ATOMIC FORCE MICROSCOPY: DIFFERENT APPROACH TO DISCOVER THE PAPER

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Abstract

Natural fibers were used as material in paper industry for centuries and then their use decayed. Currently, it is considered a new normal course to include natural fibres in the technology of production of paper as resource with high potential to be available in many countries, especially where the wood is not available. Paper sheets containing pulp from second category fibers, SCF, consisting of a mixture of bleached pulp of very short cotton fibers and chemical degumming hemp tow and respectively, from long wooden kraft, were attained. In the bleaching procedure of SCF was used peroxide delignification procedure, in the presence of a polyoxometalate ($Na_2H_3PMo_{10}V_2O_{40}$) as oxidative reagent, in aqueous solution. Paper sheets containing bleached long wooden kraft were also obtained. Mechanical, optical, and surface characteristics (atomic force microscopy) analyses of these two types of paper sheets were determined to evaluate the possible application of the SCF to be used in paper industry.

Keywords

Atomic force microscopy, hemp, paper, peroxide bleaching, polyoxometalate

1. Introduction

Natural fibers used for paper and packaging production are very diverse due to ample resources available world-wide. As the prices for obtaining paper and packaging from wooden plants are high, and the wood resources are modest in some regions of the world, new alternatives are examined in order to use annual plant fibers (e.g. cotton, flax, sisal, hemp). Another resource represent the textile wastes, which arise during manufacturing of yarn and textile fabrics, that could be used to obtain high quality paper, bacterial cellulose [1], chemically modified cellulose [2-4], and also for low grade applications (car insulation, seat stuffing, fibres for upholstery, and even building materials). The wood and non-wooden plant (e.g. flax, hemp, cotton, etc.) pulps contain residual lignin that is responsible for the yellow and even brown color of the pulp. Usually the lignin has to be removed from the pulp by delignification and this process should be selective and not harmful for the physico-chemical properties of the bleached pulp. Ecologic-friendly technologies, such as hydrogen peroxide, oxygen, ozone bleaching are alternatives to conventional chlorine-based bleaching technologies of the pulps[5]. Polyoxometalates (POMs) were reported to be used in both anaerobic and aerobic conditions of delignification of the lignocellulosic pulps of wooden plants [6]. In the anaerobic conditions the reoxidation of POM reagents is demanded in order to be reused in a secondary stage. In the application of POM as catalyst, in aerobic conditions, POM oxidizes the lignin from pulp and the reduced form of POM is reoxidized by molecular oxygen in the same phase. The Keggin type polyoxometalates were reported to be the most suitable POMs for the delignification process [6]. POMs used in delignification process are: $[PV_2Mo_{10}O_{40}]^{5}$-, $[SiW_{11}O_{40}]$ [7], $Na_{5(+2)}[Si_{1(-0.1)}MoW_{10(+0.1)}O_{40}]$ [8], $[SiW_{11}VO_{40}]_{5-}$ [9], $[SiW_{10}V_2O_{40}]^{6}$-, $[AlVW_{11}O_{40}]^{6-}$ [10], $[SiW_{11}Mn(H_2O)O_{39}]^{6-}$ [11], $[PMo_{12}\text{-}nVnO_{40}]^{(3+n)}$- (n = 1-6) [12,7].

Usually, the main physical characteristics of the paper samples (tensile strength and stiffness, breaking length, bursting strength, opacity, etc.) are evaluated using common methods and commercially available devices.

Advances in morphological characterization in cellulose research use the application of atomic force microscopy (AFM). AFM was previously used to determine the surface topography of conducting and non-conducting samples at macro- and nano-scale and also to measure surface forces and nano-mechanical properties [13]. AFM was used to determine the nanoscale structures of paper and/or cellulose, respectively, such as microfibrils [14,15], cellulose model surfaces [16] or to evaluate the structural changes of cellulose caused by process or morphology changes caused by different treatments [17-19]. Chemically modified hemp fibers suitable for thermoplastics or concrete composites [20], hardwood and softwood nanofibrillar model films [21] were also evaluated by AFM.

In the present study we have used pulp obtained from second category fibers (SCF) which contain a mixture of very short cotton fibers and chemical degumming hemp tow (Cannabis sativa L.) to attained specialty paper. Another aim of the present work was the bleaching of the SCF, accomplished by the removal of the lignin in a selective manner by using hydrogen peroxide and a polyoxometalate ($Na_2H_3PMo_{10}V_2O_{40}$) as oxidation reagent.

Materials and methods

Materials and reagents

A commercial bleached long wooden kraft pulp with the following features: burst index 6.9 kPa m^2/g; tear index 10.3 mN m^2/g; breaking length 10,500 m; opacity 88 % (Pols, Heintzel AG, Austria) has been used. The long wooden pulp has been refined to 30º SR according to ISO 5267. These data were obtained from the pulp suppliers. Second category fibers, SCF, contained 60 % very short cotton fibers (1-1.5 cm) and 40 % chemical degumming hemp tow (up to 2 cm in length). Hemp was obtained from Faltin S.A. (Falticeni, Romania). Chemicals and reagents (V_2O_5, MoO_3, H_3PO_4, Na_2CO_3, H_2O_2) used to obtain $Na_2H_3PMo_{10}V_2O_{40}$ had synthesis grade (Sigma-Aldrich).

Sample preparation

The mixture of natural fibers (cotton and chemical degumming hemp tow), 130 g, was bleached with hydrogen peroxide in the presence of polyoxometalate (POM), dried, and subjected to cutting and shredding processes up to 0.5 cm. The chemical degumming of the hemp tow has been done in FI-RI VIGONIA S.A. (Timisoara, Romania), accordingly to the method described in 22.

$Na_2H_3PMo_{10}V_2O_{40}$ was synthesized and directly used in solution (0.6 % POM reported to the mixture of fibers, w/w) in the first step of bleaching of the SCF at pH 5 and temperature 80 ºC, for one hour. The fibers were let to cool down at room temperature, filtered and washed with water. In the second step, was performed the alkaline oxidation (0.1 N NaOH) with 1.5 % H_2O_2 and 2-3 % Na_2SiO_3 by using methods described and adapted from literature 23-25. Then the fibers were let to cool down, filtered and washed with water (pH neutral). Thereafter, the pulp was formed using laboratory scale devices and typical composition for paper manufacture was applied. Paper sheets of 20 cm in diameter were made by using second category fibers, SCF, and long wooden kraft, respectively, in a HAAGE Rapid-Koethen sheet former apparatus (Emst-Haage Apparatebeau GmbH&Co., Germany, STAS 6095/3).

Mechanical characteristics

The mechanical properties of paper samples were determined by using the following devices: L&W Tensile Tester (Lorentzen&Wettre, Sweden): SR EN ISO 1924-2; for bursting test: BS20T (Tecnolab, Italy): SR EN ISO 2758; L&W Tearing Tester used Elmendorf method (Lorentzen&Wettre, Sweden): SR EN 21974; opacity and brightness: Elrepho (Lorentzen&Wettre, Sweden): ISO 2469; all properties were measured in standard conditions: SR EN 20187.

AFM

NTEGRA Probe NanoLaboratory AFM (NT-MDT, Moskow, Russia), Software Nova_1644, equipped with an M Plan Apo 100x magnification objective that has the numerical aperture of 0.70 (Mitutoyo, Kawasaki, Japan) and a RPC-TVPCI camera which helps to locate the sample position were used. For storing the optical information a CCD camera was utilized. Paper samples were added to two-sided tape on sapphire support and the measurements were carried out under ambient conditions (temperature: 22 ± 1 ºC, relative humidity: 40 ± 10). Noncontact 'Golden' silicon cantilevers (NSG30 from NT-MDT, Moskow, Russia) with a resonance frequency of 320 ± 80 kHz, were used. All samples were measured in semicontact mode ("tapping" mode) to capture simultaneously topography and phase images. Area of the paper samples has been investigated at 30 x 30 μm^2 and 15 x 15 μm^2 (with a scan velocity of 10.12 $\mu m \cdot s^{-1}$), respectively. Average roughness, Ra; Root Mean Square, RMS; Surface skewness, Ssk; and Coefficient of kurtosis, Ska were determined using ISO 4287/1 (Nova_1644).

Results and discussion

Sample preparation

The delignification and bleaching of wooden and non-wooden fibers by alternative method to chlorination bleaching and alkaline extraction is an attractive and actual challenge for the industrial application in paper industry. The use of second category fibers, SCF (very short cotton fibers and chemical degumming hemp tow), which can not be recycled for yarn and textile production, in the manufacture of paper, was applied in this work. This mixture of fibers was bleached to remove the residual lignin by using peroxide method and a polyoxometalate as oxidation reagent, in two stages, with a yield of 80 %. The pulp obtained from this bleached mixture of fibers was used to obtain paper sheets. There was also obtained paper sheets from long wooden kraft pupl commercially available in order to use as control.

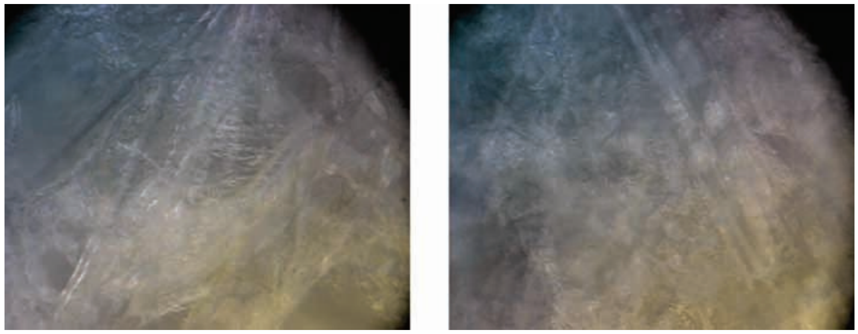
Mechanical and optical characteristics

The main mechanical and optical properties of the new paper samples obtained are exhibited in Tabel. 1. The values of mechanical properties (breaking length, burst index, tear index, etc.) of the new paper samples significantly decrease for paper containing SCF, compared to the paper obtained from long wooden kraft pulp. It is worth to mention that by using pulp containing SCF bleached by peroxide and POM, in two stages, the brightness of paper samples containing SCF decrease with maximum 19% compared with paper obtained from long wooden kraft, which is a good achievement for the final quality of the paper (Tabel 1).

Tabel 1. Mechanical and optical properties of the new obtained paper sheets.

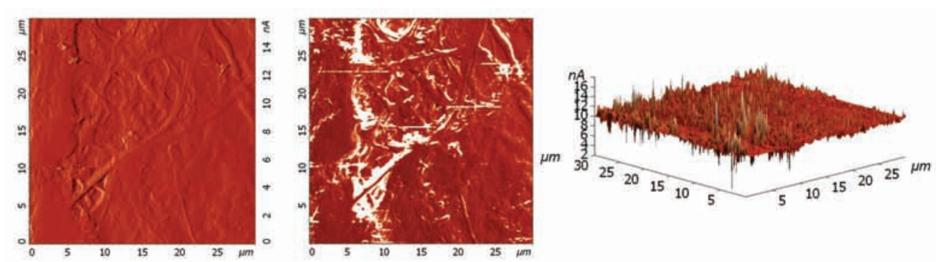
Parameter	Paper obtained from long wooden kraft	Paper obtained from pulp containing second category fibers
°SR	47	65
Weight (g/m^2)	66.2	62.0
Burst index (Nm/g)	94.96	61.9
Breaking length (m)	9500	6310
Tear index (mN m^2/g)	10.5	7.8
Tear resistance (kN/m)	6.28	3.84
Tensile strength (kPa)	324	211
Elongation (%)	1.94	2.19
Brightness (%)	85.1	69.1

a)

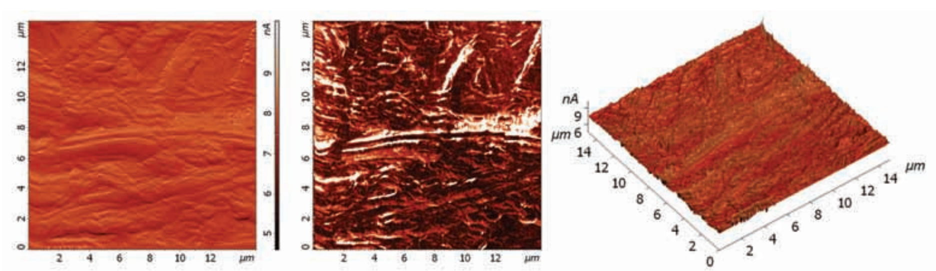


b) c)

Figure 1. Atomic Force Microscope installed at ICDISTN of "Aurel Vlaicu" University and microscopic images of paper sheets obtained from: a) long wooden kraft and b) pulp containing second category fibers (magnification 100x).



a) b) c)



d) e) f)

Figure 2. AFM images of paper samples obtained from long wooden kraft: a) 2D, b) phase, c) 3D, and from pulp containing SCF: d) 2D, e) phase, f) 3D.

Tabel 2. Characteristic parameters calculated from AFM images for the paper samples.

Sample	Average Roughness, Sa	Root Mean Square, Sq	Surface skewness, Ssk	Coefficient of kurtosis, Ska
Paper obtained from long wooden kraft	413.657 nm	503.672 nm	-0.0340474	-0.57691
Paper obtained from second category fiber	483.895 nm	574.534 nm	-0.280389	-0.812995

AFM imaging

Microscopic methods are suitable tools to determine the end-use properties of paper such as opacity, linting, absorbency, printability. Therefore, by measuring the distribution of porosity, mass and smoothness of the paper sheets at micro- and nano-scale it is possible to assess their relationship with paper properties. Atomic force microscopy was used to receive information about the roughness of the paper samples obtained from pulp containing SCF and from long wooden kraft pulp. In Fig. 1 are exhibited microscopic images of the paper sheets performed with a 100x magnification. Thereafter, was used AFM semicontact topography (tapping) mode of imaging and we performed a substraction of third order curve to obtain the final images presented in Fig. 2. As expected, the AFM phase contrast images gave little information due to the roughness and inhomogeneous properties of the paper samples (data not shown). Moreover, the simultaneous registered AFM images unveiled the less orientated fibrillar structure of fibrils in the images of paper samples obtained from second category fibers due to the inconsistent length of these fibers. This result is, probably a consequence of the manual cutting of the natural fibers. Because the samples were exposed to humid conditions during recording the AFM images, a thin contamination layer, major component being water, is presented in all the surfaces. The light parts that appears in the images most probably occurs due to the presence of more hydrophilic cellulose which is contained in the second category fibers that could present a water film of contamination and by the used paper additives on the surfaces. In Table 2 are presented the values of the Average roughness, Ra; Root Mean Square, RMS; Surface skewness, Ssk; and Coefficient of kurtosis, Ska. These parameters exhibited higher values for the paper samples containing SCF in comparison with paper obtained from long wooden kraft with 12-15%, except for the value of Coefficient of kurtosis, Ska, which increase with 29%.

Conclusions

In the present study, paper sheets were obtained from pulp containing bleached mixture of second category fibers (containing very short cotton fibers and chemical degumming hemp tow) and from long wooden kraft pulp. An eco-friendly approach, in which H_2O_2 and a polyoxometalate compound, $Na_2H_3PMo_{10}V_2O_{40}$, as oxidation reagent of lignin in the bleaching process, in a rapid two-steps procedure of SCF, was employed. Physical and mechanical properties of the obtained samples were measured and the topography of the surface of the paper samples was evaluated. Bleached second category fibers may be used as starting material to obtain specialty paper (e.g. paperboard, banknote, etc.) and which demonstrated, in contrast with the paper obtained from long wooden fibers, to exhibit more modest values for the physical and mechanical properties, except the elongation.

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