

# The use of cationic starch and starch complexes as alternative to improve fiber quality for printing and writing grades

Deusanilde J. Silva: Faculty of Chemical Engineering, UFV, Brazil, [deusanilde@ufv.br](mailto:deusanilde@ufv.br)

José Mauro de Almeida: Faculty of Forestry Engineering, UFRB, Brazil, [jmauro.almeida@gmail.com](mailto:jmauro.almeida@gmail.com)

Rubens C. Oliveira: Faculty of Forestry Engineering, UFV, Brazil, [rchaves@ufv.br](mailto:rchaves@ufv.br)

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## Abstract

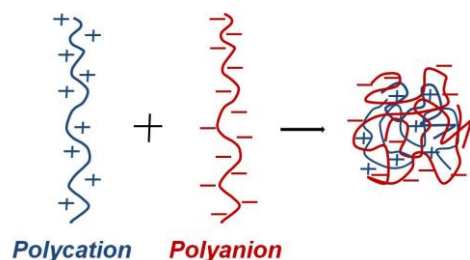
Polyelectrolyte complexes (PEC) were evaluated in this study as paper dry-strength agent. These complexes were formed between a cationic starch (CS) and an anionic carboxymethylcellulose (CMC) at different ratios of the polymers at pH 7 and ionic strength 1000 mM NaCl. Firstly, individual polyelectrolyte solutions were characterized by turbidity and charge density. The polyelectrolyte complexes formed were characterized by turbidity and charge density as well. The results showed that the charge density of cationic polyelectrolyte solution was very lower than the charge density of the anionic polyelectrolyte solution at the same solution concentration, 200 mg/L, 43.5 and 633.8 mEq/g, respectively. When the complexes were formed, the turbidity of the solution complexes was higher than the turbidity of the solution separated, cationic or anionic. The maximum turbidity, 10.5 NTU, was found when the cationic to anionic ratio was very high, 80mg of starch to 5.5 mg of CMC. It is important to consider that the charge density of the cationic solution was very lower than the charge density of the anionic solution. Therefore, the amount of anionic polyelectrolyte necessary to neutralize the cationic polyelectrolyte solution was lower as well. The results showed that the complexes of polyelectrolyte improved the fiber quality for printing and writing grade. The better result of tensile index was found when the cationic to anionic ratio was around to 70/30 when the charge density of the polyelectrolyte complexes was close to neutralization, 21.5 N.m/ The tensile strength results for the polyelectrolytes used alone were lower than all polyelectrolyte complexes, cationic starch 9,7 N.m/g and anionic polyelectrolyte 11.1 N.m/g. The tensile index with the polyelectrolyte complexes was twice higher than the tensile index with cationic starch solution alone.

**Keywords:** polyelectrolyte complexes; paper strength; cationic starch; carboxymethylcellulose.

## Introduction

Polyelectrolyte complexes (PEC) are compounds consisting of polycations and polyanions (Figure 1). They are formed spontaneously under release of the counterions by mixing solutions of polyelectrolytes with opposite charges [1, 2]. According to these authors, the drive force for PEC formation is mainly electrostatic interactions between the oppositely charged groups in the involved polyelectrolyte chains. Guo et al. (2009) reported that other weak interactions such as hydrogen bonding, van der Waals, or hydrophobic ones could also play an additional role. Because of their huge variety of applications, reaching from large scale industrial uses up to special purposes in biotechnology and medicine, fundamental research about PEC formation and the resulting structure is of high relevance at the present time [2].

One of the most important characteristics of paper products involves their dry-strength. Now a day, there are some commercial alternatives to improve paper dry-strength. The addition of paper dry-strength additives is one strategy to reach this improvement [3]. The application of mechanical energy on fibers, or use of the chemical additives such as cationic starch and polyacrylamides can be used to reach this purpose. Alternative less popular that make use of polymeric structures such as polyampholytes [3-6], as well as polyelectrolyte complexes [7-10], and polyelectrolyte multilayers added onto the cellulosic materials [11] have been studied as techniques to improve paper strength.



**Figure 1 – Illustration of polyelectrolyte complexes formation.**

Cationic polymers are frequently used in papermaking as a process additive. Among others, it is easy to find at the literature the cationic starch has been used as a dry-strength agent to improve the paper properties, through the adsorption on fiber surface [12]. Also, this additive is used for sizing emulsification and the paper surface sizing is other uses to starch in the process. On the other hand, there are in the literature some paper showing that the complexes formed with oppositely charged polymer give better dry-strength results in compared with the results with cationic polymer alone [9, 13]. Gärdlung et al. (2003) used the polyelectrolyte complexes formed by cationic poly(amideamine) epichlorohydrin condensate and anionic carboxymethylcellulose to enhance paper strength. The complexes were formed in different ratios of cationic to anionic polymers. The authors found that the addition of the complexes to the fibers before sheet preparation led to a significant increase in strength of the paper, compared to sheets prepared with the cationic polymer only. Also the authors found that the paper strength improvement was dependent upon the mixing ratio and the maximum strength was found for complexes where the anionic charge of the CMC had been neutralized to 60% [8, 9].

### Objectives

The objective of this work is to compare the strength of handmade paper by using a traditional alternative, a commercial cationic starch, and complexes of polyelectrolyte made by different ratios of cationic starch and anionic polymer.

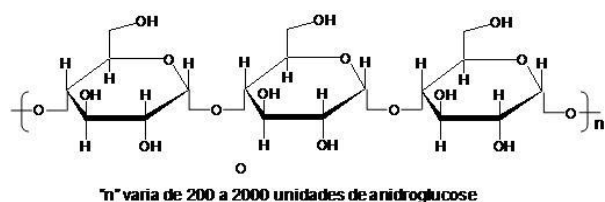
## Experimental

### Materials

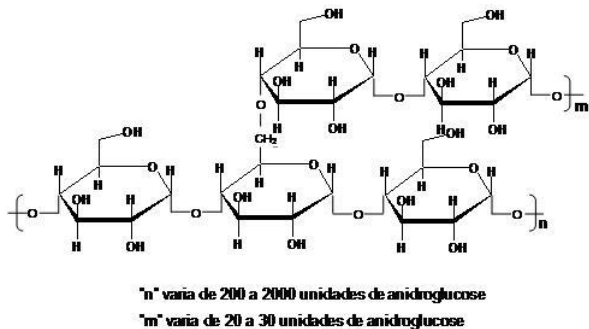
Distilled water was used in the preparation of polyelectrolyte solutions, Filtrated water was used in the preparation of paper handsheets and polyelectrolyte solutions to be used at the handsheet formation step. Sodium hydroxide and hydrogen chloride both 0.1N aqueous concentrations were used to adjust the pH. Sodium chloride 1M was used as a supporting salt to adjust the ionic strength of the polyelectrolyte solutions and fiber suspensions. Cationic and anionic polyelectrolyte standard solutions with both 0.001N were used for charge density measurements. All inorganic chemicals used in this study were of analytical grade.

### Polyelectrolytes

The cationic starch (CS) used in this study as cationic polyelectrolyte source to complex formation was supplied by Corn Product Ltda Brazil. The sample has ash maximum 2.0%, moisture around 10%, and degree of substitution (DS) 0.035-0.042. According to the supplier, the cationic starch showed 27% of amylose (Figure 2) and 73% of amylopectin (Figure 3). The starch solutions were prepared concentration 200 mg/L.

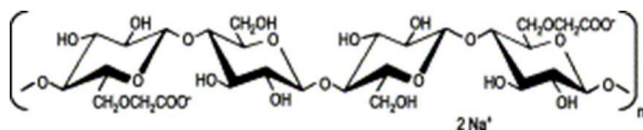


**Figure 2 – Amylose structure.**



**Figure 3 – Amylopectin structure.**

The sodium carboxymethylcellulose (CMC-Na) used in this study as anionic polyelectrolyte source to complex formation was supplied by Blanver Ltda (Figure 4). The sample showed degree of substitution 0.30-0.75 NaCl. CMC-Na solutions were prepared with 200 mg/L.



**Figure 4 – Carboxymethylcellulose salt structure.**

### **Cellulosic pulp**

Commercial pre-treated eucalyptus bleached kraft pulp was used in this study to evaluate polyelectrolyte complex to improve paper strength. The pre-treatment was performed according to Silva et al. (2009) method [6]. The pulp was washed with plenty running water through a 100-mesh screen to reduce the fines content. After this step, a sample was collected to carry out analysis with Galai CIS 100 for fines determination purpose. The pre-treated pulp showed 3.6% of fines. The suspension was dewatered by centrifugation and the wet pre-treated pulp was conditioned in a polyethylene bag under refrigeration. The moisture was determined by triplicate.

### **Methods**

#### **Polyelectrolyte solution preparation**

Cationic starch solution 200 mg/L was prepared cooking the starch 50 mg with distilled water 200 mL at 90°C during 20 min under constant stirring. After, the solution was transferred to a 250 mL volumetric flask to adjust the volume. The content of solid was measured.

Sodium carboxymethylcellulose solution 200 mg/L was prepared under vigorous stirring. In a beaker, 50 mg of CMC and 200 mL of distilled water was stirred during 30 min. The solution was transferred to a 250 mL volumetric flask to adjust the volume. The content of solid was measured.

#### **Polyelectrolyte complexes preparation**

Fresh cationic starch and CMC solutions were prepared before use at polyelectrolyte complexes formation and handsheet preparation. To measure polyelectrolyte complexes turbidity, 100 mL of cationic solution was titrated with CMC solution under stirring. After each 0.5 mL addition, 5 min were waited to form the complexes. After this, the turbidity was measured. The polyelectrolyte complexes solutions were prepared as the same way to measure the charge density and to use in paper strength evaluation. Before the complexes preparation, the cationic and anionic amount polyelectrolytes were taken for reach each cationic to anionic ratio. The studied cationic to anionic ratios were 90/10, 70/30, 50/50, 30/70 and 10/90. The time between the complexes preparation and their use was not more than 10 min. The same time for the cationic (100/0) and anionic (0/100) solutions were considered as well. The separation of complexes from the free polyelectrolyte was not done.

#### **Polyelectrolyte solution and complexes characterization**

### Turbidity

Turbidity measurements for cationic, anionic and polyelectrolyte complex solutions fixed at pH 7 and at salt concentration 10 mM were carried out with a mobile turbidimeter.

### Charge density

Charge density measurements for cationic, anionic and the solutions of polyelectrolyte complexes were done at 10 mM salt concentration and at pH 7. A 10 g aliquot of cationic 200 mg/L and anionic 200 mg/L solutions were titrated with 0.001N of anionic polyelectrolyte standard and 0.001N of cationic polyelectrolyte standard to a neutral streaming current endpoint, as determined by a Particle Charge Analyzer device from Testing Machines Inc, TMI. Also, a 10 g aliquot with cationic and anionic polyelectrolyte ratio solutions, q+/q-, 90/10, 70/30, 50/50, 30/70, and 10/90, before adsorption trials, were titrated with the same standard solutions to a neutral streaming current endpoint according to starting streaming current, cationic or anionic. The charge densities of the fiber suspensions without polyelectrolyte (reference), and after adsorption trials were measured at the same way for adsorption evaluation purpose. Three replicate runs were carried out for each solution.

### **Polyelectrolyte complexes application**

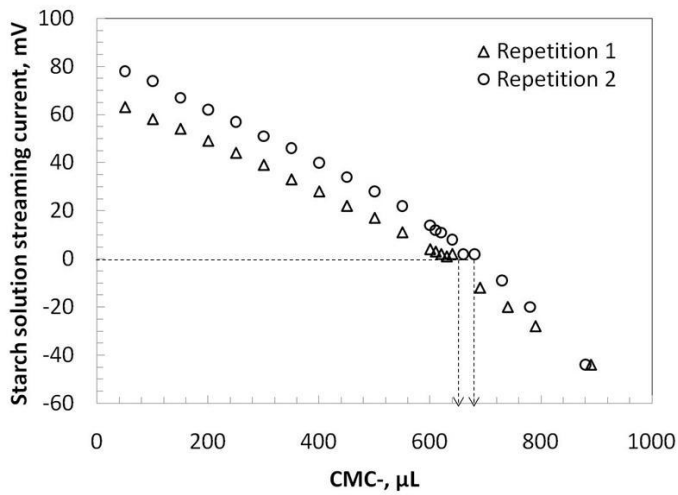
Handsheets were prepared following TAPPI method T205. The fibers slurry 1% was disaggregated at 10,000 rpm. The fiber slurry, consistency 0.2%, with pH and ionic strength adjusted, and with the polyelectrolyte or complexes solution was stirred for 10 min for adsorption on fiber surfaces. After this, handsheets were formed. After the adsorption time, an aliquot of the suspension was taken for adsorption measurement. Tensile strength was measured following the TAPPI method T404.

## **Results and Discussion**

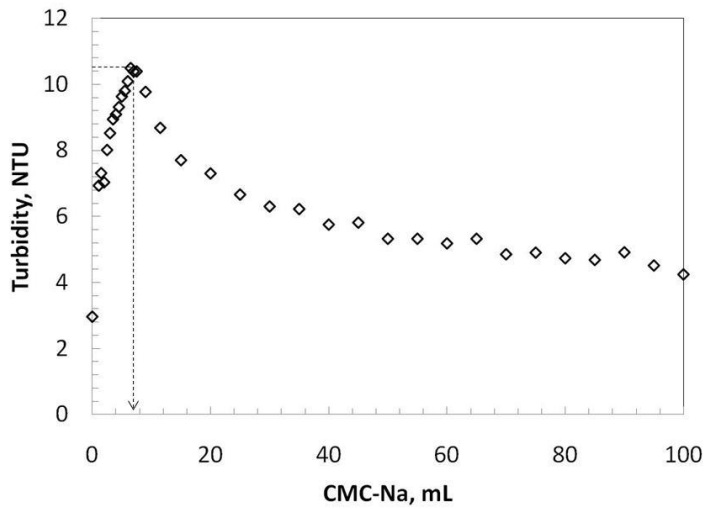
### **Polyelectrolyte complex characterization**

As we can verify, the volume of anionic CMC solution necessary to neutralize a fixed amount of cationic starch solution, 10 g, around 10,000  $\mu\text{L}$ , with the same concentration, 200 mg/L, was very low, around 660  $\mu\text{L}$  (Figure 5). It could be explained by the lower streaming current of cationic starch than the anionic CMC solution, both 200 mg/L, 77 mV and 376 mV, respectively. In this way, the CMC solution streaming current used in this study was almost 5 times higher than the cationic starch solution streaming current.

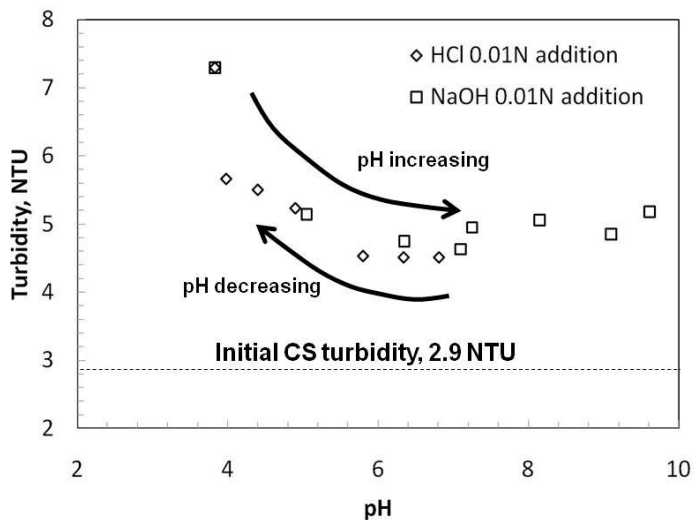
The turbidities of these solutions separately were 2.97 and 1.25 NTU for CS and CMC solutions, respectively. On the other hand, the turbidities of the complex, originated from the interaction between the polyelectrolyte, were dependent of the cationic to anionic polyelectrolyte ratios (Figure 6). This trial was carried out with a fixed amount of starch cationic solution, 100 mL. The maximum turbidity was found when the cationic to anionic ratio was 100:6.5 v/v. The ratio for the maximum turbidity was close to the ratio of charge density between cationic and anionic polyelectrolyte of the solution individually measured as mEq/g, 43.5:633.8. Also, these two results were close to the ratio between the two solution volumes in  $\mu\text{L}$  necessary to reach the neutralization, 10,000:660 (Figure 5). Amounts of volume higher than 660  $\mu\text{L}$ , the solution charge balance became negative. Considering the polyelectrolyte complexes turbidity (Figure 6), even with the reduction of the ratio of cationic to anionic polyelectrolyte until the same volumes of CS and CMC, 100 mL, the turbidity didn't reach the initial value, 2.9 NTU. We can do a hypothesis that the complexes formed remain in the solution even though the ratio of cationic to anionic polymer reduce greatly. The reversibility of these complexes was evaluated after the CS 100 mL and CMC 100 mL mix, decreasing and increasing the pH of the polyelectrolyte complexes (Figure 7) with HCl and NaOH solutions. It was verified that there are changes in turbidity values but the polyelectrolyte complexes showed turbidity values always higher than the CS solution alone for the pH range studied, pH 2.9.



**Figure 5 – Effect of anionic polyelectrolyte amount on the cationic solution streaming current. Amount of cationic solution fixed in 10 g.**



**Figure 6 - Effect of anionic polyelectrolyte amount on the turbidity of the solution. Amount of cationic polyelectrolyte fixed in 100 mL.**

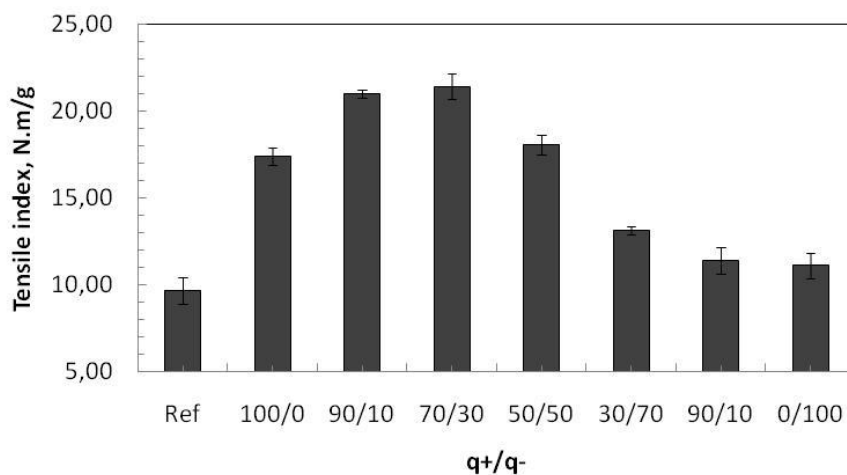


**Figure 7 – Effect of pH on the reversibility of the polyelectrolyte complexes turbidity.**

### Polyelectrolyte complexes application

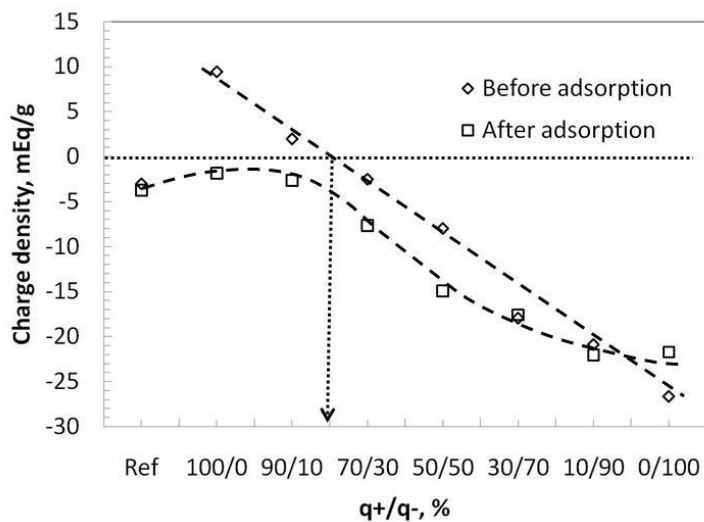
The effect of cationic and anionic polyelectrolyte ratio on the tensile strength is shown in Figure 8.

Better results were found for  $q^+/q^-$  around 70/30 when the net charge of the polyelectrolyte complexes was close to the neutralization (Figure 9 - Before adsorption line). The same results were found by Silva and co-authors when these researchers used a polymer with both cationic and anionic charge. At the isoelectric point of the polyampholyte, the authors found the maximum paper strength measured by tensile index [5, 6]. Different results were found by Gärdlund and Gernandt and co-authors when complexes of cationic polyamideamine epichlorohydrine and anionic CMC were used to improve paper strength. The authors found the maximum strength for complexes where the anionic charge of the CMC had been neutralized to 60% [8, 9]. All the tensile index results were higher than the reference trial, 9,7 N.m/g, without polyelectrolyte or complexes. The addition of CS solution individually (100/0) showed better tensile index result than the results showed by the complexes formed with lower cationic to anionic ratios and with anionic polyelectrolyte alone. It could be explained by the same negative charge density showed by the surface fibers and the net charge of the complexes in the suspension (Figure 9 – Before adsorption line). In this situation, electrostatic interactions between opposite charge can not have happened or were more difficult to happen. As we can see at Figure 8, even though the fibers and complexes had showed the same signal, the tensile index results were higher then the reference result. In this case, other kind of interaction force could be happened but it was not studied in the present work.



**Figure 8 – Effect of cationic and anionic polyelectrolyte ratio on the tensile index. The reference trial was without any polyelectrolyte addition.**

As we can see at Figure 9, the adsorption phenomena happened at different way for CS solution compared to the one for the different ratios of cationic and anionic polyelectrolyte measured by the difference between the charge density before and after adsorption. For lower SC to CMC ratios (30/70 and 10/90), the charge density differences were less evident. There was not benefit when anionic polyelectrolyte was used alone (Figure 8 – 0/100 ratio). It could be explained by the barrier energy increasing.



**Figure 9 – Effect of cationic and anionic polyelectrolyte ratios on the charge density of the complexes solution before adsorption trial on fibers, and after adsorption trial on fibers.**

## Conclusions

Polyelectrolyte complexes formed by cationic starch and anionic carboxymethylcellulose were used to be evaluated as a dry-strength agent. According to the results obtained in this study, the following conclusions can be drawn:

- ✓ It is possible to use cationic starch polymer complexes with anionic polymer dissolved in the fiber suspension for both ends to improve paper quality and to remove the anionic substances from the white water;
- ✓ The benefit of the cationic starch in complexes form showed better tensile index result than the cationic starch alone;
- ✓ In the practical way there is an optimized cationic to anionic ratio condition in order to reach better paper quality and to recycle more white water reducing the consuming of process water;
- ✓ Better conditions of cationic and anionic ratios to be used for dry strength improvement were found when the charge density of the ratio was close to the neutralization;
- ✓ The application of these results to a papermaking should be evaluated widely since the conditions found in these mills could vary widely.

## Future works

This study is part of a research line with focus on the alternatives to improve paper dry-strength. Polyelectrolytes with different charge densities and with opposite charge will be considered. Also, the conditions of adsorption trials, pH and ionic strength, the adsorption polyelectrolyte complexes studies at model surfaces, the studies of the complexes in bulk solution, and the adsorbed layer properties will be considered to help in the phenomena explanation.

## Acknowledgements

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