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Hydrophobic materials based on cellulose from vine stems

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Abstract:
The objective of this research was to investigate new paths for the preparation of cellulose derivatives to obtain advanced materials suitable for different applications. This study investigates chemical modification of paper's surface with tert-butyl and phenyl isocyanate using vapour phase technique. Two types of cellulosic materials were used: Whatman paper chosen as a reference and the paper based on fibers isolated from the vine stem. By reacting hydroxyl groups with isocyanat, hydrophobic character was acquired. The modified surfaces were characterized by FTIR-ATR and contact angle measurements.
Key Word*: Cellulose, Chemical modification, hydrophobization, contact angle.*

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I. Introduction

Cellulose is the most abundant biopolymer in the earth [1]. It can be encountered in diverse sources (plants, wood...). Cellulose fibers are known by several and particular properties, which justify the presence of that material in numerous fields. In that, due to its softness and hydrophily, this fiber was used in textile and medicine. Also, the variability of mechanical properties between dry and humid condition, makes from cellulose the best fiber for cordage especially in humidified places. Other multiple use of this biopolymer became more and more known, either by mixing cellulose with other material(matrix) in the case of green composites material([2], [3], [4], [5]) or by modifying its surface in order to change native properties. For instance, using paper in packaging application needs to have a superhydrophobic external surface. In that,cellulosic materials have been thoroughly investigated and reviewed over recent decades, as regards their surface modifications and applications [6][7][8]. In the same way, our study is located, in that we try to obtain hydrophobic paper based on cellulose extracted from Tunisian vine stems.

Tunisian vine stems waste was valorized, firstly in papermaking [9]. Then, it was used as filler with PELD to obtain a green composite material [2]. After that, this material was utilized to synthetize CMC [10] and now it is an attempt to functionalize resulting paper using t-butyl and phenyl isocyanate.

II. Material And Methods

Raw material

The stems were obtained from Monastir in December 2011 and dried under natural conditions (average relative humidity: 65%; average temperature: around 20 ◦C). They were then washed in order to eliminate sand and dried again under the same conditions. Before pulping, the stems were cut into small pieces with lengths of about 1 to 3 cm and crushed to 2.5mm. Then delignification procedure was carried out as mentioned by Mansouri et al. 2010.

Paper making

Several steps were needed for the successful preparation of handsheets from vine stem pulp. According to the standard method ISO 5263-1, the pulp was disintegrated and passed through a slotted screen with an aperture size of 0.15 mm in order to remove uncooked materials. Conventional hand sheets were prepared on a Rapid Khöten sheet former (ISO 5269-2)[2].

Different samples were described:

- PTv : paper based on cellulose extracted from vine stem unmodified.
- PTvTI: paper based on cellulose extracted from vine modified with tert-butyl isocyanate.
- PTvPI: paper based on cellulose extracted from vine modified with phenyl isocyanate.
- PWm : Whatman paper unmodified.
- PWmTI: Whatman paper modified with tert-butyl isocyanate.
- PWmPI: Whatman paper modified with phenyl isocyanate.

2.3 Modification of cellulose's surface

The modification was carried out using the following system developed by cunha et al. according to the following procedure:

Papers were placed inside the reactor onto the gas-tight holder 3. The reagent was kept in a flat-bottom flask (2) through which was passed the nitrogen stream that served as the carrier gas (controlled with flow meter 1). The reaction was conducted at room temperature (ca. 20 ºC) by streaming the N2/reagent mixture (0.1-0.5 L/min) through the filter paper for a given period of time (0.5-30 min). The by-product was removed by bubbling the gaseous waste through an outlet trap 4.

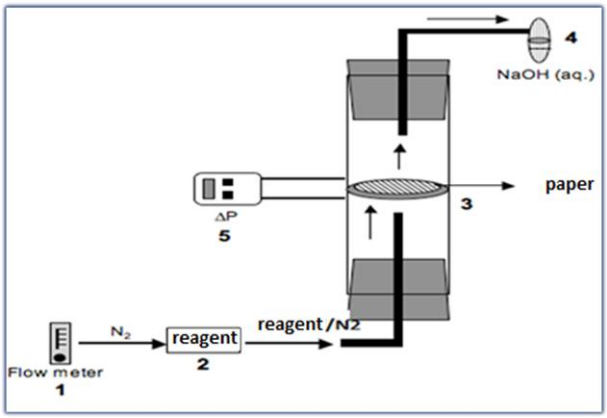
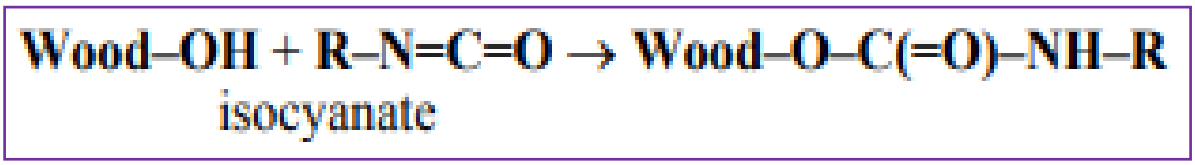


Figure 1. Schematic representation of the system used for the gas-solid reaction of cellulose [1]

Characterization of modified surfaces

-The FTIR spectra were recorded with a PARAGON 1000 Perkin–Elmer FTIR spectrometer equipped with a single horizontal Golden Gate ATR cell.

-Contact angles with water, glycerol, diiodomethane, formamide and 1-bromonaphthalene were measured with a Dataphysics device equipped with a Pulnix camera. Each retained h value (the average of 5 determinations) was the first captured by the camera following the drop deposition on the sample's surface. These values were used to calculate the dispersive and polar contributions to the surface energy of the cellulose substrates, using Owens–Wendt's approach.



III. Results

a. Contact angles

The contact angles of liquids processing different surface tensions were measured onto the unmodified and modified papers' surface. The liquids tested were water, bromonaphtalene, ethylene glycol, formamide and diidomethane. The average contact angle values measured are registered in the following table. The significant increase in the hydrophobic character of cellulosic material after chemical modification was mentioned by the rise of contact angle with water. The unmodified paper prepared from cellulose isolated from vine stem are hydrophilic (contact angle = 20°). After modification with phenyl isocyanate, the contact angle increases to 126°.

Table1 : Contact angle values of paper based on cellulose from vine stem

	(θ°)water	(θ°)brom.	(θ°)ethyl.gly.	(θ°)diiodom.	(θ°)Formamide
Unmodified paper	20,1	14,6	24,2	46,3	24
t-butylisocyanate	71.0	-	64.2	34.5	60
Phenylisocyanate	126.3	-	92.0	64.0	102.0

Whattman paper's surface was modified chemically. Also, the hydrophobic character was clearly observed when measuring the contact angle.

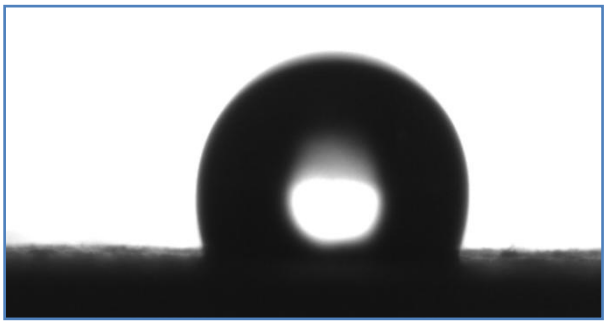


Figure 2. Drop on the modified paper surface

b. FTIR-ATR

The modified samples and unmodified paper were characterized by FTIR-ATR spectroscopy. The success of the modification was clearly confirmed, mainly on the basis of the appearance of a new band at 1738cm-1 attributed to the ester function (O- C = O)[11].

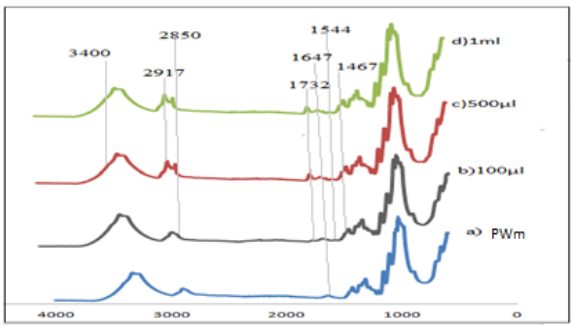


Figure 3. FTIR-ATR spectra of cellulose fibers before and after chemical modification: a)PWm, b), c) d) modified papers by different volume of t-butyl isocyanate

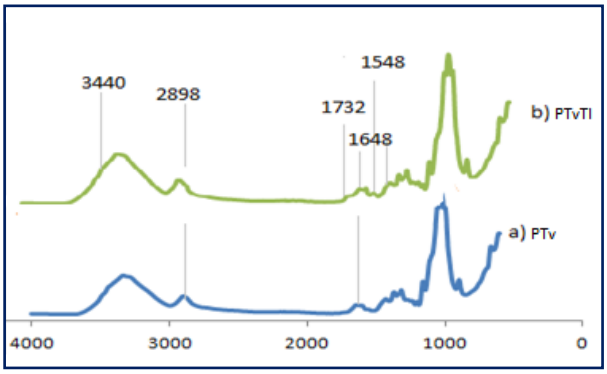


Figure 4. FTIR-ATR spectra of cellulose fibers before and after chemical modification: a)PTv, b)modified papers using t-butyl isocyanate.

IV. Conclusion

This work offered new approaches for the modification of papers' surfaces based on cellulose extracted from Tunisian vine stems. In that hydrophobic cellulose derivatives were prepared. All techniques of characterization show that the modification was carried out successfully.

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