Original Article

Thermal and structural characterization of buriti fibers and their relevance in fabric reinforced composites

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\textbf{ABSTRACT}

Engineering applications involving polymer composites reinforced with natural lignocellulosic fibers (NLFs) have greatly increased in recent decades due to advantages associated not only with favorable composite properties but also fiber sustainability and cost-effectiveness. A search for less common NLFs is currently an endeavor for the development of novel composites with improved properties. In particular, for applications above room temperature, the thermal resistance must be characterized. In the present work composites reinforced with up to 30 vol% fabric made of buriti, a relatively unknown natural fiber from Brazil, with limited reported information, were characterized by thermogravimetric/derivative (TG/DTG) and dynamic mechanical analysis (DMA). Preliminarily, the plain buriti fiber was investigated in terms of X-ray diffractometry (XRD), Fourier transform infrared spectroscopy (FTIR) and TG/DTG analysis. XRD pattern allowed, for the first time, the evaluation of a microfibril angle of $\theta$ and crystallinity index of 63%. FTIR bands for buriti fibers were also obtained with expected results. TG/DTG results indicate for the buriti fiber a limit degradation temperature around 200 $^\circ$C and for the buriti fabric epoxy composites at about 250 $^\circ$C. Dynamic mechanical analysis of composites disclosed similar viscoelastic stiffness values but an increasing glass transition temperature with the amount of buriti fabric.

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1. Introduction

In the last decades, the number of research works involving composite materials reinforced with synthetic or natural fibers has increased considerably. Synthetic fibers exhibit properties such as mechanical, thermal and morphological that make them suitable for a wide range of applications [1]. On the other hand, the processing of these fibers is associated with some drawbacks related to high-energy consumption and cost of production as well as their long-term disposal after useful life [2]. One interesting approach that has been considered in many engineering applications is the replacement of these synthetic fibers by those of natural origin, the so-called natural lignocellulosic fibers (NLFs). Indeed, this substitution is very promising as emphasized in general review articles [3–14] and specific papers [15–18]. For the interest of the present work, none of these articles presented any mention to the buriti fiber, which is now investigated. The relevance of less known NLFs is, nonetheless, an important area of investigation for novel materials. For instance, cellulose pine needles from the Himalayan region were used to facilitate graft polymerization syntheses [15]. A grass fiber, Saccharum ciliare, was investigated as possible polymer composites reinforcement [16,17]. Green polymer composites were also reinforced with Hibiscus sabdariffa, a natural bast fiber abundantly found in India [18].

In addition to the aforementioned research works, engineering applications of NLFs reinforced polymer composites have been reported [19]. In particular, several natural fiber composites are already been used in civil construction [20], and packing materials [21] as well as in automobile and aeronautical industries [22,23]. However, for the composites to be applied in some engineering areas it might be necessary to perform at temperatures above 100 °C. Therefore, thermal analysis is usually conducted to verify the isolated behavior of NLFs and their reinforced polymer composites [24].

Among the less known NLFs stands the buriti fiber extracted from the leaves of a palm tree abundant in swamp regions of the north and northeast of Brazil. Being relatively strong, buriti fibers have been traditionally used for handcrafts, including baskets and fabrics for sackcloth. An earlier publication [25] was devoted to the fruit of the buriti palm tree. More recently, the possible use of buriti fibers as reinforcement of polymer composites begin to be investigated [26–33]. Table 1 presents the physical and structural properties related so far for the different types of buriti fibers extracted from the leaf and petiole.

<table>
<thead>
<tr>
<th>Fiber Diameter</th>
<th>150–170 μm</th>
<th>1500 to 7500 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>102 ± 12 μm</td>
<td>10591/2008</td>
</tr>
</tbody>
</table>

Table 1: Fiber Diameter and Tensile Strength of Buriti Leaf Fiber.

Regarding the more recently reported results on thermal analysis, X-ray diffractometry (XRD) and infrared spectroscopy (FTIR) for the buriti leaf fiber, the following points are worth discussing. Ornaghi et al. [26] found that more prominent thermal degradation starts around 200 °C with DTG peaks at 280, 333 and 406 °C assigned to the decomposition of hemicellulose, cellulose and lignin, respectively. Santos et al. [28] indicated that thermal decomposition of pectin, lignin and hemicellulose starts at 150 °C for untreated buriti leaf fibers. They also revealed that main DSC exothermal events occur between 200 and 370 °C associated with the decomposition of the major fiber components. FTIR results in Ref. [26] disclosed stretching bands for O–H, CH2, C=O, C–H, C–O and C–O–C characteristic of lignocellulosic fiber. Their XRD results, typical of cellulose-based material, indicated that the buriti fiber is composed of cellulose I, characteristic of plant structure. Moreover, an index of crystallinity of 44.6–51.9% was calculated. However, the authors did not evaluate the microfibril angle.

As for composites reinforced with buriti leaf fibers, Santos et al. [28] investigated cardanol-formaldehyde reinforced with up to 15 wt% of buriti leaf fibers. TG curves indicate that the 10 wt% composite presents an intermediate thermal behavior in relation to the fiber and matrix. This same composite displayed a weak endothermic event, assigned to release of water, but intense exothermic peaks corresponding to thermal decomposition of the matrix. Dynamic mechanical analysis (DMA) revealed that increasing the fiber content provides a higher rigidity for the composite.

In spite of these more recent results, both the plain buriti leaf fiber and composites reinforced with buriti fabric into more commonly applied polymer matrices still require investigation. Therefore, for the first time, this work aimed to apply the buriti fabric, up to 30 vol%, as reinforcement of composites with epoxy matrix to perform thermal and structural analyses. In addition, to calculate the index of crystallinity and microfibril angle of the buriti leaf fiber used in this research.

2. Materials and methods

2.1. Materials

Fig. 1(a) shows the buriti plant, Mauritia flexuosa. Fig. 1(b) exhibits a bundle of buriti leaf fibers, while Fig. 1(c) presents the as-received fabric with an insert that displays the microscopic aspect of the fabric observed by scanning electron microscopy (SEM), model Quanta FEG 250 FEI equipment under a voltage acceleration of 15 kV. Such fabric was purchased in a local market of the city of Manaus, Brazil. The surface area of the fabric was measured as 229.6 g/m² in accordance with NBR 10591/2008 standard. The fiber length was measured in the range between 1.5 and 2 mm.

Composites were prepared by the addition of epoxy resin, as matrix, and buriti fabric, as reinforcement, in a metallic mold with dimensions of 120 × 150 mm². The epoxy resin used was the diglycidyl ether of the bisphenol A (DGEBA) mixed in stoichiometric proportion of phr = 13 with triethylentetra-
Table 1 – Properties reported for different fibers of buriti.

<table>
<thead>
<tr>
<th>Types of Buriti Fiber</th>
<th>Fiber diameter (μm)</th>
<th>Density (g/cm³)</th>
<th>Tensile strength (MPa)</th>
<th>Elastic Modulus (GPa)</th>
<th>Lignin (%)</th>
<th>Holocellulose (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leaf</td>
<td>50-75001</td>
<td>1.312</td>
<td>3.2-735</td>
<td>10.2-27</td>
<td>24.0</td>
<td>67.8</td>
<td>[26,28-30]</td>
</tr>
<tr>
<td>Petiole</td>
<td>350-950</td>
<td>1.1-1.5</td>
<td>133-260</td>
<td>9.0-15</td>
<td>NA</td>
<td>NA</td>
<td>[29,30]</td>
</tr>
</tbody>
</table>

NA = not available.

* Holocellulose = cellulose + hemicellulose.

Fig. 1 – Buriti (a) palm tree, (b) bundle of fibers, (c) fabric and insert that shows the microscopic aspect by SEM.

tramine (TETA) as hardener, both supplied by EpoxyFiber, Brazil. The buriti fabric was cut with the same dimensions of the metallic mold and then dried in an oven at 60 °C for 24 h. In order to produce the composites with 10, 20 and 30 vol%, buriti fabrics were layed down inside the mold, while still fluid DGEBA/TETA epoxy was poured over each fabric layer until the desired volume fraction was obtained.

2.2. Methods

Preliminary chemical analysis was performed by means of solvent extraction as well as weighing procedure after 2 h heating at 105 °C for water content and 1 h calcination at 600 °C for ash content.

2.2.1. Thermogravimetric analysis (TG/DTG)

TG/DTG of the fibers and composites were performed according to ASTM E1131 in a TA Instruments, model Q500. Fibers and composites were comminuted, placed in aluminum crucibles and then subjected to a temperature variation of 25–700 °C.

2.2.2. Fourier-transform infrared spectroscopy (FTIR)

FTIR analyses were performed on buriti fiber to verify the vibrations and stretching of the effective fiber bonds. The buriti fiber was mixed with KBr. The analyses were carried out in an IR Prestige 21-FTIR-Shimadzu spectrophotometer.

2.2.3. Dynamic mechanical analysis (DMA)

DMA prismatic specimens of buriti fabric were prepared with epoxy resin, measuring 50 × 13 × 5 mm³, in the volumetric fractions of 10, 20 and 30 vol%. The entire procedure followed the ASTM D4065 standard. DMA tests were performed using a model Q/800 TA Instruments equipment. The variation of storage modulus (E’), loss modulus (E”) and tangent delta (tan δ) with temperature were simultaneously recorded between −50 and 180 °C. The DMA technique is able to determine the glass transition (Tg).

2.2.4. X-ray diffraction (XRD)

XRD of the buriti fiber was performed on a model D8 Advanced Bruker diffractometer, with scan speed of 0.05 (2θ/s) power 40 mA × 40 kV and scanning from 5 to 70°. The index of crystallinity (Ic) of the fiber could be calculated by:

\[ I_c = \frac{I_{200} - I_{am}}{I_{200}} \times 100 \]  

This method was developed in 1959 by Segal et al. [34] and is based on the ratio of the height of the (200) peaks (I_{200}) and the height of the minimum (I_{am}) between the (200) and (110) peaks. Moreover, the microfibril angle (MFA) was evaluated using XRD results [35].

3. Results and discussion

3.1. Chemical and morphological analysis

A preliminary chemical analysis of the buriti fiber revealed: 58% of cellulose; 19% of lignin; 1% of hemicellulose; 6% extractives; 2% ash; and 9% of moisture content.

Fig. 2 shows SEM micrographs of the surface and internal regions of the buriti leaf fiber, Fig. 1(b), which is used to make corresponding fabric, Fig. 1(c). The images allow one to identify the typical microstructure and imperfections of this NFL, similar to previously reported ones [26,28,29,32]. The fiber surface, Fig. 2(a), has both smooth and rough regions. The roughness corresponds to holes and imperfections clearly observed with higher magnification in Fig. 2(b) and (c). Some holes appear to be associated with a network of porosity and channels for water and nutrients of the plant. A transversal cross-section...
fracture, Fig. 2(d) reveals these internal channels and porosity, in which some larger cylindrical holes can be assigned to the NFL lumen. Small cylinders might be related to microfibrils.

3.2. X-ray diffraction

The diffractogram obtained for the buriti fiber is shown in Fig. 3. An insert with deconvoluted curves used for MFA calculation is also shown in Fig. 3. This XRD pattern is typical of cellulose containing natural materials, especially NFLs with a main (002) peak corresponding to the cellulose crystalline structure [35]. Based on this peak, a microfibril angle (MFA) was preliminarily evaluated as 7.0°. An amorphous peak was detected at the angle of 16.41° and the crystalline peak was detected at the angle of 21.72°. The value of the Ic found was 63.11% and it is relatively close to that found by Ornaghi et al. [26], Segal et al. [34] and Poletto et al. [36]. This result corroborates that the cellulose content present in the buriti fiber is approximately 58%, since the Ic is directly bound to the cellulose content in the fiber [26]. In addition, the higher the cellulose content in the fiber the greater its rigidity and strength, which is also directly related to a small MFA [35].

3.3. Thermogravimetric analysis

Fig. 4 shows the TG/DTG curves of the buriti leaf fiber that compose the fabric, Fig. 1(c), reinforcing the investigated epoxy composites. In the DTG curve, the sharp oscillations up to 320 °C are due to instabilities in the TG curve. Such instabilities have not been reported in other buriti leaf fibers [26,28] and might be a consequence of electronic fluctuation in the equipment. In any case, this phenomenon did not interfere in defining a first 9.68% loss of mass, up to 180 °C, attributed to release of water, which is in agreement with the fiber moisture content. A second loss, associated with a sharp decrease in weight, from 200 to 450 °C is assigned to degradation of the fibers constituents with prominent peaks at 333 °C and a shoulder peak at 396 °C, associated with decomposition of cellulose and lignin, respectively. Similar results were found by Ornaghi et al. [26]. A similar TG curve for untreated buriti fiber
was reported by Santos et al. [28] and agrees with TG curves for several NLFs [24,37].

Fig. 5 shows (a) TG and separated (b) DTG curves for the buriti fabric reinforced epoxy composites. Only minor displacements in the level of each curve, corresponding to weight loss are observed. However a sensible change in the main peak position, associated with decomposition temperature, can be detected. Table 2 presents the related thermogravimetric parameters for the curves in Fig. 4.

By comparing with results in Fig. 4, one notice that the buriti leaf fiber suffers more thermal degradation, 9.68%, than the composites (3.33–4.27%) in the first stage of stage of water release. However, in the second stage of higher mass loss, the composites loose more mass (84.03–85.07%) than the plain fiber (74.52%). This is a known consequence of the relatively low temperature resistance of thermoset polymers beyond 300 °C [38]. As for the TG curves, Table 2, the onset temperature for intense degradation, after water release, is around 320 °C and not much affected by the amount of fiber. Again, this could be related to the epoxy limit in thermal resistance. As such, it is recommended the maximum working temperature for buriti fabric reinforced epoxy composite to be 250 °C.

3.4. Fourier-transform infrared spectroscopy

Fig. 6 shows the FTIR spectrum of the investigated buriti leaf fiber. This spectrum is very similar to the reported by Ornaghi et al. [26] and Albuquerque et al. [39]. Therefore, only a limited discussion is worth presenting. The main bands identified in
Fig. 5 – (a) Thermogravimetric analysis (TG) and (b) derivative thermogravimetry (DTG) for reinforced composites with buriti fabric.

Table 2 – Results obtained from the TG and DTG curves for the reinforced composites with buriti fabric.

<table>
<thead>
<tr>
<th>Volume fraction of buriti fabric in epoxy composite (vol%)</th>
<th>Weight loss (%)</th>
<th>$T_{\text{onset}}$ (°C)</th>
<th>$T_{\text{max}}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Stage I</td>
<td>Stage II</td>
<td>Stage III</td>
</tr>
<tr>
<td>10</td>
<td>3.33</td>
<td>85.67</td>
<td>1.71</td>
</tr>
<tr>
<td>20</td>
<td>3.80</td>
<td>85.13</td>
<td>1.59</td>
</tr>
<tr>
<td>30</td>
<td>4.27</td>
<td>84.03</td>
<td>1.67</td>
</tr>
</tbody>
</table>

Fig. 6 – FTIR spectrum for the buriti fiber.

Fig. 3 are 3447 cm$^{-1}$ for O–H stretching of moisture or hydroxyl groups in cellulose, along with 2918 and 2850 cm$^{-1}$ for CH$_2$ groups in cellulose [26]. The 1736 cm$^{-1}$ band for C=O stretching of carboxylic group of hemicellulose and 1636 cm$^{-1}$ for C=C stretching. Bands from 1460 to 1039 cm$^{-1}$ are assigned to C–H bending as well as both C–O and C–O–C stretching of groups in lignin and carbohydrates [26]. Although not identified, a possible band at 1510 cm$^{-1}$ might be related to the aromatic skeletal vibration of lignin. In addition, a small band at 897 cm$^{-1}$ was attributed to C–H deformation [26].

3.5. Dynamic mechanical analysis

Fig. 7 shows the DMA set of storage modulus ($E'$), loss modulus ($E''$), and tangent delta (tan δ) curves for epoxy composites reinforced with: (a) 10; (b) 20; and (c) 30 vol% of buriti fabric.

Based on curves in Fig. 7, Table 3 presents relevant DMA parameter for each distinct composite. The value of $E_25'$ in this table corresponds to the storage modulus at 25 °C, which gives an idea of the viscoelastic stiffness at room temperature. The value $E_{\text{peak}}'$ is that of the loss modulus at the corresponding peak. The value of $T_g$ is the temperature associated with the
tan δ peak, which may be assigned to the upper limit of the glass transition
temperature.

The results in Fig. 7 and Table 3 do not allow one to assure that the amount of buriti fabric affects significantly the DMA behavior of epoxy composites. However, few events are worth noticing in the storage modulus curves. The value of \( E' \), also
called dynamic modulus, is often associated with the viscoelastic stiffness of the material, it measured the potential stored elastic energy [40]. In Fig. 7 one may notice three distinct regions in the \( E' \) curves. The first, at lower temperature, below 90 °C, is a solid region. The second region, up to 150 °C in Fig. 7, is the beginning of a transition, where the value of \( E' \) displays a drastic decrease. The third region, above 150 °C, is known as the rubbery plateau due to the viscoelastic condition. The temperature between the first and the second region might be associated with the beginning of the transition from crystalline to a glassy structure. In Fig. 7, it is verified that this temperature for the composites increases from 72.3 to 85.0 °C with the amount of 10–30 vol% buriti fiber, respectively. These values are significantly higher than that for plain epoxy [41], also presented in Table 3. This behavior might be due to restriction caused by the buriti fabric in the mobility of epoxy chains and so retarding the beginning of glass transition temperature [24,37].

The values of \( E'' \) in Fig. 7 and Table 3 do not show much influence of the buriti fabric in the composites stiffness peaks and their temperature position. However, being the \( E'' \) peaks related to the composite internal friction, one may infer that the incorporation of buriti fabric is sensibly increasing the relaxation temperature, 64 °C, of the epoxy matrix. It should also be mentioned that possible peaks around –50 °C, not clearly defined, are attributed to secondary relaxation of the epoxy matrix.

As for the tan δ curves, Fig. 7, and related parameters in Table 3, there is no clear evidence of a significant effect cause by the amount incorporated buriti in the damping capacity

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**Table 3 – Parameters obtained by DMA for composites reinforced with buriti fabric.**

<table>
<thead>
<tr>
<th>Volume fraction of buriti fabric in epoxy composite (vol%)</th>
<th>( E'_{25} ) (GPa)</th>
<th>Lower limit of ( T_g ) (°C)</th>
<th>( E_{peak} ) (GPa)</th>
<th>Peak temperature (°C)</th>
<th>( Tan \delta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (plain epoxy)</td>
<td>1.63</td>
<td>49.1</td>
<td>0.11</td>
<td>64.0</td>
<td>0.33</td>
</tr>
<tr>
<td>10</td>
<td>1.75</td>
<td>72.3</td>
<td>0.18</td>
<td>83.1</td>
<td>0.26</td>
</tr>
<tr>
<td>20</td>
<td>1.20</td>
<td>81.3</td>
<td>0.19</td>
<td>99.7</td>
<td>0.30</td>
</tr>
<tr>
<td>30</td>
<td>2.05</td>
<td>85.0</td>
<td>0.16</td>
<td>96.7</td>
<td>0.26</td>
</tr>
</tbody>
</table>

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**Fig. 7 – DMA curves for epoxy composites reinforced with buriti fabric: (a) 10 vol%; (b) 20 vol% and (c) 30 vol%.”**
of the composites. However, their tan δ peak amplitudes are lower than that of plain epoxy, while their peak temperatures are much higher. These results corroborate the aforementioned restriction to the mobility of epoxy chains by buriti fabric incorporation. Indeed, as the upper limit of glass transition temperature, Tg, the tan δ peak is associated with a change from solid to a rubbery glassy structure. It is, therefore, suggested that the buriti fabric retards the epoxy crystalline-to-glass temperature interval from lower 49.1 to upper 54.1 °C, Table 3, by as much as 85 to 119 °C, respectively, as a consequence of 30 vol% incorporation.

4. Summary and conclusions

Thermal analyses and structural characterization of epoxy composites incorporated with up to 30 vol% of buriti leaf fiber, were for the first time investigated together with especial finding from related buriti leaf fiber.

- X-ray diffraction (XRD) of the fabric-related buriti leaf fiber revealed a crystallinity index of 63% and microfibril angle of θ. Thermogravimetric (TG/DTG) and Fourier transform infrared spectroscopy (FTIR) results were found to be similar to more recently reported ones for other buriti leaf fiber. An intense degradation peak around 320 °C recommends a maximum working temperature for these composites to be 250 °C.
- Dynamic mechanical analysis (DMA) of the composites showed significant differences to plain epoxy in terms of the effect of buriti fabric in the mobility of epoxy chain.
- The Tg interval of epoxy crystalline transition to a glassy structure, 49.1–54.1 °C at the tan δ peak, is significantly raised, 85–119 °C, respectively, due to the 30 vol% buriti fabric incorporation.

Conflict of interest

The authors declare no conflicts of interest.

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