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Proceeding Paper

Microcrystals and Microfibers of Cellulose from *Acrocomia aculeata* (Arecaceae) Characterization †

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Abstract: In the context of the so-called lignocellulose bio-refinery, the coconut shell (S) and pulp (P) of *Acrocomia aculeata* (Arecaceae) are interesting agro-industrial wastes that can be used as feedstock for the production of high value-added products. The aim of this work was to evaluate these lignocellulosic residues S and P, to obtain the microcrystal (MCC) and microfiber (MFC) of cellulose, and to characterize them to propose possible applications. First, cellulose content in the raw materials was determined, being 39.69% and 45.42% for both (S and P)) respectively, respectively. Then, the purification of residues was carried out via alkaline and bleaching treatments. Next, in order to obtain MCC and MFC from the purified cellulose, a chemical treatment with HCl (for MCC) and a mechanical treatment with a blender (for MFC) were performed. The size and morphology were observed via MEB, and properties were characterized using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and differential thermogravimetric analysis (DTG).

Keywords: coconut fruit; shell; pulp; cellulose; microcrystals; microfiber

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1. Introduction

The South American palm species *Acrocomia aculeata* (Arecaceae), commonly known as mbocayá, macaw, macauba, or just coconut palm, has attracted the attention of researchers in recent years, mainly for its great potential as a sustainable oil crop [1–3]. In Paraguay, the *A. aculeata* fruit (coconut) has been processed since 1940 [4] for oil extraction. From the process, the shell (S), pulp (P), endocarp, and almond expeller remain as waste, which can be used to obtain new products with greater added value [5,6].

Lignocellulosic wastes as S and P from coconut fruit represent a renewable cellulose source, the primary raw material for nano and micro celluloses (NCs and MCs) [7]. Cellulose derivatives with desirable properties for different applications are a current topic of study in the scientific community. Although NC is a material with exceptional properties, the high consumption of mineral acids during its extraction process is, in most cases, still a disadvantage.

Microcrystal (MCC) and microfiber cellulose (MFC) have gained increasing interest as reinforcing polymeric materials due to their availability, relatively low cost, and high mechanical resistance [8–10]. There are also numerous industrial applications for these fibers, which exploit their chemical functionality (reactivity) for crosslinking, their ability to retain water, and their hydrogen bonding capability [11].

MCC and MFC compositions must be studied for each source because characteristics such as crystallinity, thermal stability, and final chemical composition are dependent on their origin [12]. This information is essential to explore MFC and MCC uses as reinforcing

agents in developing polymeric biodegradable compounds, e.g., packaging applications with improved properties.

This work describes the characteristics of two lignocellulosic agroindustrial wastes from coconut fruit (S and P), their main components, and the methods used to obtain MCC and MFC from them. The main characteristics of the MCC and MFCs, considering their possible application as reinforcing agents in films for food packaging, are also presented.

2. Materials and Methods

2.1. Raw Materials

Coconut shell (S) and pulp (P) were provided as agroindustrial waste by Industrial Aceitera S.A. paraguayan company. They were washed to remove dirt and other impurities. Then, they were dried in an oven at 105 ± 5 °C for 3 h. Finally, sample particles between 0.85 and 2 mm were obtained using a mill IKA M20, as NREL/TP51042620 establishes them.

2.2. Compositional Analysis

The chemical composition of the constituents (S and P) was determined: organic extractive (TAPPI 204 cm-97), holocellulose, and hemicelluloses based on the standard ASTM D1104 [13,14], soluble and insoluble lignin (NREL/TP510-42618).

2.3. Cellulose Preparation

Cellulose purification was carried out via two chemical treatments: (i) alkaline treatment with 5% NaOH (*w*/*v*) solution; (ii) bleaching process, using 1.5% NaClO2 solution (*v*/*v*) with acetic acid (pH 4–5), both treatments for 120 min at 80 °C, 600 rpm, and a solid/solution ratio of 1:20. The yield was calculated based on the dry basis weight of each constituent.

Microfibrillated and Microcrystal Cellulose Preparation

MFC was prepared by blending the bleached cellulose in a high rotation brand blender (model BL 767) at 25,000 rpm at different times (5, 10, 20 min), maintaining a ratio of 1% (*p*/*v*) (fiber/solution) in a volume of 500 mL of solution. At the end of the corresponding time of the mechanical treatment, the solution was filtered, and the MFCs obtained were dried in an oven at 45 °C for 18 h.

For the MCC, the bleached cellulose was subjected to different times of acid hydrolysis (15, 30, and 60 min) with 2.5 N HCl at a constant temperature of 85 ± 2 °C and a fiber/solution ratio (1:20), with a constant stirring. The reaction was stopped with an ice bath and adding NaOH. It was filtered through a fritted glass filter and washed with distilled water until pH neutral. Subsequently, it was dried in an oven at 45 ± 5 °C for around 18 h.

2.4. Characterization of MCC and MFC

2.4.1. Fourier Transform Infrared Spectroscopy (FTIR)

The presence of functional groups was studied using a Thermo Fisher (Nicolet iS5, Thermo Fisher, Waltham, MA, USA) FT/IR (Fourier transform infrared spectrometer). For the FTIR scan, KBr pellets containing 2 mg of dry sample with 200 mg of KBr powder were prepared. Spectra in the range of 400–4000 cm^{-1} was obtained with a resolution of 4 cm^{-1}, and the signal was accumulated from 32 scans [15,16].

2.4.2. X-ray Diffraction (XRD)

X-ray diffractometer was measured using the X′Pert^3 Powder via Cu-Kα radiation at 45 kV and 40 mA in an angular range of 10° to 40°/2θ with a step size of 0.0170/2θ and a count time of 50.1650 s in each step.

The crystallinity index (CrI) was measured using Segal's Equation on the diffraction peak height intensity, as indicated in Equation (1):

$$\%CrI = \frac{I_{002} - I_{am}}{I_{002}} \quad (1)$$

where I_{002} is the maximum intensity of the diffraction peak, taken at 2θ between 22° and 23° for cellulose I, and I_{am} is the intensity of the amorphous diffraction peak taken at 2θ between 18° and 19° for cellulose I.

3. Results and Discussion

3.1. Compositional Analysis

The raw materials (S and P) were analyzed to determine the cellulose content (Table 1).

Table 1. Composition of S and P from coconut fruit.

Composition	Shell (%*w*/*w*)	Pulp (%*w*/*w*)
Extractives	6.27	17.13
Cellulose	39.65	45.42
Hemicellulose	19.22	15.89
Lignin	30.80	17.90
Ash	4.06	3.66

A higher cellulose content (45.4%) is observed in the pulp (P), but the value obtained for the shell (S) is also important (39.6%). Comparing the lignocellulosic composition of P of the coconut fruit with the non-woody and woody raw materials commonly used to obtain cellulose, such as pinewood (37–43%), eucalyptus wood (41–50%), bamboo (43%), and bagasse (42–55%), similar and even higher cellulose contents are observed. These values open the expectations for the use of these lignocellulosic wastes from coconut fruits to obtain cellulose and, after a purification process, obtain MCC and MFC from them.

3.2. Cellulose Preparation and Purification

Table 2 shows the results of the yields after the alkaline and bleached treatments. The lower yield of alkaline treatment may be due to the presence of oil in both raw materials (S and P), mainly in the shell (S), as seen in the content of extractives in Table 1 regarding the bleaching treatment, the yield is quite promising for industrial scaling.

Table 2. Alkali and bleached treatment yields.

	Time (min)	Pulp (%*w*/*w*)	Shell (% *w*/*w*)
Alkaline treatment	240	20.52	30.88
Bleaching treatment	120	45.56	58.31

Figure 1 shows the DTG traces for S and P before and after alkaline and bleaching treatments.

The purification of cellulose was verified using DTG as the functional groups and characteristic peaks of hemicellulose (around 250 °C) and lignin (a small shoulder above 390 °C) are not seen, leaving only the characteristic cellulose peak (around 340 °C), intensified in both bleached samples. In addition, the effectiveness of alkali and bleaching treatments of the coconut residues was analyzed using FTIR spectroscopy by the decrease in or disappearance of peaks characteristics of hemicelluloses and lignin.

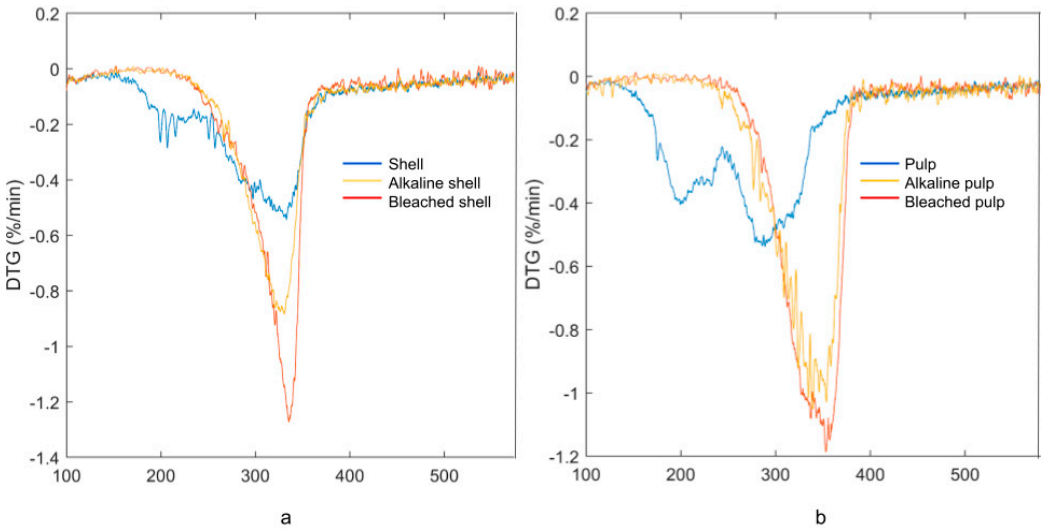

Figure 1. (**a**) DTG of S and (**b**) DTG of P before and after the alkaline and bleaching treatments.

3.3. Characterization of MCC and MFC

Fourier Transform Infrared Spectroscopy (FTIR)

Figure 2 shows the FTIR analyses performed on the MFC of the S at different times of mechanical treatment.

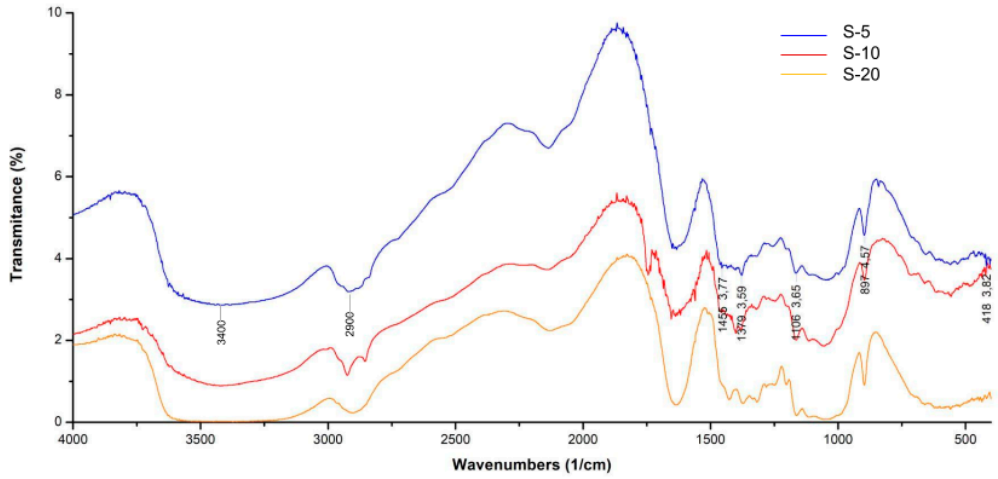

Figure 2. FTIR of the MFC of coconut shell (S) obtained at 5 (S-5), 10 (S-10), and 20 min (S-20).

Absorption bands close to 3400, 2900, 1430, 1370, 1160, and 897 cm^{-1} were associated with cellulose type I [17,18]. The peak at 2900 cm^{-1} was assigned to the CH stretching of the cellulose. The peak at 1640 cm^{-1} was due to the vibration of the adsorbed water molecules and also to the carbonyl groups, which may indicate the presence of hemicellulose [19,20]. The absorption peak at 1430 cm^{-1} was related to the crystalline band, which refers to the symmetric stretching of CH_2. The peak at 897 cm^{-1} was attributed to asymmetric stretching of the out-of-plane ring in cellulose due to β-glucoside bonding. The peak at 1640 cm^{-1} was associated with the H–O–H stretching vibration of carbohydrate-absorbed water. This indicates the presence of hemicellulose in MFCs, which favors fibrillation during mechanical treatment [20].

Other figures from the FTIR analysis for the MFC of the P and the MCC of the P and S show the same characteristic peaks of cellulose, indicating that purified MCs have been obtained using different treatments.

The crystallinity indices obtained using Equation (1) for the MCC are presented in Table 3.

Table 3. Crystallinity index for MCC and MFCs of coconut fruit.

	Sample	%CrI	Sample	%CrI
MCC	S15′	42.42	P15′	46.40
	S30′	68.19	P30′	64.36
	S60′	69.74	P60′	67.03

The peaks identified for the MCC samples correspond to Type I cellulose, and crystallinity index (%CrI) increased as the chemical treatment time increased, as observed in Table 3, for the S60 sample, with the 60 min of treatment. The increase in the crystalline index could be explained by the total or partial elimination of the hemicellulose and lignin structures, which reduced the amorphous region [21].

Regarding SEM analysis (Figure 3, a decrease in the diameter was verified for the MCFs as the mechanical treatment increased, being the best condition after 20 min treatment. The estimated diameter, after 20 min of treatment, was between 1 and 3 microns for the pulp (P) and 6 and 8 microns for the shell (S). In addition, a smaller size of the microfibers is evident in the MFCs obtained from the pulp compared to those obtained from the shell.

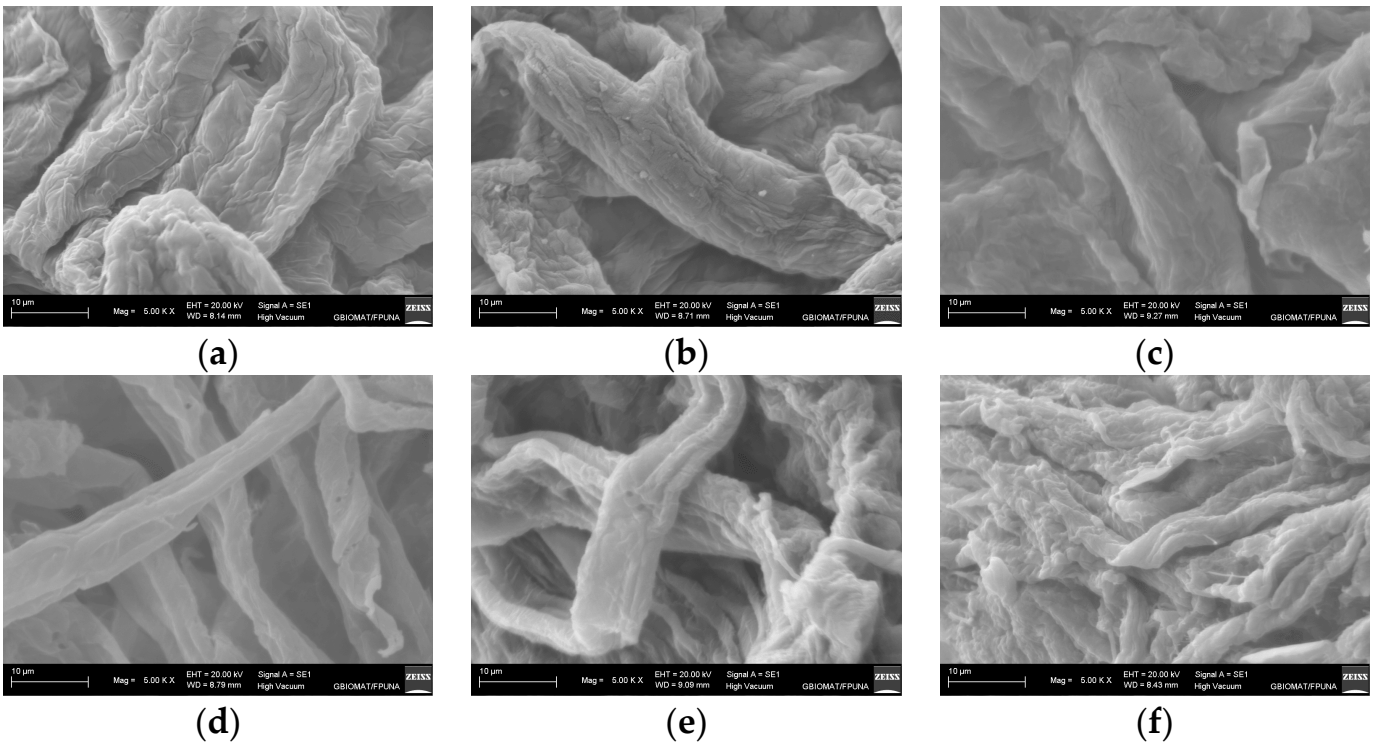

Figure 3. SEM micrographs of MFC from coconut fruit shell (**a**–**c**) and pulp (**d**–**f**) obtained after 5 min (**a**,**d**), 10 min (**b**,**e**), and 20 min (**c**,**f**) of mechanical treatment.

4. Conclusions

Coconut fruit wastes were valued by obtaining microcrystals (MCC) with high crystallinity index and cellulose microfibers (MFC) with high fibrillation. The purification treatments of the extracted cellulose were effective according to the characterizations carried out after the alkaline treatment and bleaching, verified via FTIR and TGA analysis.

In addition, high yields of purified cellulose for shell (S) and pulp (P) were obtained. Given their richness in cellulose and their (MCC) and (MFC) characteristics, S and P have the potential to be used as reinforcement for food packaging on the way to obtaining environmentally friendly materials.

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