Influence of TEMPO-oxidized cellulose nanofibrils on the properties of filler-containing papers

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Abstract

In this work, cellulose nanofibrils (CNF) were produced from a *Eucalyptus globulus* bleached kraft pulp by TEMPO-mediated oxidation and mechanical homogenization, and their effect in papermaking, namely filler flocculation and retention, dry and wet-web strength and structural properties, was studied in detail.

Cellulose nanofibrils possessing 0.6 mmol/g of carboxyl groups and a degree of polymerization (DP) of *ca.* 550 were found to promote filler flocculation and retention in the fibre mat whereas the same amount (3 wt%) of CNF having 1.5 mmol/g of carboxyl groups, a DP of *ca.* 200 and a similar mean diameter, exhibited an opposite effect. These results were interpreted with the help of flocculation studies of precipitated calcium carbonate (PCC) in the presence of CNF carried out by laser diffraction spectrometry. In addition, the mechanical and structural properties of the handsheets were analyzed revealing that the less charged CNF led to more closed matrices and, even increasing the filler retention, had a positive role on the tensile strength. A bonding mechanism between eucalypt fibres, PCC, CNF and a linear cationic polyacrylamide is proposed, consistent with the flocculation, retention and paper strength and structural properties results. It is concluded that, to be used in papermaking, the CNF must not have a high charge (nor a small length) in order to be able to flocculate the filler particles and, at the same time, to increase the filler-to-cellulosic fibres bonding.

A complementary study on the wet-web resistance of handsheets produced with the less charged CNF was conducted for moisture contents between 10 and 70% showing that this CNF can significantly improve the handsheets wet tensile strength (nearly 100%) even for water contents above 50%. The use of CNF in the paper machine may thus contribute, through the higher wet-web tensile resistance, to reduce breaks and increase the operating speeds and, through the higher filler retention, to important fibre and cost savings.

Keywords

Cellulose nanofibrils; Flocculation; Papermaking; Filler retention; Tensile strength

Introduction

Cellulose nanofibrils (CNF) are a promising and interesting material for different industrial applications as widely reported in the literature. They comprise fibrils with a high aspect ratio having diameters of less than 50 nm and lengths of a few micrometres, and can be obtained from wood or non-woody resources by using, preferentially, chemical (e.g. TEMPO-mediated or periodate-chlorite oxidations or carboxymethylation) or enzymatic pre-treatments, followed by mechanical treatments (e.g., homogenization, grinding, ultra-sonication). If only mechanical energy is used significantly lower amounts of nano-sized material are obtained. CNF possess very high stiffness (Young's modulus higher than 10 GPa) (Kangas et al. 2014) and high specific surface area (about ten times greater than that of the original fibers) (Lavoine et al. 2012), which make them highly suitable to be used as mechanical reinforcement material of diverse matrices (Eichorn et al. 2010; Khalil et al. 2014). For instance, they can enhance the strength properties of a cellulose matrix by promoting a better bonding between the cellulosic fibres (Taipale et al. 2010; González et al. 2014). In papermaking, they have also the potential to be used in a) paper coating, either to improve the barrier properties and/or the printing quality, b) as flocculant of mineral fillers or c) as rheology control additive (Klemm et al. 2011; Brodin et al. 2014). However, the research in the papermaking field is still mainly focused in the production and uses of the so-called "nanopapers" since CNF fibres have strength and gas barrier properties that make them suitable to be used as substrate for diverse applications such as in food packaging or printed electronics devices (Syverud and Stenius 2009; Henriksson et al. 2008; Fukuzumi et al 2009; Chinga-Carrasco et al. 2012; Lavoine et al. 2012; Torvinen et al. 2012; González et al. 2014).

The increase of the tensile index in lab handsheets, having only fibres and CNF, has been reported by several authors that claim that extensive hydrogen bonds are formed. Ioelovich and Figovsky (2010) found that the introduction of cellulose nanofibres increased significantly the handsheets strength while the porosity was decreased. In the same way, González et al. (2012) stated that by

incorporating 6 to 9% (w/w) of CNF in an unbeaten bleached *Eucalyptus* pulp furnish, the strength properties were similar to those of handsheets produced only with the corresponding refined pulp (23 °SR). Petroudy et al. (2014) explored the benefits of using a cationic polyacrylamide together with CNF to produce stronger handsheets without disturbing the porosity. The main drawback in all these studies was the decrease of drainability during sheet formation. However, Taipale et al. (2010) concluded that by the optimum selection of the materials and process conditions, the strength of paper can be improved without significantly affecting drainability.

The aforementioned bonding potential of the CNF is related to the high specific surface area and –OH groups available for hydrogen bonds. Besides, for the TEMPO-oxidized CNF (TOCN), it has been proposed by Saito and Isogai (2006, 2007) that the aldehyde groups derived from the oxidation at the surface of the cellulose fibres contribute to the wet strength development of the fibrous matrix because covalent bonds are formed through hemiacetal linkages between the hydroxyl and the aldehyde groups. Noteworthy that in all the studies previously referred to, no mineral fillers were used.

As well known, fillers are used to improve several paper properties (e.g., light scattering coefficient, opacity, surface smoothness) besides being cheaper than fibres, but they aggregate between fibres and prevent fibre-to-fibre bonds, thus causing a loss of paper strength (Raymond et al. 2004*;* Hubbe 2014). Therefore, the filler content in paper is limited to amounts rarely superior to 30%.

The interaction of CNF with mineral fillers, during the sheet formation, has been evaluated in a small number of studies and is not yet completely understood given the diversity of variables involved, namely e.g. the nature of fillers and nanofibrils. Ämmälä et al (2013) showed that the addition of TEMPO-oxidized and periodate-chlorite oxidized CNF to a furnish containing fibres and ground calcium carbonate (GCC) increased significantly the filler retention (from about 50-55% to 85-95%). Since GCC and oxidised CNF were all negatively charged, a patching flocculation mechanism involving Ca^{2+} ions from dissociated GCC was proposed. However, both types of CNF seemed not to have any positive effect on the handsheets tensile strength, and this was attributed to poor sheet formation. In another study, Hii et al. (2012) studied the interactions between fillers, CMF (not chemically pre-treated cellulose microfibrils) and fibres after wet pressing. Since

CMF possess a strong water retention capability which disturbs dewatering (as well as CNF), the authors used high contents of filler aiming at obtaining a better pressability. The conclusion was that by adequately selecting the CMF and the filler content it was possible to improve the strength properties without affecting the pressability of the sheet in the wet-end. Besides, the filler together with CMF also led to an increase of the handsheets light scattering and air resistance because the CMF proved to effectively bind the fillers in the fibre network. Quite recently, He et al. (2016) reported that a composite of CMF, PCC and cationic starch provided handsheets of bleached kraft pulp (BKP) fibres with better strength properties and denser sheets. The CMF were obtained only by mechanical treatment of hardwood BKP fibres.

Korhonen and Laine (2014) studied the flocculation and retention mechanisms of fillers in the presence of CNF, concluding that TEMPO-CNF and carboxymethylated CNF can be used as effective precipitated calcium carbonate (PCC) flocculants, acting by a hybrid mechanism of bridging and patching. Interestingly, chemically unmodified CMF had no flocculation ability. Thus, the authors stated that CNF must have a high number of charged groups in order to increase their electrostatic interactions with the other components of the paper matrix. Nonetheless, they did not evaluate the standard properties of paper sheets containing CNF and PCC. It must be stressed that, in spite of the different studies mentioned above, the combined effect of fibres, fillers, CNF, retention and sizing agents, supported on flocculation studies and including also the evaluation of the wet-web strength, has not yet been reported in the literature.

In this context, the objective of the present work was (a) to evaluate the filler retention and the main structural and mechanical properties of dry handsheets prepared with fibres, small amounts of TEMPO-oxidized CNF (with different carboxyl groups content and size), mineral filler (PCC), and a cationic polyacrylamide (commonly used as retention agent), (b) to study the influence of the CNF on the flocculation of the filler particles, (c) to suggest a mechanism for the interactions between the different components of the furnish when CNF and CPAM are used and, (d) to study the influence of CNF on the wet-web resistance of handsheets containing filler (by testing specimens with different moisture contents).

Materials and methods

CNF preparation and characterization

To produce the TEMPO-oxidized CNF, a bleached *Eucalyptus globulus* kraft pulp was pre-treated with NaClO and catalytic amounts of TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl radical) and NaBr according to a methodology described elsewhere (Saito et al. 2007). The cellulose fibres were previously refined at 4000 rev. in a PFI beater before chemical oxidation. Briefly, 30 g (dry basis) of refined fibres were dispersed in distilled water containing TEMPO (0.016 g per g of fibres) and NaBr (0.1 g per g of fibres) at a consistency of 1%. The mixture was stirred for 15 min at room temperature in order to assure a good dispersion of all the components. Then, a NaClO solution (12.5% active chlorine) was slowly added to the previous mixture. Two samples were produced using 5 and 11 mmol of NaClO per gram of cellulose, herein noted as CNF5 and CNF11, respectively. The pH of the medium was kept at 10 by the addition of drops of NaOH 0.1 M. The reaction was considered finished when the pH stabilized at 10 (after 2 hours). The oxidised fibres were then filtered and washed with distilled water until the filtrate conductivity reached low values (*ca.* 10 μS/cm). The fibres were then mechanically treated by high pressure homogenization: the fibres passed 5 times at 300 bar and 5 times at 600 bar (GEA Niro Soavi Panda Plus 2000, Italy).

To evaluate the "yield" of the production of nanofibrillar material, 40 mL of the dispersions (0.2 wt%) were centrifuged at 9000 rpm for 30 min: the percentage (w/w) of supernatant material was considered the yield of fibrillation (Saito and Isogai 2006; Saito et al. 2009). The results were determined in duplicate.

The nanofibrils were then characterized for the cationic demand, carboxyl groups content, degree of polymerization, specific surface area and size. The cationic demand (CD) was measured in a Mütek PCD 04 particle charge detector, by using poly-DADMAC and Pes-Na cationic and anionic titrants, respectively, according to the methodology followed by Espinosa et al. (2016). The volume of

anionic polymer consumed until the equipment registered 0 mV was used to calculate the cationic demand according to eq.1

$$CD = [(C_{PDADMAC} \cdot V_{PDADMAC}) - (C_{PESNA} \cdot V_{PESNA})]/m \quad (1)$$

where,

CD – Cationic demand (μeq/L)

$C_{PDADMAC}$ - Cationic polymer concentration (g/L)

C_{PESNA} – Anionic polymer concentration (g/L)

$V_{PDADMAC}$ – Volume used of cationic polymer (L)

V_{PESNA} – Volume used of anionic polymer (L)

m - Mass of CNF on dry basis (g)

The carboxyl's content (C_{COOH}) was determined in triplicate by conductometric titration of aqueous suspensions of CNF (acidified to pH of ca. 3) with NaOH 0.01 M. The carboxyl's content was determined from the conductivity curve according to eq.2 (Kekäläinen et al. 2014).

$$C_{COOH} = (V2 - V1)/m \cdot [NaOH] \quad (2)$$

where,

C_{COOH} - Carboxyl groups content on dry basis of CNF (mmol/g)

$V2 - V1$ - Volume of NaOH solution added between the equivalence points (mL)

m - Mass of CNF on dry basis (g)

$[NaOH]$ - NaOH concentration (mmol/mL)

The degree of substitution (DS) of carboxyl groups of the CNF was estimated from the CNF carboxyl's content, following eq. 3.

$$DS = C_{COOH} / [C_{COOH} + (1-C_{COOH} \cdot 198.1) / 162.1] \quad (3)$$

where C is the CNF carboxyl´s content (mol/g), 162.1 and 198.1 are the molar masses (g/mol) of the anhydroglucose units and of units substituted at C-6 position by COO^-Na^+ groups, respectively.

The degree of polymerization (DP) was determined from intrinsic viscosity measurements by dissolving the CNF samples in cupriethylenediamine (ISO 5351:2010). The Mark Houwink equation (eq. 3) was applied for the calculations.

$$[\eta]=K \cdot DP^{a} \quad (3)$$

where,

η – intrinsic viscosity

K,a – Mark Houwink parameters: K=2.28, a=0.76 (Henriksson et al. 2008)

DP – Degree of polymerization

AFM images were used to assess the nanofibrils diameter. AFM imaging was performed on a film prepared by solvent casting of CNF5 in an AFM microscope from Bruker Innova using the peak force tapping mode, at room temperature, in air, with a silicon cantilever with a tip with a radius of 8 nm. The size of the assessed areas was 2 μm × 2 μm. However, as well known, the results obtained, besides being operator dependent, are restricted to the analysis of a small amount of sample and therefore the corresponding mean diameter is not representative of all the material. For this reason, a mean diameter was theoretically calculated assuming a cilindrical geometry and based on the specific surface area of the nanofibrils (SSA), as reported in the literature (Espinosa et al., 2016):

$$d=4/(SSA^{x}\rho) \quad (4)$$

where,

d – CNF diameter (nm)

SSA – CNF specific surface area (m^2/g)

ρ - cellulose density = 1,6 g/cm^3

The specific surface area (SSA) of the nanofibrils was theoretically calculated from the specific surface area of a single poly-DADMAC molecule (SSA_{DADMAC}) according to equation (5) explained in detail elsewhere (Espinosa et al., 2016).

$$SSA = (CD\text{-}C_{COOH})^{x} SSA_{DADMAC} \quad (5)$$

Dynamic light scattering (DLS) measurements were made in triplicate on the supernatants obtained after centrifugation of the CNF dispersions using a Zetasizer Nano ZS (Malvern Instruments), in order to have an idea of the relative size of the fibrils, as previously reported (Gamelas et al. 2015a).

FTIR-ATR spectra of CNF films were obtained on a Bruker Tensor 27 spectrometer using a MKII Golden Gate accessory with a diamond crystal 45º top plate. The spectra were recorded in the 500–4000 cm^{-1} range with a resolution of 4 cm^{-1} and a number of scans of 256.

Handsheets preparation and characterization

Before producing the handsheets the different paper components were prepared. *Eucalyptus globulus* bleached kraft pulp (34 °SR) was used as the cellulosic fibre source for the handsheets production. After disintegration the pulp was diluted to a consistency of 1% in demineralized water. Aqueous suspensions (0.2 wt%) of each CNF were magnetically stirred for 1 hour. PCC with a median diameter (d_{50}) of the particle size distribution (as measured by laser diffraction spectrometry) of 4.4 μm and a zeta potential of +7 mV was used as filler in the handsheets production. Aqueous suspensions of PCC (1 wt%) were stirred magnetically (20 min) and sonicated (15 min, 50 KHz). A 3% starch suspension standing at 60 ºC was also prepared according to a procedure detailed elsewhere (Saraiva et al. 2010). Alkenyl succinic anhydride (ASA) was used as internal sizing agent and it was added to the starch suspension before mixture with the other components of the furnish. A 0.025% aqueous solution of a linear cationic polyacrylamide (C-PAM, commercial Percol 47, from BASF), with a high molecular weight and a low charge density, was used as retention agent. All the aforementioned additives were supplied by the industry.

According to the literature several routes may be adopted regarding the sequence of addition of the components when preparing the handsheets (Brodin et al. 2014). The most common are a) CNF addition to the mineral charges and thereafter the addition of the resultant mixture to the fiber suspension (Ämmälä et al. 2013; He et al. 2016), b) addition of all the components at once (Hii et al. 2012) or c) addition of CNF to a mixture of fibre and filler (Korhonen and Laine 2014). In the present work, preliminary studies showed that the mechanical properties of the handsheets, as well as the filler retention, had a bigger improvement by using the first strategy. Thus, PCC suspensions were mixed with the CNF dispersions at a PCC:CNF ratio of 10:1 (w/w) prior to the addition to the fibres suspension.

Handsheets were produced in a batch laboratory sheet former (255/SA model, MAVIS) using a 120 mesh screen. The aim was to achieve a basis weight of 80g/m^2. Amounts of 30, 3, 1, 0.12 and 0.02 wt% for PCC, CNF, starch, ASA and C-PAM, respectively, were used. For the handsheets production, the filler suspension (containing CNF/PCC or only PCC for comparison) was added to the fibre suspension. After 120 s of stirring, the starch/ASA mixture (at *ca.* 60 ºC)

was added. C-PAM was then added after a total time of 290 s and allowed to stir for more 5 s. The mixture was transferred into the sheet former and after 10 s of air agitation drainage was performed. The drainage time was measured.

In a first series of experiments, the sheets were collected from the web and pressed, dried, and conditioned according to the ISO 5269-1 standard. The structural properties (basis weight, thickness, bulk, and air permeability) were measured according to the corresponding ISO Standard Test Methods. Besides, the handsheets porosity was analyzed by Hg intrusion porosimetry in an AutoPore IV 9500 instrument from Micromeritics and a surface analysis was performed by field-emission scanning electron microscopy (FE-SEM) in a Carl Zeiss Merlin microscope, in secondary electron mode, without any further coating.

For the wet-web resistance tests, a rectangular metallic mold was coupled to the sheet former screen in order to form test specimens that were collected from the web and pressed. In this case, different pressure levels were used in order to obtain specimens with different moisture contents, which, next, were tested in a vertical tensile test machine with a cell load of 50 N. The handsheets were weighed before and after drying (for five hours at 105 ºC) which allowed to obtain the corresponding water content.

In both experiments the handsheets were calcined at 525 ºC for 16 h to determine the PCC effective content (and the corresponding filler retention), according to the TAPPI Standard T211 om-93.

Flocculation studies of PCC in the presence of CNF

To better understand the interaction between CNF and PCC and the filler retention mechanism, the flocculation of the mineral particles in the presence of CNF was studied by measuring the evolution of the aggregates size with time, by laser diffraction spectrometry (LDS) in a Mastersizer 2000 equipment (Malvern Instruments). Previously to the measurements, a 1 wt% aqueous suspension of PCC and a 0.2 wt% aqueous suspension of each of the CNF samples were prepared as described before for the handsheets production. For the flocculation studies a 10:1 PCC:CNF ratio was used, also similarly to the handsheets preparation. For that, 9 mL of the PCC suspension were added to the equipment vessel containing 700 mL of distilled water (total solids concentration around 0.01 wt%), and the tests were carried out by setting the pump speed at 2000 rpm. After

10 min. of agitation, 4.5 mL of the 0.2 wt% CNF suspension was added and 20 min. later sonication was applied during 15 min. The measurement was continued until the agglomerates size stabilized (*ca.* 90 min. total). Tests with only PCC were also performed for comparison. The results presented are a mean of two measurements, for the three series of experiments: PCC, PCC+CNF5 and PCC+CNF11.

Results and Discussion

CNF characterization

Cellulose nanofibrils with two different contents of carboxyl groups were produced by NaClO oxidation mediated by TEMPO as mentioned above. Their main characterization data are listed in Table 1. The nanofibres production yield was very high for both CNF samples and in agreement with values expected for TEMPO-oxidized CNF (Besbes et al. 2011; Isogai et al. 2011). The nanofibres production yield was smaller for the sample with milder chemical treatment (CNF5) confirming that bigger fibres were still present. These results were in accordance with the degree of polymerization determined for both samples: CNF5 with a higher DP than CNF11.

Insert Table 1

By doubling the amount of NaClO in the TEMPO-mediated oxidation, the cationic demand of CNF becomes much higher than that obtained for CNF5, as expected. Accordingly, the determination of the carboxyl group's content showed that CNF11 possessed more than the double of the carboxyl's of CNF5. Consequently, a degree of substitution of 0.10 and 0.26 was obtained for CNF5 and CNF11, respectively (Table 1). A similar increase of carboxyl's content with the amount of NaClO used in the oxidation reaction has been previously reported (Saito and Isogai 2004; Isogai et al. 2011). Besides, the carboxylate surface density, obtained by the ratio between the carboxyl content measured for each sample and the corresponding specific surface area calculated values, is also much higher for the CNF11 nanofibrils: 5.1 mmol/m^2 *vs.* 3.5 mmol/m^2 for CNF5. Additionally, the different carboxyl's content of the two CNF was assessed by

FTIR-ATR spectroscopy. A high intensity band at 1601 cm^{-1} due to the asymmetric COO stretching of the ionized COO^- groups was evident in the spectrum of CNF11, while for CNF5 this band was of much lower relative intensity (Fig. 1), confirming that the latter presented a considerably lower amount of carboxyl groups (Gamelas et al. 2015b).

Insert Fig. 1

The yield values, cationic demand and carboxyl groups were in agreement with the expected smaller size of the CNF11 nanofibrils. This fact was confirmed by comparing the fibrils size (Z-average) of both samples, as evaluated by DLS. It should be emphasized that DLS alone cannot be used to compute the size of the nanofibrils due to their acicular shape, but even though, it provides important and meaningful information regarding the size comparison of samples with similar structure, besides measuring a significant amount of fibrils (Gamelas et al. 2015a).

The CNF AFM image (Fig. 2a) reveals the great heterogeneity of the nanofibres size, as usual for this type of material (Besbes et al. 2011, Hänninen et al. 2015). This was confirmed by the diameter distributions plotted in Fig. 2b: values between 5 and 40 nm can be found.

Insert new Figure 2

Considering this broad range and the aforementioned limited representativity of any average value based on AFM imaging, it was decided to calculate a mean diameter using parameters representative of the whole samples – the cationic demand and the carboxyl group's content, as already supported in the literature (Espinosa et al., 2016). Values of 14.7 nm and 8.7 nm, respectively for CNF5 and CNF11, were obtained. However, it is legitimate to conclude that these differences are not significant taking into account the above referred to diversity of the nanofibrils diameter detected by AFM. Thus, based on the different degree of polymerization values, it may be concluded that both samples differ in the fibrils length rather than in the fibrils diameter. This difference was supported by the DLS Z-average values (used only for comparison purposes). Thus, the CNF

influence on filler flocculation and on the papermaking properties will be discussed based on the different carboxyl groups content and on the length.

Flocculation studies of PCC in the presence of CNF

Additional insight into the processes of PCC retention in the presence of CNF was obtained using laser diffraction spectrometry. The results of the evolution of the median (d_{50}) of the particle size distribution with time for suspensions of PCC with and without CNF are shown in Fig. 3. When measuring only PCC, the d_{50} increased slowly along the experiment, even with sonication, up to *ca.* 9 μm after 80 min, which is a common behavior for this material (Rasteiro et al. 2008). With the addition of the nanofibrils with lower carboxyl's content (and carboxyl's surface density, CNF5) to the PCC suspension, the d_{50} increased from 4.8 to 8.8 μm and continued to increase, with stirring, to a value of 10.5 μm. However, when vigorous sonication was applied, the new flocs were broken and the particle size decreased to a value similar to that observed in the curve of PCC. When sonication was stopped (while maintaining mechanical stirring), the particle size increased sharply to a d_{50} value close to 30 μm (more than 3 times the value observed in the curve of PCC), indicating a high degree of PCC re-flocculation. For the more carboxylated nanofibrils (CNF11) quite different results were obtained. Firstly, just after the addition of CNF11 to the PCC suspension, the increase of the median was very small (from 4.8 to 5.6 μm) and its value remained practically constant with time. The subsequent sonication promoted a decrease of the particle size and, even after stopping it, and with additional mechanical stirring, the evolution until the end of the experiment was not significant (not more than 0.2 μm), the d_{50} values being even smaller than those obtained for the experiment with PCC alone.

Insert Fig. 3

These results clearly indicate the disability of CNF11 in promoting both PCC flocculation and re-flocculation, probably because these nanofibrils were adsorbed at the PCC particles surface by interactions with the Ca^{2+} ions and imparted an excess of negative charge creating high repulsion between particles. On the contrary, for CNF5, the PCC particles could aggregate much easier (thus

contributing to high filler retention in papermaking, Table 2). Patching was most certainly the dominant mechanism behind flocculation, due to the very small chain length of the CNF (compared to commonly used flocculants) which prevented bridging. Besides, according to Korhonen and Laine (2014), only patch flocculants show reversible flocculation behavior.

Influence of CNF in the mechanical and structural properties of handsheets produced with PCC

Handsheets containing PCC and the aforementioned additives were produced without CNF and with the two different CNF (CNF5 and CNF11). For comparison, handsheets without PCC (and containing all the other additives) were also produced. The values of the corresponding mechanical properties (tensile index) and of the filler retention are listed in Table 2.

Insert Table 2

It is widely reported that the addition of small amounts of CNF to handsheets composed only of fibres highly increases the tensile index (Saito and Isogai 2007; González et al. 2012, 2014; Brodin et al. 2014). However, in the presence of the other additives used in papermaking (including fillers) the influence of the cellulose nanofibrils on the tensile strength seems not to be as straightforward (Hii et al. 2012; Ämmälä et al. 2013).

The results of the present study confirm that when the handsheets were produced with all the components except PCC (0% PCC, Table 2) the CNF acted indeed as a reinforcing material if a moderate TEMPO-mediated oxidation (CNF5, carboxyl's content 0.63 mmol/g and carboxyl's surface density 3.5 mmol/m^2) was used: tensile index improvement from 48.1 (±2.6) to 54.9 (±2.8) N.m/g. On the contrary, if the CNF carboxyl's surface density was high (CNF11, 5.1 mmol/ m^2), the handsheets tensile index was not significantly different from that obtained without CNF - a slight trend to decrease from 48.1 (±2.6) to 45.7 (±2.7) N.m/g was even detected. One possible explanation is that the ability of the CNF to bind with the fibres was now affected by electrostatic interactions between CNF11 and the positively charged linear CPAM. Besides, some repulsion between the highly negatively charged CNF and the fibres may have

also contributed to increase the inter-fibre distance and therefore decrease the fibre-to-fibre bonding. Thus, the tensile strength was similar or even worse than that obtained without CNF. When a lower surface charged CNF was used (CNF5), these detrimental phenomena were not significant and the potential of the CNF to enhance the fibre bonding dominated. Hence, as would be expected, an increment of the tensile strength was observed with CNF5. Furthermore, the smaller degree of polymerization of CNF11 may have also affected its reinforcing ability (Kekäläinen et al. 2014; Kobayashi et al. 2016).

When mineral fillers were added, the handsheets tensile resistance decreased significantly, as expected, due to the interference of the filler particles in the fibre-to-fibre bonding. However, with CNF5, the filler retention was clearly improved from 89.6 to 93.4% due to its positive role on PCC flocculation (Fig. 3), and even though the decrease of the tensile strength was not significant (from 25.0±0.9 to 23.6±1.0 N.m/g). This reveals that CNF5 can increase the filler retention without much disturbing the handsheets mechanical strength.

On the other side, for the CNF with a higher carboxyl groups content (CNF11) the filler retention was highly reduced (from 89.6% without CNF to 66.7%), as a result of the abovementioned particles repulsion effect that led to a decrease of the PCC flocculation (Fig. 3), and consequent loss through the wire. Also, some loss of the nanofibrils durig formation is not to be discarded, being this effect more pronounced for CNF11, with smaller DP. In accordance with the smaller filler content in the handsheet, the tensile index increased. However, this tensile increase was expected to be of higher magnitude considering the effective filler content reduction detected (Lourenço et al. 2014). This did not happened since, as stated above, on the one hand, CNF11 limit the fibre-to-fibre bonding and on the other hand the cationic polyacrylamide is preferentially linked to CNF11. As a result, it is not so available for filler retention and bridging effects, besides creating CNF-CPAM bundles that do not allow fibres to bind so effectively.

Fig. 4 attempts to explain the mechanisms behind the interactions between the fibres, the positively charged filler particles, the negatively charged CNF samples and the linear cationic polyacrylamide considering the results presented so far. When CNF5 is added to the PCC suspension, larger flocs are formed, being patching the dominant mechanism, with the nanofibrils adsorbed at the particles surface, as described above. Next, the linear cationic polyacrylamide promotes

bonds between flocs and also between flocs and fibres, by the bridging mechanism. Some bridging effect of the CNF5 nanofibrils with the fibres is not also to be discarded (Korhonen and Laine 2014). Covalent linkages between CPAM and CNF are reported in the literature (Saito and Isogai 2007). These phenomena explain the aforementioned impact of CNF5 both on filler retention and on tensile strength. The opposite occurs with CNF11 (which has more than the double of carboxylic groups) due to the referred to repulsion effects and to the formation of bundles with CPAM. Moreover, the eventual bridging between these nanofibrils and the fibres is less likely to occur with the same extent, due to their smaller DP/length.

Insert Fig. 4

FE-SEM images of the handsheets without CNF and also with CNF5 are depicted in Fig.5 for two magnifications. At 2k × magnification filler aggregates at the fibres surface and between fibres are visible for both structures. Higher resolution images (20k ×) in the areas where the precipitated calcium carbonate particles are, show a much more complex matrix when the CNF5 are used. The nanofibrils network is now visible and it is clearly evident its flocculating and binding effect.

Insert new Fig. 5

Due to the undesirable results observed with CNF11, the influence on the wet-web resistance of handsheets produced with different moisture contents was assessed only with CNF5. The results are depicted in Fig. 6. As can be seen, the CNF impact CNF on the handsheets tensile resistance was remarkable, especially for moisture contents below 60% - gains of up to 100% can be noticed. For moisture contents superior to 60% this impact was not so evident, although still positive. ~~as visible in the right plot of Fig. 6.~~ For these conditions of excess of water, the chemical interactions were expectedly weak. Remarkably, the influence of CNF was more pronounced for the wet-strength (of handsheets with water content up to 60%) than for the dry strength. Similar conclusions were reported by Saito and Isogai (2007), but in systems without mineral fillers. No studies of the CNF influence on the wet-web strength are available in the open literature for

filler-containing papers. These results are of utmost importance for the runnability of the paper machine: for moisture contents common in the drying section (7-50%), CNF may contribute, through the higher wet-web tensile resistance, to reduce break events and/or to increase operating machine speeds.

Insert new Fig. 6

Besides the mechanical resistance analysis, the drainability of the handsheets production process (evaluated by measuring the drainage time) and the structural properties of the dried handsheets were also examined. The results are presented in Table 3.

Regarding the use of CNF5, the drainage time was negatively affected (a relative increase of *ca.* 70% was detected), as a consequence of its hydrophilic character and its role on densifying the fibrous matrix, in agreement with the mechanisms described before. After drying, handsheets with less empty spaces than those produced without CNF are obtained, having a more compact 3D-structure. Accordingly, the air resistance increased significantly and the bulk decreased when CNF5 was used.

On the other side, the loss of filler detected when CNF11 was used (Table 2) was clearly confirmed by the decrease of the handsheets basis weight. The smaller filler content contributed to a higher fibre-to-fibre available bonding area, when comparing with the handsheets produced with 30% of PCC, and led, as expected, to an increase of the drainage time and of the air resistance. Even though, this increase was limited due to the abovementioned effect of CNF11 on preventing fibre-to-fibre bonding. From the smaller basis weight a higher value of bulk would be expected but this effect was balanced by the small amount of material (resulting from the filler loss) and the subsequent reduction of the handsheets thickness (114μm vs. 133μm).

Insert Table 3

Finally, the porosity of the handsheets produced with the CNF samples was evaluated by mercury intrusion porosimetry (Fig.7). The results of the total

porosity of the handsheets are in close agreement with those of the air resistance, the handsheets with CNF11 presenting intermediate values (and having also a higher percentage of larger pores).

Insert Fig. 7

One of the goals in the papermaking industry is to be able to use higher amounts of filler in paper without disturbing other properties like the mechanical strength and bulk. The results of this study revealed that by adding to a paper furnish (containing fibres, PCC, starch and a cationic polyacrylamide) 3 wt% of TEMPO oxidized CNF (containing 0.6 mmol carboxyl groups per g of pulp), it is possible to slightly increase the filler content without affecting the mechanical strength of the dry handsheets, and also to increase very significantly the tensile strength of handsheets with moisture contents up to 60 %. It was shown that this does not occur when the chemical pre-treatment is harsher, leading to high surface charged cellulose nanofibrils with small length. In spite of the aforementioned improvements, the handsheets freeness is hindered, being therefore advisable for future work to test other drainage aids. Overall, the main advance of this work is the study of the influence of different TEMPO-oxidized CNF in the papermaking properties when all the furnish components are considered, concluding that they may act as strength reinforcing agents (in the wet end section) and as flocculants if a mild TEMPO-mediated oxidation is used for their production.

Conclusions

In this work, the influence in papermaking of cellulose nanofibrils produced by TEMPO-mediated oxidation and possessing different contents of carboxyl groups and degree of polymerization has been evaluated. It was found that a CNF having 0.6 mmol/g of carboxyl groups and a yield of nanofibrillated material around 90 wt% (CNF5) was much more favorable for the PCC (filler) retention in the paper matrix than a slightly more fibrillated (97 wt% yield) but also more charged and smaller in length CNF (CNF11, with 1.5 mmol/g of carboxyl groups and a DP of 203). In fact, for furnish compositions similar to those used in papermaking (eucalyptus fibres, PCC, internal sizing agent, starch, and retention

aid), the addition of 3 wt% of CNF5 increased the filler retention relatively to that obtained without nanofibrilar material, whereas the addition of CNF11 had an opposite effect. Flocculation studies carried out by laser difraction spectrometry showed that CNF5 promoted the formation of large size flocs (with a median diameter of the particle size distribution up to almost 30 μm), which are considered to be responsible for the high filler retention. On the other hand, with CNF11, the median diameter of the PCC flocs was not larger than 5.5 μm, revealing that these more charged nanofibrils did not act as flocculant and by the contrary, caused some repulsion between particles. The influence of the CNF on the drainability and on some papermaking properties such as tensile strength and air permeability was also assessed for handsheets both without and with fillers, and the results were interpreted in terms of the reinforcing potential of the nanofibrillar material – this potential varied mainly as a function of the CNF carboxyl groups content, being also affected by their length, in such a way that the more charged and smaller CNF (1.5 mmol/g and DP of 203) exhibited a negative role on fibre bonding. A mechanism to explain the interactions between the fibres, CNF, fillers and a cationic polyelectrolyte retention agent (CPAM) was proposed.

Another important finding of this work was related to the ability of CNF5 in improving the wet-web resistance of the *E. globulus* bleached kraft pulp based handsheets with a nominal filler content close to 30% and in a wide range of moisture contents (between 10 and 70%). The well-known capability of the CNF to increase the tensile strength of cellulose matrices without minerals was now also confirmed for filler-containing papers even at high moisture contents. When CNF5 was used the tensile strength greatly increased to almost the double of the values obtained without CNF, even at moisture contents above 50%.

Overall, this study confirms that TEMPO-oxidized CNF may be used in papermaking simultaneously as reinforcing agent and flocculant, despite the complex interactions between all the paper furnish components. Nonetheless, their influence is much dependent on their structure, namely charge, but also size, as proved in this work.

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715

716 **Table 1.** CNF characterization data.

Sample	Yield (%)	CD [a] (μeq g/g)	C_{COOH} [b] (mmol/g)	DP [c]	DS [d]	SSA [e] (m^2/g)	Diameter (nm)	Z Average - DLS
CNF5	91	997	0.63	548	0.10	181	14.7	2327
CNF11	97	2188	1.56	203	0.27	307	8.7	323

717 [a] Cationic Demand; [b] Carboxyl group's content; [c] Degree of polymerization; [d] Specific Surface
718 Area.

719 **Table 2.** Tensile index of handsheets produced with CNF and PCC and also of the reference
720 (without CNF or without PCC) *.

CNF	0% PCC	30 % PCC	
	Tensile Index, N.m/g	Tensile Index, N.m/g	Filler Retention, %
0	48.1 (2.6)	25.0 (0.9)	89.6 (0.1)
3% CNF5	54.9 (2.8)	23.6 (1.0)	93.4 (0.7)
3% CNF11	45.7 (2.7)	28.5 (1.5)	66.7 (0.3)

721 *all the handsheets contained CPAM, starch and ASA; in parenthesis the standard deviation.
722

723 **Table 3** Properties of the handsheets produced with and without CNF. *

Sample	Drainage time, s	Basis weight, g/m^2	Bulk, cm^3/g	Air Resistance (Gurley), s/100 ml
30% PCC – 0% CNF	5.6 (0.1)	80.1 (0.3)	1.66 (0.01)	3.3 (0.2)
30% PCC – 3% CNF5	9.5 (0.5)	83.5 (0.4)	1.58 (0.03)	12.8 (1.4)
30% PCC – 3% CNF11	6.2 (0.2)	72.0 (0.8)	1.58 (0.04)	5.2 (0.6)

724 * in parenthesis the pooled standard deviation of two series of measurements
725
726

Figure captions

Fig 1 FTIR-ATR spectra of films of CNF5 and CNF11 highlighting the asymmetric COO stretching band.

Fig. 2 Nanofibrils diameter distribution obtained by AFM for both samples (a) and AFM image in phase imaging mode of sample CNF5 (b).

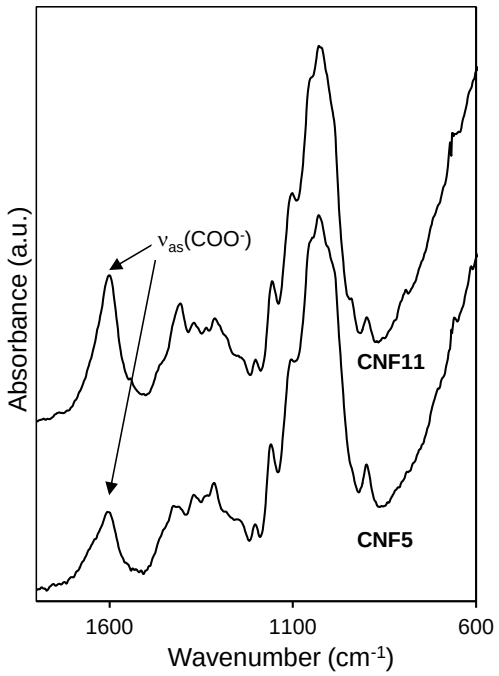
Fig. 3 Influence of the addition of CNF5 and CNF11 in the median (d_{50}) of the particle size distribution of PCC flocs measured by laser diffraction spectrometry. An experiment carried out with only PCC is also presented for comparison.

Fig. 4 Schematic representation of the bonding mechanism between PCC, CNF, fibres and retention agent (CPAM). The left side of the scheme corresponds to CNF5 and the right side to CNF11.

Fig. 5 FE-SEM images of handsheets produced without CNF5 (a,c) and with CNF5 (b,d). The narrow arrows indicate the PCC particles and agglomerates and the thicker arrows the CNF network.

Fig. 6 Tensile resistance of handsheets produced with CNF5 (square) and without CNF (cross) for different moisture contents.

Fig. 7 Hg intrusion porosity of handsheets produced with PCC (a) and with PCC and CNF5 (b) or CNF11 (c).



747

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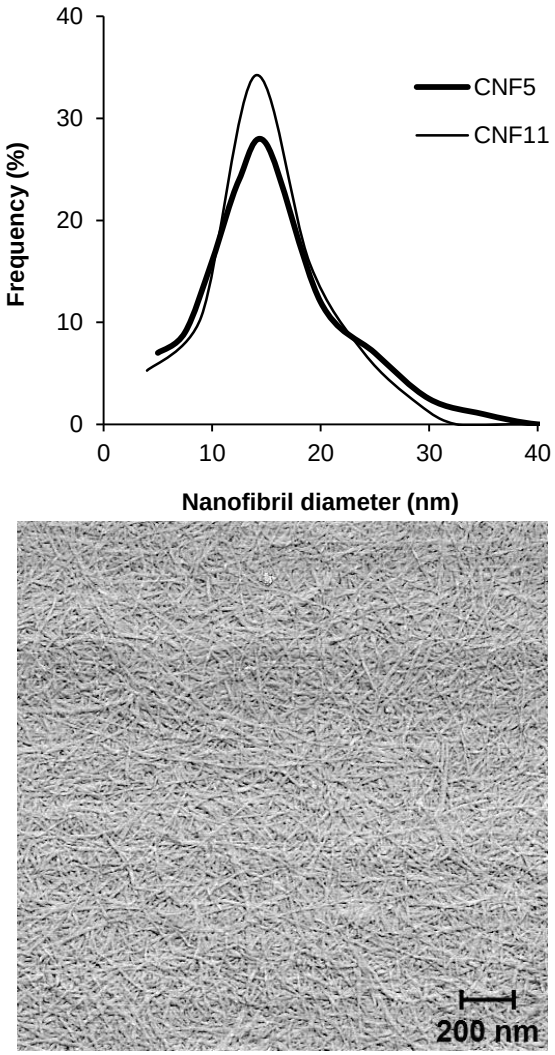
750



(a) (b)

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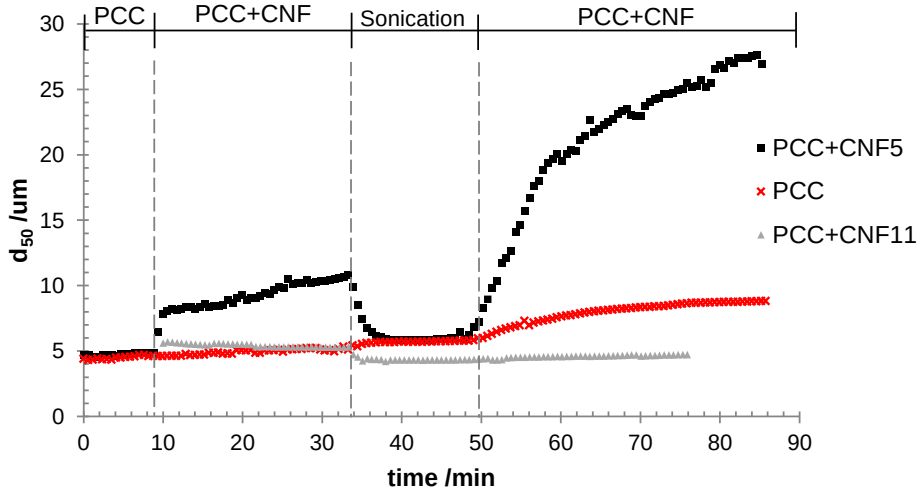

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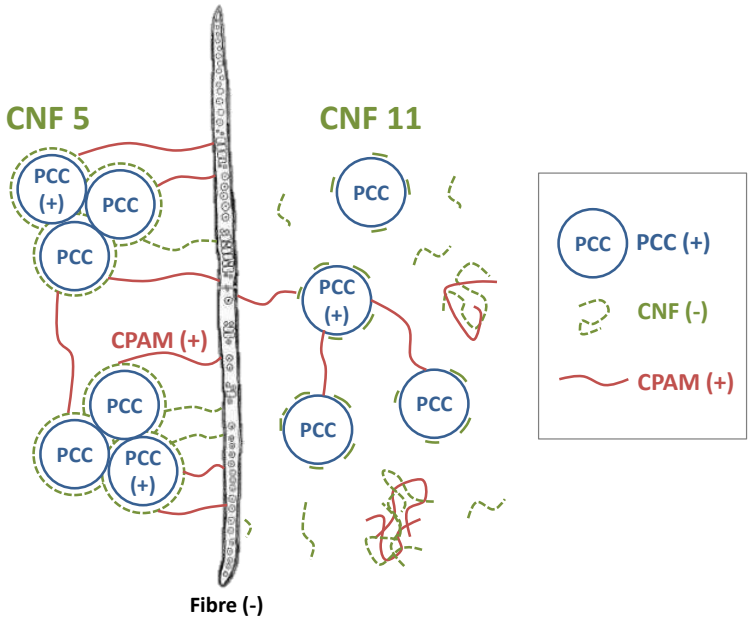

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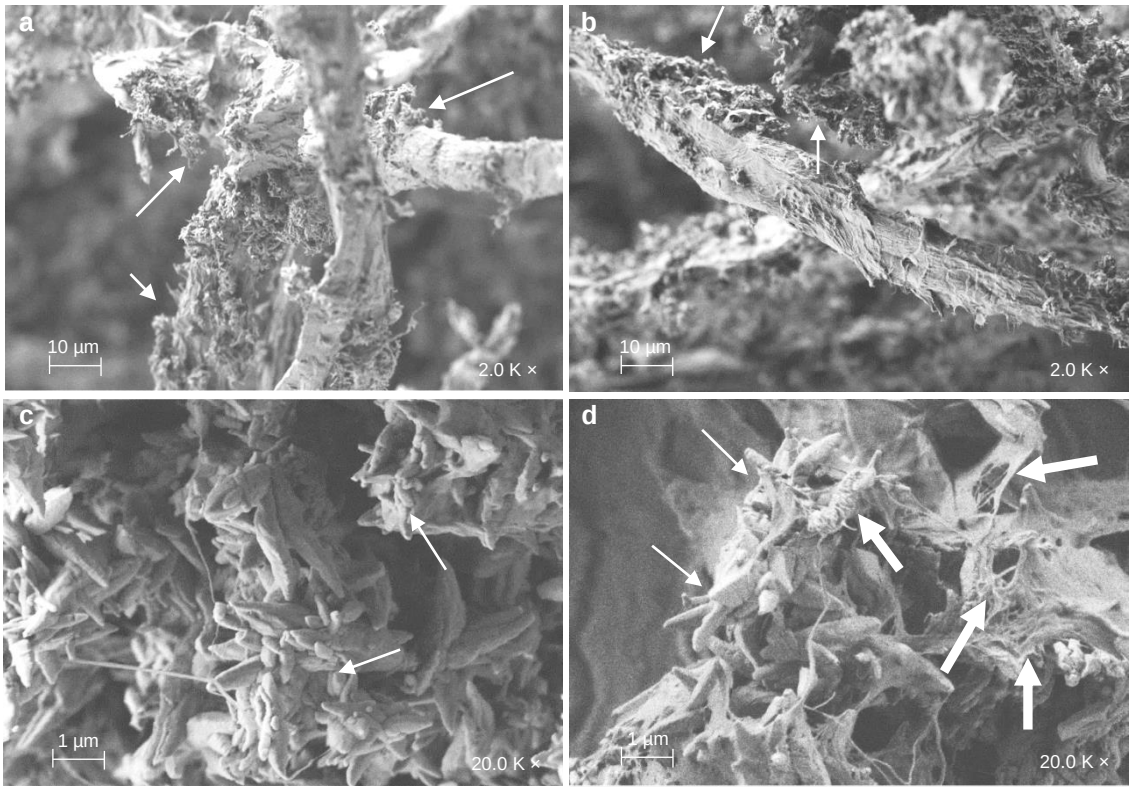

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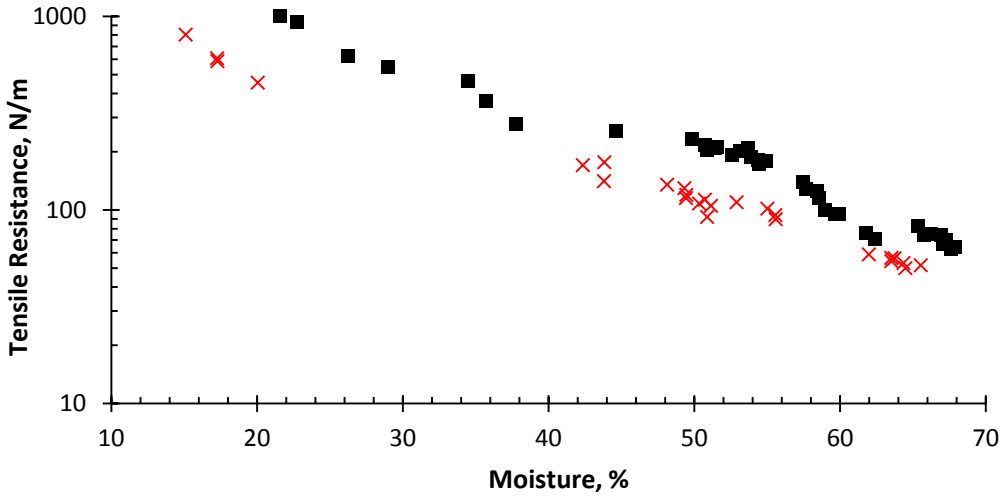

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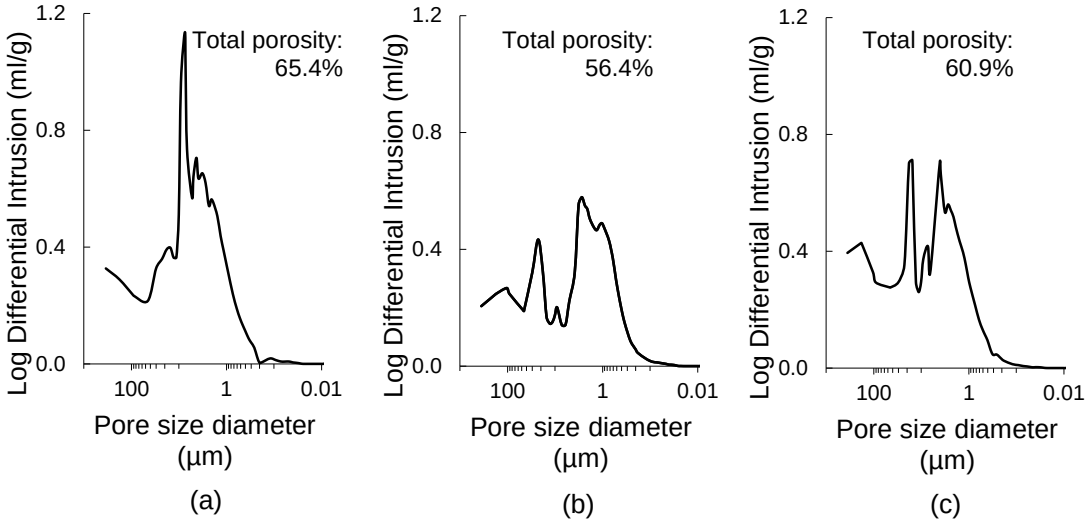

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