

PAPER SURFACE CHEMISTRY AS A TOOL TO IMPROVE INKJET PRINTING QUALITY

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Surface treatment is an important step of papermaking, namely for improving the final product quality. For uncoated printing and writing papers (P&W), surface sizing is becoming a common practice for controlling paper surface characteristics and liquid spreading and absorption. This work aims at evaluating the potential of assessing and controlling paper surface chemistry, by analyzing the impact of the application of different surface sizing formulations both on the chemical surface characteristics of the modified paper samples and on the final printing quality. For that, blends of cationic starch and minor quantities (5%, 10%, and 20% w/w) of four distinct copolymers of styrene were used, resulting in a total of 12 different surface sizing formulations. A sample surface sized only with cationic starch was taken as reference. Surface chemical properties were determined by using contact angle measurements and inverse gas chromatography. Finally, the inkjet printing quality was evaluated. The results revealed that the surface sizing treatments tested have a substantial influence on the surface energetics and partially explain the differences detected in the inkjet printing quality.

Keywords: Paper; Printing quality; Surface chemical properties; Surface sizing

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INTRODUCTION

At present there is an increasing demand concerning the printing quality of printing and writing (P&W) paper grades, and this topic is under research by several distinct groups (Lee et al. 2002; Carceller and Juppo 2004; Olkkonen and Lipponen 2007; Prinz and Schultz 2007; Moutinho et al. 2007). Printing quality is strongly influenced by the structural and chemical properties of the paper surface, being one of the most important factors concerning customer's evaluation. Thus, all the studies dealing with printing quality, paper-ink interactions and the paper surface characteristics are of utmost importance.

Chemical modification of the paper surface is nowadays a common practice in papermaking in order to improve printing quality, and surface sizing is a standard operation in many paper mills. Typically - and especially for P&W papers - starch is used for surface sizing, with the main goal of improving paper surface strength and printability. However, there is an increasing tendency to use blends of cationic starch and synthetic copolymers, in order to enhance surface sizing effects by controlling the paper

surface energy, its hydrophilic character, and the affinity towards different types of ink. The ultimate goal of this approach is to improve print quality by optimizing the balance between the absorption and spreading phenomena (Calceller and Juppo 2004; Olkkonen and Lipponen 2007; Prinz and Schultz 2007).

The most important function of the starch, used together with synthetic surface sizing agents, is to act as a binder. The synthetic surface sizing agents are used mainly to improve the paper surface resistance to water (which is crucial for many printing processes), since they are frequently polymers with some degree of hydrophobicity and the primary raw material of paper and paperboard are the hydrophilic cellulosic fibers (Moutinho et al. 2009). Typically the chemicals used to produce synthetic surface sizing agents are copolymers of styrene, maleic anhydride, acrylic acid, ester, or polyurethanes. When combined with starch, a thin reticular film is formed at the paper surface, influencing several paper properties such as hydrophobicity, surface resistance, surface free energy, and also smoothness (Prinz and Schultz 2007).

In this context, the objective of the present work is to evaluate the potential of paper surface chemistry as a tool to assess printing quality. For that, the impact of the application of different surface sizing formulations composed of blends of cationic starch and minor quantities (5%, 10% and 20% w/w) of four distinct copolymers of styrene were analyzed either in terms of the chemical surface characteristics of the modified paper samples or by assessing the final inkjet printing quality. A sample surface sized with cationic starch only was taken as reference. Both the copolymers and the formulations used were selected having in mind the feasibility of their application at an industrial scale.

Finally, it should be pointed out that this study is part of a more extensive work developed by the authors involving the eucalyptus-based printing and writing uncoated papers (Moutinho et al. 2007, 2009; Moutinho 2009).

EXPERIMENTAL

Surface Sizing

A commercial calendered uncoated base paper (80 g/m²) produced with a *Eucalyptus globulus* kraft pulp without any surface treatment was surface sized with cationic starch (St) and taken as reference. Additionally, blends of starch with four different styrene copolymers (2 co-styrene-maleic anhydride and 2 co-styrene-acrylate, with different monomer ratios) were tested in three different concentrations, as described in Table 1. These surface sized samples were not further calendered.

The surface sizing formulations were applied using a Mathis laboratory coating device, SVA-IR-B, which operates automatically with different velocities of the applicator roll. A 0.15 mm roll was used, and the application velocity was adjusted to 6 m/min. The drying process was performed in two sequential steps: using an IR drier (1.0 kW drying intensity), coupled to the applicator roll, followed by air drying for at least 10 min. The total surface sizing pick-up was 3.5 ± 0.3 g/m².

Some properties of the compounds, not available from product specifications, were determined in laboratory, and these are listed in Table 2. The information regarding the monomers proportion was derived from elemental analysis (Moutinho 2009).

Table 1. Description of Samples

Sample	Surface sizing	Formulation (% w/w)	Sample	Surface sizing	Formulation (% w/w)
St		100% Cationic Starch	StS3-05	95% Cationic Starch 5% Co-styrene-acrylate S3	
StS1-05	5%	95% Cationic Starch Co-styrene-maleic anhydride S1	StS3-10	90% Cationic Starch 10% Co-styrene-acrylate S3	
StS1-10	10%	90% Cationic Starch Co-styrene-maleic anhydride S1	StS3-20	80% Cationic Starch 20% Co-styrene-acrylate S3	
StS1-20	20%	80% Cationic Starch Co-styrene-maleic anhydride S1	StS4-05	95% Cationic Starch 5% Co-styrene-acrylate S4	
StS2-05	5%	95% Cationic Starch Co-styrene-maleic anhydride S2	StS4-10	90% Cationic Starch 10% Co-styrene-acrylate S4	
StS2-10	10%	90% Cationic Starch Co-styrene-maleic anhydride S2	StS4-20	80% Cationic Starch 20% Co-styrene-acrylate S4	
StS2-20	20%	80% Cationic Starch Co-styrene-maleic anhydride S2	-----	-----	

Table 2. Properties of the Compounds Used to Produce the Surface Sizing Formulations

Compound	Monomers proportion**	Solids content (%)	Particles mean diameter***	Surface Tension (mN/m)	pH
St - Cationic starch*	n.a.	12.0	298.8	32.9	5.0
S1 - Co-styrene-maleic anhydride	3:1	15.0	37.2	---	8.4
S2 - Co-styrene-maleic anhydride	2:1	14.6	25.4	38.51	7.6
S3 - Co-styrene-acrylate	3:4	25.7	83.6	49.99	4.3
S4 - Co-styrene-acrylate	1:2	25.5	73.8	64.33	4.7

* The cationic starch suspension was collected at the paper mill, and includes other process additives, such as optical brightener (OBA) and salt.

** Based on elemental analysis (using the equipment EA 1180 CHNS-O from Fisons Instruments).

*** Determined using the Coulter N4

Contact Angle Measurements

Contact angle measurements constitute an indirect method to easily assess paper surface energy, being fast, simple, and based on easy-to-use equations for the calculation of the surface energy components. The knowledge of these parameters is essential to assess the impact of the various sizing agents on the samples surface properties. The fundamentals of this method are well detailed in the literature, and have been previously published by the authors (Moutinho et al. 2007, 2009). In this study, the measurements were performed with the DataPhysics equipment OCA20, using the sessile drop method. The initial resting drop image was acquired by a CCD camera, and the corresponding contact angle was calculated after fitting the drop contour line. The OWRK (Owens, Wendt, Rabel and Kaeble) theory was applied to the contact angle data of five liquid probes: demineralised water, formamide, ethylene glycol, propylene glycol and diodomethane, in order to compute the total surface free energy (σ_s) and its dispersive and polar components (σ_s^d and σ_s^p) (Roe et al. 1967).

Inverse Gas Chromatography (IGC)

IGC has also proved to be a powerful and reliable tool for the characterization of solid surfaces, like fibers or paper. IGC differs from conventional chromatography since the material under analysis is not the one injected into the column but instead constitutes the surface of the stationary phase contained in the column. The principle of IGC is simple: an inert carrier gas elutes a minute quantity of a pure probe (solute) molecule through a column packed with the stationary phase under analysis, which in this case is paper. Due to the thermodynamic interactions between the two phases, the probe molecules are retained for a certain time, which is used to derive not only the dispersive component of the surface energy and its variation with temperature but also the acid-base character of the surface, based on the Lewis concept (i.e., the ability to accept and donate electrons). The methods for the calculation of the dispersive component of the surface energy (σ_s^d) and of the Lewis acid/base constants (K_a and K_b) are well described in the literature (Shen et al 1998; Carvalho et al. 2005). IGC experiments were performed using a DANI GC 1000 chromatograph, equipped with a flame ionization detector (FID). The experiments were carried out at infinite dilution with oven temperatures between 35 and 60°C using 5°C intervals. To determine the dispersive component of the surface energy, a series of n-alkane probes was used (n-hexane, n-heptane, n-octane, n-nonane, n-decane), while to assess the acid-base properties five polar probes were tested (trichloromethane (CHCl₃, acidic), dichloromethane (CH₂Cl₂, acidic), acetone (amphoteric), ethyl acetate (ETA, amphoteric), and tetrahydrofuran (THF, basic)). Natural gas (83.7 % methane) was used to determine the dead retention volume (Shen et al. 1998; Carvalho et al. 2005).

Printing Quality Evaluation

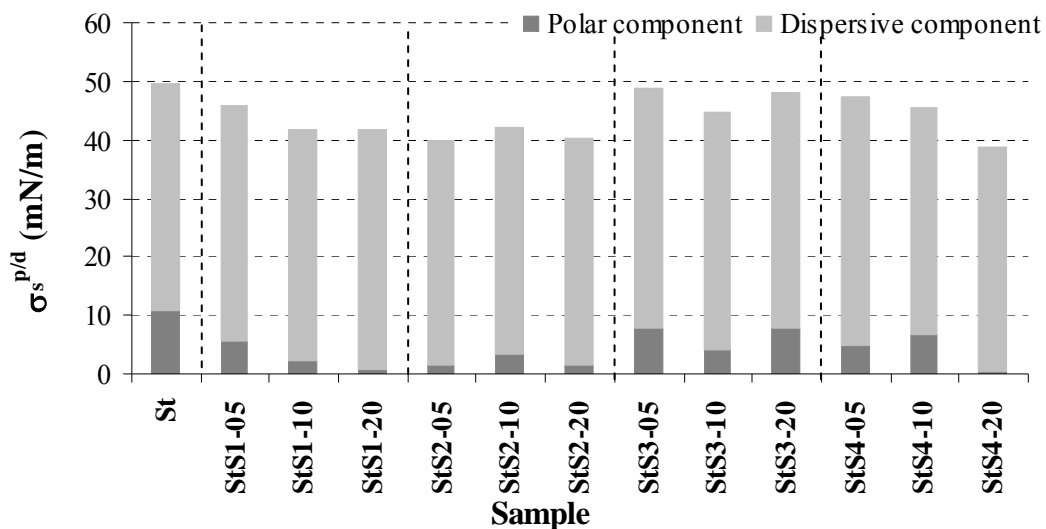
To evaluate the printing quality all the samples were printed with a specific mask using the inkjet printer HP5652. Inkjet printing quality was assessed by quantitative measurements, which include: optical density, measured by the densitometer Gretag D19C; Gamut Area, determined through the CIE Lab colour coordinates obtained for six colours by using the AvaMouse spectrophotometer (Avantes); and line gain, evaluated using the Personal Image Analysis system PIA BASF – 8042319 for a black line with yellow background. The optical density values report the color intensity achieved for a specific color, while the gamut area is used to evaluate the paper ability to reproduce a wide range of colors. The results from the printing tests were correlated to those obtained from the chemical characterization of the paper surfaces by using the Partial Least Squares tool.

Taking into account that the differences between the samples are relatively small, all the data were submitted to Analysis of Variance (ANOVA) and Principal Component Analysis (PCA), in order to validate the relevance of all the results, by analyzing inter- and intra-samples variability.

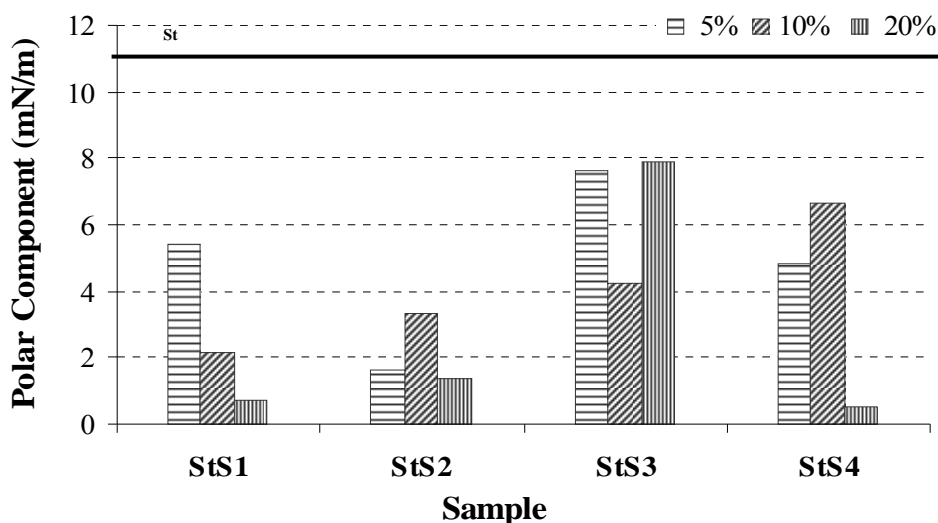
RESULTS AND DISCUSSION

Surface free energy and the corresponding dispersive and polar components of the paper samples were determined, according to the OWRK method, as indicated in the Experimental section. The values of the contact angles used for these calculations are

published elsewhere (Moutinho 2009). The results obtained are plotted in Fig. 1 –a). As can be seen, the surface free energy of the paper samples was found to be mainly dispersive. Moreover, the addition of the synthetic surface sizing agents to the cationic starch tended to decrease the total surface energy, mainly due to the decrease of the polar component rather than the dispersive one, leading to more hydrophobic surfaces. This effect was expected, since the added surface sizing agents are mainly non-polar compounds. However, since the major effect of the addition of the synthetic surface sizing agents is detected in the polar component of the surface energy, the influence of the sizing agents amount will be based on values of this component, as detailed in Fig. 1- b).



a)



b)

Fig. 1. a) Graphical representation of the polar and dispersive components of the surface energy for the various samples tested; **b)** Polar component of the surface free energy for all the samples tested.

As this figure reveals, the addition of the various synthetic agents significantly reduced the polar component of the surface energy, when compared to the standard sample (see line St above). Concerning the effect of the concentration of the sizing agent, different types of behaviours can be observed (a continuous decrease of the polar component with the increase of amount of the sizing agent, as in sample StS1, or an inflexion point as detected for the other samples). This is most certainly related to the arrangement of the copolymer molecules at the surface of the paper samples. For instance, the consistent decrease in the values of the polar component of the StS1 samples (co-styrene-maleic anhydride) suggests that the molecules of the co-polymer are always oriented at the paper surface with the styrene monomer (which is the most apolar part of the molecule) pointing outwards and the oxygen-containing monomers pointing inwards, i.e. towards the fibrous matrix, as result of some attraction from the -OH groups of cellulose. For samples StS3, the polar component exhibited a minimum at 10% concentration. Since the molecules of the co-styrene-acrylate are larger than those of the co-styrene-maleic anhydride, it is reasonable to expect that for the concentration of 20% there are no more available sites for the molecules to accommodate directly over the paper surface, and a reversion of their orientation occurs (the acrylate group, more polar, reorients outwards leading to an increase in the polar character of the surface). Figure 2 presents possible molecule orientations supporting this hypothesis.

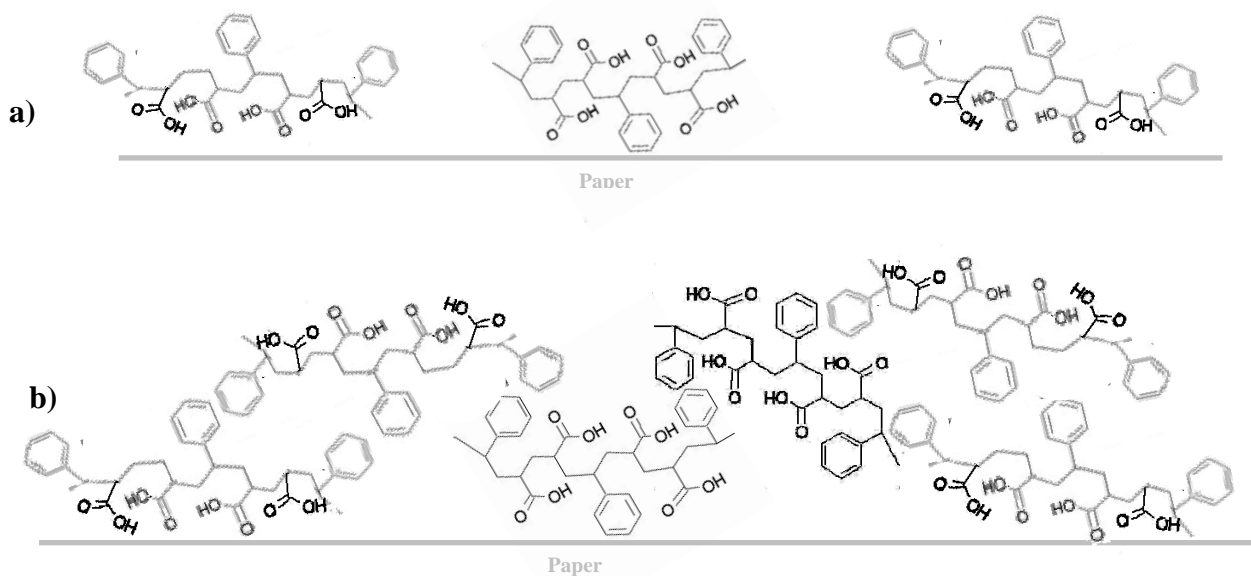


Fig. 2. Schematic representation of the molecules' orientation according to the hypothesis raised **a)** StS3 for 10% of concentration **b)** StS3 for 20% of concentration.

The results for the samples StS2 and StS4 are not solely explained by this analysis based on the orientation of the molecules, and more information from other techniques is required.

As mentioned before, the acid-base interactions based on the Lewis concept can be studied by IGC by injecting polar probes. The values of K_a and K_b obtained for all samples are plotted in Fig. 3.

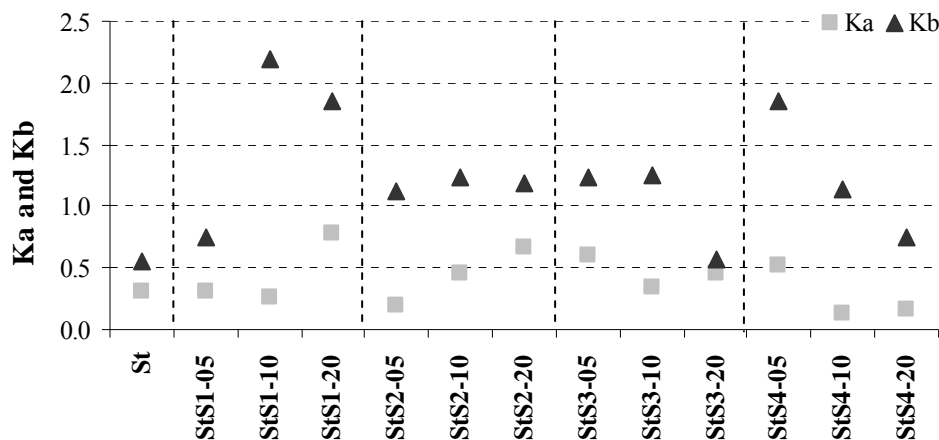


Fig. 3. Values of K_a and K_b computed from the IGC measurements for the different sizing agents and different concentrations

From this plot, it is possible to observe that the values of K_a and K_b were of the same order of magnitude, and that the K_b values were superior to those of K_a . This indicates that the surface of the papers is predominantly amphoteric with a slight tendency to donate electrons (i.e. with a moderate basic character). In comparison to the sample sized with cationic starch alone (St), it is possible to see that the impact of the addition of the synthetic surface sizing agents is predominantly apparent on the values of K_b , certainly due to the presence of the electronic cloud of the copolymers.

Additionally, it is known that the surface acid-base character is related to the availability of the hydroxyl groups (-OH) at the surface (Carvalho et al. 2005; Tze and Gardner 2001) and thus it is possible to elaborate further about the composition and orientation of the molecules of the sizing agents.

Regarding the surface sizing agent S1, the IGC results indicate that the molecules are probably oriented so that the styrene monomer is turned to the exterior, whereas the oxygen of the maleic anhydride monomer points inwards for all concentrations, in perfect agreement with the results derived from the contact angle measurements. The increase in K_a when the amount of sizing agent is increased to 20% is related to the enhancement of the electron accepting effect of the maleic anhydride monomer. Analyzing now S2, which differs from the sizing agent S1 in the styrene/maleic anhydride ratio (Table 2), the increment in K_b relative to the reference sample St is smaller than that found for samples StS1, in agreement with the corresponding smaller styrene amount (Table 2).

As for the sizing agent S3, the assumptions made regarding the orientation of this agent molecules at the paper surface when analyzing the contact angle results are confirmed in the results of Fig. 3. As explained, for the lower concentrations, the styrene monomer is the one oriented outwards, and therefore K_b is higher than K_a . The proximity of K_a and K_b for the concentration of 20% is a consequence of the higher amount of the acrylate monomer turned outwards.

With regard to the orientation of the copolymer molecules at the paper surface the results obtained by IGC for samples StS2 and StS4 are inconclusive.

Several printing quality parameters were assessed in the context of the extensive work previously reported (Moutinho 2009). However, the Principal Component Analysis (PCA) revealed that the most relevant variables to evaluate ink jet printing quality were the Optical Density for black and yellow ink, the Gamut Area and Line Gain. The values achieved for the optical densities are presented in Fig. 4 for the black and yellow colors. The dashed lines limit an interval of 0.2 units of magnitude. Values within this interval can not be considered distinct from the one of the reference sample (St) (Oittinen and Saarelma 1998).

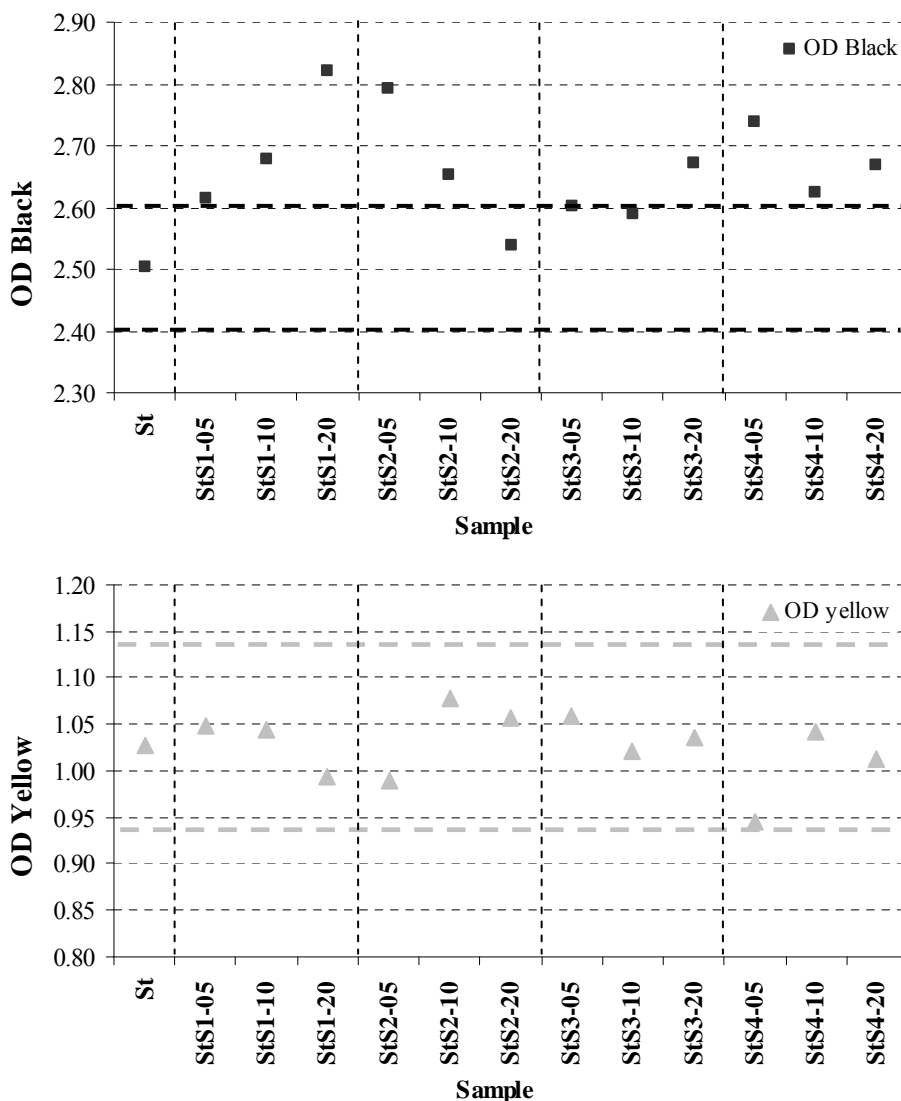


Fig. 4. Optical density values achieved for black and yellow color. The dashed lines delimit the area where the OD values can not be considered distinct from the one of the St sample.

As this figure denotes, the values of the black optical density generally were increased with the addition of the synthetic surface sizing agents in the sizing formulation. As for the yellow optical density, a slight increase relative to the reference sample was detected only in some situations, and the measurements did not allow the distinction between the samples. The increase of the optical density values is most certainly related to the increase of the surface hydrophobicity of the samples caused by the addition of the synthetic surface sizing agent. This effect was more visible when using the black ink, because it has a surface tension close to the one of the water than when compared to the yellow ink (black ink Surface tension = 68.9 mN/m; yellow ink surface tension = 35.2 mN/m). It is important to emphasize that, in spite of the small optical density differences, for both black and yellow colors, the values of all samples may be considered good in terms of printing quality (Nilsson and Fogden 2008). The results obtained for the Gamut Area and for the Line Gain are plotted in Fig. 5.

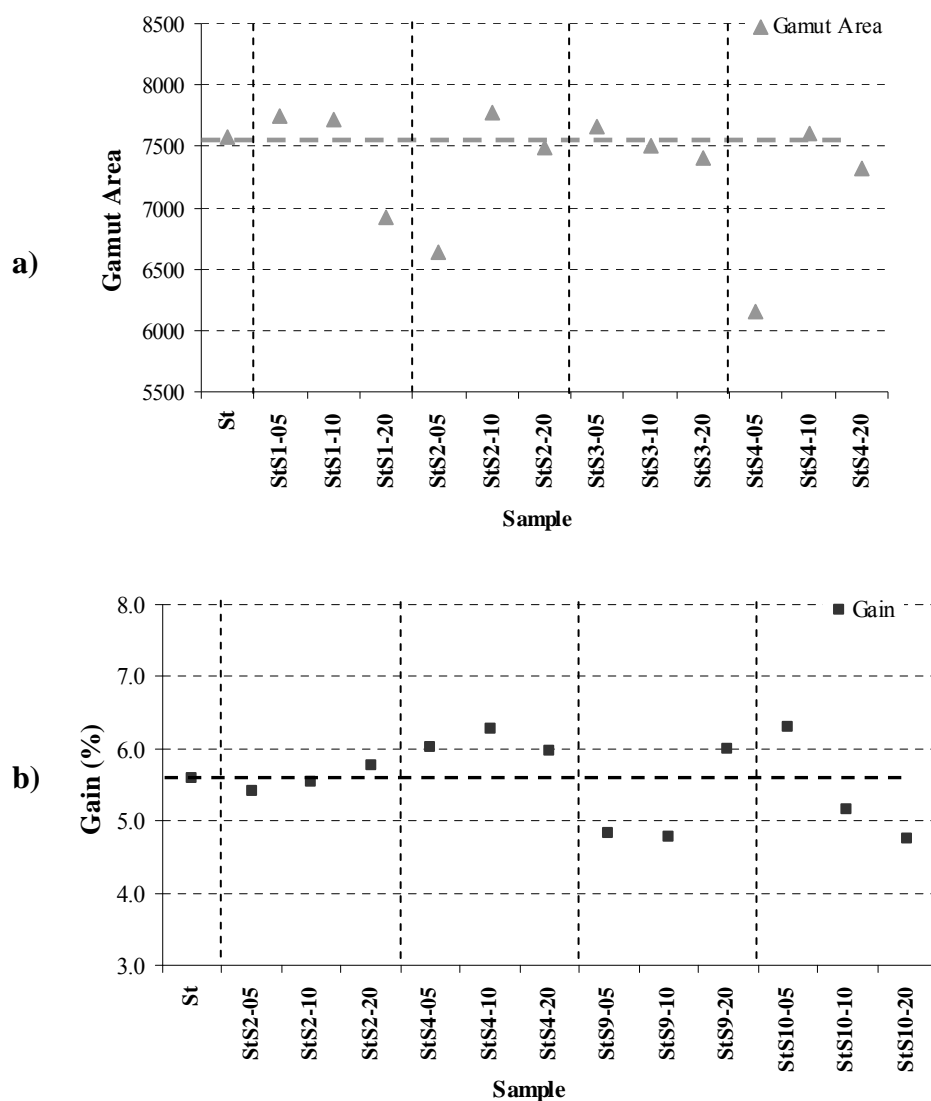


Fig. 5. a) Gamut Area values; **b)** Gain values. The dashed line refers to the value obtained for the reference sample (St)

For most of the samples the gamut area values were satisfactory (values superior to 7000 are usually accepted for this kind of papers and printing processes (Nilsson and Fogden 2008)). Compared to the reference sample St, the samples with an improved performance were StS1-05, StS1-10, StS2-10, StS3-05, and StS4-10. As for the gain values (Fig. 4-b)), it is possible to see that most of the sizing formulations improved the image definition.

The printing quality parameters usually refer to different aspects of the printed image (mainly color saturation or image definition) and thus it is convenient to analyze them all together. Combining the results obtained for the four parameters (black optical density, yellow optical density, gamut area and gain), the samples with the best printing performance seem to have been StS1-05, StS1-10, StS2-10, StS3-05, and StS4-10. In order to relate the printing quality performance of all samples with the results of the previous analyses, partial least squares (PLS) models were used. Considering the number of variables and groups in this process, a large number of models, with distinct dependent and independent variables, were taken into account. Table 3 summarizes the results of those presenting the larger degrees of explanation.

From this table it is clear that the explanation percentages as well as the correlation coefficients were in general quite small. However, it is possible to verify, for instance, that the gamut area values are quite well explained by the contact angle values, while the values of K_a and K_b consistently contributed to a relevant explanation of the three printing quality parameters that were evaluated.

Table 3. Application of PLS using Different Sets of Independent Variables

Dependent Variables Set (yy)	Independent Variables Set (xx)	Explanation %*	Correlation Coefficient
Gamut Area	Contact angle values (with 5 liquids)	23 (15; 8)	0.39
Gamut Area	(Surface Tension) + (σ_s^d σ_s^p determined by contact angle)	13 (13; 0)	0.36
Gamut Area	(Contact angle for water) + (K_a + K_b)	12 (12; 0)	0.35
Opt. density Black	Contact angle values (with 5 liquids)	10 (8; 2)	0.28
Opt. density Black	(Contact angle for water) + (K_a + K_b)	10 (10; 0)	0.31
Opt. density Yellow	Contact angle values (with 5 liquids)	17 (6; 11)	0.23
Line Gain	σ_s^p determined by IGC) + (K_a + K_b)	16 (16; 0)	0.40
Line Gain	(K_a + K_b)	12 (12; 0)	0.25
Line Gain	σ_s^d determined by contact angle) + (K_a + K_b)	17 (16; 1)	0.40
Line Gain	(Contact angle for water) + (K_a + K_b)	18 (18; 0)	0.42
*Total % (1st component; 2nd component)			

CONCLUSIONS

1. This study confirmed that the addition of the copolymers to the cationic starch increases the paper surface hydrophobicity to different degrees depending on the respective composition and concentration. It is shown that the printing and writing papers surface is predominantly dispersive, i.e., the polar and acid-base interactions have a smaller influence on paper behavior. Nonetheless, these secondary interactions

allow detailing the influence of the surface treatments, since they are more specific than the dispersive ones. In fact, the values of the polar component of the surface free energy obtained for different copolymer concentrations made it possible to formulate hypotheses concerning the orientation of the molecules at the paper surface, namely of the different functional groups.

2. The IGC analyses of the paper samples were found most useful, since they not only confirmed the results of the contact angle measurements but in some cases also complemented some of the hypotheses raised regarding the molecules orientation. As for the acid-base character it is found that the paper surface is amphoteric with a slightly basic character ($K_b > K_a$) and that the addition of the synthetic surface sizing agents to the traditional sizing formulation increases the surface ability to establish acid-base interactions due to a general increase of the K_a and K_b values (although more relevant for K_b).
3. As for the arrangement of the surface sizing molecules at the surface, the results suggest that the copolymers lie at the paper surface in a layer arrangement, and that the amount necessary to complete each layer depends on the size of their molecules. Moreover, the functional groups of the external layer mostly influence the paper surface properties, as expected.
4. The final inkjet printing performance, evaluated through the determination of several parameters related to color reproduction and image definition confirms that for better inkjet printing performances, the predominance of non-polar (rather than polar) groups turned outwards is desirable.
5. Finally, the results indicate that the addition of these synthetic surface sizing agents to the surface sizing formulation does improve the printing quality parameters, since the samples that exhibited the best overall performances were samples StS3-05 and StS4-10, which included co-styrene-acrylate copolymers in the sizing blend.

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