FUTHER ANALYSES ON HORNIFICATION PROMOTION BY WASHING CYCLES ON NATURAL VEGETABLE FIBERS

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Abstract

Several treatments on natural fibers are presented by literature as effective process to mitigate the high water absorption and reduce dimensional variation. The wetting and drying cycles treatment is pointed as an efficient treatment since they promote the stiffening of the polymer structure of the fiber cells, known as hornification. One of the main characteristics of this process is the greater dimensional stability of the fibers. In this context, the objective of the present research is to investigate the influence of wetting time, fiber/water ratio and number of wetting and drying cycles on the treatment and its effect on sisal fibers chemical and mechanical properties. The treatment of the fibers was performed in water at room temperature (T = 22 °C), varying wetting time (1h and 3h) and fiber/water ratio (1:10 and 1:40), drying process 80°C during 15 hours. Direct tensile tests, thermogravimetry analysis (TG) and infrared spectroscopy (FTIR) were performed on raw, pre-washed and treated fibers. The results revealed that lower fiber/water ratios are better to hornification promotion. Immersion times of 3 hours were efficient to increase stiffness in all studied cases.

Keywords: Natural fibres, Fiber treatments, Hornification, Mechanical properties.

1. INTRODUCTION

Composites reinforced with vegetable fibers have the potential to become the final choice of green material, since it is a material of renewable origin, has wide availability and low relative cost [1]. However, it has disadvantages, such as low chemical adhesion, high water absorption capacity. The increase of the composite moisture causes the variation in fiber volume, which results in a weaker physical interaction between the materials [2]. In this way, several studies involving physical and chemical treatments in natural fibers have been

developed to solve this problem. These treatments seek to promote the increase of surface roughness, the cleaning of the surface of the fiber and decrease the absorption of moisture [3].

The hornification reduces the water absorption capacity of the fibers and improves fiber-matrix bonding, that is because it causes structural changes in the cellulosic fibers from the wetting and drying cycles in the fibers [4,5,6]. In addition to simple and low energy consumption, this procedure increases the degree of crosslinking in the fiber microstructure, reduces the volumetric changes of natural fibers as well as promotes changes in their mechanical properties [1].

According to Ferreira et al. [5], the hornification in sisal fibers provides improvement in interfacial adhesion to the matrix. The treatment applied consisted of immersion in water for three hours followed by a slow drying, of 16 hours, at 80 ° C. In another research, Ferreira et al. [1] applied the same treatment to different fibers, subjected to 5 and 10 washing cycles. The results indicated a variation in treatment efficiency. The author attributed these differences to the nature of the fibers, such as morphology and its chemical composition. However, the variables of the treatment itself was approached by the author as a critical point for the effectiveness of drying and wetting cycles.

However, there are still several bottlenecks on the effect of this treatment on the fiber, and to what extent it can improve the fiber / matrix interface. In this context, the objective of the present research is to investigate the influence of wetting time variation, fiber / water ratio and number of wetting and drying cycles on the property of the fibers (chemical and mechanical).

2. MATERIALS AND METHODS

2.1 Materials

Sisal fibers were obtained from the Municipality of Valente-BA provided by the Association of Sustainable Development and Solidarity of the Region Sisaleira (APAEB), former Association of Small Farmers, with length ranging from 90 cm to 100 cm. These fibers were the same studied by Ferreira et al. [1,5]. According to Silva et al. [7], the microstructure of the sisal fiber is formed by numerous individual fibers (fiber-cell) with a diameter of 6 to 30 μm and a chemical composition of 54 to 66% of cellulose, 12 to 17% of hemicellulose, 7 to 14% lignin, 1% to 7% ash.

The sisal fibers were washed in hot water at 80 ° C for one hour to remove the surface residues from the extraction process, at the end of this process the fibers were dried at 40 ° C. This process was named "prewash". This procedure was executed according Ferreira et al. [5]

2.2 The fiber hornification treatment

The hornification treatment was applied to the prewashed fibers. The treatment of the fibers was performed using water at room temperature (T = 22 °C ± 2°C), varying the wetting time, and the fiber/water ratio. The drying process was performed in a muffle-type oven Quimis, at a temperature of 80 °C.

The oven was programmed to reach 80 °C at a heating rate of 1 °C/min and maintain this temperature for 15 h. After this drying time, the oven was natural air cooled to 22 °C in order to avoid possible thermal shocks in the fibers. This procedure was repeated 1 and 5 times. The treatments are best described in Table 1.

Table 1 : Description of treatments.

Treatment code	Wetting Time	Temperature	Fiber/Water Ratio	Cycles
1.A.10.1	1h	22 °C	1:10	1

1.A.10.5	1h	22 °C	1:10	5
1.A.40.1	1h	22 °C	1:40	1
1.A.40.5	1h	22 °C	1:40	5
3.A.10.1	3h	22 °C	1:10	1
3.A.10.5	3h	22 °C	1:10	5
3.A.40.1	3h	22 °C	1:40	1
3.A.40.5	3h	22 °C	1:40	5

2.3 Thermogravimetrical analyses (TGA)

TGA analyses were performed in a DGA-60H Shimadzu, getting simultaneous TGA/ DTA. Samples with 4 mg weight were subjected to a heating rate of 10 °C/min until reaching 500 °C in an open platinum crucible using 60 mL/min of nitrogen as the purge gas.

2.4 Fourier transform infrared (FTIR) spectroscopy

FT-IR analyses were performed in an IRAffinity-1 Spectrometer Shimadzu, through the attenuated total reflection technique (ATR), with resolution of 4 cm^{-1} in the range of 4000 to 600 cm^{-1}. Stored results were averages of 24 scans.

2.5 Wettability analysis

The contact angle was performed according to ASTM D-7334 [8] using the Krüss goniometer DSA25 (Krüss, Germany) by the sessile drop method at room temperature (22 ± 2°C). The contact angle measurements were performed with the deposition of deionized water droplets, with a volume of 100 μL, using a 0.507 mm diameter needle. ImageJ software was used for data processing.

2.6 Direct tensile tests

For the tensile tests, the MTS Tytron 250 electromechanical test machine was used with a 50 kN load cell, with a displacement rate of 0.3 mm / min, according to ASTM C1557 [9]. Where each fiber had a length of 40 mm and a average diamenter of 0.023 mm^2 [1, 10], fixed in paper mold for better alignment in the machine and adhering the grips of the equipment. Fifteen repetitions were used for each treatment.

3. RESULTS AND DISCUSSION

3.1 Thermogravimetrical analysis (TGA)

Figure 1 shows the thermogravimetric analysis (TGA) performed in the natural and treated sisal fibers.

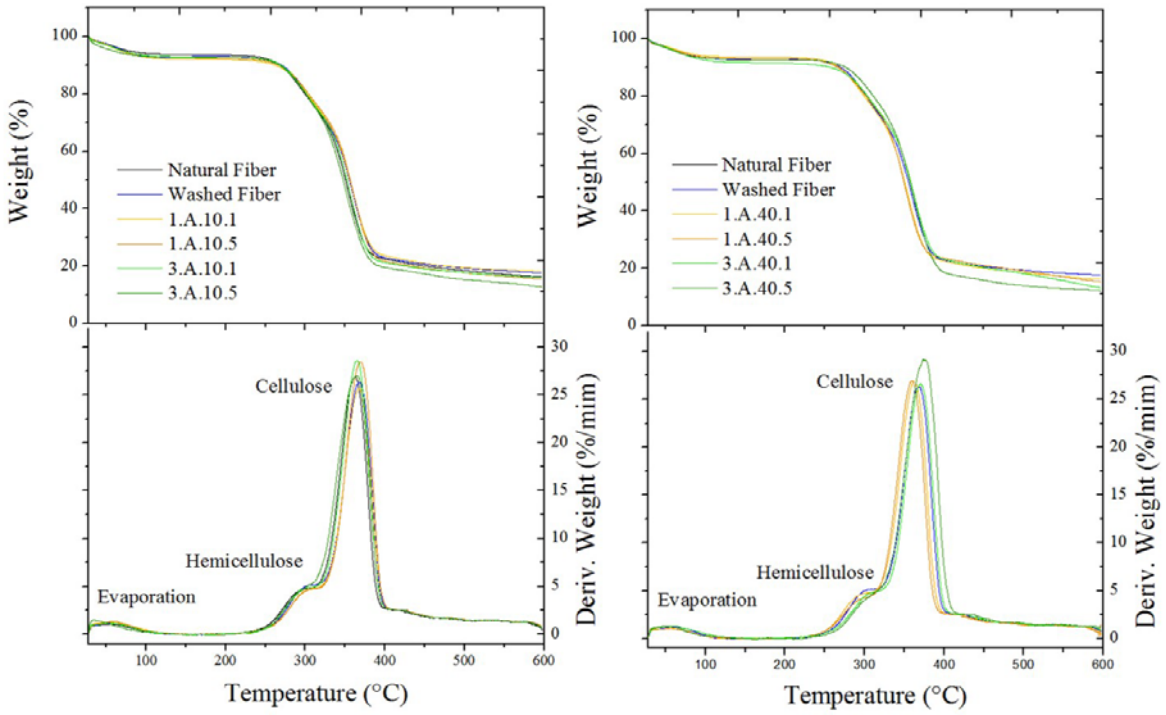

Figure 1: Thermogravimetry analysis (TG/DTG) of the sisal fibers before and after the different treatments.

According Figure 1 three decomposition intervals for all the fibers studied can be observed. The first step being water loss (about 100 ° C). The second stage occurs between 250 and 350 ° C, which corresponds to the simultaneous decomposition of cellulose, hemicelluloses, lignin and pectins [11].

At intervals between 350 and 400 ° C the third step occurs which is characteristic of cellulose degradation. At the end of the third peak there is a "shoulder" in relation to the slow degradation of lignin, which occurs between 250 and 600 ° C [1].

The results indicate that no significant difference in the thermoanalysis was observed, indicating no significant removal of soluble lignin and hemicelluloses.

3.2 Fourier transform infrared (FTIR) spectroscopy

The FTIR spectra of sisal fibers are show in Figure 2. The spectra obtained in the present study for natural and treated fibers present vibration modes according to the literature [12] and [13], observing characteristics of the lignocellulosic fibers. Sisal fibers have cellulose, hemicellulose and lignin as the most important components, and these elements present peaks in the largest region between 800 and 2000 cm^{-1} [1]. The majority of them are related to lignin, correlated with the aromatic ring groups of the groups Metoxil ($-OCH_3$), C-O-C and C = C [14,15].

An increase in peak intensity at 3400 cm^{-1} was observed to treated fibers. The increase in this peak was higher for treated fibers with longer immersion time and longer treatment cycles. This modification may be attributed to hydroxyl groups (-OH). According to Ferreira et al. [1], hornification provides increased structural hydrogen bonds due to the high energy utilized by the treatment that blocks these bonds.

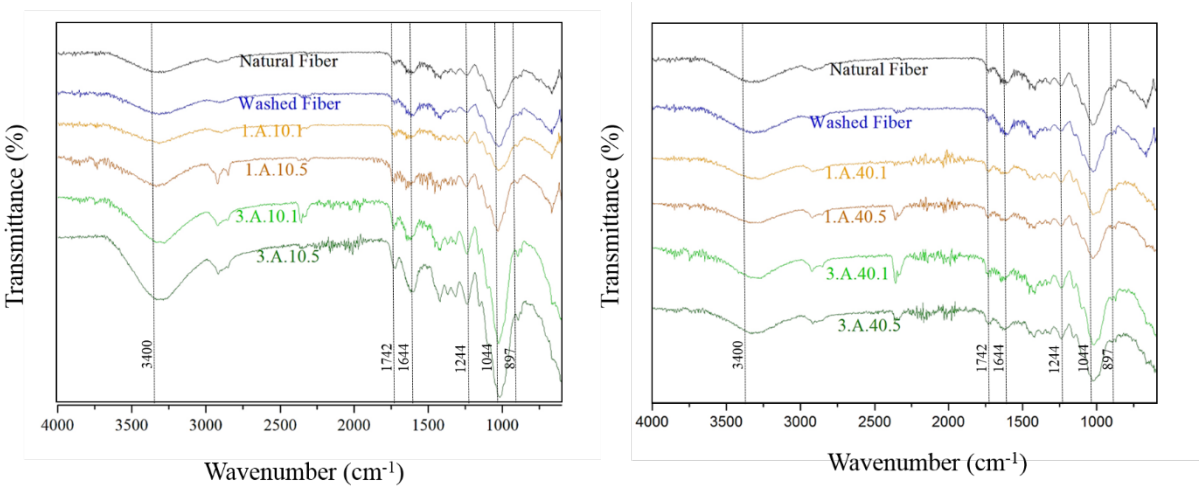

Figure 2: Infrared spectroscopy of sisal fiber before and after the different treatments.

The C = O elongation attributed to the 1742 cm^{-1} range corresponds to the carboxylic acid and ester components of the hemicelluloses [16]. The carboxylic groups are able to connect to another functional group through hydrogen bonds, which may result in an increase in the network of lignin macromolecules [17].

This mechanism promotes a better interaction between lignin, cellulose and hemicellulose, resulting in a more resistant material and in greater crystallinity, stiffness and deformation capacity [5]. Studies have also suggested that the covalent bonds between lignin and hemicelluloses exist in native wood [18]. In addition to the covalent bond between lignin and hemicellulose, there is also hydrogen bonding between hemicellulose and cellulose [5].

The peak at 1044 cm-1 is attributed to the stretching of CO and to the cellulose group vibration [15]. The peak 1644 cm^{-1} is attributed to the C = C elongation of lignin and 1244 cm^{-1} is attributed to the axial asymmetry of link =COC both to ether, esther and phenol groups [1]. According Morán et al. [19] these modifications may be correlated to absorbed water on cellulose. This water can be presented in -OH linkages, difficulting the interaction between fiber and water, resulting in a lower water absorption.

3.3 Wettability analysis

The results of contact angle measurement on all fibers are shown in Figure 3. Values and standard deviation of measurements are presented in Table 2.

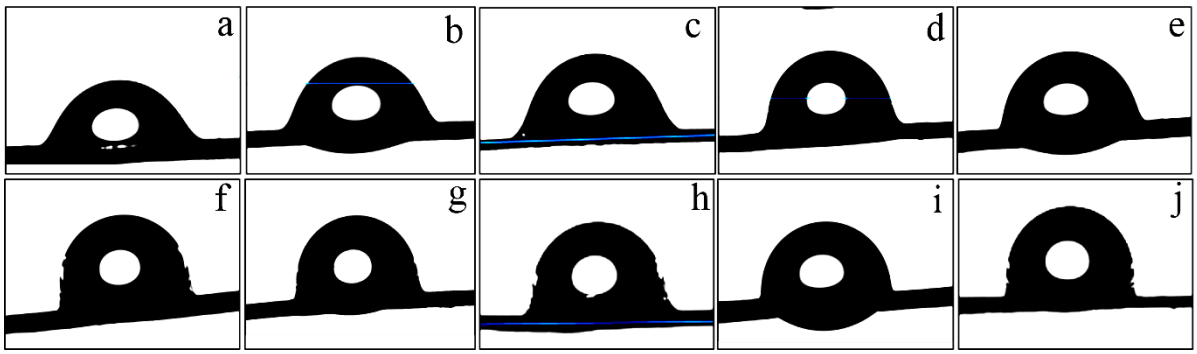

Figure 3: Images of the angle formed on the sisal fiber : a) Natural Fiber, b) Washed Fiber, c) 1.A.10.1, d) 1.A10.5, e) 1.A.40.1, f) 1.A.40.5, g) 3.A.10.1, h) 3.A.10.5, i) 3.A40.1, j) 3.A 40.5.

It is possible to observe that after treatment application the drop above the fiber present a uniform and circular shape. This significant difference between raw and treated fibers is not only present on probe geometries but in the contact angles (Table 2).

Table 2: Mean values and standard deviations for initial and final contact angles measured for water on natural fibers.

	Contact angle (deg)	
Treatment	T Initial	T Last
Natural Fiber	27.09 (10.42)	24.81 (10.93)
Washed Fiber	37.95 (17.85)	36.33 (11.09)
1.A.10.1	34.78 (20.60)	29.43 (17.52)
1.A.10.5	53.30 (9.97)	48.22 (14.57)
1.A.40.1	77.12 (20.11)	75.99 (24.52)
1.A.40.5	72.08 (12.35)	69.62 (11.78)
3.A.10.1	60.01 (12.51)	59.47 (11.55)
3.A.10.5	66.32 (9.54)	60.62 (22.34)
3.A.40.1	58.89 (15.45)	57.20 (19.89)
3.A.40.5	75.60 (8.25)	74.71 (16.39)

Treatments with lower number os cycles present a higher contact angle. The same result was obsreved to treatments with lower fiber/water ratio. This results corroborate with FTIR data. The increase in the OH groups may difficult water sorption, promoting a more hydrophobic surface.

3.4 Direct tensile tests

Typical stress-strain curves of untreated and treated sisal fibers are shown in Figure 4. The tensile strength and stiffness of sisal fiber increased after mostly treatments. It is possible to observe that one hour immersion was more effective in comparison to 3 hours in all studied ratios.

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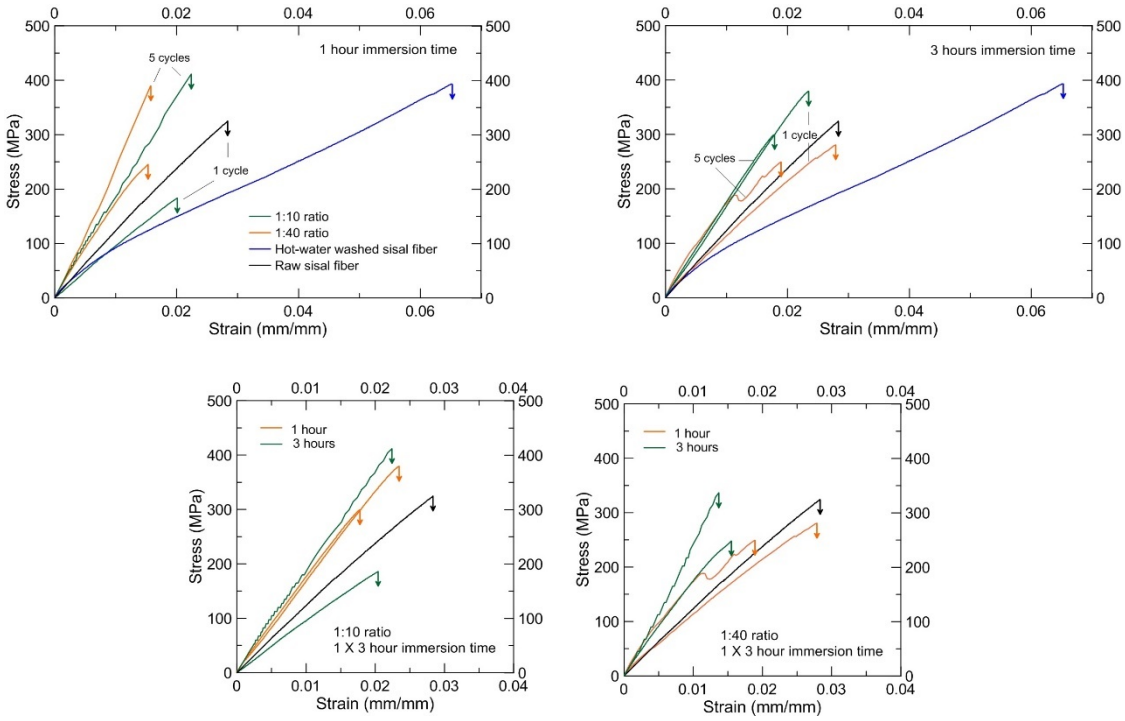

Figure 4: typical tensile curves of raw and treated fibres.

Results indicate that 5 cycles treatment was more effective in hornification promotion, even with no control of fiber/water ratio. Cycles of wetting and drying change the microstructure of vegetable fibers, which modifies the polymeric structure of the fiber-cells resulting in higher tensile strength and strain [1].

4. CONCLUSIONS

The work in hand investigated the effect treatments on sisal fibers properties. The following conclusions can be drawn from the present research. In evaluating the effect of the hornification cycles on sisal fibers, it is noted that the treatment did not cause changes in the thermal degradation of the fiber. After the treatments, the sisal fibers showed alterations in their chemical bonds, especially the acetyl group and promoted a reduction in the water absorption capacity of the fibers, allowing greater dimensional stability. When correlating the obtained results, it is emphasized that 3.A.10.5 of hornification improves characteristics of sisal fibers that reinforce its use as reinforcement in composites.

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