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Fenton pre-treated microfibrillated cellulose evaluated as a strength enhancer in the middle ply of paperboard

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SUMMARY: Microfibrillated celluloses (MFCs), produced by various pre-treatments of a fully bleached birch kraft pulp, were evaluated as strength enhancers in test sheets representing the middle ply of paperboard. The furnish consisted of hydrogen peroxide bleached high temperature spruce chemithermomechanical pulp (HT-CTMP), MFC and a retention system containing cationic starch and an anionic silica sol. The MFC was prepared via a mechanical treatment in a colloid mill after pre-treatment with Fenton´s reagent, monocomponent endoglucanase or acidic hydrogen peroxide. Addition of 5% MFC, produced with Fenton pre-treatment, resulted in improved HT-CTMP properties with respect to increased tensile index (~35%), z-directional strength (~50%), tensile stiffness index (~25%) compared to HT-CTMP test sheets prepared without MFC addition. The strength improvement was linearly correlated to the density of the tests sheet, to the surface area (BET) and to the surface charge of the enzymatic or chemically pre-treated MFCs.

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During the last decades there has been an increasing interest in the pulp and paper industry to use lignocellulosic materials for production of micro- and nanofibrillated cellulose (MFC and NFC) (Österberg, Cranston 2014). The aim is to improve existing products as well as to create new products and develop new application areas (Sandquist 2013). A variety of important industrial uses for MFC/NFC have been suggested, such as rheology modifier in foods and paints, as reinforcement in composites, as strength enhancer in papers and in barriers with low permeability to gases (Turbak et al. 1983; Zimmermann et al. 2004; Henriksson et al. 2007; Eriksen et al. 2008; Syverud, Stenius 2009). MFC was first produced by Turbak et al. (1983) by intense mechanical treatment of wood fibres by several passes through a pressurized homogenizer. The MFC production is accompanied with a high energy demand that has to be reduced to facilitate industrial production. Thus, several pre-treatment methods have been proposed to overcome this obstacle: enzymatic (Henriksson et al. 2005; Pääkkö et al. 2007), and chemical such as carboxymethylation (Henriksson et al. 2007; Bhandari et al. 2012) or TEMPO-mediated oxidation (TEMPO = 2,2,6,6-tetramethylpiperidine-1-oxyl) (Isogai, Kato 1998; Iwamoto et al. 2010; Isogai et al. 2011). The use of Fenton's reagent i.e. treatment with acidic hydrogen peroxide in the presence of ferrous ions producing hydroxyl radicals has also been suggested (Heijnesson-Hultén 2005).

The morphology and chemistry of MFC/NFC products vary significantly depending on the source of raw material and the production method used. Without chemical or enzymatic pre-treatments or fractionation, MFC products generally consist of a mixture of unaffected fibres, fibre fragments and small sized fibrils i.e. have a broad size distribution (Chinga-Carrasco 2011; Lavoine et al. 2012). In contrast, MFC produced by TEMPO-mediated oxidation, combined with mechanical treatment consist of smaller and more uniform microfibrils with a high charge density (Isogai et al. 2011).

The mechanical properties of a paper product are related to the individual fibre strength, the bonding strength per unit area and the bonded area of the fibres. One of the most commonly used methods to increase the connectivity of cellulose fibres within a paper network is by beating. During beating, the fibres are made more flexible and can easier conform to each other's surfaces. The mechanical properties of paper products are also known to be improved by addition of fines (Aaltio 1962; Retulainen et al. 1993; Retulainen and Nieminen 1996; Bäckström et al. 2008). For example, addition of fines to long fibre fraction of a bleached softwood kraft pulp increased the tensile index with 47% at a fines content of 6% (Retulainen and Nieminen 1996).

The strength of paper can also be improved by increasing the number of bonds between the fibres by adding dry strength additives like starch or carboxymethylcellulose, often together with a drainage improving additive like cationic polyacrylamide.

The benefits of using MFC/NFC as strength enhancers in paper applications have during the last years been explored by several researchers (Ahola et al. 2008; Eriksen et al. 2008; Mörseburg, Chinga-Carrasco 2009; Taipale et al. 2010; González et al. 2012; Joseleau et al. 2012; Kajanto, Kosonen 2012; Zhang et al. 2012). Da Silva Perez et al. (2010) demonstrated a clear relationship between the MFC/NFC quality and the reinforcement effect in paper sheets prepared from both softwood and hardwood pulps. The MFC with the smallest particles and the most homogenous particle size distribution gained the largest improvement in tensile and tear properties. At an addition level of 5% of MFC/NFC, the improvement was 20-25% in both tensile- and tear index compared with sheets prepared without addition of MFC/NFC. These results are consistent with an earlier study made by Eriksen et al. (2008) who evaluated the addition of MFCs with different average fibril sizes to hand sheets prepared from thermomechanical pulp. The study revealed an increased tensile index when the average fibril size of the MFC decreased. Osong et al. (2014) produced NFC from bleached kraft pulp fines and chemithermomechanical pulp (CTMP) fines by mechanical treatment in a homogeniser. The produced NFC´s were blended with bleached kraft pulp and CTMP pulp and the strength properties were evaluated on hand sheets. At an addition level of 5% NFC the strength improvement were moderate, 5-10% in z-strength and not significant for tensile index and bending stiffness when compared with sheets without addition of NFC.

Due to their large specific surface area and high aspect ratio, MFC/NFC exhibits a high water retention capacity, a property that can be desirable or undesirable depending of the field of application. In paper making, it is an advantage to enhance the paper properties without simultaneously deteriorate the drainage properties and thereby the efficiency of the paper machine. The introduction of more fibrillated materials like MFC may affect the drainage negatively (Taipale et al. 2010; Collin et al. 2012; Afra et al. 2013; Djafari Petroudy et al. 2014). However, Taipale et al. (2010) demonstrated an improvement in tensile index and Scott bond with 25% and 70% respectively, without deteriorating the drainage time by selection of suitable MFC and process conditions.

The aim of this work is to evaluate the effect of MFC products produced from a fully bleached birch kraft pulp as strength enhancers in test sheets of high temperature chemimechanical pulp representing the middle ply of paperboard and to correlate the results obtained to morphological and chemical characteristics of the MFCs determined in an earlier study (Hellström et al. 2014). The MFC´s were prepared without or with (enzymatic, Fenton, acid) pre-treatment followed by mechanical processing in a colloid mill.

Materials and Methods

Preparation of MFC products

The MFC products were prepared from a fully bleached birch (*Betula verucosa*) kraft pulp with the following properties: ISO brightness 88.6%, kappa number 0.62 and intrinsic viscosity 929 dm^3/kg. Birch fibres have proved to give MFC with good quality and with its relatively short fibre length will reduce the risk for clogging of the equipment (Tapin-Lingua 2013).The kraft pulp was pre-treated with acidic hydrogen peroxide in the presence of ferrous ions (i.e. Fenton's reagent) in two addition levels of hydrogen peroxide, 10 and 50 kg/t, hereafter denoted Fenton Low and Fenton High. For comparison an enzymatic pre-treatment was performed using a monocomponent endoglucanase (FiberCare®R, Novozymes AS, Denmark), charged at one respectively two endocellulase units (ECU) per mass unit of material, Enzyme Low and Enzyme High. Additionally, the pulp was treated at the conditions used in the Fenton pre-treatments without charge of iron representing the reference denoted Acid Peroxide. The chemical charges and conditions during the pre-treatments can be seen in *Table 1*. The pulps were thereafter mechanically treated in a colloid mill, IKA magic LAB equipped with module MK for 0, 10, 30 and 53 min. The preparation methodology and characterization of the MFC products are described in detail in a previously published study (Hellström et al. 2014).

Table 1 - The conditions employed for the chemical and enzymatic pre-treatments. The data are taken from Hellström et al. (2014)

Conditions	Acid Peroxide	Fenton Low	Fenton High	Enzyme Low	Enzyme High
H_2O_2, kg/t	10	10	50		
Fe^{2+}, kg/t		0.04	0.20		
H_2SO_4, kg/t	0.6	0.5	0.3		
pH_{start}	3.5	3.5		7.0	
FiberCare®R, ECU/g				1.0	2.0
Consistency, %	10	10		4	
Time, min.	150	150		120	
Temp., °C	90	90		50	

Sheet preparation and analysis

Test sheets representing the middle ply in paperboard, with a target basis weight of 120 g/m^2, were produced from a hydrogen peroxide bleached Norway spruce (*Picea abies*) high temperature chemithermomechanical pulp (HT-CTMP). The pulp had a Canadian Standard Freeness of 700 mL and a brightness of 70% ISO. After hot disintegration according to ISO 5263:1995, the HT-CTMP was diluted to 0.5% w/w and $CaCl_2$ (Fischer Chemicals) was added to a concentration of 0.1g/L. The conductivity was thereafter adjusted to 1200 µS/cm with sodium sulphate (Scarlau Chemie). Sheets were formed in a dynamic sheet former (DSF), Techpap supplied by Centre Technique du Papier, France, by pumping the fibre furnish from the mixing chest through a transversing nozzle into the rotation drum. In order to avoid losses of fines and MFC upon sheet making, a retention system consisting of cationic potato starch, SolBond C50 from Lyckeby, Sweden and anionic silica sol, NP 442 from AkzoNobel, Sweden was used. When MFC was charged, the amount of HT-CTMP fibres was reduced to maintain the target basis weight of the test sheets. Basis weights were used as an indirect measure of the MFC retention during sheet formation. The chemical charges used and the order of addition are presented in *Table 2*.

The DSF sheets were cut into smaller sheets (260 x 220 mm) and pressed between three blotters at 10 bars in a plane press for 10 min and thereafter dried restrained in a plane dryer from STFI, Sweden (105°C, 10 min).

Table 2 - Chemical charges and addition order for the chemicals used in the stock preparation.

Chemical	MFC product	Cationic starch	Silica sol
Charge, %	5.0	1.0	0.3
Added at time, s	0	30	45

All sheets were conditioned prior to testing in a climate room at 23°C and 53% relative humidity according to ISO 187:1999. Thickness, grammage, tensile strength and stiffness, z-directional strength and bending resistance index were determined according to ISO 534:2005, ISO 536:1995, ISO 1924-3:2005, SCAN-P 80:98 and SCAN-P 29:95, respectively. Since the dynamic sheet former produces anisotropic sheets the tensile properties are reported as geometrical mean values. For the drainage tests, a dynamic drainage analyser (DDA) from Eurocon, Sweden was used at 1500 rpm stirrer speed and -150 mbar. The furnish composition, chemical charges and order of addition were the same as during the sheet preparation, *Table 2*. The 95% confidence interval for tensile index and tensile index stiffness are based on geometrical mean values for 5 measurements in the machine direction and 5 measurements in the cross direction. Calculation of the confidence interval for bending resistance index is made from 16 separate measurements. For z-directional strength the 95 % confidence interval was determined by calculation of the pooled standard deviation for each pre-treatment method i.e. 5 samples performed in triplets.

Results and Discussion

There is no common and accepted defined size distribution of a product to be named MFC, although an ISO standardisation group is working on an international classification (SIS-CEN ISO/TS 27687:2009). According to some researchers, in 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). The products evaluated in this study contained varied portions of fibres, fibre fragments, fibrils and microfibrils in varied amounts (Hellström et al. 2014). A schematic description of the total experimental layout can be seen in *Fig 1*, Part 1 represents the preparation and characterisation of the MFC products described in Hellström et al. (2014). The outline for Part 2, which is this paper, is an evaluation of the MFC products as strength enhancers in test sheets representing the middle ply of a paper board.

The characteristics of the MFC products

The main characteristics of the MFCs are summarized in *Table 3*. As can be seen the MFCs prepared with Fenton pre-treatment had a higher specific surface area measured as Brunauer-Emmett-Teller (BET) area and a higher surface charge at a given mechanical treatment time in the colloid mill compared to MFC products produced without pre-treatment or pre-treated with acidic hydrogen peroxide or enzymes. It is also seen that Fenton pre-treatment significantly reduced the intrinsic viscosity of the pulps. Further, fractionation and scanning electron microscopy studies revealed that Fenton pre-treatment gave a MFC product that contained a higher amount of small well fibrillated particles compared to the enzymatic and acid pre-treatment methods. The enzymatic hydrolysis, as performed in this study, increased the specific surface area as a function of mechanical treatment time comparable to a pulp without any pre-treatment. Further, the total charge was not substantially altered and the intrinsic viscosity decreased by less than 100 dm^3/kg.

Strength properties

A paperboard is commonly constructed in several plies with strong outer plies produced from chemical pulp fibres and a bulky middle ply produced from mechanical or chemimechanical pulp fibres. CTMP and HT-CTMP are often used in the middle layer due to their capacity to create high bulk and high bending stiffness (Höglund 2002). However, mechanical pulps produced with high temperature processes (e.g. HT-CTMP) contain long and stiff fibres covered with lignin which generally affect the bonding ability negatively (Pynnönen et al. 2005; Klinga et al. 2008). In this respect, the optimal properties for the middle ply layer of board are bulk high enough for the required bending stiffness, and internal bond strength high enough to avoid board delamination (Klinga et al. 2005).

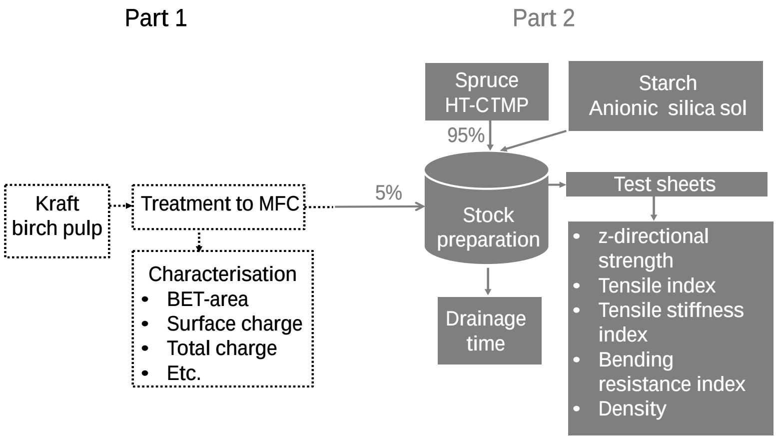

Fig 1 - Schematic description of the experimental layout. Part 1 is from Hellström et al. (2014) and Part 2 is this study.

Table 3 - Main characteristics for MFC products produced from untreated, chemically or enzymatically pre-treated birch kraft pulps mechanically processed for 0, 10, 30 and 53 min in a colloid mill. The data are taken from Hellström et al. (2014)

Analysis	*Mechanical treatment time, min*	No pre-treatment	Acid Peroxide	Fenton Low	Fenton High	Enzyme Low	Enzyme High
BET-area, m²/g	*0*	2	2		2		2
	10	4	4		6		4
	30	5	7		8		5
	53	7	9		10		6
Surface charge, µeq/g	*0*	2		5	6		7
	10	18		26	36		17
	30	23		40	44		28
	53	30		53	54		38
Total charge, µeq/g	*0*	41	38	45	58		42
Intrinsic viscosity, dm³/kg	*0*	929	445	282	186	843	844
	10	869	442	273	182	801	790
	30	884	426	268	178	807	793
	53	868	425	267	178	814	709

Strength properties

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As can be seen in *Fig 2 A-C* the z-directional strength, tensile index and tensile stiffness index increased for HT-CTMP test sheets that had been reinforced with the MFCs as described earlier. In general, sheets with MFC pre-treated with Fenton´s regent and enzymatic hydrolysis demonstrated a higher increase in strength properties compared to MFC prepared with acidic hydrogen peroxide or without pre-treatment. Fenton pre-treated MFCs improved the strength properties the most; the z-directional strength increased by about 50%, the tensile index with about 35% and the bending stiffness index with over 20%. Worth noting is the marginal difference in strength development for MFC produced with 50 kg H_2O_2/ton (Fenton High) and 10 kg H_2O_2/ton (Fenton Low) respectively indicating a possibility to reduce the hydrogen peroxide charge in the pre-treatment. Further, the change in bending resistance index is mostly within the experimental error and are slightly lower or not affected at all by the mechanical processing time (*Fig 2D*).

The levelling off in strength properties after about 30 min of mechanical treatment time probably was due to limitations in the mechanical equipment used for producing the MFCs. This assumption was based on the knowledge that the MFC products used in this study still after 53 min of mechanical processing contained a substantial amount of larger fiber fragments (Hellström et al. 2014). The improvement in strength properties were linearly proportional to sheet densities for all pre-treatments evaluated, an expected and well known relationship (Fredriksson, Höglund 1978; Rundlöf 2002). The same correlations were obtained for strength properties and surface charge (*Fig 3A-D*) and for strength properties and BET-area (*Fig 4A-D*). Deviations in both sheet preparation and furnish composition makes it difficult to compare the result obtained in this investigation with earlier published findings. However, Taipale et al. (2010) reported a 60% increase in Scott bond and 8% increase in tensile index when 5% MFC were charged to a bleached softwood kraft pulp furnish containing 1.5% cationic starch. Da Silva Perez et al. (2010) reported a tensile index increase of 20-25% when 5% MFC was added to hardwood and softwood kraft pulp furnishes and Osong et al. (2014) received 5-10% increase in z-directional strength and an insignificant increase in tensile index at 5% NFC addition level.

The strength improvement as a consequence of MFC addition is most likely due to an increased number of bonds between the stiff HT-CTMP fibers where the MFC act as a binding phase in between. In this respect a high surface area (BET) of the MFC is of importance. The MFC produced with Fenton pre-treatment have higher specific surface area and thereby a higher surface charge at a given mechanical treatment time compared to enzymatic pre-treated MFCs which indicates a possibility to reduce the energy consumption during the production of microfibrillated cellulose. The hydroxyl radicals formed in the Fenton reaction react with the cellulosic material under the formation of alkyl and carbon radicals and can lead to the opening of the anhydroglucose ring or a breakage of the cellulose chain. In both cases carbonyl groups are formed which can be further oxidised to carboxyl groups (Henniges et al. 2012; Pouyet et al. 2014). Endoglucanases are generally considered to randomly attack accessible intramolecular β-1,4-glucosidic bonds in the middle of the cellulose chain and will generate oligomers of different sizes and new reducing end groups. As a consequence, the intrinsic viscosity of the pulp fibres will decrease and the carbonyl content increase. However, the pre-treatment with endoglucanase as performed in this study resulted in a moderate decrease in intrinsic viscosity (85 dm^3/kg) without increasing the amount of carbonyl groups (Hellström et al. 2014). This indicates a mild enzymatic hydrolysis and less impact on the cellulosic material compared to the MFCs produced with Fenton pre-treatment.

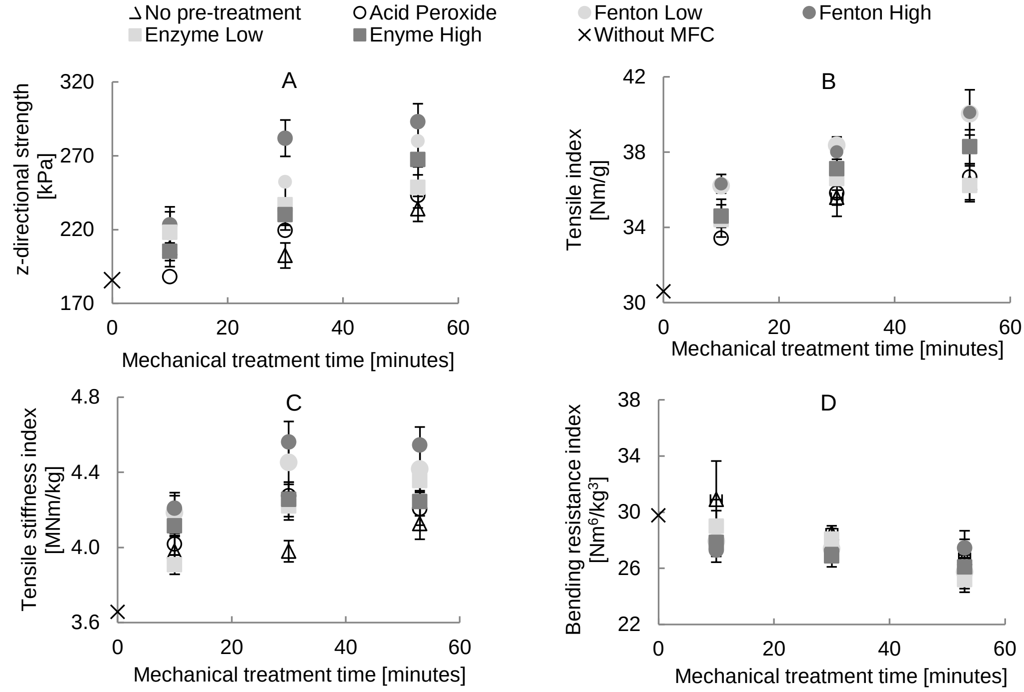
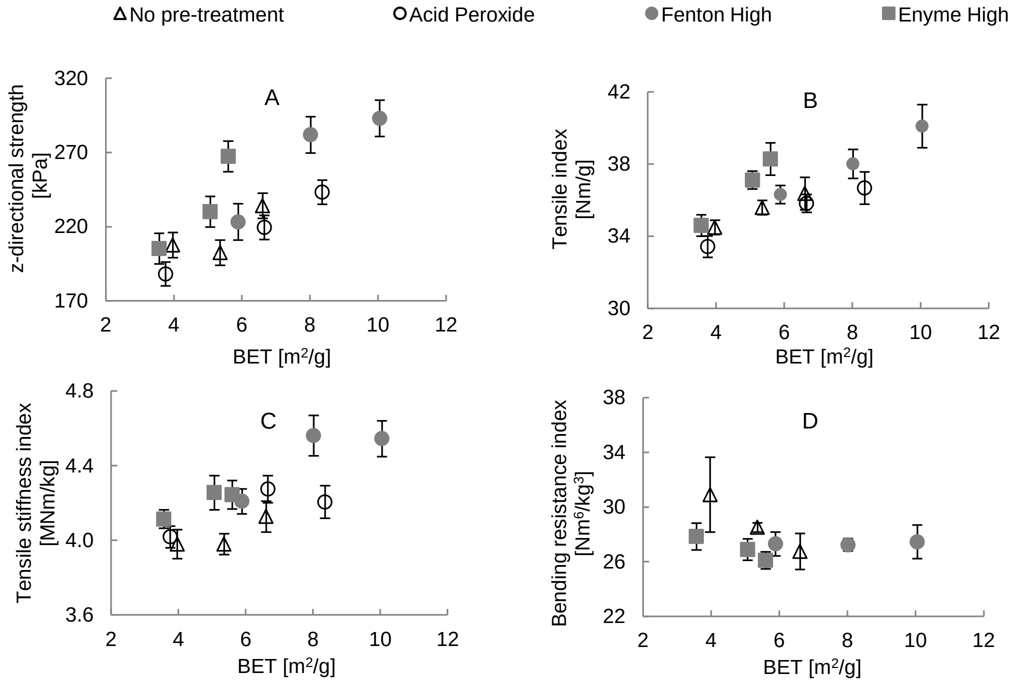


Fig 2 - Z-directional strength (A), tensile index (B), tensile stiffness index (C) and bending resistance index (D) for test sheets produced with MFC prepared without pre-treatment (No pre-treatment) as well as pre-treatment with acidic hydrogen peroxide (Acid Peroxide), Fenton´s reagent (Fenton Low and Fenton High) and enzymatic hydrolysis (Enzyme Low and Enzyme High) are in the graphs shown as a function of the mechanical treatment time in the colloid mill when producing the MFC. 95% confidence intervals are given for No pre-treatment, Fenton High and Enzyme High.



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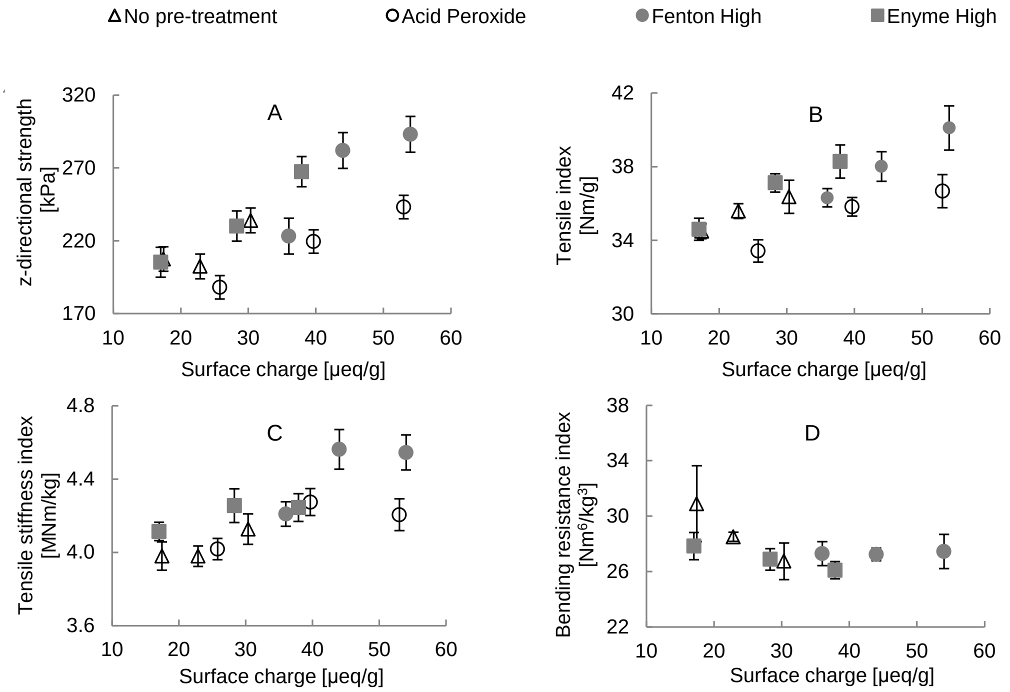

Fig 4 - Z-directional strength (A), tensile index (B), tensile stiffness index (C) and bending resistance index (D) for test sheets produced with MFC prepared without pre-treatment (No pre-treatment) as well as pre-treatment with acidic hydrogen peroxide (Acid Peroxide), Fenton´s reagent (Fenton High) and enzymatic hydrolysis (Enzyme High) are in the graphs shown as a function specific surface area (BET). Error bars show the 95% confidence interval.

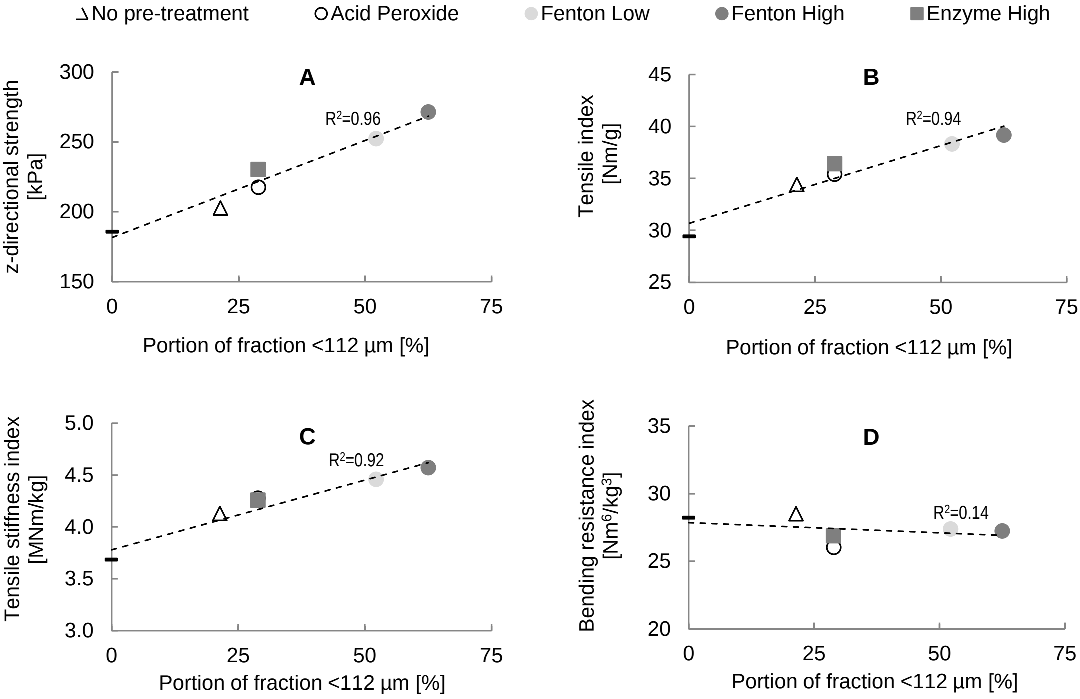

Fig 3 - Z-directional strength (A), tensile index (B), tensile stiffness index (C) and bending resistance index (D) for test sheets prepared with and without MFC (5%) as a function of the weight in percent of the MFC products that passes through a 112 µm nylon net. The MFCs were prepared without pre-treatment (No pre-treatment), pre-treatment with acidic hydrogen peroxide without addition of ferrous ions (Acidic Peroxide), Fenton´s reagent (Fenton Low and Fenton High) and enzymatic hydrolysis (Enzyme High) followed by mechanical treatment in a colloid mill for 30 min.

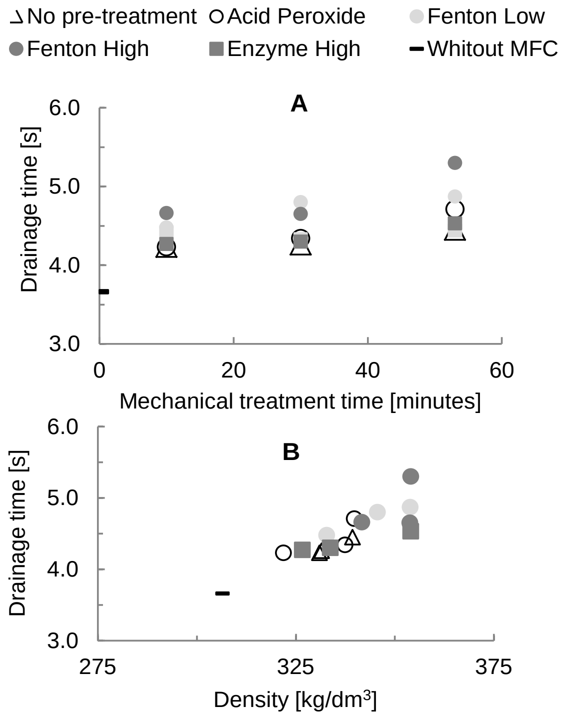

Fig 4 - Drainage time as a function of mechanical processing time in a colloid mill during the preparation of MFC (A) and drainage time as a function of sheet density (B).

There is a clear linear correlation between the weight in percent of the MFC products that passes 112 µm nylon net and the z-directional strength, tensile index and tensile stiffness index, *Fig 3 A-C*. The bending resistance index is not affected by the amount of material within this fraction, *Fig 3D*. For sheets prepared without MFC, the fraction <112 µm are considered to be zero since no small sized particles have been added. Provided uniformity in starting material and mechanical equipment when preparing the MFC, the coarse fractionation may be used for a simple and quick evaluation of the MFC as a strength enhancer in papermaking.

Dewatering

The drainage properties were measured with a DDA equipment using the furnish composition, chemical charges and addition order of chemicals as during the sheet preparation, see *Table 2*. The drainage time was increased with 20-45% (*Fig 4A*) by the addition of the differently prepared MFCs and was linearly correlated to the sheet density (*Fig 4B*) and BET-area of the MFCs (data not shown). The magnitude of the dewatering impairment are hard to compare with results presented by other researchers since it is highly dependent on the origin and beating degree of the pulp used in the furnish as well as the properties of the MFC and of the used retention system. However, Taipale et al. (2010) have shown that it is possible to improve the strength properties without deterioating the draingage by selection of approperiate MFC and process conditions.

Conclusions

Microfibrillated cellulose (MFC) prepared from a fully bleached birch kraft pulp by either mechanical treatment alone or by Fenton or enzymatic pre-treatments followed by a mechanical treatment in a colloid mill were added to a high-temperature, hydrogen peroxide bleached chemithermomechanical pulp (HT-CTMP) furnish. The pulp strength properties were assessed on test sheets formed in a dynamic sheet former. From the results it could be concluded that:

-Fenton pre-treatment resulted in MFC that when added to a HT-CTMP furnish increased the strength properties more compared to MFCs produced with monocomponent endoglucanase pre-treatment. Addition of 5% Fenton pre-treated MFC resulted in an increase in z-directional strength of about 50%, an increase in tensile stiffness index of about 25% and an increase in tensile index of 35% compared to HT-CTMP test sheets prepared without MFC addition.

-The improvement in strength properties was proportional to sheet density, to the surface area (BET) and to the surface charge of the MFC

-The strength improvement as a consequence of MFC addition is most likely due to an increased number of bonds between the stiff HT-CTMP fibres where the MFC act as a binding phase in between.

-The amount of MFC particles smaller than 112 µm correlates well with measured paper board strength properties.

-The drainage time increased with 20-45% by addition of the differently prepared MFCs and was linearly correlated to the sheet density and to the surface area of the MFCs.

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