IMPROVEMENT OF PAPER PROPERTIES OF RECYCLED UNBLEACHED SOFTWOOD KRAFT PULPS BY POLY(ALLYLAMINE HYDROCHLORIDE)

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Polyelectrolytes containing amine functional groups such as PAH (poly(allylamine hydrochloride)) can be useful, under certain conditions, for improving paper strength. In this work, the charge density of PAH was determined at different pH and ionic strengths; PAH adsorption onto the cellulosic fibers was characterized, and the effects of low PAH dosage on the papermaking properties were evaluated. It was found that the ionization of PAH is complete in acid media, but it is partial and depends on the ionic strength in neutral media. The adsorption isotherms of PAH on a recycled pulp from kraft liner allowed us to determine the amount needed to saturate the adsorption capacity of the fibers. For the three ionic strengths analyzed, the swelling of the fibers decreased when PAH was added in an amount corresponding to saturation (0.23% PAH on dried pulp). Nevertheless, the swelling was recovered when the amount of PAH was the double the saturation level (0.46% PAH on dried pulp). At these levels of addition, the papermaking properties were clearly improved, especially compressive strengths SCT (short compressive test) and CMT (concora medium test). The Page equation of tensile strength showed that PAH improved the shear bond strength, while the relative bonding area slightly decreased.

Keywords: Adsorption isotherms; Amine group-containing polymers; Charge density; Page equation; Recycling

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INTRODUCTION

The total demand of fibers for the paper industry world-wide will grow significantly in the coming years. The projection is very sensitive to the assumed demand development in China. It is estimated that 460 million tons will be required in 2015, an increase of 90 million compared to 2006. For this growth, recycled paper is expected to provide approximately 56% of the needed fiber (Dochnal 2008).

Recycled papers have lower strength compared with their corresponding virgin papers. The loss of pulp swelling (Stone and Scallan 1968; Lundberg and de Ruvo 1978), the reduction in inter-fiber bonding (Nazhad 2005; Gurnagul and Page 2001), and morphological changes such as curl and microcompressions (Page et al. 1985) are some of the causes for paper strength reduction. Hubbe et al. (2007) identified these physical changes as inherent to the drying process of the fibers themselves, in order to differentiate them from the chemical changes that occur as a consequence of the presence of contaminants such as inks, deinking agents, and papermaking additives.

In spite of the detrimental physical and chemical effects of recycling, for boxboard and other paper grades, the recycled fibers present several advantages compared to virgin fibers. These advantages include higher dimensional stability, lower apparent density, and faster drying (Hubbe et al. 2007). The disadvantage of lower paper strength can be overcome using wet-end additives.

The addition of a cationic polyelectrolyte with amine functional groups such as PAH (Fig. 1) can be an option for improving paper strength. PAH can also be useful for modifying the surface hydrophobicity of the fibers. Lee et al. (2010) evaluated the hydrophobicity of papers by means of contact angle, and they found a clear increase when the PAH was adsorbed in the outermost layer of a multilayer system. On the other hand, Lingström et al (2007), using the dynamic contact angle analyzer, found a reduction in wettability of fibers when PAH was the outermost layer adsorbed.

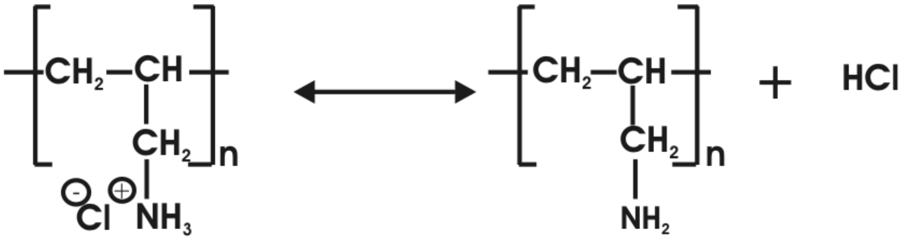

Fig. 1. Chemical structure of PAH poly(allylamine hydrochloride)

PAH is a weak polyelectrolyte. In its nonionized state, the amine groups form hydrogen bonds that are stronger than the hydroxyl groups from the carbohydrates (Emsley 1980). In addition, 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 bonds type (DiFlavio et al. 2005; Gimåker and Wågberg 2009).

Gimåker and Wågberg (2009) using different PAH dosages of low and high molecular mass (15 kDa and 150 kDa respectively) on unbleached fibers (kappa 76) found an increase in tensile strength and in strain at break. To obtain these enhancements, these authors found that PAH has to be adsorbed only on the exterior part of the fibers.

To the best of our knowledge, the effects of low dosages of PAH on packaging related properties (CMT and SCT values) of an unbleached pulp, under different ionic strengths, have not been studied yet.

In this work, PAH charge density under different pH and ionic strengths was determined using the colloidal titration method. From the adsorption isotherms of PAH on recycled kraft fibers under different ionic strengths, the amount of PAH necessary to reach the saturation level of the fibers was determined.

The effects of low PAH dosages on the tensile and compressive strengths (SCT and CMT) of the pulp were also determined and, using the Page equation for tensile strength (Page 1969), the changes in the fiber bonded area and the bond strength were estimated.

EXPERIMENTAL

Materials

Polymers

PAH (poly(allylamine hydrochloride)) with an average molecular mass of 56 kDa from Sigma-Aldrich was directly used to prepare a 0.5 g/L solution in deionized water.

KPVS (potassium polyvinyl sulfate) was supplied by AppChem (England) as a 1000 µN solution. A 200 µN KPVS fresh solution in deionized water was used for polyelectrolyte titrations.

Poly-DADMAC (polydiallyldimethylammonium chloride) with an average molecular mass of 400 to 500 kDa from Sigma-Aldrich was used to prepare a 0.0016 N solution in deionized water.

Raw material

The fibrous fraction (R100, i.e. rejected by 100 mesh) of a recycled pulp obtained from an unbleached softwood kraft-liner was used for the study. The kraft-liner (100% virgin fibers and kappa number 91.6) was supplied by Papel Misionero S.A. (Argentina). It was soaked and disintegrated in a standard laboratory disintegrator following the procedure of Mocchiutti et al. (2010). The pulp obtained was screened using a Bauer-McNett classifier according to SCAN-M6:69, and only the R100 fraction was collected. The metallic ions were removed by acid treatment (H_2SO_4 pH 2.0, 30 min) and then washed with distilled water until the pH was between 4.0 and 5.0. Then, the pulp was dewatered and stored until use. The amount of total acidic groups was 105.8 ± 1.8 µeq/g o.d. pulp (oven dried pulp) according to the conductometric titration (Katz et al.1984; $NaHCO_3$ was used instead of NaOH according to Lloyd and Horne 1993), and the amount of surface acid groups was 15.9 ± 0.6 µeq/g o.d. pulp determined by the poly-DADMAC adsorption isotherm procedure (Mocchiutti and Zanuttini 2005).

Polyelectrolyte Titrations

PAH concentration and charge density were determined by the colloidal titration method using KPVS as titrant. This method was first proposed by Terayama (1952) for strong highly charged polyelectrolytes, and then it was applied by Gärdlund et al. (2007) and Gimåker and Wågberg (2009) for weak polyelectrolytes. The OTB (o-toluidine blue) indicator was added to the PAH solution in NaCl 0.01N or 0.001N and the pH was adjusted to 2.0, 3.5, or 7.5 with HCl or NaOH. The indicator color change was on-line measured by a spectrophotometric method (Mocchiutti and Zanuttini 2007).

PAH Adsorption Isotherms

Initially, the pulp was converted to the sodium form. The pulp was washed with $NaHCO_3$ 0.01N at 1.0 % pulp consistency, and then the pH was adjusted to 9.0 with NaOH. After 30 min the pulp was washed until pH 7.5. The adsorption isotherms were carried out at that pH.

Wet samples of 0.5 g of o.d. pulp in sodium form were added to 100 mL solutions of different concentrations of PAH at pH 7.5 and NaCl 0.01N or NaCl 0.001N. Each suspension was stirred for 30 min at 25ºC to reach the adsorption equilibrium. On the filtrate, the remaining amount of polyelectrolyte was determined by the colloidal titration method.

When the treatments were carried out at 0.1N NaCl, neither the PAH charge density nor the adsorption isotherm could be determined using the colloidal titration method because, according to Eklund and Lindstrom (1991) and Sjödin and Ödberg (1996), the critical NaCl concentration in a titration medium, above which no color change of the indicator can be observed, is 0.02N NaCl.

Pulp Treatments with PAH and Handsheet Preparation

Table 1 shows the PAH dosages used for the treatments. They correspond to the amount added to saturate the fibers (0.23% on o.d. pulp) and the double of that amount (0.46% on o.d. pulp), according to the adsorption isotherms shown below.

Table 1. PAH Dosages Used for Pulp Treatments at pH 7.5, NaCl 0.001N, 0.01N and 0.1N

Pulp identification	PAH dosages (% on o.d. pulp)
Control (CON)	----
Saturation (SAT)	0.23
Double (SATx2)	0.46

Treatments were carried out at 0.5% pulp consistency, pH 7.5, and different ionic strengths (NaCl 0.1N, 0.01N, and 0.001N). The PAH solution was added to the pulp slurry at the corresponding pH and ionic strength, and left in that condition for 30 min. Then, the pulp suspension was diluted to 0.3% pulp consistency (keeping the pH and the ionic strength of the medium), and water retention value (WRV), a measure of the swelling of the pulp (the relative weight of water after centrifugation at 1750 g for 30 min). Handsheets of 120 g/m^2 were prepared according to SCAN standard methods but using deionized water with the corresponding levels of NaCl and at pH 7.5. The blotters used in sheets preparation were previously wetted in the corresponding solution. Sheets were dried under standard conditions, and then treated in an oven at 120 ºC for 10 min. Apparent density (Tappi 411 om-97), tensile strength (Tappi T494 om-01), and the compressive strengths SCT (Tappi T826 pm-92) and CMT (Tappi T809 om-99) were evaluated.

During the time in which the fibers were treated and handsheets were prepared (less than 3 hours), it can be assumed that polyelectrolyte penetration into the walls of the fibers did not take place. Gimåker and Wågberg (2009) found that the combination of high ionic strength and long adsorption time (24 hours) were necessary to detect PAH penetration throughout the fibre cell wall of a never-dried unbleached softwood kraft pulp.

Determination of the Bonding Capacity of the Fibers

The bonding capacity was determined using the Page equation for tensile strength (Page 1969), which was rearranged by Gurnagul et al. (2001) as:

$$\left[\frac{1}{T}-\frac{9}{8Z}\right]^{-1}=\frac{b}{k}-\left[\frac{b}{kSo}\right]S \qquad (1)$$

In the equation given above, the first term, $[(1/T) - 9(8Z)]^{-1}$, is the Page bonding strength index (Nm/g), and T and S are the tensile strengths and scattering coefficients of sheets prepared at different wet pressing pressure, Z is the zero-span tensile index, b is the shear bond strength per unit bonded area (it depends on drying temperature, and on the amount of polyelectrolyte adsorbed on the fibers surface), S_0 is the scattering coefficient of a sheet of unbonded fibers, and k is the coefficient related to the fiber morphology and weight. The value of k was assumed to be unchanged by PAH treatments.

For determining the bonding capacity of the fibers, handsheets of lower grammage (60 g/m^2) were prepared according to the standard method, with the exception of the pressing pressure, which was varied from 0.1 MPa to 10 MPa in geometric increments. Then, elastic modulus and tensile strength using the INSTRON 3344 universal tester and the light scattering coefficient at 681 nm (SCAN C27:76) using the Carl Zeiss Elrepho were determined. Zero-span tensile strength was determined according to TAPPI T231 cm-96 using the Clark attachment.

RESULTS AND DISCUSSION

PAH Charge Density

Figure 2 shows the PAH charge density at different pH and ionic strengths. As expected, the degree of ionization in neutral medium was lower than in acid medium. At pH 3.5, the PAH charge density was 11.18 meq /g PAH and 11.55 meq /g PAH for NaCl 0.01N and NaCl 0.001N, respectively. These values are similar to those obtained at pH 2.0, indicating that at pH 3.5, the PAH was already fully charged. These charge density values are higher than the theoretical charge 10.69 meq /g PAH that can be calculated, considering the original reagent as 100% in its ionized form (C_3H_8ClN). Nevertheless, if a fraction of the original reagent is in its nonionized form (C_3H_7N), the quantity of the chargeable groups per gram of original reagent can be higher.

At pH 7.5, the charge density strongly depends on the ionic strength of the liquid media. In NaCl 0.01N was 8.31 meq /g PAH, and in NaCl 0.001N it was 10.57 meq /g PAH.

To validate the methodology for determining the PAH charge density, which is based on the polyelectrolyte titration method, different PAH concentrations at two ionic strengths were evaluated. Figure 3 shows the PAH concentration at pH 7.5 as a function of the PAH concentration at pH 3.5 (where the PAH is fully charged) for three levels of PAH and two different ionic strengths. According to the linear regressions, the degree of ionization of PAH against KPVS at pH 7.5 was 76% and 92% for ionic strengths 0.01N and 0.001N NaCl, respectively. The figure also shows that the degree of ionization does not depend on PAH concentration.

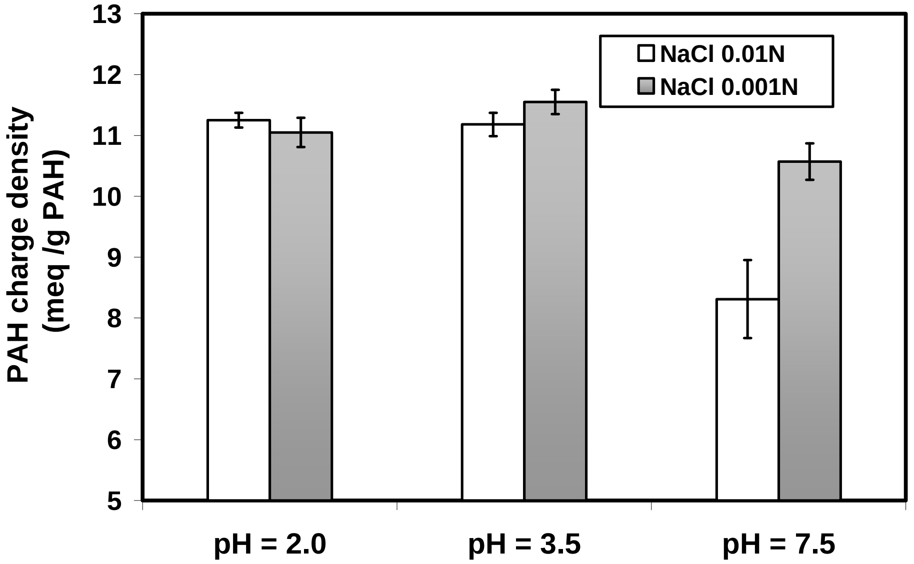

Fig. 2. PAH charge density as a function of the different pHs and ionic strengths determined by the colloidal titration method. The error bars correspond to the standard deviations of the means from three replicates of the trial.

The degree of ionization of 92%, obtained at pH 7.5 and 0.001N NaCl, is similar to the 90% found by Choi and Rubner (2005) who analyzed the influence of pH on the charge density of weak polyelectrolyte on multilayer growth using Fourier transform infrared (FTIR) analyses of dry films of PAH and anionic polyelectrolytes with high charge density such as PAA (polyacrylic acid), KPVS, and SPS (poly(sodium 4-styrene sulfonate).

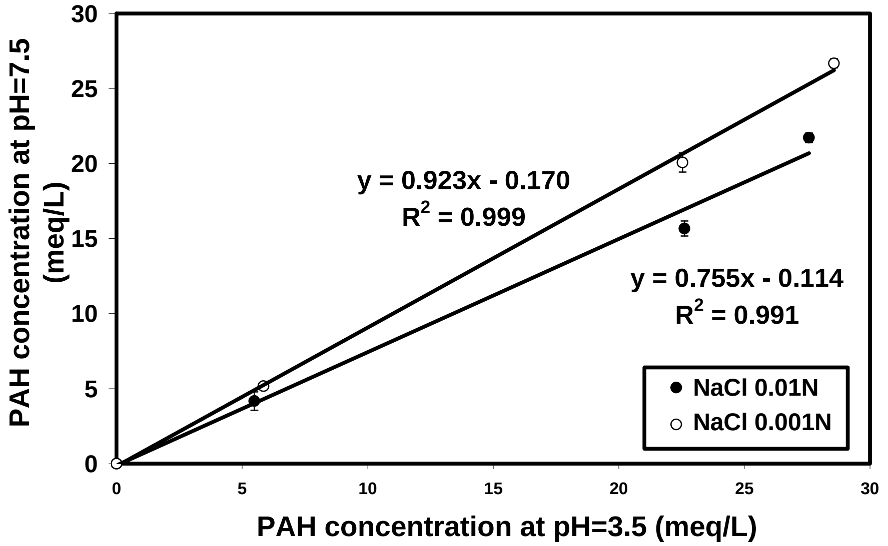

Fig. 3. PAH concentration at pH 7.5 as a function of PAH concentration at pH 3.5 (fully charged) for two ionic strengths. The linear regression indicates a slope (degree of ionization) of 0.76 for NaCl 0.01N and 0.92 for NaCl 0.001N. The error bars correspond to the range obtained from two replications of the trial.

Characterization of the PAH Adsorption onto the Fibers

Effect of ionic strength

Figure 4 shows the PAH adsorption isotherms at pH 7.5 in 0.01N NaCl and 0.001N NaCl. For these ionic strengths, the fiber saturation levels with PAH were similar in terms of accessible acid groups (16.3 μeq/g dried pulp and 16.6 μeq/g dried pulp, respectively). Nevertheless, because the PAH charge density was different at these two ionic strengths, the mass of polyelectrolyte adsorbed was different (0.20% and 0.15% of PAH on pulp, respectively).

The described behavior was observed in spite of the fact that the increment in ionic strength produces an increment in the polyelectrolyte flexibility, and thus, in the accessibility to the fiber charges, and also a reduction in electrostatic attraction between charged groups on the fiber and charged groups on the polyelectrolyte.

For 0.01N NaCl, the amount of PAH adsorbed was 16.3 μeq PAH/ g pulp (0.20% PAH on pulp), which corresponds to a dosage of 0.23% PAH on pulp. This dosage was adopted as the saturation level dosage (SAT) to evaluate swelling of the pulp and papermaking properties.

On the other hand, taking into account that the total amount of acid groups was 105.8 μeq/g o.d. pulp and that PAH only reached 15% of these groups, it can be considered that PAH was adsorbed on the more exterior parts of the fibers. Nevertheless, confocal fluorescence microscopy analysis (Gimåker and Wågberg 2009) or ESCA analysis (Horvarth et al. 2006) are required to confirm this assumption.

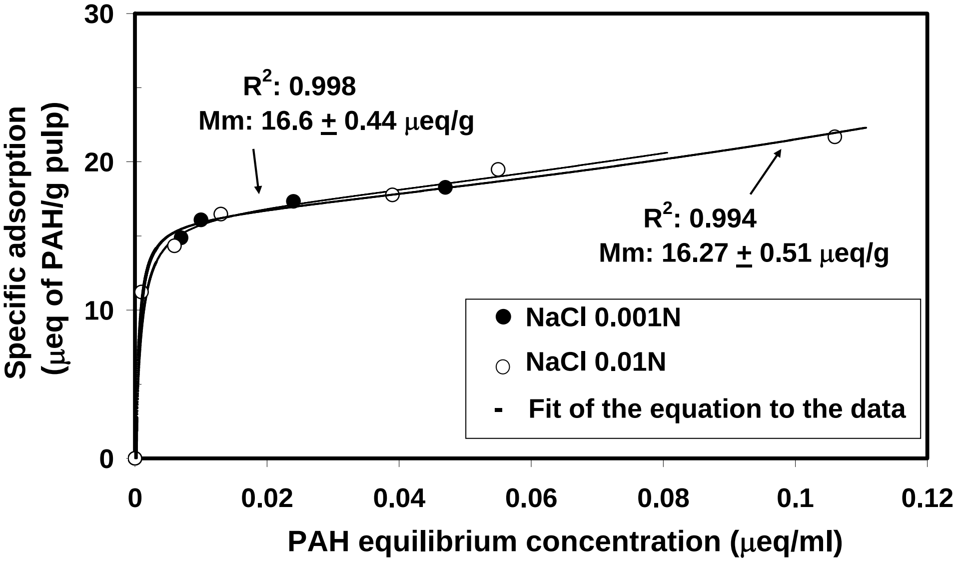

Fig. 4. PAH adsorption isotherms at pH 7.5 and NaCl 0.01N or NaCl 0.001N. The equation parameters are as follows: Mm (related to the specific surface charge of the fibers) and R^2 (the determination coefficient of the equation). The statistical hypothesis test indicates no significant differences at the 95% confidence level (p= 0.3226, higher than 0.05) in the amount of PAH adsorbed at the two ionic strength levels.

Effects of PAH addition on pulp swelling and papermaking properties

Figure 5 shows the water retention values at different ionic strengths after the addition of 0.23% and 0.46% of PAH on pulp (corresponding to the saturation dosage and to the double of the saturation dosage, respectively). The higher the ionic strength, the lower was WRV. The figure also shows that PAH added at a saturation level reduced WRV. Nevertheless, when 0.46% of PAH was added at medium or high ionic strength, WRV was recovered to the original value.

Swerin et al. (1990) and Fors (2000) found that WRV is reduced when strong cationic polyelectrolytes are adsorbed on pulps. Fors (2000) compared the WRV results of the pulp in sodium form with the WRV results of the pulp treated with poly-DADMAC, and she concluded that a strong polyelectrolyte blocks the surface charges, and thus produces deswelling.

In the case of PAH, amine groups can have different roles depending on whether they are ionized or not. It is possible that, when more PAH than the saturation level is added on pulp, the deswelling effect after the electrosorption of the polyelectrolyte can be compensated for by the swelling effect of the nonionized amine groups present in the free portion of the polymer dangling in solution

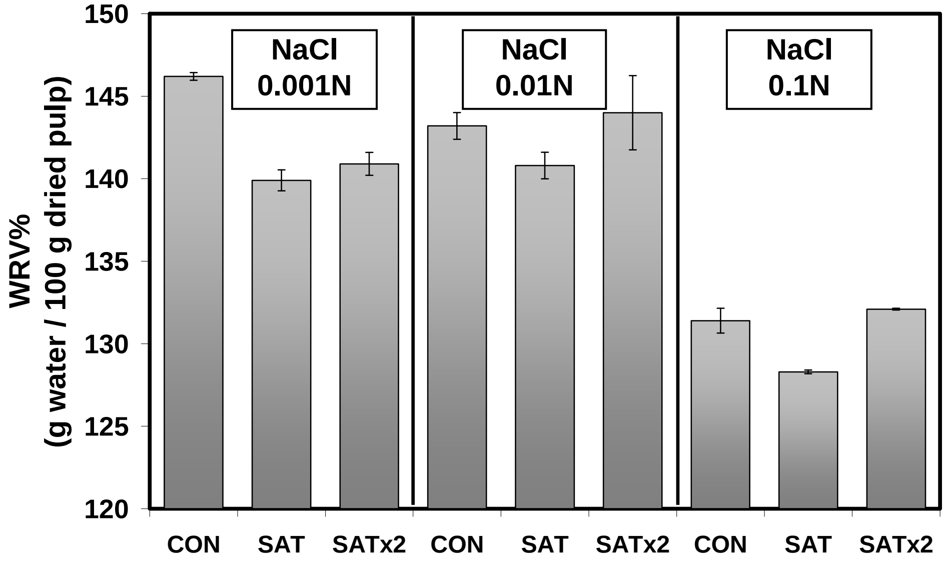

Fig. 5. Effects of PAH treatments on water retention value for different ionic strengths and pH 7.5. CON: without PAH, SAT: 0.23% PAH on o.d. pulp, SATx2: 0.46% PAH on o.d. pulp. The error bars correspond to the standard deviations of the means from three replications of the trial.

Figure 6 shows the effects of PAH treatments on tensile strength. The higher the PAH dosage, the higher the tensile strength. An increase of 23% was obtained when 0.46% of PAH was added on the fibers in NaCl 0.01N.

The apparent densities of the sheets were also determined. In NaCl 0.01N, this property was not changed by the PAH treatments (401 kg/m^3, 402 kg/m^3 and 404 kg/m^3 for the treatments CON, SAT and SATx2, respectively). The same results were obtained for all the others ionic strength conditions (data not shown). Therefore, if the apparent density is considered as indicative of the bonded area level, the improvement in the tensile strength can be attributed to an increase in specific bond strength. This concept is discussed below, using the Page equation of tensile strength.

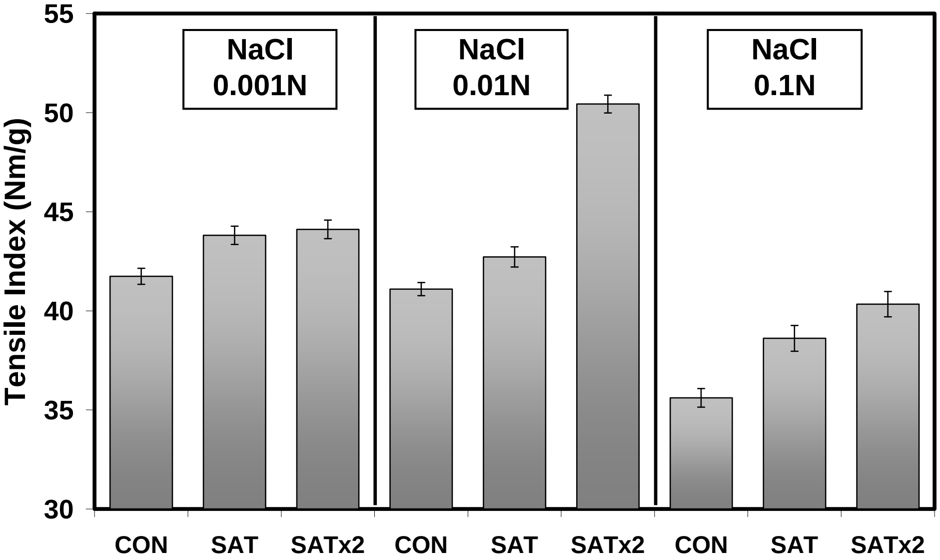

Fig. 6. Effects of PAH treatments on tensile strength for different ionic strengths and pH 7.5. CON: without PAH, SAT: 0.23% PAH on o.d. pulp, SATx2: 0.46% PAH on o.d. pulp. The error bars correspond to the standard deviations of the means from ten replications of the trial.

Figures 7 and 8 show that the addition of PAH produced favorable effects on the SCT and the CMT compressive strengths, which are clearer and higher than the tensile strength improvements, especially for the CMT results. For NaCl 0.01N and 0.46% of PAH, CMT-value was increased 132%.

It is accepted that when polyelectrolyte concentration is higher than the saturation level, the adsorption in tails and loops form takes place. Mocchiutti and Zanuttini (2005) proposed an equation based on the competition between stoichiometric (in flat form) and non-stoichiometric adsorption (loops and tails form) of poly-DADMAC on pulp.

It is possible that, when the double of the saturation level of PAH was added on pulp, the thickness of the adsorbed layer was increased. This adsorbed layer had different abilities to improve bonding. When the ionic strength was 0.01N NaCl, the amount of amine groups in non-ionized state was higher than at 0.001N NaCl, probably producing a higher amount of hydrogen bonds, and as a consequence, stronger bonding strength.

Finally, the mechanism of bonding enhancement by PAH at pH 7.5 and NaCl 0.01N was studied using the Page equation of tensile strength.

According to Gurnagul et al. (2001), to use this equation, the elastic modulus related to the fiber deformations such as curl, crimps, and microcompressions should remain unchanged during the treatments applied. Figure 9 shows that this requirement is satisfied for the PAH treatments at different pressing pressures.

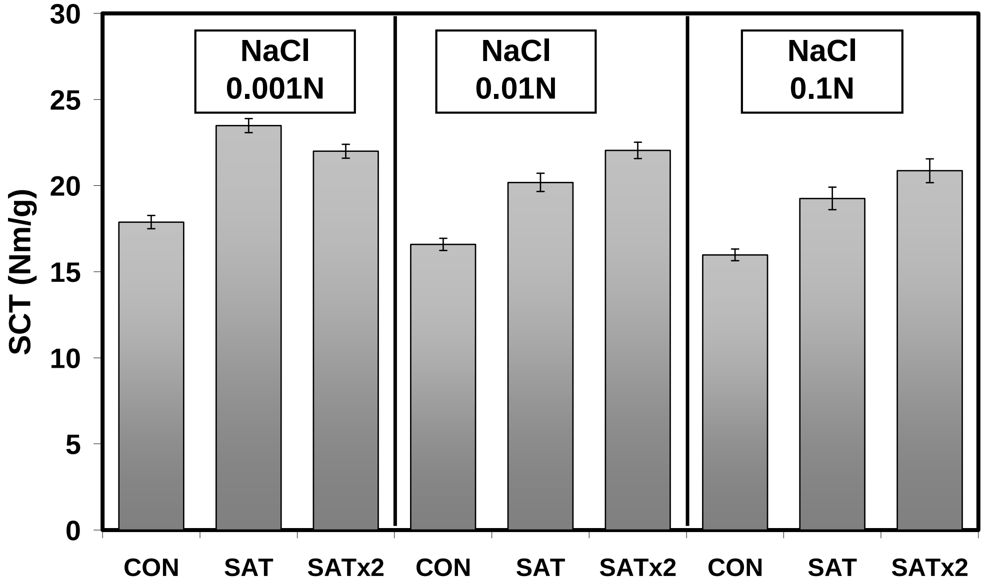

Fig. 7. Effects of PAH treatments on short compressive strength for different ionic strengths and pH 7.5. CON: without PAH, SAT: 0.23% PAH on o.d. pulp, SATx2: 0.46% PAH on o.d. pulp. The error bars correspond to the standard deviations of the means from ten replications of the trial.

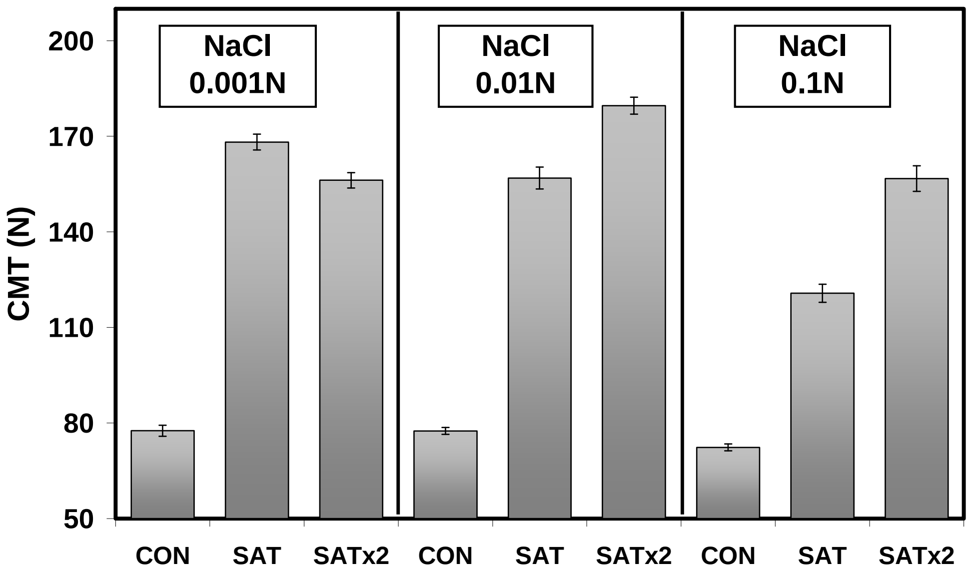

Fig. 8. Effects of PAH treatments on CMT-value for different ionic strengths and pH 7.5. CON: without PAH, SAT: 0.23% PAH on o.d. pulp, SATx2: 0.46% PAH on o.d. pulp. For any level of PAH addition at different ionic strengths the increase in CMT is remarkable. The error bars correspond to the standard deviations of the means from ten replications of the trial.

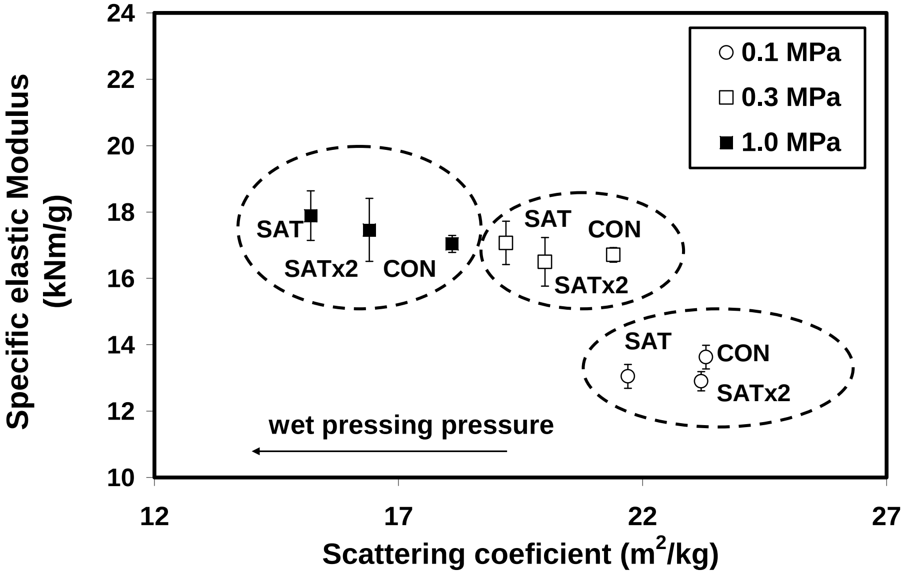

Fig. 9 Specific elastic modulus as a function of the scattering coefficient at different wet pressing pressures for the pulps treated with different amounts of PAH. CON: without PAH, SAT: 0.23% PAH on o.d. pulp, SATx2: 0.46% PAH on o.d. pulp. The error bars correspond to the standard deviations of the means from four replications of the trial.

Figure 10 shows the Page bonding strength index as a function of the scattering coefficient for 0.01N NaCl. The linear regressions indicate acceptable correlation coefficients for the different pulps.

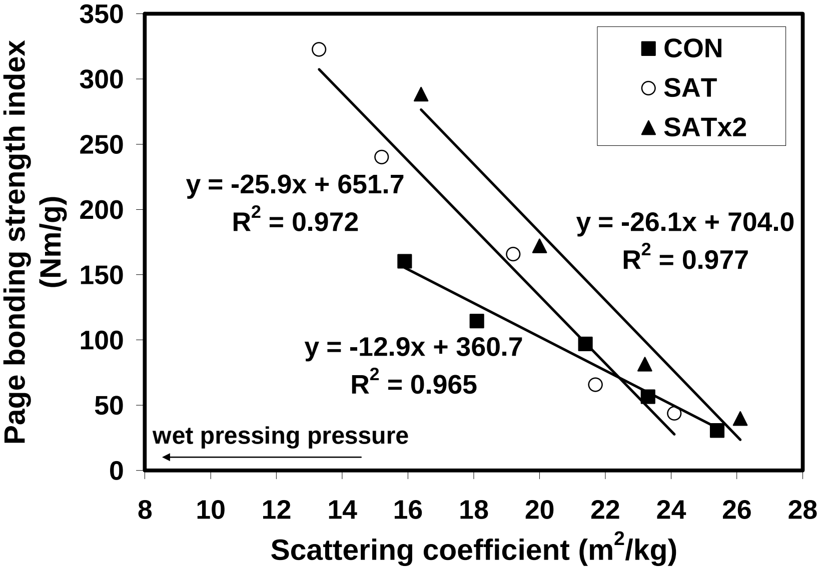

Fig. 10. The Page bonding strength index as a function of the scattering coefficient for an ionic strength of 0.01N NaCl. The addition of 0.23% PAH (SAT) or 0.46% PAH (SATx2) clearly increased the y-intercept value.

Table 2 shows the *y*-intercept and the slope of the linear regressions. Parameter (*b*/*k*), proportional to the shear bond strength, was notably increased by the PAH treatments (81% and 95% when 0.23% PAH and 0.46% PAH were added, respectively), while the relative bonded area only slightly decreased, as expected from the constant density results obtained above.

Table 2. Page Equation Parameters: Shear Bond Strength (*b/k*), Scattering Coefficient of the Sheet of Unbounded Fibers (S_0), Relative Bonded Areas (*RBA*), and the corresponding Coefficients of Determination (R^2) for the Pulps Treated with Different Amounts of PAH in NaCl 0.01N and pH 7.5

Pulp	*y*-intercept[a] (*b/k*) (kN.m/g)	Slope (*b/k*)/S_0	S_0 (m^2/kg)	RBA[b](%)= $\frac{(S_0 - S)}{S_0}$	R^2
CON	361 ± 30	12.9 ± 1.4	27.9	16.6	0.965
SAT	652 ± 48	25.9 ± 2.5	25.2	13.8	0.972
SATx2	704 ± 61	26.1 ± 2.8	27	14.1	0.977

[a] standard deviations of the regression parameters are shown,

[b] RBA results at standard wet pressing pressure (0.3 MPa)

It is concluded that the improvement in paper strength by the addition of PAH is principally due to the enhancement in the shear bond strength.

The improvement in bond strength had a higher impact on the compression properties (SCT and CMT) than on tensile strength. This behavior could be attributed to the higher stiffening of the fiber/fiber joints that PAH produced. Gimåker and Wågberg (2009) found a reduction in the creep rate at 90%RH when 15kDa PAH at low ionic strength was adsorbed on the exterior part of unbleached fibers. They suggested that this behavior could be due to the covalent linkages that PAH can form between the fibers, stiffening the fiber/fiber joint and decreasing their viscous deformation.

CONCLUSIONS

1. At acid pH, PAH ionization is complete, but at neutral pH the ionization is partial and depends on the ionic strength of the medium, being 92% and 76% for the ionic strength 0.001N NaCl and 0.01N NaCl, respectively.
2. The PAH adsorption isotherms obtained at pH 7.5 and at two ionic strengths (0.01N and 0.001N NaCl) show the same level of fiber surface charge saturation.
3. The fiber swelling was decreased when PAH was added in an amount corresponding to the saturation level. Nevertheless, the value was recovered when the amount of PAH added was the double that amount.
4. The addition of low PAH dosages on recycled fibers from kraft liner showed favorable effects on tensile strength and particularly on the compressive strengths SCT and CMT at the three ionic strengths studied. In NaCl 0.01N, the addition of 0.46% of PAH on pulp showed an increase of 23% in tensile strength, 33% in SCT strength and 132% in compressive strength CMT.
5. The Page theory of tensile strength indicated that PAH clearly improved the shear bond strength while the relative bonding area slightly decreased.

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