Surface Interactions in Paper *Surface Sizing* Solutions

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Abstract

The competitiveness of the uncoated woodfree paper market leads to a growing concern with the final quality of this product, which means for this industry a constant need for technological innovation and optimization of its various process steps. Printing quality is a critical property for the final performance of this paper grade and, it is strongly influenced by the structural and chemical properties of the paper and especially by the surface. In industry, surface sizing is the surface treatment responsible for improving the surface properties, such as strength and stiffness, and controlling the hydrophilic character of the paper. For these purposes, a solution composed of starch and other additives is typically used. The main objective of this work is to analyze the behavior of the surface sizing solution on the paper surface without any previous surface treatment. Therefore, the effects of starch concentration in the solution and temperature were studied, evaluating surface properties such as contact angle and surface tension. Furthermore, the paper samples were analyzed by scanning electron microscopy before and after the contact angle measurements. The results show that the contact angle on the top side of the paper depends on the starch content in the solution, as opposed to the bottom side. On the other hand, the temperature showed no influence on this property. It was also found that starch content does not influence the surface tension of the solution, unlike temperature.

Keywords: *Surface Sizing*, Uncoated Woodfree Paper, Contact Angle, Surface Tension, Starch

1. Introduction

The papermaking process is highly cost-sensitive and the market is extremely competitive. Specialty chemicals have been developed and applied in to assure an efficient process and meet specific end-use paper requirements [1] [2] [3].

Paper can be classified according to different criteria, either by weight, color or raw material source. This study is about the uncoated woodfree paper, which is a paper made from chemical pulp, without lignin [4].

Regarding this type of paper, the final performance depends on the quality of the fibrous matrix and the properties of the surface. The surface characteristics are controlled by surface treatments which aim to give specific qualities to the paper, according to its purpose.

Surface treatments are divided into two types: mechanical, like calendaring, or chemical such as coating and surface sizing. For Printing & Writing paper grades (P&W), calendaring and surface sizing are the treatments used while the coating is more common in magazine paper or photographic paper [4].

1.1. Motivation

Today, there is a constant increase in the importance of surface treatments in the production of uncoated woodfree paper. Printing quality is one of the parameters that is strongly affected by the physical, chemical and structural properties of the paper surface. Additionally, from the customer's perspective, this parameter is crucial to evaluate the final performance of this particular paper grade.

In the available literature, some studies and publications explore the use of coating as the surface treatment to improve paper surface properties [5] [6] [7]. However, in the production uncoated woodfree papers, surface sizing is the only chemical treatment used to control these properties.

Existing studies on surface sizing focus on evaluating the surface quality of paper, after the application of different solutions, through surface characterization techniques such as contact angle measurement or inverse gas chromatography [8] [9] [10] [11].

The lack of works exploring surface sizing in a more industrial context contributes to the importance and applicability of the present study. The complexity of the paper structure and the presence of various components make this system quite complex. Thus, to establish a possible process optimization and, consequently, a final improvement of paper characteristics, it is essential to understand the interactions between the various components present in this stage of production.

1.2. Scope

For surface sizing, a solution composed mainly of starch is applied to the surface of the paper sheet. Regarding technology, film size press is the most used, in which a film of the solution is transported and applied to the paper surface by the applicator rollers. This technology allows an independent application of the solution to each side of the paper. Usually, solids content, viscosity, and temperature are the process control parameters. The penetration of the solution into the paper structure and its uniform surface often determines the printing quality.

The behavior of a liquid on a surface is crucial for homogeneous film formation processes, where properties such as contact angle and surface tension play an important role. Thus, the present work intends to give a deeper understanding of the interactions between the surface sizing solution and the paper surface. More specifically, it aims to measure the contact angle and the surface tension of surface sizing solutions and to relate these properties to starch content and temperature.

1.3. Surface Sizing

Surface sizing is a surface treatment whose main objective is to increase the bond between the fibers by filling the pores with a solution composed mainly by starch. This treatment is used to increase the surface resistance, stiffness and printability, and to control the hydrophilic character of the fibers.

The surface sizing solution is composed typically by starch, sizing agent, optical brightening agents (OBAs), salt and defoamers [4] [12] [13] [14].

Starch is the main component of the solution and it acts as a binder to connect vessel segments and loose fibers at the surface. To be used properly, starch needs to be fully dissolved through the process of cooking [4] [15]. Afterward, starch has to be modified to keep its rheological properties and to be protected against retrogradation [15] [16]. Enzymatic or thermal conversion is usually practiced to manipulate the viscosity of the starch solution [3] [15] [17]. On the other hand, the introduction of other functional groups through chemical modifications such as oxidation, esterification or nucleophilic substitution can give other properties to the starch [1].

Surface sizing agents are compounds containing hydrophobic groups that repel water molecules and prevent their absorption by the paper sheet [1]. These agents, when combined with starch and applied to the paper surface, form a thin reticular film at the paper surface, impacting certain properties such as smoothness, surface resistance, and hydrophobicity [4]. For surface sizing, sizing agents can be cationic rosin, AKD or synthetic polymer compounds like co-styrene maleic anhydride or co-styrene-acrylate. While cation rosin and AKD are preferably applied at the wet end, syntenic polymer compounds were specially designed for surface sizing [18] [19] [20]. Compared to the other available sizing agents, polymer compounds are extremely versatile and compatible with all types of starch, and in some cases, do not need defoamers [1].

To improve the optical properties of the paper surface, like brightness and whiteness, optical brightening agents are usually applied in surface sizing. There are three types of OBAs used in the paper industry, all based on stilbene molecule. The difference between each one lies in the number of sulfonic substituents, which in turn affect their properties. In general, the whitening effect, solubility and price increase with the number of sulfonic substitutes, while the affinity to the fibers decreases [1] [21] [22].

Due to the current high-speed rate of production, together with the heat and friction between the paper and the metal parts of the machine, a favorable environment is created for static electricity to accumulate in the materials. This has serious risks such as production downtime or equipment damage. To overcome the problem is usual to add mono or divalent salt to improve the paper surface conductivity [23] [24]. The addition of a divalent salt, such as calcium chloride, further improves printing quality by enhancing the sharpness of colors on paper [25].

Defoamers are usually present on surface sizing solutions as a process chemical rather than a functional chemical. Foam is associated with operational problems, reduced efficiency and surface defects in surface treatments and must be controlled. Defoamers are sophisticated formulations made up of extremely water-insoluble surfactants with the ability to spread rapidly to gas/liquid interfaces, destabilizing the foam lamellae previously stabilized by other surfactants [1] [26] [27] [28] [29] [30].

Surface sizing performance is affected by the properties of the applied aqueous solution such as composition, viscosity or temperature, as well as the properties of the paper sheet such as weight, moisture content, porosity, surface energy, among others. These properties should be adequately controlled to ensure the desired absorption of the aqueous solution into the sheet.

2. Experimental Methods

The paper used in this study is a uncoated woodfree paper (80 g/m^2) produced from *Eucalyptus globulus* fibers without any surface treatment. Due to the inherent heterogeneity of the paper, the faces were properly identified with the respective letter: top (T) or bottom (B).

The paper samples were characterized by a roughness test using an L&W Bendtsen Tester (SE 164) according to ISO 8791-2 (2013) – Table 1.

The surface sizing solutions are composed by water, starch, sizing agent, OBA, salt and defoamer. All constituents were provided by The Navigator Company.

The solutions were prepared in the laboratory using the typical compositions of the real process conditions. At the industrial level, the solutions applied on the top and

bottom sides of the paper differ in the additives composition.

Regarding cooked starch solution, this one was sent weekly from the factory in a thermal container and stored in an oven at 70ºC upon arrival.

For each side of the paper, five formulations were studied, varying the starch content in water and the temperature, keeping the amount of the remaining additives always constant. Contact angle and surface tension measurements were performed at 50°C and 60°C.

The formulations are numbered 1 to 5, followed by the letter corresponding to the applied side. Each number corresponds to different starch content. For example, formulation 1T corresponds to formulation 1, with an 8% starch content, of the top face. Table 2 shows the starch content in water of each formulation.

Depending on the experiment, the temperature value was further added to the representative formulation code.

Table 1. Average Bendtsen roughness obtained for the top (T) and bottom (B) sides of the studied paper.

	Top (T)	Bottom (B)
Bendtsen Roughness (mL/min)	189	179

Table 2. Starch content, expressed in %, of each formulation.

Formulations	Starch content (%)
1T / 1B	8
2T / 2B	10
3T / 3B	12
4T / 4B	13
5T / 5B	14

For studying the wettability of the surface of paper and its relation with starch content and temperature, contact angle measurements were performed with a typical goniometer, using the sessile drop method. For image acquisition, a charge-coupled device (CCD) camera was used and the corresponding images were computed with the ADSA method. Values of contact angle, drop volume and drop base diameter were obtained.

Both dynamic and static contact angles were obtained. While the dynamic contact angle gives information about the behavior of the drop through the time, the static contact angle assesses the initial wetting of the surface.

For each formulation studied, an average of 4 measurements was considered. For dynamic contact angle, successive images of the solution drop were captured for 3 min. The static contact angle was defined as the average of the contact angle values before 3 seconds.

Other parameters were calculated to better understand the occurring phenomena at the surface. The wetting velocity expresses the variation rate of the contact angle and is defined as,

$$wetting\ velocity\ (°/s)\ = \frac{\theta_{60} - \theta_5}{55} \qquad (1)$$

where θ_5 and θ_{60} are the contact angle values at 5 s and 60 s, respectively [31].

For the interval 0 – 30 seconds, the absorption and the spreading coefficients were also calculated, according to equation (2) and (3), respectively [9].

$$Absorption\ Coefficient\ = \frac{V_i - V_f}{V_i} \qquad (2)$$

$$Spreading\ Coefficient\ = \frac{d_f - d_i}{d_i} \qquad (3)$$

where V and d are the drop volume and the drop base diameter, respectively, and the subscripts i and f stand for the initial and final values (after a given time interval), respectively.

Since paper is a rough and heterogeneous material, the correction of the measured contact angles would be essential if the objective was to calculate the surface energy of the paper through the Young equation. Due to the hydrophilic nature of the paper, the theory described by Wenzel would be the most appropriate and closer to reality.

In the present work, the correction will not be applied because it was not possible to measure the parameters necessary for this purpose. However, the internal consistency of the results will not be affected as the solid sample is based on the same sheet of paper, which is supposed to have a constant roughness across the surface.

The characterization of the formulations from table 2 is fundamental for a more complete interpretation of the final results of the present study. Therefore, the surface tension was also measured with the same goniometer once this equipment also allows the measurement of this property. The method used was the pendant drop method and the images were also computed by the ADSA method.

Several drops were formed and six images of each drop were acquired with a 2-second interval between each image. An average of fifty values was considered.

To visualize the internal and the surface structure of the paper, scanning electron microscopy (JM-7001F FEG-SEM, JEOL, Tokyo, Japan) was used to analyze paper samples in their initial state (without any surface treatment) and samples from contact angle measurement after drop deposition - samples 3T60 and 3B60. In this analysis, both surfaces and cross-section of the samples were observed.
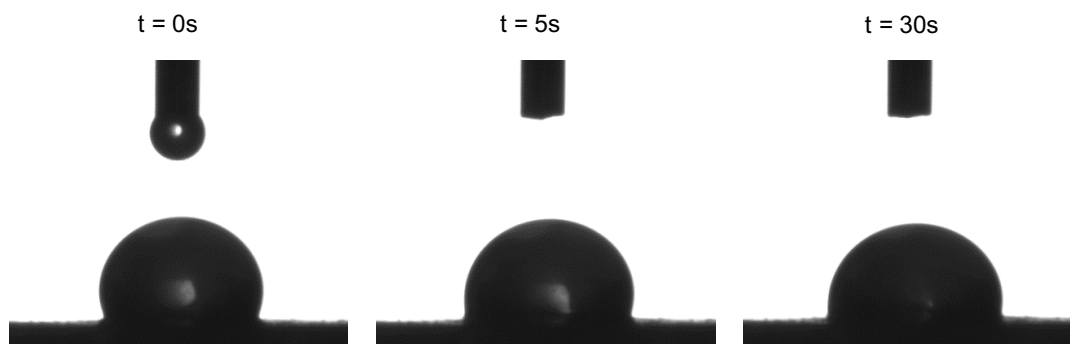
Figure 1. Drop profile for an experiment with formulation 4B50 at three different times: 0, 5 and 30 seconds.

3. Results and Discussion

Figure 1 shows the evolution of the drop profile over time through a sequence of images at three different times for one of the experiments performed with formulation 4B50.

After analyzing the obtained images, the evolution of the contact angle with time was plotted for each formulation. Figure 2 shows, as an example, the results obtained for formulation 4B50.
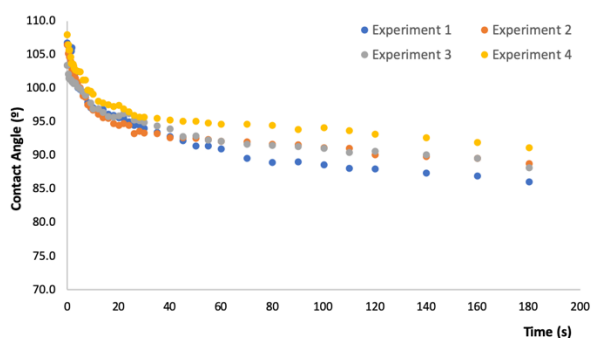

Figure 2. Temporal evolution of the contact angle for the 4 experiments performed with 4B50 formulation.

The analysis of Figure 2 shows some variability in the values, which may be due to small variations of the solution properties or to the heterogeneity of each paper sample. The industrial process of starch cooking is controlled by a macroscopic property, namely the viscosity of the solution. This approach leads to some local variability of the microscopic properties of the solution, for example different length distributions of the starch polymer chains. The retrogradation process may also introduce some variability in the properties of the solution.

The characterization of the curves by the analysis of Figure 2 also showed a characteristic behavior, namely, a fast variation of the contact angle in the initial moments (< 30 seconds) and a softer variation in the next moments (> 30 seconds). These variations may be due to spreading, absorption and evaporation phenomena. To characterize the evolution of the curves, a comparison test was also performed with the formulation 4B50 on a plastic surface, thus eliminating the absorption phenomenon – Figure 3.
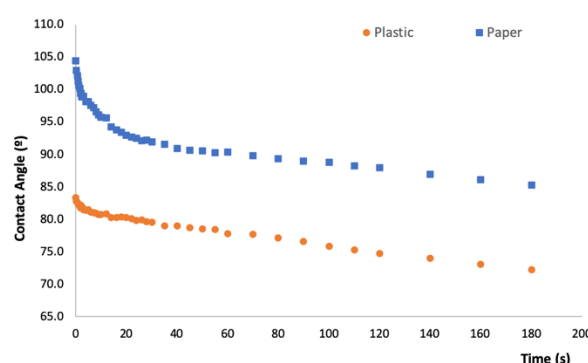

Figure 3. Temporal evolution of the average contact angle for 4B50 formulation and the plastic surface experiment.

The results on the plastic surface show a higher variation in the initial moments (<5 seconds), characteristic of the initial spread of the drop on the solid surface. After this period, the variation over time is much smaller, due solely to the evaporation phenomenon.

By transposing this analysis to paper, it is also possible to identify a sharp variation within the first 5 seconds and a slight variation from 30 seconds. The difference lies in the transition zone (5 - 30 seconds), where the curvature variation is much more gradual. This leads to a conclusion where all these phenomena occur at the same time, although there are periods in which one prevails over the other. In the initial moments, the spreading should be the one that controls the variation of the contact angle, while in the intermediate period (5 - 30 seconds) it should be the absorption. After the saturation of the paper surface with the solution, the contact angle variation is due solely to evaporation, intensified by the test temperatures. However, the last regime is not representative at the industrial level, as the contact time of the solution with the paper surface is almost instantaneous compared to the extent of the laboratory testing.

Figure 4 and Figure 5 show the temporal evolution of the contact angle as a function of starch concentration

and temperature for the top and bottom faces, respectively.

Looking at Figure 4, a dependence of the contact angle on the starch concentration is immediately noted, namely, the decrease of the wettability with the increase of starch content. This behavior may be due to the hydrophilic nature of the cellulose fibers, once the less concentrated solutions have lower contact angles. It is also possible to visualize the quick variation of the contact angle at the initial moments, either by drop spreading or drop absorption. On the other hand, the curves obtained do not show a significant influence from the temperature. In the case of formulations 1T and 2T, there is an overlap of the two curves. For the more concentrated solutions 3T, 4T and 5T, higher contact angle values at 60ºC are observed after the interval [5-10] seconds. At this temperature, the effects of evaporation will certainly be greater, causing drop evaporation at a higher rate. For more concentrated solutions, a concentration effect of the solution at the surface may also be occurring, probably decreasing the absorption effect and keeping the drop at the surface.
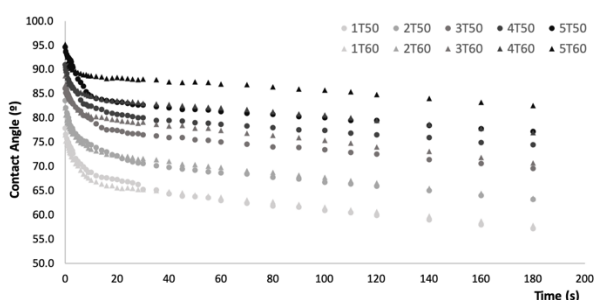

Figure 4. Temporal evolution of the average contact angle for the top side formulations (T): Circles: Experiments at 50°C; Triangles: Experiments at 60°C.
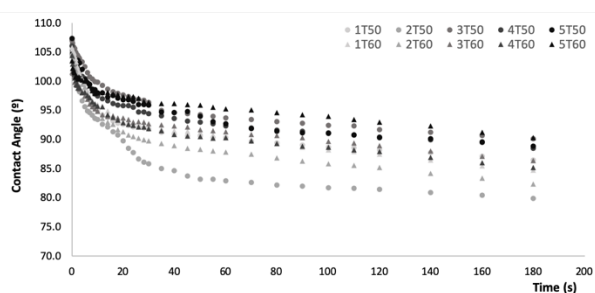

Figure 5. Temporal evolution of the average contact angle for the bottom side formulations (B) - Circles: Experiments at 50°C; Triangles: Experiments at 60ºC.

Figure 5 shows a significant difference in the contact angle values of the bottom side, compared to the top side. While at the top side, initial values comprised between 70° and 95 ° were obtained, for the bottom side, higher values were verified for the contact angles [100 ° - 108 °]. Although it is not possible to establish a direct comparison between the two sides of the paper because the formulations studied on each side are different in their composition, the behavior observed in the drop profile was quite different. This significant difference indicates that the bottom side is more hydrophobic, and this behavior may be due to the physicochemical characteristics of the surface, such as density, porosity, degree of internal sizing among others.

For the bottom side, it is not possible to identify the influence of the starch concentration on the contact angle, since the curves (except for the formulation 2Q50) are contained in a range of 8°, within the experimental dispersion of the system. Even if there is some dependency, it may not be visible because the values are all very close.

Regarding the relationship with temperature, the experiments performed at 60ºC are also inside the range verified for the experiments at 50ºC, showing a non-dependence of the contact angle with the temperature.

The values of the static contact angle (< 3 seconds) are described in Table 3 and Table 4 for the top and bottom sides, respectively.

Table 3. Static contact angle values of the top side formulations at 50ºC and 60ºC.

	Static Contact Angle	
Formulations	T = 50ºC	T = 60ºC
1T	74.8 ± 2.2	73.6 ± 2.0
2T	79.8 ± 2.9	78.6 ± 2.5
3T	84.1 ± 2.8	85.3 ± 2.8
4T	88.0 ± 3.4	87.9 ± 1.6
5T	92.4 ± 2.8	91.9 ± 2.0

Table 4. Static contact angle values of the bottom side formulations at 50ºC and 60ºC.

	Static Contact Angle	
Formulations	T = 50ºC	T = 60ºC
1B	103.0 ± 2.2	103.7 ± 2.8
2B	101.4 ± 2.6	102.1 ± 3.4
3B	105.5 ± 1.6	100.1 ± 2.5
4B	103.5 ± 2.0	100.6 ± 2.3
5B	103.6 ± 2.5	103.6 ± 3.0

By examining the static contact angle values for the top side, shown in Table 3, it confirms the increasing contact angle effect as the starch content increases. With the static contact angle being defined for the first 3 seconds of contact between the liquid drop and the surface, the phenomenon previously observed for more concentrated solutions, where the contact angle at 60°C was higher after the interval [5-10] seconds, is not visible at first glance. In fact, by assessing only the initial contact between the solution and the paper, it is found that the

Table 5. Wetting velocity (5 – 60 sec), absorption coefficient (0 – 30 sec) and spreading coefficient (0 – 30 sec) values calculated according to equations (1), (2) and (3), respectively, for the top side formulations.

Formulations	Wetting Velocity (º/s)		Absorption Coefficient		Spreading Coefficient	
	T = 50ºC	T = 60ºC	T = 50ºC	T = 60ºC	T = 50ºC	T = 60ºC
1T	0.147	0.118	0.177	0.137	0.031	0.034
2T	0.137	0.102	0.156	0.152	0.040	0.023
3T	0.121	0.076	0.094	0.099	0.036	0.040
4T	0.114	0.063	0.112	0.086	0.045	0.032
5T	0.123	0.042	0.111	0.103	0.056	0.024

Table 6. Wetting velocity (5 – 60 sec), absorption coefficient (0 – 30 sec) and spreading coefficient (0 – 30 sec) values calculated according to equations (1), (2) and (3), respectively, for the bottom side formulations.

Formulations	Wetting Velocity (º/s)		Absorption Coefficient		Spreading Coefficient	
	T = 50ºC	T = 60ºC	T = 50ºC	T = 60ºC	T = 50ºC	T = 60ºC
1B	0.147	0.167	0.0129	0.0210	0.120	0.108
2B	0.232	0.203	0.0230	0.0407	0.153	0.115
3B	0.161	0.110	0.0121	0.0036	0.089	0.077
4B	0.147	0.141	0.0370	0.0014	0.089	0.106
5B	0.154	0.124	*	0.0059	0.118	0.077

* Value without physical meaning

contact angle does not depend on the temperature in the considered time interval.

For the bottom side – Table 4 – it is verified that the studied parameters are not dependent, since the values are all very close, within the error range

Finally, the calculated values are presented for the parameters described in equations (1), (2) and (3), namely, wetting velocity, absorption coefficient and spreading coefficient, for the top side – Table 5 – and for bottom side – Table 6.

According to the values presented in Table 5 (top side), for both temperatures, it is observed a decrease in wetting velocity as the starch concentration increases, in the considered time interval. Additionally, the wetting velocity also decreases with temperature. Connecting these values to the Figure 4, the lowest velocities were calculated for the more concentrated solutions at 60°C, which agrees with the hypothesis presented previously regarding the concentration effect that may be occurring at the surface, causing the droplet to remain there longer.

As for the coefficients calculated for the top side, absorption coefficients are higher than spreading coefficients, indicating that absorption phenomena prevail over the drop spreading in the considered period. On the other hand, there is no relationship between these coefficients and starch content or temperature.

As for the values presented in Table 6 (bottom side), it appears that there is no dependence between wetting velocity and starch content. Regarding temperature, except formulation 1B, the values wetting velocity are lower at 60ºC.

The absorption and spreading coefficients for the bottom side show an inverse behavior from the one verified for the top side since now the spreading coefficients are higher than the absorption ones. In this face, and for the same interval considered, the spreading seems to prevail over the absorption. In other words, the variation of the apparent volume of the drop is smaller than the variation of its base diameter.

However, this analysis may be biased by an experimental artifact, as the results provided by the software show an increase in apparent drop volume after the initial time, which has no physical significance. Since there is no liquid added to the drop, its volume should not be increasing. This behavior occurred only on the bottom side and may be due to some paper curl caused by the absorption of the solution. Due to this apparent increase, the drop volume measured after 30 seconds is roughly equal to the initial drop (or even higher, as in the 5B50 test, which led to a negative coefficient without physical significance), which makes the spreading coefficients much lower.

Linking the results to the industrial situation to which this paper refers, the results show that the wettability of the bottom side of the paper is independent of the properties of the surface sizing solution, namely the temperature and starch content, so these parameters may not be the best option to optimize the process conditions, whose final goal is to improve printing quality.

However, on the top side, paper wettability is directly proportional to the starch content of the solution, so it may be a variable with a strong influence on printing quality once this surface presents more concrete results for this studied property.

As a further characterization of the surface sizing solutions, the surface tension was measured and the results are present in Table 7 and Table 8, for the top and bottom side, respectively.

Table 7. Surface tension values obtained for top side formulations at 50ºC and 60ºC.

Formulations	γ (mJ/m^2)	
	T = 50ºC	T = 60ºC
1T	49.7 $\pm$ 0.4	42.5 $\pm$ 0.5
2T	49.5 $\pm$ 0.3	42.6 $\pm$ 0.7
3T	49.7 $\pm$ 0.3	42.9 $\pm$ 0.8
4T	49.9 $\pm$ 0.5	43.2 $\pm$ 1.1
5T	49.4 $\pm$ 0.6	43.1 $\pm$ 0.7

Table 8. Surface tension values obtained for bottom side formulations at 50ºC and 60ºC.

Formulations	γ (mJ/m^2)	
	T = 50ºC	T = 60ºC
1B	47.0 $\pm$ 0.5	39.9 $\pm$ 0.6
2B	46.1 $\pm$ 0.3	40.1 $\pm$ 0.4
3B	47.1 $\pm$ 0.4	39.4 $\pm$ 0.4
4B	47.1 $\pm$ 0.4	39.5 $\pm$ 0.5
5B	47.2 $\pm$ 0.3	39.9 $\pm$ 0.5

Analyzing the results of Table 7 and Table 8, for the concentration range studied, it is noted that surface tension does not vary with starch content since the values obtained for the different formulations are practically the same. On the other hand, there is a temperature dependence as expected. As the temperature increases, the kinetic energy of molecules also increases, lowering the cohesive forces, and consequently, the surface tension.

As mentioned previously, the top and bottom formulations are different as regards the content of each additive. These differences may lead to the variations observed on surface tension values between the two sides. In this study, the higher surface tension values were measured for the solutions with higher salt content. Increasing the surface tension of a solution by the addition of electrolytes such as sodium chloride has been observed and is a topic of scientific interest for a long time. This increase in this surface property has been related to the surface structure [32]. On the other hand, the addition of salt to aqueous solutions with surfactants may also impact their behavior and consequently the surface tension of the solution [33].

To characterize the paper surfaces and visualize the penetration of the solution into the fibrous structure, scanning electron microscopy was used. Firstly, the aim was to make a visual and structural comparison between the top and bottom sides of the untreated paper sample – Figure 6 and Figure 7.

Figure 6. SEM image of the top side of paper sample (500x).

Figure 7. SEM image of the bottom side of paper sample (500x).

The images show the typical structure of the paper, with the interlaced cellulose fibers and the fillers (in white) around the fibers. However, no element can be found to distinguish the two faces.

The cross-sectional analysis immediately shows the presence of loose cellulose fibers on the surface, which indicates not only the need for softness and texture treatment of the paper but also the existing natural roughness, which in turn has an impact on the paper wettability - Figure 8. By enlarging the section and analyzing the Figure 9, the two sides appear to be different. It is visible the existence of voids (darker tones) between the fibers in the top side, while in the lower face the lighter tones prevail, referring to a possible higher presence of fillers. However, this conclusion may be

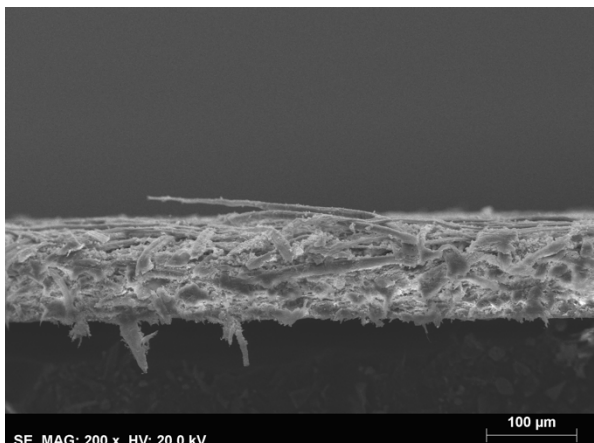being induced by deformations caused by cutting the sample.

Figure 8. SEM image of the cross-section of paper sample (200x).
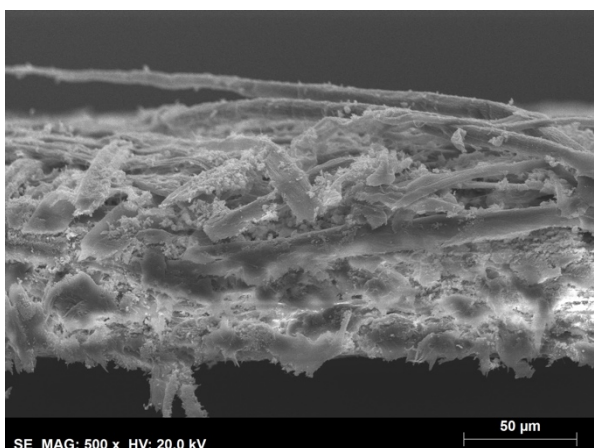

Figure 9. Enlarged SEM image of the cross-section of paper sample (500x).

After measuring the contact angles, some trials were selected, namely 3T60 and 3B60, and the cross-section was visualized to see the starch solution penetration. As an example, only 3T60 SEM images are present here. Figure 10 shows a central zone, where the drop and the surface first touched, and Figure 11 shows the periphery of the drop. The penetration seems to be more pronounced in the central zone than on the periphery of the drop, which is more likely to be due to spreading than to absorption.

4. Conclusions

The results presented in this paper show that the contact angle measurements is a relevant approach in obtaining important information about the behavior of the surface sizing solution on each side of the paper.

Firstly, all the tests showed a characteristic behavior in the contact angle evolution over time. Phenomena as spreading, absorption and evaporation were identified as
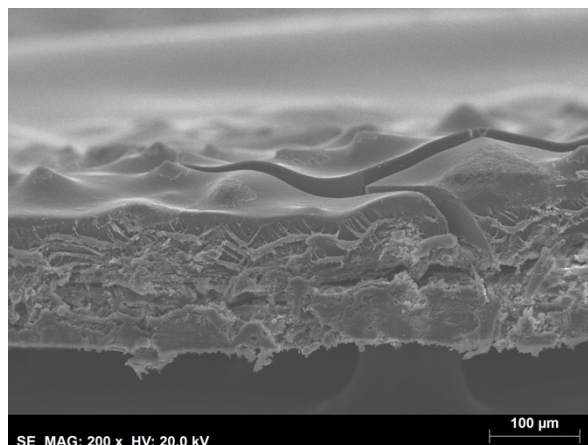

Figure 10. SEM image of the cross-section of paper sample after 3T60 experiment – central zone (200x).
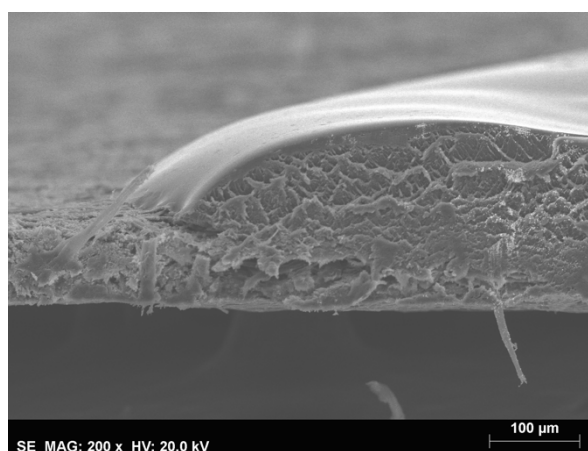

Figure 11. SEM image of the cross-section of paper sample after 3T60 experiment – peripheric zone (200x).

the occurring effects at the surface and responsible for the contact angle evolution. The interpretation given is based on the simultaneous occurrence of all these effects, although certain phenomena prevail over others in certain periods.

For the top side (T), the results showed that the starch content has a significant impact on the studied surface wettability, as there was an increase in the contact angle with the starch content. Regarding the effect of temperature, for formulations 3T, 4T and 5T, from the interval 5 - 10 seconds, a shift of the curves of 60 ° C to higher contact angles was observed, indicating probably a longer permanence of the drop at the surface. As for the values of the static contact angle, which is of major interest from an industrial point of view, the initial wetting does not depend on temperature but showed a linear relation with starch content, as reported for dynamic contact angle.

These observations suggest that starch content may have a significant influence on the quality of treatment applied, highlighting its importance as a control parameter in this process. Although there was no considerable influence of temperature on the contact

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angle, this parameter may affect other solution properties such as density and viscosity and is a critical parameter in the occurrence of starch retrogradation, which in turn implies other problems at industrial level.

For the bottom side (B), the observed scenario was quite different. Firstly, the contact angle values obtained in the initial moments for the bottom formulations (108º - 100º) are higher than those obtained on the top side. On the other hand, these values were not dependent on starch content or temperature, perhaps because they are within a small range of 8 °. The analysis of the static contact angle as a function of starch content and temperature also supports these conclusions since the values are also within a narrow range.

Regarding the surface tension, the results allowed to conclude that the starch content does not influence this property in the studied concentration range. As for the temperature, lower surface tension values were found at 60ºC, with a decrease of 7 mJ/m2, compared to the values obtained at 50ºC. This variation was expected as the increment in temperature causes a decrease in the bond strengths between molecules, and consequently, the surface tension reduction.

This paper presents information and results that may prove to be important to the industry. Surface sizing solution is a complex mixture of various components, which is applied to the surface of a material with significant variability, either by its natural source or by its process. The experimental methodology approached in this work is a useful tool to systematically analyze the behavior of this solution-surface system, and to gain an increasing knowledge about the physicochemical phenomena that control the interactions in this system

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