Influence of wet-end variables on the sizing efficiency of ASA on fine papers produced with Eucalyptus globulus *kraft pulps*

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ABSTRACT: The purpose of paper sizing is to make paper more resistant to liquid penetration. Alkenyl succinic anhydride (ASA) is a synthetic sizing agent usually used in alkaline papermaking. ASA has a fast curing size, but it can lose its ability if it is in contact with water. This work studies the influence of dissolved Ca^{2+} and HCO_3^- ions in the papermaking stock, the effect of precipitated calcium carbonate (PCC), and the influence of pH and temperature on ASA sizing efficiency using bleached Eucalyptus globulus kraft pulps. Two different types of ASA (designated P and UP) and three different emulsions of ASA were used: starch + ASA P, starch + ASA UP, and starch + ASA UP + surfactant. We concluded that a high concentration of dissolved Ca^{2+} ions in furnish diminished the sizing efficiency of ASA. Depending on the type of ASA, concentrations below 300 or 500 ppm did not reduce the sizing efficiency. The amount of dissolved HCO_3^- ions in furnish does not determine the sizing degree of ASA. According to our results, it is possible to work with relatively high PCC loading levels. If it is necessary work with high filler loading levels, however, it is better to increase the ASA concentration in stock. The pH and temperature are the limiting variables of the process; high temperature with high pH reduces the sizing performance of ASA.

Application: This study describes the influence of wet-end variables on the internal sizing efficiency of ASA. The results can be used by papermakers to better select and control paper chemistry.

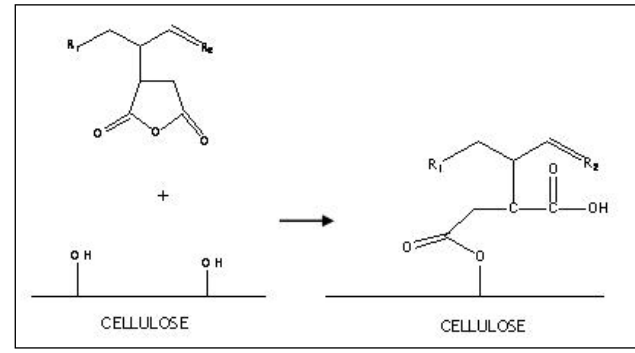
Alkenyl succinic anhydride (ASA) is a cellulose-reactive sizing agent that can impart different degrees of liquid repellence to paper by decreasing the wettability of the cellulose fibers. This synthetic sizing agent is known for its rapid on-machine cure. ASA develops sizing in the sheet faster than others sizing agents, such as alkyl ketene dimers (AKD). However, in the presence of water, or if the furnish conditions are not carefully controlled, ASA undergoes hydrolysis [1,2]. Usually, this sizing agent is used for papers with low resistance to liquids, such as fine paper grades [3].

The synthesis of ASA structures involves the reaction of an alkene (or mixture of alkenes) with maleic anhydride. The number of carbon atoms in the alkene chain typically ranges from 14 to 20, but the C16 and C18 structures are the most effective. The anhydride function in the ASA molecule reacts with the cellulose hydroxy groups to give the corresponding ester and carboxylic acid moieties. The latter is sterically shielded by the long hydrocarbon chain (**Fig. 1**), which provides hydrophobicity to the fibers [1,2].

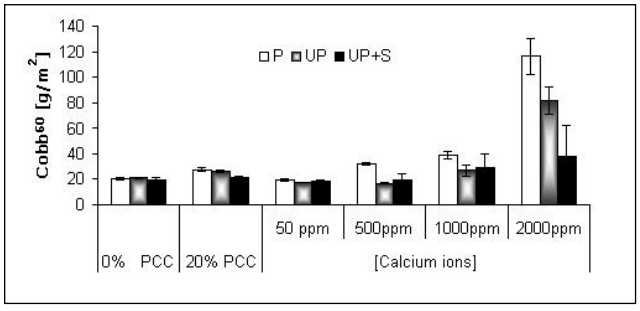
The undesired competitive reaction is the hydrolysis of the ASA anhydride function in the presence of water, which generates the corresponding dicarboxylic acid to the detriment of the sizing efficiency [1].

ASA is a yellow, oily product that is insoluble in water, but chemically sensitive to it. Therefore, an aqueous emulsion must be prepared to add the ASA to the aqueous papermaking suspension, and uniformly dispersed into it [4]. The emulsion is typically prepared with ASA, a cationic starch (or a synthetic cationic polymer), and a small amount of surfactant. The starch-to-ASA ratio is usually in the range of 2:4 [1]. The parameters affecting the quality and stability of the emulsion are

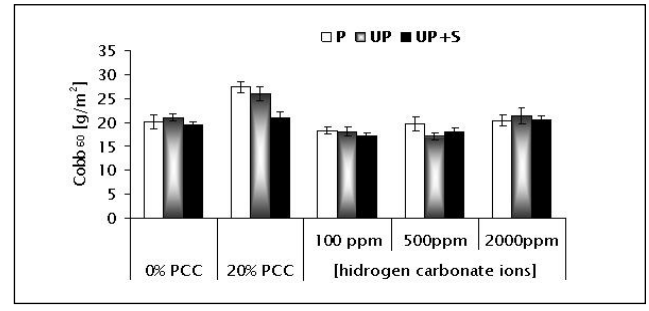
- the pH (3.5 to 4.5);
- the temperature (room temperature);
- the viscosity of the ASA sample;
- the contact time between the emulsion and the stock;
- the emulsion particle size (0.5-2 μm); and



1. Formation of a covalent ester linkage between a cellulose hydroxyl group and ASA[4].



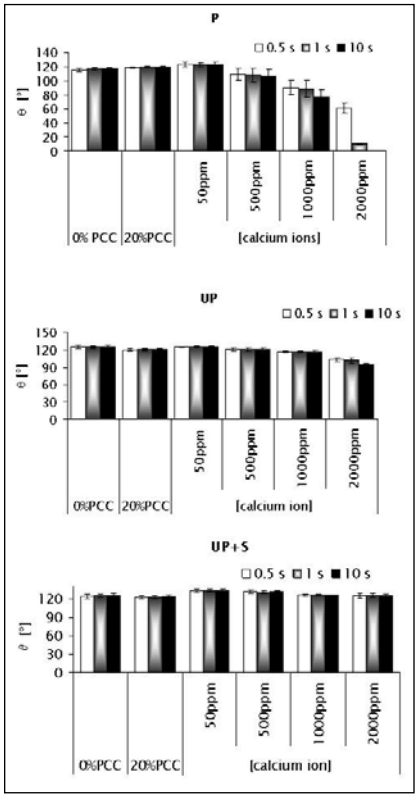
2. Influence of additional Ca^{2+} ions on the ASA sizing process using the three emulsions ASA P, ASA UP, and ASA UP+S (2% of the fiber mass) (50ºC and pH 8) determined by $Cobb_{60}$ analysis.



4. Influence of additional HCO_3^- ions on the ASA sizing process using the three emulsions ASA P, ASA UP, and ASA UP+S (2% of the fiber mass) (50ºC and pH 8) determined by $Cobb_{60}$ analysis.

• the time lag between the preparation and use, which should be as short as possible [4,5].

The emulsion process must be adjusted according to the type of ASA used [1].



3. Influence of additional Ca^{2+} ions on the ASA sizing process using the three emulsions ASA P, ASA UP, and ASA UP+S (2% of the fiber mass) (50ºC and pH 8) determined by contact angle method at 0.5, 1, and 10 s following contact of the drop of water with the paper.

The rate of esterification during the on-machine cure is also affected by some wet-end variables, including the stock pH and temperature, the calcium and bicarbonate ion concentration, the type and amount of filler particles present, and the first-pass retention levels on the machine [1,2]. Wasser [5] studied the effects of pH and temperature in the cure rate of ASA. The study showed that the cure rates decreased as the pH was lowered, and the time to develop sizing was considerably reduced as a function of increasing temperature. According to Savolainen [6], a high concentration of soluble calcium ions reduces the sizing efficiency of ASA, but a moderate concentration of bicarbonate ions improves it. This author also found that the filler, which was precipitated calcium carbonate (PCC), influenced the sizing by surface adsorption of the sizing agents, making them unavailable for fiber sizing, and by reacting with the sizing components. Fillers with a high specific surface area showed a higher tendency for chemical adsorption [7].

The purpose of our investigation was threefold:

• to study the factors affecting the ASA sizing of the fine papers produced with Portuguese *Eucalyptus globulus* kraft pulps;

• to show papermakers the benefits of ASA sizing, which only in the past few years has gained some acceptance in Europe; and

• to confirm ASA's rapid on-machine cure.

To do that, we examined the effects of the wet-end variables in the ASA sizing process by producing paper sheets from industrial bleached kraft pulp (100% *E. globulus*) in an M/K Systems former. The sizing efficiency was evaluated by a set of techniques, as previously suggested [8].

EXPERIMENTAL

Preparation of the emulsions

The commercial ASA products used to prepare the aqueous emulsions were supplied by Portuguese industries. Their specifications (provided by the suppliers) are given in **Table I**. The role of cationic starch is to stabilize the ASA emulsion. It is used to control the

SAMPLE	PROPERTIES	VISCOSITY	PURITY
Cationic starch	DS 0.027-0.032 25% C_{16} +	—	82%
ASA P	65% C_{18} non-ionic	<225 mPa s*	90%
ASA UP	100% C_{18} Non-ionic	<200 mPa s*	>95%
Surfactant	—	—	—

*Measured in laboratory.

I. Properties of materials used in the production of emulsions.

viscosity and fiber retention. The surfactant facilitates the emulsification and enhances the ASA spreading [9].

Three different emulsions were prepared, namely cationic starch + ASA P; cationic starch + ASA UP; and cationic starch + ASA UP + surfactant (ASA UP+S). The emulsions were prepared in batches at 30ºC using a commercial laboratory blender (Waring, model 7010S). The ASA P was blended at 22,000 rpm for 3.5 min., the ASA UP and ASA UP+S were blended at 18,000 rpm for 1.5 min. The ratio of cationic starch to ASA was 4:1 w/w.

The suspension (500 g) of potato cationic starch (degree of substitution = 0.027-0.032) at 3% (w/w), was cooked for 30 min. at 95 ± 5ºC with continuous mechanical agitation following the methods of the TAPPI T 491-94 water immersion test of paperboard.

The emulsion particle size was measured in a Horiba model LA-300 analyzer and found to be consistently ~1 µm, as required in this context. The use of the three ASA emulsions was limited to 3-4 h at room temperature with mechanical agitation, during which no hydrolysis or increases in particle size were detected. Given that a negligible amount of ASA (if any) was hydrolyzed in all the experiment, this parameter was not taken into account.

Preparation of paper sheets

The test sheets used in this study were prepared with a bleached kraft pulp (100% *E. globulus*). The fine papers were prepared in neutral/alkaline wet-end conditions. They had a basis weight of 80 g/m^2 and a Cobb$_{60}$ value of 28 g/m^2.

Table II lists the additives used in the preparation of the paper furnish and their dry weights, as provided by the suppliers.

PRODUCT	DRY WEIGHT
Bleached kraft pulp	92%
Cationic starch	82%
Precipitated calcium carbonate (PCC)	19.5%
Retention agent A	85%-90%
Retention agent B	90%-100%

II. Properties of the additives used in the preparation of the test sheets.

PCC was the filler used in this study.

The pulp was disintegrated and then beaten in a Valley beater (ISO 5264-1) to 25-30 ºSR, according to ISO 5267-1. The suspensions were prepared in the different conditions previously defined, and test sheets of 80 g/m^2 were fabricated in an automatic MK 9000 former. This paper machine gives rise to ready-to-use paper sheets. It comprises a suspension mixing and sheet formation section, a press, and a drying station (~110°C).

We studied the effects of dissolved Ca^{2+} and HCO_3^- ions resulting from different additions of $CaCl_2$ and $NaHCO_3$ in the stock, respectively. The furnish temperature was 50ºC, the pH 8, the ASA addition level 0.2% of the fiber mass, and the ionic concentration ranged from 50 to 2000 ppm for Ca^{2+} and from 100 to 2000 ppm for HCO_3^-. The levels of Ca^{2+} in the stock were confirmed by atomic absorption spectrophotometry.

The influence of the PCC filler in the ASA sizing process was analyzed at 50ºC and pH 8 at 0.2% ASA addition level and the filler content was in the range of 0% to 30% of the sheet weight. A supplementary study was carried out with 20% PCC and 50, 300, or 500 ppm of calcium ions added, depending on the ASA emulsion used.

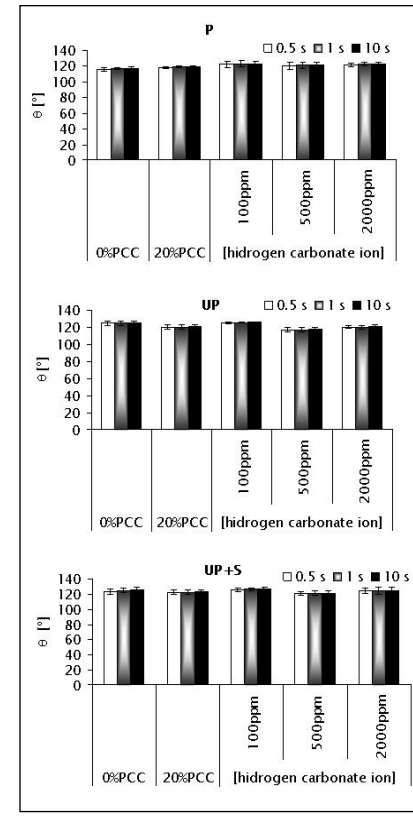
The study of the effect of stock pH and temperature at different ASA addition levels (0.1%, 0.2%, and 0.3% of the fiber mass) on paper sizing was also carried out. The pH of the paper furnish was adjusted to 5, 8, and 11. In the case of pH 8 and 11, PCC was used as filler at a concentration of 20%. The temperatures in the stock were adjusted to 40ºC, 50ºC, and 60ºC.

The order of component addition to the suspension was PCC, starch, ASA emulsion (40 s in contact with the suspension), and finally the retention agents. For pH adjustments of the stock, aqueous solutions of HCl and NaOH were used.

Sheets testing

The dried sheets were stored in a room with controlled humidity and temperature (50% RH and 23ºC, according to ISO 187) for 30 min. before characterization. Cobb$_{60}$ values were determined on 15 samples of each ASA-sized sheet, according to the ISO 535 method, using deionized water on the wire side. Contact angles (five determinations per sample) were measured with a Data-Physics model OCAH 200 at 0.5, 1, and 10 s following the contact of the drop of water with the paper (TAPPI T 458 om-94, surface wettability of paper).

The filler retention on the test sheets was determined by measuring the ash content of the paper, according to the ISO 1762 standard method.

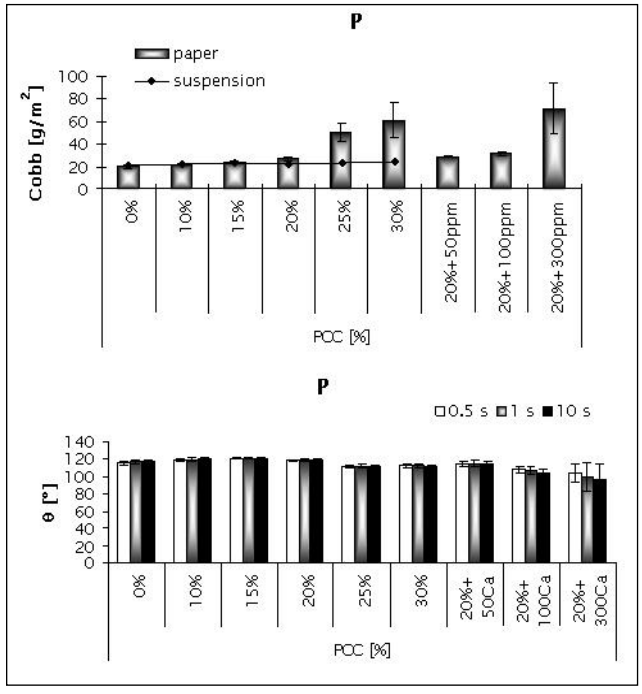


5. Influence of additional HCO_3^- ions on the ASA sizing process using the three emulsions ASA P, ASA UP, and ASA UP+S (2% of the fiber mass) (50ºC and pH 8) determined by contact angle method at 0.5, 1, and 10 s following contact of the drop of water with the paper.

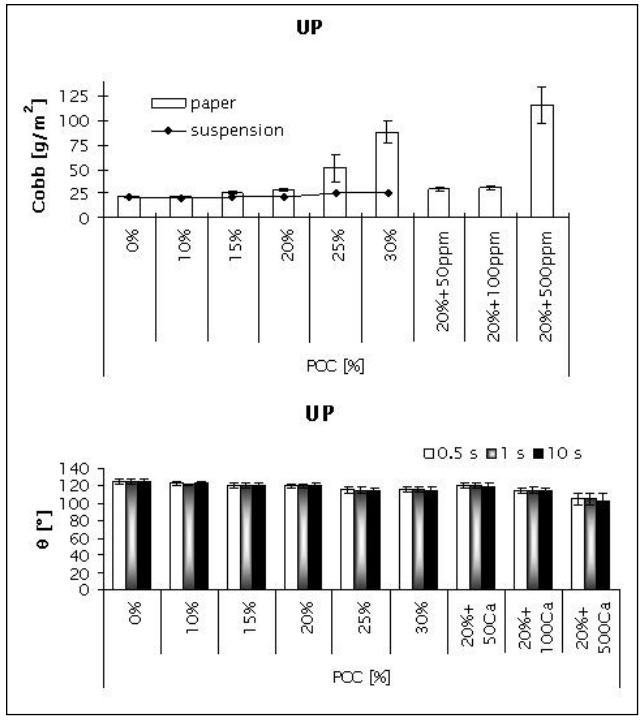
RESULTS AND DISCUSSION

Effect of the dissolved calcium ions

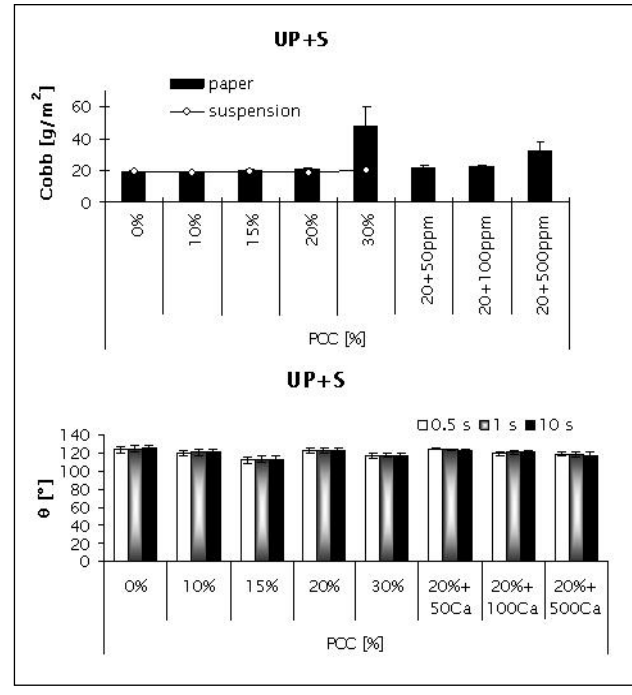
Figure 2 shows the influence of Ca^{2+} ions on the sizing efficiency, as deter-



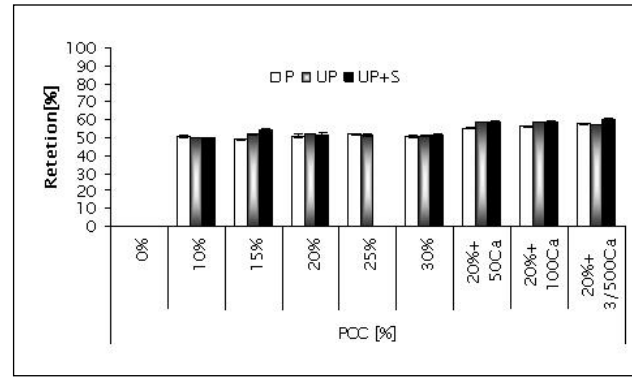
6. Effect of PCC addition level and dissolved Ca^{2+} ions on paper sizing with ASA P (0.2% of the fiber mass) at 50ºC and pH 8 determined by $Cobb_{60}$ and contact angle method.



7. Effect of PCC addition level and dissolved Ca^{2+} ions on paper sizing with ASA UP (0.2% of the fiber mass) at 50ºC and pH 8 determined by $Cobb_{60}$ and contact angle method.



8. Effect of PCC addition level and dissolved Ca^{2+} ions on paper sizing with ASA UP+S (0.2% of the fiber mass) at 50ºC and pH 8 determined by $Cobb_{60}$ and contact angle method.



9. Filler retention under different PCC concentrations and dissolved Ca^{2+} ions additions for the three emulsions: ASA P, ASA UP, and ASA UP+S.

mined by $Cobb_{60}$, for the ASA P, ASA UP, and ASA UP+S emulsions. With 500 ppm of Ca^{2+} ions, the $Cobb_{60}$ value was the same (20 g/m²) for both ASA UP and ASA UP+S, but lower for the ASA P emulsion. This study verified that the upper limit of Ca^{2+} ion concentration to be used with ASA P, without harming sizing quality, was about 300 ppm.

Similar results were obtained with the contact angle determinations (**Fig. 3**). These results indicated that high amounts of dissolved calcium ions in the stock were detrimental to the ASA sizing process, as emphasized by the contact angle values for the ASA P with 1000 ppm of Ca^{2+}. The contact angles were about 90º for the first second following the drop contact with the paper,

and decreased to ~70º within 10 s. When the Ca^{2+} concentration was raised to 2000 ppm, it became impossible to determine the contact angle after ~1 s because the water drop had already been adsorbed by the paper sheet.

The importance of the study of the influence of the calcium ion on the efficiency of ASA sizing is related to the characteristics of the white water that is used in the alkaline papermaking (the calcium ions are recycled with the water and returned to the stock) and to the strong dependence of the concentration of calcium ions on the pH of the furnish. A decrease of the wet-end process pH gives rise to an increase in the calcium ion concentration.

The dissolved Ca^{2+} ions probably adsorb onto the surface of the ASA droplets and prevent their uniform distribution on the fibers' surface, consequently limiting the formation of ester linkages. The low concentration of Ca^{2+} ions does not limit the efficiency of ASA sizing. It is important, however, to control the pH of the stock (pH = 7-8) to maintain a low dissolved calcium ion concentration.

Effect of the bicarbonate ions

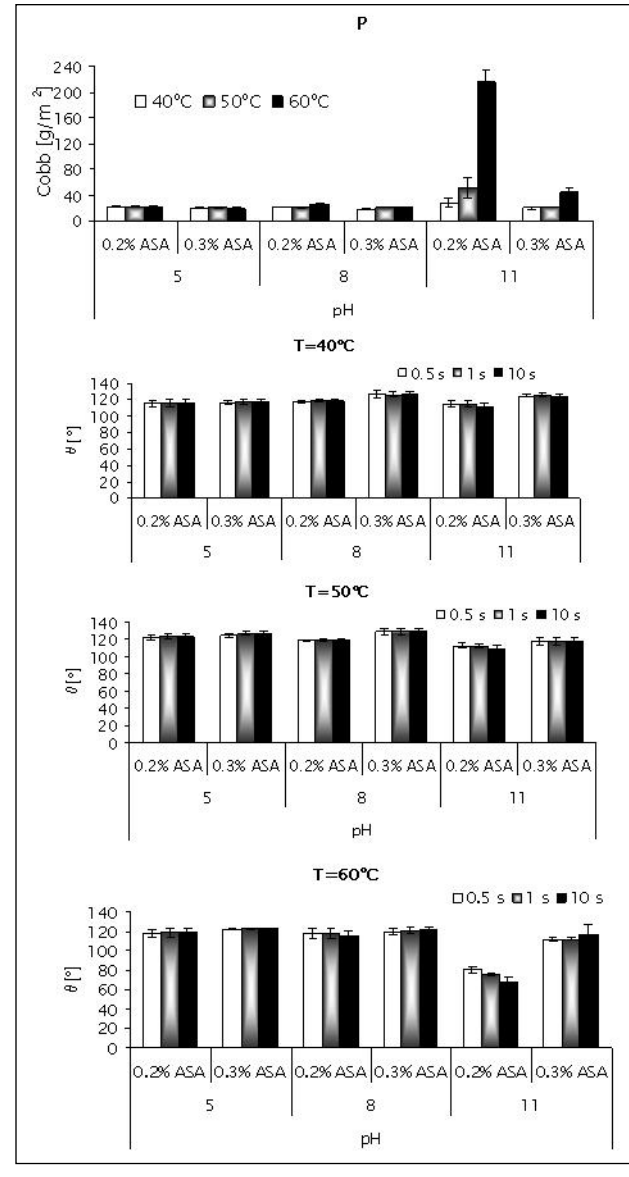
Figures 4 and **5** clearly show that the $Cobb_{60}$ values (20-23 g/m²) and the contact angle (115°-120º) for the three emulsions and for all the studied conditions were close to each other. This seems to indicate that the degree of sizing was not affected by the different bicarbonate ion concentrations of HCO_3^- at 50ºC at pH 8. In other words, concentrations of 100-2000 ppm were not harmful to the sizing efficiency of the ASA process.

The presence of HCO_3^- ions is essential for AKD to function as a sizing agent. Normally, papermakers add $NaHCO_3$ and Na_2CO_3 to increase the concentration of bicarbonate on the paper furnish. Probably these ions improve the retention of the AKD particles on the fiber surface [2]. Our results with ASA indicate a different behavior, probably because the contact time between the ASA and the alkaline stock was not sufficient for any reaction between the size agent and the bicarbonate ion to take place (swelling), or because the HCO_3^- ions could not stop the ASA from reacting with cellulose.

Effect of the PCC

The results obtained with the $Cobb_{60}$ and contact angle suggest that the degree of sizing with 0.2% ASA was dependent on filler loading. **Figures 6**, **7**, and **8** demonstrate the effect of the PCC addition level and the concentration of dissolved calcium ions, as well as the filler loading levels, for ASA P, ASA UP, and ASA UP+S, respectively. The graphics suggest that good sizing results were obtained within the level range of filler loading used in the fine paper industry, which is 15%-30%.

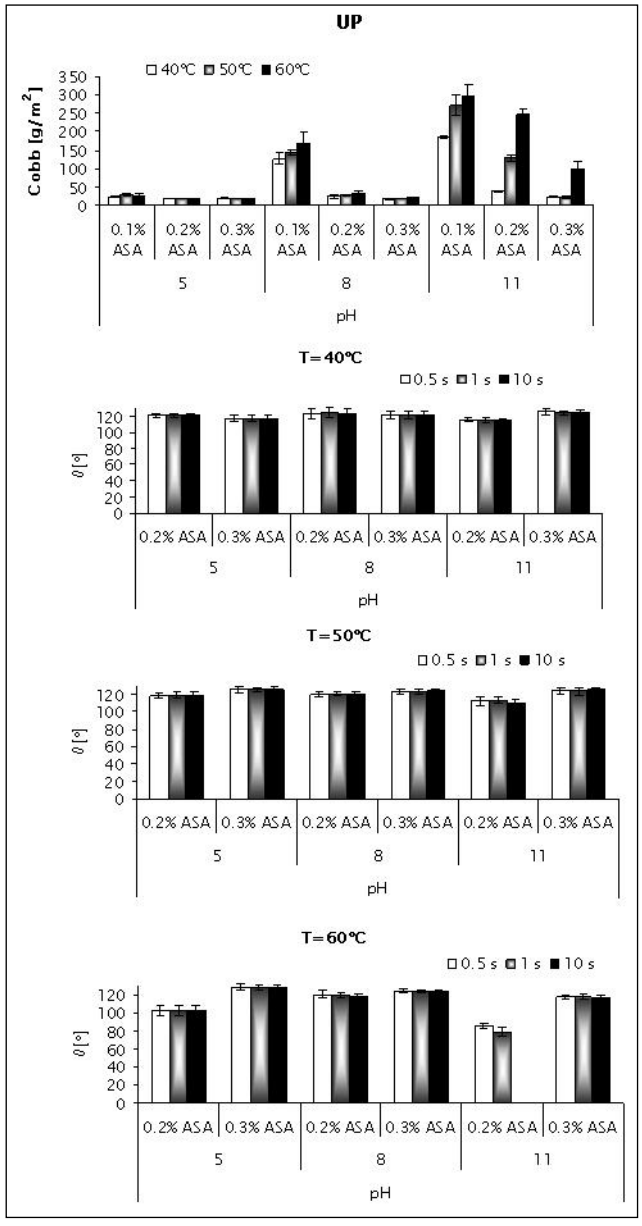
Figures 6-8 also show the role of the filler loading level on the suspension and the paper. These were studied because the mechanical retention of the paper machine was 50%. We therefore introduced 60% PCC relative to the fiber in the paper furnish to have 30% of the fiber mass in the final paper. This increase in PCC level influenced the degree of sizing so that the quantity of ASA was not effective.



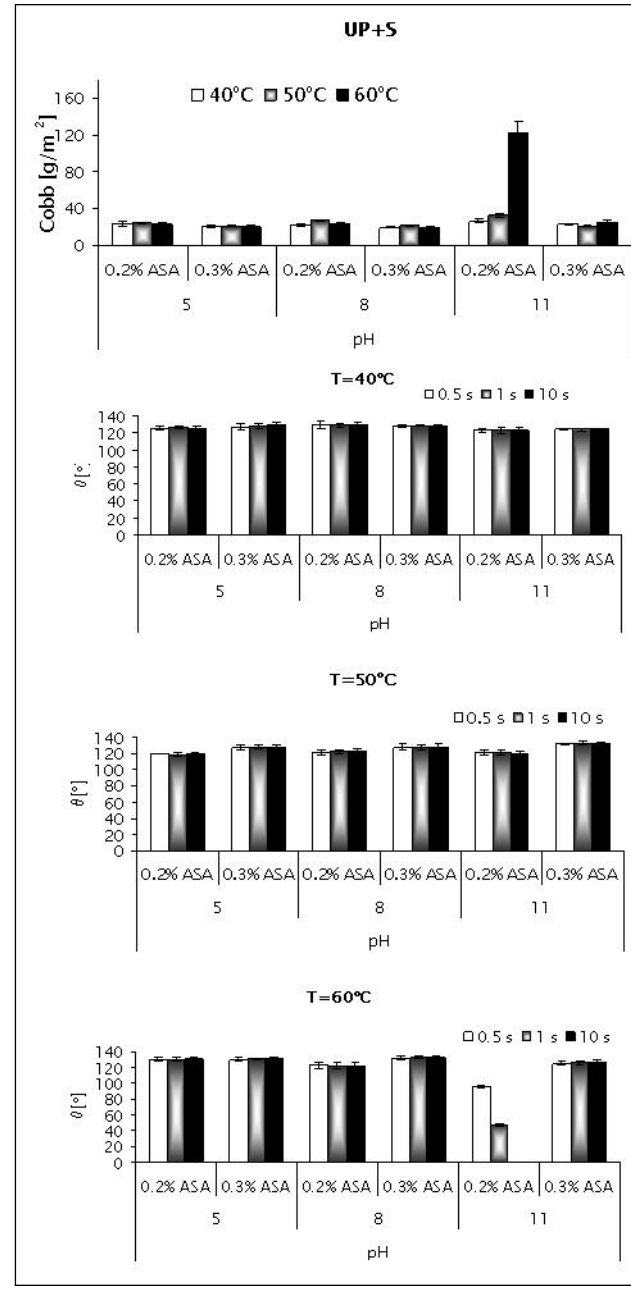
10. The influence of pH and temperature of the paper furnishes at different ASA P addition levels determined by $Cobb_{60}$ and contact angle method.

The $Cobb_{60}$ results corresponding to the PCC values on the suspension and on the paper, with 25% and 30% of filler loading levels, were different, whereas the contact angles were not affected by these changes.

We also examined the effect of three different concentrations of dissolved calcium ions in conjunction with a filler loading level of 20%. The concentrations of dissolved calcium ions used were 50 and 100 ppm, and the limit reached in this study without alteration in the degree of ASA sizing was 300-500 ppm. The dissolved calcium ion concentrations of 50 and 100 ppm, with or without added PCC, did not reduce the sizing efficiency of ASA. However, with 20% PCC, the addition of higher PCC loads did hamper ASA sizing effectiveness.



11. The influence of pH and temperature of the paper furnishes at different ASA UP addition levels determined by Cobb$_{60}$ and contact angle method.



12. The influence of pH and temperature of the paper furnishes at different ASA UP+S addition levels determined by Cobb$_{60}$ and contact angle method.

We can therefore conclude that if the filler loading must be increased, a corresponding increase in ASA loading is recommended. This is in tune with the work of Cates and coworkers [9], who found that when ASA is added to the paper furnish, it can be adsorbed on the surface of the fibers, but it can also be adsorbed on the surface of the PCC. As a result, the sizing agent adsorbed on the filler surfaces cannot contribute to the sheet hydrophobicity. Moreover, this hampers filler retention in the paper sheet [2,10].

Good filler retention was obtained with each of the three ASA emulsions (**Fig. 9**).

Effect of pH and temperature

Figures 10, **11**, and **12** show the effects of pH and temperature on paper furnish at different ASA concentrations for the three ASA emulsions. Three major trends were encountered in this context:

• ASA can successfully be used even in acidic environments (pH = 5) between 40°C and 60°C;

• the combination of high temperature (60°C) with high pH (11) is detrimental to the ASA sizing; and

• with 0.1% of added ASA and a filler loading of 20%, sizing almost failed.

This latter observation suggests that the ASA added to the furnish was entirely taken up by the PCC particles and left the fiber surface unmodified.

The temperature of the circulating water in the closed water circulation systems used in the paper industry make is difficult to control. It is therefore important to know how an increase in stock temperature influences the ASA sizing efficiency. In our study, sizing was successful even when the temperature and the ASA concentration were relatively high, namely 60ºC and 0.3%, but the best results were obtained when the temperature was 40ºC. The combination of high temperature and high pH was detrimental to the ASA sizing efficiency, probably because in these extreme conditions, the rate of ASA hydrolysis overcame that of esterification.

CONCLUSION

The main purpose of this study was to analyze the influence of different wet-end conditions on ASA sizing using Portuguese *E. globulus* kraft pulps.

We found that a high concentration of dissolved calcium ions and the association of high temperature with high pH are detrimental to the ASA sizing efficiency. If the temperature of the stock is close to 60ºC, the stock pH should be kept between 7 and 8.

The concentration of hydrogen carbonate ions did not affect the sizing quality, independent of the type of ASA emulsion used.

The PCC content in the paper furnish played an important role in the ASA sizing of E. globulus kraft pulps. However, it is possible to work without any sizing problem with the filler contents usually employed in the papermaking industry.

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LITERATURE CITED

1. Neimo, L. in *Papermaking Science and Technology*, Papermaking chemistry, Helsinki, TAPPI PRESS, 1999, Chapter 7.
2. Hodgson, K.T., *Appita J.* 47(5): 402(1994).
3. Araújo, J.A., Oliveira I., Massoquette A., et al., Proceedings of the Associação Brazileira Técnica de Celulose e Papel (ABTCP) 30th Pulp and Paper Annual Meeting, ABTCP, São Paulo, Brazil, 1997, p. 527.
4. Farley, C.E. and Wasser, R.B., in *The Sizing of Paper* (Reynold, W.F. Ed.) 2th edn., TAPPI PRESS, 1989, pp. 51-61.
5. Wasser, R.B., *J. Pulp Paper Sci.*, 13(1): 29(1987).
6. Savolainen, R.M., Proceedings of the 1996 TAPPI Papermakers Conference, TAPPI PRESS, Atlanta, p. 289.
7. Velho, J., in Mineral fillers for paper Why, What, How (Tecnicelpa Technical books Ed.), Tecnicelpa - Portuguese Association of the Pulp and Paper Technicians, 2003, pp. 185-188.
8. Gess, J.M., *Tappi* 64(1): 35(1981).
9. Cates, R.E., Dumas, D., and Evans, D., in *The Sizing of Paper* (Reynold, W.F., Ed.) 2nd edn., TAPPI PRESS, 1971, Chap. 12.
10. Zhmud, B., Seppänen, R., and Tiberg, F., Proceedings of the Pira 2001 Scientific & Technical Advances in the Internal and Surface Sizing of Paper and Board, Pira International, Leatherhead, UK, paper 6.

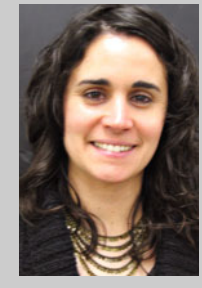
INSIGHTS FROM THE AUTHORS

Our goal with this work was to demonstrate that internal sizing with ASA is, in fact, a reliable process, in terms of influencing the variables in the wet-end paper machine. Moreover, before this work there was a lack of information in the literature concerning the internal sizing with ASA on fine papers produced with *Eucalyptus globulus*.

The stabilization of the ASA emulsion revealed itself as the most difficult stage, particularly the control and attainment of the ideal particle size. This problem was overcome by using appropriated equipment.

This work clearly demonstrated the effectiveness of the internal sizing with ASA in the paper production using *E. globulus* bleached kraft pulps. Therefore, this study represents an important contributionj to the understanding of the paper internal sizing processes.

The next step will be the assessment of the surface energy of the paper sheets produced with this internal sizing approach, as well as the evaluation of the quality of the final products.



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This research work was developed in the Science and Technology of Paper Department at the University of Beira Interior, Covilha, Portugal.

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