EVALUATING THE SURFACE ENERGY OF SURFACE SIZED PRINTING AND WRITING PAPERS

I. Moutinho*[,a], P. Oliveira[a], M. Figueiredo[a], P. J. Ferreira[a]

ABSTRACT

Printing quality is strongly influenced by the structural and chemical properties of paper surface, which depend not only on the properties of the base paper but also on the final treatment of paper surface. At present, surface treatment is an important step of papermaking for improving the final product quality and may comprise mechanical and/or chemical operations. For instance in uncoated printing and writing papers surface sizing is becoming a common practice for controlling paper roughness and mainly the spreading and absorption of liquids. Typically, only starch is used as sizing agent, but there is an increasing tendency for combining starch with synthetic polymers that enable a better control of the surface hydrophilic character.

This study aims at analyzing the influence of different surface sizing formulations on some chemical properties of paper surface, such as energy and acid-base character. For that, seven paper samples were analyzed using two distinct techniques – Inverse Gas Chromatography (IGC) and Contact Angle Measurements. The paper surface free energy and its polar and dispersive components were assessed by measurements of the contact angle with different test liquids in a OCA 20 Dataphysics equipment. Besides, the dispersive component of the surface energy and the acid-base character of the surface at different temperatures, as well as the Ka and Kb constants were evaluated by IGC in a Dani GC 1000 equipment.

The results confirmed that both the contact angle and the IGC measurements are very useful for the characterization of the paper surface chemistry. In addition, it was demonstrated that the nature and amount of sizing influences the paper surface energy and its acid-base character, and the results were interpreted considering the properties of the compounds used for surface sizing. This study is very important for better understanding the mechanisms that rule paper-ink interaction, namely for ink-jet and offset printing.

KEYWORDS

Paper, Surface Sizing, Surface Energy, Contact Angle, Inverse Gas Chromatography (IGC)

INTRODUCTION

At present, there is an increasing demand concerning the quality of printing and writing paper grades (P&W). The performance of this commodity depends on the properties of the fibrous matrix and on the characteristics of the paper surface, which are influenced by the quality

[a] Chemical Engineering Department, Coimbra University, Portugal.
Tel. +351.239.798.700; E-mail. isamim@gmail.com, paso81@gmail.com, mmf@eq.uc.pt, paulo@eq.uc.pt.

of the pulp fibers, the refining process, the chemicals added in the preparation of the furnish, the operations at the paper machine and the modifications of paper surface (Oliver *et al.* 2001; Brandão 1999). These modifications include calendering and/or chemical treatments such as coating and surface sizing (Koskela 2003; Pruszynski 2003; Brandão 1999). Today, chemical modifications of paper surface for improving printing quality is a common practice in papermaking and, as a consequence, there is a large increase in the production of new chemicals that meet specific end-use paper requirements.

For surface sizing, cationic starch alone or a mixture of cationic starch and a synthetic polymer are used to control the hydrophilic character of paper surface, preventing excessive absorption of liquids and inks (Brandão 1999). A thin reticular matrix film is formed at paper surface. This film reduces the number and size of pores as well as paper roughness, and modifies paper surface energy, so that not only liquid penetration but also liquid spreading is attenuated (Koskela 2003; Brandão 1999). Surface sizing is affected by the sizing formulation properties (composition, viscosity, pH, temperature) as well as the paper properties (basis weight, bulk, internal sizing, water content and surface energy, porosity and roughness) (Pruszynski 2003). However, these properties must be adequately controlled in order to avoid too much penetration of the surface sizing agent in the sheet structure. For selecting the most appropriate surface sizing agent for a specific paper it is essential to test its performance at lab scale. Parameters of the surface sized paper, like energy, porosity and roughness, which largely influence ink spreading, penetration and drying, have to be determined.

Many studies can be found in the open literature concerning paper coating and the characterization of paper surface, both in physical and chemical terms (Forsström *et al.* 2003). However, not many studies have been performed and published regarding surface sizing of fine papers. The objective of this study is to evaluate the influence of different surface sizing treatments on some chemical properties of paper surface, such as energy and acid-base character. For that two different techniques were applied in this work: contact angle measurements and Inverse gas chromatography (IGC).

Contact angle measurements are commonly considered convenient to determine the paper sheets surface energy, because they are fast, simple and based on easy-to-use equations for the calculation of surface energy components (Chibowski 2003; Shen *et al.* 2000; Briggs *et al.* 1989). IGC has also proved to be a powerful tool for the characterization of solid surfaces, like fibers and paper (Carvalho *et al.* 2005; Santos *et al.* 2001) and particularly those that can not be easily studied by other methods. Due to interactions between the stationary phase and the probe molecules either the dispersive component of the surface energy of the sample (γ_s^d) as his acid/base character can be achieved (Carvalho *et al.* 2005; Wålinder 2000; Cordeiro *et al.* 1995).

EXPERIMENTAL

A calendered uncoated base paper (80 g/m^2), produced with a *Eucalyptus globulus* kraft pulp and without any surface treatment, was surface sized with cationic starch (Ss), with three different blends of cationic starch and co-acrylonitrile-acrylate (Sa) and with three different blends of cationic starch and co-styrene-acrylate (Sb), as described in Table I. These surface sized samples were no further calendered.

Table 1 – Samples description

Sample	Sizing formulation (% m/m)
Ss	100% (cationic starch*)
Sa.5	95%:5% (cationic starch* : co-acrylonitrile-acrylate)
Sa.10	90%:10% (cationic starch* : co-acrylonitrile-acrylate)
Sa.20	80%:20% (cationic starch* : co-acrylonitrile-acrylate)
Sb.5	95%:5% (cationic starch* : co-styrene-acrylate)
Sb.10	90%:10% (cationic starch* : co-styrene-acrylate)
Sb.20	80%:20% (cationic starch* : co-styrene-acrylate)

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 its velocity was adjusted to 6m/min. The drying process was performed in two steps: first with an IR drier coupled to the applicator roll using a 1.0 kW drying intensity; and next with air drying for at least 10 min. The total surface sizing pick-up was 3.5 ± 0.3 g/m^2.

The Acrylate copolymers were selected due to their different hydrophobic character (Styrene is more hydrophobic than Acrylonitrile). Some properties of the compounds used in this work were determined in laboratory and the results are presented in Table 2. The monomers proportion of each copolymer was computed by calculated elemental analysis.

Table 2 – Properties of the compounds used to produce the surface sizing formulations

Compound	Monomers proportion	Solids content (%)	pH	Molecular weight (g/mol)	Molar volume (cm^3)	Surface tension (dine/cm)
Cationic starch[A]	n.a.	12.8	6.7	160.1	107.0	66.8
Co-acrylonitrile-acrylate (a)	1:1	35.2	3.4	125.1	115.5	45.9
Co-styrene-acrylate (b)	1:2	25.5	4.7	176.2	232.6	45.4

[A] The cationic starch suspension was collected at the paper mill, and includes other process additives used in industry, such as optical brightener (OBA) and salt.

For evaluating the impact of surface sizing on paper surface properties, contact angle measurements were performed with the DataPhysics equipment OCA20, using the sessile drop method (Brigs *et al.* 1989). By measuring on the same solid surface the contact angle of different liquids whose surface tension components are known it is possible to derive the total solid surface energy and its dispersive and polar components. For the surface energy calculation the OWRK method was applied. The theory behind this method and the surface tension values of the liquid probes used are presented elsewhere (Chibowski 2003; Briggs *et al.* 1989; Owens 1969). For each paper sample, pieces from at least three different sheets were used and for each liquid probe a minimum of 10 drops were measured.

Inverse gas chromatography was the other technique selected to evaluate the impact of surface sizing on paper surface properties. The main difference between IGC and conventional Gas Chromatography is that in IGC the material under analysis is the stationary phase and the compounds injected (probes) have well known properties. The principle of IGC is simple: an inert carrier gas elutes a minute quantity of a probe molecule through a column packed with the stationary phase, which in this case is paper. Due to interactions between the stationary phase and the probe molecules, the probe molecules are retained for a certain time. The application of IGC in surface characterization enables the evaluation of the dispersive component of the surface energy and its variation with temperature and also of the surface acid/base character (Carvalho *et al.* 2005).

IGC experiments were carried out using a DANI GC 1000, equipped with a flame ionization detector (FID). In order to reduce the particles size, the samples were cut into small pieces (about

2 × 2 mm²) before packing. On average, approximately 2 to 3 g of each sample were packed in stainless steel columns, 0.5 m long and 0.4 mm ID. The packed columns were conditioned for approximately 12 h under a helium flow before the beginning of the analysis. The experiments were carried out at temperatures between 35 and 60°C in 5°C intervals. The injector and detector were kept at 180 and 200°C respectively. Helium was used as carrier gas and to each sample tested the flow was selected to ensure that neither absorption nor diffusion of the probes would occur inside the column. Small amounts of each probe vapor (<1 µl) were injected into the carrier gas flow to ensure that the experiments took place at infinite dilution. To determine the dispersive component of the surface energy, a series of n-alkane probes was used, while to achieve the acid/base properties five polar probes were used: trichloromethane ($CHCl_3$, acidic), dichloromethane (CH_2Cl_2, acidic), acetone (amphoteric), ethyl acetate (ETA, amphoteric) and tetrahydrofuran (THF, basic). Natural gas (83.7 % methane) was used to determine the dead retention volume. The relevant characteristics of the probes used, such as the dispersive component (γ_l^d) of the surface tension, molecular surface area (*a*), Gutmann's modified acceptor number (AN*), Gutmann's donor number (DN) and Lewis character can be found in literature, as well as the method for the calculation of the dispersive component of the surface energy (γ_s^d) and of the acid/base properties of the surface (Wa, Ka and Kb) (Carvalho *et al.* 2005; Santos 2005; Cordeiro *et al.* 1995).

When non polar probes are used (n-alkane series), only dispersive interactions occur. By plotting $RT\ln(V_n)$ vs $2Na(\gamma_l^d)^{1/2}$ a straight line is obtained, usually referred to as the reference line. The slope of the reference line leads to the determination of γ_s^d for a given temperature:

$$2 \cdot N(\lambda_s^d)^{1/2} \cdot a \cdot (\lambda_l^d)^{1/2} + C = R \cdot T \cdot \ln(V_n) \quad (1)$$

N is the Avogadro's number, a is the cross-sectional area of the probe to be tested, R is the ideal gas constant, T is the absolute temperature and V_n is the net retention volume of the n--alkanes.

In order to obtain the acid (Ka) and base (Kb) parameters of the solid surface, the interactions of the polar probes with the samples are analyzed and the deviation from the reference line is quantified, allowing the estimation of the work of adhesion W_a^s:

$$W_a^s = \frac{R \cdot T}{N \cdot a} \ln\left(\frac{V_n}{V_{n,\mathrm{Ref}}}\right) \quad (2)$$

$V_{n,Ref}$ is the retention volume established by the n-alkanes reference line and V_n is now the retention volume of the polar probes.

By following the same procedure applied to the n-alkanes, experiments are undertaken at different temperatures in order to determine the enthalpy (ΔH^S) an entropy (ΔS^S) of adsorption from the linear relation of ΔH^S vs DN/AN*, for the series of polar probes characterized by different AN* and DN numbers, the acidic, Ka, and basic, Kb, constants are calculated:

$$\frac{\left(-\Delta H^S\right)}{AN^*} = Ka\frac{DN}{AN^*} + Kb \quad (3)$$

RESULTS AND DISCUSSION

The results of surface energy and of the corresponding polar and dispersive components, obtained by contact angle measurements, are presented in Table 3.

From Table 3 is possible to observe that, for all samples, the predominant component of surface energy is the dispersive component. Besides, sample Ss has the higher polar component and the higher polar character. The surface sizing agent *b* reduces the total surface energy and the higher is its percentage the larger is the reduction. The reduction of the surface energy relative to the starch sizing is mainly caused by the diminution of the polar component. The effect

of sizing agent *a* in the total surface energy is not evident, but once again there is a significant reduction of the polar component. These differences are due to the fact that the polar character of surface sizing agent *b* is not so pronounced, because of the presence of the Styrene monomer.

Table 3 – Surface free energy and the corresponding dispersive and polar components for the different papers, determined by contact angle measurements

Sample	Surface energy (mN/m)			γ_s^d / γ_s (%)
	Total γ_s	Polar Component γ_s^p	Dispersive Component γ_s^d	
Ss	51.25 ± 0.74	15.85 ± 0.50	35.40 ± 0.54	69.1
Sa.5	53.78 ± 0.39	10.45 ± 0.25	43.33 ± 0.31	80.6
Sa.10	48.23 ± 0.65	8.47 ± 0.38	39.76 ± 0.53	82.4
Sa.20	53.26 ± 0.44	12.33 ± 0.28	40.92 ± 0.34	76.9
Sb.5	49.18 ± 0.51	5.67 ± 0.29	43.51 ± 0.42	88.5
Sb.10	47.79 ± 0.73	10.58 ± 0.44	37.21 ± 0.58	77.9
Sb.20	40.42 ± 0.53	0.06 ± 0.04	40.36 ± 0.53	99.9

Figure 1 shows that, as expected, the increase of the polar component of the surface free energy id followed by a decrease of the contact angle with water.

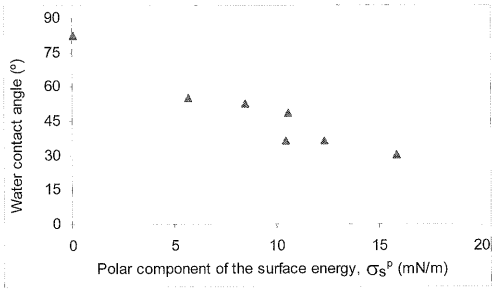


Figure 1 – Effect of the polar component of surface energy's variation in water contact angle

The analysis of the paper samples by IGC allows the determination of the surface energy's dispersive component and its variation with temperature, which is an important information for some printing technologies, namely laser printing. The results obtained for the paper samples tested in this work are presented in Figure 2.

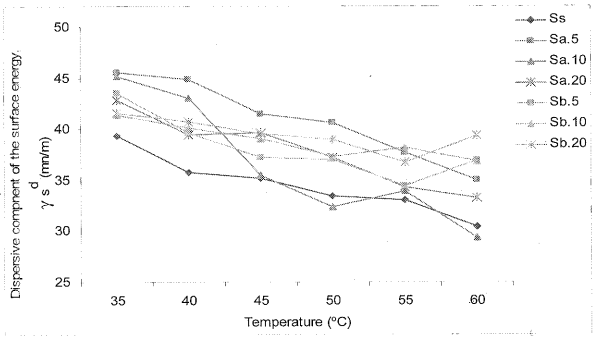


Figure 2 – Variation with temperature of the surface energy's dispersive component for all the paper samples analyzed

Sample Ss presents, in general, smaller values of γ_s^d, in agreement with the results obtained by the contact angle measurements (Table 3), and for all samples γ_s^d tends to decrease with temperature. The amplitude of variation differs from sample to sample. The application of surface sizing agent *a* increases the impact of temperature in the results (larger variation with temperature for samples Sa.5, Sa.10 and Sa.20 than for sample Ss) while the application of surface sizing agent *b* as an opposite effect (smaller variation with temperature for samples Sb.5, Sb.10 and Sb.20 that for sample Ss).

The IGC analysis allows the fitting of experimental correlations to the variation of γ_s^d with temperature, for each sample. The results are presented in Table 4, which also includes the result of the extrapolation for 25°C (in order to allow a more direct comparison with the γ_s^d values obtained by the contact angle measurements).

Table 4 – Experimental correlations for calculation of γ_s^d at different temperatures and γ_s^d values obtained for 25°C

Sample	Correlation	r^2	$\gamma_{s\,,T=25°C}^{d}$ (mN/m)
Ss	$\gamma_s^d = -0.31T + 49.37$	0.94	41.58
Sa.5	$\gamma_s^d = -0.43T + 61.37$	0.97	50.57
Sa.10	$\gamma_s^d = -0.63T + 66.36$	0.88	50.67
Sa.20	$\gamma_s^d = -0.37T + 55.59$	0.95	46.22
Sb.5	$\gamma_s^d = -0.42T + 57.08$	0.93	46.67
Sb.10	$\gamma_s^d = -0.19T + 47.71$	0.92	42.94
Sb.20	$\gamma_s^d = -0.23T + 49.79$	0.95	44.06

The good correlations presented in Table 4 ($r^2 > 0.88$) confirm the quality of the technique and enable the use of the equations for computing the values of γ_s^d at 25°C in order to better compare with the values obtained by the contact angle measurements. The resulting comparison is plotted in Figure 3 and reveals that the γ_s^d IGC results are always superior to those obtained by measuring the contact angle, although following practically the same tendency along the various samples. This is not an unexpected result, since in IGC paper roughness does not interfere with the measurements as it occurs in contact angle measurement. As a consequence, the more energetic '*sites*' of the samples are analyzed in IGC, leading to higher values.

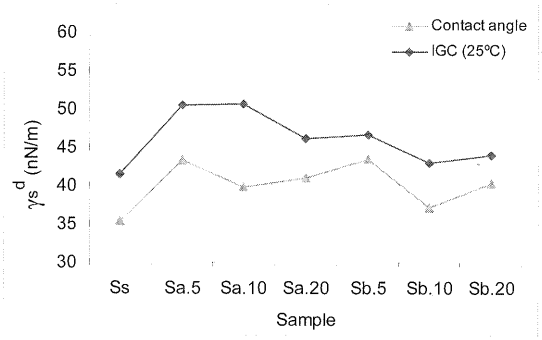
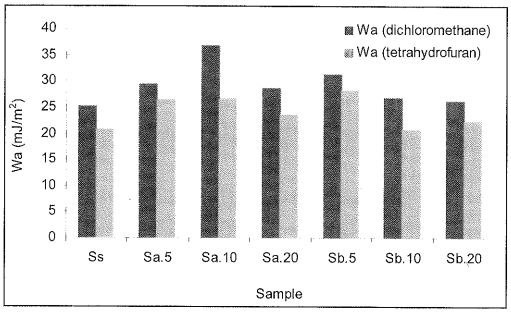
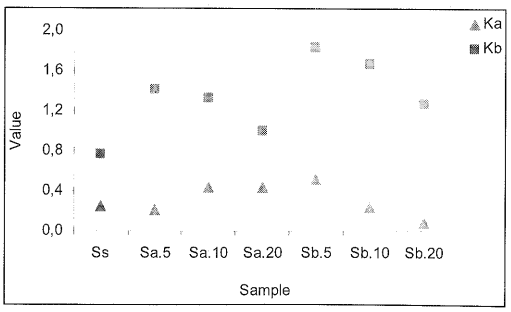


Figure 3 – γsd values from contact angle measurements and IGC.

Other valuable information obtained from IGC experiments concerns the evaluation of the acid-base character of paper surface, by computing the values of the work of adhesion and of Ka and Kb. The values obtained for the work of adhesion with an acidic (CH_2Cl_2) and a basic (THF) probe for each sample, at 40°C, are represented in Figure 4 (a), whereas the Ka and Kb values obtained for each sample are presented in Figure 4 (b).



(a)



(b)

Figure 4 – Graphical representation of: (a) work of adhesion obtained by IGC for each sample with CH_2Cl_2 and THF at 40°C; (b) Ka and Kb values obtained by IGC for each sample.

In Figure 4 (a) it is possible to see that, for all samples, the work of adhesion of the acidic probe (CH_2Cl_2) is higher than the work of adhesion of the basic probe (THF), which indicates that all paper surfaces present a basic character. The addition of the synthetic surface sizing agents increases the work of adhesion of CH_2Cl_2, and thus the basic character of the surface. By analyzing the effect of each synthetic surface sizing agent separately, it is possible to observe that for agent *a* the highest values of Wa are for 10% of incorporation and the smallest ones for 20%. This finding indicates that the effect of this compound in acid/base properties of paper increases until approximately 10% and then decreases again. On the other hand, for surface sizing agent *b* the highest values of Wa (for both probes) are obtained with 5% of incorporation and then the increase of surface sizing agent content leads to the decrease of Wa, being the smallest values obtained for 10% of surface sizing agent in the basic probe and for 20% in the acidic probe. These observations are not related with the pH of the compounds, which would be the most obvious relation, since the cationic starch presents the highest values of pH (Table 2) and sample Ss has the smallest values of Kb. The variations observed between samples with the same surface sizing agent in different amounts are possibly related to the compounds molecular volume (Table 2). Surface sizing agent *a* is smaller and the corresponding 'maximum' effect detected occurs for 10% of incorporation in the sizing formulation, while the bigger surface sizing agent *b* exerts the 'maximum' influence in the acid/base character of the surface for 5% of incorporation (for the tested formulations). This observation may indicate that after the available pores (or active sites for interaction) in paper surface are occupied, the addition of more surface sizing agent does not increase its influence on the surface acid/base properties. The values of Ka and Kb observed in Figure 4 (b) are in agreement with those obtained for Wa, since that for all samples Kb is higher than Ka, confirming the basic character of the papers surfaces as well as the increasing of the surface basic character with the addition of the synthetic surface sizing agents.

CONCLUSIONS

The results presented in this work confirm the suitability of contact angle measurements and IGC in achieving some very important chemical properties of papers surface, such as energy and acid-base character.

By contact angle measurements it was verified that the contribution of the dispersive component is bigger that the contribution of the polar component to the surface free energy of the samples evaluated in this study. The combination of the cationic starch with synthetic surface sizing agents causes the diminution of the polar component of the surface energy, and therefore the surface becomes less hydrophilic. This can be very useful to control ink penetration in printing, namely in inkjet printing. The application of a more hydrophobic surface sizing agent decreases more significantly the polar component of surface energy.

Concerning to IGC measurements it was possible to verify that the dispersive component of the surface free energy decreases with temperature for all samples tested and that the sample with only cationic starch in the surface presents the smallest values of the dispersive component. Concerning to acid/base character, all samples proved to have a basic character (which can be a consequence of the pulp production process itself) and the impact of each surface sizing agent proved to depend on the molecules size and is not directly related to the amount of compound added to the sizing formulation.

Comparing the values of the dispersive component of surface energy it was verified that IGC leads to higher values than contact angle measurements.

Comparing the surface sizing agents tested, it was verified that the application of surface sizing agent *b* significantly decreases the polar component of the surface energy, and reduces the impact of temperature variations in the dispersive component, while the application of surface sizing agent *a* has a smaller effect in the polar component diminution and increases the impact of temperature variations in the dispersive component of the surface free energy.

After all these considerations it is possible to conclude that both these techniques are very important in what concerns to the complex issue of paper surface chemistry studies and can give useful information to better understand the differences between papers that are in the origin of differences in printing quality (which many times remain without valid explanation if only surface physical properties are studied).

REFERENCES

Brandão, E. (1999). Proc. *16º Encontro Tecnicelpa*, 165-176.
Briggs, D., Rance, D.G., Briscoe, B.J. (1989) In "Polymer characterization". p. 707-732 C., Pergamon Press, Oxford.
Carvalho, M. G., Santos, J. M. R. C. A., Martins, A. A., Figueiredo, M. M. (2005). *Cellulose*. **12**: 371-383.
Chibowski, E. (2003). *Advances in Colloid and Interface Science*. **103**: 149-172.
Cordeiro, N., Neto, C. P., Gandini, A., Belgacem, M. N. (1995). *Journal of colloid and interface science*. **174**: 246-249.
Forsström, U., Fagerholm, K., Saharenen (2003). *Paperi ja Puu – Paper and Timber*. 85: **8**: 454-459.
Koskela, J. P., Hormi, O. E. O. (2003). *Appita Journal*. 56: **4**: 296-300.
Oliver, J., Chen, J., Tosto, F. (2001). *COSTJ. European*. **E11**: 1-9.
Owens, D.K., Wendt. R.C. (1969). *J. Appl. Polym. Sci.* 13 :**8**: 1741.
Pruszynski, P. (2003). *WWP Keynote lectures*. 82-90.
Santos, J. M. R. C. A., Gil, M. H., Portugal, A., Guthrie, J. T. (2001). *Cellulose*. **8**: 217- 224.
Santos, J. M. R. C. A., Guthrie, J. T. (2005). *Materials Science and Engineering*. **50**: 79-107.
Shen, W., Filonanko, Y., Truong, Y., Parker, I. H., Brack, N., Pigram, P., Liesegang, J. (2000). *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. **173**: 117-126.
Wålinder, M. E. P., Gardner, D. J. (2000). *Wood and Fiber Science*; 32: **4**: 478-488.