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Development of Cellulose Nanofibres from Coconut Husk

Chandrahara.R¹, Rajamane.N.P², Jeyalakshmi³

¹Project Officer, ²Head, Centre for Advanced Concrete Research, SRM University, Chennai

³Head, Department of Chemistry, SRM University, Chennai

¹R.chandrahara@gmail.com, ²rajamanenp@yahoo.co.uk, ³rajyashree64@gmail.com

Abstract— Cellulose is the most common abundantly available, high molecular weight linear chain organic polymer found on Earth. It is present in plants as a primary cell wall and it may be amorphous or crystalline depending on its nature and fibre form of it is very beneficial, especially when reduced to nano size. Composites made of Cellulose nano fibres attains adequate strength that fulfills necessary requirements in various fields and hence many applications. In this research work, Cellulose nanofibres were prepared from coconut husk where two pre-treatment methods were adopted before conducting concentrated Sulphuric acid hydrolysis. The pre-treatment processes include Alkali Treatment and Bleaching. The finally obtained nano fibres were characterized using different instruments such as XRD, FTIR and TGA to understand their behavior and properties.

Keywords— Coconut husk, Cellulose nanofibres, XRD, FTIR, TGA.

I. INTRODUCTION

Cellulose, an important structural component of plants have received much attention because of their low density, nonabrasive, combustible, nontoxic, low cost, and biodegradable properties. Cellulose fibers have some disadvantages too such as moisture absorption, quality variations, low thermal stability, and poor compatibility with the hydrophobic polymer matrix. However, production of nanoscale cellulose fibers and their application in composite materials have gained increasing attention due to their high strength and stiffness combined with low weight, biodegradability, and renewability. Application of cellulose nanofibers in polymer reinforcement is a relatively new research field [1]. The main reason to utilize cellulose nanofibers in composite materials is because one can potentially exploit the high stiffness of the cellulose crystal for reinforcement [2, 3].

Cellulose is a natural polymer with long chain repeating units of β -D glucose [1-4]. It has been used in many applications in many spheres of modern industry. Its existence as a common material in plants cell wall was first recognized by Anselm Payen in 1838 [5].

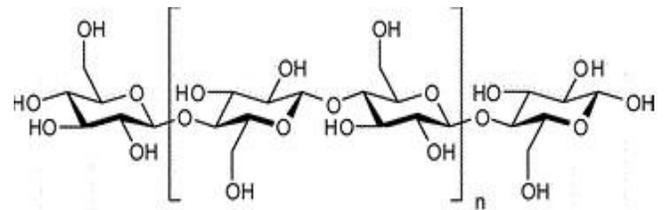


Figure (1): Cellulose

The cellulose fibers can be classified according to their origin and grouped into [6]:

- (i) **Leaf fibre:** abaca, cantala, curaua, date palm, henequen, pineapple, sisal, banana;
- (ii) **Seed fibre:** cotton; bast: flax, hemp, jute, ramie; fruit: coir, kapok, oil palm;
- (iii) **Grass fibre:** alfa, bagasse, bamboo; stalk: straw (cereal).

The bast and leaf (the hard fibers) types are the most commonly used in composite applications [7, 8]. Commonly used plant fibers includes cotton, jute, hemp, flax, ramie, sisal, coir, henequen, and kapok. Cotton contains much of cellulose in it (around 90%), however, in wood, plant leaves and stalks, it is found in combination with other materials, such as lignin and hemicelluloses. Coconut fibres, when compared to other natural fibres, are a lignocellulosic material, characterized by high toughness and durability due to its high lignin content [9]. Usually, brown coloured matured coconut fibres will be used for engineering applications.

II. EXPERIMENTAL

A. Materials

Coconut fibres were taken from outer shell of a matured coconut. Laboratory grade sodium hydroxide, sodium chlorite, glacial acetic acid, nitric acid and concentrated sulphuric acid chemicals were used for pretreatment and hydrolysis.



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B. Pre-treatment of Coconut fibres

Coconut fibres require pretreatment processes as they contain large amounts of lignin and hemicelluloses. In this research work two pretreatment processes were adopted namely 'Alkaline' and 'Bleaching' for their removal and then acid hydrolysis was carried out using concentrated sulphuric acid to obtain cellulose nano fibres.

1) Alkaline Treatment:

Sodium Hydroxide (NaOH) was used for alkaline pretreatment of coconut fibers [12, 13]. The fibres were chopped well in a mill and were sieved through 40 mesh sieve. The sieved fibres were dispersed in distilled water and the suspension was stirred for 2hrs at 50°C and filtered, and this procedure was repeated once more. The residue was dispersed in a 100ml of 2% NaOH solution and the suspension was stirred for 2hrs at 80°C, filtered and washed with water. This alkaline treatment is repeated once more and the fibres were dried at 50°C for 24 hrs.

2) Bleaching Treatment:

This process also referred as 'Delignification process' was carried out as described by Wise, Murphy, and D'Addieco [14]. The alkali pretreated fibres were undergone bleaching treatment using sodium chlorite solution and 8 to 10 drops of glacial acetic acid while heating at 60°C to 70°C so that much of the lignin content was removed in this process. The mixture was stirred at frequent intervals for 1hr, cooled in ice bath, filtered quantitatively and washed with cold water. At the end, the bleached pulps were treated with 0.05N nitric acid solution for 1hr at 70°C and washed extensively with water.

C. Sulphuric Acid Hydrolysis

After completion of pre-treatment processes, acid hydrolysis was carried out using 60 (w/w) concentrated sulphuric acid adding drop by drop until desired concentration is reached. The acid treated fibres were stirred constantly using mechanical stirrer, heating it simultaneously for 45 minutes. In these processes the hydrogen bonds breaks forming complexes and sulfate esters, depolymerization of macromolecular chains, finally change in crystallinity. Then the suspension was centrifuged at 5000rpm for 15 minutes and ultrasonicated for well dispersion of nanomaterials preventing agglomeration. Ultimately, cellulose nanofibres were obtained by freeze drying the material.

III. CHARACTERIZATION

X-ray powder diffraction analysis was conducted to analyze the sample crystallinity of raw, pre-treated and hydrolyzed coconut fibres. The crystallinity index of the material was calculated by peak height method (Figure (2)) which is an empirical method being the most common and simple method to determine the degree of crystallinity. In this approach, the X-ray apparent crystallinity (%) of cellulose is calculated from the height ratio between the intensity of the crystalline peak and the total intensity after the subtraction of the background signal (non-crystalline) measured without cellulose according to the following equation:

$$C = 100 \cdot [(I_{200} - I_{\text{non-cr}}) / I_{200}]$$

Where,

C expresses the apparent crystallinity [%] defined by Segal and co-workers [15],

I_{200} gives the maximum intensity of the peak corresponding to the plane in the sample with the Miller indices 200 at a 2θ angle of between 22- 24 degrees, and

$I_{\text{non-cr}}$ represents the intensity of diffraction of the non-crystalline material, which is taken at an angle of about 18 degrees 2θ in the valley between the peaks.

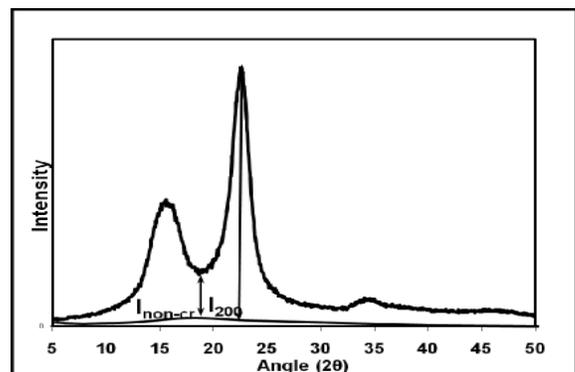


Figure (2): X-ray diffraction spectra of a cellulose I sample illustrating the Peak height method

Fourier Transform infrared Spectroscopy (FTIR) was used to analyze the bonding nature of raw coconut husk, pretreated and acid hydrolyzed fibres. Also studies were made to analyze the removal of lignins from the material at each stages of extraction. Thermogravimetric analysis (TGA) was performed to study the degradation characteristics of the cellulose nanofibres.



IV. RESULTS & DISCUSSIONS

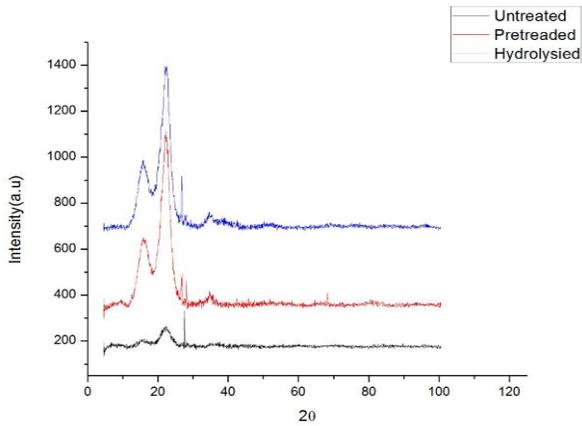


Figure (3): X-ray Crystallograph of untreated, pretreated and acid hydrolyzed coconut fiber

Figure (3) shows the crystallinity peaks for raw coconut husk fibres, pretreated coconut husk and Sulphuric acid hydrolyzed fibres. From the graph it can be seen that the raw coconut husk fibres are amorphous in nature and after the pretreatment crystallinity in the material is achieved, as also with acid hydrolysis. The amorphous nature of raw coconut husk is due the presence of large amounts of lignin, hemicellulose and others. However after pretreatment, the amorphous region of the material is subjected to alkali sodium hydroxide and Sodium chlorite bleach so that the most of lignins and hemicelluloses get dissolved leading to exposure of cellulose fibres. So in the further treatment of acid hydrolysis, the acid directly gets in contact with much of cellulose affecting a bit change in crystallinity. The crystallinity index for all three fibres is calculated by peak height method and is presented as in Table 1.

Table 1
Crystallinity Index Of Raw, Pretreated And Acid Hydrolyzed Coconut Husk Fibres

Fibres	Crystallinity Index (%)
Raw coconut husk fibre	66.62
Pretreated coconut husk	75.71
Acid hydrolyzed fibres	76.02

From the Table 1 it can be seen that there is almost 10% increase in crystallinity after pretreatment of raw coconut fibres as the cellulose is regenerated, and a bit increase in crystallinity due to acid attack on cellulose.

Also the Scherrer formula,

$$D = K\lambda / \beta \cos\theta,$$

Where,

D = diameter or mean size of the ordered (crystalline) domains.

K = dimensionless shape factor ~0.9

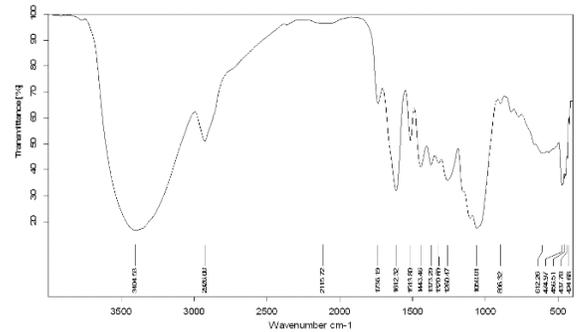
λ = X-ray wavelength

β = full width half maximum

θ = Bragg angle.

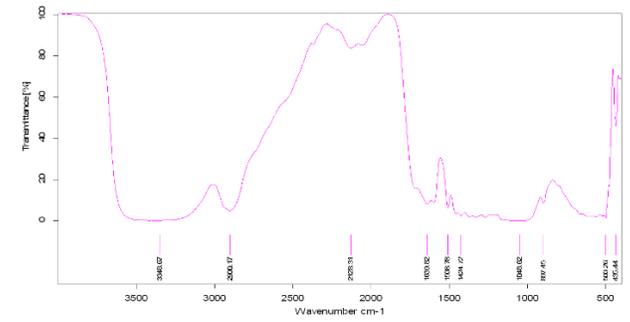
Using this formula, the average diameter of the hydrolyzed coconut fibres was found to be 25nm.

FTIR spectra for raw, pretreated and hydrolyzed coconut fibres are as shown in Figure (4) below.



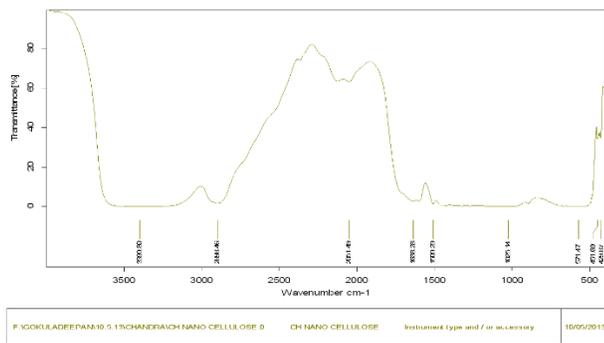
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(a) Raw coconut husk fibres



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(b) Pretreated coconut fibres



(c) Acid hydrolyzed coconut fibres

Figure (4): FTIR Spectra of Coconut fibres

Figure 4 (a), (b) and (c) shows the FTIR spectra of raw coconut husk, pretreated and acid hydrolyzed fibres respectively. Comparing the graph (a) and (b), we can observe reduction of peaks from 1736 – 1068cm⁻¹ which mentions the removal of much of lignin and hemicellulose contents by alkaline and bleaching pretreatment. The absorbance peaks at 1639, 1508, 1424 and 1048 cm⁻¹ are normalized with respect to cellulose peak at 897 cm⁻¹, assuming that a negligible amount of cellulose is removed during the bleaching process [11]. The sample residue after bleaching was more exposed to acid attack in acid treatment process since more lignin was removed. Therefore, amorphous regions are “dissolved” by acid attack and the peak ratio of lignin to cellulose increases due to the decrease in cellulose content which leads to a decrease in the absorption peak at 897 cm⁻¹ (C₁-H deformation) of glucose rings [10,11].

Vibrational frequencies (cm⁻¹) of coconut fibres with and without bleaching as well as acid treatment are tabulated as below. This Table 2 shows the peak assignments of fibres and removal of materials under different process of extraction.

Table 2
Vibrational Frequencies (Cm⁻¹) Of Coconut Fibres With And Without Bleaching As Well As Acid Treatment

Untreated fibres	Pre-treated fibres	Acid hydrolyzed fibres	Peak assignments
3404	3348	3399	O-H str.
2926	2900	2888	C-H str.
1736	-	-	C=O str. of HC (removed in pretreat)
1612	1639	1638	O-H str. def. due to H ₂ O; C=O str. of L
1513	1508	1509	C=C arom. Skeletal vibr. Of L
1443	1424	-	C-H def. of C & L (removed in acid treatment)
1373	-	-	C-H def. of HC, C & L (removed in pretreatment)
1320	-	-	CH ₂ wag of C (removed in pretreatment)
1260	-	-	C-O str. of HC & L ((removed in pretreatment)
1058	1048	1025	C-O str. (HC, L) [converted to C-O str. (C, L) in acid treatment]
896.3	897	-	Glucose ring str. C ₁ -H def. (HC,C) [removed/ peak reduced in acid process]
612	-	-	Ring bend (L) [removed in pretreatment]



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Thermogravimetric analysis of hydrolyzed coconut fibers are shown in Figure (5). The graph indicates thermal stability (TGA) and thermal decomposition (DTA) of coconut nanofibres. Red line represents TGA curve and Green line is a DTA curve. Results shows there is no water content in the material as no peak can be found at 120°C. Removal of Hemicellulose can be found by disappear of shoulder at 275°C on DTG curves and 319°C peak shows the degradation of non-sulfated cellulose. Lignin removal is reflected in the amount of residue in the range between 350 and 500°C. The thermal stability of the material is found to be 380°C - 570°C.

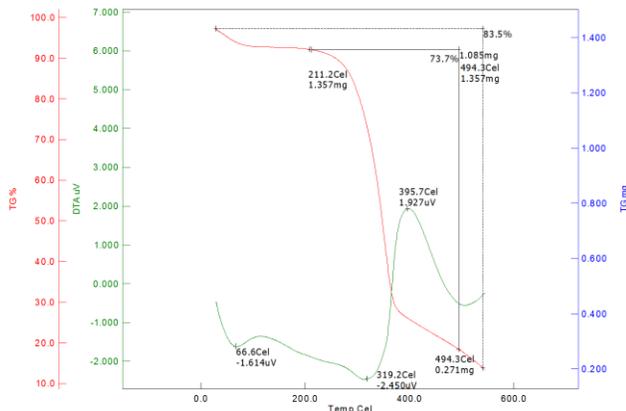


Figure (5): Thermogravimetric graph of hydrolyzed coconut fibres

V. CONCLUSIONS

Matured Coconut husk was chosen for extracting cellulose nanofibres as those fibres are highly tough and durable. Since it is a lignocellulosic material, pre-treatment processes was conducted such as alkali treatment and bleaching to remove much amount of lignin and hemicelluloses. Then, the pretreated fibres were hydrolyzed using concentrated sulphuric acid to obtain cellulose nanofibres. The raw coconut fibres, pretreated and hydrolyzed materials were characterized using different characterization techniques such as XRD, FTIR and TGA. From XRD graph, the crystalline nature of all different stages of raw, pretreated and hydrolyzed fibres were found out and the finally acid hydrolyzed fibres showed high crystalline nature than any other. Also, the average diameter of the hydrolyzed sample was found to be around 25nm.

FTIR data showed well removal of lignin and hemicelluloses in pretreatment methods, and also revealed the presence of cellulose along with different bonding natures. TGA results also confirmed successful removal of lignin and hemicelluloses; and exhibited thermal stability of the material around 380°C - 570°C. However, with all these results the finally hydrolyzed material seems to be cellulose nanofibres which is yet to be confirmed using Scanning Electron Microscope (SEM) or Transmission Electron Microscope (TEM).

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