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Green chemicals and process to graft cellulose fibers

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ABSTRACT

The treatment of additive-free hand sheet paper samples with cold plasma was carried out and showed that cellulose can be chemically linked with reactive natural products, namely myrcene (My) and limonene (LM). Contact-angle measurement and X-ray photoelectron spectroscopy (XPS) were used to ascertain the occurrence of the grafting. Indeed, the contact-angle value of a drop of water deposited at the surface of paper increased from 30° for unmodified substrate to about 105 and 107°, for LM- and My-treated samples, respectively. In fact, LM- and My-treated surfaces were rendered totally apolar. Indeed, the polar contribution to the surface energy decreased from about 23 mJ/m^2 for pristine samples to practically zero for treated ones. The treated surfaces displayed water-barrier properties; the penetration of the liquid was reduced significantly after LM and My treatments. The XPS spectra showed that the modification with LM and My gave rise to very significant change in the O/C ratio, as well as in the intensity of the C1 peak assigned to aliphatic carbon sequences.

1. Introduction

The increasing pressure of society in favor of the use of natural renewable resources, in order to propose viable alternatives to existing fossil resources, constitutes stimulating challenges for investigators. Moreover, eco-friendly processes are also an inevitable requirement in order to have a fully sustainable approach in terms of both raw material and "clean" technology.

On one hand, vegetal biomass constitutes a potential candidate to supply our needs in terms of small molecules, oligomers. and macromolecules [1–3]. Thus, for example, the family of terpenes are unsaturated reactive molecules available as a by-product of wood pulping and constitute an interesting source of "green" monomers. The most important representatives of this family are α- and β-pinene, limonene, and myrcene. On the other hand, plasma discharge is a solvent-free polymerization process that has received considerable attention in recent years, in the realm of the surface modification of various materials, such as wood and cellulose fibers from different origins [4–6].

In fact, specific gases, like CF_4 or oxygen, classically used to treat textile fibers were applied to treat chemi-thermo-mechanical pulps (CTMP) and showed that the active species of inert- or reactive-gas plasma can efficiently interact with surface molecular layers of paper and other surfaces, leading to new functionalities, such as hydrophobic surfaces in textile and adhesion- and wettability-improved properties of wood surfaces. Indeed, this technique was successfully applied to wood [7–9] and cellulose fibers from different origins [10–12], to limit the citations to recent papers only.

To the best of our knowledge, only three papers [13–15] have investigated the effect of plasma treatment of lignocellulosic fibers, as a tool to graft either acrylic monomers (methacrylic acid [13] and acrylamide [14]) or silane coupling agents [15].

This paper describes the use of monomers derived from renewable resources with a solvent-free activation process based on dielectrical plasma discharge. The efficiency of the grafting was evaluated as a function of treatment time and ground pressure, and the treated sheets were characterized using X-ray photoelectron spectroscopy (XPS) and contact-angle measurements.

2. Experimental

2.1. Materials

Bleached kraft pulps of *Eucalyptus globulus* were used as a raw material to prepare additives-free laboratory hand sheet tracing papers. The pulps were refined to 80° SR in a valley beater and paper sheets with a basis weight of 40 g/m^2 were formed in a static

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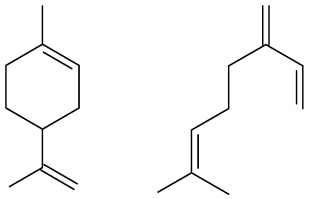
sheet former according to TAPPI T 205 sp-95; i.e., hand sheets were pressed for 7 min at 345 kPa and dried in a conditioned room at 23 °C and 50% relative humidity. The preparation of such substrate was motivated by its suitability for the characterization technique (flat surface) and its very low porosity (limitation of liquid penetration during wettability measurements).

The prepared paper samples were soxhlet-extracted with methylene chloride, for 6 h, prior to cold-plasma treatment, as established in our previous work [15]. The reagents and solvents used were commercial products with highest purity available. Two terpenes were used as coupling agents, namely limonene (LM) and myrcene (My):



LM **My**

They were commercial products supplied by Sigma-Aldrich Inc., and used as received. Before grafting, LM and My molecules adsorbed at the cellulose fibers' surface. The main interactions occurring between terpenes and cellulose macromolecules arise probably only from dispersive London-type forces.

2.2. Plasma treatment

The RF plasma generator was a EUROPLASMA apparatus equipped with a microcontroller, a vacuum system, and a 2.45 GHz microwave generator. The treatment power was 200 W and the ground pressure varied from 200, 500, to 700 mT. The treatment time varied from 30, 60, to 180 s.

Argon with a flow rate of 40 ml/min was used as the carrier gas and the system was equipped by a rotary vane pump having a capacity of 3 m^3/h. The treatment was carried out under a base pressure of 200 mTorr. This pressure target was reached after 3–5 min of pumping. The equipment used could work within a pressure interval between 1 and 1000 mTorr. A Pirani-type pressure gauge was used to measure the vacuum level and the calibration was made using nitrogen. Before proceeding with plasma discharge, the chamber was left under a stream of argon, in order to remove oxygen and vapors of water from the reaction medium. Thus, such molecules were removed before the free radical reaction initiation step.

The electrodes were cylindrical Pyrex glass tubes with a diameter and length of 60 mm. The energy input frequency was 13.56 MHz. The reaction chamber was aluminum-made cylinder with a wall thickness of 2 cm and useful dimensions of 200 × 150 mm^2, for the diameter and the length, respectively.

Three different processing conditions were tested. The first one was based on the activation of the paper surface by plasma discharge followed by its immersion into the monomeric liquid. The second approach called on the impregnation of the substrate to be treated by the chosen monomer and then the exposure of the impregnated sheet to plasma discharge. Finally, the third method was based on impregnation of the paper sample followed by its plasma activation and then again its immersion into the monomeric liquid. These methods will be designed as "activation-immersion," "impregnation treatments," and "impregnation-activation-immersion," respectively. The concentration of the grafting agent varied from one modification approach to another and was within the range of 1 to 15% w/w, of the chosen terpene with respect to oven-dried cellulose.

Table 1
Contact-angle measurement probes and their characteristics.

	Surface tension (mJ/m^2)		
	Dispersive	Polar	Total
Hexadecane	27.5	0	27.5
α-Bromonaphthalene	44.5	0	44.6
Diiodomethane	48.5	2.3	50.8
Ethylene glycol	29.0	19.0	48.0
Water	21.8	51.0	72.8

The treated paper samples were systematically soxhlet-extracted with methylene chloride, for 6 h, in order to remove the physically adsorbed unbounded polymers, before being characterized. The aim of such treatment is to be sure that detected molecules are chemically grafted. Such approach is needed more for scientific purposes than for practical ones, since in papermaking the need of chemically grafted molecules is not a systematic requirement. After the extraction, the samples were dried overnight under vacuum at 70 °C, before being characterized. The total evaporation of methylene chloride was confirmed by the absence of signals corresponding to chlorine atoms in the XPS spectra.

2.3. Characterization

The treated and untreated paper samples were characterized by contact-angle (CA) measurements and XPS. CA measurements were carried out by depositing calibrated droplets of liquid probes onto the surface of the investigated sample and measuring the angle which it forms at the equilibrium. The surface tensions of the probe molecules used in this work are summarized in Table 1. The apparatus used was a Dataphysics OCA absorption tester, equipped with a CCD camera collecting at 200 images per second. The dispersive and polar contributions to the surface energy of the investigated papers were calculated using the Owens–Wendt formalism [16].

X-ray photoelectron spectroscopy experiments were performed using a XR3E2 apparatus (Vacuum Generators, UK). This apparatus is equipped with a nonmonochromated Mg$K\alpha$ X-ray source (1253.6 eV) and operated at 15 kV under a current of 20 mA. Samples were placed in an ultrahigh vacuum chamber (10^{-8} mbar) with electron collection by a hemispherical analyzer at an angle of 90°. Signal decomposition was done using Spectrum NT, and the C_{1s} signal was shifted to ensure that the C–H signal of the decomposition occurred at 285.0 kV. Spectra were analyzed using Spectrum software.

3. Results and discussion

The optimal plasma activation conditions were shown to vary with coupling agent, but the energy applied to treat paper with both terpene coupling agents was fixed at 200 W, because this parameter was found suitable for the previously studied coupling agents [15]. Then, a first set of experiments was carried out using different operating conditions at 200 W, in order to establish the optimal working parameters. In fact, a set of experiments using a ground pressure of 700 mT was realized with varying treatment times: 30, 60, and 180 s. The contact angle of a drop of water formed at the surface of treated and untreated paper was measured, as illustrates Fig. 1, showing that a treatment time of around 60 s gave rise to a substantial improvement of the substrate hydrophobization, for both terpenes. In fact, the contact angle of a drop of water formed angles of 105 and 111°, at the surface of LM- and My-treated substrates, respectively. Prolonging the treatment time led to further improvement (less that 2%), but the gain was too modest if one considers the energy consumption associated with such prolonged treatment duration.