Original Article

Evaluation of Izod impact and bend properties of epoxy composites reinforced with mallow fibers

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ARTICLE INFO

Article history:
Received 1 May 2019
Accepted 25 October 2019
Available online 25 November 2019

Keywords:
Mallow fiber
Epoxy composite
Izod impact test
Bend test

ABSTRACT

Epoxy composites reinforced with 10, 20 and 30 vol% of a natural lignocellulosic fiber, the mallow fiber, were investigated for mechanical properties associated with Izod notch toughness and flexural resistance. For Izod tests, 150 × 120 × 10 mm plates and for three-point bend tests, 150 × 120 × 6 mm plates were fabricated in a steel mold by mixing aligned fibers with necessary percentage of diglycidyl ether of the bisphenol an epoxy resin hardened with triethylene tetramine. Each plate was kept under load of 5 ton during 24 h of curing at 25 °C. Both Izod and bend specimens were machined from corresponding plates and tested according to ASTM D256 and ASTM D790 standards, respectively. The results showed that composites with 20 and 30% of mallow fibers display a more effective reinforcement, with the predominance of fracture mechanisms, such as fiber rupture and interfacial detachment between the fibers and the matrix. The analysis of the results of both impact energies and flexural properties, was performed by the ANOVA statistics and Tukey test. Based on a 95% confidence level, the Tukey test showed that the 30 vol% of mallow fiber reinforced epoxy composites has the best performance, achieving the highest values of energy absorption, maximum flexural strength and rupture modulus. These results revealed that mallow fiber reinforced epoxy composites have promising applications as engineering materials.

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1. Introduction

Natural lignocellulosic fibers (NLFs) have, since the beginning of humankind, been playing an important role in the production of basic items such as ropes, baskets, and roofing. In past centuries, stronger NLFs became a choice for structural applications like in cables for suspended footbridges [1]. Today, these fibers continue to be increasingly used, as their handcrafted and manufactured products are a significant part

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https://doi.org/10.1016/j.jmrt.2019.10.066
2238-7856 © 2019 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
of the global economy. Indeed, a variety of textiles, carpet, canvas and nets as well papers and cardboards are produced from worldwide cultivated NLFs, such as cotton, flax, softwood, sisal, hemp, jute, bamboo and ramie. The end of the 19th throughout the 20th century witnessed the onset and extended, in large scale, the industrial use of NLFs as filler in polymer composites for cost-effective furniture, upholstery, packing, doorframes and other applications without the need of high mechanical strength [2]. By the end of the last century until the present year, sustainable issues motivated an exponential increase in research works [1–13] and industrial applications [14–20] of NLFs as effective reinforcement of stronger and stiffer polymer composites.

Although displaying several advantages, NLFs do not have uniform properties, as they are microstructurally heterogeneous and have dimensional limitations [3]. The same NLFs species may have their properties considerably affected depending on their origin, plant quality and age, as well as fiber diameter, aspect ratio and their preconditioning [1].

A typical example of a promising NFL being investigated for polymer composite reinforcement is the mallow fiber, also known as malva, mauve or aramina fiber. A strong and flexible fiber is obtained from the stems of the mallow plant (Urena lobata), illustrated in Fig. 1. Mallow fibers, up to a meter in length, are being used for sacking cordage, coarse fabrics, ropes, hammocks, carpets and other texture handicrafts [21]. Reported properties on mallow fiber, such as density of 0.996 g/cm³ [22] and tensile strength of 309 MPa [23], demonstrate a great potential for its possible use as reinforcement in polymer matrix composites (PMCs).

Indeed, recent works [24–28] investigated characteristics and properties of mallow fibers and related polymer matrix composites. In particular, photoacoustic thermal results [24] and tensile properties of mallow fiber reinforced epoxy composites [25] disclosed the possibility of using such composites for ballistic protection [26,25–28]. In another recent work [29] Charpy impact results were reported for mallow fiber epoxy composites. In order to provide a complement on the existing mechanical results of mallow fiber composites, the present work evaluated the Izod impact and bend behavior of epoxy composites reinforced with up to 30 vol% of continuous and aligned mallow fibers. A statistical analysis of the results was performed by ANOVA F and the Tukey tests.

2. Materials and methods

Mallow fibers were supplied by the Companhia Têxtil de Castanhal, Brazil. A bundle of as-received mallow fiber is illustrated in Fig. 2. The polymer used as the matrix material of the composite board was a commercially available epoxy resin, diglycidyl ether of the bisphenol A (DGEBA), hardened with triethylene tetramine (TETA), using the stoichiometric ratio of 13 parts of hardener per 100 parts of resin. The resin producer was Dow Chemical and supplied by RESINPOXY Ltda., Brazil.

Fibers from the bundle, Fig. 2, were cleaned, cut into 150 mm length pieces, dried in an oven at 80 °C for 24 h and then used to manufacture the composite plates. To fabricate the composite plates, a metal mold with an internal volume of 180 cm³ (150 × 120 × 10 mm) was used. Continuous and aligned mallow fibers were laid inside the mold in amounts corresponding to the desired volume fraction. Still fluid DGEBA-TETA epoxy was poured onto the fibers and the mold’s lid was tied–closed. The plates were processed in a hydraulic press with a maximum capacity of 30 tons. A load of 5 tons for 24 h was used to fabricate the composite plates. To calculate the volumetric percentages of each phase in the composite plate, the density of 1.00 g/cm³ [22] was considered for the mallow fibers as initial reference and the value of 1.11 g/cm³ was used for the epoxy resin (DGEBA-TETA). The percentages of mallow used in this work were 10, 20 and 30 vol%. Plain epoxy plates (0 vol%) were also fabricated for control.

The Izod impact test was performed on a Pantec CHIZ-25, 220V x60Hz pendulum using 11 and 22 J hammers. Specimens were cut and machined from the composite plates. The dimensions were specified by ASTM D256 standard [30]. Five samples for each percentage of fibers were produced with the dimensions of 62.5 × 12.7 × 10 mm. Fig. 3 shows the specimens for the Izod tests.

The three-point bending tests were performed on an EMIC DL10000 mechanical testing machine, Brazil. Specimens were cut and machined from the composite plate in the dimensions
required by the ASTM D790 standard [31]. Seven samples were produced for each percentage of fibers in the dimensions of 120 × 15 × 6 mm. The specimens prepared for the flexural tests are shown in Fig. 4.

The analysis of variance (ANOVA) was used, by means of the F test. By varying the fiber volume fraction, the objective was to verify if there were significant differences between the averages of the results obtained from the absorbed impact energy, maximum strength and flexural modulus. The confidence level used for all tests was 95%.

After verifying the existence of a significant difference between the averages of the results obtained (validity of the alternative hypothesis H1) for the various volume fractions mallow fibers, the Tukey test was also used. This test is known as a verification of the honestly significant difference (HSD). The objective was then to quantitatively evaluate each of the percentages of fibers used. The Tukey test is a hypothesis test, in which, from the obtained results, the equality hypothesis is rejected based on the Less Significant Difference (LSD), given by:

\[
LSD = q \sqrt{\frac{MSE}{r}}
\]  

where q is the total amplitude studied, which is a function of the degree of freedom (DF) of the residue and the number of treatments; MSE is the mean square error; and r is the number of replicates of each treatment [32].

3. Results and discussion

3.1. Izod impact tests

The results of Izod impact tests are presented in Table 1 and shown in Fig. 5. These results disclose a steady increase from 0 to 30 vol% of mallow fibers in the epoxy matrix. However, a comparatively much steeper increase is observed from 10 to 20 vol%, associated with a slope of 2.49 × 10³ (absorbed energy/volume fraction of mallow fibers). On the other hand, from 0 to 10 vol% and from 20 to 30 vol%, the slopes are 1.07 × 10³ and 1.37 × 10³, respectively, much lower. This steeper behavior is attributed to a change in fracture mode,
Table 2 – Variance analysis of average impact energies obtained for reinforced epoxy matrix composites with percentages of mallow fibers from 0 to 30 vol%.

<table>
<thead>
<tr>
<th>Variation causes</th>
<th>DF</th>
<th>Sum of squares</th>
<th>Average square residue</th>
<th>F (calculated)</th>
<th>F critical (tabulated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treatments</td>
<td>3</td>
<td>1065675.77</td>
<td>355225.26</td>
<td>855.43</td>
<td>3.01</td>
</tr>
<tr>
<td>Residue</td>
<td>24</td>
<td>9966.22</td>
<td>415.26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>27</td>
<td>1075641.99</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3 – Tukey test parameters used to verify the volume fraction of mallow fibers that provided better Izod impact energy results.

<table>
<thead>
<tr>
<th>Degrees of freedom from waste (DF)</th>
<th>Amplitude studied (q tab.)</th>
<th>Average Residual Square (ARS)</th>
<th>Number of repetitions of each treatment (r)</th>
<th>Minimum significant difference (m.s.d)</th>
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</thead>
<tbody>
<tr>
<td>24</td>
<td>4.17</td>
<td>415.26</td>
<td>7</td>
<td>32.12</td>
</tr>
</tbody>
</table>

Fig. 5 – Izod impact energy versus percentages of mallow fibers.

The macrographs of Fig. 6 reveal the tendency of brittle fracture in the 0 and 10 vol% specimens, and the evolution to a more ductile fracture of the composites with fiber volume fraction of 20 and 30%.

Fig. 7(a) shows the SEM micrograph for the plain epoxy control specimen, which presents a completely brittle fracture mechanism, revealed by the presence of river-mark patterns. In fact, cracks propagate transversely and catastrophically in both the plain epoxy composite and the 10 vol% fiber composites, Fig. 7(b). In these cases, there should be no effective reinforcement with the incorporation of mallow fibers, as suggested by the work of Harish et al. [33] in coir composites.

For the 20 vol% composites shown in Fig. 7(c), a greater participation of the fibers is observed in the fracture mechanism, evidencing ruptured and detached fibers from the matrix, by delamination and pull-out effect, in association with a higher impact energy absorption, as presented Table 1. Fig. 7(d), for the 30 vol% composite, shows not only fibers rupture but also delamination by their interfacial detachment from the epoxy matrix. This combination of failure mechanisms allowed the absorption of higher impact energy as compared to other volume fractions tested. These results agree with the observations of other authors who also carried out impact tests in PMCs [34–36]. An overall analysis of Fig. 7 indicates that for the control specimen (0 vol%) as well as 10 vol% of mallow fiber in epoxy composites, a predominantly brittle fracture occurred, mainly in the epoxy matrix in association with relatively low value of Izod impact energy absorption. At 20 and 30 vol%, fracture is now concentrated in the rupture of flexible mallow fibers and delamination at the fiber/matrix interface. With increasing volume fraction, the mallow fibers act as effective barriers that arrest or deviate matrix cracks and consequently increase the absorbed impact energy [29]. Thus, a related much higher energy, 498.86 J/m, is absorbed by the 30 vol% mallow fiber reinforced epoxy composites.

3.2. Bend tests

Table 5 presents the results obtained for the 3-point bending test in reinforced composites with continuous and aligned mallow fibers. An earlier work on natural fiber PMCs reported that the mechanical strength and flexural modulus increased with the percentage of incorporated fibers [37]. Indeed, both
the strength and flexural modulus raise with increasing percentage of fibers incorporated in the composites, as shown in Figs. 8-10. Typical load vs. deflection curves for the 3-points bending tested epoxy composites with different amounts of mallow fiber (0, 10, 20 and 30 vol%) are shown in Fig. 8. In this figure, it is important to note that both graphs, for plain epoxy (0 vol%) and 10 vol% mallow fibers, are limited by the end of the linear elastic regime, which characterizes a total brittle behavior. By contrast, graphs for 20 and 30 vol% in Fig. 8 display characteristic plastic curved region beyond the linear elastic regime. This partial ductile behavior might be assigned to the predominant rupture of mallow fibers, as further discussed.

Another evidence of brittle transition from 10 to 20 vol% mallow fiber composites is also revealed in Fig. 9. Indeed, a steeper change in strength, Table 5, from 10 vol% (80.47 MPa) to 20 vol% (138.84 MPa) with a greater slope of $5.9 \times 10^2$ (MPa/vol%) is an indicative of this transition. To a less extent, a similar evidence might also exist in the flexural modulus in Table 5.

The macrographs in Fig. 11 illustrates the specimens after the 3-point bend test. A visual analysis of the fracture surfaces reveals the occurrence of typically brittle mechanisms acting up to a mallow fibers percentage of 10 vol%. From this percentage on, it was observed that the fibers act as effective reinforcement of the composite (20 and 30 vol%), due to mechanisms such as fiber fracture and fiber detachment at the fiber-matrix interface.

SEM images in Fig. 12 demonstrate additional microstructure fracture mechanisms involved in the bending tests. For plain epoxy control specimens, Fig. 12(a), the predominance of the completely brittle fracture mechanism, characterized by the presence of patterns such as river-marks, is disclosed. In Fig. 12(b), for 10 vol% composites, the fiber participation was not yet effective, which made the brittle fracture mechanism still dominant in the composite [31].

For composites with 20 and 30 vol% of mallow fibers, Fig. 12(c) and (d), respectively, an effective participation of the fibers was observed in the fracture mechanism. This is evidenced by ruptured and detached fibers from the matrix (pull-out effect). Fiber reinforcement was confirmed by the significant increase in flexural strength and modulus, Table 5, in association with evidences of change in failure mechanism from brittle (0 and 10 vol%) to partially ductile (20 and 30 vol% of mallow fibers) shown in Figs. 8–11. These results are consistent with those reported.
in the literature for bend tested NLFs polymer composites [34–36].

Similar to the Charpy [29] and the present Izod impact absorbed energy results, Table 1 and Fig. 5, the bend test results in Table 5 and Figs. 8–10 raised a question regarding the possible reinforcement effect in a polymer matrix incorporated with a NLF. Indeed, as any non-treated hydrophilic NLF, the mallow fiber might have a weak bonding with a hydrophobic epoxy matrix [1–13]. However, strengthening mechanisms, such as epoxy cracks arrest by the mallow fiber, Fig. 12(c), and the relatively higher ultimate fiber strength, 309 MPa [23], retarding is rupture, Fig. 7(d), prevail over detachment, delamination and pull-out events, also illustrated in Figs. 7 and 12.

The ANOVA was also applied to verify the occurrence of differences between flexural strength, Table 6, and flexural modulus, Table 7, results obtained for the distinct mallow fiber reinforced epoxy composites.

Based on the data obtained from the analysis of variance in Tables 7 and 8, the hypothesis that the averages were equal with a level of significance of 5% was rejected. Indeed, by the
Table 6 – Variance analysis of flexural strength for reinforced epoxy composites with 0, 10, 20 and 30 vol% with mallow fibers.

<table>
<thead>
<tr>
<th>Variations causes</th>
<th>DF</th>
<th>Sum of squares residues</th>
<th>Average squares residues</th>
<th>F (calculated)</th>
<th>F critical (tabulated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treatments</td>
<td>3</td>
<td>92672.28</td>
<td>30890.76</td>
<td>77.73</td>
<td>3.01</td>
</tr>
<tr>
<td>Residual</td>
<td>24</td>
<td>9537.74</td>
<td>397.41</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>27</td>
<td>102210.02</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 10 – Variation of the flexural modulus with percentages of mallow fibers acting as reinforcement in epoxy matrix composites.

The Tukey test for comparison of average statistic test, $F$ (calculated) $(77.73) > F$ (critical) or (tabulated) $(3.01)$, for the flexural strength and $F$ (calculated) $(88.82) > F$ (critical) or (tabulated) $(3.01)$ for the flexural modulus. Therefore, the volume fraction of mallow fibers in the epoxy matrix composites showed different effects on flexural strength and flexural modulus. The Tukey test for comparison of average

was applied using a 95% confidence level to verify which volume fraction of mallow fibers gave better results in terms of bend mechanical properties. The less significant differ-

Fig. 11 – Specimens of epoxy matrix composites reinforced with mallow fibers in percentages of 0, 10, 20 and 30 vol%, after 3-point bending test.

Fig. 12 – Scanning electron microscopy of the fracture surfaces of the composites reinforced with mallow fibers, after bending test (500x). (a) 0 vol%; (b) 10 vol%; (c) 20 vol% and (d) 30 vol% of fibers.
ence (LSD) found was 31.42 and 1.47, respectively for flexural strength and flexural modulus. Table 8 for the flexural strength and Table 9 for flexural modulus show the results obtained for the differences between the average values of the properties studied in each volume fraction of mallow fibers.

These results also indicate that the composite reinforced with 30 vol% of mallow fibers displays a better performance, since it exhibited a higher value of flexural strength (191.27 MPa) and flexural modulus (10.9 GPa). These are significantly distinct from the others, because the differences found were higher than LSD (31.42 and 1.47, respectively).

Together with the ANOVA and Tukey test results for Izod tests (Tables 2-4), similar statistical results for both flexural strength (Tables 6 and 8) as well as flexural modulus (Tables 7 and 9) prove for the first timewith 95% of confidence level that, in fact, the incorporation of mallow fibers reinforces the epoxy matrix. This reinforcement effect of the mallow fiber incorporation into epoxy matrix composites was also confirmed by other works on distinct NFLs incorporated into polymer matrices [35-38].

4. Conclusions

- Izod Impact absorbed energy and 3-points bend test were performed in DGEBA/TETA epoxy composites incorporated with continuous and aligned mallow (Urena lobata) natural fibers.
- A substantial increase was found for the Izod impact absorbed energy from the plain epoxy control (1.93 J/m) to 30 vol% incorporated mallow fiber (34.67 J/m).
- Macroscopic and SEM microscopic observations revealed a transition from total brittle (0 and 10 vol%) to partially ductile (20 and 30 vol%) fracture. In spite of weak mallow fiber/epoxy interfacial bonding, the greater participation of flexible mallow fibers as well as delamination mechanism contribute to the marked reinforcement.
- A significant increase in flexural strength (191.27 MPa) and modulus (10.90 GPa) for the 30 vol% composite was also found in comparison with plain epoxy (36.6 MPa and 3.12 GPa), respectively.
- Bend curves and steeper results between 10 and 20 vol% also indicated a brittle to partial ductile transition in the quasi-static flexural properties.
- Fracture characteristics observed in both macroscopic specimens and SEM samples, revealed prevailing brittle epoxy matrix rupture (0 and 10 vol%) changing to mostly mallow fiber break together with delamination mechanism. These are similar to the fracture mechanisms observed in Izod tests.
- In both tests, Izod and 3-points bend, ANOVA and Tukey statistical analyses prove, with 95% of confidence level, that the incorporation of mallow fibers increasingly reinforces the epoxy matrix. Although similar results have been reported for other impact and bend tested natural fiber composites, this increasing reinforcement is for the first time statistically proven.

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 as well as UENF for supplying the mallow fibers.

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