CHEMICAL AND MECHANICAL PRINT STABILITY OF SUBSTRATES CONTAINING ALTERNATIVE NON-WOOD FIBRES

VALENTINA RADIĆ SELEŠ, IRENA BATES, IVANA PLAZONIĆ,
MAJA RUDOLF and IGOR ZJAKIĆ

University of Zagreb, Faculty of Graphic Arts, 10000, Zagreb, Croatia
✉ *Corresponding author: V. Radić Seleš, valentina.radic.seles@grf.unizg.hr*

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The aim of this research has been to demonstrate the use and applicability of substrates containing non-wood fibres in the printing industry, with an emphasis on flexographic printing for packaging. To obtain such substrates, laboratory papers were produced with the addition of 30% non-wood fibres (wheat, barley and triticale), in combination with recycled wood pulp. These substrates were tested for chemical and mechanical resistance after flexographic printing with conventional and ultraviolet curing inks. The results showed that all laboratory papers with the addition of 30% non-wood fibres, printed with water-based inks, had fairly good chemical and mechanical resistance, except for the prints treated with sodium hydroxide. Thus, such papers should not be used as packaging materials for alkaline products. UV-curable inks on these substrates showed low chemical resistance, thus should only be used on substrates intended for secondary packaging. The mechanical resistance of UV prints was very good, thus papers containing straw pulp could be used for various applications.

Keywords: flexographic printing, non-wood fibres, chemical stability, mechanical stability, packaging, renewable resources

INTRODUCTION

Wood and, by extension, forests are an essential element on earth. However, because of the increasing use of wood for the construction and paper industries, there is great concern about the depletion of forest resources. Regardless of environmental changes, 40% of harvested wood is still converted into cellulose pulp, and this number is expected to rise with the reduction of plastic use, as there will be a greater need for cellulose pulp. Deforestation has already accelerated over the last century, considering that the world has lost as much forest in just over 100 years as it did in the previous 9,000 years (an area the size of the United States). The UN Forest Resources Assessment (FAO) estimates that 10 million hectares of forest have been cut down each year since 2010.[1-3] Forests are very important as they store solar energy, prevent soil erosion, protect watercourses, stabilize climate and water levels, and provide habitat for many species of animals, birds, plants and insects. We need to be aware that the amount of CO_2 in the atmosphere is increasing by about 5% per decade and is considered to be the cause of climate change. When trees grow, they absorb carbon dioxide and release oxygen. In this way, they remove carbon from the atmosphere and help to reverse the “greenhouse effect”.[4]

In papermaking, the choice between virgin fibres derived from plants and secondary fibres derived from waste paper often leads to choosing virgin fibres. Certainly, this was the most common choice until 2005, when waste paper became an increasingly valued source for papermaking fibres. In 2010, in the papermaking industry, recycled fibres reached up to about 55% of the fibres used worldwide in papermaking, and the remainder was virgin fibres.[4] Since paper cannot be recycled indefinitely, since the fibres become shorter with each recycling cycle and the mechanical and optical properties of recycled paper do not meet the required standards, the pulp of recycled fibres must be enriched with virgin fibres if it is to be reused. Therefore, the paper industry has begun to rely heavily on the use of fibres from agricultural residues and annual plants, especially in areas deficient in forests.

Non-wood plants generally differ from wood in that they contain less lignin and less total cellulose, so papers without addition of other fibres tend to be of lower quality. However, our previous studies have shown that by blending recycled wood fibres with non-wood fibres, quality paper can be produced and used in unprinted packaging.[5-7] Since milder treatment is required to produce pulp from annual plants compared to wood, it is logical that the production of paper from non-wood plants becomes more common.[1-3] As environmental awareness becomes more prevalent in our society, the use of renewable resources is always welcome.

Straw is a by-product of crop farming and can originate from various cereals that have a much shorter growth cycle than wood species, and can be used as a source of fibre for pulp and thus paper.[8,9] This would be in line with EU environmental directives and would be the first transition to a circular economy, in line with the UN's Agenda 2030 and the Sustainable Development Goal 12 on "Responsible Consumption and Production".[10] Various plants are used for paper production worldwide, such as bagasse, bamboo, kenaf, rice straw, flax, hemp, and banana leaves.[11-14] In this research paper, our focus has been on straw obtained as residue after harvesting the most commonly grown cereals in Croatia: wheat (*Triticum* spp.), barley (*Hordeum vulgare* L.) and triticale (*Triticale* sp.).[15] In order to be used as long as possible in the printing industry, especially in the packaging industry, such paper must ensure adequate chemical and mechanical print stability, among other properties. Printed paper-based packaging is expected to inform and appeal to customers, as well as protect products (such as food, beverages, cosmetics) from chemical, microbiological, and physical deterioration. Nowadays, it is often considered a viable packaging solution for dry food (bread, tea, sugar, coffee, flour, biscuits, cereals), frozen food, liquid food and beverages (milk, wine), chocolate, fast food, fresh products (meat, fish, fruits, vegetables), personal care (perfumes, cosmetics) and pharmaceuticals. Moreover, considering that plant growth removes carbon dioxide from the atmosphere, the use of wood and other suitable plants as raw material for manufacturing paper-based packaging has a lower carbon footprint than materials produced from non-renewable resources, such as petrochemical derivatives, and can also be recycled and reused.[4,16,17]

The most used printing technique in the production of packaging is flexographic printing, which is the most efficient, cost-effective and versatile printing method for a wide range of substrates and the fastest developing technique of conventional printing.[18] Flexographic printing requires careful selection of suitable inks with the desired rheological properties for each substrate. Inks commonly used in this technique are solvent-based, water-based and ultraviolet (UV) curing inks.[19] Solvent-based inks contain volatile organic compounds (VOCs) and their use is banned or discouraged in many regions of the world. Today, the use of water-based and UV-curable inks is preferred due to increased safety and sustainability, and reduced costs associated with VOC control.[20]

Although the paper industry is facing a lower demand for printing, writing, and newsprint paper grades due to the rising influence of internet, new media, and paperless reading, the demand for printed paper-based packaging is expected to increase in response to the trend to replace plastic packaging and, especially, considering the rising popularity of online shopping, which enhances even more the demand for packaging solutions. On the other hand, the pulp and paper industry is under increasing environmental, political and economic pressure, so environmental sustainability and high added value will be the key mantras for the industry in the coming years.[21] In this context, the present study aims to prepare laboratory papers containing 30% non-wood (cereal straws) fibres and to investigate the applicability and usability of these newly created substrates for printed paper-based packaging, by evaluating their chemical and mechanical stability.

EXPERIMENTAL

Conversion of straw into semi-chemical pulp

The straw used in this study was obtained after harvesting winter crops from cereals available in continental Croatia: wheat (*Triticum* spp.), barley (*Hordeum vulgare* L.) and triticale (*Triticale* sp.).[22] Cleaned straw was hand-cut into 1-3 cm long pieces, which were processed into a semi-chemical pulp using the soda pulping method, followed by decantation to remove the black liquor and rinsing of the softened pulp in two cycles. The conditions of the whole process of conversion of straw into semi-chemical pulp are summarized in Table 1.[15]

Fibre length is one of the most important fibre properties as it affects the resulting paper strength properties. Long fibres increase the number of bonds per fibre, which ultimately increases the strength of the fibre network in the paper and blends well with short fibre pulp to optimise fibre cost. The differences between fibres obtained from cereal crops and different types of trees, in terms of fibre length, are shown in Table 2.

The chemical composition of straw is also very important for papermaking, especially the content of lignin and cellulose. Table 3 shows the basic chemical composition of straws, as well as that of wood raw materials, which is given for comparison.

Table 1
Conditions for conversion of straw into pulp[15]

Soda pulping		Decantation and rinsing		Fibre production in a Holländer Valley mill	
Chemical $NaOH_{(aq)}$	16%	Tap water	2x10 L	Tap water	23 L
Bath ratio straw: $NaOH_{(aq)}$	1:10			At 24 °C	40 min
At 120 °C and 170 kPa	60 min			pH	8.5-9.0

Table 2
Fibre length of straw and wood fibres used in paper production[23,24]

Raw material	Species	Fibre length (mm)	
		Min.	Max.
Straw	Wheat (*Triticum* spp.)	0.45	1.62
	Barley (*Hordeum vulgare* L.)	0.40	1.62
	Triticale (*Triticale* sp.)	0.27	2.63
Wood	Deciduous	1.00	1.80
	Coniferous	3.50	5.00

Table 3
Chemical composition of various pulps[23-26]

Raw material	Species	wt%		Brightness D65, %
		Klason lignin	α-cellulose	
Straw	Wheat (*Triticum* spp.)	24.66 ± 1.63	31.47	22.41 ± 0.55
	Barley (*Hordeum vulgare* L.)	21.71 ± 1.17	37.97	27.16 ± 0.62
	Triticale (*Triticale* sp.)	12.59 ± 1.77	44.22	19.45 ± 0.41
Wood	Deciduous	28.80± 2.60	43.70±2.60	-
	Coniferous	23.80±2.60	45.40±3.50	-

Formation of laboratory papers

Unbleached straw pulp was added to pulp of recycled wood fibres in an amount of 30% for each cereal individually. The main ingredient used in the production of laboratory paper is recycled wood pulp obtained from commercial newsprint paper.[8]

Laboratory papers weighing approximately 42.5 g/m^2 were formed using a Rapid Köthen sheet former (FRANK-PTI GmbH, Birkenau, Germany) in accordance with the EN ISO 526 9-2:2001 standard. The production process of laboratory papers is shown in Table 4.[15]

A total of four types of laboratory papers were prepared. The laboratory paper containing 100% recycled wood fibre pulp was formed as a reference paper (100R) and was used for the sake of comparing the chemical and mechanical stability of handsheets.

The abbreviations used to denote all the laboratory-prepared papers and those related to the process of testing print stability are listed in Table 5, along with their respective meaning.

Printing of laboratory papers using the flexographic technique

The printing process for all laboratory papers was carried out with two types of inks and the corresponding printing equipment. The printing process with water-based inks for all laboratory papers was carried out with an Esiproof flexographic laboratory device from RK Printcoat Instruments, in a full-tone pattern with cyan, magenta, yellow and black inks. The printing process was carried out 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 at a temperature of 23 °C and relative humidity of 50%. The engraving angle for the anilox roller was of 60°, creating hexagonal shaped cells, and providing a higher number of cells, which means an increase in ink transfer as well as homogeneity.[18] The printing process with UV-curing inks on the laboratory papers was carried out using a flexographic F1-basic printability tester in the full-tone pattern with cyan, magenta, yellow and black inks. Printing was performed at a speed of 0.5 m/s, a printing force of 300N and an anilox roller force of 200N. An anilox roller with 90 line/cm (60° raster angle) and a cell volume of 18 cm^3/m^2 were used for printing at a temperature of 23 °C and relative humidity of 50%. The prints were dried using a Technigraf Aktiprint L 10-1 UV dryer (UV-C tube, with a light source power of 120 W/cm and intensity of 60%).

Table 4
Laboratory paper production [15]

Composition (W_{pulp}, %)		Disintegration		Homogenization		Handsheet (laboratory paper)	
Recycled wood	Straw (wheat, barley or triticale)	m (pulp)	80 g	V (H_2O)	10 L	Weight	42.5 g/m^2
100	0	V (H_2O)	1.6 L	pH	7.5		
70	30	pH	8	t	5 min	Diameter	20 cm
		T	45 °C	T	45 °C		

Table 5
Abbreviations used in labelling of samples

100R	Laboratory paper with 100% recycled wood pulp (reference)
30RW	Laboratory paper with 70% recycled wood pulp and 30% wheat pulp
30RB	Laboratory paper with 70% recycled wood pulp and 30% barley pulp
30RT	Laboratory paper with 70% recycled wood pulp and 30% triticale pulp
Rev.	Revolutions
Chem. Ag.	Chemical agent
NaOH	Sodium hydroxide
$C_6H_8O_7$	Citric acid
C_2H_5OH	Ethanol
ΔE_{00}*	Euclidean colour difference
ΔH*	Hue difference
GLCM	Grey Level Co-occurrence Matrix

Chemical stability tests

All the printed laboratory papers were tested for resistance to different liquid agents in accordance with ISO 2836:2004 standard,[27] which specifies the testing procedure as a function of the chemical agent used. For all chemical stability tests, the prints were first cut to the same dimensions (2 cm x 5 cm samples) and were placed onto the lower glass plate between strips of filter paper previously soaked in the specific liquid chemical agent (where the number of filter paper was defined according to the type of the chemical agent used – for citric acid the total number of filter papers was two and for sodium hydroxide it was four). Finally, the upper glass plate was placed on top and weighed by a 1 kg weight. The contact time for alkali was 10 minutes, while for citric acid, it was 60 minutes, after which the samples were rinsed with distilled water and dried in an oven for 30 minutes. For ethanol stability assessment, the procedure was completely different – the prints were immersed for five minutes in a glass tube containing ethanol. The samples treated with alcohol were also dried in an oven for only 5 minutes. All test conditions were summarized in Table 6.[25,28]

Mechanical stability tests

Good or satisfactory rub resistance is obtained due to a combination of paper surface properties, the printing method and varnishing or sealing application (if any). To achieve satisfactory resistance, the print must not be scuffed, smeared or affected in any way by handling, transport, or use after printing.[4]

The rub resistance testing was carried out on laboratory printed papers, which were first cut into smaller samples of 5 cm in diameter. The rub resistance was tested using a Hanatek T4 Rub and Abrasion Tester at a pressure of 0.23 kg (0.5 lb), with circular movements of 20, 40, and 60 revolutions at a constant speed of 1 revolution per second, according to the BS 3110:1959 standard.[29,30]

Table 6
Test conditions for chemical stability of prints to various liquid test agents[25,28]

Test liquid agent	Receptor surface	Contact condition	Duration of exposure	Drying conditions
Sodium hydroxide (NaOH)	4 Filter papers	1 kg on 54 cm^2	10 min	30 min at 40 °C
Citric acid ($C_6H_8O_7$)	2 Filter papers	1 kg on 54 cm^2	60 min	30 min at 50°C
Alcohol (C_2H_5OH)	-	-	5 min	10 min at 40° C

Evaluation of chemical and mechanical stability of prints

Euclidean difference

The evaluation of the chemical and mechanical print stability for all the prints was performed by observing the changes in optical properties of the samples subjected to chemical and mechanical stress, compared to those of the control. Optical properties were measured using an X-Rite eXact spectrophotometer based on colour values in the CIE L*a*b* colour system, which is a quantitative relationship of colours on three axes: L* as lightness (from white to black), a* (from green to red), and b* (from blue to yellow).[31] The Euclidean colour difference (ΔE_{00}*) was used to calculate the difference between the values for the samples subjected to chemical or mechanical stress and those of the control. The ΔE_{00}* value was calculated according to Equation 1:

$$\Delta E_{00}{}^{*} = \sqrt{\left(\frac{\Delta L'}{k_L S_L}\right)^2 + \left(\frac{\Delta C'}{k_C S_C}\right)^2 + \left(\frac{\Delta H'}{k_H S_H}\right)^2 + R_T\left(\frac{\Delta C'}{k_C S_C}\right)\left(\frac{\Delta H'}{k_H S_H}\right)} \quad (1)$$

where ΔL' represents the difference in lightness between printed samples before and after the treatments, ΔC' is the chroma difference between the printed samples before and after the treatments and ΔH' represents the hue difference between the printed samples before and after the treatments. R_T stands for 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.[32] According to the tolerance definition, $\Delta E_{00}^* \leq 2$ is classified as a very small noticeable difference for a standard observer, while $\Delta E_{00}^* = 5$ is defined as a large noticeable colour difference that a standard observer can detect.[31]

Hue differences

The L*C*h colour space describes colours using cylindrical coordinates, instead of rectangular ones. In this colour space, L* indicates lightness, C* stands for chroma, and h is the hue angle. The delta for hue (ΔH*) can be positive (+) or negative (-) and is expressed as follows:[33]

$$\Delta H^* = H^*_{sample} - H^*_{standard} \quad (2)$$

GLCM analysis (mottling analysis)

To analyse the print quality after the samples were subjected to abrasion treatment, mottling was calculated using a statistical method for studying texture, which considers the spatial relationship of pixels in the Gray-Level Co-Occurrence Matrix (GLCM), also known as Gray-Level Spatial Dependence Matrix. Images of the printed samples were created with a PIAS-II digital microscope, using software that complies with ISO-13660 print quality standards. The images were then converted to grayscale and analysed with GLCM, using the GLCM Texture Plugin in ImageJ software version 1.53k.[34,35]

RESULTS AND DISCUSSION

Chemical stability of laboratory papers printed with water-based inks

Colour (ΔE*) and hue (ΔH*) differences observed on laboratory papers, containing or not straw pulp, printed using water-based flexographic inks, were analysed as indicators of chemical stability to various chemical agents.

In Figure 1, the results of ΔE_{00}*, after the samples were subjected to chemical agents (sodium hydroxide, ethanol and citric acid), are presented with filled symbols, while the results of ΔH* for all the prints are shown with open symbols. The results reveal that most cyan prints have good stability to all chemical agents, while substrates containing 30% wheat (30RW) and 30% barley pulp (30RB) exhibit high ΔE_{00}* values when exposed to sodium hydroxide, with ΔE_{00}* above the recommended reference line of $\Delta E_{00}^* = 2$ ($\Delta E_{00}^*{}_{(30RW)} = 2.36$ and $\Delta E_{00}^*{}_{(30RB)} = 2.65$). The difference in hue (ΔH*) is small for all analysed prints (Fig. 1a).

The laboratory papers printed with magenta ink showed very good stability after contact with citric acid and alcohol. However, exposed to sodium hydroxide, all the prints, regardless of the printing substrate type, recorded values above the reference line, while the control laboratory paper containing 100% recycled wood fibre pulp showed the highest value ($\Delta E_{00}^*{}_{(100R)} = 3.44$). Similar values are visible on the ΔH* scale (Fig. 2b).

Very good stability of yellow (Fig. 2c) and black prints (Fig. 2d) is indicated by the values of ΔE_{00}*, which are below the reference line. The hue difference values are also low.

Chemical stability of laboratory papers printed with UV inks

Laboratory papers printed with UV cyan ink show low stability after exposure to all chemical agents, with all ΔE_{00}^{*} values above the reference line (Fig. 2a). The lowest ΔE_{00}^{*} values are noticed for all the handsheets treated with citric acid, as well as for those containing 30% barley (30RB) and triticale pulp (30RT) after treatment with sodium hydroxide. The difference in hue is within reasonable values, with the highest difference visible on the paper containing 30% barley pulp (3RB) and treated with sodium hydroxide.

Magenta prints also show low stability after exposure to all chemical agents, except for alcohol – in which case, the treated laboratory papers exhibited ΔE_{00}^{*} values within the recommended values (Fig. 2b). The difference in hue is the greatest for the handsheets treated with sodium hydroxide, except for the paper containing barley pulp (3RB). Laboratory papers printed with yellow and black ink all show good stability within the ΔE_{00}^{*} tolerance definition (Fig. 2c-d).

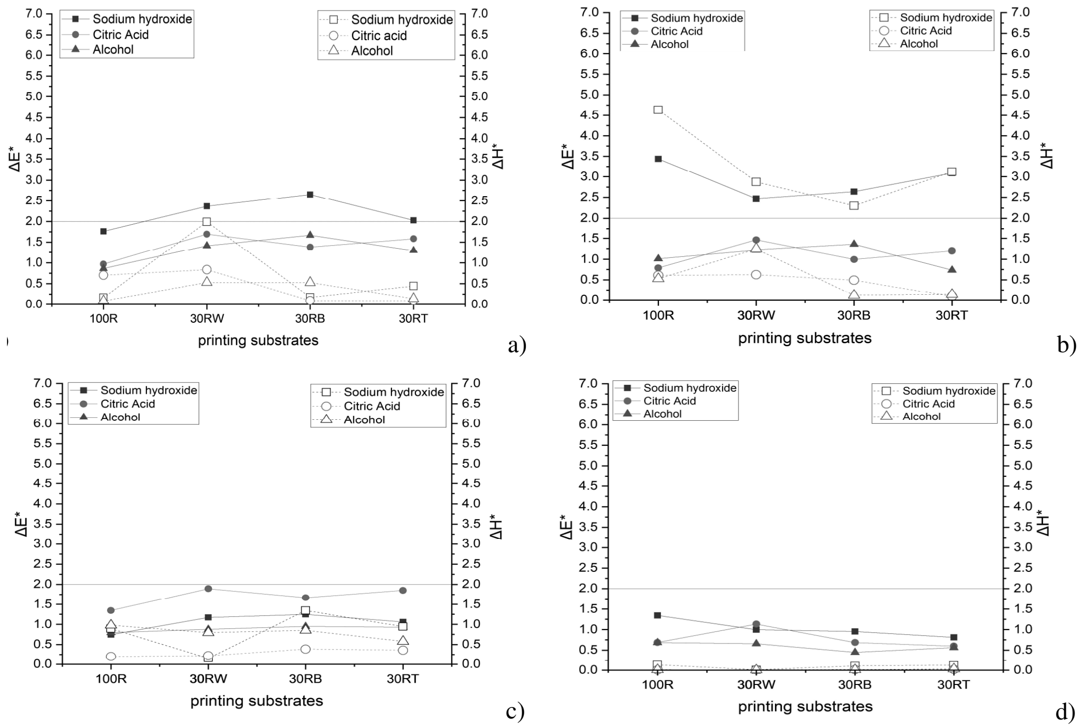
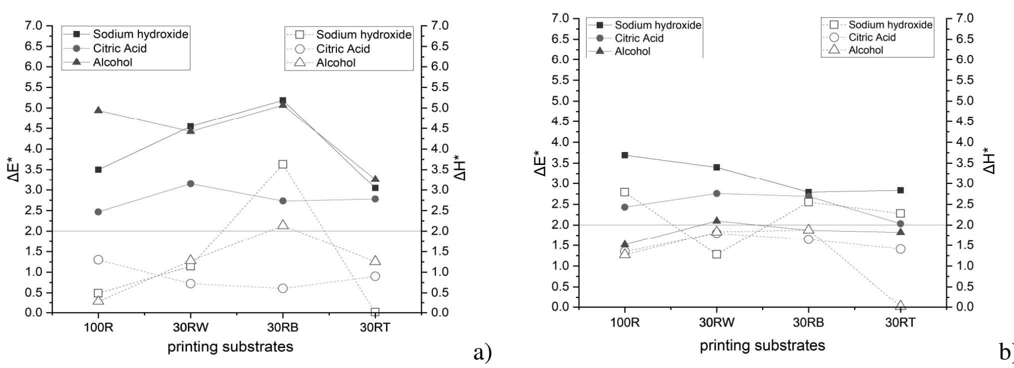


Figure 1: Colour (ΔE*) and hue (ΔH*) differences on laboratory papers with and without straw pulp, printed with water-based flexographic inks: a) cyan, b) magenta, c) yellow and d) black, after chemical stability testing



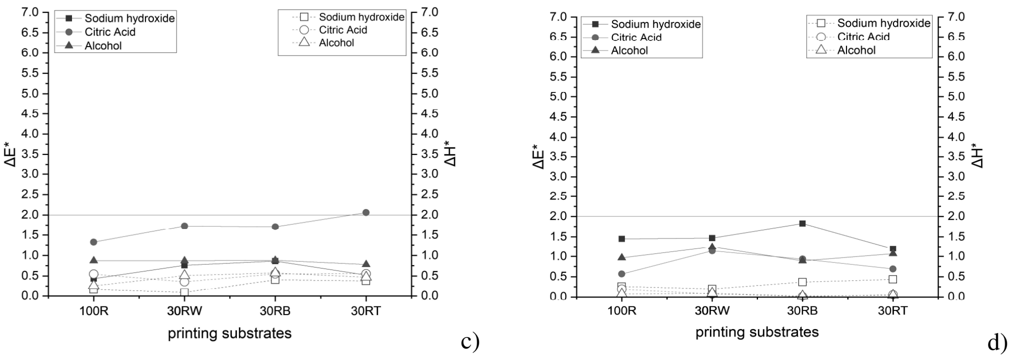


Figure 2: Colour (ΔE*) and hue (ΔH*) differences on laboratory papers with and without straw pulp, printed with UV flexographic inks: a) cyan, b) magenta, c) yellow and d) black, after chemical stability testing

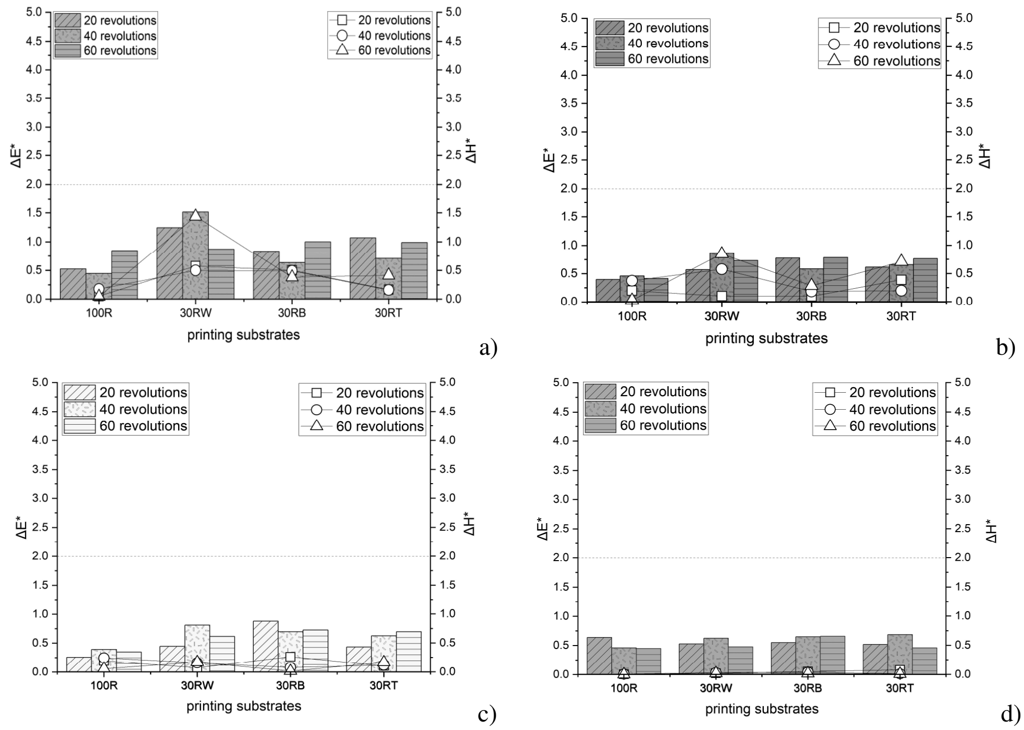


Figure 3: Colour (ΔE*) and hue (ΔH*) differences on laboratory papers with and without straw pulp, printed with water-based flexographic inks: a) cyan, b) magenta, c) yellow and d) black, after mechanical stability testing

The highest ΔE_{00}^{*} values are visible for the yellow print on the paper containing 30% triticale pulp after contact with citric acid ($\Delta E_{00}^{*}{}_{(30RT)}$ = 2.06) and for the black print on the paper containing 30% barley pulp exposed to sodium hydroxide ($\Delta E_{00}^{*}{}_{(30RB)}$ = 1.82). Differences in hue are low for all tested laboratory papers.

Mechanical stability of laboratory papers printed with water-based inks

All laboratory papers printed with cyan, magenta, yellow or black water-based ink (Fig. 3a-d) present very good colour stability after the rubbing test has been performed at three different revolution numbers. As can be seen, the ΔE_{00}^{*} values are below the reference line, even after 60 revolutions. Although the colour degradation of the prints rises with the number of revolutions, it remains within recommended values (ΔE_{00}^{*} = 2). The hue differences after the rubbing test are also low for all the prints, which mean that the flexographic prints with water-based inks have satisfactory mechanical stability.

Mechanical stability of laboratory papers printed with UV inks

All laboratory papers printed with UV inks exhibited good colour stability after the mechanical resistance test (Fig. 4). Colour degradation rises with an increasing number of rotations, and the highest colour difference caused by rubbing movements is visible on laboratory paper containing 30% barley pulp printed with magenta ink after 60 revolutions ($\Delta E_{00}{}^{*}{}_{(30RB)} = 2$). However, it is still within the recommended value. Yellow prints prove to be the most stable, considering that their Euclidean difference is the lowest for all types of paper (Fig. 4c). Hue difference values are higher on laboratory papers printed with cyan, except for that containing triticale pulp (3RT), and with magenta ink after 60 revolutions. Yellow and black prints show very low values in hue differences on all laboratory papers, thus demonstrating the best stability after the mechanical resistance test (Fig. 4c-d).

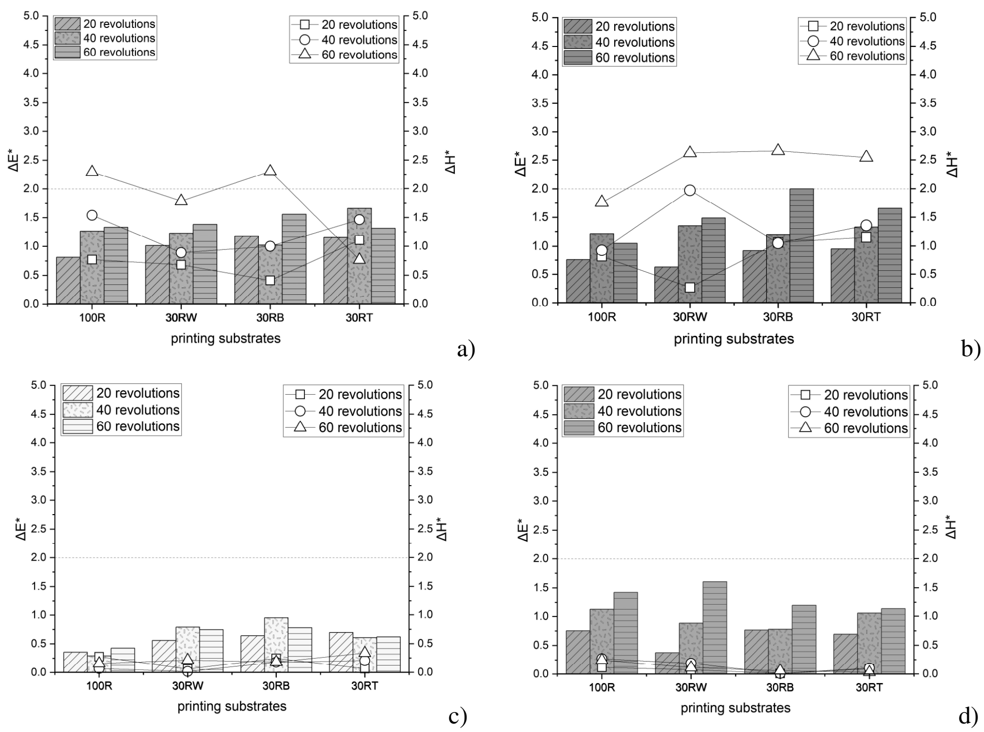


Figure 4: Colour (ΔE*) and hue (ΔH*) differences on laboratory papers with and without straw pulp, printed with UV flexographic inks: a) cyan, b) magenta, c) yellow and d) black, after mechanical stability testing

GLCM analysis

Taking into consideration the mottling analysis results presented in Tables 7-10, there are no significant changes in energy after testing mechanical stability at all rotation numbers or chemical stability of analysed printing substrates. No major variations can be seen among the prints, they all behave similarly, regardless of the type of printing substrate. The only significant change was noticed on the black printed substrates, where the energy is higher than on those printed with other inks, but the energy was reduced when the substrates containing straw pulp were printed with UV drying inks.

Table 7
Grey Level Co-occurrence Matrix parameters for mottling on laboratory papers with and without straw pulp, printed with water-based flexographic inks, after mechanical stability tests

ΔEnergy$_{(cyan)}$					ΔEnergy$_{(magenta)}$				
Rev.	100R	3RW	3RB	3RT	Rev.	100R	3RW	3RB	3RT
20	0.001	0	0.002	0.003	20	0.002	0.001	0.002	0.001
40	0.002	0.003	0.001	0.003	40	0.002	0.001	0.002	0.001
60	0.002	0.001	0.002	0.003	60	0.002	0.001	0.002	0.001
ΔEnergy$_{(yellow)}$					ΔEnergy$_{(black)}$				
Rev.	100R	3RW	3RB	3RT	Rev.	100R	3RW	3RB	3RT
20	0	-0.001	0	0	20	0.009	0.011	0.013	0.012
40	0	0	0	0.001	40	0.009	0.009	0.012	0.013
60	0	-0.001	0	0.001	60	0.012	0.011	0.011	0.012

Table 8
Grey Level Co-occurrence Matrix parameters for mottling on laboratory papers with and without straw pulp, printed with UV flexographic inks, after mechanical stability tests

ΔEnergy$_{(cyan)}$					ΔEnergy$_{(magenta)}$				
Rev.	100R	3RW	3RB	3RT	Rev.	100R	3RW	3RB	3RT
20	0.002	0.001	0.001	0.002	20	-0.005	0.001	0.001	0.001
40	0.002	0.001	0.001	0.001	40	-0.006	0.001	0.001	0.002
60	0.002	0.001	0.002	0.001	60	-0.004	0	0.003	0.003
ΔEnergy$_{(yellow)}$					ΔEnergy$_{(black)}$				
Rev.	100R	3RW	3RB	3RT	Rev.	100R	3RW	3RB	3RT
20	0	0	-0.001	0	20	0.002	0	0.002	0.003
40	0	0	0.001	0	40	0.003	-0.004	0	0.006
60	-0.001	-0.001	0.001	0	60	0.007	-0.002	0.002	0.003

Table 9
Grey Level Co-occurrence Matrix parameters for mottling on laboratory papers with and without straw pulp, printed with water-based flexographic inks, after chemical stability tests

ΔEnergy$_{(cyan)}$					ΔEnergy$_{(magenta)}$				
Chem. Ag.	100R	3RW	3RB	3RT	Chem. Ag.	100R	3RW	3RB	3RT
NaOH	0.001	0.001	0.001	0.001	NaOH	0.001	0.002	0.001	0.001
$C_6H_8O_7$	0.001	0.001	0.001	0.001	$C_6H_8O_7$	0.001	0.002	0	0.001
C_2H_5OH	0.000	0.000	0.000	0.000	C_2H_5OH	0.001	0.002	0.001	0.001
ΔEnergy$_{(yellow)}$					ΔEnergy$_{(black)}$				
Chem. Ag.	100R	3RW	3RB	3RT	Chem. Ag.	100R	3RW	3RB	3RT
NaOH	0	-0.001	0	0	NaOH	0.003	-0.004	0	-0.004
$C_6H_8O_7$	0	-0.001	0	0	$C_6H_8O_7$	0	0.004	0.002	0.005
C_2H_5OH	-0.001	0	0	0	C_2H_5OH	-0.001	0.003	0.003	0.004

Table 10
Grey Level Co-occurrence Matrix parameters of mottling on laboratory papers with and without straw pulp printed with UV flexographic inks after testing the chemical stability

ΔEnergy$_{(cyan)}$					ΔEnergy$_{(magenta)}$				
Chem. Ag.	100R	3RW	3RB	3RT	Chem. Ag.	100R	3RW	3RB	3RT
NaOH	0.001	0.002	0.001	0	NaOH	-0.004	0.002	0	0.001
$C_6H_8O_7$	0.002	0.001	0.001	0.001	$C_6H_8O_7$	-0.003	-0.002	-0.001	-0.002
C_2H_5OH	0.001	0.002	0.001	0.001	C_2H_5OH	-0.002	-0.001	0.001	0.001
ΔEnergy$_{(yellow)}$					ΔEnergy$_{(black)}$				
Chem. Ag.	100R	3RW	3RB	3RT	Chem. Ag.	100R	3RW	3RB	3RT
NaOH	0	0.001	0	0	NaOH	-0.004	-0.004	0	0.001
$C_6H_8O_7$	0	-0.001	0	-0.001	$C_6H_8O_7$	0.004	-0.005	0	0.001
C_2H_5OH	-0.001	0	0	0	C_2H_5OH	0.004	-0.003	0.002	0.003

CONCLUSION

In this research work, laboratory papers were prepared from a combination of recycled wood pulp with 30% non-wood fibres (wheat, barley and triticale straw). The obtained handsheets were evaluated in terms of their chemical and mechanical resistance after flexographic printing with conventional and ultraviolet curing inks, to examine their suitability for packaging applications. As regards the chemical stability of the prints made on paper containing a fraction of non-wood pulp, the following conclusions could be drawn from the corresponding tests:

- Laboratory papers printed with water-based flexographic inks and exposed to various chemical agents have shown that the substrates printed with cyan and magenta inks are most sensitive to sodium hydroxide, while they are quite stable when in contact with citric acid and ethanol.
- Yellow and black prints are the most stable and least sensitive to all three chemical agents.
- When printed with UV inks, the most stable prints are also yellow and black. Laboratory papers printed with cyan and magenta inks did not respond well when in contact with chemical agents.

As regards the mechanical resistance test, considering the ΔE_{00}^{*} values obtained, it can be concluded that all the laboratory papers printed with water-based flexographic inks have very good stability, as the colour differences are within the recommended values. Among the UV flexographic prints, the most stable is yellow for all the printing substrates.

Based on the findings of GLCM analysis, there were no significant changes in print quality after either chemical or mechanical resistance tests. The energy values are the same, regardless of the printing substrate used. Black prints have higher energy, compared to others, implying less mottling and minimal deterioration in quality.

Overall, all laboratory papers printed with water-based inks show good mechanical and chemical stability, with the exception of the prints subjected to sodium hydroxide. This means that these substrates containing non-wood fibres cannot be used as packaging for products with higher pH value (alkaline products). A solution to this problem would be to coat the packaging material with suitable varnishes during production to avoid colour deterioration of the prints. On the other hand, generally speaking, UV prints showed lower chemical stability than water-based ones. A possible reason for this could reside in the differences in chemical composition between these types of inks, which in turn imply different drying procedures. UV-curing printing inks consist of monomers (used to adjust the processing viscosity), prepolymers (which act as binders), pigments, photo-initiators (which trigger polymerisation) and additives. Due to their composition, drying of UV inks does not take place immediately after printing, but only under the influence of UV radiation, resulting in a solid, rigid and completely dried ink layer on the paper surface. During UV exposure, the photo-initiators react with the prepolymers and monomers, which eventually become three-dimensional cross-linking polymers. Meanwhile, drying of water-based inks is performed by evaporation of the solvent, with the ink partially penetrating the uncoated and porous substrate and the pigment penetrating the pores of the paper. Thus, it has been established that the proportion of ink cured on the substrate is of 20-30% for conventional prints and of 100% for UV prints. Since the exact composition of water-based and UV flexographic inks is not known, it can be hypothesized from the chemical stability results that in the case of UV prints, the pigments remain on the surface of the paper and are therefore more affected by chemical agents. Considering that UV flexographic inks are not recommended for printing on food packaging paper, unless it is secondary packaging, as well as the very good mechanical stability achieved in this work for the handsheets printed with such inks, such paper can be strongly suggested for other applications.

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