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AMPHOTERIC POLYMERS TO IMPROVE PAPER DRY STRENGTH

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SUMMARY: The objective of the present work is to evaluate the application of an amphoteric polymer, with acidic and basic groups on the polymer chain, as a paper dry strength additive. The polymer studied here is random terpolymer of high electrostatic charge density, and high molecular weight. The results of our work showed that the balance between the charge densities of the surface and the polymer structures is an important factor to be considered when using this polymer. The highest paper strength value, measured by tensile index, was found at the polyampholyte's isoelectric point (ca. pH of 7.3) when the charge of the fiber surface was negative and the polymer structure charge was symmetric. This observation agrees with our dynamic light scattering results which, demonstrated that at the isoelectric point there was a maximum in association among polyampholyte molecules, leading to a maximum in size of molecular aggregates. When adsorbed on an electrically charged surface, the maximum amount of adsorbed polymer, measured by the shift in resonance frequency in a quartz crystal microgravimetric balance, was observed for the same isoelectric point. Better results for paper dry strength were found when the fiber surface and the polymer structures were oppositely charged or at the isoelectric point of the polymer. Less effective addition strategies were found in the case when the fiber surfaces and the polymer structures had same sign of charge.

KEYWORDS: Nanotechnology; Polyampholytes; Paper strength; Surface charge density; Electrostatic interaction; Colloidal chemistry.

1. INTRODUCTION

The application of wet end agents in papermaking is a common practice to meet the specific demands of the process and the paper product. Mechanical strength is important in printing grades for use in modern high-speed operations. Among those chemical additives, the polyacrylamides and starches are the most often applied for the purpose of increasing the dry strength of the paper. Other additives studied to increase the dry strength of papers are the polyampholytes (Carr et al., 1977; Song, 2006; Hubbe et al., 2007; Silva et al. 2009a).

Polyampholytes are polymers that have positive and negative charges in the same molecular chain and have different properties when compared with monocharged polyelectrolytes (Bohidar, 2002). This author notes that a particular feature that these molecules is their antipolyelectrolyte behavior. When in solution, the solubility increases and the molecule expands with increasing ionic strength at the isoelectric point. Another peculiarity is that these macromolecules assume different states of aggregation under different pH conditions. At the pH of the isoelectric point, when the charge density is symmetric, polymer precipitation also occurs, the solubility is low (Patrickios, 1999), and the aggregation process increases.

According to the literature, the first work applying polyampholyte as a paper dry strength additive was published in 1977 by Carr et al. (1977). Polyampholytes based on starch were prepared by the xanthation of the cationic corn starch derivatives, which had tertiary amine groups, [$-CH_2CH_2N(C_2H_5)_2$] or ammonium quaternary [$-CH_2CHOHCH_2N^+(CH_3)_3$]. Xanthate anionic groups were introduced in aminated cationic starch. The authors showed that the addition of starch-based polyampholyte in the wet end was effective to increase the dry and the wet strength, and the strength values were higher than those obtained by starch polyelectrolytes only, either cationic or anionic (Carr et al., 1977).

More recent study concerning the use of polyampholytes as a dry strength agents for paper was undertaken by Hubbe *et al.* (2007). These authors observed an increasing in the breaking length when this kind of polymer was added to the fibers suspension. More favorable results for this application were found when the pH condition was close to the isoelectric point of the polymer.

The charge densities of the polymer and the solid surface are considered as parameters that control the adsorption behavior. The adsorption of additives on the cellulosic surface occurs in the solid-liquid interface mainly through electrostatic interactions. The charge development in aqueous medium is due to the presence of functional groups. In papermaking, where cellulosic material is used, the carboxylic groups are mainly responsible for the development of charge on the fiber surfaces (Fardim, 2005; Zhang, 2006). In the case of polymers, besides carboxylic groups, other groups such as quaternary ammonium groups also develop charge. An important aspect in an aqueous medium which influences the development of electrical charge, both surface and additives, is the concentration of hydrogen protons in the solution, which determines the pH. It is expected that at lower values of pH, the carboxylic groups, for example, are found more in the protonated form than in ionized form. On the other hand, the degree of ionization of those groups at higher pH values is higher, i.e., more deprotonated. At this pH range, the net charge of the cellulosic material is negative, as reported in the literature (Radtchenko, 2005). This author measured the charge densities of silica and cellulose surfaces by using atomic force microscopy technique. The results were as follows: silica -0.40 and -2.0 $mC.m^{-2}$, and for cellulose -0.21 and -0.80 $mC.m^{-2}$, for pH 4.0 and 9.5, respectively.

Adsorption behavior is also dependent on the concentration of electrolytes in a dispersion medium (Fleer, 1993). This author attributed adsorption, at low salt concentrations, to ion exchange mechanism that occur in the electrical double layer due to the net gain of entropy by the release of counter-ions for the liquid phase, favoring electrostatic interactions. For intermediate salt concentrations, beside the electrostatic interactions, nonionic interactions may also occur. In this case, the increasing in salt concentration reduces the repulsion between the polymer chains increasing surface adsorption. On the other hand, for high concentrations of salt, the electrostatic interaction between the polyelectrolyte and the surface charged is reduced by electrostatic screening (Fleer, 1993).

The polyampholyte behavior in solution, associated with its adsorbed layer viscoelasticity, has been studied to explain the performance of these polymers as dry strength agents (Song, 2008; Silva et al., 2008; Silva et al., 2009a; Song et al., 2010). In these studies, by using quartz crystal microbalance technique, it was observed that the energy dissipation of adsorbed layers was related to their hydration degree and, therefore, the amount of water entrapped within the aggregates formed at different pH levels.

The objective of the present work is to evaluate the application of an amphoteric polymer as a paper dry strength additive, measured by paper tensile index, for different net charge densities of the substrate and polymer.

2. EXPERIMENTAL

2.1. Materials

A milli-Q unit was used as a source of ultra-pure water in our experiments. Sodium hydroxide and hydrogen chloride, both at 0.1N aqueous concentrations, were used to adjust the pH. Sodium chloride was used as a supporting salt to adjust the ionic strength of the buffer solutions. All inorganic chemicals used in this work were of analytical grade.

Polyampholyte: The amphoteric polymer (PAmp) used was prepared by random, free-radical polymerization. The cationic monomer was N-[3-(N′,N′-dimethylamino)propyl] acrylamide (DMAPAA), a tertiary amine. The anionic monomer was methylene butanedioic acid, also known as itaconic acid (IA). Sufficient neutral acrylamide monomer was added to achieve each selected molar composition (Figure 1). The molecular weight of the polyampholyte synthesized was 2.93 x 106 Da with cationic to anionic group ratio of 5:4, as measured by NMR. Aqueous solution (1g.L-1) viscosity was 2,400 mPa.s (25 °C) and the iep was 7.5 (Wang, 2006).

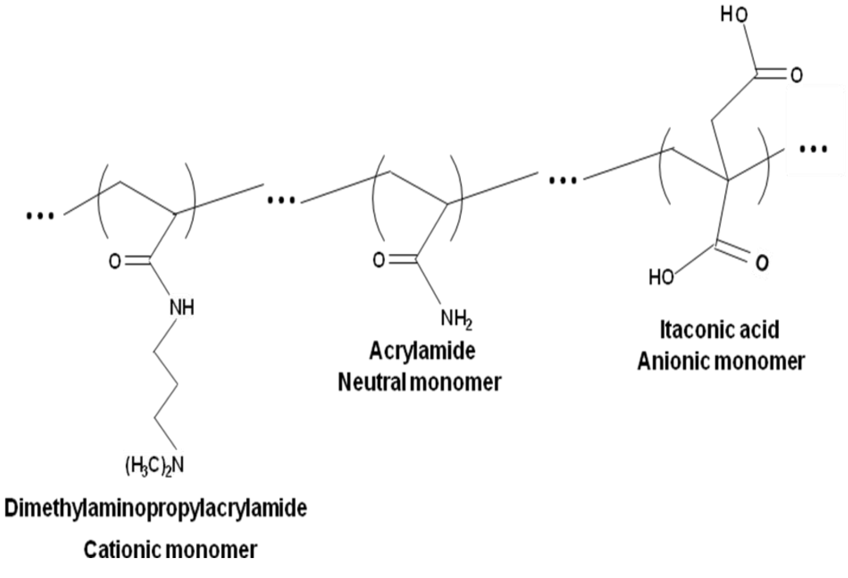

Figure 1 - Polyampholyte molecular composition prepared by random, free-radical polymerization.

Cellulosic fibers: Pre-treated Eucalyptus bleached kraft pulp from Brazil was used in this study. The pre-treatment consisted in removing the fine fraction by washing with plenty running water through a 100-mesh screen. After this step, the pH and salt (NaCl) concentration were adjusted to 6.5 and 1 mM, respectively. A sample was collected to carry out fiber analysis with a Fiber Quality Analyzer LDA02 (see Table 1). The suspension was dewatered by centrifugation and the wet pre-treated pulp was conditioned in a polyethylene bag under refrigeration. The moisture was determined in triplicate.

Table 1 - Fiber Quality Analysis.

Parameter	Mean length (mm)	Mean width (μm)	Fines (%)	Vessel (#)	Vessel length (mm)	Vessel width (μm)
Arithmetic average	0.719	16.43	0.689	6.5	0.533	133.48
Standard deviation	0.006	0.096	0.059	2.082	0.032	9.194

Note: The number of fibers counted was 3000. The fine fraction was classified as such if the fibrous elements had an effective dimension between 0.05 and 0.2 mm.

Model surface: Negatively charged silica substrates supplied by Q-Sense, Sweden were used in quartz crystal microgravimetry (QCM-D) experiments. The substrate consisted of a 50 nm silicone dioxide outer layer (active side) coated on both sides of layers consisting of Ti (10 nm), Au (100 nm) and Cr (5 nm) and quartz. Before use the silica substrates were cleaned according to the following procedure: they were immersed in a 2% w/w Hellmanex solution (HELLMA Worldwide) and placed in an ultrasonic cleaner for 20 min followed by rinsing with milli-Q water. In order to activate the silanol groups (Duval, 2002), the substrates were immersed in a 10% w/w NaOH solution for 3 min followed by rinsing with milli-Q water and drying with nitrogen gas and final conditioning in a desiccator. Before use, the substrates were exposed to UV-ozone light (28 mW.cm^{-2} at 254 nm) for 15 min.

2.2. Methods

Polyampholyte adsorption on fiber surfaces, handsheet preparation and paper strength: Handsheets were prepared following TAPPI method T205. The fibers were re-suspended as 0.5 % slurry. The required pH was adjusted at a fixed salt concentration of 10 mM and PAmp dosage of 0.3% on fiber. Fresh 1 g.L^{-1} PAmp solutions (168 mg.L^{-1} active product) were mixed under constant stirring at the selected dosage and pH. The volume of each solution added was determined to adjust the slurry consistency. The equilibration time was 30 min. The pH was continuously controlled. In order to maintain the same pH and salt concentration during the sheet formation, a calibration curve with distillated water was carried out in order to ensure the same set of conditions during formation of each handsheet. Tensile strength was measured following the TAPPI method T404.

Polyampholyte solution behavior: Solution properties with dissolved polymer were determined for each pH at a fixed salt concentration of 10 mM. Turbidity measurements for polyampholyte solutions at different pH's were carried out with a DRT-15CE turbidimeter from HF Scientific, Inc.

The theoretical maximum charge density of the PAmp used in this study was 20 mol% for the cationic groups and 16 mol% for the anionic groups (Wang, 2007). As the ionizable groups on this kind of polymer are in equilibrium with OH^- ions and H_3O^+ ions, we expect that the net charge in the bulk solution will change with pH. Charge density measurements were done at 10 mM of salt. A 10 ml aliquot of 168 mg.L^{-1} PAmp solution was titrated with 0.0025N polyvinyl sulfate potassium salt (PVSK) to a neutral streaming current endpoint, as determined by a Mütek PCD-03pH device from BTG. Three replicate runs were carried out for each PAmp solution.

The hydrodynamic diameter of the polymer in solution at different pH levels was obtained by using a dynamic scattering system, the Beckman Coulter N4 Plus. This system employs a 10-mW Helium-Neon laser (λ=632.8 nm) as a light source. The measurements of the Autocorrelation Function (ACF) were performed for each pH solution, and a set concentration of 336 mg.L^{-1} was used in order to ensure diffusion particle range per sec of recommended by the manufacturer, 5.0×10^4 to 1.0×10^6. The results from the ACF analysis were related to diffusion coefficient, and therefore the particle sizes were calculated by using Stokes-Einstein equation (Eq. 1). Each sample was investigated at three different scattering angles, 32.6, 62.3, and 90 deg. Three replicates were performed, and the results with smaller standard deviation are reported here. All experiments were performed at room temperature.

$$D = \frac{K_B T}{3\pi\eta d} \qquad (1)$$

Where, D = diffusion coefficient, K_B = Boltzmann constant (1.38×10^{-16} erg.°K^{-1}), T = temperature (°K); η = diluent viscosity (poise), and d = equivalent spherical diameter (nm).

Polyampholyte adsorption behavior on model surface: Quartz Crystal Microgravimetry with Energy Dissipation (QCM-D) was used to study polyampholyte adsorption phenomena. The instrument consisted of an E4 (Q-Sense, Sweden) coupled with a syringe pump for flow-through operation. The changes in resonance frequency of a silica quartz crystal electrode upon polyampholyte adsorption were monitored with time, enabling us to study the dynamics of the adsorption process. The energy dissipation, related to the damping of the sensor oscillation, was used to study the viscoelastic properties of the adsorbed layer. This information was relevant to understand the relationship between the structure of the adsorbed layer and the hydration behavior of the macromolecules at the interface.

The changes in QCM frequencies were assumed to be proportional to the adsorbed mass, as is the case for adsorbed rigid layers, as reported by Sauerbrey (Sauerbrey, 1959). The fundamental frequency fo (oscillating frequency without adsorbed mass) was 4.95 MHz, and the sensitivity constant (C) used in the Sauerbrey equation (Eq. 2) to calculate the added or adsorbed mass Δm was 17.7 ng.Hz^{-1}.cm^{-2}:

$$\Delta m = -\frac{C.\Delta f}{n} \qquad (2)$$

Where n is the overtone number (n = 1, 3, 5, 7). More information about this technique can be found in (Silva et al., 2008; Silva et al., 2009b; Song et al., 2010).

The thickness and the specific adsorbed PAmp layer were calculated considering the density of 1255 kg.m^{-3} (Silva et al., 2009b).

The QCM-D frequency and dissipation data were monitored with time before and after polymer injection. Rinsing with buffer solution at the end of the adsorption experiments was typically performed to determine the amount that was irreversibly adsorbed. During the measurements, the QCM liquid chamber was temperature-stabilized to 25 °C and buffer solution was injected at a flow rate of 130μL.min^{-1}. All experiments with the QCM were repeated at least two times. Although all the measurements were recorded at five harmonic frequencies in continuous mode (130μL.min^{-1} flow rate), the third overtone (15 MHz) was primarily used in the evaluation of the data presented here.

3. RESULTS AND DISCUSSION

3.1. Polymer solution behavior

In case of the highly charged (asymmetric) polyampholyte studied here, the pH responsiveness in solution was very significant. The PAmp turbidity and net charge density showed different values in the range of pH studied (Figure 2 a 3). At extreme pH's the PAmp seems to be fully solubilized, forming single or small aggregates that have little tendency to scatter light. In this case, no turbidity and small structure sizes are expected (Figure 2, left), and we have charge densities close to a single charged polyelectrolyte (Figure 2, right). On the other hand, the low values of turbidity associated with intermediate pH (pH 6 to 8.7) could be due to either (a) low light scattering efficiency when the polymers are all gathered together into a few big agglomerates, and (b) the likelihood that such agglomerates would quickly precipitate out of solution and not remain in the beam of the turbidimeter. In this case the charge of the polymer tends to symmetry. Some studies in the literature also found changes in turbidity of polyampholyte solutions with the changing in pH (Mahltig, 1999; Patrickios, 1999; Mahltig, 2000; Sezaki, 2006).

The change of the polymer charge balance with the pH affected the size of the aggregates as we can see at Figure 3, on the left. Smaller structures could be found at pH far from the iep, conditions under which the polymer presents asymmetrical positive charge (acidic pH – Figure 2, right) or negative (alkaline pH, Figure 2, right) and its behavior is closer to that of a monocharged polymer. Larger structures could be found at pH close to iep (pH 7.3). However, there was wide variation in the results for polydispersity of the structures along the pH range studied (Figure 3, right). According to the results, wider size distribution can be observed at extreme pH's where that intra and inter molecular polymer chain interaction would take place. Moreover, the tendency to lower values of polydispersity was found for intermediate values of pH close to the iep.

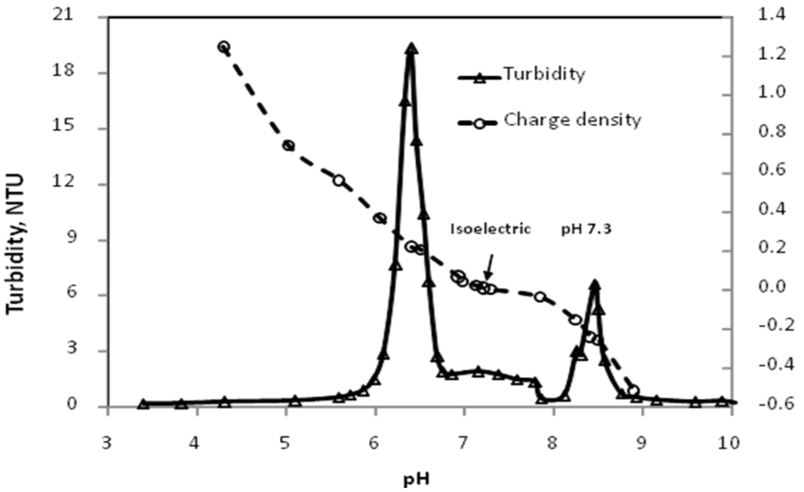

Figure 2 - Effect of pH on the turbidity and charge density of the polymer in solution.

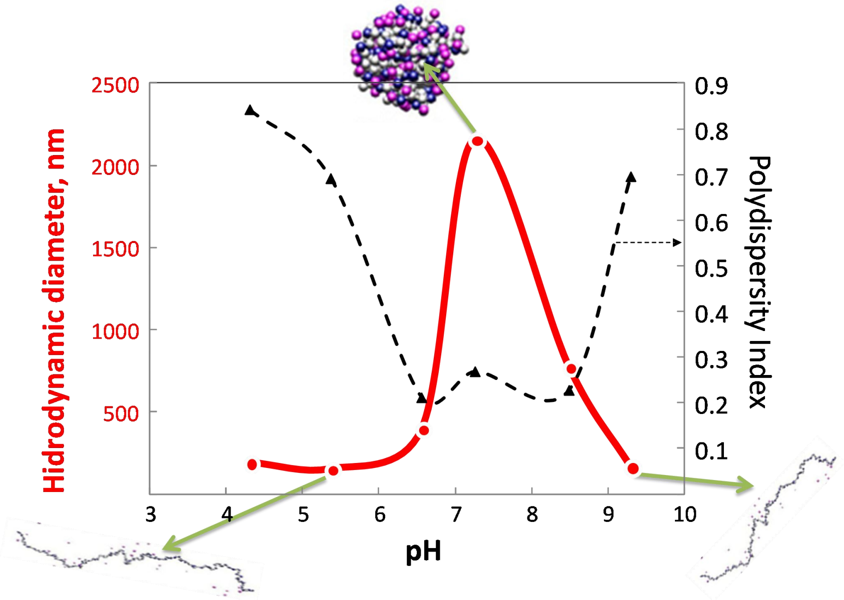

Figure 3 - Effect of pH on the hydrodinamic diameter and polydispersity index of the polymer in solution.

3.2. Effect of the polymer addition on the paper tensile strength

In Figure 4 the results of handsheet paper tensile index were plotted against PAmp charge density. This graph considers all of our results at a fixed pH (4.3) for different ionic strength (5, 10 and 100 mM), and with fixed ionic strength (10 mM) for different pH (4.3, 5.35, 6.35 and 8.48). We are also considering that the cellulosic material developed negative charge within a wide pH range, 4 up to 9.5, in agreement to what is reported in the literature (Radtchenko, 2005).

We verified that larger tensile index results were found when the PAmp and the cellulosic materials showed opposite charges (right side region of the graph). On the other hand, worse results were found were fibers and the polymer showed the same charge (left side region of the graph). In addition, the tensile index appeared to increase when the cellulose material was negative and the charge of the polymer tended to be symmetric.

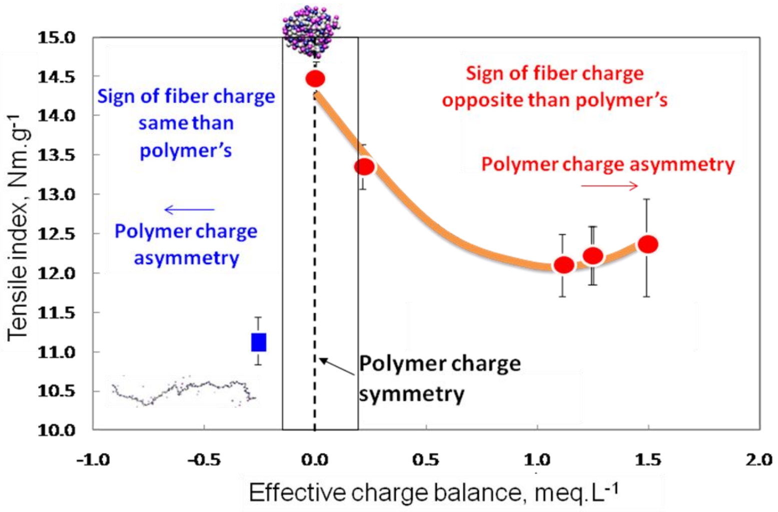

Figure 4 - Effect of PAmp charge density on the paper tensile index.

This tend can be better verified when the results of paper tensile strength are plotted against the polymer aggregate diameter (Figure 5). In this graph, the curve was built with the results where the condition or charge density is opposite for substrate, fibers, and PAmp, and the polymer charge symmetric. On the hand, the tensile index average result where the fibers and the PAmp have the same charge density is out of the curve (full triangle). It looks like an out-lier. The behaviour verified in Figure 5 showed that, besides the size the polymer aggregates, the substrate and the polymer charges, dictated by the pH of the suspension, is an important factor that has to take in an account. Even though in this case (filled triangle) the diameter is higher than the diameter results of the points where the substrate and the polymer exhibit opposite charge, the paper tensile strength was lower.

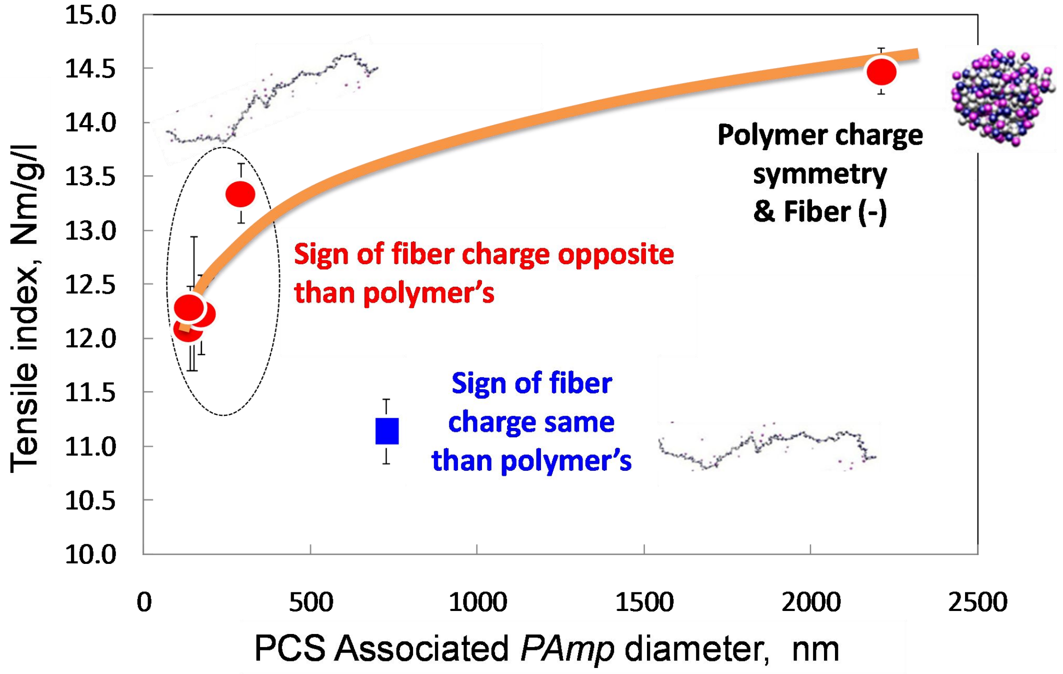

Figure 5 - Effect of PAmp structure diameter on the paper tensile index.

The Figure 6 shows the results of paper tensile strength as a function of the thickness and the specific adsorbed mass. These results where obtained from the adsorption Quartz Crystal Microbalance with Energy Dissipation analyses after rinsing step.

These results are in agreement with the last results. Higher thickness and specific adsorbed mass were found for the condition where the substrate was negative and the polymer structures showed charge symmetry. On the other hand, even though the thickness and the adsorbed mass are high for the condition with substrate and polymer with the same charge, the paper tensile strength results were lower than the other points.

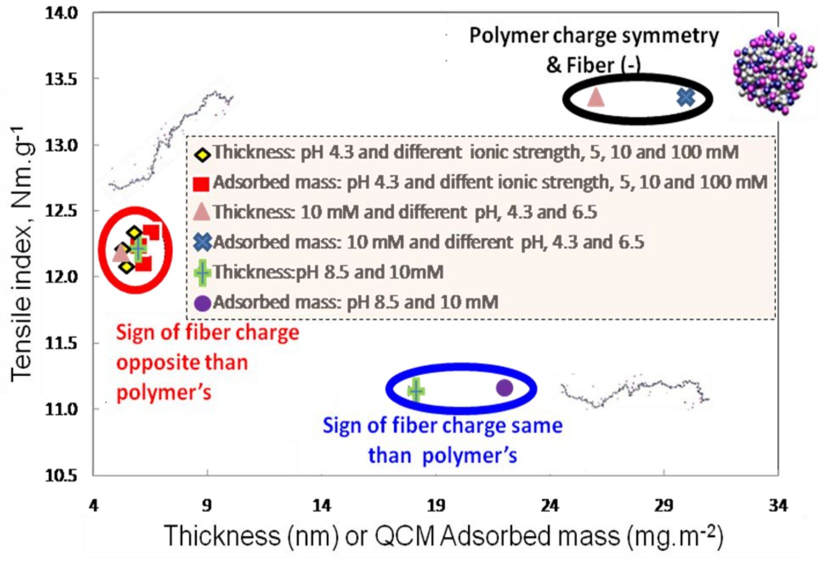

Figure 6 - Effect of thickness and the specific adsorbed mass on the paper tensile index.

4. CONCLUSIONS

According to the results obtained in this study, the following conclusions can be drawn: (a) the balance in charge densities of the surfaces and the polymer structures is an important factor to be considered when using the amphoteric polymer studied here; (b) the optimal paper strength value, measured with the tensile index, was found to be at the polyampholyte's isoelectric point (ca. pH of 7.3) when the polymer structure charge was symmetric. This is in agreement with dynamic light scattering results, which demonstrated that at the isoelectric point occurred a maximum in association among polyampholyte molecules, leading to a maximum in size of molecular aggregates, and possible more hydrated structures; (c) favorable results for paper dry strength was found when the fiber surface and the polymer structures were oppositely charge or at the isoelectric point of the polymer. Less effective addition strategies were found in the case when the fiber surfaces and the polymer structures had same sign of net charge.

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POLÍMERO ANFÓTERO PARA MEJORAR LA RESISTENCIA DEL PAPEL

RESUMEN: El objetivo de este trabajo fue la evaluación de un polímero anfótero, conteniendo grupos ácidos y básicos en su cadena, como aditivo para la resistencia en seco del papel. El polímero en cuestión fue un terpolímero aleatorio de alta densidad de carga y alto peso molecular. Se determinó que el balance entre la densidad de carga del substrato y de las estructuras poliméricas es un factor crítico a considerar en el uso de estos polímeros. El máximo valor de resistencia del papel, cuantificado mediante el índice de tensión, se consiguió a valores de pH equivalentes al punto isoeléctrico del polímero, iep (pH equivalente a 7.3); en esta condición la carga de la superficie de las fibras es negativa y la distribución de carga en el polímero es simétrica. Esta observación coincide con resultados de dispersión de luz láser de soluciones del polímero que mostró un máximo en la asociación polimérica y por tanto un máximo tamaño molecular en el iep. Al adsorberse sobre superficies con carga electrostáticas la máxima cantidad de polímero adsorbida, cuantificada mediante técnicas de microgravimetría de balanza de cristal de cuarzo, también ocurrió en el iep. Los mejores valores de resistencia en seco del papel se consiguieron en condiciones donde las carga electrostáticas del polímero y de las fibras eran de signo opuesto o en el iep del polímero. Otras estrategias de adición menos efectivas se consiguieron cuando la carga del polímero y de las fibras eran del mismo signo.

PALABRAS CLAVE: Nanotecnología; polianfóteros; Resistencia del papel; Densidad de carga superficial; Interacción electrostática; Química coloidal.