Polymer composites reinforced with natural lignocellulosic fibers, obtained from different parts of plants, have been extensively investigated in hundreds of works that were discussed in several review articles\textsuperscript{1-13}. It is currently recognized that, as composite reinforcement, the lignocellulosic fibers may compete with synthetic ones, such as glass fiber\textsuperscript{14,15}, in terms of economical, technical, societal and environmental advantages. In fact, the engineering application of lignocellulosic fibers is considered an environmentally friendly alternative to replace more expensive, non-recyclable and energy-intensive synthetic fibers\textsuperscript{16}. Important industrial sectors, from packing and sport appliances to house construction and automobiles\textsuperscript{17-19}, are already using lignocellulosic fiber reinforced composites in components. However, some drawbacks such non-uniform dimensions and heterogeneous properties as well as incompatibility with a hydrophobic polymer matrix, reduce the potential of lignocellulosic fiber to be used as composite reinforcement\textsuperscript{11}. In particular, a low interfacial strength causes a weak adhesion between the hydrophilic fiber and the polymeric matrix\textsuperscript{12}.

In Brazil, the variety of lignocellulosic fibers is an additional motivation for the study of new polymer composites reinforced with these fibers\textsuperscript{20}. Among them, attention is now being focused on that extracted from the stem of the malva plant, Figure 1, originally from Asia and today cultivated in meadows of rivers, particularly in the Amazon region. The malva, also known as mallow, belongs to the \textit{malvaceae} family, which comprises several species, such as the \textit{Malva sylvestris} and the \textit{Urena lobata} L.. Its fiber has been of economical interest for textile and simple items production in low-income areas. Review papers\textsuperscript{1,13} indicate the malva fiber as composite reinforcement. Preliminary tests with malva fiber revealed tensile strength of 214-497 MPa and Young’s modulus of 8.8 GPa. These values are superior than traditional natural fibers, such as bamboo and coir\textsuperscript{16}. A Fourier Transform Infra-Red spectroscopy analysis was also reported for the malva fiber\textsuperscript{22} showing particular bands not found in other lignocellulosic fiber. The incorporation of malva in polyester composites improved the dynamic mechanical viscoelastic stiffness\textsuperscript{23}. A photoacoustic thermal characterization\textsuperscript{24} showed that the malva fiber is a good thermal insulator. Pullout tests found a malva fiber critical length of 2.6 mm and interfacial shear strength of 3.1 MPa with respect to an epoxy matrix\textsuperscript{25}.

Despite these recent investigations, the mechanical properties are yet to be evaluated for the malva fiber polymer composites. These properties are basic requirements for any engineering application. Therefore, the objective of this work was, for the first time, to investigate the mechanical behavior of composites reinforced with malva fiber by evaluating their flexural properties.

\textbf{Keywords:} epoxy composite, malva fiber, flexural behavior, fracture analysis
2. Experimental Procedure

2.1. Materials

The malva fiber investigated in this study was of the species *Urena lobata* L., commercially supplied by the Brazilian firm Castanhal Textil. Figure 2 illustrates the as-received bundle of malva fibers as well as some long and continuous fibers separated for composite reinforcement. As the composite matrix, a diglycidyl ether of the bisphenol A (DGEBA) epoxy resin with equivalent weight of 187.3 g(eq) mixed with triethylene tetramine (TETA) as hardener in stoichiometric proportion of parts per hundred, phr, 13 was used.

2.2. Methods

2.2.1. Preparation of composites

The as-received fibers were cleaned and dried before use. Composites with 0, 10%, 20% and 30% in volume of aligned malva fibers were manufactured through accommodation of the fibers in a 152 × 122 × 10 mm rectangular mold and mixed with the DGEBA/TETA epoxy resin. The mold was kept under pressure of 20 MPa at room temperature (RT) for 24 hours for curing the resin. The cured rectangular plates were cut into 6 specimens with dimensions of 122 × 25 × 10 mm, maintaining the fiber aligned along the length.

2.2.2. Testing

The specimens were RT three points bend tested in a model 5582 Instron machine with 100 kN of capacity at a strain rate of $1.6 \times 10^{-2} \text{ s}^{-1}$ and a span-to-depth ratio of 9, according to the ASTM D790-03 norm. The flexural rupture strength, $\sigma_f$, was calculated by the following equation:

$$\sigma_f = \frac{3F_mL}{2bd^2}$$

where $F_m$ is the maximum applied load until rupture, $L$ the distance between supports, $b$ and $d$ are the width and thickness of the specimen, respectively

2.2.3. Fractography

The fracture surface of the specimens was characterized after gold sputtering by scanning electron microscopy, SEM, in a model 6460 LV Jeol microscope, operating at a voltage of 20 kV for the secondary electron beam.

Figure 1. Malva plant (a) and fibers drying after extraction (b).

Figure 2. Bundle of malva fibers (a) and separated long and continuous fiber for composite reinforcement (b).
3. Results and Discussion

3.1. Flexural testing

Figure 3 illustrates the typical appearance of load vs. elongation curves obtained in bending tests for epoxy composites reinforced with different amounts of malva fibers. These curves were recorded directly from the Instron machine and revealed that malva fibers reinforced epoxy composites present limited plastic deformation, with a tendency for rupture just beyond the elastic limit. After an approximately straight line, a sudden fracture occurs, indicating a brittle behavior for both pure epoxy and malva fiber composites. This is mainly a consequence of the limited plasticity of the brittle epoxy matrix. From the curves in Figure 3, the value of the maximum loads, $F_{\text{m}}$, and the corresponding deflection were obtained. The flexural rupture strength was then calculated by the Equation 1, while the deflection to rupture and the flexural elastic modulus obtained from corresponding curves and stress/strain ratio.

Figure 4 shows the variation of the flexural rupture strength of the neat epoxy as well as the epoxy matrix composites reinforced with up to 30 vol% of continuous and aligned malva fibers. In this figure, it is worth noticing the significant reinforcement caused by incorporation of continuous and aligned malva fibers into the epoxy matrix. Indeed, up to 30 vol% an increasing straight (dashed) line can be adjusted to the experimental points. Based on the principles of fiber reinforcement[24] the results in Figure 4 are expected since the strength of the malva fibers, 214-497 MPa[22], is considerably higher than that of the epoxy matrix, 28-90 MPa.

Figure 5 displays the variation of total deflection until rupture for the neat epoxy specimen and for the epoxy matrix composites reinforced with up to 30 vol% of continuous and aligned malva fibers. One should note in this figure that there is a tendency to decrease the total deflection with the incorporation of malva fiber. However, within the standard deviations (error bars) this decrease is negligible and might not be assigned to any particular mechanism.

Figure 6 shows the flexural modulus of elasticity dependence on the volume fraction of incorporated malva fibers in epoxy matrix composites. It should be noticed in Figure 6 that, similar to Figure 4, there is a clear linear tendency between the flexural modulus of elasticity and the volume fraction of malva fibers. A sharp rise in flexural modulus indicates a marked increase in bending stiffness of the epoxy matrix by the incorporation of malva fibers. This increase is comparable to that obtained for the flexural rupture strength in Figure 4. Indeed, any elastic modulus is measured as the ratio between the stress and corresponding strain inside the initial elastic stage. Consequently, the stiffness is directly dependent on the strength. Since the strain, which in the case of a bend tests is associated with the deflection, does not show much change with incorporated malva fiber, Figure 5, then one should expect the same linear type of relation for both strength and flexural elastic modulus as actually shown in Figures 4 and 6. In fact, the elastic modulus of the malva fibers, of 8.8 GPa, is much higher than that of

![Figure 3](image-url) Load (N) versus deformation (mm) curves, for malva/epoxy composites with different amounts of malva fibers: (a) 0%; (b) 10%; (c) 20% and (d) 30% in volume.
the epoxy matrix, around 2 GPa. Based on the theory of fiber reinforcement, this justifies the marked linear increase in stiffness observed in Figure 6.

A simple explanation for the linear relationship found in the variation of the flexural strength ($\sigma_f$), Figure 4, and flexural modulus ($E_f$), Figure 6, can be given by the Rule of Mixtures applied to composites reinforced with continuous and aligned fibers:

$$\sigma_f = \sigma_m(1-v_f) + \sigma_f v_f \quad (2)$$

$$E_f = E_m(1-v_f) + E_f v_f \quad (3)$$

where $\sigma_m$ and $E_m$ are the strength and modulus of the matrix; $\sigma_f$ and $E_f$ the tensile strength and modulus of the fiber; and $v_f$ the volume fraction of the fiber.

Figure 7 compares the experimental results for the: (a) flexural strength, Figure 4, and (b) flexural modulus, Figure 6, with corresponding Equations 2 and 3. The plots of these equations extend to the limit values obtained for the tensile strength, 214-497 MPa, and the tensile modulus, 8.8 GPa, of malva fibers. It is important to note in Figure 7 that the extension of experimental points linear adjustment reaches the corresponding values of strength and modulus of the neat (100%) malva fibers.

The Rule of Mixtures was previously applied in bend test results of polyester composites reinforced with two different lignocellulosic fibers: curaua and piassava. In both cases, the flexural strength followed straight lines similar to that shown in Figure 4. A relevant distinction occurred for the curaua fiber, which fails to match its theoretical Rule of Mixtures.
Mixtures line, Equation 2, due to fiber surface conditions. On the contrary, the piassava fiber experimental results fit well the Rule of Mixtures, Equation 2, owing to the improved fiber adherence. In the case of malva fibers, the experimental results, Figure 7, fit well the Rule of Mixtures for the lower value of fiber tensile strength. This agrees with the fact that the lower malva fiber tensile strength, 214 MPa, is associated with fibers with thicker diameter and more defects. The lower strength of the thicker fibers in the present work, using fibers with different diameters, will be the limitation of the composites strength.

3.2. Fractography

Fracture analysis contributes to explain the improvement provided by the malva fiber reinforcement to the epoxy matrix of the investigated composites. Figure 8 displays the SEM fractograph of a bend tested sample of neat epoxy, i.e., 0% of malva fiber. In this figure, one should note the brittle aspect of the rupture, with river patterns corresponding to crack propagation without obstacle. This is responsible for a relatively low breaking load, Figure 3a, and corresponding lower flexural rupture strength, as shown in Figure 4.

The incorporation of malva fiber causes composite reinforcement in association with changes in the fracture behavior. Figure 9 shows SEM fractographs of bend tested epoxy composites reinforced with 10, 20 and 30 vol% of aligned malva fibers. The main point to be observed in this figure is the well adhered malva fiber into the epoxy matrix. Indeed, only few holes associated with fiber pullout were detected. Moreover, the fractured epoxy in between the fibers displays evidence of crack being arrested at the fibers interface. This is strongly demonstrated by the broken matrix around a fiber in Figure 9a.

In particular, the homogeneous distribution of fibers throughout the fracture surface and their good adherence to the epoxy is illustrated, with lower magnification for the 30 vol% malva fiber composite, in Figure 10. In the figure inset, typical river patterns indicate (arrow) a crack arrest by a malva fiber. This corresponds to a strengthening mechanism, which improves the mechanical properties of natural fiber reinforced polymer composites and justifies the results shown in Figures 4, 6 and 7. As previously discussed, a good fiber adherence to the polymeric matrix is the basic condition for the match between the experimental results and the Rule of Mixtures, as shown in Figure 7, for both flexural strength and modulus.

4. Final Remarks

As a final remark, the novel flexural results of epoxy matrix composites incorporated with up to 30 vol% of continuous and aligned malva fibers revealed a significant reinforcement effect. Both the flexural strength and the flexural modulus, which is associated with the composite stiffness, increase with the amount of malva fiber, according to linear relationships that match the corresponding Rule of Mixtures fundamental equations. This is an unique result that not only confirms the best possible reinforcement of the malva fibers to the epoxy but also indicates an effective adhesion between fiber and matrix.
5. Conclusions

- Bend tests performed on epoxy matrix showed a linear increase in both flexural rupture strength and flexural modulus of elasticity up to 30 vol% of continuous and aligned malva fibers.
- These strength and modulus linear relationships match with the fundamental Rule of Mixtures and indicate the best possible reinforcement, which is an unique behavior and most convenient for engineering application.
- SEM fractographic analysis confirms not only an effective adhesion of the malva fiber to the epoxy matrix but also the crack arrest by the fiber that contributes to the superior flexural reinforcement behavior.

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