



Effect of chemical treatments on properties of green coconut fiber

A.I.S. Brígida^a, V.M.A. Calado^b, L.R.B. Gonçalves^c, M.A.Z. Coelho^{a,*}

^a Departamento de Eng. Bioquímica, Escola de Química, Universidade Federal do Rio de Janeiro, 21949-900 RJ, Brazil

^b Departamento de Eng. Química, Escola de Química, Universidade Federal do Rio de Janeiro, 21949-900 RJ, Brazil

^c Departamento de Eng. Química, Universidade Federal do Ceará, 60455-760 CE, Brazil

ARTICLE INFO

Article history:

Received 25 August 2009

Received in revised form 24 September 2009

Accepted 6 October 2009

Available online 13 October 2009

Keywords:

Green coconut fiber

Chemical treatment

SEM

Thermal analysis

FTIR

Wettability

ABSTRACT

Green coconut fiber, a lignocellulosic material native from Brazilian northeast coast, was chemically treated by three methods: NaOCl, NaOCl/NaOH or H₂O₂. The effect of these treatments on the structure, composition and properties of fibers was studied using SEM, FTIR, XPS, TGA and other analyses. SEM showed that treatment with H₂O₂ is the most efficient in terms of waxy and fatty acid residues removal but it does not modify the surface chemical composition, that it can be seen by FTIR and wettability results. The chemical composition and FTIR analyses revealed a reduction of the hemicelluloses content in the fibers treated with NaOCl/NaOH and, consequently, this fiber showed a greater exposure of cellulose and a reduction in thermal stability. The fiber surface treated with NaOCl is morphologically similar to the natural fiber surface, have the element Cl on your surface and it is a little more hydrophilic than the natural fiber.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

Lignocellulosic fibers, also called “plant” fibers, “natural” fibers or “vegetable” fibers, include bast (or stem or soft sclerenchyma) fibers, leaf or hard fibers, seed, fruit, wood, cereal straw, and other grass fibers. They are materials rich in lignin, hemicellulose and cellulose and are used for various applications, depending on their composition and physical properties. In the last two decades, the world fiber production increased 0.8 million ton. However, the last few years have shown signals of a possible stabilization in world production. China has been singled out as the world largest producer and, contrasting to world production behavior, its production has been increasing in these recent years. Brazil maintains its position as the fifth largest fiber producer in the world, with 1.3 million ton in 2007 (FAO, 2008). Traditionally, these fibers are used by artisans or industrial sectors, in the textile industry or as an energy source. An increasing world trend towards the maximum utilization of natural resources through new processes and products has been driving to the study and exploration of such rich renewable natural materials, generating new applications to lignocellulosic fibers in the automotive industry, production of adhesives, ethanol, lactic acid, active carbon, furfural among others (Reddy & Yang, 2005), or in the development of composites (John & Thomas, 2008).

* Corresponding author. Tel.: +55 21 25627564; fax: +55 21 25627622.
E-mail address: alice@eq.ufrj.br (M.A.Z. Coelho).

Fibers of banana, jute, piassava, sponge-gourd, sugarcane, coconut, rice straw, sisal and mainly cotton are the most important commercial varieties of Brazilian fibers and they are responsible for 93% of the national production (Satyanarayana, Guimarães, & Wypych, 2007). Some plants are cultivated only for fiber extraction and improvement, however, in most cases, the sources of fiber are agricultural byproducts, and these could become a main source for not only fibers but also chemicals and other industrial products. The cultivation of coconut (*Cocos nucifera* L.) in Brazil is a good example of this situation. In 2007, about 2.77 billion tons of coconuts were produced, in a cultivated area of 273,459 ha (FAO, 2008). Such coconut production is intended mainly for copra-extraction in the industry of coconut milk and grated coconut. In this industry, the coconut used is a mature coir, about 10 or 11 months of age. However, a less but considerable part of this production is targeted to the consumption of “in nature” coconut water or the production of industrialized coconut water. The coconut used is a green coir, about 6–8 months of age. These differences in the coconut coir ages promote distinct chemical characteristics in the fibers and water content (van Dam, van Den Oever, Teunissen, Keijsers, & Peralta, 2004). The mature coconut agroindustrial byproducts (mature pith and fiber) have some applications as textiles (mats, carpets), building (thermal insulation) and automotive (cushions, seat covers, lation) (Silva, Souza, Machado, & Hourston, 2000). Although green coconut husk is rich in micronutrients (Neto, Ferreira, Bezerra, Sousa, & Cavalcanti, 2004), with physical-chemical properties of great potential in various applications (Dey, Chakraborty, & Mitra, 2005; Rosa et al., 2002; Tomczak, Sydenstricker,

& Satyanarayana, 2007), it is currently disposed in landfills. In response to socio-environmental demand, some forms of exploitation of this waste are being studied. Studies about the use of green coconut husk and its derivatives (endocarp, fiber and pith) range from application in agronomy to biotechnological processes. Among the various applications suggested, use in solid state fermentation (Coelho, Leite, Rosa, & Furtado, 2001), some can stand out such as agricultural substrate (Carrijo, Liz, & Makishima, 2002), source of tannin for industrial applications (Brígida & Rosa, 2003), reinforcement for polymeric composites (Corradini et al., 2006), as a support for amylase (Dey, Nagpal, & Banerjee, 2002) and lipase immobilization (Brígida, Pinheiro, Ferreira, & Gonçalves, 2007, 2008). For a number of these applications, the characteristics of the fiber surface are very important to obtain a high quality product.

Chemical treatments of surface fibers have been reported to improve their wettability and to modify their microstructure, surface topography, surface chemical groups and tensile strength (Rout, Tripathy, Nayak, Misra, & Mohanty, 2001; Silva et al., 2000). These changes may have positive influence on the interaction between matrix and polymer (in case of composites), adsorbent and adsorbate (for use as adsorbent of metals and pigments), enzyme and support and/or functionalizing agent and support (for immobilization process).

Therefore, the aim of this study was to investigate the effect of different chemical treatments carried out in green coconut fiber surfaces on physical and chemical properties targeting potential applications of these fibers. For this purpose, three different chemical treatments were used: treatment with H_2O_2 , NaOCl and NaOCl/NaOH and characteristics like morphology, chemical composition, thermal stability and surface constituents from natural and treated green coconut fiber were evaluated.

2. Materials and methods

2.1. Materials

Green coconut fiber was obtained from green coconut husks through a process developed by Embrapa Agroindústria Tropical (CNPAT/EMBRAPA), Ceará, Brazil. Before being chemically treated, green coconut fibers were previously cut and sieved to obtain particles between 32 and 35 mesh, washed with distilled water and dried at 60 °C for 24 h. All chemicals used were of analytical grade.

2.2. Chemical treatments

The coconut fibers were submitted to chemical treatments as described below. After this, treated fibers were thoroughly rinsed with distilled water and dried under vacuum for 2 h.

2.2.1. Treatment with H_2O_2

Two grams of coconut fibers was submitted to oxidation using 40 mL of a H_2O_2 solution in basic medium (0.05 g NaOH and 18 mL of H_2O_2 30%, v/v, for 100 mL of solution), at 85 °C for 2 h.

2.2.2. Treatment with NaOCl

Five grams of fibers was soaked in 100 mL of 0.4% NaOCl (v/v, in glacial acetic acid) for about 2 h at 85 °C.

2.2.3. Treatment with NaOCl and NaOH

This treatment was performed by soaking 5 g of fibers in 100 mL of NaOCl 4–6% (v/v): H_2O (1:1) for 2 h at 30 °C and, after that, the fibers were washed with water and soaked in 100 mL of 10% NaOH for 1 h at 30 °C.

2.3. Morphologic characterization

The morphologic characterization of natural and treated fibers was conducted using an optical microscope and also a scanning electron microscope. A Nikon SMZ800 microscope with a 10× objective was used to determine the diameter of the fiber. A set of at least 20 fibers was tested to get meaningful results. Image Pro® Software was employed to analyze the fiber images (1 μ m was equivalent to 32.0624 pixels). In order to study the surface texture and cross-sections of coconut fibers and to evaluate changes in the surface provoked by the chemical treatments, natural and treated fibers were analyzed by scanning electron microscopy (SEM) using a Zeiss DSM 940A operating at 15 kV. All samples were glued onto special stubs and gold-coated with a Sputter Emitech K550 to avoid electrostatic charge and to improve image resolution.

2.4. Chemical constituents and density characterization

Klason lignin, which is based on the isolation of lignin after hydrolysis of polysaccharides (cellulose and hemicellulose) by concentrated sulphuric acid (72%), and cellulose content of fibers were determined using the standard methods TAPPI T13M-54 and TAPPI T222-OM-93, respectively. The fiber density was measured by the pyknometry.

2.5. Fourier transform infrared (FTIR) spectroscopy

Fourier transform infrared (FTIR) spectroscopy was carried out to qualitatively identify the constituents of coconut fiber. Both the untreated (raw) and chemically treated coconut fibers were examined. Fibers were dried, ground into fine particles and 2.5 mg were mixed with 250 mg of KBr, compressed into pellets, and then analyzed with Mattson 7000 FTIR spectrophotometer. To obtain FTIR spectra, 10 scans were collected for wave number ranging from 4000 to 500 cm^{-1} .

2.6. Thermal gravimetric analysis (TGA)

Thermogravimetric analysis (TGA), conducted to evaluate the thermal stability of the fibers, were obtained using a Perkin-Elmer Pyris 1, under nitrogen atmosphere with a flow rate of 40 mL/min in the balance and 20 mL/min in the sample. The mass of the samples was between 5 and 6 mg. This experiment was carried out in a temperature interval of 30–650 °C, at a heating rate of 10 °C/min. The weight loss and its derivative (DTG) as a function of temperature were analyzed.

2.7. Wettability

A NIMA DST 9005 tensiometer, with a balance accuracy of 10^{-9} N, was used to evaluate natural and treated fibers wettability using a washburn cup in water and *n*-hexane. The tension caused by the fluid in contact with the fiber was monitored for 200 s.

2.8. X-ray photoelectron spectroscopy (XPS)

The chemical part of sample surface was analyzed by X-ray photoelectron spectroscopy (XPS). X-ray photoelectron spectra were collected using a Physical Electronics PHI Quantum 2000 ESCA instrument equipped with a monochromatic AlK α X-ray source, operating at 25 W, with a combination of electron flood gun and ion bombarding for charge compensation. The take-off angle was 45° in relation to the sample surface. The analyzed area was 500 × 400 μ m. Two types of spectrum were collected: a survey spectrum and low resolution spectrum of the C_{1s} (278–300 eV),

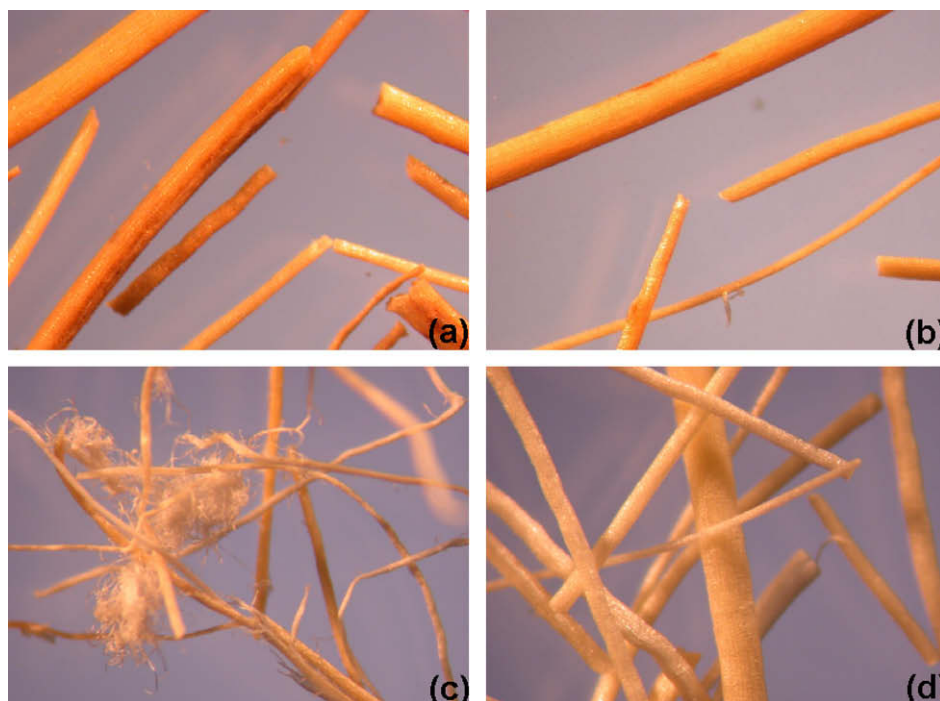


Fig. 1. Natural green coconut fiber (a), NaOCl treated fiber (b), NaOCl/NaOH treated fiber (c) and H_2O_2 treated fiber (d) obtained in an optical microscope using a 10 \times objective.

N_{1s} (392–408 eV), O_{1s} (524–540 eV), Mg_{1s} (1294–1312 eV), Si_{2p} (94–110 eV), Cl_{2p} (194–208 eV) and Ca_{2p} ($2p_{1/2}$, $2p_{3/2}$) (338–358 eV). For XPS peak analysis, C_{1s} peak position was set at 285 eV and used as a reference to locate the other peaks.

3. Results and discussion

The characterization of modified coconut fibers is important because the induced changes affect the success of potential applications. Thus, morphological and chemical modifications, and their impact on the material resistance were studied after chemical treatments.

3.1. Morphological characterization

The first aspect analyzed was the chemical treatment effect on fiber morphology by optical and scanning electron microscopies of the fibers. Using an optical microscope, it was possible to observe that natural green coconut fiber has a light brown color (Fig. 1a)¹ that differs considerably from a mature coconut fiber, which has a dark brown color. The chemical treatment with NaOCl preserves the light brown color (Fig. 1b). The treatment with NaOCl and NaOH makes it even more lighter (Fig. 1c), while the use of H_2O_2 changed the fiber color to yellow (Fig. 1d). The observations suggest that H_2O_2 was the most efficient in removing pigments, which was expected since H_2O_2 is widely used for the bleaching of fibers (Reyes, Peralta-Zamora, & Durán, 1998).

The results of diameter determination for natural and treated green coconut fibers are shown in Table 1. A set of at least 20 fibers were used for each run. A natural dispersion of values can be observed for all fibers studied in this work (natural or treated). For instance, the fiber treated with NaOCl presented an average diameter of $148 \pm 92 \mu\text{m}$, ranging from 69 to 495 μm , showing large size and

shape irregularities. This variation in the diameter values was also observed by Silva et al. (2000), with minimum and maximum values of 269 and 419 μm , respectively, and an average diameter of $337 \pm 55 \mu\text{m}$ for the diameter of a single fiber. Different studies have reported average diameters ranging from 40 to 400 μm for Brazilian coconut fibers (Satyanarayana et al., 2007). Plant and soil type, usage and climatic conditions may be the cause of these deviations in the fiber diameter. Chemical treatments with NaOCl or H_2O_2 , did not change the green coconut fiber diameter. However, the treatment with NaOCl and NaOH caused a significant reduction in the average diameter of coconut fiber by as much as 1:3 of the natural fiber value.

Although the reactions have been carried out in short fibers ($\sim 2 \text{ mm}$) and under constant stirring, all treatments resulted in heterogeneous surfaces. The non-uniformity obtained in this study is, probably, caused by heterogeneous distribution of impurities observed (Fig. 2a) in the natural fiber, showing that a slight increase in the reagent concentration and/or in the exposure time must be applied to obtain more uniform fibers, fully free from impurities. Scanning electron microscopy showed that NaOCl treated fiber surface was identical to the natural one (Fig. 2a), and it did not remove globular protrusions or patches of waxy and fatty acids present on the fiber surface at regular intervals (Fig. 2b). For rice husk, a material with less lignin amount, however, this treatment

Table 1
Diameter of natural and treated green coconut fibers.

| Fibers | Average diameter (μm) | | | |
|--------------------------------|------------------------------------|---------|---------|--------------------|
| | Maximum | Minimum | Average | Standard deviation |
| Natural | 495 | 69 | 157 | 87 |
| NaOCl treated | 495 | 69 | 148 | 92 |
| NaOCl/NaOH treated | 165 | 7 | 44 | 28 |
| H_2O_2 treated | 511 | 103 | 153 | 58 |

¹ For interpretation of the references to color in this figure, the reader is referred to the web version of this paper.

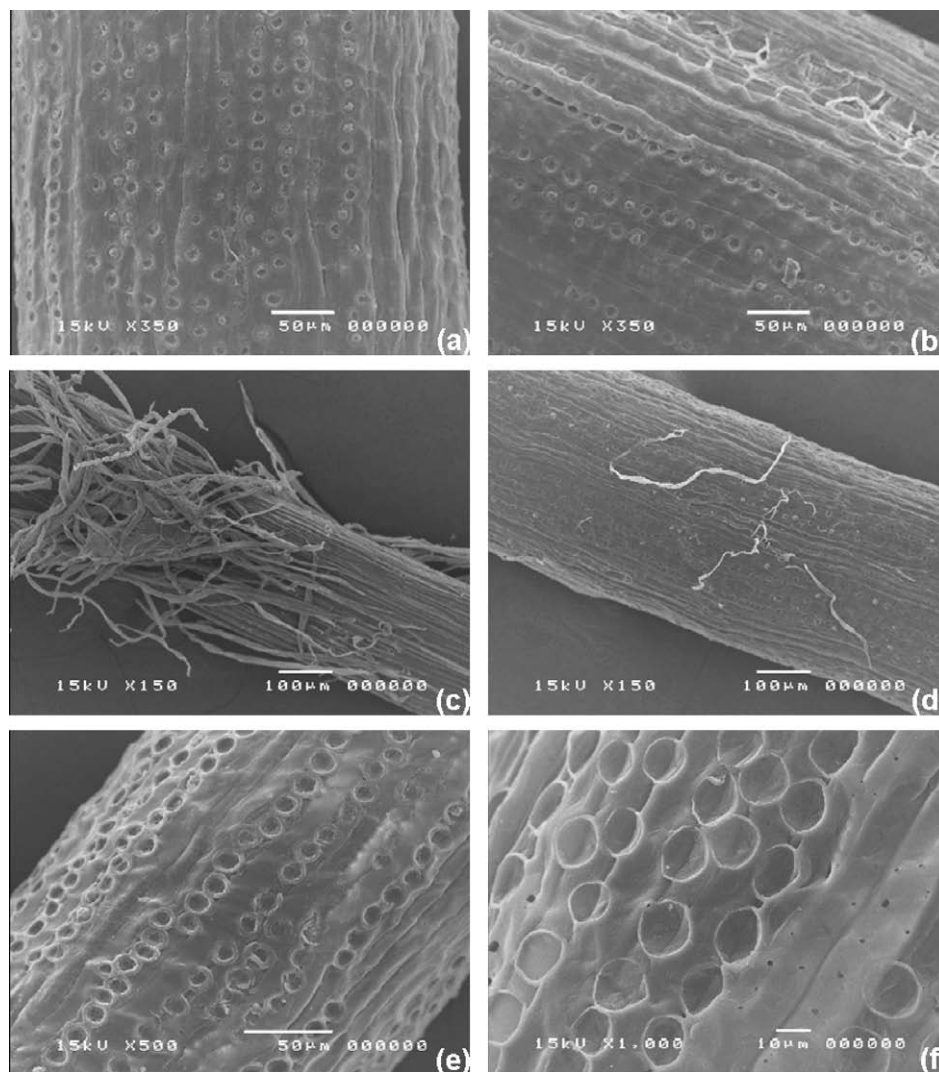


Fig. 2. Natural green coconut fiber, 350 \times (a), NaOCl treated fiber, 350 \times (b), NaOCl/NaOH treated fiber showing partial disintegration, 150 \times (c) NaOCl/NaOH treated fiber showing the presence of wax and fatty acid residues, 150 \times (d), H_2O_2 treated fiber, 500 \times (e) and H_2O_2 treated fiber, 1000 \times (f).

was efficient and promoted a uniform treatment of the fiber (Reyes et al., 1998).

The treatment with NaOCl and NaOH produced a scratch formation and a partial disintegration of the fiber, probably because of the removal of part of the hemicellulose and lignin that interconnects the cellulose fibrils (Figs. 1 and 2c). Comparing this treated fiber surface with natural and NaOCl treated fiber surfaces, it is possible to observe a reduction on waxy and fatty acids (Fig. 2d). Besides, a larger removal of the parenchyma cells was observed, making the surface of the fiber wavier. Similar results were also observed by other authors using only NaOH (Rout et al., 2001; Martins, Kiyohara, & Joekes, 2004).

The H_2O_2 treatment seems to be the most efficient in the removal of waxy and fatty acids residues (Fig. 2e and f). Although the waxy removal has been observed, pit like openings were preserved (Fig. 2e). But, in some parts, where the chemical attack was probably stronger, the fibers appeared to be deformed, with a smoother surface (Fig. 2f).

3.2. Chemical characterization

The amount of cellulose and non-cellulosic constituents in a fiber determines its structure and properties and it influences the moisture content (Reddy & Yang, 2005). In Table 2 the influence

of chemical treatments on density and some chemical constituents is reported. Only the treatment with NaOCl/NaOH results in a significant mass and volume loss affecting the fiber density. This treatment caused a mass loss and also reduced considerably the fiber volume. Therefore, the density of this fiber was larger than natural fiber density, becoming similar to palm fiber (1030 kg/m³) density (Spinacé, Lambert, Fermoselli, & Paoli, 2009).

Comparing the three treatments, only the treatment with NaOCl and NaOH affected the fiber cellulose content. The observed increase may be explained by hemicellulose partial removal, what can be confirmed by the disintegration observed in Fig. 2c. The amount of insoluble lignin is not modified in all fibers while a reduction in the soluble lignin was observed.

Table 2

Density and chemical composition of natural and treated green coconut fibers.

| Fiber | Density (kg/m ³) | Cellulose (%) | Klason lignin | |
|--------------------|------------------------------|------------------|-----------------|-------------------|
| | | | ASL (%) | AIL (%) |
| Natural | 825 \pm 18 | 45.93 \pm 1.50 | 2.92 \pm 0.43 | 40.22 \pm 5.79 |
| NaOCl treated | 790 \pm 17 | 41.89 \pm 2.50 | 2.05 \pm 0.20 | 45.23 \pm 15.44 |
| NaOCl/NaOH treated | 1057 \pm 115 | 62.77 \pm 5.90 | 1.41 \pm 0.01 | 43.71 \pm 11.40 |
| H_2O_2 treated | 804 \pm 30 | 43.95 \pm 1.50 | 1.18 \pm 0.01 | 41.55 \pm 6.00 |

3.3. Fourier transform infrared spectroscopy

The FTIR spectra of natural and treated green coconut fibers are shown in Fig. 3. All these spectra reveal a broad and intense peak at $\sim 3340\text{ cm}^{-1}$ suggesting hydrogen-bonded $\nu(\text{O—H})$ stretching vibration from the cellulose and lignin structure of the fiber. FTIR analyses also reveal a reduction in hemicellulose content in the fibers treated with NaOCl and NaOH (Fig. 3). The characteristic bands of hemicellulose, observed in the natural green coconut fiber around 1728 cm^{-1} , are not present in NaOCl and NaOH treated fibers. This phenomenon has been verified by Rout et al. (2001) that used NaOH in the treatment of fiber surfaces. The spectra of the fibers treated with NaOCl and NaOH also presented such characteristic. The band at 1238 cm^{-1} is related to the vibration $\nu(\text{C—O})$ of esters, ethers and phenols groups attributed mainly to a presence of waxes in the epidermal tissue (Herrera-Franco & Valadarez-González, 2005), and the disappearance of this band in the treated fibers results from the removal of those waxes.

The hydrogen peroxide tends to oxidize the hydroxyl groups from cellulose in the fiber surface to carboxyl groups giving the fiber a soft cationic potential (Reyes et al., 1998; Shukla & Pai, 2005). This oxidation is confirmed by the spectra of the H_2O_2 treated fibers (Fig. 3) at 1728 cm^{-1} . The carbonyl signal initially present is from lignin and hemicellulose; after the treatment, the formation of carboxyl groups is observed, whose axial vibration of C=O intensifies the peak. The band at 1238 cm^{-1} in H_2O_2 treated fiber spectrum is intensified by the presence of carboxyl groups formed, representing the axial vibration of O—C—C (Bilba, Arsene, & Ouen-sanga, 2007). Between 1370 and 1390 cm^{-1} , the absorption peak refers to a symmetrical and an asymmetrical deformation of C—H in cellulose and hemicellulose groups. In spectra of NaOCl and NaOH treated fibers and H_2O_2 treated fibers, these bands are more accentuated, what can be an indicative of a larger exposition of cellulose and hemicellulose on the fiber surface.

3.4. X-ray photoelectron spectroscopy

The surface element distribution of the coconut fibers was obtained by X-ray photoelectron spectroscopy (XPS) analysis. Mass

Table 3

Mass surface concentration (%) determined by XPS quantitative analysis of natural green coconut fiber and different treated coconut fibers.

| Fiber | C _{1s} | O _{1s} | N _{1s} | Si _{2p} | Ca _{2p} | Mg _{1s} | Cl _{2p} | Na _{1s} | O/C |
|------------------------|-----------------|-----------------|-----------------|------------------|------------------|------------------|------------------|------------------|------|
| Natural | 69.05 | 27.36 | 2.04 | 1.10 | 0.46 | – | – | – | 0.40 |
| NaOCl | 59.89 | 34.43 | 1.32 | 0.39 | 0.13 | 0.96 | 2.89 | – | 0.57 |
| NaOCl/ NaOH | 63.39 | 30.41 | 0.86 | 0.97 | 0.29 | 0.19 | 0.30 | 3.60 | 0.48 |
| H_2O_2 | 65.01 | 33.23 | 0.81 | 0.78 | 0.17 | – | – | – | 0.51 |

surface concentrations of samples have been obtained by numerical integration of the spectra peaks and are reported in Table 3. The main elements detected using XPS were carbon and oxygen. Small amounts of nitrogen, silicon and calcium were also present in natural fiber. Cellulose, hemicellulose and pectin have an O/C ratio of 0.83 while lignin has a ratio of just 0.35 (Sgriccia, Hawley, & Misra, 2008). Since the O/C ratio of natural and treated green coconut fibers is inferior to 0.83, the surface must have a significant proportion of lignin and waxes. However, considering the increase in the O/C ratio observed for all treated fibers (Table 3), and considering the chemical composition of the fibers (Table 2), it is possible to state that all chemical treatments evaluated in this work reduced the proportion of waxes on the surface, increasing cellulose exposition. The increase in cellulose on the fiber surfaces provides more hydroxyl groups that can react with epoxide groups, in the epoxy resin production, and with silane groups, for instance in the fiber functionalization for enzyme immobilization by covalent attachment. Some lignocellulosic materials present silicon in their composition, which provides stability (Rosas, Bedia, Rodríguez-Mirasol, & Cordero, 2008). In natural and treated green coconut fibers, there are peaks at 486 cm^{-1} because of SiO_2 and at 1122 cm^{-1} because of SiC (Fig. 3). During the treatments using NaOH, SiO_2 is converted to Na_2SiO_3 which can justify the appearance of Na in NaOCl and NaOH treated fiber surface (Table 2).

3.5. Thermal analysis

The data obtained from the thermograms of natural and treated fibers (TG and DTG curves) are summarized in Table 4. Three

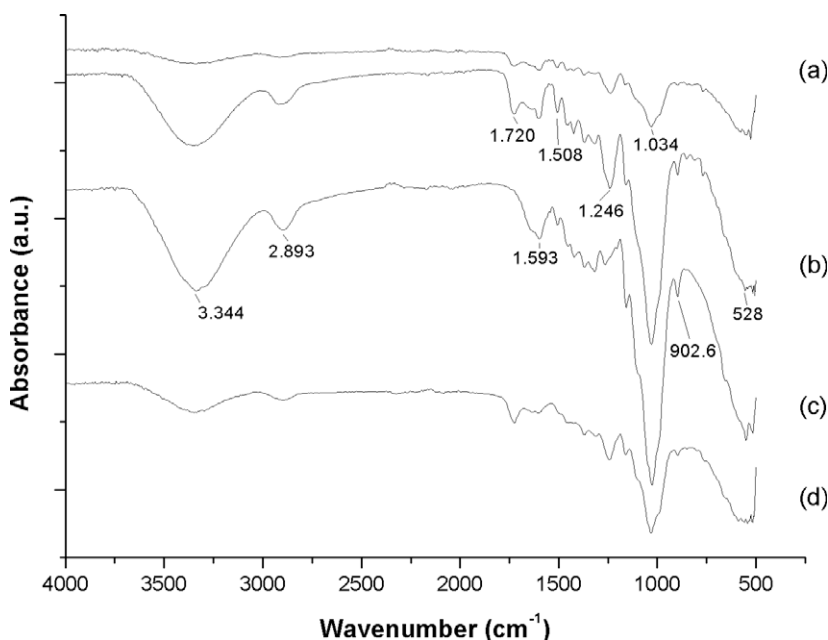


Fig. 3. FTIR spectra of different chemically modified green coconut fiber: (a) natural, (b) H_2O_2 treated, (c) NaOCl/NaOH treated, and (d) NaOCl treated.

Table 4

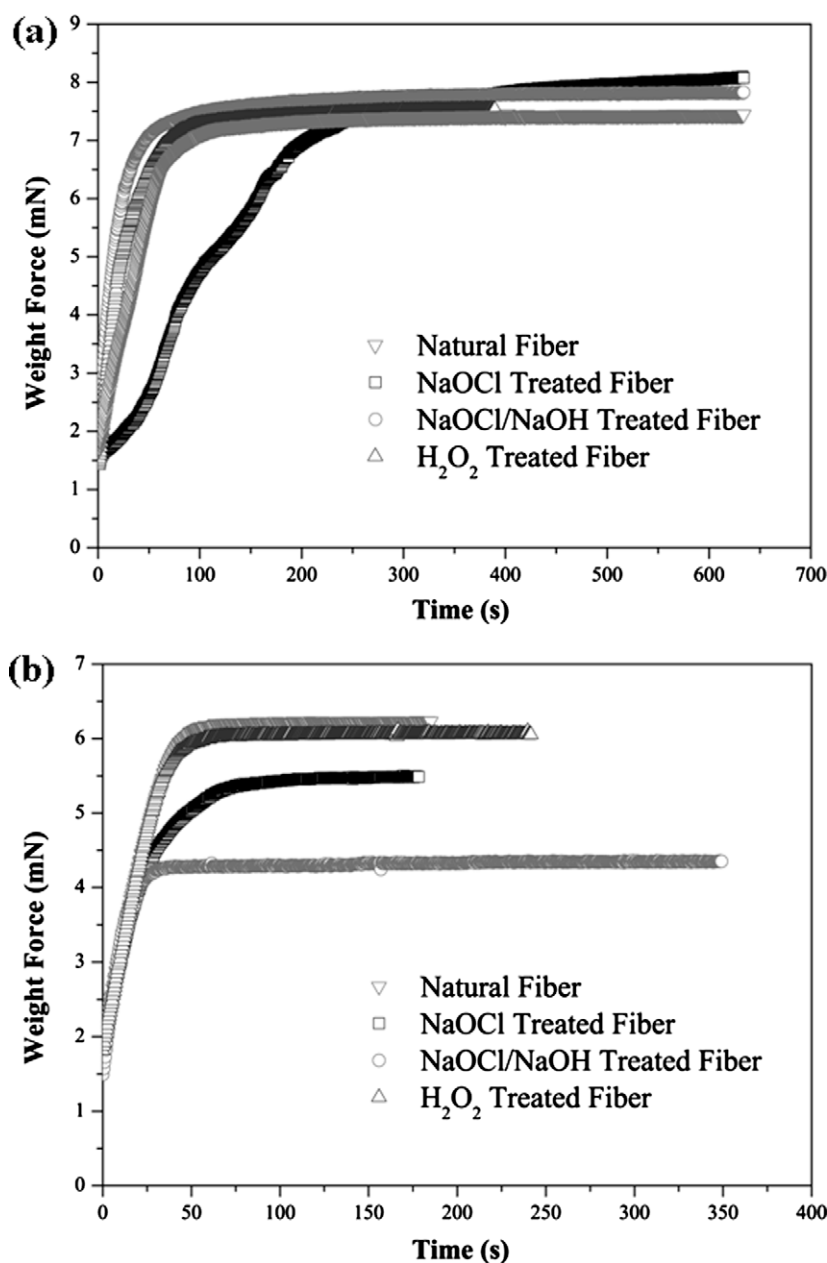
Thermogravimetric results of natural and chemically treated green coconut fibers.

| Fiber | Transition temperature range (°C) | Transition peak (°C) | Onset (°C) | Weight loss (%) |
|---------------------------------------|-----------------------------------|----------------------|------------|-----------------|
| Natural | 30–100 | 50 | – | 4.79 |
| | 220–340 | 310 | 268.8 | 28.82 |
| | 340–500 | 370 | 310 | 47.42 |
| H ₂ O ₂ treated | 30–80 | 50 | – | 3.53 |
| | 220–340 | 315 | 274.1 | 27.86 |
| | 340–500 | 400 | 312.4 | 43.27 |
| NaOCl treated | 30–90 | 50 | – | 3.46 |
| | 200–330 | 290 | 255.8 | 23.53 |
| | 330–500 | 370 | 306.9 | 49.74 |
| NaOCl/NaOH treated | 30–100 | 50 | – | 6.39 |
| | 230–550 | 350 | 294.4 | 67.52 |

degradation steps can be seen at TG curves. Some fibers, such as curaua, present four degradation processes (Spinacé et al., 2009).

The first weight decay is related to moisture loss with a peak observed at 50 °C for all samples. Because of the higher cellulose exposure, the fibers treated with NaOCl/NaOH presented 1.6% more water, which is inferior that one reported by other authors that use alkaline treatment (Silva et al., 2000).

The treatment of green coconut fibers with H₂O₂ promoted an increase in thermal stability. The opposite effect is observed for the fibers treated with NaOCl/NaOH. For the fibers treated with NaOCl/NaOH, the absence of detectable levels of hemicellulose in the TG, and the loss of weight caused mainly by the degradation of cellulose and lignin justifies the occurrence of only two peaks for this sample (50 and 350 °C). This phenomenon was also reported by d'Almeida, Barreto, Calado, and d'Almeida (2008) studying curaua and caroa fibers that also have low hemicellulose levels. As cellulose and lignin begin their process of degradation at 200 and 310 °C, respectively, peaks in the DTG curves were only observed at 350 °C. Silva et al. (2000) also reported a decrease in thermal stability after treatment with NaOH.

**Fig. 4.** Testing of wetting in water (a) and hexadecane (b) for natural and treated coconut fibers.

3.6. Wettability

The wettability of a surface in a solvent can be evaluated by the contact angle between the surface and the solvent. The weight force against contact time observed for the fiber–water and fiber–hexadecane systems, respectively, are shown in Fig. 4. In studies of wettability of coconut fibers in water (Fig. 4a), it was observed that the interaction fiber–solvent varies slightly depending on the chemical treatment applied. The interaction fiber–water for natural and H₂O₂ treated fibers were equal, with values of 7.3 and 7.4 mN, respectively, for the system at equilibrium. The fibers treated with NaOCl or NaOCl/NaOH presented values of 8.0 and 7.7 mN, respectively. Based on these results, it is possible to assume that only the fibers treated with NaOCl or NaOCl/NaOH have become a little more hydrophilic than the natural fiber. This was expected because NaOCl/NaOH treated fiber has more cellulose exposed on the surface, as shown before.

In the studies using hexadecane (Fig. 4b), it was observed that the interaction fiber–solvent varied considerably with the chemical treatment. The interaction fiber–hexadecane for natural and H₂O₂ treated fibers was similar, with values of 6.2 and 6.1 mN, respectively. Nevertheless, the fibers treated only with NaOCl or NaOCl/NaOH presented smaller forces at equilibrium, 5.5 and 4.3, respectively. These low values resulted from a reduction in hydrophobic sites caused by the removal of lignin. The studies of wettability show that the treatment with H₂O₂ does not modify the hydrophilic/hydrophobic nature of green coconut fiber.

4. Conclusions

In this work, we have reported the use of three different chemical treatments on green coconut fiber and its morphological and chemical characterization. The fiber morphology analyses showed that the treatment with H₂O₂ is indicated for applications where decolorized fibers are required and when the presence of waxes and fatty acids on fiber surface are undesirable. Chemical characterization showed the composition of the fiber surfaces and the relationship of these characteristics with thermal resistance and with hydrophilic/hydrophobic character. The treatment with NaOCl/NaOH was the most efficient in hemicellulose removal and, consequently, in cellulose exposition. High amount of cellulose on fiber surfaces provides free hydroxyl groups that can react with the epoxide groups, in epoxy resin production, and with silane groups, for instance, in the functionalization for enzyme immobilization by covalent attachment. Therefore, cellulose presence increases the potential of using this fiber when free OH is fundamental. Fiber treatments with H₂O₂, through the oxidation of hydroxyl groups to carboxyl groups (confirmed by FTIR), promoted a smooth cationic potential on fiber surface. This characteristic is necessary to fiber applications as metal adsorbents, for example. Furthermore, this treatment is shown to maintain the native hydrophilic/hydrophobic characteristic of green coconut fiber and to increase its thermal stability.

Acknowledgments

We are grateful to Dr. Leonardo Rodrigues de Andrade for the SEM work and to Prof. João A.P. Coutinho for the fruitful discussions about the results. The authors also thank financial support from CAPES, CNPq, FAPERJ, FCT and CICECO.

References

- Bilba, K., Arsene, M.-A., & Ouensanga, A. (2007). Study of banana and coconut fibers: Botanical composition, thermal degradation and textual observations. *Bioresource Technology*, 98, 58–68.
- Brígida, A. I. S., & Rosa, M. F. (2003). Determinação do teor de taninos na casca de coco verde (*Cocos nucifera* L.). *Proceedings of the Interamerican Society For Tropical Horticulture*, 47, 25–27.
- Brígida, A. I. S., Pinheiro, A. D. T., Ferreira, A. L. O., & Gonçalves, L. R. B. (2007). Immobilization of *Candida antarctica* lipase B by covalent attachment to green coconut fiber. *Applied Biochemistry and Biotechnology*, 136, 67–80.
- Brígida, A. I. S., Pinheiro, A. D. T., Ferreira, A. L. O., & Gonçalves, L. R. B. (2008). Immobilization of *Candida antarctica* lipase B by adsorption to green coconut fiber. *Applied Biochemistry and Biotechnology*, 146, 173–187.
- Carrijo, O. A., Liz, R. S., & Makishima, N. (2002). Fibra da casca de coco verde como substrato agrícola. *Horticultura Brasileira*, 20, 533–535.
- Coelho, M. A. Z., Leite, S. G. F., Rosa, M. F., & Furtado, A. A. L. (2001). Aproveitamento de resíduos agroindustriais: Produção de enzimas a partir da casca de coco verde. *Boletim CEPPA*, 19, 33–42.
- Corradini, E., Morais, L. C., Rosa, M. F., Mazzetto, S. E., Mattoso, L. H. C., & Agnelli, J. A. M. (2006). A preliminary study for the use of natural fibers as reinforcement in starch–gluten–glycerol matrix. *Macromolecular Symposia*, 245, 558–564.
- d'Almeida, A. L. F. S., Barreto, D. W., Calado, V., & d'Almeida, J. R. M. (2008). Thermal analysis of less common lignocellulose fibers. *Journal of Thermal Analysis and Calorimetry*, 91, 405–408.
- Dey, G., Nagpal, V., & Banerjee, R. (2002). Immobilization of α -amylase from *Bacillus circulans* GRS 313 on coconut fiber. *Applied Biochemistry and Biotechnology*, 102–103, 303–313.
- Dey, G., Chakraborty, M., & Mitra, A. (2005). Profiling C₆–C₃ and C₆–C₁ phenolic metabolites in *Cocos nucifera*. *Journal of Plant Physiology*, 162, 375–381.
- Food and Agriculture Organization of the United Nations – FAO. (2008). Database agricultural – Production – Crops primary – Coconut. July 20. Available from: <http://faostat.fao.org>.
- Herrera-Franco, P. J., & Valadarez-González, A. (2005). A study of the mechanical properties of short natural-fiber reinforced composites. *Composites: Part B*, 36, 597–608.
- John, M. J., & Thomas, S. (2008). Biofibres and biocomposites. *Carbohydrate Polymers*, 71, 343–364.
- Martins, M. A., Kiyohara, P. K., & Joekes, I. (2004). Scanning electron microscopy study of raw and chemically modified sisal fibers. *Journal of Applied Polymer Science*, 94, 2333–2340.
- Neto, C. P. C. T., Ferreira, F. F. H., Bezerra, F. C., Sousa, R. F., & Cavalcanti, M. L. F. (2004). Efeito de diferentes substratos na aclimatização “ex-vitro” de mudas de Violeta Africana (*Saintpaulia ionantha* Wendl). *Revista de Biologia e Ciências da Terra*, 4, 2–6.
- Reddy, N., & Yang, Y. (2005). Biofibers from agricultural byproducts for industrial applications. *Trends in Biotechnology*, 23, 22–27.
- Reyes, J., Peralta-Zamora, P., & Durán, N. (1998). Hidrólise enzimática de casca de arroz utilizando-se celulases. Efeito de tratamentos químicos e fotoquímicos. *Química Nova*, 21, 140–143.
- Rosa, M. F., Bezerra, F. C., Correia, D., Santos, F. J. S., Abreu, F. A. P., Furtado, A. A. L., et al. (2002). *Utilização da casca de coco como substrato agrícola*. Fortaleza: Embrapa Agroindústria Tropical. 22p. (Documentos, 52).
- Rosas, M., Bedia, J., Rodríguez-Mirasol, J., & Cordero, T. (2008). Hemp-derived activated carbon fibers by chemical activation with phosphoric acid. *Fuel*, 88, 19–26.
- Rout, J., Tripathy, S. S., Nayak, S. K., Misra, M., & Mohanty, A. K. (2001). Scanning electron microscopy study of chemically modified coir fibers. *Journal of Applied Polymer Science*, 79, 1169–1177.
- Satyanarayana, K. G., Guimarães, J. L., & Wypych, F. (2007). Studies on lignocellulosic fibers of Brazil. Part I – Source, production, morphology, properties and applications. *Composites: Part A*, 38, 1694–1709.
- Sgriccia, N., Hawley, M. C., & Misra, M. (2008). Characterization of natural fiber surfaces and natural fiber composites. *Composites: Part A*, 39, 1632–1637.
- Shukla, S. R., & Pai, R. S. (2005). Adsorption of Cu(II), Ni(II) and Zn(II) on modified jute fibres. *Bioresource Technology*, 96, 1430–1438.
- Silva, G. C., Souza, D. A., Machado, J. C., & Hourston, D. J. (2000). Mechanical and thermal characterization of native Brazilian coir fiber. *Journal of Applied Polymer Science*, 76, 1197–1206.
- Spinacé, M. A. S., Lambert, C. S., Feroselli, K. K. G., & Paoli, M. A. (2009). Characterization of lignocellulosic curauá fibers. *Carbohydrate Polymers*, 77, 47–53.
- Tomczak, F., Sydenstricker, T. H. D., & Satyanarayana, K. G. (2007). Studies on lignocellulosic fibers of Brazil. Part II – Morphology and properties of Brazilian coconut fibers. *Composites: Part A*, 38, 1710–1721.
- van Dam, J. E. G., van Den Oever, M. J. A., Teunissen, W., Keijsers, E. R. P., & Peralta, A. G. (2004). Process for production of high density/high performance binderless boards from whole coconut husk. Part 1: Lignin as intrinsic thermosetting binder resin. *Industrial Crops and Products*, 19, 207–216.