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Evaluation of changes in the optical properties of high yield fibrous materials under thermal treatment

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The plants raw materials are huge source with good stock and annualy renewable origin of fibers which are needed for different kinds of industries. The wood is one of the most important and easy for processing and treatment raw material for humanity. The wood consists of non-homogenous organic matter, which after chemical and mechanical treatment converts to fibrous materials. The Cellulose is one of the most important components obtained from fibrous materials. Another very actual and usable material in present day is the high yield fibrous material. This material is suitable and perspective for using in composition of packing papers and corrugated boards.

Except the well-known and usable wood species like *Populus* in the last years in many regions like South-East Europe there is a big demand and interest for *Paulownia*. The *Paulownia* belongs to group of fast growing hardwood species, which makes it one of perspective sources of high yield fibrous materials.

In this research chemical mechanical pulps (CMP) from *Populus* and *Paulownia* woods are obtained. Then they were bleached in two stages with H_2O_2 and Rongalyt C.

The artificial thermal ageing has been made. The measuring, tracing and evaluation of optical properties have been performed of the obtained CMP before and after artificial ageing at temperature of 90°C for 0, 6, 12, 24, 36, 48 and 72h.

The aim of this work is to obtain chemical mechanical masses of *Populus* wood and *Paulownia* wood, to bleach them, to age at 90°C and evaluate their optical and color characteristics.

Key words: *fiber materials, thermal ageing, corrugated cardboard, packing industry, chemical mechanical pulp*

1. INTRODUCTION

The timber as natural source and after improving of its properties or after its revision is a universal raw material for meeting various human needs [1, 2].

Fibrous materials with yield of over 65% from the starting raw material are called high-yield. The high yield is due to the initial composition of the starting material or due to partial dissolution of lignin and hemicelluloses [3].

The process of bleaching of high yield fibrous materials differs from bleaching process of pulp. The aim of bleaching of high yield fibrous materials is to discolor lignin and other coloring substances in such manner that they not pass in solution, i.e. without degradation to products with low molecular weight, soluble in water or in alkali solutions [4 - 6].

There are three basic methods for bleaching of high yield fibrous materials: by oxidation, by reducing agents and combined bleaching. To achieve the best results it is preferable to use a combined bleaching.

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Over time, during prolonged storage of each fiber material irreversible changes in its properties occur. This process is accompanied by changes in the chemical composition and reduction of mechanical strength of material. Ageing of the fibrous materials is a complex process whose nature has not yet been sufficiently clarified, as in the course of this process many factors influence - the type and chemical composition of the fibrous material, pH of the medium, storage conditions, the degree of impact of light rays on the fibers and microbiological factors.

The thermal aging is due to oxidative processes that take place under the action of heat, air oxygen, and hydrolysis under the action of moisture or of their synergy action. Thermal destruction is associated with decrease of strength and causes smaller or greater changes in the chemical composition and properties. The content of lignin is the main factor which depends on the ageing of the fibrous mass [3, 7].

Features and characteristics of *Paulownia* species. *Paulownia* from family Scrophulariaceae includes nine highly adaptive species with valuable timber. These are: *P. elongata, P. tomentosa, P.*

fortuneii, P. australis, P. fargesii, P. albiphloea, P. catalpifolia, P. taiwaniana and P. kawakamii [6].

Paulownia Populus

All species of the genus *Paulownia* are fast growing with excellent timber, but most promising in this respect are *P. elongata* (the emerald tree) and *P. fortunei*, which for 8-10 years can reach 20m tall and a trunk diameter of 30-40cm.

Features and characteristics of species *Populus.* *Populus* are kind of fast-growing wood species. They reach a height of about 25m. They grow quickly and live up to 400 years. Typical for poplar is that it has large number of equally spaced conductive vessels that allow increasing the area of interaction with chemical reagents during chemical processing [2, 4, 5, 7].

2. EXPERIMENTAL

Used raw materials

The wood is split into chips with standard size 15x20x3mm [1].

The fibrous materials used in this study are: CMP - chemical mechanical pulp from poplar wood from species *Populus deltoides clon* - 235-15, obtained in the laboratory; CMP – from timber of *P. tomentosa*, obtained in laboratory conditions.

For obtaining CMP the following chemical reagents are used: Na_2SO_3, pure analysis, NaOH. Bleaching reagents are: H_2O_2, Rongalyt C ($NaHSO_2.CH_2O.2H_2O$), supplied by BASF;

The reagents Na_2SiO_3 and MgSO4 were applied for stabilization of H_2O_2. NaOH was added to reach the pre-determined pH level (10.5). In order to bond the metals ions, the pulp was treated with the complexion agent EDTA. The following parameters of the produced CMP have been determined: Yield [%], determined by weight method in comparison to the mass of the absolutely dry timber; Grinding degree, as determined by the device Schopper – Riegler (°SR) per EN ISO 5267 – 1/AC: 2004; Microscopic analysis of the fibers determined on a light microscope OLYMPUS DX53.

For all used fibrous materials the degree of Brightness R457 (ISO 2470:2002) was determined before and after ageing thanks to the appliance by Spectrophotometer Gretag Magbeth Spectroeye.

A. Production of CMP. Production of CMP is performed according to preliminary determined optimal regime: NaOH 7%, Na_2SO_3 5%, temperature 80°C, treatment duration - 120 min and liquor-to-wood ratio 1:5.

Chips from poplar wood and wood species *Paulownia* with standard size are digested. Chips pour with required amount of solution of NaOH and Na_2SO_3 and placed in a tempering container to maintain a constant temperature.

After completion of specified period according to the technological regime, the used solution was removed and the chips have been washed to neutral reaction. The treatment continued by chips refining in a Sprout-Valdron laboratory mechanical refiner. Further fiber materials was washed away and sorted out manually between two sieves.

The yield of CMP is calculated by the mass method. After soaking for 24 hours in distilled water, the treated chips were washed to reach neutral pH and dried into a drying apparatus at 105°C to achieve absolute dry state.

The yield of CMP is determined by weight method. After 24 hours soaking in distilled water, chips were washed until neutral reaction and dried to constant weight at 105°C

B. Bleaching of the different types of fibrous materials. The samples of CMP are bleached in two-stage: I stage - bleaching with H_2O_2, II stage - bleaching with Rongalyt C. The conditions of bleaching are given in Table 1.

Table 1. Conditions of bleaching CMP

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	80	120	10	10.5
II stage	1.5% Rongalyt C	80	60	6	5

First stage of bleaching

First-degree bleaching is performed with H_2O_2 - 2%. To maintain pH = 10.5 additives of NaOH - 2%, Na_2SiO_3 - 5%, $MgSO_4$ - 0.5% were used. For binding of heavy metal ions EDTA - 0.5% is used. All reagents are expressed in percent with respect to absolutely dry fibrous material.

Certain amount of fibrous material is weighted and placed in a plastic bag. In it a bleaching solution is added and the mass is stirred to complete homogenization. Then the bag is placed in a thermostatic container that provides a constant temperature in time of bleaching. The fibrous mass in the bag is homogenized periodically to ensure uniform bleaching.

This scheme applies to both fibrous materials. After completion of the first stage of the bleaching fiber material is washed to pH = 7 and then the second stage of bleaching is performed.

Second stage of bleaching

In time of bleaching of both fibrous materials in the second stage Rongalit C - 1.5% and EDTA - 0.5% are used under conditions shown in Table 1. The method of bleaching is similar to those used in the first stage. After completion of the bleaching process the fibrous mass is washed again to pH = 7.

Samples of all fibrous materials before and after bleaching have been prepared. After drying of these samples the degree of brightness and yellowness is determined.

C. *Ageing of CMP.* Samples of unbleached, single-step bleached and two-steps bleached CMP were subjected to thermal ageing for 72 hours at temperature of 90°C. For all used fibrous materials the degree of Brightness R457 (ISO 2470:2002) was determined before and after ageing thanks to the appliance by Spectrophotometer Gretag Magbeth Spectroeye. Furthermore, the degree of brightness of bleached samples was determined at the 0th, 6th, 12th, 24th, 36th, 48th and 72th hours from the start of the artificial thermal ageing [2, 3, 5 and 7].

Microscopic analysis of fibrous materials

Microscopic images have been made by light microscope OLYMPUS BH 53. Before observations a small part of study mass was taken and placed in a test tube. Distilled water is added and mass is shaken vigorously until a uniform suspension with concentration of about 0.05% is obtained. A few drops of fibrous suspension are applied to a slide. Excess water is removed with filter paper. Carefully the fibers are distributed in the drop and later the drop is dried under a lamp at a temperature of about 60°C. Once the slide is cooled for a while a drop of staining solution is applied on the fibers and they are covered with a glass roof, making sure no air. As staining solution for identifying the fibrous material a reagent of Herzberg (ISO 9184-3: 1990) - [Cl-Zn-I] is used.

3. RESULTS AND DISCUSSION

The results data of the chemical analysis and physical characteristics of the two types of woods are: for *Populus deltoides clon* - 235-15 lignin is (21%), cellulose (50.9%), for *Paulownia Tomentosa* lignin e (20.2%) and cellulose (39.2%). The yield and grinding degree of resulting CMP are defined: the yield of the type *Paulownia tomentosa* is 86% and 13°SR, the yield the type *Populus deltoids clon* -235-15 is 88% and 12°SR.

CMP are bleached in two stages. The artificial thermal ageing of bleached and unbleached under different conditions CMP is made. In order to study the kinetics of the process a thermal aging is carried out at temperature of 90°C. The change of the degree of whiteness with time of 0, 6, 12, 24, 36, 48 and 72 hour s was observed. The obtained kinetic curves of Fig 3 and 4 *(Paulownia* and *Populus*) show that whiteness declines over time; the process is accelerated with increasing of temperature.

Figure 1 shows the changes of brightness at the process of artificial ageing. Figure 2 shows the changes of the yellowness at the process of artificial ageing. From Fig. 1 it can be seen that the degree of whiteness decreases for all fibrous materials. In the same conditions of preparation and bleaching of fibrous masses higher degree of whiteness is achieved with the samples of *Paulownia*.

From Fig. 2 it can be seen that regardless of the type of test specimens their yellowness (%) is increased with time. There are almost identical values for yellowness of unbleached CPM of *Paulowvnia* and two-stage bleached poplar CPM.

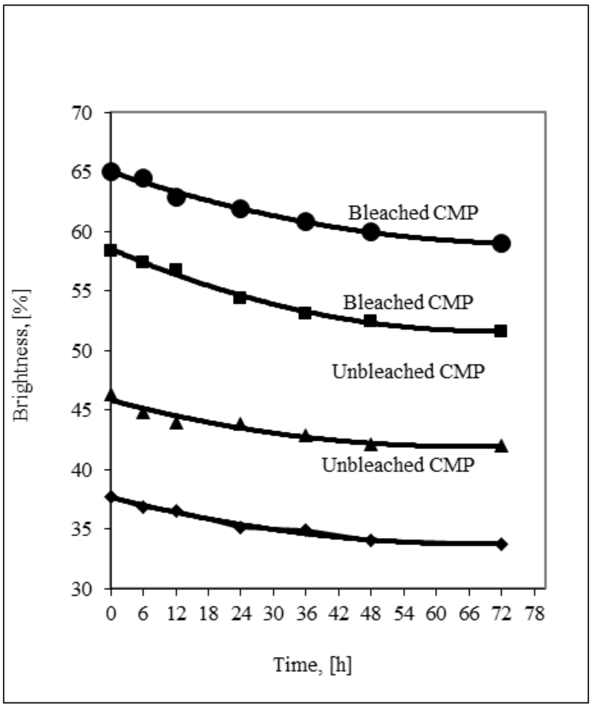


Fig. 1. Change in the degree of Brightness of bleached and unbleached CMP samples in artificial thermal ageing at 90°C.

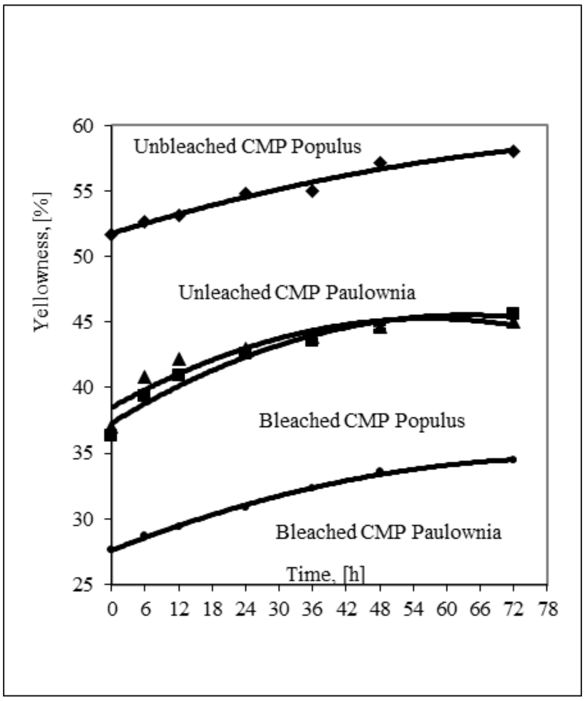
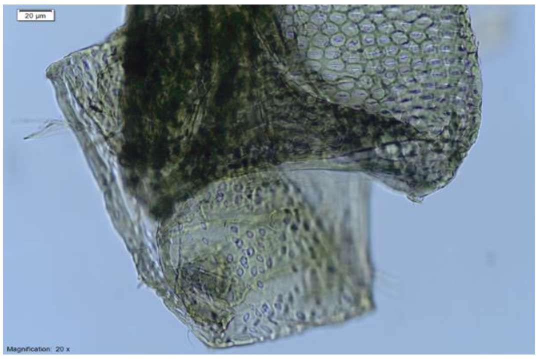


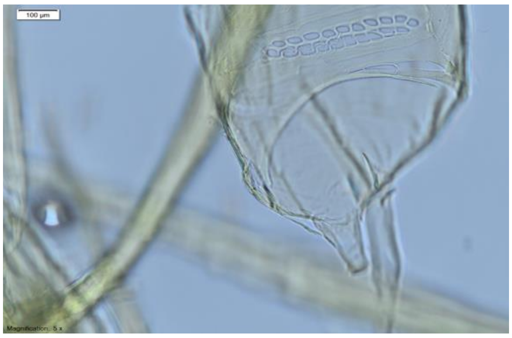
Fig. 2 Change in the degree of Yellowness of bleached and unbleached CMP samples in artificial thermal ageing at 90°C**.**

From Figures 1 and 2 (at 90°C) it can be seen that CPM from *Paulowvnia* in bleached and unbleached state the degree of whiteness is higher and the degree of yellowness is lower compared to bleached and unbleached CPM of *Populus*. CPM from *Paulowvnia* has better properties regardless of the way they are received and bleached.

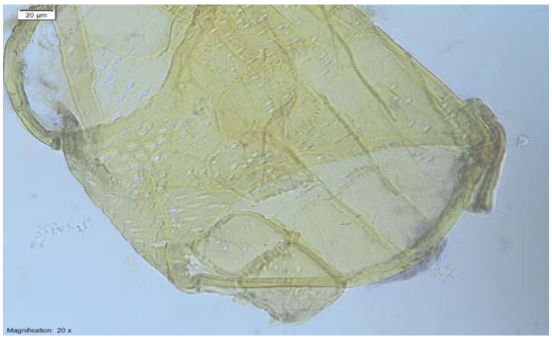
Ageing is a complicated process which does not obey formal kinetic principles. The reaction proceeds usually on certain places called active centers, which over time deplete. The active centers are in fact different functional groups primarily of lignin, which in time of the ageing process due the oxidation can form conjugated double bonds with aromatic ring. This way the destroyed during bleaching chromophores can recover. The next microscopic images are made from different CMP.



Picture 1. Unbleached CMP of *Paulownia* **Picture 2.** Bleached two-stage CMP of *Paulownia*



Picture 3. Unbleached CMP of *Populus*



Picture 4. Bleached two-stage CMP of *Populus*

At pictures 1 and 3 (unbleached CPM of *Paulownia*) characteristic elements of CPM - coarse fibers with uneven and irregular shape can be seen. They are typical for hardwood structural elements - the trachea, libroform cells and torn fibers, probably from production and grinding of fibrous mass. Tracheas have tapered edges.

Picture 2 shows structural elements which have more twisted and more disorganized parts in comparison to those who did not undergo drastic conditions of bleaching.

Picture 3 shows typical poplar wood vessels with open ends with extensions. There are sections of fibers with torn edges, preferably bundles of fibers and also small particles.

Picture 4 shows samples of poplar after bleaching. Characteristic fibers can be seen: with pores and libroform bundles of fibers and vessels with varying size and shape as thick tubes with mesh construction. More wide and shorter fibers typical for hardwood and wide variety of structural elements are well visible, in comparison with softwood.

If compare structural components of the microscopic images of two types of wood *Populus* and *Paulownia*, we can say that *Populus* has smaller number of pores in the walls of trachea and smaller number of tracheas which leads to higher density of poplar wood. The presence of tracheas negatively affects physical and mechanical properties of fibrous materials, but improves water permeability.

4. CONCLUSIONS

1. Poplar wood and wood from *Paulowvnia* are fast-growing hardwood species. Poplar wood has a density (451kg/m^3) and rich carbohydrate part, suitable for obtaining of CMP

2. Chemical-mechanical masses of species *Populus deltoides clon* - 235-15 and *Paulownia tomentosa* are obtained at pre-established regime with yield respectively 88% and 86%, and degree of grinding respectively 12ºSR and 13ºSR.

3. Microscopic pictures show typical for hardwood species large numbers of structural elements and larger numbers of pores in the walls of the trachea, which is indicative for their lower density, especially for type *Paulownia*;

4. CPM after two-stage bleaching reaches whiteness for *Paulownia tomentosa* 65.6% and for *Populus deltoides clon* **-** 235-15- 57.99%;

5. At the same conditions of obtaining and bleaching *Paulownia* tomentosa has higher degree of whiteness [%] and lower degree of yellowness, which is maintained in the aging process too.

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ИЗСЛЕДВАНЕ НА ПРОМЕНИТЕ В ОПТИЧНИТЕ СВОЙСТВА НА ВИСОКОДОБИВНИТЕ ВЛАКНЕСТИ МАТЕРИАЛИ ПРИ ТЕРМИЧНА ОБРАБОТКА

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(Резюме)

Растителните суровини са голям и ежегодно възобновявящ своите резерви суровинен източник. Дървесината е не само една от най-старите и най-лесно обработваните суровини, но и една от най-важните за човечеството. По своята същност тя е нехомогенна органична материя чрез чиято химична преработка се превръща в различни видове влакнести материали. От тях се използва предимно целулозата, но днес интерес представляват и високодобивните влакнести материали. Този материал е подходящ и перспективен за използване в състава на различни видове опаковъчни хартии и картони.
Освен добре познатия ни дървесен вид *Populus*, през последните години в Югоизточна Европа има интерес към изследване и използване на вида *Paulownia*, който също спада към групата на бързо растящите дървесни широколистни видове и прави този вид един от перспективните източници на високодобивни влакнести материали.

От двете дървесини са получени химикомеханични маси (ХММ). След това те са избелени двустепенно (H_2O_2 and Rongalyt C) и подложени на термично стареене.

Проследени са измененията в оптичните свойства на получените ХММ преди и след изкуствено термично стареене от 90^{o}C на 0, 6, 12, 24, 36, 48 and 72h. Направен е микроскопски анализ на получените влакнести материали.

Целта на настоящето изследване е получаване, избелване и стареене при 90^{o}C на химикомеханични маси, получени от тополова (*Populus*) дървесина и дървесина от *Paulownia* и оценяване промените в оптичните и цветови характеристики.