Bulgarian Chemical Communications, Volume 49, Special Issue L (pp. 126 – 129) 2017

Investigation of color characteristics changes of semi chemical pulp samples in process of ageing

R. Boeva[1]*, I. Spiridonov[1], Ž. Pavlović[2], G. Vladić[2]

[1]*Department of Pulp, Paper and Printing Art, University of Chemical Technology and Metallurgy, 8, Kl. Ohridski Blvd., 1756 Sofia, Bulgaria*

[2]*Department of Graphic Engineering and Design, Faculty of Technical Sciences, University of Novi Sad, Serbia*

Submitted November 26, 2016; Revised February 3, 2017

The fibrous species are the main raw materials needed for production of the various types of papers for printing and graphic industry, corrugated boards and packaging papers. Because of increasing demands, lack of materials, high value of raw fiber resources and of course of ecological reasons – there is substantial and increasing necessity of processing of wood for manufacturing of high yield fibrous material (HYFM).

In this study was utilized semi chemical pulp which was obtained from hardwood fibrous material.

The semi chemical pulp used in experiment was bleached in two different stages. It have been performed investigation of the changes in the optical properties of bleached and unbleached type of fibrous materials before and after artificially thermal ageing at of 105°C at 0, 6, 12, 24 and 36h.

For complete characterization of obtained and tested materials it have been made a complete characterization and estimating of color characteristics and differences in CIE Lab system during all of processing and ageing. The changes in the optical properties and colors before and after aging have been determined.

The experimental results and properties of samples in this study shows that the tested Semi Chemical Pulp hardwoods could be used completely for producing of corrugated boards and added to packing papers composition. The benefits of replacement of cellulose with semi chemical pulp are leading to cheaper and more ecological products for printing and packing industry.

Key words: semi chemical pulp, fiber materials, thermal ageing, corrugated cardboard, packing paper

1. INTRODUCTION

The main raw materials for the production of paper and paperboard - fibrous material are derived from various types of wood or annual plant materials by treatment with chemical reagents under certain conditions.

The advantages of HYFM (high yield fiber materials) are almost complete preservation of the original chemical composition of the starting timber or only partial dissolution of lignin and hemicelluloses. The usage of HYFM in the composition of high quality papers and boards are limited by their low degree of brightness. This necessitates them to be bleached [1, 2].

The availability in the mass of HYFM of heavy metal ions such as Fe^{3+}, Mn^{2+}, Cu^{2+} etc., are affecting at the bleaching process. The whitening effect becomes smaller and this causes in increasing expense of bleaching agent. In order to prevent the influence of metal ions are used complexing agents. For this purpose most often are used polyphosphates, EDTA, etc. The result is increasing of degree of brightness with additionally approx. 3%. Ageing processes of HYFM are very intensive, which acceleration is a consequence of the higher content of lignin [5].

In the study an investigation of color characteristics changes of semi chemical pulp samples of in process of ageing after two bleaching process is conducted.

2. EXPERIMENTAL

Production of CMP

As a fibrous material in this work is used neutral-sulphite semi chemical pulp (SCP), produced in the factory conditions from hardwood. Bleaching reagents are used: H_2O_2, pure analysis, Rongalyt C from BASF [2, 3].

The composition of the bleaching solution, $H2O2$ stabilizers are used - Na_2SiO_3 and $MgSO_4$. To achieve the required pH of about 10.5 is added NaOH. As complexing agents for connecting of heavy metal ions is used a solution of EDTA – 0.5%.

Bleaching of the semi chemical pulps

The conditions of the bleaching process (established in previous investigations) are shown in Table 1. Semi chemical pulps are treated at the two-stage bleaching:

- First stage of bleaching – with H_2O_2;
- Second stage of bleaching - Rongalite C from BASF.

*) To whom all correspondence should be sent:
E-mail: r_boeva@abv.bg

Table 1. Conditions of bleaching semi chemical pulp

Type of Bleaching	Quantity of reagent, (%)	T, (°C)	Duration of process, (min)	Concentration of fibrous materials, (%)	pH of the solution
I stage	2% H_2O_2	75	120	10	10.5
II stage	1.5% Rongalyt C	75	60	6	5

First stage of bleaching

In a first degree of bleaching for maintaining pH=10.5 are used additives of: NaOH - 2%, Na_2SiO_3 - 5%, $MgSO_4$ - 0.5%. For binding of heavy metal ions is used EDTA - 0.5%.

In order to achieve better degree of brightness, it is required to ensure mixing of the fiber material and facilitating the uniformly distribution of whitening mixture. After completion of the first stage of the bleaching fiber material is washed to pH=7 and then passes to the second degree of bleaching.

The fibrous mass is placed in a polyethylene bag where the bleaching solution is poured. The additional reagents are added and the solution is mixed till reaching complete homogenization. Later the bag is placed in thermostatic container which ensures constant temperature during the whole process of bleaching. In order to achieve better degree of degree of brightness, it is required to ensure mixing of the fiber material, thus facilitating the uniformly distribution of whitening mixture [2, 3, 6, 7].

Second stage of bleaching

In the bleaching of SCP in second degree is used Rongalit C ($NaHSO_2.CH_2O.2H_2O$) and EDTA - 0.5%, and the conditions are shown in Table 1. The process of bleaching is similar to the one described in the first stage. After completion of the process, the fibrous mass is washed away again to adjust pH 7.

Ageing of fibrous materials

The samples of both bleached and unbleached fiber materials, are dried and then submitted to artificial thermal ageing. Are determined the degree of brightness and yellowness for 0, 6, 12, 24 and 36 hours from the beginning of artificial thermal aging at 105°C.

For a more complete characterization the color characteristics are measured with a densitometer-spectrophotometer under the following conditions: standard light illuminant - D65, standard observer - 10°, geometry of measurement 45°/0° or 0°/ 45°, polarizing filter.

In the system CIE L*a*b* are measured the following main parameters: CIE L* (lightness), CIE a* - red-green coordinate, CIE b* - yellow-blue coordinate.

3. RESULT AND DISCUSSION

The utilization of HYFM in various brands of paper and cardboard is limited because of the low level of whiteness. SCP is bleached in two stages. After the bleaching is conducted artificial thermal ageing at 105°C.

Picture1. Semi chemical pulps.

By advancing the process of artificial thermal ageing change the brightness decreased most at the beginning of the process ageing.

In order to track the influence of ageing at 105°C on the properties of various fibrous materials, bleached and unbleached has traced change of the degree of Brightness and Yellowness over time (0, 6, 12, 24 and 36h).

On Fig. 1 and 2 are presented the kinetic regularities showing these changes in the brightness and yellowness of SCP depending on time at 90°C.

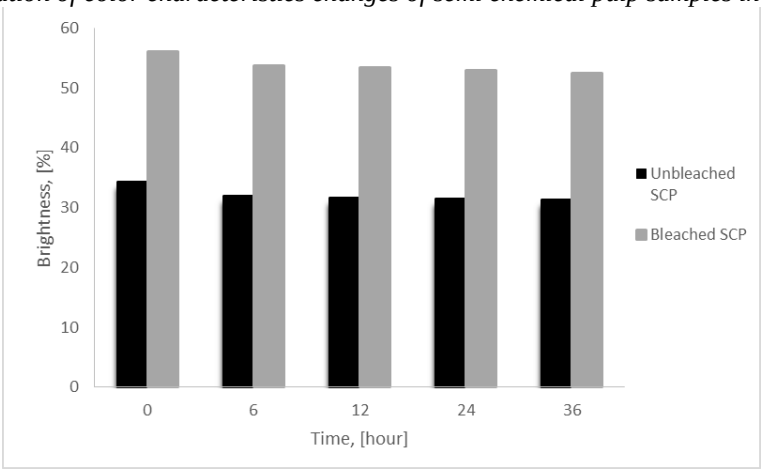

Fig. 1. Change of the Brightness of the bleached and unbleached samples of SCP in artificial ageing of 90°C

Fig. 1 shows that the degree of Brightness decreases at all samples, regardless of the manner of obtaining and bleaching of fibrous materials, but in differing amounts. It is seen further that the higher degree of brightness of the bleached samples were reserves in the process of artificial thermal ageing. There is a difference in the change in the degree of brightness in relation of the starting brightness depending on the conditions of obtaining and type of bleaching of the corresponding fibrous material. All this results shows that the fibrous materials and their production of paper and paperboard must be used and stored at lower temperatures.

Fig. 2 shows that the degree of Yellowness increase at all samples in the process of artificial thermal aging with the progress of the process.

In Table 2 are presented CIE L*a*b* color characteristics of the bleached and unbleached SCP samples before and after ageing.

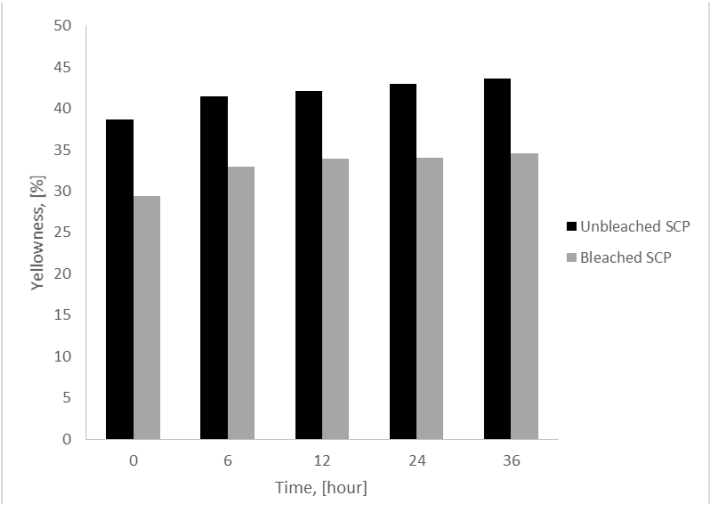

Fig. 2. Change of the Yellowness of the different samples of SCP in artificial ageing of 90°C.

Table 2. Color characteristics of the bleached and unbleached SCP samples before and after ageing

Type of samples	Before ageing			After ageing		
	L*	a*	b*	L*	a*	b*
Unbleached SCP	68.38	7.95	18.61	70.12	7.68	20.54
Bleached SCP	84.41	2.95	17.96	83.71	3.30	19.46

Unbleached semi-chemical pulp has higher values of CIE b* during the ageing, indicating that there is a color shifting in yellow direction – Db=1.93. Before and after the ageing the CIE a* coordinate of Unbleached SCP has the relatively same values, comparable to measurement accuracy. The obtained results for Bleached SCP are similar - higher values of CIE b* during the ageing, indicates color shifting in yellow direction – Db=1.5.

The value of color difference - DE_{ab} before and after ageing of Unbleached SCP (DE_{ab} =2.83) is approximately two times bigger than Bleached SCP (DE_{ab} =1.69). The reason is better chemical stability resulting at less color shifting at bleached samples during the artificial ageing process.

3. CONCLUSIONS

On the basis of the present investigation it is established:

- The conducted two stage bleaching increases the degree of brightness of SCP. This expands the possibilities for its use in preparing various types of paper, cardboard and their production of packaging.
- At ageing of fibrous materials, they modify their optical properties. Conducted artificial thermal ageing at 105°C showed a decrease in the degree of brightness in different degrees in the studied samples.
- Unbleached SCP has higher values of CIE b* during the ageing, indicating that there is a color shifting in yellow direction. Before and after the ageing the CIE a* coordinate of Unbleached SCP has the relatively same values, comparable to measurement accuracy. The obtained results for Bleached SCP are similar - higher values of CIE b* during the ageing, indicates color shifting in yellow direction.
- The value of color difference - DEab before and after ageing of Unbleached SCP is approximately two times bigger than Bleached SCP. The reason is better chemical stability resulting at less color shifting at bleached samples during the artificial ageing process.

Acknowledgments:*The authors thank the Scientific Research Centre (contract №11523) at the UCTM Sofia for the financial support of these investigations.*

REFERENCES

1. L. Wilson, What the printer should know about paper, Moscow, 2005.
2. R. Boeva-Spiridonova, E. Petkova, *J. Chem. Technol. Metall.*, **42**, 41 (2007).
3. R. Boeva, G. Radeva, *J. Chem. Technol. Metall.*, **49**, 585 (2014).
4. K. M. Han, R. Dharmawardhana, R. S. Arias, C. Ma, V. Busov, S. H. Strauss, *Plant Biotechnol J*, **9**, 162 (2011).
5. M. El-Sakhawy, *Polymer Degrad. Stability*, **87,** 419 (2005).
6. M. Area, H. Cheradame, *BioResources*, **6,** 5307 (2011).
7. Z. Zhou, A. Jääskeläinen, I. Adorjan, A. Potthast,P. Kosma,T. Vuorinen, *Holzforschung*, **65**, 289 (2011).
8. N. Kachin, I. Spiridonov, *Cellulose Chem. Technol.*, **39**, 255 (2004).
9. N. Kachin, I. Spiridonov, Printing Processes, Part 1, Theoretical bases, Pleiada, Sofia, 2000.

ИЗСЛЕДВАНЕ НА ПРОМЕНИТЕ В ЦВЕТОВИТЕ ХАРАКТЕРИСТИКИ НА ОБРАЗЦИ ОТ ПОЛУЦЕЛУЛОЗНА МАСА В ПРОЦЕСА НА СТАРЕЕНЕ

Р. Боева[1]*, И. Спиридонов[1], Ж. Павлович[2], Г. Владич[2]

[1]Катедра „Целулоза, хартия и полиграфия“, Химикотехнологичен и металургичен университет, бул. „Климент Охридски“ 8, България,
[2]Катедра по графично инженерство и дизайн, Университет в Нови Сад, Факултет по технически науки, Нови Сад, Сърбия

Постъпила на 26 ноември, 2016 г.; приета за печат на 3 Февруари, 2017 г.

(Резюме)

Влакнестите материали са основната суровина, необходима за производството на различни видове хартии и картони за нуждите на полиграфичната и опаковъчната промишленост. Поради нарастващите изисквания към суровинните ресурси и влакнестите материали и разбира се по екологични причини - съществува необходимост от преработването на дървесината за производството на високодобивни влакнести материали (ВДВМ).

Като влакнест материал в това изследване е използвана полуцелулоза, получена от широколистна дървесина. Полуцелулозата е избелена двустепенно. Проследени са измененията в оптичните свойства на влакнестите материали (в избелен и неизбелен вид) преди и след изкуствено термично стареене от 105ºС на 0, 6, 12, 24 and 36h.

За цялостно охарактеризиране на получените материали е извършена оценка на цветовите характеристики в системата CIE Lab по време на стареене. Определени са промените в оптичните свойства и цветовите характеристики преди и след стареене.

Получените резултати от изследваните образци показват, че полуцелулозата има добри свойства и може успешно да се използва при производството на различни видове хартии и картони. Ползите от замяната на целулозата с полуцелулоза водят до получаване на по-евтини и по-екологични продукти за печатната и опаковъчната промишленост и в някой случаи и до по-добри показатели.