Energy consumption of the nanofibrillation of bleached pulp, wheat straw and recycled newspaper through a grinding process

Sébastien Josset, Paola Orsolini, Gilberto Siqueira, Alvaro Tejado, Philippe Tingaut, and Tanja Zimmermann

KEYWORDS: Energy consumption, Nanofibrillated cellulose, Fibrillation, Grinding, Waste materials

SUMMARY: Cellulose nanofibrils (CNF) are steadily gaining attention since this material is a renewable alternative to artificial polymers. Moreover, waste products from cellulose-based industries (*e.g.* paper mills) or from agriculture can be used as raw material for CNF isolation. However, the up-scaling from the laboratory to the industry can only be achieved if the energy costs are low enough to compete against low-price petroleum derivatives. The objective of this work is to present an energy-related study of the direct fibrillation of cellulose-based materials using a grinding process. Two waste materials, namely wheat straw and recycled newspaper, have been investigated as starting materials, together with bleached wood pulp for comparison purposes. The mechanical properties and specific surface areas of the resulting fibrillated materials are then presented and systematically compared with each other. The properties of the bleached wood-pulp fibres exhibited the highest values that were reached already at low energy inputs. The different properties of CNF isolated out the waste materials could reach values close to their maxima for energy inputs as low as about 5 kWh/kg compared to the *ca.* 10 kWh/kg needed with high pressure homogenization.

ADDRESSES OF THE AUTHORS:
Sébastien Josset (Sebastien.Josset@empa.ch)**, Paola Orsolini** (Paola.Orsolini@empa.ch)**, Gilberto Siqueira** (Gilberto.Siqueira@empa.ch)**, Philippe Tingaut** (Philippe.Tingaut@empa.ch)**, Tanja Zimmermann** (Tanja.Zimmermann@empa.ch): Empa, Swiss Federal Laboratories for Materials Science and Technology, Laboratory of Applied Wood Materials, Überlandstrasse 129, 8600 Dübendorf, Switzerland
Alvaro Tejado (Alvaro.Tejado@tecnalia.com): Tecnalia Research & Innovation, Área Anardi 5, 20730 Azpeitia – Gipuzkoa, Spain
Corresponding author: Sébastien Josset

Due to environmental concerns, increasing oil prices and more drastic international regulations, there is a need for green alternatives for the elaboration of functional materials (*i.e.*, packaging, construction, purification technologies, automotive or biomedical applications for instance). In this context, the use of natural renewable polymers has steadily gained a strong interest over the last three decades, and still remains one challenge of the 21st century. Plants contain the largest amount of organic polymers on Earth, cellulose representing among them about 1.5×10^{12} tons of the total annual biomass production (Klemm et al. 2005; Siro, Plackett 2010). Different types of nanomaterials can be isolated from cellulose using physical, enzymatic and/or chemical treatments. Among the most popular nanoelements that have been the object of intensive studies over the last years, cellulose nanocrystals (also called cellulose "nanowiskers") and "cellulose nanofibrils (CNF)" materials, which are in focus of this study, have been mainly envisaged.

Apart from the advantages related to the native biopolymers, such as low densities, renewability and biodegradability, cellulose nanomaterials also possess very specific characteristics, such as high aspect ratios and high specific strengths (Bledzki, Gassan 1999; Samir et al. 2005; Ishii et al. 2011). CNF consist of long, flexible and interconnected fibrils, with diameters from 10 to 100 nm and aspect ratios from 50 to 100 (Turbak et al. 1983; Boldizar et al. 1987; Zimmermann et al. 2004; Gardner et al. 2008).

Besides the costs of the starting material, the different CNF production processes are significantly energy consuming, but only few works have focused up to now on the energy costs of the CNF production, which are however of major importance for their subsequent use at the industrial level (Spence et al. 2011; Jonoobi et al. 2012; Qing et al. 2013). Two main CNF production methods have been reported: homogenisation and grinding processes (Herrick et al. 1983; Turbak et al. 1983; Taniguchi, Okamura 1998; Abdul Khalil et al. 2014). In a very interesting study related with the energy consumption of these different fibrillation techniques, Spence et al. (2011) the homogenisation process has been shown to be the most expensive method for CNF isolation.

The main difficulty with the homogenisation process, commonly used in other industrial fields, is inherent to the morphology of the starting material which often tends to clog the production apparatus. Moreover, the direct fibrillation of cellulosic materials using homogenisation has been shown to require relatively large energy inputs of about 27 kWh/kg (Lindström, Winter 1988). For these reasons, a pre-treatment of the fibrous material is usually performed in order to decrease the size of the cellulose fibres and ease the fibrillation process. This pre-treatment can be performed mechanically, but it has been shown that chemical or enzymatic pre-treatments could also lead to significant improvements in terms of energy consumption – up to 98% energy savings - and/or properties (Saito et al. 2006; Henriksson et al. 2007; Pääkkö et al. 2007; Henriksson et al. 2008; Wagberg et al. 2008; Ankerfors 2012). These aspects are discussed in recent publications of Tejado et al. (2012), Ankerfors et al. (2012) and Abdul Khalil et al. (2014).

The fibrillation method used in the present work is the grinding process first reported in 1998 (Taniguchi,

Okamura 1998; Iwamoto et al. 2005). Indeed, the fibrillation is the result of the shearing forces occurring between two ceramic stones, one rotating, and the other acting as a stator. The fibres are usually processed sequentially, passing several times through the adjustable clearance between grinding stones, until the desired quality is reached (Iwamoto et al. 2007). CNF with diameters down to 15 nm have been reported after fibrillating a water suspension of pre-treated wood fibres with this technique (Abe et al. 2007).

One of the main advantages of the use of a grinding process can be seen in its simplicity and its robustness. Compared to high pressure homogenization processes, it does not have blocking problems generated by larger fibers. However, the CNF obtained through this method appears to be less homogeneous in terms of fibril diameters compared with CNF processed by high-pressure homogenisation since large bundles of fibrils can still be observed (Qing et al. 2013). Moreover, degradation of the pulp fibers resulting from the high shear forces generated by the grinding stones was reported in the literature (Iwamoto et al. 2007).

Wood-based fibres have been widely used to produce CNF, however, other less expensive plant-based or even waste materials are increasingly being considered, including wheat straw, sugar beet pulp, potato pulp, bagasse, sludge, etc. (Alemdar, Sain 2008; Siro, Plackett 2010; Zimmermann et al. 2010). The present study deals with the fibrillation of different materials through the "super-grinding" technique mentioned above.

The objective of this work is to provide an energy-related description of CNF production from cellulosic waste materials, and assess a potential reuse of those materials. The first material is issued from the processing of wheat straw through a bio-refinery plant (WS), whereas the second one consists of fibres obtained from recycled newspapers (NP). Bleached wood-pulp fibres (ECF) have also been processed into CNF for comparison purposes. Among microscopic observations and mechanical characterisations, the specific surface area (SSA) was determined to estimate the "fibrillation degree" of the materials at the different grinding stages.

Materials and Methods

Materials

Three materials have been used in this study.

Elemental Chlorine Free (ECF) fibers from bleached softwood-based pulp-fibers (*Picea abies* and Pinus spp.) were obtained from *Stendal* (Berlin, Germany) and used as reference material.

The recycled newspapers (NP) were obtained from *Ecopulp* (Koria, Finland) and processed as received. This material is based on recycled thermo-mechanical pulp obtained from newspapers, without inks removal.

The wheat straw (WS) is an agricultural waste product used for bioethanol production and was used as received from the *Compagnie Industrielle de la Matière Végétale (*Estillac, France). This fibre material has been pre-treated prior to use in bio-refinery. Pre-treatments of the wheat straw pulp included the impregnation of the raw material with a mixture of acetic acid/formic acid and water (85% acids/15% water) followed by the extraction of the lignin at 105°C for 3 h by adding hydrogen peroxide (H_2O_2) directly in the acidic media. This leads to the formation of peracetic and performic acids which react with the lignin. The slurry was then washed and treated in alkaline conditions to extract silica and finally washed with water (Kham et al. 2005).

The costs of these different materials are respectively about 700 €, 150 € and 400 € per dry tonne. Their chemical compositions can be found in *Table 1*.

Fibrillation

The three materials were obtained in wet state, with water contents higher than 70 wt.%. 20 l slurries were prepared from the different materials, adjusting the dry solid content to 2 wt.%. These slurries were allowed to stay at room temperature for 24 h in order to let the fibres swell. This swelling time is necessary to allow the inclusion of water molecules between the microfibrils, leading to an easier fibrillation process. This phenomenon is driven by osmotic forces due to the presence of charged groups on the cellulosic chains, depending on the nature of the material and on its pre-treatment (*e.g.* bleaching) (Ankerfors 2012).

The slurries were processed with a "Supermass Colloider" (MKZA10-20J CE) from the company *Masuko Sangyo Co.,Ltd.* (Kawaguchi/Saitama, Japan) equipped with non-porous grinding stones made out of SiC/Al_2O_3 particles in resin. The rotating grinding stone was driven at the nominal velocity (*ca.* 1500 rpm, motor-load: 15 kW).

The slurries were grinded 10 times through the device while recording the energy consumption with a power-meter. This value was normalised by the dry weight of the material processed.

For each grinding cycle, the stones were first carefully brought close to contact, as noticed by the starting of a low friction-sound, then the slurry was poured into the hopper and, as soon as it touched the stones, these were tightened as close as possible, so that the clearance appeared to be "negative" on the monitor. The clearance was adapted to limit the temperature increase of the slurries to 50°C leading to flow-rates of *ca.* 5 l/min. Concerning the first two grinding cycles of the ECF, the flow-rate was set to *ca.* 10 L/min in order to prevent excessive water squeeze-out which leads to engorgement at the early fibrillation stages.

Two independent samples of *ca.* 50 ml of the suspensions were collected at each stage for further analysis.

Table 1 - Chemical analysis of the materials. ECF: elemental chlorine free bleached wood-pulp fibers; NP: recycled newspaper-based material; WS: wheat straw-based material

Material	ECF	NP	WS
Cellulose	81.3%	47.3%	83.1%
Hemicellulose	12.6%	18.9%	5.6%
Lignin	0.0%	17.8%	1.3%
Ash	0.3%	10.3%	4.6%
Total	94.2%	94.3%	94.6%

Mechanical tests

For each material, films (diameter 9 cm) were prepared by filtering the CNF suspensions over a metallic filter with pore size of 5 μm, and subsequent hot-pressing of the wet cakes. Each film was first hot-pressed at 120°C at 1000 N/cm^2 for 10 min between two metal meshes, these placed between two felts and then 1 min under the same conditions, but directly between the heating metal-plates of the press. The films were prepared from suspensions collected at different grinding cycles (*i.e.* 0, 2, 4, 6, 8 and 10 grinding cycles, respectively). Two films were prepared per cycle. Out of each paired-films, 12 dog-bone shaped specimens were punched out (length 5 cm, surface 330 mm^2, width of the central part 4 mm). They were allowed to equilibrate 18 h at 23°C and 50% RH.

Mechanical properties in tension were determined using a Zwick Z010/TH2A (Zwick GmbH& Co. KG, Ulm, Germany): Young's modulus (E), Tensile strength (σ at F_{max}) and elongation to break (ε at F_{max}). The pre-load applied was 0.2 N, the loading speed 2 mm/min. The Young's modulus (E) was determined using the strain curve between elongations from 0.05% and to 0.25%. The results presented are the mean values and the standard deviation of at least 5 values.

The statistical analysis of the mechanical properties was performed using Matlab R2011b. For each material and each mechanical property, a multiple comparison of the mean differences vs. the energy consumed was performed using the Tukey–Kramer method (TKM) at a 5% significance level (Kramer 1956).

Aerogels preparation through critical point drying

The water of the slurries was exchanged with ethanol, which shows higher solubility in liquid CO_2. For each sample, 10 g of suspension (2 wt.% solid content) were vigorously stirred with 30 ml of an ethanol:isopropanol (E95, 95% v/v:5% v/v) mixture and filtered on a metal mesh (pore size ca. 5 μm) to obtain a wet filtration cake of about 2 g. This filtration cake was re-dispersed in 40 ml of E95 and filtered to obtain again a wet filtration cake. This second step was repeated one more time with E95 and finally once with absolute ethanol (99.9% v/v). Each filtration cake was placed in a metal mesh, rolled to form a tube (*ca.* 60 mm length, diameter *ca.* 10 mm, pore size 300 μm) and stored in a closed vessel to avoid premature drying before aerogel preparation.

After this water-to-ethanol exchange, the ethanol was replaced by liquid CO_2 in a pressurised chamber (model: E3000, *Quorum Technologies*, Newhaven, U.K.). The pressurised chamber was first cooled down to 10°C, and filled with liquid CO_2 (pressure: 60 bar). The system was let to equilibrate for one hour, the reason of the use of mesh-tubes being the increase of the diffusion of the liquid species (*i.e.* ethanol and liquid CO_2). Then, the upper CO_2 inlet was closed and liquid CO_2 slowly allowed to flow out through the underneath exhaust, until the surface of the liquid CO_2 reached the top of the samples situated at the mid-height of the chamber. This flushing step was repeated twice and the chamber was filled again and let for one hour. This whole procedure was realised five times. The samples were stored in a desiccator.

Specific surface area (SSA) measurements

The Brunauer–Emmett–Teller (BET) surface area was determined according to a multipoint BET method by N_2 physisorption on a surface area. For each measurement, an amount comprising between 60 mg and 200 mg of each aerogel was dried overnight at 105°C and the dry weight of each sample was determined. An automated device from *Micrometerics* (Ottawa, Canada, model: SAP 2020) was used to determine the B. E. T. surface of the aerogels. Prior to the measurement at 77 K with N_2, each sample was degased for one hour to remove the water adsorbed during the transfer to the measurement cell (20°C to 75°C within 30 min, then 75°C 30 min, 5 μmHg).

Optical microscopy

For each material, 1 ml of slurry collected after 0, 7 and 10 grinding cycles was diluted to *ca.* 0.1% w/w and a droplet dried over a glass slide at 105°C for 10 min. After this fixation step, the fibres were double-stained with astra blue and safranin (Gerlach 1977).

Electron microscopy

For each material, 1 ml of slurry collected after 0, 7, 9 and 10 grinding cycles was diluted to *ca.* 0.1% w/w and placed on a mica platelet. All samples were sputter coated directly with a platinum layer of about 8 nm (BAL-TEC MED 020 Modular High Vacuum Coating Systems, BAL-TEC AG, Liechtenstein). SEM images were taken with a FEI Nova NanoSEM 230 instrument (FEI, Hillsboro, Oregon, USA) at an acceleration voltage of 5 kV.

Statistical analysis of the mechanical properties

Many parameters during the preparation of the samples can lead to heterogeneities; the Tukey-Kramer Method (TKM) was used to determine if the observed differences were significant. This method supposes that the mean values are obtained from normally distributed populations which have the same finite variance (Kramer 1956).

Due to the sample size ($5<n<10$) in this work, it is difficult to assess if these assumptions are observed. However, the standard deviation can be used to estimate the variance and it has been shown that the TKM is robust to deviations from the normal distribution (Driscoll 1996).

Briefly, the TKM makes comparisons of all possible pairs in a group of average values and tests if their differences are significant. In this work, for each material and each property, average values and variances were calculated at 0, 2, 4, 6, 8 and 10 grinding cycles and the TKM was then used to compare each pair of averages. For a better reading of the results, each average value is usually classified as belonging into one or more arbitrary group which are denominated by letters. If two average values have one or more group in common, they cannot be considered as different at the chosen significance level (5% in this work).

Results

Microscopies

Fig 1 and *2* present optical and electronic micrographs of the starting materials, as well as after 7 and 10 grinding cycles, respectively. The ECF fibers appeared in blue under the optical microscope since they only contain cellulose which is preferentially stained by the astra blue. The fibers of the recycled newspaper (NP) and of the wheat straw (WS) displayed both blue and red colours, since these fibers contain both cellulose and lignin, the latter being preferentially stained in red by the safranin. Both ECF and WS starting materials are composed of relatively intact fibers with diameters around 50 µm, while on the contrary to the NP ones are already fibrillated as a consequence of the refining processes.

For all materials, fibrils could be observed at the early grinding stages but large amounts of macroscopic fibers were still present. The proportion of these large fibers appeared to be progressively reduced during the grinding process and a network of interconnected nanofibers could be observed for all materials after 10 grinding cycles, even if some fibers can still be observed at the end of the treatment in all cases as shown on the (*Fig 2* and *3*).

Energy consumption

The evolution of the energy consumption upon grinding cycles for the three materials is presented in *Fig 3A*. For all materials, the energy consumptions increased almost linearly after two grinding cycles, with an energy-consumption rate of *ca*. 0.7 kWh/kg per grinding cycle. On a dry-weight base, the whole treatment of the ECF fibers (10 cycles) consumed 5.25 kWh/kg, the WS fibers 5.75 kWh/kg and the NP fibers 6.75 kWh/kg.

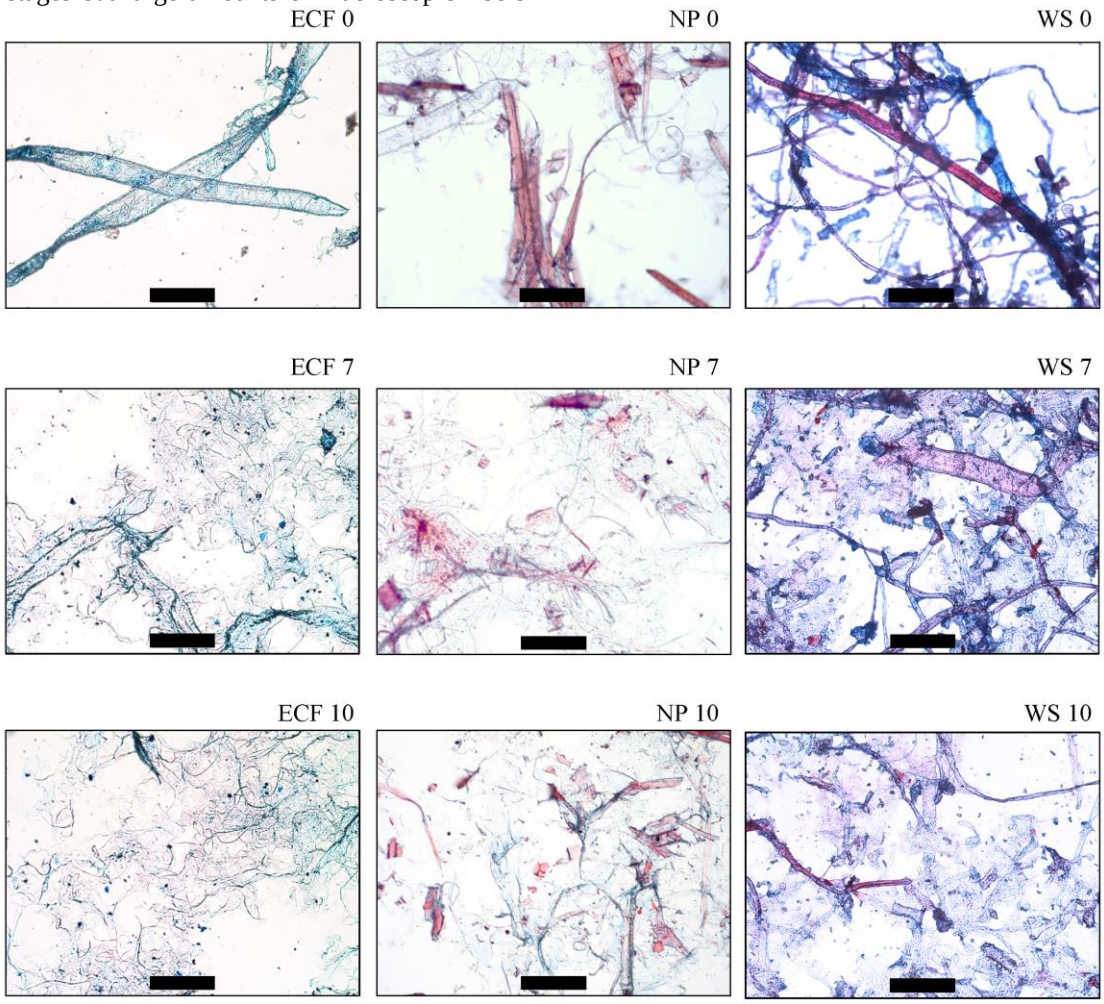

Fig 1 - Optical micrographs of the different materials after 0, 7 and 10 grinding cycles. The samples were double stained with astra blue and safranin. Scale bar is 100 µm.

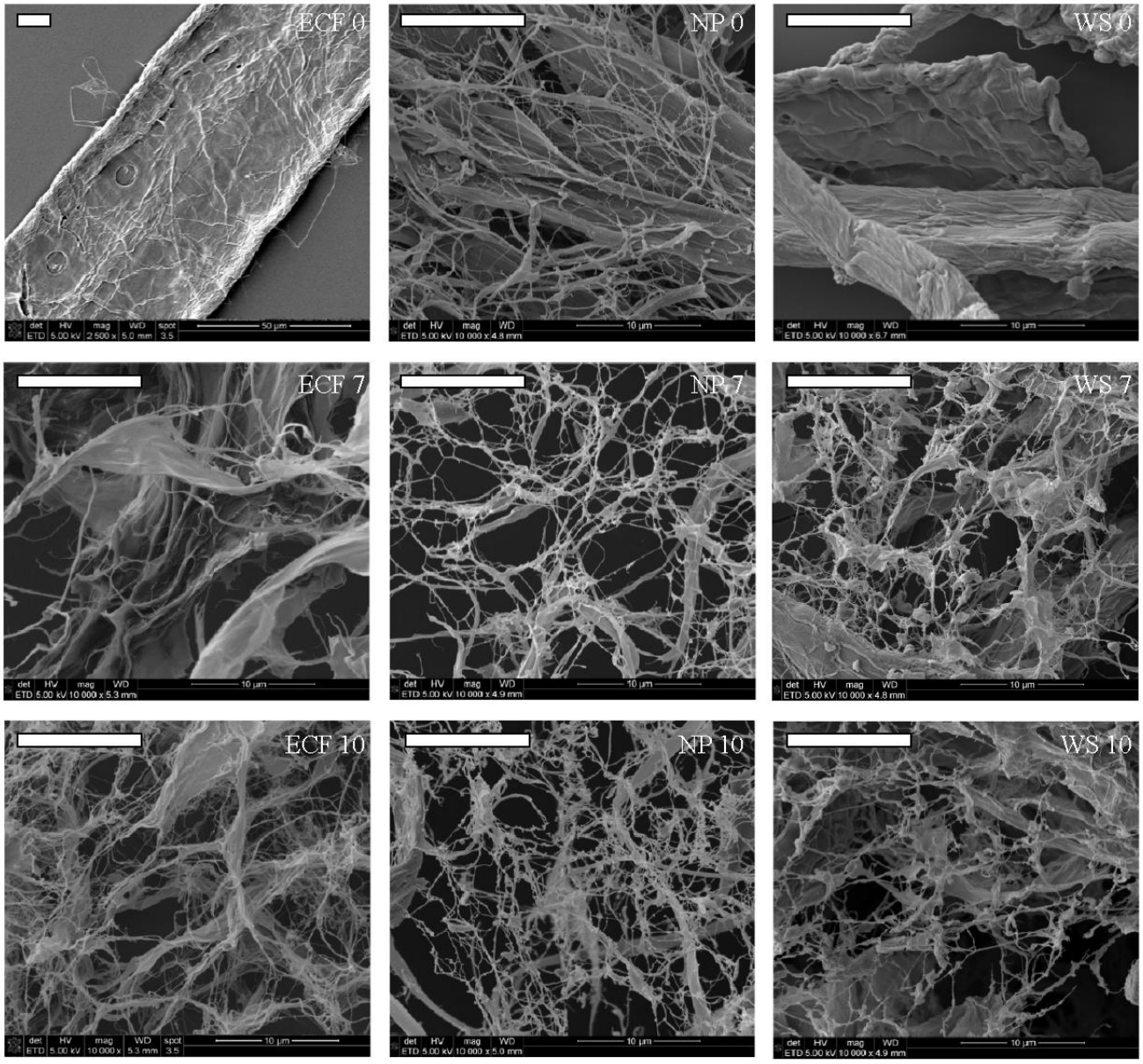

Fig 2 - SEM micrographs of the different materials after 0, 7 and 10 grinding cycles. Scale bar is 10 µm.

SSA measurements through N_2 adsorption

Specific Surface Area (SSA) measurements can be performed in the liquid phase by dye adsorption techniques *e.g.* with methylene blue or Congo red, (Jonoobi et al. 2012) but the results have been shown to be affected by the chemical composition of the fibres (Spence et al. 2011). Moreover, the remaining ink and more generally the chemical composition of the water matrixes would have biased such spectrophotometric measurements. Hence, SSA determinations through N_2 adsorptions (Brunauer–Emmett–Teller theory) were preferred in this work since they are considered to be independent from the chemical composition.

However, the samples need to be completely dried prior to the measurements and this is a major difficulty with CNF which tend to aggregate through a process called "hornification" (Young 1994; Eyholzer et al. 2010), obviously leading to very low SSA. Sehaqui et al. (2011b), showed that supercritical CO_2 drying leads to much higher SSA in comparison to other drying techniques, *e.g.* oven drying or freeze drying. Hence, this procedure was used to prepare the samples.

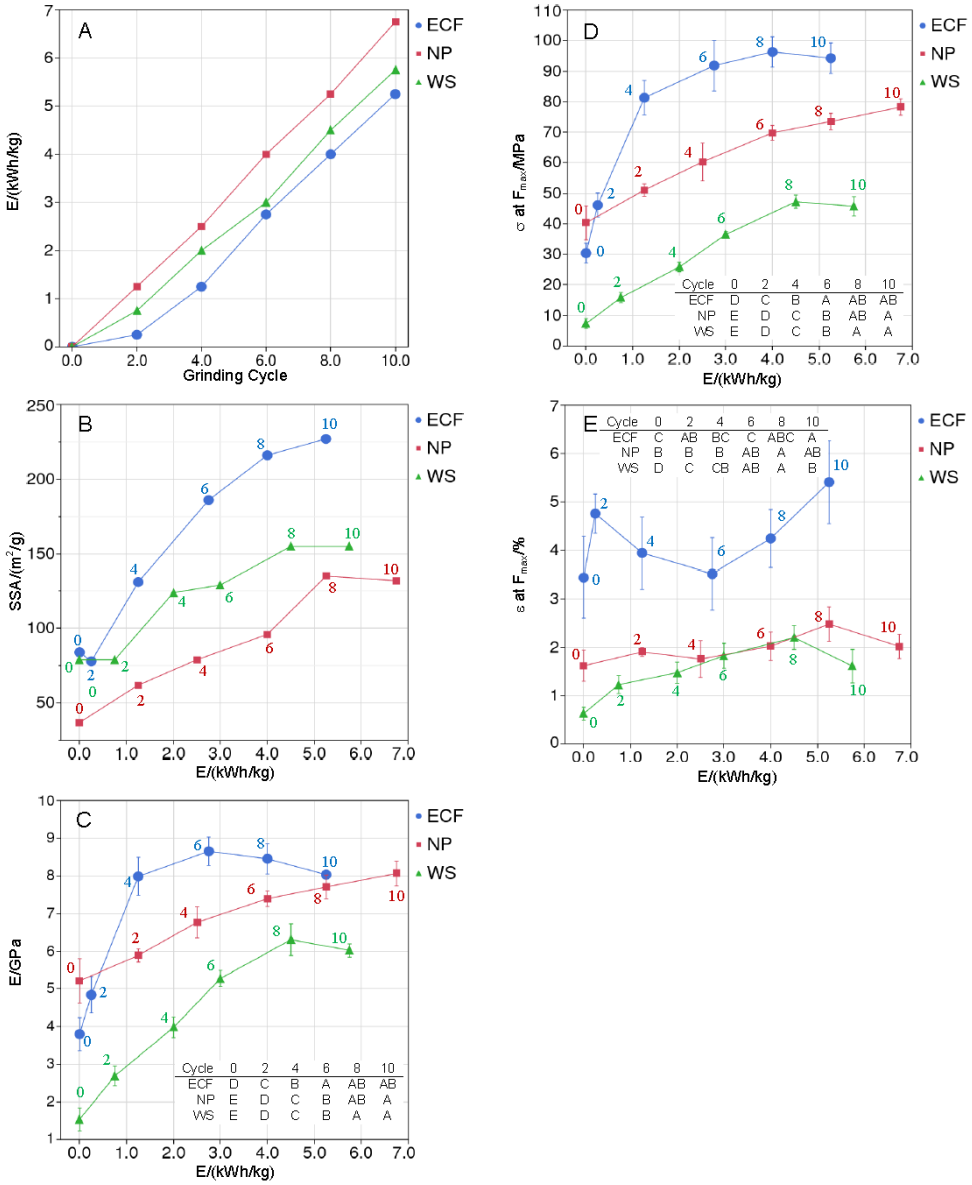

Fig 3 - Properties of each NFC materials from bleached softwood pulp (ECF), recycled newspaper (NP), and wheat straw (WS) after 0, 2, 4, 6, 8 and 10 grinding cycles. A) Energy consumed vs. grinding cycle. B) Specific surface area vs. consumed energy. C) Density vs. consumed energy. D) Young's modulus vs. consumed energy. E) Tensile strength vs. consumed energy. F) Elongation at break vs. consumed energy. For the mechanical properties, the mean values and the standard deviation of at least five measurements are depicted. The table indicates for each material which averages can be considered different at 5% significance level: if two values have at least one letter in common, they cannot be considered different at this significance level.

As shown in *Fig 3B*, the SSA of the three materials significantly increased during the grinding process. A direct comparison between the materials indicates that the CNF from ECF presented a higher SSA than NP and WS, after all grinding cycles. For all materials envisaged in this study, a gradual increase of the SSA has been observed with the grinding cycles, as expected. These results are in agreement with a progressive fibrillation of the materials upon grinding cycles previously observed with SEM (*Fig 1*). After 8 grinding cycles, the increase in SSA was slowed for the ECF which reached after 10 cycles a final SSA of 226 m^2/g for 5.25 kWh/kg. Both NP and WS even reached plateaus of respectively 132 m^2/g (for 6.75 kWh/kg) and 155 m^2/g (for 5.75 kWh/kg). This latter trend could be associated with the highest fibrillation level reachable for these two materials with this grinding technique.

Young's modulus

An increase of the Young's modulus (E) has been generally observed upon fibrillation for all materials studied here, but different trends were observed between the samples (*Fig 3C*).

CNF films prepared from ECF and WS nanofibers displayed the same profile, with a rapid increase of E during the first grinding cycles before reaching a plateau above which any variation in E could no longer be considered as significant. This plateau has been reached at an earlier stage for the films prepared from ECF compared with those from WS (*i.e.*, 1.25 kWh/kg versus 4.5 kWh/Kg, respectively), which may indicate that the

energy demand for a full fibre fibrillation through grinding is lower for ECF than for WS fibers (*Fig 3C*). In contrast, the recycled fibers of the NP material showed a regular increase of E at a rate of *ca.* 400 MPa/(kWh/kg) upon fibrillation. However, the TKM methods showed that there is no statistically significant difference between the E values obtained from the films made out of fibers grinded 8 and 10 cycles. The films prepared with this material reached a similar value than the ECF fibers (8 GPa) but for 5.25 kWh/kg instead of 1.25 kWh/kg.

The *Fig 3C* allows a direct comparison between samples concerning the energy consumption required per material to reach a specific E value. Looking at an energy consumption between 3.0 and 5.5 kWh/kg (*i.e.*, between 4 and 10 grinding cycles, respectively, see graph), the highest stiffness could be reached for the CNF films prepared from ECF, with a E above 8 GPa, followed by the CNF prepared with NP and finally the WS fibers.

Tensile strength

The tensile strengths (σ) of the 3 different materials are depicted in *Fig 3D*. In the case of the ECF fibres, the tensile strength rapidly increased during the first grinding cycles and, similarly to the other mechanical parameters, did not vary significantly from its maximum (between 90 and 100 MPa) after 1.25 kWh/kg despite further energy inputs.

For the waste materials, the increase in the tensile strength was almost linear at the beginning of the process and both materials reached a plateau after 6 (WS) and 8 (NP) grinding cycles. The NP reached 75 MPa whereas the WS peaked between 40 and 50 MPa for energy inputs larger than 4 kWh/kg. Once again, this result seems to indicate that the degree of crosslinking density between cellulose nanofibers in the ECF films was higher than for the other materials prepared from NP and WS.

Strain at break

The evolution of the strain at break (ε) with the energy consumption is presented in *Fig 3E*. For all materials envisaged in this study, a higher ε has been measured for films elaborated with fibrillated material as compared with samples prepared with non-fibrillated fibres. A direct comparison between samples led to the same trend already observed for E and σ, the highest value being measured for films elaborated with ECF nanofibres.

Thus, the ECF fibre films exhibited the highest elongation potential of the three materials. The films made out of non-fibrillated fibres could be strained up to 3%. After the whole grinding treatment, they resisted to stress leading to deformation of more than 5%. The evolution between the starting material and the final product was however not absolutely consistent since the dispersion of the results was quite high for this material.

The elongation potential of the waste materials remained quite low, increasing from 0.5% to 1.5% for the WS, whereas the NP did not present significant changes at all (*ca.* 2% strain during the whole grinding process).

Discussion

The high-energy demand for the CNF isolation processes is frequently reported as an issue which limits its application and commercialization (Siro, Plackett 2010; Ankerfors 2012). Recent reports indicate that the energy consumption during the isolation of CNF is in the range of 5 to 30 kWh/kg, when using bleached cellulose pulp without pre-treatment (Zimmermann et al. 2010; Klemm et al. 2011; Spence et al. 2011; Wang et al. 2012). In this work, energy consumptions between 5 and 7 kWh/kg for high quality CNF were recorded (10 passes through the grinder) and are therefore in a similar range. However, those values can be reduced to *ca.* 1.5 kWh/kg when using sludge (Jonoobi et al. 2012) or enzymatic pre-treatments (Rezayati Charani et al. 2013). For TEMPO-oxidized bleached-cellulose pulp, the energy required for isolation is reported to be lower than 2 kWh/kg (Isogai et al. 2011).

The fibrillation of wheat straw is quite well documented in the literature but to the best of our knowledge, the literature concerning the fibrillation of newspaper material is very scarce, with only one reported value concerning the costs engaged for its fibrillation of 95$/kg (Spence et al. 2011).

Concerning the Young's modulus values, other authors have reported the tensile properties of cellulose nanofibres films. For instance, a value of 14 GPa for E has been obtained by Henriksson et al. (2007) for CNF films produced out of pre-enzymatically treated bleached pulp. For TEMPO-oxidized CNF network, Sehaqui et al., (2011a) found a value of 13.5 GPa for E. Yano and Nakamura (2004), reported values of E for CNF films equal to *ca.* 16 GPa, but in this case the CNF was produced via high pressure homogenisation.

Zimmerman et al. (2004) showed that CNF produced via high pressure homogenisation can demand energy amounts in the range of 8.5 - 14.8 kWh/kg. The CNF films they obtained presented E values ranging from 5.5 to 6.0 GPa. In the present work, up to three times lower energy inputs were required to produce films with E values comprised between 6 and 9 GPa.

The tensile strength values of the films elaborated with CNF from ECF are comparable with the literature data for films prepared with nanofibers from bleached softwood pulp (Syverud, Stenius 2009; Qing et al. 2013). The lower values obtained for WS and NP samples, compared to CNF from bleached softwood pulp (ECF), can be attributed to the differences on the chemical composition of the samples. Compared to WS, ECF presents higher hemicellulose content and according to Iwamoto et al. (2008), hemicelluloses contribute to the adhesion between nanofibers in the dried state, leading to an improvement in the strength and stiffness of the films produced out of them.

Concerning the mechanical performance of CNF from recycled newspaper, inorganic components (e.g. inks, impurities) might have increased the stiffness (similar performance compared with ECF after 10 fibrillation cycles), but however decreased tensile strength of the resulting films (Syverud, Stenius 2009; Sehaqui et al. 2011a; Sehaqui et al. 2013). The CNF produced from NP exhibited the lowest SSA of the three materials with 132 m^2/g in comparison to the 227 m^2/g and 155 m^2/g obtained respectively with the CNF from ECF and WS. This could have led to low tensile properties but the

presence of impurities could have positively contributed to the observed values of E (*ca.* 8 GPa) and σ (*ca.* 80 MPa) close to those obtained with the ECF CNF (respectively 8 GPa and 95 MPa).

The elongations at break values for ECF samples are in the same range of the ones reported in the literature (e.g. 2.5 to 8.0% for cellulose nanofibers network produced from untreated bleached cellulose pulp or pre-treated via TEMPO oxidation or enzymes (Henriksson, Berglund 2007; Syverud, Stenius 2009; Sehaqui et al. 2011a; Spence et al. 2011). However, it can be observed that elongation at break for waste materials remained low independently of fibrillation degree. Similar to the other properties, it might be influenced by the presence of inorganics components and lignin which rendered the samples more brittle.

Conclusion

Here we prove that CNF films out of this material reach similar mechanical properties than the ECF fibres, even if its elongation at break was sensibly lower than for the films made out the other materials, as well as its specific surface area. The fact that this material appears already fibrillated prior to the treatment surely participates to these results and makes it an interesting low-cost starting material for CNF production.

Finally, it could be observed that the films of the three cellulosic materials tested in this study reached maxima in their mechanical properties for low energy inputs. Especially in the case of the ECF, only 1.25 kWh/kg were needed to obtain high increases in tensile strength and stiffness. For the other materials, the energy inputs for reaching the best mechanical properties of the prepared films were higher and around 4 to 5 kWh/kg.

Acknowledgements

The authors gratefully acknowledge the financial support from the European Commission, under the INNOBITE project (Grant Agreement nº 308465, FP7-ENV-2012-6-3-1), as well as the Swiss National Science Foundation. The authors further thank E. Strub and A. Huch for the electronic microscopy, Dr. M. Santhosh for the BET measurements, and M. Rees for the mechanical characterisations.

Literature

Abdul Khalil, H. P. S., Davoudpour, Y., Islam, M. N., Mustapha, A., Sudesh, K., Dungani, R. and Jawaid, M. (2014): Production and modification of nanofibrillated cellulose using various mechanical processes: A review, Carbohydrate Polymers, 99(0), 649-665.

Abe, K., Iwamoto, S. and Yano, H. (2007): Obtaining Cellulose Nanofibers with a Uniform Width of 15 nm from Wood, Biomacromolecules, 8(10), 3276-3278.

Alemdar, A. and Sain, M. (2008): Isolation and characterization of nanofibers from agricultural residues – Wheat straw and soy hulls, Bioresource Technology, 99(6), 1664-1671.

Ankerfors, M. (2012): Microfibrillated cellulose: Energy-efficient preparation techniques and key properties. Department of Fibre and Polymer Technology Royal Institute of Technology, Stockholm.

Bledzki, A. K. and Gassan, J. (1999): Composites reinforced with cellulose based fibres, Progress in Polymer Science, 24(2), 221-274.

Boldizar, A., Klason, C., Kubat, J., Naslund, P. and Saha, P. (1987): Prehydrolyzed Cellulose as Reinforcing Filler for Thermoplastics, International Journal of Polymeric Materials, 11(4), 229-262.

Driscoll, W. C. (1996): Robustness of the ANOVA and Tukey-Kramer statistical tests, Computers & Industrial Engineering, 31(1–2), 265-268.

Eyholzer, C., Bordeanu, N., Lopez-Suevos, F., Rentsch, D., Zimmermann, T. and Oksman, K. (2010): Preparation and characterization of water-redispersible nanofibrillated cellulose in powder form, Cellulose, 17(1), 19-30.

Gardner, D. J., Oporto, G. S., Mills, R. and Samir, M. (2008): Adhesion and surface issues in cellulose and nanocellulose, Journal of Adhesion Science and Technology, 22(5-6), 545-567.

Gerlach, D. (1977): Botanische Mikrotechnik (2.Aufl.), Georg Thieme Verlag, Stuttgart.

Henriksson, M. and Berglund, L. A. (2007): Structure and properties of cellulose nanocomposite films containing melamine formaldehyde, Journal of Applied Polymer Science, 106(4), 2817-2824.

Henriksson, M., Berglund, L. A., Isaksson, P., Lindström, T. and Nishino, T. (2008): Cellulose Nanopaper Structures of High Toughness, Biomacromolecules, 9(6), 1579-1585.

Henriksson, M., Henriksson, G., Berglund, L. A. and Lindström, T. (2007): An environmentally friendly method for enzyme-assisted preparation of microfibrillated cellulose (MFC) nanofibers, European Polymer Journal, 43(8), 3434-3441.

Herrick, F. W., Casebier, R. L., Hamilton, J. K. and Sandberg, K. R. (1983): Microfibrillated cellulose: morphology and accessibility, J. Appl. Polym. Sci.: Appl. Polym. Symp 37:797-813 (United States) ITT Rayonier Inc., Shelton, WA.

Ishii, D., Saito, T. and Isogai, A. (2011): Viscoelastic Evaluation of Average Length of Cellulose Nanofibers Prepared by TEMPO-Mediated Oxidation, Biomacromolecules, 12(3), 548-550.

Isogai, A., Saito, T. and Fukuzumi, H. (2011): TEMPO-oxidized cellulose nanofibers, Nanoscale, 3(1), 71-85.

Iwamoto, S., Abe, K. and Yano, H. (2008): The Effect of Hemicelluloses on Wood Pulp Nanofibrillation and Nanofiber Network Characteristics, Biomacromolecules, 9(3), 1022-1026.

Iwamoto, S., Nakagaito, A. N. and Yano, H. (2007): Nano-fibrillation of pulp fibers for the processing of transparent nanocomposites, Applied Physics A-Materials Science & Processing, 89(2), 461-466.

Iwamoto, S., Nakagaito, A. N., Yano, H. and Nogi, M. (2005): Optically transparent composites reinforced with plant fiber-based nanofibers, Applied Physics A, 81(6), 1109-1112.

Jonoobi, M., Mathew, A. P. and Oksman, K. (2012): Producing low-cost cellulose nanofiber from sludge as new source of raw materials, Industrial Crops and Products, 40, 232-238.

Kham, L., Le Bigot, Y., Delmas, M. and Avignon, G. (2005): Delignification of wheat straw using a mixture of carboxylic acids and peroxoacids, Industrial Crops and Products, 21(1), 9-15.

Klemm, D., Heublein, B., Fink, H. P. and Bohn, A. (2005): Cellulose: Fascinating biopolymer and sustainable raw material, Angewandte Chemie-International Edition, 44(22), 3358-3393.

Klemm, D., Kramer, F., Moritz, S., Lindström, T., Ankerfors, M., Gray, D. and Dorris, A. (2011): Nanocelluloses: A New Family of Nature-Based Materials, Angewandte Chemie International Edition, 50(24), 5438-5466.

Kramer, C. Y. (1956): Extension of multiple range tests to group means with unequal numbers of replications, Biometrics, 12(3), 307-310.

Lindström, T. and Winter, L. (1988): Mikrofibrillär cellulosa som komponent vid papperstillverkning STFI-meddelande C159.

Pääkkö, M., Ankerfors, M., Kosonen, H., Nykänen, A., Ahola, S., Österberg, M., Ruokolainen, J., Laine, J., Larsson, P. T., Ikkala, O. and Lindström, T. (2007): Enzymatic Hydrolysis Combined with Mechanical Shearing and High-Pressure Homogenization for Nanoscale Cellulose Fibrils and Strong Gels, Biomacromolecules, 8(6), 1934-1941.

Qing, Y., Sabo, R., Zhu, J. Y., Agarwal, U., Cai, Z. Y. and Wu, Y. Q. (2013): A comparative study of cellulose nanofibrils disintegrated via multiple processing approaches, Carbohydrate Polymers, 97(1), 226-234.

Rezayati Charani, P., Dehghani-Firouzabadi, M., Afra, E., Blademo, Å., Naderi, A. and Lindström, T. (2013): Production of microfibrillated cellulose from unbleached kraft pulp of Kenaf and Scotch Pine and its effect on the properties of hardwood kraft: microfibrillated cellulose paper, Cellulose, 20(5), 2559-2567.

Saito, T., Nishiyama, Y., Putaux, J.-L., Vignon, M. and Isogai, A. (2006): Homogeneous Suspensions of Individualized Microfibrils from TEMPO-Catalyzed Oxidation of Native Cellulose, Biomacromolecules, 7(6), 1687-1691.

Samir, M., Alloin, F. and Dufresne, A. (2005): Review of recent research into cellulosic whiskers, their properties and their application in nanocomposite field, Biomacromolecules, 6(2), 612-626.

Sehaqui, H., Allais, M., Zhou, Q. and Berglund, L. A. (2011a): Wood cellulose biocomposites with fibrous structures at micro- and nanoscale, Composites Science and Technology, 71(3), 382-387.

Sehaqui, H., Zhou, Q. and Berglund, L. A. (2013): Nanofibrillated cellulose for enhancement of strength in high-density paper structures, Nordic Pulp & Paper Research Journal, 28(2), 182-189.

Sehaqui, H., Zhou, Q., Ikkala, O. and Berglund, L. A. (2011b): Strong and Tough Cellulose Nanopaper with High Specific Surface Area and Porosity, Biomacromolecules, 12(10), 3638-3644.

Siro, I. and Plackett, D. (2010): Microfibrillated cellulose and new nanocomposite materials: a review, Cellulose, 17(3), 459-494.

Spence, K. L., Venditti, R. A., Rojas, O. J., Habibi, Y. and Pawlak, J. J. (2011): A comparative study of energy consumption and physical properties of microfibrillated cellulose produced by different processing methods, Cellulose, 18(4), 1097-1111.

Syverud, K. and Stenius, P. (2009): Strength and barrier properties of MFC films, Cellulose, 16(1), 75-85.

Taniguchi, T. and Okamura, K. (1998): New films produced from microfibrillated natural fibres, Polymer International, 47(3), 291-294.

Tejado, A., Alam, M. N., Antal, M., Yang, H. and Ven, T. M. (2012): Energy requirements for the disintegration of cellulose fibers into cellulose nanofibers, Cellulose, 19(3), 831-842.

Turbak, A. F., Snyder, F. W. and Sandberg, K. R. (1983): Microfibrillated Cellulose, A New Cellulose Product: Properties, Uses and Commercial Potential., Journal of Applied Polymer Science: Applied Polymer Symposium, 37, 815-827.

Wagberg, L., Decher, G., Norgren, M., Lindstrom, T., Ankerfors, M. and Axnas, K. (2008): The Build-Up of Polyelectrolyte Multilayers of Microfibrillated Cellulose and Cationic Polyelectrolytes, Langmuir, 24(3), 784-795.

Wang, Q. Q., Zhu, J. Y., Gleisner, R., Kuster, T. A., Baxa, U. and McNeil, S. E. (2012): Morphological development of cellulose fibrils of a bleached eucalyptus pulp by mechanical fibrillation, Cellulose, 19(5), 1631-1643.

Yano, H. and Nakahara, S. (2004): Bio-composites produced from plant microfiber bundles with a nanometer unit web-like network, Journal of Materials Science, 39(5), 1635-1638.

Young, R. A. (1994): Comparison of the properties of chemical cellulose pulps, Cellulose, 1(2), 107-130.

Zimmermann, T., Bordeanu, N. and Strub, E. (2010): Properties of nanofibrillated cellulose from different raw materials and its reinforcement potential, Carbohydrate Polymers, 79(4), 1086-1093.

Zimmermann, T., Pöhler, E. and Geiger, T. (2004): Cellulose fibrils for polymer reinforcement, Advanced Engineering Materials, 6(9), 754-761.

Manuscript received November 25, 2013
Accepted February 7, 2014