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VALORIZATION OF STRAW PULP FOR THE PAPER INDUSTRY BASED ON THE WATER RESISTANCE OF PRINTS MADE WITH DIFFERENT PRINTING TECHNIQUES

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Abstract

Nowadays, all kinds of industries are facing surging prices and uncertainty about the supply of natural raw materials, which are closely related to their shortage. The paper industry and therefore, the graphic industry is facing the same problem. The graphic industry supports all economic activities with its products, whether it is information, news, entertainment, education, advertising or packaging, so it can be said that printed products play a major role in daily life. Today, the packaging sector is rapidly developing and growing and the graphic and paper industry play an important role in the production and design of packaging. Therefore, it is necessary to expand the sources of raw materials for the production of packaging, especially to annually available renewable sources. Considering the fact that packaging becomes waste very quickly after using the product it protects, from the moment of production until delivery to the consumer, the goal is to produce reusable packaging in an environmentally safe way without endangering the consumer or the product. Not only is it desirable that the packaging could be recycled for environmental reasons, but it is also important that it is of good quality and that it can carry printed information. In this research, studied papers as one of the most common substrates for printing and widely used packaging material were made from the pulp of recycled fibers refined with 30% pulp of cereal straw of the Croatian climate. Printed laboratory-made papers in full tone with conventional black ink by offset, flexographic printing and gravure printing were subjected to a test of chemical resistance to water. Given that, packaging most often comes into contact with water during transportation, storage and handling, recommendations for choosing the optimal printing technique when printing paper with straw pulp will be based on the tested water resistance of the prints.

Key words: *straw pulp, water resistance, packaging, prints, printing techniques*

Introduction

All types of industries are facing surging prices and uncertainty about the supply of natural raw materials, which are closely related to their scarcity. The pulp and paper industry has an enormous influence on global forests, as this sector accounts for 13-15% of total wood consumption and uses between 33-40% of all industrial wood traded globally (Mcguire, 2022). Therefore, full utilization of available renewable resources is the most fundamental parameter for clean production technology in any industry (Malik et al., 2020). Due to their abundance and cost-effectiveness, non-wood plants are reasonable candidates for pulp and paper production as increasing urbanization and population are the main factors driving demand for commercial and packaging printing. As a biobased and biodegradable material, paper is a widely used packaging material and is regaining its importance today (Fadiji et al., 2017). Paper and paperboard-based materials have long been used in the packaging industry. According to the World Packaging Organization (WPO), 60% of the world's total pulp production is used for packaging. Considering the fact that packaging becomes waste very quickly after using the product it protects, from the moment of production until delivery to the consumer, the goal is to produce reusable packaging in an environmentally friendly way without endangering the consumer or the product. Indeed, in the field of packaging, paper serves various purposes as to protect goods like single material for wrapping, in laminates or for secondary packaging and also as barcode labels (Lindner, 2018). Paper and cardboard are sheet materials made up from an interlaced network of cellulose fibers and as a packaging material it plays a crucial role in maintaining the quality of products during use by providing protection from physical, chemical and environmental challenges (Mujtaba et al., 2022; Gadhave & Gadhave, 2022). As a substrate for printing, paper undoubtedly serves as a tool for communicating with customers and marketing goods. Therefore, paper and cardboard occupy the most significant share among packaging materials (Figure 1).

Figure 1. Proportion of major packaging materials in 2021
(Source: https://www.jiangyinforward.com/news/north-american-packaging-market-and-development-trends-in-2021.html)

Undoubtedly, paper packaging is more in demand in the food and beverage industry due to its ease of recycling, potential to reduce air pollution, and ability to clean up the environment. It is interesting to note that the food industry uses over 50% of the paper and cardboard used for packaging (Kirwan, 2011). The pulp and paper sector is expected to thrive as a result consequence of increasing consumer knowledge about negative environmental effects of plastic and the environmental friendliness of paper packaging made from cellulose fibers. Today, the world's largest user and producer of pulp and paper is China, and Asia-Pacific region currently controls the pulp and paper industry (Aytac & Korkmaz, 2022).

Therefore, it is not surprising that the lack of wood fibers and the abundance of the non-wood fibers have led to non-wood fibers being the main raw materials for the Chinese paper industry with a percentage of even 60% (Hammett et al., 2001). This turn towards alternative raw materials for the paper industry worldwide is necessary and inevitable. Given that the production of straw is ecological and energy-saving, i.e., there is no waste and it can be fully used, straw is an interesting alternative lignocellulosic raw material for the pulp and paper industry. The yield of straw is between 4 and 5 tons of straw per hectare, which makes it an easily available material. After harvesting the cereal crops, large amounts of straw remain, which creates a large amount of waste. With intensive cultivation of cereals, it can be calculated that 4-5 tons of straw remain per hectare, which depends on the variety and the year. The ratio of grain yield and straw yield is approximately 50:50 (Glasnović et al., 2008). According to the announcement of the State Statistical Office of the Republic of Croatia in 2023, in 2022 the harvested area of wheat in Croatia was 161,000 ha, and barley 63,000 ha, which is approximately 224,000 ha for 2022 (Cvjetićanin & Kanižaj, 2023). If we calculate with a lower value, that 4 tons of straw remain per hectare, we arrive at a figure of 896,000 tons of straw per year from only two types of cereal. However, nowadays, in the total pulp consumption of the world, the proportions of wood pulp, wastepaper pulp, and non-wood pulp are 63%, 34%, and 3%, respectively (Liu et al., 2018). This means that globally the main source to produce plant-derived cellulose fibers for pulp and paper production is still wood (Eugenio et al., 2019).

In this research, we studied water resistance of prints made with different printing techniques widely used in packaging printing on papers made of pulp from recycled fibers enriched by the addition of 30% straw pulp. Water resistance is only one of several chemical stabilities that printed packaging must possess.

Materials and Methods

Commercial paper made from pulp of recycled fibers was used as a control sample, as the purpose of this research was valorization of straw pulp for paper industry if it is used as a supplement to pulp of recycled fibers. First the paper weighing approximately 42.5 g/m^2 was formed by Rapid-Köthen sheet former (FRANK-PTI) in laboratory conditions according to the standard EN ISO 5269-2:2004. As a source of virgin fibers, crop residues left in Croatian fields after the harvest of wheat, barley and triticale were collected and manually cut into pieces up to 3 cm long. The straw, cleaned of grain and impurities, was converted into a semi-chemical pulp using the soda pulping method (Plazonic et al., 2016). The obtained unbleached wheat pulp was blended with a recycled wood fiber pulp in ratio 30:70. At same laboratory conditions paper without addition of straw pulp into the recycled pulp was also formed and was used as a reference sample in this research. In total four different printing substrates were prepared in laboratory conditions and some of their properties determined in previous studies are summarized in Table 1.

Table 1. An overview of laboratory-made substrate properties

Laboratory-made printing substrate with straw pulp	Reference (0% straw pulp)	30% wheat pulp	30% barley pulp	30% triticale pulp
Thickness (μm) (Plazonić et al., 2016)	94.0 ± 2.79	101.5 ± 5.32	99.1 ± 4.06	99.4 ± 6.20
Surface roughness, R_a (μm) (Plazonić et al., 2016)	4.15 ± 0.34	4.59 ± 0.51	4.24 ± 0.41	4.40 ± 0.39
Water absorption percent after 5min, M_{5min} (%) (Plazonić et al., 2016)	171.23	268.50	256.53	264.48
Contact angle with water (°) (Plazonić et al., 2021)	60.22 ± 1.34	61.46 ± 2.39	60.08 ± 2.48	61.85 ± 1.87

All papers, laboratory and commercial, were printed in full tone with conventional black ink by fast growing print techniques, especially in the field of packaging printing (offset, flexographic and gravure printing). In Table 2 basic information is given about the ink used, the printing device and the conditions under which the printing of all printing substrates was done.

Table 2. Summarized information of printing procedures used in the research

Printing technique	Offset	Flexographic	Gravure
Ink type	SunPak FSP low migration ink, manufacturer Sun Chemicals.	Water-based ink.	Sunprop ink, manufacturer Sun Chemical
Printing device	Prüfbau multipurpose printability testing machine.	Esiproof flexographic laboratory device from RK Printcoat Instruments using an anilox roller, with a total volume of 39.1 cm^3/m^2 and engraved with a line screen of 40 line/cm.	KPP Gravure laboratory device with a 65 shore impression roller and a 100 lines/inch engraving plate (RK Rint Coat Instrument Ltd).
Printing conditions	Speed of 0.5 m/s and a pressure of 600 N, temperature of 23 °C and a relative humidity of 50%.	Temperature of 23 °C and a relative humidity of 50%.	Speed of 20 m/min, temperature of 23 °C and a relative humidity of 50%.

All black prints produced by three different printing techniques on laboratory-made papers with 30% straw pulp were tested for resistance to water in accordance with ISO 2836:2004 standard. The test method itself can be described as immersion of the four strips of filter paper in the water used for the test and then draining them until no free water dripped from the filter papers. Two saturated strips of filter papers were placed on the lower glass plate on which the test specimen of print pre-cut to size 20 mm x 50 mm was placed and covered with the remaining two strips of saturated filter papers and another glass plate. On top, a 1 kg mass was placed and left for 24 hours. The test specimen was then dried in an oven preheated to 40 °C for 30 minutes.

The water resistance of prints made with different printing techniques on papers from pulp of recycled fibers enriched by addition of 30% straw pulp and on reference and control papers (without addition of straw pulp) was evaluated based on the changes in the colorimetric values of the black prints after water treatment. The values of ΔL^*, Δa^* and Δb^* provide a complete numerical description of the color differences between a black print after water resistance testing and a black print before water resistance testing (i.e., target color) and are calculated according to the Equations 1-3:

$$\Delta L^* = L^*_{AWT} - L^*_{BWT} \quad (1)$$

$$\Delta a^* = a^*_{AWT} - a^*_{BWT} \quad (2)$$

$$\Delta b^* = b^*_{AWT} - b^*_{BWT} \quad (3)$$

Where: ΔL^* represents a lightness difference between black print after water resistance testing (AWT) and black print before water resistance testing (BWT), Δa^* represents a redness or greenness difference between black print after water resistance testing (AWT) and black print before water resistance testing (BWT) and Δb^* represents blueness/yellowness difference between black print after water resistance testing (AWT) and black print before water resistance testing (BWT).

The L^*, a^* and b^* values before and after water resistance testing of all black prints were measured using an X-Rite SpectroEye spectrophotometer under an illuminant D50, 2° standard observer. Generally, L^* represents lightness from black to white on a scale of 0 to 100, while a^* and b^* represent chromaticity with no specific numeric limits. Negative a^* corresponds to green, positive a^* corresponds to red, negative b^* corresponds to blue and positive b^* corresponds to yellow. In the case of ΔL^*, Δa^*, Δb^*, the higher the value, the greater the difference in that dimension.

To calculate the difference between the two colors within the L*a*b* system caused by the influence of water on the black prints, the distance between their points on the sphere was mathematically calculated according to Equation 4, using the untreated sample as a reference.

$$\Delta E_{00}^{*} = \sqrt{\left(\frac{\Delta L'}{k_L S_L}\right)^2 + \left(\frac{\Delta C'}{k_C S_C}\right)^2 + \left(\frac{\Delta H'}{k_H S_H}\right)^2 + R_T \frac{\Delta C'}{k_C S_C}\frac{\Delta H'}{k_H S_H}} \qquad (4)$$

Where: ΔE_{00}^* represents the total color difference, $\Delta L'$ represents the difference in lightness between black prints before and after water treatment, $\Delta C'$ represents the chroma difference between the black prints before and after water treatment and $\Delta H'$ represents the hue difference between the black samples before and after water treatment. R_T represents the rotation function while k_L, k_C, k_H represent the parametric factors for variation in experimental conditions and S_L, S_C, S_H represent the weighing functions.

In addition to quantifying the total color difference between a water treated sample and standard color of untreated sample, ΔE_{00}^* was intended to be a single number metric for Pass/Fail tolerance decisions (Table 3).

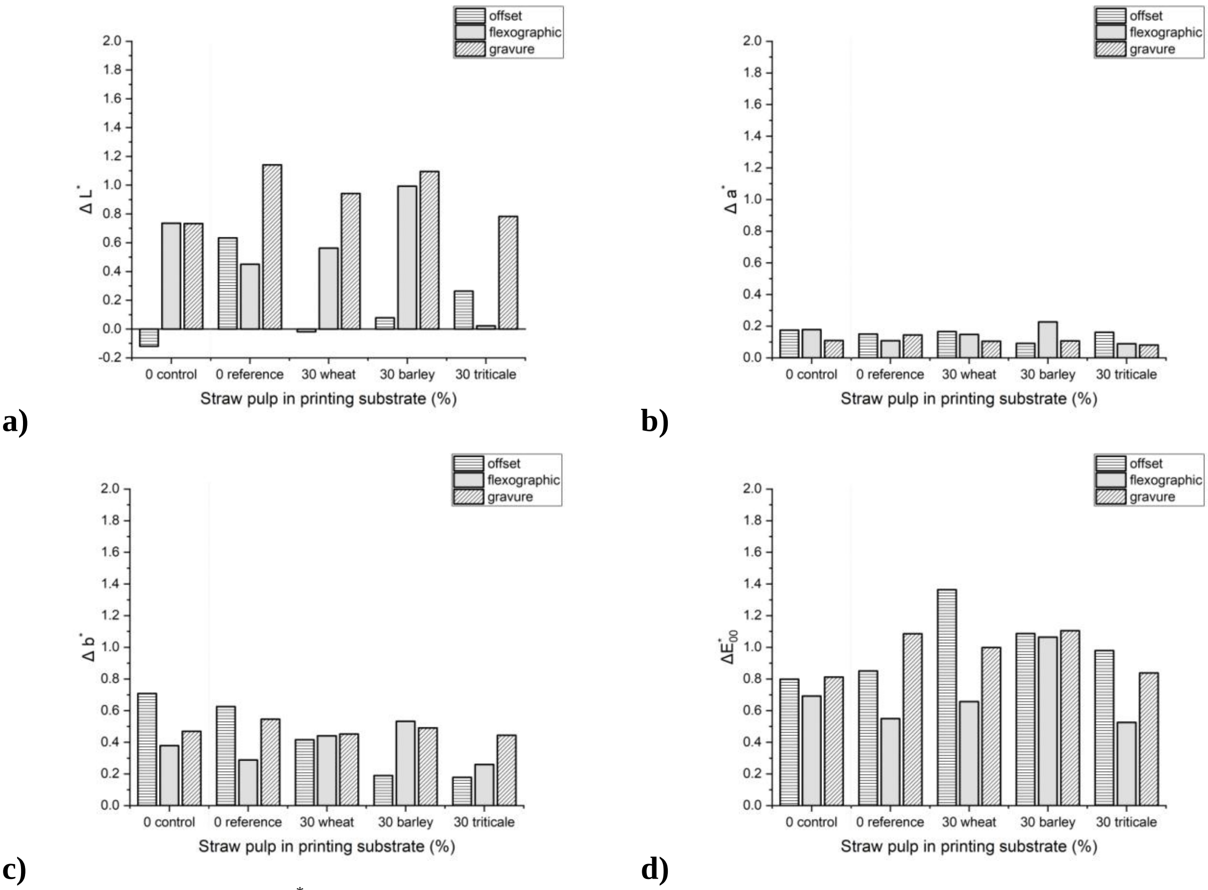
Table 3. The relation between the perceptual difference in color of a standard observer and the ΔE_{00}^* value (Mokrzycki & Tatol, 2011)

Value	Perceptual difference in color
$0 < \Delta E_{00}^* < 1$	observer does not notice the difference
$1 < \Delta E_{00}^* < 2$	only experienced observer can notice the difference
$2 < \Delta E_{00}^* < 3.5$	unexperienced observer also notices the difference
$3.5 < \Delta E_{00}^* < 5$	clear difference in color is noticed
$5 > \Delta E_{00}^*$	observer notices two different colors

Effectively a ΔE_{00}^* tolerance value defines an acceptance range around the standard or target color. The lower the ΔE_{00}^* value, the closer the sample is to the standard, in our case untreated sample (BWT). A ΔE_{00}^* value of 0.00 means the color of the sample is identical to the color of the standard.

Results and Discussion

The main structural component of wood and non-wood fibers is cellulose, which, being highly hydrophilic, interacts with water. Therefore, cellulose-based paper has the same affinity for water. From the results presented in Table 1, it can be seen that all analyzed laboratory-made papers have a hydrophilic surface (θ water < 90º). It is well known that water uptake (as liquid and from humid air) weakens the paper by breaking the hydrogen bonds and alters the dimensional stability of paper over time (Barletta et al., 2020). Figure 2 presents the results of water resistance of black prints made with three types of printing techniques on laboratory-made papers with straw pulp and those without straw pulp as reference and control samples. The water resistance of all black prints is expressed by the change of three colorimetric values (ΔL^*, Δa^*, Δb^*) and the total color difference (ΔE_{00}^*).



***Note:** In Figure 2.d) the ΔE_{00}^* results for flexographic prints are part of a doctoral dissertation (Radić Seleš, 2022)

Figure 2. Color accuracy of black prints after water treatment expressed through: a) ΔL^*, b) Δa^*, c) Δb^*, d) ΔE_{00}^*

From Figure 2a it is clearly visible that generally, in terms of changing the lightness of black color, the most resistant black prints are prints made by offset printing technique, while the prints with the highest lightness change caused by water are gravure black prints. After water treatment all printing substrates, especially those prepared in a laboratory, printed by gravure technique show higher lightness value indicating that the black color of the prints becomes brighter than the original color. The water has no significant influence on redness/greenness difference in black color regardless of the printing substrate and printing technique used (Figure 2b). It is visible that all prints after water treatment have slightly increased a^* print color value (Δa^*_{max} = 0.23), enhancing slight redness of all prints. A slightly stronger influence of water was observed on blueness/yellowness difference in black color (Figure 3c) than on redness/greenness difference. Water contact has increased b^* print color value as well, and the maximum increase was observed for control substrate printed by offset printing technique (Δb^*_{max} = 0.71). The total color difference calculated from measured color values indicates good water resistance of the prints made on printing substrates with addition of straw pulp (ΔE^*_{max} = 1.40), and thus the possibility of using straw pulp for the packaging sector of the paper industry. Namely, the addition of wheat, barley or triticale pulp into pulp of recycled fibers provides papers which have similar and good water resistance after printing with all printing techniques that are widely used in packaging printing (Figure 2d).

Conclusions

Straw pulp for the paper industry was evaluated as a promising source of fiber due to the good water resistance of prints made with different printing techniques (offset, flexographic and gravure). In fact, all prints have a total color difference (ΔE_{00}*) lower than the value 1.4, which proves that the changes in the black color of the prints are within the tolerances for the graphic industry. Compared to other straw, triticale straw provides paper substrates on which black prints with conventional offset, flexographic and gravure inks are the most resistant to water. The smallest difference in black color after water treatment (ΔE_{00}^*) is generally observed for flexographic prints, regardless of the composition of the paper substrate.

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