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The effect of Fenton chemistry on the properties of microfibrillated cellulose

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Abstract A fully bleached birch kraft pulp was
treated with acidic hydrogen peroxide in the presence
of ferrous ions (Fenton's reagent) and thereafter treated
mechanically in a colloid mill to produce a product
containing microfibrillated cellulose (MFC). The pro-
duced MFC products were chemically and morpho-
logically characterized and compared with MFC
products produced without pretreatment as well as
with enzymatic hydrolysis. Fenton treatment resulted
in an increase in total charge and number of carbonyl
groups while the intrinsic viscosity decreased. The
Fenton treated pulps were easier to process mechan-
ically i.e. they reached a higher specific surface area at
a given mechanical treatment time and the MFC
produced had a stable water-fibre suspension for at
least 8 weeks compared to enzymatic pretreated pulps
and pulps not subjected to any pretreatment.

Keywords Microfibrillated cellulose · Fenton
chemistry · Enzymatic hydrolysis · Carbonyl
groups · Carbohydrate composition · Total and
surface charge · Suspension stability

Introduction

In the early 1980s, Turbak et al. (1983) subjected a
wood pulp suspension to high shear forces by making
multiple passes through a pressurized homogenizer.
The resulting product, a gel-like mixture consisting of
unaffected fibres, fibre fragments, fibrils and micro
fibrils was denoted microfibrillated cellulose (MFC).
The new product, derived from wood which is an
abundant and renewable raw material, suggested a wide
range of potential commercial uses, such as a rheology
modifier in foods and paints, for reinforcing compos-
ites, as a strength enhancer in paper and in barriers with
low permeability to gases, such as O_2 and CO_2 (Turbak
et al. 1983; Zimmermann et al. 2004; Henriksson et al.
2007; Eriksen et al. 2008; Syverud and Stenius 2009).

Despite major research efforts to develop commer-
cially viable processes, i.e. to overcome the major
drawbacks of high energy consumption (Klemm et al.
2011; Sandquist 2013), low efficiency and clogging of
the equipment (Klemm et al. 2011), MFC production is
still restricted to pilot plant scale. Products are
available from some companies and organizations:
for example, Borregaard (Norway), Daicel (Japan),
Rettenmeier (Germany) and Innventia (Sweden).

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Several of the processes are using enzymatic hydrolysis as a pretreatment in order to reduce energy consumption. The total capacity for pilot plants worldwide is estimated at 150 tonnes annually (Siqueira et al. 2010; Siro and Plackett 2010; Sandquist 2013).
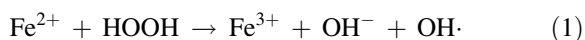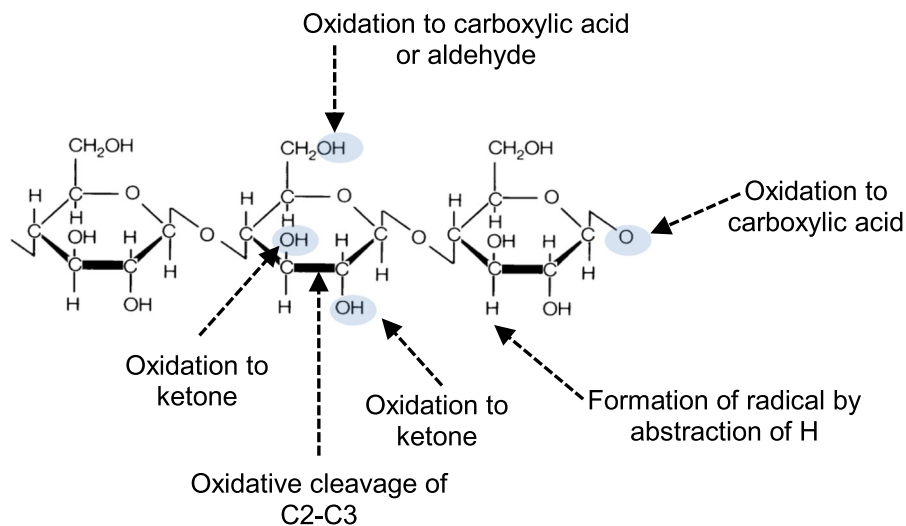
Cellulose is a linear polymer connected by 1→4-glucosidic linkage of β-D-glucose and is the main component in a variety of living species such as wood, annual plants and in some bacteria. In the cell walls, the cellulose chains form a network built from the smallest cellulosic structure, the so called elementary fibril. The elementary fibrils are packed into larger bundles forming agglomerates with various dimensions, stabilized by intermolecular hydrogen bonds (Andresen et al. 2006; Stenstad et al. 2008). This hierarchical structure is deconstructed during the generation of the MFC, yielding a product with more or less individualized cellulose aggregates and thus a continuing size distribution and high aspect ratio (length/diameter). The lateral size of the elementary fibril is dependent on the cellulose species and varies from about 3 nm for natural wood and up to 15 nm for algal celluloses (Klemm et al. 2005). The average diameter of the cellulose nanoparticles in MFC products is commonly in the range of 10–100 nm and with lengths from 0.5 up to 50 μm (Chinga-Carrasco 2011; Lavoine et al. 2012; Sandquist 2013). For a properly produced MFC, the main part of the cellulose components should have a diameter of 100 nm or less (Chinga-Carrasco 2011; Abdul Khalil et al. 2012).

Various mechanical treatment methods have been used to manufacture MFC, for example the Gaulin homogenizer (Turbak et al. 1983) in which the pulp suspension is forced through a small-diameter orifice at 53 MPa. An alternative to the Gaulin homogenizer is the more commonly used microfluidizer, where the diluted pulp is pumped through a z-shaped chamber under pressure as high as 207 MPa (Siqueira et al. 2010). Another category is commercial grinders equipped with a specially designed grind stone. Each of the mentioned mechanical treatment methods requires high energy consumption per unit weight of the product. For example, the energy demand for a homogenizer has been reported to be as high as 30,000–70,000 kWh/t depending on the number of passes (Eriksen et al. 2008; Taipale et al. 2010). The high energy demand is an obstacle to overcome and a variety of pretreatments to reduce the energy consumption have therefore been proposed.

TEMPO-mediated oxidation (TEMPO = 2,2,6,6-tetramethylpiperidine-1-oxyl), carboxymethylation and enzymatic hydrolysis are the most frequently used non-mechanical pretreatment methods applied for MFC production (Lavoine et al. 2012). TEMPO mediated oxidation (Iwamoto et al. 2010; Isogai et al. 2011) and carboxymethylation (Henriksson et al. 2007; Bhandari et al. 2012) introduce charged groups into the fibre walls, which leads to an extensive repulsive effect that will enhance fibre delamination and overwhelm the hydrogen bond network of the fibres. Another method has been proposed by Pääkkö et al. (2007) who demonstrated that a mild enzymatic hydrolysis with endoglucanase in combination with high pressure shear forces produced MFC with a well-defined diameter and a high aspect ratio. Endoglucanase belongs to the cellulase class of enzymes, catalyzing the cleavage of the β-1,4-glucosidic bond in the cellulose molecule. Different cellulases have established different strategies to approach their solid substrate. Endoglucanase randomly cleaves bonds in the middle of the chains (Henriksson et al. 2005). Both enzymatic and chemical modification may reduce the energy consumption down to 1,000–10,000 kWh/t (Isogai 2009; Siro and Plackett 2010; Taipale et al. 2010; Tejado et al. 2012). Chemical modification is often linked with high chemical charges, up to several hundred kilograms per tonne of pulp, including non-environmentally friendly chemicals and generates an MFC product with a high cationic demand.

The application of Fenton chemistry to lignocellulosic materials has been described in various scientific studies, for example to enhance the fermentability of prehydrolysates obtained from steam explosion pretreatment of biomass (Oliva et al. 2005), to decrease the energy demand in mechanical pulping (Walter et al. 2009) and to enhance the enzymatic hydrolysis response for cotton substrates (Jain and Vigneshwaran 2012). In the Fenton reaction, active oxygen species, such as hydroxyl radicals (OH·) are formed through the one-electron reduction of hydrogen peroxide, catalyzed by transitional metal ions such as soluble ferrous ions (Fe^{2+}) (Fenton 1894; Haber and Weiss 1934), see reaction (1). The classical Fenton mechanism was proposed by Haber and Weiss in 1934 and further development of the radical intermediate concept was made by Barb et al. (1951). The main reaction is given below.

Fig. 1 Positions in the cellulose chain possible to participate in oxidation reactions (partly adapted from Norimoto 2001)

Oxidation to carboxylic acid or aldehyde

Oxidation to carboxylic acid

Oxidation to ketone

Oxidation to ketone

Formation of radical by abstraction of H

Oxidative cleavage of C2-C3

$$Fe^{2+} + HOOH \rightarrow Fe^{3+} + OH^- + OH\cdot \qquad (1)$$

The produced ferric ions are slowly regenerated into ferrous ions by reaction with hydrogen peroxide under formation of hydroperoxyl radicals (HOO·) or may react with a present reductant i.e. the iron will react as a catalyst in the oxidation system. The formed hydroxyl radical may also oxidize Fe^{2+} to Fe^{3+} or decompose H_2O_2 to water and HOO·. The pH range for Fenton reactions utilizing free iron is restricted to an upper pH of about 3–4 due to precipitation of ferric iron at a higher pH (Pignatello et al. 2006). Besides the described theory including free radicals, some researchers claim the participation of the ferryl ion (FeO^{2+}) as an active intermediate (Sychev and Isak 1995). The presence of hydroxyl radicals in the reaction between acidic hydrogen peroxide and ferrous ions in a cellulosic substrate has been demonstrated by Walter et al. (2013). Organic compounds like lignocellulosic materials, oxidized in radical chain reactions, encompass a series of complex reactions including numerous radical intermediates and consecutive reactions. The reaction mechanisms is not fully elucidated, but are suggested to involve the formation of various radicals like alkyl and carbon radicals produced by hydrogen abstraction. The hydroxyl groups in cellulose and hemicelluloses are susceptible to direct oxidation of the C2, C3 and C6 hydroxyl groups, the resulting aldehyde or keto group may initiate further degradation reactions such as dehydration and cleavage of the glycosidic linkages (Wang et al. 2011; Henniges et al. 2012; Jeong et al.

2014; Lai 2001). Figure 1 shows the positions in the cellulose chain that may be subjected to oxidation.

The aim of this work was to study the effect of using Fenton chemistry as a pretreatment when producing MFC from a fully bleached birch kraft pulp. The produced MFC products were chemically and morphologically characterized and compared with MFC products produced using enzymatic hydrolysis as pretreatment. The effect of the MFC products as strength enhancer in paperboard will be evaluated in a later study.

Experimental

Materials

Pulp

The pulp used in this study was a commercially produced fully bleached birch (*Betula verucosa*) kraft pulp delivered dried in sheets. The properties of the pulp were as follow: ISO brightness 88.6 %, Kappa number 0.62 and viscosity 930 dm^3/kg. The metal content in the pulp was (mg/kg): Al 2.3, Ba 1.4, Ca 100, Cr < 0.1, Cu 0.6, Fe 1.9, K 10, Mg 30, Mn 0.3, Na 230, P < 10, S 140.

Chemicals

Hydrogen peroxide KR 59 from Akzo Nobel, Bohus, Sweden, was diluted with de-ionized water to a concentration of 389 g/L, and sulfuric acid 98 % pro

analysis from Sigma Aldrich, Germany, was diluted to 0.5 M using de-ionized water. A stock solution containing 5 g Fe/L was prepared on a daily basis using a reagent grade ferrous sulfate (Fe$_2$SO$_4$ × 7 H$_2$O) from Scharlau, Spain. The enzyme used was a monocomponent endoglucanase (FiberCare®R) provided by Novozymes AS, in Denmark, which was used without further purification. The enzyme activity expressed in endo cellulase units (ECU) per mass unit of material was determined to 4,300 ECU/g. The phosphate buffer used in the enzymatic treatment was prepared from 11 mM KH$_2$PO$_4$ and 9 mM Na$_2$HPO$_4$ giving a pH between 6.8 and 7. For the charge density measurements, the following chemicals were used: sodium chloride reagent grade from Scharlau, Spain, polydiallyldimethyl-ammonium chloride (Polydadmac) solution with a molecular weight of 200,000–350,000 g/mol from Sigma Aldrich, USA, polyethenesodiumsulfonate (Na-PES) from Paper Test Equipment, hydrochloric acid 37 % and sodium

calculated as dry material was diluted with de-ionized water to 0.5 % w/w where after the pH was adjusted to pH 6.5–7.0 with 0.05 M NaOH and required to be stable for at least 1 h before the electrolyte concentration was adjusted to 110–140 μS/cm with NaCl, corresponding to 0.4–0.7 mM NaCl. The electrolyte concentration was selected to avoid the increase in adsorption that occurs at high electrolyte concentrations when the distance between the charges becomes greater than the thickness of the double layer (Horvath et al. 2005) but is high enough to minimize the charge increase due to a small variation in electrolyte concentration. Polydadmac (50 mL, 2,000 μeq/L) was added to the fibre suspensions and the samples were stirred using a magnetic stirrer for 120 min. Five mL of the sample, fibres included, was diluted with 5 mL de-ionized water and thereafter titrated with PES-Na (1,000 μeq/L) using a PCD-03 from MÜTEK. The surface charge was calculated using the formula below:

$$q = \frac{V_{PolyD} \cdot C_{PolyD} \cdot m_2 - V_{NaPES} \cdot C_{NaPES} \cdot \left(m_1 \cdot \frac{100-PC}{100} + V_{PolyD} + V_{H_2O} + V_{NaOH} + V_{NaCl}\right)}{m_1 \cdot m_2 \cdot PC \cdot 10}$$

hydroxide 0.1 M from Scharlau, Spain. For the post-oxidation and reduction of the pulps before measurement of the intrinsic viscosity, sodium chlorite (puriss) from Sigma Aldrich, Germany, and sodium borohydride (purpose grade) from Fischer scientific, United Kingdom, were used.

Methods

Charge determination

The total charge was determined on untreated and Fenton or enzymatic pretreated pulps according to Katz et al. (1984) using a titration unit, 712 Conductometer, Metrohm. Katz et al. (1984) report the reproducibility to be in the range of ± 4 mmol/kg. The surface charge was determined on pulp suspensions by polyelectrolyte titration with a streaming current detector. The analysis was performed without an acidic wash and without transferring the pulps to its sodium form. The procedure was as follows: 0.5 g

where q is the surface charge (μeq/g), V_{PolyD} is volume of Polydadmac (mL), C_{PolyD} is the concentration of the Polydadmac solution (μeq/L), V_{NaPES} is the volume of Na-PES used in the polyelectrolyte titration (mL), C_{NaPES} is the concentration of titrant (μeq/L), V_{H_2O} is the volume of water (mL), V_{NaOH} is the volume of sodium hydroxide used for pH adjustment (mL), V_{NaCl} is the volume of sodium chloride used for conductivity adjustments (mL), PC is the pulp consistency of the fibre suspension to be analysed (w/w %), m_1 is the weight of the fibre suspension to be analysed (g) and m_2 is the amount of sample used in the polyelectrolyte titration (g). The 95 % confidence interval was determined to ±2.3 μeq/g by calculation of the pooled standard deviation for five sets of samples performed in triplets.

Product stability

The stability of the bio-fibre products was measured as the degree of sedimentation of a 0.5 % (w/w) fibre

suspension in a 24 mL test tube (radius 0.7 cm and height 15.5 cm) kept in room temperature. The sedimentation degree was determined after 2 and 56 days and reported as suspension stability measured as non-separated fibre solution in percent, i.e. 100 % suspension stability corresponds to a fully stable product.

Intrinsic viscosity

The intrinsic viscosity was based on the standard method ISO 6351-1:2010 utilizing cupricethylenediamine as solvent. A departure from the applied method was made for the Fenton treated pulps since the efflux time for the Fenton treated pulps were outside the specified limit. Some of the pretreated samples were post-oxidized with sodium chlorite according to Mishra et al. (2011) aiming to reduce the formed carbonyl groups and thereby minimize the alkali induced β-alkoxy elimination caused by the alkalinity of the cupricethylenediamine. The intrinsic viscosity was also measured after a reductive treatment with sodium borohydride (2 % $NaBH_4$, 30 min, room temperature, 5 % consistency) (Roncero et al. 2003).

Fibre properties

Determination of the length-weighted mean length and width of the fibres was performed using a L&W Fibre Tester. It is worth noting that the fibre length is defined as the average length measured on fibres with lengths ranging from 0.2–7.5 mm. Objects shorter than 0.2 mm are defined as fines. The measured range for width is 10–100 μm. The equipment is therefore not optimal for measurements on MFC products but will nevertheless give useful information about the size distribution of the remaining fibre material.

Carbohydrate analysis

Pretreated pulp samples were dried, milled and submitted to an acid hydrolysis using sulphuric acid (1.6 M H_2SO_4, 120 °C, 60 min). The liberated monosaccharides (glucose, xylose, mannose, arabinose, galactose) were quantified by HPLC-Dionex using fucose as internal standard.

Enzyme activity

Endoglucanase activity was analyzed at pH 5.0 using hydroxylethyl cellulose (Fluka 54290) as a substrate. The activity was expressed ECU per mass unit of material according to Ghose (1987).

Carbonyl groups

The determination of the carbonyl group content was performed by reaction with hydroxyl ammonium chloride, which forms an aldoxime with the carbonyl groups in the pulp sample. After reaction, the content of carbonyl groups is proportional to the amount of nitrogen in the sample, which is determined by chemiluminescence using an Antek MultiTek from PAC after catalytic combustion.

Residual hydrogen peroxide

The amount of residual hydrogen peroxide is determined in a slightly acidified potassium iodide solution in the presence of a trace of ammonium molybdate as a catalyst. The liberated iodine is titrated with a thiosulfate solution with the use of starch as indicator (Schumb et al. 1955).

Metal ions

The metal ions in the pulp samples were determined after wet combustion with nitric acid in a microwave system with an inductively coupled plasma (ICP) instrument (Iris radial, Thermo ICP s/n 10773). The report limits (mg/kg) were: Al 1.0, Ba 0.2, Ca 20, Cr 0.1, Cu 0.1, Fe 0.5, K 10, Mg 20, Mn 0.1, Na 5, P 10, S 20.

Chemical oxygen demand

The chemical oxygen demand (COD) was measured on filtrates, filtered through glass microfibre filters GF/A (Whatman) using HAC Lange Classic COD Cuvette Tests and a Dr. Lange Xion 500 spectrophotometer.

Brunauer–Emmett–Teller (BET)—area

An MFC sample (50 g, 0.5 % w/w) was placed in a 500 mL round flask and freeze dried. The specific

surface area Brunauer–Emmett–Teller (BET) was thereafter determined by adsorption of N_2 at 177 K using a Micrometrics TriStar 3000 instrument, which operates according to ISO 9277:1995.

Fractionation

The fractionation was performed in a stirred ultrafiltration cell (Model 8400) from Amicon. The trials were performed at room temperature. Five hundred mg of oven dry material was diluted with 300 mL de-ionized water and transferred to the ultrafiltration cell with a pre-weighted nylon wire/membrane mounted. The stirring speed was set to 500 rpm and a pressure of 0.5 bar was obtained by using compressed air. The filtrate was continuously sampled in a glass bottle. When 150 mL filtrate had been collected, the volume in the ultrafiltration cell was readjusted to 300 mL with de-ionized water. The procedure was repeated until a total volume of 3,000 mL had passed through the cell and the output filtrate was clear of fibre fragments. After thorough cleaning with de-ionized water, the wash water was evaporated together with the screen and the fibre material was dried overnight at 105 °C. After cooling in a desiccator, the screen with the fibre material was weighted and the portion of the fraction was calculated. The procedure was repeated allowing the collected filtrate to pass through the next screen. Altogether three screens with varied pore sizes were used: a 112 μm nylon net from Derma AB, Sweden, a 20 μm nylon net (NY20) from Millipore and a 0.1 μm Durapore®Membrane Filter (VVPP) from Millipore. Three screening stages give four fraction levels: >112, 20–112, 0.1–20 and <0.1 μm. The final permeate is too diluted for appropriate measurement of the solid content and is therefore calculated as the residual not found in the other screening stages. It will therefore be less accurate.

Scanning electron microscopy

For the scanning electron microscopy (SEM) analysis, the MFC product was diluted to 0.1 % (w/w) and freeze dried on an adhesive tape on a sample holder. The samples were examined by high resolution scanning microscopy at 375× magnification with a LEO 1530 FEG-SEM from ZEISS, applying an acceleration voltage of 200 kV.

Chemical and enzymatic pretreatments

Fenton treatment

A pulp sample was disintegrated as described in ISO standard 5253:1995. The fibre suspension was thereafter drained on a Büchner funnel equipped with a 112 μm nylon wire screen (from Derma AB, Sweden). The filtrate was recycled once through the wet fibre pad to avoid the loss of fines. Sixty gram of the disintegrated pulp, calculated as oven dry, was suspended in de-ionized water to 10 % consistency. The dilution water contained a sufficient amount of sulphuric acid to obtain an initial pH of 3.5 and ferrous ions to a molar ratio $H_2O_2/Fe = 411$. The hydrogen peroxide was charged in two levels, 10 kg/t, hereafter denoted *Fenton Low* and 50 kg/t denoted *Fenton High*. For the acidic hydrogen peroxide reference, sulphuric acid and 10 kg H_2O_2/t were combined without the addition of ferrous ions and is hereafter denoted *Acid Peroxide*. An acidic reference without hydrogen was also performed, denoted *Acid*. After thoroughly mixing, the pulp slurry was transferred to a plastic bag and placed in a water bath (90 °C). The reaction time was set to 150 min to obtain a uniform reaction and to ensure that all hydrogen peroxide was consumed; except for *Acid Peroxide*, the residual hydrogen peroxide was 6.5 kg/t. At the end of the trial, the pulp suspension was drained on a Büchner funnel (112 μm nylon wire) and washed as described above. Residual hydrogen peroxide, pH and the COD were measured on the filtrates. To reduce the amount of residual chemicals, the pulp was washed with de-ionized water at 3 % (w/w) consistency, dewatered on a Büchner funnel (112 μm nylon wire) and the filtrate was recycled once. After conditioning in room temperature overnight in a sealed plastic bag, the pulp consistencies were determined (ISO 638:2008). The pretreated samples were stored in a refrigerator until the mechanical treatment and analyses were performed. The conditions during the chemical treatment are summarized in Table 1.

Table 1 The conditions employed for the chemical and enzymatic pretreatments

Conditions	Units	Acid	Acid Peroxide	Fenton Low	Fenton High	Enzyme Reference	Enzyme Low	Enzyme High
H_2O_2	kg/t		10	10	50			
Fe^{2+}	kg/t			0.04	0.2			
H_2SO_4	kg/t	0.6	0.6	0.5	0.3			
pH_{start}		3.5	3.5	3.5	3.5	7.0	7.0	7.0
FiberCare®R	ECU/g						1.0	2.0
Consistency	%	10	10	10	10	4	4	4
Time	minutes	150	150	150	150	120	120	120
Temperature	°C	90	90	90	90	50	50	50

Enzymatic treatment

The enzymatic treatments were performed as described by Pääkkö et al. (2007) beside the choice of raw material, birch kraft pulp was used instead of sulphite pulp (40 % pine and 60 % spruce) and the exclusion of pre-milling before treatment. The birch kraft pulp was wet disintegrated according to ISO standard 5263:1995. One hundred grams of the pulp, calculated as oven dry, was dispersed in 11 mM phosphate buffer to a final pulp concentration of 4 % (w/w). Monocomponent endoglucanase was charged in two levels, 1.0 ECU/g denoted *Enzyme Low* and 2.0 ECU/g denoted *Enzyme High*. After mixing thoroughly, the sample was transferred to a plastic bag and incubated in a water bath (50 °C) for 120 min. The sample was mixed manually every 30 min. At the end of the trial, the pulp suspension was drained on a Büchner funnel (112 μm nylon wire) and washed as described earlier. The monocomponent endoglucanase was denatured at 80 °C for 30 min and the pulp was thereafter washed once with de-ionized water. The consistency was determined (ISO 638:2008) and the pretreated samples were stored in a refrigerator until further use. A pulp sample was treated as described above with the exception that no enzyme was charged for use as a reference (denoted *Enzyme Reference*). The conditions during the enzymatic treatment are summarized in Table 1.

Mechanical treatment

Mechanical treatment was conducted in a colloid mill, IKA magic LAB equipped with module MK. The grinding gap between the stator and rotor was adjusted to 0.159 mm and the operation was performed at 20,000 rpm. Ten grams of pulp calculated as oven dry was disintegrated in 800 mL de-ionized water for 2 min. After adjusting the pulp consistency to 1 % (w/w), the pulp suspension was fed into the colloid mill and processed for 10, 30 and 53 min. The inlet funnel was continuously cooled with water maintaining the temperature of the pulp suspension to between 25–30 °C throughout the mechanical treatment.

Results and discussion

The effect of chemical and enzymatic pretreatments

In this investigation, a fully bleached birch (*B. verucosa*) kraft pulp was treated with acidic hydrogen peroxide in the presence of ferrous ions (i.e. Fenton's reagent) and thereafter treated mechanically in a colloid mill with the aim to produce MFC. The resulting MFC product consists of a mixture of unaffected fibres, fibre fragments, fibrils and microfibrils. The MFC products produce in this study were chemically and morphologically characterized and compared with MFC products produced with enzymatic (monocomponent endoglucanase) pretreatment as well as with an MFC product produced with acid pretreatment. The conditions employed for the Fenton and enzymatic pretreatment and for the references can be seen in Table 1 accompanied by sample denotations.

Table 2 shows the amount of hydrogen peroxide consumed in the Fenton reaction, the amount of released organic material measured as COD and the carbohydrate composition of untreated and pretreated pulps. As can be seen, the more hydrogen peroxide

Table 2 Consumed hydrogen peroxide, the amount of solubilized material (chemical oxygen demand, COD), and carbohydrate composition for untreated and pretreated birch kraft pulps

Denotation	Consumed				Carbohydrate composition			
	H_2O_2 (kg/t)	COD (kg/t)	Glucan (%)	Mannan (%)	Xylan (%)	Galactan (%)	Arabinan (%)	Total (%)
Untreated pulp		1	72.8 ± 1.4	<0.1	24.9 ± 0.5		<0.1	97.7 ± 3
Acid		1						
Acid peroxide	3.5	5	72.7 ± 2.2	<0.1	27.4 ± 1.2		<0.1	100.1 ± 3
Fenton low	10	21		<0.1		<0.1	<0.1	
Fenton high	50	50	75.2 ± 1.0	<0.1	24.6 ± 1.9	<0.1	<0.1	99.8 ± 3
Enzyme reference		1	72.0 ± 0.7	<0.1	25.1 ± 0.1	<0.1	<0.1	98.0 ± 3
Enzyme high		2	72.5 ± 1.6	<0.1	25.8 ± 1.0	<0.1	<0.1	98.4 ± 3

The chemical charges and explanation of denotations can be found in Table 1

that is consumed in the Fenton reaction, the more material is solubilized. The dissolved material corresponded to a yield loss of about 2 % for *Fenton Low* and about 4 % for *Fenton High*; the yield calculation is based on the theoretical amount of oxygen required to oxidize pure cellulose (0.84 g cellulose corresponds to 1.0 g COD) (Süss and Kronis 1998). Neither the *Acid* nor the enzymatic treatments increased the COD, whereas a minor increase was obtained for the *Acid Peroxide* sample. Despite the variation in the amount of dissolved material, no significant difference in the carbohydrate composition for *Untreated Pulp* could be seen compared to pulps treated with Fenton chemistry or with enzymatic treatment; all variations were within the experimental error.

The total charge of the pulp increased for *Fenton High*, whereas the changes in total charge obtained with the other pretreatments were low or within experimental error (Table 3). No significant change in surface charge could be seen for any of the pretreated pulps. Thus, to obtain a significant increase in carboxylic groups within the pulp at the prevailing conditions, the high charge of hydrogen peroxide (50 kg/t) is required. Furthermore, the Fenton reaction was not restricted to the fibre surfaces but occurred throughout the fibre cell walls. Intrinsic viscosity measurements were performed to assess the change in the degree of cellulose polymerization during the pretreatment. The enzymatic pretreatment marginally affected the intrinsic viscosity while the Fenton pretreatment already at low consumption of hydrogen peroxide lowered the viscosity significantly (Table 3;

Fig. 2). The main part of the decrease in viscosity is caused by oxidation of the cellulose as a result of the Fenton reaction and a minor part is a consequence of acid hydrolysis when compared with untreated and acid treated pulp. For the combination of acid and hydrogen peroxide (*Acid Peroxide*), the consumption of hydrogen peroxide, the increase in carbonyl group content and the decrease in viscosity indicate a detectable amount of Fenton reaction. The Fenton reaction is probably due to the transition metals present in the starting pulp (Cu 0.6, Fe 1.9 and Mn 0.3 mg/kg).

Interestingly, the amount of carbonyl groups in the Fenton pretreated pulp increased significantly (Table 3). Aldehyde, ketone and carboxyl groups are formed during the oxidation of cellulose. The type and amount of the oxidized functionalities depends on the nature of the oxidant and the conditions of oxidation. In contrast to the naturally occurring aldehyde groups located at the reducing end groups, carbonyls in cellulose (at C-2 and/or C-3) are always introduced by oxidative treatments (Potthast et al. 2005). Hydroxyl radicals are proposed to abstract hydrogen connected to C-2 or C-3 carbons and introduce a carbonyl group (Gierer 1997). The introduction of carbonyl groups along the carbohydrate chain increases the chemical instability, becoming "hot spots" where cleavage of the cellulose chain may occur. The strong alkalinity of the cupriethylenediamine solvent used when measuring the intrinsic viscosity may cause fragmentation of the cellulose chain at the oxidized points by β-alkoxy elimination and thereby result in a low viscosity
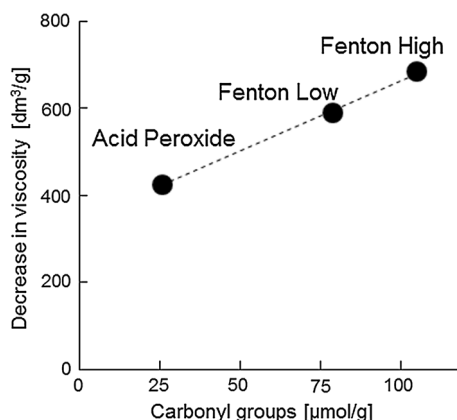
Table 3 Intrinsic viscosity, degree of polymerisation (DP), total and surface charges and amount of carbonyl groups in untreated and pretreated birch kraft pulps

Denotation	Intrinsic viscosity (dm³/kg)	DP[a]	Total charge (µeq/g)	Specific surface charge (µeq/g)	Carbonyl groups (µmol/g)
Untreated pulp	930	2,720	40	2	13
Acid	870	2,490			
Acid peroxide	450	1,050	38		23
Fenton low	280	660	45	5	79
Fenton high	190	450	58	6	105
Enzyme high	840	2,380	42	7	15

[a] DP values calculated using the formula $\eta = 0.42\ DP$ for $DP < 950$ and $\eta = 2.28\ DP^{0.76}$ for $DP > 950$ (Marx-Figini 1978)
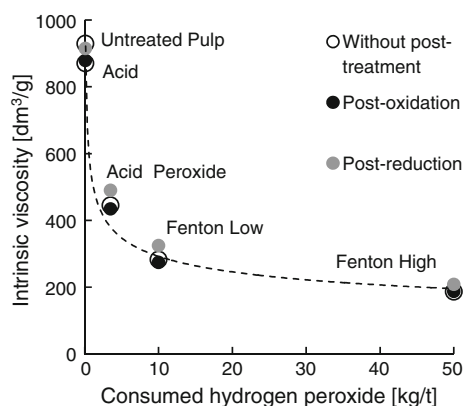
Fig. 2 Intrinsic viscosity as a function of consumed hydrogen peroxide for *Untreated Pulp*, *Acid*, *Acid Peroxide* and *Fenton* pretreated birch kraft pulps

Fig. 3 The decrease in viscosity for *Acid Peroxide* and *Fenton* pretreated birch kraft pulps as a function of the carbonyl group content

(Roncero et al. 2002; Potthast et al. 2005). To investigate whether the lowered viscosity caused by the *Fenton* treatment originates from oxidation along the cellulose backbone or if the increase in carbonyl groups reflects the generation of new reducing end groups upon chain scission, a post-oxidation (sodium chlorite) and a post-reduction (sodium borohydride) were performed after the *Fenton* treatment and *Acid Peroxide* treatment (Mishra et al. 2012; Roncero et al. 2003). The viscosity measurements without post-treatment and after post-oxidation and post-reduction respectively were almost identical and a function of the amount of consumed hydrogen peroxide (Fig. 2). This indicates that under the studied conditions, the Fenton reaction introduces new reducing end groups by cleaving the cellulose backbone. The introduction of hydroxyl radicals by γ-radiation of cellulose is reported to cause similar effects i.e. a decrease in molar mass and an increase in carbonyl group content (Henniges et al. 2012). As can be seen in Fig. 3 the

decrease in viscosity caused by oxidation is linearly proportional to the amount of new carbonyl groups formed during *Fenton* and *Acid Peroxide* treatments.

The fibre dimensions (length and width), the fines content and the specific surface area BET were not affected by the *Acid Peroxide*, the *Fenton* or the *Enzymatic* pretreatments. The data is shown in Table 4 (for the mechanical treatment time 0 min).
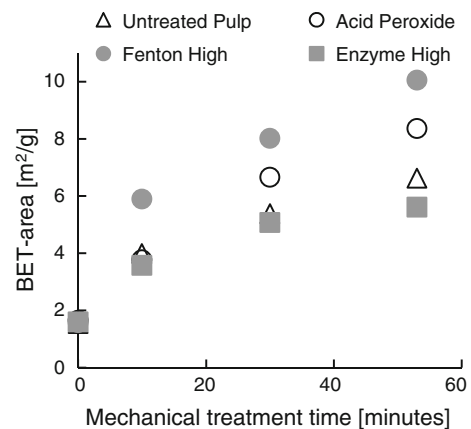
The effect of mechanical treatment

The pretreated samples and reference pulps were suspended in de-ionized water and treated mechanically in a colloid mill, IKA magic LAB at 1 % consistency for 10, 30 and 53 min. With increasing mechanical treatment the fibre length decreased for all samples including the sample without pretreatment, *Untreated Pulp* (Table 4). The effect is most pronounced for *Fenton Low* and *Fenton High*. The fibre

Table 4 Length weighted mean fibre length and width, fine content (<0.2 mm), surface charge and surface (BET) area for untreated and pretreated samples before and after mechanical treatment in the colloid mill

Denotation	Mechanical treatment time (min)	Length weighted fibre length (mm)	Length weighted fibre width (μm)	Fines < 0.2 mm (%)	Surface charge (μeq/g)	BET-area (m²/g)
Untreated Pulp	0	0.79	20.6	7.9	2	1.5
	10	0.82	20.3	8.3	17	4.0
	30	0.77	20.5	10.5	23	5.4
	53	0.75	21.3	11.5	30	6.6
Acid Peroxide	0	0.79	20.6	8.1		1.7
	10	0.78	20.2	9.5		3.8
	30	0.69	21.1	13.8		6.7
	53	0.64	21.9	15.9		8.4
Fenton Low	0	0.78	20.2	8.0	5	
	10	0.66	20.2	15.0	26	
	30	0.52	19.2	22.9	40	
	53	0.51	18.9	22.9	53	
Fenton High	0	0.77	20.5	8.4	6	1.6
	10	0.57	19.4	12.2	36	5.9
	30	0.44	18.6	28.1	44	8.8
	53	0.35	17.3	34.2	54	10
Enzyme High	0	0.80	20.7	8.2	7	1.6
	10	0.81	20.3	8.0	17	3.6
	30	0.75	19.9	11.8	28	5.1
	53	0.70	19.7	14.4	38	5.6

length after 53 min of mechanical processing is reduced from 0.79 to 0.75 mm for the *Untreated Pulp* and to 0.51 and 0.35 mm for *Fenton Low* and *Fenton High* samples, respectively.

After 10 min of mechanical processing, *Untreated Pulp*, *Acid Peroxide* and *Enzyme Reference* showed a small reduction in fibre width followed by an increase in width at longer treatment times. The increased fibre width indicates removal of the primary wall, allowing water penetration into the cell walls and breakage of intra fibre hydrogen bonds resulting in swelling of the fibres (Brännvall and Annergren 2004). This was not seen for *Fenton Low*, *Fenton High*, *Enzyme Low* and *Enzyme High* where the fibre widths were descending in the studied time interval. The decrease in fibre width was most pronounced for *Fenton Low* and *Fenton High* whose fibre widths decreased from 20.5 μm down to 18.9 and 17.3 μm, respectively. As a consequence of increased defibrillation/delamination of the fibre wall, the surface area and the surface charge will increase while the total fibre charge will remain at the

Fig. 4 The specific surface area (BET) as a function of mechanical treatment time in the colloid mill for *Untreated Pulp*, *Acid Peroxide*, *Fenton High* and *Enzyme High samples*

same level (Bhardwaj et al. 2004). For the chemical pretreatments tested in this study, the surface charge, specific surface area and fines content all increased
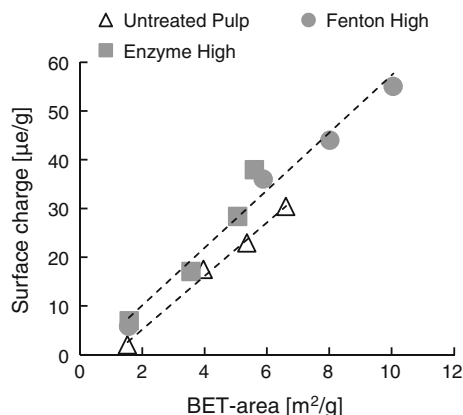
Fig. 5 The surface charge as a function of specific surface area (BET) for *Untreated Pulp*, *Fenton High* and *Enzyme high* samples at different mechanical treatment times in the colloid mill

with increasing mechanical treatment time, Table 4. The increases were most pronounced for the Fenton treated pulps. The development of the specific surface area (BET) as a function of mechanical treatment for untreated and pretreated pulps can be seen in Fig. 4. The steep development in surface area for *Fenton High* compared with *Untreated Pulp* suggests a potential to reduce the energy consumption in the mechanical processing stage when producing MFC. The BET-area was not measured for *Fenton Low* but since the development of surface charge as a function

of mechanical treatment time are almost identical for *Fenton Low* and *Fenton High* a similar progress of the specific surface area may be expected (Table 4). This assumption is supported by the linear relationship between surface charge and specific surface area measured for *Untreated Pulp*, *Fenton High* and *Enzyme High* (Fig. 5).

The studied pretreatments generated a large variation in size profiles of the pulps after mechanical processing, Fig. 6. After a mechanical treatment time of 30 min, the fraction of large fibres, i.e. fibres that do not pass a 112 μm nylon net, range from 79 % for the *Untreated Pulp*, 71 % for *Acid Peroxide*, 68 % for *Enzyme High*, 48 % for *Fenton Low* down to 37 % for *Fenton High*. This result combined with the increase in the smaller sized fractions indicates that the pretreatment resulted in a pulp that is easier to process mechanically in the following order *Fenton High* > *Fenton Low* > *Enzyme High* > *Acid Peroxide*, see Fig. 6. This is also supported by the SEM visualization of the MFC products (Fig. 7). In the image of *Fenton High*, a more intense defibrillation and fewer unaffected fibres can be seen when compared to the *Untreated Pulp*. It is worth noting that a very small portion of the total fibre fraction passed a 0.1 μm membrane filter and the amount was almost the same for *Untreated pulp*, *Acid peroxide*, *Fenton* and *Enzyme*

Fig. 6 The weight in percent of untreated and pretreated samples, refined for 30 min in a colloid mill, after successive fractionation with finer and finer filters/membranes. **a** The amount of material that do not pass a nylon net of 112 μm; **b** the amount of material that pass a nylon net of 112 μm but not a nylon net of 20 μm; **c** the amount of material that pass a nylon net of 20 μm but not a membrane filter of 0.1 μm. The final permeate was calculated as the residual not found in the other fractions (**d**)
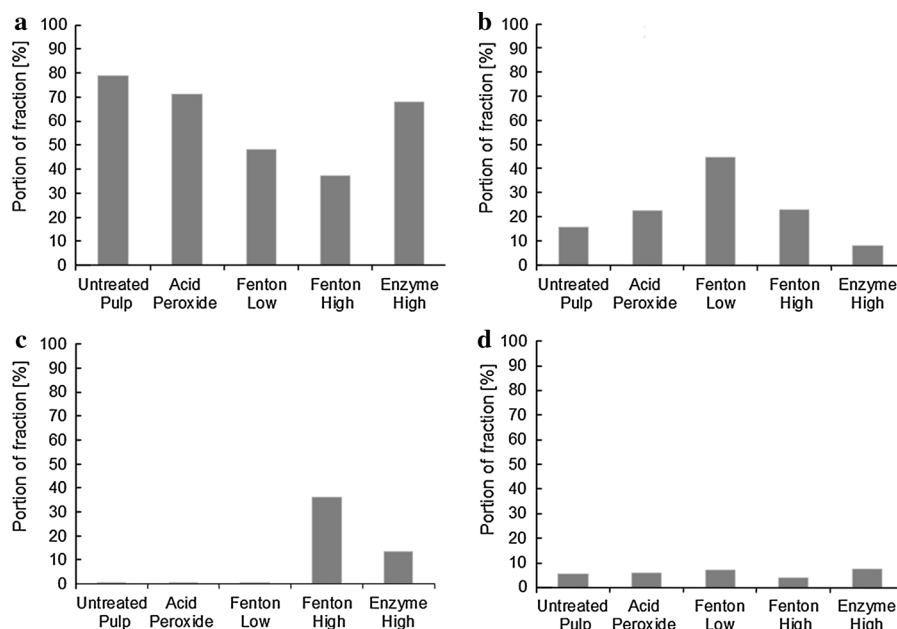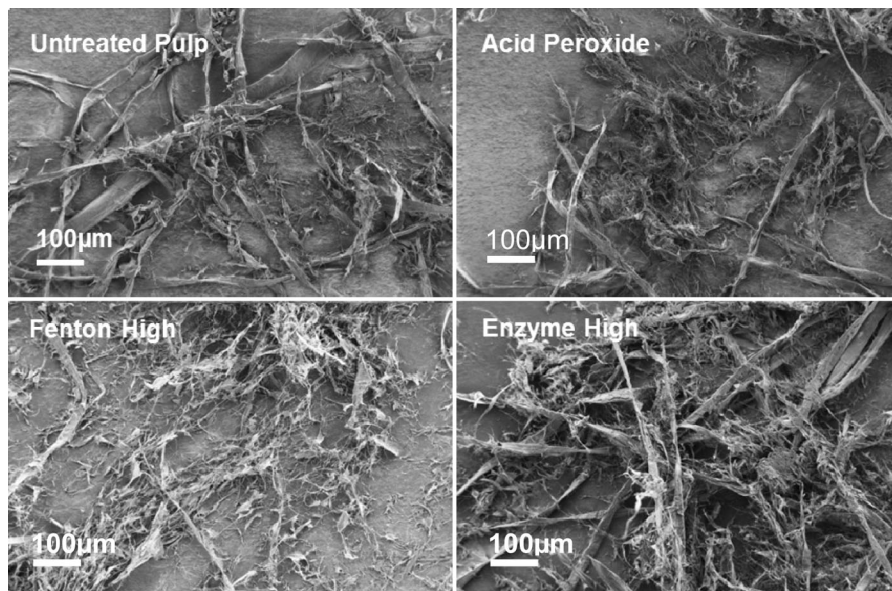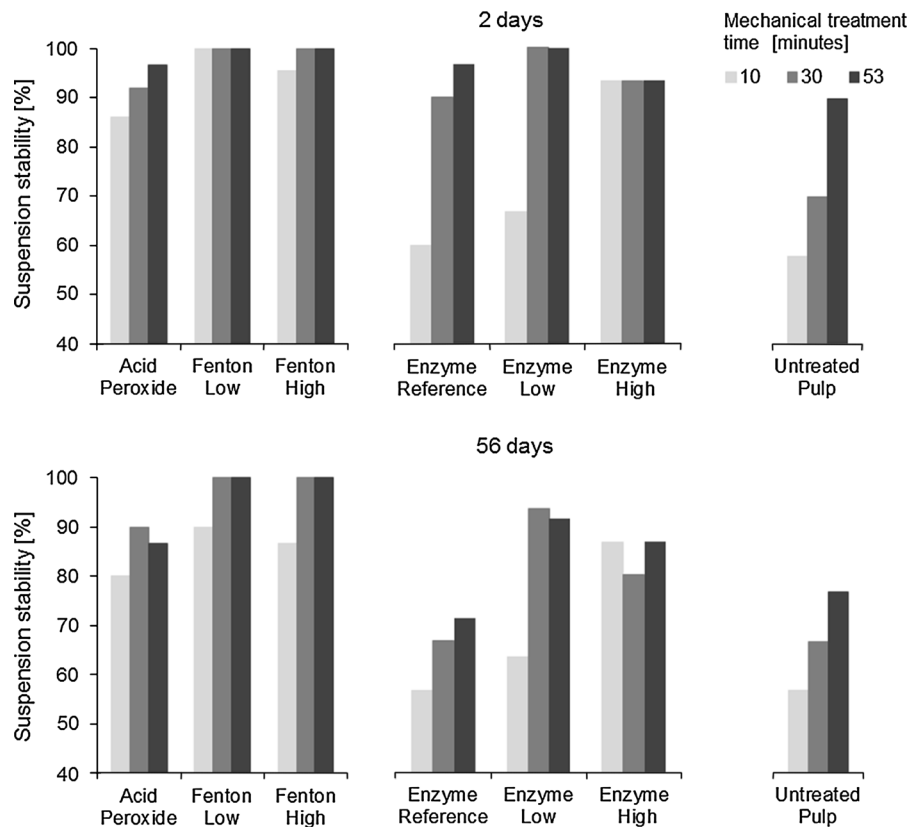
Fig. 7 Scanning electron microscopy images of *Untreated Pulp*, *Acid Peroxide*, *Fenton High* and *Enzyme High* samples after 30 min of mechanical treatment in the colloid mill

Fig. 8 Suspension stability measured after 2 and 56 days for untreated and pretreated pulp samples after 10, 30 and 53 min of mechanical treatment in the colloid mill

pretreated pulps. The fractionation study revealed that only a small portion of the processed pulps was in the size range of MFC.

Mechanical processing of fibres in a water suspension causes structural changes of the fibres such as increased fibre swelling, fibre shortening, internal and external fibrillation (Brännvall and Annergren 2004). A quick and easy indication of the extent of fibrillation is to measure the suspension stability which depends on the dimensions of the dispersed material, their polydispersity and their surface charge (Marton and Robie 1969; Hubbe and Orlando 2008). Prior to mechanical treatment, the two-phase nature of the water-fibre suspension is apparent since sedimentation occurs rapidly for all of the suspensions. An increase in mechanical processing consistently provided an increase in product stability. After running a stability test of diluted (0.5 %) pulp water suspension for 2 days, Fenton Low (10, 30, 53 min), Fenton High (30, 53 min) and Enzyme Low (30, 53 min) were entirely stable but after 56 days of testing only Fenton Low (30, 53 min) and Fenton High (30, 53 min) remained stable, see Fig. 8.

It is obvious that the treatment with Fenton chemicals gives the birch pulp outstanding characteristics and such pulps are therefore well suited for further processing to MFC. The use of Fenton chemistry as pretreatment for MFC production will be studied further and the use of such products as strength enhancers in paperboard will be presented in future studies.

Conclusions

The Fenton pretreatment increased the total charge of the birch kraft pulp, decreased the viscosity and introduced new carbonyl groups. The addition of 10 or 50 kg/t hydrogen peroxide resulted in a yield loss of 2 and 4 %, respectively. The enzymatic hydrolysis did not substantially change the total charge or the carbonyl group content of the pulp and did not release any organic material. The Fenton pretreated pulps were easier to process mechanically, i.e. they reached a higher specific surface (BET) area and thereby a higher surface charge at a given mechanical treatment time, indicating a potential to lower the energy in the final mechanical processing stage. The Fenton pretreatment produced disintegrated pulp fibres that to

some extent can be referred to as microfibrillated cellulose (MFC). These suspensions were stable in a sedimentation experiment which was stable for at least 8 weeks in a water suspension (0.5 % consistency). Furthermore, the Fenton pretreatment gave an MFC product that contained a higher amount of small well-fibrillated particles, as indicated by fractionation and scanning electrone microscopy, compared with the enzymatic and acid pretreatment methods studied.

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