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BLAŽ BAROMIĆ 2015

19. MEĐUNARODNA KONFERENCIJA
TISKARSTVA, DIZAJNA I GRAFIČKIH KOMUNIKACIJA

ZBORNIK RADOVA
PROCEEDINGS

Senj, 16. - 19. rujan 2015. godine, Hrvatska
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I thank for the participation and cooperation in the creation of the Proceedings to all authors, Conference participants, Conference organizers, members of Organizing and Scientific and Review Committees, sponsors, donators and the team which designed and realized the Proceedings!

Editor

KARAKTERISTIKE UBRZANO STARENIH PAPIRA S NEDRVNIM VLAKANCIMA JEČMA

CHARACTERISATION OF ACCELERATE AGED PAPERS WITH NON-WOOD BARLEY FIBRES

Ivana Plazonić[1], Irena Bates[1], Marina Vukoje[1], Željka Barbarić-Mikočević[1]
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SAŽETAK

Papirne tiskovne podloge mijenjaju svoja fizikalna, kemijska i optička svojstava tijekom starenja. Sam sastav papira snažno utječe na njegovu postojanost tijekom starenja. Cilj ovog istraživanja je utvrditi optičke promjene u laboratorijskim papirnim podlogama nakon dva tretmana ubrzanog starenja. Promatrane laboratorijske papirne podloge izrađene su miješanjem izdvojenih vlakancima ječma s recikliranim drvnim vlakancima u masenom omjeru 10:90, 20:80 i 30:70. Kao kontrolni uzorci korišteni su laboratorijske papirne podloge izrađene od recikliranih drvenih vlakanaca. Sve laboratorijske papirne podloge su ubrzano starene koristeći standardizirane metode: s povišenom temperaturom i s xenon lampom. Promjene u optičkoj stabilnost laboratorijskih papirnih podloga promatrane su nakon tretmana ubrzanog starenja u obliku razlika relativnih refleksijskih vrijednosti, svjetline i Euklidove razlike boja.

Ključne riječi: ubrzano starenje, papirna podloga, optička stabilnost, vlakanca ječma

ABSTRACT

Paper as a printing substrate upon ageing varies in the physical, chemical and optical properties. Paper composition strongly influence on its permanence during aging. The aim of this study is to determine the optical changes in the paper substrates by artificial ageing. The research was carried out with laboratory paper substrates made by mixing isolated barley fibres with the recycled wood fibres in a weight ratio 10:90, 20:80 and 30:70. Cellulose fibres in form of the pulp were isolated from barley straw in a process known as chemical pulping. Laboratory paper substrates made only from recycled wood fibres was used as a control paper. All paper substrates were artificially aged using standard techniques of accelerated ageing: dry-heat and treatment with a xenon arc lamp. The changes in the optical stability of paper substrates were analysed after accelerated ageing and presented in form of relative reflectance spectra differences, brightness differences and Euclidean differences.

Key words: accelerated ageing, paper substrate, optical stability, barley fibres

1 INTRODUCTION

Ageing can be defined as the irreversible changes that occur slowly over time and in the case of paper substrate ageing process results with the deterioration of useful properties that can render it unsuitable for its primary usage. Therefore, an accelerated ageing test is a practical way to predict the physical and chemical changes occurring naturally in a paper in a relatively short period of time. In a practice a numerous accelerated ageing tests with various aging conditions are used for evaluation and ranking paper substrates on their permanence. Heat, light and moisture are the most important environmental influences on the stability of papers. Some of the standard techniques of accelerated ageing are moist-heat (80 °C and 65% RH), dry-heat (105 °C) and treatment with a xenon arc lamp [1]. The concept of accelerated ageing test is simple. Namely, the rate of most chemical reactions in a paper sample increases when temperature is increased and those chemical changes affecting the physical properties of a paper. Paper optical stability is extremely important in graphic industry because it contribute, more than any other factor, to the overall paper appearance and appeal [2]. The optical properties of the paper are very sensitive to its structure. Paper is by large the prevalent cellulose product. Accelerated ageing causes chemical and physical changes that occur in organic materials during deterioration [3]. Pure cellulose absorbs visible light only to a small extent (380 – 550 nm), while absorption in near UV spectral region (300 – 380 nm) is more pronounced. It is therefore in that spectral range most of the damage in cellulose is induced during exposure to electromagnetic radiation [4]. Except for cellulose fibres, which can be either virgin or recovered by their origin, there are many other organic and inorganic components in the paper network structure (such as fillers, adhesives, pigments, binders, etc.) that strongly influence on the paper optical stability. The brightness (B), the lightness (L*) of the CIEL*a*b* colour system and the whiteness (W) of paper decline, while the yellowness and the b* (shift to yellow) and a* (shift to red) coordinates of the CIEL*a*b* 20 colour system increase after exposing to accelerated ageing.

In this work artificial ageing tests of thermal oxidation and photo-oxidation under Xenon arc lamp were performed on paper substrates containing non-wood barley fibres. Straw is a by-product of different kinds of crops and it's left behind harvesting in huge amount in many countries in the world. Virgin fibres isolated from agricultural residues could be a great replacement for wood fibres in some grades of paper [5, 6]. The issue of optical stability of papers are important data for defining the possible application of that particular paper.

2 EXPERIMENTAL PART

2.1 Materials

The materials studied were laboratory paper substrates in the form of 42.5 g/m^2, 20 cm diameter representing papers containing non-wood fibres isolated from barley straw. Raw material for making laboratory paper substrates were virgin barley fibres and recycled wood fibres. Barley fibres were isolated form straw after crop harvesting by chemical pulping according to two different alkaline methods (Figure 1.).

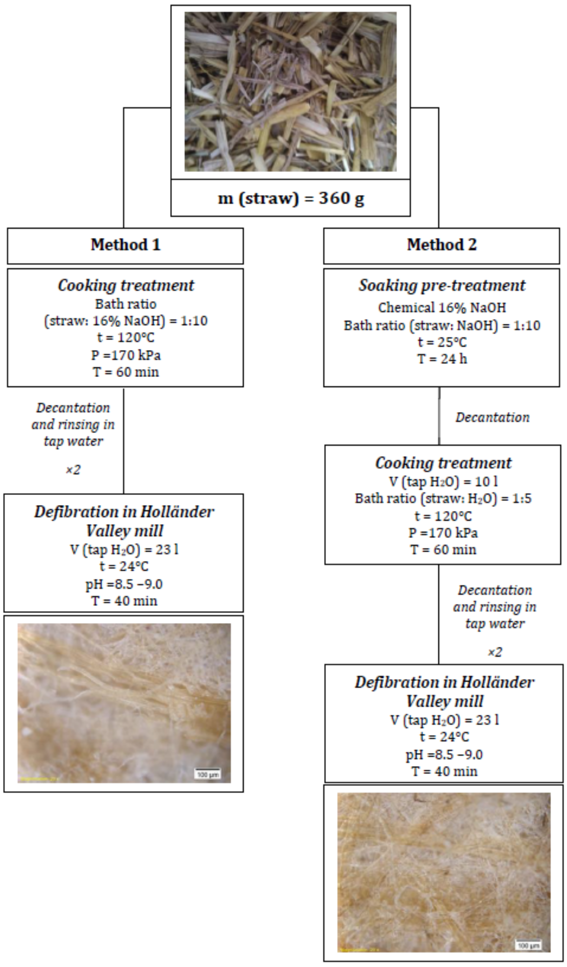

Figure 1 General process flow of cellulose isolation from straw

Each isolation method provided virgin barley fibres which were mixed together with recycled wood fibres in defined weight ratio for laboratory paper substrate production. In total, 7 different types of laboratory paper substrates (42.5 g/m^2, 20 cm diameter) were produced by

Rapid Köthen Sheet Machine and named according to Table 1. Laboratory paper substrates formed only of recycled wood fibres were used as control paper substrate in the process of comparing the optical stability of papers with non-wood straw fibres.

Table 1 Paper substrate marks and composition

Paper substrate	%		
	Recycled wood fibres	Virgin fibres isolated from barley	
		Method 1	Method 2
N	100	0	0
1NJ1	90	10	0
2NJ1	80	20	0
3NJ1	70	30	0
1NJ2	90	0	10
2NJ2	80	0	20
3NJ2	70	0	30

2.2 Methods

Aging Treatments

In order to obtain optical stability of those paper substrates under controlled degradation levels, two different accelerating ageing treatments were carried out as a simulation of different degradation processes that naturally occurs in cellulosic materials.

- *Thermal oxidation*: it was carried out on all laboratory prepared paper substrates at 60°C in oven for 24 hours in absence of light. These dry-heat accelerated ageing test is based on the standard INGEDE Method 11p where accelerated ageing conditions correspond to 1-2 months of natural ageing. It is well known that thermal oxidation induces the breakage of chemical bonds in cellulose and the formation of carbonyl, carboxyl, and hydroperoxide groups [7].

- *Photo-oxidation*: all laboratory prepared paper substrates were exposed in a Cofomegra Solarbox 1500e Xenon Test Chamber with a Xenon light source for 24 hours. Irradiation was kept at a constant power of 550W/m^2 and at a temperature of 60°C. Photooxidative reactions result in an increase of carbonyl content, carboxyl, and hydroperoxide groups [7].

Optical properties analysis

Characterisation of accelerate aged papers with non-wood barley fibres was discussed through optical properties analysis (reflectance spectra, ISO D65 brightness and Euclidean difference deteriorations) and compared to control paper substrate (marked with N). Monitored optical measurements were repeated 10 times on upper side (felt side) of each paper substrate. Papers reflectance spectra measurements were processed using SpectroEye spectrophotometer with standard illuminant D65 and 2 degree observer, in the interval of the wavelengths from 400 nm to 700 nm for every 10 nm. Spectrophotometric results are presented as average value of ten measurements of the laboratory made paper samples and were statistically processed in Origin Lab 8.0.

Reflectance spectra values (R) were measured for all samples before ageing ($R_{non\ aged}$) and after accelerated ageing (R_{aged}) and gained results are presented as ΔR according to Equation (1):

$$\Delta R = R_{non\ aged} - R_{aged} \tag{1}$$

Colorimetric analysis of the unaged and aged paper substrates were processed using Colour Touch 2 spectrophotometer (with illuminant D65) in order to determine the variation of optical properties induced by the aging treatments. Brightness, by TAPPI T 452 standard, is defined by reflection value of the observed sample on the wavelength of 457 nm, at which the reflected light is measured which passes through the blue filter. The brightness (R457) method was developed to monitor the bleaching of pulp, because at these short wavelengths (from 400 to 500 nm) reflectivity is changed the most [8]. Brightness reduction of laboratory paper substrates is corresponding to ISO 2470-2 standard. Colorimetric CIE L*a*b* values of all laboratory paper substrates before and after accelerated ageing were measured on the same spectrometer as the brightness. In the CIE L*a*b* colour space the value L* represents the lightness of the colour and the value +a* represents redness or the value –a* represents greenness, and the +b* value represents yellowness or the value –b* represents blueness [9]. The colour differences or Euclidean difference (ΔE_{00}^*) of all analysed paper substrates were calculated with the following Luo equation [10], using the corresponding starting material (unaged paper substrate) as reference:

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

3 RESULTS AND DISCUSSION

The changes in the optical stability of all laboratory made paper substrates after exposing to accelerated ageing were analysed and gained experimental results are presented at Figures 2-4.

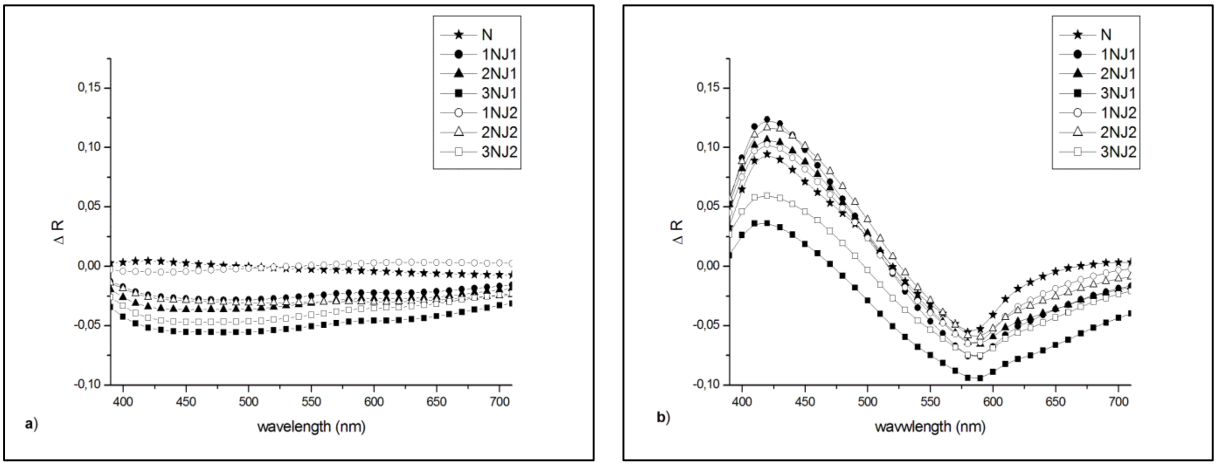

Figure 2. Relative reflectance spectra differences (ΔR) of all paper substrates influenced by: a) dry-heat accelerated ageing; b) xenon lamp accelerated ageing

It is obtained how control paper substrate (marked with N) after dry-heat accelerated ageing treatment doesn't show reflectance differences in the whole measured wavelength range (Figure 2a). The addition of barley fibres have slightly influence on optical stability of made paper substrate. Namely, all paper substrates with barley fibres (1NJ1, 2NJ1, 3NJ1, 1NJ2, 2NJ2, and 3NJ2) comparing to the control substrate gave higher monitored reflectance values after exposing them to dry-heat accelerated ageing. Maximum changes are visible in samples with a 30% weight proportion of barley fibres, whereby Method 1 used for fibres isolation achieved highest reflectance differences in the whole measured spectrum.

After exposure to UV/VIS radiation by xenon lamp all laboratory paper substrates show major changes in reflectance values (Figure 2b) compared to those aged only by thermal treatment (dry-heat). The most significant reflectance changes are noticed in the blue part of the spectrum at approx. 420 nm and in red part of the spectrum negative reflectance differences are observed at approx. 580 nm (Figure 2b). All examined paper substrates after treatment by xenon lamp have similar deviations in whole spectrum, which are increasing or decreasing depend on the weight ratio of barley fibres in paper substrates. Laboratory paper substrates made of raw materials containing 30% of barley fibres had the highest reflectance deviation, if compared to a control paper (N).

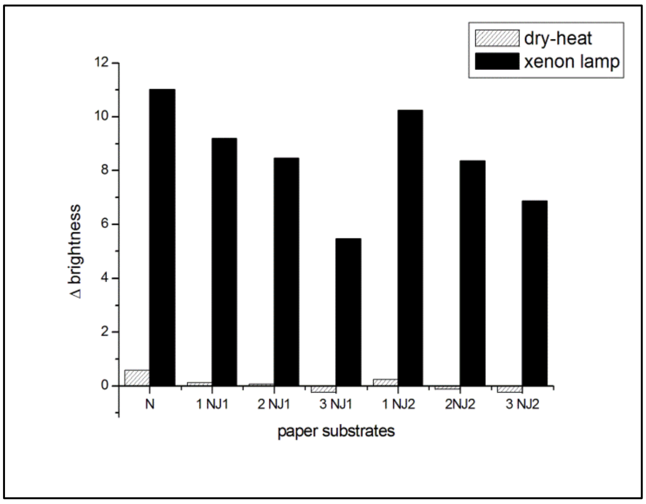

Figure 3 Brightness differences (Δ brightness) of all paper substrates influenced by dry-heat and xenon lamp accelerated ageing

Brightness differences after dry-heat and xenon lamp accelerated ageing for laboratory paper substrates made with barley fibres and control sample without barley fibres (N) are presented at Figure 3. The smallest change of brightness is visible in all substrates after dry-heat ageing, while brightness differences after xenon lamp ageing are extremely high. Degradation of paper components (cellulose, hemicellulose, lignin) caused by UV radiation is stronger than the one caused only by thermal treatment. One of the major sources of deterioration of materials made from natural fibres is affected by light. Cellulose component of paper substrates has the tendency to undergo yellowing (brightness reversion) upon exposure to the sunlight or artificial UV/VIS light. Namely pure cellulose absorbs visible light only to a small extent, while the absorption in the near UV spectral region is more pronounced [1, 11]. On the other hand, high lignin content contributes yellowing of the paper. It is general knowledge that lignin molecules, when exposed to oxygen in the air, begin to change and become less stable. The lignin will absorb more light, giving off a yellow colour. The addition of non-wood barley fibres in paper substrate compared to the control substrate (N) provides better brightness stability.

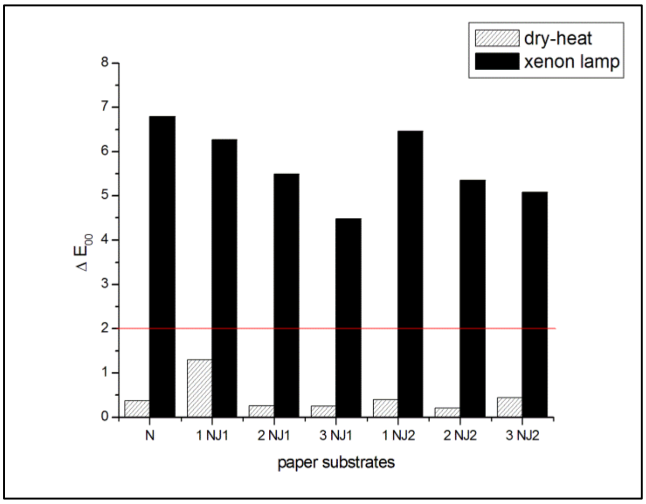

Figure 4 Euclidean differences (ΔE_{00}*) of all paper substrates influenced by dry-heat and xenon lamp accelerated ageing

The calculated colour differences or Euclidean difference (ΔE_{00}*) values by equation 2 shows same trend as the gained brightness differences. Colour difference values caused by dry-heat ageing are minor, while the differences values are up to ΔE_{00}*=7 for paper substrates aged by xenon lamp (Figure 4.). Namely, according to tolerance definition ΔE_{00}*≤ 2 is classified as very small noticeable difference for standard observer while ΔE_{00}*=5 is defined like big noticeable difference in the colour whose standard observer can recognized [12].

3 CONCLUSION

The aim of the research was to point out the influence of non-wood barley fibres in paper substrates on the optical stability of papers after exposing them to accelerated ageing. Taking into account all obtained results, the following could be concluded:

- Both used methods for fibres isolation from straw (Method 1 and Method 2) provide barley fibres which form paper substrates of approximately equal optical stability.
- After both used accelerated ageing techniques it was noticed that dry-heat accelerated ageing demonstrate negligible optical changes of all observed paper substrates.
- UV/VIS radiation significantly affects the optical deterioration of all paper substrates.

- The addition of 30% barley fibres in paper suspension, regardless of their isolation method, provide better optical stability then paper substrates made only from recycled fibres.

- Virgin barley fibres in paper substrates exposed to UV radiation improve the optical resistance of the paper substrate.

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