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New products made with lignocellulosic nanofibers from Brazilian amazon forest

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Abstract. The biodiversity of the Amazon forest is undoubtedly rich; hence there is considerable variety of plant fibers regarding their morphological, chemical and structural properties. The legal exploration of the Brazilian Amazon is based on sustainable management techniques, but the generation of a relevant amount of plant wastes still can`t be avoided. The correct destination of such materials is a challenge that Brazilian companies have to face. In this context, the National Council of Science and Technology (CNPq) promoted the creation of investigation nets on sustainability of Brazilian agribusiness. The Brazilian Net on Lignocellulosic Composites and Nanocomposites was then created, with partnership between several national and international research institutions. Until the moment, the results showed that Amazon plant fibers that are discarded as residues have great potential to nanofiber production. Nanopapers with considerable high mechanical and physical strength, proper opacity and great crystalline index were produced by using a clean and simple mechanical method. Those materials are candidates to several uses such as packaging, substrates transparent conductive films, gas barrier films, solar cells and e-papers.

1. Introduction

Lately, there is a genuine interest and need to decrease society`s dependency on petroleum bio-based products. Inspired by this environmental awareness and new standards, the development of biodegradable materials with improved performance is crucial [1, 2].

This context, combined with new technology development in nanotechnology field, strongly favors the use of cellulose. The annual biomass production of cellulose in nature is about 1 trillion tons, making it a virtually inexhaustible source of raw material that may be obtained from non-wood plants, woods, bacteria and tunicate forms [3, 4].

Since the biodiversity of the Amazon forest is undoubtedly wide, this tropical environment certainly offers an enormous potential to provide cellulose sources. It should be mentioned that the legal exploration of the Brazilian Amazon is based on sustainable management techniques, but the generation of a relevant amount of plant wastes still can`t be avoided. In this context, the National Council of Science and Technology (CNPq) promoted the creation of investigation nets on sustainability of Brazilian agribusiness. The Brazilian Net on Lignocellulosic Composites and Nanocomposites was then created, with partnership between several national and international research institutions. One of the goals of this partnership is to investigate the potential of wastes from wood processing for the production of nanopapers. Those materials are candidates to several uses such as packaging, substrates transparent conductive films, gas barrier films, solar cells and e-papers. Partial results from such efforts are given in this work.

2. Methodology

Veneers for saw wood of three certified Amazonian species were selected, namely *Cordia goeldiana, Brosimum parinarioides*, and *Parkia gigantocarpa*. Those species are legally used by a Brazilian panel company for tropical plywood production within the terms of sustainable management of the Amazon forest. Low-quality veneers for plywood production from the four species were reduced in a hammer mill and transformed into sawdust in a disintegrator.

2.1. Cellulose isolation

The sawdust was previously submitted to chemical modification through two stages: 1) Alkali treatment with NaOH at 5% in a digester, at 150˚C for 30 min; 2) Bleaching with H_2O_2 at 24% and NaOH at 4% under mechanical stirring at 60˚C for 2 h.

2.2. Nanopaper production

The bleached fibers were immersed in distilled water at a proportion of 1% (m:m). The fibers were then submitted to fibrillation in a grinder resulting in a suspension of structures known as microfibrillated celluloses (MFC`s). After 40 cycles the suspensions were poured on Petri dishes and the nanopapers were formed after about 5 days.

2.3. Nanopaper and MFC`s properties

The following analyses are presented:

- Scanning electron microscopy (SEM) investigation: The SEM micrographs of the *C. goeldiana* MFC's and raw sawdust were taken using a JEOL scanning electron microscope (SEM) model JMS 6510 with an acceleration voltage of 10 kV. The samples were previously sputter coated with gold before examination;

- Strength to water deterioration: Four 2 cm – diameter samples were obtained from the nanopapers of each species and previously dried at 100˚C for 24 h. The samples were then weighted and immersed in water for 24 h under soft mechanical stirring. The samples were dried once again at the above mentioned conditions. After weighting, the percentage of mass loss was calculated;

- Tension strength: The analysis was carried out according to ASTM D882-12 (ASTM, 2012);

- X-ray diffraction: The diffractograms of the nanopapers were recorded on a Rigaku diffractometer model XRD 600 operating at 30 kV, 30 mA and CuKα radiation (λ = 1540 Å). The samples were placed on aluminum holders and scanned in 2θ/min ranges varying from 5 to 37.5˚ (2˚ min^{-1}). The extension of crystalline (CI) was estimated on the basis of areas under crystalline and amorphous peaks after appropriate baseline correction. The diffractograms were fit by placing Gaussian shaped peaks and the crystalline index (CI) was calculated by Eq. 3;

$$CI = (Ca/Ta)100$$

Where: Ca is the sum of the areas under the crystalline peaks; and Ta is the sum of the areas under the crystalline peaks and amorphous peak.

- Opacity change acquired by nanopapers is visually presented.

3. Results and Discussion

The difference between the raw wood sawdust and the obtained nanomaterial can be examined by SEM micrographs (figures 1 and 2). The raw sawdust presents bundles of fibers connected by amorphous bending materials which are intended to be removed by alkali and bleaching treatments. Afterwards, by only submitting the fibers to high mechanical shearing forces, disintegration of the fibers occurs, leading to the formation of MFC`s. Generally, MFC`s consists of nanofibril aggregates, whose lateral dimensions range between 10 and 30 nm [4]; hence those were successfully obtained previously to drying for nanopapers production.

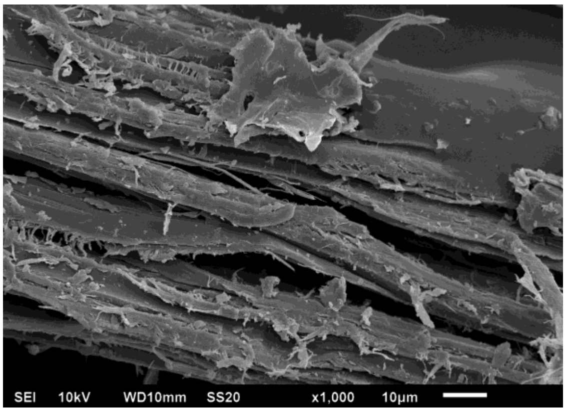

Figure 1. Micrograph of a fiber bundle from *C. goeldiana* raw sawdust (X 1000)

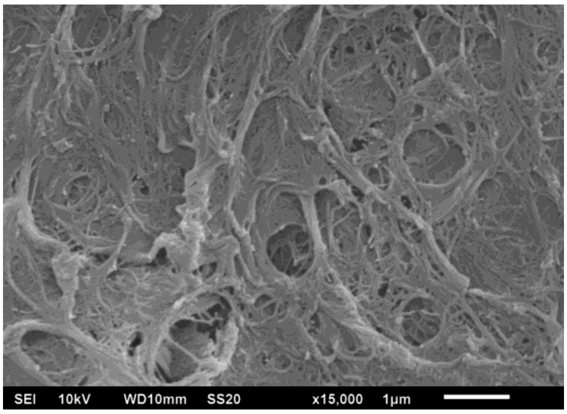

Figure 2. Micrograpn of microfibrilated fibers from *C. goeldiana* (X 15000)

Water deterioration analyses clearly showed high strength of the nanopapers produced from hardwood wastes. Among the four samples of each species, two from *B. parinaiodes* and *P. gigantocarpa* nanopapers showed no detectable mass loss, while the same happened for one sample obtained from *C. goeldiana* nanopapers. The remaining samples present mean deterioration ranging from 14 to 17% and the values were similar among nanopapers from different species (figure 3). Cellulose is a relatively stable polymer that does not readily dissolve in water [5]. As the nanopapers are basically comprised of MFC`s closely connect in a net, high water strength was achieved.

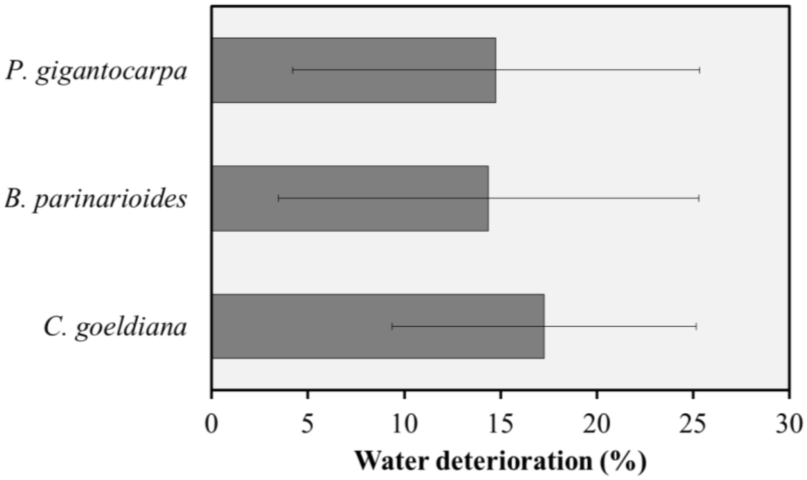

Figure 3. Water deterioration index of the nanopapers

Tension strength and crystalline indexes of the nanopapers are depicted in table 1. *C. goeldiana* nanopapers had the greatest mechanical strength. The nanopapers from this species were less bleached which suggests a higher amount of residual lignin which could act as a binder between the MFC's improving tension strength.

Table 1. Crystal index and mechanical strength of the nanopapers

Species	Tension Strength (MPa)	Crystalline index (%)
C. goeldiana	50.7$^{(7.6)}$	91
B. parinarioides	37.0$^{(6.6)}$	93
P. gigantocarpa	42.0$^{(6.6)}$	86

Crystalline indexes of the nanopapers ranged from 86 to 91%. The high and different values are related to previous removal of amorphous materials and the fibrillation process. The microfibrils consist of monocrystalline mesomorphous cellulose domains in a larger amount linked by amorphous domains that occur in smaller amount [1, 3, 6]. In cellulosic materials from several sources the length of crystallites ranges from 50-150 nm, while the disordered domains are 25-50 nm [3].

Changes in properties from micro to nano scale can be also clearly observed when a film made from cellulose bleached fibers is compared to a film made from cellulose nanofibers (figures 4, 5 and 6). It should be mentioned that the paper and nanopaper present in the pictures have exactly same chemical constitution and only a mechanical processing applied to achieve nanoscale was able to completely modify the opacity property.

Figure 4. Uncovered picture

Figure 5. Picture covered by *B. parinarioides* paper

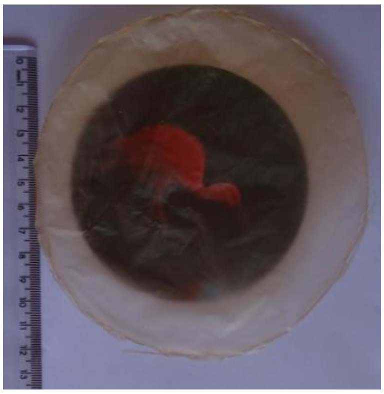

Figure 6. Picture covered by *B. parinarioides* nanopaper

4. Conclusion remarks

Nanopapers were produced from Amazon hardwood processing wastes in this work and showed promising results. High mechanical and physical strength were observed combined with high crystal index and opacity change. By using a simple and clean mechanical process it is possible to assure the utilization of wastes from Amazon wood processing avoiding them from injuring the environment.

Acknowledgments

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