

THE USE OF POLYELECTROLYTE WITH CELLULOSE NANOCRYSTALS ASSOCIATION AS AN ALTERNATIVE TO IMPROVE PAPER STRENGTH

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ABSTRACT

Structures consisting of cationic polyelectrolyte and anionic cellulose nanocrystals at different charge ratios, $q+/q-$, were manufactured for use in improving handmade paper strength properties. Eucalyptus bleached pulp with low fines content was used in the paper manufacturing. Cationic starch sample was used as the polyelectrolyte to be associated with nanocrystals isolated from cotton fibers. All study was done on the basis of charge densities of both materials, cationic starch and cellulose nanocrystals. Reference test was conducted for comparison purpose. Results of tensile index of cationic polyelectrolyte (9.8 N.m.g⁻¹) and cellulose nanocrystals (9.1 N.m.g⁻¹) separately applied were higher than the reference test (8.2 N.m.g⁻¹).

The association of cationic polyelectrolyte and the anionic cellulose nanocrystals at different charge ratios, $+q/q-$, resulted in suspensions with different charge balancing when compared to the suspensions with the original constituents only. This enabled the formation of structures with desired charge densities, i.e. with positive residual to adsorption in fiber surfaces. The best result of tensile index was achieved when the value of charge density of the structures in suspension was near neutral, $q+/q- = 100/100$.

Keywords: Adsorption on solid-liquid interface, cationic starch, polyelectrolyte and cellulose nanocrystal structures, anionic cellulose nanocrystal, paper strength

INTRODUCTION

The dry-strength of printing and writing paper grades is considered one of the most important properties. Commercial alternatives to increase this property are the mechanical energy application to the fibers and the addition of chemical additives such as cationic starch and polyacrylamides. Non-commercial alternatives have been studied as techniques for improving paper strength, which make use of polymeric structures containing positive and negative charges, such as polyampholytes [Hubbe *et al.*, 2007; Silva *et al.*, 2009; Silva *et al.*, 2010], polyelectrolyte complexes [Silva *et al.*, 2012; Yamaguchi *et al.*, 2008; Heermann *et al.*, 2006; Gärdlung *et al.*, 2003; Gernandt *et al.*, 2003], and polyelectrolyte multilayer added onto cellulosic materials [Eriksson *et al.*, 2006]. These studies showed that association of oppositely charged additives in the structures formation achieved better results in comparison to the use of these additives alone. Gärdlung *et al.* (2003) used structures formed with a cationic polyamide-amine-epichlorohydrin (PAE) and an anionic carboxymethylcellulose (CMC) to increase paper strength. The structures were formed in different contents of cationic and anionic polyelectrolytes in order to achieve different ratios between positive and negative charges, $q+/q-$. The authors found that the addition of such structures to a fiber suspension led to a significant increase of paper strength compared with handsheets prepared with cationic polyelectrolyte only. Furthermore, the authors observed increase in paper strength with the increasing $q+/q-$ ratio in

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the structures. Highest paper strength was obtained when the anionic polyelectrolyte was neutralized by 60% ($q+/q- \sim 0.6$) [Gärdlung *et al.*, 2003]. Similar results were found by Heermann *et al.* (2006) using diallyl dimethyl ammonium chloride (poly-DADMAC) and anionic polyelectrolyte carboxymethylcellulose (CMC) to develop structures with different $q+/q-$ ratios. These authors noticed increase in paper strength with the increasing of $q+/q-$ ratio. The best result was achieved when this ratio reached 40% replacement ($q+/q- \sim 0.40$). From this point on, there was decrease in resistance. Studies by Silva *et al.* (2012) using cationic starch as positive polyelectrolyte associated with carboxymethylcellulose (CMC) as negative polyelectrolyte also showed that the formation of structures contributed to increase paper strength when compared with polymers used alone. Best results were obtained when the ratio $q+/q-$ was found near the neutral point, i.e. all the starch being neutralized by the CMC. In 2010, Silva *et al.*, studying the application of polyampholytes as dry strength agents, found the best results when these polymers were close to the isoelectric point ($q+/q- = 1$). Considering results reported in literature on use of structures formed by polyelectrolytes with positive and negative charge densities, the main target of this study was the use of structures manufactured through the association of cationic polyelectrolyte with anionic cellulose nanocrystals as a paper dry-strength additive. In this study, cellulose nanocrystals obtained from cotton fibers were isolated for use in combination with cationic starch.

EXPERIMENT

Structures with different ratios of charge density, $q+/q-$, were formed by the use of modified cationic starch, 200 mg.L⁻¹, and a suspension of cellulose nanocrystals obtained from the acid hydrolysis of cotton fibers. The modified starch was supplied by Corn Products Brasil Ltda. The sample with a maximum ash content of 2.0%, moisture content 10% and degree of substitution (DS) from 0.035 to 0.042. According to the supplier, the cationic starch presents an amylose content of 27% (**Figure 1**) and an amylopectin content of 73% (**Figure 2**). The starch solutions were prepared at 200 mg.L⁻¹ of concentration for all tests.

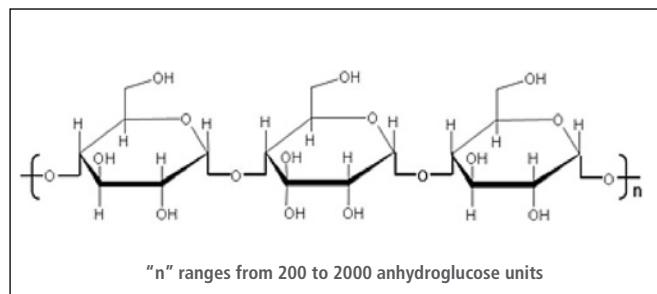


Figure 1. Amylose structure

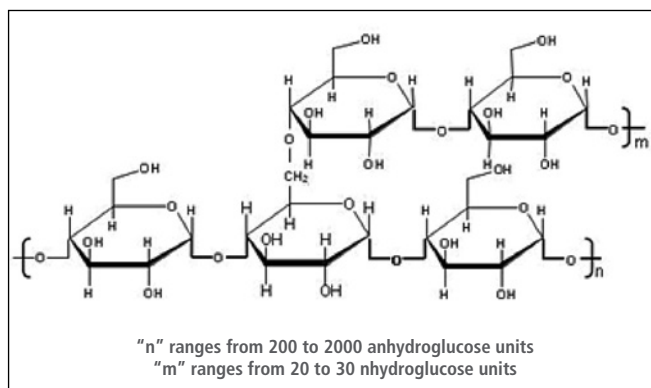


Figure 2. Amylopectin structure

In this work, bleached and pretreated commercial eucalyptus kraft pulp was used to evaluate the adding of structures formed by cationic starch and cellulose nanocrystals as paper dry-strength agents. The pretreatment was performed according to the method suggested by Silva *et al.* (2009). The pulp was washed with excess of tap water through a 100 mesh screen in order to reduce fines content. After this step, samples were collected to perform analysis with CIS100 Galai for determining amount of fines. The pretreated pulp showed an average of 3.3% fines. The suspension was dewatered by centrifugation and the wet pretreated pulp was packed in polyethylene bags maintained under refrigeration (4°C). Moisture content was determined in triplicate. Distilled water was used to prepare the polyelectrolyte solution and the cellulose nanocrystal suspension. Filtered water was used to prepare paper handsheets. Aqueous solutions of sodium hydroxide and hydrochloric acid, both with 0.1 N concentration, were used for pH adjustment. 1 M sodium chloride was used to adjust the ionic strength of the polyelectrolyte solution and fiber suspensions. Standard solutions of anionic and cationic polyelectrolytes, both with 0.001 N concentrations, were used in cationic starch solution and cellulose nanocrystal suspension charge density analysis, respectively. All inorganic chemical reagents used in this study were of analytical grade.

Preparation of cotton fiber cellulose nanocrystal

The suspension of cotton fiber cellulose nanocrystals was prepared based on method described by Silva *et al.* (2011) and by Vieira *et al.* (2012). Firstly, it was carried out a solid-liquid extraction of approximately 6 g cotton with acetone in a Soxhlet apparatus, performing six cycles per hour during four hours. After drying under a hood for three hours at room temperature for evaporating the acetone and followed by the drying in a desiccator with silica gel for twenty four hours, the cotton fibers were subjected to the isolation procedure (Silva *et al.*, 2011; Vieira *et al.*, 2012). Two hydrolyses were made with approximately 3 g

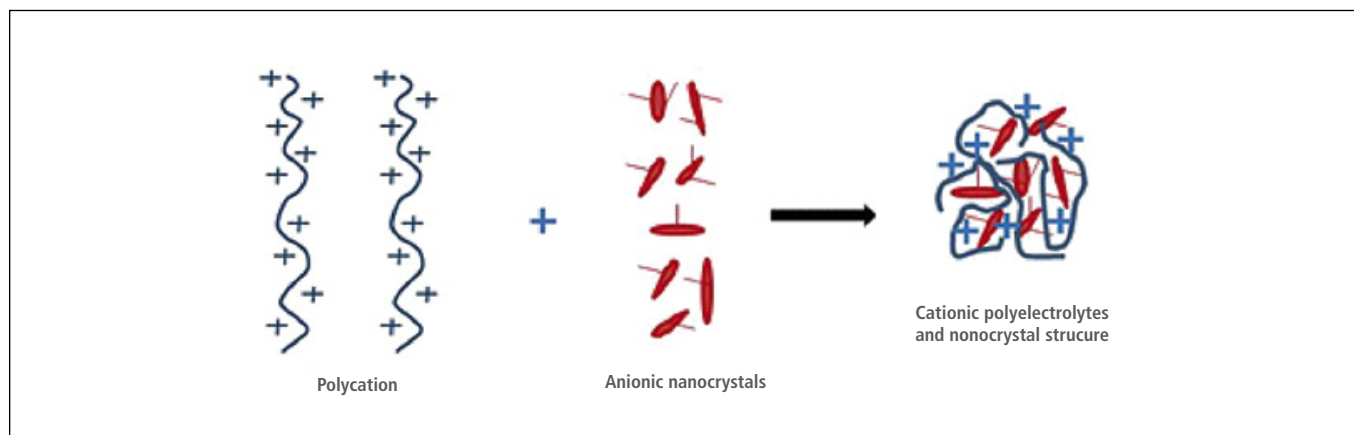


Figure 3. Cationic polyelectrolytes and nanocrystal structure formation

each to be used in initial tests and in the structure formation, for the adsorption on fiber surfaces and subsequent sheet formation for tensile testing. Were obtained nanocrystal suspensions with 5.5 pH, 250 mL per each 3 g, totaling 500 mL.

Characterization of cellulose nanocrystal by microscopy

The nanocrystals were analyzed with a transmission electron microscope (Zeiss EM 109 TEM) operating at 80 kV at the Nucleus of Microscopy and Microanalysis (NMM), UFV. Firstly, the 10x diluted suspension was submitted to 20 minutes of ultrasound in a conventional device manufactured by Cristófoli, at a frequency of 42 KHz. A drop of nanocrystal suspension was added to a 300 mesh grid covered with Formvar 0.4% for two minutes. The excess liquid was removed with filter paper, and the reaction was covered with a drop of 2% uranyl acetate for ten minutes. The samples were dried overnight in a desiccator with silica gel and, then, images were taken. Three samples were prepared.

Measurements of turbidity

Turbidity measurements of the cationic polyelectrolyte solutions, of the anionic nanocrystal suspension and of the dispersions with both materials at fixed values of pH and ionic strength of 7 and 10 mM NaCl, respectively, were performed with a portable turbidimeter from Policontrol, model AP 2000 IR.

Measurements of starch solution and nanocrystal suspension charge density

Aliquots of about 10g of the cationic starch solution of 200 mg.L⁻¹ (polycation) and nanocrystal suspension (polyanion) as obtained in the hydrolysis isolation processes were titrated with standard solution of polyelectrolyte of opposite charge - both 0.001 N - with Particle Charge Analyzer device from TMI Inc., up to neutralization. The charge densities of fiber suspensions without polyelectrolyte (reference),

and after the adsorption process of each test, were measured in same way to evaluate the adsorption process. Two repetitions were performed for each test.

Quantification of the nanocrystal volume suspension required to neutralize the cationic polyelectrolyte

Ratios between the polycation and the polyanion, q⁺/q⁻, were determined by potentiometric titration of 10g of cationic starch solution, 200 mg.L⁻¹, with the anionic nanocrystal suspension. From these results, volumes of cellulose nanocrystal suspension necessary to achieve the studied ratios q⁺/q⁻ of 100/0, 100/50, 100/100 and 0/100 were established.

Structure preparation

For the ratios 100/50 and 100/100 a volume of starch solution containing the equivalent of 2% of the additive, based on dry pulp, was neutralized in 50% and in 100% of the initial charge density of the starch, respectively. Firstly, the starch solution was placed in a beaker containing distilled water. Under stirring, the volume of the suspension corresponding to the predetermined ratio of nanocrystals was added. The incubation time was 5 min. The pH and ionic strength of the medium were respectively 6.5 ± 0.3 and 10 ± 0.5 μS.cm⁻¹.

Figure 3 illustrates the structure formation.

For test with the cationic starch alone, q⁺/q⁻ =100/0, or nanocrystal suspension, q⁺/q⁻ =0/100, and for the reference test, q⁺/q⁻ =0/0, the preparation procedure was the same. Calculations were previously made based on the concentration of the starch solution, 200 mg.L⁻¹, and considering that in each charge determination test approximately 10 mL of starch solution was used. In this case, 0.002 g of starch was in fact neutralized with approximately 405 μL of nanocrystal suspension. Considering these data, volumes of starch solution and nanocrystal suspension required for all the treatments

Table 1. Starch solution, nanocrystal suspension and distilled water volumes used in the tests

q+/q-	Starch solution, mL	Nanocrystal suspension, mL	Distilled water, mL
0/0	0	0	200
100/0	16	0	184
100/50	16	32,4	151,6
100/100	16	64,8	119,2
0/100	0	64,8	135,2

based on 16 g of dry pulp were calculated (**Table 1**). The volume of distilled water previously added to the beaker, in addition to the starch solution and the suspension, was necessary for completing the 200 mL.

Adsorption structures on the fiber surfaces

The volume with the structures formed by starch and nanocrystals was added to the fiber suspension previously disaggregated (1% consistency at 10,000 rpm) with $\sim 0.22\%$ consistency, and pH and ionic strength adjusted to ~ 6.5 and $\sim 70 \mu\text{S}\cdot\text{cm}^{-1}$, respectively. The consistency was adjusted to 0.2%. The entire content was stirred for 10 min for the adsorption of the structures on fiber surfaces to happen. Then, handsheets were made according to standard TAPPI T205. After the adsorption time, an aliquot was withdrawn for the adsorption evaluation. The tensile strength was carried out according to standard TAPPI T404. Tensile tests were performed in six replicates.

RESULTS AND DISCUSSION

Characterization of nanocrystal by transmission electron microscopy

According to **Figure 4**, cotton fiber nanocrystals can be

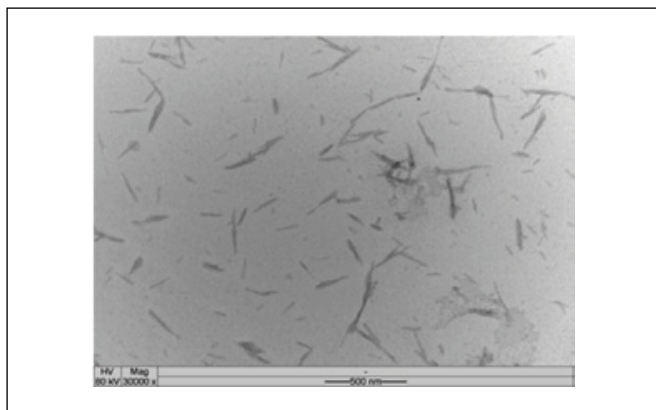


Figure 4. Photomicrograph of cotton nanocrystals as seen in transmission electron microscope, 30,000X

observed individually and randomly distributed over the surface of the used substrate (300-mesh grid covered with Formvar film). The nanocrystals appearance was of similar morphology as that presented in literature, namely: as needles with high length/width ratio (Elazzouzi-Hafraoui *et al.* 2008).

Characterization of polyelectrolyte and cellulose nanocrystal structures

The charge densities of the starch solution, $200 \text{ mg}\cdot\text{L}^{-1}$, and the cotton nanocrystal suspension were respectively $+9.3 \text{ mEq}\cdot\text{g}^{-1}$ and $-71.5 \text{ mEq}\cdot\text{g}^{-1}$. This latter value is normal since the isolation procedure was performed with sulfuric acid. Therefore, the nanocrystal suspension showed, in module, a charge density ~ 7.7 higher than that of the starch solution. This reflected the low volume, $405 \mu\text{L}$, of this suspension necessary to neutralize $\sim 10\text{g}$ of starch solution, $200 \text{ mg}\cdot\text{L}^{-1}$, as seen in **Figure 5**. The formation of structures with the cationic polyelectrolyte and the cellulose nanocrystals can be verified with the increasing of the solution turbidity (**Figure 6**). Considering the turbidity values of

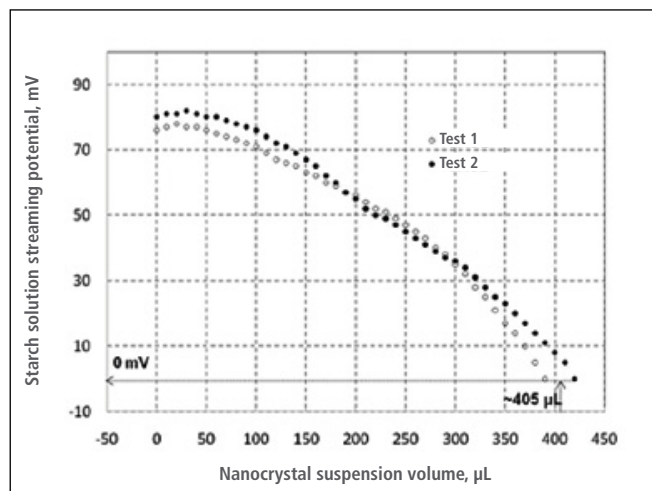


Figure 5. Potentiometric titration of the starch solution with nanocrystal suspension

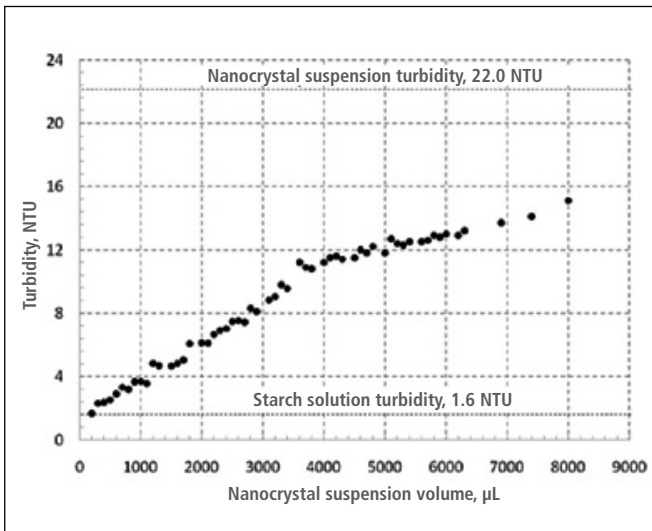


Figure 6. Effect of the nanocrystal suspension addition on solution turbidity

the materials individually, the turbidity of starch solution showed off lower than the nanocrystal suspension, 1.6 NTU and 22.0 NTU, respectively. Unlike found by Silva *et al.* (2012) for the turbidity curve when carboxymethylcellulose (CMC) solution was added to the cationic starch solution, which exhibited maximum turbidity point of 10.5 NTU. In this study, the turbidity of the starch solution increased with the addition of cellulose nanocrystal suspension (Figure 6). This can be explained, in part, by the higher turbidity value of the nanocrystal suspension used in this study, 22.0 NTU, compared to the turbidity of the CMC solution used by those authors, 1.25 NTU.

Effect of nanocrystals and starch structures on paper strength

The effect of application of polyelectrolyte structures formed by cationic starch and cellulose nanocrystals on handsheet tensile strength index can be seen in Figure 7. As per this figure, the

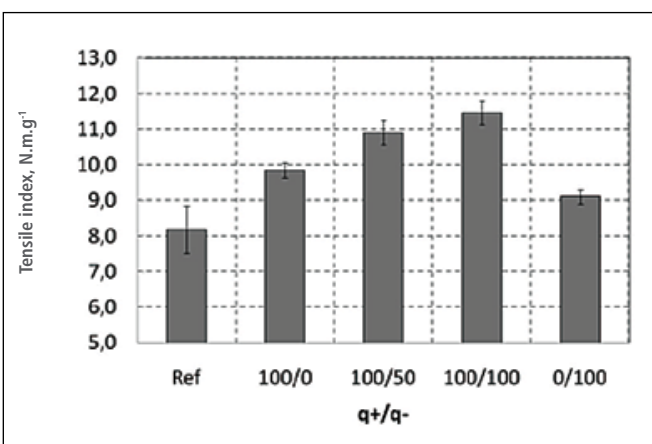


Figure 7. Effect of cationic polyelectrolyte and anionic nanocrystals ratio on the paper tensile index. The reference test was conducted without addition of any materials

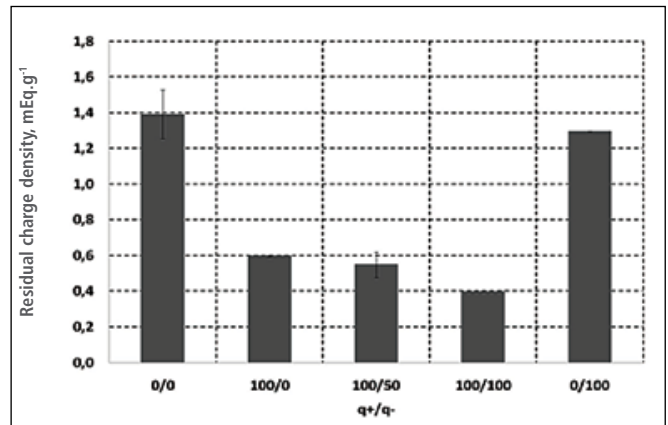


Figure 8. Effect of cationic polyelectrolyte and anionic nanocrystals ratio on the charge density of the filtrate from the fiber suspension after adsorption

highest tensile value index was achieved when ratio between positive and negative charges was near to neutral, $q+/q- = 100/100$. Similar results were found by Silva *et al.* (2012) when using cationic starch and CMC for the formation of structures. Moreover, Heermann *et al.* (2006), using the cationic polyelectrolyte diallyl dimethyl ammonium chloride (poly-DADMAC) and the anionic carboxymethylcellulose (CMC) for structure formation, observed the greatest resistance when the ratio reached replacement of 40% ($q+/q- \sim 0.40$). On the other hand, Gärdlung *et al.* (2003), using polyamide-amine-epichlorohydrin (PAE) cationic and carboxymethylcellulose anionic noticed highest resistance value when the anionic polyelectrolyte was neutralized by 60% ($q+/q- \sim 0.6$). Tests performed in this study adding the association of the two materials, $q+/q- = 100/50$ and $q+/q- = 100/100$, achieved better results than with materials used alone. The adsorption of these structures on the fiber surface can be verified by the lower values of filtrate charge densities of the related fiber suspensions after the adsorption process in comparison to the reference test (Figure 8). The addition of cationic starch solution alone (100/0) showed higher tensile index than the result presented by cellulose nanocrystals only. This fact can be explained by the negative charge density produced by both fiber surface (developed when in aqueous suspension) and cellulose nanocrystals. In this condition, the electrostatic interactions between opposite charges are difficult to happen. However, according to Figure 7, although fibers and nanocrystals having the same charge, results of tensile index were higher when compared to the reference test, $q+/q- = 0/0$. In this case, another type of interaction may have happened. However, this assumption was not studied in this work.

CONCLUSIONS

Cationic polyelectrolyte and cotton fiber cellulose nanocrystal structures were formed for application as paper dry-strength agents. According to the results attained in this study, the following conclusions can be drawn:

- The association of cationic polyelectrolyte with anionic nanocrystals was favorable in increasing paper strength, in this work measured by the tensile strength index;
- Best result for tensile index was attained when using starch and nanocrystal structures with charge ratio close to the neutrality;
- Although fibers nanocrystal cotton is relatively easy to isolate

in comparison with other biomass, commercial use of cationic starch and cellulose nanocrystal structures to increase paper strength must be carefully investigated, since the nanocrystal isolating step is still a laborious stage and is undergoing laboratory attempts.

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