

Evaluating the surface energy of laboratory-made paper sheets by contact angle measurements

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ABSTRACT: Contact angle is one of the most useful tools to easily assess the surface energy of paper sheets. However, the results obtained should be treated with some caution, since these measurements are significantly influenced by the properties of the liquids used and of the paper surface. Our study compares the values of the contact angle and of the surface energy of laboratory handsheets produced with demineralized water and with white water (collected from the paper mill). In addition, and to assess the influence of paper roughness on the contact angle measurements, some 3-D topographical parameters were computed by profilometry. Complementary measurements were also performed with commercial paper samples. The results clearly demonstrate that the kind of water used in the sheet-making process has a more pronounced influence on the surface energy of the paper sheets than whether the paper sheets were made in a laboratory sheet former or in an industrial paper machine.

Application: This study clarifies factors that have influence on the practical determination of the surface energy of paper sheets by contact angle measurements. The results show the influence of the water used in the sheet-making process on the surface energy of paper sheets and are specially useful for experiments carried out in the laboratory.

For many paper grades, particularly printing and writing papers, the physical and chemical surface characteristics are of utmost importance because of their influence on ink-paper interactions, namely wetting, adhesion, and absorption [1,2]. Therefore, it is crucial to assess the surface characteristics and to relate them with these parameters. One of the most common procedures for doing that involves measuring the contact angle between the sample and some specific liquids. From the results, we can evaluate the potential of inks to spread or penetrate. We can also obtain the total paper surface energy and the corresponding polar and dispersive contributions.

Contact angle methods, including the sessile drop method, are considered the most convenient for determining paper sheet surface energy. They are fast, simple, and based on easy-to-use

equations for the calculation of surface energy components [3-5]. Nonetheless, the measurement of the contact angle depends on many factors related to the paper structure and to the properties of the liquids that are used. Although some relevant studies can be found in the literature, many related issues remain to be studied.

The motivating factor for our study was the fact that previous studies obtained opposite results for the relationship between the polar and the dispersive components of the surface free energy computed from contact angle measurements in commercial printing and writing papers and in laboratorial paper sheets [6]. Both kinds of papers were produced with the same pulp furnish, the only difference being the process of sheet formation and the water that was used.

In this work we compare and discuss the results of the contact angle

measurements obtained in laboratory handsheets prepared with the same pulp furnish, but using two different kinds of water: demineralized water (as is common practice in laboratory) and white water collected from a paper mill circulation water system. We also tested commercial paper sheets produced with the same type of pulp. To separate the influence of the water from that of the paper surface roughness on the surface energy, complementary profilometry tests were performed.

The final objective of the study was to evaluate how paper surface energy is affected by the water used in the production of laboratory paper sheets. This is an important matter since the advent of new water-based inks has increased research in paper surface chemistry, with most of the experiments being carried out at laboratory scale. In this scenario, it is essential to guarantee that both the physical and the chemical sur-

face characteristics of laboratory paper sheets used in this research are as close as possible to those of the commercial paper sheets.

EXPERIMENTAL

Sample preparations

Handsheets were made in laboratory, according to the ISO 5269/1 standard, using a commercial *Eucalyptus globulus*-based kraft pulp bleached with an elemental chlorine-free (ECF) sequence. This pulp was collected at the headbox sampling point of a paper mill. It therefore included all the furnish additives: filler (precipitated calcium carbonate [PCC]), cationic starch, retention aids, and internal sizing agents.

First, the handsheets were produced using demineralized water (HS-1). Next, and to better simulate the prevailing conditions at the paper mill, white water collected from the paper machine was used. However, the high amount of solids in the resulting fibrous suspension prevented the water from draining from the sheet former, making it virtually impossible to obtain handsheets. For this reason, a second and more successful attempt of producing handsheets was made after a previous settling of the white water overnight, so that only the supernatant was used (HS-2). At least five handsheets of each kind (HS-1 and HS-2), with 90 ± 5 g/m² oven-dry (o.d.) basis weight, were produced and conditioned at $23^\circ\text{C} \pm 1^\circ\text{C}$ and $50\% \pm 2\%$ relative humidity.

Depending on the raw materials used, the pulping and bleaching process, the washing efficiency, the paper type produced, and all other production conditions, the white water usually contains many dispersed and dissolved material. This includes fillers and process chemicals, such as surface active agents, polymers from the bleaching chemicals and the sizing and retention aids, ions from inorganic salts, and other dispersed minerals and particles [7]. Therefore, to monitor the white water system, the measurement of several parameters is usually recommended [8]. In this study, both the demineralized water and the white water supernatant were analyzed in terms of pH, conductivity, and calcium ion concentration (by atomic absorption spectrophotometry). The results are presented in **Table I**. The analysis of the settled solids by Fourier transform infrared (FTIR) spectroscopy confirmed that the white water contains a very high percentage of PCC.

To compare the contact angle values of the paper sheets

Parameter	Demineralized water	White water
pH	7.3	7.7
Conductivity ($\mu\text{S}/\text{cm}$)	202	820
Ca ²⁺ content (mg/L)	7.97	36.7

I. Properties of the demineralized water and of the white water.

produced in laboratory with those produced in industry, we also studied a sample of a commercial paper, corresponding exactly to the same pulp furnish of the laboratory handsheets (CP-1). However, due to process restrictions in the paper mill, it was only possible to collect paper samples with surface sizing. For this reason and because the laboratory handsheets did not have any surface treatment, a commercial paper having no surface treatment was analyzed (CP-2). This paper was also produced with an E. globulus-based kraft pulp, bleached with an ECF sequence, and with identical additives.

Contact angle measurements

The contact angle of a liquid over a solid surface reaches equilibrium, as described by the well-known Young equation [3,9,10]:

$$\sigma_s = \sigma_{sl} + \sigma_l \cdot \cos \theta \quad (1)$$

where, σ_s is the solid surface free energy, σ_{sl} is the solid/liquid interfacial free energy, σ_l the liquid surface tension, and θ the contact angle formed between the liquid drop and the solid surface. On the other hand, the solid/liquid interfacial free energy can be expressed by Dupre's equation [3,5,9,11]:

$$\sigma_{sl} = \sigma_s + \sigma_l - W_a \quad (2)$$

where W_a is the work of liquid adhesion. This work of adhesion results from two types of intermolecular forces: the van der Waals dispersive forces, always present, and the nondispersive or polar forces, which include the dipole forces and the acid-base forces, present solely between polar molecules [3,11,12]. Owens and Wendt [13] and Kaelble and Uy [14] proposed that both the dispersive and the polar interactions between the two phases could be approximated by a geometric mean expression, and therefore Eq. (2) becomes [3]:

$$\sigma_{sl} = \sigma_s + \sigma_l - 2 \left(\sqrt{\sigma_s^d \cdot \sigma_l^d} + \sqrt{\sigma_s^p \cdot \sigma_l^p} \right) \quad (3)$$

In this equation the superscripts d and p stand respectively for the dispersive and polar components of the liquid surface tension and of the solid surface energy, considering that [3,10,12]:

$$\sigma_l = \sigma_l^d + \sigma_l^p, \quad \sigma_s = \sigma_s^d + \sigma_s^p \quad (4)$$

Combining Eqs. (1) and (3) gives:

$$\frac{1 + \cos \theta}{2} \cdot \frac{\sigma_l}{\sqrt{\sigma_l^d}} = \sqrt{\sigma_s^p} \cdot \sqrt{\frac{\sigma_l^p}{\sigma_l^d}} + \sqrt{\sigma_s^d} \quad (5)$$

Liquid	Surface tension σ_l (mN/m)	Polar component σ_l^p (mN/m)	Dispersive component σ_l^d (mN/m)	σ_s^d / σ_s (%)
Water	72.8	48.1	24.7	33.9
Water/Ethylene glycol	57.7	39.1	28.5	49.4
Formamide	58.1	25.8	32.3	55.6
Ethylene glycol	48.3	17.4	30.9	64.0
Propylene glycol	35.4	9.0	26.4	74.6

II. Surface tension and the corresponding polar and dispersive component of the liquid probes used.

Thus, by measuring on the same solid surface the contact angle of different liquids whose surface tension components are known, we can plot $(1 + \cos\theta)/2 \cdot (\sigma_l/(\sigma_l^d)^{1/2})$ versus $(\sigma_l^p/(\sigma_l^d)^{1/2})$ and fit the points to a straight line in order to calculate σ_s^p and σ_s^d , respectively from the slope and from the intersection with the vertical axis [3], and then derive the total solid surface free energy (Eq. 4).

In this work, the contact angles were measured with a DataPhysics OCA20 using the sessile drop method [3]. For that, the initial resting drop image (<3 s after application of the liquid) was acquired by a CCD camera and the corresponding contact angle was calculated after fitting the drop contour line to an ellipse. Five liquids were used as probes: demineralized water, water:ethylene glycol mixture (50/50 wt.%), ethylene glycol, propylene glycol, and formamide. The respective values of the total surface tension and the corresponding dispersive and polar components were calculated in a previous study [6] with the same equipment, by using the pendant drop method [15]. **Table II** lists these values, with a coefficient of variation always inferior to 1%, where the liquids are presented in decreasing order of the corresponding polar component, σ_l^p .

For each paper sample (HS-1, HS-2, CP-1, CP-2), pieces from at least three different sheets were used and for each liquid probe a minimum of 10 drops were measured.

Perfilometry measurements

To find the contribution of the surface topography to the contact angle results, measurements of some 3-D parameters were carried out using an AltiMet profilometer Altisurf 500 and PaperMap software. For each paper sample, we scanned samples measuring $4 \times 4 \text{ mm}^2$. From the 2,000 profiles obtained for each specimen the following parameters were computed:

- average roughness (S_a , μm), defined as the arithmetic average of the absolute values of the surface height deviations measured from the best fitting plane;
- maximum peak height (S_p , μm)

and maximum valley depth (S_v , μm), both measured relatively to the mean plane; and

- interfacial area ratio (S_{dr}), which indicates the complexity of the curvilinear surface compared with the support surface [16].

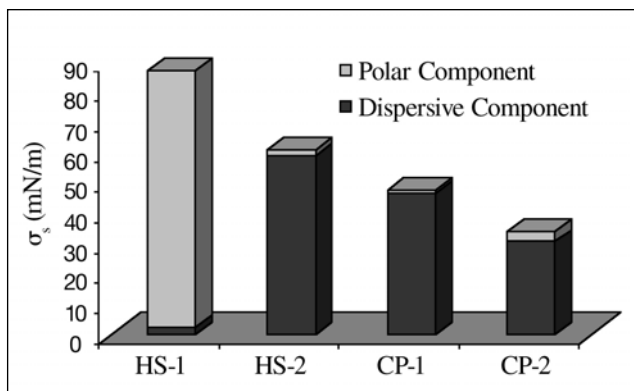
RESULTS AND DISCUSSION

Table III summarizes the results obtained for the different paper samples, in terms of the total surface free energy and polar and dispersive components. Each value is the average of at least 10 measurements.

Although different surface energies were obtained for the different samples, the most striking evidence is the inversion of the relative contributions of the surface energy components found for the handsheets HS-1, when compared with the other papers. Considering only the handsheets made in laboratory (HS-1 and HS-2), it is clear that for those produced with demineralized water (HS-1) the contribution of the polar component is much larger than that of the dispersive component, whereas the opposite is found for the handsheets made with the white water (HS-2). The predominance of the dispersive component over the polar component, also found in both commercial papers analyzed (CP-1 and CP-2), is in agreement with results reported in other works [6,17,18]. The contribution of both components to the total surface energy is more evident in **Fig. 1**. It is important to notice that values of the dispersive component as small as that of handsheets HS-1 were obtained by the authors for other handsheets, also produced with demineralized water, and analyzed by inverse gas chromatography (IGC) [19, 20].

Sample	Surface energy σ_s (mN/m)	Polar component σ_s^p (mN/m)	Dispersive component σ_s^d (mN/m)
HS-1	87.2 ± 3.0	84.8 ± 2.9	2.42 ± 0.43
HS-2	60.8 ± 3.3	1.76 ± 0.69	59.1 ± 3.3
CP-1	47.6 ± 1.8	0.94 ± 0.30	46.7 ± 1.8
CP-2	34.1 ± 2.4	3.38 ± 0.97	30.7 ± 2.2

III. Surface free energy and the corresponding polar and dispersive components of the different papers.



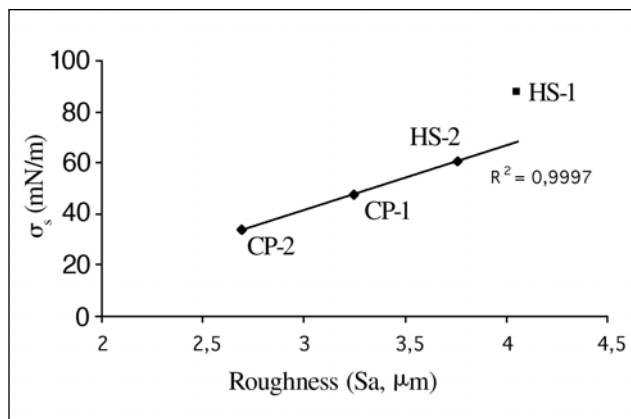
1. Contribution of the polar and dispersive components to the total surface free energy of the different papers (Table III).

These results will be published separately.

Because paper sheets are far from homogeneous, surface roughness is a parameter to consider when analyzing and interpreting surface energy data evaluated from contact angle measurements. To investigate the contribution of this parameter, we also analyzed some results derived from profilometry (Table IV).

As expected, the laboratory-made paper sheets have a rougher surface than do the commercial paper sheets. The laboratory sheets were also found to be more heterogeneous, as shown by the higher values of the surface peaks (Sp) and valleys (Sv), and of the interfacial area ratio (Sdr). The differences between handsheets HS-1 and HS-2 can be explained mainly by the existence of fines and fillers in the white water, which tend to fill the valleys at the surface of handsheets HS-2, making it smoother.

Figure 2 depicts surface energy as a function of surface roughness for the samples tested. It shows a perfect linear correlation for the papers produced with white water. Additionally, this figure shows that the differences in roughness obtained for the various samples are of the same magnitude, regardless of the sheet-making process, leading to the conclusion that topography can not explain the much larger polar component of the surface energy of handsheets HS-1,



2. Paper surface free energy as a function of paper roughness (Tables III and IV).

visible in Fig. 1.

The preponderance of the polar component of the paper surface energy detected for the handsheets produced with the demineralized water (HS-1) most certainly derives from the ionizable groups of the fibers and fines (mainly dissociated carboxylic groups from the hemicelluloses, but also hydroxyl groups), and from some residual fillers, which are also anionic in character [8,21]. Furthermore, some remaining extractives eventually present in the furnish may have been removed by the demineralized water during the handsheet-making process, also rendering the surface more hydrophilic.

When white water is used, which has a quite distinct composition, we expect a variation in the charge of the furnish components because this charge depends on the pH, concentration of dissolved ions, and conductivity of the water phase. The results in Table I show that the pH, and particularly the Ca^{2+} ion and the electrolyte concentration of the white water used, are much larger than those of the demineralized water. Together with roughness, that explains the differences found in the surface energies of handsheets HS-1 and HS-2. The slightly alkaline pH is due to the dissociation of the calcium carbonate and the resulting formation of hydroxyl ions.

This dissociation inevitably leads to an increase in the concentration of Ca^{2+} ions. The strong adsorption of these ions on the negatively charged groups of the fibers and fines, by electrostatic forces, balances the charge, thus reducing the surface energy and especially the polar component. Other chemicals used in the papermaking process may also have contributed to the high concentration of Ca^{2+} . The high salt concentration of the white water, expressed by the large conductivity value, decreases the thickness of the fibers double layer, which also contributes to a reduction of the repulsion forces [8].

The comparison between the results obtained for the two commercial papers (Fig. 1) confirms the effect of the surface sizing treatment in reducing the polar interactions at the

Sample	S_a (μm)	S_p (μm)	S_v (μm)	S_{dr} (%)
HS-1	4.06	12.25	17.93	25.97
HS-2	3.76	12.53	14.88	18.60
CP-1	3.25	9.55	12.55	13.97
CP-2	2.69	7.74	10.34	9.81

Sa - average roughness; Sp - maximum peak height;

IV. 3-D topographical parameters of the different papers.

Sample	Contact angle (°)				
	Water	Water /Ethylene glycol	Formamide	Ethylene glycol	Propylene glycol
HS-1	26.8 ± 2.1	23.1 ± 1.9	15.6 ± 0.9	21.3 ± 1.0	33.6 ± 2.4
HS-2	121.4 ± 1.9	86.3 ± 1.6	53.9 ± 1.4	53.2 ± 1.2	48.3 ± 2.0
CP-1	106.8 ± 0.9	88.4 ± 0.9	75.0 ± 1.2	63.4 ± 0.5	56.5 ± 1.6
CP-2	102.6 ± 1.9	—	52.4 ± 1.7	45.6 ± 1.5	39.0 ± 1.5

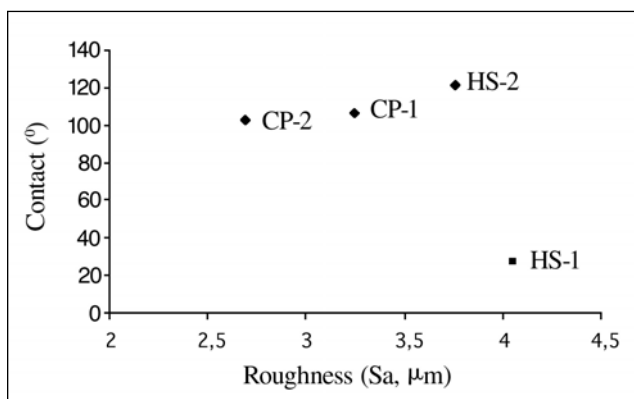
V. Values of the contact angle obtained for each paper with different liquid probes.

paper surface. Indeed, a smaller contribution of the polar component to the total surface energy was found for the paper with surface sizing (CP-1), despite having a rougher and more energetic surface.

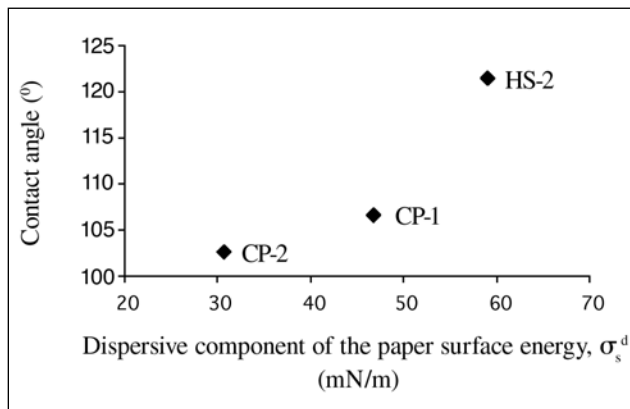
From this discussion, we can conclude that using two distinct types of water in the production of the handsheets induces much larger differences in the paper sheet surface energy than does the sheet-making process itself (lab sheet former versus industrial paper machine) and that it would be expected, considering only the differences in the surface roughness.

Table V lists the values of the contact angles measured with the distinct liquid probes (sequenced as in Table II). The results of HS-1 and HS-2 indicate that the production of laboratory handsheets with white water leads to much higher contact angles, independently of the liquid tested. Such large differences can not result from the distinct surface textures of both samples, as may be concluded from the plot of **Fig. 3**. They are most likely a consequence of the reduction found for the paper surface energy, in particular, of its polar component (Fig. 1).

Although surface heterogeneity may contribute to the differences of the contact angles with water of samples HS-2, CP-1, and CP-2, the high values of this parameter are mainly due to the extremely low polar components of the surface energy of these samples. Furthermore, and as depicted in **Fig. 4**, the contact angle increases with the dispersive com-



3. Paper contact angle with water as a function of paper roughness (Tables IV and V).

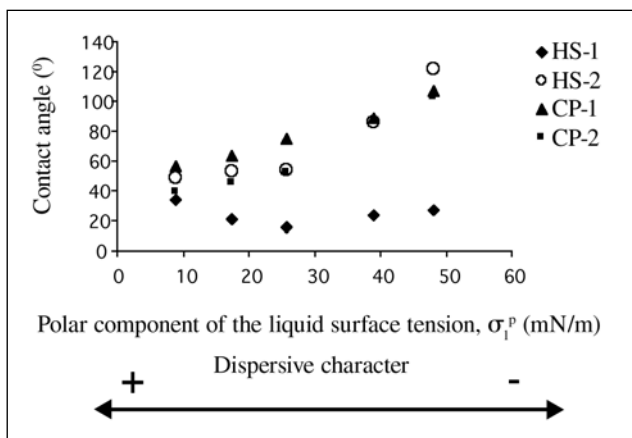


4. Paper contact angle with water as a function of the dispersive component of the paper surface free energy (Tables III and V).

ponent of the corresponding paper surface energy. This was expected since the interactions with a polar liquid tend to decrease as the nonpolarity of the surface increases.

Table V also shows that for handsheet HS-2 the values of contact angle decrease from water to propylene glycol, that is, as the contribution of the dispersive component of the liquid surface tension increases (Table II). This trend, not observed for HS-1, can be explained by the highly dispersive character of the surface of handsheets HS-2, and reflects the increasing predominance of the dispersive interactions. A similar tendency was found for both commercial papers (CP-1 and CP-2), which also have a dispersive rather than polar surface energy. **Figure 5** clearly illustrates this behavior and shows, once again, the proximity between the values of the samples produced with white water, whether they are laboratory (HS-2) or commercial paper sheets (CP-1 and CP-2).

The results reported in Table V and in Fig. 5 also demonstrate that, as expected, surface sizing leads to an increase in the contact angle (higher contact angles were determined for sample CP-1). In addition, we see that the values of the contact angle for handsheets HS-1, whose surface has more affinity to polar interactions, besides being quite small, seem not to be much affected by the polar component of the liquids surface tension. In fact, the extremely high polar character of the surface of handsheets HS-1 somehow minimizes the effect of the differences in the polarity of the probe liq-



5. Paper contact angle with the different liquids as a function of the polar component of the liquid probes surface tension (Tables II and V).

uids. Factors such as molecular orientation become decisive for defining the nature and intensity of the interactions between the solid and the liquid.

CONCLUSIONS

The results of this study clearly demonstrate the influence of the water with which laboratory sheets are produced in their

surface properties. In fact, the contact angles measured with various liquids in handsheets made with demineralized water are considerably lower (up to five times inferior) than those obtained in handsheets made with white water (collected at the paper mill). This leads to differences in the calculated surface energies, the most striking being the totally opposite relative contributions of the dispersive and polar surface energy components. Perfilometry measurements performed with the various samples reveal that although an increase in roughness leads to higher surface energies, the differences in the samples' surface roughness are not sufficient to explain that inversion. The results were then interpreted in terms of the chemical properties of the two types of water used and the resulting interface phenomena.

Additional analyses undertaken with commercial paper sheets produced with an identical pulp resulted in values very close to those obtained for the laboratory handsheets made with the white water. This fact validates the conclusion that the kind of water, rather than the sheet-making process, plays a decisive role in the surface energy of the final product. **TJ**

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INSIGHTS FROM THE AUTHORS

While performing contact angle measurements in a study of paper surface sizing in industrial and laboratorial sheets, we found significant differences for which we needed to find the origin.

This research complements the work that has been performed, as it allows an exhaustive analysis of the factors that affect contact angle measurements and also reveals the relevance of the water used in the paper manufacturing to the paper chemical properties. This work differs from previous research because there is no information concerning a systematic analysis of these same parameters as was undertaken here.

The most difficult aspect of this research was the development of a correct and reliable methodology for the preparation of the laboratorial sheets using the water collected at the paper mill.

This research showed the importance of the chemical properties in the paper production and highlighted the particular influence of the water used in the sheet making process on the surface energy of the paper sheets. Additionally, it revealed that this influence is much more pronounced than the fact of producing the paper sheets in a laboratory sheet former or in an industrial paper machine.

As far as we know, paper engineers were not aware of



Moutinho



Ferreira



Figueiredo

the tremendous differences found in the paper surface properties as a result of the water used in the papermaking process and this study gives relevant information regarding the measurement of contact angles in paper sheets prepared in laboratory.

After this study, all the work regarding surface sizing will take into consideration the results presented here where we intend to compare laboratorial and industrial papers.

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HANDSHEETS

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