CHEMICAL, PHYSICAL, MECHANICAL, THERMAL AND MORPHOLOGICAL CHARACTERIZATION OF CORN HUSK RESIDUE

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Received May 7, 2014

This work describes the chemical composition, physical characteristics, thermal resistance, mechanical properties, crystallinity index and morphology of corn husk residue collected from disposal areas of small street markets. Each sample was cleaned manually, sun dried, cleaned manually once more, chopped into small pieces, ground in a hammer mill and then classified by a 35 mesh Tyler sieve. The results are discussed and also compared to the characteristics of other lignocellulosic biomass used to produce biofuels and composites. According to the results, corn husk has low lignin content and similar amounts of hemicellulose and α-cellulose to those of the other fibers considered. In addition, the corn husk biomass showed better tensile property than piassava and coir and similar maximum safety temperature to that of caroa and olive husks. The crystallinity index of corn husk was 21-26% and surface morphology showed the presence of a large number of microfibrils in its structure.

Keywords: corn husk fiber, lignocellulose, residue, characterization waste

INTRODUCTION

Nowadays, it is not enough for products to meet technical and economical requirements; it is also important that they have sustainable characteristics. This necessity motivates academic and industrial researches to develop innovative solutions, which can be noted from the large number of technical papers investigating the use of agro-industrial residues as raw materials for producing energy, biofuels, composites and nanomaterials.[1-5]

Specifically, lignocellulosic biomass can be transformed into bioethanol via biochemical or thermochemical conversion. These processes involve the degradation of biomass into fragments of hemicellulose and cellulose, which are hydrolyzed into sugars that are converted into bioethanol, subsequently followed by a purification process.[2] Furthermore, the fractioning of lignocellulosic biomass can produce, in addition to the cellulose and hemicellulose streams, a lignin stream that can be used to produce low molecular weight chemicals with high added value, such as benzene, phenol, methanol, acetic acid and dimethyl sulfoxide.[6]

A further example found in the technical literature about the uses of lignocellulosic feedstock is the production of composites, regarded as promising materials that can replace petrochemical based composites.[7]

Agroindustry is an economic sector that generates immense amounts of lignocellulosic residues. This renewable biomass usually comes from non-edible plants or parts of them. It is mainly composed of cellulose, hemicelluloses, lignin and minor contents of proteins, lipids and ash. Among the many crop residues are corn and rice husks, wheat straw and sugarcane bagasse.[2]

Cellulose is the major component of the lignocellulosic biomass. It is a semicrystalline biopolymer of glucose molecules with β(1 – 4)

glycosidic linkage naturally organized as microfribrils, and has strong mechanical properties. In general, the mechanical properties of a natural fiber are influenced by its chemical composition, internal fiber structure, microfibril angle, cell dimensions and the presence of defects. The main function of cellulose in the plant cell is structural.[2,6,8]

Hemicellulose is an amorphous biopolymer with low molecular weight. Its backbone chain is primarily composed of xylan $\beta(1 \rightarrow 4)$-linkages that include D-xylose and L-arabinose. Hemicellulose binds bundles of cellulose fibrils to form microfibrils and is also crosslinked with lignin, creating a complex network of bonds that provide structural strength and prevent microbial degradation of the plant. The portion of cellulose and hemicelluloses in the lignocellulosic material is named holocellulose.[2,6,8]

Lignin is a macromolecule that is composed of aliphatic and aromatic constituents. Its structure is very complex and consists of a three-dimensional randomized network. The main functions of lignin in the plant are to act as a biological barrier and a binder to retain hemicelluloses and celluloses in order to shape the cell walls.[6]

Different properties can be found in lignocellulosic materials, depending on the lignin, hemicellulose and α-cellulose proportions. Knowledge of the composition and properties of lignocellulosic biomass is obligatory for the development of processes and/or products that use biomass.[8-9] For example, in production of bioethanol and biodiesel, the biomass needs to be pretreated to make it more suitable for subsequent cellulose hydrolysis. The best pretreatment strategy and conditions depend strongly on the type of lignocelluloses. Alkaline hydrolysis, which is a slow process, is more attractive for biomass feedstock with lower lignin content, but also introduces a negative effect on the bioethanol fermentative processes. In addition, the ash present in lignocellulosic biomass makes the heat generation process more difficult.[2-3]

The ability of lignocellulosic residues to absorb moisture should be considered when composites are developed, since an increase in the moisture content of the lignocellulosic residue decreases the electrical resistivity and also affects the dimensional stability of the composites. When the purpose is to obtain lightweight composites, lignocellulosic biomass with lower density can be used as filler. Lignocellulosic fibers do not show a good relationship between crystallinity and strength, as observed in pure cellulose fibers. The presence of substantial amounts of non-cellulosic components, mainly lignin, which contributes to the strength of fibers and the variations in the dimensions of unit cells, is the major reason for the absence of this relationship. Therefore, the composition and morphology of lignocellulosic biomass must be considered to choose the best lignocellulosic type. Additionally, the composite processing parameters depend on the lignocellulosic thermal behavior.[7,10]

Therefore, this paper describes the chemical composition, physical characteristics, thermal resistance, mechanical properties, crystallinity index and morphology of corn husk residue. Samples of corn husk were collected from five street market disposal areas from different places in Rio de Janeiro state, Brazil. The properties are also compared to other types of lignocellulosic biomass used for producing biofuels and composites.

EXPERIMANTAL

Corn husk residue samples

Five corn husk samples were collected from small street markets in four districts of Rio de Janeiro city and one in the neighboring city of Duque de Caxias, in Rio de Janeiro state, Brazil. Table 1 shows the sample codification and provides information about the places the samples were collected from.

Table 1
Codification of sample and respective collection place

Corn husk	Street market location
Sample # 1	Rio das Pedras, Jacarepaguá district, Rio de Janeiro city
Sample # 2	Nova Campina district, Duque de Caxias city
Sample # 3	Freguesia, Jacarepaguá district, Rio de Janeiro city
Sample # 4	Tijuca district, Rio de Janeiro city
Sample # 5	Jardim América district, Rio de Janeiro city

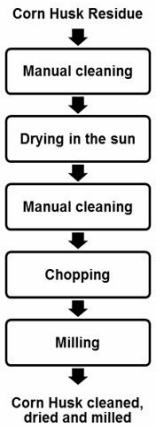

Figure 1: Laboratory procedure applied to corn husk samples

The samples were cleaned manually in order to remove foreign materials. Then they were dried by exposure to the sun for four days. After this period, the samples were again cleaned manually and chopped into small pieces. During this step, individual fibers were also randomly removed from each corn husk sample to perform tensile testing and evaluate their morphology. Finally, each corn husk sample was milled using a hammer mill and classified by a Tyler sieve (35 mesh), to make each sample homogenous. Figure 1 describes this procedure.

Characterization of corn husk agro-residue samples

Moisture content

The moisture content was measured based on the ASTM D1348-94 standard (Reapproved 2008). This procedure was performed in triplicate.

Density

The density was determined based on the ASTM D854-10 standard using a glass pycnometer and ethanol (puriss. p.a.) as liquid test. This procedure was performed in triplicate.

Chemical composition

Prior to determining the chemical composition, all the corn husk samples were dried in an oven with air circulation at 60 ^{o}C for 24 hours in order to eliminate the moisture content. All procedures were performed in triplicate using the following standards.

The amount of inorganic material present in the biomass, defined as ash content, was measured based on the standard method of Technical Association of Pulp and Paper Industry (TAPPI) T413-om-11(Ash in wood, pulp, paper and paperboard: combustion at 900 ºC). Extractive and water soluble components were determined based on the standards TAPPI T204-cm-07 (Solvent extractives of wood and pulp) and T207-cm-08 (Water solubility of wood and pulp). Holocellulose, which is composed of hemicellulose and α-cellulose, was measured using the acid chlorite method.[11] The α-cellulose content was measured based on the TAPPI T 203 cm-09 (Alpha-, beta-, and gamma-cellulose in pulp) and the content of hemicellulose was calculated by subtracting the amount of α-cellulose from the total amount of holocellulose. The lignin content was estimated by using equation (1).

Lignin Content (%) = 100% - (% extractive + % ash + % holocellulose) (1)

Scanning electron microscopy (SEM)

The morphology of corn husk fiber was investigated by using a JEOL JSM-6510LV scanning electron microscope with electron bean acceleration of 10kV in vacuum mode. For sample preparation, the fibers were cut into longitudinal and transversal sections and were affixed on metal support stubs using carbon tape.

Thermogravimetric analysis

The thermal stability was carried out in a Q500 series thermogravimetric analyzer (TA Instruments), using sample amounts of about 20 mg, scanning temperature from 25 to 860 ^{o}C, heating rate of 20 ^{o}C/min under nitrogen atmosphere.

X-ray diffraction (XRD) analysis

X-ray diffraction patterns of corn husk samples were recorded with a Rigadu Miniflex diffractometer at room temperature from 5 to 40^{o}, using CuKα irradiation (1.54 Å) at 40 kV and 30 mA. Different approaches have been used to measure the crystallinity index. As a consequence, different results were observed even if the sample was the same. In this study, the crystallinity index was calculated by the deconvolution method, which separates amorphous and crystalline contributions from the diffraction spectrum. This procedure was performed by using a curve-fitting process (Fityk 0.9.8 software). The peak function used was Gaussian and the crystallinity index was calculated by dividing the crystalline peaks' area by the total scattering area.

Tensile properties

The tensile properties of the corn husk fibers were evaluated based on the ASTM C1557-03 standard (2013) using an Oswaldo Filizola AME-5kN universal testing machine with 500 N load cell. The Dynaview Standard/Pro version 2.6.7 software was used for data acquisition. The gauge length of the tensile specimen was 30 mm and the tensile speed was 3 mm/min. The fiber diameter was determined from five measurements along fiber length using a micrometer (Mitutoyo, ±0.001 mm). The shape of cross-section was considered circular. The minimum number of specimens for each tested corn husk sample was 20.

Data analysis

Data analysis was performed using the Statistica 8 software (StatSoft) with 95% level of confidence and assuming normal distribution.

RESULTS AND DISCUSSION

It is well known that the properties of lignocellulosic materials can be influenced by many factors, such as type, variety, climate, harvesting method, plant maturity, extraction process, as well as the experimental procedure conditions used for the analysis. Since these factors introduce and increase variability in the results, it is advisable to estimate the confidence interval for the mean, instead of using only the test average, because this statistical parameter provides a range that contains the most probable true mean value for the property. Table 2 shows the mean intervals of density, moisture content and chemical composition of corn husk samples determined in this study.

Density

Regarding density, the interval for the mean obtained in this study was in accordance with the corn husk value reported in the literature (1270 kg/m^3).[12] It is higher than the nominal values of curauá (1000 kg/m^3), palm (1030 kg/m^3) and coconut (1150 kg/m^3), but lower than those of banana (1350 kg/m^3) and sisal (1450 kg/m^3).[13] The low density values of lignocellulosic biomass make it an attractive raw material for production of lightweight composites when compared to the synthetic fibers, such as fiberglass (2500 kg/m^3).[14]

Table 2
Properties of corn husk residue samples

Property	Sample					Mean	Confidence limits for mean (95%)
	#1	#2	#3	#4	#5		
Density, kg/m^3	1160±40	1250±40	1270±40	1310±40	1280±40	1254	1180-1320
Moisture content, wt%	8.1±0.1	8.3±0.1	8.6±0.1	7.4±0.1	8.2±0.1	8.1	7.6-8.7
Ash content, wt%	6.4	3.5	5.8	6.0	3.5	5.0	3.3-6.8
Extractive and water soluble components, wt%	10.2±0.8	11.1±0.8	14.0±0.8	15.4±0.8	18.9±0.8	13.9	9.6-18.3
Holocellulose, wt%	78±1	69±1	73±1	70±1	75±1	73.1	68.4-77.8
Hemicellulose, wt%	39	33	40	37	40	37.5	34.0-41.0
α-Cellulose, wt%	40	36	33	33	33	35.3	31.3-39.3
Lignin, wt%	5	16	7	9	2	7.9	1.5-14.3

Table 3
Composition of corn husk residue samples and other lignocellulosic materials (wt%)

Lignocellulosic materials	Ash, wt%	Hemicellulose, wt%	α-Cellulose, wt%	Lignin, wt%
Corn husk residue samples	3-7	34-41	31-39	2-14
Corn stover[10]	4-7	28	38-40	7-21
Curauá[16]	-	30	63	5
Banana[10,17]	5	6-8	60-65	5-10
Sugarcane bagasse[17]	1-4	27-32	32-55	19-25

Moisture content

The equilibrium moisture content of corn husk residue is also in accordance with the value reported in the literature (9 wt%) and with those for other lignocellulosic materials, such as curauá (9.1 wt%), bamboo (9.16 and 10.16 wt%), coconut (11.36 wt%), banana (10.71 wt%) and sisal (9.76 wt%).[10,13] The moisture content of lignocellulosic biomass is an important property for composites development and for thermochemical conversion. For example, in polymer composites, moisture content can reduce the adhesion between fibers and polymeric matrix. Furthermore, high moisture content increases the costs of thermochemical conversion.

Chemical composition

As to chemical composition, the results showed that corn husk is a lignocellulosic biomass with low content of lignin and similar amounts of hemicellulose and α-celullose. Also, considerably high levels of ash content and extractives, as well as of water soluble materials, were observed. Comparing the mean intervals for ash, α-cellulose, hemicellulose and lignin of corn husk to those of other lignocellulosic materials, as shown in Table 3, the chemical composition obtained in this study is similar to the values reported in the technical literature for corn stover. Regarding ash content, it can retard the enzymatic hydrolysis efficiency.[15] Consequently, the high value of ash verified for the corn husk samples indicates that this biomass should be submitted to pretreatment so as to reduce its ash to an acceptable level if used, for instance, as raw material for producing biofuels.

X-ray diffraction analysis

Crystallinity index is a term used to describe the ordered structure of a material. In biomass, cellulose is considered the only component responsible for the crystalline contribution, whereas hemicellulose and lignin are amorphous parts. However, cellulose has a portion of imperfect crystallites that also contribute to the amorphous content in lignocellulosic biomass. Usually, four crystalline peaks of the crystal polymorph I of cellulose (101, 10i, 002 and 040) are used to calculate the crystallinity index.[18-19] However, as shown in the XRD diffraction spectra of the corn husk samples (Figure 2), these peaks are not well resolved, and only one peak at $2\theta = 22.6^{o}$ is easily observed, which corresponds to the (002) crystallographic plane. Despite the low resolution of the XRD diffraction spectra, the crystallinity index of corn husk could be determined, resulting in a mean interval of 21-26%. As expected, the interval of the crystallinity index was lower than the confidence intervals of α-cellulose content in the lignocellulosic biomass, as shown in Table 2. By dividing the crystallinity index by the α-cellulose content, as suggested by Xu, Shi and Wang,[19] the mean of α-cellulose crystallinity (a percentage of the crystalline component in cellulose) was found to be 67%.

Thermogravimetric analysis

The thermal (TGA) and differential (DTG) thermogravimetric curves of the five corn husk samples are shown in Figure 3, where it is possible to observe four degradation processes. Table 4 shows the estimated means of the weight loss and the temperature of the maximum decomposition rate for each degradation process.

The first peak corresponds to the vaporization and removal of bound water in the samples, which occurs for all lignocellulosic fibers. The second and third peaks can be mainly related to the degradation of small molecules (sugar, protein, wax etc.) and depolymerization of hemicellulose. Finally, the fourth peak is related principally to the cellulose thermal degradation. About lignin, it is known that its decomposition happens slowly over a broad temperature range (200-500 ^{o}C). Consequently, a portion of the lignin starts to degrade in the same step as hemicellulose.

Additionally, other important characteristics can be determined from TGA and DTG curves, such as the initial decomposition temperature and the temperature of maximum decomposition rate. Figure 3 shows that corn husk presents reasonable thermal stability.

The interval estimated for the initial decomposition temperature of corn husk samples was 187-197 ^{o}C. This means that 187 ^{o}C can be considered the maximum safe temperature for using this corn husk without degradation. In comparison with other lignocellulosic biomass materials presented in the literature, corn husk has lower thermal resistance than piassaba (225 ^{o}C), sisal (302 ^{o}C) and luffa cylindrica (250 ^{o}C); but similar resistance to caroa (190 ^{o}C) and olive (201 ^{o}C) and higher than that of buriti palm (150 ^{o}C).[21-22]

The interval estimated for the initial decomposition temperature obtained in this study suggests that the use of corn husk without any previous treatment as reinforcement fiber for polymer composite production can be restricted, because most polymer composites are processed at 180-200 °C.

Tensile properties

Tensile properties are useful to ascertain whether a fiber can be a candidate for being used as reinforcement in polymer or ceramic composites. A stress-strain curve of one corn husk fiber specimen (Sample #5) is shown in Figure 4. In the early portion of the curve, the corn husk fiber shows linear proportionality of stress and strain. As the strain increases, a deviation from this linear proportionality appears and a yield region can be observed. This curve pattern suggests that corn husk fibers can have a slightly ductile behavior, although presenting brittle rupture behavior.

Table 5 shows the statistics for the stress at rupture of corn husk samples in comparison with the data for sisal, piassava, coir, jute and curauá.[20]

As can be noted, corn husk fibers show higher stress at rupture than piassava and coir, but the results are significantly lower than those for sisal and curauá fibers. The difference in the tensile behavior of lignocellulosic fibers can be caused by the cellulose content, crystallinity degree, maturity and also the part of the plant that the fibers are taken from. In addition, there is a higher coefficient of variation for all fibers. Unlike synthetic fibers, which are produced with precise dimensional characteristics, natural fibers show non-uniform diameters, irregular cross-sections and superficial defects, which are not easily perceived. These facts contribute to the high standard deviation values of this test.

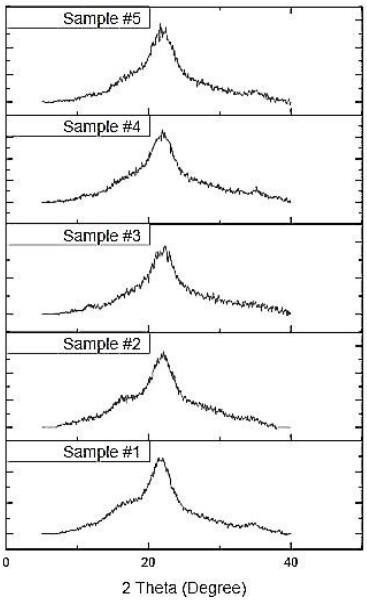

Figure 2: XRD diffraction spectra of corn husk samples

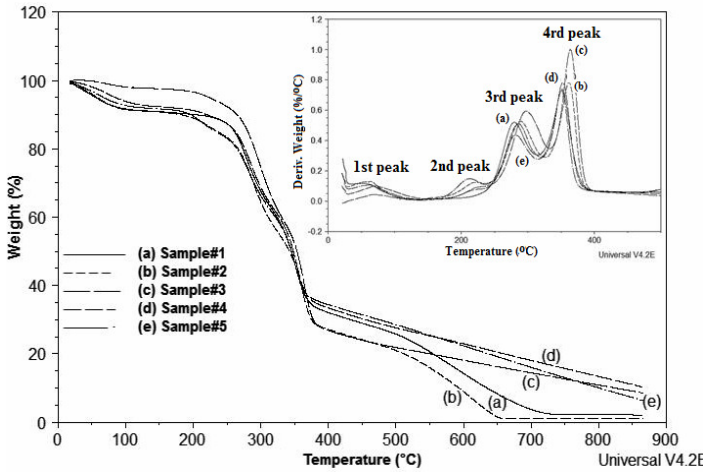

Figure 3: TGA and DTG curves of corn husk samples

Table 4
Thermal properties of corn husk samples obtained by TGA/DTG

TGA/DTG analysis	Weight loss (%)	Temperature at maximum rate of decomposition (°C)
1st peak	3-10	54-73
2nd peak	2-8	211-225
3rd peak	23-34	276-295
4rd peak	30-38	348-364

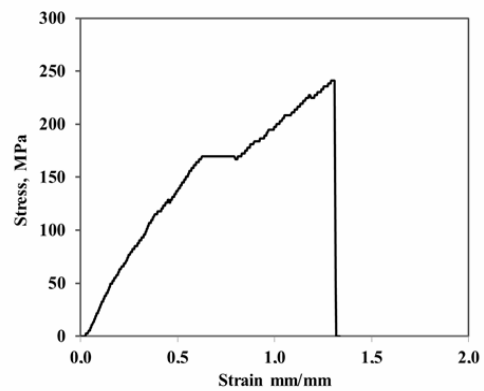

Figure 4: Stress-strain curve of a test specimen of the corn husk (Sample #5)

Table 5
Comparison of tensile properties of lignocellulosic fibers

Lignocellulosic fiber	Mean (MPa)	Standard deviation (MPa)	Coefficient of variation (%)
Corn husk - Sample #1	256	101	39%
Corn husk - Sample #2	201	53	26%
Corn husk - Sample #3	201	60	30%
Corn husk - Sample #4	180	54	30%
Corn husk - Sample #5	249	47	19%
Sisal[20]	484	135	28%
Piassaba[20]	131	36	27%
Coir[20]	90	35	39%
Jute[20]	249	89	36%
Curauá[20]	543	260	48%

Scanning electron microscopy

The morphology of corn husk fiber was analyzed by SEM. According to Figure 5, which shows a longitudinal section of corn husk fibers, it is possible to see three ribs on the adaxial surface (white asterisks) and a large number of microfibrils randomly distributed (white arrows).

The opposite longitudinal corn husk view is shown in Figure 6. In this image, it is still possible to see part of the adaxial surface with some visible microfibrils (white arrows), but principally the abaxial surface (white circle) and some stomata (white arrowhead).

Figure 7 shows the transversal section of corn husk fibers, where it is possible to see the adaxial surface (white star) with the microfribrils (white arrows) and two ribs (white asterisks).

The SEM images confirm that corn husk fiber has an irregular cross-section, non-uniform surface, a significant number of short microfibrils, lumens (vessel structures) and some impurities on the surface, which are typical of raw natural fibers. The amount and the size of lumens, which are correlated to the voids in the structure, affect the fiber tensile behavior. The more and the bigger the lumens are, the lower the fiber's tensile resistance, which is not desirable for use in composites. Furthermore, the reinforcement potential of a lignocellulosic fiber in a composite is related, among other factors, to its ability to form a percolated network in a polymer matrix, which depends on the fiber aspect ratio and also on the fiber and polymer interaction. The higher the aspect ratio is, the greater the fiber's reinforcement capability will be. Thus, thinner fibers generally produce stronger and stiffer composites.[23] As to impurities, they can disturb the fiber and polymer adhesion. Therefore, to improve the interface adhesion, it is advisable that corn husk fibers be treated and chemically modified before being used in composites.

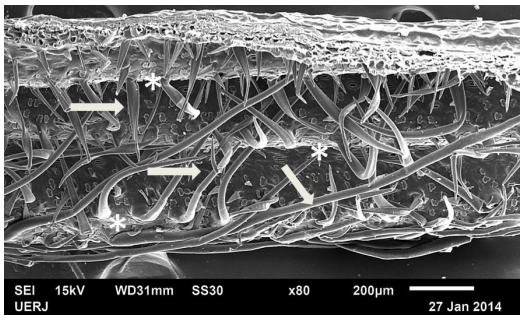

Figure 5: Adaxial SEM morphology of longitudinally cut corn husk fiber (x80 magnification)

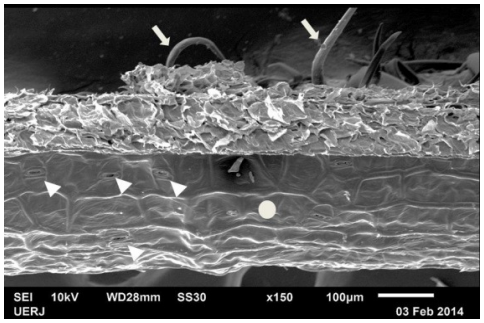

Figure 6: Abaxial SEM morphology of longitudinally cut corn husk fiber (x150 magnification)

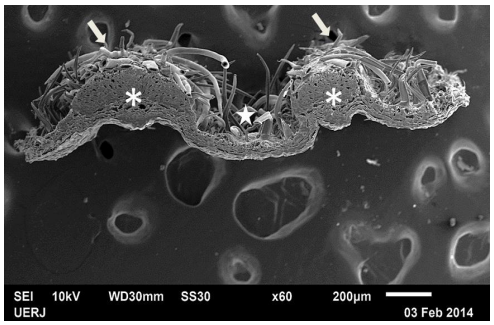

Figure 7: SEM morphology of transversely cut corn husk fiber (x60 magnification)

CONCLUSION

Five corn husk samples collected from disposal areas of small street markets were characterized. The moisture content of corn husk, which is an important property in making composites and for thermochemical conversion, was similar to those of curauá, bamboo, coconut, banana and sisal. Density was also in accordance with the corn husk value reported in the literature.

The chemical composition of corn husk comprised 34-41% hemicellulose, 31-39% cellulose, 2-14% lignin, 3-7% ash, 10-18% extractives and water soluble components. This composition was similar to the values reported in the literature for corn stover.

In addition, the corn husk crystallinity was 21-26% and the maximum safety temperature was 187 ^{o}C, which can restrict its use in some composite applications. On the other hand, the stress-strain curve of the corn husk samples indicated that the fibers had a slightly ductile behavior and the tensile strength results were similar to those of piassava and coir fibers. The longitudinal and transverse surface morphology of corn husk fiber showed the presence of a large number of microfibrils on the adaxial surface.

ACKNOWLEDGEMENTS: We thank the merchants at the street markets for donating the corn husk samples, Prof. Eloisa Mano (Instituto de Macromoleculas) for allowing the use of the Oswasdo Filizola machine and Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPERJ) for financial support.

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