THERMAL AND STRUCTURAL CHARACTERISTICS OF WASTE DERIVED BIOMASS FOR POTENTIAL APPLICATION IN NANOMATERIALS

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Abstract

In recent years, the interest in the use of cellulose nanowhiskers (CNW) in polymeric composite materials has increased significantly. In this work, we have investigated the thermal and structural characteristics of unripe coconut husk fibers, palm oil pressed mesocarp fibers and cotton linter, from Brazilian agribusiness wastes, as well as their extracted cellulose nanostructures. The performed assays were thermogravimetric (TG) analysis, X-ray diffraction (XRD) and transmission electron microscopy (TEM). The aim of this work was to evaluate the performance of these fibers as sources for nanocellulose extraction, as well as the quality of the several nanocelluloses for nanomaterial applications.

Introduction

The consumption of coconut water is an important economic activity in coastal regions. However, it has caused environmental concerns, due to the difficult disposal of the unripe coconut shell, which represents 80% of the gross weight of the fruit. Unripe coconut shells are agricultural wastes with high potential for biomass recovery, but with very few implemented actions in Brazil (ROSA, 2001).

The development of an agroenergy program, which involves palm and cotton oils for biodiesel production also generates concerns about the byproduct wastes.

The palm oil pressed mesocarp fiber is a waste of the oil extraction, which has significant quantities of lignocellulosic materials (GUTIERREZ; SANCHEZ; CARDONA, 2009).

The linter is a byproduct of cotton production chain. It is defined as a layer of short fibers between 3 mm and 12 mm length, which remain attached to the seed after the removal of the long fibers (lint). It is composed of almost pure cellulose, serving as an important raw material for chemical industry, as in the manufacture of hydrophilic cotton (rayon and cellulose acetate) and paper money, for instance (SSA, 2004, LU; WENG; CAO, 2005).

The concern of the modern society to reduce environmental impact and to find solutions for the depletion of non-renewable natural resources has encouraged the research and development of sustainable technologies environmental-friendly materials.

In this context, the natural fibers are presented as an alternative to the cellulose nanowhiskers (CNW) extraction and nanocomposites preparation (ALEMDAR; SAIN, 2008).

The whisker is a single filamentous crystal that can be obtained from various sources. The development of new materials appears as an option for adding value to agricultural wastes and helps to reduce their negative environmental impacts.

The use of cellulose nanowhiskers as reinforcement in nanocomposites has attracted considerable attention in the recent decades, especially because of the exceptional mechanical characteristics of these materials in polymeric matrices. The main method for cellulose nanowhiskers production is the transverse cleavage by acidic hydrolysis with sulfuric acid.

Furthermore, the replacement of synthetic fibers by natural polymeric ones from agricultural wastes is a particularly attractive alternative due to their biodegradability, renewability and relative low costs.

Unripe coconut husk fiber, palm oil pressed mesocarp fiber and cotton linter were characterized by TG and XRD. Sequentially, the nanocellulose whiskers were evaluated by TEM.

Experimental

Unripe coconut husk fibers (CF), palm oil pressed mesocarp (FD) and cotton linter (FL) were initially milled in a knife mill and passed through a sieve of 35 Mesh. Since FC and FD samples have a high content of impurities, that could reduce the accessibility of crystalline cellulose, these fibers were subjected to a pretreatment in accordance with the methodology of Dinand (1996), modified by Malainine (2003). Then, FC was treated with $NaClO_2$ (1% w/w) in acidic medium in order to remove the lignin from the fiber (WISE, 1946, ROSA, 2009). Due to the lack of papers about lignin removal from the FD, they were subjected to a "greener" methodology, in which it was used a H_2O_2 solution (20% v/v) in basic medium for 1 h at 45°C.

As FL had negligible amounts of impurities, it was not subjected to any chemical pretreatment before the acidic extraction of cellulose nanowhiskers.

The cellulose nanowhiskers were prepared by acidic hydrolysis with concentrated sulfuric acid (60-64% w/w) as described in literature (CRANSTON; GRAY, 2006, MEDEIROS, 2008a, 2008b; ORTS, 2005) with minor modifications. Afterwards, samples of partially hydrolyzed celluloses were centrifuged and water dialysed until pH (6-7) constant.

The thermal stability of the fibers was investigated by thermogravimetric (TG/DTG), performed under a nitrogen atmosphere with gas flow rate of 50 mL/min with a heating rate of 10 °C/min and temperature range from 25 to 800°C.

The measures for X-ray diffraction of the fibers, with or without treatment, were performed in a model Xpert MPD diffractometer with Co tube at 40KV and 30mA. The crystallinity index (ICr) of cellulose was calculated by the equation: $\%ICr = (1 - I_{am} / I_{002}) \times 100$, where I_{002} is the maximum intensity of diffraction of the (002) lattice peak at a 2θ angle between 26° and 27° and I_{am} is the intensity of diffraction of the amorphous material, which is taken at a 2θ angle between 21° and 22° when the intensity is minimal.

This method was developed by Segal (1959) and it has been widely used for the study of crystallinity of natural fibers.

Cellulose nanowhiskers were contrasted with uranyl acetate 20% (w/v) and were observed with a transmission electron microscopy Morgagni 268D at CETENE.

Results and Discussion

Figure 1 illustrates the decomposition profile of coconut, palm and cotton fibers under an inert atmosphere.

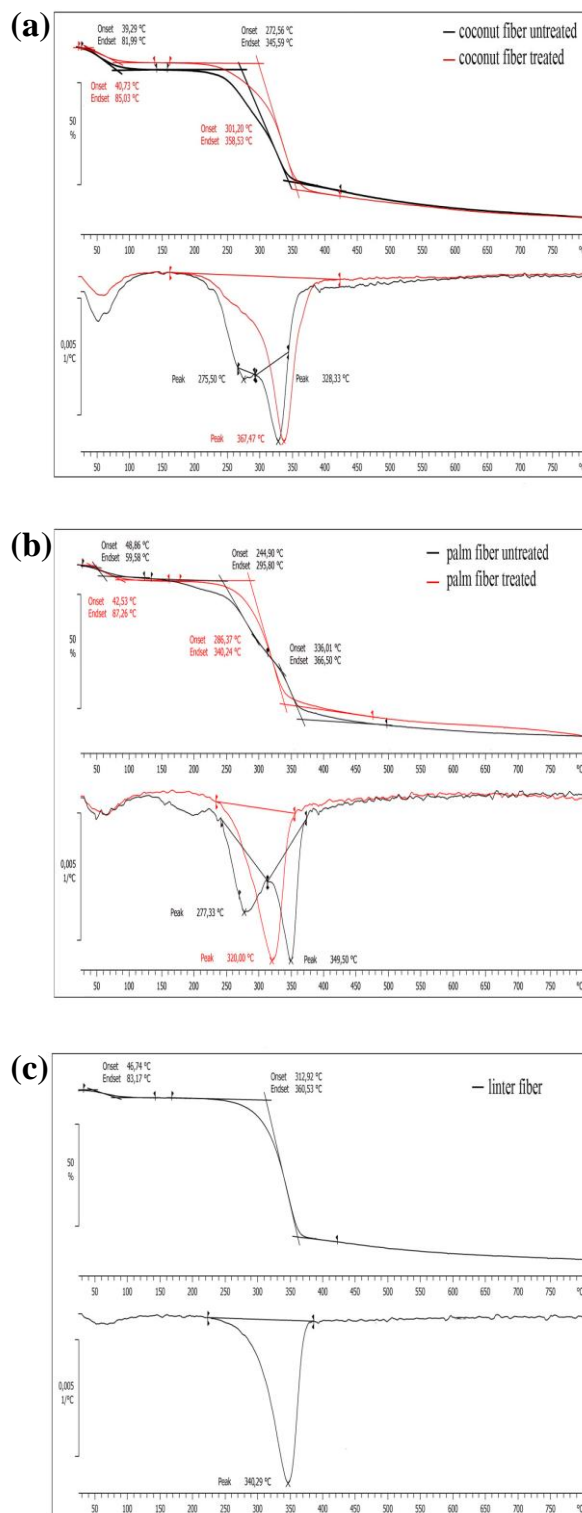The higher onset of degradation temperatures indicates the better thermal stability of the material.

Figure 1: Thermal decomposition profile of: (a) untreated and treated coconut fibers; (b) treated and untreated palm oil fibers and (c) raw linter.

Figure 2 shows the diffractograms of the fibers. The major peaks to the crystallographic plans of cellulose are related to the following Bragg angles (2θ) with intesities of 17,422° (plan 101), 19,169° (plan 101) and 26,518° (plan 002) as indicated by the International Centre for Diffraction Data - ICDD.
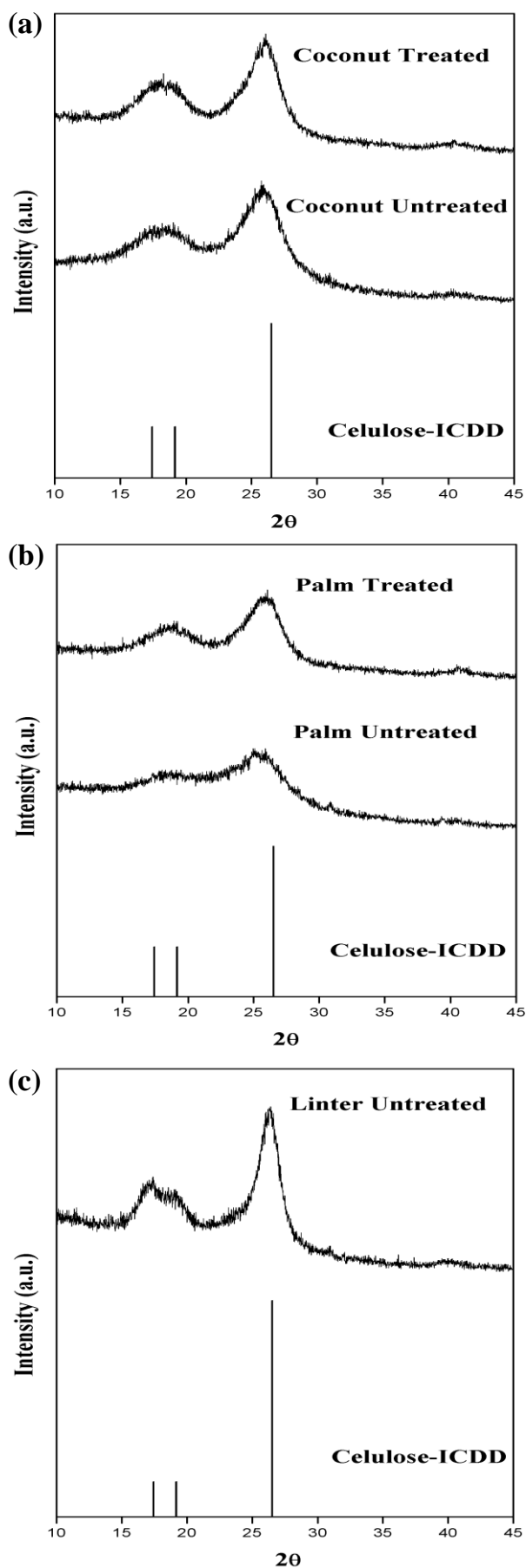
(a)

(b)

(c)

Figure 2: X-Ray Diffractograms of the fibers (a) coconut, (b) palm, (c) cotton linter

The calculated crystallinity index and the initial thermal degradation temperature T (onset) of the several samples are presented in Table 1, as follows:

Table 1: Initial thermal degradation temperature T (onset) and crystallinity index (ICr) of fibers studied.

Sample	T onset (°C)	ICr(%)
Untreated Coconut	272,56	43,10
Treated Coconut	301,20	56,88
Untreated Palm	244,90	25,67
Treated Palm	286,37	47,03
Untreated Linter	312,92	64,42

It is observed an increase in crystallinity as well as an increase in thermal stability of fibers subjected to prior treatment. The increase in the percentage of crystallinity index of the treated fibers occurs because of the removal of cementing material, which leads to a better packing of cellulose chains. As for higher thermal stability of the materials treated these changes can be interpreted in terms of removal some substances which decompose earlier than the major components, cellulose and lignin, leading to higher thermal stability of the second step of degradation (main event).

In general, the tested treatments lead to positive effects upon fibers thermal degradation and crystallinity.

The most thermal stable material was cotton linter, which starts its degradation at a higher temperature than all the others fibers, with or without treatments. It must be correlated to the highest cristallinity index in the fiber.

Plotting the crystallinity index versus onset temperature, it was verified a linear fit, as is showed in figure 3.
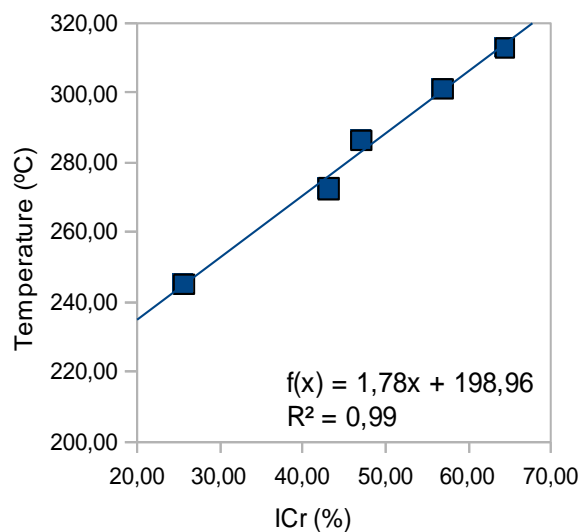

$$f(x) = 1,78x + 198,96$$
$$R^2 = 0,99$$

Figure 3: Correlation of onset temperature of thermal degradation as a function of crystallinity index.

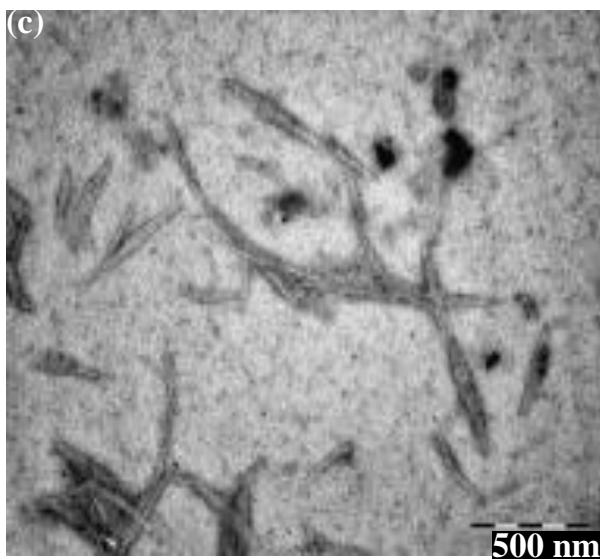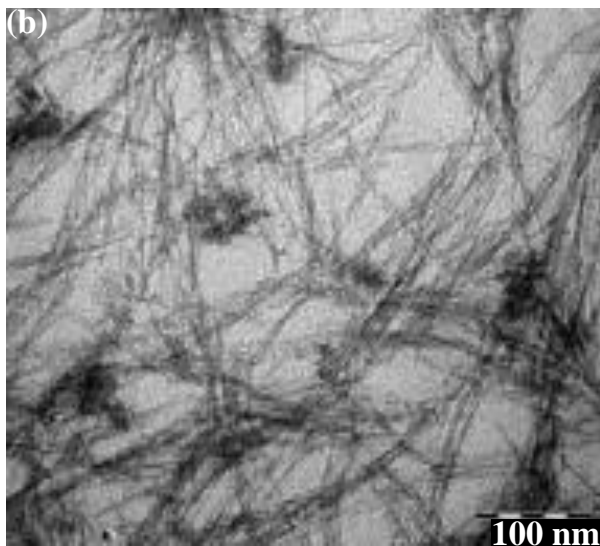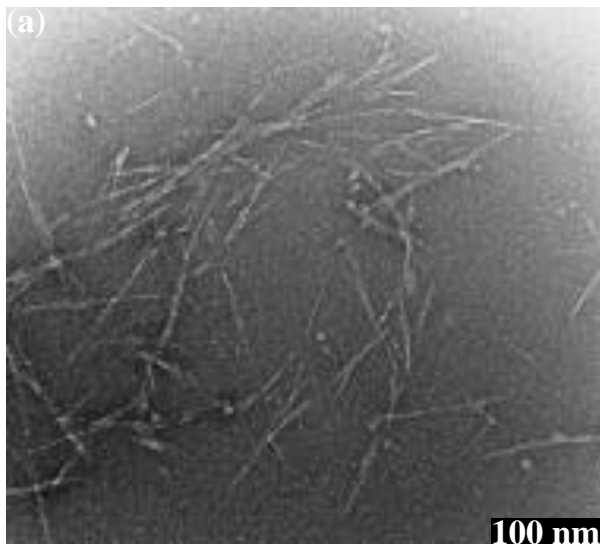The morphology of the analyzed nanofibers is shown in figure 4.

Figure 4: Transmission Electron Microscopy of cellulose nanowhiskers from (a) unripe coconut husk fiber, (b) palm oil pressed mesocarp fiber and (c) cotton linter.

It is noticeable by a few individualized nanofibers that there is a needled format in the nanostructures, which confirms the structural model proposed by Battista and Smith (1962), suggesting that the microfibrils consist of monocrystalline cellulose domains arranged in bundles.

Conclusions

Chemical treatments have improved thermal stability as well as removed the amorphous fraction of fibers, which was evidenced by the increased crystallinity of the treated ones.

The linter showed thermal stability and crystallinity index quite attractive, even that it was not subjected to any kind of chemical treatment.

TEM observed nanocrystals have showed attractive dimensions for a potential incorporation as a reinforcing agent in composites.

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