A comprehensive study on nanocelluloses in papermaking – the influence of common additives on filler retention and paper strength

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Abstract

Nanocelluloses are being explored and produced at an impressively increasing pace. Due to their good characteristics as reinforcement agent, their application in the most diverse fields has proven to be very beneficial. Their use in papermaking has been investigated in several studies, but the industrial implementation is still in a preliminary stage. In the present study, the influence of nanocelluloses, produced by four different treatments (mechanical, enzymatic hydrolysis, TEMPO-mediated oxidation and carboxymethylation) in the properties of filler-containing laboratory handsheets was assessed. Furthermore, five series produced with different additives, among internal strength and sizing agents as well as a retention agent, allowed to investigate the interactions between the common additives used in paper production and nanocelluloses. It was found that the different properties of the studied nanocelluloses led to very different interactions with the paper components. In this sense, by properly selecting the furnish to use (in terms of nanocellulose typology and presence or absence of each additive), high improvements of filler retention and dry and wet-web strength, as well as reduced surface roughness and water penetration, could be achieved.

Keywords

Cellulose nanofibrils; mineral filler; nanocellulose; paper additives; strength

Introduction

The manufacturing of printing and writing papers usually comprises the addition of several compounds. Natural fibers are the main raw material but mineral fillers are also used to improve optical properties and, mainly, to reduce production costs, with incorporation levels attaining values as high as 30% (Raymond et al. 2004; Thorn and Au, 2009; Hubbe 2014). In order to optimize the production process and improve paper properties, several natural or synthetic components are added to the furnish. On the one hand, strength additives, such as cationic starch, are used to improve the physical strength properties of paper. On the other hand, internal sizing agents, such as alkyl ketene dimer (AKD) and alkenyl succinic anhydride (ASA) are added to make paper reasonably hydrophobic. Additionally, retention agents, such as cationic polyacrylamides (CPAM) are used to retain the mineral fillers in the paper matrix. Other additives such as optical brightening agents, dyes, waxes, etc., are also included, although not directly affecting the papers' strength (Neimo 1999; Thorn and Au, 2009).

Nanocelluloses, a renewable and biodegradable cellulose-based nanomaterial, have been widely explored as paper additive due to their excellent functional properties (Brodin et al. 2014; Boufi et al. 2016; Osong et al. 2016; Lengowski et al. 2019). When produced from wood, industrial processes based on high mechanical intensity are applied for the isolation of the fibrils and it is common practice to use enzymatic or chemical pretreatments to reduce the energetic consumption and aid on the production of the cellulose nano or microfibrils (CNF and CMF, respectively). In papermaking, two main generations of studies regarding nanocellulose addition to the bulk can be found (Bardet and Bras 2014): the first relates to the direct addition of CNF or CMF to pulp suspensions, which highly enhances paper strength due to increased number of hydrogen bonds between fibrils and fibers (González et al. 2012, Petroudy et al. 2014, Delgado-Aguilar et al. 2015). Despite the confirmed great potential, the studies revealed that the water retention was much increased, mainly harming the process drainability and holding off the possibility for industrial

implementation. In this sense, the second generation of studies, focused on the resemblance to the industrial practice, was conducted by exploring the nanocellulose combination with several polyelectrolytes or mineral materials for improvement of the papermaking properties (Ahola et al. 2008, Korhonen and Laine, 2014, Merayo et al. 2017, Rice et al. 2018, Tajik et al. 2018). In fact, some market reports state that nanocelluloses are starting to be implemented at papermaking industrial facilities (Klemm et al. 2018).

Although the interactions of nanocellulose with different additives have been already assessed, recent results have proved that the influence of the nanofibrils in papermaking containing additives is highly dependent on the presence or absence of mineral fillers (Ankerfors et al. 2014, Diab et al. 2015, Lourenço et al. 2017, 2019a, 2019b, He et al. 2016a, 2016b, 2017). In this sense, it is of relevance to thoroughly understand the different and complex interactions and mechanisms between all the paper components. In addition, if functionalized CNF are used, these interactions are even more complex, particularly during the wet-end, and the effect of the aforementioned paper additives (especially sizing and retention agents) can be highly affected.

The number of publications regarding papermaking with nanocelluloses and mineral fillers is still very scarce. Most of the publications regarding the manufacturing of fine papers containing both components state that it is necessary to add additives in order to flocculate the mineral charges, modify their surface and/or bind them to the fibres, in a way that the paper properties are enhanced. The most usual additive is cationic starch, not only due to its availability and low price, but mainly because this additive promotes bridges between CNF and fillers, increasing the levels of flocculation and retention in the paper matrix (He et al. 2016a, 2016b) as also the mechanical resistances (Ankerfors et al. 2014, Laine et al 2010). Ämmälä et al (2013) were the first to state that CNF are potential retention aids for use in fine paper production instead of traditional polymers. However, in their study, poor formation was obtained and therefore the handsheets mechanical strength was not enhanced by using CNF. In general, the paper properties are reported to be significantly improved when CNF are combined with polyelectrolytes (Korhonen and Laine 2014, Hii et al 2012, Ottesen et al 2016, Hietaniemi et al. 2015, Diab et al 2015). Previous studies performed by our group revealed that nanocelluloses can partially or totally substitute retention additives in

papermaking, if the nano/micromaterials possess specific characteristics and if a proper selection of the furnish and mixing conditions is taken into account (Lourenço et al. 2019a, 2019b).

In the present article, a comprehensive study of the influence of common paper additives in the properties of handsheets containing mineral fillers and nanocellulose was carried out. For that, different cellulose nano or microfibrils were produced from bleached eucalyptus kraft pulp. The new products were characterized and used to flocculate precipitated calcium carbonate particles. The flocs were then added to papermaking furnishes with variable compositions in terms of additives (starch, ASA and CPAM). The results of filler retention and of the papers' structural, optical and mechanical properties were thoroughly analysed.

Materials and Methods

CNF/CMF production and characterization

CNF/CMF were produced from an industrial bleached eucalyptus kraft pulp (BEKP): 30 g (dry basis) of the never dried fibres were disintegrated and refined at 4000 rev. in a laboratory beater (PFI type, model MK-V, 1983). After an additional mechanical, chemical or enzymatic pre-treatment the fibres were mechanically treated, at 1% consistency, in a high pressure homogenizer (HPH, GEA Niro Soavi, model Panther NS3006L), with one pass at 500 bar and a second pass at 1000 bar. Four different pre-treatments were applied as follows.

a) Mechanical refining

The fibres were further beaten until a total of 15000 PFI rev. (including the initial refining). After the HPH treatment, sample "CMF-Mec" was obtained.

b) Enzymatic hydrolysis

The methodology detailed by Tarrés et al. (2016) was followed to produce CMF-E sample. Briefly, the beaten fibres were suspended in water (3.5% consistency) and the pH was adjusted to 5 with sodium citrate buffer. The suspension was heated to

50 °C under constant mechanical stirring and the enzyme was added (300g per ton of pulp). A commercial endoglucanase (endocellulase, 10% of exocellulase and 5% of hemicellulose) was used. The hydrolysis was stopped after 2 h by heating the suspension to 80°C for 15 min. The resulting suspension was cooled to room temperature and thoroughly washed with demineralized water until low filtrate conductivity was reached. After the two passes in the HPH, sample "CMF-Enz" was obtained.

c) TEMPO-mediated oxidation

The beaten fibres were properly mixed in an aqueous suspension with NaBr and TEMPO at room temperature. Then, a NaClO solution containing 3 mmol NaClO per gram of fibre was slowly added to the mixture, while maintaining the pH constant at 10 with NaOH, for two hours, according to the methodology described by Saito et al. (2007). The samples were thoroughly washed with water, until the conductivity of the filtrate was low. After HPH, sample "CNF-TEMPO" was obtained.

d) Carboxymethylation

The beaten fibres were washed with ethanol, to perform a solvent-exchange, and subsequently impregnated in an isopropanol and monochloroacetic acid (MCA) mixture for 30min (9% of MCA relative to the fibres). The fibres were then added to a system with isopropanol and methanol, in the presence of sodium hydroxide (MCA/NaOH ratio of 1.6), where the carboxymethylation reaction took place for three hours, at 60 °C. The pre-treated fibres were then filtered and washed, firstly with distilled water, secondly with acetic acid (0.1 M) and finally with distilled water until the conductivity of the filtrate was low, according to the methodology described in detail by Wågberg et al. (2008). The fibres were finally taken into the HPH originating the sample "CNF-Carbox".

The CNF/CMF produced were fully characterized for their fibrillation yield (gravimetry of centrifuged suspensions), content of carboxyl groups (C_{COOH}, conductometric titration), intrinsic viscosity (viscosimetry in

cupriethylenodiamine) and charge (zeta potential, electrophoretic mobility) as detailed elsewhere (Lourenço et al. 2017). The degree of polymerization (DP) was calculated from the intrinsic viscosity values by applying the Mark-Houwink equation with the parameters defined by Henriksson et al. (2008), namely K=2.28 and a=0.76 (DP>950) or K=0.42 and a=1 (DP<950). A modified centrifugal water retention value (WRV) was measured according to the procedure detailed by Dimic-Misic et al. (2018), on mixtures containing BEKP (WRV_0=1.3 g/g) and 3% of CNF/CMF. Field emission-SEM images were acquired in the films sputter-coated with gold in a Carl Zeiss Merlin microscope, in secondary electron mode (Supplementary Material).

PCC flocculation in the presence of CNF/CMF

Flocculation tests with industrial scalenohedral precipitated calcium carbonate (PCC) and each one of the CNF or CMF produced were conducted by Laser Diffraction Spectrometry (LDS) in a Mastersizer 2000 apparatus (Malvern Instruments) equipped with the Hydro2000MU module, according to the procedure detailed elsewhere (Lourenço et al. 2019a). Briefly, PCC (aqueous suspension at 1 wt%) was mixed with CNF/CMF suspensions (0.2 wt%) in the equipment vessel and, after 20 min of mechanical stirring (2000 rpm), sonication (14 µm of tip displacement) was applied for extra 15 min to break the flocs. The zeta potential of the PCC particles, measured by electrophoretic mobility in a Zetasizer Nano ZS (Malvern Instruments) was +7 mV and the median of the particle size distribution (d_{50}), determined by LDS, was 4.2 µm.

Papermaking potential

The new CNF/CMF were used in the production of laboratory handsheets together with mineral fillers and different additives. Their influence on filler retention and on the paper structural and mechanical properties was assessed. A semi-automatic laboratory sheet former (300-1 model, LabTech) equipped with a 120 mesh screen was used for the tests and isotropic handsheets obtained.

The formulations were prepared with fibre (BEKP refined up to 33 ºSR), PCC, CNF/CMF, a mixture of starch with alkenyl succinic anhydride (ASA), and a linear

cationic polyacrylamide (CPAM). All the additives were supplied by a paper production mill. In order to properly assess the interactions between all the paper components, 5 different series, varying in the presence/absence of additives, were produced. The amounts added are listed in Table 1 and were selected based on preliminary studies, regarding the CNF/CMF amount (see Supplementary Material), and on the industrial practice, regarding the additives amount.

Table 1 Amounts (%) of each component added in the production of laboratory handsheets *.

Component	Series				
	-	S	SA	CPAM	SA-CPAM
BEKP	67.00	66.00	65.88	66.98	65.86
PCC	30	30	30	30	30
CNF/CMF	3	3	3	3	3
Starch (S)	-	1	1	-	1
ASA (A)	-	-	0.12	-	0.12
CPAM	-	-	-	0.02	0.02

* For each series, a reference without CNF/CMF, was also produced.

For the handsheets production, the BEKP was disintegrated and diluted to a consistency of 0.4% in demineralized water. The PCC and CNF/CMF suspensions were prepared as in the flocculation experiments. The cationic tapioca starch was cooked in water at 3%, according to the procedure detailed by Saraiva et al. (2010). Since ASA is not water dispersible and must be used as an emulsion, it was firstly stabilized by mixing with the aforementioned cooked starch suspension, standing at 60 ºC. CPAM (commercial Percol 47, from BASF, with high molecular weight and low charge density) was diluted in water to 0.025%. The handsheets were made according to the procedure described in detail by Lourenço et al. (2017), either for dry and wet-web tests. Briefly, the PCC-CNF/CMF flocs were added to the BEKP. In the series with additives, the starch or starch/ASA mixture were subsequently added after 120 s and CPAM after 265 s of magnetic stirring. In all series, the furnish was transferred into the sheet former after a total time of 270 s. In the handsheets former, at a solids concentration of *ca.* 0.02 wt%, air agitation and decantation (5 and 10 s., respectively) were succeeded by drainage. The handsheet was removed and proper pressing was performed in order to obtain specimens with high moisture for the wet-tensile vertical tester (Instron, 2519-102 model equipped with a 50 N static load cell). For the dry specimens, after pressing and conditioning, the optical, structural and mechanical properties were measured according to the corresponding ISO standards. Additionally, the handsheets were calcined at 525 °C

for 16 h to determine the PCC effective content (and the corresponding filler retention), according to the TAPPI Standard T211 om-93.

Results and discussion

CNF/CMF characterization

Four different pre-treatments were used to produce cellulose nano/microfibrils with distinct characteristics: cellulose microfibrils a)-CMF-Mec (produced only by mechanical fibrillation) and b)-CMF-Enz (produced by enzymatic hydrolysis); cellulose nanofibrils c)-CNF-TEMPO (produced by TEMPO-mediated oxidation) and d)-CNF-Carbox (produced by carboxymethylation). Table 2 depicts the results of the characterization of the gels obtained.

Table 2 Characterization of the CNF/CMF produced.

	Sample	Yield (%)	C_{COOH} (μmol/g)	Intrinsic viscosity (ml/g)	DP	ζ Potential (mV)	Apparent WRV (g/g)
	BEKP	-	145	905	2628	-26	-
a)	CMF-Mec	8	123	817	2296	-25	2.2
b)	CMF-Enz	19	136	554	1378	-28	2.2
c)	CNF-TEMPO	81	885	164	366	-69	9.2
d)	CNF-Carbox	72	403	522	1345	-59	8.7

From the wide range of fibrillation yields it is possible to conclude that the different pre-treatments provided very different samples. The microfibrillated samples, obtained by only mechanical treatment or enzymatic hydrolysis, present, as expected, low fibrillation yields since the treatment applied did not introduce any functional groups on the surface of the fibres to aid the HPH fibrillation. The very high yield of the TEMPO-CNF is in accordance with the high content of carboxyl groups obtained and is well documented in the literature (Besbes et al. 2011, Kobayashi et al. 2016, Lourenço et al. 2017). For the carboxymethylated CNF the yield was lower due to the used procedure, as explained before (Lourenço et al. 2019a). In fact, from the FE-SEM images (Supplementary Material), it is possible to clearly distinguish both the CMF and CNF samples, as the latter presented a

spider-web-like structure, contrary to the former. Additionally, and as expected, for these two samples (c) and d)), the stronger the chemical treatment, the higher the content of carboxyl groups in the CNF.

The huge difference in the content of carboxyl's obtained with the different pre-treatments was also reflected in the intrinsic viscosity, and by calculation, on the degree of polymerization, with the TEMPO-CNF presenting much shorter polymer chains. The carboxymethylated sample presented values similar to those obtained for the enzymatic CMF. Nonetheless, it is possible to state that an effective breaking of the cellulose chain occurred as these DP are half of the ones measured for the BEKP. In addition, the CMF-Mec, although intensively beaten (15000 PFI rev.), did not show small fibrils. This confirms that a proper pre-treatment is mandatory for the efficient fibrillation in the HPH.

As expected, the functionalizations of the cellulose structure introduced negative charge on the fibres, and high zeta potential values (absolute value) were obtained for the TEMPO and carboxymethylated samples. By the contrary, for the mechanical and enzymatic cellulose microfibrils, the charge of the initial fibres was not altered since no functional groups were added. The apparent WRV gives an indication of the swelling of the samples, with the TEMPO and carboxymethylated CNF presenting nearly 4 times the network swelling level of the mechanical and enzymatic CMF. These values are in accordance with the higher number of fibrils at the nanoscale and much higher charge of the functionalized CNF samples, as reported in the literature (Dimic-Misic et al. 2013).

PCC flocculation in the presence of CNF/CMF

The interactions between PCC and the produced cellulose nano/microfibrils were analysed by flocculation tests performed by laser diffraction spectrometry (Figure 1). The mechanical CMF initially flocculated the PCC particles, but the agitation and sonication applied broke the flocs and therefore values around 8 µm (similar to the normal aggregation of PCC) were obtained after the 90 min of measurement. On the contrary, the enzymatic CMF led to high PCC flocculation due to bridging mechanisms occurring between the long CMF chains and the PCC particles (Lourenço et al. 2019b), with final floc sizes of *ca.* 26 µm, even after applying the shear forces. In the case of the TEMPO-mediated CNF, floc sizes of around 38 µm were obtained. Finally, for the carboxymethylated CNF, a much stronger

flocculation occurred, originating flocs with sizes up to 63 µm. With both the functionalized CNF (TEMPO and carboxymethylated), strong reflocculation occurred after breaking the flocs (visible after stopping sonication), explained by patching mechanisms (Lourenço et al. 2019a, 2019b). Besides, the longer chains of the carboxymethylated samples (higher DP) also contribute to bridging mechanisms, forming therefore the bigger flocs.

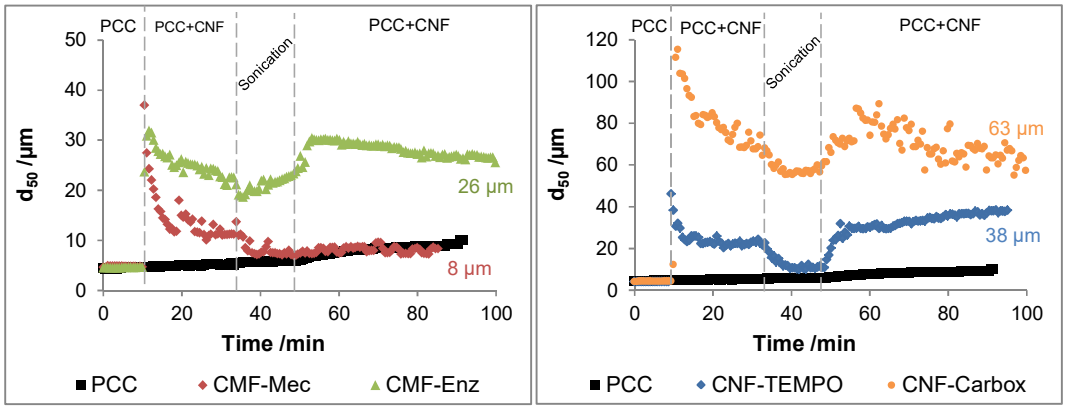

Fig. 1 Evolution of the median of the particle size distribution (d_{50}) of suspensions containing precipitated calcium carbonate (PCC) and CNF/CMF, evaluated by Laser Diffraction Spectrometry. A test with only PCC (and no added CNF/CMF) was conducted for comparison. Special attention should be paid for the different d_{50} scale of the two graphs.

Papermaking potential

The effect of the produced CNF/CMF on laboratory handsheets containing BEKP and PCC and common papermaking additives (starch, ASA and/or CPAM) was investigated. As well-known, in reference handsheets (without CNF/CMF), all these additives are essential to retain the mineral filler in the paper matrix, otherwise very low retentions are obtained (Figure 2, series "Ref": 46% without additives vs 91% with SA-CPAM). The amounts of starch and CPAM used led to similar effects on PCC retention, but their combination produced the optimum value. However, the strong PCC flocculation detected in the presence of CNF/CMF led to high filler retention, even in the absence of additives. When comparing the obtained results to the current reference (the one that simulates the P&W commercial papers - with PCC and all additives but without CNF –identified with a horizontal line in Figure 2), slight filler retention increments were even observed, with the benefits of not using, e.g., expensive CPAM. This is visible in Figure 2, e.g., with "CMF-Enz" for

the series with only starch and ASA (SA) or with the TEMPO and carboxymethylated CNF for the series with only starch (S), which also allow for the ASA and CPAM substitution. With CMF-Mec no significant PCC retention increase was observed, since these CMF were not able to flocculate PCC, as shown above. It must be taken into account that the conductivity of the water used at large scale is much higher than that used at laboratory facilities, which may affect the retention of the components of the furnish.

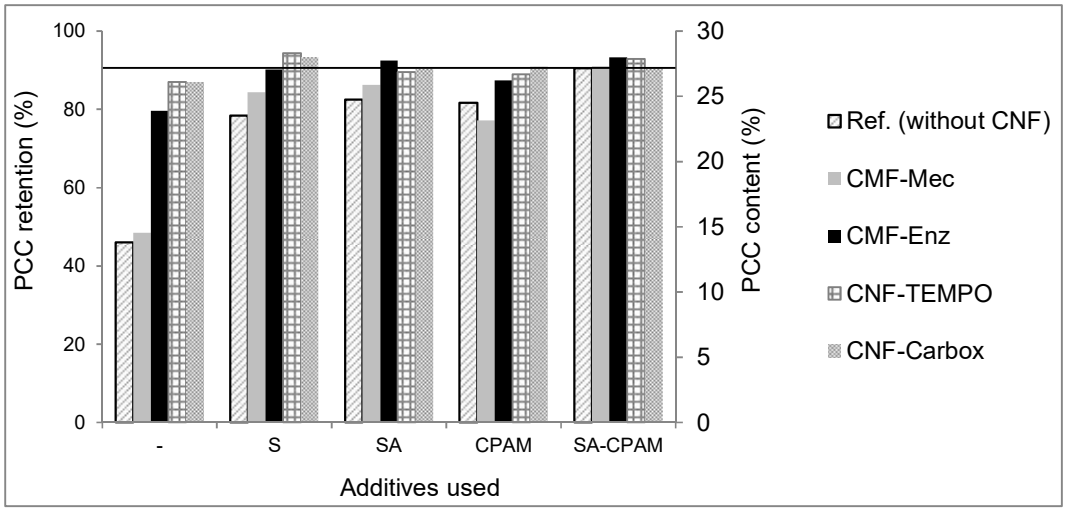

Fig. 2 Filler retention and filler content of handsheets produced with the different cellulose nano/microfibrils and additives. The horizontal line indicates the current reference (handsheets without CNF and all the additives). S: starch; SA: starch and ASA; CPAM: cationic polyacrylamide

Since the mechanical properties of paper are much dependent on the amount of filler, which is known to disturb the bonding between fibres, a normalization of the tensile index was performed by considering the effective filler content of the handsheets. Therefore, a "filler-tensile factor" was computed by comparing this value to that of the current reference handsheets without CNF and with all additives (eq.1). Values higher than 1 correspond to handsheets with a normalized tensile index superior to that of the reference handsheets, and vice-versa (Lourenço et al. 2019a). It should be noted that the reference used derives from an industrial process, representing the results obtained by a procedure optimized in industry. If other reference was used instead (without additives, for example), the factors obtained would be higher, i.e. with better CNF/CMF performances.

$$\text{Filler-tensile factor} = \frac{(\text{Tensile Index} \times \text{Filler content})_{\text{with CNF}}}{(\text{Tensile Index} \times \text{Filler content})_{\text{without CNF and with additives}}} \quad (1)$$

From the results depicted in Figure 3 it is possible to conclude that the additives strongly influence the bonding between fibres, PCC and CNF/CMF. When the additives were used (S, A and/or CPAM), none of the functionalized CNF samples (carboxymethylated and TEMPO) was able to improve the paper strength, probably because the highly negative CNF bonded with the cationic additives instead of bonding with the fibres, as reported previously (Lourenço et al., 2017, 2019a). In fact, CNF-TEMPO and CNF-carboxymethylated only improved tensile when no additives were present. On the contrary, if the nanocellulose was not functionalized, as in the case of CMF-Mec or CMF-Enz, the additives presence had distinct influence: in the case of the enzymatic CMF, the tensile index was always improved in the presence or absence of the different additives, and filler-tensile factors superior to 1 were obtained. In addition, by removing only CPAM from the furnish (Figure 3, series "SA"), the highest tensile increments were obtained for CMF-Enz, suggesting that the high chain length of these microfibrils is overcoming the effect of CPAM. The length of the nanocelluloses seems to be determinant to their reinforcement potential (Lourenço et al., 2019b). In opposition to the CMF-enzymatic, the longer fibrils of CMF-mechanical were not able to improve the tensile strength of the handsheets unless a strength agent (cationic starch, in this study) was present. The higher fibrillation degree of the enzymatic, compared to the mechanical CMF, promoted stronger hydrogen bonding with the cellulosic pulp fibres, and thus better strength properties.

Furthermore, the interaction of CMF-Mec with CPAM proved to be detrimental, since the handsheets produced with these microfibrils and all additives (SA+CPAM) were weaker than the similar but without CPAM (series "SA").

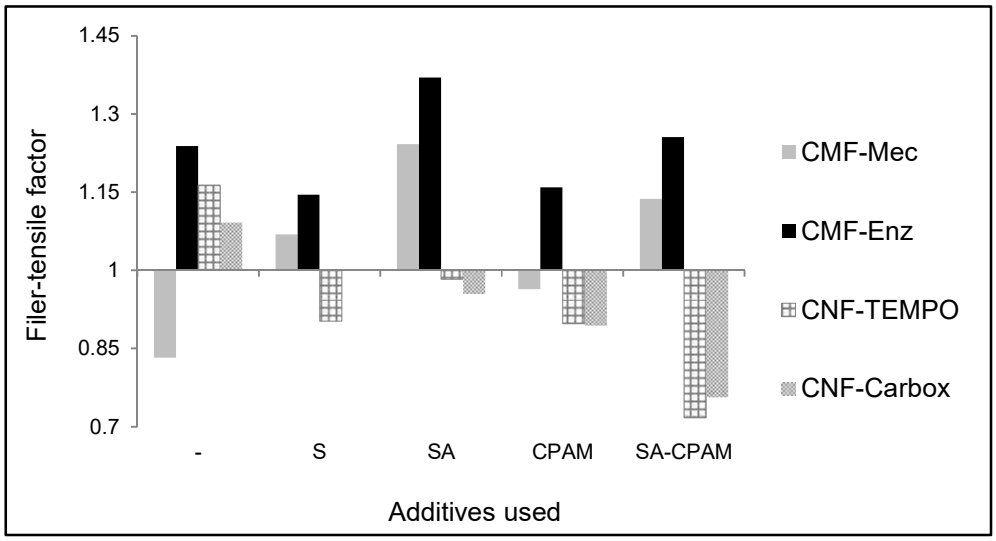

Fig. 3 Tensile index normalized to the same filler content of handsheets produced with the different cellulose nano/microfibrils and additives, relative to the current reference (handshets without CNF and with all additives). S: starch; SA: starch and ASA; CPAM: cationic polyacrylamide

The influence of the distinct CNF/CMF on the wet-web resistance of handsheets for different moisture contents was assessed for selected furnishes. The formulations were selected from the ones that originated the same effective filler content of the current reference (average of all selected samples of 27%±1, corresponding to a filler retention of 90%) and the highest increases in dry tensile index, namely: CMF-Mec+SA+CPAM; CMF-Enz+SA; CNF-TEMPO and CNF-Carbox (both without additives). The results are depicted in Figure 4. As can be seen, the CNF/CMF impact on the handsheets wet tensile resistance was remarkable with gains of up to 100%, when compared to the current reference with all the additives (starch+ASA+CPAM). Remarkably, the influence of the nanocelluloses was more pronounced for the wet-strength (of handsheets with water content up to 70%) than for the dry strength.

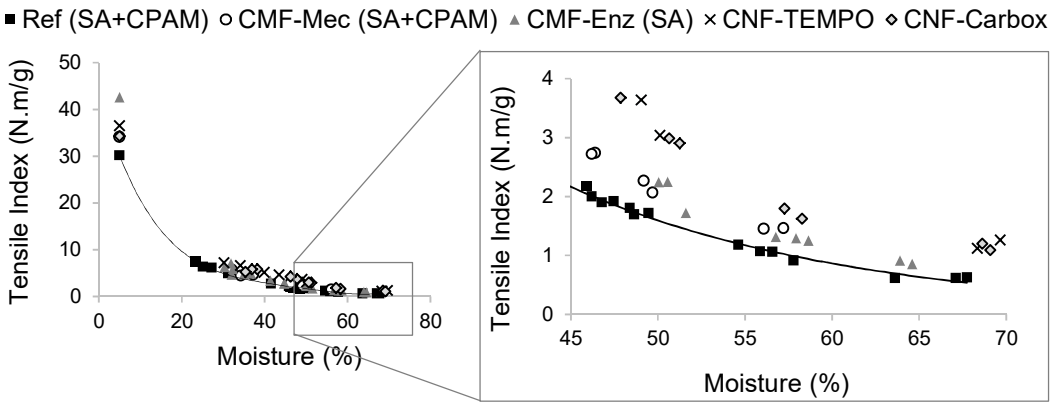

Fig. 4 Wet web tensile index of selected handsheets produced with the different cellulose nano/microfibrils, compared to the current reference (handshets without CNF and with all additives). S: starch; SA: starch and ASA; CPAM: cationic polyacrylamide

As expected, the structural properties of the handsheets containing the cellulose nano/microfibrils and the different paper additives were very distinct. Figure 5 depicts the results of the air resistance, as measured by the Gurley method, and of the Bendtsen roughness. The air resistance of the handsheets produced with the chemically modified CNF (TEMPO and Carbox) increased substantially in comparison to the reference handsheets without nanofibrils. This increase means that the structure was much more closed, and evidences the worsening of the process drainability. If microfibrils were used instead, such as the case of CMF-Mec and CMF-Enz, typically the air resistance was not so disturbed, although still very high for an efficient drainage in a paper machine. The influence of additives in the structural properties was also very pronounced and has a relevant role in understanding the mechanisms involved in the process. Without additives, all the CNF/CMF samples led to very closed structures. Nonetheless, it must be taken into account the different contents of filler obtained (Figure 2): with lower contents of PCC (series without additives) it is easier for the cellulosic fibres and CNF/CMF to establish stronger hydrogen bonds. The presence of the additives in the furnish resulted in much lower air resistance values, being the lowest ones those obtained for handsheets produced with all the additives (starch, ASA and CPAM). As for the surface roughness, it was noticed that the mechanical and enzymatic CMF always improved the smoothness of the handsheets, since the structure was more compact. The addition of additives had a great influence on the roughness of the functionalized CNF-containing handsheets: generally, in the presence of additives, the roughness was higher than that of the reference handsheets (without CNF), which may be due to the abovementioned preferential bonding between the anionic CNF and the cationic additives, originating big agglomerates. Nonetheless, in the absence of additives, the functionalized CNF led to an improvement of the surface roughness.

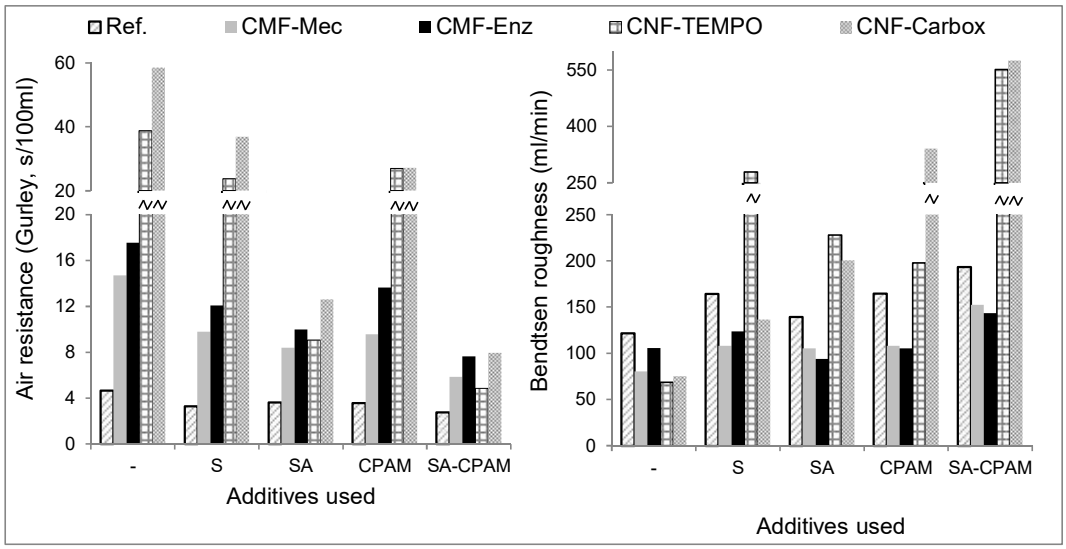

Fig. 5 Structural properties of handsheets produced with the different cellulose nano/microfibrils and paper additives. S: starch; SA: starch and ASA; CPAM: cationic polyacrylamide

The results presented can be synthesised in four cases (Figure 6):

1. Reference handsheets in the presence of additives: The high PCC retention is caused by bridging between the linear CPAM and the filler and cellulosic fibres and also by entrapment due to electrostatic interactions between cationic starch and cellulosic fibres, as well documented in the literature (Hubbe et al. 2009; Ghasemian et al. 2012). As also widely reported, in the absence of additives, PCC is not entrapped and due to the small particles size it is lost through the web wire of the paper machine, leading to low filler retention (Hubbe and Gil, 2016).
2. CMF-Mec in the presence of additives: As in case 1, PCC retention is high due to the presence of additives. However, in addition, the CMF fibrils are able to establish hydrogen bonds with the cellulosic fibres and therefore strength is enhanced, if in the presence of starch, but mainly ASA.
3. CMF-Enz and CNF (TEMPO and Carbox) in the absence of additives: These three types of nanocellulose proved to efficiently flocculate PCC (Figure 1) as explained above, and therefore filler retention is high due to the high size of flocs that cannot be easily lost through the web wire. The strong hydrogen bonding generated between the nanocellulose and the cellulosic fibres improves strength. Additionally, if additives were used in the handsheets production, starch and ASA were still helpful in further improving retention, and, when using CMF-Enz, the additives also helped improving strength.
4. CNF (TEMPO and Carbox) in the presence of additives: The high PCC flocculation ability leads to high retentions in the matrix, as explained, but due

to the high negative charge of the cellulose nanofibrils, there is preferential bonding with the cationic additives, and therefore neither the CNF, neither the additives, are available to bond with the fibres, promoting a huge reduction of strength, especially when all additives are present.

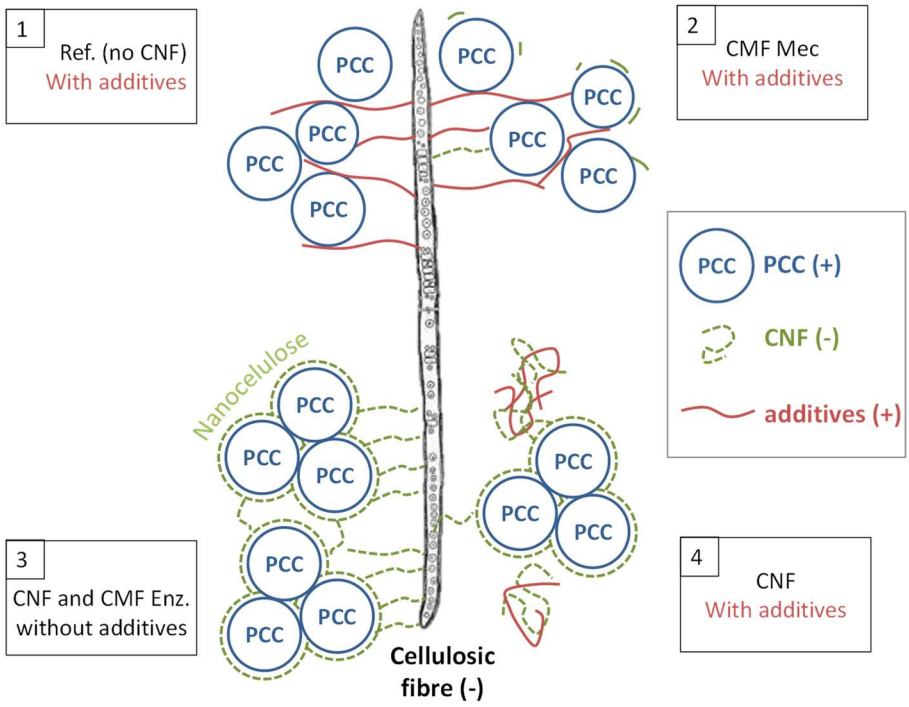

Fig. 6 Schematic representation of the interactions occurring during paper formation, between cellulosic fibres, nanocelluloses, PCC filler and cationic additives. For ease of perception the size of the different components is not at real scale

The water uptake behaviour was evaluated by the water retention value of the fibrous mat and by the handsheets capillary rise Klemm test (Figure 7). For the reference handsheets (without nanocellulose) the sizing effect of ASA and starch is very evident, and the lowest WRV was therefore measured in the series containing these additives ("SA"). However, the cellulose nano and microfibrils addition to the furnish generated completely different results, which depended on the type of CNF/CMF used but also on the interactions with the additives. In the series containing additives, the handsheets produced with functionalized CNF generally retained more water, in accordance to the measured apparent WRV of the CNF (Table 1), which could mean that in an industrial process the drying of the

handsheets is harmed. As for the non-functionalized CMF, it is easily perceived that the handsheets with mechanical CMF followed the same trend of the reference ones, with a great influence of the sizing additives on WRV, but the ones with enzymatic CMF retained much more water. On the other side, the capillary rise results, being mostly influenced by the preferential channels formed during formation of the handsheets, show that in the presence of all of the cellulose nano and microfibrils there is a high reduction of water penetration. This effect was more pronounced in the absence of starch and ASA and the results are directly related to the much more closed structure (increased air resistance) of the handsheets containing nanocellulose.

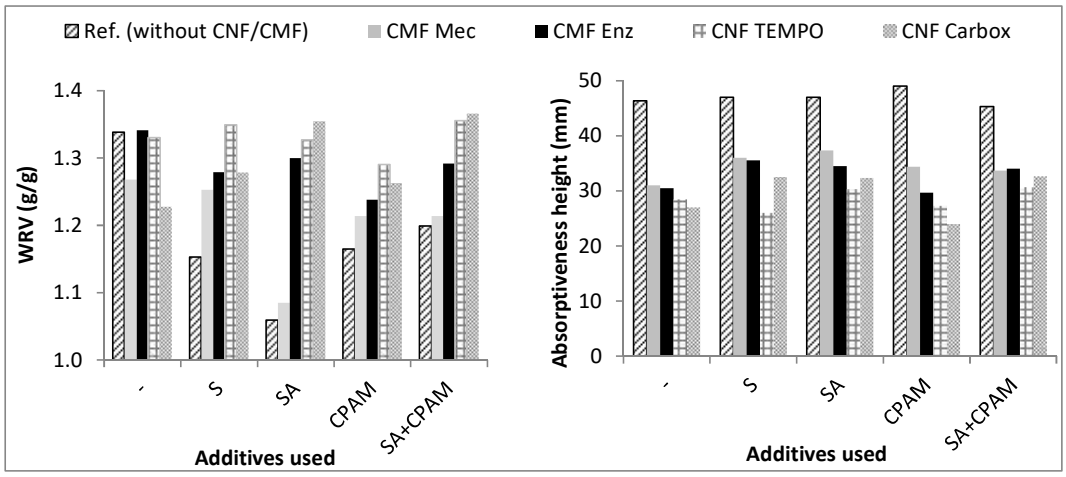

Fig. 7 Influence of different paper additives (starch, ASA and CPAM) in the water retention value (WRV) and water absorption (capillary rise, Klemm test) of handsheets containing PCC and cellulose nanofibrils. S: starch; SA: starch and ASA; CPAM: cationic polyacrylamide

Figure 8 presents a radar plot with some more relevant paper properties of the handsheets produced with selected furnishes. It can be concluded that, in comparison with current reference handsheets (produced with BEKP, PCC, cationic starch, ASA and CPAM), it is possible to slightly increase filler retention while simultaneously increasing strength (tensile and tear, according to Figure 9) and reducing the roughness, at the cost of decreased bulk but mainly reduced drainability (as estimated by the Gurley air resistance). The best formulation tested was the one containing flocs of PCC and enzymatic CMF, starch and ASA: a filler retention of 92.5%, dry tensile strength of 40.4 N.m/g, tear strength of 6 mN.m^2/g, wet-web tensile strength of 2.25 N.m/g (at 50% moisture), Bendtsen surface roughness of 94 ml/min, and Gurley air resistance of 10.0 s (100 ml) were obtained,

to which correspond increases relative to the current reference (without CMF and with starch+ASA+CPAM) of 2.2%, 34%, 20%, 32%, -51% and 260%, respectively.

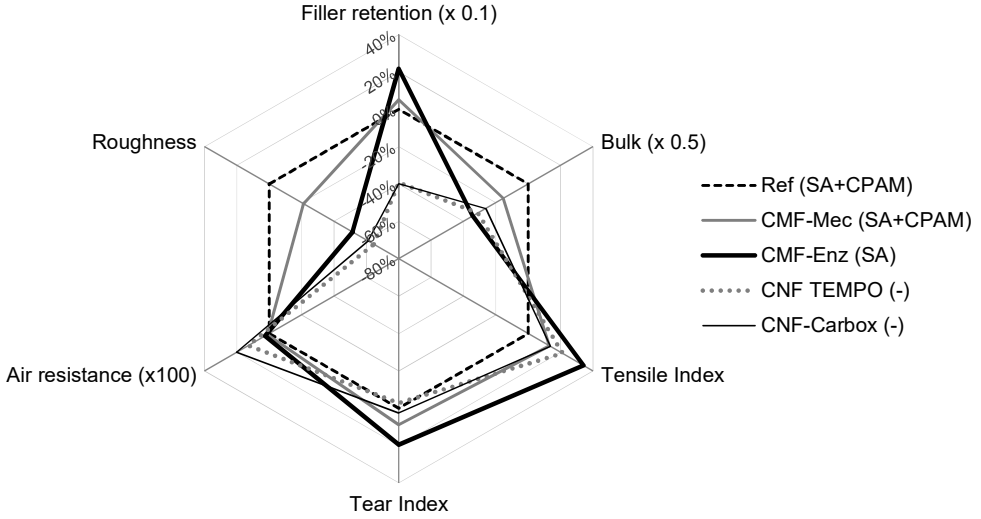

Fig. 8 Improvement percentage of the properties of handsheets produced with selected furnishes, in comparison to the current reference handsheets (without CNF/CMF and with all additives). S: starch; SA: starch and ASA; CPAM: cationic polyacrylamide

The results of the study performed can also allow for cost savings. Table 3 presents the costs estimation for the production of the different CNF and CMF and for their addition in papermaking. A huge difference is visible between the functionalized nanofibrils and the microfibrils obtained by only mechanical process or enzymatic hydrolysis, since the chemicals used in the first case boosted the production costs. Considering the higher filler retentions obtained (Figure 2), and especially the substantially higher strength achieved (Figure 3) by using the enzymatic microfibrils, it is expected to replace a large amount of fibres by filler: it is possible to produce handsheets with a tensile index of 40 N.m/g, with 14% of PCC or with 28% of PCC if 3% of CMF-Enz are used (sample CMF-Enz in series "SA"). Significant cost savings can be therefore attained (assuming PCC to be 7 times cheaper than fibre). Additional savings related to the possibility of replacing non-biobased additives can also be anticipated.

Table 3. Costs estimation for CNF/CMF production and its addition in papermaking.

Material used	Production costs (€ / kg dry CNF)*	Cost of addition to paper €/paper tonne***

	Chemicals*	Energy**	Total	
CMF-Mec	0.7	0.39	1.1	12
CNF-Enz	0.8	0.38	1.2	15
CNF-TEMPO	61.4	0.35	61.7	1831
CNF-Carbox	95.5	0.46	96.0	2859

514 * Fibre cost estimated at 700€/tonne; excluding cost of water consumption
515 ** Energy cost assumed to be 0.075 €/kWh.
516 *** Substitution of 3% of fibre by 3% of CNF/CMF
517
518

519 Conclusions

520 The major conclusion of the present work is that the use of nanocelluloses in
521 papermaking is much influenced by their interaction with all the paper components,
522 in such a way that the presence or absence of the latter can significantly alter the
523 nanocellulose inputs. In this sense, different types of nanocelluloses, with distinct
524 characteristics, will have different interactions with mineral fillers, internal strength
525 and sizing agents or retention systems. If the nanocelluloses are highly negatively
526 charged, such as the case of TEMPO-oxidized or carboxymethylated CNF, there is
527 a great probability that they will interact preferentially with cationic additives, such
528 as cationic starch and cationic polyacrylamide, hindering therefore their availability
529 to flocculate mineral fillers and establish bonding sites with the cellulosic pulp. On
530 the other hand, the nanocelluloses must possess appropriate length, usually obtained
531 after severe mechanical treatment aided by pre-treatments, in order to establish
532 effective bonding with the cellulosic pulps. From the results obtained, it was
533 concluded that an enzymatic hydrolysis was the pre-treatment that produced fibrils
534 with the most suitable characteristics for the abovementioned desired purposes.
535 In the present work, it was concluded that nanocelluloses obtained only by
536 mechanical treatment with a degree of polymerization slightly inferior to that of the
537 original pulp were not able to properly retain filler particles in the matrix, unless
538 combined with retention agents, but could slightly improve paper's strength if
539 starch was used as additive. On the other hand, TEMPO-oxidized or
540 carboxymethylated nanofibrils, highly negatively charged or with very small degree
541 of polymerization, were efficient in retaining fillers and improving strength,
542 provided no cationic additives were present in the furnish. Finally, the best results
543 were obtained using the enzymatic microfibrils, since it was possible to
544 simultaneously improve filler retention and strongly improve the paper's dry and

wet tensile index, without the need to use CPAM, a non-biobased paper additive. These outcomes were explained by their chain length, half of the original pulp, which promoted strong bridging mechanisms with the mineral filler, as supported by flocculation studies, and also with the furnish pulp.

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