

## LUFFA CYLINDRICA AS A LIGNOCELLULOSIC SOURCE OF FIBER, MICROFIBRILLATED CELLULOSE, AND CELLULOSE NANOCRYSTALS

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In this work the annual plant called *Luffa cylindrica* (LC) has been characterized and used to prepare macroscopic lignocellulosic fibers and cellulosic nanoparticles, viz. microfibrillated cellulose (MFC) and whiskers, each of which can be used as a reinforcing phase in bionanocomposites. The morphological, chemical, and physical properties of LC fibers were first characterized. The contents of lignin, hemicellulose, and other constituents were determined, and scanning electron microscopy (SEM) observations were performed to investigate the surface morphology of the LC fibers. Sugars contents were determined by ionic chromatography, and it was shown that glucose was the main sugar present in the residue. MFC and whiskers were prepared after chemical treatments (NaOH and NaClO<sub>2</sub>), purifying cellulose by eliminating lignin and hemicellulose. Transmission electron microscopy (TEM) and SEM made it possible to determine the dimensions of LC whiskers and MFC. Tensile tests were carried out to investigate the mechanical properties of LF nanoparticles.

*Keywords:* Whiskers – Microfibrillated Cellulose (MFC) – *Luffa cylindrica* – mechanical properties.

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### INTRODUCTION

Huge quantities of natural fibers are produced yearly worldwide from biomass. Each source of natural fibers, e.g. cotton, flax, sisal, or palm tree, displays its own morphological characteristics and chemical composition. These resources already have been used for several centuries, but their importance is growing in our society because of the search for sustainable solutions in materials. This point is confirmed by the declaration of 2009 as the year of natural fibers according to the Food and Agriculture Organization of the United Nations (FAO).

The main components of natural fibers are cellulose, lignin, and hemicelluloses. They are therefore referred to as lignocellulosic materials. In lower quantities pectins, pigments, and extractives can be found (Dufresne in press). Each constituent provides different properties that contribute to the overall properties of the fiber and justify its use as reinforcing material. Since hemicelluloses display lower resistance, they are responsible for thermal and biological degradation and also moisture absorption. Lignin is thermally stable but sensitive to UV degradation (Saheb and Jog 1999). Natural fibers

such as flax, hemp, straw, kenaf, jute, and sisal are usually listed as raw material when used as a reinforcing phase in biocomposites (Dufresne in press).

Meanwhile, over the last decades there has been an increasing interest in reinforcing composite materials with nanosized particles, i.e. for the preparation of nanocomposites (Bondenson et al. 2006). The push for nanocomposites can be related to the large window of opportunities opened to overcome the limitations of traditional micrometer-scale composites (Dufresne in press). Moreover, nanocomposites can provide extraordinary properties never found in conventional composites (Azizi Samir et al. 2005).

Cellulose fibers can be used to process nanocomposite materials. They naturally occur as micrometer-scale entities, and the first step consists in going from this scale to nanometer scale. There are two different possibilities to obtain nanoelements from cellulose sources. It is possible to produce either microfibrillated cellulose (MFC) or nanocrystals, also called whiskers. MFC consists of high aspect ratio cellulose nanofibrils prepared by mechanical homogenization of cellulose fibers (Herrick et al. 1983). Through this process, cellulose fibers are opened up and unraveled to expose smaller fibrils and microfibrils (Herrick et al. 1983; Turbak et al. 1983). MFC is produced as a dispersion in water or other polar solvents. The lateral dimension of MFC is in the order of 10-100 nm (Lu et al. 2008; Nakagaito and Yano 2005), and the length can be in the micrometer scale, both parameters depending on the preparation method.

Whiskers are high-purity single cellulose crystals obtained after treatment of fibers under controlled conditions (Azizi Samir et al. 2005). Stable aqueous suspensions of cellulose nanocrystals are prepared by acid hydrolysis of the biomass. Geometrical characteristics of these nanoparticles depend on the nature of the cellulosic substrate and acid hydrolysis process conditions such as time, temperature, and purity of the material (Beck-Candanedo et al. 2005; Viet et al. 2009). This hydrolysis treatment, generally performed using sulfuric acid and bleached fibers, consists in the disruption of amorphous cellulosic regions surrounding and embedding cellulose microfibrils while leaving the crystalline domains intact (Dufresne in press). Recent papers and reviews confirm the impact of using such cellulose nanoparticles (whiskers or MFC) on thermomechanical properties of bionanocomposites (Azizi Samir et al. 2005; Habibi et al. 2008; Bondenson and Oksman 2007; Bendahou et al. 2008; Siqueira et al. 2009).

*Luffa cylindrica* (LC) is a tropical plant, belonging to the family of *Cucurbitacea*, with fruits possessing a netting-like fibrous vascular system. The LC's struts are characterized by a microcellular architecture with continuous hollow microchannels, which form vascular bundles and yield a multimodal hierarchical pore system (Zamperi et al. 2006). This specific morphology makes it possible to imagine a specific composition on crystallinity cellulose.

The chemical composition of LC fibers depends of several factors, such as plant origin, weather conditions, soil nature, etc. For instance, the cellulose content varies from 55 to 90%; the lignin content is within the range 10 to 23%; the hemicellulose content is around 8 to 22%; extractives nearly 3.2%, and ash 0.4% (Satyanarayana et al. 2007; Tanobe et al. 2005). The choice of this source is related to its high cellulose content (Satyanarayana, et al. 2007). The density of LC is around 0.82 to 0.92 g/cm<sup>3</sup> (Satyanarayana et al. 2007; Tanobe et al. 2005), which is lower than the density of some

common natural fibers like sisal (1.26 to 1.45 g/cm<sup>3</sup>) (Sydendtricker et al. 2003; Li et al. 2000), hemp (1.48 g/cm<sup>3</sup>), coir (1.25 g/cm<sup>3</sup>), ramie (1.5 g/cm<sup>3</sup>), and cotton (1.51 to 1.6 g/cm<sup>3</sup>) (Wambua et al. 2003; Bledzki, and Gassan 1999).

One of the main uses of LC is as bath sponges, but they are also used as filler in the production of composites materials, materials of adsorption in water treatments stations during the step of ion exchange, etc. (Tanobe et al. 2005). However, according to Davis et al. (1993), the main market for LC is the cosmetic industry, which uses LC in various bath and cosmetic products. Only few papers have been dedicated to this source of fiber.

In this manuscript, we investigate the morphology and chemical composition of LC fibers with the objective to evaluate the use of this natural material as a source of nanoreinforcement phases in bionanocomposites. The possibility to obtain MFC and whiskers from this source was also studied, and these new bionanoparticles were thoroughly characterized.

## **EXPERIMENTAL SECTION**

### **Materials**

Native LC fibers, originally from Southeast Brazil, were purchased in Belo Horizonte (Minas Gerais, Brazil).

### **Fibers Preparation**

LC fibers were cut with a FRITSCH Pulverisette mill, until fine particulate fibers were obtained. The ensuing fibers were treated with 4 wt% NaOH solution at 80°C for 2 h under mechanical stirring. This treatment was done 3 times, in order to purify cellulose by removing other constituents present in the fibers. After each treatment the, fibers were filtered and washed with distilled water until the alkali was completely eliminated. A subsequent bleaching treatment was carried out to remove lignin and whiten the fibers. The solution used in this treatment was made by equal parts of acetate buffer, aqueous chlorite (1.7 wt% in water), and distilled water. The bleaching treatment was performed 4 times at 80°C, under mechanical stirring, with each treatment lasting 2 h. After each treatment, the fibers were filtered and washed with distilled water.

### **Whiskers Preparation**

Acid hydrolysis was achieved at 50°C with 65 wt% sulphuric acid (pre-heated), for 40 min, using mechanical stirring. The fiber content during the whole chemical treatment ranged between 4 and 6 wt%. The suspension was diluted with ice cubs to stop the reaction and washed until neutrality by successive centrifugations at 10,000 rpm and 10°C for 10 min each step and dialyzed against distillate water, in that sequence. Afterwards, the LC whiskers suspension was homogenized by using an Ultra Turax T25 homogenizer for 5 min and filtered using glass filter n°1. Some drops of chloroform were added to the whiskers suspension, which was stored at 4°C.

### Microfibrillated Cellulose (MFC)

A solution of bleached LC fibers (2.0% w/v) was pumped through a microfluidizer processor, Model M-110 EH-30. The slurry was passed through the valves that applied a high pressure. Size reduction of products occurred into an Interaction Chamber (IXC) using cells of different sizes (400  $\mu\text{m}$  and 200  $\mu\text{m}$ ). The number of passes was varied in order to optimize the fibrillation process.

### Analytical Methods

After hydrolysis with  $\text{H}_2\text{SO}_4$ , neutral sugars were analyzed by ion chromatography (Dionex DX500) with a CarboPac PA-1 column and guard column and an electrochemical detector ED40 with a gold electrode. The products of hydrolysis were filtered (0.45 $\mu\text{m}$ ), neutralized with sodium hydroxide, and diluted 20 times. To determine the sugar concentration in the solution, an internal standard was added at 1.0  $\text{mgL}^{-1}$ .

The chemical composition of LC fibers was determined by the methods shown in the following sequence: holocellulose, cellulose, and hemicellulose (TAPPI T257 om-85), lignin (TAPPI T222 om-88), ash (TAPPI T211 om-85), and extractives (TAPPI T264 om-88). A minimum of three samples of each material was tested, and averaged values were obtained.

### Scanning Electron Microscopy (SEM)

A field emission scanning electron microscope (FESEM), model Quanta 200 FEI, with accelerating voltage of 12.5 kV was used to study LC fibers and MFC surface topography. The samples were mounted onto a substrate with carbon tape and coated with a thin layer of gold.

### Transmission Electron Microscopy (TEM)

A Philips CM200 transmission electron microscope (TEM) was used to observe LC whiskers, using an acceleration voltage of 80 kV. A drop of diluted suspension of sisal whiskers was deposited on a carbon-coated grid. The samples were stained with a 2 wt% uranyl acetate solution to obtain a negative coloration of the samples.

### Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analysis was performed with a Mattson 5000 spectrometer, equipped with single reflection ATR attachment and a ZnSe crystal.

### X-Ray Diffraction

X-Ray analyses were recorded in a PANALYTICAL X' PERT PRO MPD-Ray diffractometer with Ni-filtered Cu  $\text{K}\alpha$  radiation ( $\lambda=1,54\text{\AA}$ ) generated at a voltage of 45 kV and current of 40 mA, and scan from 5° to 60°.

The crystallinity index was calculated using the Buschle-Diller and Zeronian (1992) equation,

$$I_c = \frac{1 - I_1}{I_2} \quad (1)$$

where  $I_1$  is the intensity at the minimum ( $2\theta=18^\circ$ ) and  $I_2$  is the intensity associated with the crystalline region of cellulose ( $2\theta=22.5^\circ$ ).

### Morfi Analyses

The length of bleached fibers was determined by Morfi analyses using TECHPAP LB 01 Morfi equipment (fiber content of 0.300 g/L).

### Tensile Tests

Tensile strength tests were carried out with a RSA3 (TA Instruments, USA) equipment with a 100 N load cell. Measurements were performed with a cross head speed of  $10 \text{ mm}\cdot\text{min}^{-1}$  at  $25^\circ\text{C}$ . The samples were prepared by cutting strips from the films 30 mm long, and the distance between jaws was 10 mm. The width and the thickness of the samples were measured before each measurement. The width of the specimens was around 4 mm, and the thickness was around 0.02 mm and 0.01 mm for MFC's and whisker's films, respectively. The Young's modulus values were determined from the initial slope of tensile curves. Five samples were used to characterize each sample.

## RESULTS AND DISCUSSION

### Fibers Analysis

The composition, i.e. lignin, cellulose, hemicellulose, extractives, and ash content, was measured for LC fibers. All results are reported in Table 1. These values agree with those reported in the literature (Turbak et al. 1983; Lu et al. 2008), which are given in Table 2. Table 2 also presents the chemical constituents values taken from the literature for other annual plants such as sisal, ramie, cotton, and hardwood. The cellulose content of LC is similar to sisal and ramie, but lower than for cotton. It is higher than that of hardwood. The lignin and hemicellulose content is higher than for sisal, ramie, and cotton, but lower than for hardwood. The compositions reported for the various species generally display a broad range of values, since it is well known that the climatic conditions, type of soil, extractive method, age, and digestion process influence not only the structure of fibers but also the chemical composition (Sydendtricker et al. 2003; Bledzki and Gassan 1999).

The sugar analysis of hydrolysis residue was performed and results are reported in Table 3. It is shown that glucose is the main sugar present in the residue, confirming its cellulosic nature and indicating that LC could be a good source for the preparation of cellulose whiskers and MFC.

Figure 1 shows SEM micrographs of raw LC fibers (before and after the milling process), and of bleached fibers. From this morphological analysis, it is possible to observe the rough surface of the fibers before the milling process (panels A and B). On the other hand, the morphology of LC fibers is completely different after milling (panels C and D). The fibers display a more homogeneous aspect with smooth surfaces which corresponds to cellulose hornification, as already proven during dry refining of fibers and is explained by a zipping-up of void volume (Crawshaw and Cameron 2000). Obviously, the milling process cuts the fibers and modifies their length, which is important for the

preparation of MFC and cellulose whiskers, because the specific area of the fibers can strongly influence the hydrolysis process. It is important to have a homogeneous mixture of fibers with similar dimensions to avoid a too high or too low hydrolysis reaction in the same batch. Figures 1E and 1F prove that NaOH and bleaching treatments lead to fiber fibrillation and breaking-down of the fiber bundles into smaller fibers. The lengths of bleached fibers were determined by Morfi analysis, and an average value around 470 $\mu$ m was reported.

**Table 1.** Chemical Composition of *Luffa cylindrica* Fibers

Component	Content (wt%)
Ash	0.7 $\pm$ 0.2
Extractives	3.1 $\pm$ 0.5
Total Klason Lignin	15.2 $\pm$ 1.0
Cellulose	65.5 $\pm$ 0.5
Hemicellulose	17.5 $\pm$ 0.5
Holocellulose	83 $\pm$ 1

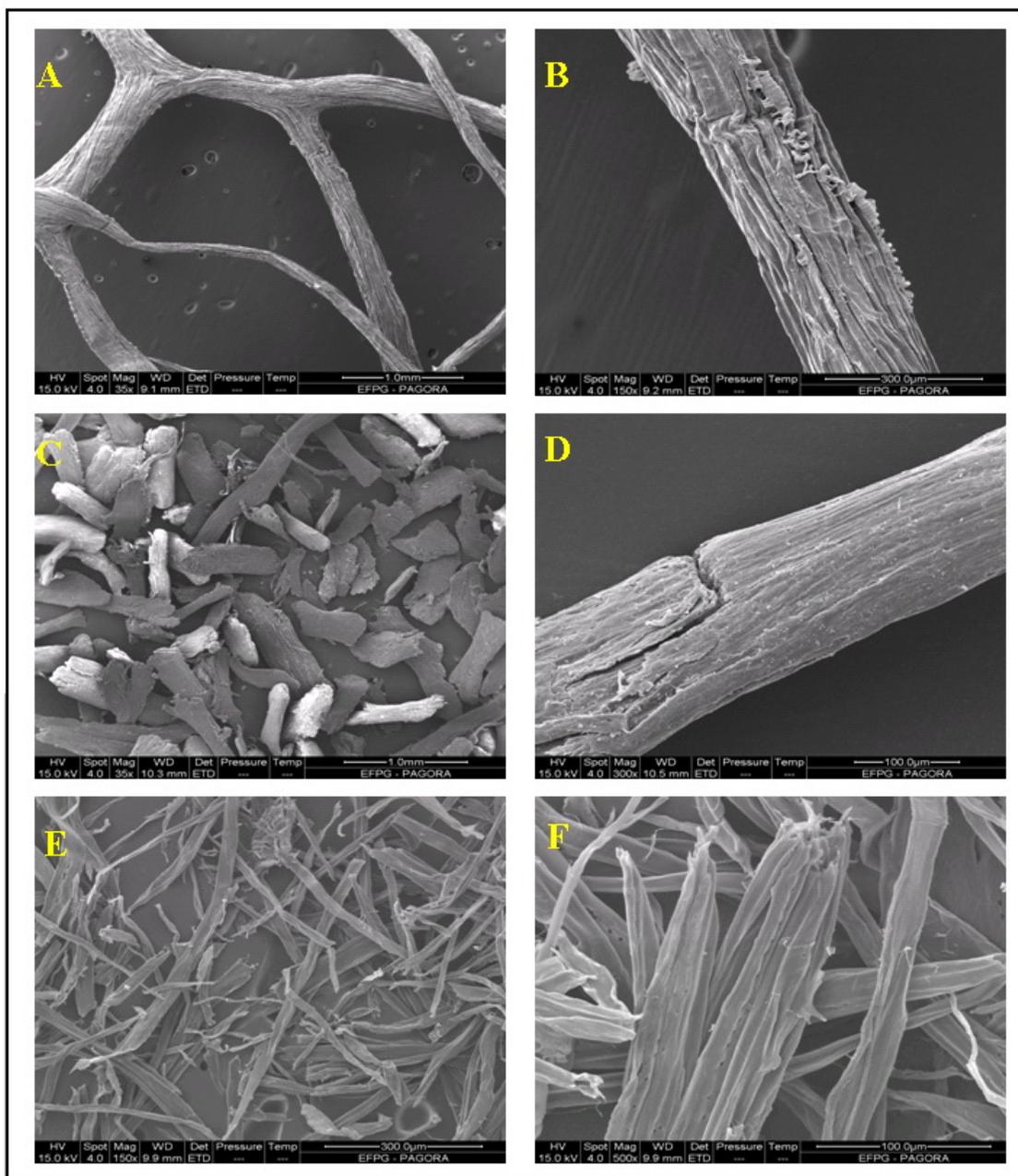
**Table 2.** Chemical Composition of Some Lignocellulosic Sources

Fiber	$\alpha$ – Cellulose (wt%)	Hemicellulose (wt%)	Lignin (wt%)	Reference
Sisal	60 – 75.2	10.0 – 16.5	7.6 – 12.0	(Satyanarayana et al. 2007; Sydendtricker et al. 2003; Bledzki and Gassan 1999)
Ramie	68.6 – 85.0	3.0 – 13.1	0.5 – 0.6	(Satyanarayana et al. 2007; Bledzki and Gassan 1999)
Cotton	82.7 – 90.0	5.7 – 6.0	–	(Satyanarayana et al. 2007; Bledzki and Gassan 1999)
<i>Luffa cylindrica</i>	60.0 – 63.0	19.4 – 22.	10.6 – 11.2	(Satyanarayana et al. 2007; Tanobe et al. 2005; Hanini and Bouaziz 2003)
Hardwood	40.0 – 45.0	32.0 – 33.0	17.0 – 26.0	(Hanini and Bouaziz 2003)

**Table 3.** Sugar Composition of *Luffa cylindrica*'s Hydrolysis Residue

Source	Sugar composition (wt%)*			
	Arabinose	Galactose	Glucose	Xylose
<i>Luffa cylindrica</i> fibers	0.74 $\pm$ 0.01	0.58 $\pm$ 0.07	67.22 $\pm$ 2.57	12.26 $\pm$ 0.14

\* Expressed in relative weight percentages.

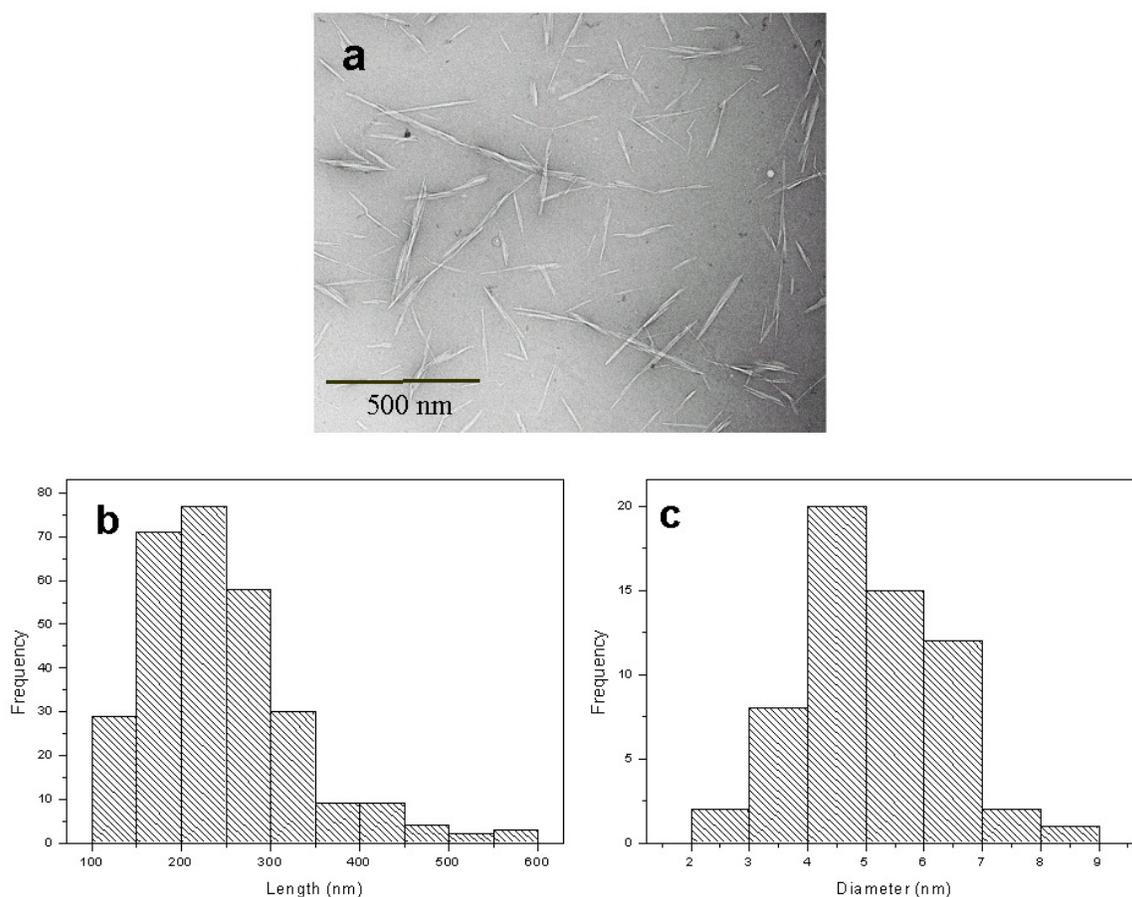


**Fig. 1.** Scanning electron micrographs of *Luffa cylindrica* fibers before the milling process (A and B), milled fibers (C and D) and bleached fibers (E and F)

The morphology of LC fibers is classical, and they can be bleached with quite high yield, as their lignin content is lower than the one of wood. It is also possible to have a homogeneous mixture of cut cellulose fibers after milling and bleaching treatment, which is a preliminary condition before whiskers and MFC preparation. The milled fibers could also be used in fiber reinforced polymer composites that have been strongly developed in the last few years, such as wood-polymer composites (Bledzki and Gassan, 1999).

## Whiskers and MFC

Milled and bleached LC fibers were mixed with 65 wt% sulphuric acid during a short time to limit glucose formation. After washing and dialysis, a whiskers suspension was obtained. Figure 2a shows a transmission electron micrograph of well dispersed LC whiskers. They classically occur as stiff rod-like nanoparticles. The average length (Fig. 2b) and diameter (Fig. 2c) were determined using digital image analyses (Image J). The geometrical average length and diameter of LC whiskers were  $242 \pm 86$  nm and  $5.2 \pm 1.3$  nm, respectively. Figures 2b and 2c also show the histograms corresponding to these measurements. For the determination of the length of LC whiskers, 292 measurements were performed, whereas 60 measurements were done in order to determine their diameter. Therefore, the aspect ratio of LC whiskers is around  $L/d = 46.8$ . It is very similar to that reported for some other annual plants already used for the preparation of cellulosic whiskers, e.g. sisal whiskers ( $L/d = 43$ ) (Siqueira et al. 2009), wheat straw ( $L/d = 45$ ) (Helbert et al. 1996), or rachis of the date palm tree ( $L/d = 43$ ) (Bendahou et al. 2009).



**Fig. 2.** Transmission electron micrograph of a dilute suspension of *Luffa Cylindrica* nanocrystals. Length and diameter histograms of *Luffa cylindrica* whiskers.

Figure 3 shows an SEM image of LC MFC. They display a classical morphology and occur as very long entangled cellulosic filaments. The diameter of LC MFC was determined by digital image analysis (Image J) of SEM micrographs. About 50 measurements were done in order to determine the diameter. The result of this analysis shows that the diameter was around  $55 \text{ nm} \pm 15 \text{ nm}$ . The length of MFC was not determined. The film formed when the MFC suspension was dried did not allow the determination of its length, which is generally considered as practically infinite.

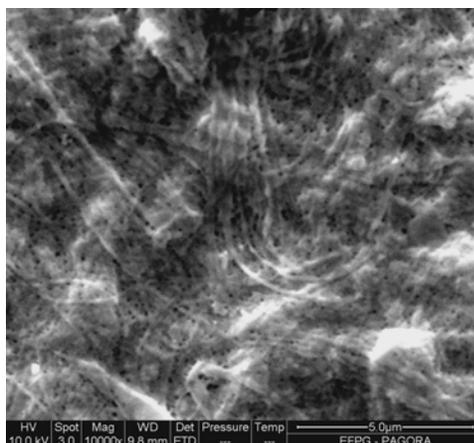


Fig. 3. Scanning electron micrograph of *Luffa cylindrica* MFC

### Physical and Chemical Properties

Figure 4 shows infrared spectra of untreated LC fibers, MFC and whiskers. It can be seen in Figure 5 that the peak at  $1735 \text{ cm}^{-1}$ , present in the untreated LC fiber, disappeared after treatments with NaOH 4% and NaClO<sub>2</sub>, which were performed before MFC and whiskers preparation. The band in the spectrum near  $1730 \text{ cm}^{-1}$  is assigned mainly to C=O stretching vibration of the carbonyl and acetyl groups in the xylan component of hemicellulose and also chemical groups of lignin as studied by Kataoka and Kondo (1998). The band near  $1240 \text{ cm}^{-1}$ , which appears in the untreated fibers FTIR spectrum corresponds to axial asymmetric strain of =C–O–C. It is commonly observed when =C–O–, e.g. in ether, ester, and phenol groups are present. The former band isn't found in the spectra of *Luffa cylindrica* MFC and whiskers. It can also be explained by the elimination of lignin and hemicellulose by chemical treatments.

The other bands are well-known and specific to cellulose. We can quote as an example the large band at  $3300\text{-}3500\text{cm}^{-1}$  related to O-H groups or the C-H band at  $2900 \text{ cm}^{-1}$ . Bands between  $800 \text{ cm}^{-1}$  and  $1500 \text{ cm}^{-1}$  are also specific to cellulose, and some of them have been studied in detail to determine the crystalline organization and allomorph composition (Akerholm et al. 2004). In our case, X-ray diffraction was preferred for such measurements.

The crystallinity index ( $I_c$ ) of the various samples was calculated from the intensity of the peaks from crystalline region of XRD curves, as shown in Fig. 5. LC untreated fibers displayed a value  $I_c = 81.3\%$ , LC MFC  $I_c = 90\%$ , and LC whiskers  $I_c = 96.5\%$ .

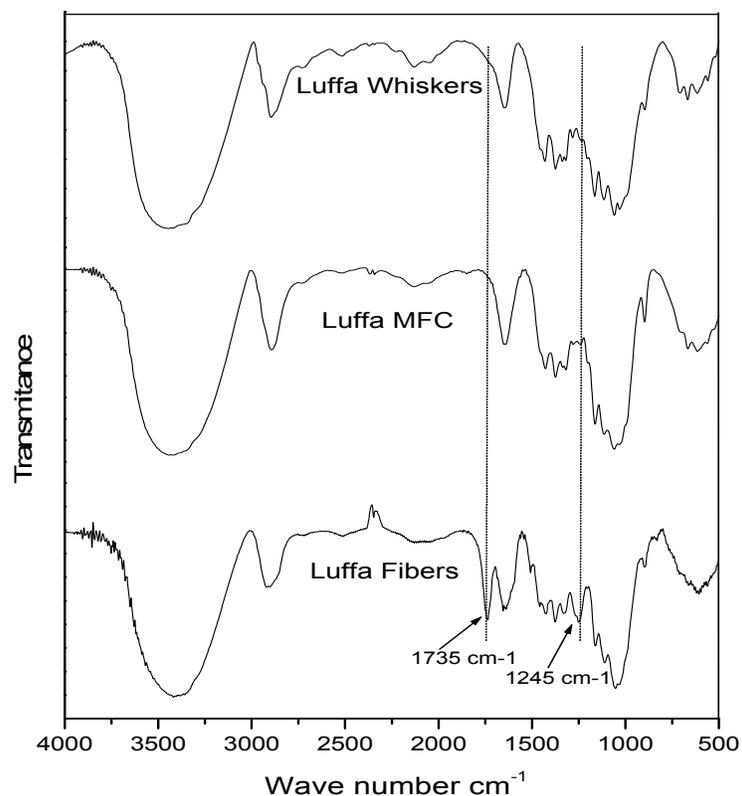


Fig. 4. FTIR spectra of *Luffa cylindrica* fibers, MFC and whiskers

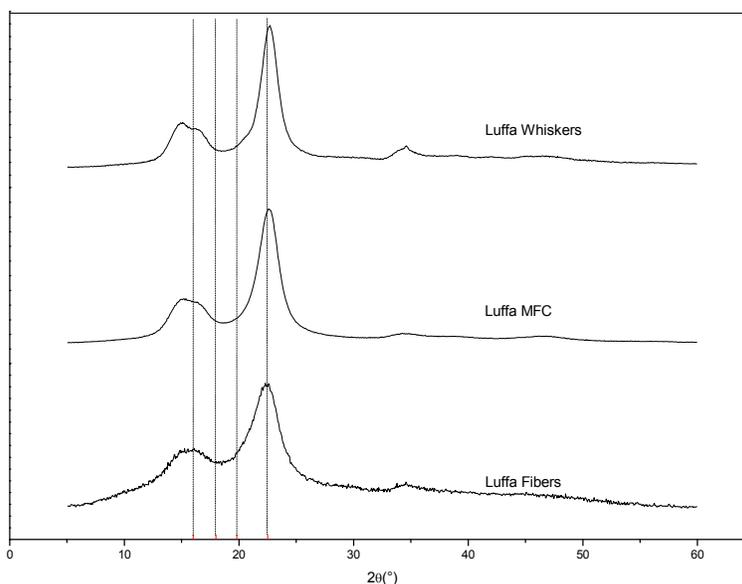


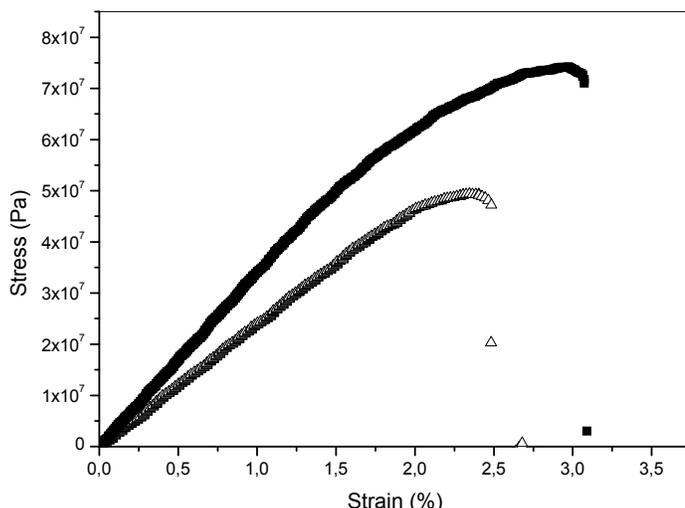
Fig. 5. X-ray diffraction patterns of *Luffa cylindrica* fibers, MFC and whiskers

The increase of the degree of crystallinity for LC MFC and whiskers compared to the initial raw fibers can be explained by the partial elimination of amorphous regions from the fibers during alkali and bleaching treatments, performed before MFC and whiskers preparation. The preparation of LC nanocrystals involves an acid hydrolysis

treatment with  $H_2SO_4$ . This treatment allows removal of cellulosic amorphous domains (Dufresne 2008). Actually, this step consists of the disruption of amorphous regions surrounding and embedding cellulose microfibrils while leaving the microcrystalline segments intact. So, the increase of the degree of crystallinity when comparing LC whiskers with LC MFC was expected and confirmed the effectiveness and quality of the treatment.

### Mechanical Properties

Typical stress-strain curves obtained from tensile tests performed at room temperature on films obtained by water evaporation of aqueous suspensions of LC whiskers and MFC are reported in Fig. 6. The tensile or Young's modulus, as well as the strength and elongation or strain at break, were determined from these plots. Average results are reported in Table 4. From these data it is seen that LC MFC films displayed a higher stiffness (tensile modulus) than LC whiskers films. The presence of residual pectins at the surface of microfibrils and possibility of entanglements (Azizi Samir et al. 2004) can result in higher modulus values. According to Dufresne et al. (1997), pectins act as a binder between cellulose microfibrils and improve the mechanism of load transfer toward microfibrils when the sample is subjected to a mechanical stress. Actually, this mechanism is mainly governed by hydrogen bonding and/or covalent connections between pectins, hemicelluloses, and microfibrils.



**Fig. 6.** Typical stress-strain curves obtained from tensile tests performed on films resulting from the water evaporation of an aqueous suspension of *Luffa cylindrica* whiskers ( $\Delta$ ) and MFC ( $\blacksquare$ )

**Table 4.** Mechanical properties of *Luffa cylindrica* whiskers and MFC films

Sample	Young's Modulus (GPa)	Strain at break (%)	Strength (MPa)
Whiskers	$2.41 \pm 0.215$	$4.5 \pm 2.7$	$68.1 \pm 24$
MFC	$3.05 \pm 1.07$	$4.2 \pm 1.3$	$53.1 \pm 19$

Whiskers consist of more pure cellulose nanoparticles than MFC because pectins and hemicelluloses are eliminated during the hydrolysis step. Another reason for this difference could be the possibility of entanglements between cellulose microfibrils as recently described for nanocomposites (Azizi Samir et al. 2004). Despite standard deviations approaching the absolute values, it is worth noting that whisker's films displayed a higher strength than MFC's films. However, these films were very brittle. Then, the determination of the mechanical properties of the former is more difficult. Many samples break before starting the mechanical analysis when fixing them in the jaws of the equipment. This also explains the higher standard deviation observed for whisker's films for other parameters as strain at break and strength.

## CONCLUSIONS

1. The chemical composition of *Luffa cylindrica* (LC) fibers was determined by TAPPI methods. Morphological differences of LC fibers, microfibrillated cellulose (MFC), and whiskers were observed by microscopic analysis.
2. FTIR spectroscopy shows the modification of fibers after chemical treatments, by the disappearance of the bands at 1240 and 1735  $\text{cm}^{-1}$ .
3. The crystallinity of cellulose from LC fibers, MFC, and whiskers was determined by x-ray diffraction analysis, which shows a significant increase of the crystallinity index of MFC and whiskers compared to the untreated fibers. The high crystallinity index of LC fibers, allied to the relatively low lignin and hemicelluloses contents and also the simple process used to purify the fibers by removing hemicelluloses and lignin, are the main factor that confirms the interest to work with LC as a new source for the preparation of cellulose nanoparticles, as whiskers and MFC.
4. The use of these nanoparticles as a reinforcing phase in nanocomposites is expected to open high value valorization of these fibers and will be reported in the near future.

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