



Exploring the synergistic effect of anionic and cationic fibrillated cellulose as sustainable additives in papermaking

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Abstract While cationic cellulose has yet to find a place in the paper industry, manufacturers show certain interest in a more recent material: cellulose nanofibers (CNFs), generally with negative surface charge. This work suggests both to be combined to increase the mechanical properties of recycled paper while preventing the use of synthetic polyelectrolytes as retention agents. On one hand, a bleached pulp was cationized by etherification, both as-is and following mechanical refining (15,000 PFI revolutions) and submitted to high-pressure homogenization, generating two different kinds of cationic CNFs. On the other, the same pulp was submitted to an enzymatic pretreatment and high-pressure homogenization, producing a negatively charged cellulose micro/nanofiber (CMNF). Two different cellulose-based systems consisting of each type of cationic CNF and the enzymatic CMNF were applied in the papermaking of

both virgin and recycled paper. This study demonstrates the effective use of the cationic CNFs as retention agents during sheet formation, which together with the enzymatic CMNFs significantly enhanced the mechanical properties of both types of paper. The study found that refining before cationization favored the retention effect, primarily due to increased surface area and charge of the cationic CNFs, where remarkable increases in the breaking length of virgin (125.1%) and recycled paper (46.5%) were reached. The synergy between cationic CNFs and enzymatic CMNFs outperformed the use of commercial polyacrylamide, a non-biodegradable polyelectrolyte. This research highlights the potential of tailored CNFs in producing high-performance papers, while promoting sustainability and offering a plausible strategy to increase paper recycling rates.

Keywords Cationization · Pulp and paper · Nanocellulose · Recycling · Wet-end chemistry

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Introduction

According to the Food and Agriculture Organization of the United Nations (FAO), from 2010 to 2021 the annual production of paper and paperboard increased by 6% (FAO 2021). In Europe, the annual turnover from the production of pulp, graphic, hygienic, packaging and specialized paper grades and products accounted for over 180 billion euros

(European-Commission 2022; CEPI 2023). Noticeably, the pulp and paper industry is an important and increasing sector for economy and society, where innovation and sustainability are decisive features for leading the segment.

One of the central operations on which the industry is focusing in the last decades is improving the paper recycling rates. Recycling paper reduces the need of extracting new raw material for pulp production and decreases the required energy consumption in the process. Current recycling rates in Europe are of 71.4%, according to the Confederation of European Paper Industries (CEPI), and the objective is to increase them up to 76%. Nevertheless, there are challenges that still need to be overcome for achieving this objective. Paper cannot be recycled for infinite times, since there is a noticeable decrease of its strengthening capacity over time due to the hornification of fibers, an irreversible deterioration caused by repeated drying and processing cycles (Wan et al. 2011; Hubbe 2014; Solhi et al. 2023). Currently, processes employed to recover paper properties, such as mechanical refining, are becoming inefficient or insufficient. Therefore, it is necessary to improve recycling rates, while maintaining or even enhancing mechanical characteristics of the final product, at the same time that sustainability requirements are met.

Key approaches to achieve this outcome involve the use of additives, such as strengthening agents and retention aids. Strengthening agents are able to interact with fibers and promote the bonding between fiber and fibrils, thus creating a stronger network and improving mechanical properties. These agents should interact with water, be compatible with the cellulose surface and be biodegradable so to meet environmental regulatory requirements (Ashori et al. 2013). Examples of strength additives are cationic starch, polyacrylamides and micro/nanocellulose fibers. This latter type of agent has been gaining considerable attention from both academia and industry, as it constitutes a sustainable material that has been well proven to enhance mechanical properties of papers (Lavoine et al. 2012; Rol et al. 2019a; Li et al. 2021). The phenomenon behind this is due to their high specific surface area, which improves the bonding between fibers and fibrils at the same time that they are able to better arrange the stress peaks through the network during loading (Taipale et al. 2010). Hollertz et al. (2017) produced three different

types of carboxymethylated cellulose nanofibers and applied them in the preparation of unbleached kraft pulp handsheets. These cellulose nanofibers (CNFs) were able to increase the tensile strength of the papers probably due to the increased densification of the sheets and the chemical cross-linking between fibers and nanofibrils. Ang et al. (2020) produced CNFs by applying mechanical refining and high-pressure homogenization over de-inked recycled pulp and was able to increase the tensile index of bleached eucalyptus kraft pulp paper by 83% with a 20 wt.% CNF addition. Another route that is interesting to consider when producing micro/nanocellulose fibers is the enzymatic hydrolysis (Henriksson et al. 2007). Treating fibers with enzymes, such as endoglucanases, is attractive since it does not employ harsh and expensive chemicals and usually requires mild reaction conditions (Lourenço et al. 2019). For instance, CNFs from enzymatically treated pulps were produced by Jo et al. (2021) and applied in bleached hardwood kraft pulp handsheets. At a 2 wt.% application, tensile index was increased by 52.7% and the burst index by 210.2%.

Similar agents can also be used as retention aids, namely cationic polymers such as cationic polyacrylamides and cationic starch. Retention agents' main purpose is to help in the retention of fines and other additives (such as mineral fillers and some strengthening agents like CNFs) in the pulp slurry. This approach optimizes the utilization of resources and avoids the loss of these components to white water, which can have a detrimental effect on paper properties since this water is usually recirculated in the process. These components are usually smaller than the mesh size of the screens used during the forming step in the paper machine and therefore are washed away together with the water contained in the initial slurry. Considering the importance of improving mechanical properties of paper, retaining fines onto the fiber network is essential, especially when considering recycled pulp where the percentage of fines is higher (Odabas et al. 2016). The retention is possible due to the flocculation capacity of the retention agents, usually of cationic nature, over these components, which are often negatively charged. More recently, the development and application of cationic cellulose nanofibers (CCNFs) has also been explored and they could be potentially used as retention agents (Aguado et al. 2017; Lu et al. 2020;

Pedrosa et al. 2022a). Common routes employed to produce cationic cellulose derivatives include cellulose oxidation with sodium periodate followed by cationization with Girard's reagent T ((2-hydrazinyl-2-oxoethyl)-trimethylazanium chloride, GT) (Sirviö et al. 2011; Huang et al. 2020; Pedrosa et al. 2022b; Borja et al. 2022). Another alternative is to react the cellulose with some epoxy reagents, e.g. N-oxiranyl-methyl-N-methylmorpholinium, or 2,3-epoxypropyl-trimethylammonium chloride (EPTAC) or even with its precursor (3-chloro-2-hydroxypropyl)trimethylammonium chloride (CHPTAC) under alkaline media (Yan et al. 2009; Hasani et al. 2009; Moral et al. 2016; Pedrosa et al. 2022b). Owing to several factors, cationic derivatives of cellulose have not been as successful in the pulp and paper industry as those of starch (Farrell and Hauser 2013; Sharma et al. 2021). One reason is the reluctance of manufacturers to use chemically modified fibers with the pulp stock, mainly because it implies altering the already existing equipment and the supramolecular structure of cellulose, which could ultimately lead to changes in paper performance. However, a major drawback is inherent to cellulose, which is less reactive than starch. Its repeating units, namely anhydroglucose units (AGU), are linked to each other and through intra- and intermolecular hydrogen bonds, giving way to cellulose I α and cellulose I β crystalline networks (French 2014). Furthermore, when suspended in water, the hydrophobic effect hinders the penetration of the solvent through the fibrils (Alves et al. 2015). It is common to address the setbacks presented by the supramolecular structure of cellulose with the use of sodium hydroxide (Yokota et al. 2022).

Nevertheless, interesting studies investigating the application of cationic cellulose in papermaking have been performed and show their potential as retention agents. For instance, Aguado et al. (2017) investigated the flocculation capacity of three different soluble cationic derivatives of cellulose over precipitated calcium carbonate (PCC), ground calcium carbonate (GCC) and kaolin. The main conclusions were that high degrees of polymerization (DP) and high charges favored the flocculation of these mineral fillers. Another example is the work of Pedrosa et al. (2022a), who produced different CCNFs, either with Girard's reagent T or by cationization with CHPTAC, and applied them in the retention of PCC. Results demonstrated that the best

CCNFs, with a degree of substitution (DS) of 0.13 for the CHPTAC treated derivative and a DS of 0.16 for the Girard's reagent one, were able to increase the retention rate from 43 to 62% for an incorporation of 0.4 wt.%. Finally, Lu et al. (2020) studied the effect of adding CCNFs in the flocculation of fines and its influence on the wet web strength of papers produced with softwood bleached kraft pulp. The researchers concluded that CCNF can effectively improve the interactions between fibers and fines, thus enhancing wet web strength performance without hindering greatly the dewatering rate. For instance, with an addition of 5 wt.% CCNFs with the highest charge, the breaking length of the wet web increased by 46%.

Considering the aforementioned challenges and opportunities, namely the potential performance of anionic and cationic CNFs as strength and retention agents, respectively, and the need of exploring to a further extent the use of both of them in papermaking, this work defines a dual-CNF strategy to improve the mechanical properties of recycled paper. To the best of the author's knowledge, the proposed approach has been scarcely explored in the literature so far, and underlines the strengthening effect of anionic CNFs, here represented by the use of enzymatically hydrolyzed fibers, combined with the retention potential of CCNFs, enabling a fully cellulose-based system. For this, first anionic and cationic CNFs were produced and characterized. The second stage was to study the effects of this dual-CNF system in virgin pulp paper, in order to assess the different electrostatic interactions that could be happening between fibers and CNFs. Finally, with the results obtained for virgin pulp, the study concludes with their application in recycled pulp and the effects on the paper properties are evaluated. The present study suggests that it is possible to tailor different CCNFs by applying mechanical refining prior to the cationization reaction. In addition, the combination of anionic CNFs, produced via enzymatic hydrolysis, and CCNFs increased the mechanical properties of both virgin and recycled paper, surpassing the effects of the combination between anionic CNF and commercial polyacrylamide, the reference non-biodegradable polyelectrolyte that is conventionally used as retention agent in papermaking. Thus, the study highlights the potential of cellulose-based additives for obtaining high-performance papers, while minimizing the use

of chemicals and increasing the sustainability within the industry.

Experimental section

Materials

For producing CNFs and virgin pulp paper, bleached kraft eucalyptus pulp (BKEP) was used and kindly provided by Torraspapel SA (La Montañanesa, Spain). Recycled pulp used for papermaking was made by mixing 65% of liner paper and 35% of fluting, both provided by Saica Paper (Zaragoza, Spain). For the enzymatic pre-treatment, FiberCare® U solution was used and acquired from Novozymes (Bagsværd, Denmark). The aqueous solution of (3-chloro-2-hydroxypropyl)trimethylammonium chloride (CHPTAC) at 60 wt.% used for cationization was acquired from Merck (Barcelona, Spain). A commercial cationic polyacrylamide (CPAM) with an anionic demand of 2252 µeq/g and high molecular weight ($\sim 10^6$ g/mol) was used for comparison. Other reagents used during the experimental tests were purchased from Merck (Barcelona, Spain).

Production of cellulose micro/nanofibers

First, BKEP was disintegrated at 3000 rpm for 20 min at a 1.5 wt.% consistency by means of a device complying to the ISO standard 5263-1 (ISO 2004). After dispersion, fibers were filtered with a nylon cloth of 200 mesh in order to reduce the excess of water and stored at 4 °C until further use.

For the enzymatic reaction, the pulp was suspended in distilled water reading a 3 wt.% consistency. Sodium acetate/acetic acid buffer (0.1 M) was then added to maintain the pH at 4.8 and the reaction media was then heated up to 50 °C. Then, the enzyme was added at a dosage of 240 mg/kg and the reactor was kept under gentle agitation for 3 h. To stop the reaction, the medium was diluted with water at 90 °C. The treated pulp was filtered with a nylon cloth of 200 mesh, washed thoroughly with water, and suspended in distilled water at 1 wt.%. In order to generate the micro/nanofibers, the diluted suspension was submitted to a high-pressure homogenizer (HPH) NS1001L PANDA 2 K-GEA (GEA Niro Soavy, Parma, Italy)

with the following sequence: 3 passes at 300 bar, 3 passes at 600 bar, and 3 passes at 900 bar.

For the CCNFs, one of them was made by using unrefined BKEP after disintegration. For the second type, the disintegrated pulp was subjected to mechanical refining in an NPFI-02 PFI mill (Metrotec SL, Gipuzkoa, Spain), for 15,000 revolutions at a 10 wt.% consistency (Kerekes 2005). This PFI refined BKEP was analyzed in a MorFi Compact Analyzer (Tech-PAP, Grenoble, France) for morphology inspection.

Next, both types of pulp (unrefined and refined) were subjected to the same reaction conditions. First, the fiber was mercerized at approximately 9 wt.% consistency with a 20 wt.% NaOH solution for 90 min at room temperature. This first step is necessary for breaking the crystalline structure and promoting the swelling of the cellulose chain, thus providing more accessibility of the –OH groups to the epoxy moieties in the subsequent reaction (Moral et al. 2016). Then, the cationization reaction proceeded by adding CHPTAC at a 9:1 molar ratio (CHPTAC:AGU) and distilled water until a consistency of 2 wt.% was reached. The reaction was performed at 60 °C for 3 h. To stop it, excess HCl (3 wt.%) was added to the media, which was washed thoroughly and filtered with filter paper of 14–18 µm pore size. The cationic fibers were then subjected to different degrees of fibrillation in the same HPH used for producing the enzymatically hydrolyzed cellulose micro/nanofibers (CMNFs).

Characterization of fibers and CNFs/CMNFs

Optical microscopy

Suspensions of cationic fibers (0.5 wt.%) were analyzed with an optical microscope (LEICA DMR-XA) equipped with a Nikon F90 camera, to check morphological aspects visually. The equipment had a 0.2 µm resolution and reflected light images were taken in 5× magnification. Subsequently, images were treated using FiJi ImageJ Software.

Degree of substitution

The DS of the fibers was measured by conductometric titration of chloride ions, considering that there is one counterion per trimethylammonium group, according to the method previously described in literature (Hasani et al. 2008; Pei et al. 2013; Rol et al.

2019b). First, 0.4 dry gram of fiber was suspended in 200 mL of distilled water. The conductimetric titration was performed by adding 0.2 mL of a 0.06 M AgNO_3 aqueous solution every 30 s into the suspension. The DS can be calculated according to Eq. 1:

$$DS = \frac{n_{\text{AgNO}_3}}{n_{\text{cellulose}}} = \frac{C_{\text{AgNO}_3} * V_{\text{AgNO}_3}}{\frac{m_{\text{cellulose}}}{M_{\text{AGU}}}} \quad (1)$$

where C_{AgNO_3} relates to the molar concentration, V_{AgNO_3} to the volume of the AgNO_3 solution used in the equivalence, $m_{\text{cellulose}}$ to the amount of cellulose (dry), and M_{AGU} to the molar mass of AGU (162 g/mol).

Pulp viscosity

The viscosity of cationic fiber suspensions at 0.1 wt.% consistency was determined using a Brookfield viscosity meter (Model PCE-RVI 2). The viscosity was measured in a 50 mL cylindrical container, at a constant temperature of 25 °C and with a cylindrical spindle (diameter=1.8 cm, height=6.5 cm). The rotation frequency of the spindle was set at 60 rpm.

Anionic and cationic demands

The cationic and anionic demands of fibers and CNFs/CMNFs were determined by potentiometric back titration (Serra-Parareda et al. 2021a) with a Mütek PCD-06 particle charge analyzer (BTG Instruments, Wessling, Germany). For the cationic demand, the sample (0.02 g, on the basis of dry pulp weight) was soaked in excess polydiallyldimethylammonium chloride solution (polyDADMAC, 0.001 mol/L). Then, the sample was centrifuged at 2,300 g for 20 min and 10 mL of the supernatant was titrated with a negative polymer aqueous solution, namely sodium polyethylene sulfonate (PES-Na) at 0.001 mol/L, until the isoelectric point (0 mV) was reached. For the anionic demand, the inverse procedure was performed; samples were soaked in excess PES-Na and titrated with polyDADMAC instead.

Yield of nanofibrillation and transmittance at 600 nm

The yield of nanofibrillation was determined by centrifugation (Serra-Parareda et al. 2021a). For this, a 0.2 wt.% CNF suspension was centrifuged at 4000 g

for separation of the micro- and nanofibrillated parts, assuming that the micro-sized fibrils sediment while the nano fraction stays stable in the supernatant. The supernatant was discarded, while the sediment was retrieved and oven-dried at 105 °C for 24 h. The dry sample was weighed, and the yield was calculated according to Eq. 2.

Yield of nanofibrillation(%)

$$= \left(1 - \frac{m_{\text{dry sample}}}{m_{\text{diluted sample}} * \%Sc} \right) * 100 \quad (2)$$

Transmittance at 600 nm, an additional parameter used to assess the degree of nanofibrillation of a fiber, was measured on a CNF suspension at 0.2 wt.% consistency using a Shimadzu UV-160 spectrophotometer (Isogai et al. 2011; Fujisawa et al. 2011).

Papermaking of virgin and recycled pulp and characterization of paper sheets

Neat BKEP paper consisted solely of virgin pulp. As mentioned previously, enzymatic CMNFs (ENZCMNFs) were the strengthening agent selected for the study. They were added to the pulp at a 3 wt.% concentration (with respect to dry fiber weight) and then the slurry was mixed at 3000 rpm for 60 min (Serra-Parareda et al. 2021a). The slurry was then displaced in a 5 L jar, where tap water was added until the consistency was 1 wt.%. Following that, the retention agent (either CPAM or CCNFs) was added and mixed with the slurry for 20 min for optimal interaction before preparing the paper sheets (Serra-Parareda et al. 2021a). Three different concentrations of retention agent were tested: 0.05, 0.10 and 0.25 wt.%. Slurries with BKEP and retention agent only, *i.e.*, without any type of negatively charged CMNFs, were also prepared. For the recycled paper, similar steps were taken, but using a mixture of 65% of liner and 35% of fluting instead of BKEP. Figure 1 shows a schematic overview of the described process.

BKEP and recycled fibers (65% liner, 35% fluting) without any addition of agents were analyzed in a MorFi Compact Analyzer (TechPAP, Grenoble, France) for morphology inspection.

Paper sheets of basis weight 75 g/m² were prepared in a Rapid-Köthen sheet former, model 786-FH (ISP, Gipuzkoa, Spain), according to the standard

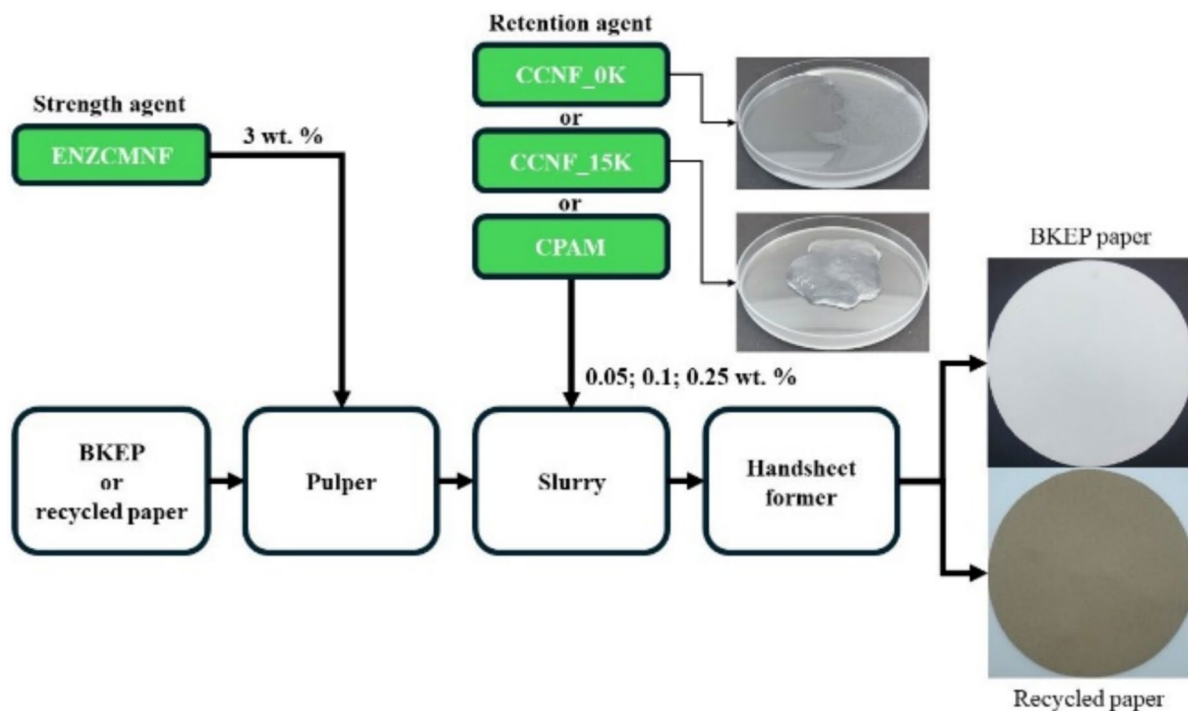


Fig. 1 Schematic diagram of paper production using enzymatic CMNF (referred as ENZCMNF) as strengthening agent, three different kinds of cationic retention agent—a commercial

polyacrylamide (CPAM) and the two types of CCNFs here named as CCNF_0K and CCNF_15K—and two different pulps (BKEP and recycled)

ISO 5269-2. The drainability of the slurries was assessed by measuring the Schopper-Riegler degree ($^{\circ}$ SR) with an equipment from PTI (model 95,587) that complies to ISO 5267/1.

Tensile strength at constant elongation rate was measured according to ISO 1924-2 and reported as breaking length (BL). Paper sheets were also characterized in terms of Elmendorf tear index (ISO 6383-2), Scott bond (ISO 16260), Mullen burst index (ISO 2758) and air permeability (Gurley porosity, ISO 5636-5) (ISO 2011). Five paper sheets of each composition were conditioned at 23 ± 1 °C and at relative humidity of 50% for 24 h before testing. The resulting average of these five samples was taken for determination of all paper properties.

Look through (LT) index was assessed by means of a sheet formation index inspector (TechPAP 2D formation tester, Grenoble, France). The index is based on the transmittance of diffused light and is a function of the average flocs contrast intensity, the total number of flocs, and how homogenous the flocs are distributed in the analyzed area.

The turbidity of whitewater effluents from paper-making was measured with an optical turbidity meter from Thermo Scientific, model Eutech TN-100/T-100 (Singapore) and results are presented in Nephelometric Turbidity Units (NTU).

Results and discussion

Production and characterization of CNFs/CMNFs

ENZCMNFs presented a cationic demand of 158.6 ± 6.7 $\mu\text{eq/g}$, a yield of nanofibrillation of $5.4 \pm 0.2\%$ and a transmittance of 2.75% after homogenization. Considering these aspects, the suspension could be characterized as a mixture of micro and nanosized fibers, thus justifying the name already given to this material. These values are slightly lower than those found by Mazega et al. (2023), who applied a refining stage prior to the enzymatic reaction.

Figure 2 depicts the morphological changes that BKEP fibers underwent due to PFI treatment and cationization. Firstly, Fig. 2a represents the neat pulp fiber without any source of treatment other than the initial disintegration. One can observe that the fibers are long, homogeneous and there are no apparent fines present in the media. Figure 2b shows the morphological changes that the BKEP fibers without any mechanical refining suffered after cationization. It is possible to notice that the reaction hardly changed the morphology of the long and smooth fibers but increasing to some extent the number of smaller fractions. Figure 2c, on the other hand, highlights the effect of the 15,000-revolution PFI refining over the neat BKEP, where the presence of smaller fractions is clearly higher in comparison to Fig. 2a. Indeed, the morphological changes were quantified with a MorFi

analyzer, and it was possible to observe that, from the BKEP to the refined BKEP, the mean arithmetic length decreased from 398.5 μm to 251 μm , the mean length-weighted fiber length from 696.5 to 488.25 μm and the fines content in length increased from 12.98 to 14.47%. Interestingly, after cationization, the PFI-treated fibers exhibited significantly different morphological features than the unrefined cationized fibers, as shown in Fig. 2d. In this case, the cationic fibers presented straight regions that intercalate with round ones, resembling ganglia-like areas. Possibly, these rounder areas correspond to more amorphous, swollen, and disintegrated regions in comparison to the straighter ones. Since PFI refining disintegrated the fiber to a further extent, allowing a swelling effect, the accessibility into the cellulose chains by the cationic reagent increased. This led to an intensification

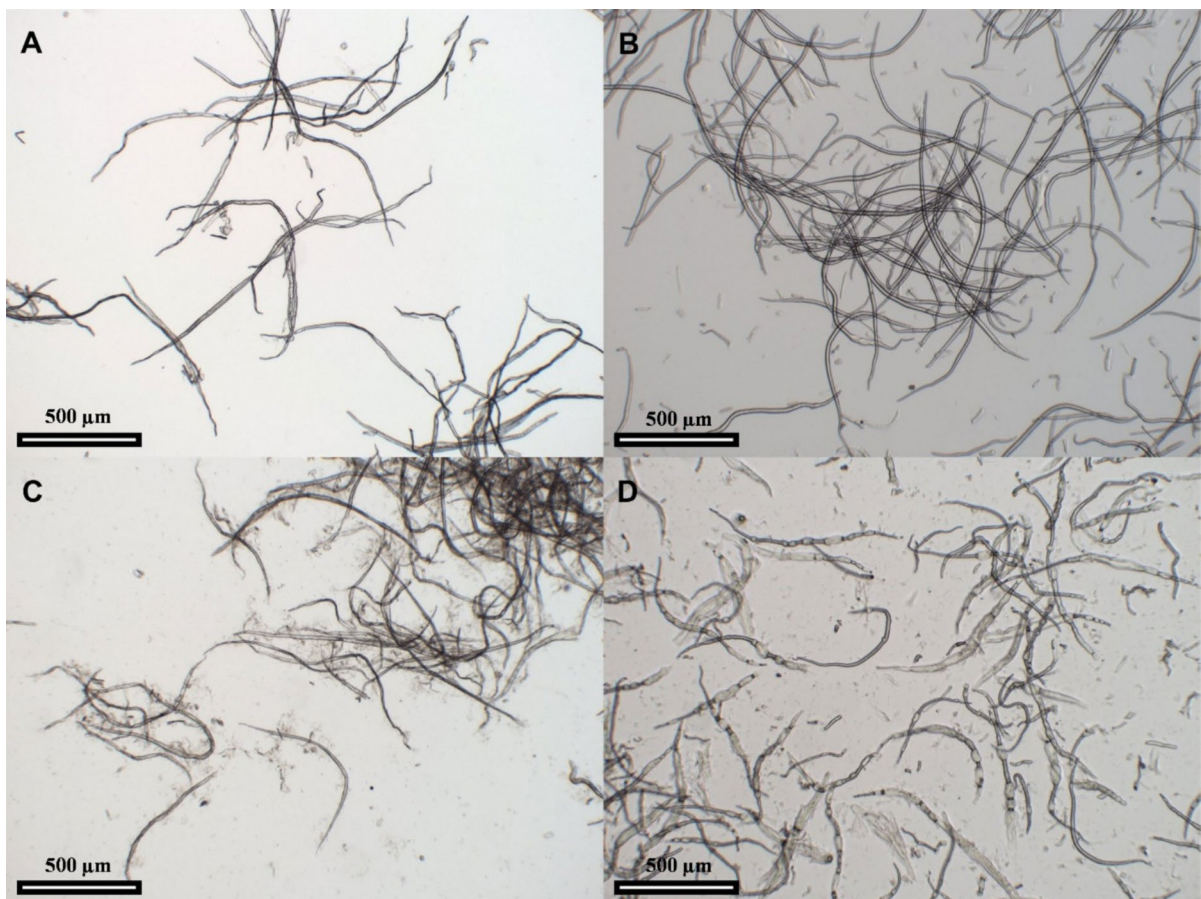


Fig. 2 Optical microscopy images of a) BKEP pulp prior cationization treatment b) BKEP pulp after cationization treatment c) PFI refined BKEP pulp prior to cationization treatment d) PFI refined BKEP pulp after cationization treatment

of the cationization process that changed the fibers' morphology considerably. This characteristic of the cationization process has been reported in literature by other authors (Huang et al. 2020; Pedrosa et al. 2022b).

The differences between the cationic fibers can be perceived not only in their morphology, but also in the values of their anionic demand, degree of substitution and viscosity, as depicted in Table 1. It can be noted that PFI refining caused an increase in all of these properties. For the cationization performed on the unrefined pulp, the anionic demand achieved was 230 $\mu\text{eq/g}$; for the cationic pulp produced from refined fibers, it accounted for 492 $\mu\text{eq/g}$. The degree of substitution also increased, from 0.21 to 0.25, respectively. For anionic CNFs, polyDADMAC adsorption has been previously reported to adequately correlate with surface area (Serra-Parareda et al. 2021b); thus, a parallelism could be established for CCNFs here. In this sense, while the slight increase in DS was due to the diminishment of mass transfer limitations during cationization, the high increase in anionic demand corresponds to a larger specific surface area. Finally, the viscosity of a 0.1 wt.% suspension increased from

71.11 to 82.69 mPa.s, for the unrefined and refined fibers respectively. Increase in viscosity can be related to the increase in surface charge and fine content.

After cationization, the fibers were fibrillated in the HPH. Different degrees of fibrillation were obtained and their effect on the anionic demand (Fig. 3), energy consumed (Table 2) in the HPH, yield of nanofibrillation (Table 2) and transmittance at 600 nm (Table 2) was investigated. It was found that, as the number of passes and pressure gradually increased in the homogenizer, the anionic demand of the CCNFs also increased until reaching a plateau, for both types of cationic fiber. This indicates that, similarly to what happens with anionic CNFs (Balea et al. 2021), as the fibrillation process increases the surface area of the cellulosic chains, there is an increased exposure of the quaternary ammonium groups grafted during cationization, implicating that the PES-Na polyelectrolyte used during the back titration has a greater number of cationic groups available to interact with. This suggests that the interaction between the cationic and OH^- functional groups did not happen only in the surface of the cellulose chain, but rather involved a diffusion phenomenon. Nevertheless, this

Table 1 Characterization of the obtained cationic fibers

Type of cationic fiber	Anionic demand ($\mu\text{eq/g}$)	Degree of substitution	Viscosity* (mPa.s)
Unrefined	230 \pm 8	0.21 \pm 0.02	71.11 \pm 2.67
PFI refined	492 \pm 11	0.25 \pm 0.01	82.69 \pm 3.19

*Measured on a 0.1 wt.% suspension

Fig. 3 Anionic demand of CCNFs at increasing HPH intensity

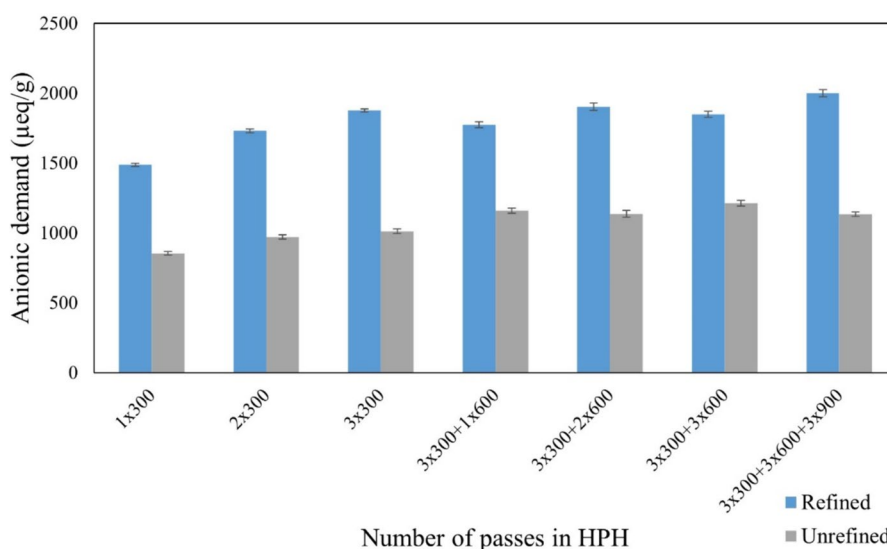


Table 2 Characterization of CCNFs

Original cationic fiber	Degree of fibrillation	Anionic demand ($\mu\text{eq/g}$)	Energy consumed (kWh/kg)	Yield of nanofibrillation (%)	Transmittance at 600 nm (%)
Not PFI refined	1 \times 300 bar	854 \pm 13	6.03	12 \pm 1	13 \pm 0
	3 \times 300 bar + 1 \times 600 bar	1161 \pm 19	9.79	30 \pm 2	29 \pm 1
	3 \times 300 bar + 3 \times 600 bar + 3 \times 900 bar	1135 \pm 15	45.61	> 95	59 \pm 2
PFI refined	1 \times 300 bar	1488 \pm 12	9.54	29 \pm 2	29 \pm 2
	3 \times 300 bar + 1 \times 600 bar	1774 \pm 22	24.50	79 \pm 2	65 \pm 4
	3 \times 300 bar + 3 \times 600 bar + 3 \times 900 bar	2000 \pm 25	76.47	> 95	88 \pm 3

happens until a certain point where there are no significant changes in the number of functional groups exposed, maintaining similar anionic demands.

It was also found that the different cationic fibers provided different anionic demands for the same conditions in the HPH, thus reinforcing that the increase in the demand for different substituted fibers is not due to the homogenization itself, but rather from the previous PFI pretreatment applied to the pulp. For the 15,000 revolutions in the PFI, a single pass at 300 bar already elevated the anionic demand up to 1500 $\mu\text{eq/g}$, while for the cationic fiber without PFI pre-treatment, this first pass increased the demand until 854 $\mu\text{eq/g}$. The highest anionic demand was achieved with the PFI treated fiber, for the most intense fibrillation (3 passes at 300 bar, 3 passes at 600 bar and 3 passes at 900 bar), providing a value of 2000 $\mu\text{eq/g}$. On the other hand, the highest demand achieved for the unrefined cationic fiber was 1161 $\mu\text{eq/g}$, already obtained with 3 passes at 300 bar and 1 pass at 600 bar.

The investigation regarding the yield of nanofibrillation, energy consumed and transmittance was done for three different levels that would be representative of the evolution in the fibrillation degree. It was chosen an initial point (1 pass at 300 bar), an intermediate point (3 passes at 300 bar and 1 pass at 600 bar) and a final point (3 passes at 300, 3 passes at 600 and 3 passes at 900 bar). From Table 2, it is noticeable that the yield and the transmittance are also quite distinct between samples subjected to the same fibrillation intensity. For instance, the yield of nanofibrillation achieved for the refined pulp is higher for all fibrillation intensities. Even though in the most intense level, where the yield from both samples was considered the same, it is possible to see that the

transmittance is different, thus indicating that there is a difference in the fiber size not distinguished during the sedimentation technique. Another point worth to mention is that the CCNF produced from the refined fiber reaches, with only one pass at 300 bar, the same yield of nanofibrillation that the CCNF produced from the unrefined cationic pulp does at the intermediate level. Finally, an aspect important to highlight is the amount of energy consumed for each of the fibrillation degrees evaluated in Table 2. Of course, for the cationic fibers that were previously refined, the refining is an extra process that consumes energy. On the other hand, this translates as a lower energy demand in the HPH, when the aim is to obtain higher surface charge. For instance, taking the same previously given example, with 9.54 kWh/kg it was possible to obtain a CCNF with an anionic demand 28% higher than the CCNF from the unrefined cationic fiber obtained with approximately the same amount of energy. Nevertheless, if it is wished a CCNF with 2000 $\mu\text{eq/g}$, higher fibrillation intensities are needed, and so more energy is spent. In addition, an important remark to make is that it was only possible to obtain higher surface charge when the PFI treatment was applied. Thus, from an industrial point of view, it would be relevant to balance what kind of CCNF is needed and for which application, with the energy spent during the process.

Therefore, two clearly different CCNFs were chosen to study their application as retention agents in papermaking. One is the CCNF obtained from the initial cationic fiber with no PFI refining, at a degree of fibrillation of 3 passes at 300 bar and 1 pass at 600 bar. The reasons for this choice are that, from this degree of fibrillation on, there is no significant change in the anionic demand achieved and in addition there

is a reasonable amount of nanosized fibers in the suspension. These CCNFs will, from now on, be referred as CCNF_0K. The second one is the CCNF produced from the PFI-treated cationic fiber at a degree of fibrillation of 3 passes at 300, 3 passes at 600 and 3 passes at 900 bar, named here as CCNF_15K. For this case, it was possible to reach an anionic demand of up to 2000 $\mu\text{eq/g}$ and a high content of nanosized fibers.

Virgin pulp paper production and characterization

From the MorFi analysis, virgin fibers presented a mean arithmetic length of 398.5 μm , a mean length-weighted fiber length of 696.5 μm and contained 12.98% of fines in length. Since the length-weighted length takes into consideration the fiber length in the denominator part of the average calculation, this mean is not as sensitive as the arithmetic length is to

the fine content (Robertson et al. 1999). Because of this, the mean fiber arithmetic length presents a lower value than the length-weighted one.

From Fig. 4, it is noticeable that every paper produced with ENZCMNF and CCNFs promoted a remarkable improvement in the strength properties of BKEP paper. In general, higher cationic charges reflected in better BL. The highest result was for the 0.25% of CCNF_15K, which presented a BL of 3368 m, representing an increase of 125.1% in the strength of the paper comparing to the neat BKEP sample (1496 m). The °SR for this point corresponded to 21, while the measured value for the neat pulp was of 17.

The BLs achieved for the papers produced with 0.05, 0.1 and 0.25% of CCNF_0K presented an increasing trend with increasing concentration, and an optimum value of 2726 m was reached with the 0.25% concentration. This represents a rise of 82.2%

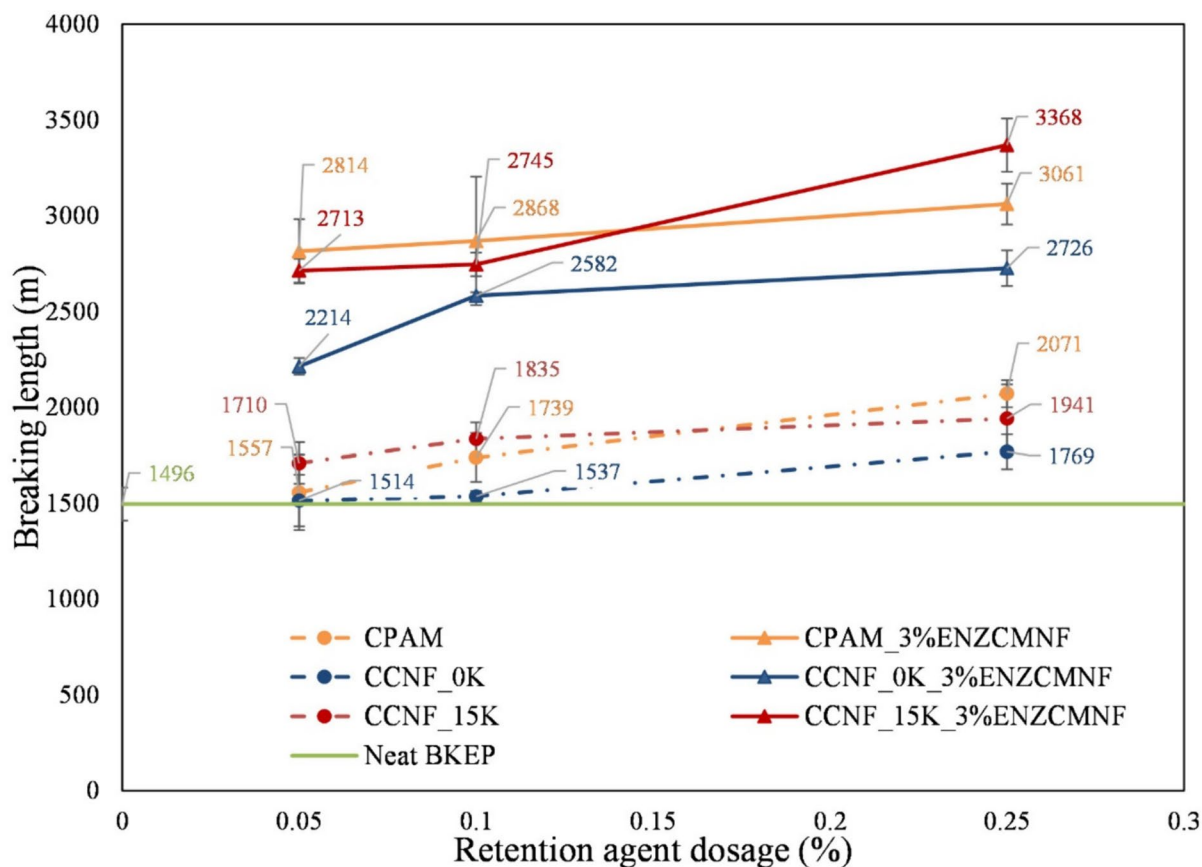


Fig. 4 Effect on the breaking length of BKEP paper using different retention agents

in the strength property of the paper. In addition, the °SR measured was of 21 for this paper composition. The CCNF_15K also presented a similar trend, where the BLs for the 0.05 and 0.1% were quite similar, however attaining a noticeable rise in the property for the 0.25% point. High increases in the tensile properties are obtained at the same time that the increase in the °SR is not as high. These results are comparable with other found previously in literature. For instance, Delgado-Aguilar et al. (2015b) tested different negatively charged CNFs in the papermaking of hardwood pulp, among them ENZCMNFs. For this type of nanofiber, at a 3 wt.% addition, the increase in the BL achieved was of 89% approximately and the °SR increased from 17 to 27. Lourenço et al. (2019) generated cellulose microfibrils (CMFs) by treating fibers with an enzymatic hydrolysis and high-pressure homogenization. These CMFs were able to increase the strength capacity of bleached eucalyptus kraft paper up to 22%, when using precipitated calcium carbonate (PCC), cationic starch, alkenyl succinic anhydride and cationic polyacrylamide as additives.

Moreover, papers containing only retention aid, that is, with no addition of any strengthening agent, resulted in higher tensile property as well, comparing to neat BKEP. In the case of 0.25% of CCNF_0K, an increase of 20.65% was attained. For the CCNF_15K, all the compositions tested provided higher strength, however the best result was of 1941 m for the 0.25% concentration, which represents an increase of 29.7%. This could be a sign that the perceived increase in the strengthening capacity when adding only the retention agents could be mainly caused by the improved ability of retaining fines and promoting the bonding between fibers/fines in the paper network. This behavior is in accordance with the literature. Lu et al. (2020) investigated the effect of three types of CCNFs with different charge densities in the making of softwood bleached kraft pulp paper. The researchers concluded that higher charge densities favored the retention of fines in the network because of the stronger electrostatic interactions that take place between fines and fiber, improving wet web performance. The best result achieved was with the highest charge CNF, which promoted an increase of 46% in the BL of wet web at a CCNF concentration of 5 wt.%.

The effect of CPAM was also assessed and compared to the effect of the CCNFs in the BL, as depicted in Fig. 4. First, analyzing the effect of this

retention agent without any strengthening aid, one can observe that for the 0.05 and 0.10 wt.% points, CCNF_15K provided better BLs, although in the 0.25 wt.% the opposite is noticed. Now, observing the values related to the papers produced with ENZCMNFs, the best value achieved for the CPAM was also at 0.25%, like the other retention agents. The BL was of 3061 m, lower than the BL attained for the CCNF_15K. The corresponding °SR was of 20.

Table 3 shows the values obtained for the Scott bond, burst and tear index for the different produced papers. For all these properties, the papers containing CCNF_15K and ENZCMNF outperformed the other paper formulations. The best improvements in respect to the neat BKEP paper were achieved for 0.25% concentration. The Scott bond grew 305.5%, the burst index 143.1% and the tear index 155.96%. Increases in these properties reflect that the negatively charged CMNFs and the CCNFs synergistic effect promoted the bonding between fibers and fines, not only improving the tensile properties of the paper sheets. These results are comparable with other works reported in literature, such as González et al. (2013), who reported an increase of 316.57% in the Scott bond and 150% in the burst index with the addition of 3 wt.% TEMPO-CNF, 0.8 wt.% of colloidal silica and 0.5 wt.% of cationic starch in biorefined BKEP paper.

At both 0.05 and 0.1% concentrations of retention agent, papers produced with ENZCMNF and CCNF_0K performed similarly to the papers made with CPAM for the Scott bond and burst index. However, the CCNF_0K provided better results than the CPAM at the 0.25% point. On the other hand, this is not the case for the tear index, where the CPAM provided better results than the CCNF_0K for 0.05 and 0.25% of retention agent.

Considering these results, it is noticeable that the cationic cellulose-based retention agents have competitive performance when compared to the commercial one, specially the CCNF_15K. Also, we highlight the point with 0.25% of CCNF_15K, where it outperformed the CPAM. In addition, the decrease in the drainage rate caused by the additives could be related to an enhancement in the fines retention and better fiber-fines connections. Nevertheless, the action of these agents does not hinder considerably the drainage capability up to unpractical values. All of this indicates the suitability of these fully cellulose-based systems for improving paper properties.

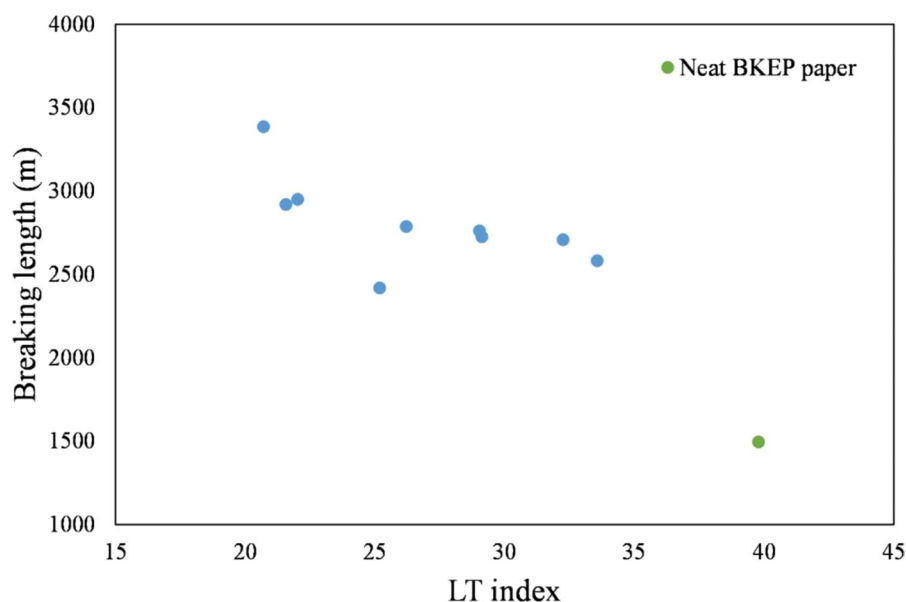
Table 3 Effect of different retention agents on Scott bond, burst index, tear index and air permeability in BKEP paper

% of ENZC-MNF	Retention agent	% of retention agent	Scott bond (J/m ²)	Mullen burst index (kPa.m ² /g)	Tear index (mN.m ² /g)	Air permeability (s/100 cm ³)
0	No cationic agent	0	25.3 ± 2.0	0.58 ± 0.01	1.99 ± 0.23	1.62 ± 0.24
0	CPAM	0.05	31.8 ± 1.6	0.59 ± 0.01	2.14 ± 0.21	1.50 ± 0.07
0	CPAM	0.10	27.9 ± 2.5	0.62 ± 0.04	2.20 ± 0.37	1.46 ± 0.11
0	CPAM	0.25	34.7 ± 4.0	0.74 ± 0.03	2.86 ± 0.65	1.47 ± 0.12
3	CPAM	0.05	74.7 ± 8.9	1.06 ± 0.06	3.63 ± 0.32	1.94 ± 0.05
3	CPAM	0.10	66.1 ± 8.9	1.12 ± 0.05	3.57 ± 0.51	1.88 ± 0.05
3	CPAM	0.25	59.3 ± 7.5	1.15 ± 0.07	4.16 ± 0.70	1.81 ± 0.12
0	CCNF_0K	0.05	33.8 ± 3.1	0.61 ± 0.03	1.70 ± 0.27	1.62 ± 0.03
0	CCNF_0K	0.10	28.6 ± 1.7	0.62 ± 0.03	2.47 ± 0.58	1.69 ± 0.10
0	CCNF_0K	0.25	28.9 ± 2.8	0.72 ± 0.04	2.50 ± 0.40	1.57 ± 0.07
3	CCNF_0K	0.05	74.6 ± 11.9	1.03 ± 0.13	3.26 ± 0.20	1.89 ± 0.10
3	CCNF_0K	0.10	65.3 ± 6.3	1.13 ± 0.08	3.95 ± 0.97	1.82 ± 0.17
3	CCNF_0K	0.25	84.4 ± 25.5	1.30 ± 0.12	3.85 ± 0.73	1.96 ± 0.14
0	CCNF_15K	0.05	37.4 ± 1.1	0.68 ± 0.04	2.51 ± 0.29	1.70 ± 0.06
0	CCNF_15K	0.10	32.6 ± 2.9	0.71 ± 0.03	2.91 ± 0.52	1.54 ± 0.07
0	CCNF_15K	0.25	30.0 ± 2.1	0.64 ± 0.04	2.97 ± 0.81	1.51 ± 0.08
3	CCNF_15K	0.05	84.0 ± 11.1	1.15 ± 0.12	4.13 ± 0.50	1.93 ± 0.14
3	CCNF_15K	0.10	85.0 ± 10.1	1.35 ± 0.05	3.95 ± 0.71	2.02 ± 0.19
3	CCNF_15K	0.25	102.6 ± 18	1.41 ± 0.08	5.58 ± 0.72	2.05 ± 0.27

The formation of the papers using 3 wt.% of ENZCMNF and 0.05, 0.10 and 0.25 wt.% of the cationic retention agents was inspected by the LT index.

From Fig. 5, we can observe that there is a decreasing trend on the BL when the LT index increases. In this type of analysis, the highest the index, the worse the

Fig. 5 Breaking length of BKEP paper sheets (reinforced with 3% ENZCMNF and with different dosages of the retention agents tested) as a function of look through index. Data is provided as supplementary material (Table S1)



paper formation is. This is because there is a higher transmittance of light, which is caused by the disposition of bigger flocs in the paper network. Considering this, the decrease in the mechanical properties can be related to a worsening in formation indeed.

Recycled pulp paper production and characterization

From the MorFi analysis, recycled fibers presented a mean fiber arithmetic length of 257.2 μm , a mean length-weighted fibre length of 652.75 μm and a 28.83% of fines in length. Comparing it with the virgin pulp, in this case the proportion of fines is higher, which correlates with a lower mean fiber arithmetic length. The mean length-weighted fiber length is also lower, but not drastically, in comparison to the virgin pulp, since it is not affected largely by the number of fines.

The study executed with the BKEP pulp served the purpose of assessing the potential performance of the

CCNFs over the strength properties of paper, at commonly applied doses of retention agent. Bearing in mind that high increments on BL were achieved when using both ENZCMNFs and CCNFs for BKEP, the same dosages were studied for the recycled paper. The effect of using solely cationic polymers was not considered here since their effects were already assessed for the virgin pulp and did not present an increase as high as the one using the combined system. Considering this, Fig. 6 shows the evolution of the BL of recycled paper in respect to retention agent dosage. One can observe that the improvements reported in respect to the neat pulp are not as pronounced as they were for the BKEP case. This could be occurring since the BL of neat recycled paper is already approximately 86% higher than that of the neat BKEP. Even though the mean fiber length is smaller in comparison to the BKEP, there is a higher content of fines in the recycled pulp used, which is beneficial for the paper strength. In addition, possibly, the capacity of

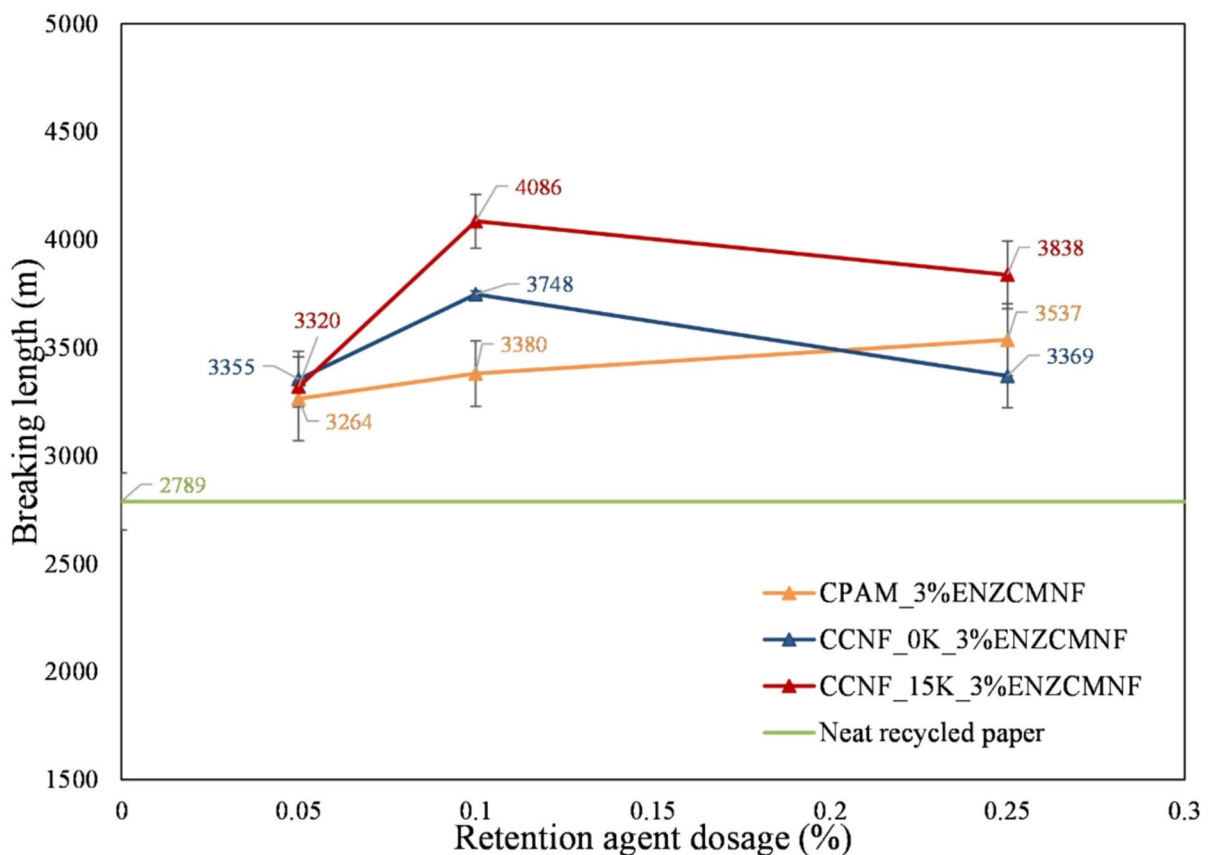


Fig. 6 Effect on the breaking length of recycled paper using different retention agents

improvement of the anionic/cationic system applied here poses a limitation, especially if we consider that the same dosages of retention agent were applied in a slurry that is intrinsically more negative than the BKEP pulp, due to the higher presence of fines.

From Fig. 6, all retention agents performed similarly at the 0.05 wt.% point, where BL increased between 17 and 20% approximately. However, when the concentration increased to 0.10%, there was a considerable difference between retention agent performance. The CCNF_15K promoted the highest increase, achieving a 46.5% improvement in respect to neat paper. The increase in the °SR was somewhat more pronounced if compared to the BKEP papers. For this composition, the °SR increased from 34.5 (neat recycled pulp) to 45.5, representing almost 32% of increase. Other authors when incorporating CNFs and cationic retention agents in other pulp slurries also experienced an increase in °SR (Delgado-Aguilar et al. 2015a). Perhaps, optimization of dosage could be done in order to avoid the decrease in the dewatering rate without compromising the mechanical properties due to increased flocculation.

Subsequently, CCNF_0K promoted a 34.4% and CPAM a 21.2% increase in the BL at the same 0.10 wt.% dosage. Similar increases in the °SR were noted as well, of 45 and 47 respectively. Interestingly, when 0.25% of retention agent was added, it is possible to see a decrease in the mechanical performance for both CCNFs, while for the CPAM the BL continued to increase, and in this case, it was higher than the CCNF_0K. It is interesting to point out as well that in the case of CCNF_15K, every paper composition tested with it surpassed the performance of the CPAM. Another highlight is that the highest BL achieved (which used CCNF_15K) required less than half of the CPAM dosage required to obtain its best BL performance. Similar improvements in the tensile properties of recycled paper are reported in the

literature using negatively charged CNFs and other retention systems, ranging from 28 to 108.32% (Balea et al. 2016; Merayo et al. 2017; Zeng et al. 2021).

The different trend observed for the CCNFs with the recycled pulp, in comparison to the one experienced by the virgin pulp, could be due to the different natures of the fibers, especially considering that the recycled pulp slurry is more anionic than the BKEP. This is due to the higher fine content, which increases the presence of OH- groups available for interaction. Considering this, the electrostatic interactions between the CCNFs, ENZCMNF and the fibers/fine is more intense and at 0.25% of concentration, papers experience a decrease in mechanical performance.

The effect of the retention agents (for the concentration of agent respective to the highest BL achieved in each case) in Scott bond, burst index, tear index and air permeability is presented in Table 4. Noticeably, there was an increase in all of the properties, apart from the tear index, which did not have a substantial change. Indeed, all of these properties are highly related to relative bonded area, which is enhanced by the addition of the ENZCMNFs and retention agents, whereas the tear index is more dependent on fiber length, which is not affected by the additives (Page 1969; Škulcová et al. 2017). Here, it is possible to observe as well that CCNF_15K caused similar increases to the properties as CPAM did but requiring a lesser amount of it. For this specific CCNF, the increase on the Scott bond was of 72%, the burst index of 26% and the tear index of 12% in respect to the neat pulp. The retention caused by the addition of the strengthening and retention agents can be also seen by the increase in the air permeability value, indicating the filling of voids in the paper network by fines and fiber.

Figure 7 shows how the turbidity of white water changed with different concentrations of the retention agents. One can notice that CCNF_15K usually

Table 4 Effect of different retention agents on Scott bond, burst index, tear index and air permeability in recycled paper

% of ENZC-MNF	Retention agent	% of retention agent	Scott bond (J/m ²)	Mullen burst index (kPa.m ² /g)	Tear index (mN.m ² /g)	Air permeability (s/100 cm ³)
0	No cationic agent	0	143.3 ± 11.4	1.67 ± 0.11	6.6 ± 0.6	9.1 ± 0.4
3	CPAM	0.25	244.7 ± 12.8	2.19 ± 0.10	7.1 ± 0.2	19.8 ± 1.6
3	CCNF_0K	0.10	212.8 ± 1.7	2.05 ± 0.16	6.4 ± 0.3	18.9 ± 1.4
3	CCNF_15K	0.10	247.2 ± 9.8	2.10 ± 0.14	7.4 ± 0.8	19.5 ± 1.3

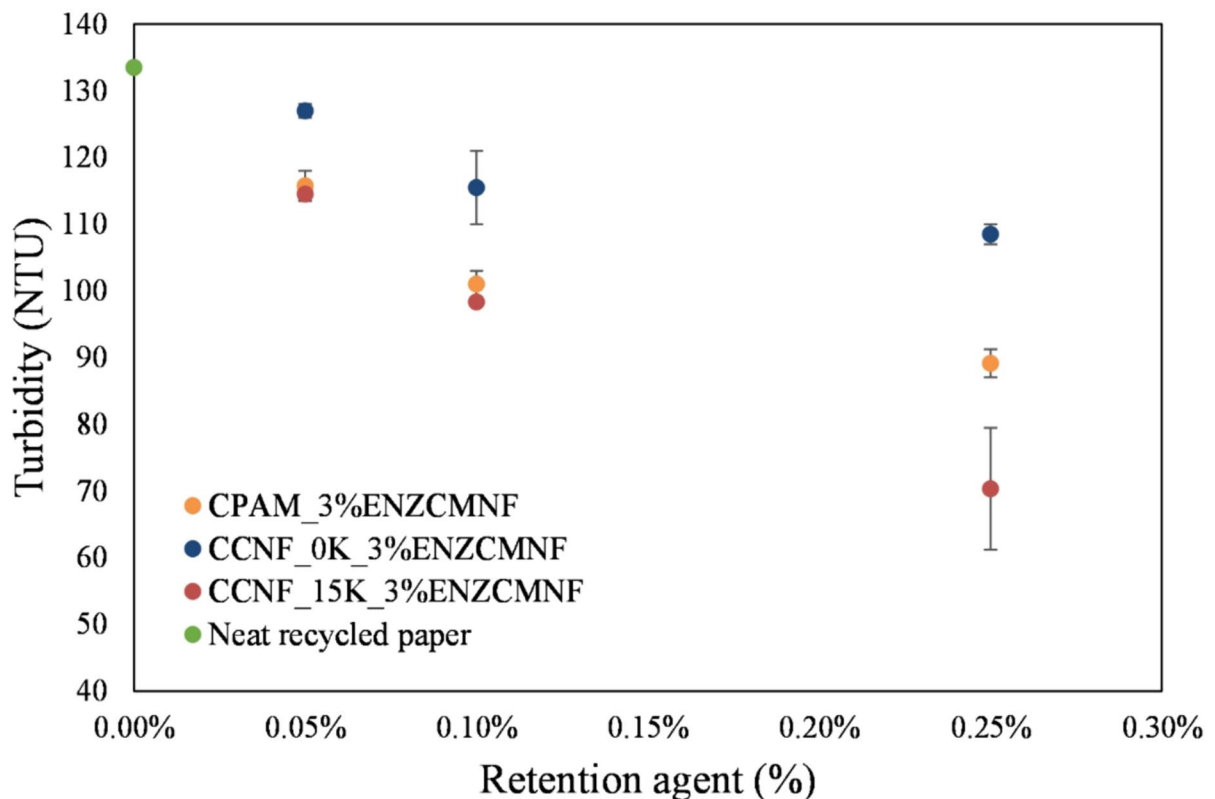


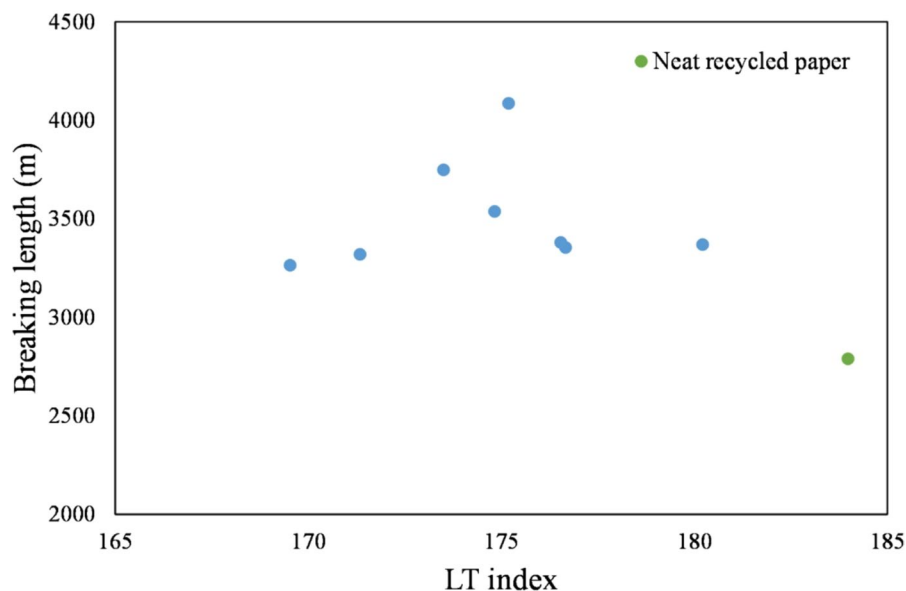
Fig. 7 Turbidity measurements as a function of retention agent addition in recycled paper reinforced with 3 wt.% ENZCMNF

presented the lowest turbidities, meaning the highest retentions, especially at 0.25 wt.%. CPAM followed closely to the values presented by CCNF_15K for 0.05 and 0.10 wt.% and presented an intermediate value between the CCNFs for the 0.25 wt.% concentration. This behavior makes sense, considering that CCNF_15K and CPAM present higher charges in comparison to CCNF_0K, and thus can retain more fines in the paper network.

Examining Fig. 8, where the BL of the papers is put as a function of the LT index, it is possible to observe that the trend followed is not the same as the one presented for the virgin pulp case. Although the LT index increases, the BL of the papers also increases until it reaches a limit. From the index value of 175 onward, the mechanical strength of the paper experiences a decrease. For what it seems, although there is an improvement in the retention of fines when all retention agents are increased, the formation of flocs in the paper network does not hinder the paper strength up to a certain point and the interactions

between fiber/fine/agents compensate some of the mal formation. Bastida et al. (2023) have also reported similar behavior, where flocculation was favored due to the cationic system used in recycled paper, but still presenting increases up to 40% in the tensile index. As it is known, the mechanical strength of paper is dependent on a range of variables, such as formation, but also fiber bonding. For instance, it is noticeable that the lowest breaking length and the lowest LT index corresponded to the neat recycled pulp. On the other hand, all papers produced with negatively charged CMNFs and retention agent presented better look through index in comparison to the neat pulp, similar to what was observed for the virgin paper, even though there is more fine retention, and subsequently, floc formation, when the agents are added. However, these flocs are apparently more well distributed in the paper network as compared to the neat paper. Another possible explanation is that, since the cationic retention agents have a good compatibility and interaction with the negatively charged CMNFs

Fig. 8 Breaking length of recycled paper sheets (reinforced with 3% ENZCMNF and with different dosages of the retention agents tested) as a function of look through index. Data is provided as supplementary material (Table S2)



at these dosages, the synergistic effect between these additives favor the network formation (Delgado-Aguilar et al. 2015a; Merayo et al. 2017).

On interaction mechanisms

The positive charge of both CPAM and CCNFs is due to quaternary ammonium groups, but they are radically different in some important respects. Even though their anionic demand was found to be similar, cationic groups were more spaced in the case of the commercial polyelectrolyte. For CCNFs, a DS of 0.25 could seem in the low range if considering soluble derivatives, but it theoretically corresponds to the monosubstitution of nearly all AGU on the surface of nanofibers (Chaker and Boufi 2015). In contrast, for a CPAM copolymer with an anionic demand of 2252 $\mu\text{eq/g}$, the ratio of non-quaternized acrylamide units (71 g/mol) to cationic monomers (159 g/mol) is 4.

At an atomistic level, the attraction potential between retention agents and ENZCMNFs is mainly driven by ion–dipole interactions between the quaternary ammonium ion (formal charge +1) and the permanent dipole between oxygen and hydrogen in hydroxyl groups (dipole moment: $\mu = 1.85$ D). More specifically, the negative partial charge of the oxygen atom explains the negative surface charge of hydroxy polymers even in moderately acidic media (Drechsler

et al. 2019). An identical adsorption mechanism is postulated for BKEP, whose surface charge is slightly negative. In the case of the recycled pulp, encompassing liner and fluting, the non-negligible presence of carboxyl groups also opens the way to ionic bonds, less abundant but higher in attraction potential (E):

$$E \propto \left| \frac{q_{NR4+} \times q_{COO-}}{r} \right| > \frac{q_{NR4+} \times \mu_{O-H}}{r^2} \quad (3)$$

where q is the charge of either ion and r is the interatomic distance. Figure 9 schematizes the most common interactions, both in the case of cationic cellulose and in the case of CPAM. The larger space between quaternary ammonium groups in the latter favors a bridging flocculation mechanism, but the main reason why cannot be discussed at an atomistic scale. The mobility and length of high-DP CPAM chains allows for pulp–CNF bridges, while CCNFs are postulated to work mostly by charge neutralization and/or generation of cationic patches (Aguado et al. 2023). By reducing or suppressing the energy barrier for aggregation (mainly based on electrostatic repulsion), tight adsorption is possible. This caused agglomeration, leading to a less homogeneous formation of isotropic sheets, but also an enhancement of the mechanical properties. Hence, it could be hypothesized that this kind of tight adsorption onto fibers aided in fiber–nanofiber additive interactions.

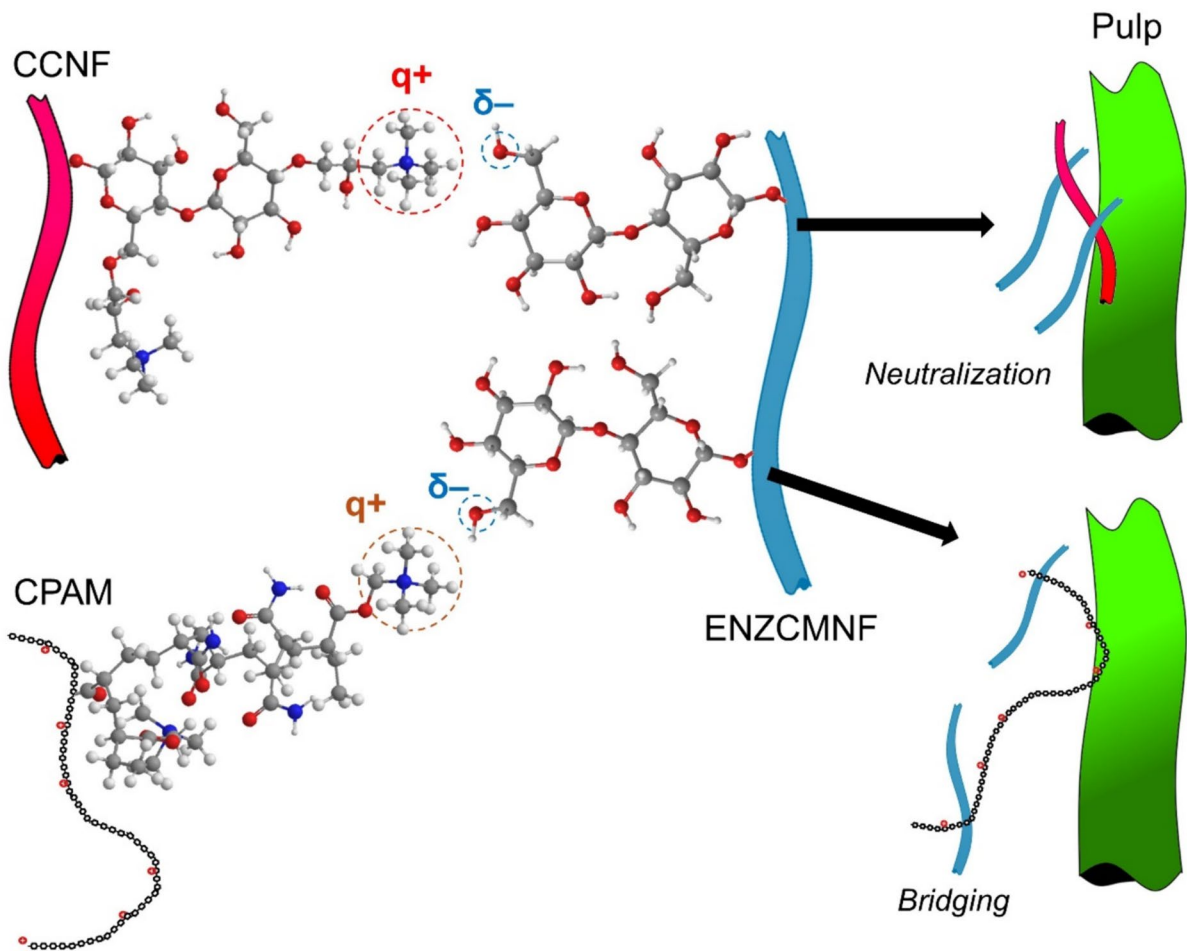


Fig. 9 Ion–dipole interactions between cationic retention aids and enzymatic nanofibers, and postulated flocculation mechanisms

Conclusions

This work successfully showed the use of cationic cellulose nanofibers to retain fines and micro/nanocellulose with moderate negative charge during sheet formation. In turn, said negatively-charged micro/nanocellulose, which was produced by enzymatic and mechanical processes, succeeded at increasing the mechanical properties of both virgin paper (BKEP) and recycled paper (65% liner, 35% fluting). For the former case, breaking length was improved 125% and the burst index, the tear index and the internal cohesion were more than doubled when using highly charged CCNFs, involving a refining stage prior to cationization, along with enzymatic CMNFs (3 wt.%). As for the latter, the breaking length increased from 2.8 to 4.1 km by using 3 wt.% enzymatic CMNFs

and 0.1 wt.% highly charged CCNFs, while burst index, the tear index and the internal cohesion also increased, although not as much as in the case of virgin pulp. Overall, the combination of both kinds of nanocellulose showed great potential, either to produce stronger virgin paper or to compensate for the losses of mechanical performance of packaging paper after several recycling cycles.

In nearly every performance indicator, better results were obtained when carrying out a refining stage (15,000 PFI revolutions) before the cationizing reaction. This was attributed mainly to the increase in the surface area of CCNFs and increase in charge. Remarkably, in terms of mechanical properties, the synergy between CCNFs and enzymatic CMNFs surpassed the combination of the latter with CPAM, a non-biodegradable polyelectrolyte being

conventionally used as retention agent in papermaking. It is also worth noting that their dosage (by weight) was the same for comparison purposes, that their charge density was in the same range (anionic demand $\sim 2000 \mu\text{eq/g}$), and that their effects on drainability were similar. However, while CPAM was present in the medium as dispersed long chains of high molecular weight, CCNFs were solid particles with a highly charged surface. This affected the adsorption and flocculation mechanisms, and thus the response of fiber-nanofiber systems when subjected to different kinds of mechanical stress. This research highlights the ability to tailor CCNFs with different surface charges and characteristics through PFI treatment, as well as obtaining high-performance papers minimizing the use of chemicals, underscoring the potential of cellulose-based additives in promoting sustainability within the papermaking industry.

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Data availability Raw data of the present work can be made available upon request.

Declarations

Conflict of interests The authors have no competing interests to declare that are relevant to the content of this article.

Ethical approval and consent to participate Authors declare that the manuscript is not submitted to any other journal at the time of submission for simultaneous consideration, that the submitted work is original and has not been published elsewhere in any form, that results are presented under the principles of

honesty, without fabrication, falsification or inappropriate data manipulation and that no data, text or theories by others are presented as our own.

Consent for publication All authors have revised the last version of the submitted manuscript and we approve its submission.

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