POTENTIALS OF LIGNOCELLULOSIC AGRICULTURAL RESIDUES IN PAPER PRODUCTION

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ABSTRACT

Surface characteristics of printing substrates are of the utmost importance to all types of paper that interact with ink. During all types of printing processes, the behaviour of the liquid phase (ink or dye) on the paper is directly defined by the paper cellulose-based surface. The printed ink spreads and penetrates more into paper fibres when the paper surface is rougher and more permeable. Contact angle measurements by sessile drop method are considered the most appropriate for determining the paper sheet surface energy. Paper as hydrophilic material has a high absorption rate resulting in a low contact angle. The objective of this study was to evaluate the surface free energy of laboratory-made papers containing straw pulp obtained from residues after the harvest of the most cultivated cereals in Croatia (wheat, barley and triticale). The obtained surface free energy results are promising for straw pulp usage in the manufacture of printing paper.

Keywords: *laboratory paper, straw pulp, contact angle, surface free energy, sessile drop method*

INTRODUCTION

Proper choice of raw material for pulp and paper production is a very important part of papermaking industry. As a traditional raw material, wood is still the most common used source, but the utilization of non-wood sources in papermaking has been increasing in the last few years. The straw, as a harvesting residue, is a fibre resource available from the annually renewable crops, produced abundantly in numerous regions all over the world. Straw of the most cultivated cereals in Croatia (wheat, barley and triticale) was chosen for analysis of its suitability for pulp and paper production. Previous research based on the chemical composition of straw has indicated how wheat, barley and triticale straw can bring competitiveness and vitality to the paper industry as an alternative non-wood raw material [1]. Straw of the above-mentioned species has nearly the same cellulose content as most wood species, lower content of lignin and higher amount of ash and solvent extractives. The research presented in this paper focuses on the possibility of obtaining pulp from the wheat, barley and triticale straw as well as its use in producing printing substrates at a laboratory scale. As printing processes are greatly affected by surface properties of substrate such as surface and interfacial tension, surface energy and adhesion, evaluation of the surface free energy is the first step for achieving a high print quality on the printing substrate [2]. Namely, each paper viewed as a potential printing substrate has a unique structure in terms of surface roughness, porosity and surface free energy which is the result of manufacturing technology [3]. For paper as a printing substrate, surface free energy measurement can provide a good understanding of paper surface properties using a relatively simple approach [4]. The surface free energy of paper can be determined from the contact angle measurement achieved by a test liquid drop on a paper substrate [5]. This indirect method to access the surface free energy of paper by measuring the contact angle with liquids of known surface tension is a fast technique based on few equations [6]. In this study, unprinted laboratory papers containing straw pulp in different weight ratios were experimentally compared to those made only from recycled wood pulp and results were associated with topographical parameters. This research is of great importance for getting better insight into paper-ink interactions which occur during any type of printing process.

EXPERIMENTAL

Laboratory papers preparation

Straw as agricultural residue after the harvest of the most cultivated cereal species in Croatia (wheat, barley and triticale) was collected, purified and manually cut into 1 to 3 cm long pieces. Straw of each cereal type was converted into semi-chemical pulp by soda pulping method under conditions summarized in Table 1 [7].

Table 1. Pulping conditions

Straw	Pulping conditions
Wheat	Temperature of 120 °C, alkali level of 16 % for 60 min and a 10:1 liquid biomass ratio.
Barley	
Triticale	

The obtained unbleached straw pulps were mixed with recycled wood pulp in different ratios (10 %, 20 %, and 30 %). According to standard EN ISO 5269-2:2001, laboratory papers of approx. 42.5 g/m^2 were formed by a Rapid-Köthen sheet former (FRANK-PTI). Laboratory papers made only with recycled wood pulp were used as a reference for comparison in evaluating the surface free energy of laboratory-made papers containing straw pulp. In total, 10 types of laboratory papers were formed. Abbreviations used in marking laboratory paper samples are listed in Table 2.

Table 2. Abbreviations used for laboratory made paper samples

Abbreviation	Pulp composition
N	100 % recycled wood pulp
1NW	10 % wheat pulp + 90 % recycled wood pulp
2NW	20 % wheat pulp + 80 % recycled wood pulp
3NW	30 % wheat pulp + 70 % recycled wood pulp
1NB	10 % barley pulp + 90 % recycled wood pulp
2NB	20 % barley pulp + 80 % recycled wood pulp
3NB	30 % barley pulp + 70 % recycled wood pulp
1NTR	10 % triticale pulp + 90 % recycled wood pulp
2NTR	20 % triticale pulp + 80 % recycled wood pulp
3NTR	30 % triticale pulp + 70 % recycled wood pulp

Surface properties determination

Surface free energy of paper sheets is assessed from contact angle measurements at room temperature of (23.0 ± 0.2) °C by sessile drop method using a Dataphysics OCA30 Goniometer (DataPhysics Instruments GmbH, Filderstadt, Germany). The sessile drop method is an optical contact angle method that involves directly measuring the contact angle for a 1 μl drop of a standard test liquid (whose surface tensions are known and listed in Table 3) on a horizontal solid surface of the paper sheet (Figure 1). Contact angles of liquids were defined from average values of twenty liquid droplets placed at different areas of the same paper sample. The CCD camera, which is a part of the Goniometer device, is used to take a drop image immediately after contact with the paper sheet.

Table 3. Surface tension and the corresponding dispersive and polar component of test liquids

Test liquid	γ_l (mJ m^{-2})	γ_l^d (mJ m^{-2})	γ_l^p (mJ m^{-2})	Polarity [γ_l^p/ γ_l^d]
Water	72.80	21.80	51.00	2.34
Glycerol	64.00	34.00	30.00	0.88
Formamide	58.00	39.00	19.00	0.49
Diiodomethane	50.80	50.80	0.00	0.00

Surface free energy of laboratory papers was determined using the Owens, Wendt, Rabel and Kaelble (OWRK) method based on Young's equation:

$$\gamma_s = \gamma_{sl} + \gamma_l \cdot \cos\theta \qquad (1)$$

where: γ_s is the total surface free energy of the solid (mJ m^{-2}), γ_{sl} is the interfacial tension between solid and liquid, γ_l is the surface tension of the liquid, and θ is the contact angle (°).

The illustration of the contact angle formed by sessile liquid drop on a paper surface is presented in Figure 1 [8].

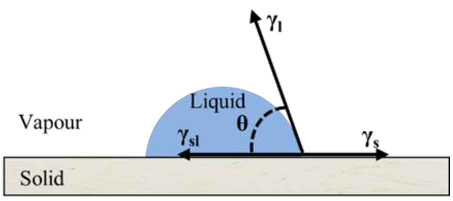

Figure 1. Diagram showing the interfacial tensions and contact angle formed by a liquid drop which describes the interaction of Young's equation (Eq.1)

The total surface energy (γ_s) is divided into a dispersive part (γ^d) and a polar part (γ^p) according to the equation:

$$\gamma_s = \gamma^d + \gamma^p \qquad (2)$$

These calculations are integrated into the software (SCA20, Version 2.01) and are carried out automatically.

As contact angle values could be affected by the sample surface topography, the roughness of samples is also determined using a portable surface roughness tester TR200 (PortableTesters, Pittsburgh, USA). Measurements were provided by the stylus method, vertical to the paper surface. Surface roughness measurements can be described with few roughness parameters. The most commonly used parameters for analysing papers surface roughness are arithmetic mean surface roughness (R_a) and maximum peak height (R_z) which are calculated according to equations (ISO 4287-1:1997):

$$R_a = \frac{1}{L} \int_0^1 |Z(x)|\, dx \qquad (3)$$

$$R_z = R_p + R_v \qquad (4)$$

where: R_p is the maximum profile peak height of the assessed profile and R_v is the maximum profile valley depth of the assessed profile.

The reported R_a and R_z values are the average of 10 measurements corresponding to different regions and in different directions of the paper surface.

RESULTS AND DISCUSSION

The values of arithmetic mean surface roughness (R_a) and maximum peak height (R_z) are listed in Table 4. R_a values of all analysed paper samples are in the range from 4.06 to 4.59 µm. R_z values, as expected, cover a wider range of values from 23.14 to 31.96 µm. From the results, it is evident that the addition of any straw pulp into recycled wood pulp slightly increases roughness values of laboratory-made papers. It is important to emphasize how all papers used in this study were laboratory papers without any surface finishing treatment, but still their average roughness values are within the range for uncoated papers (R_a value in range from 3 to 5 µm) [9].

Table 4. Topographical parameters of laboratory-made papers

Paper sample	R_a (μm) [10]	R_z (μm)
N	4.15 ± 0.34	23.65 ± 3.28
1NW	4.13 ± 0.43	23.15 ± 2.63
2NW	4.24 ± 0.34	23.63 ± 2.56
3NW	4.59 ± 0.51	31.96 ± 3.80
1NB	4.06 ± 0.36	23.60 ± 3.05
2NB	4.21 ± 0.35	23.14 ± 3.36
3NB	4.24 ± 0.41	24.39 ± 2.49
1NTR	4.25 ± 0.56	23.68 ± 2.50
2NTR	4.37 ± 0.34	24.99 ± 1.29
3NTR	4.40 ± 0.39	23.73 ± 3.28

Inhomogeneity of the laboratory-made papers as a printing substrate due to its topographical parameter values (R_a and R_z) is clearly visible through high standard deviations (SD) of average roughness and maximum peak height values. However, all laboratory-made papers used in this study have quite similar texture.

The contact angles measured for four different liquids are summarized in Table 5. Water, having a predominant polar component over the dispersive component, glycerol and formamide with slightly higher dispersive component than the polar component and diiodomethane, which has no polar component because of its molecular symmetry, were used (Table 3). From the results presented in Table 5, it can be seen how all analysed laboratory papers show hydrophilic surface (θ water < 90º). Namely, the network of cellulose fibres that have a high affinity to water is the base material in paper [11]. Unsized laboratory papers in contact with water rapidly absorb water as evidenced by a contact angle of less than 90º. It is also evident that the addition of straw pulp into recycled wood pulp for making laboratory papers changes water contact angle by up to 9.5 % in comparison with papers made only from recycled wood pulp. In general, papers containing straw pulp show slightly higher hydrophobicity than those made only with recycled wood pulp (N) which can be explained with the addition of lignin component within the straw pulp [12]. Presence of lignin in a paper sheet increases the hydrophobic character of the paper [11].

Table 5. Contact angles measurements on laboratory-made papers

Paper sample	Contact angle (°)			
	Water	Glycerol	Formamide	Diiodomethane
N	60.22 ± 1.34	78.41 ± 1.90	48.96 ± 3.59	38.91 ± 2.68
1NW	57.79 ± 1.89	78.94 ± 1.84	44.58 ± 3.36	39.19 ± 2.60
2NW	63.32 ± 3.34	79.39 ± 1.64	51.18 ± 2.29	37.09 ± 1.51
3NW	61.46 ± 2.39	80.08 ± 2.14	49.67 ± 1.38	36.11 ± 1.52
1NB	61.46 ± 1.65	80.28 ± 3.19	47.24 ± 3.09	38.75 ± 2.08
2NB	56.84 ± 2.11	78.69 ± 1.59	44.00 ± 3.02	36.91 ± 2.08
3NB	60.08 ± 2.48	78.39 ± 2.36	46.73 ± 2.69	38.72 ± 2.26
1NTR	61.22 ± 1.76	78.77 ± 2.71	36.93 ± 3.37	39.79 ± 1.83
2NTR	65.98 ± 2.21	78.04 ± 2.19	39.92 ± 4.34	38.29 ± 2.12
3NTR	61.85 ± 1.87	73.93 ± 2.24	38.95 ± 3.09	38.40 ± 1.65

If we look at the contact angles measured on the laboratory papers, we can see that they are quite similar, regardless of the different composition of the paper listed in Table 2. From this we can conclude that the calculated free surface energy of all analysed papers will be similar, as well as the proportion of polar and disperse components. Table 6 summarizes the results obtained for all paper samples without (N) and with straw pulp, in terms of the total surface free energy (γ), dispersive (γ^d) and polar (γ^p) components and dispersive index (X^d) calculated by the ratio of the dispersive component to the total surface free energy. All listed values are the average value of at least 10 parallel measurements.

Table 6. Surface free energy and the corresponding dispersive and polar components for the laboratory-made papers determined by contact angle measurements

Paper sample	Surface free energy (mJ m^{-2})			X^d (%)
	Total γ	Dispersive components γ^d	Polar components γ^p	
N	40.92	30.69	10.23	75.00
1NW	41.90	30.66	11.24	73.17
2NW	40.18	31.63	8.55	78.72
3NW	40.70	31.57	9.13	77.57
1NB	40.64	31.19	9.45	76.75
2NB	42.59	31.28	11.31	73.44
3NB	41.38	31.18	10.20	75.35
1NTR	42.54	32.98	9.56	77.53
2NTR	42.06	34.67	7.39	82.43
3NTR	43.55	34.10	9.45	78.30

As can be seen from Table 6, paper samples assessed show total surface free energy (γ) between 40.18 and 43.55 mJ m^{-2}. These results obtained for laboratory papers containing straw pulp are within the range intended for uncoated papers (30 - 50 mJ m^{-2}) reported by Örtegren. While, by the same researcher the approximate surface energy values of coated inkjet paper are higher, in the range from 40 to 60 mJ m^{-2} [13]. As well, from Table 6, it is possible to observe that for all paper samples (without and with straw pulp) the predominant component of surface energy is the dispersive component (γ^d) which has a similar value for all papers (ranging from 30.66 mJ m^{-2} to 34.67 mJ m^{-2}).

For a more visual display of the surface, results obtained for free energy, total surface free energy and the dispersive/polar components of 10 papers in total are presented in Figure 2.

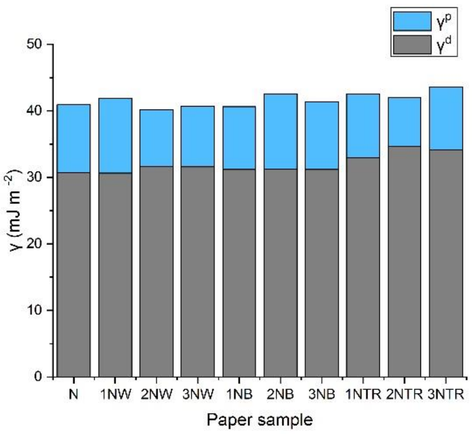

Figure 2. Contribution of the dispersive and polar components to the total surface free energy of laboratory-made paper samples

CONCLUSION

In this research evaluation of the surface free energy was conducted on laboratory-made papers containing semi-chemical straw pulp (wheat, barley and triticale) in different share. It is important to emphasize that these papers formed at a laboratory scale have not undergone any surface treatment that is characteristic of commercial paper production. However, the results obtained on such papers show how attention should definitely be given to straw as a lignocellulosic material for paper production. Value of topographical parameter R_a is slightly increased by the addition of any straw pulp type and consequently rises with the increase in the proportion of straw pulp in the paper. However, these uncoated and unsized surfaces of all laboratory-made papers are within the range for uncoated commercial papers. Regardless of paper composition (portion and type of straw pulp) all analysed laboratory papers show hydrophilic surface (θ water < 90°). Calculated total surface free energy (γ) varies between 40.18 and 43.55 mJ m^{-2}, which is within the range for uncoated commercial papers. For all paper samples (without and with straw pulp) the predominant component of surface energy is a dispersive component (γ^d).

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