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Comparative Study of Extraction of Cellulose Nanocrystals (CNC) from Wood Pulp

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Abstract. The present work is a study on cellulose nanocrystals extracted from the wood Pulp of the joineries in order to exploit this cellulosic waste (recycling). After a bibliographic study, we selected four different extraction technics to be followed. The extracts obtained have undergone several physical and structural characterizations to evaluate the influence of the extraction method on the yield in quality and quantity of the CNCs.
Fourier transform infrared spectroscopy (FT-IR) was used to highlight the evolution of the chemical composition thus confirming the elimination of extracellulosic substances during the chemical treatment of the extraction process. X-ray diffraction analysis determined the crystallinity of the CNC. According to the results of the thermogravimetric analyzes, the degradation of the CNCs occurs at a low temperature in the region of 200 ° C. The morphology of cellulose nanocrystals has been studied by optical microscopy.

Keywords: biopolymer, biomass, cellulose, cellulose nanocrystals, whiskers.

1 Introduction

Synthetic polymer materials are in permanent development, but the challenge for scientists today is the development of new materials that will satisfy our needs and at the same time be compatible with the environment and renewable sources. This has led to much research on biopolymers and composites in the last two decades and we are witnessing a rapid development of nanocomposite polymers which are polymer matrices reinforced by a filler that has at least one dimension less than 100 nm [1].

Natural fiber-reinforced composites have attracted the attention of the research community mainly because they are turning out to be an alternative solution to the ever-depleting petroleum sources [2].

Among the various organic nano particles, cellulose nano particles have encountered an enormous consideration for diverse causes. Nevertheless, cellulose has several substantial

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practical applications such as being renewable, biodegradable, environmentally friendly, low-priced, and possessing enormous mechanical strength [3].

Cellulose is the most abundant polymer and it is the main component of most plant biomass. Nano cellulose and its derivatives present a new brand of nano technology that appear to have very wide applications in a variety of domains where physical characteristics such as strength, weight, rheology, and optical properties can be affected in a very positive manner. Also, the cellulose nano crystal (CNC) is one of the strongest and stiffest organic molecules, that has a modulus of 145 GPa, a strength estimated at 7500 MPa, high surface areas (~250 m^2 /g), hydrophilic, and quite amenable to surface activation [4,5].

However, owing to the fact that they have an easily accessible hydroxyl functional group which allows them to be able to be chemically modified, they can find advantageous applications in the field of health care. In this context of drug delivery CNC is a suitable nanomaterial for a wide range of applications, such as enzyme immobilization, synthesis of antimicrobial and medical materials, green catalysis, biosensing, synthesis of drug carrier in therapeutic and diagnostic medicine, etc. [6-9].

The main composition of natural fibers is cellulose, hemicellulose and lignin. The cellulose is surrounded by amorphous hemicellulose and the whole is immersed in the lignin matrix.

The quantity of cellulose synthesized by the plant is estimated at 50-100 billion tons per year, which are in the form of biofilm synthesized and arranged regularly. This mode of biogenesis generally leads to crystalline microfibrils practically free from defects having axial physical properties close to those of the perfect crystal [10,11].

Isolation, characterization, and search for applications of novel forms of cellulose, termed nanocrystals or whiskers, is generating much activity currently.

Preparation of cellulosic nanocrystals in laboratory are frequently reported. The CNC extraction process is a chemical process, which consists to use a strong acid for the hydrolysis of the amorphous celluloses regions.

The objective of this treatment is to dissolve the low cohesion regions (amorphous parts) so that the highly crystalline insoluble residue is transformed into a stable suspension by vigorous mechanical shear action. The resulting nanocrystals are in the form of stick particles (whiskers) [4,12,13].

2 Experimental

2.1. Materials

The wood pulp is recovered from a carpentry waste which we have subjected a preliminary treatment common to all the extraction methods and then to divide into four parts, each of one will undergone the extraction protocols selected [14-17].

2.2. Preparation of nanocrystals of cellulose

2.2.1. Pretreatement

- **Drying:** 2 hours at 120 ° C;

- **Sieve:** 50 µm;
- **Drying:** 2 hours at 120 ° C;

2.2.2. Extraction

The nano whiskers of cellulose was extracted from wood pulp according to the steps summarized in the table I (below)

Table 1 Extraction steps of whiskers from wood pulp according to four technics

Steps Method	Alkaline treatment	Bleaching	Hydrolysis	Filtration
Method I	NaOH (5%) T=70°C, t=1h	NaClO (50%) + acetate buffer	Sulfuric acid (65%) t =30 m, T=45°C	Centrifugation + ultrasounds
Method II	Toluene + Ethanol t=24h NaOH (2%), T=80°C, t=2h	NaClO (50%) t=6h	Sulfuric acid (65%) t=30m, T=45C	/
Method III	NaOH (2%), T=15°C t=1h; Demineralized water T= 80°C, t=1h;	/	Hydrochloric acid t=1h T=45°C	Lyophilisation T= -30°C, t=96h ;
Method IV	$Na_2 SO_3$ (5%) T=74°C, t=2h NaOH (17,5%), t=2h;	NaClO (0.7%) + acid acetic, t= 24h ;	Sulfuric acid (64%), t=45min, T=45°C;	Centrifugation t=25min

Table 2 Comparative results of the influence of the concentration of the NaClO solution on the bleaching steps, according to Method I

Samples	Concentration in NaClO (%)	Methods	Duration of treatment	Bleaching	Hydrolysis acid
I	50	I		White paste	Yellow solution
II	70	I		Yellow paste	/
III	80	I	24h	Yellow paste	/
IV	100	I		White paste	Brown solution
V	50+ acetate buffer	I		Very white paste	Brown solution

2.2. Methods of Characterization

2.2.1. Morphological Characterizations

A. FT-IR Spectroscopy

The changes in the chemical composition of the cellulose fibers after chemical treatment was conducted through FTIR spectroscopy. A FTIR SPECTUM1000 PERKIN ELMER was exploited to provide the spectrum of each sample. Spectra were taken at a resolution in the range of 4000–400 cm−1.

B. X-ray diffraction analysis (XRD)

XRD analysis was carried. The scans were performed in the range 2q = 2–70°.

C. Optical Microscope

The scan was carried out with an enlargement (×400).

2.2.2. Thermal Characterizations

D. Thermogravimetric analysis (TGA)

TGA was performed to study the thermal characteristics of the CNW samples. The thermal behavior of each sample was determined, using a type Perkin Elmer TGA 4000, across a temperature range of 30–800 °C, at a heating rate of 10 °C/min, in a nitrogen environment.

3 RESULTS AND DISCUSSION

3.1. Fourier transform infrared spectroscopy (FTIR)

CNW were characterized by FTIR analysis in order to follow the chemical composition over the process, this method revealed the presence of some characteristic functional groups corresponding to the cellulose structure and the influence of the method in the type of functional groups in the surface of cellulosic chain.

Figure 1 shows the FTIR spectra of wood pulp CNW.

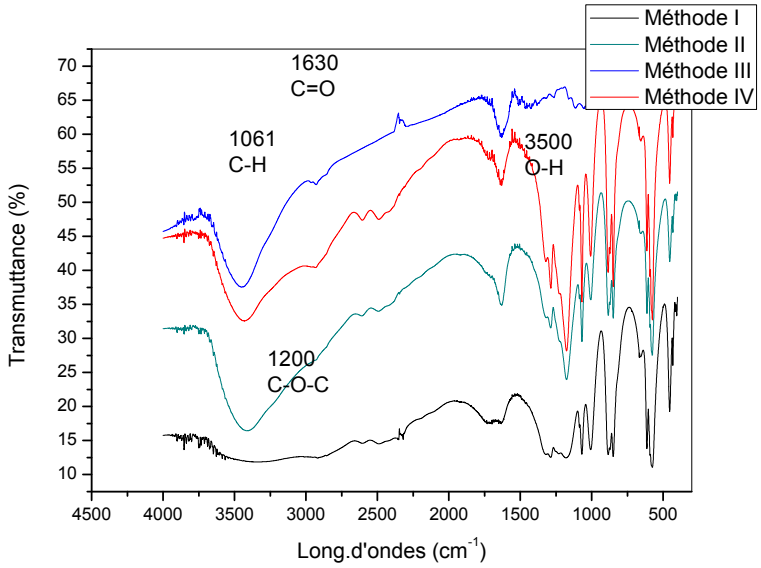

Fig. 1 FT-IR Spectrum of CNW

We observe that the all FTIR spectra are similar, with a few differences in the spectra (method III) in the range of 1500-500 cm^{-1}.

The peak at 3700 and 4000 cm^{-1} correspond to the hydroxyl groups (−OH). The peak at 1600 cm^{-1} is attributed to C=O Stretching of aliphatic aldehyde. The peak at ~1200 cm^{-1} is assigned to asymmetric stretching vibrations de la liaison C-O-C. The peak at 1061 cm^{-1} is attributed to C-H bonds of cellulose. Then, the peak at 550, 800 cm^{-1} were attributed to C=O stretching vibrations of carbonyl and acetyl groups presents in lignin and hemicellulose, in the other hand, absence of the peak at 1037, et 1515 cm^{-1}, which are attributed to C-O-C bonds of diethyl ether and C=C of aromatic compound respectively.

The peak at 1205 cm^{-1} who is intense for the FTIR spectra of method (I, II, IV), attributed to the S=O bond because of the esterification reaction which occurs during the hydrolysis acid with sulfuric acid and we observe the absence of this peak in the FTIR spectra of method III. For the FTIR spectra of method I, absence of the peak at 3500 cm^{-1} which is corresponding to the stretching of O-H bonds.

The peaks in the FTIR spectra can be too exploited for the evaluation of the type of CNW crystallinity (cellulose I, cellulose II or mixed of the two components and the amorphous cellulose). According to O'connor [18], the range 1500-850 cm^{-1} indicates a lot about the crystalline structure of the cellulosic material. The peaks at 1420-1430 cm^{-1} and 893-897 cm^{-1} are very important to elucidate the crystalline structure and from the spectral quotition (1420/893 cm^{-1}) and (1375/2900 cm^{-1}) we can calculate the cellulose crystallographic plane and the crystallinity index respectively in the cellulose samples, the spectral quotition (1430/897 cm^{-1}) gives the evidence that the fraction contains cellulose I. By this analysis, we can deduce that according the FTIR spectra of the treated wood pulp, the method IV presents a high crystallinity (the peak at 850-1500 and 1420-1430 cm^{-1}), while they are very low or nonexistent in the FTIR spectra of method III [18, 19, 20].

3.2. X-ray diffraction analysis (XRD)

XRD analysis was carried out to investigate the crystalline behavior of wood pulp CNW. The figure 2 reports the XRD pattern of CNW extracted by the two methods III and IV.

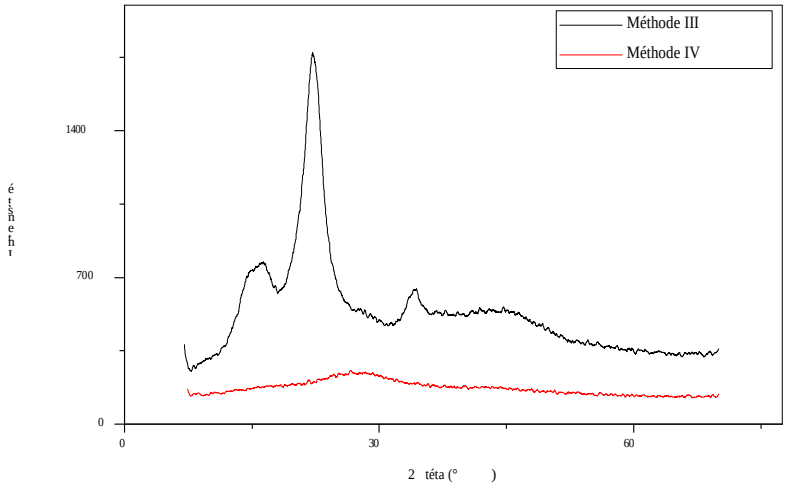

Fig.2 Xrd patterns of CNW

We observe that the XRD pattern of method III exhibits a sharp peak which leads us to note that these CNW are partially crystalline relatively high, while the CNW extracted by method IV, the XRD pattern presents a large peak, which demonstrates a low level of crystallinity, so we can conclude that the suspension obtained by method IV still contains various constituents of fiber components. This result is not concording with what was observed on the FTIR results.

The diffraction peaks at the angle 2θ in the region of 22° corresponds to the cellulose crystallographic plane 002.

3.3. Optical Characterization

From the microscope characterization of the CNCs (FIG. III), a clear difference can be observed in the shape and size of the CNCs between these obtained by method I, II and III, IV. The CNCs obtained in suspension (I, II) are very small, could not separate. It is known that the electrostatic repulsion of the sulphate ester groups on the surface of the CNCs introduced during the acid hydrolysis step with sulfuric acid after reaction with the hydroxyl groups is at the origin of the formation of very high CNC suspensions stable in water and the introduction of each negative group has the effect of increasing the stability of the suspension.

In the case of the centrifugation results of Method III and IV, precipitates are obtained with a larger size, this can be explained by formation of agglomerations due to the absence of the negative charges in the surface of the CNCs in the case of method III.

Fig. 3 CNW Images corresponding to each method (from I to IV from the left)

3.4. Thermogravimetric analysis (TGA)

Figure IV shows thermal analysis curves (TG and DTG) of CNW obtained by the fourth methods.

The appearance of the thermograms attributed to each extraction technic shows that the state and the structure of the extracts are different from one method to another. Samples experiencing premature loss of mass compared to others that show better stability at elevated temperature.

The TG curves show three stages of weight loss, while its decomposition occurs in two main stages. The beginning of CNC degradation occurs at a higher temperature, after 200 ° C for CNCs obtained with acid hydrolysis by sulfuric acid, while that obtained by hydrochloric acid, the decomposition occurs at a higher temperature (300 ° C). Above this temperature it can be seen that the thermal stability gradually decreases towards the degradation of the CNC.

In all cases, a small weight loss was found in the range of 35-150 ◦C, due to water loss of adsorbed moisture on the surfaces of CNW including chemisorbed water and/or intermolecular H-bond water or to the evaporation of water from low molecular weight compounds (present in cellulose). The first step of degradation basically corresponds to the cellulose degradation such as depolymerization, dehydration and decomposition of the glycosyl units. Thermal degradation of CNCs occurs at low temperatures, the onset temperature of CNW was 210 °C and the last degradation stage was attributed to breakdown of the charred residue [21, 22].

This behavior is predictable since the introduction of the sulfate groups decreases the thermal stability of the CNCs due to the dehydration reaction of the cellulose.

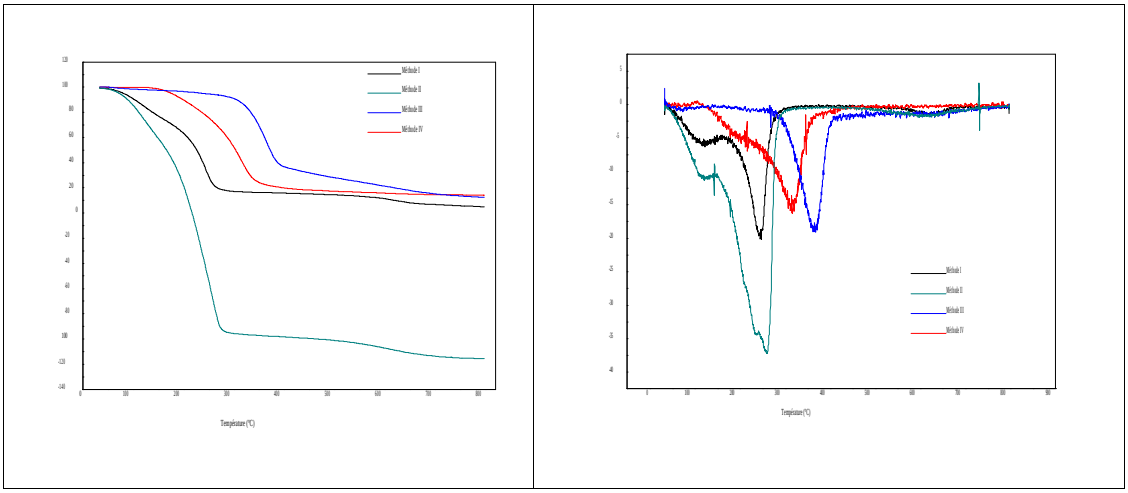

Fig.3 Tga and dTg thermograms of CNW

4 CONCLUSION

The work on Cellulose nano crystals commonly called CNC or Wiskers, has greatly interested us due its novelty, its economic and ecological impact.
In this paper, CNW were extracted from wood pulp (recycling).
At the end of the work we were able to arrive at several conclusions:
-It is possible to carry out the bleaching step with NaClO at an optimal concentration at 50% (v/v) in the case of substitution of sodium chlorite.
- Bleaching by the addition of acetic acid remains the most and indicated for a better yield.
- Characterization by optical microscope showed that the hydrolyze acid by sulfuric gives a stable suspension because the sulfate ester groups are favorably formed on the surface of the nanoparticles, this creates a double layer of electrostatic repulsion between the nanoparticles in the suspension.

-Most of the extracts have similar chemical structures from the IFTR analyzes.
- IFTR analysis revealed the difference in crystallinity in the different samples.
- The degree of crystallinity in the extracts depends on the extraction technique used.
- The thermal stability of the nanowhiskers is affected by the chemical treatments specific to each extraction method.

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