Study of natural fibers from waste from sponge gourd, peach palm tree and papaya pseudstem

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Abstract— *Lignocellulosic wastes from agro-industry are usually discarded, despite their technical potential for use to reinforce composites. Because of increasing environmental concerns, scientific interest is growing to characterize fiber residues from peach palm tree trunks, papaya tree trunks and sponge gourds. The peach palm residues were obtained from the portion of the trunk not suitable for hearts of palm, while the papaya trunk residues were obtained from trees cut down after three years of fruit production and the sponge gourd waste material came from leftover gourds not suitable for making bath sponges. The materials were characterized regarding moisture content, density, ash content, lignin and holocellulose content, and soluble content, and were submitted to thermogravimetric analysis, Fourier transform infrared spectroscopy (FTIR), X-ray diffraction, mechanic property and morphological analysis by scanning electron microscopy. The moisture, extractives and ash contents of the papaya pseudsterm and peach palm wastes were very near each other. The sponge gourd fibers had the highest concentrations of α-cellulose and hemicellulose and lowest levels of extractable soluble, and ash. The characterization results show that these waste materials are comparable with other agro-industrial residues described in the literature for use in making composites, so they have good potential for use as polymer reinforcement.*

Keywords— lignocellulosic fibers, peach palm tree, papaya pseudstem, sponge gourd.

I. INTRODUCTION

Concern over the use of resources from fossil sources has prompted development of composites for various applications containing cellulose as a substitute for synthetic materials derived from petroleum [1]. The cellulosic materials or lignocellulosic fibers obtained from agro-industrial waste can be burned to generate energy (e.g., sugarcane bagasse), but the majority are discarded in dumps/landfills or are burned without proper control, causing environmental problems, especially atmospheric emissions. For this reason, there is a need to find uses for these materials in line with good sustainability practices, involving economic, social and environmental questions [2].

A wide range of lignocellulosic fibers can be used to reinforce polymers. These include agricultural fibers such as stems and leaves as well as wood fibers [1]. Fibers can be considered composites of fibrils bounded by a matrix formed by lignin and hemicellulose. Cellulose is main responsible for the resistance of fibers, because of its high degree of polymerization and molecular orientation. In turn, lignin not only keeps the fibers together, it also acts as a stiffening agent for the cellulose molecules within the fiber wall. Besides these components, fibers contain inorganic compounds and molecules that are extractable with organic solvents, such as pectins, simple carbohydrates, alkaloids, saponins, polyphenols, gums, resins, fats, greases and others. Woody plants typically contain 40-50wt% cellulose, 20-30wt% hemicellulose and 20-28wt% lignin, besides other substances in smaller concentrations [3]. Study of the chemical composition is important to understand the influence of fibers on the characteristics of the composite of interest [4].

It is necessary to investigate the chemical composition of fibers because this can vary according to many factors, such as species, variety, soil type, climate conditions, plant part and age of the plant from which the fiber is extracted. In one study [5], the chemical compositions of fibers from banana plants, sugarcane bagasse and sponge gourds were determined and the samples were also characterized by X-ray diffraction, thermal analysis and microscopy to evaluate morphology. The crystallinity indices, obtained by X-ray diffraction, for the banana tree, bagasse and sponge gourd fibers were 39, 48 and 50%, respectively. All the materials came from Brazil. The morphological study of the fibers revealed different sizes and arrangements of cells composing the fibers, with thick non-spherical cells [5]. Another characterization study was carried out

by Tanobe and collaborators [6], who evaluated sponge gourd fiber from southeastern Brazil before and after different chemical treatments (2% NaOH and 3% methacrylamide) for surface modification. They observed that the treatment with NaOH was more effective to prepare the surface for subsequent use as reinforcement of composites. Teixeira and collaborators [7] characterized sugarcane bagasse by thermogravimetry, X-ray diffraction and morphological analysis, concluding that this bagasse can be used to obtain whiskers. Other studies to characterize cellulosic residues from various plant sources and countries can be mentioned, such as: coconut shells [8,9], wheat and rice stalks [10](origin not mentioned), banana plants (India) [11-13] and palm (Thailand) [9].

By looking for in the literature, we verified that no articles have been published about the characterization of fibers extracted from the peach palm or papaya tree trunks for the last ten years. In the case of the peach palm, only part of the trunk is used (to produce hearts of palm), while papaya trees have a short productive lifetime, after which they are cut down. In both cases, the remaining material is generally discarded or burned. For this reason, the research group of the Center for Excellence in Recycling and Sustainable Development (NERDES), located at the Universidade Federal do Rio de Janeiro (UFRJ), has taken the initiative to study these materials. The fibers extracted from the trunks of peach palm (*bactris gasipaes*) and papaya pseudstem (*Carica papaya*) were characterized for subsequent use in composites. Waste fibers from mature sponge gourds (*Luffa Cylindrica*) were characterized as well because they also have technical and commercial potential. Fibers are known to improve properties when added to polymers to produce composites. The reinforcement is highly dependent of the interaction between the polymeric matrix and the filler. To insure that the fiber-filled composite will have better performance, characterization of the fiber is very important as filler and matrix must present special features as to develop a strong interface.

II. MATERIAL AND METHODS

2.1 Raw materials

The fibers analyzed were obtained from: peach palm trunks, from the city of Silva Jardim (Rio de Janeiro State); papaya pseudstem trunks, from the city of Mucuri (Bahia State); and waste material from producing bath sponges from sponge gourds, obtained from the city of Bonfim (Minas Gerais State).

2.2 Fiber processing

2.2.1 Processing of peach palm fibers

The top parts of the trunks (used for making hearts of palm) were cut off and the remaining parts were transported to the NERDES laboratory where they were processed in a shredding machine (Fortalmag model TCVS-R). The moist fibers obtained were naturally dried in the sun and then ground in a knife mill (Solab model SL-32), to attain uniform fiber size. The yield was calculated by the ratio between the dried fiber mass and trunk mass before processing, according to Equation 1. Fig. 1 shows the peach palm trunks, before and after cutting.

FIGURE 1: PHOTOGRAPHS OF PEACH PALM TRUNKS: A) STANDING TREE; B) FELLED TRUNK; C) TRUNK CUT INTO DISKS (Elaborated by Mônica Castedo, Sep. 2014)

$$\% \text{ yield} = \frac{M2}{M1} \times 100 \quad (1)$$

Where: M1= mass of trunks *in natura* (kg), M2 = mass of dried fibers (kg).

2.2.2 Processing of papaya tree fibers

The papaya trees, after three years of production, were felled and the trunks were taken to the NERDES laboratory for processing. The trunks were first weighed and then ground in a sugarcane grinder (Maqtron 721 Turbo) to separate the fibers from the other constituents. The fibers were dried in the sun and then weighed, after which they were further ground in a knife mill (Solab model SL-32) to obtain uniform size. The yield was calculated by Equation 1. Fig. 2 shows the papaya tree trunks before and after cutting.

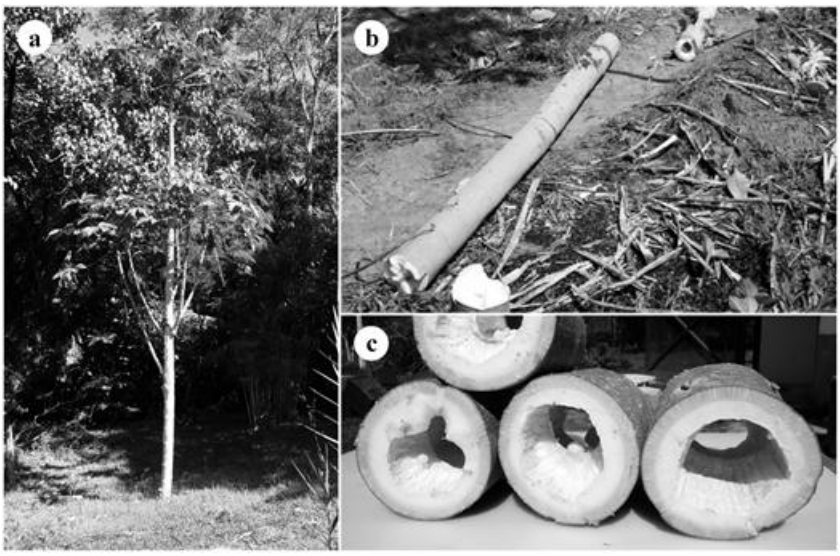

FIGURE 2: PHOTOGRAPHS OF PAPAYA TREE TRUNKS: A) STANDING TREE (by Mônica Castedo, Sep. 2014) B) FELLED TRUNK (by Viviane Escócio, Sep. 2014), AND C) TRUNK SEGMENTS (by Mônica Castedo, Sep. 2014)

2.2.3 Processing of sponge gourds

The sponge gourd (*Luffa cylindrica)* residues were ground in a knife mill (Solab model SL-32) to obtain uniform size. The calculation of the yield was performed by the producer, with Equation 1, where M1 represents the mass of 12 gourds after harvest and M2 represents the mass of the scrap from transforming the 12 gourds into bath sponges. Fig. 3 shows the gourds before harvest, the sponge material and the fibers.

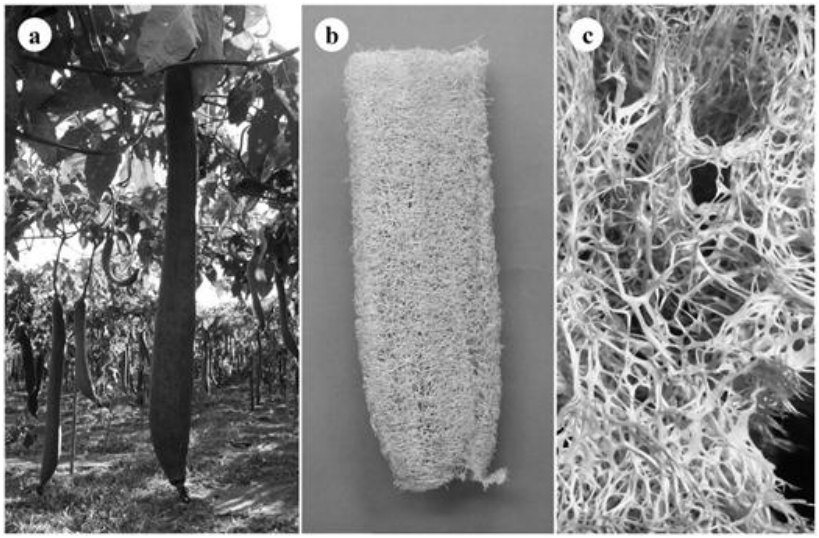

FIGURE 3: PHOTOGRAPHS OF SPONGE GOURD MATERIAL: A) GOURDS (FRUITS) ON THE TREES; B) SPONGE GOURD C) SPONGE GOURD FIBERS (by Viviane Escócio, August 2014)

2.3 Characterization of the peach palm, papaya tree and sponge gourd fibers

The characterization of the fibers involved determining the moisture content, density, ash content, lignin content, soluble content by extraction as well as analysis by thermogravimetry, Fourier-transform infrared spectrometry (FTIR) and X-ray diffraction, tensile strength property and morphological analysis by scanning electron microscopy.

2.3.1 Moisture content

The moisture content of the fibers was determined according to the ASTM D1348-61 standard. The test was carried out in triplicate and the moisture was calculated by Equation 2.

$$\% \text{ Moisture} = \frac{(M2 - M1)}{M2} \times 100 \quad (2)$$

Where: M1 = mass of the sample dry (g) and M2 = mass of the sample wet (g)

2.3.2 Density

The density of the fibers was determined with a pycnometer according to the ISO 8962 standard, by applying Equation 3.

$$\text{Density} = \frac{\rho(M3 - M1)}{M3 - M1 + M2 - M4} \quad (3)$$

Where: ρ = density of ethanol at the testing temperature(g/ml), M1 = mass of the clean and dry pycnometer (g), M2 = mass of the pycnometer with ethanol (g), M3 = mass of the pycnometer containing 2 g of fiber (g), and M4 = mass of the pycnometer containing fiber and ethanol (g).

2.3.3 Soluble extractives

The concentration of the water-soluble extractives was measured according to the TAPPI T212 om-98 standard. The test was carried out in quadruplicate.

2.3.4 Ash content

The ash content was determined according to the TAPPI T211 om-93 standard, carried out in triplicate. The ash content was calculated by the ratio between the final and initial masses, according to Equation 4 (average of three measurements).

$$\% \text{ Ash} = \frac{M1}{M2} \times 100 \quad (4)$$

Where: M1= final ash mass (g) and M2= initial fiber mass (g).

2.3.5 Determination of the contents of lignin, holocellulose, α-cellulose and hemicellulose

2.3.5.1 Determination of lignin content

The lignin was extracted from the fibers by the method described by Klason according to the TAPPI T222 om-22 with modifications, in which the polysaccharides were removed by solubilization and the lignin was extracted from the residue by acid hydrolysis.

The fiber (3 g of sample) was extracted in a Soxhlet device with a solution of ethanol/benzene (3:1 v/v), kept boiling for 16 h. Then the material was placed in an oven at 60 ºC for 16 h to eliminate possible resins, which can interfere with quantification of the lignin content. Twenty-five mL of 72% sulfuric acid solution (H_2SO_4) was added to the solution, which was left standing for 2 h. Then distilled water was added to the reaction medium to reduce the solution's concentration to 3%v/v. The sample was them transferred to a reflux condenser system, heated to boiling and maintained at that temperature for 4 h. Afterward, the solution was filtered and the extracted fiber was washed with water until neutralization and placed in an oven at 100 ºC for 16 h [14]. The resulting solid was weighed. This procedure was carried out in triplicate and the values are the average of these analyses. The percentage of fiber without lignin was calculated by Equation 5.

$$\% \text{ Fiber} = \frac{(Mi - Mf)}{Mi} \times 100 \quad (5)$$

Where: Mi = initial dry fiber mass (g), Mf = final extracted and dried fiber mass (g).

2.3.5.2 Determination of holocellulose content

The holocellulose content was measured according to the TAPPI T19m-54 standard. The final mass of the funnel plus the sample was measured (M3) and the holocellulose content was calculated by Equation 6:

$$\% \text{ Holocellulose content} = \frac{(M3 - M2)}{M1} \times 100 \quad (6)$$

Where: M1 = mass of the sample dry (g) and M2 = mass of the clean and dry funnel (g)

2.3.5.3 Determination of α-cellulose and hemicellulose contents

The α-cellulose and hemicellulose contents were quantified based on the TAPPI T19m-54 standard. The final mass of the funnel plus the sample was measured (M3) and the contents of α-cellulose and hemicellulose were calculated by Equations 7 and 8, respectively.

$$\% \ \alpha \text{ Cellulose content} = \frac{(M3 - M2)}{M1} \times 100 \quad (7)$$

$$\% \text{ Hemicellulose content} = \% \text{ holocellulose} - \% \ \alpha \text{ cellulose} \quad (8)$$

2.3.6 Thermogravimetric analysis

The thermogravimetric analysis (TG/DTG) was performed with a TA Instruments model Q500 analyzer, with N_2 flow of 60 mL/min, at a heating rate of 20 °C/min and temperature range from room temperature to 850 °C. Three samples of each fiber type were analyzed.

2.3.7 Crystallinity index

The cellulose samples (ground and passed though a #70 mesh screen) were submitted to X-ray diffraction in a Rigaku Miniflex diffractometer. The test was carried out using a CuKα cathode (1.54 Å), scanning from 5 to 40°, voltage of 40 kV and current of 30 mA. The crystallinity index was calculated by the deconvolution method, which separates the diffraction spectra of the amorphous and crystalline contribution. This procedure was performed by curve fitting with the Fityk 0.9.8 software. The diffractograms were fitted using a Gaussian curve and the crystallinity index was calculated by dividing the area under the crystalline peaks by the total dispersion area. As suggested by Xu et al. [15] the percentage of crystalline component in cellulose can be estimated by dividing the crystallinity index (calculated by deconvolution method of biomass) by the α-cellulose content.

2.3.8 Fourier transform infrared spectrometry (FTIR)

FTIR was applied to evaluate the functional groups present in the fiber samples, using a Perkin-Elmer model 1720X spectrophotometer with KBr pellets in the range of 400 to 4000 cm^{-1}.

2.3.9 Tensile strength of the fiber

To test the tensile strength, the fibers extracted from the peach palm trunks were carefully selected to avoid samples with apparent defects (folds, cracks, abrupt color changes, indications of contamination, etc.) to rule out the influence of defects on the test results, except in the samples representative of groups. The sponge gourd fibers were too short and the papaya tree fibers were too fragile for realizing of the testing.

The fibers were extracted from four trunks, called groups 1 to 4. From each group, twenty five fibers were selected (test specimens) with length of 30 mm. Adhesive tape was placed on the ends (Fig. 4) to facilitate handling and avoid causing any damage to the fiber by the pressure produced by tightening the clamps. The thickness of each test specimen was measured with a micrometer (0.01 mm) at five positions along the length.

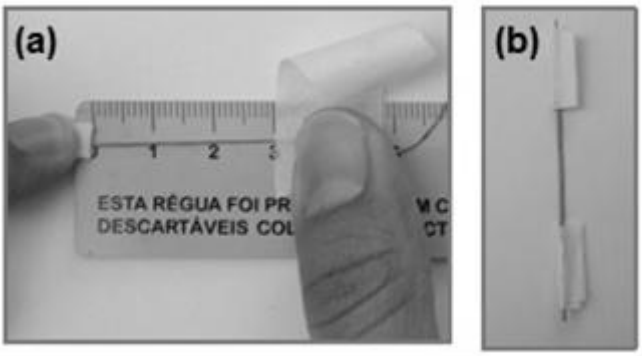

FIGURE 4: PHOTOGRAPHS OF PREPARATION OF SAMPLES FOR TENSILE STRENGTH TEST: A) LENGTH OF THE FIBER ANALYZED, B) TEST SPECIMEN WITH ADHESIVE TAPE ON THE ENDS (Elaborated by A. M. F. de Sousa, May 2012)

There is no standard procedure for testing the uniaxial traction of natural fibers. Therefore, it was relied on the ASTM D3822 (2007) standard as a reference for this test. The test was conducted with an Oswaldo Filizola AME 5 kN universal testing machine with a 5 kN load and speed of testing of 3.0 mm/min. The data were processed by the Dynaview Standard/Pro version 2.6.7 software. When placing the sample in the clamps, it was taken care to centralize it to avoid damage to the fiber. The transversal area was calculated assuming the fibers had circular cross sections.

2.3.10 Morphology

The morphology of the fibers was observed in longitudinal and cross sections by scanning electron microscopy (SEM) using a Jeol microscope (model JSM-6510LV). The samples were gold sputtered with a Denton vacuum (Desk V) system.

III. RESULTS

3.1 Fiber yield after processing and estimate of yearly availability of waste material

The yields obtained from the process of fiber recovery from the peach palm and papaya tree trunks are shown in Table 1. The fiber yields were 6.0 and 8.0 wt%, respectively. Regarding the sponge gourds, data provided by producers in the region of Bonfim (Minas Gerais) indicate the waste generated while making bath sponges is about 30 wt% of the total amount of material processed, because the mass of 12 gourds is 0.75 kg and the mass of the scrap from transforming the 12 gourds into bath sponges is 0.25 kg.

TABLE 1
FIBER YIELDS FROM AGRO-INDUSTRIAL WASTES: PEACH PALM TREE AND PAPAYA TREE

Fiber type	Initial residue mass (kg)	Dry fiber mass (kg)	Yield (%)	Estimated production in Brazil (t/year)
Peach palm	50	3	6	20,000
Papaya	119	9.52	8	39,034

By using the data available from the sites of the Brazilian Institute of Geography and Statistics (*Instituto Brasileiro de Geografia e Estatística* - IBGE) [16], we estimated the potential production of lignocellulosic fibers that can be extracted from waste material from papaya tree and peach palm trunks, applying the yields after processing measured in this study. According to the IBGE, in 2015 Brazil's papaya fruit production was 1,463,770 t (IBGE 2016) and the output of hearts of peach palm was 109,409 t [16].

In relation to papaya tree fibers, each tree produces an average of 35 kg of fruit a year, meaning approximately 41,822,000 papaya trees are needed to produce the yearly fruit crop (1,463,770,000 kg of papaya fruit/35 kg per tree). Considering that each trunk weighs an average of 35 kg and that the trees are typically cut down every three years [17], the quantity of waste from trunks is 487,923 t/year. Applying the fiber yield of 8 wt%, the yearly fiber output is 39,034 t. For peach palm, the annual production of hearts of palm is 109,409 t. Since the waste corresponds to 75% of the total weight of the tree, the estimated waste material is 328,227 t/year, with the remaining 25% sold mainly in the domestic market in various forms (whole and chopped hearts of palm). Based on the total quantity of waste and the fiber yield from processing (6 wt%), the

estimated yearly production is about 20,000 t. These calculations do not consider production for home use and subsistence farming.

3.2 Moisture content, density, soluble extractives and ash content

Fibers are hydrophilic due to the presence of hydroxyl groups in their structure [3]. Since moisture has a negative influence on the mechanical properties of composites, this value was measured for the fibers analyzed. Hemicellulose is considered mainly responsible for water absorption by fibers, although non-crystalline cellulose and lignin also absorb water [18]. According to the Table 2, which shows the moisture levels in the different fibers, the papaya tree fiber had the lowest moisture level. The values for all the fiber types can be considered low when compared to those normally found for wood, which are between 10-18% [19].

TABLE 2
MOISTURE LEVELS, AVERAGE DENSITY AND SOLUBLE EXTRACTIVES OF PEACH PALM TREE, PAPAYA TREE AND SPONGE GOURD FIBERS

Fiber type	Density (g/cm^3)	Moisture content (wt%)	Soluble extractives
Peach palm	1.20 ± 0.02	9.5 ± 1.7	11.6 ± 3.2
Papaya	1.21 ± 0.11	9.1 ± 0.7	10.3 ± 1.5
Sponge gourd	1.25 ± 0.05	10.7 ± 0.7	2.1 ± 1.4

In Table 2 also presents the density results for the three types of fiber. The values found experimentally here are lower than those of mineral reinforcements, of which the most commonly used are calcium carbonate (density = 2.70 g/cm^3), fiberglass (2.54 g/cm^3), talcum (2.7 g/cm^3) and kaolin (2.6 g/cm^3) [20,21]. Lower density values allow obtaining lighter composites (lower specific mass).

To quantify the percentage of extractives soluble in hot water, such as low-molar-mass polysaccharides and inorganic impurities, the fiber samples were stirred in distilled water (70 °C). The results are reported in Table 2. The value for the sponge gourd fiber is very near that reported in the literature [22], 2.3 wt%.

The average values found for the ash contents of the peach palm, papaya tree and sponge gourd fibers were 0.55 ± 0.2, 3.3± 0.5 and 3.4 ± 0.7 wt%, respectively. According to the literature [6,22,23], these values correspond to silicates, oxalates, sulfates and carbonates of Ca, Na, K and Mn, which are commonly found to be present in or adhered to the surface of natural fibers in the form of their respective salts. The values for the papaya tree and peach palm fibers are very close (3.3 ± 0.5 and 3.4 ± 0.7 wt%) and the value for the sponge gourd sample (0.5± 0.2 wt%) is similar to that reported in the literature [6] which is 0.4 wt%.

3.3 Contents of holocellulose, *α*-cellulose, hemicelluloses and lignin

Table 3 shows the holocellulose, cellulose, lignin and hemicellulose concentrations in the fibers. The values for sponge gourd fiber are near those found in the literature [5, 6]. The composition of fibers depends on various factors, such as origin and type, plant age and part from which they were extracted. This variation makes it important to characterize the material to be used to reinforce a polymer matrix. It was not find any published studies characterizing the fibers of peach palm and papaya tree, but the values found here are near those for other natural fibers, such as banana plant, sugarcane bagasse and coconut shell. The percentages of the constituents did not add to 100%, a phenomenon that according to Guimarães et al. [5] can be due to the experimental conditions, including methodology, causing loss of proteins or polysaccharides during cellulose isolation, loss of sugars from the inverse reaction during hydrolysis, overlap of some constituents (e.g., lignin residues in the cellulose or ash), presence of impurities of protein or products, and presence of other components not quantified (e.g., waxes/oils).

TABLE 3
PERCENTAGE COMPOSITION OF THE CONSTITUENTS OF PEACH PALM TREE, PAPAYA TREE AND SPONGE GOURD FIBERS

Fiber type	Holocellulose content (wt%)	*α*-cellulose content (wt%)	Hemicellulose content (wt%)	Lignin content (wt%)
Peach palm	58.6 ± 0.2	55.5 ± 0.7	3.1 ± 0.5	8.3 ± 1.5
Papaya	67.0 ± 0.5	62.0 ± 2.8	5.0 ± 2.4	15.1 ± 0.2
Sponge gourd	78.7 ± 0.9	63. 4 ± 1.0	15.3 ± 0.4	14.7 ± 0.5

The lignin content in the papaya tree fibers was higher than peach palm tree fiber. This value is also higher than sisal fibers (7.6-7.98 wt%) [24]. High lignin concentration can promote good interaction with polymers that have hydroxyl groups in their structure.

3.4 Thermogravimetry

The results of the thermogravimetric analysis are shown in Table 4 and Figs. 5, 6 and 7. The three fibers have the same degradation profile. The initial mass loss corresponds to the vaporization and removal of bound water in samples, which occurs for all lignocellulosic fibers. The intense peak (336-381ºC) is referring to the degradation of cellulose and a less intense peak (206-297ºC) referring to the degradation of hemicellulose in the derivative mass loss curves (DTG). In Fig. 5, referring to degradation of the peach palm tree fibers, the initial peak (hemicellulose) is more intense (286ºC) than those of papaya tree (269ºC) (Fig. 6) and sponge gourd (297ºC) fibers (Fig. 7). According to Tanobe et al. [6], in sponge gourd fibers the degradation of hemicellulose occurs in the range of 200 to 260ºC, of cellulose from 240 to 350°C and of lignin from 280 to 500°C. The differences in results can be explained by the fact that the composition of lignocellulosic fibers depends on their species, variety, soil type, climate conditions, plant age etc. [5,6,24]. Other authors [25,26] have reported the degradation of hemicellulose and cellulose in wood as occurring between 207-330°C and 343- 367°C, respectively.

TABLE 4
THERMOGRAVIMETRY RESULTS FOR PEACH PALM TREE, PAPAYA TREE AND SPONGE GOURD FIBERS

Fiber type	T_{onset} (ºC)	Peak 1 (ºC)	Peak 2 (ºC)
Peach palm	238± 37	286±49	344±7
Papaya	254±7	269±7	346±6
Sponge gourd	291±16	297±0	369±12

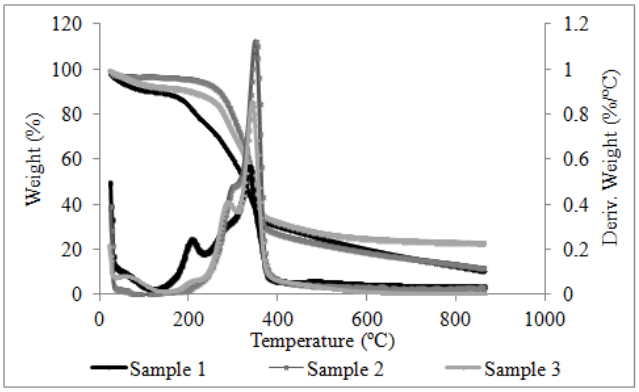

FIGURE 5: THERMAL DEGRADATION AND FIRST DERIVATIVE MASS LOSS CURVES OF THREE SAMPLES OF PEACH PALM FIBER IN N_2

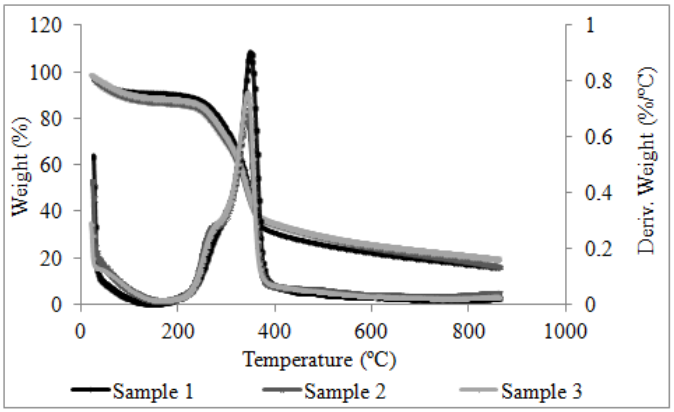

FIGURE 6: THERMAL DEGRADATION AND FIRST DERIVATIVE MASS LOSS CURVES OF THREE SAMPLES OF PAPAYA TREE FIBER IN N_2

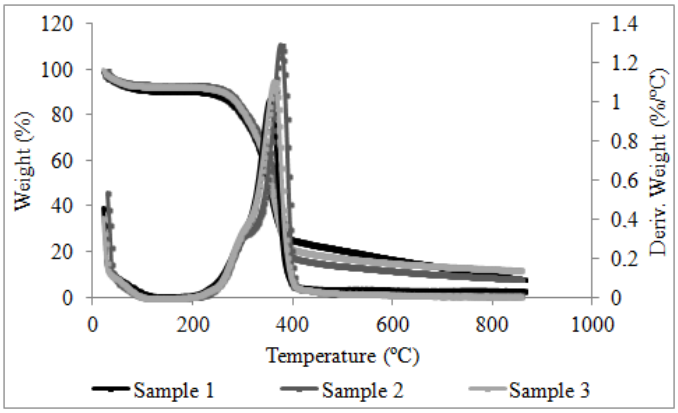

FIGURE 7: THERMAL DEGRADATION AND FIRST DERIVATIVE MASS LOSS CURVES OF THREE SAMPLES OF SPONGE GOURD FIBER IN N_2

In general, the peach palm fiber samples showed greater variation regarding thermal degradation. The degradation of the papaya tree and sponge gourd fibers was similar. The degradation of cellulose in the three fiber types occurred between 336 and 381°C, similar to the values reported in the literature of 240-350°C [5]. The decomposition reactions of cellulose usually occur by the cleavage of glycosidic, C-H, C-O and C-C bonds, as well as dehydration, decarboxylation and decarbonilation. The formation of water from cellulose occurs at several reactions involving its degradation. The most abundant product from the degradation of cellulose is levoglucosan, which is carbonized at around 600°C, releasing water [27].

3.5 Infrared spectrometry

Fig. 8 shows the infrared spectra of the peach palm tree, papaya tree and sponge gourd fibers. The bands shown indicate absorption of the groups that are characteristic of their constituents: lignin, hemicellulose and cellulose. The bands show the presence of alkenes, aromatic groups and functional groups like esters, ketones and alcohol.

The O-H bond stretching absorption occurs in the region of 3342-3364cm^{-1}. In the 1034–1029cm^{-1} region, the absorption can be attributed mainly to carbohydrates (cellulose and lignin), including the stretching of the C–O–C and C–O bonds (primary and secondary hydroxyl groups). The bands in the 1720-1745cm^{-1} region can be attributed to the non-conjugated C-O bond (vibration of aliphatic carboxylic acids and ketones, mainly due to the groups present in hemicellulose). The bands at 1594cm^{-1} can be attributed to the carbonyl group present in lignin. The presence of moisture might have contributed to the deformation bands of the water molecules near 1650cm^{-1}and also to the intensity of the broad band of the OH group in the region near 3400cm^{-1}. The C=C stretching absorptions, generically called skeletal vibrations of the aromatic ring of lignin appear in the 1500-1600cm^{-1} region, and stretching band of the symmetric and asymmetric C-H bond is in the region of 2887- 2904cm^{-1}. The spectrum is similar to those of other fibers found in the literature [5, 6, 28].

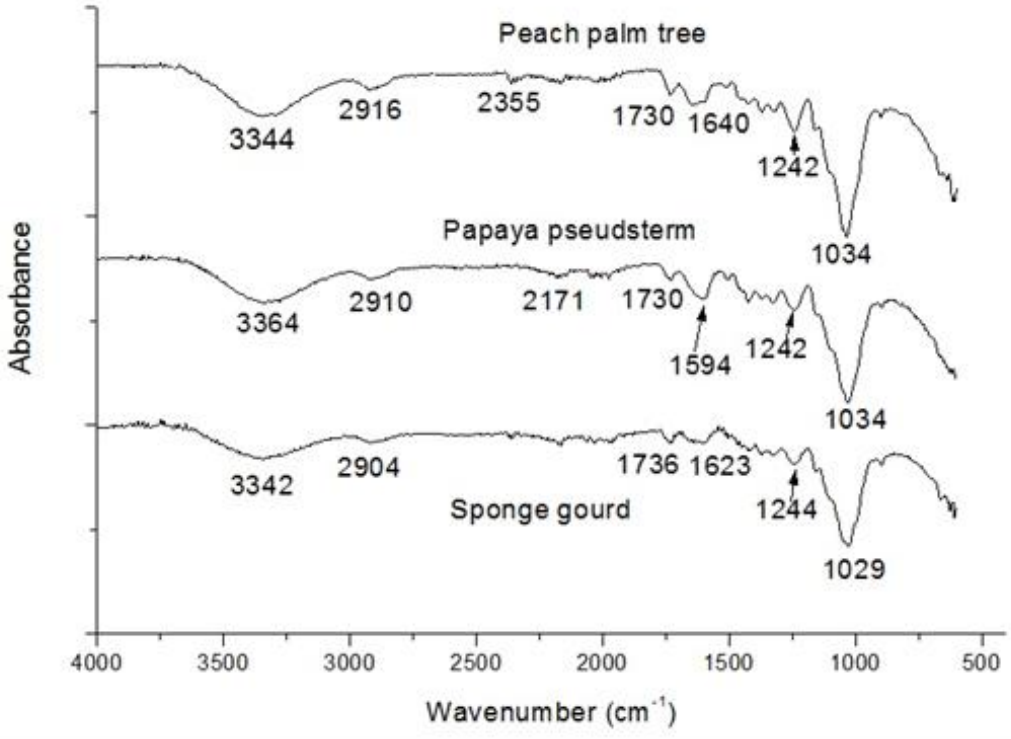

FIGURE 8: FTIR SPECTRA OF PEACH PALM TREE, PAPAYA TREE AND SPONGE GOURD FIBERS

3.6 X-ray diffraction

The diffractograms of the three fibers are shown in Fig. 9. In a lignocellulosic material, cellulose is considered the only component responsible for the crystalline contribution, whereas hemicellulose and lignin are the amorphous parts, although cellulose is composed of both crystalline and amorphous parts. Four crystalline peaks of the crystal polymorph I of cellulose (101, 10i, 002 and 040) was used to calculate crystallinity index [15,29]. As expected, the crystallinity index (CI) should be lower than the α-cellulose content in the lignocellulosic material as shown at Table 5. CI of α-cellulose was calculated by taking into account its content in the composition of each fiber studied by deconvolution method.

TABLE 5
CRYSTALLINITY INDEX (CI) OF THE PEACH PALM TREE, PAPAYA TREE AND SPONGE GOURD FIBERS

Fiber types	α-cellulose content (wt%)	Lignocellulosic Crystallinity index (%)	α-cellulose Crystallinity index (%)
Peach palm	55.5 ± 0.7	49.6	89
Papaya	62.0 ± 2.8	38.4	61
Sponge gourd	63. 4 ± 1.0	49.2	78

Crystallinity index varies significantly depending on the method chosen for measurement. French and Citrón [30] used the method developed by Segal et al. [31] with different peak widths at half maximum height (pwhm) for cellulose Iβ and II. The values obtained for crystallinity indexes were 99 and 47% in different pwhm. The crystallinity index of α-cellulose found in this work for the peach palm fibers, papaya and sponge gourd were comparable to those obtained by French and citron [30].

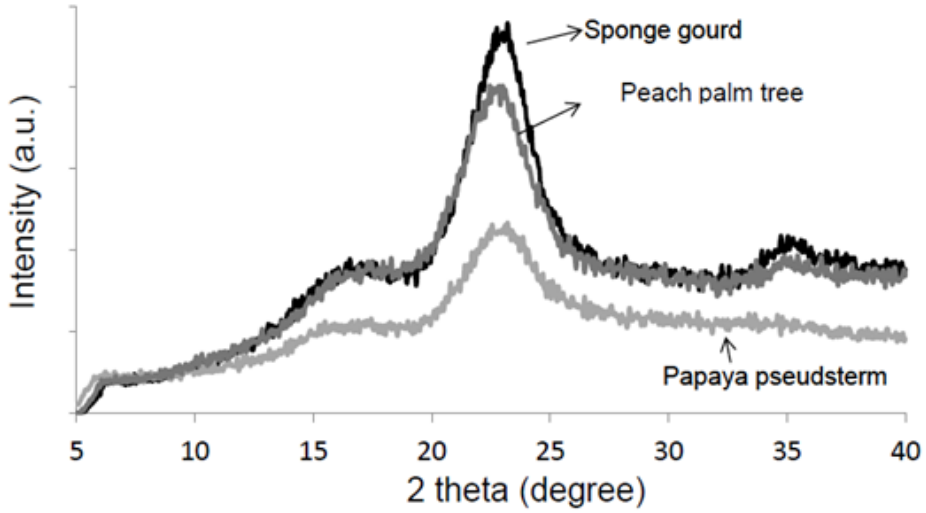

FIGURE 9: X-RAY DIFFRATOGRAMS OF THE PEACH PALM TREE, PAPAYA TREE AND SPONGE GOURD FIBERS

3.7 Tensile strength

The mechanical resistance was tested in four groups of fiber specimens. The fibers in each group were obtained on different dates, to assure having samples representative of the heterogeneity of natural products [6]. The tensile strength results of the four groups of peach palm fibers and the statistical treatment of the data are shown in Table 6 and Figs. 10 and 11. It can be seen that the tensile strength results are similar among the four groups.

The statistical treatment of the data from the four groups (Fig. 11) produced values slightly higher than those found in the literature for coconut shell fibers (140-225 MPa) [32], suggesting the peach palm tree fibers are slightly more resistant.

TABLE 6
TENSILE STRENGTH OF THE SAMPLE GROUPS OF PEACH PALM FIBERS

Statistical summary	1	2	3	4
Number of data	23	24	25	24
Mean, MPa	241	227	278	226
Standard deviation, MPa	76	70	82	79
Coefficient of variation, %	31.4%	30.8%	29.5%	34.7%

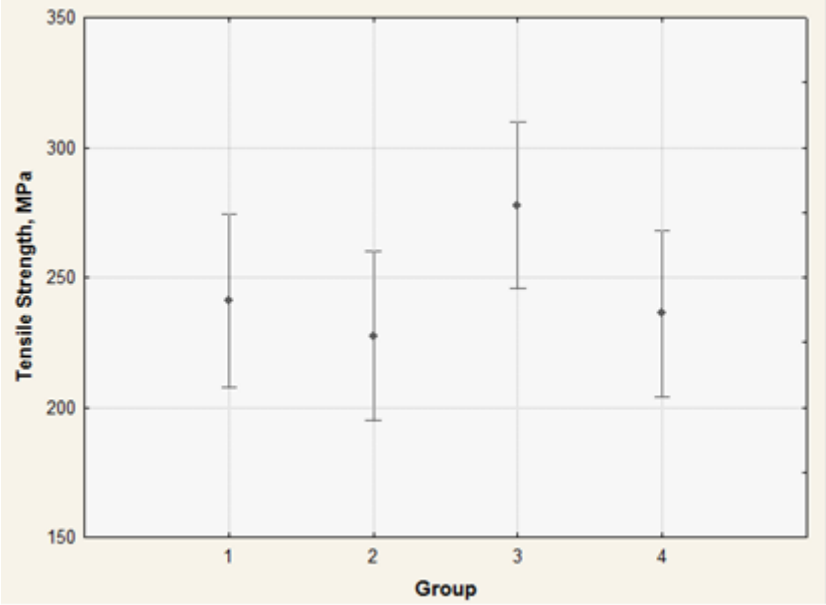

FIGURE 10: COMPARISON OF THE TENSILE STRENGTH OF THE GROUPS OF PEACH PALM FIBERS

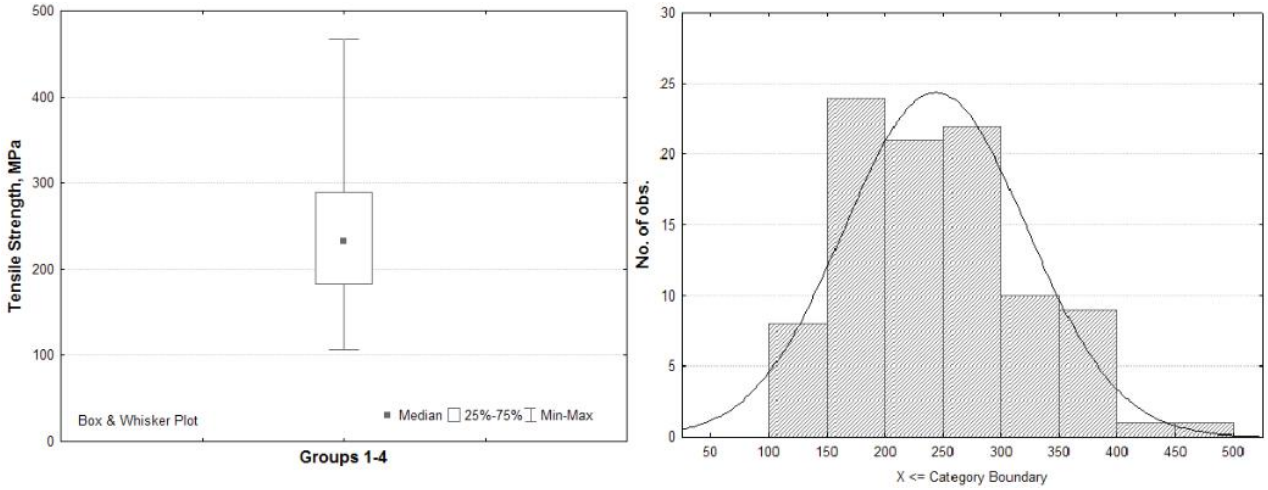

FIGURE 11: BOX AND WHISKER PLOT AND HISTOGRAM OF GROUPS 1 TO 4 OF PEACH PALM FIBERS

The mean tensile strength of the peach palm fibers is 240±15 MPa. The high dispersion of the results is due the natural irregularity of plant fibers. The tensile strength of the sponge gourd and papaya tree fibers could not be measured because their short length and great fragility, respectively.

3.8 Morphology

Figs. 12 (a, b, c, d, e and f) show the micrographs of the fibers. Each lignocellulosic fiber has a complex layered structure, composed of a thin primary wall, initially deposited during growth of the cells, surrounding a secondary wall [3]. In the micrographs showing longitudinal sections, it is possible to observe this primary layer, which is similar for papaya tree and peach palm fibers. The longitudinal sections are smoother, and the papaya tree has more surface irregularities. The cross sections reveal the cellular structure. There is greater similarity of the longitudinal sections of the papaya tree and peach palm fibers, both having a higher quantity of channels. According to Silva et al [3], the secondary wall is formed by three layers, where the middle layer determines the fiber's mechanical properties and consists of helicoidal microfibrils formed by long cellulose chains and organized along the fiber. These microfibrils result from the packing of from 30 to 100 extended cellulose chains. The cell structures of the sponge gourd and papaya tree fibers are more compact than of the peach palm fiber (micrographs of cross section). The latter fiber has large and well-defined channels, while the others do not, although this might have resulted from the difficulty of visualizing the surface due to the scalpel cut**.**

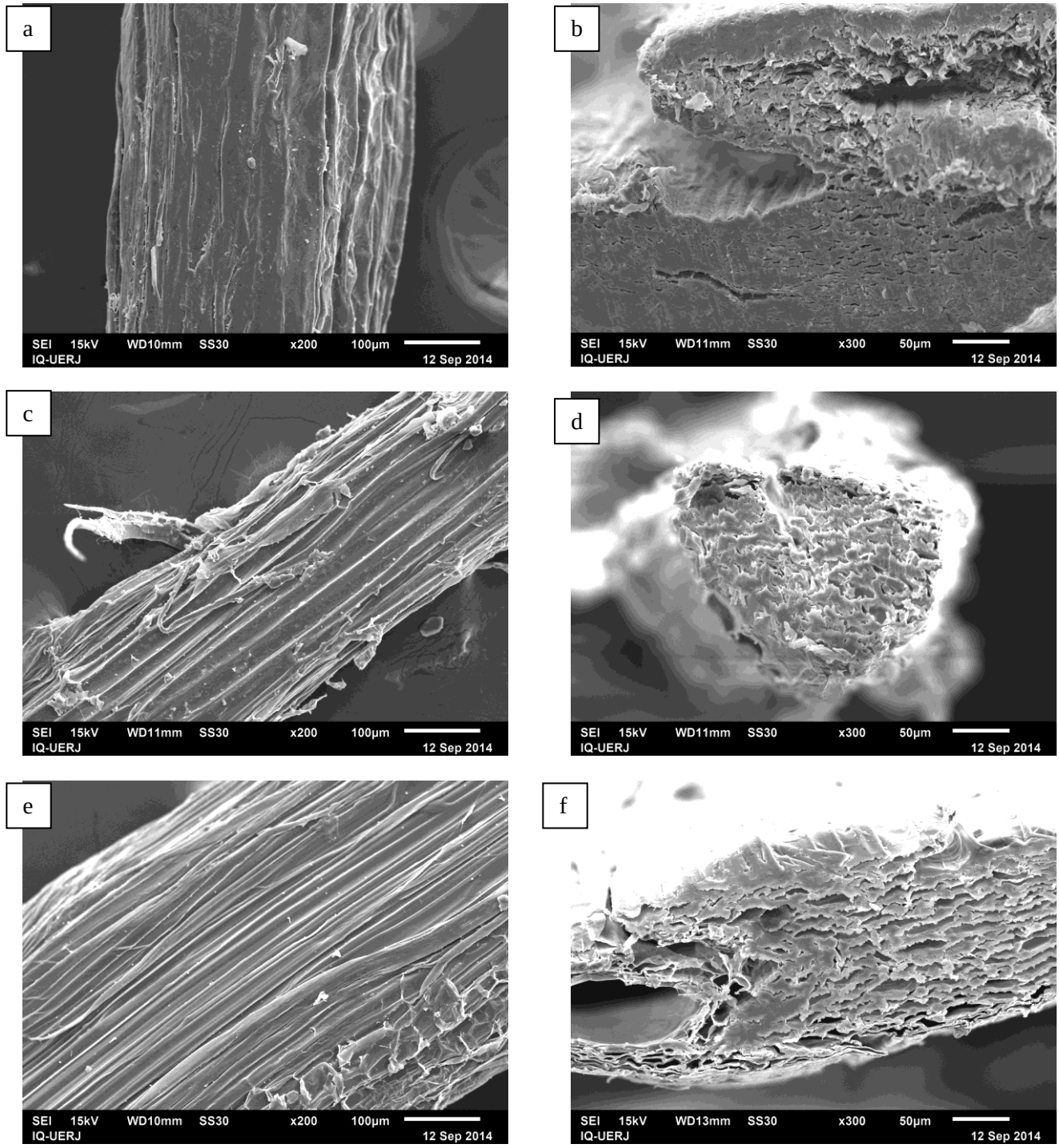

FIGURE 12: MICROGRAPHS OF THE FIBERS: A) LONGITUDINAL SECTION OF A SPONGE GOURD FIBER; B) CROSS SECTION OF A SPONGE GOURD FIBER; C) LONGITUDINAL SECTION OF A PAPAYA TREE FIBER; D) CROSS SECTION OF A PAPAYA TREE FIBER; E) LONGITUDINAL SECTION OF A PEACH PALM FIBER; AND F) CROSS SECTION OF A PEACH PALM FIBER.

IV. CONCLUSION

The characteristics of the agro-industrial waste fibers analyzed here, from peach palm trees, papaya trees and sponge gourds, are comparable to those of other studies of natural fibers from waste materials (coconut shells, sponge gourds, sugarcane bagasse and banana plants), even though the materials come from different places. Knowledge of the structure and compositions of these three waste materials will provide data for comparison in future studies, in particular for peach palm and papaya tree, for which this is the first published report. The sponge gourd fiber presented higher hemicellulose and

cellulose concentrations than the othe two fibers so probably the presence of hemicellulose and cellulose could be directly related to the absorption of water. The sponge gourd fiber had the highest concentrations of holocellulose, and consequently of α-cellulose and hemicellulose, and the lowest levels of soluble extractives and ash. The papaya tree and peach palm fibers had moisture, extractives and ash values very near each other. These waste fibers can be used effectively to reinforce polymers, while reducing the environmental impacts caused by inadequate disposal or burning.

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