CHARACTERIZATION OF NATURAL FIBERS: WOOD, SUGARCANE AND BABASSU FOR USE IN BIOCOMPOSITES

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Natural fibers have received increasing attention in recent years. New properties are achieved when these fibers are used in composites. A comparative study of three different natural fibers, supplied by agroindustrial residues, was carried out to investigate their potential to be used as reinforcement in biocomposites. The following characterization techniques were used: thermal analysis (TGA/DTG), optical microscopy, dimensional analysis and morphological analysis by SEM and FTIR. The specimens of natural fibers used were: wood flour, sugarcane and babassu, without prior treatment. TGA/DTG analysis confirmed that the thermal stability of babassu was lower than that of wood and sugarcane fiber. FTIR analysis showed the existence of similar groups corresponding to cellulose, hemicellulose and lignin in the natural fibers. SEM micrographs showed a non-homogeneous and random size distribution of the vegetal fibers, with pores and cracks as pits and tylose. The results showed the potential of the fibers to be used as reinforcement in polymer biocomposites for several applications.

Keywords: natural fibers, wood, sugarcane, babassu, biocomposite

INTRODUCTION

The search for new materials, combining natural fibers with biodegradable or non-degradable polymers, appears as a viable solution to current environmental problems. Natural fiber may confer reinforcement to composites and, moreover, the use of fibers derived from residues can minimize environmental pollution and reduce the costs of the produced materials. Composites reinforced with natural fibers are gaining more acceptance in structural applications due to their relative cheapness and recyclability. Specialists have been encouraged to develop biodegradable composites using renewable agro-based materials.[1-3] The characteristics of natural fibers, such as their hydrophilic nature, high moisture absorption, poor reactivity and compatibility with polymeric matrices, influence the mechanical properties of the composite materials.[1,4]

Cellulose, hemicellulose, lignin, pectins and waxes are the main components of vegetal fibers. Cellulose, the most important structural component, is a natural polymer and its crystallinity functions as a bond between cellulose microfibrils. Hemicelluloses, which are essential components of the plant cell wall, associated with cellulose, are responsible for moisture absorption in natural fibers. Lignin, which is hydrophobic, is a complex hydrocarbon polymer that gives rigidity to plants and assists in the transportation of water. Pectin gives plants flexibility. Lastly, waxes consist of different kinds of alcohols and, along with oils, they cover the fiber surface and have the role of protecting the fiber.[5-7]

The greatest risk in composites reinforced with natural fiber is their degradation when exposed to outdoor conditions (long-term stability), as compared to composites with synthetic fibers. This is attributed to the characteristics of natural fibers, which are susceptible to biodegradation. The effects of degradation, mainly due to weathering conditions, such as temperature, humidity and UV radiation, among others, affect the performance of the product and incur changes in the chemical, physical and mechanical properties of the materials.[2,6]

In this study, three different vegetal fibers will be evaluated. Babassu is a palm largely cultivated in Brazil due to its industrial applications, mainly in cosmetic industries, but also for biodiesel production and in food and detergent industries.[8,9] Sugarcane is another vegetal fiber abundant in Brazil, it is crushed for the extraction of its juice and the fibrous residue is known as bagasse. Sugarcane bagasse constitutes a typical example of an agricultural by-product, which is abundantly available worldwide, including Brazil.[10,11] Wood fibers, specifically wood flour, are widely used as biodegradable filler. WPCs (wood plastic composites) have already found wide acceptance on the global market. Moreover, vegetal fillers are made from industrial by-products.[12]

In this paper, a comprehensive characterization of wood, babassu and sugarcane fibers, including their physical, morphological and thermal properties, is reported. The extensive characterization of these fibers should reveal new information of relevance to the research community.

EXPERIMENTAL

Materials

The natural fibers: wood flour (*Pinus ellioti*), sugarcane (*Saccharum* spp), and babassu (*Orbignya phalerata*) were used without any prior surface treatment or drying in the oven. All three natural fibers were supplied by "Inbrasfama" (Paraná – Brazil). The natural fibers used were agroindustrial residues (Fig. 1).

Moisture content

The moisture content of natural fibers was determined gravimetrically and then the samples were placed in an oven set at 105 ºC for 5 h. The oven dry weight was taken and used to calculate the moisture content. The moisture content in percentage was calculated using the sample weight before and after oven drying. The mass loss that was found after drying was assigned to moisture. Thus, moisture content (MC) was estimated by the following relation:

$$MC = \frac{M1 - M2}{M1} x\,100 \quad (1)$$

where MC: moisture content (%), $M1$: initial wet weight, and $M2$: final dry weight.

Particle size distribution

The particles of wood flour, sugarcane and babassu were separated using an automatic vibratory sieve shaker. The particle size distributions of the fibers were determined by sieve separation (Bertel). The device was equipped with the following sieves (in order from the largest to the smallest): 35, 45, 60, 80, 170 and 325 mesh. Natural fiber (100 g) was placed on top of the 35 mesh sieve and then subjected to vibration for 20 min. Then, the amount of fiber on each sieve was determined gravimetrically.

Optical microscopy

Natural fibers were analyzed by an optical microscope (Leitz Laborlux 12MES – Leica). The images were processed with Axio Vision 4.8 Zeiss image analysis software.

Surface morphology by Scanning Electron Microscopy (SEM)

The surface morphologies of the natural fiber strands were examined using a FEI Quanta LX 400 SEM. The scanning images were obtained with an accelerating voltage of 15 kV and magnification of 80-1.000x. The layers were not surface coated prior to scanning.

Thermogravimetric analysis (TGA)

The thermal stability behavior of the wood, sugarcane and babassu was assessed by TGA using a TGA-50H analyzer (Model Shimadzu). The samples, weighing 8.3 mg (*Pinus*), 10.6 mg (babassu) and 8.8 mg (sugarcane), were placed in an alumina crucible to avoid any temperature variation during the thermocouple measurements. Then, the temperature was increased from 20 to 1.000 ºC, at a heating rate maintained at 10 ºC/min and under nitrogen atmosphere at a flow rate of 50 mL/min.

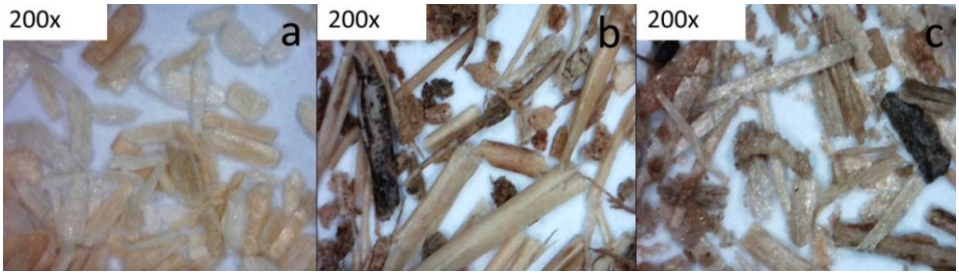

Figure 1: General aspect of the natural fibers used: (a) wood, (b) babassu and (c) sugarcane fibers

Table 1
Moisture content of wood, babassu and sugarcane fibers

Moisture content			
Time (h)	Wood (%)	Babassu (%)	Sugarcane (%)
1	8.25	9.25	8.00
2	8.50	9.25	8.95
3	8.55	9.25	8.95
4	8.55	9.85	8.95
5	8.55	9.85	8.95

Table 2
Particle size distribution of natural fibers

Sieve	Wood (%)	Babassu (%)	Sugarcane (%)
35 mesh (500 µm)	5.00	25.69	26.01
45 mesh (354 µm)	33.95	31.83	26.99
60 mesh (250 µm)	34.76	21.97	19.85
80 mesh (178 µm)	20.01	12.19	12.10
170 mesh (89 µm)	5.32	7.15	10.06
325 mesh (45 µm)	0.96	1.16	4.99
Background	0.00	0.00	0.00

Fourier Transform Infrared Spectroscopy (FTIR)

A Shimadzu Prestige-21 FTIR spectrophotometer was used to obtain the FTIR spectra of the three natural fibers. All the spectra were recorded in the wavenumber range of 800-3600 cm^{-1}, operating in ATR (attenuated total reflectance) mode.

RESULTS AND DISCUSSION

Moisture content

Table 1 shows the measured moisture content of different natural fibers: wood flour, babassu and sugarcane. According to the results shown, it can be observed that the sample of babassu fibers has higher water content, when compared to those of wood flour and sugarcane, while the lowest moisture content of the fibers corresponded to wood flour. It is well known that natural fibers are hydrophilic, which is traceable to the presence of cellulose, hemicelluloses and the hydroxyl groups in the cell walls. However, it is believed that there are differences in the composition of the fibers studied, as well as in their morphology, namely, babassu fiber probably has a greater number of functional groups (hydroxyl) and/or a greater surface area.[13,14]

Particle size distribution

An important parameter in fiber composite technology is fiber size. The particle size distributions obtained are listed in Table 2. It is important to note that the sugarcane and babassu have a considerably broader particle size distribution, compared to that of the wood flour. As can be noted in Table 2, the major part of the wood fiber has particle sizes ranging between 45 and 80 mesh. It can be concluded from the measurements that a very small part (6% w/w) of the wood fiber had sizes lying between 170 mesh and background. Sugarcane and babassu fibers showed a wider distribution among the sieves of 35-80 mesh and a narrow one for sizes smaller than 170 mesh.

Thermogravimetric analysis of fibers

Figure 2 offers important information about the thermal properties and degradation behavior of the fibers under study. The TGA curves show the mass loss of wood flour, babassu and sugarcane fibers. It may be noted that all the samples had three thermal decomposition events, and in addition, an early event in the range of 50-120 ºC, which is attributed to loss of moisture and possibly of some extractives. This early weight loss represented 6.31% for *Pinus* wood, 7.34% for the sugarcane and a slightly higher value for babassu – of 9.80%, which is consistent with the hydrophilic character of these fibers. These results confirm the moisture content data listed in Table 1.

In the case of wood flour, the TGA curve revealed several decomposition steps: the first step at 260 ºC (23.10%) was associated with the decomposition of the hemicellulose; the second step at 360 ºC (40.95%) corresponded to the degradation of cellulose; and the final step above

400 ºC (15.23%) was due to the degradation of the lignin fraction.[15,16] However, the sugarcane fiber starts degrading at 220 ºC and the process ends at 405 ºC. The region between about 260 ºC and 340 ºC refers to the possible decomposition of hemicellulose (28.67%); then, around 350 ºC, there is a weight loss due to cellulose degradation (39.69%), similarly to the data found in the literature.[17,18] For the babassu fiber, degradation started at 200 ºC (22.21%), a stage that is related to the decomposition of hemicellulose, notably exhibiting a lower degradation temperature than those found for the wood flour and sugarcane fibers. In the second stage of decomposition, a weight loss of the fibers is attributed to the decomposition of cellulose (38.65%). Finally, in the last stage, at about 510 ºC, the weight loss is attributed to the degradation of lignin (14.73%).[19,20]

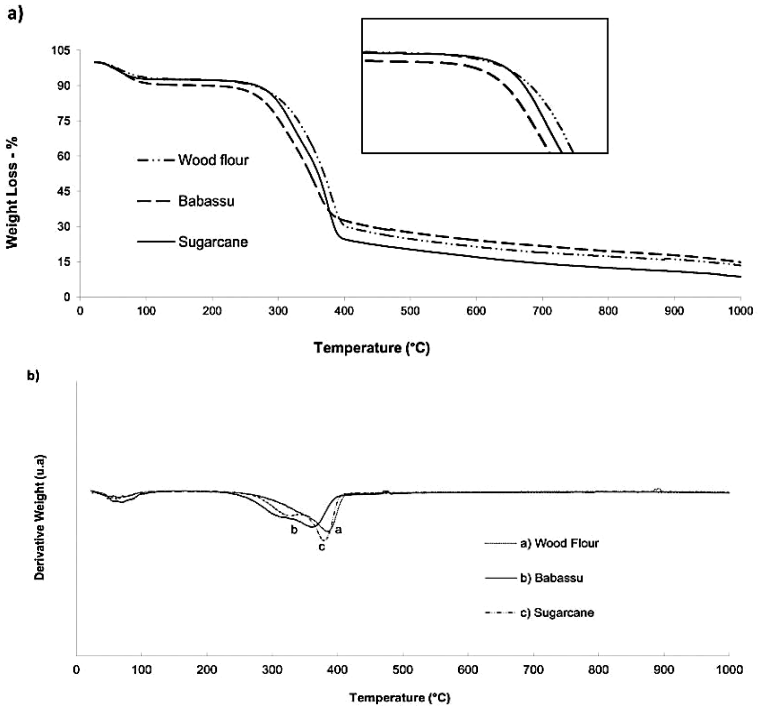

Figure 2: Comparative curves of TGA (a) and DTG (b) of the natural fibers

Table 3
Data collected from the TGA and DTG curves of wood, babassu and sugarcane natural fibers

Natural fiber	Weight loss (%)	TGA T (ºC)	Hemicellulose (%)	Cellulose (%)	Lignin (%)	Ash (%)	DTG Peak1 (ºC)	Peak2 (ºC)	Peak3 (ºC)
Wood	6.91	262	23.10	40.95	15.23	13.82	350	395	420
Babassu	9.80	197	22.21	38.65	14.73	14.61	300	360	440
Sugarcane	7.34	268	28.67	39.69	14.82	9.50	340	390	420

Higher thermal stability is related directly to a high fraction of hemicellulose, and the wood and sugarcane fibers exhibit this property, considering their higher degradation temperature in the first decomposition stage noted on the TGA and DTG curves. On the other hand, babassu fiber can be suitable for compounding with polymers that can be processed at a lower temperature because of its lower thermal stability. Also, differences in the fibers under investigation may be observed when overlapping the DTG curves, namely, the babassu fiber shows lower cellulose content, judging by the lower amplitude of the curve, compared with those of the other fibers. Table 3 lists the thermal

properties of the studied natural fibers (wood, babassu and sugarcane). As detailed in Figure 2, all of them presented three stages of decomposition (weight loss). It may be also observed that the babassu fiber showed higher ash content and lower content of hemicellulose and cellulose, indicating that it may contain a higher content of inorganic compounds than the other fibers.

Optical microscopy of fibers

Figure 3 shows optical microscopy images of the natural fibers studied. A great heterogeneity in the dimensions of the fibers, which differ in terms of length, diameter and particle size (as powder), may be remarked. This heterogeneity can also be seen in the particle size distribution (Table 2), especially in sugarcane, very little in babassu and wood flour. The babassu fiber (Fig. 3b) has a more fibrillar physical aspect; these features were also observed by Ishizaki *et al.*[21] Natural fibers are usually a fibrous lignocellulosic residue obtained from previous processing in grinding mills, and are formed of a heterogeneous set of particles (grains and fibers) of various sizes. The particle sizes of these fibers depend primarily on the type of equipment used in processing and, in a less significant way, on the variety of the plant. This can be also seen in the SEM micrographs of Figure 3.[22]

Surface morphology by Scanning Electron Microscopy (SEM) of fibers

Figure 4 presents micrographs of the fracture surface of the vegetal fibers evaluated after the grinding process. As may be noted in the micrograph of Figure 4a, the wood fiber has a fibrillar and irregular surface, as evidenced by optical microscopy (Fig. 3). In addition, the direction of the fibers (mono-oriented) and the presence of empty slots on the surface should be remarked. Figure 4b shows the morphology of the babassu fiber surface, and it can be observed that these fibers have cylindrical shape, but different diameters. Also, it may be noted that the interior of the fiber is porous (similar to a cellular structure). The micrograph corresponding to sugarcane fiber (Fig. 4c) reveals an irregular distribution of sizes and shapes, as already observed in Figure 3c. It also displays an irregular surface with mono-oriented fibers. Additionally, it should be noted the apparent presence of a waxy coating on the fiber, which is probably due to extractives. It must be mentioned that all images display a few white particles, which are signaled in the images by arrows, and which may be crystals. According to the authors Pereira *et al.*,[23] Fidelis *et al.*[24] and Silva *et al.*,[25] the surfaces of natural fibers can present coating with waxes and other fatty acids that are present on natural fibers, since the latter did not undergo any chemical treatment. Cunha *et al.*[10] carried out the SEM analysis of sugarcane bagasse samples (3000x) and noted the presence of sugar crystals on the surface of the material, which indicates, according to the authors, the extraction process to which the material was subjected.

Moreover, the presence of "pits" may be observed (Fig. 4c), these are small orifices distributed along natural fibers, throughout the cell wall. The "pits" have a certain role in the growth and maintenance of the plant, namely, to transport water and nutrients throughout the cells to the roots and leaves. The presence of "pits" assists in the mechanical anchoring of the fiber with the polymer matrix.[27,28] It is worth mentioning that the surface of the babassu fiber has a number of cylindrical protrusions distributed homogeneously (Figure 5). This aspect may be irregular due to the presence of tylose, which is a coating of wax composed of fatty deposits that adhere to the fiber surface.[29-31] Muensri *et al.*[31] also reported the presence of tylose in their study of untreated vegetal fibers. They subjected the fibers to $NaClO_2$ treatment in order to remove impurities from the fiber surface, which removed the tylose. In vegetal histology, tylose is described as the projection of parenchyma cells into the tracheal elements, through the pits, blocking them. The tylose refers to the vesicular expansions of axial parenchyma of the cells adjacent to the vessels or fibrous tracheids, enclosed inside extractive substances (gums, resins, oils, waxes, crystals, *etc.*). This phenomenon occurs in the core of the trunk, after the cessation of cell activity, leading to the plant's death. Various structures formed by cell wall modification, among them carbohydrates, gels, tyloses and phenolic acids, have the function of protecting plants from infectious agents.[32,33]

Fourier Transform Infrared Spectroscopy (FTIR)

Natural fibers are composed of three main molecules: cellulose, hemicelluloses and lignin, which have different characteristics and specific infrared absorptions. FTIR spectroscopy was used to identify the functional groups present in the

samples and the main differences in the chemical structure of each vegetable fiber. Figure 6 shows the FTIR spectrum of wood, babassu and sugarcane fibers with the typical functional groups. The chemical structure of the three fibers was analyzed and typical peak bands were identified, with the main changes in the bands related to the functional groups shown in Figure 6. A more pronounced band from hydroxyl (OH) stretching appeared at 3320 cm^{-1}, whereas the band at 2890 cm^{-1} is related to symmetric C-H vibrations. Similar results were obtained by several authors.[1,34,35]

According to Bedane *et al*.,[36] the presence of characteristic bands around 3320 cm^{-1} can indicate especially water loss, *i.e*., weight loss, as also evidenced in Table 3 and Figure 2, which present the weight loss observed in the TGA curves of the fibers. The basic features of the adsorbed water spectrum are very similar and were observed in the OH stretching band for all three natural fibers, with an emphasis on sugarcane fiber, followed by babassu. Babassu and sugarcane samples presented little peaks at approximately 1500 and 1550 cm^{-1}, which correspond to unsaturation (C=C) in the molecules, which may be related to the waxes, extractives and lignin, and is in agreement with the lignocellulosic natural fibers.[37]

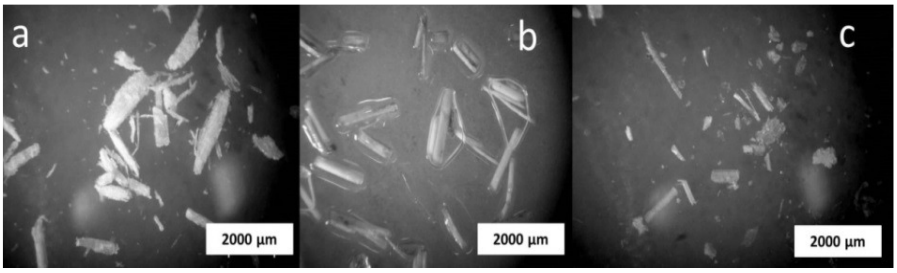

Figure 3: Micrographs of fibers of: (a) wood, (b) babassu and (c) sugarcane

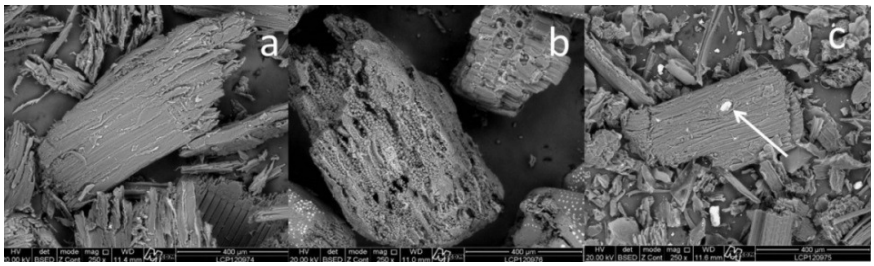

Figure 4: SEM surface of natural fibers at 250x magnification: (a) wood, (b) babassu and (c) sugarcane

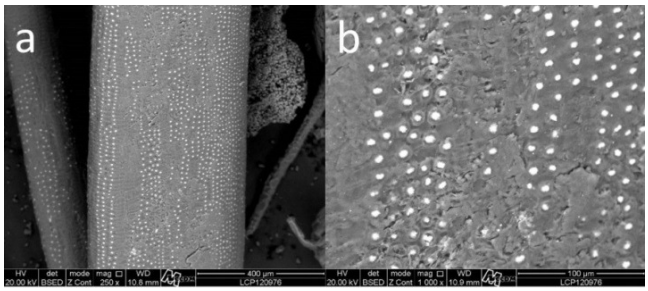

Figure 5: SEM surface of babassu fiber at 250x (a) and 1000x magnification (b)

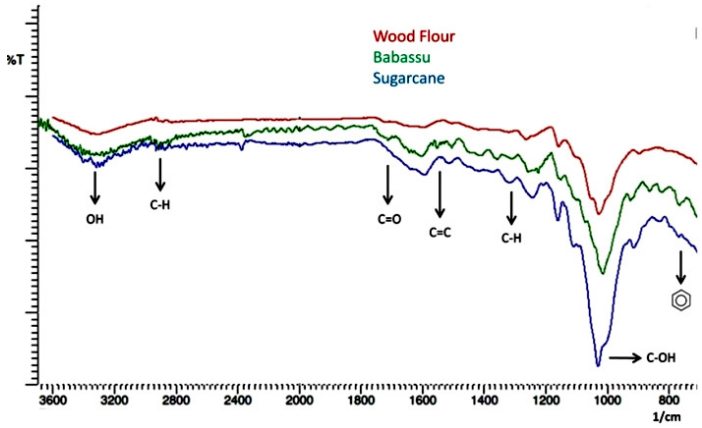

Figure 6: FTIR spectra of wood, babassu and sugarcane fiber

The peak at 1320 cm^{-1} represents the C–H bending vibration and the band at 1375 cm^{-1} is attributed to the bending vibration of the CH_3 group. The absorption band in the region around 1720 cm^{-1} is attributed to the carbonyl group C=O stretching vibration from the acetyl groups of the hemicelluloses.[38] The intense peak near 1030 cm^{-1} can be attributed to the carbonyl peak relating to the structure of cellulose.[39] These bands were more intense for sugarcane and babassu fibers. Thus, these results show high similarity between the natural fibers. However, for the use of these fibers in the manufacturing of biocomposites, these small variations in their structures can have an influence, because depending on the amount of each fiber used, it can significantly alter its characteristics, especially its properties as in aging and degradation.[40] The bands at 860, 765 and 710 cm^{-1} can be assigned to ester vibrations and monosubstituted aromatic rings, due to the lignin fraction in the fiber.[41]

CONCLUSION

The physical, chemical and thermal characteristics of three natural fibers (wood flour, babassu and sugarcane) were discussed in this study. TGA analysis revealed that the wood and sugarcane fibers presented higher thermal stability (above 260 ºC) than babassu (below 200 ºC). The micrographs showed a non-homogeneous and random size distribution of the natural fibers, with the presence of pores and cracks as pits (sugarcane) and tylose (babassu). FTIR spectroscopy analyses showed, in general, similarities in the chemical compositions of the three different vegetable fibers, with little variation. However, the results indicated small differences in some important bands influenced by the specific characteristics of each fiber and its content of cellulose, hemicellulose and lignin, which was also evidenced by the TGA analysis results. Thus, the results confirm the potential of the investigated fibers to be used as reinforcement in biocomposites for various applications. However, further studies are required to clarify if surface treatments of the fibers are necessary or not.

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