Influence of the combined use of cationic starch and cationic polyacrylamide on the quality of printing paper

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ABSTRACT: The influence of combined use of cationic starch (CS) and cationic polyacrylamide (C-PAM) on the properties of printing paper made from Portuguese pulps was studied with the aim of correlating the quality of sheet formation with its physical properties. Calcium-carbonate-filled paper sheets, made from a mixture of bleached kraft pulps from Eucalyptus globulus (beaten at 30°SR) and Pinus sylvestris (beaten at 23°SR), were prepared in the presence or absence of CS as a dry strength additive and C-PAM as a retention aid. Three levels of addition of CS were tested; 2%, 3%, and 4% (w/w). As expected, the combined use of these two additives improved the retention of fillers, but it also compensated for the decrease in paper strength. In fact, the internal cohesion strength, and tensile and tear indexes, were significantly improved. It was also found that when CS is used alone, it acts mainly as a retention aid, but when it is used with the C-PAM, it acts mainly as a dry strength additive. Thus, the addition of 3% or 4% CS was not enough to maintain the mechanical properties of filled papers, not only because of the increase of fillers but also because of the degradation of the paper formation.

Application: With the combined use of CS and C-PAM, a good compromise can be found between the formation quality and the mechanical properties of printing and writing grades of paper.

Cationic starch (CS) is one of the oldest of the dry strength additives used in the papermaking industry and is still the most important, not only because of its competitive price but also as a result of its dry strength properties and its capacity to retain fines and fillers in paper bulk [1]. On the other hand, cationic polyacrylamide (C-PAM) is a synthetic polyelectrolyte that promotes the retention of fine particles and fillers, which enhance the optical properties of printing papers but have the drawback of inducing a loss of mechanical resistance in the paper produced [2]. That is why it is necessary to combine the use of these families of additives. The goals are to promote the maximum retention of small size particles, to increase the brightness and the opacity of paper, and to compensate for the loss of mechanical properties resulting from the introduction of mineral fillers.

Unfortunately, the use of CS and C-PAM in particular and polyelectrolytes in general is known to provoke the degradation of the paper formation. The mechanism by which polyelectrolytes interact with pulp fibers is based on the flocculation process, which leads to some detrimental effects on paper properties. In fact, the use of such wet end additives negatively affects the air permeability, the opacity, and the paper formation, even though it increases the retention of fines and fillers [3,4].

According to Korteoja *et al.* [5,6], the physical properties of the paper depend on the uniformity of the formation and on the organization of the fibers within the paper mat structure. Thus, a paper with poor formation is not as strong as its better formed counterpart. It was also demonstrated that when paper is submitted to tension stresses, the low basis weight areas usually deformed before the denser ones do [7].

In this study we tried to correlate the quality of paper formation with the physical properties obtained for the papers produced with the combined uses of CS, C-PAM, and calcium carbonate in paper made from a mixture of bleached kraft pulp from *Eucalyptus globulus* and *Pinus sylvestris*.

EXPERIMENTAL

Materials

The paper furnishes were a mixture of bleached kraft pulps, 85% from *Eucalyptus globulus* and 15% from *Pinus sylvestris. E. globulus* pulp was beaten to 30°SR, and *P. sylvestris* fibers were refined at 23°SR in a Valley beater. The pulp compositions and the papermaking conditions were close to those used in the production of printing paper in Portugal.

A commercial cationic starch derived from potato and modified by alkyl chains bearing quaternary ammonium groups with a degree of substitution of 0.034 was used in this study. Aqueous solutions of cationic starch having a concentration of 5% (w/w) were prepared and gelatinized

	Additive-free	0.02% C-PAM	2% CS	Both
Basis weight, g/m²	59.9	61.5	61.0	60.0
coeff. of variation	2.8	2.3	1.6	1.7
Thickness, mm	116	123	114	112
coeff. of variation	2.1	2.9	3.2	2.8
Density, g/cm³	0.52	0.50	0.53	0.54
Air permeability, m/Pa·s	21.0	30.1	25.0	24.4
coeff. of variation	4.9	3.4	5.7	4.2
Tensile index, N·m/g	41.2	27.5	35.7	40.9
coeff. of variation	4.8	5.2	7.2	4.0
Burst index, kPa·m²/g	1.43	1.17	1.67	1.72
coeff. of variation	4.9	3.6	10.9	7.5
Tear index, mN·m²/g	8.15	6.18	7.06	8.67
coeff. of variation	4.4	5.3	4.3	2.0
Internal cohesion, J/m²	98	98	161	178
coeff. of variation	5.0	5.2	9.0	9.9
PCC in paper, %	°	7.8	10.6	11.8
Whiteness, %	87.7	89.1	84.2	81.4
coeff. of variation	0.2	0.2	0.2	0.2
Opacity, % ISO	78.6	83.5	88.0	91.2
coeff. of variation	0.4	0.5	0.3	0.4
Scattering coeff., m²/kg	0.16	0.46	0.61	1.00
coeff. of variation	0.01	0.02	0.01	0.02
Absorption coeff., m²/kg	44.1	56.7	59.3	62.0
coeff. of variation	0.7	2.2	1.2	1.5

I. Properties of sheets without additives and with 20% PCC and either 0.02% C-PAM or 2% CS or both.

		Cationic Starch		
	Additive-free	2%	3%	4%
Basis weight, g/m²	59.9	60.0	64.7	65.2
coeff. of variation	2.8	1.7	1.8	2.7
Thickness, mm	116	112	128	128
coeff. of variation	2.1	2.8	3.2	3.3
Density, g/cm³	0.52	0.54	0.51	0.51
Air permeability, m/Pa·s	21.0	24.4	36.1	34.1
coeff. of variation	4.9	4.2	2.9	2.8
Tensile index, N·m/g	41.2	40.9	27.7	29.0
coeff. of variation	4.8	4.0	2.2	6.9
Burst index, kPa·m²/g	1.43	1.72	1.23	1.41
coeff. of variation	4.9	7.5	8.1	7.8
Tear index, mN·m²/g	8.15	8.67	5.36	5.42
coeff. of variation	4.4	2.0	9.4	11.1
Internal cohesion, J/m²	98	178	108	123
coeff. of variation	5.0	9.9	5.9	5.6
PCC in paper, %	°	11.8	14.4	14.6

II. Properties of sheets made without additives and with 20% PCC, 0.02% C-PAM, and different amounts of CS.

by boiling for 30 min under a gentle manual permanent mixing. Before being stored, the solution was diluted to 1% (w/w).

The filler used was a slurry of precipitated calcium carbonate (PCC) with a solid content of 17% supplied from an industrial source. The specific BET-surface area and the average particle size were given by the suppliers as being 4.2–4.8 m²/g and 2.75 μm, respectively. The retention aid used for all the papers was a commercial cationic polyacrylamide.

Sheet forming

Paper sheets having a basis weight of 60 g/m² were elaborated in the presence or absence of the additives mentioned. Papers of *E. globulus* and *P. sylvestris* were prepared with an automatic sheet former, where handsheets were only dried and slightly pressed at 100–110°C. The residence time of the paper samples in the drying section was about 260 s.

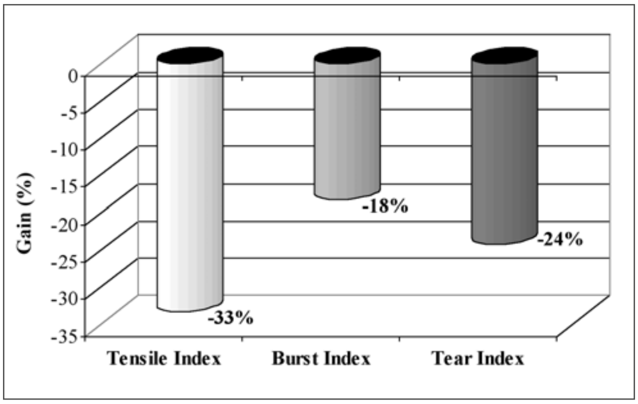
A first set of filled papers was elaborated in presence of 20% PCC, 2% CS, and 0.02% C-PAM to determine the effect of the combined use of these two additives. (The quantities given here are in wt/wt percentages with respect to o.d. pulps.) A reference set of free-additives paper samples was also elaborated.

Finally, a set of experiments was prepared to deal with filled papers prepared in the presence of different amounts of CS (2%, 3%, and 4%). The preparation of the samples involved the addition of 20% PCC to a 4-L pulp suspension (1.5 g/L consistency). This stock was mixed at 1200 rpm for about 1 min. After a homogeneous suspension was reached, different amounts of CS (2%, 3%, and 4%) were added to the stock. The suspension was stirred for 5 min more before 0.02% C-PAM was added.

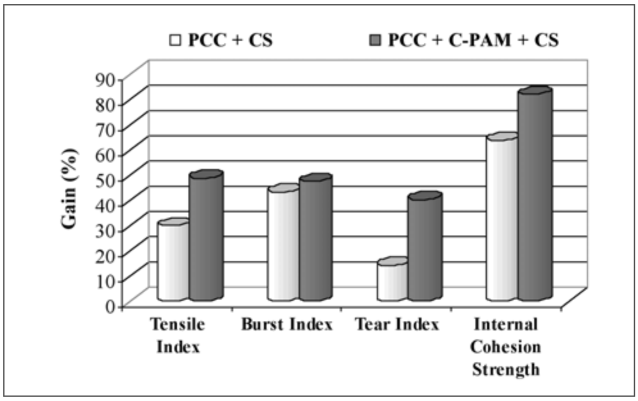
All the quantities added were optimized in previously published studies [8,9].

Handsheet characterization

The physical properties of the prepared sheets were determined according to relevant standard methods. All the data obtained are presented as the arithmetic means of 10 measurements, except for the thickness, which was based on 20 values.



1. Gain in tensile, burst, and tear indexes for sheets made with PCC and C-PAM.



2. Gain in tensile, burst, and tear indexes and internal cohesion strength for sheets made with PCC + CS and with PCC + C-PAM + CS.

Formation parameters were determined by a method developed by Costa [10], which is based on an image analysis technique. Accordingly, the images of paper samples were obtained by normalized light transmission and were then analyzed.

First- and second-order statistics were employed to determine some relevant paper formation parameters: first- and second-order entropy, contrast, and homogeneity.

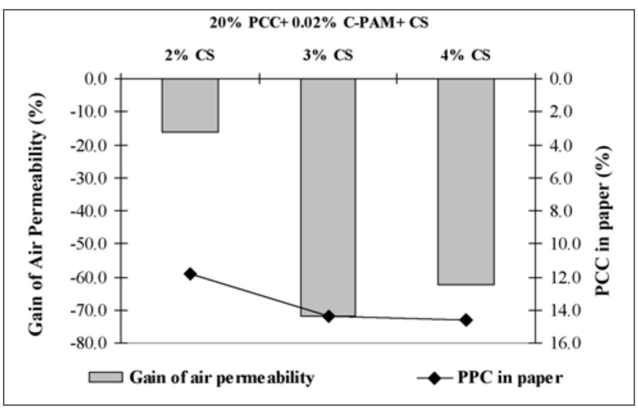
The retention of filler was evaluated at 575±25°C by the incineration method described in TAPPI T 413 om-85.

RESULTS AND DISCUSSION

The physical properties of papers made from pulps without and with the addition of CS and C-PAM are reported in Table I, which shows that the retention of PCC increased from 8% to 12% when these two wet end additives were used. The addition of 2% CS increased the paper density and consequently its overall mechanical properties, which confirms the expected increase of interfiber bonds, induced by the cationic amylopectine and amylose macromolecules.

The air permeability increased with the addition of PCC and C-PAM, because the addition of filler reduced the fiber–fiber bonding and created more fiber–air interfaces. On the other hand, with the addition of cationic starch, which promotes fiber bonding, the fiber–air interfaces decreased, with the air permeability also decreasing. The opacity increased because the retention aid enhanced the retention of fillers.

As expected, the mechanical properties of papers made with PCC and C-PAM without CS decreased with increasing filler content in the paper. Thus, decreases of 33%, 18%, and 24% for the tensile index, burst index, and tear index, respectively, were observed, as shown in Fig. 1. The results reported in Table I and Fig. 2 show the influence of the CS addition. As the filler content increases in paper, the mechanical properties are enhanced considerably (tensile and tear indexes and internal cohesion strength). These results indicate that CS acted mainly as a dry strength additive and C-PAM acted mainly as a retention aid.

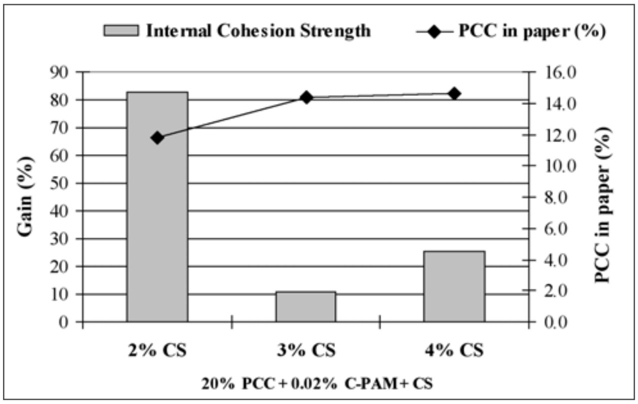


3. Gain in air permeability and PCC retention values in paper made with different amounts of CS.

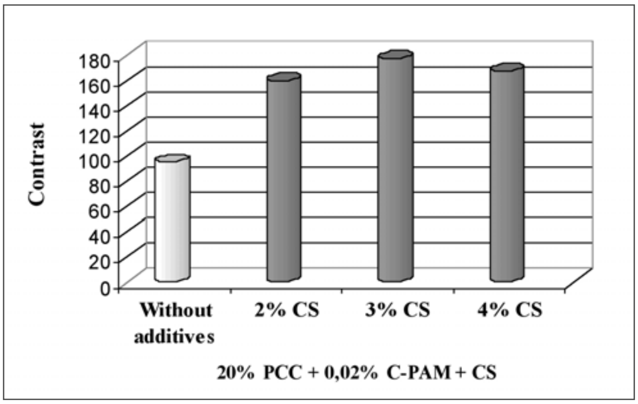
The physical properties of papers made without additives and with PCC, C-PAM, and different amounts of CS are reported in Table II. These data and Fig. 3 show that the air permeability was significantly increased by CS addition. In fact, the air permeability increased from about 20 mm/Pa·s to about 35 mm/Pa·s when CS was added to the pulp stock. On examining the formation of the paper samples, one can observe that the addition of CS contributes to the formation of flocks, thus decreasing the quality of paper formation.

The mechanical properties increased with the addition of CS, which compensated for the decrease in paper strength caused by the addition of the filler.

It is commonly known that the influence of cationic starch on paper strength is pronounced essentially in the z direction. In other words, the internal cohesion strength is the property most affected by the addition of cationic starch. Figure 4 shows that the internal cohesion strength increased by 80%, 12%, and 25%, for CS additions of 2%, 3%, and 4%, respectively. The higher retention of PCC in paper and the probable lower retention of CS could



4. Influence of the amount of CS on the internal cohesion strength and the retention of PCC in the paper samples.



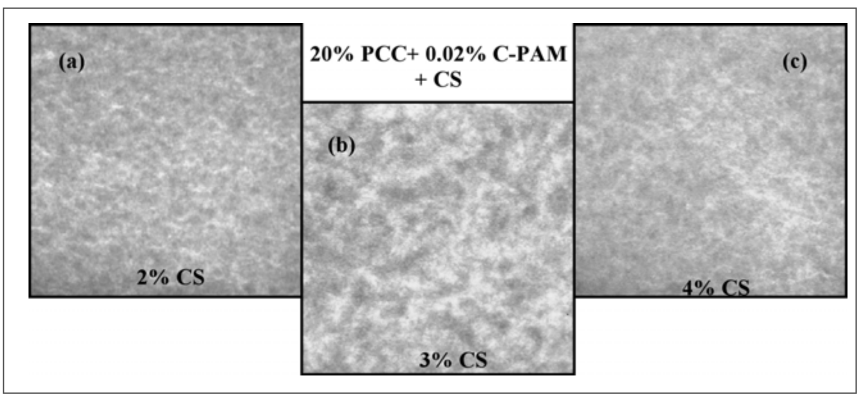
5. Values obtained for the contrast for sheets made with C-PAM, PCC, and different amounts of CS.

explain, at least partially, the modest gain in internal cohesion strength for higher levels of CS addition.

The formation parameters were determined according to Costa's method [10], and the data are reported in Table III. An increase in first- and second-order entropies for all amounts of CS indicates a decrease in the formation quality of paper with the addition of both CS and C-PAM, justifying the conclusion that the mechanism of these additives is indeed one of flocculation. This indication is more accentuated for the results of contrast and homogeneity, which denotes clearly the degradation of paper formation quality with the combined use of C-PAM and CS. In fact, the combination of these two additives increased the contrast by 39%, if one compares them with the sheets made with C-PAM only.

	1st order entropy	2nd order entropy	Contrast	Homo-geneity
No additives	5.22	7.11	95	0.123
20% PCC, 2% CS	5.63	7.52	141	0.102
20% PCC, 0.02% C-PAM				
0% CS	5.75	7.57	115	0.111
2% CS	5.86	7.73	160	0.096
3% CS	5.99	7.85	178	0.088
4% CS	6.01	7.84	168	0.093

III. Formation parameters of filled papers prepared from a blend of* E. globulus *and* P. sylvestris *using different amounts of cationic starch.

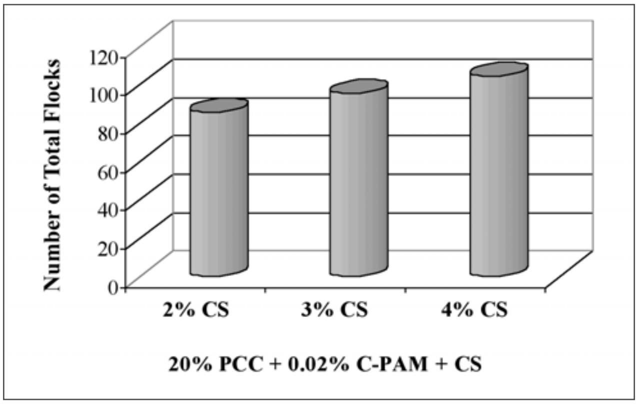


6. Grey level density images using light transmission on paper sheets containing (a) 2%, (b) 3%, and (c) 4% CS.

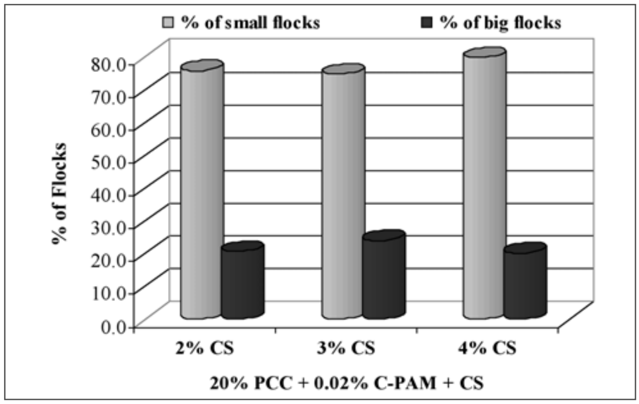
On the other hand, with an increase of the amount of cationic starch, the data show an increase for first- and second-order entropies and for contrast and a decrease for homogeneity for the 3% CS, which denotes a degradation of paper formation. For 4% CS added, an improvement was observed in the formation parameters, as reported in Fig. 5.

Figure 6 shows the differences obtained for the formation parameters, and the degradation of formation is clearly shown for 3% CS addition. The improvement of formation with 4% CS can be justified by the size of the formed flocks, and they can be classified as follows: (i) small flock sizes of 1.2 mm and 3 mm and (ii) big flock sizes of 6, 10, and 16 mm.

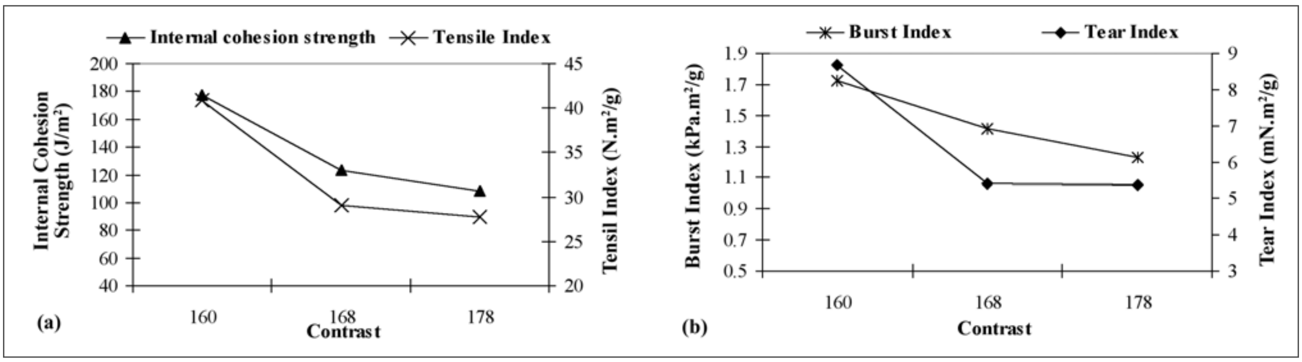
Thus, this parameter was determined as a function of the CS addition, as shown in Figs. 7 and 8. From these figures, one can observe that: (i) the total number of flocks increased with increasing amounts of CS, (ii) the percentage of small flocks passed through a minimum for 3% CS addition, (iii) the percentage of small flocks was the highest for 4% CS, and (iv) the percentage of big flocks was largest for the samples containing 3% CS. These data verify the opposite trend observed for the formation qual-



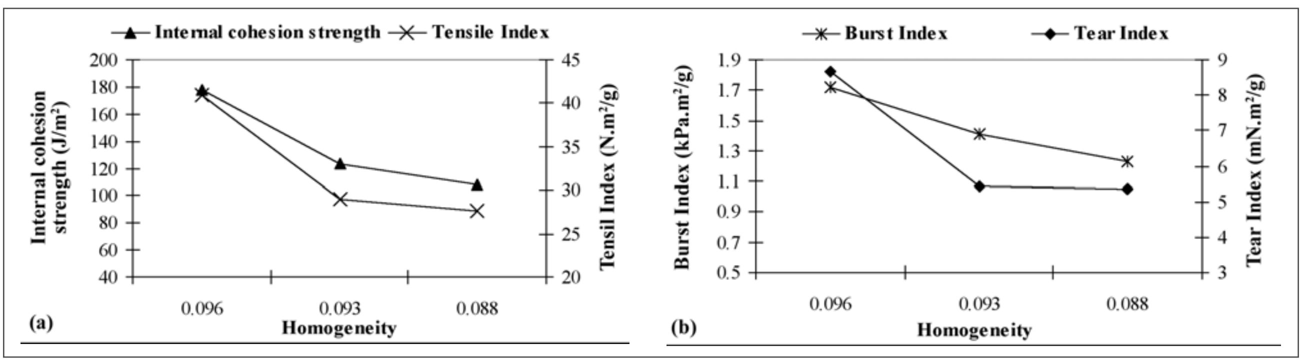
7. ***The total number of flocks for sheets made with PCC, C-PAM, and different amounts of CS.***



8. ***The percentages of small and big flocks for sheets made with PCC, C-PAM, and different amounts of CS.***



9. ***The evolution of (a) tensile and internal cohesion strength and (b) burst and tear indexes as a function of values of contrast for sheets made with PCC, C-PAM, and different amounts of CS.***



10. ***The evolution of (a) tensile and internal cohesion strength and (b) burst and tear indexes as a function of values of homogeneity for sheets made with PCC, C-PAM, and different amounts of CS.***

ity of paper prepared with 4% CS.

We carried out the correlation of the formation parameters with mechanical properties for the sheets made with different amounts of CS. Figures 9 and 10 present the correlations between the values obtained for the tensile, burst, and tear indexes and internal cohesion strength as a function of the contrast and the homogeneity values for all samples made with CS. The results point out that the increase of contrast and the decrease of homogeneity, indicating a degradation of the paper formation, induced a decrease in the quality of mechanical properties.

These original correlations can be considered a useful tool to find the compromise between the quality of the formation of paper and its mechanical properties. Even if the retention of CS decreased for the highest amount of added CS (4%), the quantity of retained CS in the sheets was higher than for the lower additions (2% and 3%), as summarized in Table IV.

CS, %	Max. retention, %	Added CS g/L	Added CS mg/g	Adsorbed CS g/L	Adsorbed CS mg/g
2	94.4	0.18	20	0.17	18.9
3	95.5	0.23	30	0.22	28.6
4	77.5	0.31	40	0.24	31.0

***IV. Retention of CS in papers prepared from a pulp blend of* E. globulus *and* P. sylvestris.**

CONCLUSIONS

Quantitative formation parameters like contrast and homogeneity can be established on the basis of image treatment. Increasing additions of CS induced an increase in the total number of the flocks, and the addition of 3% CS provoked the highest values of big flocks in the sheet samples.

The contrast and the homogeneity were correlated to the mechanical properties of the paper samples, and direct correlations were found. Thus, the tensile, burst, and tear indexes and the internal cohesion strength were found to decrease with decreasing homogeneity and increasing contrast. **TJ**

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LITERATURE CITED

1. Roberts J.C., *Paper Chemistry*, Blackie, Glasgow & London, United Kingdom, 1991.
2. Eklund, D., and Lindström, T., *Paper Chemistry—An Introduction*, DT Paper Science Publication, Grankulla, Finland, 1991.
3. Marton, J., and Marton, T., *Tappi* 59(12): 121(1976).
4. Björklund, M., and Wågberg, L., *Colloids Surfaces* 105: 199(1995].
5. Korteoja, M.J., Lukkarinen, A., Kaski, K., *et al., TAPPI J.* 79(4): 217(1996].
6. Korteoja, M.J., Lukkarinen, A., Kaski, *et al., J. Pulp Paper Sci.* 23(1]: J18(1997].
7. Wong, L., and Kortschot, M.T.J., *J. Pulp Paper Sci.* 22(6]: J213(1996].
8. Gaiolas, C., Costa, A.P., Silva, M.S., *et al., Appita J.* 52(2]: 12(2004]
9. Gaiolas, C., Mendes, P., Silva, M.S., *et al., Appita J.* 58(4]: 282(2005].
10. Costa, A.P., "Contribuição ao estudo do factor de formação da folha de papel," Ph.D. thesis, University of Beira Interior, Covilhã, Portugal 2001.

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INSIGHTS FROM THE AUTHORS

Today, there is a tendency to use higher filler content even in light papers, which justifies combining these fillers with dry strength additives and retention aids. Except for common fillers such as calcium carbonates and clay, wet-end additives represent a significant part of the total cost of the paper produced. Consequently, it is important to optimize the use of these additives and determine their influence on the formation quality of paper.

To the best of our knowledge, no other research has been carried out on the combined use of cationic starch and C-PAM and their influence on the quality of paper made with Portuguese pulps. The increasing knowledge in this field could allow us to find a rational use of this family of additives and an optimized balance between costs and the quality of the products. As a result, the competitiveness of these wet-end additives could increase considerably.

The most difficult aspects of this research were the normalization of light transmission and the establishment of the most relevant statistical criteria to quantify the formation parameters. We found a direct correlation between the formation parameters and the mechanical properties. We also found that 4% cationic starch is better than 3% in terms of the quality of formation.

The next step is to gain a deeper knowledge about the adsorption of the polyelectrolytes onto the surface of lignocellulose fibers.

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