Enzymatic nanocellulose in papermaking – the key role as filler flocculant and strengthening agent

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Abstract

Nanocelluloses have been increasingly used in composites since their reduced size, high aspect ratio and stiffness confer great strength to the materials. In papermaking, it has been proved that harsh and expensive chemical pre-treatments to generate nanofibrils, such as TEMPO-mediated oxidation, are not the most favourable and therefore the use of cellulose microfibrils (CMF) have gained extra attention, especially those produced with the aid of enzymatic hydrolysis. In the present work, strategies to improve filler flocculation and the papermaking properties, by using enzymatic CMF, are provided. The CMF degree of polymerization was found to be directly related to precipitated calcium carbonate flocculation, leading to higher retentions in the fibre matrix. Besides, the paper dry and wet strengths were much improved, allowing in return the production of high-filler loaded handsheets with reduced requirements for common paper additives.

Keywords

Enzymes; Filler retention; Nanocellulose; Papermaking; Paper strength

Abbreviations

CMF, cellulose microfibrils; LDS, laser diffraction spectrometry; DLS, dynamic light scattering; DP, degree of polymerization; PCC, precipitated calcium carbonate; CPAM, cationic polyacrylamide; BEKP, bleached eucalyptus kraft pulp

1. Introduction

Nanocelluloses are a promising material, for a wide range of applications. They exhibit unique characteristics, such as reduced size and high specific surface area, high tensile strength, crystallinity and transparency, being for that the object of growing attention, mainly as reinforcing material in composite structures.

In papermaking, their use has been recently reported as they are able to improve strength, filler retention and/or other specific properties such as water absorption (Boufi et al., 2016; Guimond, Chabot, Law, & Daneault, 2010; Tarrés et al., 2016a). Different raw-materials and methodologies can be used to produce these new fibrous structures, usually including mechanical treatments to fibrillate the fibres. To avoid intensive mechanical energy and overcome some inherent technical difficulties, it is common practice to apply to the fibres chemical or enzymatic pre-treatments, originating therefore the cellulose nano or microfibrils (CNF and CMF, respectively) (Abdul Khalil et al., 2014, Lindström, Naderi, & Wiberg, 2015; Nechyporchuk, Belgacem, & Bras, 2016; Osong, Norgren, & Engstrand, 2016).

Although TEMPO-mediated oxidized CNF have been widely employed in composites and papermaking, several drawbacks arise due to their specific properties. In papermaking, the tiny fibrils create a strongly entangled network which leads to severe drainage problems, making this a difficult keypoint that several authors tried to solve, but without complete success (Ankerfors, Lindstrom, & Söderberg, 2014; Rantanen, Dimic-Misic, Kuusisto, & Maloney, 2015; Su, Zhang, Batchelor, & Garnier, 2014; Taipale, Österberg, Nykänen, Ruokolainen, & Laine, 2010). Besides, a highly negative charge of the TEMPO-CNF can lead to filler flocculation problems and therefore diminish its retention in the paper matrix (Korhonen & Laine, 2014; Lourenço et al., 2017). In fact, it has been found that it is not necessary, neither appropriate, to apply fibrils with such reduced size as the ones obtained by TEMPO-oxidation.

In this sense, enzyme-assisted methodologies to produce CMF have been widely explored. Enzymes have been used for a long time to degrade or modify lignin and hemicelluloses, while maintaining the cellulose component of the fibres (Janardhnan & Sain, 2006; Tarrés et al., 2016b; Zhu, Sabo, & Luo, 2011). Recently, the exploitation of enzymes for isolation of cellulose has made it possible to produce CMF with high yields of almost pure cellulose. In this sense, fibrils with diameters in the range of 20-100 nm and lengths up to 100 μm have been obtained. Several authors have reported the

influence of enzymatic-CMF as an additive in papermaking, mainly as reinforcing material. Increases of strength between 40 to 60% were found in the pulp handsheets with this type of CMF (Petroudy, Syverud, Chinga-Carrasco, Ghasemain, & Resalati, 2014; Sehaqui, Zhou, Ikkala, & Berglund, 2013; Tarrés et al., 2016b). However, the research regarding the production of fine papers still needs to explore the CMF effects in conditions similar to those of the papermaking industry, namely by considering the complex interactions between cellulosic pulps, CMF, mineral fillers, and the wide range of additives commonly used to produce these paper grades. Some studies have already addressed the theme, with different types of nanocellulose, fillers or addition strategies (Ankerfors et al., 2014; Diab et al., 2015; He, Yang, Cho, Yong, & Jong, 2017; Hii, Gregersen, Chinga-Carrasco, & Eriksen, 2012; Lourenço et al. 2017; Lourenço, Godinho, Gamelas, Sarmento, & Ferreira, 2019). Also, several works have reported the useful interactions between CMF and mineral fillers (Liu, Maloney, Dimic-Misic, & Gane, 2017; Tenhunen et al., 2018). The present study intends to provide strategies that allow optimizing the production of enzymatic CMF in order to achieve the highest increments on the properties of fine papers, containing mineral fillers, namely precipitated calcium carbonate (PCC). Additionally, focus is also given on the previous flocculation of PCC with the CMF so that flocs with appropriate characteristics to the target application are obtained.

2. Materials and Methods

2.1. Enzymatic hydrolysis

The cellulose microfibrils were produced from an industrial bleached eucalyptus kraft pulp (BEKP) with *ca.* 85% of cellulose and 14% of glucuronoxylan. Previously to the enzymatic reaction, 30 g (dry basis) of the never dried fibres were disintegrated and refined at 4000 rev. in a PFI beater in order to make the fibrils more accessible. Three different commercial enzymes were used to produce distinct CMF samples: Enzyme “a” (endocellulase, 10% exocellulase and 5% hemicellulose), Enzyme “b” (endocellulase with 10% hemicellulose), and Enzyme “c” (endocellulase). Bovine serum albumin (Sigma-Aldrich, USA) was used to determine their protein concentration, according to the Bradford method (Bradford, 1976) and values of 5.0, 5.8, and 6.2 mg/ml, respectively, were obtained. The methodology detailed by Tarrés et al. (Tarrés et al.,

2016b) was used as starting point for the CMF production: briefly, the beaten fibres were suspended in water (3.5% consistency) and the pH was adjusted to 5 by the addition of sodium citrate buffer. The suspension was heated to 50 °C under constant mechanical stirring and the enzyme was added (300 g per ton of pulp). The cellulose 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.

2.2. Mechanical treatment

A sample without enzymatic pre-treatment was produced for reference. For that, BEKP was refined up to 15000 PFI rev. Both the mechanical reference fibres and the enzymatically pre-treated fibres were submitted to mechanical energy, at 1% consistency, in a high pressure homogenizer (HPH, GEA Niro Soavi, model Panther NS3006L). Samples "CMF-Ref", "CMFa", "CMFb" and "CMFc" were obtained after two passes: the first at 500 bar and the second at 1000 bar. An additional study to assess the influence of the HPH in the CMF properties was conducted with fibres pre-treated with Enzyme "a" and with increased passes (2, 4 and 6). However, due to technical difficulties, and differently from the previous samples, it was not possible to attain 1000 bar on the second pass and forward. Total pressures of 1250, 2750 and 4250 bar, respectively, were used to produce samples "CMFa-2P", "CMFa-4P" and "CMFa- 6P", respectively.

2.3. CMF characterization

The CMF produced were fully characterized for their fibrillation yield, zeta potential, degree of polymerization (DP) and ensemble Z-average hydrodynamic equivalent size. The "yield" of production of nanofibrillar material was evaluated in duplicate by gravimetry after centrifugation (9000 rpm for 30 min) of 40 mL of the dispersions (0.2 wt%). The zeta potential (ζ) of the 0.2% CMF aqueous dispersions was measured in triplicate in a Zetasizer Nano ZS (Malvern Instruments). The DP was determined from intrinsic viscosity measurements in cupriethylenediamine (ISO 5351:2010) by applying the Mark-Houwink equation parameters, K=2.28, a=0.76 (Henriksson, Berglund, Isaksson, Lindstrom, & Nishino, 2008). Dynamic light scattering (DLS) measurements

were performed on the centrifugation supernatants using a Zetasizer Nano ZS equipment (Malvern Instruments), in order to have an idea of the relative size of the fibrils, as previously reported (Gamelas et al., 2015, Lourenço et al., 2017).

2.4. PCC flocculation in the presence of CMF

In order to understand the influence of the produced CMF in filler flocculation, tests were conducted by Laser Diffraction Spectrometry (LDS) in a Mastersizer 2000 apparatus (Malvern Instruments) equipped with the Hydro2000MU module. An industrial scalenohedral precipitated calcium carbonate (PCC) was used as filler. Its zeta potential, measured by electrophoretic mobility in the Zetasizer Nano ZS instrument was +7 mV and the median of the particle size distribution, by volume (d_{50}), determined by LDS was 4.2 μm.

The filler and CMF were mixed in the equipment vessel, at a 10:1 mass ratio and a total solids concentration of around 0.01 wt%. After 20 min. of agitation, sonication was applied during 15 min. to break the flocs and then stopped to test if any re-flocculation occurred. This procedure was firstly proposed for filler particles (without CNF) by Rasteiro et al. (Rasteiro et al., 2008). Tests with only PCC were also performed for comparison.

2.5. Papermaking potential

In order to evaluate the behaviour of the new CMF in terms of retention in the fibre matrix and influence on the structural and mechanical properties, handsheets were produced in a semi-automatic laboratory sheet former (300-1 model, LabTech) using a 120 mesh screen.

The used formulations contained fibre (BEKP industrially refined up to 33 ºSR), PCC and CMF. Besides, a series was performed with common paper additives: cationic starch, alkenyl succinic anhydride (ASA) and a linear cationic polyacrylamide (CPAM) used as internal strength, sizing and retention agents, respectively.

For the handsheets production, PCC and CMF suspensions were prepared and mixed as in the flocculation experiments (stirring followed by ultrasonication). Afterwards, the PCC-CMF flocs (33%) were added to the BEKP (67%). In the series with additives, an

emulsion of starch and ASA was subsequently added to the fibre-flocs suspension, followed by CPAM, according to the procedure described in detail elsewhere (Lourenço et al., 2017). The furnish was transferred into the sheet former where air agitation and decantation were followed by drainage. The sheet was collected from the former, and pressing and conditioning were performed according to the ISO 5269-1 standard. The structural and mechanical properties were measured according to the corresponding ISO standards.

Water retention measurements were made according to SCAN-C 62:00 on never dried handsheets (collected immediately after drainage). The wet-web tensile was also measured in a tensile vertical tester (Instron, 2519-102 model equipped with a 50 N static load cell) for different moisture levels, according to the procedure previously described (Lourenço et al., 2017). Besides, 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.

3. Results and discussion

3.1. CMF characterization

Table 1 depicts the results of the characterization of the CMF suspensions obtained. The zeta potential of all the samples was similar to that of the original BEKP, i.e., slightly negative due to the pulp production process. As expected for these types of materials, the yield of fibrillation was low, when compared to nanocelluloses obtained using chemical pre-treatments, with values superior to 70% (Isogai, Saito, & Fukuzimi, 2011; Lourenço et al., 2019), and the standard deviation of the results was quite big due to presence of fibrils with large size, which confer higher heterogeneity to the material. Nonetheless, by analysing the yield values it is possible to distinguish the influence of the different enzymes used in the CMF production, with enzymes “a” and “c” leading to higher yields (higher levels of fibrillation). The determination of the degree of polymerization revealed that the enzymatic treatments applied reduced to more than half the average DP of the original BEKP. Since DP is roughly proportional to the length of the nanofibres (Shinoda et al., 2012), it can be concluded that the size of the fibres,

namely the length, was significantly reduced. However, and as expected, the DP values are of higher magnitude than those obtained for TEMPO-oxidized CNF (Lourenço et al. 2017, 2019; Shinoda, Saito, Okita, & Isogai, 2012). The DP values obtained are in accordance with the measured protein concentration of the enzymes used, with CMFa presenting the highest DP. Although CMF-c presents the lowest DP, meaning that, in average, the fibrils have the smaller length, the supernatant evaluated by DLS reveals that the smallest fraction of the sample (nanofibrils) has the largest equivalent hydrodynamic diameter of all the samples. Since enzyme "a" has a small percentage of exocellulases, in contrast to enzymes "b" and "c" that are composed only of endocellulases, the mechanisms of fibrillation and fiber shortening are expectedly different, producing therefore microfibrils with different structure. The reference CMF was produced with the triple of the refining energy of those applied for the enzymatic microcelluloses and even though the DP was only slightly reduced, proving that only by the enzymatic pre-treatment a substantial breakage of the cellulose chains occurs. The effect of the HPH on fibrillation was translated into a decrease of the DP of *ca.* 330 between the samples with 2 and 6 passes, as higher shear forces helped partially break the cellulose chains. Moreover, it seems that by increasing the intensity of the mechanical treatment, a higher number of fibrils are being released from the surface of the fibres (thus increasing the yield).

Table 1 Characterization of the CNF/CMF produced.

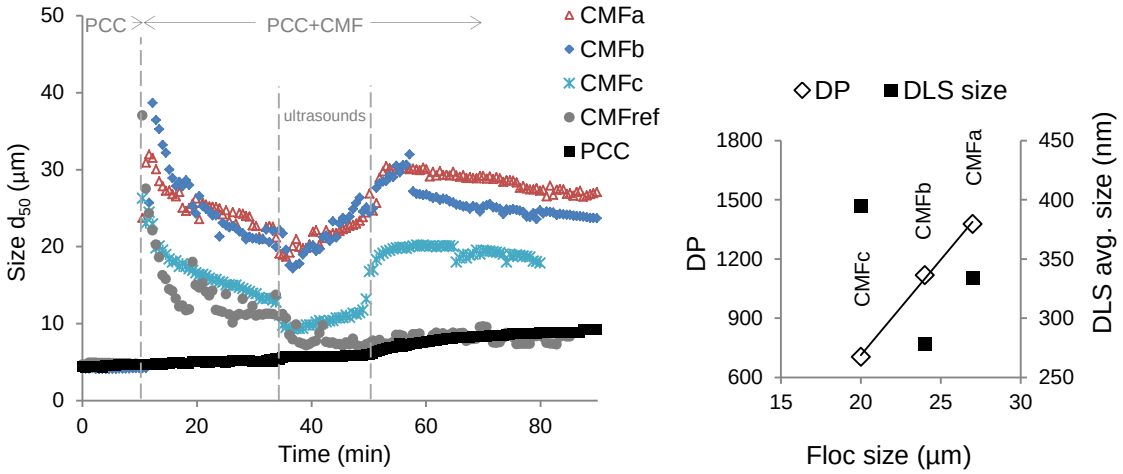
Sample	Enzyme (g/tonne)	Passes / pressure (bar) in the HPH	ζ Potential (mV)	Yield (%)	DP	DLS avg. size (nm)
BEKP	-	-	-25 (8)	-	2628 (127)	-
CMF-Ref	-	2P /1500	-25 (3)	5 (3)	2296 (57)	356 (86)
CMFa	300	2P / 1500	-28 (1)	20 (11)	1378 (9)	334 (10)
CMFb	300	2P / 1500	-28 (1)	10 (6)	1118 (43)	278 (4)
CMFc	300	2P / 1500	-31 (3)	20 (4)	704 (75)	387 (65)
CMFa (2P)	300	2P /1250	-29 (3)	22 (8)	1834 (7)	428 (17)
CMFa (4P)	300	4P / 2750	-33 (3)	24 (11)	1747 (61)	483 (14)
CMFa (6P)	300	6P / 4250	-33 (1)	26 (14)	1504 (12)	550 (14)

(standard deviation within parentheses)

3.2. PCC flocculation in the presence of CMF

The interactions between the cellulose microfibrils and PCC were analysed by

flocculation tests performed by LDS (Fig. 1a). The reference CMF (only mechanical treatment) caused an initial flocculation of PCC, but the shear forces applied, either by mechanical stirring or ultrasonication, broke the flocs, and final sizes similar to those of PCC were obtained. The type of enzyme used in the production of CMF led to distinct flocculation results, with the CMFc flocculating PCC much less than the ones produced with the other two enzymes ("a" and "b"), in accordance with the lower DP value of the former CMF. In fact, Fig.1b reveals that the size of the PCC flocs is directly influenced by the DP of the CMF used, rather than by their hydrodynamic equivalent diameter. The effect of sonication on the flocculation behaviour was also distinct when the different enzymes were used to produce CMF: CMFa and CMFb did not deflocculate when sonication was applied, in contrast to CMFc and to what was expected for the PCC-nanocellulose flocculation (Lourenço et al., 2017, 2019; Korhonen et al., 2014), which could also contribute to the formation of larger floc sizes. These results can be determinant for papermaking when CMF are used as additive and therefore this type of flocculation studies (which include ultrasound to simulate the shear forces in stock preparation and headbox of the industrial process) can be used as a starting point for selecting the conditions to produce an optimized CMF. In this work, stabilized flocs with *ca.* 27, 24 and 20 µm were obtained for CMFa, CMFb and CMFc, respectively.

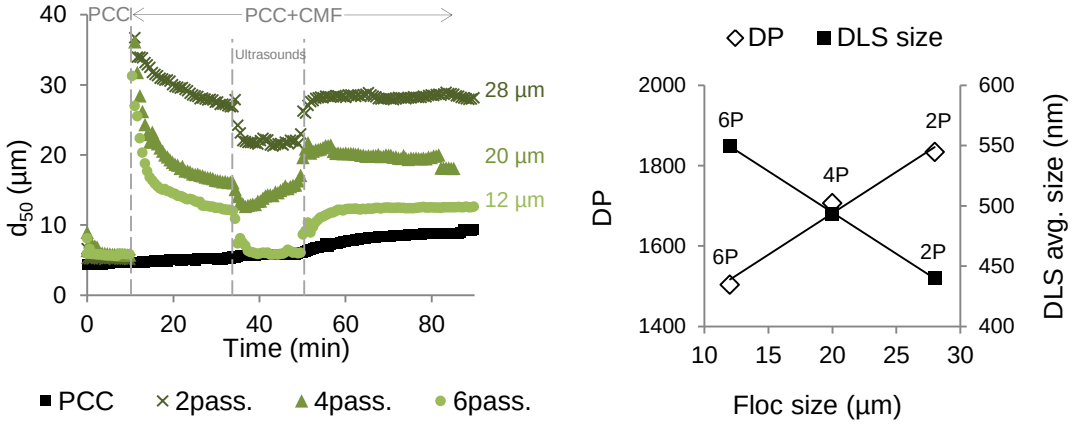


(a) (b)

Fig. 1. (a) Evolution of the size of PCC flocs in the presence of CMF, evaluated by LDS, and (b) influence of the degree of polymerization and DLS average size of CMF on the final flocs size.

In order to assess the influence of the CMF length on PCC flocculation, an additional study was performed with cellulose microfibrils produced with increased passes in the

HPH. By analysing the flocculation behaviour depicted in Fig. 2a, it is possible to state that increased passes in the HPH are harmful for PCC flocculation since the fibrils become not only smaller in length (lower DP), but intrinsically weaker. In fact, with the increased passes, the shear forces applied during the flocculation tests led to relative breaking of the PCC flocs and the "6 pass" sample almost failed to create PCC flocs (observable at a total time of 90 min of measurement). As concluded previously, the floc size was also found to be directly influenced by the CMF degree of polymerization, but in this additional study, performed with the same enzyme, it was possible to conclude that floc size was inversely related with the DLS average size of CMF (Fig 2b).



(a) (b)

Fig. 2. Influence of CMF-Enz produced with 2, 4 or 6 passes in the HPH on the a) evolution of the median of the particle size distribution (d_{50}) of PCC suspensions, and b) the correlation between the CMF properties (degree of polymerization and DLS average size) and the PCC-CMF flocs size.

From the results presented, it is possible to state that the size of PCC-CMF flocs is influenced by: a) the type of enzyme used in the CMF production, being directly related to the DP of CMF (Fig. 1b) and b) the mechanical treatment intensity during CMF production (Fig. 2b), wherein a higher intensity provides CMF with lower DP and lower potential for PCC flocculation.

3.3. Papermaking potential

The effect of the incorporation of CMF on laboratory handsheets was investigated. From Fig. 3 and 4 it is clearly visible that the CMF presence leads to a high increase of

strength and in some cases, of filler retention. This can be explained by the formation of strong bonding between fibres and nano and microfibrils (González et al., 2012; Hii et al., 2012; He, Cho, & Won, 2016) and to the formation of big filler flocs (Korhonen & Laine, 2014; Lourenço et al., 2017, 2019).

In a common printing and writing paper, produced with BEKP and PCC, it is usual practice to add additives such as internal sizing, strength and retention agents to improve the paper properties. This effect was clear for the reference handsheets (without CMF) in the presence and absence of additives, with huge increases of filler retention (Fig. 3) and consequent effects on strength (Fig. 4). The same effect was observed with the reference CMF (with only mechanical treatment). However, it was found out that, in most of cases, the enzymatic microfibrils presence was able to substitute or reduce the need of the aforementioned additives, as higher retentions and tensile indices were obtained in comparison to the reference handsheets without additives (Fig. 3 and 4). By testing the same formulations in the handsheet production, it was possible to increase filler retention in 77% and 65% (without additives) or in 2 and 3% (with additives) by using CMFa and CMFb, respectively. As for CMFc, no significant increments were obtained for the filler retention in the absence of additives, which could be due to the much smaller degree of polymerization of the microfibrils (Table 1), not being able therefore to substitute the long chains of the CPAM used as retention agent. In the presence of additives, the incorporation of that CMF also led to no substantial variations.

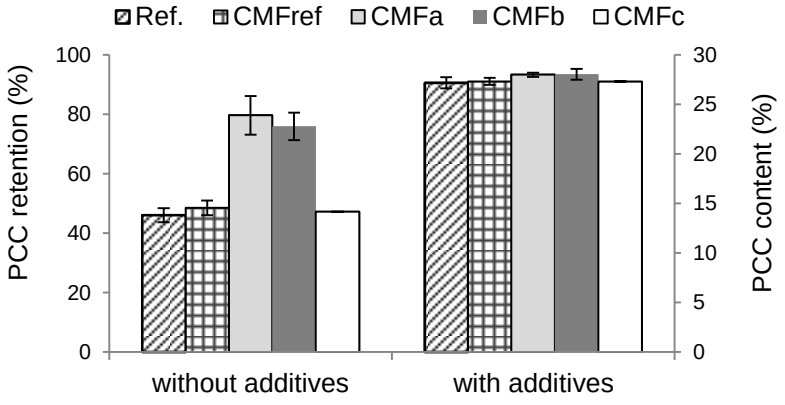


Fig. 3 Influence of enzymatic cellulose microfibrils (CMF) on filler content and retention of handsheets produced without and with additives (cationic starch, ASA and cationic polyacrylamide). Reference handsheets without CMF (Ref.) and with CMFref (only mechanical treatment) are presented for comparison.

As for the tensile index (Fig. 4), increases relative to the reference handsheets (without CMF) of 4, 0 and 16% (without additives) and 22, 18 and -4% (with additives), respectively for CMFa, CMFb and CMFc, were obtained. The reference CMF (without enzymatic pre-treatment) was also able to increase the tensile index by 14 and 13%, respectively. When analyzing these results, it is of utmost importance to consider the filler retention values abovementioned, since the handsheets mechanical resistance is known to be directly influenced by the filler content (Lourenço, Gamelas, & Ferreira, 2014). Although similar filler contents were obtained in the presence of additives, in their absence, the microfibrils CMFa and CMFb were able to generate handsheets with a much higher filler content and similar or slightly higher mechanical resistance. Inversely, the CMFref led to very strong handsheets in the absence of additives, but it must be taken into account the much lower effective filler content achieved in comparison to the handsheets produced with enzymatic CMFa or CMFb (absolute reduction of -10%). To further explore these results, a new series of handsheets with CMFa and without additives, containing more 5% of added filler, was produced (62, 35 and 3% of BEKP, PCC and CMF, respectively). The results obtained are also shown in Figure 4. These handsheets were found to have the same effective filler content of the reference handsheets with additives, but showed a remarkable 19% increase in the tensile index. This conclusion indicates that it is possible to produce handsheets without additives and increased strength, by using 3% of enzymatic CMF.

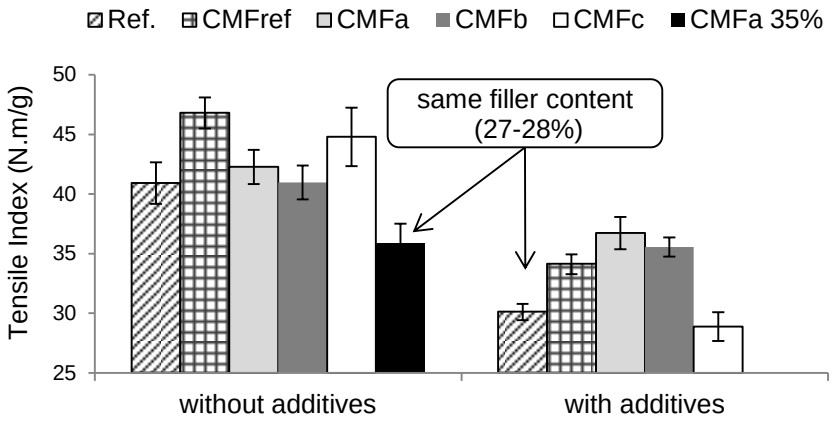


Fig. 4. Influence of enzymatic microcellulose fibrils (CMF) on tensile index of handsheets produced without and with additives (cationic starch, ASA and cationic polyacrylamide). The extra black column refers to handsheets produced with addition of 35% of PCC. Reference handsheets without CMF (Ref.) and with CMFref (only mechanical treatment) are presented for comparison.

The influence of the CMF on the wet-web strength of the handsheets (without additives) was also analyzed (Fig. 5). For high moisture contents, a different trend from the one observed for the dry handsheets was registered: at 46% moisture content, tensile increases relative to the reference (without CMF) of 104, 91 and 28% for CMFa, CMFb and CMFc, respectively, were observed. It must be taken into account that CMFc led to low retention values (in the absence of additives), with values below 50%, while, for the same conditions, CMFa and CMFb were able to increase this value to more than 75%. Furthermore, these values are still below the filler retention of the reference handsheets with additives (> 90%). Considering that the increase of tensile index is directly proportional to the decrease of filler content (Lourenço et al., 2014), the present results obtained must be carefully analysed. The wet tensile strengths of CMFa and CMFb were similar and always superior to the values obtained with CMFc, even considering the huge differences of filler retention/content. As expected, for the dry section the filler content is highly influencing the results (as observable for CMFc with only 14% of filler, in comparison to the reference handsheets with 27%), but for the high moisture section, the interactions between the microfibrils and BEKP fibres seem to be dominant and overcoming this filler content differences.

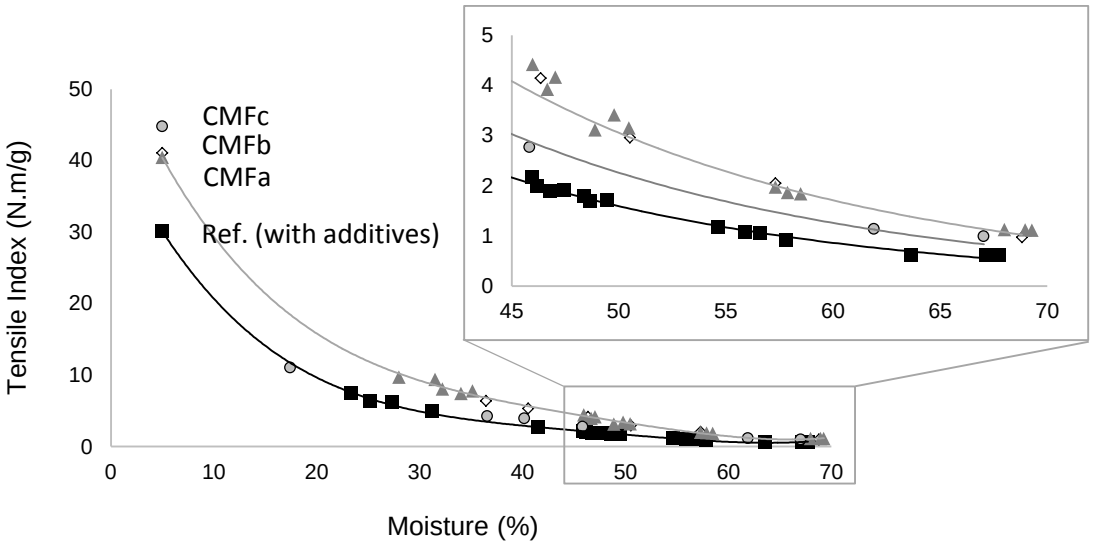


Fig. 5. Wet web tensile index of handsheets produced with the enzymatic cellulose microfibrils (without additives), compared to reference handsheets (without CMF and with additives)

As expected, the presence of the cellulose microfibrils granted distinct structural

properties to the handsheets. Fig. 6 reveals the results of the air resistance, as measured by the Gurley method, and of the Bendtsen roughness. The major drawback of using CMF in papermaking is the reduced drainability, since the sheet structure becomes much more closed due to the increased bonding. The air resistance measured in the produced handsheets is directly related to the process drainability, which can be improved if the filler content is increased: Fig. 6 reveals, for CMFa, a decrease of air resistance of 34% when 5% more of filler is used. Although the handsheets produced with CMFc and without additives were found to possess low filler effective content, which theoretically would close even more the paper structure, a lower air resistance value was obtained. Although these values are still considered high for an efficient drainage in a paper machine, an optimization of the conditions (filler content, use of other additives, addition of long fibre, etc.) could lead to smaller values, as proven by other authors (Dimic-Misic, Maloney, Liu, & Gane, 2017). In contrast, the handsheets roughness was highly reduced since CMF binds all the components, creating a net-like structure without so many loose fibrils. The roughness of CMF-containing handsheets (without additives) with the same filler content of the reference handsheets (without CMF and with additives) was found to be 46% smaller.

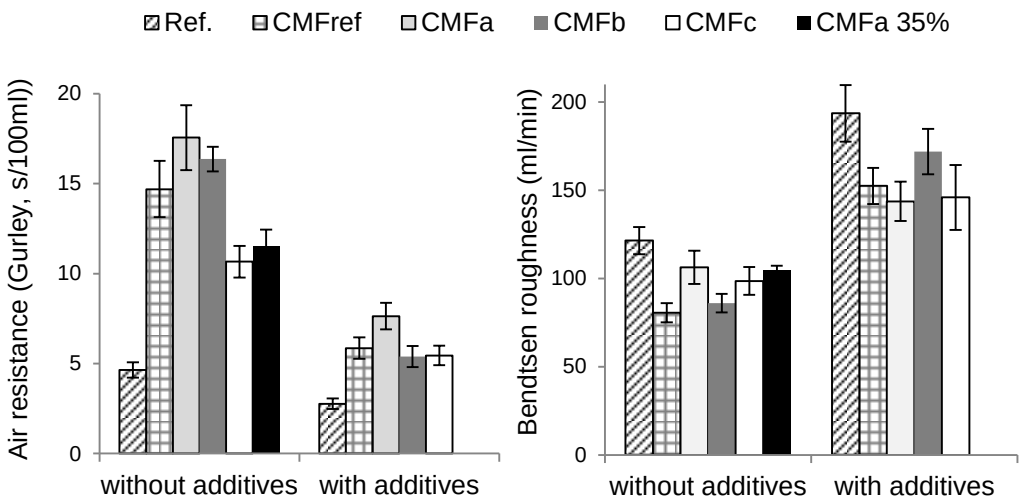


Fig. 6. Air resistance and roughness of handsheets produced with cellulose microfibrils. Reference handsheets without CMF (Ref.) or with CMFref (only mechanical treatment) are presented for comparison.

The capacity of the fibres mat to retain or absorb water was evaluated by the water retention value (WRV) and that of the handsheets by the capillary rise Klemm test (Fig.

7). Generally, in the presence of the cellulose microfibrils, the fibre mat retained more water, as expected. This could mean that the CMF-containing sheets are more difficult to dry in the dryer section of the paper machine. Additionally, if additives were not used, the WRV was even higher. On the other hand, the capillary rise is reduced in the CMF presence, which means that there is lower penetration of liquids than with the reference handsheets without CMF, such as e.g., the surface sizing formulations applied in the paper machine size press. This is directly related to the more closed handsheets, as the Gurley air resistance shows a linear correlation (R^2>0.9) with the capillary rise (Supplementary data).

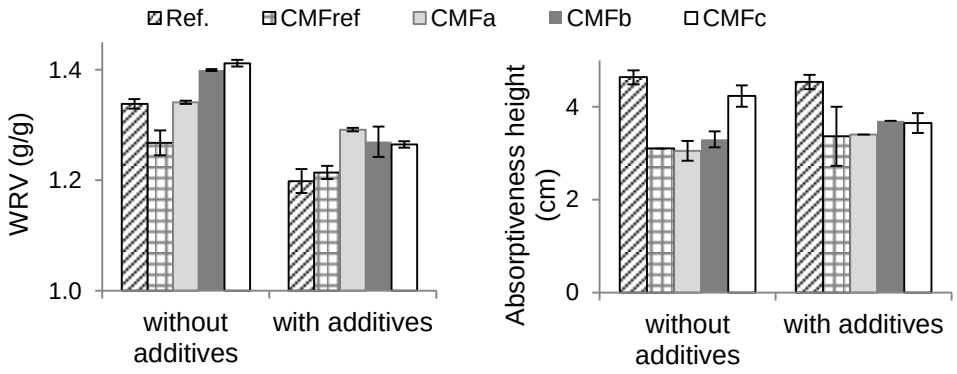


Fig. 7. Influence of enzymatic cellulose microfibrils (CMF) in the handsheets water retention value (WRV) and water absorption (capillary rise, Klemm test).

The results obtained help in defining a pathway to use cellulose microfibrils as retention and strength additive in papermaking, namely on the production of fine papers. Further studies must be carried out in order to optimize the CMF production and their application, specifically regarding the type and amount of paper additives to use.

4. Conclusions

Cellulose microfibrils (CMF) were produced by enzymatic hydrolysis followed by high pressure homogenization. A reference CMF obtained without enzymatic pre-treatment was also used for comparison purposes. Different enzymes were tested, originating CMF with different degree of polymerization and size. Flocculation studies revealed that enzymatic CMF are able to flocculate PCC, contrary to the reference CMF (only intensive mechanical treatment). A direct relation between the enzymatic CMF degree of polymerization and the generated flocs size was found. Additionally, exceeding

mechanical treatment intensity during the enzymatic CMF production seemed to degrade the fibres, with poor PCC flocculation as a consequence.

When added to papermaking furnishes, enzymatic CMF were able to increase filler retention and strength. Moreover, some of the CMF produced were able to partially substitute the effect of retention agent (cationic polyacrylamide) and reduce the requirements for internal strength additives (e.g. cationic starch). Furthermore, the wet-web strength was highly increased when CMF were used and it was presumed that, at high moistures, the fibre-CMF interactions were stronger than the disruption caused by the presence of mineral filler particles.

One of the drawbacks of incorporating CMF in papermaking was the reduced drainability, which could be overcome by optimization of the process (3% enzymatic CMF and 5% more filler reduced air resistance by 50%). In fact, the CMF-containing fibre mats retained more water (WRV), thus hindering drying of the paper web. However, as a positive outcome, surface roughness and water penetration (capillary rise, Klemm test) were reduced.

The results obtained reveal the great aptitude of enzymatic-CMF to improve the properties of handsheets containing filler and provide important correlations between the CMF production and final paper properties, giving solutions to overcome difficulties such as reduced drainability or use of expensive synthetic polymers.

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