DUAL-ADSORPTION OF POLY(ALLYLAMINE HYDROCHLORIDE) AND LIGNOSULFONATE ONTO RECYCLED CELLULOSIC FIBERS

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The effects of the dual-polyelectrolyte adsorption of poly(allylamine hydrochloride) (PAH) and lignosulfonate (LS) on a recycled unbleached softwood kraft pulp were studied and the method used for the determination of LS concentration was discussed. Adsorption isotherms of LS on untreated and on previously PAH-treated pulps at neutral pH, and different ionic strengths were built, and the effects of the amount of PAH on LS adsorption were considered. It was found that even at low dosages of PAH, for which fibers remain anionic, high levels of LS adsorption at room temperature and short adsorption time can be achieved. Besides, it was found that the increase in ionic strength also increased the amount of LS adsorbed. The highest values on papermaking properties were obtained using only PAH. Nevertheless, when compared to the reference pulp, the PAH/LS system clearly improved the wet tensile strength and the compressive strength, avoiding paper non-uniformity or charge-reversal problems.

Keywords: recycled unbleached softwood kraft pulp, dual-polymer treatment, poly(allylamine hydrochloride), lignosulfonate, adsorption isotherms, papermaking properties, paper uniformity

INTRODUCTION

The surface of cellulosic fibers can be conveniently modified by the adsorption of polyelectrolytes. Recently, several authors have shown the beneficial effects of the adsorption of cationic polyamines, such as PAH (poly(allylamine hydrochloride)) or PVAm (poly(vinylamine)) on paper strength. Particularly, Gimåker and Wågberg[1] applied high PAH dosages (up to 3% w/w) of different molecular mass onto unbleached fibers to show improvements in tensile strength and in strain at break when the polyelectrolyte had been adsorbed only on the exterior part of the fibers. Then, Mocchiutti *et al.*[2] used low PAH dosages (0.2-0.5% w/w) on a similar kind of pulp and they found clear strength improvements, especially on compressive strengths SCT (short compressive test) and CMT (concora medium test). More recently, Marais and Wågberg[3] compared the results obtained also using low PAH or PVAm dosages of different molecular mass onto unblea-

ched, bleached refined and not refined pulps, and they found greater improvements using PAH (56 kDa) instead of polyvinylamines or PAH (15 kDa).

In a paper machine, the dosage of the cationic polyelectrolyte influences the paper machine runnability and the papermaking properties. At a dosage level corresponding to the charge neutralization, a high-charge and medium-molecular-weight cationic polyelectrolyte produces coagulation[4] and handsheet non-uniformity.[5] It is known that paper non-uniformity produces economic loss, paper strength decrease, and variation of local basic weight of typical machine-made paper.[6] Strazdins[7] found optimum single-pass retention, and faster drainage and production rates in paper machine when the system had a near-neutral or slightly anionic charge. On the other hand, when the amount of cationic polyelectrolyte is higher than the charge saturation level, the charge-reversal in the furnish

can lead to restabilization effects,[4,8] improving the formation quality, and the paper strength properties.[1,2,3] Nevertheless, in practice it would be expensive and would probably affect the drainage rate. Besides, the polyelectrolyte can end up in the white water and can cause a great variety of difficulties,[9] especially in closed paper machine water loops.

In order to take advantage of the cationic polyelectrolytes, avoiding paper non-uniformity or charge-reversal problems, the dual-polymer technique can be applied.

The dual-polymer deposition of polyelectrolyte on surfaces, formed by the consecutive adsorption of two polyelectrolytes of opposite charges is a simple method for modifying the interfacial properties of different materials. Hubbe *et al.*[10] showed that a dual-polymer dry-strength treatment with poly(dimethyldiallylammonium chloride) (poly-DADMAC) and carboxymethylcellulose (CMC) can modify the surface of unbleached softwood kraft pulp and significantly improve the compressive and tensile strengths. Recently, Galván *et al.*[11] showed that the tensile strength of recycled unbleached kraft pulp can be improved by 30%, when a dosage of 1% xylan on pulp was added on a previously PAH treated pulp. This technique can also be used to increase the effectiveness of high speed papermaking, adding first an excess of a high-charge and low-molecular-mass cationic polyelectrolyte, and then, after a shear stage, an anionic polyelectrolyte with low charge and high molecular mass.[12] The objective of adding the anionic polyelectrolyte is to flocculate the cationic floc fragments previously formed.[12]

As anionic polyelectrolyte, lignosulfonate can find applications in papermaking, especially when the paper has no requirements of optical properties.

Lignosulfonate (LS) is an inexpensive and renewable biopolymer derivative from the sulfite pulping process. It is an amphiphilic compound that contains hydrophobic groups (aliphatic and aromatic groups) and hydrophilic groups (sulfonic and carboxyl acid groups and phenolic hydroxyl groups).[13] Due to the hydrophilic groups, LS is soluble in water and exhibits polyelectrolyte behavior.[13]

Lignosulfonates are used as surfactants, but in contrast with the common ones, they have generally been characterized as compact and spherical structures where the sulfonic acids and carboxylic acids (polar groups) are positioned mainly on the surface of a hydrophobic hydrocarbon core and thus they can interact with the other molecules.[14] They are also used for other applications, such as concrete water reducers, dispersants for water coal-slurry, corrosion and scale inhibitors.[15]

Although the use of LS is increasing, a high proportion of them are disposed of as waste, likely causing environmental hazards.[16] Therefore, it is interesting to find new applications for this product, such as modifying the interfacial properties of different materials.

Particularly, the behavior of lignosulfonates during their adsorption as polyanions for building multilayers with polycations, such as poly-DADMAC, has been widely studied.[15,17,18] Qian *et al.*[17] showed that the aggregation state and molecular conformation of lignosulfonate when it is adsorbed on poly-DADMAC and then dried, depends on the pH of the liquid medium. When the pH values were lower, a self-assembled film with higher surface roughness and higher thickness was obtained. On the other hand, Ouyang *et al.*[18] showed that the increase in ionic strength of the liquid medium increased the amount of lignosulfonate adsorbed on poly-DADMAC.

In this work, the surface properties of a recycled unbleached softwood kraft pulp were modified by the consecutive adsorption of PAH and LS. First, the pulp and the lignosulfonate were chemically characterized, and the method used for LS concentration determination was selected. Then, the LS adsorption on an untreated and a previously PAH-treated pulp was analyzed at different ionic strengths and different dosages of PAH and the papermaking properties were evaluated. Finally, the recyclability of the paper prepared with the addition of PAH and LS was discussed.

EXPERIMENTAL

Preparation and characterization of the whole pulp and the fibrous fraction

The starting material was an industrial liner paper (100% virgin fibers) supplied by Papel Misionero S.A. Argentina. Two different pulps were prepared following the procedure described in Mocchiutti *et al.*[2] In brief, the paper was soaked and disintegrated in a standard disintegrator. A fraction of the pulp obtained was separated (the whole pulp) and the rest was classified using a Bauer McNett classifier (Scan method M6:69) and the R100 fraction (the fibrous fraction) was collected. Then, both pulps were

converted to the acid form (HCl pH 2.0, 30 min), and then they were converted to the sodium form (0.01N NaHCO$_3$ and NaOH pH 9.0, 30 min). Finally, the pulps were washed at a final pH 7.5. On the extractive-free pulps (Tappi T280-pm 99), the total lignin and ash content (technical report NREL/TP 510-42618, USA) were determined. Total acid groups were determined using the method of Katz *et al.*,[19] but NaHCO$_3$ was used instead of NaOH according to Lloyd and Horne.[20] Surface acid groups were estimated using the polyelectrolyte titration method[21,22] and a previously proposed equation.[22] The cationic polyelectrolyte used was a poly-DADMAC of *Mw* 400-500 kDa.

Preparation and characterization of polyelectrolytes

PAH (poly(allylamine hydrochloride)) with an average molecular mass of *Mw*: 56 kDa from Sigma-Aldrich was directly used to prepare a 0.5 g/L solution in deionized water. The PAH solution concentration and charge density were determined by the polyelectrolyte titration method using potassium polyvinyl sulfate KPVS as titrant and o-toluidine blue (OTB) as indicator,[21] and at pH 7.5.[2] The charge density of PAH was 6.3 meq/g PAH, 8.3 meq/g PAH, and 9.9 meq/g PAH for 0.1, 0.01 and 0.001N NaCl, respectively.

Lignosulfonate (LS)

Spray dried powder from liquid sodium lignosulfonate was supplied by Tembec, Canada. It was separated from spent acidic sulfite pulping liquor of softwoods. A 1 g/L LS solution was prepared and ultrafiltrated (cut-off 10 kDa) to remove the low *Mw* lignosulfonate and low *Mw* impurities, and finally LS was freeze-dried. For this LS, the amount of sulfonic and carboxylic acid groups was determined by the conductometric titration,[20] following the procedure of Qiu *et al.*[23] A volume of the LS solution was ion-exchanged through a cationic exchange resin Tulsion T-42 NaFF. The resin was previously washed with 3.7% (w/w) HCl for 60 min, and then with deionized water until the filtrate conductivity was lower than 6.0 μS/cm.

Titration curves were obtained using an INOLAB 730 conductometer, with a four-electrode-laboratory conductivity cell (WTW-Tetra Con 325). To estimate the LS concentration, two methods were used: a) direct UV absorption spectroscopy at 280 nm,[24,25] b) modified Pearl-Benson method[26] based on a specific chemical reaction, where the phenolic units in lignin react with acidified sodium nitrite to form a nitrosophenol, which, upon the addition of alkali, is tautomerized to an intensely colored quinone mono-oxime that can be measured at 430 nm.[27] The measurements were performed in a CECIL 3055 spectrophotometer. Due to the lack of commercially available pure LS, the classified and freeze-dried LS was used as a calibration standard for both methods.

The molar mass measurements of the LS were performed by Waters HPLC in 0.1M NaOH eluent using PSS's MCX 1000 and 100 000 Å columns with UV detection at 280 nm (30 ºC, flow rate 0.5 mL/min). The average molar masses (*Mn*, *Mw*) and the molar mass distributions were calculated relative to the polystyrene sulphonate (Na-PSS, 3 420-148 500 g/mol) standards using the Waters Empower 2 software. For the SEC analysis, the lignosulfonate sample was dissolved overnight in 0.1 M NaOH (1 mg/mL) and filtered with 0.45 μm PTFE membrane syringe filters (VWR).

Other polyelectrolytes

Poly-DADMAC (poly(diallyldimethylammonium chloride)) with an average molecular mass of 400-500 kDa from Sigma-Aldrich was used to prepare a 1.6 mN 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. The other reagents used were purchased commercially as analytical grade products.

LS and PAH/LS adsorption isotherms

Initially, the PAH necessary to saturate the adsorption capacity of the fiber surface at pH 7.5 and 0.01N NaCl was determined by building the PAH adsorption isotherm according to Mocchiutti *et al.*[2] Then, PAH/LS adsorption isotherms were obtained in a similar way as described in Galván *et al.*[11] In brief, wet samples of PAH treated fibers (0.5 g pulp treated with 0.15%, 0.30% and 0.60% PAH on pulp) were added to a 100 mL solution of different concentrations of LS at pH 7.5, and stirred for 30 min. Three ionic strengths were considered (0.001, 0.01, and 0.1N NaCl). Fibers were rinsed with 200 mL of conditioned water at the same pH and ionic strength as during the adsorption stage. The amount of LS adsorbed was estimated indirectly by measuring the LS concentration in the original solution as well as in the filtrate after adsorption, using the UV spectroscopy and modified Pearl-Benson methods. Prior to the determinations, the filtrates were additionally filtered through fiberglass filter (retention 0.5 μm) to separate fines. LS adsorption isotherms on untreated pulp were also made under the same conditions as described above, but without adding PAH. To account for the lignin released from the pulp during the adsorption process, a control treatment was made under the same conditions as the PAH and LS adsorption treatments, but without adding PAH or LS.

PAH/LS pulp treatments for handsheet preparation

PAH/LS pulp treatments were carried out at 0.5% pulp consistency, pH 7.5 and 0.01N NaCl. The pulp slurry (fibrous fraction) was added to the PAH solution at 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 using conditioned water (pH 7.5 and 0.01N NaCl) and added to the LS solution also at 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 reference pulp was also prepared in the same manner, but without adding PAH or LS. For each treatment, six handsheets of 120 g/m^2 were prepared according to SCAN standard methods, 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 (23 ºC, 50% RH) and the paper formation was qualitatively assessed by looking at the light passing through the sheet. Tensile strength (Tappi T494 om-01), wet tensile strength (ISO 3781:1983), short compression test SCT (Tappi T826 pm-92) and concora medium test CMT (Tappi T809 om-99) were determined on all the sheets.

Scanning Electron Microscopy (SEM)

From pulps treated with PAH and lignosulfonate, hand sheets were made, freeze dried and observed in a Scanning Electron Microscopy (SEM) JEOL, JSM-35C equipped with a digital image acquisition SemAfore. The observation was made in the mode of secondary electron images, using an accelerating voltage of 20 kV.

Effects of PAH and LS after recycling

To evaluate the recyclability of the paper after the PAH and the dual-polyelectrolyte PAH/LS treatment, for each treated pulp, twelve handsheets were formed and dried under standard conditions. Six of them were used for the determination of the paper physical properties, and the other six handsheets were repulped to evaluate the effect of recycling. This study was made using the whole pulp.

RESULTS AND DISCUSSION
Pulp characterization

Table 1 shows some of the chemical characteristics of the commercial pulp used in this work. The high total lignin content is typical of unbleached high yield chemical pulps. The amount of total acid groups was similar to that reported by other authors on a similar unbleached pulp,[28,29] but the amount of surface acid groups (21 µeq/g pulp) was significantly higher than the results obtained by Horvarth and Lindström[28] (3.4 µeq/g pulp), probably because they used a poly-DADMAC of higher molecular mass (920 kDa compared to 500 kDa used in this work) to estimate the surface charges of cellulosic fibers, which has lower access to the anionic charge of the fibers.

Lignosulfonate characterization

Table 2 shows some of the characteristics of the LS used in this work, and Figure 1 shows its relative molecular weight distribution. The number-average (*Mn*) and weight-average (*Mw*) molecular masses were 2500 Da and 25000 Da, respectively. The upper limit of molecular mass of 1.6×10^3 kDa is in good agreement with the results obtained by other authors using an ammonium lignosulfonate from spruce wood sulfite liquor.[30] The table also shows the acid groups content. At neutral pH, both anionic groups, the sulfonic (HSO_3^-, p*Ka* = 1.5) and carboxylic groups (COO^- p*Ka* = 5.1) are ionized.[30] The phenolic hydroxyl group is ionized only at high pH values, since its p*Ka* is 10.5.[30]

Table 1
Characteristics of the fibrous fraction (R100) and the whole pulp

Parameter	Fibrous fraction Value $\pm$ SD[b]	Whole pulp Value $\pm$ SD[b]
Fibrous fraction (R100) (% of the whole pulp)[a]	84.3	–
Extractives (% on o.p.)	0.22	0.27
Ash (% on o.p.)	0.067	0.134
Insoluble lignin (% on o.p.)[b]	11.92 $\pm$ 0.10	12.14 $\pm$ 0.07
Soluble lignin (% on o.p.)[b]	0.530 $\pm$ 0.002	0.546 $\pm$ 0.030
Total lgnin (% on o.p.)[b]	12.40 $\pm$ 0.10	12.65 $\pm$ 0.04
Surface acid groups (µeq/g pulp)	21.0 $\pm$ 0.5	25.7 $\pm$ 0.5
Total acid groups (µeq/g pulp)	90.60 $\pm$ 0.16	91.70 $\pm$ 0.03
Charge ratio (surface/total acid groups)	0.23	0.28

[a] Fibrous fraction obtained from Bauer McNett classifier; [b] Values referred to original pulp (o.p.); SD: standard errors

Table 2
Characteristics of the lignosulfonate

Parameter	Value
Mn (g/mol)	2500
Mw (g/mol)	25000
Sodium content (%)	6.5
Calcium content (%)	0.18
Reducing sugar content (%)	6.7
Ash content at 900 ºC (%)	23
Sulfonic acid groups (meq/g LS)	1.49 (15.3% w/w LS)[a,b]
Carboxylic acid groups (meq/g LS)	0.48 (3.2% w/w LS)[a,b]
Total acid groups (meq/g LS)	1.97

[a] The values were obtained considering the molecular mass of the sulfonic and carboxylic acids in their sodium form (103 g/mol and 67 g/mol, respectively); [b] Determined on freeze-dried LS
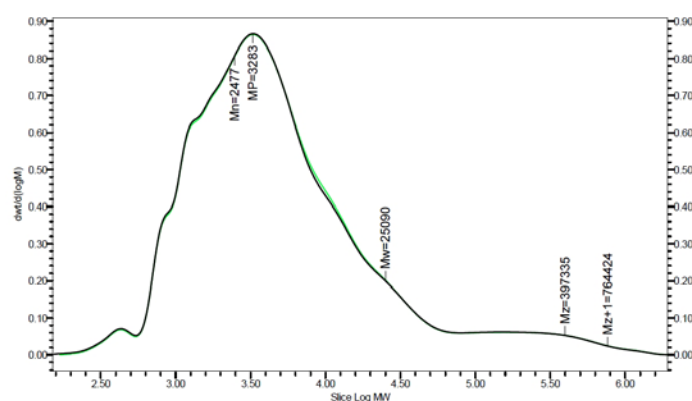
Figure 1: Molecular weight distribution of lignosulfonate, the *Mn* and *Mw* values are shown
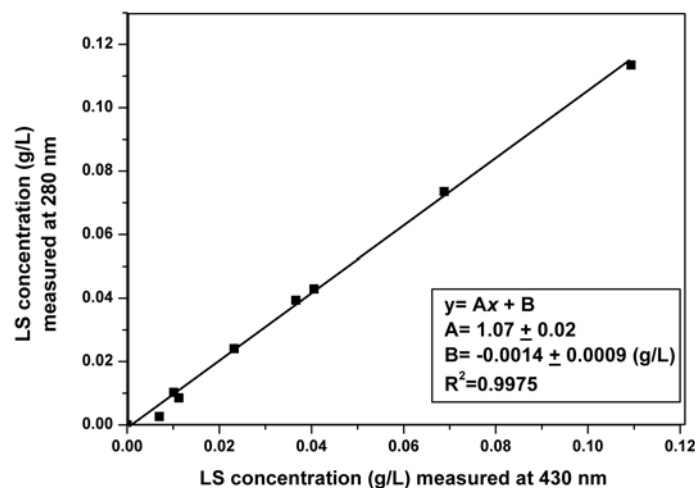

Figure 2: LS concentration directly measured at 280 nm as a function of LS concentration measured at 430 nm after the color reaction between lignosulfonate and acidified sodium nitrite

Determination of LS concentration by different methods

Figure 2 shows the LS concentration measured at 280 nm (UV spectroscopy method) as a function of the LS concentration measured at 430 nm (Pearl-Benson method). According to

Dence,[27] the Pearl-Benson method is the most widely used. It is less affected by interfering impurities (i.e. phenolic impurities) than the UV spectroscopy method.[27] Nevertheless, the linear regression obtained in this work indicates an acceptable correlation between the two methods.

The direct UV spectroscopy method was selected for the rest of the work since it is fast and easy to use.

The coefficient of determination and the slope calculated from the calibration curve, at 280 nm and pH 7.5, were $R^2 = 0.9996$, and 11.5 L/g.cm, respectively (figure not shown). Using a similar sodium lignosulfonate, Deng *et al.*[15] found similar calibration slope values (14.01 L/g.cm at pH 7.0).

Adsorption isotherms

First, the PAH adsorption isotherms at pH 7.5 in 0.01N NaCl was built and the dosage of PAH needed to saturate the adsorption capacity of the fibers was determined; it was 0.30% PAH on pulp (figure not shown). Similar results were previously shown using the same pulp and the same liquid medium conditions.[2]

Table 3 shows the dosages of PAH and LS used for building the adsorption isotherms of LS on untreated and on previously PAH treated pulps. The PAH dosages were selected from the PAH adsorption isotherm. When the ionic strength of the liquid medium is 0.01N NaCl, they correspond to: a) PAH (0.15%): half the amount necessary to saturate the adsorption capacity of the fiber surface, b) PAH (0.30%): the saturation level, and c) PAH (0.60%): double of the saturation level.

Figures 3, 4 and 5 show LS adsorption isotherms obtained at different ionic strengths by the addition of increasing amounts of LS on untreated pulps and also on pulps previously treated with different amounts of PAH, according to Table 3. The figures show that the amount of LS directly adsorbed on untreated pulp was low. For the highest ionic strength studied (0.1N

NaCl), only 0.2% LS could be adsorbed on pulp when 3% LS was added. On the other hand, the figures show that a clear increase in the amount of LS adsorbed takes place, when the pulp was previously treated with low dosages of PAH, even dosages lower than the fiber charge saturation levels. In particular, for a dosage of 3% LS on pulp, when the ionic strength had been increased from 0.001N to 0.1N NaCl, the amount of LS adsorbed on a previously PAH treated pulp (0.6% PAH on pulp) increased from 0.5% LS on pulp up to 1.8% LS on pulp. Similar results were obtained in a previous work[11] using xylan, another anionic natural polymer.

According to the theory of van de Steeg *et al.*,[31] when only electrostatic attraction exists between polyelectrolyte and surface, the increase in ionic strength always decreases the amount of polyelectrolyte adsorbed, while when non-electrostatic attraction also exists, the increase in ionic strength increases the amount of polyelectrolyte adsorbed. According to the balance between electrostatic and non-electrostatic attraction, the increase in salt concentration will increase or decrease the adsorption.

In the present work, the results show that non-electrostatic attraction could exist between the hydrophobic groups of the LS and the backbone of PAH, and also cation–π interactions between the cation of the polyelectrolyte and the electron rich π-system of the aromatic rings of the LS. Several authors[18,32] proposed the cation–π interaction as the main driving force for the adsorption of lignosulfonate on poly-DADMAC in a layer-by-layer adsorption.

Table 3

Conditions used for building LS adsorption isotherms on untreated pulps and previously PAH treated pulps [a]

Treatments	First layer PAH dosage (% on pulp)	Second layer LS dosage (% on pulp)
LS	–	
PAH (0.15%)/LS	0.15	
PAH (0.30%)/LS	0.30	1%, 2%, 3%, 4%
PAH (0.60%)/LS	0.60	

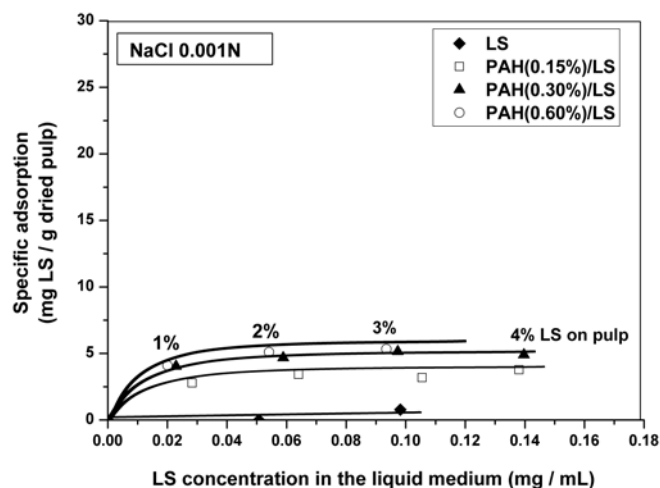[a] The LS isotherms were built at pH 7.5 and 0.001N, 0.01N and 0.1N NaCl

Figure 3: LS specific adsorption on untreated and previously PAH treated pulps as a function of LS concentration at pH 7.5 and NaCl 0.001N; LS dosages are indicated in the plot
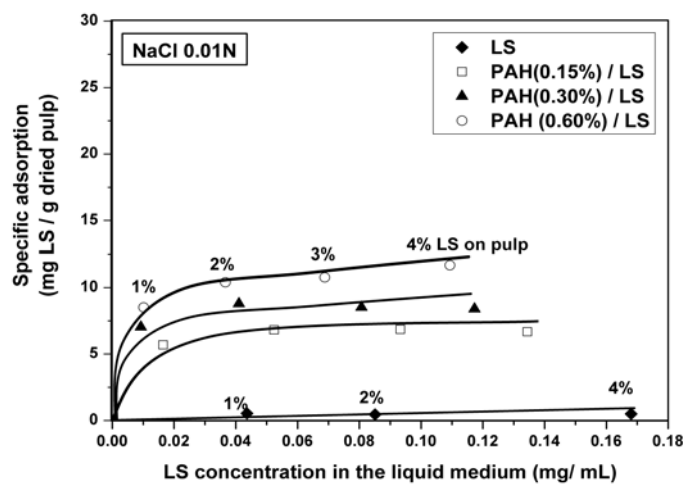

Figure 4: LS specific adsorption on untreated and previously PAH treated pulps as a function of LS concentration at pH 7.5 and NaCl 0.01N, LS dosages are indicated in the plot
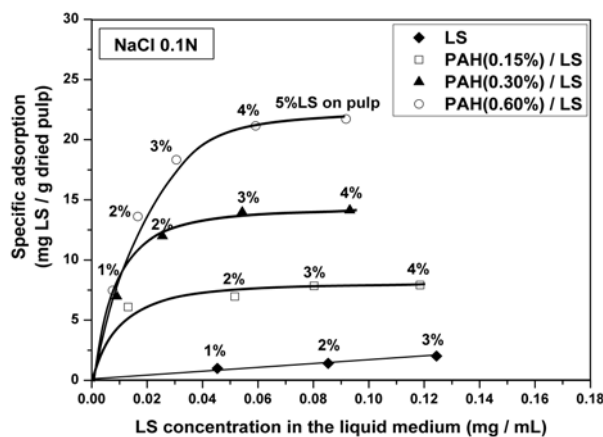

Figure 5: LS specific adsorption on untreated and previously PAH treated pulps as a function of LS concentration at pH 7.5 and NaCl 0.1N, LS dosages are indicated in the plot

Besides, using fluorescent excitation spectroscopy, Ouyang et al.[18] showed that the cation–π interaction between LS and poly-DADMAC was improved when the ionic strength of the liquid medium had been increased, resulting in an increase in the amount of lignosulfonate adsorbed,[18] as found in this work.

On the other hand, changes in the LS conformation and aggregate formations can also occur when the ionic strength is increased, as reported by Qian *et al.*,[17] when the pH of the liquid medium was decreased from 7.0 to 4.0.

Papermaking properties

Table 4 shows the dosages of PAH and LS used for studying the effects of the dual-polyelectrolyte adsorption on papermaking properties.

Paper formation

The quality of paper formation was assessed visually by looking at the light passing through the sheet (Figure 6). The figure clearly shows that the addition of 0.30% PAH on pulp (amount corresponding to the saturation level of the fibers at NaCl 0.01N and pH 7.5) produced fiber coagulation, and thus a detriment in sheet uniformity. Nevertheless, when LS was adsorbed as a second layer onto PAH saturated fibers, the sheet uniformity significantly increased with respect to the PAH treated pulp, probably due to restabilization effects.

Scanning Electron Microscopy (SEM)

The concept of layer-by-layer adsorption on a flat surface differs from the situation on a cellulosic fiber, where external fibrils exist. It is probable that PAH is adsorbed on the surface of fibrils, where a high proportion of hemicelluloses and thus, carboxylic groups are present,[33] and then, LS is adsorbed on these PAH-enriched areas. As a consequence, the fibrils can appear clearly different under the microscope. The photographs in Figure 7 show that the addition of PAH and LS produces flocculation of the fibrils, which become visible under the microscope.

Table 4

Conditions used for PAH an PAH/LS treatments for hand sheet preparation[a]

Treatments	First layer PAH dosage (% on pulp)	Second layer LS dosage (% on pulp)
REF	–	–
PAH (0.3%)	0.30	–
PAH (0.3%)/LS (1%)	0.30	1.0

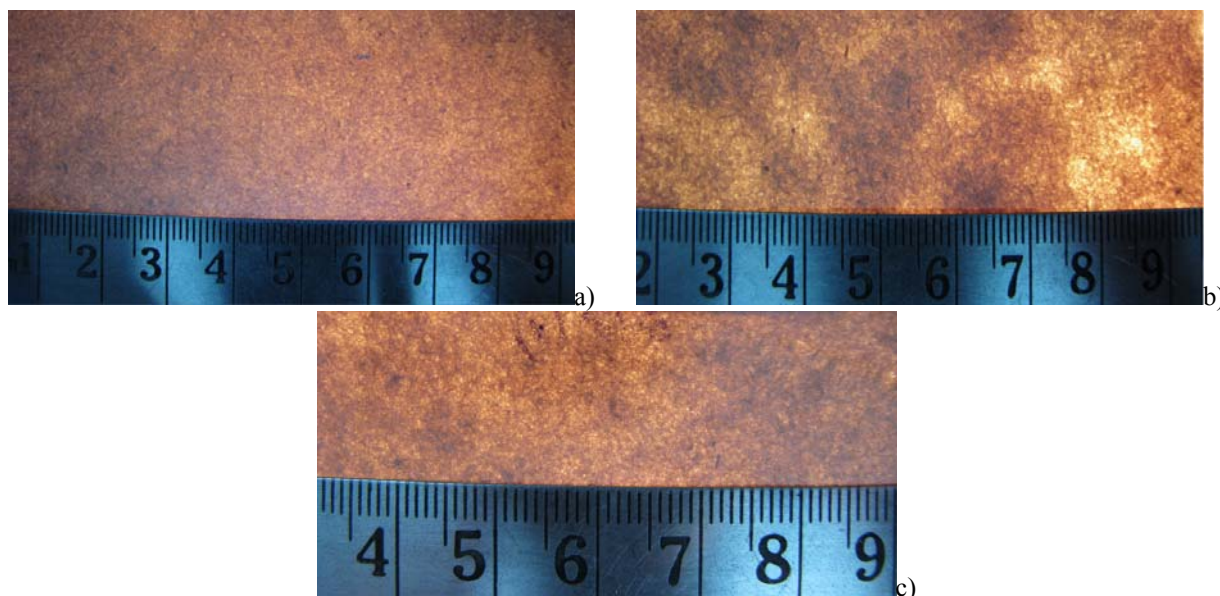[a] Treatments were made at 0.5% pulp consistency, pH 7.5 and 0.01N NaCl

Figure 6: Back light photographs of handsheets. Sheet uniformity is clearly improved when LS is adsorbed on PAH treated pulp: (a) REF: reference pulp, (b) PAH: 0.30% PAH on pulp, (c) PAH/LS: 0.30% PAH and 1% LS on pulp

Table 5
Effects of recycling on papermaking properties and their corresponding statistical significant relative changes (in %)[a]

Treatments	Tensile index (Nm/g)			Wet tensile index (Nm/g)			CMT (N)		
	1st cycle	2nd cycle	Relative change (%)	1st cycle	2nd cycle	Relative change (%)	1st cycle	2nd cycle	Relative change (%)
REF	33.5±0.8	31.2±1.7	nsd[b]	1.4±0.1	1.0±0.1	-28.6	99.6±5.1	86.2 ± 5.9	-13.5
PAH	34.5±1.4	30.6±1.5	-11.3	5.4±0.3	2.4±0.1	-55.6	143.1± 9.6	87.7± 5.2	-38.7
PAH/LS	28.8±0.9	31.7±1.1	+10.1	3.1±0.1	2.3±0.1	-25.8	103.7±6.2	81.4±4.3	-21.5

[a] Treatments were made at 0.5% pulp consistency, pH 7.5 and 0.01N NaCl. The standard deviations of the means from six replicates of the trial are shown; [b] nsd: non-statistical difference

a)   b)

Figure 7: Photographs of handsheets obtained by scanning electron microscopy: (a) REF: reference pulp, and (b) PAH/LS: 0.30% PAH and 1% LS on pulp
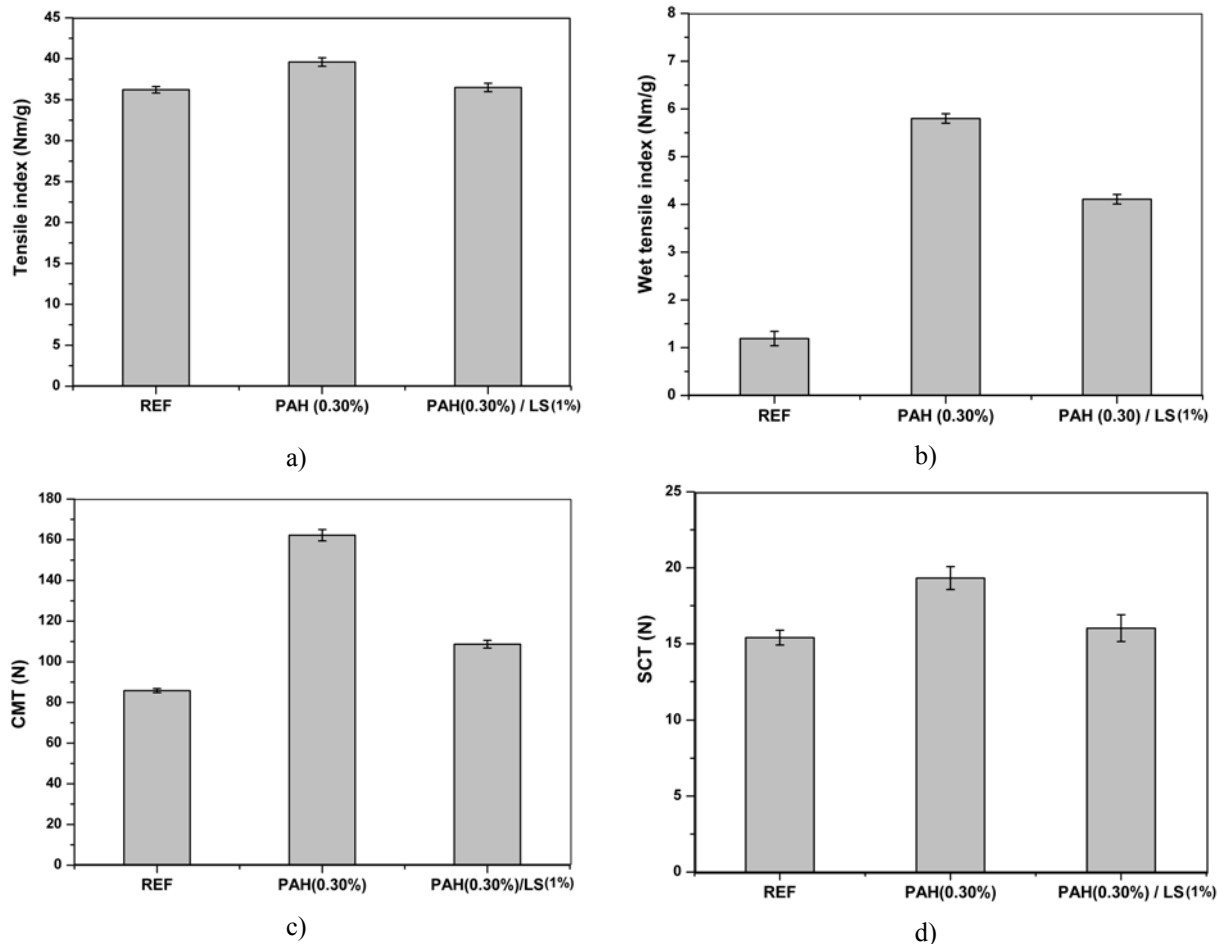
a)

b)

c)

d)

Figure 8: Paper physical properties as a function of different treatments made at pH 7.5 and 0.01N NaCl; the error bars correspond to the standard deviations of the means from ten replications of the trial. (a) Dry tensile strength, (b) Wet tensile strength, (c) CMT, (d) SCT

Physical properties

Figure 8 shows the effects of the different treatments (Table 4) on papermaking properties. The figure shows that the highest values of papermaking properties were obtained using only PAH. Nevertheless, comparing with the reference pulp, the PAH/LS system improved the wet tensile strength and the compression strength CMT, avoiding paper non-uniformity or charge-reversal problems.

Effects of recycling on papermaking properties

Table 5 shows the effects of recycling on the papermaking properties of the reference, PAH and PAH/LS treated pulps, and their corresponding relative changes. As expected, all the physical properties decreased after recycling, mainly the wet tensile strength. The effect of recycling is more pronounced when only PAH was adsorbed on pulp, reaching similar values to those of the reference pulp after recycling, in CMT and tensile strength.

CONCLUSION

The results obtained by the UV spectroscopy method at 280 nm and by the modified Pearl-Benson method were similar, indicating that the UV spectroscopy method, which is easier and faster, can be used to determine the concentration of the lignosulfonate used.

The LS adsorption isotherm on untreated pulp shows that very low amounts of LS (0.2% LS on pulp) can be adsorbed on pulp when the ionic strength is high (0.1N). At lower ionic strength, the amount of LS adsorbed is significantly lower.

The PAH pretreatment makes it possible to achieve high levels of LS adsorption. The increase in ionic strength leads to an increase in the amount of LS adsorbed as the second layer, which suggests a non-electrostatic interaction between PAH and LS, as the cation–π interaction.

The addition of LS on a previously PAH treated pulp increased the uniformity of the sheets, compared to PAH treated pulps, using a PAH dosage corresponding to the saturation level of the fiber charges.

The highest values of papermaking properties were obtained using only PAH. Nevertheless, compared to the reference pulp, the PAH/LS system clearly improved the wet tensile strength and the CMT paper, avoiding paper non-uniformity or charge-reversal problems.

The effect of recycling is more pronounced when only PAH is adsorbed on pulp, reaching similar values to the reference pulp after recycling, in CMT and tensile strength.

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