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ORIGINAL ARTICLE

Effects of mercerization in the chemical and morphological properties of amazon piassava

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Abstract

The objective of this work was to investigate the effects of mercerization on chemical, morphological and thermal properties of Amazon Piassava Fibers. The effect of this treatment was studied using XRF, SEM, XRD and TGA. The fibers have been treated in 5% and 10% NaOH for 60 min. The XRF results for treated and untreated fibers showed that there is a decrease in the amount of SiO_2 by increasing the NaOH concentration. It has been possible to observe through SEM in untreated fiber that the surface presents a well arranged pattern of silicon rich star-like protrusions. For the two concentrations, SEM allowed to notice that the removal of deleterious surface impurities and fiber roughness was enhanced. The removal of organic material after treatment can be observed in the TGA analysis. XRD analysis indicate an increase in the crystallinity index, 0.19 to 0.31 after the treatment for 10% concentration solutions.

Keywords: *alkaline treatment, mercerization, piassava fibers, superficial modification.*

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1. Introduction

The increasing global demand for consumer goods has exerted a rising pressure on the Earth's resource consumption. This has led to increased interest in the development of sustainable materials[1].

Among such renewable resources are the lignocellulosic materials or vegetable fibers. Brazil, specifically the Amazon region, is rich in renewable resources and possesses wide variety of vegetable fibers[2].

As a result, the use of natural fibers as a viable reinforcement in composite materials is increasing and has gained a significant research interest, possibly due to features like high specific modulus, non-toxicity, biodegradability, low cost and abundance[3]. Natural fibers like flax, hemp, jute and sisal have been well known as potential adequate reinforcements for engineering fiber composites[4-8]. Nevertheless, the Piassava Fiber (Leopoldinia Piassaba) in despite of their availability in Amazon, has been used mainly as raw material in craft and as home utensils as brooms or brushes and there is a lack of specific studies focused on Piassava Amazon fiber uses and their properties in composites materials.

On the other hand, the issue of fiber-matrix interaction in composites materials has received increasing attention. However, natural fibers have structural compounds (cellulose, hemicelluloses, lignin and other substances) that allow moisture absorption from the environment. The interaction between the hydrophilic fibers and their hydrophobic matrix causes fiber swelling within the matrix[9]. This results in the weakening of bonding strength at the interface, therefore leading to dimensional instability, matrix cracking and poor mechanical properties of the composites[10,11].

In order to enhance the effectiveness of interfacial bonding between fiber and matrix, fiber surface needs to be modified. There are many types of treatments, such as, for instance, sodium hydroxide (NaOH) or mercerization, which is being widely used to modify the cellulosic molecular structure[5,12]. According to John, 2007, This modification promotes the access to penetrate chemicals causing reaction with water molecules and move out them from the fibre structure, while the remaining reactive water molecules form fibre-cell-O-Na bonds[11]. This process increase the fibres moisture resistance property due to reduction of hydropylic hydrowyl groups[10,13]. Besides, another important modification done by mercerization is the increase in the surface roughness caused by the disruption of hydrogen bonding in the network structure. Consequently, there is improvement in the composite mechanical properties[6,14].

The main objective of the present study consists of clarifying the effect of mercerization on chemical, morphological and thermal properties of the Amazon Piassava Fibers (Leopoldinia piassaba), filling the gap of information about the surface modifications after the treatment, which could improve the interface adhesion between Amazon Piassaba Fiber and polymer matrix

2. Materials and Methods

2.1 Materials

The Piassava fibers used in the present investigation were purchased from O. A. NunesNeta - ME (Brazilian company), located in Manaus.The fibers presented a moisture content of 13%, measures in laboratory. The NaOH was obtained by Nuclear Company, supplier Instrumental Technical Ltda, Manuas-Am.The fibers were cut at a nominal length of 1 cm.

2.2 Methods

2.2.1 Mercerization

For mercerization treatment, a commercial NaOH solution was used.

The fibers were cut at a nominal length of 1 cm and soaked in two different NaOH concentrations (5% and 10% by weight) for 60 min. Then, the fibers were rinsed several times with water to remove the excess NaOH solution, until achieving pH 7, and afterwards dried at room temperature conditions of 36 °C for 24hrs to remove excess water. The effects of the mercerization in the fibers were investigated using the following techniques: XRF, SEM, XRD and TGA.

2.2.2 X Ray Fluorescence (XRF)

The measurements of the sample elemental composition were performed through the X-ray fluorescence (XRF) technique using an Epsilon3-XL spectrometer (PANalytical) with 15 W maximum power. A semiquantitative analysis of the spectra was performed with the Omnian package.

2.2.3 Scanning Electron Microscopy (SEM)

The piassava fiber's microstructure was investigated using an SEM Hitachi TM3000. The microscope was operated under an accelerating voltage of 15 kV. A pre-coating with a thin layer of approximately 20 nm of gold was done to make the fiber conductive and suitable for analysis.

2.2.4 X Ray Diffraction (XRD)

X-ray diffraction studies were performed under ambient condition in the equipment EMPYREAM PIXcel 3D (Panalytical), using Cu Ka radiation (1.5406Å), operating at 40 Kv and current of 40Ma. The scan was taken at a range of $5° < 2\theta < 45°$ at a rate of 1°/min and step size 0.0001°. Crystallinity index (Ic) and percentage crystallinity (% Cr) were calculated using Equations 1 and 2[15,16],:

$$Cr\% = \frac{I_{22}}{I_{22} + I_{18}} x100 \quad (1)$$

$$Icr = \frac{I_{22} - I_{18}}{I_{22}} \quad (2)$$

The method was for empirical measurements to allow rapid comparison of samples, where I_{22} and I_{18} are the crystalline and amorphous intensities at 2θ scale to 22° and 18°, respectively[17,18].

2.2.5 Thermo Gravimetric Analysis (TGA)

Thermal analysis of fibers (TGA/DTGA) was performed in natural and treated fibers. The tests were performed in a SDT Q600 simultaneous TGA/DTA/DSC from TA Instruments. Samples weighing 10 mg were submitted to a heating rate of 10 °C/min until reaching 600 °C in a platinum crucible using 100 ml/min of nitrogen as the purge gas.

3. Results and Discussions

The XRF results are shown in Table 1. After the mercerization process, there is a decrease of the SiO_2 content from 34.9% of the natural fiber to 9.6% and 6.6% for 5 and 10% concentration solutions, respectively. The treatment processes can enhance removal of surface impurities and increase fiber roughness. This is advantageous for fiber to matrix adhesion as it facilitates mechanical interlocking from the increased surface area available for contact with the matrix and improves the composites mechanical properties[19].

Moreover, Table 1 shows that after the treatment there is presence of sodium in the fiber. This is possible since the treatment changes the fiber structure and there is the reaction of sodium hydroxide with cellulose. This reaction is shown in Equation 3[3].

$$Cellulose - OH + NaOH \rightarrow Cellulose - O^{-}Na^{+} + H_2O + Surface\ Impurities \quad (3)$$

Figure 1 shows SEM micrographs of the fiber surface morphology and the protrusions, which are Si rich particles[20,21].

The surface topography of piassava (Fib 2b) is rougher than before treatment (Figure 2a) and the surface looks cleaner. This occurs because the mercerization removes lignin, pectin, waxy substances, and natural oils that cover the external surface of the fiber cell wall, revealing the fibrils,

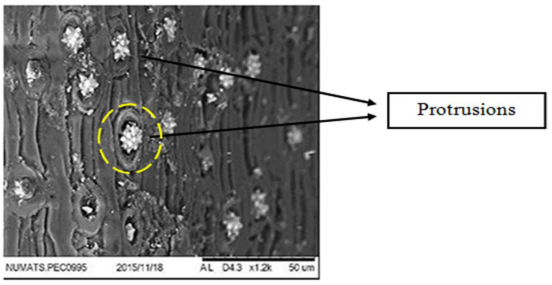

Figure 1. SEM of piassava fiber untreated: protrusions.

Table 1. Chemical elements presentin the untreated and treated Piassava fiber samples obtained by the X-ray fluorescence.

Element	Fiber in Natura (w.%)	5% NaOH (w.%)	10% NaOH (w.%)
Na	**0.000**	**8.435**	**22.842**
Mg	0.541	0.026	0.169
Al	21.109	6.491	8.194
Si	**34.965**	**9.664**	**6.668**

resulting in a rough surface topography of the fiber[3,21]. Then, with the higher solution concentration there is a roughness increase (Figure 3a and 3b).

Figure 4a shows the transversal cross-section of the untreated piassava sample. After treatment (Figure 4b), the cell wall thicknessvaried from 3 μmto 1 μm, which can be attributed to the removal of organic materials, suchas lignin and other substances[3].

The results of the thermogravimetric analysis are presented in Figure 5. It is possible to observe in the untreated fiber decomposition behavior a small low temperature weight loss (11.88%), between 25 and 112 °C, that can be attributed to water in the form of absorbed moisture or combined water[22]. The onset of the fiber thermal degradation began at about 180 °C, with the decomposition of hemicellulose. According to the literature[11], the TGA curve of hemicellulose presented three stages of decomposition (from 25 to 180 °C, from 180 to 280 °C and 280 to 500 °C). The peak at 361 °C could be associated with the decomposition of cellulose. This value is higher than the reported for the pure cellulose sample[11] and the piassava (*Attaleafunifera*)[10]. The thermal decomposition of lignin ranged from 150 to 450 °C[11] and is dependent on specie. A clear peak for lignin was not observed in this curve.

From Figure 5 it is also possible to observe the TGA and DTGA curves for the mercerized fibers. The mercerized (5-10% NaOH) fibers showed lower decomposition temperatures compared to the untreated fiber. For the main fiber decomposition region (200-400 °C), the treated fibers had a higher weight loss than the untreated fiber, indicating lower thermal stability.This is probably due to the removal of organic materials such as lignin,pectin, waxy substances, and natural oils, evident in the curves of DTGA for mercerized fibers, where the peak around 250 °C was not visible, indicating the removal of hemicellulose from the fiber[3,23].

To study the effectiveness of chemical treatment in piassaba fibers, XRD analysis was performed whose result is shown in the diffractogramin Figure 6.The figure shows

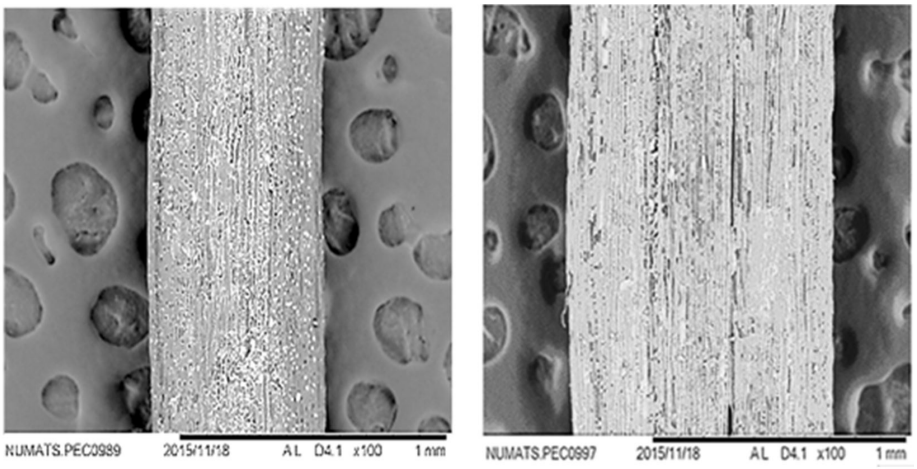

Figure 2. SEM of piassava fiber (a) untreated; (b) 5% NaOH treated.

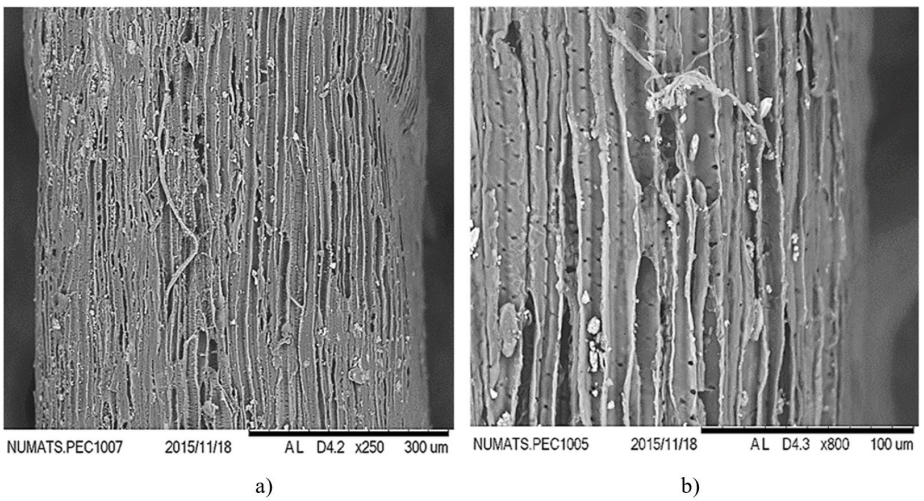

Figure 3. SEM of piassava fiber treated 10% NaOH, view of fibrils (a) x250; (b) x800.

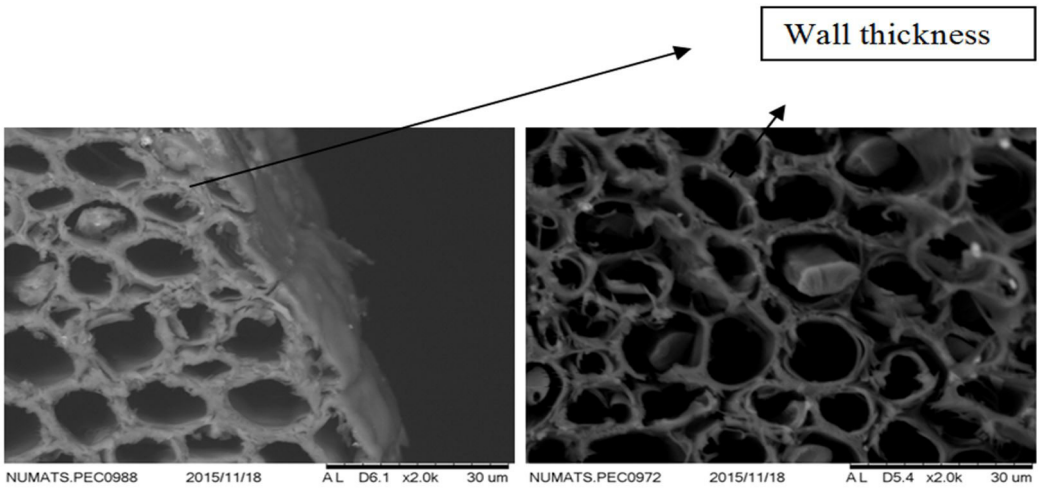

Figure 4. SEM of transversal cross-section piassava fiber (a) untreated; (b) 10% NaOH.

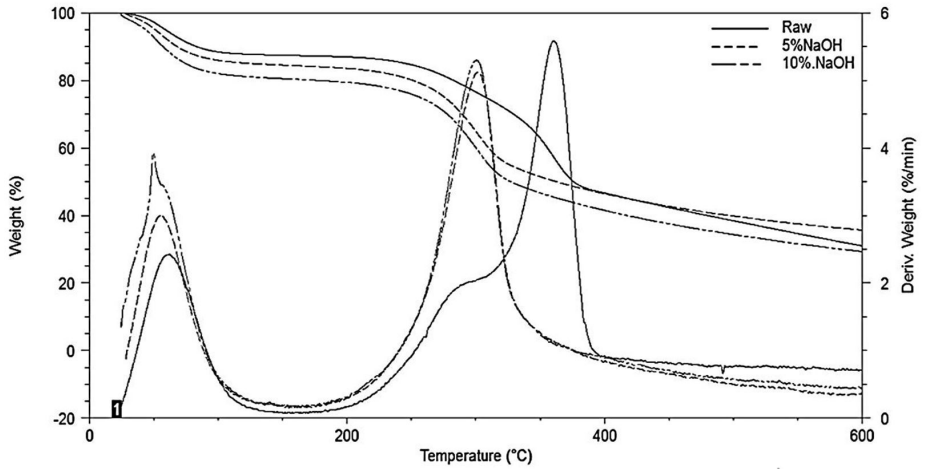

Figure 5. TGA and DTGA curves for treated and untreated fiber.

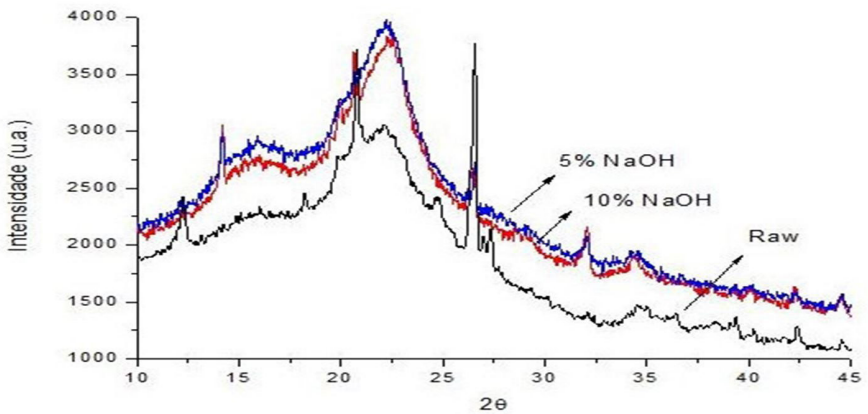

Figure 6. XRD curves of piassava fibers treated and untreated.

Table 2. XRD data of raw and chemical treated piassava fibers.

Sample	I_{22} (at 2θ scale)	I_{18} (at 2θ scale)	C.I.	%Cr.
Untreated	3093.94	2499.56	0.19	55.31
5% NaOH	3982.73	2790.97	0.30	58.79
10% NaOH	3835.82	2615.45	0.31	59.45

that piassava fiber (untreated and treated) there are three broad diffraction peaks at 2 θ, the most intense being the 22° corresponding to the crystalline part of the fiber, and halos at 16° and 35º referring to the amorphous part of the fiber, such as the hemicellulose and lignin present in the fibers microfibrils.The result obtained is very similar to those of other lignocellulosic fibers, and reflects the crystalline lattice of cellulose I [24-28].

Table 2 shows the results of percentage crystallinity (% Cr) and crystallinity index (C.I) of untreated and treated piassava fiber. The untreated fiber at 2θ scale gave peaks at 22.0 and 18.0 with relative intensity is 3093.94 and 2499.56. Percentage crystallinity (%Cr) and crystallinity index (C.I) of untreated piassava fiber are 55.31 and 0.19 respectively whereas percentage crystallinity of alkali treated fibers (5% and 10%) were 58.79 and 59.41. Whereas crystallinity index of alkali treated fibers are 0.30 and 0.31 respectively.

The increase of crystallinity index in alkaline treated piassava fibers indicated that the chemical treatment induced the crystallinity and it increase due to the removal of amorphous materials like hemicellulose, lignin, and some other[23,29-31].

Through alkalization, an increase of composite quality is to be expected due to the improved fibre–matrix adheshion[5].

4. Conclusions

The effects of mercerization on the amazon piassava (*Leopoldinia piassaba*) were presented. The results of the XRF showed that there is a higher sodium concentration when the fiber is treated with the 10% NaOH solution. The fibers present silicon rich star-like protrusions that are removed after the mercerization process. XRD revealed increase in the crystallinity index due to the removal of amorphous materials like hemicellulose, lignin, and some other.

The fiber surface appears cleaner and rougher after the treatment. Thermal analysis of treated fibers displays lower thermal stability compared to the untreated fibers. These surface modifications could improve the interface adhesion between fiber and matrix, resulting in composites with enhanced mechanical properties.

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