Characterization of Brazil nut fibers

Patricia Y. Inamura, Felipe H. Kraide, Maria J.A. Armelin, Marcos A. Scapin, Esperidiana A.B. Moura, Nelida L. del Mastro*

Energy and Nuclear Research Institute, IPEN-CNEN/SP, Av. Prof. Lineu Prestes, 2242, zip code 05508-000, São Paulo, SP, Brazil

Abstract

The fruit from Brazil nut (*Bertholletia excelsa)* is characteristically a spherical capsule. When ripe, the capsule releases seeds through its lower portion. In this work, an attempt has been made to characterize the Brazil nut capsule or bur and shell fibers by various techniques. The organic composition was established and elementary composition was determined by Instrumental Neutron Activation Analysis (INAA) and Wavelength Dispersive X-ray Fluorescence Spectrometry (WDXRF). Possible applications of these fibers must be considered as novel markets for lignocellulosics have been identified in recent years, representing an exceptional opportunity for sustainable technological development.

Keywords: *Fibres, thermal properties, thermal analysis, chemical analysis*

*Corresponding author: nlmastro@ipen.br;

Phone: +55 11 3133 9829; Fax: +5511-3133-9765

1. Introduction

The agro-industry generates innumerable sources of biomass that are not sufficiently nor adequately utilized. The use of lignocellulosic fibers and their constituents as raw materials in the production of polymeric and composite materials represent an exceptional opportunity for sustainable technological development [1,2]. In order to think about potential and future exploitation and applications of lignocellulosics, properties and performance of fibers under environmental or other conditions must be known. The necessity of developing a detailed chemical composition and physical properties data bases of the many natural fibers which are potentially available in the world was pointed out by Rowell et al. [3].

Many lignocellulosic fibers were studied and several of their properties, such as chemical and physical nature and mechanical strength have been already evaluated. The chemical composition of fibers from piassava, sisal, coir, flax, hemp, sugarcane bagasse, banana, curauá, pineapple, cotton lint, bamboo, jute, ramie and rice straw, for instance, were subjected to different important studies [4,5,6,7,8]. The available properties of some of these fibers reported so far can be understood in terms of their observed structure.

Besides a small utilization in artistic handicraft, very few works on Brazil nut shell and bur fibers were performed which revealed some further application. One that is possible to mention comes from our laboratory [9].

The Brazil nut (*Bertholletia excelsa*) tree occurs only in the Amazon basin river, thus it is produced in Brazil and also in parts of Bolivia and Peru. The Brazil nut is one

of the most valuable non-timber forest products of the Brazilian Amazon and one of the few which reaches the international market, and come entirely from wild collection rather than from plantations.

Brazil nuts, the commercially harvested, edible seed, are considered to be one of the most valuable products that can be harvested from undisturbed rainforest. The tree is large and stands out of other trees tops in the forest and can reach up to 50 m, with a trunk diameter that reaches from 10 to 12 m and it lives over 500 years. The fruits, known to Brazilians as *Castanha do Pará,* are characteristically a spherical capsule, with a thick, hard, dark brown surface (Fig. 1). The fruits are difficult to be collected: each hard outer bur can weigh over 1 kg and contain between 14 and 25 seeds (nuts) inside, surrounded by yellow pulp that is rich in vitamins, fats and proteins [10,11].

Figure 1. Brazil nut (*Bertholletia excelsa*) shell and bur fiber

Brazil nut is an angular nut with a very hard hull. Their nut almond is very white, with a dark brown tegument with high energy content and rich in proteins of high biological values. A tree may produce more than 150 kg of nuts a year and the species is propagated naturally. It is difficult to estimate the nut production because there is a

significant variation in burs number from one year to another and among the trees. For example, new Brazil nut trees produce 30 to 50 burs per year, whereas mature trees, 200 to 400 years old, can reach up to 1,000 burs produce in just one year [11]. In this work, an attempt has been made to characterize the Brazil nut bur and shell fibers by several techniques.

2. Experimental

2.1. Material

Brazil nut shell and bur fibers from the residues disposed by the processing industries of Brazil nuts were provided by Amazon Brazil Nuts.

2.2. Fiber Characterization

The Brazil nut shell and bur fibers were evaluated following the standard procedures and all analyses were performed at least in triplicate. The extractives present in the fiber were removed via Soxhlet extraction with toluene/ethanol for 4 h/70 °C, subsequently replaced by water (100 °C/4 h).

The lignin content was determined by Klason method. This method is one among many others used to evaluate the lignin content, which is based on acid hydrolysis of polysaccharides. Subsequently, the gravimetric determination of soluble and insoluble lignin, according to TAPPI T13M-54 was carried out. For insoluble lignin content, the extractive-free fiber was weighed; after that, 72% w/v sulfuric acid solution was added, homogenized and maintained in an incubator at 25.0 ± 0.5 °C for 24 h. The solution was transferred to a 1L flask and 560 mL distilled water was added, followed by a 4 h reflux. The insoluble lignin was washed several times with water and dried in an oven at 105 ± 2 °C until constant weight.

The soluble lignin content was determined by the filtrate obtained from the insoluble lignin percolation. This filtrate was analyzed by UV-Visible Spectrophotometer, model UV-1601, Shimadzu and the absorbance was measured at wavelengths from 280 to 215 nm. The lignin concentrations (g/L) in diluted samples were calculated by the following expression:

$$C\ (g/L) = \frac{4.53(A_{215})-A_{280}}{300} \quad (1)$$

C (g/L) = concentration in g/L of soluble lignin Klason in diluted samples

A_{215} = absorbance value at 215 nm

A_{280} = absorbance value at 280 nm

The total lignin content of the sample was quantified by the sum of soluble and insoluble lignin determinations.

For cellulose content determination, 25 mL of nitric acid-glacial acetic acid were added in 1 g of extractive-free, dried Brazil nut bur and shell fiber. The sample was maintained under reflux at 120±3°C for 25 min. The system was cooled to room temperature and the cellulose residues were percolated in sintered glass, washed with 500 mL of hot water and then with 25 mL of ethanol. The sample was dried in oven at 105 ± 2 °C until constant weight and then cooled and weighed.

The moisture content of Brazil nuts bur and shell fibers was performed in triplicate. Samples of 1 g were weighed and then placed in an oven at 105±2 °C until constant weight. The samples were cooled in a desiccator and then weighed and quantified.

The determination of density for porous materials of varying composition such as lignocellulosic materials, must consider the pores and microcracks of the samples. The measurement was performed in triplicate. The Brazil nuts bur and shell fibers were dried in the oven at 105±2 °C until constant weight. After dried, the 5 g of samples were completely submerged in graduated cylinders partially filled with distilled water. The assays were maintained in solution for 24 hours to determine the variation of the water.

2.3. Thermogravimetric Analysis (TG)

Brazil nut shell and bur fibers thermal stability was evaluated by a thermogravimetric analyzer TGA-50 (Shimadzu, Japan). Sample with 5.0 ± 1.0 mg was placed in a platinum cell, under air atmosphere with a flow rate of 50 mL/min. The experiment was conducted from ambient temperature (25 ºC) to 600 ºC at a heating rate of 10 ºC/min.

2.4. Scanning Electron Microscopy (SEM)

The Brazil nut shell and bur fibers morphological characterization were accomplished by means of a Philips, XL 30 SEM. Powder sample was fixed in carbon, introduced into a vacuum sputter coater until reach the critical point drying and then coated with gold. Therefore, the analysis was performed using secondary electrons. The scanning electron microscope was equipped with an energy-dispersive X-rays spectroscopy (EDS) system that gathered a spectrum of elements.

2.5. Wavelength Dispersive X-ray Fluorescence (WDXRF) Analysis

The pressed powdered samples (grain size ca 100 μm) were prepared according to Scapin et al. [12]. A Rigaku Co. X-ray fluorescence spectrometer, model RIX 3000 was used with the proper measurement conditions [12].

2.6. Instrumental Neutron Activation Analysis (INAA)

For INAA, the sample and the elemental synthetic standards aliquots were irradiated at the IEA-R1 nuclear research reactor for 16 h under a thermal neutron flux of about 40 10^{12} n cm^{-2} s^{-1}. Therefore, reasonable decay time, samples and standards were measured using a hyperpure Ge detector coupled to a gamma ray spectrometer. The radioisotopes were identified according to half lives and gamma ray energies and the element concentrations were calculated by comparative method.

3. Results and Discussion

Fiber chemical components are distributed through outer cell wall, which is composed of primary and secondary wall layers. Chemical composition differs between different plants and also different parts of the same plant, according to the geographic location, age, climate and soil conditions, among other factors [3].

The Brazil nut shell and bur fibers chemical composition is presented in Table 1. The cellulose content found to Brazil nut bur fiber, 53.3%, is in the range for jute fiber, 45-63% [3] and somewhat higher was found for sugarcane bagasse, 54.3-55.2% [5]. For Brazil nut shell fiber, the cellulose content of 40.0% was similar to the coir fiber [13].

Table 1

Chemical composition (%) of Brazil nut bur and shell fiber

	Brazil nut bur fiber	Brazil nut shell fiber
Cellulose (%)	53.3 (1.1)	40.0 (0.9)
Lignin (%)	35.8 (0.8)	59.5 (0.6)
Extractives (%)	7.49 (0.23)	5.40 (0.06)

Data expressed as mean (standard deviation)

The lignin content of Brazil nut bur and shell fiber, 35.8% and 59.5%, respectively, found in the present work was considerably higher than that from bamboo,

20 - 25% [14] and 36.14% for coir fiber [15], but inferior to that found in piassava, ~48% [4].

The moisture content and density of Brazil fibers are presented in Table 2. Similar results for moisture were found for cotton, jute or flax, 10.0% [13] and curauá fiber, 9.10% [16]. The density values were in the same range found for banana fiber, 1350 kg m^{-3} [17] and not so far from that of curauá fiber, 1100 ± 91 kg m^{-3} [16]. A major limitation for all cellulosic fibers is the hydrophilic nature if used as reinforcement in plastic. This hydrophilicity influences the all mechanical properties as well as other physical properties of the fiber itself [13]. For that reason moisture determination is an important issue as moisture presence can prevent composite formation [16].

Table 2

Moisture content and density of Brazil fibers

	Moisture content (%)	Density (kg m^{-3})
Brazil nut shell fiber	14.73 (0.09)	1,398.05 (0.06)
Brazil nut bur fiber	10.29 (0.03)	1,313.07 (0.03)

Data expressed as mean (standard deviation)

In general terms, the chemical composition and density values obtained here are consistent with data from other fibers reported in the literature [3,5,6].

The thermogravimetric analyses (TG) of Brazil nut bur and shell fiber are presented in Fig. 2 and 3, respectively, as an instrumental output of mass versus increasing temperature. The numerical derivative TG trace is also shown. Distinct transformation regions, all indicating mass loss, can be observed. The first one indicates a weight loss at the beginning of the analysis (about 55-75 °C) and then a thermal

stability until 230 ºC. The weight loss of 6.7% at the lower temperatures can be related to water evaporation [4,6,8]. Weight losses (11.5%) were showed at 260 °C and 310 °C (44.9%), and at 426 °C, another weight loss of 22.4% can also be seen. According to the literature [18,4,6] the degradation temperature showed at about 260 ºC can be attributed to decomposition of hemicellulose. The lignin onset temperatures at 426 °C (Fig. 2) and 451 °C (Fig. 3) are similar as those reported before for lignin degradation [18].

Silva et al. [2] showed similar degradation temperature stages for sisal fiber/polyurethane resin-based composites and other authors obtained similar results for other lignocellulosic fibers [5,6].

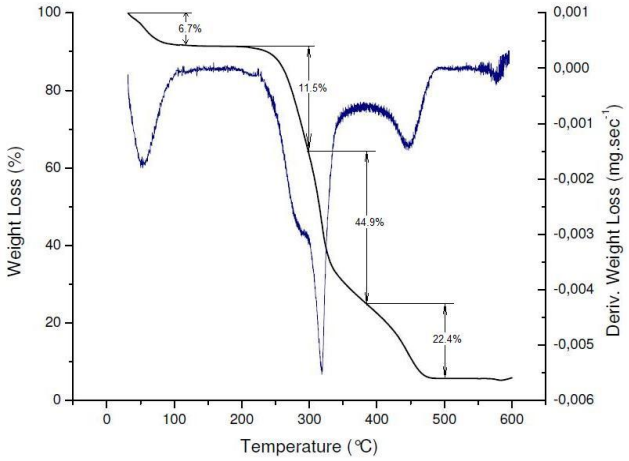

Figure 2. Thermogravimetric analysis of Brazil nut bur fiber

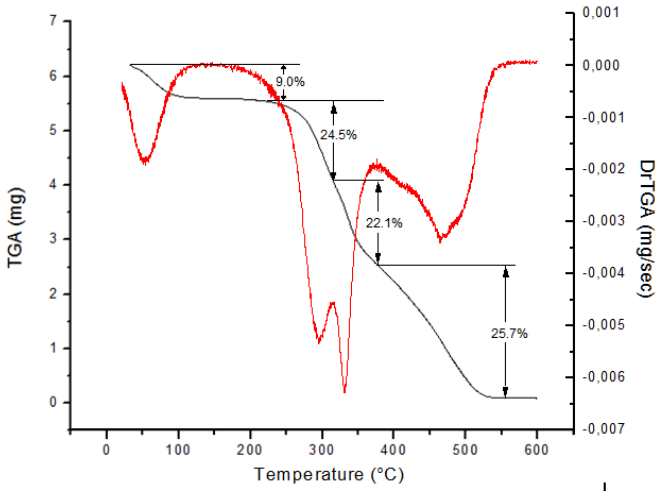

Figure 3. Thermogravimetric analysis of Brazil nut shell fiber

Fig. 4 and 5 shows some cross and longitudinal section microphotographs of the Brazil nut shell fiber. Can be observed that shell fiber present different morphology, depending of the fiber layers. And Fig. 6 and 7 presents cross and longitudinal section microphotographs of the Brazil nut bur fiber. In the Fig. 6b and Fig. 7 could be observed that the bur fiber presents irregular fibers, in different directions, like polymers cross-linking. And this quality can be given by the difficulty to fracture the fiber. It is possible to see an array of protruded features. These protrusions, shown in detail in the Fig. 4 d, would be, according to some authors, Si rich particles [19].

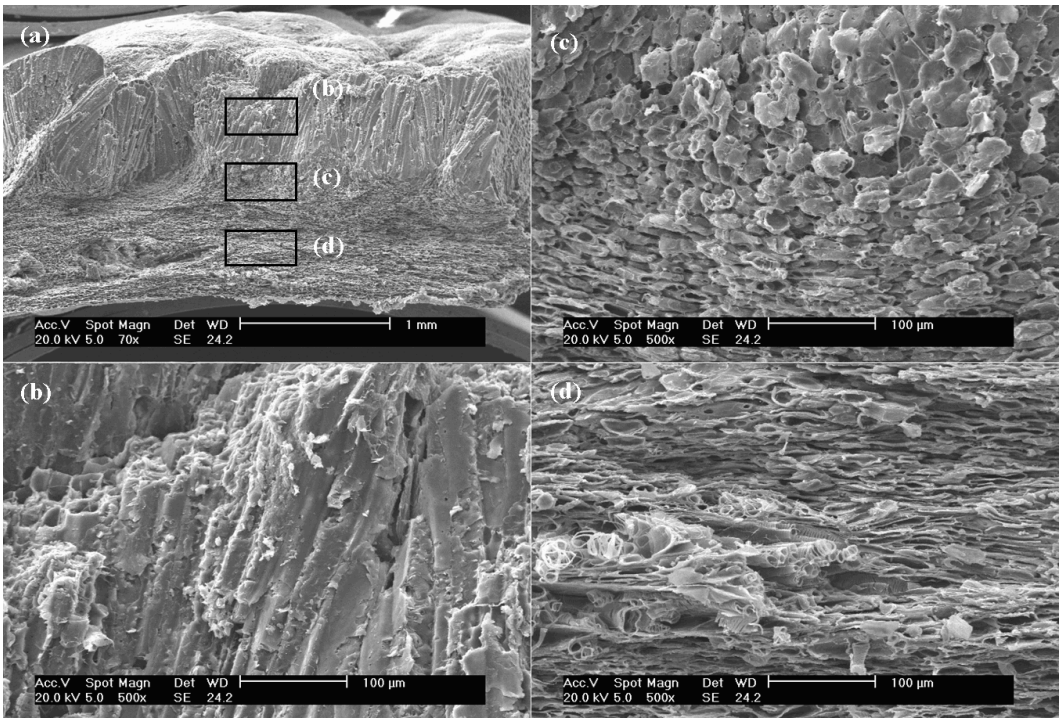

Figure 4. SEM cross-section images of Brazil nut shell fiber: (a) 70x; (b) superior, (c) central and (d) inferior parts of fiber, 500x.

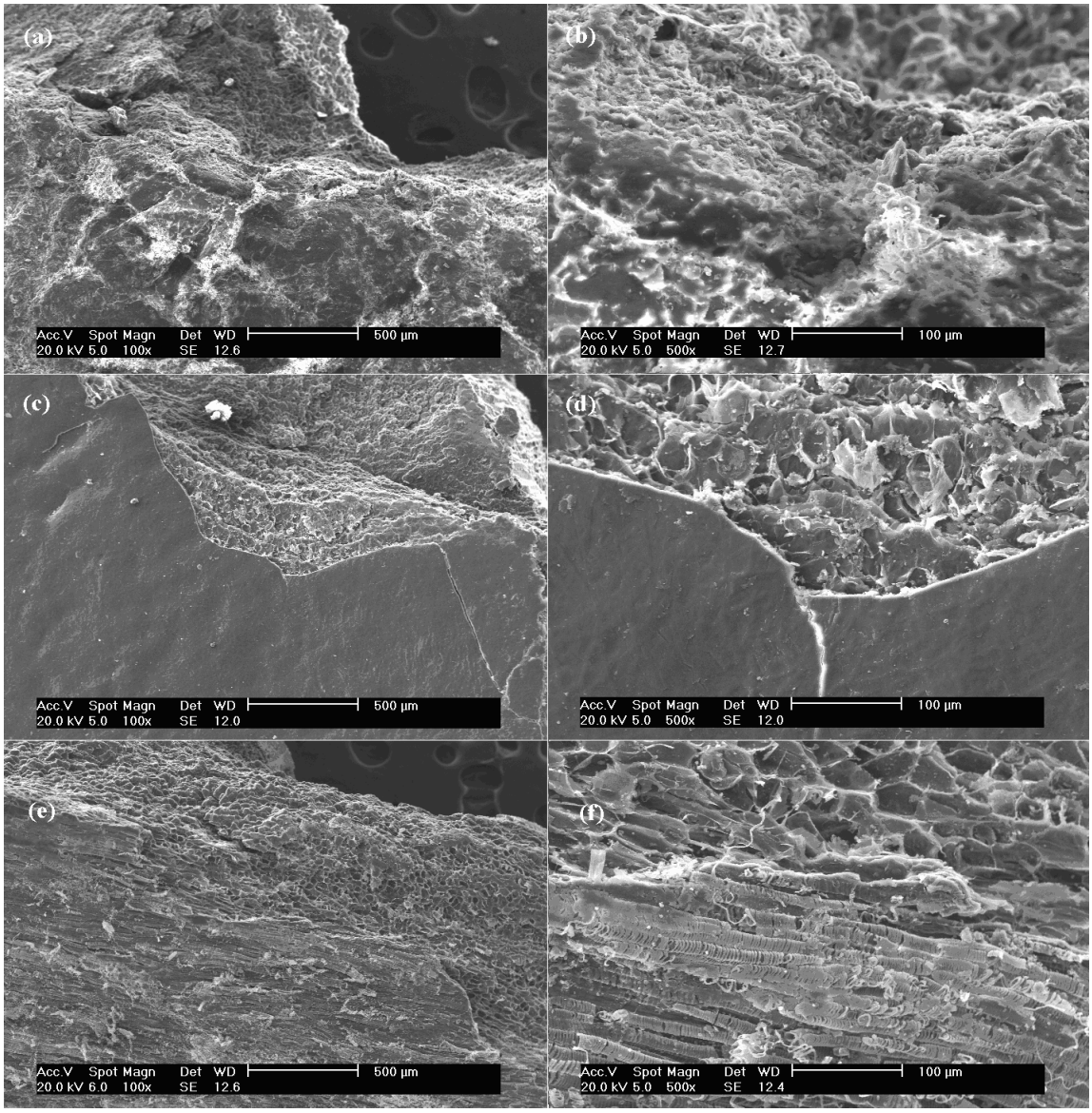

Figure 5. SEM longitudinal section images of Brazil nut shell fiber: (a) and (b) external micrograph of fiber, 100x and 500x; (c) and (d) internal micrograph of fiber, 100x and 500x; (e) and (f) central micrograph of fiber, 100x and 500x, respectively.

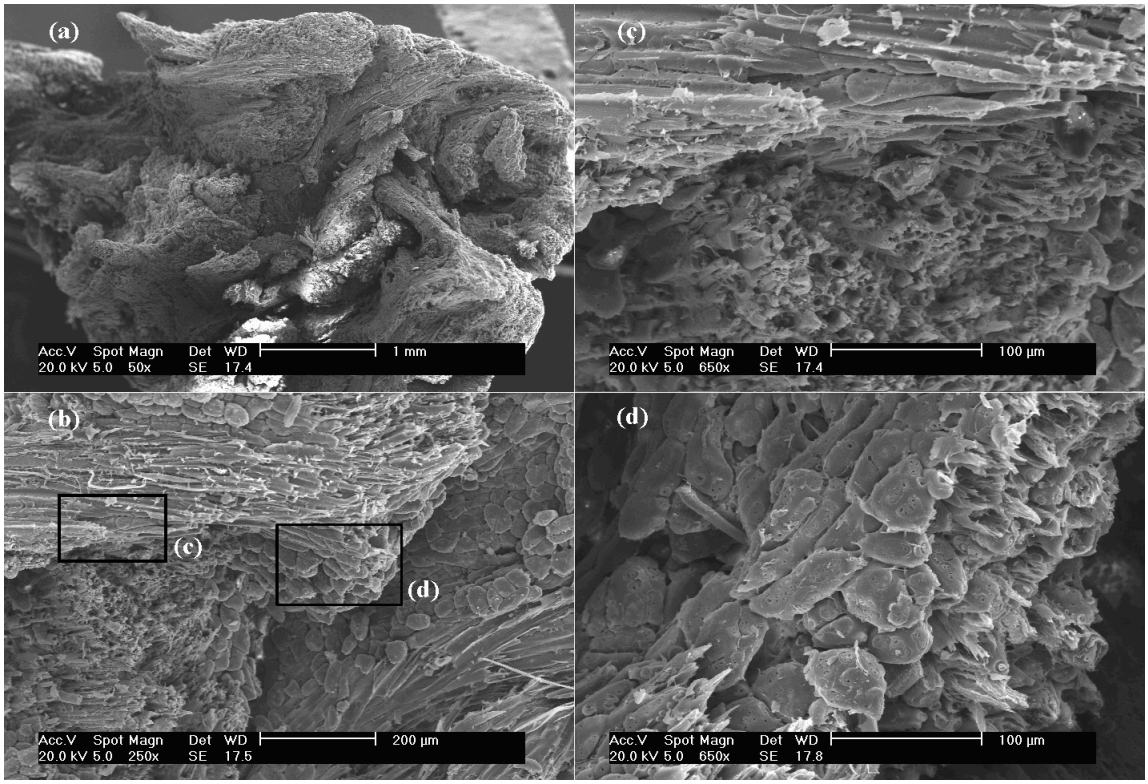

Figure 6. SEM cross-section images of Brazil nut bur fiber: (a) 50x; (b) 250x; (c) 650x; and (d) 650x.

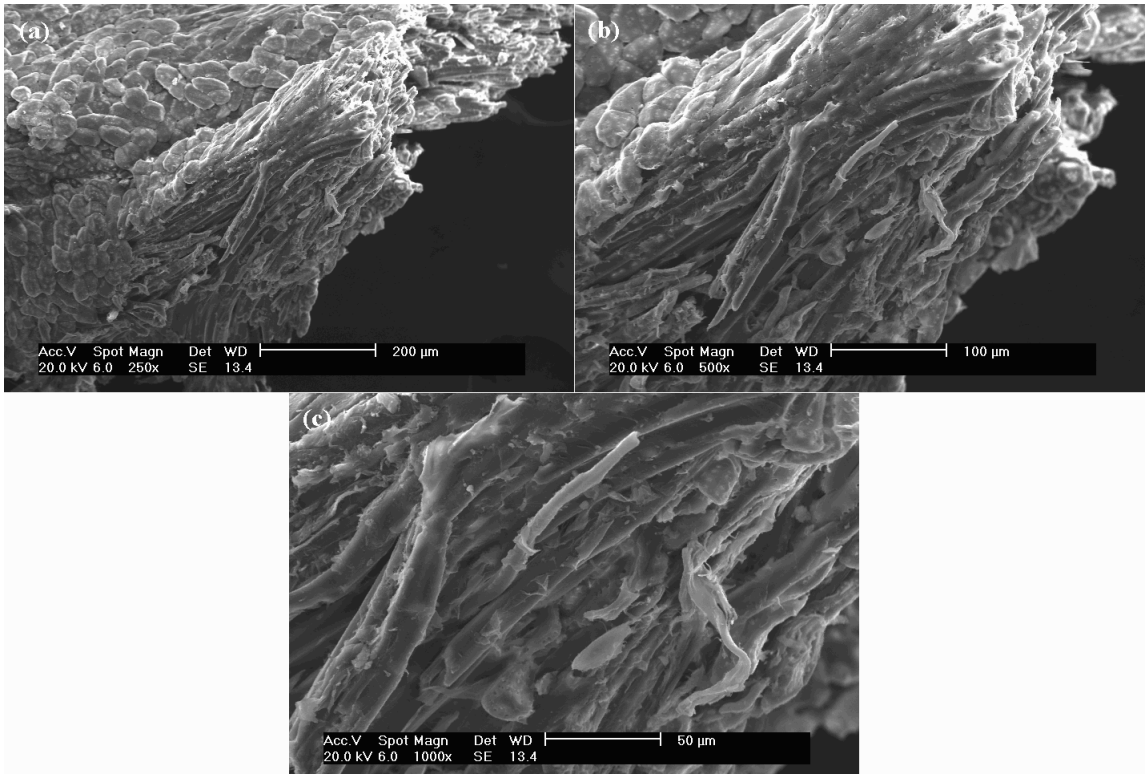

Figure 7. SEM longitudinal section images of Brazil nut bur fiber: (a) 250x; (b) 500x; (c) 1000x.

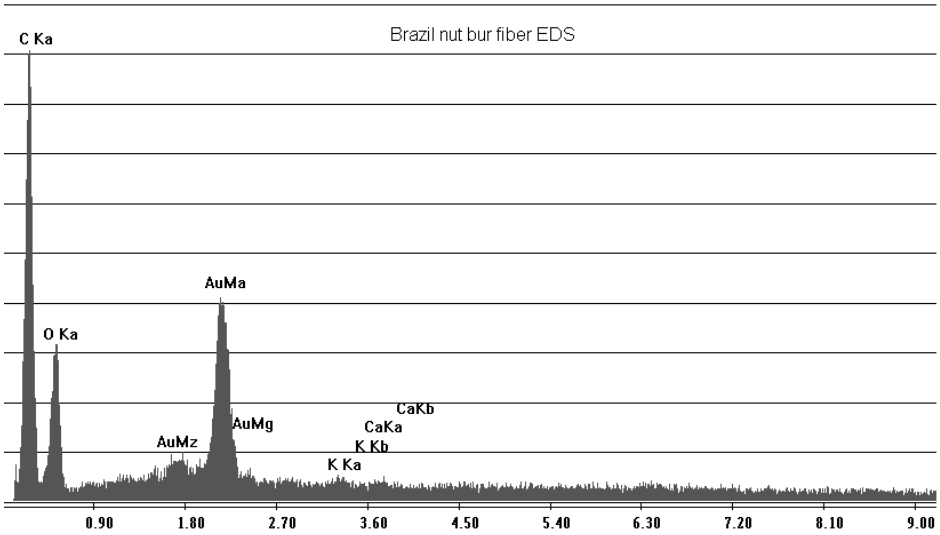

Figure 8. EDS spectrum of Brazil nut bur fiber.

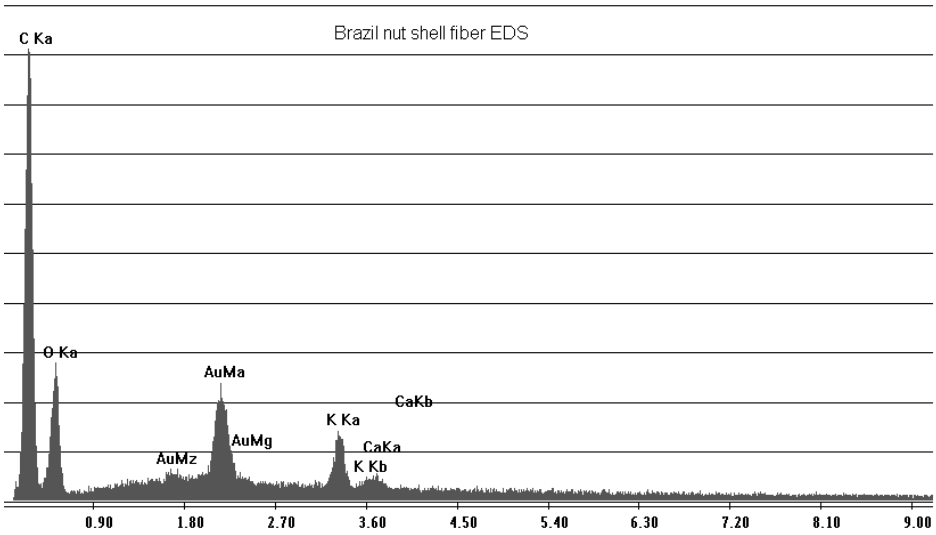

Figure 9. EDS spectrum of Brazil nut shell fiber.

Although EDS has reduced accuracy in inhomogeneous and rough samples, the elements identified (Figs 8 and 9) are consistent with the data found by other methods presented as follows in Tables 3, 4, 5 and 6.

Data of elementary composition of both kinds of fiber from Brazilian nut were obtained through the application of INAA as it is shown in Table 3 and 4. The Wavelength Dispersive X-ray Fluorescence (WDXRF) technique was also used to determine the level of nutrient elements (Table 5 and 6).

Table 3

Inorganic composition of Brazil nut bur fiber using INAA

Element	Unit	Conc. ± Uncertainty*	Conc. ± Uncertainty*
Br	µg/g	84 ± 4	89 ± 3
Ca	—	—	
Cr	µg/g	39 ± 1	—
Cs	µg/g	1.74 ± 0.04	—
Co	µg/kg	1900 ± 58	1317 ± 22
Fe	µg/g	11437 ± 41	10882 ± 94
K	µg/g	4576 ± 83	4403 ± 93
Mn	µg/g	49.2 ± 0.3	51.5 ± 0.3
Na	µg/g	53.2 ± 0.3	44.8 ± 0.4
Rb	µg/g	16.6 ± 0.6	16.0 ± 0.5
Sb	µg/kg	36 ± 4	
Sc	µg/kg	9.7 ± 0.6	
Se	µg/kg	188 ± 83	208 ± 44
Th	µg/kg	19 ± 4	
Zn	µg/g	19.8 ± 0.7	15.2 ± 0.4

*Uncertainty arising only from radioactive counting.

Table 4

Inorganic composition of Brazil nut shell fiber using INAA

Element	Unit	Conc. ± Uncertainty*	Conc. ± Uncertainty*

Br	µg/g	30 ± 1	29 ± 1
Ca	µg/g	10787 ± 137	12962 ± 101
Cr	µg/g	2.84 ± 0.06	2.81 ± 0.09
Cs	µg/g	1.37 ± 0.04	0.83 ± 0.02
Co	µg/kg	1280 ± 22	1264 ± 22
Fe	µg/g	1506 ± 10	1384 ± 11
K	µg/g	7376 ± 160	6998 ± 145
Mn	µg/g	22.7 ±0.2	23.8 ± 0.2
Na	µg/g	62.2 ± 0.3	62.4 ± 0.5
Rb	µg/g	42 ± 1	40 ± 1
Sb	µg/kg	20 ± 2	
Sc	µg/kg	12.4 ± 0.4	
Se	µg/kg	471 ± 46	441 ± 43
Th	µg/kg	17 ± 3	20 ± 3
Zn	µg/g	15.5 ± 0.5	16.3 ± 0.4

*Uncertainty arising only from radioactive counting.

Table 5

Inorganic composition of Brazil nut bur fiber using WDXRF

Elem./Comp	µg g^{-1}	Elem./Comp	µg g^{-1}
Fe_2O_3	14462 ± 300	Br	78 ± 10
K_2O	8229 ± 100	MnO	67 ± 10
SO_3	1996 ± 100	NiO	31 ± 10
Al_2O_3	1651 ± 100	CuO	25 ± 10
CaO	1080 ± 100	ZnO	21 ± 10
Cl	697 ± 30	As_2O_3	16 ± 10
SiO_2	625 ± 30	SrO	<10
MgO	555 ± 30	ZrO_2	<10
P_2O_5	447 ± 30	SnO_2	<10

Table 6

Inorganic composition of Brazil nut shell fiber using WDXRF

Elem./Comp	µg g^{-1}	Elem./Comp	µg g^{-1}	Elem./Comp	µg g^{-1}
K_2O	34381 ± 500	Cl	290 ± 30	ZrO_2	<10
SO_3	9356 ± 100	MnO	160 ± 20	SnO_2	<10
CaO	6684 ± 100	CuO	111 ± 20		
Al_2O_3	6533 ± 100	Br	94 ± 10		

Fe_2O_3	6380 ± 100	ZnO	87 ± 10
MgO	3214 ± 100	Rb_2O	83 ± 10
BaO	2711 ± 100	NiO	83 ± 10
SiO_2	2019 ± 100	As_2O_3	37 ± 10
P_2O_5	1735 ± 100	SrO	34 ± 10

As Skinner & Jahren [20] pointed out, the process of biomineralization creates heterogeneous accumulations in vegetal tissues with inhomogeneous distributions that reflect the environment in which they are formed. Vegetal material can contain carbonate, phosphate, oxalate, silica, iron, or sulfur-containing minerals with particular chemistries. The knowledge of the mineral composition of the fiber can be important for the correct analysis of some properties of this material, as inorganic elements are related to metabolism of living organisms.

Comparing present data from INAA and WDXRF, it is possible to perceive a correlation between the abundance in the shell fiber of Ca and K and the important quantities of K_2O, SO_3 and CaO. Likewise, the abundance of Fe and K correlated well with the highest quantities of Fe_2O_3 and K_2O in the bur fiber.

4. Conclusion

This work presents an investigation on the thermal behavior, chemical and elementary composition of Brazil nut fibers. Their characteristics are comparable to those of fibers already studied by other groups. The chemical analysis showed that Brazil nut bur fiber is a lignin-rich fiber. This material, nowadays a leftover, could result to be useful as other lignin-rich fibers, considering that many lignocellulosic materials are suited for composite material development. As poor information is

available on this kind of fiber until now, the present paper is a contribution to elucidate characteristics of Brazil nut shell and bur fibers.

Acknowledgements

The authors want to express their thanks to Eng. Elizabeth S.R. Somessari and Eng. Carlos Gaia da Silveira for guidance in the irradiation operation. Financial support from the University of Sao Paulo is also acknowledged.

References

[1] Bastioli C. Biodegradable Materials - Present Situation and Future Perspectives. *Macromol. Symp.* **1998**, 135, 193-204.

[2] Silva, R.V.; Ueki, M,M,; Spinelli, D.; Bose Filho, W.W..; Tarpani, J.R. Thermal, Mechanical, and Hygroscopic Behavior of Sisal Fiber/Polyurethane Resin-based Composites. *J. Reinf. Plast Compos*. **2010**, 29, 1399-1417.

[3] Rowell, R.M.; Han, J.S.; Rowell, J.S. Characterization and factors effecting fiber properties. In *Natural Polymers and Agrofibers Based Composites*; Frollini, E., Leão, A.L., Mattoso, L.H.C., Eds.; Embrapa Instrumentação Agropecuária: São Carlos, 2000; pp.115-132.

[4] d'Almeida, J.R.M.; Aquino, R.C.M.P.; Monteiro, S.N. Tensile mechanical properties, morphological aspects and chemical characterization of piassava (Attalea funifera) fibers. *Compos. Part A.* **2006**, 37, 1473–1479.

[5] Satyanarayana, K.G.; Guimarães, J.L.; Wypych, F. Studies on lignocellulosic fibers of Brazil. Part I: Source, production, morphology, properties and applications. *Compos. Part A.* **2007**, 38, 1694–1709.

[6] Tomczak, F.; Satyanarayana, K.G.; Sydenstricke,r T.H.D. Studies on lignocellulosic fibers of Brazil: Part III – Morphology and properties of Brazilian curauá fibers. *Compos. Part A*. **2007**, 38, 2227–2236.

[7] Moura, E.A.B.; Nogueira, B.R.; Ortiz, A.V. In *Changes in physicochemical, morphological and thermal properties of electron-beam irradiated ethylene-vinyl alcohol copolymer (EVOH) as a function of radiation dose*, Proceedings of AccApp, Vienna, IAEA, 2010.

[8] Corrêa, A.C.; Teixeira, E.M.; Pessan, L.A.; Mattoso, L.H.C. Cellulose nanofibers from curaua fibers. *Cellul*. **2010**, 17, 1183–1192.

[9] Inamura, P.Y.; Kasawa, C.T.S.; Colombo, M.A.; Moura, E.A.B.; Mastro, N.L. del. In *Changes in Gelatin/Brazil Nut Shell Fiber Composite Treated by Electron Beam Radiation*, Proceedings of APSRC, India, September, 2010.

[10] Vianna, P.R. *Estudo da castanha-do-Brasil*. Brasília: Ministério da Agricultura, Comissão de Financiamento da Produção, 1972.

[11] APIZ - Zoro Indigenous People Association. Good practices of harvest, storage and trade of Brazil nut. Defanti, Eds.; Brasil, 2008; pp. 10. *(In Portuguese*).

[12] Scapin, M.A.; Salvador, V.L.R.; Cotrim, M.E.B.; Pires, M.A.F.; Sato, I.M. In *Uncertainty Measurement Evaluation of WDXRF and EDXRF Techniques for the Si and U_{total} Determination in U_3Si_2 used as Nuclear Fuel Material*, Proceedings of INAC. Rio de Janeiro, Brazil, 2009.

[13] Bledzki, A.K.; Reihmane, S.; Gassan, J. Properties and modification methods for vegetable fibers for natural fiber composites. *J. Appl. Polym. Sci*. **1996**, 59, 1329-36.

[14] Kozlowski, R.; Rawluk, M.; Barriga, J. In *State of the art-production, processing and applications of fibrous plants*, Proceedings of SINTEX-2004, Natal, Brasil, 2004; Sivam, R.L., Araújo, R.C, Eds.; [CDROM], Paper No.TIP-1-00, 2004.

[15] Espert, A.; Vilaplana, F.; Karlsson, S. Comparison of water absorption in natural cellulosic fibres from wood and one-year crops in polypropylene composites and its influence on their mechanical properties. *Compos. Part A*. **2004**, 35, 1267–1276.

[16] Spinacé, M.A.S.; Lambert, C.S.; Fermoselli, K.K.G.; De Paoli, M.A. Characterization of lignocellulosic curaua fibres. *Carbohydr. Polym.* **2009**, 77, 47-53.

[17] Idicula, M.; Malhotra, S.K.; Joseph, K.; Thomas, S. Dynamic mechanical analysis of randomly oriented intimately mixed short banana/sisal hybrid fiber reinforced polyester composites. *Compos. Sci. Technol.* **2005**, 65, 1077-1087.

[18] Ramiah, M.V. Thermogravimetric and differential thermal analysis of cellulose, hemicellulose, and lignin. *J. Appl. Polym. Sci.* **1970**, 14, 1323–37.

[19] Calado, V.; Barreto, D.W.; d'Almeida, J.R.M. The effect of a chemicaltreatment on the structure and morphology of coir fibers. *J. Mater. Sci. Lett.* **2000**, 19, 2151-2153.

[20] Skinner, H.C.W.; Jahren, H.C.W. Biomineralization. In *Treatise on Geochemistry*; ISBN (set): 0-08-043751-6, Elsevier, 2003, 8, pp. 117–184.