Guaruman fiber: another possible reinforcement in composites

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\textbf{ARTICLE INFO}

Article history:
Received 2 May 2019
Accepted 1 November 2019
Available online 3 December 2019

Keywords:
Guaruman fiber
Natural lignocellulosic fiber
X-ray diffraction
Density
Morphology characterization

\textbf{ABSTRACT}

Natural lignocellulosic fibers (NLFs) have been investigated, especially in the past decades, as promising reinforcement in composite materials for engineering applications. The interest regarding the use of NLFs is associated with advantages such as low density and high mechanical strength as well as low toxicity and cost-effectiveness. In addition, NLFs are also considered as environmentally friendly materials. Indeed, they are biodegradable and obtained from renewable resources. In this paper, a relatively unknown Amazonian NFL, the guaruman fiber, was for the first time physically characterized by X-ray diffraction (XRD). The density of the fibers was measured and statistically analyzed by the Weibull distribution. It was verified that the guaruman fiber presents one of the lowest densities, 0.50–0.64 g/cm$^3$, for NLFs ever reported in the literature. Furthermore, it was disclosed for the first time the crystallinity index, 60–67\%, mechanical strength, 614 MPa, microfibril angle, 7.3–8.2\°, and cross-section morphology microstructure for the guaruman fiber.

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1. Introduction

Natural fibers are commonly classified by their origin. They can be related to animal, mineral or vegetable sources. Those from vegetable origin are known as natural lignocellulosic fibers (NLFs). Such fibers have brought attention due to their mechanical properties but also because of their low cost of production. Monteiro et al. [1] showed that many NLFs present specific mechanical properties comparable to synthetic ones, especially to glass fiber. As for their cost of production, Satyanarayana et al. [2] showed that in many cases such fibers are considered as residue of some industries and that a proper destination is mostly desired as a by-product. As such they are cost-effective as compared to any synthetic fiber.

NLFs exhibit a structure that can be compared to a natural composite material. They are basically constituted of two
different phases: a crystalline and an amorphous one [1–6]. The main crystalline phase is the cellulose microfibril, which can be seen as a reinforcement phase, while the lignin could be considered as the amorphous matrix. These two phases are organized and the amount of each phase results in the macroscopic properties exhibit by the NLFs. Thakur et al. [6] discussed how the type and degree of polymerization of the cellulose as well as the amount and microfibril angle affected the mechanical properties of the fibers.

NLFs are known to present a cell order composed of three distinct walls, with different microfibril angle (MFA) [6,7]. In the primary wall, the MFA are randomly oriented exhibiting several degrees of alignment. In the second wall, three layers are found. The first and the third ones, S1 and S3 respectively, exhibit transversely oriented microfibrils. On the other hand, in the second one (S2) the MFAs are axially oriented. Finally, the last wall is associated with the lumen channel [6]. In fact, the orientation of the microfibrils in the second layer S2 is the main responsible for the tensile strength of the fiber. Indeed, lower MFA results in higher tensile properties [8].

Among the numerous reported NLFs, that extracted from the Amazonian plant, locally known as guarumã, here spelled as “guaruman” for English facility, has been traditionally used in the north of Brazil to fabricate simple items, such as ropes, fabrics, nets and rugs. From private communication of local producer, it was indicated that the stalk of the guaruman plant is mechanically divided in longitudinal splints that are then manually separated with a stiletto into thinner fibers. Fig. 1 illustrates the guaruman plant (a) as well as the splints divided from the stalk (b) and final separated fibers (c, d).

Basic characteristics recently revealed that the guaruman fiber emerges as a promising NLF for reinforcement of polymer matrix composites [9]. Thus, the objective of this work was to investigate the guaruman fiber, which is still a scientifically unknown Amazonian fiber, in terms of its density, mechanical properties, cross-sectional aspects, microfibril angle and degree of crystallinity. These characteristics might be relevant for composite fabrication, which should be further investigated.
2. Materials and methods

The guaruman fiber was obtained from a local market in the state of Pará, Brazil. The fiber is extracted from the stalk of the plant, botanically named Ishinosiphon kornii. Following the chemical and morphological characterization [9], the density, mechanical properties, microfibril angle and degree of crystallinity are now evaluated and characterized for the guaruman fiber.

The density was preliminary evaluated by measuring the fiber cross-section dimensions and length. Each fiber was measured in five different positions and in two different angles, 0° and 90°. First, the fibers were dried in an air oven for 24 h at 80 °C. The mass of each fiber was then measured in an electronic (0.0001 g) precision scale model AG-200, Gehaka, Brazil. Standard evaluation, as per ASTM 3800 [10], of the fiber density was also performed by the Archimedes method [11,12], considering an ellipsoidal-shaped fiber cross-section with approximate $A_e$ area of

$$A_e = \frac{\pi ab}{4}$$

(1)

where $a$ and $b$ are the larger and smaller ellipse axes, respectively. Two hundred fibers were considered for this purpose.

The dispersion in the cross-section shapes, given by the average values of $a$ and $b$ for 200 guaruman fibers is shown in the histogram of Fig. 2 with percentage frequency related to 10 arbitrary intervals. Results of guaruman fiber densities will further be related to the corresponding cross-section $(a + b)/2$ average intervals in Fig. 2.

The density results for each interval in Fig. 2 were statistically evaluated using the Weibull Analysis (WA) software. This statistical analysis is based on the cumulative Weibull frequency distribution function ($F(x)$).

$$F(x) = \exp \left[ -\left( \frac{x}{\beta} \right)^{\gamma} \right]$$

(2)

where $x$ is the measured density, $\beta$ the Weibull modulus, also known as shape parameter associated with uniformity of data. Moreover, $\gamma$ is the scale parameter, with precision adjustment given by $R^2$. Eq. (2) can be modified to adjust a linear graph

$$\ln \left[ \ln \left( \frac{1}{F(x)} \right) \right] = \beta \ln x - (\beta \ln \gamma)$$

(3)

in which $\beta$ is a linear slope. A single slope is associated with a unimodal distribution of densities in the present work. A series of measured values of density ($x$) are taken experimentally. These values are input into WA software and a slope is plotted based in the aforementioned frequency distribution function. This provides important information and verifies if the measurements taken experimentally are in accordance to each other and does not deviate from a common value. The quality of these measurements can be verified by the $R^2$ parameter; close to 1, the more reliable the data obtained.

Scanning electron microscopy (SEM) was performed to disclose the cross-section shape of the fiber as well as to observe microfibrils. The procedure for this analysis consisted in the insertion of the guaruman fibers in liquid nitrogen for 25 min. Then the fibers were mechanically broken and the fractured surface was analyzed. Furthermore, microfibrils were also observed on the surface of the fiber. The SEM analysis was carried out in a Quanta FEG 250 with a Bruker detector, produced by Thermo Fisher Scientific.

X-Ray diffraction (XRD) analysis was performed on both XPert Pro MRD System equipment as well as D8 Discover XRD Bruker with Co Kα radiation (1.789 A) by PANalytical. The microfibril angle (MFA) was evaluated by a proposed method [7,25] based on the cellulose (002) peak. The crystallinity index (CrI) calculations followed the method described by Segal et al. [13]. It was used the maximum intensity or the area of the peaks (101) and (002) above the background of the diffractogram [10–12]. These peaks are associated with the amorphous and crystalline phases of the fibers. The crystallinity index is then calculated by:

$$\text{CrI} = \left( \frac{I_{002} - I_{am}}{I_{002}} \right) \times 100$$

(4)

For the preliminary tensile test of the guaruman fiber 3360 Instron equipment was used in accordance to the ASTM standard D-2101. The tests were carried out at room temperature and a constant deformation velocity of 1 mm/s was applied, this is equivalent to a strain rate of $10^{-2}$ s$^{-1}$. The procedure consisted in randomly selecting 10 fibers with average cross-section within each interval of the histogram shown in Fig. 2. The fiber gage length was 80 mm. Moreover, cardboard were used to avoid direct contact between the fiber and the grip as well as to prevent damaging the fiber due to slippage. The results were then statistically analyzed in terms of mean and standard deviation.

3. Results and discussion

The average cross-section dimensions frequency for the investigated guaruman fibers, shown in Fig. 2, reveals an almost normal distribution within the interval from 6 to 26 μm with
15.4 μm as mean value. For each interval in Fig. 2, the average density of about 20 fibers was measured and statistically analyzed by the Weibull method.

Density measurements for the two hundred investigated guaruman fibers with distinct cross-section area were performed by both mass/volume and the Archimedes technique. Table 1 presents the average values of guaruman fiber density for each interval in Fig. 2 of average cross-section dimensions. In this table, it should be noticed a tendency of higher density for thinner fibers in both techniques. Moreover, the density values obtained by the Archimedes technique, although superior in mean values, within corresponding standard deviations, are comparable to those obtained by mass/volume. In principle, this difference would be attributed to the intersection of the liquid medium, used by the Archimedes technique, with the fiber’s porosity. In either case, the guaruman density values are among the lowest reported for NFLs [1,2]. Indeed, the mean values in Table 1 for the mass/volume densities of 0.50 g/cm³ and for the Archimedes densities of 0.64 g/cm³ are significantly below those of most common NFLs applied as polymer composites reinforcement, such as jute, flax, cotton, pineapple, ramie and sisal [1].

Weibull statistical analysis was performed for the densities measured by both mass/volume and Archimedes techniques, corresponding to each interval in Fig. 2. Linear graphs, Eq. (3), for the guaruman fiber densities using both techniques disclosed unimodal distribution for all intervals. Table 2 presents the Weibull parameters provided by WA software associated with the shape parameter, β; scale parameter, θ; and precision adjustment, R². In this table, it is worth mentioning that the θ values follow the same tendency of the guaruman fiber average density of increasing values for decreasing cross-section dimensions shown in Table 1. Furthermore, R² falls between the experimentally acceptable 84–98% range of reliability. By contrast, relatively low values of θ indicate only a tolerable uniformity of data. This is expected for NFLs owing to natural defects and heterogeneous morphological aspects [14–18] to be further discussed regarding the guaruman microstructure.

SEM analyses reveal the morphologies of the cross-section and surface of the guaruman fiber. Fig. 3 shows the microstructure of fractured samples in liquid nitrogen. It was verified that the guaruman fiber has peculiar morphological aspects. The fiber transversal fracture, Fig. 3(a), is associated with an irregular shape tending to an ellipsoidal cross-section with highlighted contour. Fig. 3(b) and (c) display, with higher magnification, details of the guaruman fiber cross-section. In Fig. 3(b), relatively larger holes (left side), with a honeycomb configuration, correspond to the lumen where nutrients flow through the plant. The cylindrical-shaped elements next to the lumen (right side) in Fig. 3(b) and covering most of the cross-section, Fig. 3(c), are assigned to the cellulose-based microfibrils composing the fiber walls [6,7].

As for the guaruman fiber surface, Fig. 4 shows typical SEM images. With lower magnification (400×) in Fig. 4(a), one should notice the white longitudinal stripes (narrow bands) with a tendency to separate at the left bottom of the image. Similar stripes have been reported for other natural fibers, such as sisal, bamboo, coir and piassava [1] as well as in curaua fiber [14]. These stripes were associated with microfibrils that are based on cellulose chains and constitute the strongest part of a NFL. Indeed, during the fiber rupture, its microfibrils tend to split apart [1,14], as shown in Fig. 4(a). With higher magnification (3000×), Fig. 4(b), a typical microfibril, pointed out by arrow, is being detached from the surface of the guaruman fiber. In the left side of this picture, two other white stripes resembling apparent protrusions might not be solely attributed to microfibrils. For these relatively large protruded white stripes, a possible explanation is that they could be more as part of lignin, which joins the microfibrils, deformed during the guaruman extraction process. The results in Fig. 4 are consistent with those recently disclosed for guaruman fiber [9].

As aforementioned, the orientation of the MFA is responsible for the NFL strength [1,8]. The measurement of MFA can be accomplished by direct visualization of surface marks using optical microscopy, confocal reflectance microscopy, SEM and field emission scanning microscopy (FESEM) [7]. In particular, Abe et al. [19–22] and Brandstrom et al. [23,24] used SEM images of protrusions on the surface of conifer and spruce trees, respectively, fibers (wood tracheids) to evaluate corresponding MFAs. Uncertainties regarding similar measurements on the surface, Fig. 4(b), of guaruman fibers refrained the use of this technique in the present work. Another more precise method to calculate MFA is based on XRD [7,13].
Fig. 3 – SEM of a guaruman fiber cross-section: (a) highlighted ellipsoidal contour; (b) lumen large holes; and (c) top view of cylindrical microfibrils.

Fig. 4 – SEM of guaruman fiber surface: (a) 400× and (b) 3000× of magnification.

Fig. 5 shows XRD patterns of samples associated with different conditions of guaruman fiber-related: (a) vertical splint; (b) horizontal splint; and (c) bunch of tied fibers. One should notice that in all three conditions, the peak that is associated with the direction (002) is the prominent peak. This peak is related to the crystalline part of the fiber and, therefore, was the peak used for evaluating MFA [25]. In fact some minor difference in such spectra could also be observed, but one should verify that the intensity in these three cases varies. This behavior could be associated with the condition of analysis, aforementioned vertical, Fig. 5(a) and horizontal splint, Fig. 5(b) as well as bunch of tied fibers, Fig. 5(c). While in the two first conditions the maximum intensity is about 700 a.u., in the third one such intensity goes to more than 8000 a.u. This suggests that only main peaks would appear in Fig. 5(c), while in the other two conditions secondary peaks would be related with the position of the splint.

Applying this way to the distinct XRD patterns in Fig. 5, the corresponding MFAs were calculated and presented in Table 3.

One should notice in Table 3 that almost the same values of MFAs were obtained, regardless the type of sample. A mean value of 7.8° might be consider, which is comparable to MFA values reported for other NFLs [26].

Table 3 – Microfibril angle for distinct types of guaruman fiber-related samples.

<table>
<thead>
<tr>
<th>Guaruman Fiber</th>
<th>Microfibril angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vertical splint</td>
<td>7.3</td>
</tr>
<tr>
<td>Horizontal splint</td>
<td>8.2</td>
</tr>
<tr>
<td>Tied fibers</td>
<td>7.9</td>
</tr>
</tbody>
</table>

Preliminary tensile properties evaluated for the guaruman fiber are shown in Table 4, together with average values of density and MFA. In this table, for comparison, corresponding values related to other NFLs used as polymer composites reinforcement [1] are also presented. As compared to other NFLs, the relatively small MFA, 7.8°, of the guaruman fiber fits well with its superior tensile strength of 614 MPa, which is an expected result [8].

Fig. 6 shows XRD pattern of a guaruman fiber powder sample used to evaluate the crystallinity index (CrI), according to Eq. (4). This evaluation gives a CrI=60% based on the intensity, 1697 a.u., for the (101) peak observed at 2θ=17.2° and 4187 a.u. for the (002) cellulose peak at 2θ=25.7°. Another proposed method [13], based on the corresponding areas of the same peaks gives CrI=67%. These results are close enough
Fig. 5 – XRD patterns of guaruman fiber-related samples of: (a) vertical splint; (b) horizontal splint; and (c) tied fibers.

Table 4 – Average values of tensile properties of guaruman fiber as compared to other common NFLs.

<table>
<thead>
<tr>
<th>Natural lignocellulosic fiber</th>
<th>Density (g/cm³)</th>
<th>Tensile strength (MPa)</th>
<th>Young’s modulus (GPa)</th>
<th>Microfibrilar angle (°)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Guaruman</td>
<td>0.57</td>
<td>614</td>
<td>21</td>
<td>7.8</td>
<td>PW^a</td>
</tr>
<tr>
<td>Jute</td>
<td>1.45</td>
<td>597</td>
<td>20</td>
<td>8.0</td>
<td>[1,26]</td>
</tr>
<tr>
<td>Ramie</td>
<td>1.50</td>
<td>685</td>
<td>44</td>
<td>6.2</td>
<td>[26]</td>
</tr>
<tr>
<td>Hemp</td>
<td>1.45</td>
<td>539</td>
<td>35</td>
<td>7.5</td>
<td>[1,5]</td>
</tr>
<tr>
<td>Sisal</td>
<td>1.38</td>
<td>478</td>
<td>19</td>
<td>20.0</td>
<td>[1,26]</td>
</tr>
<tr>
<td>PALF^*</td>
<td>1.44</td>
<td>180</td>
<td>59</td>
<td>11.5</td>
<td>[1,26]</td>
</tr>
<tr>
<td>Coir</td>
<td>1.52</td>
<td>135</td>
<td>5</td>
<td>51</td>
<td>[1,26]</td>
</tr>
</tbody>
</table>

^a Present work.
^* Pineapple leaf fiber.

Fig. 6 – XRD pattern of a guaruman fiber powder sample for crystallinity index evaluation.
and might not require further discussion on possible reason for the small difference between them. Indeed, they are within the range of values reported for many NFLs [26].

4. Summary and conclusions

Basic characteristics and properties of a relatively unknown guaruman fiber from the Amazonian region are reported for possible application as polymer composite reinforcement.

- Densities measured by both mass/volume and Archimedes techniques and analyzed by the Weibull statistical method revealed a tendency to decrease with increasing fiber cross section dimensions.
- These densities mean values of 0.50 g/cm³ (mass/volume) and 0.64 g/cm³ (Archimedes) are among the lowest reported so far for natural lignocellulosic fibers (NSF).
- Microfibril angles (MFA) of 7.3–8.2° were found by X-ray diffraction in different guaruman fiber-related samples. These relatively low MFAs are coherent with a superior tensile strength of 614 MPa, as expected for NFLs.
- A crystallinity index (Crl) of 60–67% was obtained by XRD in powder samples of guaruman fiber. This Crl is within the range of values reported for several NFLs.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

The authors thank the Brazilian supporting agencies CAPES, CNPq and FAPERJ for the funding. It is also acknowledged the LNDC/COPPE-UFRJ for some of the DRX analysis as well as the tensile tests.

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