Cationic and anionic polyelectrolyte complexes of xylan and chitosan. Interaction with lignocellulosic surfaces

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ABSTRACT

Cationic (CatPECs) and anionic (AnPECs) polyelectrolyte complexes from xylan and chitosan were formed, characterized and adsorbed onto unbleached fibers for improving the papermaking properties. They were prepared at a level of 30% of neutralization charge ratio by modifying the order of addition of polyelectrolytes and the ionic strength (0.01 N and 0.1 N NaCl). The charge density, colloidal stability and particle size of polyelectrolyte complexes (PECs) was measured using polyelectrolyte titration method, Turbiscan and Zetasizer Nano equipments, respectively. All the complexes were stable even after seven days from PEC formation. DRIFT spectra of complexes were also analyzed. The adsorption behavior of them onto cellulose nanofibrils model surfaces was studied using quartz crystal microbalance with dissipation monitoring, and surface plasmon resonance. It was found that the PEC layers were viscoelastic and highly hydrated. Finally, it is shown that the adsorbed PECs onto cellulosic fibers markedly improved the tensile and crushing strengths of paper.

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1. Introduction

Polyelectrolyte complexes (PECs) are obtained by combining cationic with anionic polyelectrolytes. Electrostatic interactions, and to a lesser extent, hydrogen bonding and hydrophobic interactions are present in PEC formation (Thünemann, Müller, Dautzenberg, Joanny, & Löwen, 2004). PECs present the advantages over single polyelectrolytes in creating new nanostructured units (Ankerfors & Wågberg, 2014, Chapter 1) with high surface/volume ratio and structural sizes of biological components (Müller, Keßler, Fröhlich, Poeschla, & Torger, 2011).

Natural polyelectrolyte complexes find potential uses such as films, coatings and hydrogels. Particularly, Karaaslan, Tshabalala, and Buschle-Diller (2010) prepared hydrogels of xylan and chitosan for potential applications such as controlled drug delivery vehicles for antibiotics or antiulcer drugs in the stomach.

They also have potential applications in papermaking processes as strength additive (Gärdlund, Forsström, & Wågberg 2005). In this case, they can be formed in situ or pre-formed before letting them interact with the fibers (Ankerfors & Wågberg, 2014). The advantage of using pre-formed PECs is the possibility of knowing their structure and colloidal properties prior to the addition to the fibers (Ankerfors & Wågberg, 2014).

In our previous work we studied the effects of PECs added onto high quality unbleached fibers (Mocchiutti, Galván, Peresin, Schnell, & Zanuttini, 2015) and it was shown that the use of a synthetic cationic polyelectrolyte, poly(allylamine hydrochloride) (PAH), together with an anionic and natural one, such as xylan, considerably increased the paper properties. Nevertheless, in order to reduce the use of synthetic materials for lessening environmental impact, chitosan is proposed to be used in this work as an alternative of cationic polyelectrolyte.

Chitosan (Ch) is a natural, linear and weak polyelectrolyte of β-(1,4)-N-acetyl-ᴅ-glucosamine units, derived from the deacetylation of chitin which is present in shrimps and crustaceans (Rinaudo, 2006). Chitosan has excellent properties such as biocompatibility, biodegradability, non-toxicity, etc. (Kumar, 2000). In recent years, a high number of investigations have been carried out to find different applications of chitosan, such as packaging material (Van
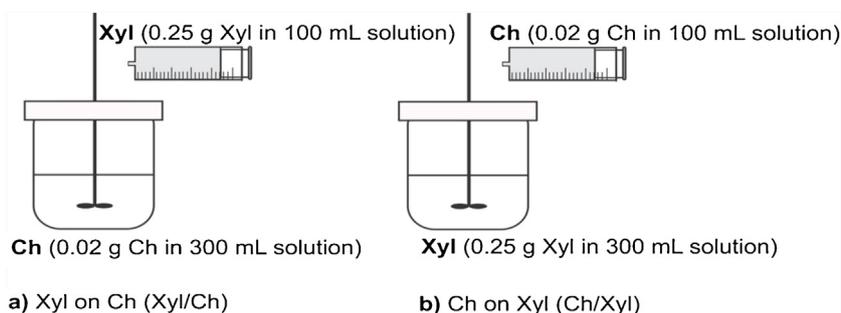
Fig. 1. Preparation of complexes under both orders of polyelectrolyte addition. Turbidity and streaming current measurements were made while a polyelectrolyte solution (Xyl or Ch solution) was added at a flow rate of 40 mL/h on a solution of the polyelectrolyte of opposite charge that is under continuous stirring (400 rpm). The mass of polyelectrolytes used is shown in the schematics.

den Broek, Knoop, Kappen, & Boeriu, 2015) and papermaking in the form of promising retentions aids for the paper industry (Li, Du, Wu, & Zhan, 2004).

On the other hand, hardwood xylan (Xyl) is an anionic, weak and linear polyelectrolyte whose chemical structure is characterized by a backbone of β-D-xylopyranose units, linked by $(1 \rightarrow 4)$ bonds to which, on average, 4-O-methylglucuronic acids are substituted every 10 units, with acetyl groups in a ratio of two to each three xylose units (Sjöström, 1993).

The order of addition, mixing ratio, concentration and molecular weight of polyelectrolytes, such as ionic strength and pH of the surrounding medium, affect the complexation process. Particularly, Müller et al. (2011) found a significant dependence of poly(ethyleneimine) (PEI) and poly(acrylic acid) (PAC) particle size on the order of addition of polyelectrolytes. To the best of our knowledge, the effect of the order of addition of natural polyelectrolytes such as chitosan and xylan has not yet been analyzed in the literature.

The aims of this work were to obtain and characterize natural PECs of chitosan and xylan, and to adsorb them onto unbleached recycled kraft fibers with the objective of improving paper strength. PECs were prepared by modifying the order of addition of the polyelectrolytes and the ionic strength of the liquid medium. The adsorption process of these pre-formed complexes onto cellulose nanofibrils model surface was investigated by using quartz crystal microbalance with dissipation (QCM-D) and surface plasmon resonance (SPR) measurements. Cellulose nanofibrils were used as a model substrate for fibers. Finally, the effects of the addition of these complexes on tensile and crushing (Concora Medium Test) strengths of the paper were determined.

2. Experimental

2.1. Characterization of the polyelectrolyte solutions

2.1.1. Xylan

Anionic polyelectrolyte, 4-O-methyl-glucuronoxylan (Xyl) isolated from beechwood by alkaline extraction, was supplied by Sigma-Aldrich (product number X-4252). The average molecular weight was M_w: 18.7 kDa and polydispersity of 1.8 determined by size-exclusion chromatography (SEC).

Fresh solutions of xylan were daily prepared by adding the commercial solid xylan to 10^{-4} N NaOH solution prepared in 0.01 N or 0.1 N NaCl, and heating it in a water bath at 95 °C for 15 min to dissolve xylan, as performed in other reports (Galván, Mocchiutti, Cornaglia, & Zanuttini, 2012).

To determine the xylan purity, a HPAEC-PAD (high pH anion-exchange chromatography system with pulsed amperometric detection) was used. The acid-hydrolysis of xylan, previous to the chromatographic analysis, was made following the procedure described in Sluiter et al. (2011), except that barium hydroxide was used for the neutralization of the hydrolysates. A Waters chromatography system with CarboPAc PA1 guard and analytical columns (Dionex) was employed. The system operation conditions were: eluent 16 mM NaOH, flow rate: 1.0 mL/min and column temperature: 40 °C. The amount of residual lignin (acid soluble and insoluble lignin and ash) was also measured as reported by Sluiter et al. (2011).

The xylan charge density was determined using two methods: the polyelectrolyte titration and the Scott method (1979). The polyelectrolyte titration was made at the two ionic strengths considered (0.01 N and 0.1 N NaCl) and pH 6.0, and using, as titrant, a solution of 250 μN pDADMAC (poly(diallyldimethylammonium chloride)) with an average molecular weight of M_w: 400–500 kDa from Sigma-Aldrich. To detect the end point of titration, streaming current measurements (Chemtrac ECA 2100 equipment) were used. On the other hand, the Scott method implies an acid hydrolysis of xylan in concentrated sulphuric acid at 70 °C for 10 min, followed by a colorimetric reaction of the chromogens formed with the 3-5-dimethyphenol. The difference in absorbance at 450 and 400 nm is measured (using a CECIL 3055 spectrophotometer) and it is related to the xylan uronic anhydride concentration.

2.1.2. Chitosan

The cationic polyelectrolyte used was chitosan (Ch) from Sigma-Aldrich (product number 448877). The viscosity average molar mass was determined using a capillary viscometer Cannon-Fenske number 75 in a water bath at 25 °C, giving a value of M_V: 189.8 kDa. The degree of deacetylation (DD) of chitosan was 79.6% ± 0.7%. It was determined using the linear potentiometric titration method reported by Jiang, Chen, & Zhong (2003).

A solution of 1.0 g/L in 0.1 M acetic acid was prepared according to Rinaudo, Pavlov, & Desbriéres (1999). The solution was sonicated for 10 min, stirred for 30 min and finally filtered using a glass filter of 1.5 μm of porosity. The amount of chitosan retained in the filter was weighted and used to calculate the correct final chitosan solution concentration.

The charge density of chitosan at two ionic strengths (0.01 N and 0.1 N NaCl) and pH 6.0 was determined by the polyelectrolyte titration method (Terayama, 1952). For the titrations, a 200 μN potassium (polyvinyl sulfate) (KPVS) solution in deionized water was prepared from a 0.001 N standard solution supplied by AppChem, England.

2.2. Polyelectrolyte complex formation. Construction of the streaming current and turbidity curves

Complexes were obtained by the dropwise addition method and using a syringe pump for adding the anionic (Xyl) or the cationic (Ch) solution at a flow rate of 40 mL/h on a solution of the poly-

electrolyte of opposite charge under 400 rpm continuous stirring (Fig. 1) (Mocchiutti et al., 2015). Two ionic strengths (0.01 N and 0.1 N NaCl) were considered. The pHs of the polyelectrolyte solutions were previously adjusted to 6.0.

PEC formations were monitored by streaming current (SC) measurements. Taking into account the SC titration curves as a function of the polyelectrolyte charge ratios, cationic (named CatPECs) and anionic (named AnPECs) complexes at a level of 30% of the neutralization charge ratio were selected for their characterization and adsorption studies.

The turbidity was also followed during the formation of PECs using a turbidimeter (Hanna HI93703C) as reported by other authors (Hubbe, Moore, & Lee, 2005). The average of three measurements of turbidity, after manually shaking the cuvette between each reading, is reported.

2.3. Characterization of the cationic and anionic complexes

2.3.1. Charge density

PEC charge densities were determined by the polyelectrolyte titration method using streaming current measurements for detecting the end point of titration. The conditions of the complex formation were kept during the titration (0.01 N or 0.1 N NaCl, and pH 6.0).

2.3.2. Particle size and zeta potential measurements

A Zetasizer Nano ZS90 apparatus (Malvern Instruments, U.K.) was used to determine the particle size and the zeta potential of PECs. All measurements were made at 25 °C and pH 6.0. The intensity distribution curve was used to report the average particle size, and the volume distribution curve to report the relative amounts of material in each peaks (Malvern manual). On the other hand, the Smoluchowski model was used to calculate the zeta potential values, and the parameters employed were: dielectric constant 78.6 and viscosity 0.8910 cP, and 78.5 and 0.8990 cP for 0.01 N and 0.1 N NaCl concentrations, respectively. The refractive index of water (1.334) was used due to the high content of water present in PEC particles (Cegnar & Ker, 2010).

2.3.3. Colloidal stability

The Turbiscan Classic was used to assess colloidal stability of the PECs suspensions at two ionic strengths (0.01 N and 0.1 N NaCl) and the two orders of addition of polyelectrolytes. Measurements were performed immediately after the complexes preparation (0 h), after 48 h and 7 days and before and after shaking the tubes.

2.3.4. Polyelectrolyte complex spectroscopic characterization

The Diffuse Reflectance Fourier Transform Infrared (40 scans at 4 cm^{-1}) of the polyelectrolyte and polyelectrolyte complexes were obtain with a Shimadzu FTIR- 8000 Spectrometer, equipped with a MCT detector cooled with liquid N$_2$, using a diffuse reflectance accessory Barnes Analytical/Spectra – Tech at 9 mm/s. Films were prepared by casting chitosan, xylan and PECs solution.

2.4. Pulp preparation

Industrial liner paper (100% virgin softwood fibers from *Pinus elliottii and Pinus taeda*) supplied by Papel Misionero S.A. (Argentina) was soaked for 12 h in water. Then, following the procedure described in Mocchiutti et al. (2015), the sheets were re-pulped, classified (only the fibrous fraction, was collected), acidified up to pH 4.0, and stored until use.

The chemical characteristics of the pulp used in this work were previously reported in Galván, Mocchiutti, Schnell, Liitia, and Zanuttini (2013). Particularly, the surface acid groups were
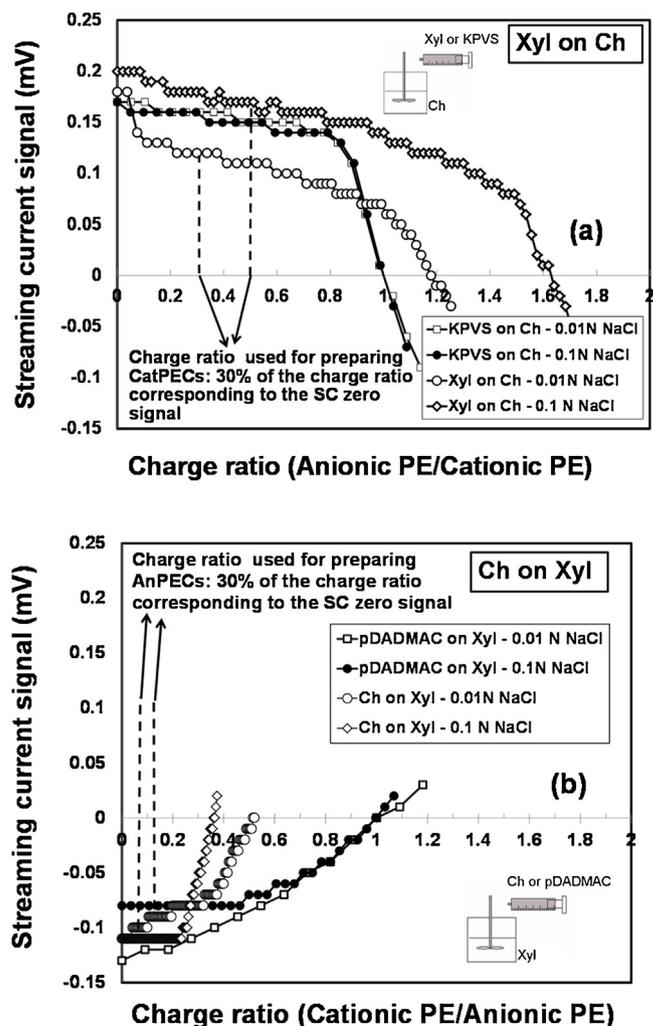

Fig. 2. Effect of the addition of (a) an anionic polyelectrolyte solution (KPVS or Xyl) on chitosan (Ch) solution, (b) a cationic polyelectrolyte solution (pDAMDAC or Ch) on xylan (Xyl) solution on the streaming current signal at different ionic strengths and pH 6.0. The amount of xylan and chitosan used for preparing the CatPECs and AnPEcs are shown.

21.0 ± 0.5 μeq/g pulp, the total charge was 90.6 ± 0.2 μeq/g pulp and total lignin was 12.65 ± 0.04% on the original pulp.

2.5. Preparation of cellulose nanofibrils (CNFs) and CNF model surface

CNFs were prepared similarly to what has been reported by Galván, Peresin, Mocchiutti, Zanuttini, and Tammelin (2015). In brief, the industrial liner paper described above, was mechanically processed using a Masuko grinder (three passes) followed by disintegration in a fluidizer, 20 passes. The resulting CNF suspension was centrifuged and the supernatant was collected and stored for later use.

CNF model surfaces were prepared by high shear spin-coating (WS400BNPP Spincoater-Laurell Technologies Corporation, PA, USA) on gold substrates either for QCM-D or SPR measurements.

Gold crystals for QCM-D measurements were provided by Q-Sense AB, Sweden and the SPR gold slides, by BioNavis Oy, Finland. Prior to the CNF deposition, the gold substrates were first cleaned using UV/ozonator (BioForce Nanoscience UV/O3 ProcleanerTM Ames, IA, USA) for 15 min, followed by immersion into a 3.3 mg/mL aqueous poly(ethyleneimine) solution for 30 min. Poly(ethyleneimine) acts as an anchoring polymer that improves

the coverage of the fibrils on gold. The finer fraction of nanocellulose suspension was spin-coated (20 s, 3000 rpm) on a previously hydrated, clean gold substrate. Thin CNF films were subsequently rinsed with MilliQ-water, dried with nitrogen and placed in an oven for 10 min at 80 °C to evaporate the remaining water and fix the CNF film on the substrate. Finally, the CNF thin films were allowed to swell overnight in 0.01 N NaCl solution at pH 6.0, prior to the QCM-D and SPR runs.

2.6. Quartz crystal microbalance with dissipation monitoring (QCM-D) measurements

The QCM-D E4 (Q-Sense AB, Gothenburg, Sweden) was used to evaluate the adsorption of PECs onto cellulose nanofibrils. While CatPECs were adsorbed directly onto CNF model surfaces, in the case of AnPECs, the CNF surfaces were previously treated with chitosan in order to have the proper charge available for the adsorption phenomena to occur. After a stable baseline was obtained with 0.01 N NaCl at pH 6.0, PECs or chitosan solutions were injected and the adsorptions were monitored. Once the adsorption stage was complete and the signal stable, the surfaces were rinsed with 0.01 N NaCl at pH 6.0 to remove loosely bound material. All QCM-D measurements were performed using 100 μL/min constant flow rate at 23 °C and duplicates were made to ensure reproducibility.

The fundamental frequency (f_0) used was 5 MHz. All the data were processed with the QTools software and its overtones ($n = 3$, 5, 7, 9 and 11) and f_0 were used to determine the amounts of mass adsorbed of PECs.

The data was fitted to the Voigt viscoelastic model and the following parameters were considered: fluid density (1000 kg/m^3); fluid viscosity (0.001 kg/ms); the density of the film was assumed to be constant (1200 kg/m^3).

2.7. Surface plasmon resonance (SPR)

A SPR Navi 200 (BioNavisOy, Ylöjärvi, Finland) equipment was employed for determining the dry mass of the PECs on the CNF substrate. It can be monitored in real time if there is a difference between the refractive index of the adsorbate in the layer and in the bulk solution (Jung, Campbell, Chinowsky, Mar, & Yee, 1998). The mass adsorbed of layers of complexes were calculated according to Jung et al. (1998) and Galván et al. (2015). In this work, the refractive index was assumed to be 1.5 RIU for chitosan (Jiang et al., 1996) and PECs.

All SPR measurements were performed using 100 μL/min flow rate at 23 °C. The SPR measurements were stabilized using a 0.01 N NaCl solution at pH 6.0 for 10 min and then, the chitosan or PECs solutions were injected until a constant ∆SPR angle was obtained. Finally, surfaces were rinsed with buffer solution in order to remove loosely bound material. All experiments were performed in duplicate to assure reproducibility.

2.8. Atomic force microscopy (AFM)

Images of chitosan, CatPECs and AnPECs adsorbed on CNF model surface were analyzed by using a Nanoscope IIIa Multimode scanning probe microscope (Digital Instruments Inc. Santa Barbara, CA, USA). The images were scanned using tapping mode with a silicon cantilever supplied by μMasch (Tallin, Estonia). Scan sizes of 2×2 μm^2 were employed.

2.9. Pulp treatments with PECs and handsheet preparation

Treatments of fibers using CatPECs and AnPECs were carried out at 0.15% pulp consistency, pH 6.0 and 0.01 N NaCl. The pulp slurry was added to the chitosan or PEC solutions. The pH and ionic

Table 1
Characterization of the xylan powder.

	(%) w/w
Xylan purity by HPAEC-PAD	89.5
Soluble lignin	8.84 ± 0.14
Insoluble lignin + ash	2.81 ± 0.16

Table 2
Chitosan and xylan charge densities determined by polyelectrolyte titration, at pH 6.0 and two ionic strengths.

NaCl (N)	Chitosan (meq/g)[a]	Xylan (meq/g)[a]
0.01	+3.78 ± 0.07	−0.61 ± 0.01
0.1	+3.94 ± 0.03	−0.72 ± 0.04

[a] The standard deviations of the means from two replicates of the trial are indicated.

strength of the medium were adjusted to the selected conditions, and kept under stirring for 30 min. Before adding the AnPECs to the pulp, it was treated with a 0.82% chitosan over dry pulp. A reference (Ref) treatment was also prepared, under the same conditions as explained before but without adding any additive. For each treatment, five handsheets of 120 g/m^2 were prepared according to SCAN standard methods but in controlled conditions, using deionized water that was adjusted at pH 6.0 and 0.01 N NaCl. Apparent density (TAPPI 411 om-97), dry tensile strength (TAPPI 494 om-01), crushing strength CMT (Concora Medium Test) (TAPPI T809 om-99) and wet tensile strength (ISO: 3781:1983) of the handsheets were evaluated.

3. Results and discussion

3.1. Characterization of polyelectrolytes

Table 1 shows the purity of the xylan powder determined by HPAEC-PAD after acid hydrolysis, and the amount of soluble lignin and insoluble material (insoluble lignin and ash) present in the xylan powder. In order to convert the amount of xylose to xylan, a factor of 1.18 was considered assuming a ratio of 4-O-methylglucuronic acid to xylose of 1:10. The purity value of 89.5% was used in the rest of the work.

Table 2 shows the chitosan and xylan charge densities determined at two ionic strengths. The table shows that, at pH 6.0 and using the polyelectrolyte titration method, the charge density of chitosan was more than six-fold higher than xylan ones. That means that, for example when xylan is added on the chitosan solution, about six-fold higher mass of xylan should be added to the chitosan solution to reach the neutralization between them. The table also shows that when ionic strength was increased from 0.01 N to 0.1 N NaCl, the charge density values of both polyelectrolytes was slightly increased. Additionally, the charge density of xylan was determined using the Scott method. The value obtained was −0.71 ± 0.02 meq/g, in agreement with those results obtained by the polyelectrolyte titration method. The low charge density of xylan could affect its solubility, nevertheless by dissolving it in an alkaline medium (10^{-4} M NaOH) and at 95 °C this problem was avoided.

3.2. Streaming current curves and selection of the complexes to be analyzed (CatPECs and AnPECs)

Fig. 2(a) shows the effects of the addition of xylan solution on chitosan solution (Ch) on the streaming current signal. For comparison, the addition of the PVSK (a strong and high charge density anionic polyelectrolyte with high molecular weight) was considered. Two ionic strengths and pH 6.0 were considered. The results
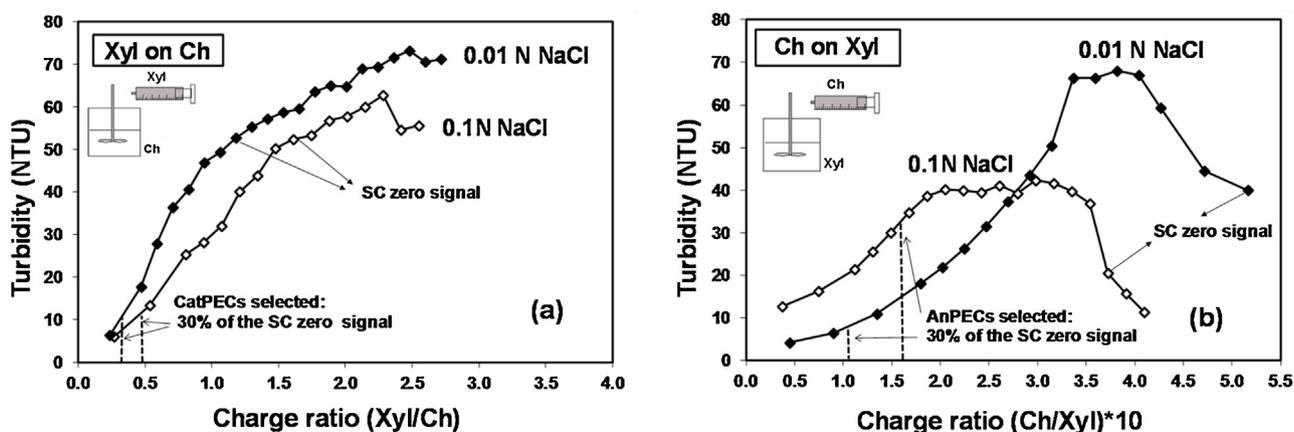
Fig. 3. Formation of polyelectrolyte complexes monitored through turbidity measurements as a function of the charge ratios at pH 6.0, two ionic strengths (0.01 N and 0.1 N NaCl) and different order of addition: (a) xylan on chitosan solution (Xyl on Ch), and (b) chitosan on xylan solution (Ch on Xyl). A charge ratio multiplied by 10 is adopted when AnPECs were used. The SC zero signal and the corresponding 30% of the SC zero signal selected for preparing the CatPECs and AnPECs are shown.

Table 3
Polyelectrolyte complexes characterization at pH 6.0 and two ionic strengths.

NaCl (N)	Complexes prepared	Mass ratio		Average particle size[a] (nm)	PdI	Charge density (meq/g)		z-Potential (mV)
		%Xyl	%Ch			Expected values	Experimental values	
0.01	CatPEC	68	32	387 ± 16	0.21	+0.71	$+0.56 \pm 0.02$	14.7 ± 0.3
	AnPEC	98	2	220 ± 4	0.16	−0.50	-0.47 ± 0.02	-12.6 ± 0.6
0.1	CatPEC	73	27	414 ± 29 (71.8%) 4904 ± 23 (28.2%)	0.24	+0.55	$+0.53 \pm 0.02$	18.6 ± 0.4
	AnPEC	98	2	302 ± 59 (74.9%) 4583 ± 346 (25.1%)	0.28	−0.63	-0.48 ± 0.03	-9.5 ± 0.3

[a] The intensity PSD distribution curve was used for reporting the size of each peak, and the volume PSD distribution curve for reporting the relative amounts of each peak in the distribution.

Table 4
Calculated mass (Δm), water content and mass ratio of layers of chitosan, cationic and anionic complexes adsorbed on CNF model surface from QCM-D and SPR data.

	Δm_{QCM-D} (mg/m^2)	Δm_{SPR} (mg/m^2)	% coupled water	Mass ratio (Dry mass: water)
Chitosan	3.5 ± 0.2	1.8 ± 0.1	49	1:1
CatPECs	42.1 ± 0.7	1.6 ± 0.1	96	1:25
AnPECs	22.7 ± 1.3	4.3 ± 0.1	81	1:4

indicate that, when KPVS was replaced by a weak anionic polyelectrolyte (Xyl) with low charge density and low molecular weight, the amount of titrant needed to reach the SC zero signal is significantly increased. In the case of higher ionic strength values (0.1 N

NaCl), the amount of xylan needed to reach the zero signal was even higher.

Fig. 2(b) shows the effects of the addition of chitosan solution on xylan solution (Xyl) on the streaming current signal. For comparison, the addition of pDADMAC (a strong and high charge density
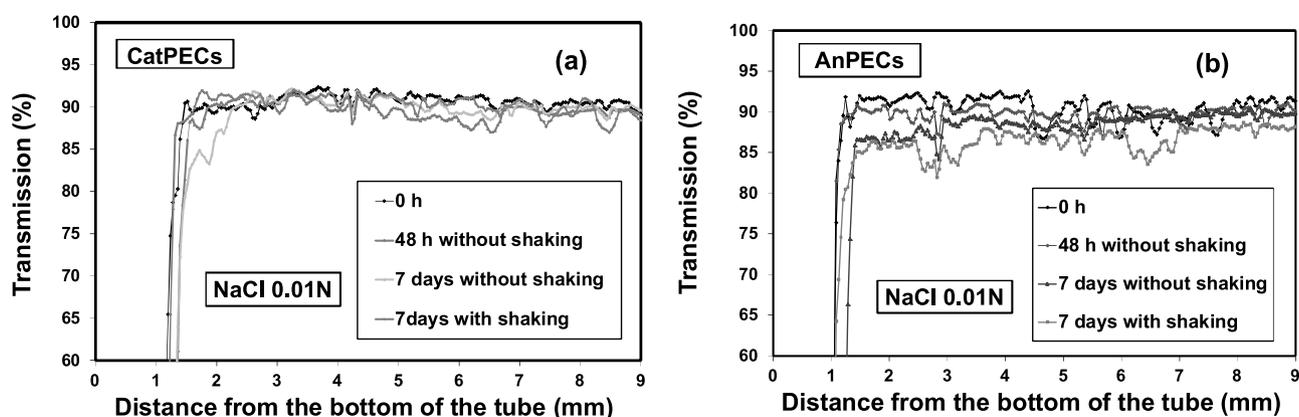

Fig. 4. Stabilities of the complexes: Transmission of a) cationic complexes (CatPECs) and b) anionic complexes (AnPECs) solutions as a function of the distance from the bottom of the tube at 0.01 N NaCl by using the Turbiscan optical analyzer at pH 6.0. The first 9 mm from the bottom of the 60 mm tube are shown.

cationic polyelectrolyte with high molecular weight) was considered. The results show the opposite behavior, i.e., lower amount of titrant is needed to reach the SC zero signal when pDADMAC was replaced by chitosan.

For both orders of addition, the deviation from the stoichiometry suggests that some of the anionic groups of xylan are inaccessible for chitosan. Due to that, it could be expected that the PECs formed during titration retain water. This gel-like structure is potentially favorable for improving papermaking properties and also potentially useful for other applications.

From Fig. 2(a) and (b), the polyelectrolyte charge ratios for the following studies were selected. The addition corresponding to a 30% of that needed to reach the zero SC signal was considered. The characteristics of these complexes, as well as their interaction with lignocellulose surfaces, and the effects as papermaking additives are analyzed in detail in the following sections.

3.3. Turbidity curves

The effects of the order of polyelectrolyte addition and the ionic strength were also studied by monitoring turbidity values as a function of the polyelectrolyte charge ratios (Fig. 3). The curves show different shapes, which are related to the structural conformation of the PECs in solution. When xylan was added on a chitosan solution (Fig. 3a), i.e. in an excess of chitosan, the turbidity of the system was gradually increased even beyond the ratio corresponding to SC zero signal, indicating that colloidal-type complexes were formed since the beginning of the xylan addition. They were formed by adding a low molecular weight xylan (guest polyanion) on one with a high molecular weight chitosan (host polycation).

On the other hand, when chitosan was added on a xylan solution (Fig. 3b), a decrease in turbidity was observed before reaching the SC zero signal for both ionic strengths, indicating less complex stability. In fact, large aggregates were visually observed at the end of the curves.

Similar results were obtained by Schatz, Domard, Viton, Pichot, & Delair (2004). They evaluated the stabilities of polyelectrolyte complexes formed by a chitosan of high molecular weight and dextran sulfate of low molecular weight. They found that an excess of chitosan could act as host and accommodate several molecules of the dextran resulting to particles electrostatically stabilized by a large hydrophilic corona of excess component. On the other hand, when the chitosan in default was added to dextran in excess, colloids were formed in a rather small range of molar mixing ratios and then flocculation or poor stability occurred.

Fig. 3(b) also shows that, at the lower ionic strength studied (NaCl 0.01N) the turbidity values are higher at high charge ratio of (Ch/Xyl).

It would be expected that the cationic (CatPECs) and anionic (AnPECs) complexes selected for studying (shown in the figure) are colloidally stable at both ionic strengths.

3.4. Characterization of CatPECs and AnPECs

3.4.1. Particle size, charge density and z-potential

Table 3 shows the mass ratios used for preparing the selected cationic and anionic complexes at pH 6.0 and the two ionic strengths. The particle size, polydispersity index, charge density and z-potential are also indicated. All complexes had a high proportion of xylan. The table shows that when the lower ionic strength was used, monomodal distributions of particle sizes were obtained for both complexes. It also shows that when chitosan of high molar mass was in excess (CatPECs), the particle size of the complexes obtained were larger than when xylan was in excess. This result also agrees with the one obtained by Schatz et al. (2004). Using different chitosans of high molar mass and dextran sulfate of low
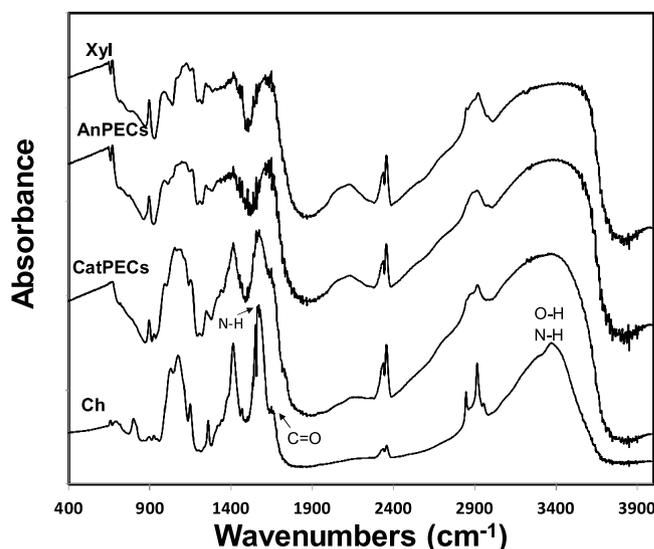

Fig. 5. DRIFT spectra of chitosan (Ch), xylan (Xyl), cationic (CatPECs) and anionic (AnPECs) polyelectrolyte complexes films cast from aqueous solutions at pH 6.0 and NaCl 0.01N.

molar mass, these authors showed that chitosan chain length was the main parameter impacting the sizes of PECs: A higher molar mass of chitosan leads to a higher particle size.

On the other hand, when the higher ionic strength was used, two populations were found. The population of larger particle sizes indicates that some small aggregates were formed.

In all cases, the polydispersity index was between 0.1–0.3, indicating rather broadly distributions in sizes.

Table 3 also shows that the charge densities of the complexes were lower than the expected ones which can be considered as a deviation from the 1:1 stoichiometry. The low charge densities are in agreement with the low z-potential values obtained and can affect the complex stability. Potential values between 10 and 30 mV are related to complexes that show incipient instability (Galván et al., 2015).

3.4.2. Colloidal stability

Fig. 4(a) and (b) shows that the CatPECs and AnPECs formed at pH 6.0 and 0.01 N NaCl were stables. They only show an incipient instability after 7 days from complex formations. Nevertheless, in the case of CatPECs, the shaking of the tubes reversed this slight effect. Similar results were obtained for CatPECs and AnPECs at 0.1 N NaCl (data not shown).

DRIFT spectra were used for comparing individual polyelectrolytes and their PECs. As shown in Fig. 5 the characteristic absorption bands of chitosan at around 1564 cm^{-1} and 1645 cm^{-1} are assigned to the N—H deformation of the amino group and to the amide (I) bond (C=O stretching), respectively (Karaaslan, Tshabalala, & Buschle-Diller, 2012). In CatPECs both bands were also observed. On the other hand, as it was expected, Xyl and AnPECs spectra were similar due to AnPECs has low amount of chitosan (mass ratio: 98% Xyl-2% Ch). A broad band at 3200–3500 cm^{-1} O—H stretching were observed in all the spectra. Particularly, Ch spectrum shows this band centered on 3346 cm^{-1} due to overlaying bands of N—H and O—H stretching caused by the elongations and stresses groups (Macea et al., 2015).

3.5. Adsorption of PECs on CNF model surfaces monitored by QCM-D and SPR

QCM-D and SPR techniques were used to obtain information about the viscoelastic properties of PECs adsorbed onto cellulose
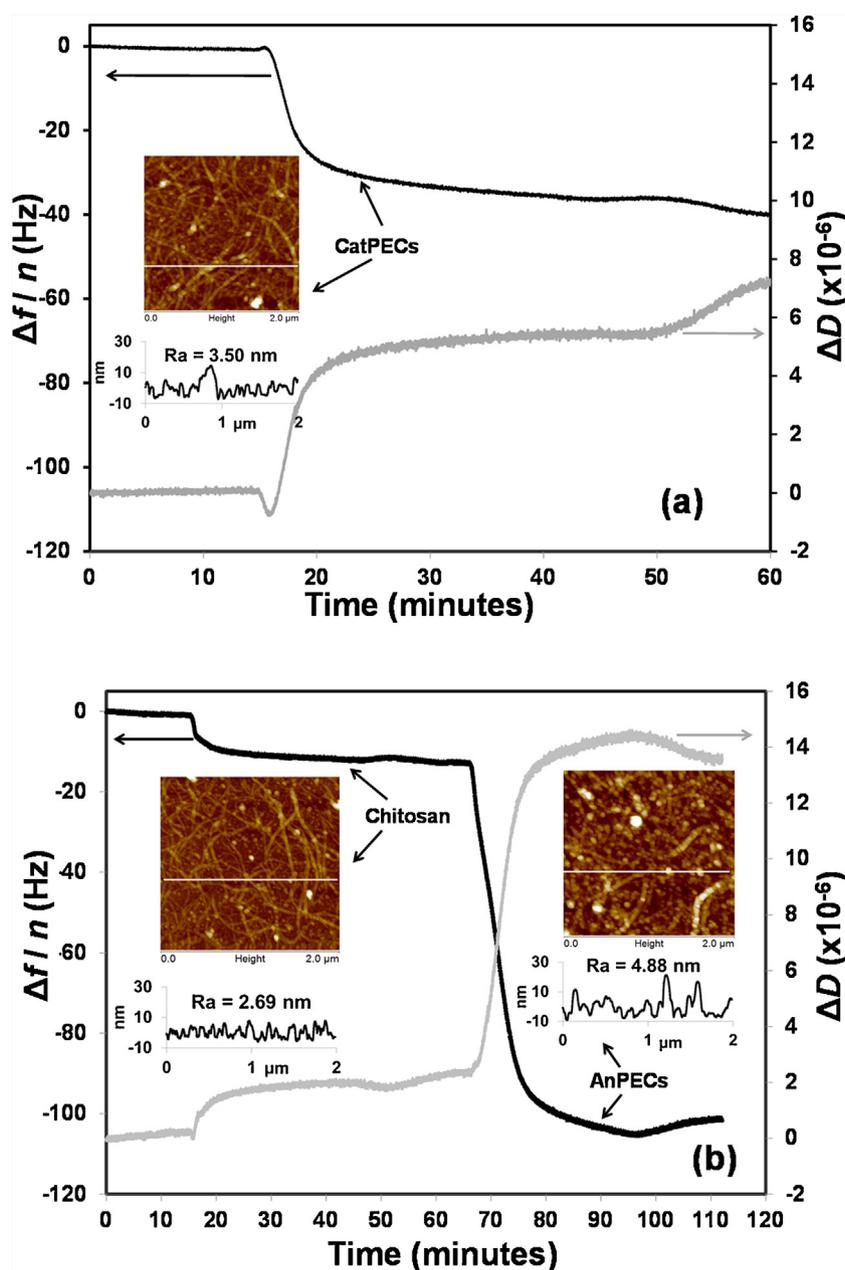
Fig. 6. Change in frequency (Δf) and dissipation (ΔD) as a function of time for complexes adsorption on CNF model surface monitored by QCM-D. (a) adsorption of cationic complexes and (b) adsorption of anionic complexes. The PEC concentrations were 50 ppm. The third overtones ($n=3$) are shown. Insets: $2 \times 2\,\mu m^2$ AFM height images and corresponding roughness profiles.

nanofibrils prepared from the liner kraft fibers. A model surface was used because the pulp fibers cannot be used for direct surface interaction studies on a molecular level (Tammelin, 2006). The QCM-D technique is also used for determining both the dry mass and the coupled water of the PECs adsorbed, whereas the SPR technique is only used for determining the dry mass of complexes.

Fig. 6 illustrates the changes in frequency (Δf) and dissipation (ΔD) as a function of time when CatPECs and AnPECs at pH 6.0 and 0.01 N NaCl are adsorbed on the CNF model surface. For both complexes, a high increase in dissipation values was observed, indicating that the adsorbed complexes form soft and viscoelastic layers.

Using QCM-D, Eriksson, Shannon, and Wagberg (2005) related the viscoelastic properties of polyelectrolyte multilayer (PEM) of PAH and PAA (polyacrylic acid) adsorbed onto silicon oxide surface with the results in papermaking properties of bleached softwood

kraft fibers. They concluded that more open, viscous and water-rich multilayer produces stronger paper. We can expect that soft and viscoelastic layer of CatPEC and AnPEC with high amount of coupled water can improve the strength of paper.

Particularly, Fig. 6(a) shows the CatPEC adsorption. A sharp decrease in the change in frequency (approx. −36 Hz) indicates a high mass adsorption. An additional decrease in frequency and an increase in dissipation after rinsing with buffer (pH 6.0 and 0.01 N NaCl) was observed (approx. 50 min) probably due to the adsorption of free chitosan. A similar behaviour was found by Ahola, Österberg, & Laine (2008) using the QCM-D technique for studying the adsorption of nano-aggregates of nanofibrils and poly(amideamine) epichlorohydrin (PAE) on cellulose model surfaces.

On the other hand, Fig. 6(b) shows the AnPECs adsorption. The CNF surfaces were previously treated with chitosan. The figure also

shows a decrease in the change in frequency (approx. −90 Hz) indicating its adsorption.

Fig. 6 also shows the roughness profiles obtained by AFM images. The adsorption of chitosan onto CNF layer slightly increased the roughness indicating a uniform adsorption layer. Higher topographical changes were observed when CatPECs or AnPECs were adsorbed. The images also show that chitosan as well as the complexes are adsorbed with a spherical morphology.

Fig. 7 shows the SPR sensograms upon adsorption of the complexes on CNF surface. Since ΔSPR angle is linearly proportional to the mass adsorbed on the surface, Δm_{SPR}, it can be concluded that higher mass of AnPECs was adsorbed compared to CatPECs.

Specifically, Table 4 shows the mass adsorbed and percent of water content of the layers of PECs calculated using: The Voight-model for determining Δm_{QCM}, and the equation proposed by Jung et al. (1998) for determining Δm_{SPR}. The mass of complex determined by QCM-D was found to be significantly higher than the one obtained from SPR measurements, indicating that the PEC structures, particularly CatPECs, were highly hydrated. Due to the high content of water of the adsorbed PEC layers it could be expected to behave as hydrogel, as was reported by Orelma (2012). The coiled structure of the complexes with inaccessible charges could explain the high amount of water retained. The amount of water coupled in the chitosan layer was lower than in both complex layers. This is due to the fact that chitosan is a polyelectrolyte with a high charge density. It is known that a highly charged polyelectrolyte forms a flat layer with no water coupled in their structure (Tammelin, 2006).
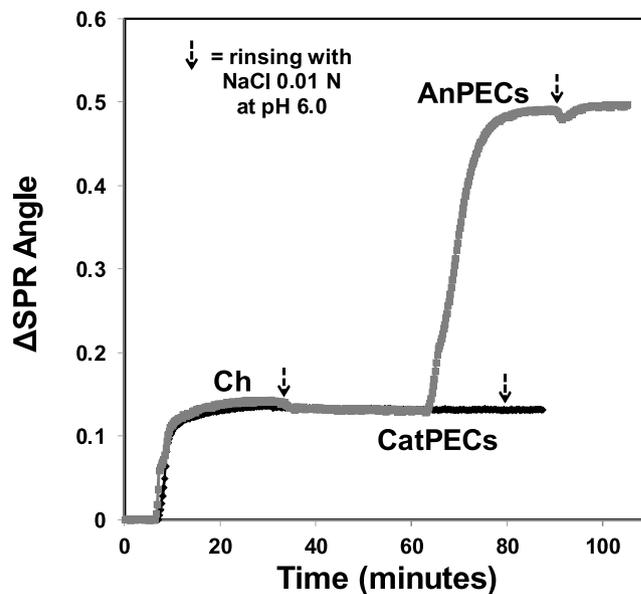

Fig. 7. SPR sensograms for the adsorption of cationic complex (CatPECs) and anionic complex (AnPECs) on CNF model surface. When AnPECs were used, the surface was previously treated with chitosan (Ch). Liquid medium condition: 0.01 N NaCl at pH: 6.0. The PEC concentrations were 50 ppm.

3.6. Dosages used of complexes added to the pulp

Table 5 shows the dosages of xylan and chitosan added to the pulp. A dosage of 1.8% xylan on pulp was selected. Then, knowing
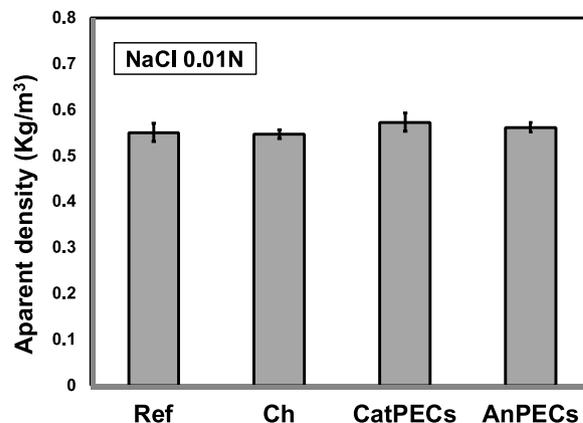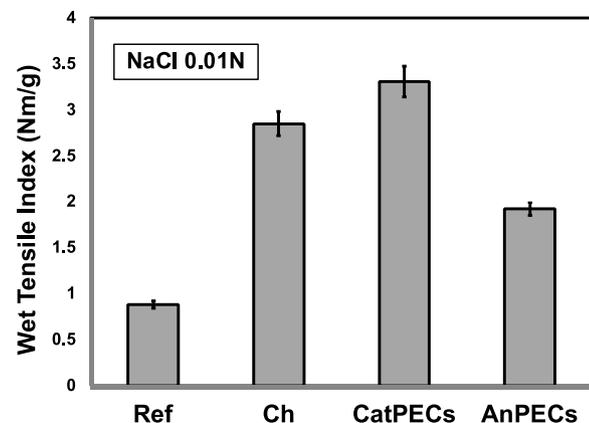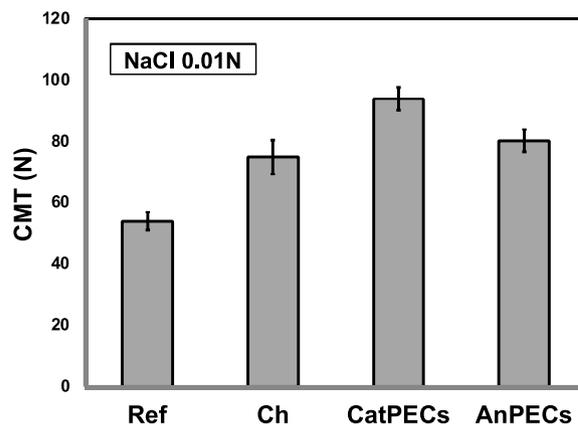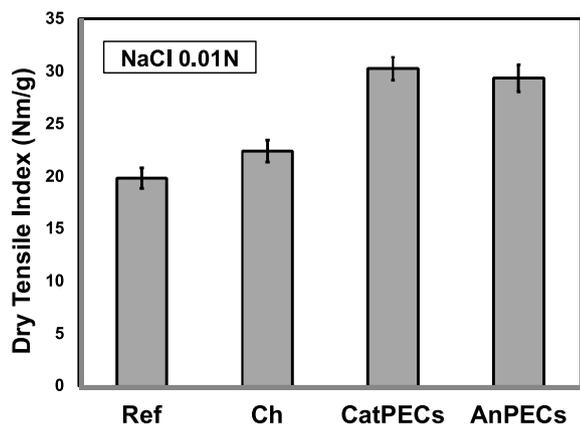

Fig. 8. Paper physical properties as a function of the different treatments at pH 6.0 and 0.01 N NaCl. Ref: reference pulp; Ch: 0.83% chitosan treated pulp; CatPECs: 0.83% chitosan + 1.8% xylan; AnPECs: 1.8% xylan + 0.01% chitosan on pulp previously treated with a 0.82% chitosan solution.

Table 5
Amount of xylan and chitosan used for evaluating the effects on physical properties of paper at 0.01 N NaCl.

PECs	First layer (Ch)	Second layer (PEC)	
	(% on pulp)	Xyl (% on pulp)	Ch (% on pulp)
CatPECs	–	1.8	0.83
AnPECs	0.82	1.8	0.01

the ratio between xylan and chitosan needed for preparing the 30% of the SC zero signal CatPECs and AnPECs (Fig. 2), the amount of chitosan was determined. When AnPECs were used, the pulp was previously treated with an excess of chitosan to ensure its adsorption on fibers with cationic loops and tails dangling in solution. The dosage of chitosan used for the first layer was such that the total amount of chitosan added was the same for both cases (0.83% Ch on pulp).

3.7. Paper physical properties

The effects of chitosan and PEC treatments (Table 5) at pH 6.0 and NaCl 0.01 N on papermaking properties are shown in Fig. 8. Compared to the reference pulp, all the strength properties were increased when PECs were added on pulp, mainly when CatPECs were used. Particularly, the addition of CatPECs and AnPECs on pulp increased 53% and 48% the dry tensile strength and 74% and 49% the compressive strength (CMT), respectively. It is probably that the adsorbed CatPECs increased the physical properties more than the AnPECs due to the higher amount of coupled water in their structure.

Wet tensile strength in Fig. 8 shows that this property increased when chitosan or CatPECs were added. Nevertheless, compared to the pulp treated with Ch alone, the addition of AnPECs decreased the wet tensile strength probably due to the fact that the presence of free xylan charges made the fibers more hydrophilic. The apparent density was not significantly changed.

Several authors have shown increments in wet and dry paper strengths using pre-formed PECs and have attributed these improvements to the increase in the adhesion between the fibers (Ankerfors and Wågberg, 2014). In recent years, the most widely discussed and accepted molecular mechanism for complexes adhesion behavior is based on the similarity with the gecko's feets behavior, where the geometry of the adhering surfaces, and not the chemistry, is the dominating effect. Ankerfors, Lingström, Wågberg, and Ödberg (2009) showed that PAH/PAA complexes form a random array of contact points (or pillars) at the solid-liquid interface that could create efficient joints between two treated surfaces, and increase the adhesion between the fibers. Probably this kind of phenomena occurs with the natural polyelectrolyte complexes of chitosan and xylan studied in this work.

4. Conclusions

The order of addition of the polyelectrolytes as well as the ionic strength of the liquid medium affects the stoichiometry of polyelectrolyte interactions during the formation of PECs. In both cases, the deviation indicates that a part of the ionic groups of xylan are inaccessible to chitosan and remains free in the structure of the complex.

Average particle size of the CatPECs and AnPECs prepared were in between 220 nm and 387 nm when the ionic strength of the liquid medium was 0.01 N NaCl. When a higher ionic strength was used (0.1 N NaCl), some small aggregates were formed. Nevertheless, the complexes were stable at both ionic strengths studied. They only showed an incipient instability after seven days from PEC formation.

Layers of CatPECs and AnPECs adsorbed on cellulose nanofibrils model surface showed viscoelastic behaviors. The complex layers were highly hydrated and showed hydrogel-like properties. They were adsorbed with a spherical morphology.

These PECs with high amount of water retained were beneficial for significantly increasing the tensile and crushing (Concora Medium Test) strengths of papers. These results indicate that they are potential agents for using in the paper industry.

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