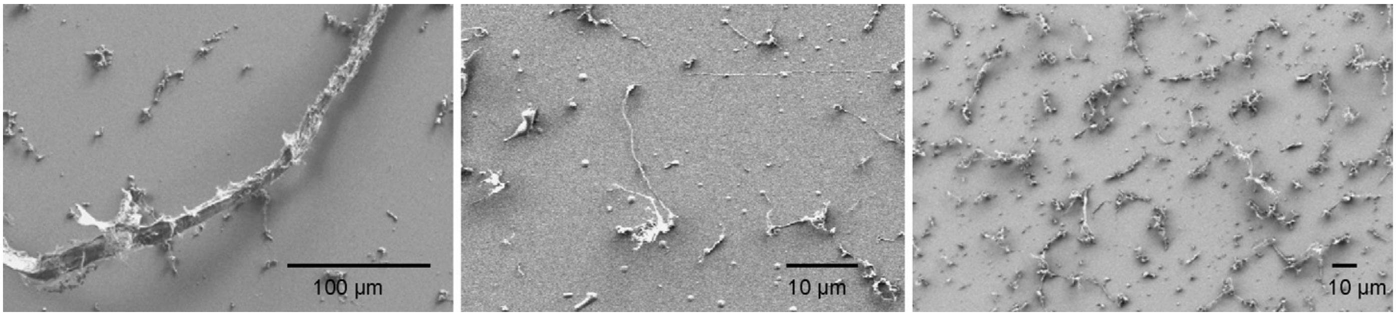

Fig. 4. FESEM images of the original pulp (left), pulp after 10 min of micronization (middle), and pulp after 45 min of micronization (right). The amount of pearls used in wet milling was $0.94\,dm^3$.

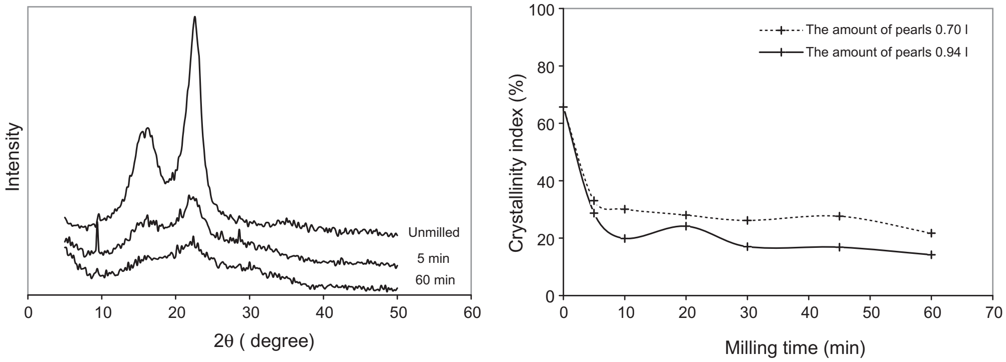

Fig. 6. WAXD analysis of samples: (a) diffractograms obtained prior and after micronization (the amount of pearls used was 0.70 l) and (b) calculated crystallinity indexes.

significantly higher decrease (from 80 to 30 μmol/g) was obtained when a higher pearl filling volume was used. This charge reduction during milling may be attributed to the dissolution of hemicelluloses, which contributes significantly to fiber anionicity. This was supported by the small mass losses observed after milling. It was also visually observed that samples were more aggregated when a larger amounts of pearl was used. This could be due to a reduction in the charge of these particles, i.e. a smaller repulsion between them.

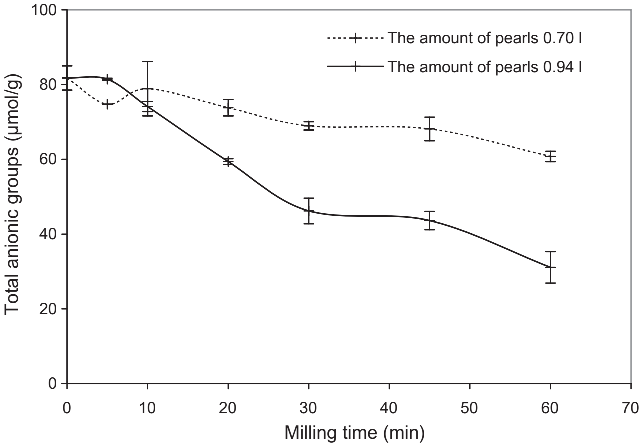

Fig. 7. Total anionic charge of micronized and untreated pulp samples.

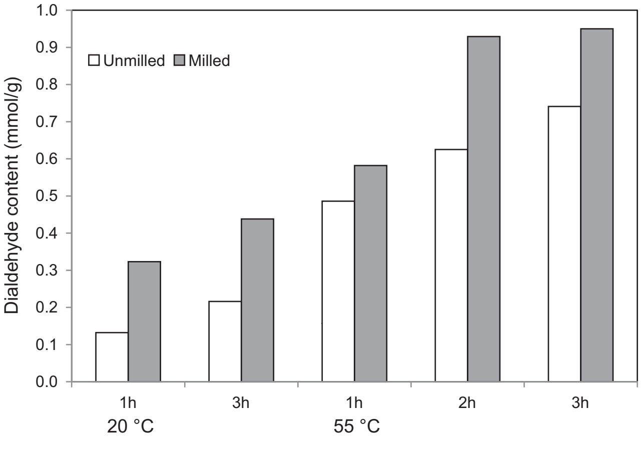

Fig. 8. Dialdehyde contents of micronized and untreated pulp samples.

3.5. *Reactivity of micronized cellulose in regioselective oxidation*

To evaluate the chemical accessibility and reactivity of the micronized celluloses samples, they were oxidized to 2,3-dialdehyde cellulose during milling. Fig. 8 shows the dialdehyde contents of the milled samples and original pulp. It was found that the micronized celluloses had a noticeably higher reactivity towards oxidation than the unmilled reference in all the conditions tested. This is probably due to the creation of a new reactive surface and the loosening of crystalline structure of cellulose during wet stirred media milling. Furthermore, the simultaneous micronization and chemical modification, i.e. reactive milling, provides a new route for producing minuscule cellulose derivatives.

4. Conclusions

Highly accessible cellulose microfibers were produced from kraft wood pulp by a novel method based on a single mechanical treatment with a wet stirred media mill. The method resulted in microfibers with a length of below 50 μm and a diameter ranging from a few hundreds of nanometers to 1 μm after just 5 min of milling. A substantial increase in BET specific surface area was measured from an initial value of 2.2 m^2/g to 25–60 m^2/g indicating a large accessible surface area of microfibers. Furthermore, the amount of reactive amorphous sites was increased according to the crystallinity index which decreased from 65% to 20–30%. This was supported by the significantly increased reactivity of microfibers compared to the reference pulp in the periodate oxidation reaction of cellulose to dialdehyde cellulose. The oxidation reaction conducted simultaneously with cellulose micronization, i.e. reactive milling, was also found to be a potential new route for producing minuscule cellulose derivatives.

Acknowledgements

This work was carried out in the Future Biorefinery Programme of Forestcluster Ltd. Ms. Katja Kilpimaa is gratefully acknowledged for her kind assistance in FESEM imaging while thanks also go to VTT Espoo for their pulp analysis.

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