Impacts of the carboxymethylcellulose adsorption onto eucalyptus bleached fibers and their effects on paper properties

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Abstract
Eucalyptus is becoming one of the most important fiber sources for papermaking worldwide. Ongoing scientific and technical advances with eucalyptus fibers are directed at modifying fiber properties for specific paper properties. An important component in the development of new or improved eucalyptus materials is the surface chemistry of the fiber. Also it has been well recognized for many years that carboxyl groups of cellulosic fibers have a major impact on various unit operations in pulp and paper manufacture as well as on the properties of the final product. In this context, the present study aims to discuss the impacts of the carboxymethylcellulose (CMC) adsorption onto eucalyptus bleached fibers and their effects on paper properties. The treatment of CMC adsorption to the fibers resulted in changes of the superficial charge density of fibrous material, being reported an increase in the range of 10-16% in the content of carboxylic groups, depending on the CMC amount adsorbed (0.4-3.75%). In addition, the modified pulps presented development of absorption properties, marked by increased rates of water retention value (7-28%) and a distinguished reduction of the fiber hornification phenomenon (70%). Moreover, increase in refinability was observed, with significant reduction in energy demand (24%) during this stage. Improvements on physical-mechanical properties were found and are, remarkably, dependent on the development of fiber-fiber linkages due to the treatments. Conclusively, the CMC adsorption treatment onto cellulosic fibers, when applied to the paper industry, paying attention to their inherent peculiarities, can produce products with differentiated quality aspects that are higher than the currently produced.

Keywords: eucalyptus; fiber modification; carboxymethylcellulose.

Introduction
The polymer adsorption on the cellulosic fibers surface helps to increase its charge density, improving the strength properties of paper formed. A polymer variety has the potential of adsorption to the fiber, including carboxymethylcellulose (CMC), an anionic polymer derived from cellulose. In the paper manufacturing process, the CMC can be used as an additive to improve the sizing of paper surface, and as a component of coating color [1,2]. CMC can be adsorbed to the fiber wall, increasing its surface charge density and by improving strength properties of paper formed [3].

Anionic polyelectrolytes, such as CMC, are generally not adsorbed on cellulose fibers due to electrostatic repulsion between the negatively charged fiber surface and the anionic polyelectrolyte. Thus, to retain the anionic polymer in the fiber is necessary to use a cationic system [3,4]. Alternatively, specific methodologies promote the adsorption of CMC on the fiber surface, without the use of cationic additive. According the literature CMC can be adsorbed by controlling the electrical conductivity and degree of substitution (DS) of the polymer [5]. CMC with high DS and low molecular weight can be adsorbed to the fibers surface, under specific conditions (1 hour, 60 ^{o}C, pH 12.5) [2,6].

It is believed that the CMC adsorption mechanism on the pulp fiber is governed by intermolecular hydrogen bonds between substituted segments of the polymer chain and the fiber surface. In adsorption, the CMC charged groups experience repulsion, resulting in an extended conformation of the modified fiber. It is suggested that water molecules trapped after CMC adsorption are located in this extended conformation [3,4].

In papermaking process, improvements in retention of chemical additives are achieved by the CMC adsorption to cellulosic fibers. Additionally, the CMC adsorption generates a uniform charge along the fiber surface [5]. The literature reported that cellulose pulp treatment with CMC increased its water retention value and, consequently, the strength of internal linkages in the paper formed [2,4].

The CMC adsorption on cellulose pulps opens new possibilities for the paper industry. Studies have shown that in the fibers the adsorption is comparable to the refining effect. Also, the treated fibers showed an increase in strength properties, while elastic properties are less affected. The effects are explained by the increased strength of fiber-fiber linkages [1,3,7].

Thus, this study aims to evaluate the CMC adsorption to bleached eucalyptus pulp, so as to obtain a pulp chemically and structurally modified, showing an improvement in its refinability and physic-mechanical properties of paper formed.

Experimental

MATERIALS

A commercial bleached eucalyptus pulp (1.72 microkappa; 90.3% ISO brightness; 11.37 mPa.s intrinsic viscosity and 18 Schopper Riegler degree) was used as starting material for this project. It was used a commercial carboxymethylcellulose sodium salt (Chromate Chemicals Ltda.), with a minimum purity of 99.5%.

METHODS

Carboxymethylcellulose adsorption to the kraft pulp

The CMC adsorption on the pulp was carried out according to the methodology proposed by the literature [2], with modifications. In a flask containing the equivalent of 50 g of dry pulp, the treatment liquor was added (CMC, sodium hydroxide and water), reaching a final consistency equivalent to 5% and a pH equal to 12.5. After complete homogenization, the mixture (pulp and liquor) was pre-heated and transferred to a thermostat, which was kept under stirring and temperature of 60 ^{o}C. After treatment period, 90 minutes, the pulp was washed with distilled water to 9 m^3 per ton of dry pulp. All treatments were performed in triplicate. For a systematic understanding of the CMC adsorption effects on the pulp, different charges of the polymer were evaluated, these being equivalent to 0.5, 1.0, 2.0 and 4.0%, resulting in cellulosic pulps CMC1, CMC2, CMC3 and CMC4, respectively. All data were compared with the reference pulp (REF), ie one that was not subjected to the polymer adsorption treatment.

Cellulosic pulp quality

Chemical characteristics

All samples were analyzed according to TAPPI - "Technical Association of Pulp and Paper Industry" test procedures, as well as literature reviews [8,9,10]. All samples were analyzed in duplicate.

Morphological properties

Samples prepared in water suspension of fibrous material in the consistency of 0.001% and dispersant added (2 % pulp basis) were prepared for coarseness, number of fibers per gram, fines content, and length and width determination. Analyses were performed in equipment Galai CIS-100.

Absorbing properties

The hydrophilicity of the pulp treated and reference was measured by analyzing the water retention value (WRV), in accordance with ISO 23714:2007.

In regards to hornification analysis the correlation demonstrated by the literature [11], which reflects some fiber structure changes including the width, attributed to the fibers morphology when they suffer the collapse of the lumen and rolling the middle lamella fiber wall, were used. The correlation is given by the equation:

$$\text{Hornification (\%)} = (WRV_0 – WRV_1)*100/WRV_0$$

Where, WRV_0 = pulp that has not undergone drying water retention value and WRV_1 = pulp that has been dried water retention value.

Paper produced refining and properties evaluation

The pulps, after rehydrated for four hours, were refined in PFI mill laboratory using the mill revolutions intervals to allow the physical and mechanical properties development with the refining action. For all pulps were obtained four refine points, corresponding to the following revolutions numbers: 0, 500, 1000 and 2000.

For pulps without refining and their respective refined pulps physical-mechanical tests laboratory sheets were formed, which were stored in an controlled environment (relative humidity of 50 $\pm$ 2% and temperature 23 °C $\pm$ 1). All tests were performed according to TAPPI procedures.

Statistical analysis

The initial experiments (adsorption treatment and cellulosic pulp chemical, morphological and absorbing evaluation) statistical analysis was carried out using the software Statistica 6.0 and Microsoft Office Excel 2007. A variance analysis (ANOVA), using a 5% level significance by Tukey test, was performed. Curve Expert 1.4 and Microsoft Office Excel 2007 software were used for statistical analysis of data obtained in the physic-mechanical tests performed in papers produced at different refine levels. The data for each test, depending on the energy demand of the refining step, were statistically analyzed by regression analysis. The adjusted equations were compared by F test, using the identity test models and adopting a significance level of up to 5% probability according to the methodology presented by the literature for linear and nonlinear models [12,13]. The generated equations (energy demand of refining step versus physic-mechanical property) for each property were compared in order to check equality between them. If so, the equations that had been reduced to equal a single equation. The remaining equations, statistically different, were not reduced.

Results and Discussion

CMC Adsorption on pulp

The CMC adsorption on the pulp was indirectly measured by analyzing the pulp reference and treated glycans contents. The choice of the parameter, glycans content, are due to the fact that CMC is a polymer derived from cellulose, so its chain is composed of glucose units. Thus, the CMC adsorption will be expressed in terms of glycans added to the pulp, as shown in Figure 1.

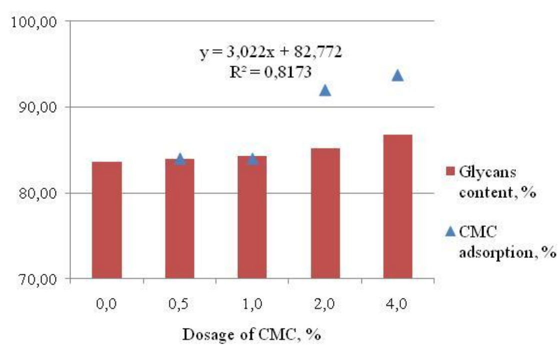

Figure 1. Glycans content and carboxymethylcellulose adsorption (CMC), in percentages, for cellulose pulps reference and treated with CMC at charges equivalent to 0.5, 1.0, 2.0 and 4.0%.

The CMC adsorption on pulp was satisfactory, according to the treatment conditions used (60 °C, 90 min, pH 12.5), with minimum and maximum observed adsorptions equivalent to 84.00 and 93.75%, respectively. The results are in agreement with the literature that reported approximately 80% CMC adsorption on bleached softwood pulp [1]. The authors suggest that CMC is adsorbed mainly on the fiber outer surface, the fiber and porosity controls the polymer adsorption. They further report that CMC adsorbed is strongly linked to the fiber, being an irreversible process, unaffected by subsequent washing steps or intensive refining.

According to the literature the CMC anionic carboxylate groups and the fiber surface nature contribute to the effect of electrostatic repulsion and commitment of the phenomenon of CMC adsorption on fibers [5]. It is known that the CMC substitution degree strongly influences its adsorption, knowing that its rise penalizes cellulosic fibers adsorption.

It was proposed that the mechanism of CMC adsorption to cellulosic fibers occurs through the non-substituted segments in the CMC chain, ie, those that do not contain carboxylate groups, which interact via hydrogen bonds to the fiber [4].

Quality of the pulp

The modifications in bleached eucalyptus pulp resulting from the CMC adsorption treatment were evaluated in relation to chemical, morphological and absorbent pulp and physico-mechanical properties of paper produced. Thus will be presented and discussed the results obtained for the reference pulp (REF) and adsorbed to CMC at charges equivalent to 0.5, 1.0, 2.0 and 4.0%, corresponding to pulps CMC1, CMC2, CMC3 and CMC4 respectively.

Chemical analysis

Table 1 shows the chemical analysis results obtained for the reference pulps and CMC adsorbed pulps, the values for each analysis were evaluated statistically by Tukey at 5% probability.

Table 1. Pulp reference (REF) and carboxymethylcellulose (CMC) adsorbed chemical analysis at charges equivalent to 0.5, 1.0, 2.0 and 4.0% (CMC1, CMC2, and CMC3 CMC4, respectively)

Parameters	REF	CMC1	CMC2	CMC3	CMC4
Glycans, %	83,63 a *	83,98 a	84,33 a	85,17 b	86,77 c
Xylans, %	14,35 a	14,48 a	14,24 a	13,28 b	12,09 c
Uronic acids, %	0,85 a	0,74 b	0,68 bc	0,66 c	0,55 d
Hexenuronic acids, %	0,15 a	0,15 a	0,14 ab	0,13 bc	0,12 c
Carbonyl group, meq/100g	6,68 a	7,39 b	7,49 b	7,40 b	7,78 b
Carboxyl group, meq/100g	4,57 a	4,33 a	4,75 a	4,43 a	4,58 a

*Averages followed by same letter in same row do not differ significantly by Tukey test at 5% probability.

As observed and discussed earlier, there is a tendency to increase the glycans content in pulps with CMC adsorption. There is a 3.75% maximum percentage increase in the glycans content when the pulp is treated with 4% CMC, corresponding to 93.75% adsorption.

The pulp xylans content presents apparent decrease in value due to the CMC adsorption, though. Due to the pulp chemical analysis is made on percentage content from pulp analyzed, the reduction is apparent, because there is increased glycans content, while the xylan content is kept unchanged. Same trend is observed for uronic and hexenuronic acids contents. In summary, the CMC adsorption treatment promotes a change in the pulp chemical composition, with an increase in the relative percentage glycans content.

To characterize the pulp functional groups profile were performed measurements of the contents of carbonyl and carboxyl groups. As noted, a significant increase in the carboxylic groups content, due to the CMC adsorption treatment. However, among themselves, the treated samples showed no significant difference. The increase is due to the carboxylic groups content present in the CMC. On the other hand, the content of carbonyl groups remained unchanged due to the adsorption treatment.

It is well substantiated that the increased carboxylic groups content can impact positively on papermaking process, as well as the final product properties. According to the literature, CMC adsorption on pulp reduces the difference in charge density along the fiber surface, making the pulp anionic sites more uniform, a phenomenon that can result in improved additives retention in wet end paper machine [5].

Morphological analysis

The reference and CMC adsorbed pulps were analyzed morphologically for the following parameters: coarseness, number of fibers per gram, fines content, fibrous material length and width, and the results are presented in Table 2.

Table 2. Fibrous material morphological analysis for cellulose pulps reference (REF) and carboxymethylcellulose (CMC) adsorbed at charges equivalent to 0.5, 1.0, 2.0 and 4.0% (CMC1, CMC2, and CMC3 CMC4, respectively)

Parameters	REF	CMC1	CMC2	CMC3	CMC4
Coarseness, mg/100m	4,47 a*	4,70 a	4,89 a	4,91 a	5,57 a
Number fiber per gram, million	32,15 a	28,38 a	28,61 a	33,50 a	28,22 a
Length, mm	0,79 a	0,81 a	0,81 a	0,77 a	0,78 a
Width, mm	32,56 a	31,86 a	32,65 a	32,81 a	31,07 a
Fines, %	11,62 a	11,96 a	11,82 a	11,01 a	12,74 a

*Average followed by same letter in same row does not differ significantly by Tukey test at 5% probability.

There was no significant difference by Tukey test at 5% probability for any of the morphological parameters analyzed in this study. So, apparently, the differences resulting from the CMC adsorption on pulp appear to be more related to fiber-fiber interactions.

Absorbing properties evaluation

In order to evaluate CMC adsorption treatment effect on absorbent properties of the pulps were measured: the water retention value (WRV), related to the hydration capacity and swelling properties of the fibers, and the effect of hornification as defined by the literature [14] as the relative loss in the hydration capacity of the fibers after drying step. The results are presented in Table 3.

Table 3. Water retention value (WRV) and hornification phenomenon to the cellulose pulps reference (REF) and adsorbed with carboxymethylcellulose (CMC) at charges equivalent to 0.5, 1.0, 2.0 and 4.0% (CMC1, CMC2, CMC3 and CMC4, respectively)

Parameters	REF	CMC1	CMC2	CMC3	CMC4
WRV_0, % **	106,83 a *	114,38 a	117,81 ab	125,75 bc	136,41 c
WRV_1, % **	83,12 a	105,81 b	109,98 bc	116,32 c	130,27 d
Hornification, %	22,20 a	7,50 b	6,65 b	7,50 b	4,50 b

* Average followed by same letter in same row does not differ significantly by Tukey test at 5% probability. ** WRV_0 is the pulp water retention value that was not subjected to drying step, and WRV_1 is the pulp water retention value that was subjected to drying step at 105 ^{o}C.

The pulp CMC adsorption treatment leads to an increase in the WRV, being observed a maximum increase of 27.68% for the pulp treated at a charge equivalent to 4% CMC. The literature reported similar results, however, the authors used a softwood pulp in their studies [2,3]. Commonly, the WRV is used to determine the pulp swelling capacity. Thus, CMC adsorption contributed to the pulp swelling increase. Also, with the CMC adsorption, there was reduction of the of fibers hornification phenomenon. An average of 70% reduction was observed for the treated pulps. According to the literature the hornification phenomenon has been associated with the formation of irreversible or partially reversible hydrogen bonds in the pulp due to the step of drying or water removal [15]. Thus, the CMC adsorption appears to reduce the irreversibility of hydrogen bonds, improving the fiber swelling properties, and reducing, therefore, the hornification phenomenon.

Refining and paper properties evaluation

The reference cellulose pulps and the pulps obtained by CMC adsorption treatment were refined in a PFI mill laboratory and evaluated for their physic-mechanical properties; with the aim of characterizing the quality for tissue paper production, *P&W* (print and writing paper) or other relevant category, depending on the acquired characteristics.

Figure 2 shows the reference pulp and pulp obtained by CMC adsorption treatment behavior during the refining stage. The energy demand was chosen because it represents a widely discussed variable among papermakers, always seeking to reduce its value. It is noteworthy that in papermaking process, the refining stage is among the most energy demanding.

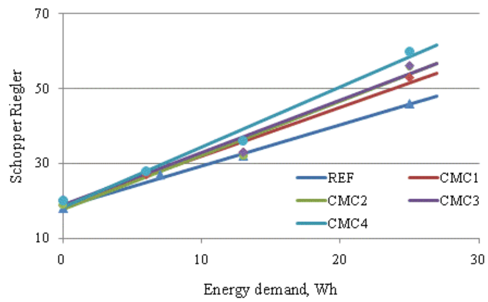

Figure 2. Refining degree (Schopper Riegler) for reference cellulose pulp (REF) and pulps obtained by CMC adsorption treatment at charges equivalent to 0.5, 1.0, 2.0 and 4.0% (CMC1, CMC2, CMC3 and CMC4, respectively).

As observed, the treated pulp exhibited a tendency to lower energy demand to achieve the same refining degree, expressed by Schopper Riegler degree (^{o}SR). It was observed a 24% average reduction for the pulps CMC adsorbed. The downward trend in the refining stage to the treated pulps is related to their WRV increase, which reflects in an increased resistance to pulp drainage (increasing ^{o}SR).

To facilitate papermaking properties comparisons, among the treatments levels applied to the pulp, curves of the property developing in function of the energy demand in the refining stage were plotted. For best understanding of the results, some properties, often measured in tissue paper segments and *P&W*, are graphically presented (Figure 3) and will be further discussed.

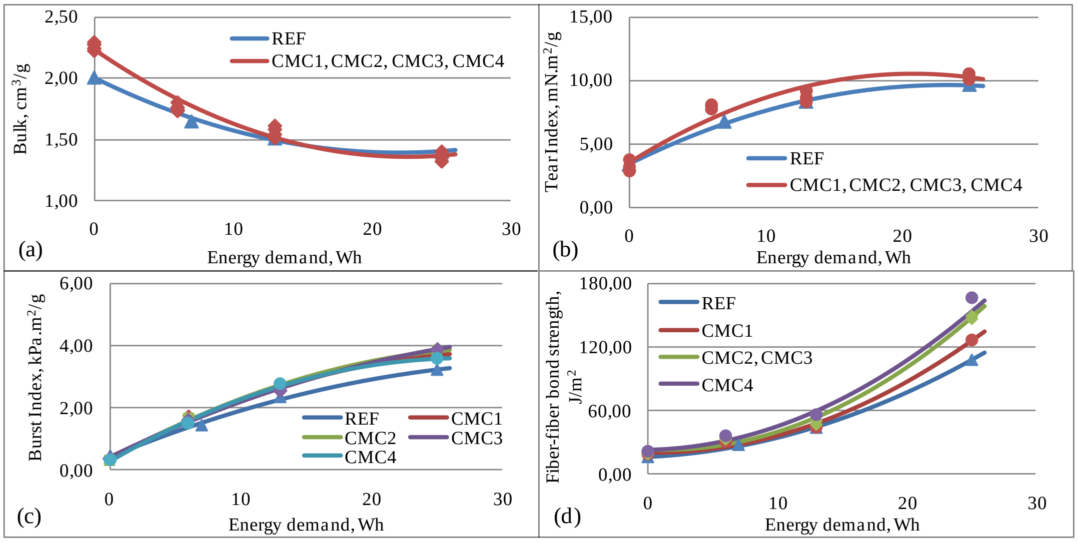

Figure 3. Bulk (a), tear index (b), burst index (c) and fiber-fiber bond strength (d) properties curves as a refining energy demand function for produced paper from the CMC adsorption treatment to the reference pulp.

Physico-mechanical properties

Bulk

There was a tendency to increase bulk as a function of the CMC adsorption treatment, until the energy demand value in the refining stage equivalent to 15 Wh. However, after this energy demand amount there was a small reduction in property value. Note that the polymer adsorption can impact on the property assessed, so that it can be controlled, considering the quality of the final product required. That is, if the product demands the highest bulk the controlled application of refining stage is recommended; in our study to values of 15 Wh of energy demand. However, among themselves, the treatment levels evaluated were not significant. Thus, the lowest charge of CMC evaluated (1%) would be sufficient for the adsorption treatment in order to promote the observed changes in bulk property.

Tear index

Tear index property was positively influenced by the CMC adsorption treatment. It was found an average of property increase equivalent to 6.59% and a maximum of 18.92% for paper produced from the pulp adsorbed with CMC, and refined in the range of 0-25 Wh of energy demand.

According to the literature, tear index is greatly affected by fiber-fiber bond strength, length, thickness and total number of fibers participating in breakage of the sheet [16]. As previously reported there were no morphological differences to the cellulosic pulp with CMC adsorbed, so the increase in tear index property was basically in function of the fiber-fiber bond development.

Burst index

There was a tendency to increase burst index property in function of the CMC adsorption treatment. Average and maximum increases equivalent to 4.56 and 29.88%, respectively, were observed, arising from the CMC adsorption treatment.

Fiber-fiber bond strength

The CMC adsorption treatment promoted increased fiber-fiber bond strength property, relating positively to the treatment dose applied to the pulp. Increments ranging from 2.38 to 54.98% were observed, being the maximum value the one corresponding to the paper produced from pulp treated with 4% CMC, at the maximum refining point (25 Wh of energy demand). It is worth to note that during the refining stage of the treated pulp, expressed by energy demand, the property increasing trend is more pronounced.

The CMC adsorption on fibers promotes an increase of its surface charge density, which implies the development of fiber-fiber linkages properties. According to the literature, CMC adsorption conceives new possibilities for modification of cellulosic fibers and produced paper properties, citing as its main advantage is the increase in internal resistance properties of the paper [3]. In this study, the development of fiber-fiber bond strength was evident and infers extremely important, representing one of the main effects of treatment for modifying the pulp.

Conclusions

- Effective CMC adsorption to the pulp in the range of 84.00 to 93.75% was achieved using controlled treatment conditions (60 ^{o}C, 90 minutes and pH 12.5).
- Chemical analysis confirmed the increased glycans content of the treated pulps, for the polymer adsorbed on the pulp is a cellulose derivative and, therefore, is composed of glucose units.
- Morphologically the CMC adsorption on pulp did not impacted in coarseness parameters, number of fibers per gram, fines content, fibers width and length.
- The pulps adsorbed with CMC showed water absorption properties development, marked by an increase in water retention value and reducing the phenomenon of hornification.
- The treated pulps had higher Schopper Riegler degree values, and therefore had better refinability. The energy demand for treated pulps was significantly reduced compared with the reference pulp (average reduction equivalent to 24%).
- The development of physical-mechanical properties of paper formed from the pulp treated with CMC has been substantially evidenced. In summary, the changes in properties are due especially to the development of fiber-fiber linkages promoted by the CMC adsorption on pulp.
- Conclusively, according to the observed results is permissible to think of the industrial application of CMC adsorption on pulp, paying attention to the industrial requirements. The polymer quality and the treatment parameters (time, temperature and pH) are major factors in the CMC adsorption effectiveness on cellulosic fibers.

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