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Curaua Fibers/Epoxy Laminates with Improved Mechanical Properties: Effects of Fiber Treatment Conditions

*Paulo H. M. Cardoso, Fernando L. Bastian, Rossana M. S. M. Thiré**

Summary: The use of lignocellulosic fibers as reinforcement in polymer composites has increased worldwide recently. Vegetal fibers have low cost and they are commonly available in Brazil. The curaua fibers in particular are of great importance for the development of the Amazon region. The mechanical behavior of the composites reinforced with fibers depends on the effectiveness of the transfer of the applied load by the matrix to the fibers, which is determined by the magnitude of the interfacial bonding between fiber/matrix phases. In this paper, curaua fibers were treated with 0.25–2% (w/v) NaOH solution under tensile loading to improve fiber-matrix adhesion in curaua fibers/epoxy laminates. Composites with 40 vol.% curaua fibers were obtained. Maximum improvement in the composite properties was observed for those containing curaua fibers treated with 0.5% NaOH under tensile loading. Composites with good bending properties were obtained by using a simple, low cost and environmental friendly method for curaua treatment. This method employed low concentration of chemical solutions, which are neutralized during the process, and no need of heating.

Keywords: composites; curaua fibers; epoxy; mechanical properties; modification of vegetal fibers

Introduction

Many of the current technologies require materials with combinations of properties that cannot be performed by traditional materials. The possibility of obtaining materials with high strength and low specific weight was one of the main reasons for the use of the polymeric composites in different areas. The environmental concerns have encouraged scientists to develop environmental friendly composite materials.[1–3]

The use of lignocellulosic fibers as reinforcement in polymer composites has been grown worldwide in order to replace synthetic fibers such as glass and carbon fibers.[1–3] These vegetable fibers provide many advantages over synthetic ones, such as low density, high flexibility, non-toxic, high deformation, easy processing, low cost, biodegradability and, in addition, they are obtained from renewable sources.[1–4] However, the lignocellulosic fibers have some disadvantages: they can only be used with low temperature processing, besides their hydrophilic character can induce high moisture absorption and makes them incompatible with several polymers (they are usually hydrophobic). This incompatibility affects the interface fiber-matrix adhesion, leading to composites with low mechanical strength.[2–4]

Lignocellulosic fibers are composed mainly of cellulose, hemicelluloses and lignin. Their hierarchical structure can be described as highly crystalline, spirally wound cellulose fibrils immersed in a matrix of amorphous hemicellulose and lignin. Cellulose content and the microfibrilar angle (the angle between the fiber axis and cellulose microfibrils) are the main contributors to the strength and stiffness of natural

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PEMM/COPPE, Federal University of Rio de Janeiro,
PO Box 68505, 21945-970, Rio de Janeiro, RJ, Brazil
E-mail: rossana@metalmat.ufrj.br

fibers. Some studies reported that higher cellulose content and/or lower microfibrilar angle usually lead to vegetal fibers with higher mechanical properties.[3,5,6]

In order to increase fiber-polymeric matrix compatibility and improve the interfacial adhesion, it is necessary to modify the surface of lignocellulosic fibers using chemical or physical treatments like alkaline treatment, coupling agents, plasma and others.[2–5] Alkaline treatment is frequently used due to its simplicity and economic viability. During this treatment, hemicellulose, lignin, pectin, wax and oil covering materials are partially eliminated, without affecting the cellulose fraction.[1] The effective alkaline concentration depends on the type of the fiber. However, concentrations near to 4–5 wt.% appear to be optimal concentration to improve the mechanical properties of different natural fibers.[6] In addition, the application of tension load during the alkali treatment can improve structural and mechanical properties of fibers by minimizing their shrinkage and decreasing the microfibrilar angle due to the orientation of cellulose microfibrils along the fiber axis.[1,7]

The major vegetal fibers used in composite materials are curaua, sisal, jute, ramie, bamboo, kenaf, bagasse, hemp and others. Some authors have been called attention to the main applications for these fibers such as: ropes, handcrafts, rugs, civil and automotive industries.[2–5] Curaua, *Ananas erectifolius* species, is originally from the Amazon region in Brazil. It is catalogued in the pineapple family/bromeliads.[1] These fibers are extracted from the plant's leaves. Some authors report their chemical composition is around 73.6% of cellulose, 9.9% of hemicellulose, 7.5% of lignin and 0.9% of ashes.[2,8] In Brazil, curaua fiber is produced especially in the State of Pará, where small communities grow them along with other crops, such as cassava, vegetables and beans. Thus, besides the environmental appeal, there is the social reason for seeking new applications for this fiber. Although it is recognized that curaua is one of the strongest and most flexible vegetal fiber,[8] there are few works in literature that investigate curaua fibers-reinforced thermoset resin composites.

The aim of this work was to evaluate the effect of NaOH solution concentration used in the treatment of curaua fibers on the bending properties of curaua fibers/epoxy composite laminates. The fibers were treated with low concentrated (0.25–2%(w/v)) of NaOH solution under tensile tension in order to produce composites with improved mechanical properties.

Experimental Part

Treatment of Curaua Fibers

Curaua fibers were obtained from native producers in Pará, Brazil. A bundle of curaua fibers was soaked in NaOH solution with different concentration (0.25, 0.5, 1 and 2% (w/v)) under 5 N of tensile loading, for each 1g of fibers with 1 m of length. One end of the fibers bundle was fixed with clamps and the tensile load was applied along the fibers length. The treatment was carried out at room temperature for 30 minutes. After this time, hydrochloric acid was used to neutralize the fibers immersed in the alkaline solution. Then, the fibers were rinsed several times with water and dried at room temperature.

Characterization of Curaua Fibers

The evaluation of the diffraction pattern of the fiber after modification was carried out with a XRD 6000 Shimadzu Diffractometer, operating with CuKα radiation ($\lambda = 0.1542\,\text{nm}$) at 30 kV and 30 mA. Scattered radiation was detected at room temperature in the angular region between $2\theta = 5^\circ$ and $2\theta = 50^\circ$ at a rate of 2°/min and a step size of 0.02°. The crystallinity index of the cellulose was calculated according to the Segal Method (Equation 1).[9]

$$I_c = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \qquad (1)$$

Where I_c is the crystallinity index of cellulose, $I_{(002)}$ the maximum intensity of the peak corresponding to the plane (002), and

I_{am} the intensity of the amorphous phase, which is considered the minimum intensity between the diffraction peak of the planes (002), at $2\theta = 22°$ and the diffraction peak of the planes (101), at $2\theta = 16°$.[9] Data were normalized using Kolmogorov-Smirnov test ($\alpha = 0.05$). Afterwards, Student t test with $\alpha = 0.05$ was used to assess the significance of the results of crystallinity degree.

The presence of lignin and hemicellulose in curaua fibers after treatment was verified by Infrared Spectroscopy Fourier Transform (FTIR). The analysis was performed in a Thermo Scientific Nicolet 6700 FT-IR spectrometer, ZnSe crystal and attenuated total reflectance (ATR) analysis was performed in the range of wavenumber of 650–4000 cm^{-1}, resolution of 4 cm^{-1} and 64 scans per sample. Helium pycnometry is an accurate method to measure the density of the fibers and porous materials. For this reason, the density of untreated and treated fibers was determined using a helium gas pycnometer (Quantachrome Ultrapycnometer 1000). Five measurements of each sample were conducted at 23 °C. Prior to the analysis, the fibers were dried in an oven at 100 °C for 1 h. The morphological analysis of the longitudinal section of the fibers was performed in a JEOL JSM 6460 LV scanning electron microscope at voltage of 15–20 kV. The samples were coated with gold prior to the analysis.

Manufacture of Composites

Composites with both untreated fibers and treated ones were prepared by manual lamination using a mechanical laminator.[10] Prior to the manufacture, the fibers were dried at 60 °C for 2 h. An epoxy system, MC130 resin and FD154 hardener, was supplied by the Epoxyfiber company (Rio de Janeiro, Brazil). The volumetric ratio of the components was 100:50 (epoxy:hardener), as recommended by the supplier.

Characterization of Composites

The volume fraction of fibers in the composites ($\%V_f$) was calculated based on the volume of the composites (Equation 2) and on the volume of the curaua fibers in the composites (Equation 3), according to the Equation 4.

$$V_c = \mathrm{W} \times \mathrm{L} \times \mathrm{T} \tag{2}$$

Where V_c, W, L and T correspond to the volume, width, length and thickness of the composites, respectively. W, L and T were measured with a digital caliper.

$$V_f = \frac{\mathrm{m}_f}{\rho_f} \tag{3}$$

Where V_f, m_f and ρ_f correspond to the volume, mass and density of fibers in the composites, respectively. ρ_f was determined by pycnometry, as previously described.

$$\%V_f = \frac{V_f}{V_c} \tag{4}$$

Where V_f correspond to the volume of fibers in the composites and V_c correspond to the volume of the composites.

Three-Points Bending Tests of the composites were carried out in an universal testing machine Instron model 5567 with electromechanical drive and cell load of 2 kN under a cross-head speed of 1 mm/min at room temperature. The experimental conditions and the specimen's dimensions followed the standard ASTM D7264–07 (*Standard Test Method for Flexural Properties of Polymer Matrix Composites)*, Procedure A. At least five specimens of each treatment were tested. The data were normalized using Kolmogorov-Smirnov test ($\alpha = 0.05$). Afterwards, Student t test with $\alpha = 0.05$ was used to assess the significance of the results. The morphological analysis of the composite laminates was performed in a JEOL JSM 6460 LV scanning electron microscope, at a voltage of 15–20 kV. The images of the fracture surface (Au-coated) were taken on specimens from the flexural tests.

Results

FTIR Analysis

Figure 1 shows the spectra of untreated and treated curaua fibers. All spectra show a

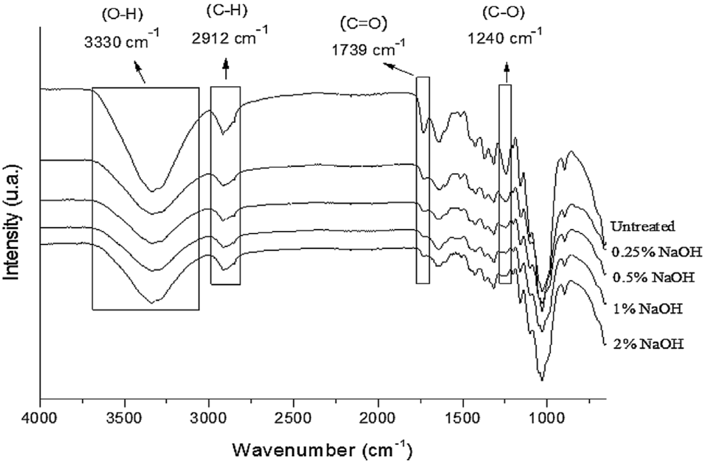

Figure 1.
FTIR spectra of curaua fibers subjected to treatment with different concentration of NaOH solution under tensile load application.

broad band at 3300 cm^{-1} related to O-H stretching which refers to hydrogen bonding present in the structure of amorphous cellulose and of water. The reduction in the intensity of these bands after treatment of the fibers may have been due to the breaking of hydrogen bonds of the amorphous cellulose molecules.[2,8,11] It is also assumed that the reduction of this band may be related to the reduction of water absorbed by the fibers after treatment due to the reduction of the hydrophilic character of these fibers.

The band 2912 cm^{-1} is related to symmetric and asymmetric C-H stretching of saturated hydrocarbons from cellulose and hemicelluloses.[8,11] Thus, the decrease of this band may be related to the partial removal of hemicellulose. The band of 1739 cm^{-1} which is associated with the C=O stretch of carboxylic acid and ester present in hemicelluloses was observed. Thus, the decrease of this band portrays the partial removal of this component.[2,12] The wavelength of 1240 cm^{-1} refers to C-O stretch of acetyl grouping present in hemicelluloses and lignin. Mitigation of this peak also indicates the partial removal of hemicelluloses.[1,11,12]

The bands 1510 and 1600 cm^{-1} are related to C=C vibration of aromatic rings present in lignin. However, these bands continued to be observed regardless of the concentration of the NaOH solution used.[12,13] It is known that lignin molecules are more resistant to chemical attack due to the presence of strong C—C linkages and aromatic groups.

These results suggested that all treatments promoted partial removal of only hemicellulose.

X-Ray Diffraction

XRD was performed in order to investigate if the treatment led to any change in the crystalline pattern or in the degree of crystallinity of the curaua fibers. The obtained diffractograms are shown in Figure 2.

It was possible to observe that the treatment did not modify the diffraction pattern of the fibers. All the diffractograms of untreated and treated fibers show diffraction peaks at $2\theta = 16^\circ$, $2\theta = 23^\circ$ and $2\theta = 35^\circ$ assigned to the planes $(10\bar{1})$, (002) and (040) of cellulose I, respectively.[14] It can be stated that the crystalline phase of cellulose I is present in the fibers, regardless the treatment used. These results indicated that there was no polymorphic transformation of cellulose I (native form) to cellulose II, which could occur if alkaline treatments were used under severe conditions (NaOH concentration higher than 10 wt.%).[14] For

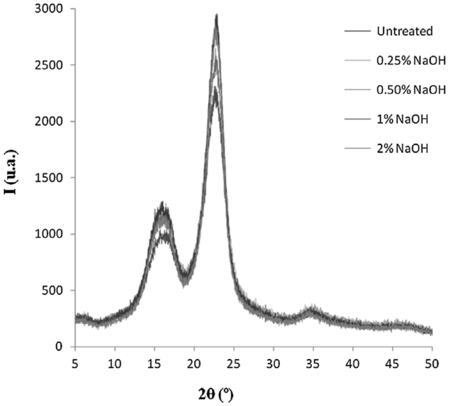

Figure 2.
XRD spectra of curaua fibers subjected to treatment with different concentration of NaOH solution under tensile load application.

the application of fibers as reinforcement in composites, the conversion from cellulose I to cellulose II is undesired, since this transformation is associated with a significant decrease in the mechanical properties of the fibers.[14]

Table 1 shows the average values of the crystallinity index (I_c) of untreated and treated fibers and their respective standard deviations. Statistical tests revealed that there were no significant changes in I_c values of untreated fibers and those of fibers treated with 0.25–1% NaOH solution. The use of higher concentration (2%) led to a slight increase in the I_c of the fibers. It can be presumed that the increase in crystallinity index could be associated to the partial removal of amorphous phase of the fibers (hemicellulose, as shown by FTIR analysis results), which increase the relative content of cellulose (crystalline phase). Other suggestion is that the removal of impurities and the amorphous constituents from the fibers can improve the packing of cellulose chains, resulting in increasing of crystalline index.[14]

Table 1.
Crystallinity index of untreated and treated curaua fibers.

NaOH concentration (%)	Crystallinity index, Ic (%)
0	74.7 ± 4.3
0.25	77.9 ± 4.5
0.5	78.9 ± 2.8
1	79.8 ± 2.6
2	81.9 ± 1.9

Helium Pycnometry Analysis

The analysis of both untreated and treated fibers showed that the treatment does not affect significantly their density. The density of the untreated and of all treated fibers was (1200 ± 65) kg/m^3, in average. This value is in the range of density of other vegetal fibers, but, as expected, it is lower than of the glass fiber.[2]

SEM Micrographs

The surface morphology of both untreated and treated fibers was observed by scanning electron microscopy (Figure 3). For untreated fibers, a compact surface with impurities was observed. After the treatment with 0.25% NaOH, it can be observed that the surface impurities were leached (Figure 3b). According to Figure 3c, the treatment with 0.5% NaOH promoted an increase in the surface roughness and it was also possible to see exposed cellulose microfibrils. It is expected that these changes in fibers morphology would provide more physical anchoring positions to the polymer chains. However, when more concentrated NaOH solutions were employed (Figure 3d and 3e), microfibrils exposure and defibrillation process could be observed. As reported by previous work, a higher degree of defibrillation can damage the mechanical resistance of the fibers.[4]

Mechanical Properties of Laminates

The calculated volume fraction of fibers was about 40% for all samples, which is relevant, since these vegetal fibers are very flexible making it difficult to mechanically compress them during rolling. Probably, the applied pressure compressed the intrafiber voids, allowing a great amount of fiber incorporation.

The values of obtained elastic modulus and flexural strength of the composites are shown in Figure 4 and 5, respectively.

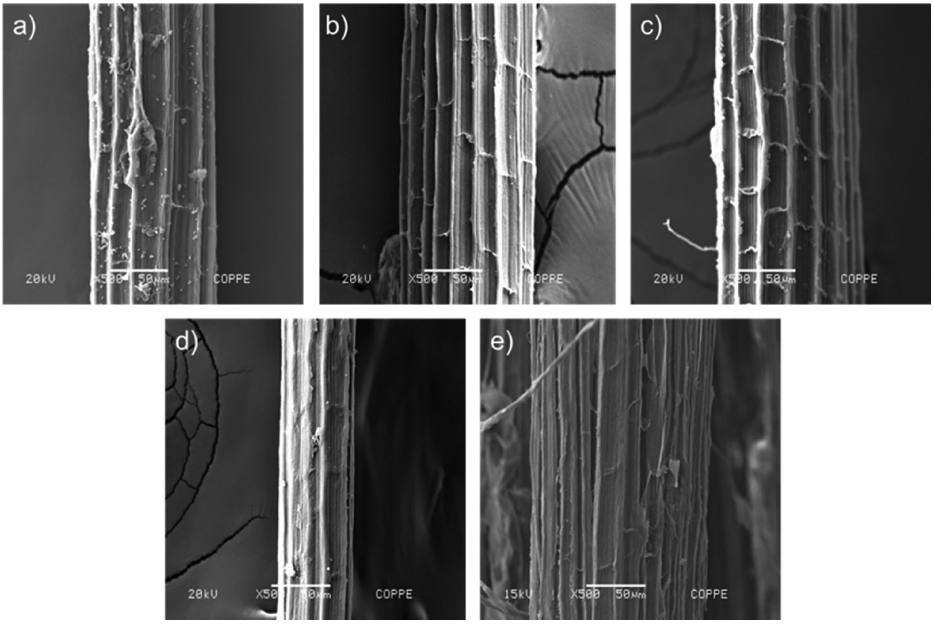

Figure 3.
SEM micrographs of untreated curaua fibers (a) and fibers subjected to treatment with different concentration of NaOH solution under tensile load 0.25% NaOH (b), 0.5% NaOH (c), 1% NaOH (d) and 2% NaOH (e).

Statistical tests revealed that there was a significant difference only between the properties of the composites containing fibers treated with 0.5% NaOH and the other composites. Hence, it was possible to observe that the treatments with 0.25, 1 and 2% NaOH solutions did not change the bending properties of the composites compared to the composites with untreated fibers.

It can be assumed that only a small amount of amorphous molecules and impurities was removed from fibers treated with 0.25% NaOH, which was not enough to promote the decrease in hydrophilicity character of fibers and/or the increase in their surface area. On the other hand, the low mechanical strength of the composite containing fibers treated with 1 and 2% NaOH may be related to the defibrillation

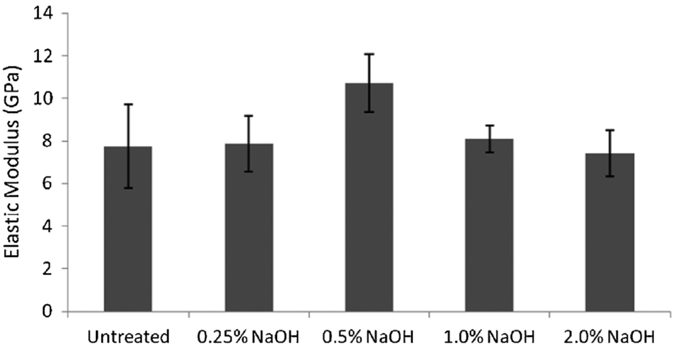

Figure 4.
Elastic modulus of curaua fiber/epoxy composites containing fibers subjected to treatment with different concentration of NaOH solution under tensile load application.

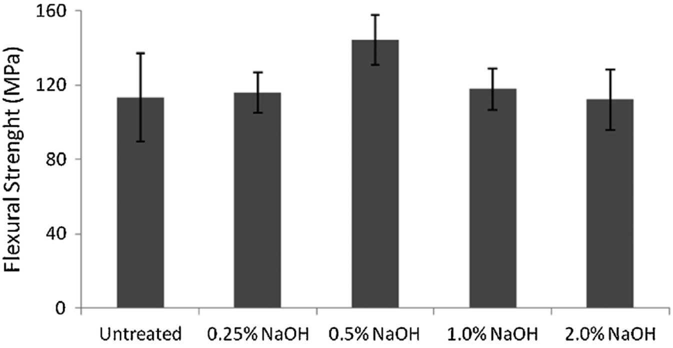

Figure 5.
Flexural strength of curaua fiber/epoxy composites containing fibers subjected to treatment with different concentration of NaOH solution under tensile load application.

by breakage of hydrogen bonds and by removal of hemicellulose. Due to the network modification, the microcrystalline microfibrils should be more likely to irreversible slippage, leading to increased permanent deformation of the fibers.[14,15] This observation is in agreement with the morphology of the damaged fibers shown in Figure 3d and 3e.

On the other hand, the treatment with 0.5% NaOH under tension load allowed an increase in elastic bending modulus of about 38% (from 7.74 GPa to 10.70 GPa) and an increase in the flexural strength of approximately 27% (from 113.45 MPa to 144.39 MPa), compared to untreated composite fibers, demonstrating the effectiveness of this treatment. These improvement were higher than observed for alkali treated flax/epoxy, linen/epoxy and bamboo/epoxy composites.[16] Those fibers were treated with 5 wt.% NaOH solution for 30 min without tensile load application. Compared to the untreated fabric composites, the flexural strength of treated flax, linen and bamboo composites increased 16.1%, 16.7% and 13.6%, respectively, while their flexural modulus showed an increase of 7.2%, 9.1% and 6.3%, respectively.

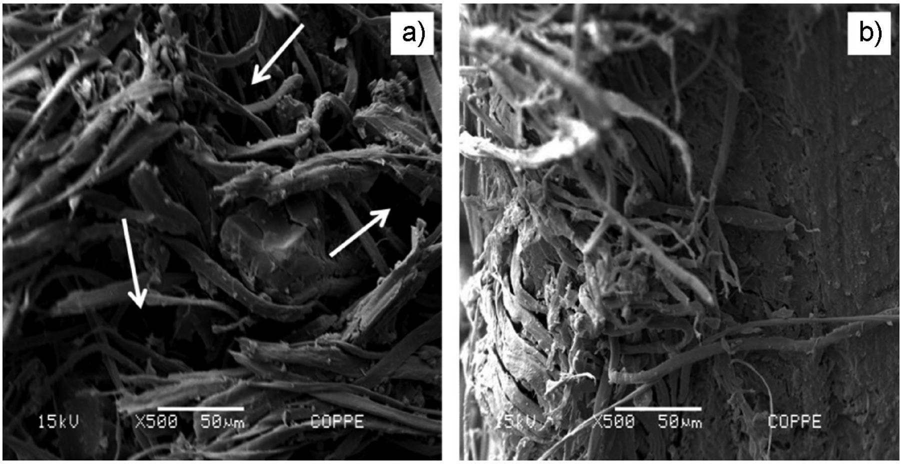

Figure 6.
SEM micrographs of fractured surfaces of composites containing untreated fibers (a) and fibers treated with 0.5% NaOH under tensile loading (b).

SEM Micrographs of Laminates

Scanning electron microscopy was used to investigate the fracture surfaces of the laminates after the bending tests and to assess the fiber-matrix adhesion of these materials (Figure 6).

In Figure 6a, some voids at the fiber/matrix interface of the untreated fibers/epoxy laminate can be visualized, pointed out by indication white arrows, this occurring despite of some wettability of the fibers by the polymer. This suggests that the voids appeared during the bending tests as consequence of a weak interface. However, the fracture surface of the composite laminates manufactured with fibers treated with 0.5% NaOH under tensile load (Figure 6(b)) showed that there was higher compatibility between fibers and matrix and higher affinity on the interface, even during the bending tests. In this case, no voiding occurred at the interface. This observation could explain the improvement of the mechanical properties of these composites, as observed in Figure 4 and 5.

Conclusion

The treatment of the curaua fibers with 0.5% NaOH solution under tension load allowed to obtain curaua fibers-reinforced epoxy composite laminates with better mechanical properties than those containing untreated fibers, possibly due to the increase in fiber-matrix interfacial adhesion. It can be supposed that the partial removal of hemicellulose and the increase in surface roughness of the fibers after treatment could explain this improvement in fiber-matrix compatibility. It is worth noting that these composites were obtained using lower concentration of NaOH solution and lower immersion time than those reported in the literature. Besides, the treatment was carried on at room temperature. Probably, the application of tension load during the alkali treatment might have contributed for the effectiveness of the treatment with mild conditions.

Regarding the mechanical properties, the obtained composites could be considered potential candidates to be used as substitute materials for several conventional materials, including some used in structural applications. In addition, these composites could be an alternative to increase the aggregate value of curaua fibers.

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