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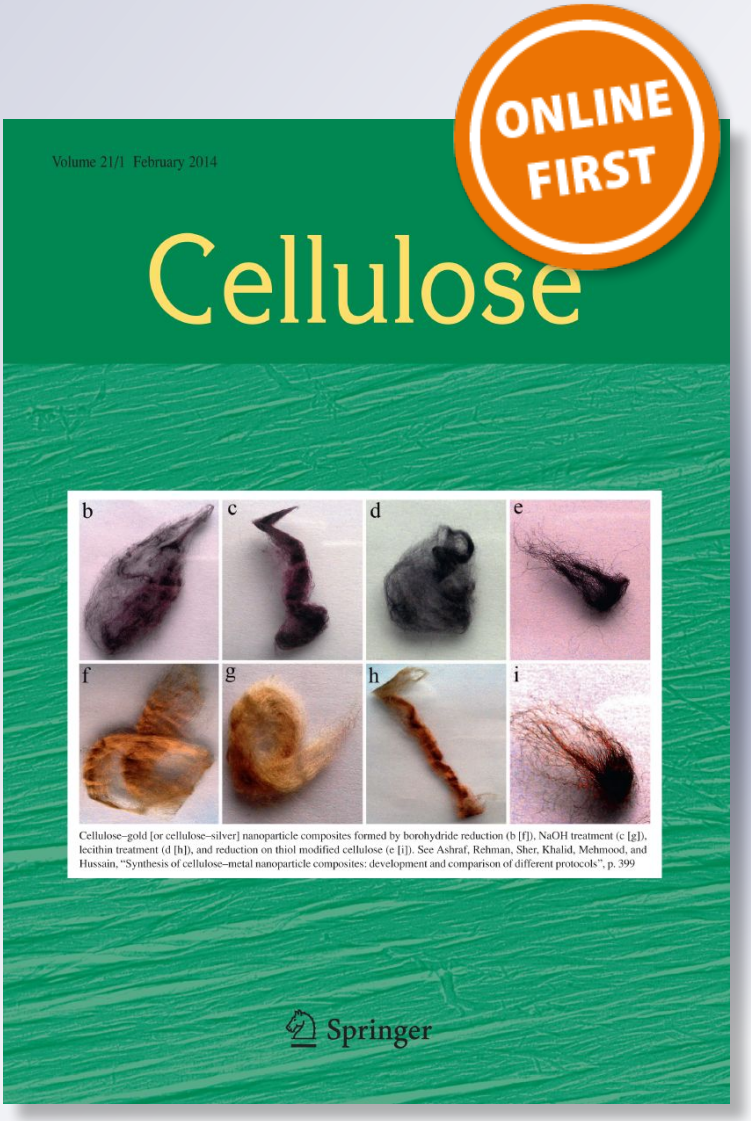

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ORIGINAL PAPER

Polyelectrolyte complexes for assisting the application of lignocellulosic micro/nanofibers in papermaking

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Abstract A novel procedure based on the addition of polyelectrolyte complexes (PECs) onto the pulp containing lignocellulosic micro/nanofibers (LCMNF) is presented. This procedure allows increasing paper strength avoiding an excessive loss in drainability. LCMNF were obtained from partially delignified kraft pine sawdust using a high-pressure homogenizer. Cationic complexes (CatPECs) were prepared by adding the anionic polyelectrolyte solution (polyacrylic acid) on the cationic polyelectrolyte solution (poly(allylamine hydrochloride)). According to turbidity and surface morphology changes, an interaction between CatPECs and LCMNF could be established. Different CatPEC dosages (from 0.3 to 1.0% on pulp) were added on a recycled unbleached softwood kraft pulp containing 3% of LCMNF. For a PEC dosage of 0.75% on pulp, an optimum balances between negatively and positively charged materials [near to zero value of the logarithm of the colloidal titration ratio (logCTR)] was found. Britt Dynamic Drainage Jar test showed a high retention of fines and LCMNF for all PEC dosages. A maximum in retention value was obtained for the addition of 0.75% of PECs on pulp, dosage that was suggested as optimum by the logCTR. In addition, the best drainability value (18°SR) was obtained for this PEC addition level. Papermaking properties were clearly improved for all dosage of PECs. Particularly for a dosage of 0.75% of PECs on pulp, tensile strength was noticeably increased (+48%) and both compressive resistance Concora Medium Test (CMT) and Short-span Compressive Test (SCT) were markedly increased (+64% and +39%, respectively). These results suggest that PECs are a possible alternative to assist the application of LCMNF in papermaking.

Keywords Colloidal charge · Recycled paper · Polyelectrolytes · Poly(allylamine hydrochloride) · Polyacrylic acid · Cellulosic nanomaterials

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Introduction

Cellulose nanofibers and microfibers (CNF and CMF, respectively) have gained increasing interest in the recent years, especially for the paper industry as sustainable and promising strength additive. In fact, those CNF obtained by means of mechanical methods are of interest of papermakers due to their lower cost and potential application as dry and wet strength

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additive that, in addition, can be in situ produce (Boufi et al. 2016). This application is of special interest for recycled paper production, since no structural damages are caused and life span of paper products can be significantly increased although the low quality of the raw material (Delgado-Aguilar et al. 2015a, b; Merayo et al. 2017a). Delgado-Aguilar et al. (2015a) studied the use of CNF as alternative to mechanical refining for recycled paper production, reaching significantly higher paper tensile strength and stiffness with 1.5% CNF addition. Other basic but advantageous properties and characteristics such as high availability as a renewable material, large specific surface area and high aspect ratios, thermal stability, biodegradability and biocompatibility, makes CNF a material of interest for other productive sectors (Brodin et al. 2014).

CNF can be obtained from several raw materials, such as hardwood, softwood, agricultural residues and even waste paper (Ahola et al. 2008; González et al. 2012; Jonoobi et al. 2012; Merayo et al. 2017a). Usually, CNF are produced from woody and bleached pulps due to the commercial availability and large use in other sectors. However, the yield in terms of material utilization from the tree to the final product is low, usually below 50%, meaning that more than 50% is considered as waste that needs to be valorized. To avoid further processing of the raw material, recent studies have shown the feasibility of producing CNF and CMF containing lignin, also called lignocellulosic nanofibers (LCNF) and lignocellulosic micro/nanofibers (LCMNF). Comparatively to cellulose nanofibers (CNF), unbleached fibers, present advantages as high yield, low production cost, low environmental impact and, at appropriate lignin and hemicellulose content, the same reinforcing potential (Rojo et al. 2015; Tarrés et al. 2017).

The main limitation when using CNF or LCNF as strength additive is the need of dosing the appropriate amount of retention agents to ensure the adsorption of the nanofibers and to avoid an excessive loss in drainability during pulp dewatering in the paper production process (Ahola et al. 2008; Taipale et al. 2010). Synthetic polyelectrolytes are widely used in the paper industry to increase fines and filler retention and therefore, to improve paper quality and reduce material and energy costs (Korhonen and Laine 2014). Several studies have been focused in the use of polyelectrolyte complexes (PECs) as paper strength additive, by pre-forming the PECs and letting them interact with fibers (Lofton et al. 2005; Gärdlund et al. 2005; Eriksson et al. 2006; Mocchiutti et al. 2016). PECs are formed mainly by electrical interactions (Coulomb interactions) between the cationic and the anionic polyelectrolytes (Ankerfors 2008). Structure of PECs depends on pH, ionic strength, polymer concentration, molar mass, etc.

PECs are advantageous with respect to single polyelectrolytes in creating new nanostructured units (Ankerfors and Wagberg 2014; Schnell et al. 2017) with high surface/volume ratio and structural sizes of biological components. PECs are used in a wide variety of industrial applications such as coatings and wastewater treatment (Ankerfors 2008). In our previous works, the effects of the addition of polyelectrolyte complexes of poly(allylamine hydrochloride) (PAH) and polyacrylic acid (PAA) onto high quality unbleached fiber were studied (Mocchiutti et al. 2015). It was shown that the mechanical properties of the paper, such as compressive resistance (CMT), could be significantly increased by using PECs.

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.

For all the above, in this work, the efficiency of PECs as retention and strength agent on a recycled pulp-nanocellulose system was evaluated. Stable colloidal suspensions of PECs of PAA and poly(allylamine hydrochloride) (PAH) was considered. Interactions and flocculation efficiency of LCMNF with PECs was analyzed by the addition of PECs on LCMNF suspension under different stirrings rates. Then, the effects of PEC dosage added, between 0.3 to 1.0%, on a recycled unbleached softwood kraft containing 3% of LCMNF was analysed. Colloidal titration ratio method (CTR) was employed to analyse, in this system, the total colloidal charge and to determine the dosage corresponding to the neutral point. Britt Dynamic Drainage Jar was used to evaluate the global retention of fines and LCMNF. Finally, the effects of PEC additions on drainability and papermaking properties of the pulp were evaluated.

Experimental

Preparation of LCMNF

A laboratory sodium-antraquinone pulp of *Pinus pinaster* sawdust from Mas Clarà (Domeny, Spain) was used to obtain LCMNF (Vallejos et al. 2016). Pine sawdust pulp was bleached and refined before nanofibrilation. The bleaching process was performed at 70 °C and using 8 wt% NaClO on pulp, according to Delgado-Aguilar et al. (2016). Then, the pulp (Kappa N° 25), at 10 wt% was mechanically refined in a PFI mill (NPFI 02 Metrotec SA) according to ISO 5264-2:2011 at 20,000 revolutions. The fibrillation process was performed using a high-pressure homogenizer (NS1001L PANDA 2K-GEA, Niro Soavi Parma, Italy) at 1 wt%, following the sequence of 3 passes at 300 bar, 3 passes at 600 bar and 3 passes at 900 bar. The resulting LCMNF suspension was kept at 4 °C in a hermetic plastic bag.

Characterization of LCMNF

Chemical characterization and nanofibrillation yield

The surface acid groups content was determined by direct polyelectrolyte titration as described Junka et al. (2013). This method was found to be a more suitable than indirect polyelectrolyte titration, which produced apparent high surface charge values. A solution of 450 μN of poly-DADMAC (poly (diallyldimethylammonium chloride)) from Sigma-Aldrich with an average molecular weight of 400–500 kDa was used as titrant. This solution was previously titrated using a standard solution of 1000 μN of KPVS (potassium (polyvinyl sulfate)) from AppChem Ltd UK (England). Titrations were performed at 0.001 N NaCl and pH 7.5, using a streaming current detector (Chemtrac CCA 3100) for determining the equivalence point. The content of total acid groups was determined by the conductometric method (Katz et al. 1984) but using $NaHCO_3$ instead of NaOH as titrant, as was suggested by Lloyd and Horne (1993).

The fibrillation yield was determined by centrifugation of the LCMNF suspension at 0.14% consistency at 4.500 rpm for 20 min. The dry weight of the supernatant, called nanofibrilated fraction was obtained from the difference between the total and the centrifugation sediment which was considered as micro fibrillated fraction. Also, to indicate the nanocellulose fraction, transmittance measurements were performed on LCMNF suspension of 0.1% concentration. A UV–Vis Shimadzu spectrophotometer set (UV-160A) and a range of length between 400 and 800 nm was used. Distilled water was used as reference.

Determination of LCMNF size distribution

The average diameter of the nanofibrilated fraction was determined by atomic force microscopy (AFM). The sample was placed on a glass holder and vacuum-dried. A SPM/AFM Microscope (Agilent 5400) was used in tapping-mode at cantilever drive frequency of 300–330 kHz. Images were scanned on, at least, five different areas of the sample.

On the other hand, the micro fibrillated fraction of the LCMNF was re-dispersed in water and fractionated by fiber length using a Bauer McNett (SCAN M6:69) classifier. The 100 and 200 mesh screens were considered. A sample of +100 and +200 mesh fractions was taken to determine average fiber diameter by optical microscopy. The suspension containing the shortest fibers (passing through the 200 mesh) was collected in buckets and acidified (pH 4.0) for a better settling of the material. Sediment was neutralized and average diameter was determinate by scanning electron microscopy (SEM). Gold coating was necessary. Finally, all the fractions were dried at 105 °C and weighed.

Preparation and characterization of polyelectrolyte complexes (PECs)

Polyacrilic acid (PAA) and poly(allylamine hydrochloride) (PAH) supplied by Sigma-Aldrich with average molecular weights of Mw: 5 kDa and Mw: 56 kDa, respectively, were used to obtained the polyelectrolyte complexes. First, polyelectrolyte solutions of 0.25 μeq/L of PAH and 1 μeq/L of PAA at 0.01 N NaCl and pH 7.5 were prepared as previously reported by Mocchiutti et al (2015). Then, cationic complexes with 50% of free cationic charges were formed by adding the anionic polyelectrolyte solution of PAA at a dosage of 30 mL/h onto cationic PAH solution under controlled mild stirring.

Particle size 71.5 ± 14.0 nm (94.4%), zeta potential +32.5 ± 2.4 mV and charge density 1.87 ± 0.08 μeq/g of these cationic complexes was previously determined by Mocchiutti et al (2015).

Interaction between LCMNF and PECs

The interaction between LCMNF and PECs was followed by turbidity and by scanning electron microscope (SEM). PEC suspension (37 mg/L) was added to LCMNF suspension (150 mg/L) under continuous stirring. Two flow rates (30 and 120 mL/h) and two stirring speeds (600 and 1200 rpm) were considered. Change in turbidity was followed by a HACH 18,900 instrument. It is assumed that flocculation is reflected in a decrease in turbidity. In addition, samples were taken and dried on glass holder to observe the flocculation level by scanning electron microscopy (SEM).

Pulp preparation

Industrial liner paper (100% virgin softwood fibers from Pinus elliottii and Pinus taeda) supplied by Papel Misionero S.A (Argentina). The pulp was prepared as described previously by Mocchiutti et al. (2015). In brief: sheets were soaked 24 h and disintegrated for 15 min. Then, the pH of pulp suspension was adjusted to 4.0 and after 30 min, it was centrifuged and stored until use.

Colloid titration ratio

An optimum balance between negatively and positively charged materials in fiber slurry can be critical to the profitable operation of a paper machine. Colloidal Titration Ratio (CTR) was carried out here to evaluate the effect of CatPEC addition onto the total charge of the pulp slurry containing 3% of LCMNF. The colloid titration ratio can be calculated as the ratio between the cationic and the anionic polyelectrolyte in terms of charge equivalents that are absorbed by the pulp slurry and are determinated by indirect colloidal titration (Halabisky 1977). Different addition levels of PECs (0.3, 0.5, 0.75 and 1.0%) and 0.25 g of o.d. pulp at 0.4% pulp consistency was considered. First, 25 ml (0.01 N) of standardized solution of poly-DADMAC or the anionic polymer sodium polyethylene sulfonate (NaPES) was added. After 1 min of stirring, the suspension was centrifuged at 3000 rpm for 15 min and the excess of polyelectrolyte in the supernatant was titrated using the polyelectrolyte with opposite charge. A streaming current detector device (Mutek PCD-04) for determining the equivalence point was used. Afterward, dried weight of pulp was determined.

Retention

To evaluate the ability of PECs as retention agent, CatPECs (0.3, 0.5, 0.75 and 1%) were added to suspensions of 1.2 g o.d. of pulp at 0.2% pulp consistency containing 0.036 g of LCMNF (3% on pulp). A Britt Dynamic Drainage Jar was used at 600 rpm. Filtered water conditioned at pH 7.5 and 300 μS/cm conductivity was used. The suspension passing through a metal screen of 0.75 μm was considered, after discarding the first 15 ml. A filter paper of nitrocellulose (0.22 μm) was used to quantify the dry amount of LCMNF and fines existing in the suspension. Set of experiment without PECs was also carried out. Retention was calculated as the proportion of the fines and LCMNF (that not pass through of metal screen). The sum of the mass of LCMNF added and the fines present in the pulp was considering as 100% of retention. The P-200 fraction of Bauer McNett classification (SCAN M6:69) was considered as the amount of fines present in the pulp (13 wt%). The evaluation was done by duplicated.

Handsheet preparation and evaluation

At 0.4% pulp consistency, in conditioned water at pH 7.5 and 300 μS/cm of ionic strength, the pulp was treated for 60 min in a standard disintegrator in presence of 3 wt% of LCMNF. Then, the pulp slurry was added to the PEC solutions and kept under mild stirring for 30 min. Different dosages of PECs (0.3, 0.5, 0.75 and 1.0%) were studied. A control treatment (Ref) without additives (LCMNF, PECs) was also made. For each treatment, six handsheets of 120 g/m^2 were prepared according to SCAN standard methods. Rapid-Kothen sheet was used for formation, pressing and drying (ISO 5269-2:2004). Apparent density (Tappi 411 om-97), tensile strength (Tappi T494 om-01), CMT (Concora Medium Test) (Tappi T809 om-99) and SCT (Short Compression Test) (Tappi T 826 pm-92) were evaluated on all sheets. A sample of the sheets formed, were pressed and lyophilized to be

observed by scanning electron microscopy (SEM; Phenom ProX, Phenom-World, Netherlands).

Results and discussion

Characterization of LCMNF

Chemical characterization and nanofibrillation yield

Table 1 shows the results of fibrillation performance and the chemical characterization of LCMNF. The low values of nanofibrillation yield and transmittance bring to the light that only a small portion of the fibers are in the nano domain.

The surface charge was approximately a 58% lower than the total charges value obtained by conductometric titration. This percentage can be considered as delamination efficiency index (42%). Junka et al. (2013) indicated that, in case of full fibrillation of the fibers, the surface charge of nanomaterial should be equal to the total charge of the material.

The obtained value of surface charge is lower than values reported by others. Korhonen and Laine (2014) obtained a total charge value of 65 μeq/g for a mechanical CNF (bleached kraft hardwood pulp).

Determination of LCMNF

Figure 1 shows the AFM image of the nanometric fraction. The typical dimensions of CNF produced by homogenization are around 20–40 nm in width and several micrometers in length (Lavoine et al. 2012).

Table 2 shows that the average diameter of the isolated supernatant fraction obtained by centrifugation is slightly higher (48 ± 10 nm). The analysis performed in optical microscopy for the microfibrilar fraction, showed that the higher fraction of LCMNF (76.1%) has an average diameter of 127 ± 57 nm and a 6.1% of the LCMNF present higher diameter (Table 2).

Table 1 Characterization of LCMNF

Nanofibrillation yield (%)	17.8 ± 0.42[a]
Total charge, μeq/g CNF	34.60 ± 1.66[a]
Surface charge (after sonication), μeq/g CNF	14.40 ± 0.43[a]
Transmittance at 800 nm, %	15.1

[a]The standard deviations of the average values from two replicates are indicated

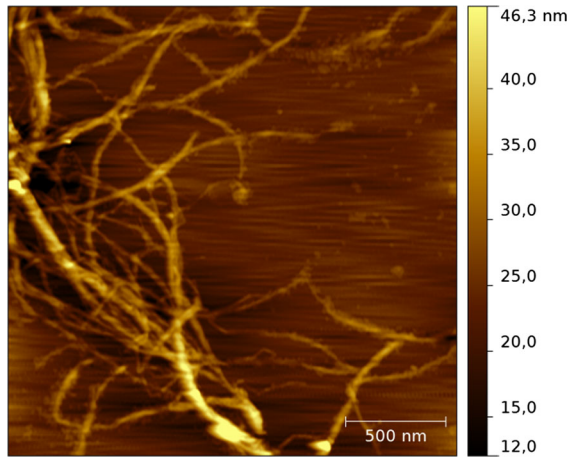

Fig. 1 AFM image of the nanometric fiber fraction onto glass holder. The image size is 2 × 2 μm

Interaction between LCMNF and PECs

Figure 2a shows the turbidity of the LCMNF suspension as function of the amount of PEC added at two flow rates (30 and 120 mL/h) and at a stirring speed of 300 rpm. Turbidity is decreased until a plateau, indicating that flocculation occurred gradually from the beginning but it was completed at 0.12 mg PEC/mg LCMNF mass ratio approximately. Besides, no significant difference was observed when flow rate was varied.

In this system, the major driving force that leads to flocculation is the electrostatic interaction. Considering the surface charges of LCMNF and PECs (14.4 and 1870 μeq/g respectivelly), the point of theoretical neutrality corresponds to 0.01 mg PEC/mg LCMNF mass ratio approximately. It can be expected that the PEC dosage necessary to allow retention of the LCNMF in a papermaking system be close to this theoretical neutral level.

Flocculation of nanocellulose can withstand a wide dosage of flocculant agent. Merayo et al (2017b) indicated that CNF allow the addition of higher flocculant dosage before overdosing effect occurs.

Figure 2a includes SEM images corresponding at two mass ratios of mg PEC/mg LCMNF, showing that the size of the aggregates grows as PEC amount is

Table 2 Diameter of the fibers corresponding to the nanofibrillar and microfibrillar fractions

	Fraction	% (wt)	Average diameter (nm)
Microfibrilar	> 100 Mesh	2.1	3413 ± 2050[a]
	100/200 Mesh	4.0	3170 ± 2120[a]
	< 200 Mesh	76.1	127 ± 57[b]
Nanofibrilar		17.8	48 ± 10[c]

Bauer McNett portions are indicated for microfibrilar fraction. Values are the average of, at least, fifty determinations
Microscopy used: [a]Optical, [b]SEM, [c]AFM

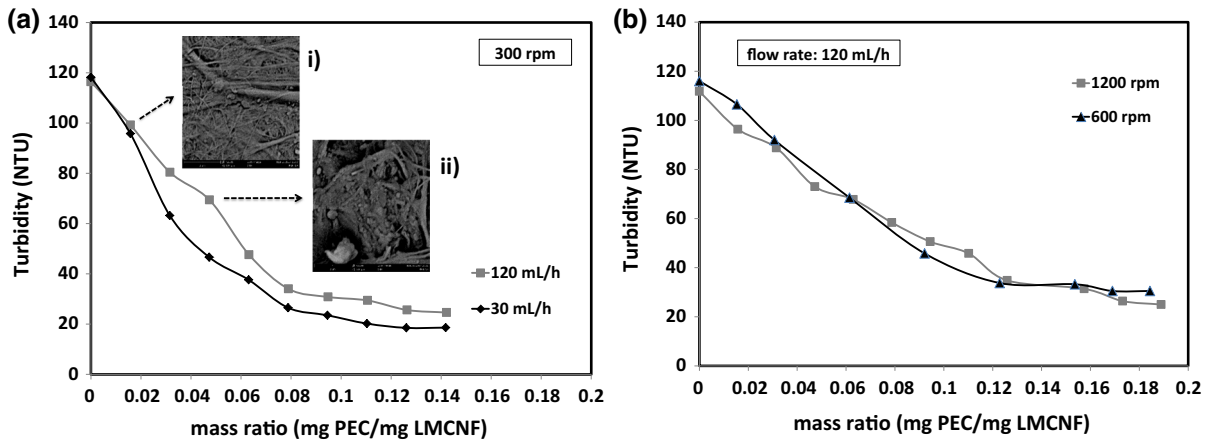

Fig. 2 Interaction between LCMNF and PEC, monitored through turbidity measurements as a function of the mass ratio (PEC/LCMNF), at **a** 30 and 120 mL/h flow rate at 300 rpm and **b** 600 and 1200 rpm stirring speed. Insets: SEM images: (i) at 0.02 PEC/LCMNF mass ratio (ii) at 0.05 mg PEC/mg LCMNF

increased. Higher dosages lead to flocs of excessive size that may not be desired in a paper system.

Korhonen (2015) evaluated the interaction between polyelectrolyte complexes and different fillers. In this study, continuous monitoring of turbidity was carried out, taking into account that bigger aggregates scatter light in a lower magnitude and, thus, a decrease on turbidity can be observed as bigger the aggregates are.

Figure 2b shows the turbidity of the LCMNF suspension as function of mg PEC/ mg LCMNF mass ratio at higher stirring speeds (600 rpm and 1200 rpm) for a flow rate of 120 mL/h. In this case, the flocculation was completed at a higher mass ratio ($\approx$ 0.17 mg PEC/mg LCMNF) compared to the curves obtained at 300 rpm. Anyway, PEC produced a clear flocculation of LCMNF in both cases.

PECs on pulp-LCMNF system: colloid charges

The balance between the negative and positive colloidal charges present in pulp slurries according to the Colloid Titration Ratio (CTR) technique at different PEC dosage was studied. In some cases and at large scale, this technique is used to glimpse the paper machine performance. An effectively control of wet-end additives will result in better machine drainage and improve filler retention.

Figure 3 shows the logarithmic CTR (logCTR) as function of the amount of PEC added. The value of REF corresponds to the initial charge of fiber-LCMNF slurry. A negative value of logCTR indicates that the sample absorbs more cationic than the anionic polymer. As expected, when the PECs dosage was increased, the value of logCTR also increased. A dosage of 0.75% of PECs was found to be the optimal,

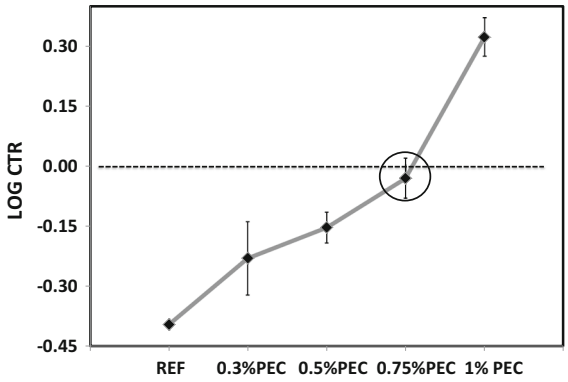

Fig. 3 Total charge of the pulp slurry containing 3% of LCMNF as a function of the PEC dosage

since the value of logCTR was near to zero, indicating that charges are neutralized.

In fact, Carrasco et al. (1998) reported that a logCTR value near to zero corresponds to the best fine-particle retention. Also, these authors found a good correlation between the logCTR and zeta potential values derived from micro-electrophoresis.

PECs on pulp-LCMNF system: retention

Table 3 shows the retention percentage of LCMNF and fines at different dosages of PECs. The percentage was increased with the addition of PECs, thus asserting the existence of interactions between the complexes, LCMNF and fines presents on the fiber slurry. Although the best retention value corresponds to 0.75% of PEC addition, there is no significant difference ($p < 0.05$) in the percentage of retention between the dosages of 0.75, 0.50 and 0.30% of PECs.

It is observed when 1.0% of PECs was added, the value of the retention was decreased. This result is in accordance with the values of logCTR, which showed, for this PEC addition, a value clearly beyond the charge neutrality.

Considering the turbidity curve (Fig. 2), the level of 0.75% of PEC could be high in terms of PEC/LCNMF mass ratio (0.25 mg PEC/mg LCMNF), which corresponds to a high level of flocculation. The benefit of the nanocellulose on paper strength could be hindered by an extreme flocculation. Nevertheless, PECs interact with other anionic elements that the papermaking system includes like fillers, fines and fibers decreasing the flocculation level.

Table 3 Retention of LCMNF and pulp fines for a different dosages of PECs in a Britt Dynamic Drainage Jar

% PEC addition	% (fines + LCMNF) retention[a]
0% PEC (REF)	89.7 ± 0.41
0.30% PEC	95.8 ± 0.08
0.50% PEC	95.4 ± 0.09
0.75% PEC	96.3 ± 0.04
1.0% PEC	94.2 ± 0.33

[a]Average of two determinations

Effect of PECs and LCMNF addition on papermaking properties

Figure 4a shows the effect of PECs and LCMNF addition on tensile strength and drainability. Compared to the reference pulp (REF), tensile strength was increased when PECs and LMCNF were added onto the pulp. However, as expected, pulp drainability was affected (increase on °SR). The highest increase in tensile strength (+48%) and the best drainability result (18°SR) was obtained for a PEC dosage of 0.75% on the pulp containing 3% of LCMNF. Thus, it becomes apparent that by appropriate selection of additives and process conditions, a significant enhancement of the mechanical properties can be achieved without affecting the drainability.

On the other hand, a mechanical refining (1000 revolution at PFI mill) on the reference pulp showed a 63% increase in tensile index. However, compared to LCMNF addition, a higher lost in drainability (22.0°SR) was detected.

Although, mechanical refining develop similar increase in paper strength, the use of nanocellulose offer another benefits. In previous works, it was stated that the use of CNF instead to mechanical refining for recycled paper production presents environmental advantages, such as lower energy consumption during processing. In addition, the number of recycling instances that fiber can withstand is increased. (Delgado-Aguilar et al. 2015b).

Figure 4b shows the effect of PECs and LCMNF addition on compressive strength, CMT and SCT. A notable enhancement on CMT (+64%) and SCT (+39%) was achieved with respect to the reference pulp when 0.75% of PECs was added. In fact, this

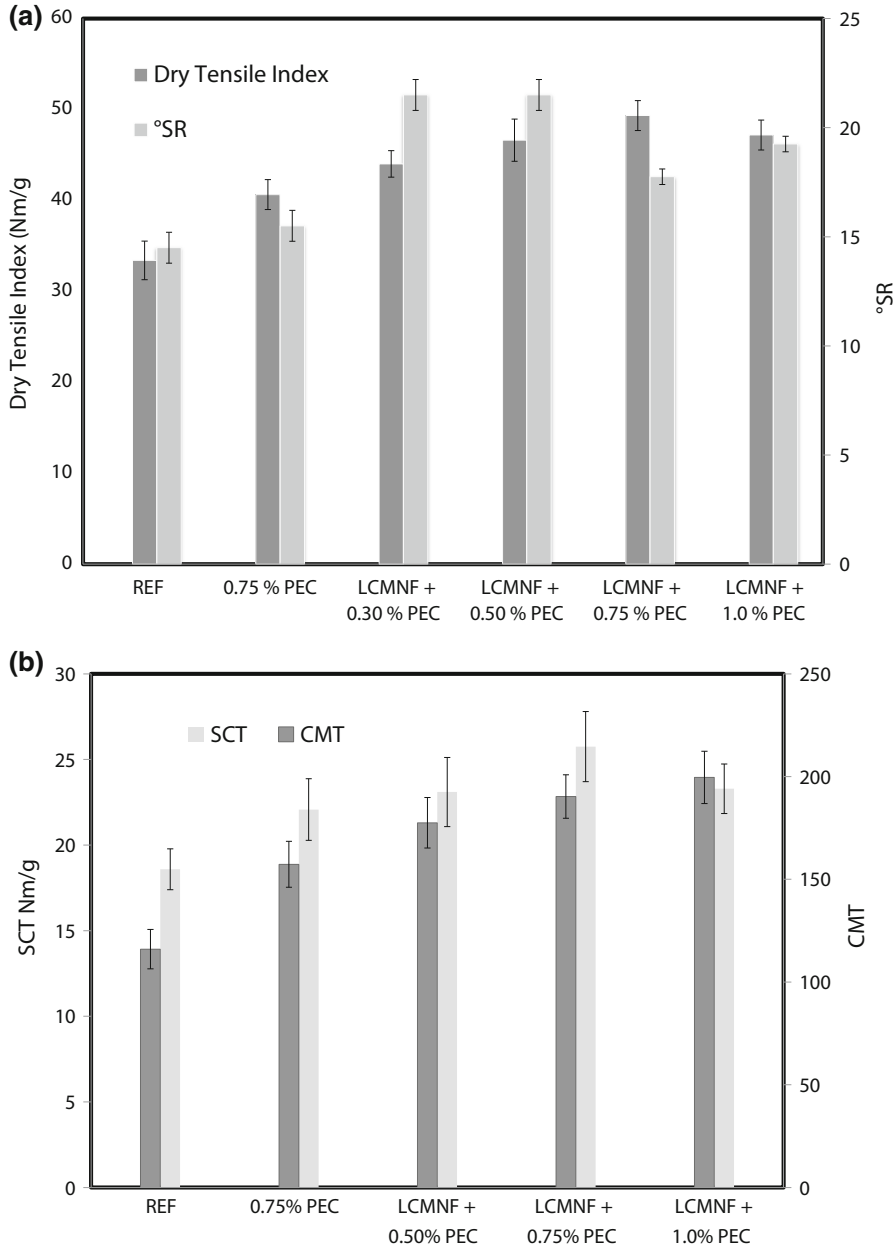

Fig. 4 Effect of PECs and LCMNF addition on dry tensile index and drainability (**a**) and compressive strength (CMT and SCT) (**b**) (value of handsheets). (REF: only pulp)

addition level has been indicated above as the optimum in terms of surface charge and retention.

In addition, others LCMNF dosages (1.5% and 4%) with 0.75% of PECs lead to lower improvement in paper strength compared with 3% of LCMNF addition (data not shown).

It can be expected that, the paper sheets with LCMNF and PECs show a higher degree of fiber bonding. The SEM photographs in Fig. 5 show the difference between reference handsheet and the one containing 3% of LCMNF and 0.75% of PECs. Compared to the reference handsheet, it exhibits a better-consolidated. In fact, apparent density was slightly higher (0.537 ± 0.008 kg/m^3 against 0.517 ± 0.007 kg/m^3).

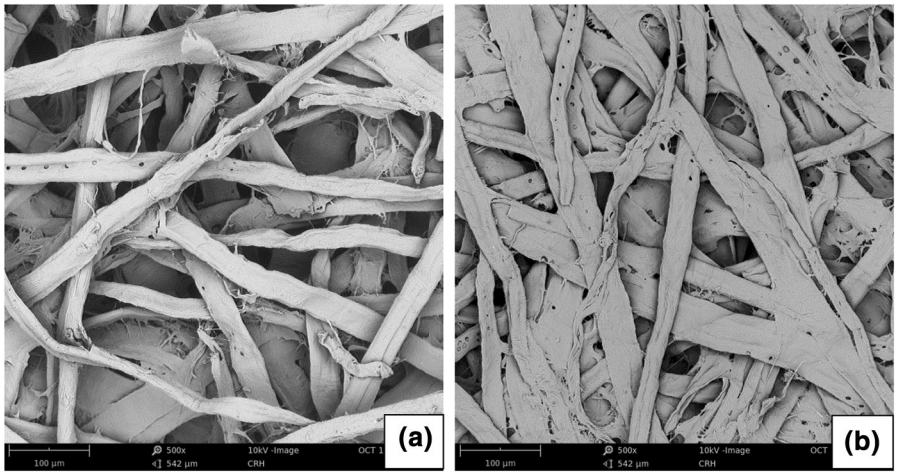

Fig. 5 Photographs of handsheets obtained by scanning electron microscopy: **a** REF: reference pulp and **b** 0.75% PEC and 3% LCMNF on pulp

Conclusions

A novel procedure for the application of lignocellulosic micro/nanofibers (LCMNF) to reinforce recycled paper is proposed, considering the addition of LCMNF in combination with PECs formed by PAA (polyacrylic acid) and PAH (poly (allylamine hydrochloride)). The procedure showed an acceptable drainage and retention and a notable enhancing of mechanical properties of the final paper.

PECs showed a clear interaction with LCMNF and the addition of 0.75% of PECs on recycled softwood kraft pulp previously mixed with 3% of LCMNF showed the most favorable results. For this dosage of PECs, a maximum retention and pulp drainability (°SR) was obtained. Colloidal charge (logCTR) showed a close to zero value and tensile strength, CMT and SCT was increased 48%, 64% and 39%, respectively. These results suggest that polyelectrolyte complexes are a promising alternative to assist the application of LCMNF in papermaking.

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