DUAL-POLYELECTROLYTE ADSORPTION OF POLY(ALLYLAMINE HYDROCHLORIDE) AND XYLAN ONTO RECYCLED UNBLEACHED KRAFT PULPS

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The effects of a double polyelectrolyte adsorption of poly(allylamine hydrochloride) (PAH) and xylan (Xyl) on a recycled unbleached softwood kraft pulp were studied. The kinetics of PAH adsorption on this pulp was analyzed by building adsorption isotherms and by estimating the surface nitrogen adsorbed through the X-ray photoelectron spectroscopy (XPS) technique. It was found that at pH 7.5, 0.01N NaCl, and short adsorption time, PAH is mainly adsorbed on the fiber surface. Adsorption isotherms of xylan on untreated and on previously PAH-treated pulps at different ionic strengths were built, and the effects of the amount of PAH on xylan adsorption were considered. It was found that when ionic strength was lower than 0.01N NaCl, a PAH pretreatment was necessary to achieve high levels of xylan adsorption at room temperature and short adsorption times. Nevertheless, when ionic strength was 0.1N NaCl, 0.3% xylan on pulp could be directly adsorbed on untreated pulp. Finally, it is shown that the dual-polyelectrolyte adsorption on this pulp is a feasible technique for improving paper tensile strength.

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INTRODUCTION

From an environmental and economic point of view, recycled fibers are highly desirable as a source for paper and board production. However, the principal limitation is their lower strength in comparison with their corresponding virgin papers due to the physical and chemical changes that affect fibers during the previous papermaking process (Hubbe et al. 2007).

Wet-end additives such as cationic starches or polyacrylamides are commonly used in industrial practice to increase the specific bonding strength of fibers. Nevertheless, the maximum dosage of cationic starch that can be applied is limited, and synthetic polyelectrolytes can increase the paper strength properties up to a certain maximum value.

The layer-by-layer deposition (LbL) of polyelectrolyte on surfaces, formed by the consecutive adsorption of polyelectrolyte of opposite charges, is a simple method for modifying the interfacial properties of different materials. Hubbe et al. (2003) showed that a dual-polymer dry-strength treatment with poly(dimethyldiallylammonium chloride)

(pDADMAC) and carboxymethylcellulose (CMC) can significantly improve the compressive and tensile strengths of an unbleached softwood kraft pulp. Other authors showed that the strength of bleached softwood pulps can be increased by building polyelectrolyte multilayers (up to 8 layers) of two synthetic weak polyelectrolytes, poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA), (Wågberg et al. 2002; Eriksson et al. 2006).

Taking into account the raw material considered in this research, and the relative low value of the final paper products that can be obtained, only one dual-polyelectrolyte adsorption is considered in the present work.

As a cationic polyelectrolyte, PAH, which is a synthetic linear weak polyelectrolyte with amine groups, has been studied in detail for improving paper strength of unbleached fibers (Gimåker et al. 2009; Mocchiutti et al. 2011). A characteristic of PAH is that, at high drying temperature, the amine groups can react with carboxylic groups, producing amides (Eriksson et al. 2006), or with aldehydes from the lignocellulosic fibers producing imines and N-C-N bond types (DiFlavio et al. 2005; Gimåker and Wågberg 2009), and thus additional fiber-to-fiber bonds can be established.

As an anionic polyelectrolyte, hemicelluloses such as O-acetyl-4-O-methylglucuronoxylan from hardwoods, L-arabino(4-O-methyl-D-glucurono)xylans from softwoods (Sjöström, 1993), or both from gramineous plants (Sun et al. 2004), provide an interesting option because they are a class of natural polymers, abundant in nature, renewable, biodegradable, and having a natural affinity to cellulose.

Xylan constitutes the main hemicellulose of hardwoods and gramineous plants, and it can be a by-product of alkaline pulping processes. According to Sixta et al. (2011), streams of dissolved xylan with low lignin content can be separated by high alkalinity pre-extraction in hardwood soda-antraquinone pulping processes.

In particular, the hardwood xylan chemical structure is characterized by a backbone of β-D-xylopyranose units, linked by (1→4)-bonds to which, on average, 4-O-methylglucuronic acids are substituted every 10 units, and acetyl groups in a ratio two to each three xylose units (Sjöström 1993). However, the ratio of glucuronic acid to xylose units on the xylan that is isolated depends on the extraction method employed and it can be higher for eucalyptus wood (Magaton et al. 2011).

The presence of glucuronic acids on xylan impairs its adsorption on cellulosic fibers that are anionic. Silva et al. (2011) found that at high temperatures (90ºC to 170ºC) and long adsorption times (1 to 4 h), low uronic acid content xylan had greater adsorption on eucalyptus pulp than enriched methylglucuronic acid xylan. Under those conditions of adsorption, the mechanism of adsorption is through the formation of aggregates that have a non-electrostatic affinity to the cellulose surface. This type of xylan adsorption has shown a favorable decrease in the beating energy but a slight improvement in strength properties of eucalyptus pulp.

An alternative that can lead to a favorable xylan adsorption, at room temperature, is to chemically modify the xylan through cationization by reaction in alkaline medium with epoxides containing quaternary amines, as it is usually done on starches (Köhnke and Brelid 2009; Ren et al. 2009; Köhnke 2010). The electrosorption of xylans on fibers can thus be possible. However, this option has also shown slight improvements in paper tensile strength (Ren et al. 2009; Köhnke 2010).

This paper analyzes the dual-polyelectrolyte treatment with PAH and xylan as a polyelectrolyte bilayer on an unbleached recycled softwood kraft pulp. First, the PAH behavior was characterized during its adsorption onto the pulp. Then, the xylan adsorption on an untreated and also on a previously PAH-treated pulp was studied at different ionic strengths and different dosages of PAH. Finally, the effects of the dual-polyelectrolyte treatment on tensile strength were determined, considering two different drying temperatures (23ºC and 120ºC).

EXPERIMENTAL

Materials and Methods

Preparation and characterization of polyelectrolytes

PAH (poly(allylamine hydrochloride)) with an average molecular mass of M_w: 56 kDa from Sigma-Aldrich was directly used to prepare a 0.5 g/L solution in deionized water. The PAH solution concentration was determined by the polyelectrolyte titration method using KPVS as titrant and o-toluidine blue (OTB) as indicator (Gimåker et al. 2009; Mocchiutti et al. 2011). At pH 7.5, the PAH charge densities used were 8.30 meq /g PAH IN NaCl 0.01N, and 10.6 meq /g PAH in 0.001N NaCl according to Mocchiutti et al. (2011).

4-O-methyl glucuronoxylan isolated from birch wood by alkaline extraction (Sigma-Aldrich product number X-0502) was used without further purification. HPAEC-PAD analyses of neutral sugars, using a Carbopac PA-10 column and a 16 mM NaOH mobile phase, showed 96.8% xylose and 3.2% galactose. For these analyses, the xylan was hydrolyzed in 2N trifluoroacetic acid (TFA) for 1h at 121ºC, according to Mortimer et al. (2010). Similar results regarding the neutral sugar content were obtained by Köhnke et al (2010). Besides that, these authors reported the following chemical composition of the same commercial xylan: 79.0% neutral carbohydrates, ash 10.4% and Klason lignin 0.6%.

Xylan molecular mass was analyzed by SEC in combination with refractive index and UV detectors using a 2 PSS MCX column and a 0.5 M NaOH in HPLC water as mobile phase. The M_w was 21.5 kDa and the M_n was 7.4 kDa.

Fresh xylan solutions (0.6g/L) were daily prepared by adding the commercial solid xylan to NaOH 10^{-4} N solution and heating it in a bath at 95ºC for 15 min to dissolve xylan (Linder et al. 2003). As was done by Salyers et al. (1981), xylan solution concentration was determined using the phenol/sulphuric acid spectrophotometric method (Hodge and Hofreiter 1962). The xylan charge density was determined by indirect polyelectrolyte titration (Terayama 1952; Mocchiutti and Zanuttini 2007), and the values obtained at pH 7.5 were 1.11 meq/g and 0.97 meq/g xylan in 0.001N and 0.01N NaCl, respectively. The xylan charge density was also determined by conductometric titration, and it was 0.99 meq/g xylan. Katz et al.'s (1984) method was applied, but NaHCO₃ was used instead of NaOH according to Lloyd and Horne (1993).

At 0.1N NaCl, neither the PAH charge density nor the xylan charge density could be determined using the polyelectrolyte titration method because, according to Eklund and Lindström (1991) and Tanaka and Ichiura (1999), the critical NaCl concentration in a

titration medium, above which no color change of the indicator can be observed, is 0.02 N NaCl.

KPVS (potassium polyvinyl sulfate) solution was supplied by AppChem (England) as a 1000 µN concentration. A 200 µN KPVS solution in deionized water was prepared for polyelectrolyte titrations. The solution concentration was frequently checked by polyelectrolyte titration using pDADMAC as titrant (Terayama 1952; Mocchiutti and Zanuttini 2007).

Raw material

The fibrous fraction of a recycled pulp obtained from an unbleached softwood kraft-liner paper was used for the study. The paper (100% virgin fibers and kappa number 91.6) was supplied by Papel Misionero S.A. Argentina. Fibers were prepared following the procedure described in Mocchiutti et al. (2011). In brief: the paper was soaked, and pulp was disintegrated and classified using a Bauer McNett classifier. Only the R100 fraction (R100, i.e. rejected by 100 mesh) was collected. Then, the pulp was converted to the acid form (HCl pH 2.0 to 30 min), and then it was converted to the sodium form (0.01N $NaHCO_3$ and NaOH pH 9.0, 30 min). Finally, the pulp was washed at a final pH 7.5.

PAH adsorption isotherms

PAH adsorption isotherms were obtained following the procedure described in Mocchiutti et al. (2011). In brief: Wet samples of 0.5 g of o.d. pulp in its sodium form were added to 100 mL solutions of different concentrations of PAH and 0.01N NaCl at pH 7.5. Each suspension was stirred for 8 min, 30 min, or 180 min at 25ºC and then filtered. Fibers were rinsed with 200 mL of conditioned water at the same pH and ionic strength as during the adsorption stage, and they were stored for XPS analysis as it is described below. On the filtrate, the remaining amount of PAH was determined by the polyelectrolyte titration method.

From the PAH adsorption isotherms, the PAH dosage necessary to saturate the adsorption capacity of the fiber surface was obtained using the equation proposed by Mocchiutti and Zanuttini (2005), which can be rewritten as,

$$\frac{M}{Ms} = \frac{rx}{(1-x)(1-x+r\,x)} \qquad (1)$$

where $x=c/a$; c is the polyelectrolyte concentration in solution (mg/mL); a is the polyelectrolyte conc. of saturation in the solution (mg/mL); M is the specific total mass of polyelectrolyte adsorbed on fibers (mg/g pulp); Ms is the specific mass of polyelectrolyte corresponding to the stoichiometric adsorption on fiber surface charges (mg/g pulp), and r is a parameter related to the affinity between the surface and the polymer.

PAH/xylan and xylan adsorption isotherms

To adsorb xylan as the second layer, PAH treated fibers were added to a 100 mL solution of different concentrations of xylan at pH 7.5 and stirred for 30 min. Three ionic strengths were considered (0.001, 0.01, and 0.1N NaCl).

The amount of xylan adsorbed was determined indirectly by measuring the xylan concentration in the original solution as well as in the filtrate after adsorption, using the phenol/sulphuric acid spectrophotometric method. Prior to phenol/sulfuric acid measurements, the filtrates were additionally filtered through a fiberglass filter (retention 0.5 μm) to separate fines. Xylan adsorption isotherms on untreated pulp were also made under the same conditions as described above but without adding PAH. To account for the sugar release from the pulp during the adsorption process, a control treatment was made under the same conditions as the PAH and xylan adsorption treatments but without adding PAH or xylan.

X-ray photoelectron spectroscopy (XPS) analyses

The mat of fibers treated with PAH was pressed twice at 2.5 kg/cm^2 between blotters (5 min and 2 min), and then it was dried at 23ºC and 50% RH, and used for XPS analyses.

XPS analyses were performed in a multi-technique system (SPECS) equipped with a monochromatic Al X-ray source and a hemispherical PHOIBOS 150 analyzer operating in the fixed analyzer transmission (FAT) mode. The spectra were obtained with a pass energy of 30 eV, and the Al-Kα X-ray source was operated at 200 W and 12 kV. To compensate the charging effect, a low energy electron flood gun was employed. The working pressure in the analyzing chamber was less than 5×10^{-7} Pa. The XPS analyses were performed on the samples after being evacuated overnight in the load-lock chamber at room temperature. The X-ray incident angle was 90º in relation to the sample surface. The high-resolution O 1s, N 1s and C 1s spectra were recorded for each sample. The data treatment was performed with the Casa XPS program (Casa Software Ltd, UK). The peak areas were determined by integration employing a Shirley-type background. For the quantification of the elements, sensitivity factors provided by the manufacturer were used. The curve fit of the C 1s spectrum was performed employing Gauss–Lorentzian components with a full width at half maximum (FWHM) between 1.7 and 2.0 eV.

*PAH/xylan pulp treatments for handsheet preparation*

PAH/xylan pulp treatments were carried out at 0.5% pulp consistency, pH 7.5, and 0.01N NaCl. The pulp slurry was added to the PAH solution at the adjusted pH and ionic strength, and left under mild stirring for 30 min. Then, the suspension was filtered, and the web mat of fibers was washed and added to the xylan solution also at the adjusted pH and ionic strength. After mild stirring for 30 min, the pulp suspension was diluted to 0.3% pulp consistency (keeping the pH and the ionic strength of the medium). A sample was separated for determination of water retention value (relative weight of water after centrifugation at 1750 g for 30 min). A PAH-treated pulp as well as a control pulp were prepared. They were treated in the same manner, but without adding xylan or without adding PAH or xylan, respectively. For each treatment, ten handsheets of 120 g/m^2 were prepared according to the SCAN-C 26:76 standard method but using deionized water adjusted to 0.01N 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 (23ºC, 50% RH, SCAN P2:75) but, in order to evaluate the effect of the drying

temperature, five sheets were additionally treated in oven at 120ºC for 10 min. Dry tensile strength (Tappi T494 om-01) was determined on all the sheets.

RESULTS AND DISCUSSION

Kinetic of PAH Adsorption

Figure 1 shows PAH adsorption isotherms at different adsorption times (8 min, 30 min, and 180 min). The figure shows that at 180 min the amount of PAH adsorbed was clearly higher.
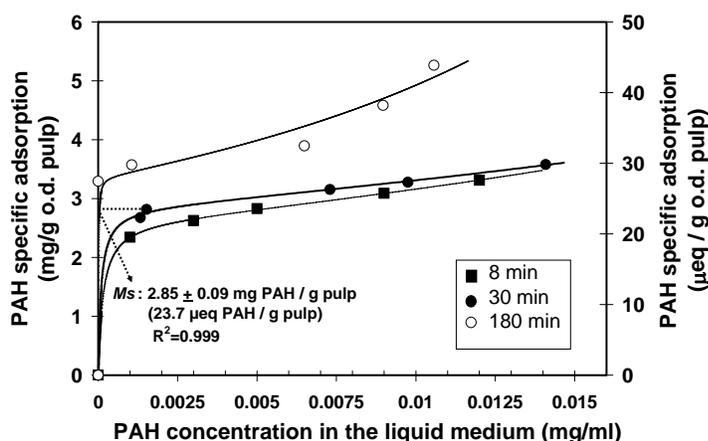

Fig. 1. PAH specific adsorption as a function of PAH equilibrium concentration at different times, pH 7.5 and NaCl 0.01N. Equation (1) was fitted to data points to obtain the values of the parameters. The amount of PAH is expressed in mg PAH/g pulp, and in µeq PAH /g pulp, considering a charge density of 8.30 meq/g PAH.

To assess where the additional amount of PAH is located, fibers were analyzed by XPS. This technique makes it possible to determine the amount of surface nitrogen, and it can be associated with the presence of PAH only on the fiber surface in a depth up to around 10 nm. The XPS results are shown in Fig. 2, where it can be observed that the content of fiber surface nitrogen was similar irrespective of the treatment time. The discrepancy with Fig. 1, which shows that the amount of PAH adsorbed at 180 min was higher, can be ascribed to the fact that adsorption takes place not only on the fiber surface but also inside the fiber wall when extended adsorption time is applied, which could not be quantified by XPS because it is a surface technique.

To discuss the location of polyelectrolytes on pulps, such as pDADMAC, several authors used the XPS technique together with the polyelectrolyte titration (Horvath et al. 2006). Other authors used the fluorescent confocal microscopy to show the location of cationic dextran and copolymer of acrylamide and pDADMAC (Horvath et al. 2008), or PAH on fibers (Gimåk er et al. 2009).

Gimåker et al. (2009) found that to obtain paper significant strength improvements, the adsorption of the PAH has to be restricted to the exterior surface of the fibers. Thus, for the rest of this work, an adsorption time of 30 minutes was adopted.

On the other hand, from the isotherm obtained at 30 min in Fig. 1, the PAH necessary to saturate the adsorption capacity of the fiber surface was obtained using the equation proposed by Mocchiutti and Zanuttini (2005). The equation parameter *Ms* was in this case 2.85 ± 0.09 mg PAH/g of dried pulp (23.7 µeq PAH/g of dried pulp) and it corresponds to a PAH dosage of 3.0 mg/g o.d. pulp. This is in agreement with previous results obtained for the same pulp at 0.01N NaCl and also at 0.001N NaCl (Mocchiutti et al. 2011).
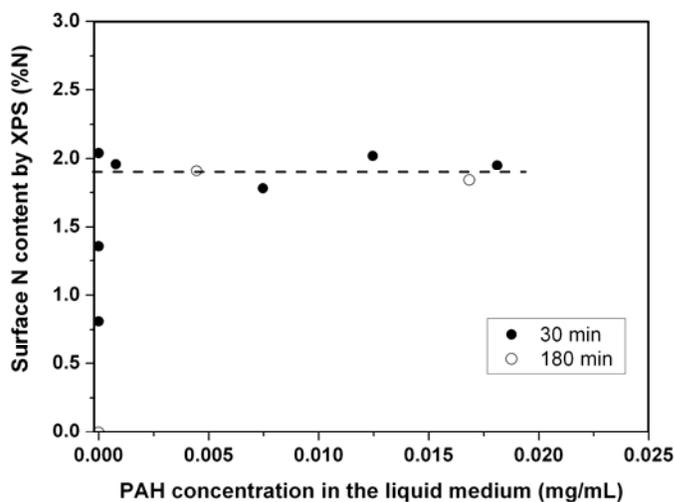
Fig. 2. Surface nitrogen content determined by XPS as a function of PAH equilibrium concentration where PAH adsorption took place, at pH 7.5, NaCl 0.01N for 30 and 180 min

PAH/xylan and xylan adsorption isotherms at different ionic strengths

Table 1 shows the dosages of PAH and xylan used for building the isotherms. The PAH dosages were selected from the PAH isotherms obtained at 30 min and 0.01N NaCl (Fig.1.), and correspond to the half of the fiber saturation level, PAH(0.15%), b) the saturation level, PAH(0.30%), and c) the double of the saturation level, PAH(0.60%) when the adsorption was made in 0.01N NaCl.

Table 1. Conditions Used for Building Xylan Adsorption Isotherms on Untreated Pulps or on Previously PAH-Treated Pulps (pH 7.5, and at Different Ionic Strengths: 0.001N, 0.01N, and 0.1N NaCl).

TREATMENTS	FIRST LAYER	SECOND LAYER
	PAH dosage (% on o.d. pulp)	Commercial xylan dosage (% on o.d. pulp)
Xyl	-----	1.0 – 5.0
PAH (0.15%) /Xyl	0.15	1.0 ; 2.0 ; 3.0 ; 4.0
PAH (0.30%) /Xyl	0.30	1.0 ; 2.0 ; 3.0 ; 4.0
PAH (0.60%) /Xyl	0.60	1.0 ; 2.0 ; 3.0 ; 4.0

Figures 3, 4, and 5 show xylan adsorption isotherms obtained at different ionic strengths by the addition of increasing amounts of xylan on untreated pulps and also on pulps previously treated with different amounts of PAH, according to Table 1.

Figures 3, 4, and 5 show that the amount of xylan directly adsorbed on untreated pulp was low. Nevertheless, for the highest ionic strength studied (0.1N NaCl) up to 0.3% xylan could be adsorbed on pulp. This behavior could be due to a decrease in the mutual repulsion between charged groups of xylan and cellulosic fiber, allowing a higher adsorption by non-electrostatic affinity, as was discussed by Fleer (1993) in his general theory of polyelectrolyte adsorption. On the other hand, the increment in ionic strength could also affect the solubility of xylan, since the polymer solvency has a great influence on the driving force of adsorption.
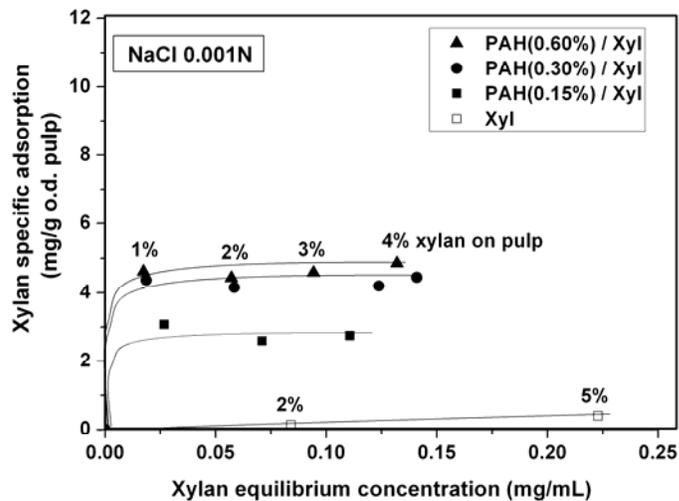
Fig. 3. Xylan specific adsorption on untreated and on previously PAH treated pulps as a function of the xylan equilibrium concentration at pH 7.5 and NaCl 0.001N. Dosages of the commercial xylan used are indicated in the plot (% xylan on pulp).
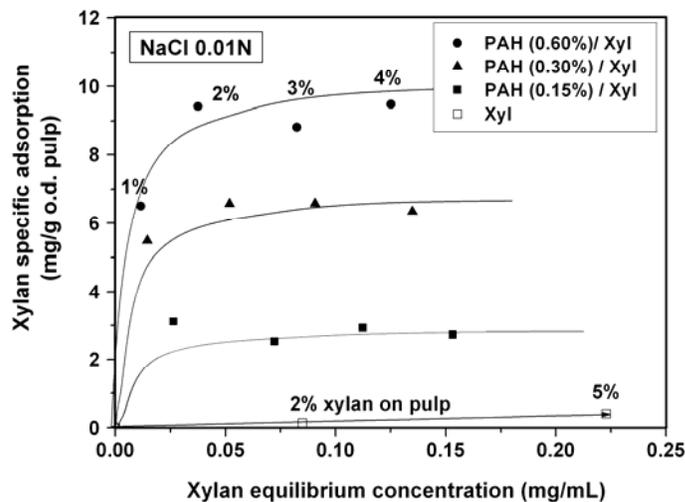
Fig. 4. Xylan specific adsorption on untreated and on previously PAH treated pulps as a function of the xylan equilibrium concentration at pH 7.5 and NaCl 0.01N. Dosages of the commercial xylan are indicated in the plot (% xylan on pulp). In this case, the dosage 0.3 % PAH on pulp corresponds to saturation of fiber surface charges when the ionic strength corresponds to 0.01N NaCl.
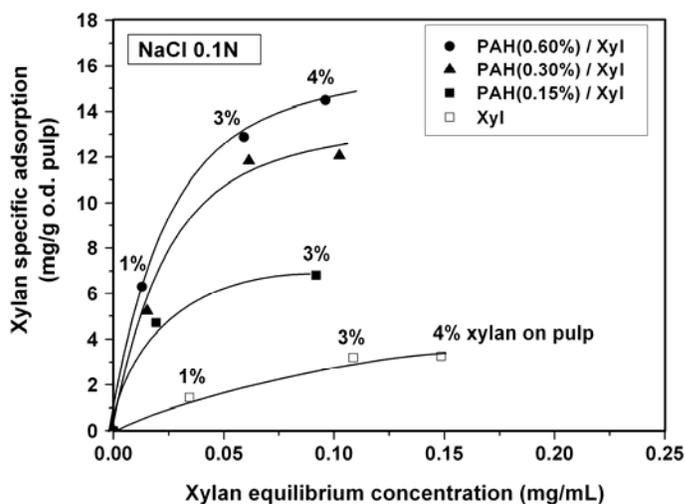
Fig. 5. Xylan specific adsorption on untreated and on previously PAH treated pulps as a function of the xylan equilibrium concentration at pH 7.5 and NaCl 0.1N. Dosages of the commercial xylan are indicated in the plot (% xylan on pulp).
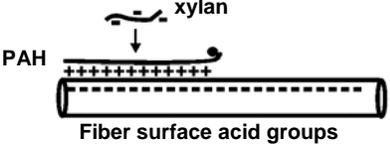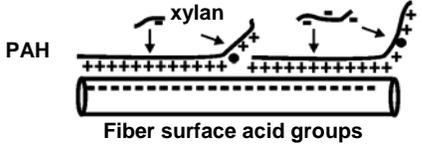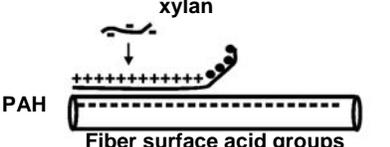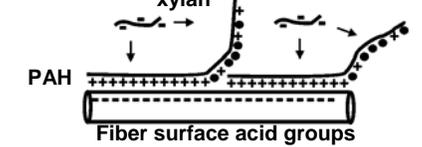
The figures also show that the amount of xylan adsorbed was significantly increased when the fibers had been previously treated with PAH. The amount of xylan adsorbed as a second layer depended on the amount of PAH previously adsorbed. The higher the amount of PAH adsorbed, the higher the amount of xylan adsorbed in the second layer. In particular, for a dosage of 1.0 % of commercial xylan on pulp, 65% of this xylan was adsorbed when pulp was previously treated with 0.6% PAH on o.d. pulp (PAH(0.60%)) in 0.01N NaCl or 0.1N NaCl. The figures also show that, in general, the increase in ionic strength leads to an increase in the amount of xylan adsorbed as a second layer.

Taking into account the results shown in Figs. 3 and 4, the adsorption of PAH and xylan at 0.01N NaCl and 0.001N NaCl is idealized in Fig. 6. The amount of fiber surface acid groups considered is 24 μeq/ g pulp, and the amount of PAH adsorbed on pulp is 12 μeq/g PAH for cases I and III, and 29 μeq/g PAH for cases II and IV, which corresponds to PAH dosages of 0.15% and 0.60 % PAH on pulp, respectively, when the ionic strength is 0.01N NaCl.

When the amount of PAH adsorbed is half of the fiber saturation level (12 μeq/g PAH), the PAH is adsorbed in flat form (case I). The increase in ionic strength from 0.001N to 0.01N NaCl (case III), reduces the PAH charge density from 11 μeq/g PAH to 8 μeq/g PAH, and thus, more mass is necessary to block the same amount of fiber surface charges. Bare fiber surface has no interaction with xylan and thus, it can be assumed that xylan is adsorbed only on the PAH layer. Xylan probably competes against anionic fiber charge for the electroadsorption onto the PAH.

When the amount of PAH adsorbed is more than the saturation level (29 μeq PAH/g pulp, cases II and IV), the PAH is adsorbed with loops and tails dangling in solution. Here, xylan can be adsorbed on the segments of PAH adsorbed, and also on the charges existing in the free segments of the PAH. The contribution of these free chain ends is higher for 0.01N NaCl (case IV), probably because they are longer and they have higher flexibility.

It is expected that when the ionic strength is 0.1N NaCl, the amount of xylan adsorbed increases due to the additional adsorption by non-electrostatic affinity or due to a decrease in the xylan solubility.

	Dosages: **PAH (half of the saturation level)** **1% Xyl on pulp**	**Dosages:** **PAH(double of the saturation level)** **1% Xyl on pulp**
NaCl 0.001N	**PAH adsorbed:** 1.1 mg /g pulp ~ 12 µeq/g pulp **Xylan adsorbed:** 3 mg/g pulp ~ 3 µeq/g pulp **Fiber surface acid groups:** 24 µeq/g pulp I	**PAH adsorbed:** 2.7 mg / pulp ~ 29 µeq/g pulp **Xylan adsorbed:** 4 mg/g pulp ~ 4 µeq/g pulp **Fiber surface acid groups:** 24 µeq/g pulp II
NaCl 0.01N	**PAH adsorbed:** 1.5 mg / pulp ~ 12 µeq/g pulp **Xylan adsorbed:** 3 mg/g pulp ~ 3 µeq/g pulp **Fiber surface acid groups:** 24 µeq/g pulp III	**PAH adsorbed:** 3.6 mg / pulp ~ 29 µeq/g pulp **Xylan adsorbed:** 6 mg/g pulp ~ 6 µeq/g pulp **Fiber surface acid groups:** 24 µeq/g pulp IV

Fig. 6. Idealized models for adsorption of polyelectrolyte onto fiber surfaces at different ionic strength and pH 7.5, considering the results obtained in Figures 3 and 4. For the scheme, the following charge densities are considered for the polyelectrolytes: 8 µeq /mg PAH in 0.01N NaCl, 11 µeq /mg PAH in 0.001N NaCl, and 1 µeq /mg xylan. The pulp surface charge considered is 24 µeq /g pulp (according to Figure 1). In PAH polymer, amine groups are indicated as ionized (**+**) or non.ionized (●). In xylan polymer, charges are indicated (**-**).

Effects of PAH/xylan addition on pulp swelling and paper strength
   Table 2 shows the dosages of PAH and xylan used for studying the effects of the dual-polyelectrolyte adsorption on pulp swelling and paper tensile strength.

Table 2. Conditions Used for Pulp Treatments with PAH and Xylan at 0.5% Pulp Consistency, pH 7.5, and 0.01N NaCl

TREATMENTS	FIRST LAYER	SECOND LAYER
	PAH dosage (% on o.d. pulp)	Xylan dosage (% on o.d. pulp)
Ref	-----	----
PAH (0.30%)	0.30	----
PAH (0.30%) /Xyl	0.30	1.0
PAH (0.60%) /Xyl	0.60	1.0

        Figure 7 shows that the PAH added at a saturation level slightly reduced the water retention value (WRV). Nevertheless, when xylan was added as the second layer, the WRV obtained depended on the dosage of the PAH used as the first layer. When PAH was added at the saturation level (0.30%) followed by the adsorption of xylan, the pulp

swelling decreased. However, when the double of the saturation level of PAH was added, the WRV slightly improved, probably due to a higher amount of water imbibed within the loops and tails of the PAH adsorbed.
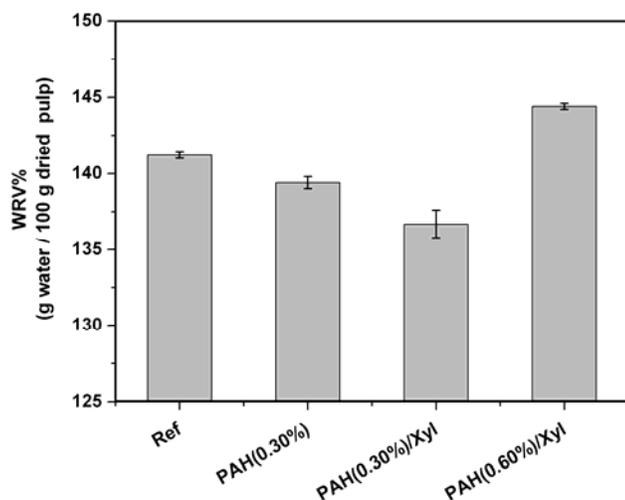
Fig. 7. Effects of PAH and PAH/Xylan treatments on water retention values at pH 7.5 and NaCl 0.01N. The error bars correspond to the standard deviations of the means from three replications of the trial.

Figure 8 shows the effects of the different treatments of PAH and PAH/Xyl (Table 2) on tensile strength for both drying conditions applied. The figure shows that both polyelectrolytes, the PAH and the xylan, contributed to improve paper strength. For standard (unheated) drying conditions, and compared to the reference pulp, the PAH increased the tensile strength by approximately 13%, while the dual-polyelectrolyte adsorption increased this property by 24% and 31%, when PAH(0.30%)/Xyl and PAH(0.60%)/Xyl were adsorbed on pulp, respectively.

Figure 8 also shows a slight improvement in tensile strength for all cases when the additional drying treatment was applied (120ºC), and a trend similar to that shown for the standard drying conditions. Although several authors showed increments in paper strength due to reactions of PAH functional groups with fibers, under the mild drying conditions used in this work (120ºC for 10 min) additional improvements due to the PAH were not observed.

Lingström and Wågberg (2008) compared the effects on tensile strength of the PAH/PAA system with the pDADMAC/poly(styrene sulfonate) (PSS) system, where both polyelectrolytes are strong and produce thinner films. According to these authors, the number of free chain ends (tails) is important for the development of strong adhesion between polyelectrolyte multilayer covered surfaces.

In our case, both PAH and xylan are weak polyelectrolytes, and xylan has a low charge density, so a thick bilayer can be expected, which is favorable to strength enhancements.

For future work, the fast and effective adsorption of xylan when a cationic polyelectrolyte is previously adsorbed encourages studying the effects of a dual-polymer

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adsorption of other cationic polyelectrolytes with amine group, including natural ones such as chitosan.
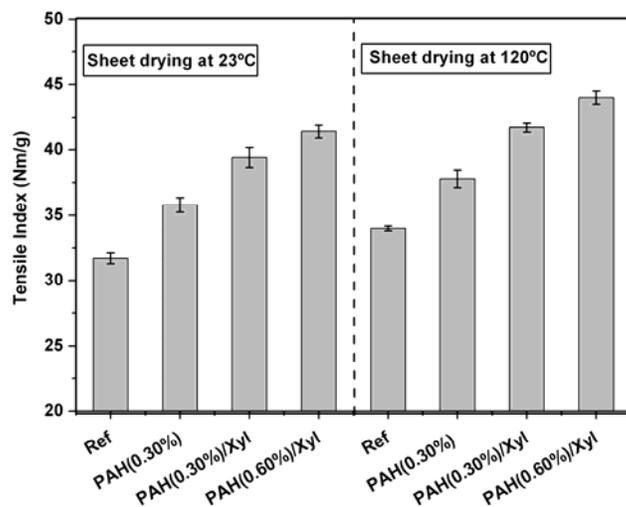
Fig. 8. Tensile strength as a function of the different treatments at 23ºC or 120ºC, pH 7.5 and 0.01N NaCl. The error bars correspond to the standard deviations of the means from ten replications of the trial.

CONCLUSIONS

1. Kinetics of medium molecular mass PAH adsorption on a recycled unbleached softwood kraft pulp at pH 7.5 and 0.01N NaCl indicates that at short times (lower than 30 min) the adsorption is restricted to the external fiber surface. Nevertheless, at longer times, PAH penetrates into the cell walls of fibers.
2. Xylan's adsorption isotherms on untreated pulp show that 0.3% of xylan can be adsorbed on pulp when the ionic strength is 0.1N. At lower ionic strength, the amount of xylan adsorbed is significantly lower.
3. Pulp pretreatment with PAH makes it possible to achieve high levels of xylan adsorption. The increase in ionic strength leads to an increase in the amount of xylan adsorbed as the second layer.
4. The short xylan adsorption times and room temperature needed for this procedure are in contrast to the drastic conditions used in the literature for the direct adsorption of xylan.
5. PAH/Xylan dual-polyelectrolyte treatment increases the pulp swelling when the amount of PAH adsorbed as the first layer is higher than the amount corresponding to the fiber saturation level.
6. The dual polyelectrolyte adsorption on unbleached recycled softwood kraft pulps can be a feasible technique for improving paper tensile strength.

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REFERENCES CITED

DiFlavio, J.-L., Bertoia, R., Pelton, R., and Leduc, M. (2005). "The mechanism of polyvinylamine wet-strengthening," *13th Fund. Res. Symp.*, Cambridge, UK, September 2005, 1293-1316.

Eklund, D. and Lindström, T. (1991). "Colloidal Stability," In: *Paper Chemistry. An Introduction.* DT Paper Science Publications, Finland, Ch. 5, 106-133.

Eriksson, M., Torgnysdotter, A., and Wågberg, L. (2006). "Surface modification of wood fibers using the polyelectrolyte multilayer technique: Effects of fiber joint and paper strength properties," *Ind. Eng. Chem. Res.* 45(15), 5279-5286.

Fleer, G. J., Cohen-Stuart, M. A., Scheutjens, J. M. H. M., Cosgrove, T., and Vincent, B. (1993). "Electrostatic effects: Charged surfaces and polyelectrolyte adsorption," In: *Polymers at Interfaces*, Chapman & Hall, London, Ch. 7, 343-375.

Gimåker, M., and Wågberg, L. (2009). "Adsorption of polyallylamine to lignocellulosic fibres: Effect of adsorption conditions on localisation of adsorbed polyelectrolyte and mechanical properties of resulting paper sheets," *Cellulose* 16, 87-101.

Hodge, J. E., and Hofreiter, B. T. (1962). *Methods in Carbohydrate Chemistry*, Academic Press, New York, San Francisco, and London.

Horvath, A. E., Lindström, T., and Laine, J. (2006). "On the indirect polyelectrolyte titration of cellulosic fibers. Conditions for charge stoichiometry and comparison with ESCA," *Langmuir* 22(2), 824-830.

Horvath, A. T., Horvath, A. E., Lindström, T., and Wågberg, L. (2008). "Diffusion of cationic polyelectrolytes into cellulosic fibers," *Langmuir* 24, 10797-10806.

Hubbe, M. A., Jackson, T. L., and Zhang, M. (2003). "Fiber surface saturation as a strategy to optimize dual-polymer dry strength treatment," *Tappi J.* 2(11), 7-12.

Hubbe, M. A., Venditti, R. A., and Rojas, O. J. (2007). "What happens to cellulosic fibers during papermaking and recycling? A review," *BioResources* (http://www.bioresources.com), 2(4), 739-788.

Katz, S., Beatson, R. P., and Scallan, A. M. (1984). "The determination of strong and weak acidic groups in sulfite pulps," *Svensk Papperstidning* 87, 48-53.

Köhnke, T., and Brelid, H. (2009). "Adsorption of cationized barley husk xylan on kraft pulp fibres: Influence of degree of cationization on adsorption characteristics," *Cellulose* 16, 1109-1121.

Köhnke, T. (2010). "Adsorption of xylans on cellulosic fibres - Influence of xylan composition on adsorption characteristics and kraft pulp properties," *PhD. Thesis. Chalmers University of Technology*, Göteborg, Sweden.

Köhnke, T., Lund, K., Brelid, H., Westman, G. (2010). "Kraft pulp hornification: A closer look at the preventive effect gained by glucuronoxylan adsorption," *Carbohydrate Polymers* 81, 226-233.

Linder, A., Bergman, R., Bodin, A., and Gatenholm, P. (2003) "Mechanism of assembly of xylan onto cellulose surfaces," *Langmuir* 19, 5072-5077.

Lingström, R., and Wågberg, L. (2008). "Polyelectrolyte multilayers on wood fibers: Influence of molecular weight on layer properties and mechanical properties of papers from treated fibers," *J. Colloid Interface Sci.* 328, 233-242.

Lloyd, J. A., and Horne, C. W. (1993). "The determination of fibre charge and acidic groups of radiata pine pulps," *Nordic Pulp Paper Res. J.* 8(1), 48-57.

Magaton, A., Colodette, J., Pilo-Veloso, D. and Gomide, J. (2011). " Behavior of eucalyptus wood xylans across kraft cooking," *J. Wood Chem. Technol.* 31(1), 58-72.

Mocchiutti, P., and Zanuttini, M. A. (2005). "A useful equation for estimating the surface charge of pulp fibers," *Tappi J.* 4(5), 18-22.

Mocchiutti, P., and Zanuttini, M.A. (2007). "Key considerations in the determination of polyelectrolyte concentration by the colloidal titration method," *BioResources* (http://www.bioresources.com) 2(3), 399-407.

Mocchiutti, P., Galván, M. V., Inalbon, M. C., and Zanuttini, M. A. (2011). "Improvement of paper properties of recycled unbleached softwood kraft pulps by poly(allylamine hydrochloride)," *BioResources* (http://www.bioresources.com) 6(1), 570-583.

Mortimer, J. C., Miles, G. P., Brown, D. M., Zhang, Z., Segura, M., Weimar, T., Yu, X., Seffen, K. A., Stephens, E., Turner, S. R. and Dupree, P. (2010). "Absence of branches from xylan in *Arabidopsis gux* mutants reveals potential for simplification of lignocellulosic biomass," *PNAS*, 107(40), 17409-17414.

Ren, J., Peng, F., Sun, R., and Kennedy, J. (2009). "Influence of hemicellulosic derivatives on the sulfate kraft pulp strength," *Carbohydrate Polymers* 75, 338-342.

Salyers, A. A., Gherardini, F., and O'Brien, M. (1981). "Utilization of xylan by two species of human colonic *Bacteroides*," *Appl. Environ. Microbiol.* 41(4), 1065-1068.

Silva, T. C. F., Colodette, J. L., Lucia, L. A., de Oliveira, R. C., Oliveira, F. N., and Silva, L. H. M. (2011). "Adsorption of chemically modified xylans on eucalyptus pulp and its effect on the pulp physical properties," *Ind. Eng. Chem. Res.* 50(2), 1138-1145.

Sixta, H., Guetsch, J., Nousiainen, T., and Wollboldt, P. (2011). "Progress and challenges in the isolation of xylan from Eucalyptus wood," *5th International Colloquium on Eucalyptus Pulp,* May 9-12. Porto Seguro, Bahia, Brazil.

Sjöström, E. (1993). *Wood Chemistry. Fundamentals and Applications. Second Edition.* Academic Press Inc., San Diego, California, USA.

Sun, R. C., Sun, X. F., and Tomkinson, J. (2004). "Chapter 1: Hemicelluloses and their derivatives," In: *Hemicelluloses: Science and Technology,* ACS Symposium Series 864, USA, Ch. 1, 2-22.

Tanaka, H., and Ichiura, H. (1999). "A novel and simple method for determining the cationic demand of suspensions using chromophoric labeled cationic polymers. *Colloid and Surfaces A: Physicochemical and Engineering Aspects* 159, 103-107.

Terayama, H. (1952). "Method of colloid titration (a new titration between polymer adsorption)," *Journal of Polymer Science* 8(2), 243-253.

bioresources.com

Wågberg, L., Forsberg, S., Johansson, A., and Juntti, P. (2002). "Engineering of fibre surface properties by application of the polyelectrolyte multilayer concept. Part I: Modification of paper strength," *J. Pulp Pap Sci*. 28, 222-228.