Innovative system based on natural polyelectrolyte complex and cellulose micro/nanofibers to improve drainability and properties of recycled paper

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Abstract In this work, the efficiency of a polyelectrolyte complex (PEC) to retain different cellulose micro/nanofibers (CMNFs) during paper formation and to improve the physical properties of recycled unbleached fiber paper was analyzed. CMNFs were obtained from a commercial bleached eucalyptus pulp (BEP) using a PFI refiner followed by a chemical treatment with oxalic acid at two different concentrations. Finally, the pulp was fibrillated using a high-pressure homogenizer at three different intensities. The PEC was formed by addition of the xylan (Xyl) solution on chitosan (CH) solution with a Xyl/CH mass ratio of 80/20. The required dosages of PEC solution to neutralize the charges of different nanocellulose fractions were determined by ζ-potential measurements, and the CMNF retentions on recycled unbleached fibers were evaluated in a Britt Dynamic Drainage Jar. The results showed that the maximum retention was obtained when the neutral PEC-CMNF system was added to pulp. Besides, a significant decrease on °SR was observed when PEC and PEC-CMNF systems were added to the untreated pulp, limiting the negative effects of nanocellulose addition on pulp drainability. The incorporation of PEC-CMNF systems to the handsheets increased the tensile index (up to 28%), Mullen index (up to 40%) and internal bonding (up to 255%). Finally, the compressive strength of the handsheets, namely SCT and CMT, increased up to 30 and 70%, respectively. These simultaneous improvement on drainability and mechanical properties makes the proposed PEC-CMNF system a promising solution for the production of packaging paper.

Keywords Oxalic acid · Paper property · Xylan · Chitosan · Internal bonding · Drainability · Nanocellulose

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Introduction

The environmental and economic benefits of paper recycling have been extensively reported and proven (Villanueva and Wenzel 2007; Serra-Parareda et al. 2022). Indeed, according to the European Paper

Recycling Council (EPRC), the recycling rate in European for all paper and board in 2021 was 71.4%. Concretely, 78% of paper and cardboard was recycled in the same year in Spain, bringing to light the relevance of paper and board recycling (ASPAPEL 2022). However, despite the figures above, paper and board recycling processes often need to be reanalyzed to meet the objectives of improving quality, reducing costs, and complying with environmental laws. Paradoxically, higher recycling rates result in negative effects on recycling processes, as fibers suffer irreversible structural damages that negatively affect the mechanical properties of recycled paper (Delgado-Aguilar et al. 2015b). This can be improved by, for example, mechanical refining (Chen et al. 2012) or the addition of strength agents (Asa'ari et al. 2010; Mocchiutti et al. 2011), but the extensive physical deterioration of fibers limits the benefits of these strategies to recover paper properties.

In last years, many studies have been carried out on the addition of cellulose nanofibers (CNFs) to improve the physical properties of paper (Delgado-Aguilar et al. 2015a; Osong et al. 2016; Merayo et al. 2017), as well as other strategies such as enzymatic refining (Lecourt et al. 2010; Torres et al. 2012; Delgado-Aguilar et al. 2015c). The production of CNFs usually encompasses two different stages, namely (i) pretreatment followed by (ii) fibrillation (Alila et al. 2013). The pretreatment stage is determinant both for the fibrillation stage, but also for the resulting characteristics of CNFs. The literature reports several methods for pretreating the fibers, such as TEMPO-mediated oxidation, carboxymethylation, cationization, enzymatic hydrolysis or mechanical refining (Saito and Isogai 2004; Henriksson et al. 2007; Naderi et al. 2014; Prado and Matulewicz 2014). In the case of the processes involving chemical reactions (i.e. oxidation, carboxymethylation or cationization), it is possible to obtain individualized CNFs with tailored surface, incorporating functional groups that will provide them unique characteristics. However, these processes are vaguely optimized and require the use of special equipment and expensive chemical reagents (Serra et al. 2017). One alternative to produce of CNFs is the use of oxalic acid. The treatment with this reagent produces carboxylation through Fischer-Speier esterification between one carboxylic group of the oxalic acid and one hydroxyl group on the accessible surface of the cellulose (Chen et al. 2016; Ji

et al. 2019). Oxalic acid has some advantages, such as its low price, it can be easily recovered and corrosion in equipment is controllable (Xie et al. 2018). Due to the interesting properties and characteristics of CNFs, such as high intrinsic mechanical performance, biodegradability, biocompatibility, and non-toxicity, they have been proposed for a myriad application, including nanocomposites, biomedicine, electronics and, also, paper production, among others (Lee et al. 2014; Lin and Dufresne 2014; Boufi et al. 2016; Hoeng et al. 2016; Xue et al. 2017). Nevertheless, due to the high specific surface area of CNFs, together with their high hydrophilicity, their incorporation into papermaking processes have a negative impact on pulp drainability (Sharma et al. 2020). Besides, their retention during the paper web formation is also challenging due to their small size and high anionicity. This results in ineffective dosage of CNFs and poor distribution, which negatively affects their reinforcing capacity (Merayo et al. 2017). This, together with the interactions of CNFs with other colloidal dissolved substances, also known as anionic trash, is limiting the industrial deployment of CNFs in papermaking at large scale (Tarrés et al. 2018). However, previous works have reported that the use of appropriate amounts of polyelectrolytes, such as polyacrylamide, cationic starch, or others, can overcome this situation mainly due to the ionic interactions that they generate between CNFs and fibers. These interactions are essential because the pores of the paper web are not small enough to retain nanostructured fibers (Ämmälä et al. 2013; Brodin et al. 2014; Schnell et al. 2018).

Over the past decades, polyelectrolyte complexes (PECs) have attracted great interest due to their unique flocculating properties (Lu et al. 2002; Nyström et al. 2003). Advantages of PECs for flocculation of fillers have been previously reported by (Korhonen et al. 2013), where it was shown that they appear more effective than single polyelectrolytes. Besides, PECs can be used in significantly wider concentration ranges and flocculation can be recovered after a high-speed stirring, mainly due to the presence of opposite charge polyelectrolytes. Electrostatic interactions and, to a lesser extent, hydrogen bonding and hydrophobic interactions are present in PEC formation (Thünemann et al. 2004). Further, it has been reported that PECs can be used as dry/wet strength additives (Torgnysdotter and Wågberg 2006; Ankerfors et al. 2009; Mocchiutti et al. 2016) and fine

retention aids (Nyström and Rosenholm 2005; Schnell et al. 2018). In previous studies, the authors analyzed the addition of lignocellulosic micro/nanofibers (LCMNFs) in combination with PECs based on synthetic polyelectrolytes such as polyacrylic acid (PAA) and polyallylamine chloride (PAH) (Schnell et al. 2018). An acceptable drainage capacity (18°SR) was found, together with an excellent fine and LCNMF retentions (96.3%) and a notable improvement in mechanical properties of paper (48% increase on tensile strength; 64% increase on corrugating medium test CMT and 39% increase on short-span compression test SCT). However, while the need of replacing synthetic by bio-sourced PECs is urgent, the former was used. Chitosan (CH) is a cationic polysaccharide obtained by deacetylation of chitin, which is widely present in nature in crustaceous, insects and certain fungi (Rinaudo 2006). Structurally, CH is a linear and weak polyelectrolyte of β-(1–4)-linked N-acetyl-D-glucosamine (GlcNAc) and D-glucosamine (GlcN), and the presence of GlcN imparts its cationic character (Li et al. 2018). It has excellent properties such as biocompatibility, biodegradability, and non-toxicity, among others (Ravi Kumar 2000; Mocchiutti et al. 2016). Another interesting polyelectrolyte is xylan (Xyl), which can be extracted from sugarcane bagasse and mostly contains arabinoglucuronoxylan (AGX). Xyl is extracted from hemicellulose, which is second most abundant polysaccharide in nature after cellulose, and its chemical composition depends on the source that is extracted from. Its chains consist of 30–100 units of β-D-xylopyranose with 1,4-glycosidic linkages. AGXs have single units of 4-O-methyl-D-glucuronic acid and α-L-arabinofuranosyl attached at positions 2 and 3, respectively, to the β-(1–4) skeleton of D-xylopranose (Peng et al. 2012). Due to the presence of glucuronic acids, hemicelluloses can be considered as anionic polyelectrolytes. This polysaccharide usually exhibits a degree of polymerization below 200 and, contrary to cellulose, hemicelluloses is only constituted by an amorphous phase (Kaur et al. 2019).

Natural PECs can be formed due to the anionic nature of xylan and the cationic nature of chitosan. These can be used for different applications such as films (Schnell et al. 2017; Solier et al. 2020, 2022b); hydrogels (Schnell et al. 2018) and strength agents for papermaking (Mocchiutti et al. 2016). However, to the best of our knowledge, the use of natural PECs

as a retention agent for cellulose micro/nanofibers (CMNFs) in papermaking has never been evaluated.

In this paper, the addition of CMNFs and previously formed xylan/chitosan complexes on pulp is analysed. CMNFs were obtained from a commercial pulp treated with a PFI mill followed by a chemical treatment with oxalic acid at 25 and 50 wt%. Then, the pulp was passed through a high-pressure homogenizer (300, 600 and 900 bar). CMNFs were characterized by measuring nanofibrillation yield, transmittance, and surface charge. The length and size of CNF fraction were determined by TEM microscopy and the hydrodynamic size by dynamic light scattering (DLS). The retention of fines and CMNFs with different PEC dosages was evaluated. Finally, the drainage capacity and the papermaking properties corresponding to packaging paper were analysed.

Experimental

Materials

Chitosan was supplied by Sigma Aldrich (product number 448877), with a viscosity average molar mass of M_v: 190 kDa and a degree of deacetylation of $79.6\% \pm 0.7\%$, as determined in a previous work (Mocchiutti et al. 2016). A solution of 2.5 g/L of chitosan at low acetic acid concentration (0.25%w/v) was prepared according to Schnell et al. (2017).

Xylan was obtained by alkaline extraction from sugarcane bagasse according to Solier et al. (2022a, b). Briefly, extractions were made at 50 °C and 1:25 bagasse:liquor ratio using an alkali charge of 40 wt% on bagasse, during 180 min. The extracted hemicellulose was precipitated from the extraction liquor using ethanol in a 1:1 v/v liquor:ethanol ratio, to be later separated by centrifugation (15 min, 1800 G-force) after being reserved overnight at 4 °C. The composition determined by HPLC and molecular weight by HPLC-SEC were previously reported by Solier et al. (2020): xylose 0.67, arabinose 0.18, glucuronic acid 0.02, insoluble lignin 0.07 and soluble lignin 0.06 w/w, the molecular weight: 55 kDa.

CMNF preparation

CMNFs were obtained from industrial bleached eucalyptus pulp (BEP) supplied by Suzano Papel e

Celulose S.A. (Aracruz, Brazil). The pulp was soaked in water for 24 h and disintegrated for 5 min at 1.5 wt% consistency in water. Then, the water content of pulp was removed by centrifugation and pulp was stored at a low temperature (4 °C) to prevent any degradation.

The fibers were mechanically pretreated using a PFI mill refiner according to the SCAN-C 18:65 standard at 10 wt% consistency and for 10,000 revolutions. Then, a chemical pre-treatment was carried out according to the technique described by Chen et al. (2016). In a typical experiment, 15 g of pulp were introduced in a batch reactor containing oxalic acid at two concentrations: 25 and 50 wt%. The reaction was carried out at 90 ℃ under stirring (250 rpm) for 1 h. Then, the suspension was thoroughly filtered in a Büchner funnel and using a 400-mesh nylon cloth, adding additional water to wash the pre-treated fibers until achieving a low conductivity of the filtrate. Finally, the pulp was neutralized to pH 7.0 with a NaOH solution. In all cases, the pulp was homogenized at 0.75 wt% consistency through a laboratory high-pressure homogenizer (HPH) (NS1001L PANDA, 2000-GEA, GEA Niro Soavi, Italy) according to the following sequence: 2 initial passes at 300 bar followed by either 3 passes at 300, 600, and 900 bar. Energy consumption was measured with a Circutor CVM-C10 measuring equipment, which directly provided the consumed energy in real time. This equipment also provides cumulative energy consumption in certain periods of time, as previously set by the user. The obtained CMNFs were stored at 4 °C for further use and characterization. Figure 1 shows the flow diagram of the production process of CMNFs, and Table 1 shows the nomenclature of each CMNFs according to processing conditions.

Table 1 Nomenclature of cellulose micro/nanofibers according to the treatment used

| CMNFs	Oxalic acid (wt%)	Homogenization (bar)
$CMNF_{25,300}$	25	300
$CMNF_{25,600}$	25	600
$CMNF_{25,900}$	25	900
$CMNF_{50,300}$	50	300
$CMNF_{50,600}$	50	600
$CMNF_{50,900}$	50	900

Characterization of CMNFs

Prior characterization, the CMNF suspensions were sonicated for 2 min using a Sonics & Materials ultrasonic homogenizer VC 505 (500 W, 40% amplitude) to ensure an appropriate dispersion.

The yield of nanofibrillation was determined by centrifuging (2800 G-force) an aqueous suspension of 0.1 wt% CMNF for 20 min. The dry weight of the supernatant, corresponding to the nanosized fraction, was obtained from the difference between the initial weight (W_i) and the centrifugation sediment (W_s) which was considered as micro fibrillated fraction (CMF) (Eq. 1):

$$Yield\ (\%) = \left[1 - \frac{W_s}{W_i}\right] * 100 \tag{1}$$

Transmittance measurements of 0.1 wt% CMNFs suspensions were performed at 800 nm in a spectrophotometer Shimadzu UV-160A (Kyoto, Japan) using distilled water as a reference.

Fig. 1 Stages of CMNF preparation
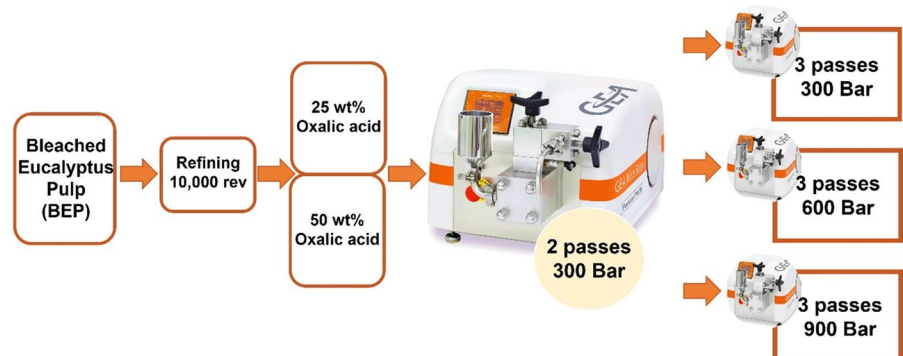
Characterization of the nanosized fraction of CMNF suspensions

The nanosized fraction of each CMNF suspension (CNF) was obtained by means of centrifugation of a 0.1 wt% suspension for 20 min at 2800 G-force. The supernatant was collected, while the sediment was discarded.

The diameter and length distributions of CNFs were determined by transmission electron microscopy (TEM) (JEOL, JEM-2100 Plus, Tokyo, Japan). Observations were made in HRTEM mode, with an acceleration voltage of 100 kV. An aliquot of the CNF suspensions, diluted at 0.001 wt%, was mounted on a glow-discharged carbon coated Cu grid. 300 diameter and 100 length measurements were performed using Image J processing software.

The ζ-potential and hydrodynamic size of the CNFs were determined using a Zetasizer Nano (ZEN 3600, Malvern, UK). The refractive index was set at 1.59. All measurements were made at 25 °C.

Preparation and characterization of polyelectrolyte complexes (PECs)

The PEC formation with a mass ratio: 80 wt% Xyl/20 wt% CH was carried out by adding a xylan solution (2.5 g/L in NaCl 0.01N) to a chitosan solution (0.065 g/L in 0.01 N NaCl) under continuous stirring (300 rpm) at flow rate of 90 mL/h. The pH values of both solutions were adjusted to 5.0 prior mixing.

The particle sizes and ζ-potential of the cationic complex was determined by dynamic light scattering (DLS) using a Zetasizer Nano equipment (ZEN 3600). All measurements were made at 25 °C and pH 5.0. The refractive index used was 1.33 due to the high-water content of the PEC particles (Cegnar and Kerč 2010; Mocchiutti et al. 2016).

PEC-CMNF system added to pulp

Pulp preparation

For this study, test liner recycled pulp (TLRP) supplied by Saica S.A. (Zaragoza, Spain) was used. The morphological analysis of fibers was performed using a MorFi Compact analyzer (TechPAP, Grenoble, France), assisted by an image analysis system involving the software MorFi v9.2. In addition, the fines

content by weight was measured by filtering the pulp suspension through a 200-mesh screen with Bauer McNett classification (SCAN M6:69). We define "fines" as those particles whose length is less than 75 μm.

A sample of paper (30 g, odw) was disintegrated in a standard disintegrator at 3,000 rpm for 20 min at 1.5 wt% of pulp consistency. The resulting pulp was centrifuged, filtered in a 75-mesh cloth, and stored in hermetic plastic bags at 4 °C to prevent any degradation.

Out of the obtained CMNFs, those fibrillated at 600 bar during high-pressure homogenization were excluded from the study with recycled pulp, and those selected to evaluate the effects of the PEC-CMNF system over pulp and paper properties were: $CMNF_{25,300}$; $CMNF_{25,900}$; $CMNF_{50,300}$, and $CMNF_{50,900}$.

Determination of the neutralization point of the PEC-CMNF system

The required PEC dosages to neutralize the charges of the nanosized fraction were determined by ζ-potential measurements. For this, 10 mg of CMNFs were prepared in 5 ml 0.01N NaCl solution and different volumes of PEC solution were gradually added. Finally, the suspensions were centrifuged at 2430 G-force for 20 min and the ζ-potential of the supernatants were measured to find the neutral points. These dosages were used to define the neutral PEC-CMNF systems (Ne) for different CMNFs. In addition, the anionic (An) and cationic (Cat) systems were obtained by decreasing and increasing in a 50%, respectively, the amount of PEC from neutrality.

Evaluation of the retention capacity of PEC

The ability of PEC as retention agent was evaluated using a Britt Dynamic Drainage Jar, according to Schnell et al. (2018). Different dosages of PEC were added to 0.2 wt% suspensions containing a 3 wt% dosage of CMNFs. The suspension was stirred at 900 rpm for 20 min. Three PEC dosages were defined according to the neutralization point, and values of 50% above and below it. The suspension passing through a metal screen (with holds of 75 μm) was obtained without discontinuing the stirring, and after discarding the first 15 mL. A filter paper of cellulose acetate (0.45 μm) was used to quantify the dry amount of CMNFs and fines existing in the

suspension. A set of experiment without PEC was also carried out. Retention was calculated as the proportion of the fines and CMNFs retained at the metal screen. The sum of the mass of CMNFs added and the fines present in the pulp was considering as 100% of retention.

Incorporation of CMNFs and PEC into the pulp and handsheet preparation

CMNFs were incorporated into the pulp in a standard disintegrator operating at 3,000 rpm for 60 min, according to a previously reported method (Delgado-Aguilar et al. 2015a). The CMNF dosage was set at 3 wt% and the pulp consistency, at 1.5 wt%. Then, different PEC dosages were incorporated into the suspension, and this kept under gentle stirring (250 rpm) for 20 min.

The Schopper-Riegler degree (°SR) of the pulps was determined using a Schopper-Riegler equipment (mod. 95587 PTI) in accordance with ISO 5267/1.

A reference sample (Ref) without additives (CMNFs, PEC) was considered. For comparison, the addition of PEC without CNMF was also considered for three levels of PEC addition, which were defined as 1.2, 2.4 and 3.3% by weight with respect to the pulp. For each treatment, five handsheets of 75 g/m^2 of basis weight were prepared in a Rapid-Köthen sheet former, including the pressing and drying stages, according to ISO 5269-2. Handsheets were conditioned at 23 ± 1 °C and a relative humidity of 50% for 48 h before testing. Air permeability (ISO 5636-5), Tensile strength at constant elongation rate (ISO 1924-2), Mullen Index (ISO 2758), Internal

Bonding (TAPPI T569), SCT (ISO 9895:1989) and CMT (TAPPI T809 om-99) were determined for all the prepared handsheets. The presented results are the average of five measurements for each property.

Results and discussion

CMNF characterization

In the present work, two levels of chemical pre-treatment using oxalic acid to obtain CMNFs were analyzed. A yield of 94 and 71% was obtained for the pulp treated with 25 and 50 wt% oxalic acid solution, respectively.

Figure 2a shows the results of transmittance as function of the nanofibrillation yield for the obtained CMNFs. As expected, both transmittance and nanofibrillation yield were enhanced at increasing severity of the oxalic acid treatment, as well as at increasing high-pressure homogenization intensity. In the case of the treatment with oxalic acid, the increase on the nanofibrillation yield and the transmittance was attributed to the higher presence of carboxylic groups, which impart high repulsive forces and, in addition, are more voluminous than hydroxyl groups present in untreated cellulose. Indeed, the nanofibrillation yield was increased by a factor of 6.4, 3.8, and 3.3 when the oxalic acid concentration was doubled, for the first, second and third fibrillation level, respectively. This reveals the high influence of the oxalic acid over the resulting characteristics of the CMNF suspensions. On the one hand, the influence of the carboxylic groups on the fibrillation degree has been previously
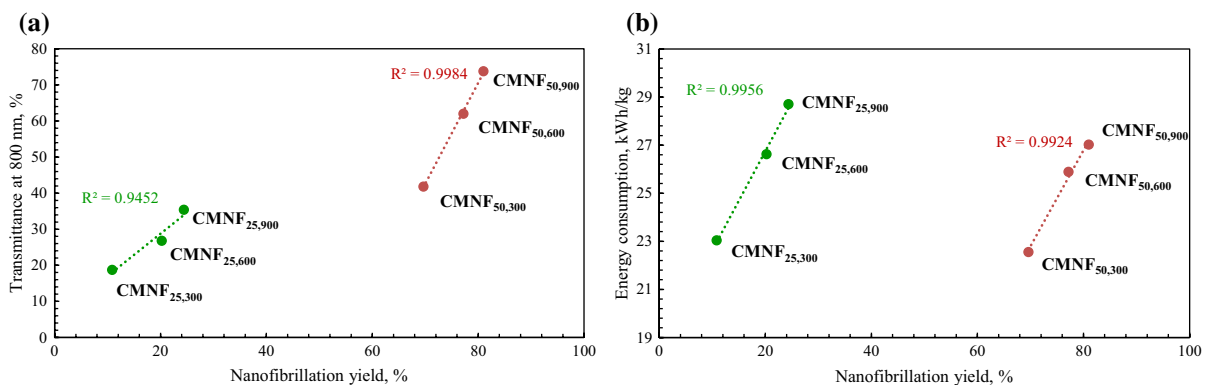
Fig. 2 **a** Transmittance and **b** Energy consumption as a function of nanofibrillation yield for different CMNFs

reported by other authors (Besbes et al. 2011; Serra et al. 2017). On the other, oxalic acid also hydrolyzes the cellulose chain, leading to fiber/nanofiber length reduction and rod-like structures at severe conditions (Bakar et al. 2022). An interesting alternative to avoid this effect is to obtain CNFs by esterification using a treatment with N-succinylimidazole, achieving a regioselective C6-OH surface modification, which can be reversed by mild post-treatments. Beaumont et al. (2021), reported that this chemical modification has the advantage of not compromising the degree of crystallinity and degree of polymerization of native CNFs.

Transmittance has been reported as a robust indicator of the nanofibrillation yield, finding strong correlations between both parameters, mainly due to the low light-scattering capacity of nanosized fibers (Xu et al. 2016; Serra-Parareda et al. 2021). As expected, the light transmittance of the suspensions increased with the nanofibrillation yield, following in both cases (25 and 50 wt% of oxalic acid) a linear tendency as the intensity of the high-pressure homogenization was increased.

Figure 2b shows the energy consumption of the high-pressure homogenizer as a function of the nanofibrillation yield. As expected, the energy consumption increased at increasing pressure of the homogenizer. In addition, at constant pressure in the homogenizer, the energy consumption slightly decreased with the oxalic acid concentration. Surprisingly, the differences on energy consumption between the two oxalic acid treatments were not significant, while both transmittance and the nanofibrillation yield were noticeably enhanced.

Characterization of the nanosized fraction of CMNF suspensions

Regarding the nanosized fractions, after appropriate fractionation of the CMNF suspensions as described above, Table 2 shows their average diameter and length determined by TEM. No significant differences were observed in the average diameters of any CNF (from 10.3 ± 2.6 nm to 12.5 ± 4.2 nm). However, a decrease in the average lengths and aspect ratios were observed for 50 wt% oxalic acid treatment compared to those obtained for 25 wt% oxalic acid. These results are in accordance with those found by Bastida et al., (2022). The same behavior was observed when the pressure of the homogenizer increases. This length reduction effect is derived from the hydrolysis capacity of oxalic acid, as previously discussed (Bakar et al. 2022). Figure 3 shows the images of the CNFs determined by TEM and the histograms of diameter and length.

On the other hand, ζ-potential of the CNFs slightly increased when the concentration of oxalic acid was increased from 25 to 50 wt%. All the CNF suspensions were considered stable, as the absolute value was higher than 25 mV (Lieberman et al. 2020). The introduction of carboxylate groups on the cellulose surface led to greater stability, as they conferred strong electrostatic repulsion between nanofibers (Malucelli et al. 2019).

Table 2 Average diameter and length determined by TEM, Aspect ratio, and ζ-potential determined by Dynamic Light Scattering (DLS) of the CNF fraction

CNF	Average diameter (nm)[a]	Average length (nm)[b]	Aspect ratio (length/diameter)	ζ-potential (mV)[c]
CNF$_{25,300}$	12.5 ± 4.2	1204 ± 298	96.3	-26.5 ± 4.6
CNF$_{25,600}$	12.5 ± 3.7	622 ± 161	49.8	-27.1 ± 5.2
CNF$_{25,900}$	12.4 ± 2.8	601 ± 181	46.2	-29.6 ± 5.8
CNF$_{50,300}$	12.0 ± 3.5	793 ± 227	66.1	-32.3 ± 4.2
CNF$_{50,600}$	11.9 ± 2.4	474 ± 174	39.8	-33.2 ± 4.2
CNF$_{50,900}$	10.3 ± 2.6	358 ± 84	34.8	-34.6 ± 6.2

[a]Values are the average of three hundred replicates of the trial

[b]Values are the average of hundred replicates of the trial

[c]Values are the average of two replicates of the trial
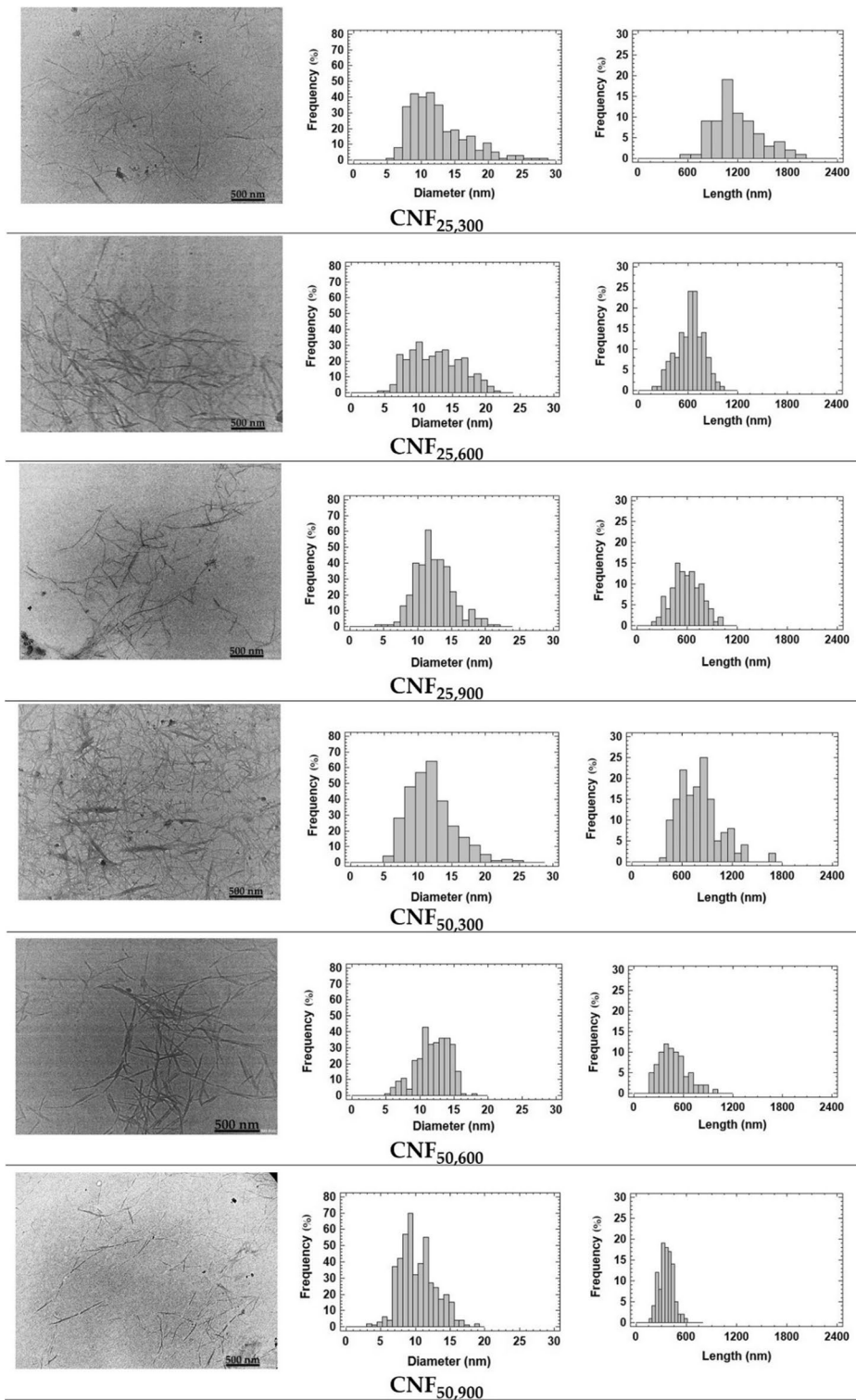
Fig. 3 TEM images and histograms of diameter and length

Some authors used the DLS hydrodynamic diameter combining with TEM or SEM microscopies to estimate the nanofibril lengths (Gamelas et al. 2015; Kunaver et al. 2016; Mao et al. 2017). However, it must be noted that DLS is a technique based on the Brownian motion of macromolecules in solution and relates this motion to the particle size. DLS assumes spherical geometries, providing misleading results when particles with a certain aspect ratio are measured. This is often solved by calculating the equivalent spherical diameter of a cylinder. The advantage of DLS relies on its easiness and non-destructive character, but results are strongly influenced by physic-chemical features such as chemical composition, heterogeneity, topography, surface charge density, dispersing medium, viscosity, and also particle orientation (Kaushik et al. 2015). Considering that DLS results must be critically considered, Fig. 4 shows the average particle size determined by this technique as a function of the nanofiber length determined by TEM for the CNF fraction, as the latter measures the dimensions of the particles in the dry state, while DLS has the implications described above. Despite the differences in both techniques, a linear correlation was found between the particle size (DLS) and the average length values (TEM), exhibiting correlation factors (R^2) of 0.9051 and 0.9835 for the CNFs treated with 25 and 50 wt% of oxalic acid, respectively.
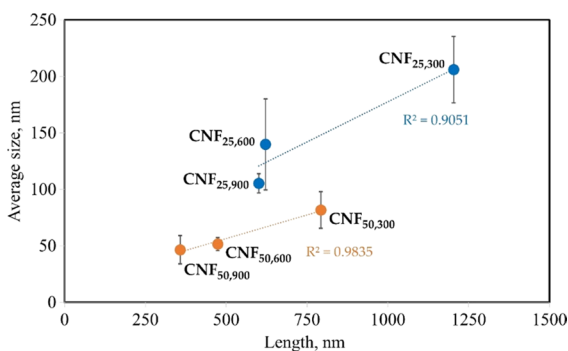

Fig. 4 Average size by DLS as a function of nanofiber length determined by TEM for different CNF suspensions

Determination of the neutralization point of the PEC-CMNF system

The charge and size of PEC in solution by DLS were $+4.5 \pm 0.3$ mV and 221.9 ± 6.4 nm, respectively, with a polydispersity index of 0.207, indicating its cationic character.

Aiming at determining the optimal dosage of PEC over the CMNF/pulp system, prior to handsheet preparation, different PEC-CMNF suspensions were prepared. Figure 5 shown the ζ-potential values as a function of PEC/CMNF mass ratio, and the neutralization points are shown in Table 3. It is observed that the obtained with higher pressure in the homogenizer and those obtained using 50 wt% oxalic acid concentration, required a higher PEC dosage to be neutralized, mainly due to their higher surface charges (Table 2).
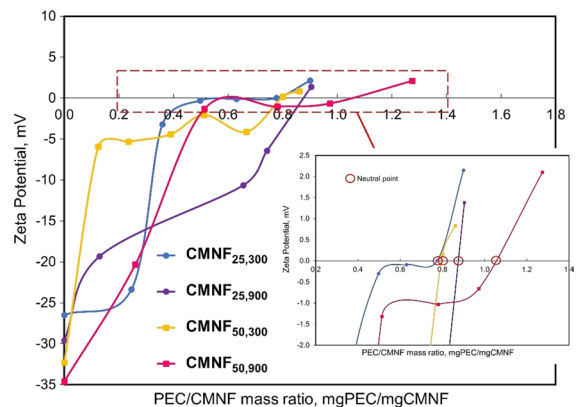
Fig. 5 ζ-potential as a function of PEC/CMNF mass ratio

Table 3 PEC/CMNF mass ratio corresponding to neutralization points determined by ζ-potential measurements

CMNF	PEC/CMNF mass ratio (mg PEC/mg CMNF)
CMNF$_{25,300}$	0.78
CMNF$_{25,900}$	0.88
CMNF$_{50,300}$	0.79
CMNF$_{50,900}$	1.06

PEC-CMNF system added to pulp

Although the effect of CMNFs and fines was analyzed together, it is known that the presence of fines plays an important role in papermaking. As reported by Odabas et al. (2016), on the one hand, the fines cause a higher sheet density, improved bonding and therefore better wet and dry strength. On the other, a high content of fines also results in impaired drainage. In addition, Espinosa et al. (2016) reported that the excessive presence of fines may hinder the interactions between CMNFs and paper fibers, particularly those fines known as non-reinforcing, which are not bonded to the fiber surface (Espinosa et al. 2016). According to the morphological analysis of fibers, the content of fines in length was 37.2%. In addition, the amount of fines present in the pulp was 10.2%.

PEC-CMNF systems were prepared at three levels of PEC dosages corresponding to: (a) neutral system (Ne) obtained by addition of PEC according to the mass ratio indicated in Table 3, (b) anionic (An) and cationic systems (Cat) obtained by 50% lower and higher PEC addition, respectively.

Retention

The retention of CMNF and fines, and PEC/CMNF mass ratio for the anionic, neutral and cationic PEC-CNF systems are shown in Table 4. In general, high retention (between 79.8% and 98.4%) was observed. Particularly, a maximum retention was obtained for the addition of neutral PEC-CMNF system, regardless the CMNF type. In all cases, a decrease in retention values was observed at higher PEC dosages. This was attributed to the excess of PEC, leading to a higher level of flocculation in the system. Schnell et al. (2018) found a similar effect when synthetic

cationic PECs were added to and unbleached recycled pulp.

Drainability

Figure 6 shows the °SR for the different pulps, including the reference (Ref), the recycled pulp containing different PEC dosages, and the pulps containing PEC and CMNFs. Favorably, the °SR significantly decreased when PEC was incorporated into the pulp, regardless the dosage. The effect of increasing PEC content resulted in increased drainability, this is a decrease of the °SR. This can be attributed to an increase on the flocculation of fibers and fines and, thus, promoting the water drainage from the system during paper formation. Indeed, this effect was observed during paper preparation, as it will be later discussed. Flocculation can be qualitatively observed in Fig. 7.

On the other hand, as expected, the addition of CMNFs slightly increased °SR values compared to
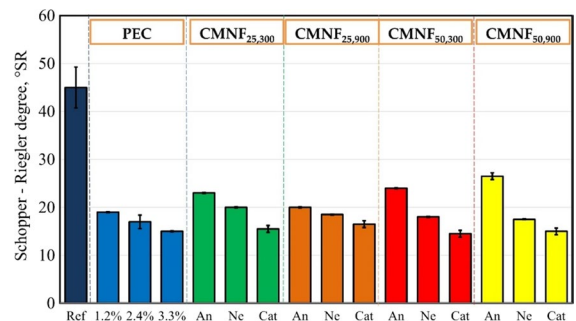
Fig. 6 Schopper-Riegler degree (°SR) of different treatments: Reference (Ref), dosage of PEC alone on pulp (1.2%, 2.4% and 3.3%) and Anionic (An), Neutral (Ne) and Cationic (Cat) PEC-CMNF systems. The error bars correspond to the standard deviations of the means from two replicates of the trial

Table 4 Retention of fines and CMNFs for different dosages of PECs determined in a Britt Dynamic Drainage Jar. Between brackets, the corresponding PEC/CMNF mass ratio is indicated

PEC-CMNF system	% Retention of fines and CMNF*			
	$CMNF_{25,300}$	$CMNF_{25,900}$	$CMNF_{50,300}$	$CMNF_{50,900}$
Anionic	88.4 (0.40)	98.3 (0.45)	94.0 (0.40)	91.9 (0.55)
Neutral	95.5 (0.80)	98.4 (0.90)	96.9 (0.80)	94.1 (1.10)
Cationic	91.0 (1.20)	79.8 (1.30)	79.1 (1.20)	93.4 (1.50)

*The amount of fine present in the pulp was 10.2%
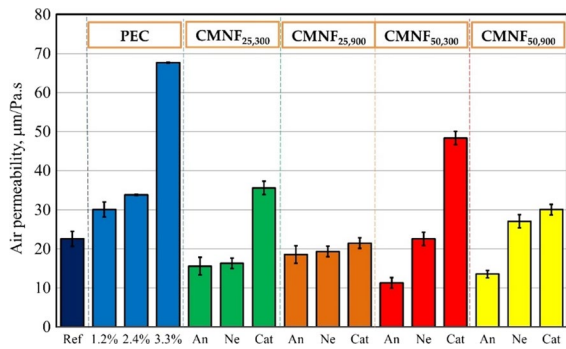
Fig. 7 Air permeability of different treatments: Reference (Ref), dosage of PEC alone on pulp (1.2%, 2.4% and 3.3%) and Anionic (An), Neutral (Ne) and Cationic (Cat) PEC-CMNF systems. The error bars correspond to the standard deviations of the means from five replicates of the trial

those containing PEC. This increase on the °SR can be attributed to the pore filling-ability of the CMNFs, together with the higher water retention capacity of CMNFs compared to pulp fibers (Taipale et al. 2010; Sharma et al. 2020). Indeed, the highest °SR was obtained when incorporating a 3 wt% of CMNF$_{50,900}$ and using the anionic PEC-CMNF formulation, highlighting the role of the nanofibrillation yield of CMNFs on pulp drainability, which is directly linked to their capacity to retain water (Delgado-Aguilar et al. 2016). However, this can be improved with cationic systems, achieving a controlled flocculation. Nevertheless, in all cases, the obtained drainage rates accounted below 33°SR, which ensures good runability in the paper machine (Delgado-Aguilar et al. 2015a).

Table 5 provides °SR values, selected from the literature and for a 3 wt% CNF addition on pulps obtained from different raw materials, while using different retention agents, compared to the present work.
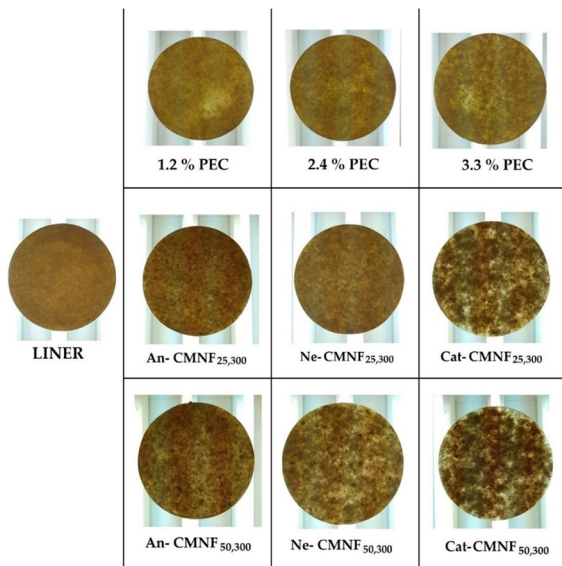
Paper properties

Figure 7 shows the air permeability for a reference treatment (Ref), different PEC and PEC-CMNF dosages on pulps. The values of air permeability increased at increasing PEC dosages. This can be attributed to the increase in flocculation of the fibers and fines that the addition of PEC generates, as revealed in Fig. 8.

On the other hand, as expected, the addition of CMNFs decreased the porosity compared to the pulps treated with PEC. The effect of nanocellulose on paper permeability has been ascribed to the decrease the pore size of the paper (Tanpichai et al. 2019).

The highest permeability was observed for the cationic PEC-CMNF systems, where a lower quality of sheet formation was also observed, promoting the air flow through the structure of paper. Concretely, 50 wt% oxalic-acid CMNFs in anionic systems exhibited the lowest permeability. These CMNFs showed a higher yield of nanofibrillation compared to CMNFs obtained with 25 wt% oxalic acid. The air permeability of paper indicates not only the porosity (void volume/total volume) of paper, but also the complexity of the network structure. This is related mainly to increased fibrillation, fiber flexibility and fines generation (Taipale et al. 2010).

Table 5 Schopper-Riegler degrees (°SR) for different systems reported in the literature and compared to the present work

Pulp	CNF (3%)	Retention agents	°SR	References
Bleached kraft hardwood (BKHW)	TEMPO-CNF	Colloidal silica and cationic starch in amounts of 0.8 and 0.5 wt%, respectively	26	Delgado-Aguilar et al. (2015c)
Bleached kraft softwood pulp (BKSP), from spruce	APSCNF (APS) ammonium persulfate oxidation	Polydiallyldimethylammonium chloride (Poly-DADMAC) 0.5 wt%	45	Filipova et al. (2018)
Bleached thermomechanical pulp (BTMP), from spruce	Mechanical-LCMNF	Poly-DADMAC 0.5 wt%	18	Serra-Parareda et al. (2021)
Laboratory sodium-antraquinone pulp of Pinus	LCMNF	PEC PAH/PAA 0.75 wt%	18	Schnell et al. (2018)
Commercial BEP	CMNF-oxalic acid	PEC Xyl/Ch	15	Present work

Fig. 8 Sheets images of different treatments

Figure 9a, b shows the tensile index and the Mullen index of paper for a reference treatment (Ref), different PEC and PEC-CMNF dosages on pulps, respectively. As expected, both properties evolved similarly. However, the cationic systems negatively affected these properties, which can be attributed to the presence of flocs in the system that hinder the sheet formation, as shown in Fig. 8. Particularly, the highest increase in tensile index (40%) was observed when 2.4% PEC was added to the pulp, and the highest increase in Mullen index (40%) was found for the combined action of PEC and $CMNF_{25,300}$ in a neutral system. The obtained CMNFs exhibited a notable aspect ratio, but low nanofibrillation yield, indicating that the network-forming capacity of micro-sized fibrils contribute to a higher extent than inter-fiber bonds generated by surface fibrillation.

Internal bonding (Fig. 9c) was increased in 119% for a 2.4% PEC addition and can be attributed to the increase on bonding between fibers and fines due to
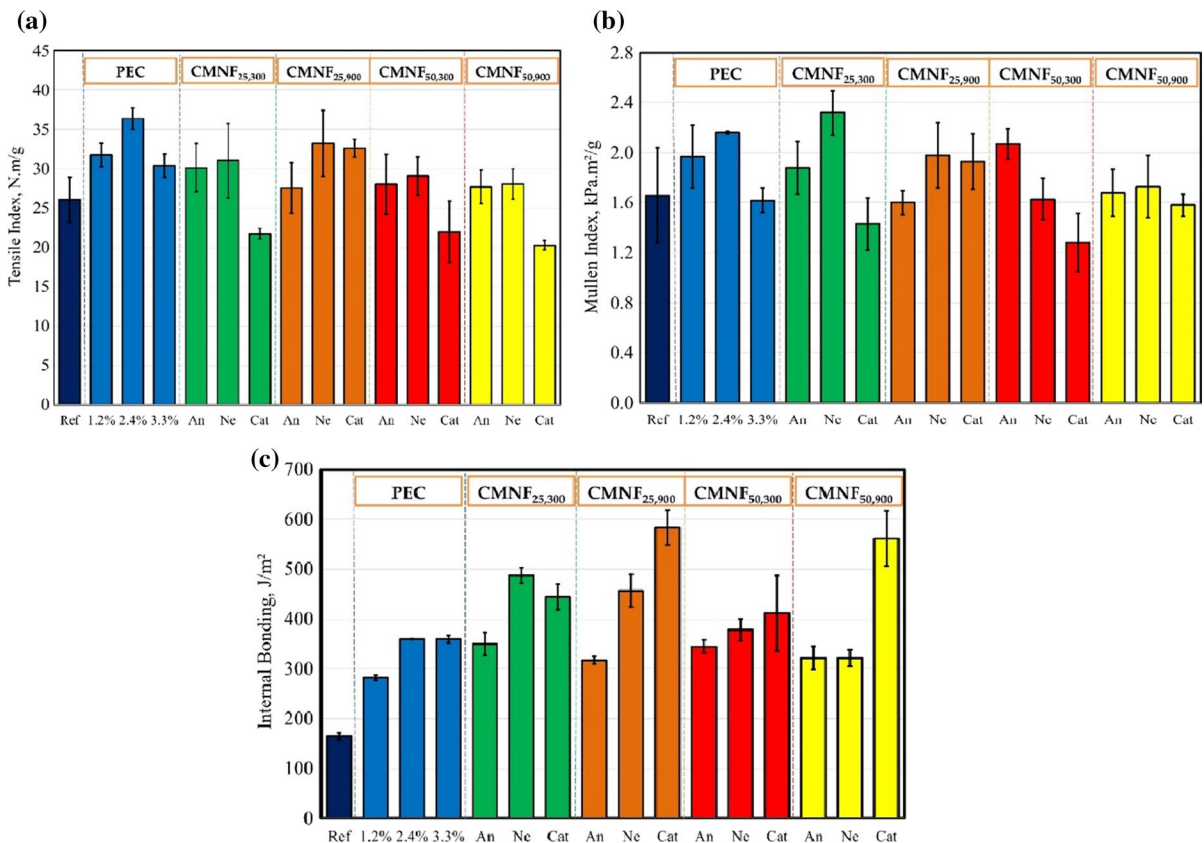
Fig. 9 **a** Tensile index, **b** Mullen index, and **c** Internal bonding of the obtained papers with different treatments. The error bars correspond to the standard deviations of the means from five replicates

the cationic character of PEC. For the cationic systems and CMNFs obtained at high pressure, internal bonding remarkably increased (between 241 and 255%), mainly due to a greater fibrillation, surface area and increased number of bonds between fibers. CMNFs are expected to coat the surface of the fibers facilitating contact at the molecular level during drying and fill the pores, thus expanding the possible adhered area, which would result in increased strength (Brodin et al. 2014).

In contrast to the tensile index, the enhancement of internal bonding was greater through the addition of the PEC-CMNF system, indicating that improper formation apparently affects tensile in more extent than delamination strength. This can be attributed to the fact that, during the internal bonding test, in-plane delamination occurs by detachment of the paper layers, while in the tensile test, according to Page's theory (Page et al. 1969), the failure is localized in single line that will ultimately become the line of rupture.

Table 6 shows the SCT index of paper for a reference treatment (Ref), different PEC and PEC-CMNF dosages on pulps. In general, no significant differences in SCT index for different treatments are observed. However, this compressive strength was increased a 30% when a treatment with $CMNF_{50,900}$ in cationic system was used. Table 6 also shows the CMT compressive strength. It was observed that the crushing resistance of corrugated paper increased at increasing PEC dosages, achieving improvements of up to 41%. On the other hand, the combined action of CMNFs and PEC enhanced the CMT compressive strength with respect to the addition of PEC. As for SCT, the maximum CMT value was found for the addition of $CMNF_{50,900}$ in a cationic system, reaching a 70% enhancement, which was attributed to the higher yield of nanofibrillation of these CMNFs. The improvement in CMT was higher than that reported by other authors. Ehman et al. (2020) reported increments in CMT strength from 11 to 27% when handsheets were prepared using unbleached industrial chemimechanical pulp (CMP). The authors used 3 wt% TEMPO-CNFs, LCNFs and $Al_2(SO_4)_3$ under the presence of a rosin resin emulsion.

Conclusions

The developed cationic polyelectrolyte complex based on xylan and chitosan has been found to be effective as retention agent for CMNFs prepared with oxalic acid. Depending on the requirements of paper, the addition of PEC with or without CMNFs may be of interest. Particularly, the addition of only PEC in neutral system, the tensile index improved up to 40%. PEC-CMNF system exhibited noticeable improvement on pulp drainability, which is convenient to ensure an appropriate runability of the paper machine. On the other hand, the proposed systems strongly influenced the characteristics of the obtained papers. Internal Bonding was notably improved, achieving an enhancement of 255% when the cationic system was used. Besides, SCT and CMT were increased in 30 and 70%, respectively, when the CMNFs prepared at the highest oxalic acid concentration and severer fibrillation conditions were incorporated into the pulp slurry. Overall, an acceptable retention, together with the simultaneous improvement on (i) pulp drainability, (ii) air permeability, (iii) paper delamination strength and (iv) compression strength, make the combination of PEC with CMNFs a promising alternative to be considered in packaging paper production.

Table 6 CMT and SCT Index of Reference (ref), addition dosage of PEC alone on pulp (1.2%, 2.4% and 3.3%) and addition of Anionic (An), Neutral (Ne) and Cationic (Cat) PEC-CMNF systems

Samples	SCT index (Nm/g)[a]	CMT (N)[a]
Reference (Ref)	18.6 ± 1.7	54 ± 5
1.2%	17.3 ± 1.6	54 ± 1
2.4%	19.5 ± 2.9	69 ± 3
3.3%	16.3 ± 1.5	76 ± 1
An-CMNF$_{25,300}$	19.5 ± 2.6	74 ± 2
Ne-CMNF$_{25,300}$	20.9 ± 1.7	65 ± 4
Cat-CMNF$_{25,300}$	19.0 ± 1.9	85 ± 6
An-CMNF$_{25,900}$	20.4 ± 2.3	70 ± 7
Ne-CMNF$_{25,900}$	19.1 ± 0.2	76 ± 1
Cat-CMNF$_{25,900}$	21.9 ± 1.7	76 ± 6
An-CMNF$_{50,300}$	19.2 ± 0.1	69 ± 1
Ne-CMNF$_{50,300}$	18.0 ± 0.3	81 ± 4
Cat-CMNF$_{50,300}$	20.9 ± 2.0	79 ± 4
An-CMNF$_{50,900}$	21.9 ± 1.8	89 ± 2
Ne-CMNF$_{50,900}$	21.5 ± 1.8	89 ± 6
Cat-CMNF$_{50,900}$	24.1 ± 1.2	92 ± 7

[a]Values are the average of three measurements

Declarations

Conflict of interest Authors declare that they have no known competing interests or personal relationships that could have appeared to influence the work reported in this paper.

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 this work is not part of a single study, 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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