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Complexes of xylan and synthetic polyelectrolytes. Characterization and adsorption onto high quality unbleached fibres

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ABSTRACT

In this work, polyelectrolyte complexes (PECs) were formed by adding polyacrylic acid (PAA) or 4-O-methylglucuronoxylan (Xyl) on poly(allylamine hydrochloride) (PAH) solutions, at different ionic strength and neutral pH. Turbidity curves, charge densities of the cationic complexes determined by polyelectrolyte titration method, and *z*-potential values showed clear differences between both complexes. Stirring favourably reverses the effects of sedimentation of Xyl/PAH complexes, as demonstrated by colloidal stability tests. Adsorption studies on silica surfaces, performed by Quartz Crystal Microbalance with Dissipation (QCM-D) showed that PAA/PAH adsorbed complexes layers were rigid, while the corresponding Xyl/PAH layers were viscoelastic. Despite the different conformations, both complexes were adsorbed as spherical particles, as observed by Atomic Force Microscopy (AFM). Adsorption isotherms performed on fibre suspensions showed that the ionic strength of the liquid medium determines the amount of PEC retained. Finally, it was found that the papermaking properties were significantly increased due to the addition of these PECs.

1. Introduction

The use of polyelectrolyte complexes (PECs) obtained by combining a cationic polyelectrolyte with an anionic polyelectrolyte, have been increasing in the last few years. They are produced for industrial application such as coatings (Ball, Michel, Toniazzo, & Ruch, 2013), binders, and flocculants for water purification (Ankerfors, 2008) as well as for the food industry, where colloidal stability of the products is necessary (Gärdlund, Wågberg, & Gernandt, 2003).

Particularly, in the paper industry several studies have been focused on achieving remarkable improvements in paper strength properties by pre-forming polyelectrolyte complexes and letting them interact with fibres (Eriksson, Torgnysdotter, & Wågberg, 2006; Fatehi, Kititerakun, Ni, & Xiao, 2010; Gärdlund, Forsström, Andreasson, & Wågberg, 2005; Lofton, Moore, Hubbe, & Lee, 2005). This alternative, compared with the well known dual system (Galván, Mocchiutti, Cornaglia, & Zanuttini, 2012; Hubbe, Moore, & Lee, 2005) or multilayer system (Eriksson et al., 2006; Wågberg, Forsberg, Johansson, & Juntti, 2002), has the advantages of being simpler to apply, and requiring lower investment for the industry (Ankerfors, 2008).

The driving force for the formation of PECs has been described in terms of electrical interactions (Coulomb interactions) between oppositely charged polyelectrolytes and entropy gain caused by the release of counterions (Ankerfors, 2008; Chen, Heitmann, & Hubbe, 2003; Koetz & Kosmella, 2007). Furthermore, intermacromolecular hydrogen bonding, van der Waals, dipole–dipole and hydrophobic interactions can also occur (Koetz & Kosmella, 2007). Complexes, once formed, can undergo structural rearrangements (Koetz & Kosmella, 2007).

PECs can have different structures depending on pH, salt concentration, polymer concentration, molar mass, etc. According to the structural characteristics of the simple polyelectrolytes used, there are two borderline models (Michaels & Miekka, 1961) suitable to describe the conformation that they can acquire: (a) the ladder model, which assumes that the two polyelectrolytes have enough flexibility and acceptable charge density to bind cooperatively, and (b) the scrambled eggs model, obtained when two polyelectrolytes with high and similar molecular mass are mixed. Nevertheless, experimental structures usually correspond to an intermediate model (Hubbe, Sundberg, Mocchiutti, Ni, &

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Pelton, 2012; Philipp, Dautzenberg, Linow, Koetz, & Dawydoff, 1989).

Currently, there exists an increasing interest on replacing synthetic polymers by natural polymers, such as xylan (Xyl). Estimations are that global economic activity based on chemical bioresources will grow from EUR 21 billion in 2008 to 40 billion in 2020, representing an annual increase of 5.3% in volume (Pöyry, 2012). These chemicals can be used for the manufacture of many biomaterials, being packaging one area with great potential (Pöyry, 2012).

Xylan is a natural polysaccharide found in high proportion in grasses and hardwoods, were it represents the 20–35% of the lignocellulosic biomass. Recently, new pilot-scale processes have been developed for separating and isolating hemicelluloses from the rest of the lignocellulosic matrix, such as cellulose and lignin. These advances open a new world of possible applications for this renewable source (Gatenholm & Tenkanen, 2004).

The aims of this work are to characterize polyelectrolyte complexes of polyacrylic acid (PAA) and poly(allylamine hydrochloride) (PAH), (PAA/PAH), and Xyl/PAH, and analyze the effects of the application of these complexes onto high quality unbleached softwood kraft fibres, while evaluating the feasibility of replacing PAA by xylan for improving papermaking properties. A comprehensive characterization of the PECs was performed, including the building of turbidity curves, the determination of charge densities, *z*-potential values, particle sizes, and the colloidal stabilities. Then, PEC retention isotherms on unbleached softwood kraft pulp, and adsorption analysis on silica surfaces using Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D) were built, and the morphology of the adsorbed PEC layers was investigated using Atomic Force Microscopy (AFM). Finally, the effects of PAH and PECs on the papermaking properties were evaluated, according to standardized methods.

2. Experimental

2.1. Preparation and characterization of polyelectrolytes

PAH with an average molecular mass of Mw: 56 kDa from Sigma–Aldrich was directly used to prepare a 0.25 meq/L solution at the corresponding ionic strength, as reported previously by our group (Galván, Mocchiutti, Schnell, Liitiä, & Zanuttini, 2013). The charge densities were 6.3 meq/g PAH, 8.3 meq/g PAH and 9.9 meq/g PAH for 0.1, 0.01 and 0.001 N NaCl, respectively.

The anionic polyelectrolyte used was 4-O-methyl-glucuronoxylan, isolated from beechwood by alkaline extraction (Sigma–Aldrich product number X-4252) with an average molecular mass of Mw: 18.7 kDa, and polydispersity of 1.8 determined by size exclusion cromatography (SEC). As previously published (Galván et al., 2012; Linder, Bergman, Bodin, & Gatenholm, 2003), fresh xylan solutions (1 meq/L) were daily prepared by adding the commercial solid xylan to NaOH 10^{-4} N solution and heating it in a water bath at 95 °C for 15 min to dissolve xylan. As described by Salyers, Gherardini, and O'Brien (1981), xylan solution concentration was determined using the phenol-sulphuric acid spectrophotometric method (Hodge & Hofreiter, 1962).

The other anionic polyelectrolyte used was a PAA with an average molecular mass of Mw: 5 kDa from Sigma–Aldrich. PAA is a synthetic polymer that it has been used in several studies by others (Ankerfors, 2008; Gärdlund et al., 2005; Norgren, Gärdlund, Notley, Htun, & Wågberg, 2007). The exact concentration of the commercial solution of PAA (49.09 g PAA/100 ml sol.) was determined gravimetrically (Gärdlund et al., 2003) and directly used to prepare a 1 meq/L solution at the corresponding ionic strength. The xylan and PAA charge densities were determined by indirect polyelectrolyte titration at pH 7.5 and different ionic strengths (Mocchiutti & Zanuttini, 2007; Terayama, 1952). For xylan, the charge density was also determined by conductometric titration using the Katz's method (Katz, Beatson, & Scallan, 1984), but $NaHCO_3$ was used instead of NaOH according to Lloyd and Horne (1993).

2.2. Polyelectrolyte complex formation procedure

Complexes were formed in a Britt Dynamic Drainage Jar using a syringe pump for adding the anionic polyelectrolyte solution of PAA or Xyl (1 meq/L) at a dosage rate of 30 ml/h on a 0.25 meq/L PAH solution that is under continuous stirring (300 rpm), in a similar way as other authors (Ankerfors, 2008; Gärdlund, Wågberg, & Norgren, 2007). Different ionic strengths (0.001 N, 0.01 N and 0.1 N NaCl) and pH 7.5 were considered. At this pH, PAH in solution is partially ionized, however in the presence of a negative polyelectrolyte, PAH can be further ionized. Choi and Rubner (2005) quantified the degree of ionization of weak polyelectrolytes (PAH and PAA) in bilayer films and their results indicated that, the degree of ionization of a weak polyelectrolyte can be increased from its solution value when it interacts with another polyelectrolyte of opposite charge.

2.3. Turbidity curves

The anionic polyelectrolyte solution of PAA or Xylan (1 meq/L) was added to the cationic polyelectrolyte solution (0.25 meq/L), as described above, and turbidity was followed using a Hanna HI93703 C turbidimeter (Hubbe et al., 2005). The averages of three measurements, after manual stirring the cuvette between each reading are reported.

2.4. Characterization of the cationic polyelectrolyte complexes

2.4.1. Polyelectrolyte titration method

The charge densities of the cationic PECs were determined by polyelectrolyte titration method and using KPVS (potassium (polyvinyl)sulfate) as titrant and OTB (o-toluidine blue) as indicator (Mocchiutti & Zanuttini, 2007; Terayama, 1952). Before titrating, pH of the solutions at the corresponding ionic strengths was adjusted to pH 7.5 with NaOH.

2.4.2. z-Potential and particle size measurements

Cationic polyelectrolyte complex solutions at the corresponding ionic strength and pH 7.5 were analyzed using a Zetasizer Nano Series (Malvern Instruments, United Kingdom).

2.4.3. Colloidal stability determination

Turbiscan Classic equipment was used to assess colloidal stability of PEC suspensions. The dispersion is scanned along a cylindrical glass cell. The light is emitted by an electro luminescent diode ($\lambda_{air} = 850$ nm) and two optical sensors receive light transmitted through the sample (180° from the incident light) and light backscattered by the sample (45° from the incident radiation).

Colloidal stability was measured at pH 7.5 at different ionic strengths (0.001 N, 0.01 N, and 0.1 N NaCl) immediately after the complexes preparation (0 h), after 1 h, and 48 h, before and after stirring the tubes.

2.5. Pulp preparation

Industrial liner paper (100% virgin softwood fibres from *Pinus elliottii* and *Pinus taeda*) supplied by Papel Misionero S.A. Argentina was cut in sheets of approximately 30 g which were randomly selected and soaked for 12 h. Then, the sheets were repulped in a standard disintegrator for 2 min at 1.5% pulp consistency using distilled water. The pulp obtained was left in these conditions for 24 h in order to ensure the wetting of the fibre. Then, the pulp was again disintegrated for 17 min and classified using a Bauer McNett classifier (Scan method M6:69) collecting the R100 fraction. This fibrous suspension was resuspended in deionized water and pH was adjusted to 4.0 using HCl, and left in that conditions for 30 min. Finally, the pulp was concentrated by centrifugation and stored at low temperature until use.

2.6. PAH and PEC retention curves

Wet samples of 0.5 g of o.d. pulp were added to 330 mL complex suspensions of different concentrations, at pH 7.5, and different ionic strengths (0.001 N, 0.01 N and 0.1 N NaCl), while being continuously stirred using a Britt Dynamic Drainage Jar (600 rpm) for 30 min. 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 (Hubbe et al., 2005). The amount of complexes which was not retained was determined using the polyelectrolyte titration method, for PAA/PAH complexes, or the phenol–sulfuric acid method (Hodge & Hofreiter, 1962), in the case of Xyl/PAH complexes (PEC_{C+P}).

For Xyl/PAH complexes, a set of experiments were carried out using the same procedure as describe above, but no fibres were added (PEC_C), and a set of test was performed for determining soluble and fine materials (S/F) (Hubbe et al., 2005). Finally, the amounts of Xyl/PAH retained were calculated according Eq. (1). All determination were made by phenol–sulfuric acid method,

$$\text{Amount of complex retained} = \frac{(\text{PEC}_\text{C} - \text{PEC}_\text{C+P} - \text{S/F})\,\text{mg}}{g_\text{pulp}} \quad (1)$$

where, PEC_C, is the amount of PEC on the filtrate in the absence of fibres, mg; PEC_{C+P}, is the amount of PEC on the filtrate in the presence of fibres, mg; S/F, is the amount of soluble and fines released from the pulp, and determined in the absence of complex, mg.

For Xyl/PAH complexes a second set of measurements was obtained by discontinuing the stirring before taking the sample, and after discarding the first 15 mL (Hubbe et al., 2005).

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

Adsorption of polyelectrolyte complexes onto silica surfaces was studied by using a Quartz Crystal Microbalance with Dissipation Monitoring QCM-D E4 (Q-Sense AB, Gothenburg, Sweden). QCM-D allows simultaneous measurement of the adsorbed amount and the viscoelastic properties of the adsorbed layer. The fundamental frequency (f_0) used was 5 MHz. Detailed principles of this method are described by Rodhal, Hook, Krozer, Brzezinski, and Kasemo (1995). Data obtained from QCM-D can be fit using different models, depending on the viscoelastic properties (determined by changes in dissipation) of the adsorbed layers.

In the case of rigidly adsorbed layers ($\Delta D \sim 0$), the mass adsorbed was calculated using Sauerbrey Eq. (2):

$$\Delta m = \frac{-C \cdot \Delta f}{n} \quad (2)$$

where Δm, is the adsorbed mass, mg/m^2; C, is the sensitivity constant 0.117 mg m^{-2} Hz^{-1} for the QCM-D crystals utilized; $\Delta f = (f - f_0)$, is the change in resonance frequency, Hz; n, is the number of the overtone ($n = 1, 3, 5, 7\ldots$).

Sauerbrey equation is only valid in the case of evenly distributed adsorbed layers with mass smaller than the mass of the crystal, and the mass is usually overestimated in the case of viscoelastic layers, due to high energy dissipation caused by friction losses (Orelma, 2012).

For soft adsorbed layers, ($\Delta D > 0$), the data was fitted using the Voight model. This is an iterative model that utilizes both changes in dissipation and in frequency to calculate adsorbed mass. Detailed principles of Voight model can be found in the article by Voinova, Rodhal, Jonson, and Kasemo (1999). The following parameters were considered for the fluid density: 1000 kg/m^3, fluid viscosity: 0.001 kg/ms, and film density: 1200 kg/m^3.

All the data was processed by using QTools software and the third overtone was used to determine the adsorbed mass for rigid complexes (Sauerbrey equation), while the third, fifth, seventh and ninth overtones were used to determine the layer thickness of viscoelastic complexes (Voight model).

The silica substrates were cleaned by exposing them to UV/ozone (Bioforce Nanosciences UV/O_3 Procleaner^{TM} Ames, IA, USA) for 10 min (Ahola, Salmi, Johansson, Laine, & Österberg, 2008). Different polyelectrolyte complexes concentrations at pH 7.5 and 0.01 N NaCl kept under continuous stirring were passed through the sensor chambers at a flow rate of 100 μL/min for 30 min. After that, surfaces were rinsed with 0.01 N NaCl in order to remove material that was only loosely bound to the surface. At the end of each QCM-D run, MilliQ-water, was circulated through the chamber. The sensors were finally dried with N_2, and placed in a desiccator in order to keep the surface free from contamination, for further morphological analysis by AFM. Two replicas were made for each solution concentration.

2.8. Atomic force microscopy (AFM)

The images of the QCM-D silica surface after complexes adsorption 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 silicon cantilevers with a nominal resonance frequency of 320–360 kHz, supplied by μMasch (Tallin, Estonia). No image processing except flattening was performed.

2.9. Pulp treatments with polyelectrolyte complexes and handsheets preparation

Treatments were carried out at 0.15% pulp consistency, NaCl 0.01 N and pH 7.5. The pulp slurry was added to the PAH (with a dosage of 0.66% on pulp) or PEC solutions (PAA/PAH and Xyl/PAH complexes formed with dosages of 0.66% PAH, 0.25% PAA and 2% Xyl) at adjusted pH and ionic strength, and kept under mild stirring for 30 min. A control treatment (Ref) was also made, under the same conditions as explained before but without adding any additional additives.

For each treatment, six handsheets of 120 g/m^2 were prepared according to SCAN standard methods but using deionized water that was adjusted to 0.01 N NaCl and pH 7.5. The blotters used in the sheets preparation were previously wetted in the same conditioned water. Sheets were dried under standard conditions. Apparent density (Tappi 411 om-97), tensile strength (Tappi T494 om-01), CMT (Cóncora Medium Test) (Tappi T809 om-99) and wet tensile strength (ISO: 3781:1983) were evaluated on all the sheets.

The use of complexes did not produce major problems of stickiness to wire, stainless steel plates or blotters during preparation of handsheets. This is an advantage compared to the stickiness observed when handsheets were prepared after the addition of PAH alone.

Table 1
Polyelectrolytes and polyelectrolyte complexes charge densities at pH 7.5 and different ionic strength.

NaCl (N)	Charge density (meq/g)[a]					
	PAA	Xyl	PAA/PAH		Xyl/PAH	
	Experimental values	Experimental values	Expected Values	Experimental values	Expected values	Experimental values
0.001	-9.3 ± 0.2	-0.86 ± 0.02	+3.23	$+2.22 \pm 0.11$	+0.76	–
0.01	-9.5 ± 0.6	-0.96 ± 0.04	+2.90	$+1.87 \pm 0.08$	+0.80	$+0.37 \pm 0.01$
0.1	-10.1 ± 0.4	-0.59 ± 0.04	+2.40	$+1.44 \pm 0.08$	+0.50	$+0.30 \pm 0.02$

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

3. Results and discussions

3.1. Polyelectrolytes characterization

Table 1 shows the charge densities of PAA and Xyl at different ionic strengths determined using the polyelectrolyte titration method. According to one-way ANOVA (Analysis of Variance), there was no difference between the value of charge density of xylan at 0.001 N and 0.01 N NaCl ($p = 0.1170 > 0.05$), but at high ionic strength, i.e. 0.1 N NaCl, charge density was significantly lower ($p = 0.0036 < 0.05$). The charge density of the PAA was not modified ($p = 0.2189 > 0.05$). The xylan charge density was also determined by conductometric titration in 0.001 N NaCl, and it was -0.76 ± 0.01 meq/g xylan, in agreement with the results obtained using polyelectrolyte titration method at the same ionic strength.

3.2. Turbidity curves

Turbidity as a function of different mass ratios of PAA and PAH at different ionic strengths are shown in Fig. 1(a). The turbidity maximums at ionic strength values of 0.001 N and 0.01 N NaCl were reached at mass ratios of 0.78 and 0.79, respectively. Using pDADMAC (poly(diallyldimethyammonium chloride) and CMC (carboxymethylcellulose) polymers, Lofton et al. (2005) related the maximums in turbidity with the theoretical point of charge neutralization. The figure shows that at the beginning of the titration curves, the turbidity did not increase probably because water-soluble complexes with non-stoichiometric mixing ratio were obtained. The conformation they acquire could correspond to the ladder model (Ankerfors, 2008). With increasing PAA/PAH mass ratios, the turbidity gradually increased. Such increase can be attributed to the formation of colloidal stable PECs, up to the point where complex aggregations occur (maximum point). Finally, the turbidity slightly decreased which could be explained by restabilization effects, as indicated by Hubbe et al. (2005) for the case of high charge density polyelectrolyte complexes. When PAA/PAH complex was formed in 0.1 N NaCl, the turbidity increased faster, and the maximum was reached at a mass ratio of 0.58. Deviations from the stoichiometric reaction can occur in the presence of salt in which case polyelectrolytes tend to form denser structures. According to Vanerek and van de Ven (2006), at high ionic strength, the polyelectrolyte complexes become unstable and undergo secondary macroscopic flocculation due to screening of charges by the electrical double layer.

Fig. 1(b) shows the turbidity as a function of different mass ratios of Xyl/PAH at different ionic strengths. As expected, the shapes of the curves obtained using low-charge-polyelectrolytes, like xylan, and with similar molecular mass as the PAH, are different to those observed in Fig. 1(a) for PAA/PAH. With increasing Xyl/PAH mass ratios, the turbidity gradually increased reaching a plateau, indicating that colloidal (no soluble) complexes were formed since the beginning of the xylan addition. This can be explained by the low solubility of xylan which is reduced as its charges are cancelled by the formation of complexes.

The conformation of Xyl/PAH complexes could be described by the scrambled egg model. It is improbable that a ladder structure can be formed in this case. The ladder model requires polyelectrolytes of high flexibility (Koetz & Kosmella, 2007) and high charge density.

The figure also shows that, at highest ionic strength (NaCl 0.1 N) studied, the turbidity values were higher.

3.3. Conditions selected for the formation of the cationic complexes

To prepare PAA/PAH cationic complexes containing 50% free PAH charges, the amount of PAA needed to add to the PAH solution was selected from the turbidity curve (Fig. 1(a)), and it was the 50% of the maximum turbidity reached.

In the case of Xyl/PAH cationic complexes, since the turbidity curves did not show a clear maximum, the amount of xylan needed to be added to reach 50% free PAH charges was selected taking into account the simple polyelectrolyte charge densities experimentally obtained at the corresponding ionic strengths (Table 1) and pH 7.5. Values were calculated using the following Eq. (3):

$$\text{Mass ratio} = \frac{\text{mg}_{\text{Xylan}}}{\text{mg}_{\text{PAH}}} = \frac{\rho_{\text{PAH}}\,(\text{meq/g})}{\rho_{\text{Xylan}}\,(\text{meq/g})} \times 0.5 \qquad (3)$$

where mg_{Xylan}, amount of xylan, mg; mg_{PAH} amount of PAH, mg; ρ_{xylan}, Xylan charge density, meq/g; ρ_{PAH}, PAH charge density, meq/g.

3.4. Cationic complexes characterization

3.4.1. Charge densities of cationic complexes

Theoretical expected charge densities of the cationic complexes considering the charge densities of the polyelectrolytes at different ionic strengths, together with the experimental charge densities of the complexes obtained using the polyelectrolyte titration method are summarized in Table 1. From the reported values it can be observed that experimental results were lower than the expected values, which can be probably explained by deviations from 1:1 stoichiometry. Using strong, linear, and high-mass polyelectrolytes, Chen et al. (2003) showed that the streaming current titration results were dependent on the order of addition of the two polyelectrolytes, and the PECs obtained, appear to have an excess of the later added polyelectrolyte. According to one-way ANOVA, PAH/PAA charge densities significantly decreased ($p = 0.0073 < 0.05$) when the ionic strength of the liquid medium increased, while PAH/Xil charge densities were not modified ($p = 0.1783 > 0.05$). The charge densities of the Xyl/PAH complexes were clearly lower than the PAA/PAH complexes. The table also shows that the charge density of the Xyl/PAH complex could not be determined at 0.001 N NaCl probably because the value was too low to be detected using the polyelectrolyte titration method.

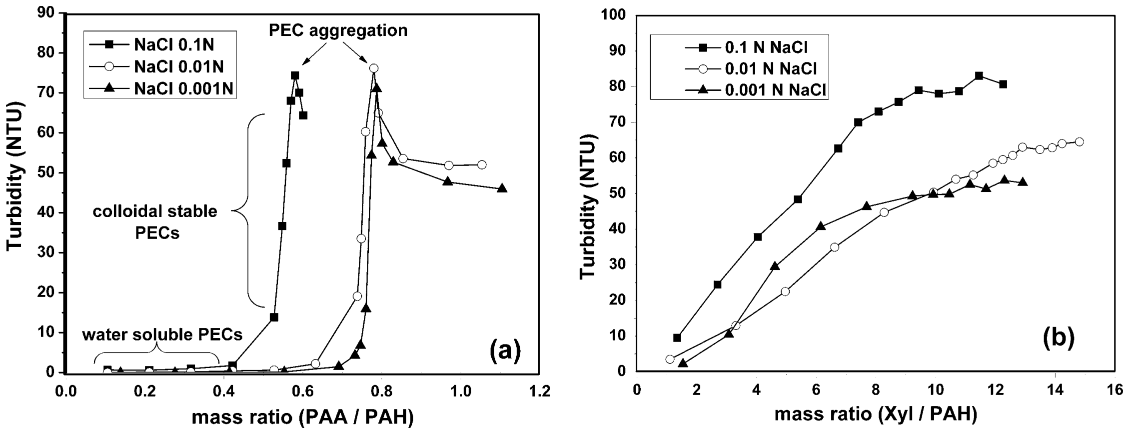


Fig. 1. Formation of polyelectrolyte complexes monitored through turbidity measurements as a function of mass ratio of (a) (PAA/PAH) and (b) (Xyl/PAH) at different ionic strengths and pH 7.5.

3.4.2. z-Potential and particle size measurements

Zetasizer was utilized to measure *z*-potential and size of the PAA/PAH and Xyl/PAH cationic complexes at different ionic strength; results are shown in Table 2. The sizes of PAA/PAH complexes, were all similar at different ionic strengths, the majority being between 70 and 95 nm. This was not the case for Xyl/PAH complexes, where it was observed that the sizes were significantly greater than PAA/PAH complexes, especially at 0.1 N NaCl (280–930 nm) which corresponds to a higher turbidity (Fig. 1b). At 0.001 N NaCl, the particle size of the Xyl/PAH complexes could not be determined, presumably for the same reason why this particular suspension was not able to be titrated using the polyelectrolyte titration method (Table 1). The standard deviations of the zeta-potential values when the ionic strengths were 0.001 N and 0.1 N were high probably because the true value is near to zero.

3.4.3. Colloidal stability

Fig. 2 shows the colloidal stabilities of the cationic complexes at pH 7.5, and different ionic strengths using the Turbiscan optical analyzer. Tests were carried out at 0 h, after 1 h, and 48 h before and after manual stirring the tubes. Fig. 2(a) shows that cationic PAA/PAH complexes were highly stable at 0.1 N NaCl. The results obtained at 0.001 N and 0.01 N NaCl indicated even higher stability (data not shown). This was not the case for Xyl/PAH complexes at 0.01 N, and 0.1 N NaCl, respectively (see Fig. 2(b) and (c)). Nevertheless, the stirring reversed the effects of sedimentation that occur after 1 h and 48 h. Results obtained at 0.001 N were similar to that obtained at NaCl 0.01 N (data not shown). The sedimentation and the subsequent re-dispersion by stirring can be a practical advantage, because it allows concentrating suspensions for storage and transport purposes.

3.5. PAH and PEC retention curves

Fig. 3(a) shows the specific retention of the PAH and PAA/PAH complexes at neutral pH and at different ionic strengths as a function of the PEC concentrations. The specific retention levels of PAA/PAH complexes on pulp at 0.001 N and 0.01 N NaCl were similar. Nevertheless, for 0.1 N NaCl the retention of PECs significantly increased. The figure also shows that the use of PECs, instead of simple polyelectrolytes (PAH), allow high amounts of cationic additive retention to be retained. For example, when 1.4% PEC on pulp was added, 1.08% PEC was retained, where 0.85% corresponded to PAH and 0.23% corresponded to PAA.

The isotherms could be fitted well by the Langmuir model, since they defined plateaus that indicate saturation of the fibre surfaces charges by the formation of monolayer of complex.

Fig. 3(b) shows the specific retention of Xyl/PAH complexes at different ionic strengths as a function of the PEC concentration determined by phenol–sulfuric acid method and using Eq. (1). The figure also shows the results obtained by discontinuing the stirring in the Dynamic Jar before taking the sample. As found for PAA/PAH complexes, the specific retention levels of Xyl/PAH complexes on pulp at 0.001 N and 0.01 N NaCl were similar. On the other hand, the amount of PEC retained was higher when the stirring was discontinued due to the formation of a fibre mat, except when the ionic strength of the liquid medium was 0.01 N NaCl, where no differences were found. On the other hand, the increase in ionic strength produced a decrease in the specific retention levels of the PECs on pulp, contrary to the results obtained when PAA/PAH complexes were used. For PAA/PAH and Xyl/PAH, the retention curves at 0.001 N and 0.01 N NaCl were similar. For both complexes, PAA/PAH and Xyl/PAH, there was no major difference between the corresponding retention curves at 0.001 N and 0.01 N NaCl.

Table 2
Zeta potential and Size measurements of PAA/PAH and Xyl/PAH complexes at different ionic strengths.[a]

NaCl concentration (N)	PAA/PAH		Xyl/PAH	
	Zeta potential (mV)	Size (nm)	Zeta potential (mV)	Size (nm)
0.001	+37.9 ± 3.6	80.6 ± 3.4 (94.8%) 3318 ± 264 (5.2%)	+9.8 ± 6.8	–
0.01	+32.5 ± 2.4	71.5 ± 1.4 (94.4%) 3033 ± 626 (5.6%)	+23.8 ± 4.4	279.6 ± 1.2 (97%) 4705 ± 48 (3.0%)
0.1	+28.7 ± 2.1	95.4 ± 2.4 (91.4%) 1532 ± 606 (4.3%) 3643 ± 310 (4.3%)	+7.3 ± 6.8	928.8 ± 102 (93.2%) 5200 ± 126 (6.8%)

[a] The standard deviations of the means from two replications of the trial are shown.

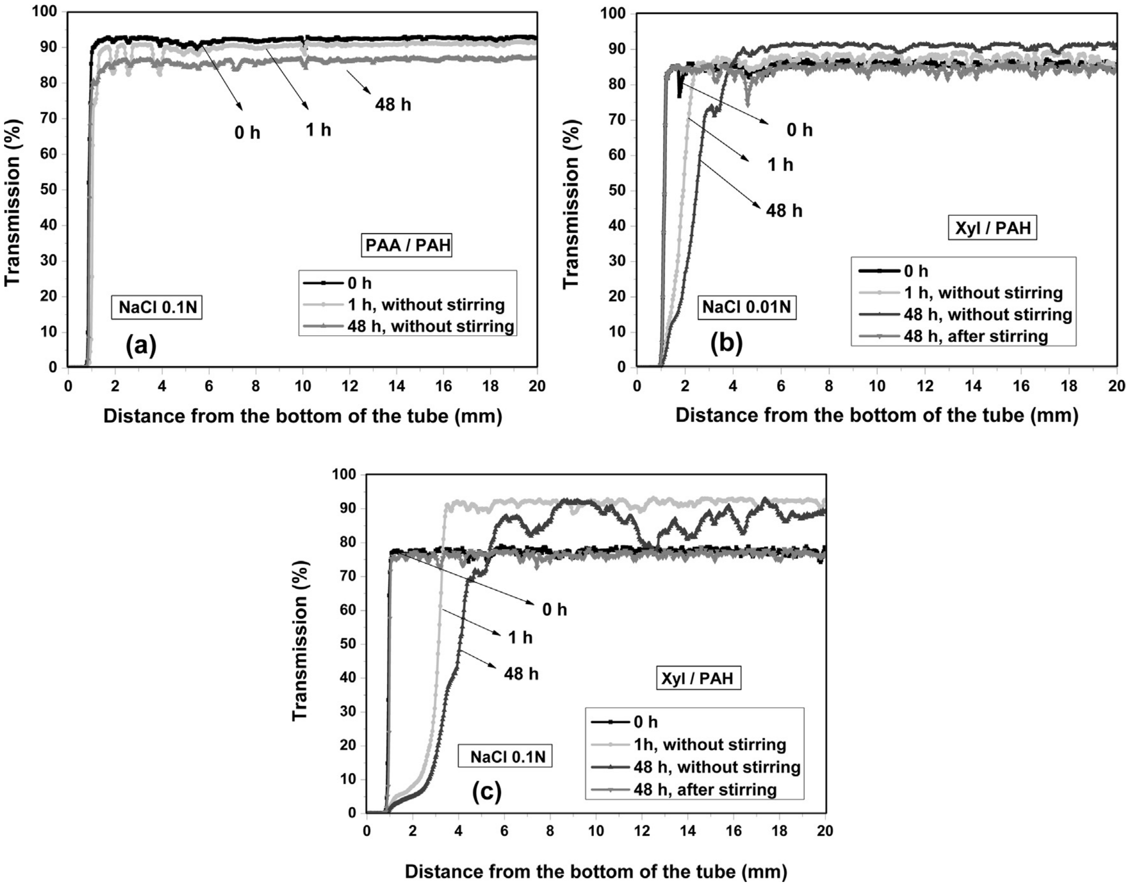


Fig. 2. Stabilities of the complexes: transmission of PAA/PAH and Xyl/PAH complexes at different ionic strengths as a function of the distance from the bottom of the tube by using the Turbiscan optical analyzer.

Differently from PAA/PAH, the isotherms of Xyl/PAH did not reach plateaus, probably because more than one mechanism of adsorption could exist, i.e., electroadsorption, non-electrostatic affinity and also, due to their higher size, mechanical retention.

3.6. Adsorption of PECs on model surfaces: QCM-D analysis

Fig. 4 shows the changes in frequency as well as changes in dissipation as a function of time, for silica quartz crystals when PAA/PAH and Xyl/PAH complexes at 0.01 N NaCl were adsorbed. Two concentrations of PAA/PAH and Xyl/PAH were selected considering the lowest and highest concentration used to build the retention curves (indicated by dot-circles in Fig. 3(a) and (b). Almost non-existing changes in dissipation were observed for the case of the adsorbed PAA/PAH complex layer, indicating that the PECs pack very well on the surface, forming a rigid structure. On the other hand, Xyl/PAH complexes form a more viscoelastic layer, as indicated by the large variations in dissipation values. Due to the different viscoelastic behaviour of both systems, two different models were utilized to obtain adsorbed mass values; Sauerbrey model was used in the case of PAA/PAH complexes, while Voigt viscoelastic model was used for Xyl/PAH complexes. Additionally, results indicated that the higher the concentrations of the PEC solutions, the higher were the changes in frequency, indicating higher adsorbed mass

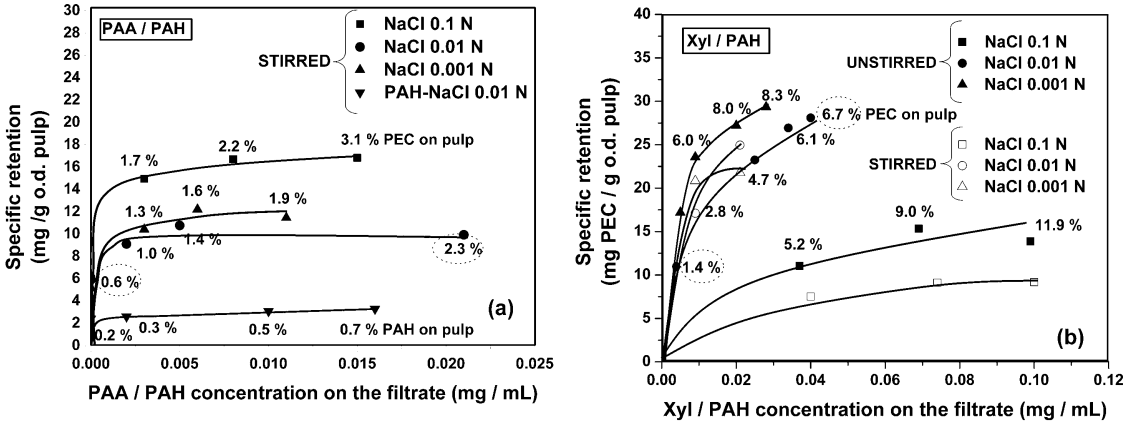


Fig. 3. Specific retention of (a) PAH and PAA/PAH and (b) Xyl/PAH complexes as a function of the PEC concentrations, at different ionic strengths and neutral pH.

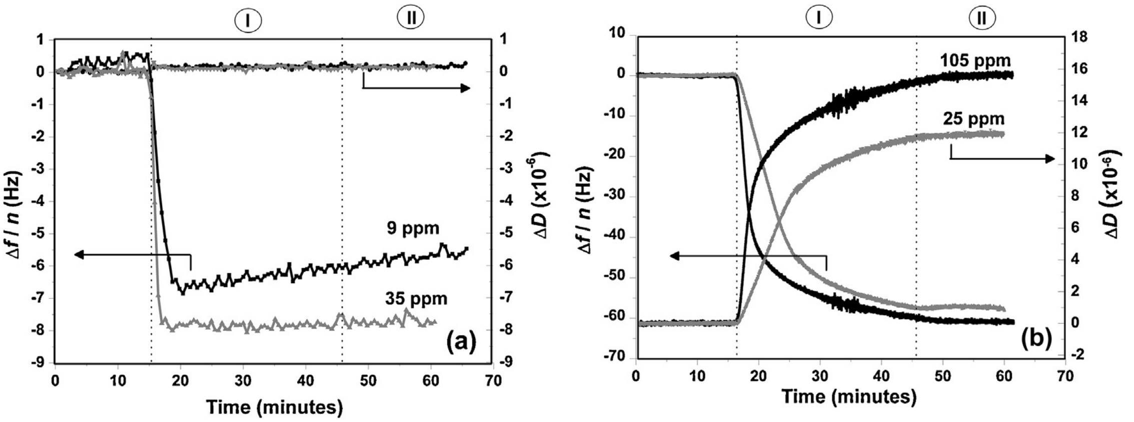


Fig. 4. Changes in frequency of silica surface and dissipation due to the adsorption of (a) PAA/PAH, and (b) Xyl/PAH complexes at different concentrations, pH 7.5 and NaCl 0.01 N. (I) PEC adsorption, (II) Rinse with NaCl 0.01 N.

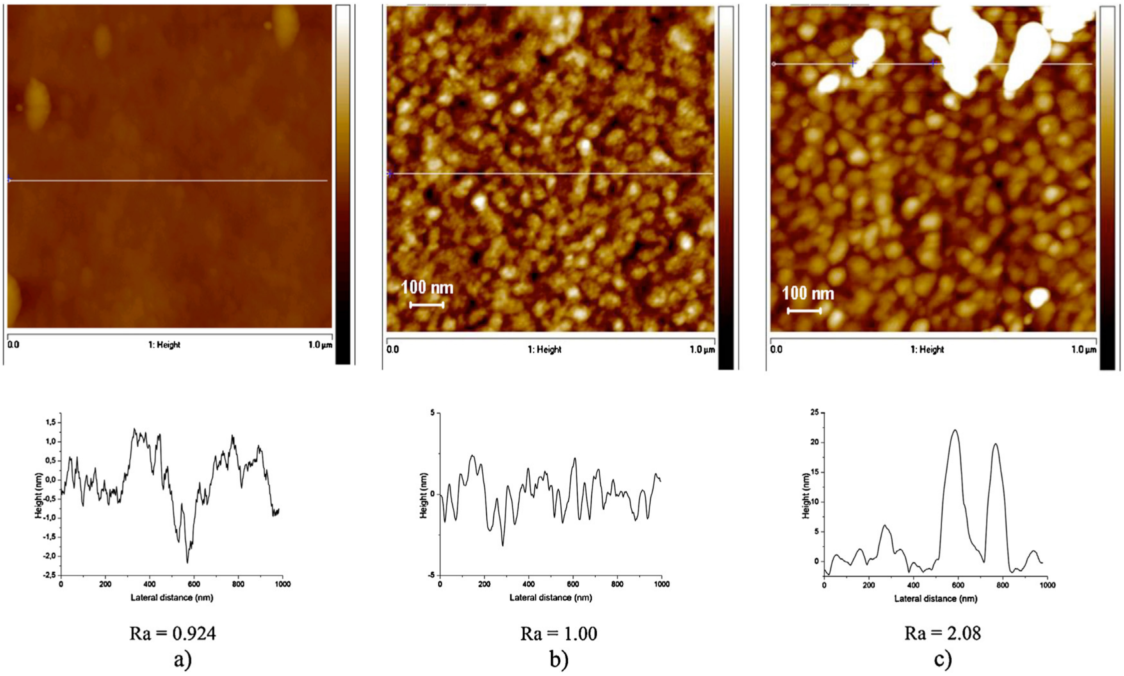
of material. This last result agrees well with specific retention values obtained directly on bulk fibres suspension (Fig. 3). It was also found that the amount of mass adsorbed calculated for Xyl/PAH complexes were notably higher than in the case of the PAA/PAH complexes (57.8 ± 0.25 mg/m^2 and 1.4 ± 0.01 mg/m^2, for Xyl/PAH and PAA/PAH complexes, respectively) when the PEC concentrations were 25 ppm of Xyl/PAH and 35 ppm of PAA/PAH.

3.7. *Morphology of PECs*

Morphology of PECs was investigated by Atomic Force Microscopy (AFM). Fig. 5 shows that both PAA/PAH and Xyl/PAH complexes were spherical. The average diameters obtained from 65 measurements were 39.9 ± 7.2 nm, and 58.1 ± 7.7 nm for PAA/PAH and Xyl/PAH, respectively. For Xyl/PAH some bigger complexes were observed, in agreement with results obtained by Zetasizer. The discrepancy between PEC sizes determined by AFM and those reported using electrophoresis are due to the fact that in the case of AFM, the diameters were measured on air dried adsorbed complexes. AFM data also shows that roughness average of the Xyl/PAH complexes adsorbed on silica was higher than the PAA/PAH complexes, principally due to the formation of aggregates.

3.8. *Effect of PAH and PEC additions on papermaking properties*

The effects of addition of the different PECs on apparent density, dry tensile strength, wet tensile strength and CMT of high quality unbleached fibres is shown in Fig. 6. Results indicated that the apparent density of the sheets is not affected by treatments, however all the strength properties were significantly increased by the addition of PAH or PECs, especially when PECs were added. Both complexes produce a similar effect on tensile and crushing strengths. Particularly, compared to the reference treatment, an increase of 50% and 141% in dry tensile index and CMT were obtained respectively, when Xyl/PAH was added on the fibres. In the case of wet tensile strength, similar results were obtained for the addition of PAH and Xyl/PAH, being the addition of PAA/PAH treatment with the highest impact. This behaviour could be attributed



Ra = 0.924
a)

Ra = 1.00
b)

Ra = 2.08
c)

Fig. 5. Topographic AFM images of (a) Silica, (b) PAA/PAH complexes, (c) Xyl/PAH complexes adsorbed on quartz crystals coated with silica. Ra: is the roughness average. The image size is 1×1 µm. The *z*-scale is from −5 to +5 nm.

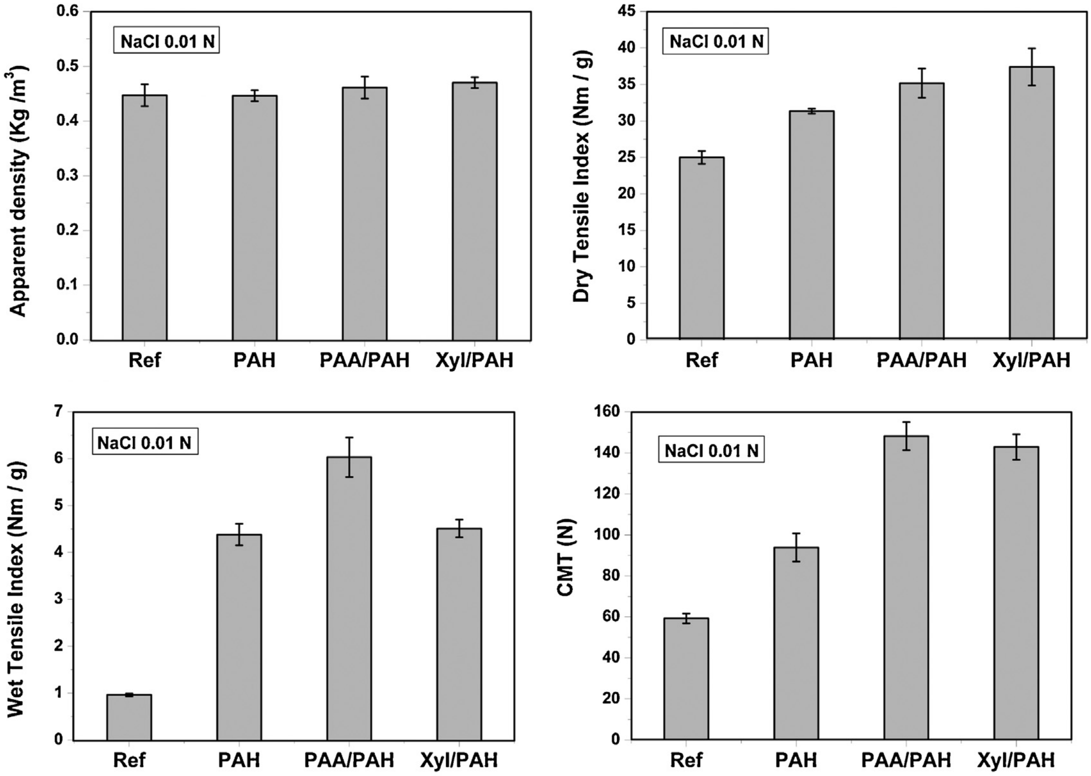


Fig. 6. Paper physical properties as a function of the different treatments, pH 7.5 and 0.01 N NaCl. The error bars correspond to the standard deviations of the means from ten replications of the test.

to more hydrophilic character of Xyl/PAH complex presents compared to PAA/PAH complex. In fact, it was observed that Xyl/PAH complex sheets took water faster than PAA/PAH complex sheets when they were immersed in water for the test.

4. Conclusions

Different shapes of the turbidities curves as a function of mass ratios of the polyelectrolytes were obtained. For PAA/PAH complexes, maximums in turbidity were reached, which is typical of polyelectrolytes with high charge densities. On the other hand, Xyl/PAH complexes showed a gradual increase of turbidity until a plateau was reached, indicating that colloidal complexes were formed since the beginning of the anionic polyelectrolyte addition.

Xyl/PAH complexes were between four and ten times larger in comparison to PAA/PAH complexes, and the increase in ionic strength, increased the size of the Xyl/PAH complexes as studied by Zetasizer.

Adsorption studies with QCM-D provided valuable data regarding adsorption and structural behaviour of the PECs layers, while using a very small amount of sample. It was observed by QCM-D that PAA/PAH complexes were rigid while Xyl/PAH complexes were viscoelastic, while AFM images showed that both complexes were spherical.

Even though Xyl/PAH complexes were not stable; it was found that the effect of sedimentation was reversed by simply stirring the suspension, which represent a practical advantage for its industrial application.

The increase in ionic strength, increased the amount of PAA/PAH complexes adsorbed on high quality unbleached fibres, while decreased the amount of Xyl/PAH complexes adsorbed. Particularly, the use of PECs, instead of simple polyelectrolytes, allows reaching high amounts of cationic additive adsorbed.

Finally, it was observed that both complexes considerably increased the papermaking properties indicating that it is possible to use a natural polyelectrolyte such as xylan instead of synthetic PAA, especially when high CMT strength is desired.

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