Original Article

Charpy impact test of epoxy composites reinforced with untreated and mercerized mallow fibers


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A R T I C L E   I N F O

Article history:
Received 10 November 2017
Accepted 13 March 2018
Available online 23 August 2018

Keywords:
Mallow fibers
Epoxy composite
Merceration
Charpy impact test

A B S T R A C T

The mallow fiber (Urena lobata, linn) is demonstrating a great potential as reinforcement in polymer matrix composites. The difficulty in the use of the mallow, as in other natural lignocellulosic fibers (NLFs), is its hydrophilic compatibility with polymeric matrices that are typically hydrophobic. In order to improve the adhesion between the fiber surface and polymeric matrices, mallow fibers were subjected to mercerization treatment. In this work composites were produced with epoxy matrix reinforced with 30 vol% of mallow fibers, both untreated and mercerized. By means of XRD analysis it was verified the variation of crystallinity in fibers treated with different NaOH solutions as well as immersion times and agitation. After this XRD preliminary analysis, a treatment of 5% NaOH solution for 24 h without agitation was selected. The objective was to compare the Charpy impact energy of composites specimens produced with untreated mallow fibers and treated for the higher crystallinity obtained after the selected mercerization. For the analysis of impact energy the Tukey test was applied from which it could be assured, with a confidence level of 95%, that the epoxy specimens reinforced with 30 vol% of untreated mallow fibers, had the best performance.

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1. Introduction

Unlike synthetic fibers, natural lignocellulosic fibers (NLFs) do not have uniform properties. In fact, they are microstructurally heterogeneous and have dimensional limitation. The same type of NLF may considerably vary its properties depending on their origin, quality and age of the plant, as well as fiber diameter, aspect ratio and its preconditioning. This could significantly affect the performance of polymer composites reinforced with NLFs [1-12]. Another difference between NLFs and synthetic fibers is their interaction with water. Due to the

* Paper was part of technical contributions presented in the events part of the ABM Week 2017, October 2nd to 6th, 2017, São Paulo, SP, Brazil.
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https://doi.org/10.1016/j.jmrt.2018.03.008
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presence of hydroxyl groups NLFs are hydrophilic, with high affinity with humidity. The fiber moisture content can vary between 5 and 10 wt% [2,3].

The water on the surface of a NLF, reinforcing a composite, acts as a release agent at the interface of a hydrophobic polymer matrix. Further, due to evaporation of water, voids may appear in the matrix, resulting in loss of mechanical properties. One solution to reduce the moisture content and improve the interfacial adhesion is drying the NLF followed by pretreating the fibers by chemical modification of the surface [13–22].

Pretreatment enables the creation of increased roughness on the surfaces, which contributes to better adhesion to the polymer matrix. Among the different techniques for pretreating to produce NLFs surface modification, one of the most used is the alkaline treatment, also known as mercerization [17]. The mercerization removes both the waxes and greases as a portion of hemicellulose and lignin, enhancing the packing of the cellulose molecules and increasing crystallinity of the fibers. This results in a rougher surface with larger contact surface, aiding in mechanical anchoring and promoting an increase in both the elastic modulus and the tensile strength [23,24].

The mallow fiber (Urena lobata, linn) although widely used for making cordage in clothes as well as carpets, paper money, crafts among others [25], does not have so far a great use as reinforcing component in industrial composite products. However, physical and mechanical properties such as tensile strength have shown [26,27] a promising potential for using mallow fibers as reinforcement in polymer matrix composites (PMCs). Table 1 presents some of these properties.

In this context, there is the possibility of using PMCs reinforced with mallow fibers in dynamic applications such as ballistic armor. Therefore, increased crystallinity of the mallow fibers and consequently the adhesion to the polymer matrix, through the mercerization treatment, may provide improvement in the mechanical properties of the composites. This could be the case of Charpy impact energy, which is investigated in the present work.

### Materials and methods

The mallow fibers were provided by the State University of North Fluminense (UENF) and acquired from the Textile Company Castanhal, Brazil Fig. 1 shows the as received mallow fibers. The polymer used as the material of the composite plate matrix was a commercial epoxy resin diglycidyl ether type of bisphenol A (DGEBA) cured with triethylene tetramine (TETA), using the phr of 13 parts of hardener to 100 parts of resin.

Mallow fibers were added in two different situations as reinforcement in the manufacture of epoxy composite plates. In the first case the untreated fibers were cleaned, cut to a length of 150 mm and dried in a stove for 24 h. In the second case, mallow fibers were subjected to NaOH mercerizing treatment in the combination of parameters, according to Table 2.

The choice of immersion times was based on the effectiveness of the treatment. Indeed, a minimum of 3 h was needed to reveal visible microstructural changes. By contrast, more than 48 h treatment caused serious degradation to the fiber integrity. A 24 h treatment time was selected as middle in between the extreme conditions.

After a preliminary selection based on the value of crystallinity obtained by X-ray diffraction (XRD), one specific treatment, the CP4 in Table 2 was applied. These treated mallow fibers were then incorporated into epoxy matrix for impact test. Charpy test specimens with untreated fibers were added into epoxy matrix in the volumetric fractions of 0%, 10%, 20% and 30%. Specimens with 5% NaOH for 24 h treated fibers, relative to CP4 in Table 2, were added into the epoxy matrix in the volumetric fraction of 30%. Fig. 2 shows the various composite plates produced. These plates were cut in several Charpy specimens according to the standard [28].

The crystallinity index (\(I_c\)) of the cellulose was calculated by means of Eq. (1).

\[
I_c = 1 - \frac{I_1}{I_2}
\]

where \(I_1\) is the intensity of the minimum of diffraction, related to the amorphous part and \(I_2\) is the intensity of the maximum of diffraction, related to the crystalline part. This method was developed in 1959 by Segal et al. [29], and has been widely used for the study of natural fibers [30,31]. The XRD analyses

### Table 1 – Physical and mechanical properties of the mallow fibers.

<table>
<thead>
<tr>
<th>Material</th>
<th>Diameter (µm)</th>
<th>Length (mm)</th>
<th>Specific mass (kg/m³)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
<th>Modulus of elasticity (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mallow</td>
<td>42.6</td>
<td>23.8</td>
<td>1374</td>
<td>160</td>
<td>5.2</td>
<td>17.4</td>
</tr>
</tbody>
</table>

### Table 2 – Types of specimens produced from the variation of the mercerization parameters.

<table>
<thead>
<tr>
<th>NaOH Concentration (%)</th>
<th>3 h</th>
<th>24 h</th>
<th>48 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%</td>
<td>CP1</td>
<td>CP4</td>
<td>CP7</td>
</tr>
<tr>
<td>10%</td>
<td>CP2</td>
<td>CP5</td>
<td>CP8</td>
</tr>
<tr>
<td>20%</td>
<td>CP3</td>
<td>CP6</td>
<td>CP9</td>
</tr>
</tbody>
</table>

Fig. 1 – Mallow fibers as received by UENF.
were performed in a Shimadzu diffractometer, model XRD-6000, scan speed of 4°/min, power 30 mAh x 40 kV and scanning from 5° to 80°.

Fourier transform infrared (FTIR) analysis was conducted in a model IR Prestige 21-FTIR Shimadzu equipment. Samples of mallow fibers, both untreated and mercerized treated, were first milled followed by sieved for 20 mesh and then mixed with KBr. The mixture was then pressed to produce a film suitable for the analysis. Table 3 shows the FTIR absorption bands for a natural fiber [32].

Dynamic mechanical analysis (DMA) test was carried out from 20 to 200 °C in a model DMA Q800 TA Instrument using single cantilever 3 points bending specimens according to standard. A heating rate of 3 °C/min and nitrogen atmosphere was applied for the test.

A total of 7 specimens for Charpy impact test were obtained by cutting each composite plates according to ASTM D6110 dimensions [28]. The tests were performed in a PANTEC instrumented pendulum, Model XC-50, 1 × 220 V × 60 Hz. Fig. 3 illustrates the prepared specimens for the Charpy tests.

After impact tests, fragments of the ruptured specimens were collected and analyzed by scanning electron microscopy (SEM), in a model Quanta FEG FEI equipment.

### 3. Results and discussion

Fig. 4 shows the FTIR spectra for: (a) untreated and (b) mercerized treated mallow fibers. These spectra reveal significant changes in the wavenumber interval from 800 to 1800 cm⁻¹. By comparing the values in Table 3 to the results of Fig. 4 one notice that the strong absorption band around 1050 cm⁻¹ for the untreated fiber, Fig. 4(a), which might correspond to the C - O stretching in cellulose, hemicellulose and lignin, has been considerably attenuated in the mercerized treated fiber, Fig. 4(b). Similarly, the absorption band around 1400 cm⁻¹ for the untreated, Fig. 4(a), which could be associated with CH₂ bending or wagging in lignin, is practically inexisten in the treated fiber. One may then conclude that merceirization significantly affects the participation of lignin, which is a bonding substance for the cellulose, in the mallow fiber.

Fig. 5 shows DMA results for: (a) neat epoxy and (b) epoxy composites reinforced with 30 vol% of mallow fibers. By comparing the two graphs, in general, it is observed an increase in onset of softening temperature of the storage modulus E', as well as displacement to higher of the peaks in the loss modulus “E” and tangent delta. A possible interpretation for this behavior is an interference of the mallow fibers in the mobility of the epoxy chains, which postpones the occurrence of glass transition temperature.

The results obtained from the Charpy impact test for epoxy matrix composite reinforced with continuous and aligned mallow fibers, in percentages 0, 10, 20 and 30 vol% without treatment as well as 30 vol% with treatment, CP4 in Table 2, disclosed a good ability to absorb energy as compared to other polymer composites reinforced with NLFs [23]. Fig. 6 shows the results of Charpy absorbed energy (J/m) test for each group. It should be noticed that, as in other works [23,34], occurs an increase in average energy values with the fiber volume fraction used in the composite. High impact energy values can be related to low interfacer bonding, obtained by pullout tests, between the fibers and the matrix [35].

A low interfacer bonding between the mallow fiber and the epoxy matrix allows for easier decohesion during the impact, which causes fracture by delamination. This mechanism of fracture is more effective in composites with greater amount of reinforcement mallow fibers, above 10 vol%.

In this case, it can increase the path to be followed by the crack, and therefore the absorbed energy required for fracture of the composite. Perhaps, because of this, there was a relative reduction of impact energy in the specimens produced with merceirized fibers as presented in Fig. 6. Due to the increased crystallinity of the fibers and consequently better adhesion to the epoxy matrix, cracks found difficult to propagate and create fractured surfaces that would be associated with higher impact energy.

### Table 3 – FTIR absorption bands for a natural fiber [32].

<table>
<thead>
<tr>
<th>Frequency (cm⁻¹)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3200–3600</td>
<td>OH stretching</td>
</tr>
<tr>
<td>2905</td>
<td>CH₂ and CH₃ stretching</td>
</tr>
<tr>
<td>1740</td>
<td>Carbonyl (C=O) stretching of carboxylic acid or ester</td>
</tr>
<tr>
<td>1650</td>
<td>H–O–H bending of absorbed water</td>
</tr>
<tr>
<td>1616</td>
<td>Benzene ring stretching (lignin)</td>
</tr>
<tr>
<td>1500</td>
<td>Benzene ring stretching (lignin)</td>
</tr>
<tr>
<td>1440</td>
<td>CH₃ bending in lignin</td>
</tr>
<tr>
<td>1411</td>
<td>CH₂ and CH₃ bending</td>
</tr>
<tr>
<td>1357</td>
<td>CH₂ bending</td>
</tr>
<tr>
<td>1320</td>
<td>CH₃ wagging (lignin)</td>
</tr>
<tr>
<td>1235</td>
<td>C–O stretching of acetyl (lignin)</td>
</tr>
<tr>
<td>1150</td>
<td>C–O–C antisymmetric bridge stretching in cellulose and hemicellulose</td>
</tr>
<tr>
<td>1110</td>
<td>O–H association in cellulose and hemicellulose</td>
</tr>
<tr>
<td>1028</td>
<td>C–O stretching in cellulose, hemicellulose and lignin</td>
</tr>
<tr>
<td>879</td>
<td>β-Glucosidic linkage</td>
</tr>
<tr>
<td>600</td>
<td>Out of plant OH bending</td>
</tr>
</tbody>
</table>
Fig. 3 – Specimens with mallow fiber for Charpy test. (a) 0 vol%; (b) 10 vol%; (c) 20 vol%; (d) 30 vol% without treatment and (e) 30 vol% with treatment.

Fig. 4 – (a) FTIR to mallow fibers untreated; (b) FTIR to mallow fibers treated.

Fig. 5 – (a) DMA to neat epoxy; (b) DMA to epoxy composites reinforced with 30 vol% of mallow fibers.

Fig. 7 shows the diffractograms obtained for each mercerized sample, according to the various combinations of the parameters: concentration, immersion time and agitation. In this figure, 5% NaOH, 24 h immersion and without agitation, CP4 was found in Fig. 7(a) to have a fiber crystallinity index (Ic) of 84.49%. This is higher than the value obtained for the other mercerization combinations and for the untreated mallow fibers (82.24%) in Fig. 7(b).

From the results obtained, the analysis of variance (Table 4) rejects the hypothesis that the means are equal to 5% significance level for the statistical “F”, on this account: F calculated >F critical (tabulated). Therefore, the volume fraction of mallow fibers in epoxy matrix composites as well as the treatment of mercerizing has different effects on the Charpy impact energy.

The Tukey test was applied for comparison, using a confidence level of 95%, to determine which volumetric fraction of mallow fibers provided better results in terms of Charpy impact energy. The less significant difference (LSD) obtained was 77.34. The results for the differences between the mean values of Charpy impact energy are shown in Table 5.

Based on these results, with 5% significance level, the reinforced composite with 30 vol% mallow fibers without treatment showed better performance since it exhibited a higher average energy value of Charpy impact (905.49 J/m).
Table 4 – Analysis of variance of the average impact energies obtained for the epoxy matrix composites reinforced with percentages from 0% to 30 vol% of mallow fibers.

<table>
<thead>
<tr>
<th>Variation causes</th>
<th>DF</th>
<th>Sun of squares</th>
<th>Mean square</th>
<th>F calc.</th>
<th>F crit (tab.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treatments</td>
<td>4</td>
<td>3468899.11</td>
<td>867224.78</td>
<td>348.18</td>
<td>2.69</td>
</tr>
<tr>
<td>Residue</td>
<td>30</td>
<td>74721.76</td>
<td>2490.73</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>34</td>
<td>3543620.88</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5 – Results for the differences between the mean values of Charpy impact energy in the volume fractions of mallow fiber 0 to 30% after application of the Tukey test.

<table>
<thead>
<tr>
<th>Volumetric fraction of mallow fibers</th>
<th>0%</th>
<th>10%</th>
<th>20%</th>
<th>30% without treatment</th>
<th>30% with treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>0</td>
<td>46.59</td>
<td>470.63</td>
<td>809.41</td>
<td>65.36</td>
</tr>
<tr>
<td>10%</td>
<td>46.59</td>
<td>0</td>
<td>424.04</td>
<td>762.83</td>
<td>18.77</td>
</tr>
<tr>
<td>20%</td>
<td>470.63</td>
<td>424.04</td>
<td>0</td>
<td>338.78</td>
<td>405.27</td>
</tr>
<tr>
<td>30% without treatment</td>
<td>809.41</td>
<td>762.83</td>
<td>338.78</td>
<td>0</td>
<td>744.05</td>
</tr>
<tr>
<td>30% with treatment</td>
<td>65.36</td>
<td>18.77</td>
<td>405.27</td>
<td>744.05</td>
<td>0</td>
</tr>
</tbody>
</table>

Fig. 6 – Results of Charpy impact test for the epoxy matrix composites reinforced with mallow fibers.

This is significantly distinct from the others because the differences are higher than LSD (77.34). Another important point to emphasize is the comparatively lower for the impact energy (161 J/m) of 30 vol % treated mallow fiber composite (CP4), Fig. 4, which is much lower than those of 20% and 30 vol % and treated mallow fiber composite.

One possible explanation would be that the percentage of 10 vol% in mallow fibers were not sufficient to produce an effective reinforcement in the epoxy matrix, which is associated with low results in Charpy impact energy. In all test specimens there was a similar complete rupture, making valid the results. In Fig. 8 it is shown the specimens ruptured after the Charpy test.

By visual analysis it can be seen a brittle fracture tendency in specimens with 0% and 10 vol% untreated and 30 vol% treated, which was confirmed by the impact energy values presented in Fig. 4. This figure shows a higher increase of more than 6 times in going from 10% to 20 vol% mallow fibers. The SEM images in Figs. 9–11 show the way fracture mechanisms are involved in the impact process.

In Fig. 9(a) and (b) it is perceived clearly the brittle fracture mechanism by the presence of “river marks”, both in the specimen with 100% epoxy as well as the composite with 10 vol% of fiber. These show that there was no effective reinforcement with low percentage of fibers.

For untreated composites with 20 vol% of mallow fibers it was observed a greater amount of energy absorption owing to

Fig. 7 – (a) Diffractogram for untreated mallow fibers; (b) diffractogram for mallow fibers mercerizing (CP4).
fracture mechanisms. Indeed, Fig. 10(a) revealed broken and detached fibers of the matrix, and a very effective encasement of the broken fibers by the epoxy matrix. On the contrary, the mercerized treated mallow fiber composite, evidence of delamination, i.e. separation between fiber and epoxy matrix, is observed in Fig. 10(b).

In the image of Fig. 11(a) for the untreated 30 vol% mallow fiber composites one sees the fibers rupture, and the interfacial detachment from the epoxy matrix. These failure mechanisms led to the high absorption of impact energy as compared to the other percentages of untreated mallow fiber composites. However, the image of Fig. 11(b) for the mercerized-treated 30 vol% shows the fracture surface like those of composites reinforced with untreated 0% and 10 vol% fibers. Thus, the fracture was brittle and the absorbed energy was similar to that measured for reinforcement with 10 vol% fiber.

Finally, Table 6 displays a comparison between the young modulus and tensile strength obtained in quasi-static, test velocity of 2 mm/mm, and the impact energy. In this table one should notice that a relationship exists between the quasi-static mechanical properties and the absorbed impact energy. Indeed, the higher the amount of mallow fiber in the composite, the higher the stiffness, strength and impact energy. This emphasize the relevant effect of mallow fibers as reinforcement of epoxy composites.

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**Fig. 8** – Specimens completely fractured after Charpy impact test. (a) 0 vol%; (b) 10 vol%; (c) 20 vol%; (d) 30 vol% without treatment and (e) 30 vol% with treatment.

**Fig. 9** – (a) Epoxy composite with 0 vol% mallow fibers; (b) composite with 10 vol% mallow fibers.

**Fig. 10** – (a) Composite with 20 vol% mallow fibers; (b) mallow fiber detail in composite with 20 vol% of fibers.
The Charpy impact energy increase with the volume fraction of mallow fibers incorporated into the epoxy matrix. Among the specimens evaluated by the Tukey test with 95% confidence level, the composite with 30 vol% of mallow fibers without treatment was the one that exhibited the best results in terms of Charpy impact energy. This particular case indicates that natural fiber treatment is not beneficial to the composite performance.

Predominantly brittle fracture occurs in composites with volume fractions of 0% and 10 vol% mallow fibers untreated as well as 30 vol% mercerized fibers. These composites play significantly lower Charpy impact energy than composite reinforced which untreated 20 and 30 vol% of mallow fibers.

An index of crystallinity was obtained by XRD of 84.49% for CP4, which was treated with 5% NaOH, 24 h immersion and without treatment. However, the improvement in crystallinity did not reflect as an increase in Charpy impact energy.

Composites with 20% and 30 vol% mallow fibers without treatment provided a more effective reinforcing action. In these composites the fibers rupture was predominant mechanisms. This is evidenced by the average Charpy impact energy obtained, of the order 900 J/m.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

The authors thank the support to this investigation by the Brazilian agencies: CNPq, CAPES and FAPERJ, and UENF for supplying the mallow fibers.

4. Conclusions

Table 6 – Comparison between tensile strength, young modulus and Charpy impact energy to composites reinforced with mallow fibers.

<table>
<thead>
<tr>
<th>Percentage of mallow fibers</th>
<th>Tensile strength (MPa)</th>
<th>Young modulus (GPa)</th>
<th>Charpy impact energy (J/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>32.98 ± 14.61</td>
<td>3.89 ± 0.03</td>
<td>96.07 ± 21.15</td>
</tr>
<tr>
<td>10%</td>
<td>90.01 ± 21.35</td>
<td>11.60 ± 0.11</td>
<td>142.66 ± 8.23</td>
</tr>
<tr>
<td>20%</td>
<td>109.85 ± 21.70</td>
<td>15.73 ± 0.17</td>
<td>566.71 ± 52.54</td>
</tr>
<tr>
<td>30%</td>
<td>177.49 ± 17.80</td>
<td>20.50 ± 0.10</td>
<td>905.49 ± 94.56</td>
</tr>
</tbody>
</table>

References


Characteristics and applications of the mallow fiber. Available in http://www.ebah.com.br/content/ABAAAAyJAAG/fibra-malva [access 05.12.16].


