Processing and properties of continuous and aligned curaua fibers incorporated polyester composites

Sergio Neves Monteiro\textsuperscript{a,*}, Felipe Perisse Duarte Lopes\textsuperscript{b}, Denise Cristina Oliveira Nascimento\textsuperscript{b}, Ailton da Silva Ferreira\textsuperscript{b}, Kestur Gundappa Satyanarayana\textsuperscript{c}

\textsuperscript{a}Materials Science Department, Instituto Militar de Engenharia (IME), Rio de Janeiro, RJ, Brazil  
\textsuperscript{b}Universidade Estadual do Norte Fluminense Darcy Ribeiro (UENF), Advanced Materials Laboratory (LAMAV), Campos dos Goytacazes, RJ, Brazil  
\textsuperscript{c}Acharya Institutes, BMS College of Engineering & Poornapragna Institute of Scientific Research, Bangalore, India

\textbf{ABSTRACT}

This paper presents systematic studies carried out on the processing and characterization of continuous and aligned curaua fibers-polyester composites. Laminates of these composites with (0 to 40 vol. \%) curaua fibers were press-molded at room temperature, cured for 24 hours and tested for strength properties. Resulting fracture surfaces were analyzed by scanning electron microscope. Composites showed high flexural properties, which is attributed to a complex mechanism of individual interaction of the microfibrils with the matrix during crack initiation and further propagation through a model of stress concentration due to the specific fiber/matrix interface geometry. Impact test results showed a remarkable increase in the notch toughness with the amount of incorporated curaua fibers, which is attributed to the difficulty of breaking down the fibers and preferential de-bonding of the fiber/matrix interface, which in turn contributes to an elevated absorbed energy.

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\textbf{1. Introduction}

Amongst the various natural fibers available in Brazil, increased attention is being given to the curaua fibers, particularly in recent times [1-13]. These fibers are extracted from the leaves of a plant (\textit{Ananas erectifolius}), identified with the family of the pineapple, native of the Amazon region. The curaua fiber is relatively soft, nevertheless it is one of the natural lignocellulosic fibers with potential as polymer composite reinforcement [3,4,8,10-13]. In addition to their conventional use in nets, blankets and carpets, curaua fiber reinforced composites are already being applied in the automobile industry [14,15]. Both interior and exterior components are already on the market and a major reason is the technical advantage of a higher impact resistance. This is of great importance in case of a crash event and applies equally for an automobile headrest or a cyclist helmet.

Strength properties of polymer composites containing short/chopped curaua fibers are reported to be relatively higher [16]. Since long and aligned fibers provide greater resistance to applied loads in composites, [17] the use of continuous and aligned curaua fibers as reinforcement for polyester composites, both in terms of processing and properties is the main objective of this work.
The unique microstructure of each curaua fiber shows a bundle of microfibrils, which may assist in adhesion to the polymeric matrix [7]. However, the mechanism of the observed rupture of these microfibrils is still not clear. Thus, another objective of this work was to investigate the rupture mechanism responsible for the flexural fracture of polyester composites reinforced with different amounts of curaua fiber. This investigation was carried out without any fiber treatment, with a view to minimize the cost of the final product.

A critical length value of 10.2 mm, measured in pullout test [18], indicates that curaua fiber with length above 150 mm should be considered as long enough for composite reinforcement. On the other hand, this value of the critical length of curaua fiber is associated with a low interfacial resistance of fiber/polymer, which makes it very favorable for use in impact resistant applications. Higher impact strength of curaua-polyester composite can be expected considering the fact that a composite with low interfacial strength has an inefficient transfer of energy from the matrix to the fiber, requiring more energy to break. This is because a large energy will be devoted to the breaking of extensive delaminated interfaces. Moreover, the cracks formed in pullout test of the fiber tend to branch out [19]. A large number of cracks lead to a greater area of fracture, and hence higher energy associated with the toughness of the composite. It is therefore expected that polymer composites reinforced with long fibers of curaua would be relatively tougher.

It is well reported [20] that impact resistance of polymeric composites with short and randomly oriented lignocellulosic fiber reinforcements, tested with notched and fixed Izod specimens resulted in absorbed energy values lower than 60 J/m for all fibers investigated with polypropylene as matrix. Recent studies by the authors on the impact resistance of thermostet polymer composites reinforced with long and aligned lignocellulosic fibers [21-25], revealed a much higher value for the impact energy. In particular, polyester composite reinforced with 40% of curaua fiber exhibited value of 170 J/m [22], which is more than three times the maximum obtained by any short and randomly oriented lignocellulosic fiber composites [20]. This remarkable result served as motivation for this work to confirm it with the Charpy test.

According to the ASTM D 256 norm, there are significant differences between both Charpy and Izod tests [26] that could lead to distinct results. In practice, the Izod test simulates the actual situation of a component fixed into a system, which is hit at a point away from a stress raiser like a groove or a flange. By contrast, the Charpy test simulates a component free standing in a base, which is hit at the same level of a stress raiser. Hence, still another objective of this work was to evaluate the impact resistance of polyester-matrix composites reinforced with different percentages of continuous and aligned curaua fibers by both Charpy and Izod impact methods.

2. Experimental procedure

2.1. Materials

Curaua fibers were obtained from a commercial plantation in the state of Pará, located in the Amazon region, north of Brazil. The length and diameter of the fibers were statistically evaluated from a random lot of 100 fibers using the histogram shown in Fig. 1. These dimensions of the curaua fibers are similar to that observed in any other lignocellulosic fiber [27] with heterogeneity and significant dispersion in values. From these, average values for length (L) and diameter (d) were found as 846 mm and 0.07 mm, respectively, with this length being more than 15 times its critical length of 10.2 mm [18]. This is considered a condition for long and continuous fiber in terms of composite reinforcement, which assures an effective strengthening of the matrix [28]. The as-received curaua fibers were cleaned with water and dried in an oven at 60 °C for 24 hours. As matrix, an unsaturated orthophthalic type polyester, hardened with 0.5% of methyl ethyl ketone catalyst, was used.

2.2. Methods

Polyester matrix composites were prepared with different amounts, up to 40% in volume of curaua fibers. Rectangular plates of size 152 × 122 × 10 mm composites were molded by mixing long and aligned curaua fibers with the resin and
catalyst/hardener mentioned. To ensure that the desired amount of curaua fibers were placed throughout the length and width of 122 mm of the mold, additional amount of polyester resin mixed with the catalyst was added with the fibers. A pressure of 0.53 MPa was applied on the mold during the curing time of 24 hours to facilitate the impregnation of resin through the fibers. After curing, the laminate was cut into 6 specimens parallel to the fibers.

Specimens with $112 \times 25 \times 10$ mm of dimensions were subjected to 3 points bend test in an Instron testing machine (model 5582) with 1 kN load cell at a strain rate of $1.6 \times 10^{-2}$ s$^{-1}$. The test span-to-depth ratio was kept as 9, which is within the range required by standard for this type of test [29]. Based on the maximum load value of $Q_m$ obtained in each test, the maximum stress associated with the resistance of the composite was calculated using the equation:

$$\sigma_m = \frac{3LQ_m}{2bd^2}$$  \hspace{1cm} (1)

where $L$ is the distance between supports equal to 90 mm, width $b$ equal to 25 mm and thickness of 10 mm. Then, the experimental flexural strength was determined by the equation:

$$\sigma_e (\text{MPa}) = 54 \times 10^{-3} \frac{Q_m (\text{N})}{s}$$  \hspace{1cm} (2)

where $Q_m$ was the maximum load attained during the test.

Samples of dimensions $125 \times 12.7 \times 10$ mm and $63 \times 12.7 \times 10$ mm were cut in the direction of alignment of the fibers for Charpy and Izod impact tests, respectively, according to ASTM D256 [26]. Notches of 2.54 mm deep with 45° angle and radius of curvature of 0.25 mm at the bottom of the notch were made using a German steel mill as per DIN 847 standards. The samples were tested using EMIC machine in respective configurations with appropriate pendulum hammer. The impact energy was obtained with 2.7 J hammer for the 25% and 30% curaua fiber composites. For pure polyester specimens up to 20% curaua fiber, and with a 5.4 J hammer for the 25% and 30% curaua fiber composites. In each composition, 10 samples were tested to ensure statistical validation.

Fracture of the composites was analyzed using gold sputtered tested composite surfaces by scanning electron microscopy (SEM) in JEOL microscope (model JSM-6460 LV), imaging between 15 and 20 kV.

3. Results and discussion

3.1. Flexural strength

Fig. 2 presents the variation of the flexural strength of the composites as a function of the volume fraction of curaua fibers. In this figure a straight line is drawn from the strength of the pure polyester resin, corresponding to $V_f = 0$ vol.% to the tensile strength of the curaua fiber reported elsewhere [1]. This value of the fiber strength was considered as the other linear limit at $V_f = 100$, of the rule of mixtures [28] for the composite strength ($\sigma_f$):

$$\sigma_f = \sigma_c (1 - V_f) + \sigma_i V_f$$  \hspace{1cm} (3)

where $\sigma_c$ is the polyester strength and $\sigma_f$ the curaua fiber strength.

The experimental values for the composite strength in Fig. 2 can be adjusted with a dashed straight line within the experimental values (up to 50 vol.%). A comparison of this experimental line with the predicted solid line of the rule of mixtures indicates that a difference exists between the theoretical value, calculated by this rule and the corresponding experimental value:

$$\Delta \sigma = \sigma_e - \sigma_f = 2.8 V_f$$  \hspace{1cm} (4)

Eq. (4) shows that the experimental values can be almost three times lower than the theoretical maximum given by the rule of mixtures. Although many factors should affect the experimental values, the main reason for this difference might be the stress concentration at the fiber/matrix interface.

The special configuration of the microfibrils that compose each curaua fiber, shown in Fig. 3, could be responsible for a significant stress concentration at the fiber/matrix interface. The model presented in Fig. 4a simulates each curaua fiber as a set of close-packed parallel cylinders corresponding to the microfibrils observed in Fig. 3. In Fig. 4b it can be seen a transversal section of the modeled fiber where each fiber is composed of several microfibrils, probably more than 50. This results in sharp reentrants, enlarged in Fig. 4c. Considering that the resin (grey region) occupies the reentrants space in Fig. 4a, this would correspond to a stress concentration $\sigma_i$ at the interface given by [29]:

$$\sigma_i = \sigma_0 \left[1 + 2 \frac{a \rho}{r} \right]^{1/2}$$  \hspace{1cm} (5)

where, $\sigma_0$ is the applied stress in the composite, ‘a’ and $\rho$ are the depth and radius of curvature of the reentrants respectively. Then, for the condition $a = 0$, in Fig. 4c,

$$\sigma_i = 3\sigma_0$$  \hspace{1cm} (6)
Eq. (6) indicates that it is possible to have a reduction of up to three times the theoretically predicted value of the composite strength, given by Eq. (4), owing to the stress concentration caused by the reentrants in the fiber surface on the polyester matrix seen in Figs. 4b and 4c. The difference between the predicted strength and the experimentally obtained, 2.8 $V_f$ in Eq. (4), is in reasonable agreement with the reduction of three times caused by the stress raisers at the fiber/matrix interface. One reason for the small discrepancy between Eq. (6) and (4) can be attributed to the difficulty in attaining total penetration of the still fluid polyester resin into the edges of the reentrants during the processing of the composite.

It is possible to imagine that the filamentary morphology of the curaua fiber can contribute to the rupture of the composite by cracks developed through debonding of the microfibrils. An analysis of microstructural aspects of the interaction between curaua fiber and polyester matrix is presented in Fig. 5. It is verified that curaua fiber is composed of several microfibrils, Fig. 5a, as in other lignocellulosic fiber. During the application of load, some of these can break while others remain intact. This clearly indicates that a single curaua fiber acts itself as a mini-natural composite with relatively long and continuous microfibrils [27], each one capable of absorbing the load transferred from the matrix. It was observed that while the microfibrils have not separated in the fiber, the polyester resin was fragmented, Fig. 5b. This suggests that, as long as the fiber is well embedded in the polymeric matrix, it is difficult to separate the microfibrils, which leads to efficient adhesion and ability to transfer mechanical load from the matrix to the entire fiber. In Fig. 5b, the fiber surface showed a number of microfibrils adhering to/coated with polyester. This highlights a topography of the microfibrils allowing the penetration of polyester between them while the latter was still in liquid stage during processing of the composite. Thus, besides the effect of continuous and aligned fiber, mini composites of microfibrils with an average diameter of 8mm may be formed, increasing the fiber surface to which they belong. Since these microfibrils can individually resist the mechanical load despite other microfibrils are already broken, observed strength levels, which are comparable with the values reported for other lignocellulosic fiber incorporated polymer composites [30], can be expected.
Fig. 5 displays the general aspect of the surface fracture of 30% curaua fiber-polyester composite, wherein some fibers adhering very well to the polyester matrix can be seen. These fibers suffered rupture at one end, while other fibers have been pulled out from the matrix and left holes in their original locations, which can be seen (marked by arrows). Most of the fracture surface, however, corresponds to a rupture associated with the polyester matrix. This corroborates the proposed mechanism of crack nucleating at the interface by stress concentration and propagating throughout the matrix, shown in Fig. 4c.

3.2. Impact tests

Fig. 6 shows the variation of Charpy and Izod impact energies, respectively, with the volume fraction of curaua fibers in polyester composites. It is observed that the incorporation of long curaua fiber into polyester matrix significantly increases the toughness of the composite. This increase with the amounts of fiber content, within the limits of standard deviation, can be considered linear up to 40% of fiber in the case of Charpy and an exponential function in Izod up to 30%. It is also important to

Fig. 5 – Morphology of Curaua fiber and its composite: (a) Tensile fractured curaua fiber; (b) fiber surface after detachment from the polyester matrix; (c) non-uniform rupture mechanism of a 30% curaua fiber reinforced composite.

Fig. 6 – Impact energy as a function of amount of curaua fibers. (a) Charpy impact energy; (b) Izod impact energy.
mention that in both types of impact tests, with increasing fiber fraction, relatively high dispersion of impact values is reflected with higher standard deviations, which is a consequence of non-uniform behavior and recognized as a characteristic of lignocellulosic fibers [27]. Further, the curves shown in Fig. 6 are consistent with the results reported in literature about impact strength values, since the reinforcement of polymer matrices with both synthetic [31] as well as natural fibers [21-25] increases the impact strength of composites.

In Table 1, the present results of both Charpy and Izod tests are compared with those values obtained [1,20-25,32] in notched specimens of various polymer-matrix composites reinforced with natural fibers. It can be seen that the both Charpy and Izod values obtained with the continuous and aligned curaua fibers are significantly higher than the values reported for polypropylene composites reinforced with 50% of short and randomly oriented lignocellulosic fibers and even continuous and aligned coir (40%)-polyester composites [1]. In the case of Charpy, it is almost 4 times that obtained for notched short curaua fibers-polypropylene composites in Izod impact test. Since this is not the proper way of comparison, the values with similar test with the present composite are also included for comparison. The greater impact resistance of the polyester in comparison with the polypropylene matrix could be one reason for the superior performance of the present result. However, there are other important factors related to the impact fracture characteristic of polymeric reinforced with continuous and aligned natural fibers.

The relatively low interface strength between a hydrophilic lignocellulosic fiber and a hydrophobic polymeric matrix contributes to an ineffective load transfer from the matrix to a longer fiber resulting in relatively greater fracture surface and higher impact energy needed for the rupture [19]. Another factor is the flexural compliance of a long fiber during the impact test, which will be further discussed.

It is also observed that the incorporation of continuous and aligned curaua fibers results in a marked change with respect to pure polyester (0% fiber) totally transverse fracture to the specimen axis (fiber alignment) occurs. Even with 10% fiber, the fracture is no longer completely transversal. This indicates that the cracks nucleated at the notch will initially propagate transversally through the polyester matrix, as expected in a monolithic polymer. However, when the crack front reaches a fiber, the crack/fracture will proceed through the interface. As a consequence, after the Charpy or Izod hammer hit the specimen, some long fibers will be pulled out from the matrix. This is illustrated in Fig. 7, which shows macro photographs of Izod tested samples. But owing to their compliance, most fibers will not break, but simply bend. In fact, for fiber contents above 10%, the area of fracture is not fully separated because a part is attached to the longitudinal part of the fibers. This indicates that the cracks generated in the notch by the impact, initially propagate transversally in the matrix, without the specimens being not separated at all as can be seen in this figure.

For these amounts of long curaua fibers, part of the specimen was bent enough to allow the impact hammer to continue its trajectory without carrying away the top part of the specimen, as expected in an impact tests. This is in accordance with the mechanism of fracture in composites with weak interfacial resistance [19]. Although it seems paradoxical,

<table>
<thead>
<tr>
<th>Composite system</th>
<th>Amount of fiber vol. (%)</th>
<th>Test Method</th>
<th>Impact strength (J/m)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Curaua/Polyester</td>
<td>40 (continuous &amp; aligned)</td>
<td>Charpy</td>
<td>170</td>
<td>Present work</td>
</tr>
<tr>
<td>Curaua/Polyester</td>
<td>30 (continuous and aligned)</td>
<td>Izod</td>
<td>190</td>
<td>Present work</td>
</tr>
<tr>
<td>Piassava/Polyester</td>
<td>40 (continuous)</td>
<td>Charpy</td>
<td>94</td>
<td>[21]</td>
</tr>
<tr>
<td>Coir/Polyester</td>
<td>40 (long &amp; aligned)</td>
<td>Izod</td>
<td>121</td>
<td>[25,32]</td>
</tr>
<tr>
<td>Curaua/Polypropylene</td>
<td>50 (short &amp; random)</td>
<td>Izod</td>
<td>54</td>
<td>[1]</td>
</tr>
<tr>
<td>Wood/Polypropylene</td>
<td>50 (short &amp; random)</td>
<td>Izod</td>
<td>28</td>
<td>[1]</td>
</tr>
<tr>
<td>Coir/Polypropylene</td>
<td>50 (short &amp; random)</td>
<td>Izod</td>
<td>46</td>
<td>[1]</td>
</tr>
<tr>
<td>Flax/Polypropylene</td>
<td>50 (short &amp; random)</td>
<td>Izod</td>
<td>38</td>
<td>[1]</td>
</tr>
<tr>
<td>Jute/Polypropylene</td>
<td>50 (short &amp; random)</td>
<td>Izod</td>
<td>39</td>
<td>[1]</td>
</tr>
<tr>
<td>Sisal/Polypropylene</td>
<td>50 (short &amp; random)</td>
<td>Izod</td>
<td>51</td>
<td>[1]</td>
</tr>
</tbody>
</table>

As a consequence, after the Charpy or Izod hammer hit the specimen, some long fibers will be pulled out from the matrix. This is illustrated in Fig. 7, which shows macro photographs of Izod tested samples. But owing to their compliance, most fibers will not break, but simply bend. In fact, for fiber contents above 10%, the area of fracture is not fully separated because a part is attached to the longitudinal part of the fibers. This indicates that the cracks generated in the notch by the impact, initially propagate transversally in the matrix, without the specimens being not separated at all as can be seen in this figure.

For these amounts of long curaua fibers, part of the specimen was bent enough to allow the impact hammer to continue its trajectory without carrying away the top part of the specimen, as expected in an impact tests. This is in accordance with the mechanism of fracture in composites with weak interfacial resistance [19]. Although it seems paradoxical,
a low interfacial resistance leads to higher toughness, because it increased the area of fracture and, consequently, greater energy is absorbed in impact. The value of the impact toughness in this case cannot be compared with others in which the specimen is totally split apart. Anyway, the fact that a specimen is not completely separated into two parts underestimates the impact toughness. In other words, had all the fibers been broken, the adsorbed impact energy would be higher. Fractograph evidences illustrate this rationale.

Fig. 8 presents the SEM analysis of the fracture surface of Charpy tested specimens and provides a better understanding of the mechanisms responsible for the high toughness of composites reinforced with continuous and long curaua fibers. In the case of pure polyester typical brittle fracture of a polymer was observed as reported elsewhere [22]. The propagation of a single crack, nucleated at the notch, caused the failure/collapse. The crack is associated with voids and imperfections formed during the processing.

Fig 8a shows an effective adhesion between the fibers and the polyester matrix, where cracks preferentially propagate. Some of the fibers were pulled out from the matrix, while others were broken during the impact. By contrast, the part of the specimen in which the rupture preferentially occurred longitudinally through the fiber/matrix interface, reveal that most of the fracture area is associated with the fiber surface.

Fig. 8b shows evidence of interfacial debonding. This behavior corroborates a mechanism of fracture through cracks that spread preferentially between the fiber and matrix due to low interfacial resistance [19]. The greater fracture area (Fig. 8) associated with the long and aligned fibers, acting as reinforcement for the composite, justify the higher absorbed impact energy (Fig. 6) with increasing amount of curaua fibers.

4. Conclusions

- The experimental values of the fracture stress, corresponding to the flexural strength of the continuous and aligned curaua fibers-polyester composites, cured at room temperature, are significantly lower than the theoretical value predicted by the rule of mixtures. The stress concentration determined by a geometrical model of the curaua fiber/polyester matrix interface is in reasonable agreement with the difference between theoretical and experimental values.
- The rupture mechanism in flexural tests of polyester matrix composites reinforced with aligned curaua fibers is related to the filamentary morphology of these fibers. However, most of the observed fracture surfaces of the composites correspond to the rupture of the polyester matrix as predicted by the model.
- The curaua composites show a significant increase in the notch toughness, measured in Charpy/Izod impact tests, particularly those with higher fiber contents. This increase in toughness is apparently due to the weak fiber/polyester interfacial shear stress. This results in a higher absorbed energy as a consequence of a longitudinal propagation of the cracks throughout the interface, which generates larger rupture areas.
- Increased notch toughness in composites with curaua fibers above 10% are associated with incomplete rupture of the specimen owing to the bend flexibility, i.e., flexural compliance, of the curaua fibers. Fractographic studies of tested impact specimens confirmed these findings.

Acknowledgements

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