

Effect of Surface Treatments on the Thermal Behavior and Tensile Strength of Piassava (*Attalea funifera*) Fibers

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ABSTRACT: Piassava (*Attalea funifera*) fibers subjected to several surface chemical treatments and as-received raw fibers were compared with respect to their thermal and tensile behaviors. The thermal degradation of the raw fibers was characterized by three main stages that corresponded to water release at low temperatures, decomposition of hemicellulose, and decomposition of α cellulose. Mercerization acted mainly on hemicellulose removal, and there was no change in the hydrophilic behavior of the fibers. The removal of hemicellulose split the fibers into microfibrils and favored the thermal decomposition of α cellulose. The same behavior was observed when the fibers were subjected to mercerization and acetylation. The

fibers subjected to only acetylation showed thermal behavior similar to that of the raw fibers. With the acetylation treatment, a minor decrease in the hydrophilic character of the fibers was noted. Despite some differences in the thermal behavior, the tensile strengths of the raw and treated fibers were statistically equal. Complementary Fourier transform infrared and scanning electron microscopy analysis corroborated the thermogravimetric analysis/differential thermogravimetry results. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 2508–2515, 2011

Key words: fibers; FT-IR; strength; thermogravimetric analysis (TGA)

INTRODUCTION

Nowadays, the use of lignocellulosic-fiber-reinforced composites is being considered by many different industries, including the automotive industry, for which interior panels and cushion seats are already being manufactured with coir, flax, or sisal fibers.¹ These fibers, along with hemp and jute, are among the most characterized and most studied lignocellulosic fibers.^{2–6} However, many other less studied fibers, such as banana,⁷ sponge gourd,^{8,9} and piassava fibers,¹⁰ are suitable as reinforcements in polymer matrix composites because of several different characteristics. Banana fibers, for example, which are extracted from many species of banana trees (*Musa* sp.), are disseminated worldwide and are a low-price material obtained from the cut and disregarded banana tree.⁷ On the other hand, the fibers obtained from the dried fruit of the sponge gourd

(*Luffa cylindrica*) form a natural mat that can be favorably used to increase composite toughness.⁸

The use of lignocellulosic fibers has, in fact, many advantages well discussed in the literature. The great advantage of these fibers is, however, the fact that they are neutral with respect to the emission of CO₂.¹¹ This is an extremely important aspect and makes lignocellulosic fibers suitable materials in the context of the Kyoto protocol.

Usually, the main disadvantage of using lignocellulosic fibers with polymeric matrices is the very weak interface that develops between hydrophilic fibers and hydrophobic matrices. Weak interfaces result in ineffective stress transfer to the fibers. Therefore, the mechanical behavior of many natural-fiber-reinforced composites is characterized by strength values below the theoretically expected ones. Better interfaces can be obtained by the modification of the fibers by physical or chemical treatments.^{9,12–15} Some treatments can, however, affect the mechanical and/or thermal behavior of the fibers and can compromise their final use as reinforcements in composites.¹⁶ Moreover, some treatments that promote better interfaces with specific fibers are not suitable for use with other fibers because of differences in the compositions of the fibers.

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In this work, piassava fibers (*Attalea funifera*) were subjected to several surface chemical treatments designed to promote a better fiber–matrix interface. The thermal behavior and tensile strength of the treated and as-received fibers were evaluated, and the effect of each treatment is presented and discussed.

EXPERIMENTAL

Piassava (*A. funifera*) fibers, obtained from the southern region of Bahia State, Brazil, were used in this work. These fibers were subjected to the following chemical surface treatments: (1) mercerization, (2) mercerization and acetylation, and (3) acetylation. Raw fibers in their as-received condition, washed with flowing tap water, were also analyzed.

Mercerization is an old and effective chemical process used by the paper industry, and it is one of the most used treatments for natural fibers. It has been successfully applied to enhance fiber–matrix adhesion in different lignocellulosic-fiber-reinforced composites.¹² It is used to remove lignin and hemicellulose from the fiber surface and increase the fiber surface roughness. The mechanical interlock between the fiber and the resin matrix is thus increased as well as the fiber-to-matrix adhesion. The removal of lignin can also favor a subsequent acetylation step because the reactive hydroxyl sites on the cellulose molecule are exposed and are more readily available for further reactions.

In this work, the fibers were immersed for 1 h at the ambient temperature in solutions with 10 or 15 wt % NaOH. They were then washed in flowing tap water and left immersed in tap water for 24 h to remove any NaOH residue. A following step of 24-h immersion in distilled water always produced solutions with a pH around 7, and this indicated that the fibers were conveniently washed.

Acetylation is designed to reduce the number of free hydroxyl groups of cellulose by substituting hydroxyl groups with acetate groups. Therefore, the polarity of the fibers is reduced and their compatibility with the common polymeric matrices used in composites can be improved.^{15,17} This treatment was performed for raw fibers just washed in tap water and for fibers previously mercerized with a 15 wt % NaOH solution. The fibers were immersed in a solution with acetic anhydride, glacial acetic acid (1.5 : 1.0 wt/wt), and some drops of sulfuric acid, which was used as a catalyst for the reaction. The reaction occurred in an ultrasonic bath at room temperature for 3 h. The fibers were subsequently washed and remained immersed in tap water for 24 h. After another period of immersion in distilled water for 24 h, the fibers were once again washed in tap water and cleaned for 30 min in an ultrasonic water bath.

After each treatment, the fibers were dried at 60°C for 12 h.

The efficiency of the treatments was followed by Fourier transform infrared (FTIR) analysis with a PerkinElmer Spectrum One spectrometer (Shelton, Connecticut), and scans were run between 400 and 4000 cm^{-1} . This region of the spectrum contained the characteristic carbonyl band related to the acetyl group (1780–1740 cm^{-1}), the hemiacetals from the anomeric C1 carbons (1750–1636 cm^{-1}), and the band associated with the axial vibration of hydroxyl groups (3500–3300 cm^{-1}).

The thermogravimetric analysis (TGA) of raw and treated fibers was performed at a heating rate of 10°C/min from 30 to 700°C with a Pyris 1 TGA analyzer from PerkinElmer. The experiments were conducted under a nitrogen atmosphere with a gas flow of 20 mL/min. Raw and treated fibers were also analyzed with scanning electron microscopy (SEM). The SEM analysis was performed on gold-sputtered samples with a Zeiss 960 DSM microscope (Oberkochen, Germany) operated in the secondary imaging mode at 15–20 kV.

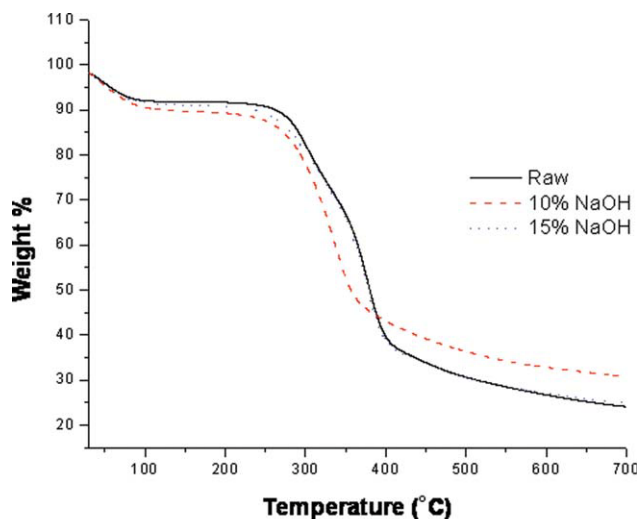
The tensile strength of single piassava fibers was measured with the procedures recommended by ASTM Standard D 2101 on a mechanically driven machine that had a 10-kN capacity and was equipped with pneumatic action grips. An optimum holding pressure of 0.3 MPa was experimentally found to give reliable test data. With this clamping pressure, neither fiber slippage nor fiber crushing at the grips occurred. The test speed was 1 mm/min, and 15 specimens with a gauge length of 30 mm were tested per fiber condition.

RESULTS AND DISCUSSION

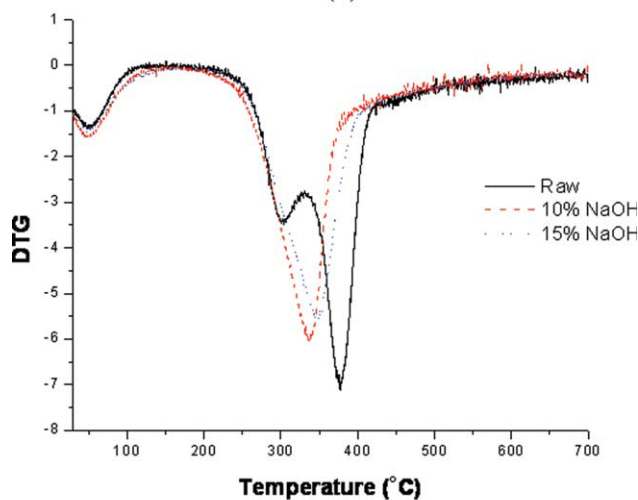
Raw fibers

Figure 1 shows the thermal behavior of the raw fibers. The curve shows a low-temperature weight loss that can be attributed to a loss of water in the form of absorbed moisture or combined water. The weight loss ($\approx 8.3\%$) was similar to the values reported for other lignocellulosic fibers, such as sponge gourd (9.4%)⁹ and jute (10.2%)¹⁸ but was higher than the value of 5.2% reported previously for piassava fibers.¹⁰ Because the fibers tested in this work came from the same lot of fibers tested earlier but their tests were separated by approximately 1 year, this difference could be related to normal water uptake by the stocked fibers.

The weight loss observed between 272 and 351°C could be attributed to the thermal decomposition of hemicellulose and the rupture of the glycoside link of the cellulose molecule.^{19,20} The rupture of α and β aryl–alkyl–ether linkages, originating from thermal degradation reactions of lignin, also contributed to the observed weight loss.²¹ The weight loss occurring



(a)



(b)

Figure 1 (a) TGA and (b) DTG curves for the raw and mercerized piassava fibers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

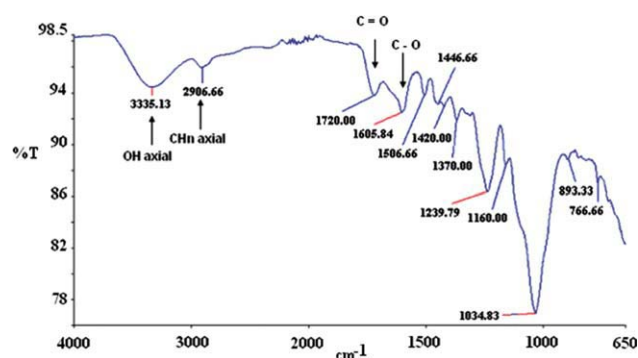


Figure 2 FTIR spectrum of the raw piassava fibers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

between 351 and 410°C involved the decomposition of cellulose oligomers, which evolved into levoglucosans and low-molecular-weight volatile compounds such as ketone, aldehydes, furans, and pyrans.²⁰ The peak value of 372°C in the differential thermogravimetry (DTG)

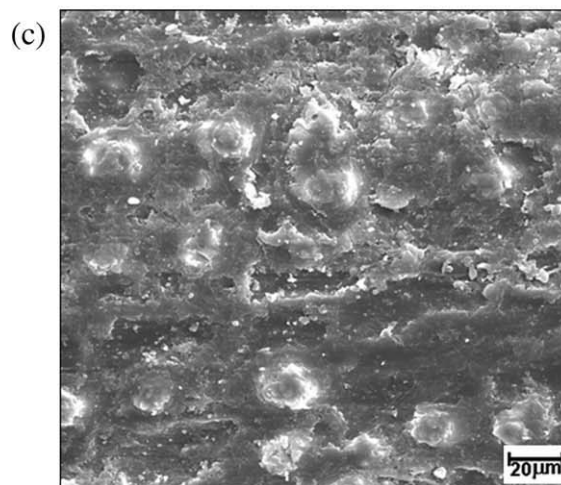
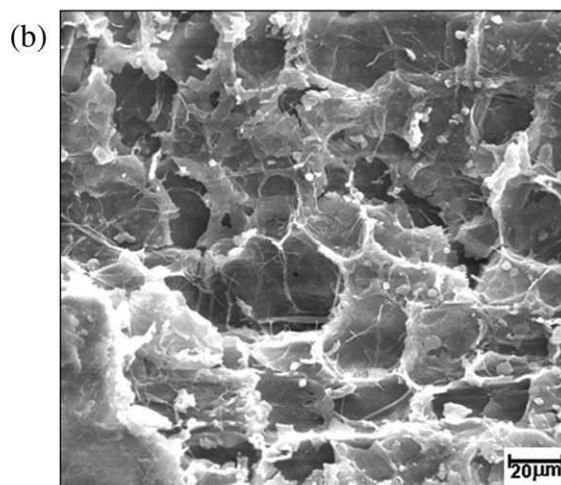
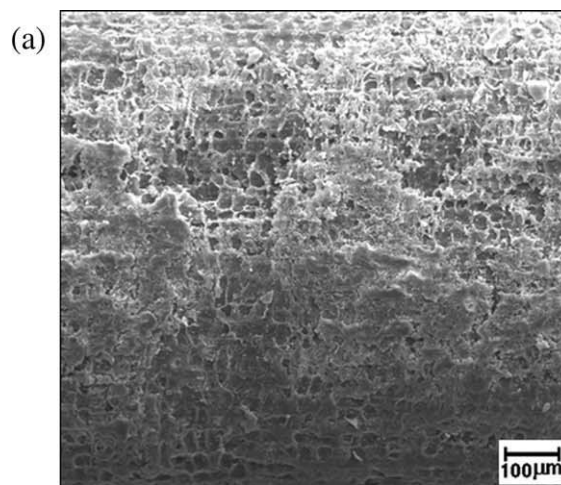


Figure 3 (a) Overall aspect of the piassava fibers, (b) organic residue attached to the surface of the fibers and parenchymal cells, and (c) array of protrusions.

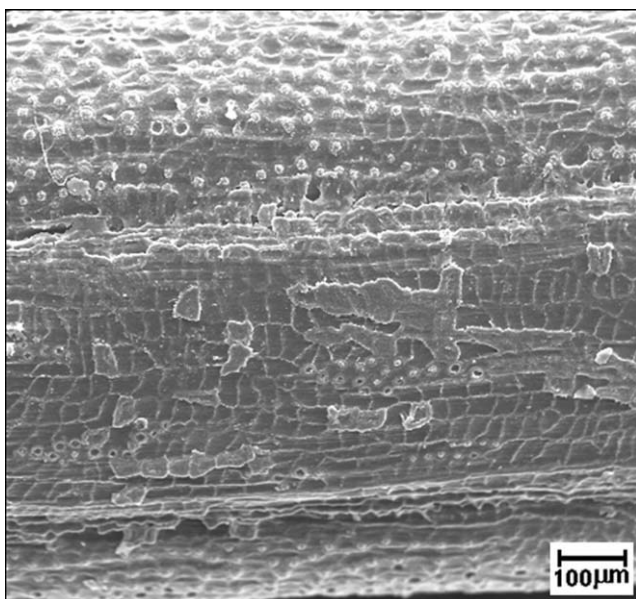


Figure 4 Surface morphology of mercerized fibers in a 10 wt/wt % alkali solution. The array of protruded silicon-rich features was completely exposed.

curve was in close agreement with the value reported for the thermal decomposition of α cellulose of jute fiber.¹⁹

In the FTIR spectra of the raw fibers (Fig. 2), the following could be observed: (1) a strong signal at 3335 cm^{-1} , which was characteristic of the axial vibration of the hydroxyl groups of cellulose (the hydroxyl groups of carbons 2, 3, and 6 of glucose); (2) signals in the region of the axial vibration of CH ($2990\text{--}2950\text{ cm}^{-1}$); and (3) hemiacetal signals due to

the anomeric carbons at 1730 cm^{-1} (C=O) and around 1605 cm^{-1} (C—O and C—C).^{22,23}

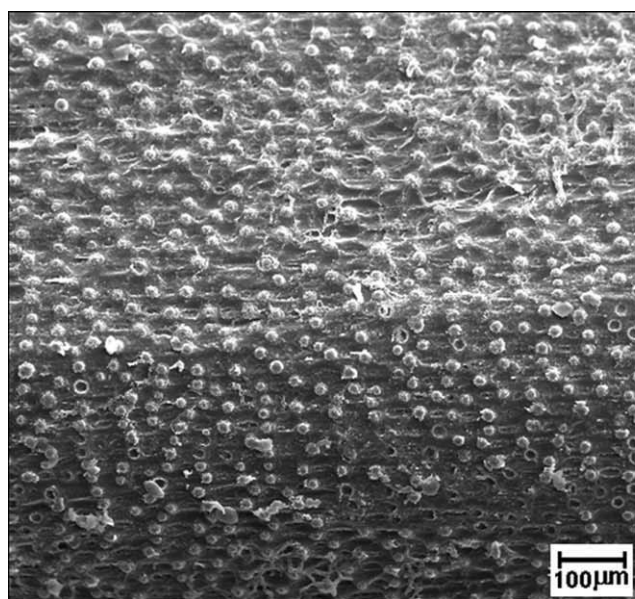
The overall surface morphology of the raw piassava fibers is shown in Figure 3(a), in which one can see residues from organic material (probably vestiges of leaves from which the fibers were extracted and parenchymal cells). These aspects are shown in detail in Figure 3(b). In some regions in which the outer surface was apparently removed during the mechanical separation of the fibers from the soft tissue of the palm leaf, arrays of protruded features could also be seen [Fig. 3(c)]. These protrusions were silicon-rich particles, as detailed elsewhere.¹⁰

Treated fibers

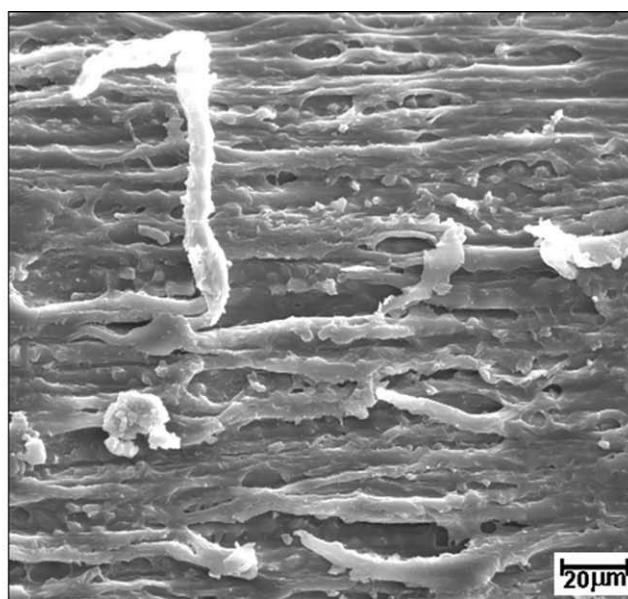
Mercerization

TGA of the fibers subjected to mercerization treatments is also shown in Figure 1, and the following main aspects were observed:

1. The low-temperature weight loss was not substantially modified, and this implied that the treatment did not basically modify the hydrophilic character of the fibers.
2. The peak with respect to hemicellulose decomposition was attenuated for the 10 wt % treatment and completely disappeared when the 15 wt % treatment was used. This result was in close agreement with reported results showing that an alkali treatment removes hemicellulose and causes fibrillation of lignocellulosic fibers.²⁴



(a)



(b)

Figure 5 Surface morphology of mercerized fibers in a 15 wt/wt % solution: (a) a cleaned surface without any trace of the outer surface layer and (b) a deeply etched region with fibrils detached from the surface.

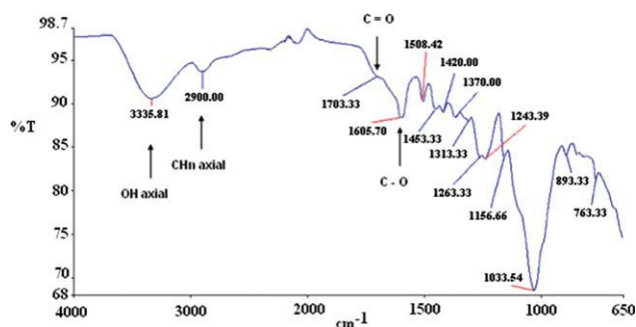


Figure 6 FTIR spectrum of the NaOH-treated fiber in a 15 wt/wt % solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

- The peak temperature related to the decomposition of α cellulose decreased to 353 and 340°C for the 10 and 15 wt % treatments, respectively. This behavior could also be attributed to hemicellulose removal, which split the fibers into microfibrils with an accompanying increase in the surface area available for reaction; this favored thermal degradation. Similar behavior has been observed for sponge gourd fibers.⁹

Mercerization promoted an almost complete removal of the outer surface layer of the fibers and exposed the array of protrusions covering the entire fiber length (Figs. 4 and 5). The degree of etching was, however, dependent on the alkali solution used. With the treatment with the 10 wt % solution, the surface was uniform, although some areas of the outer layer residue could still be observed (Fig. 4). The use of a stronger alkaline solution (15 wt %) eliminated any residue of the outer surface layer [Fig. 5(a)], but in many areas, the protrusions were also removed, and the detachment of fibrils from the fibers could be seen [Fig. 5(b)]. This result corroborated the thermal analysis and indicated that this treatment split the fibers because of hemicellulose removal.

Figure 6 shows a typical spectrum of the FTIR analysis of the mercerized fibers. The signal corresponding to the axial stretching of the O—H group ($\sim 3400\text{ cm}^{-1}$) increased with the alkaline treatment. According to Paul et al.,²⁵ this could be attributed to the formation of new hydroxyl groups resulting from the rupture of crosslinked bonds from both lignin and hemicellulose during the alkaline treatment. Moreover, the signal at 1720 cm^{-1} almost disappeared. The reduction of this signal could be due to the removal of hemicellulose or some of its constituents such as uronic acid.^{25,26} This result corroborated the TGA and SEM analysis performed.

The signal reduction that was associated with the axial vibration of the C—H group from both cellulose and hemicellulose at 2906 cm^{-1} also corroborated the hypothesis that the alkaline treatment effec-

tively reduced the hemicellulose content.²⁶ In Figure 6, one can also note a signal reduction at 1240 cm^{-1} related to the C—O stretching vibration of the acetyl group associated with lignin components.²⁶

Acetylation

The fibers subjected to acetylation showed behavior that was almost similar to the behavior presented by the raw fibers (Fig. 7). A slight tendency of a decreasing amount of water loss at a low temperature (7.6%) in comparison with the value obtained for the raw fibers (8.3%) seemed to indicate that the acetylation treatment increased the hydrophobic behavior of piassava fibers; this accorded with what was observed when this same treatment was used with sponge gourd fibers.⁹ The difference, however, was very small and may indicate that the acetylation treatment performed was not as effective as

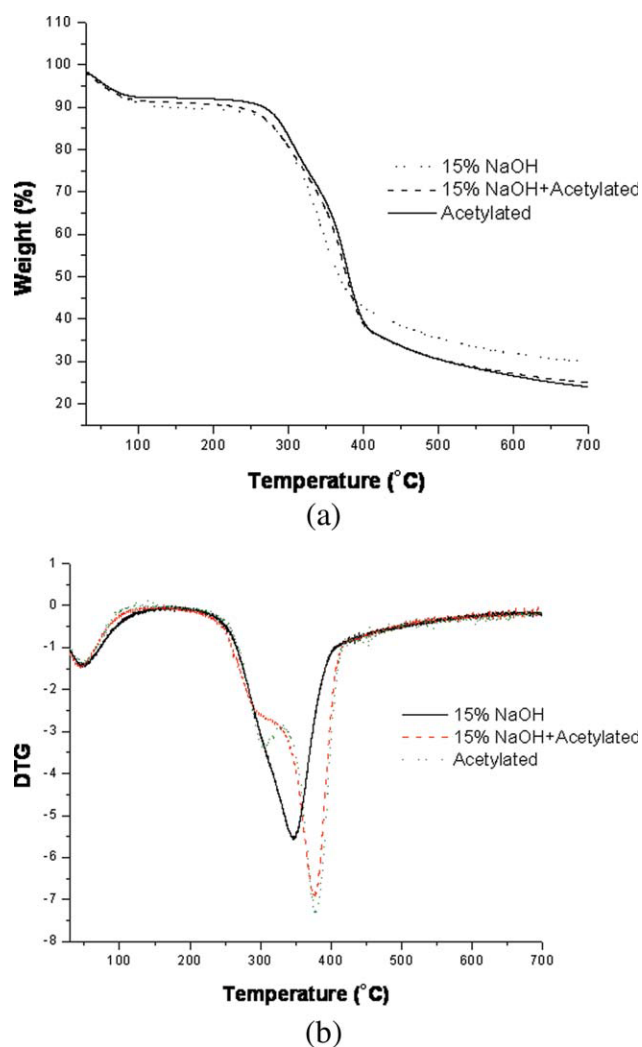


Figure 7 TGA curves of the mercerized and acetylated fibers and the acetylated fibers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

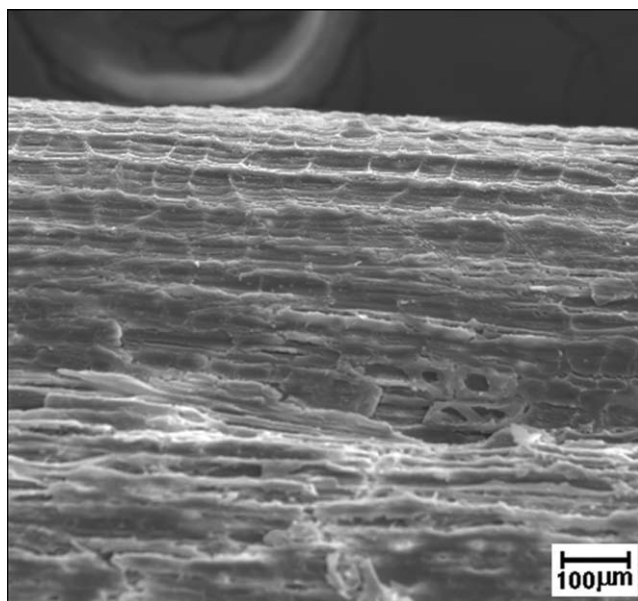


Figure 8 Regions of the surface of the acetylated fibers. The outer surface appeared to be free of any residue.

expected. After each treatment, the fibers were manipulated with exactly the same procedures in a laboratory with controlled temperature and humidity. Therefore, the results from the low-temperature water release could be used comparatively to ascertain the amount of water contained in the fibers after each treatment.

The presence of the hemicellulose decomposition stage (between 274 and 351°C) and α cellulose (between 354 and 451°C) in almost the same temperature range obtained for the raw fibers showed that the acetylation treatment in fact did not significantly modify the thermal behavior of piassava fibers.

The SEM analysis did not show fibril formation when the fibers were subjected to acetylation. Also, the SEM analysis showed that the surface morphology of the acetylated fibers was most uneven. Large areas showed exposed protrusions similar in aspect to those shown in Figure 4, but others showed the regu-

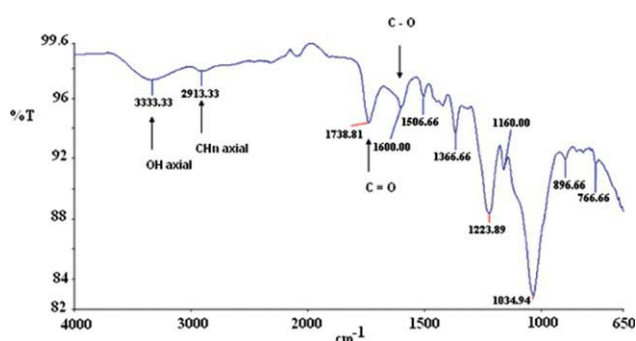


Figure 9 FTIR spectrum of the acetylated fiber. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

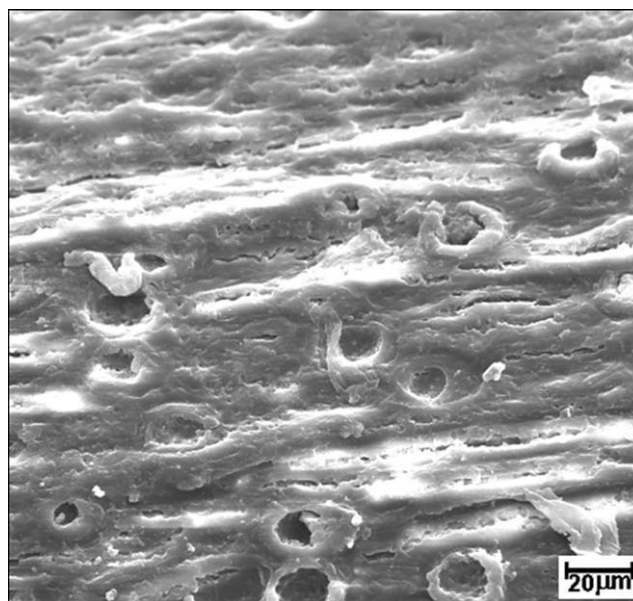


Figure 10 SEM analysis of the mercerized and acetylated fibers. The surface was clean, with many areas having no protrusions and many incipient fibrils (as shown).

lar pattern of parenchymal cells observed for the raw (untreated) fibers. These areas were, however, clean of any organic residues, as shown in Figure 8.

The FTIR spectrum of the acetylated fibers (Fig. 9) showed a strong increase in the signal in the region associated with the carbonyl band between 1800 and 1700 cm^{-1} in comparison with the raw fiber spectrum (Fig. 2). There was also a signal shift from 1720 (Fig. 2) to 1739 cm^{-1} (Fig. 9), which indicated that acetylated fiber esters such as acetate were present.²² Figure 9 also shows that the signal corresponding to the hydroxyl band decreased, and this indicated the substitution of the hydroxyl group by an acetate group. However, the degree of reduction indicated that under the experimental conditions used in this work, only partial substitution occurred. The FTIR analysis of the mercerized-acetylated fibers (not shown here for the sake of brevity) presented a similar behavior. However, because of a smaller reduction of the hydroxyl band for these previously mercerized fibers, it appears that the acetylation step is not as effective as the direct acetylation of raw fibers.

TABLE I
Tensile Strength of Piassava Fibers

Surface treatment	Tensile strength (MPa)
Raw (untreated)	127.0 \pm 35.6
Mercerized (10 wt %)	105.8 \pm 26.2
Mercerized (15 wt %)	116.5 \pm 33.8
Acetylated	99.3 \pm 56.6
Mercerized (15 wt %) and acetylated	105.5 \pm 20.0

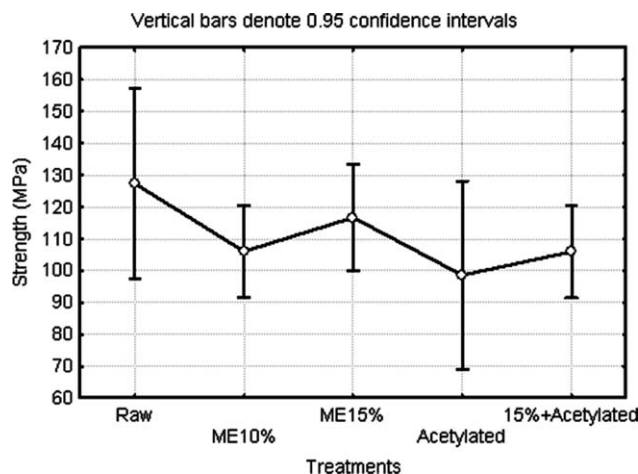


Figure 11 Variation of the tensile strength of the raw and treated fibers (ME = mercerization).

Acetylation and mercerization

The thermal analysis of the fibers subjected to mercerization (15% NaOH) and acetylation showed similarities but also differences in comparison with mercerized fibers. In short, as shown in Figure 7, the hydrophilic behavior was not changed, and the thermal degradation temperature of α cellulose was reduced, as also observed for mercerized fibers. However, a shoulder was observed at 296.5°C. The peak observed in the raw fiber thermogram at 303°C (Fig. 1) was associated with hemicellulose thermal degradation.¹⁹ However, it vanished completely when the fibers were subjected to mercerization with the 15 wt % solution, as shown in Figure 7. Therefore, the shoulder observed when the fibers were mercerized and acetylated might be due to the weight loss of acetyl groups. Similar behavior was observed when sponge gourd fibers were acetylated.⁹

The SEM analysis of the fibers subjected to this two-step treatment, that is, mercerization followed by acetylation, also showed the complete removal of the outer surface layer and many protrusions with the formation of incipient fibrillation (Fig. 10).

The tensile strengths and standard deviations of the raw and treated fibers are listed in Table I. Although the treatments appeared to have changed the tensile strength, the standard deviation was high enough to mask this result. In fact, by using the Fisher test (least-square difference) with 5% significance, we can say that there was no difference between the treatments. Between the raw fiber and the acetylated fiber, there was a marginal statistical difference ($P = 0.073$). However, this result was not conclusive because the standard deviation of the strength values was high for all treatments, and this tended to mask the least-square difference test.²⁷

Figure 11 shows the average values with the 0.95 confidence intervals.

CONCLUSIONS

The following conclusions were obtained from the results:

1. The surface treatments, that is, mercerization, mercerization and acetylation, and acetylation, did not modify the tensile strength of the piassava fibers. This is a relevant result because it implies that the fibers were not degraded by these chemical treatments.
2. The mercerization treatment removed the outer surface layer of the fibers and exposed the inner structural features. The effect of this treatment was dependent on the alkali concentration, and for the highest value used (15 wt % NaOH), fibrils were exposed at the fiber surface. Although the degradation temperature of the fibers subjected to mercerization decreased in comparison with that of the raw fibers, the surface aspects generated—protrusions and fibrils—could contribute to the increase in the fiber-to-matrix adhesion in composites because of the increase in the fiber surface area.
3. Similar results were obtained when a second treatment step, acetylation, followed mercerization. Therefore, this two-stage treatment does not present any advantage with respect to the mercerization treatment alone.
4. The fibers subjected only to acetylation showed thermal behavior similar to that of the raw fibers, but a minor decrease in the fiber hydrophilic character was also noted. The FTIR spectrum of the acetylated fibers showed that acetylated esters such as acetate were present. Therefore, this treatment was effective in modifying the fiber surface and again could contribute to enhancing the fiber-to-matrix interface in composite materials.

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