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DWARF-GREEN COCONUT FIBERS: A VERSATILE NATURAL RENEWABLE RAW BIORESOURCE. TREATMENT, MORPHOLOGY, AND PHYSICOCHEMICAL PROPERTIES

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Dwarf-green coconut fibers were modified by alkali treatment and characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), as well as thermogravimetric (TGA), mechanical, and dielectric analyses. Changes in composition, structure, and morphology of the coconut fibers were observed after sodium hydroxide treatments due to the removal of lignin, hemicellulose, and other impurities. The XRD data were in agreement with the morphological analysis, where the crystallinity fraction increased with the concentration of alkali solution and fell off above 10%. The infrared spectrometry showed the partial dissolution of hemicellulose, lignin, and pectin, which was clearly identified by the band at 1736 cm^{-1}. Thermogravimetric analysis showed a double degradation process for the untreated dwarf-green coconut fibers, while a single one was observed after the pretreatment. The tensile properties showed an increased elongation at break, modulus, and strength, and the dielectric results showed a decrease of all parameters (permittivity, dielectric loss, and conductivity), reflecting the reduced dipole and ion mobility associated with the loss of amorphous components.

INTRODUCTION

A great interest towards the development of composite materials reinforced with natural fibers has emerged in the last decade (Martins and Mattoso 2004; Mohanty and Nayak 2004b; Thomsen et al. 2006; Bérnard et al. 2005; Bledzki and Gassan 1999; Ramakrishna and Sundararajan 2005; Ray et al. 2002b; Herrera-Franco and Valadez-González 2005; Wambua et al. 2003; Mwaikambo and Ansell 2006). One of the principal

advantages is given by the widespread availability of fibers, their low cost, weight, biodegradability, CO_2-neutral renewable nature, and good mechanical properties. Coconut (*Cocos nuciferas L.*), is one of the most widely planted tree species in tropical countries. According to Faostat (FAO 2008) Brazil is the fourth producer, followed by the Philippines, Indonesia, and India, with an annual production of 3 million tons of nuts.

Historically, the Northeast of Brazil is the largest Brazilian production region for coconut: Bahia state occupies the first place with 35.2%, followed by Pará with 12.2% and Ceará with 11.9% (AGRIANUAL 2008). Brazil presents a peculiarity with respect to the coconut fruit. While is globally known as an oleaginous one and used only in the final stage of maturing for production of oil and other products, in Brazil it is also consumed at an immature stage thanks to the quality of its juice. Due to this peculiarity, the production of dwarf-green coconut is growing in Brazil in the most recent years. The average production of green coconuts is 200 fruit/tree, and fruit harvesting is facilitated by the tree size reaching a maximum height of 10 meters, Fig. 1. The traditional variety, called giant coconut, is very different from the dwarf-green coconut, being tall (20-30 meters), and having a later start its production (from 6 to 9 years of age), giving an average of 70 fruits/tree.

Fig. 1.   Typical tree of dwarf-green coconut
(Source:http://www.ceplac.gov.br/radar/coco.htm)

According to the Brazilian Company of Agricultural Research, about 70% of the total litter disposed on the beaches of the Northeast of Brazil corresponds to green coir. In Fortaleza, just in the Future's Beach and in the Coastal Avenue in the high season (December to February and July) 40 tons/day of green coir are disposed (EMBRAPA, 2008).

As a consequence, this large amount of waste material is becoming a problem in many cities in Brazil as well as in the main producer countries (India, The Philippines, Malaysia, Sri Lanka, Jamaica, and others). For this reason, the development of alternatives that make possible the reduction of the high amount of the green coir shells

sent to waste disposal sites is very important in order to reduce their environmental impact. Among other solutions, the use of green coir fibers as reinforcement of composites could be an interesting and useful application.

Coir (from Malayalam Kayar, cord), a coarse fiber extracted from the fibrous outer shell (mesocarp part of the fruit) of a coconut, is characterized by a length varying from 10 to 200 mm, and it is coated with wax of non-polar aliphatic origin presenting globular formations (Ray et al. 2002b; Van Dam 2004b). Chemical treatments can change the surface polarity, increasing the fiber-resin adhesion, a key property in composite materials. As a consequence there is a growing interest to produce novel bio-based composite materials with a high percentage of renewable materials.

The treatment depends on the type and concentration of the alkali solutions, temperature, time of treatment, tension applied to the material, and additives (Silva et al. 2000, Mannan 1993). Several studies reported the surface modifications of fibers (Martins and Mattoso 2004; Mohanty and Nayak 2004b; Thomsen et al. 2006; Bérnard et al. 2005; Bledzki and Gassan 1999, Ramakrishna and Sundararajan 2005; Ray et al. 2002c; Herrera-Franco and Valadez-González 2005; Wambua et al. 2003; Mwaikambo and Ansell 2006); AGRIANUAL 2008; EMBRAPA 2008; Esmeraldo 2006, Calò et al. 2007; Maffezzoli et al. 2004, Pothan et al. 1997a; Pothan and Thomas 2003b; Karnani 2004; Mohanty et al. 2000a; Rout and Mishra 2001; Geethamma et al. 1998a; Vijayalakshmi et al. 2000; Savastano 2000b; Goda et al. 2006; Gomes et al. 2007; Ray and Sarkar 2001a) to improve interfacial bonding between fiber and matrix.

Recently, novel bio-composites were obtained using jute, sisal, sugarcane bagasse, and banana fibers in combination with cardanol-based phenolic resins deriving form CNSL, which are nowadays considered to be very attractive renewable bio-sources to use in eco-friendly processes (Ray et al. 2002b; Esmeraldo 2006; Calò et al. 2007; Pothan et al. 1997a; Pothan and Thomas 2003b; Karnani 2004; Mohanty et al. 2000a).

In this paper the effect of alkali treatment on the structure and surface of dwarf-green coir fibers was investigated using different characterization techniques devoted to studying either the morphology or the physicochemical and mechanical properties. The dwarf-green coir fibers used originated from the Northeast of Brazil, and more specifically from Fortaleza.

EXPERIMENTAL

Materials

The coir fibers were collected from fresh husk and supplied by Empresa Brasileira de Pesquisa Agropecuária, Fortaleza-Brazil located in the Federal University of Ceará. The fibers were previously selected (approximately 20 cm in length) and washed at room temperature for one hour with a neutral detergent and distilled water to remove eventual residues. Finally, the fibers were dried. A mild chemical attack was performed using NaOH and NaClO (Aldrich) solution.

In a typical experiment 20.0 g of dried coir fibres were treated with 50.0 mL of alkali solutions at different percentage weight concentration (2%, 5%, 8%, 10%, 12%, and 15%) in the range of temperature of 60 to 70 °C, for 6 hours. Then the fibers were

washed several times with distilled water to remove any sodium hydroxide excess from the surface, i.e. until the water no longer showed any alkalinity. Subsequently, the fibers were dried at 60 °C for 24 h. The fibers were dipped in $NaClO/H_2O$ solution (2.5 %/L), under heating (60 °C) for 4 hours. At this point, the bleached fibers were subsequently washed with distilled water until free from any chemicals.

Methods

The determination of lignin was based on the ASTM Test Method (ASTM D1106-96). The method involves a pre-treatment to remove the acid components, followed by separation of the residual insoluble matter, leaving the lignin as a final residue. The cellulose content was obtained by the Yokoyama procedure (Yokoyama et al. 2002) by the oxidation with sodium chlorite and acetic acid, destroying all the lignin, and leaving cellulosic compounds.

Morphological characterization by scanning electron microscopy (SEM) was used to observe the surface morphology and the microstructure of the fibers. The micrographs were obtained by the electronic microscope model DSM 960/Zeiss, with 20 kV electron beam. The samples were coated with silver using a BALZERS 5CD50 apparatus. The composition of topographic features identified at the surface of the fibers was determined by energy dispersive X-rays spectrometry (EDS).

The thermal stability of the fibers was evaluated by thermogravimetric analysis (TGA). The decomposition analyses were performed under either nitrogen or air atmospheres in a constant flow of 60 cm^3 min^{-1}, with a heating rate of 5.0 to 10.0 ^oC and a sample mass of 10 mg. Dynamic experiments were performed using a Shimadzu Thermogravimetric Analyser TGA 50H, AC115V. The curves were obtained in a Shimadzu TGA-50H with temperature programs from 30 to 800 ^oC at a heating rate of 5 to 10 $^oC/min$.

The X-ray diffraction (XRD) patterns were obtained at room temperature (300 K) by step scanning, using powdered samples. The coir fibers samples were powdered, and the particle size selected using a ϕ = 250 μm mesh screen. These particles were compacted in a cylindrical mold of 1.5 cm diameter and submitted to the pressure of 111 MPa. A five seconds integration time was applied for each step with a Cu-Kα tube at 40 kV and 25 mA using the Bragg-Bretano geometry. The coir fibers crystallinity fraction (Eq. (1)) was obtained through separation and integration of crystalline and amorphous peak areas under the diffraction X-rays plot as,

$$C\% \ = \frac{\sum I_C}{\sum (I_C + I_A)} \tag{1}$$

where I_c is the area under the diffractogram of the crystalline phase and the I_A is the area under the diffractogram of the amorphous phase.

The dielectric properties (permittivity-K, dielectric loss-D, and dielectric conductivity-σ) of the fibers were obtained from a HP 4291A Material Impedance Analyzer, covering the region of 100 Hz to 40 MHz at 300 K. The mechanical properties

were measured using an INSTRON 5569 dynamometer. The tensile tests were carried out on five samples for each kind of fiber (unmodified and after treatment), using an average length of 5.4 cm. The fibers were fixed in a rectangular window, with 2.0 cm of width and 5.5 cm of length, according with the standard ASTM method (ASTM WK20144 Revision of D3039/D3039M-07). A rate of elongation of 2.0 mm/min., using a 50 N load cell was used.

Infrared measurements were performed using a Perkin Elmer 2000 spectro-photometer in the 4000 to 400 cm^{-1} wavenumber range. The samples were previously dried, ground to powder, and pressed (10 μg of sample to 100 mg of KBr) in a disk shape for measurements.

RESULTS AND DISCUSSION

Treatments and Composition of Coir Fibers

The potential use of natural fibers as composite material reinforcement is strictly related to the ability of a hydrophobic resin to wet out and bond to the fibers (Mohanty and Nayak 2004b; Bledzki and Gassan 1999; Herrera-Franco and Valadez-González 2005; Ray et al. 2002b; Van Dam 2004b; Silva et al. 2000; Mannan 1993; Esmeraldo 2006; Pothan et al. 1997a; Goda et al. 2006; Gomes et al. 2007; Ray and Sarkar 2001a; Almeida et al. 2006; Campana et al. 2002; Maldas et al. 1997; Calado and Barreto 2000). This can be achieved by matching the physicochemical characteristics of the fiber surface on the matrix. Renewable materials, when used as reinforcement in thermoplastic matrix, can give rise to new composite materials with lower cost and interesting mechanical properties.

Numerous treatments are available (alkali, silane, cyanoethylation, acetylation, use of different coupling agents, mercerization) and frequently each one of them has been explained in terms of a different theory of adhesion. One of the oldest methods, still economically viable, is alkaline treatment (alkali solution at low concentrations) leading to surface cleaning by partially removing hemicelluloses and lignin, at the same time promoting a decrease in the diameter and an increase in fiber crystallinity (Ray et al. 2002b; Van Dam et al., 2004b; Goda, et al. 2006; Gomes et al. 2007; Ray and Sarkar 2001a; Calado and Barreto 2000; Xiao et al. 2001).

On the basis of results previously obtained for other vegetable fibers (Esmeraldo 2006; Pothan et al. 1997a; Goda et al. 2006; Gomes et al. 2007; Ray and Sarkar 2001a; Calado and Barreto 2000; Xiao et al. 2001), in consideration of the optimized mechanical and physical properties for the application as composite reinforcements (Ray et al. 2002c; Herrera-Franco and Valadez-González 2005; Esmeraldo 2006; Campana et al. 2002; Calado and Barreto 2000; Eichorn et al. 2001; Peijs 2000; Joseph et al. 2002; Tita 2002), the alkali treatment was employed in this work. The qualitative effect of the NaOH treatment is shown in Fig. 2.

Fig. 2. Dwarf-green coir fibers before and after alkali treatment

Traditional coir fibers have been characterized by different authors, who have observed that many factors can influence their properties, including weather conditions, whether they are green or mature, the age of the plant, the type of soil, and the extraction method (Bledzki and Gassan 1999; Ray et al. 2002b; Pothan et al. 1997a; Karnani 2004). Similar considerations hold for dwarf-green coir fibers, even if the properties of the fibers are still under examination. Table 1 shows the chemical composition of principal macro-components of traditionally studied coir fibers of different types, maturation degree, and origin.

Coconut coir is the seed-hair fiber obtained from the outer shell (endocarp) or husk of the coconut. Table 1 shows large differences between the chemical compositions of its fibers. This results because the best growth conditions are in well drained, sandy soils that retain sufficient moisture, are not always wet, so providing a good and effective germination, as well as vegetative growth.

Plant cell wall material is composed of three important constituents: cellulose, lignin, and hemicellulose. Lignin fills the spaces in the cell wall between cellulose, hemicellulose, and pectin components, and it is covalently linked to hemicellulose. Lignin confers mechanical strength to the cell wall (stabilizing the mature cell wall) and therefore the entire plant. Lignin resists attack by most microorganisms, and anaerobic catabolism tends not to attack the aromatic rings (Kirk 1971; Latorre et al 2005; Djarwanto and Tachibana 2010). Lignin represents nature's cement, along with hemicellulose, in order to exploit the strength of cellulose, while conferring flexibility (Biagiotti et al 2004).

As shown in Table 1, coir fibers contain an average percentage of lignin in the order of 30-45%. This amount is relatively higher if compared with other kinds of fibers, such as sisal (6.5-12%), ramie (0.6-0.7%), hemp (3-5%), flax (2-5%), banana (5%), jute (10-15%), malva (10%), cotton (0.2-1%), bucha (11.2-15.2), sugarcane (15-24%), kenaf (15-19%), paina (15.1%), cuaura (7.5%), and pineapple (12%). For this reason their performances as composite reinforcement are not as good as those of other vegetable fibers associated with the high microfibrillation degree already mentioned and variable diameter (Van Dam et al. 2004b).

Table 1. Chemical Composition of Coir Fibers

α−Cellulose	Hemicellulose	Lignin	Origin	Reference
36-43	----	41-45	India	Geethamma et al. (1998a)
43.4	0.25	45.8		Khedari et al. (2005)
46	21	31		Khalil et al. (2001)
47	15	31		Hill et al. (1998)
47.7	25.9	17.8		Raveendran et al. (1995)
64	-----	-----	India	Edwards et al. (1997)
----	-----	27.2-33.8		Kelley et al. (2004)
33.3-35.5	16.8-18	33.6-36.6	Philippines	Hill et al. (1998)[1,2]
36.3	-----	31.9 (AIL)	Philippines	Van Dam et al. (2004b)[3]
		0.8 (ASL)	Philippines	Van Dam et al. (2004b)[3]
53	-----	40.8		Savastano Jr et al. (1997a)
43.4±1.2	4.0±0.3	48.3±1.9	Brazil	Razera (2006)[4]
45.1±0.8	5.0±0.7	44±1.0	Brazil	Razera (2006)[5]
44.2	56.3[6]	32.8	Malaysia	Khalil et al. (2006)
20-30	7-9	65-70	Sri Lanka	<http://www.enviromulchuk.co.uk/E_Coir.htm>
43.44	0.25	45.84	India	<http://www.ccriindia.org/Portal/cict/articles/agritex.pdf>
34.9	16.8	32.1	Thailand	Asasutjarit et al. (2005)
23-43	3-12	35-45	Brazil	<http://www.cpatc.embrapa.br/publicacoes_2005/cot-36.pdf>[7]

33-40	0.15-0.25	41-46	Brazil	<http://www.cpatc.embrapa.br/publicacoes_2005/cot-36.pdf>[8]
34.9±35.5	17.3±18.0	35.7±36.6	Philippines	van Dam et al. (2006c)[9]
35.1(0.3)	16.8(0.3)	33.6(0.1)	Philippines	van Dam et al. (2006c)[10]
32-43	0.15-0.25	40-45	Malaysia	Taj et al. (2007)
36-43	0.15-0.25	41-45	India	Bismarck et al. (2001)
Dwarf-green coir				
30-34	9-11	57-64	Brazil	this work
Dwarf species				
32.65	7.95	59.4	Jamaica	Jústiz-Smith et al. (2008)

[1] The values are respectively the minimum and maximum obtained by different maturities degree. [2] Two different varieties were analyzed: Rennel Island Tall (RIT) and Laguna Tall (LAGT). Highest quality from Kerala (India) were used for comparison in fibers testing. [3] The author concluded that only slight differences can be observed between mature coconut husks of different origin, and all are suitable as input feedstock for boards production. [4] Mature coconut fibers. [5] Green coconut fibers. [6] % of Holocellulose (mixture of cellulose and hemicellulose, a fibrous residue that remains after the extractives, lignin and the ash-forming elements have been removed). [7] Green coconut fibers (7-8 months – white fiber); [8] Mature coconut fibers (11-12 months – brown fiber). [9] Six different varieties were analyzed: Tagnanan Tall (TAGT), Baybay Tall (BAYT), Laguna Tall (LAGT), Catigan Green Dwarf (CATD), Rennel Island Tall (RAT) and Agta Tall (AGAT). Average values of varieties (TAGT), (BAYT), (LAGT), (RIT) and (AGAT). [10] Only (CATD) values.

Table 1 also indicates a cellulose content of dwarf-green coir fiber lower than that of lignin, which is consistent with published data (Ramakrishna and Sundararajan 2005; Van Dam et at. 2004; Geethamma et al. 1998a; Jústiz-Smith et al. 2008; Khedari et al. 2005; Khalil et al. 2001; Hill et al. 1998; Raveendran et al. 1995; Edwards et al. 1997; Kelley et al. 2004; Savastano Júnior et al. 1997a; Razera 2006; Khalil et al. 2006; <http://www.ccriindia.org/Portal/cict/articles/agritex.pdf>;<http://www.cpatc.embrapa.br/publicacoes_2005/cot-36.pdf>; <http://www.enviromulchuk.co.uk/E_Coir.html>; van Dam et al. 2006c) .

An interesting point is the similarity between the lignin content for the dwarf-green coir fibers for Brazil, Jamaica, and Sri Lanka, countries that are also characterized by a predominantly tropical climate. Ford et al. (1989), for example, studied the temperature effects on lignin, hemicellulose, and cellulose in tropical and temperate grasses. Thirteen tropical species and 11 temperate grasses were grown in controlled environment under day/night temperatures of 21/13, 27/19, and 32/24°C. In the tropical group a relatively low proportion of cellulose was observed, whereas hemicellulose and lignin contents generally tended to increase with increasing temperature.

In the species of temperate grasses, lignin, hemicellulose, and cellulose levels all showed a consistent increase with growth temperature. At each growth temperature the lignin content in the tropical group appeared to be more closely associated with hemicellulose than with cellulose. In fact, according to the Table 1, for the Brazil, Sri Lanka, and Jamaica countries, the lignin content of the fibers was are more closely associated with hemicellulose than with cellulose.

The high lignin content also made it possible to observe the resistance of fibers to rotting under wet and dry conditions and to have a better tensile strength. This behavior was observed to be more effective when samples of dwarf-green coir were used due the higher lignin percentage compared to the green or mature coir fibers samples. Sun et al. (2004) also observed the same behavior when investigating the content of cellulose from lignocellulosic fibers.

The morphological characteristics of coconut husk pith and fiber surface structures are shown in Fig. 3, where clear differences are shown between the surface morphology of the untreated and treated fibers. The fibers in Fig. 3a shows globular structures in regular intervals (porous) and other constituents, probably organic residues (Mohanty and Nayak 2004b; Almeida et al. 2006) of the extraction of the fibers. The fibrils are covered from a cuticle layer, i.e. wax of aliphatic origin (Esmeraldo 2006; Ratta 1999). Fig. 3b shows the surface a little more defined when compared with 3a. The fibers were washed only with water and removed part of the surface impurities and the aspect of fibers is more defined.

After treatment with 5% NaOH solution, the impurities and wax cuticle layers of the fibers surface were removed. The fibrils were starting to separate from each other because the lignin, the cementing component, had been removed by the action of the alkaline solution, leading to an increase of the surface area and potentially improving the fiber-matrix adhesion in composites.
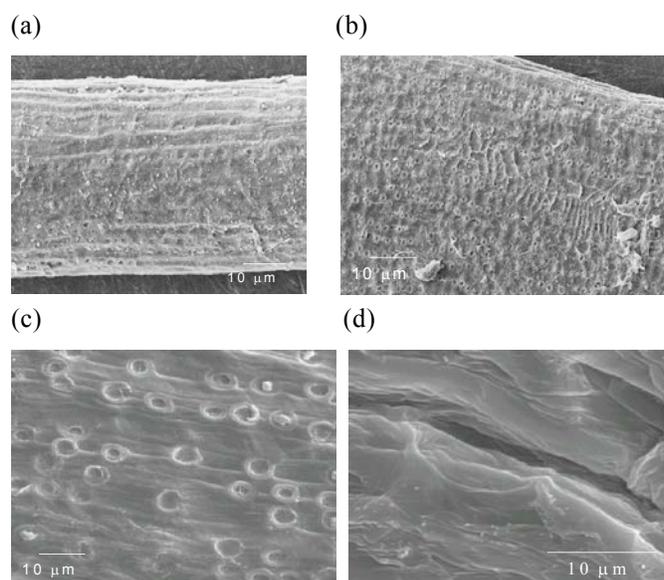
(a)   (b)

(c)   (d)

Fig. 3. Scanning electron microscopy for dwarf-green coir fibers: (a) untreated, (b) washed with water, (c) and (d) after alkali treatment with 5% and 10% NaOH, respectively

The cleaning treatment also produces changes to hydrogen bonding interactions of hydroxyl groups of cellulose, resulting in the deformation of individual microfibrils (Gañan and Mondragoni 2005). The treatment with 10% NaOH, Fig. 3d, showed a more effective result in the lixiviation of the cuticle layer in removal of bonding material. Under this condition, the most external layer of the fiber was eliminated, revealing the fibrillar structures. The cavities became more defined, and the surface fibers became rougher than in the former pictures.

The characteristics observed in Fig. 3 reveal that the chemical treatment was able to modify the outer layer of the fibers. It was verified that concentrations lower than 5% did not lead to significant alterations of the surface of fibers, while solutions containing NaOH concentration higher than 10% and temperatures above 90 ^{o}C resulted in defibrillation and significant damage to the fibers.

The alkali treatment, besides removing impurities from the fibers surface, as well as lignin and hemicellulose, also reduced the fibers' diameter. The average diameter was 136 μm for the untreated fibers, 128 μm after washing with distilled water, and 109 to 106 μm, respectively, after alkaline treatment with 5% and 10% NaOH solutions.

XRD Analysis

The XRD data are in agreement with the morphological analysis. The crystallinity fraction increased with the concentration of alkali solution and fell off for concentrations of NaOH higher than 10%. The crystallinity fraction was 33.74% for untreated fibers, and this was raised to 40.94%, and 41.41% after treatment with 5% and 10% NaOH, respectively.

Figure 4 presents two main peaks, representing the planes 002 and 101 at $2\theta = 22.46^o$ and $2\theta = 16.7^o$ respectively, characteristics of the cellulose crystalline phase

(Almeida et al. 2006; Maldas et al. 1997; Campana Filho et al. 1997). The curves obtained for the dwarf-green coir fibers shows a larger amorphous phase, associated with the large content of lignin. According to Ouajai (2005), the dwarf-green coir fibers have a lower crystalline fraction due the lower amount of cellulose (ca. 42 %) compared with the other lignocellulosic fibers: 75% for sisal, 83% for cotton, 63.5% for jute, 72.4% for ramie, 71% for flax, and 63.5-82.2% for hemp (Bledzki and Gassan 1999; van Dam et al. 2004b; Goda et al. 2006; Gomes et al. 2007; Almeida et al. 2006; Peijs 2000; Khedari et al. 2005; Edwards et al. 1997; Gañan and Mondragoni 2005; Medeiros 2003; Geerhamma et al. 2005b; Gassan and Bledzki 1999).
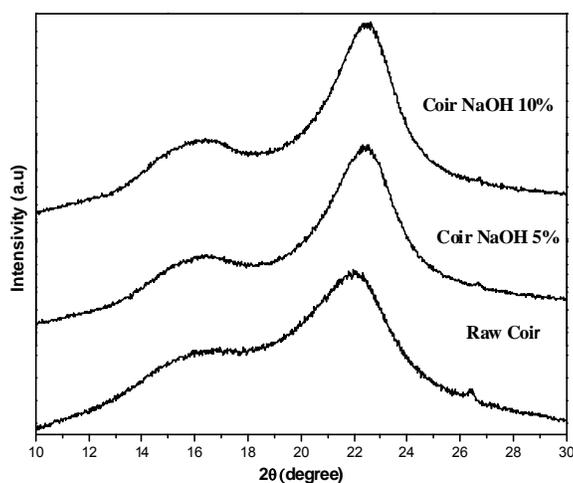

Fig. 4. XRD of dwarf-green coir fibers after and before alkali treatment

Infrared Analysis

Infrared spectrometry also was used to analyze the effect of the treatment on the surface structure of the fibers (Fig. 5). The IR spectra of the untreated and treated fibers show the peaks typically found by others authors, with the frequencies in agreement with the literature, for characteristics of lignocellulosic fibers (Herrera-Franco and Valadez-González 2005; van Dam et al. 2004b; Xiao et al. 2001; Kelley et al. 2004; Gassan and Bledzki 1999). The partial dissolution of hemicellulose, lignin, and pectin are clearly identified in the band at 1736 cm^{-1} ascribed to C=O stretching (Yu et al. 2004), which disappeared when the fibers were treated by a sodium hydroxide solution.

The hydroxyl band at 3440 cm^{-1} is characteristic of the stretching vibration of cellulose hydroxyls bonded to carbons 2, 3, and 6 of the glucose (van Dam et al. 2004b; Joseph et al. 2002). It appears broadened, depending on the chemical treatment and due to changes of the inter- and intra-molecular hydrogen bonding in polysaccharides (van Dam et al. 2004).

Thermogravimetric Analyses

The TG and DTG (derivative of the thermogravimetry curve) curves for the dwarf-green coir fibers shown in Figs. 6 and 7, indicate that the range of thermal degradation decreased after chemical treatment (Karnani 2004; Mohanty 2000a). Either when the fibers were degraded in air or in N$_2$, the DTG curves show the first peak below

100 °C as the result of evaporation of residual moisture (Pothan et al. 1997a; Pothan and Thomas 2003b; Eichorn et al. 2001).
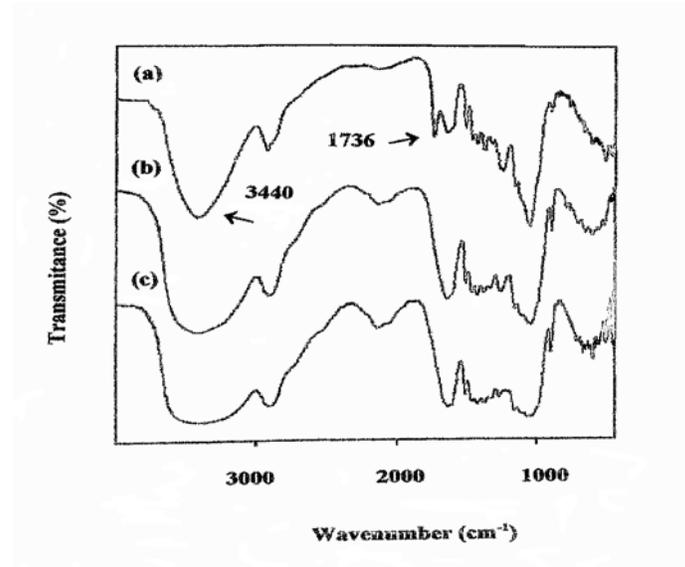

Fig. 5. Infrared spectra of the dwarf-green coir fibers before and after chemical treatment: (a) untreated; (b) treated with NaOH 5 %; and (c) treated with NaOH 10 %
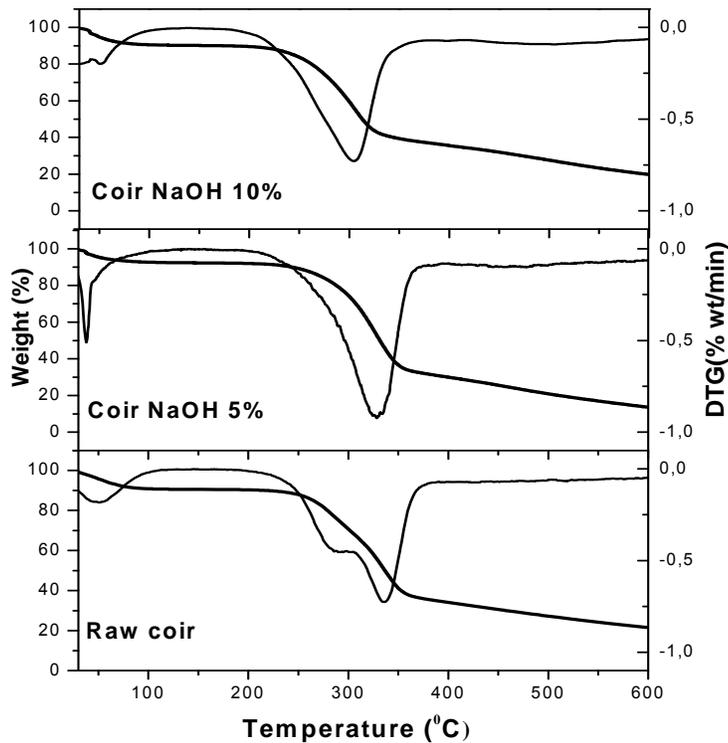

Fig. 6. TG and DTG of unmodified and NaOH treated dwarf-green coir fibers in nitrogen gas flow

Thermal degradation processes during the TG experiments in N_2 atmosphere for unmodified and treated coir fibers are revealed in Fig. 6. The treated fibers showed a single degradation peak in contrast to the double peak observed for untreated fibers. This is a further indication of a higher homogeneity resulting from NaOH treatments. The results also indicate that the macrocomponents were removed by the alkali solutions.

The degradation process of treated fibers is attributed to α-cellulose and to residual hemicellulose pyrolysis, which is shifted to lower temperature when the amount of lignin is reduced (Mitra et al. 1998). Varma et al. (1986) and van Dam et al. (2004b) report that weight losses above 200°C can be attributed to oxidation and condensation of carbohydrates, while the phenolic components of lignin are considered to be more stable. Also Vázquez-Torres et al. (1992) after extraction and characterization of coconut lignin samples, verified that their decomposition starts from approximately 380 °C.

The degradation produced a significant amount of char: 12.4% for unmodified natural fibers and 9.5% and 2.0% for those treated with NaOH 5% and 10% respectively. These results showed that the pretreatment with NaOH reduced the hemicellulose, making the product more stable than the untreated fibers and the increasing the amount of residual char (van Dam et al. 2004b; Vásquez-Torres et al. 1992).

Thermal degradation in a N_2 atmosphere was characterized by an overlapping of processes that may occur in the same range of temperature, and that can be separated only by looking at one of the peaks of the DTG output. In an oxidative atmosphere, these processes were separated, and two peaks were clearly detected, with one of them observed within an interval of temperature smaller than in a N_2 atmosphere (Fig. 7). The results can be justified by the presence of free radicals (van Dam et al. 2004; Vásquez-Torres et al. 1992; Calado and Barreto 2000; Peijs 2000; van Kreveler 2000), which allows a more effective degradation at lower temperatures.

Mechanical and Electrical Properties of Coir Fibers

According to Table 2, it is possible to observe a slight increase of the tensile properties after the chemical treatment with NaOH. Natural fibers are a bundle of microfibrils bound together by amorphous lignin, waxy materials, and others impurities, and the arrangement of microfibrils is a determining factor of the luster and strength of the fiber (Pothan et al. 1997a; Pothan and Thomas 2003b; Ray and Sarkar 2001a; Padilha 1997). According to Goda et al. (2006) and Gomes et al. (2007), after application of tensile stress, the microfibrils in the untreated fiber tend to slip one on another, retaining to the original alignment.

As shown in Table 2, the increase of elongation at break after treatment can be attributed to the content of cellulose contained in this kind of fiber. It was visibly more pronounced when treated with 10% NaOH, associated with the high content of lignin, and consequently with the high values of microfibrillar angles (41–45°) (Vijayalakshmi et al. 2000). The cellulose content increased after alkali treatment and is responsible for a consistent growth of tensile strength and elastic modulus without exhibiting a decrease of the elongation to break. The high value of elongation obtained for the coir mature in comparison with dwarf-green, could be justified by a higher proportion of lignin in the mature coir. The proportion of lignin increases as the cycle of maturation of the fruit is completed.
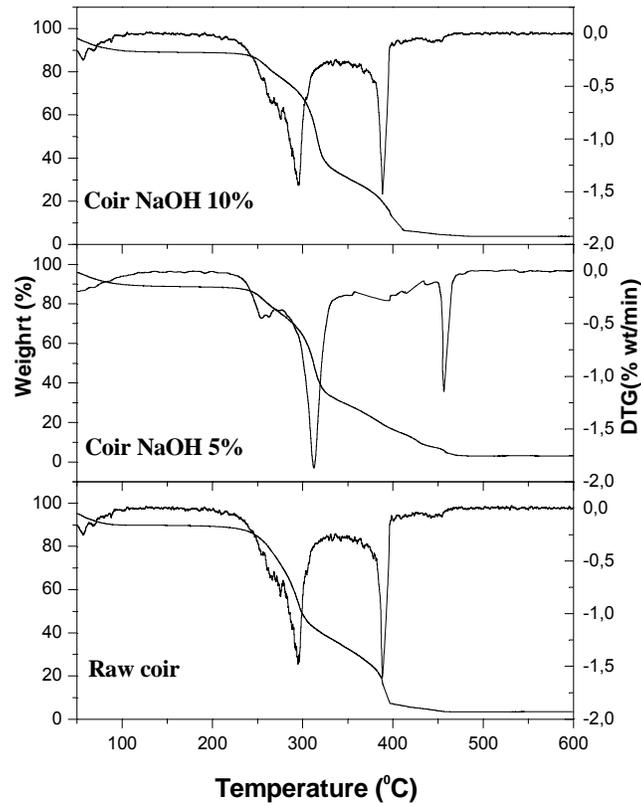
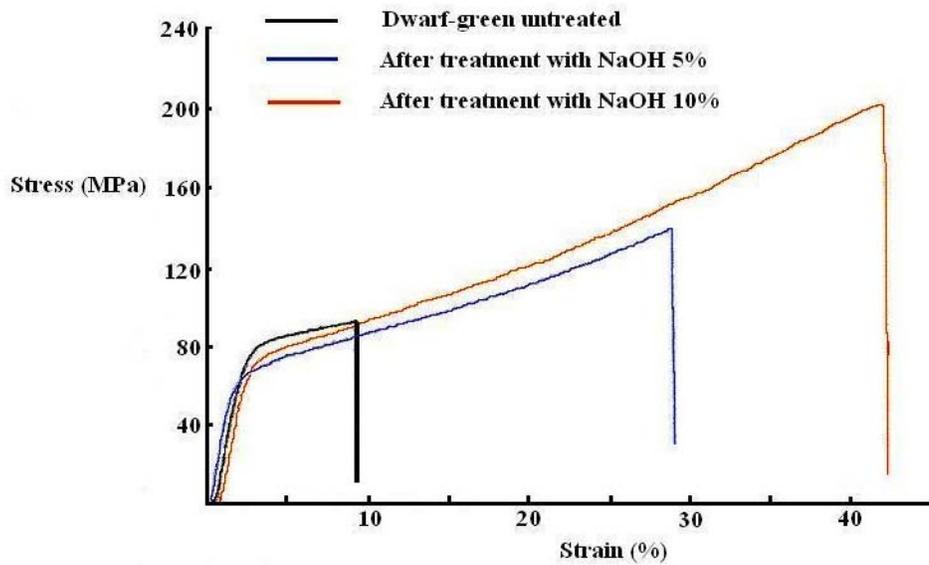**Fig. 7.** TG and DTG of unmodified and NaOH treated coir fibers in air

Fig. 8. Stress *vs.* strain curves to dwarf-green coir fibers, untreated and after chemical treatment with NaOH

Table 2. Mechanical Parameters for Coir Fibers

Fibers	Elongation at Break (%)	Tensile Strength (MPa)	Young's Module (GPa)	References
Cotton	7.0-8.0	----	5.5-12.6	Bledzki and Gassan (1999) Peijs (2000)
Sisal	2.0-2.5	----	9.4-22.0	Bledzki and Gassan (1999) Maldas et al. (1997) Peijs (2000)
Ramie	3.6-3.8	----	61.4-128	Goda et al. (2006) Gomes et al. (2007) Peijs (2000)
Hemp	1.6	----	30-60	Bledzki and Gassan (1999) Mwaikambo and Ansell (2006) Maldas et al. (1997) Peijs (2000)
Flax	2.7-3.2	----	27.6-50.0	Bledzki and Gassan (1999) Wambua et al. (2003) Maldas et al. (1997) Joseph et al. (2002) Tita (2002)
Banana	7.0	----	12.0	Tita (2002)
Jute	1.5-1.8	----	14.8-26.6	Bledzki and Gassan (1999) Maldas et al. (1997) Peijs (2000) Herrera-Franco et al. (2001)
Piassava	----	----	1.07-4.59[*]	Maldas et al. (1997)
Coir mature	30.0	180	4.0-7.0	Bledzki and Gassan (1999) Vijayalakshmi et al. (2000) Maldas et al. (1997) Calado and Barreto (2000) Peijs (2000)
Mature coir	8.0±1.0	120±5.0	------	Razera (2006)
Green coir	13.0±1.0	118±5.0	------	Razera (2006)
Coir	23.9-51.4	-----	2.8	Geethamma, (1998a)
Coir	15-40	131-175	4.0-6.0	Chand et al. (1988)
Coir	22.0(7)	24.0(83)	6.0(1.8)	Van Dam et al. (2004b)
Coir	30.0	175	4.0-6.0	Brothers (2003)
Coir	15.0-25.0	220	6.0	Schmidt (1989)
Dwarf-green coir	19.9 ± 7.8	110 ± 20	2.2 ± 0.98	this work
Dwarf-green coir after treatment with NaOH 5%	19.2 ± 6.5	150 ± 40	2.4 ± 0.6	this work
Dwarf-green coir after treatment with NaOH 10%	21.7 ± 5.8	190 ± 60	2.6 ± 1.4	this work

* Without the correction of the elastic contribution of the test machine.

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Although the properties are dispersed in a broad range, some general trends could be established by comparing the mechanical behavior of the different fibers. A proper comparison should be done among fibers with comparable amounts of lignin. The ramie, for example, has the higher values of modulus (61.4-128 GPa) and the lower lignin content in the composition (0.6-0.7) (Goda et al. 2006; Gomes et al. 2007; Tita 2002). In contrast, the dwarf-green coir fibers showed a high content of lignin (57-64) and lower modulus values (4.0-7.0 GPa).

It is also possible to observe from Table 2 that the modulus values obtained for the coir fibers in others works (Bledzki and Gassan 1999; Vijayalakshmi et al. 2000; van Dam et al. 2004b; Maldas et al. 1997; Calado and Barreto 2000; Peijs 2000; Gassan and Bledzki 1999) were double or more the values found in this work. The results could be justified considering that during the maturation of the nut, the amount of extractables decreases. Van Dam et al. (2004b) observed the changes in chemical composition of husks and fibers comparing nuts of different maturity. They demonstrated a gradual increase of glucose associated with the formation of cellulose and dramatic changes in others sugars as a function of maturation.

The dielectric properties: permittivity (K), dielectric loss (D), and dielectric conductivity (σ) for the untreated and treated dwarf-green coir fibers as a function of frequency, also are reported in this work (Table 3 and Figs. 9 a-c).

Table 3. Dielectric Parameters for the Dwarf-Green Coconut Fibers

Fibers	Thickness(μm)	1 kHz		
		K	D	$\sigma \ (\Omega^{-1}.m^{-1}).10^{-7}$
Untreated	480	158.41	0.568	50.96
Treated with NaOH 5%	640	45.35	0.063	1.64
Treated with NaOH 10%	1095	25.03	0.328	4.65

The dielectric permittivity is essentially the sum of all contributions from the various dielectric processes that may take place within the sample. According to Fig. 9a, the permittivity values (capacity of polarization of the sample when submitted to an electric field) decreased with the increase of NaOH concentration when compared with the untreated fibers. It is known that the physical-chemistry properties of cellulose are mainly dependent on the amorphous regions of cellulose. These results can be explained by considering the lower mobilities of outermost electrons in cellulose crystals compared with those in amorphous phases, such as lignin and hemicellulose.
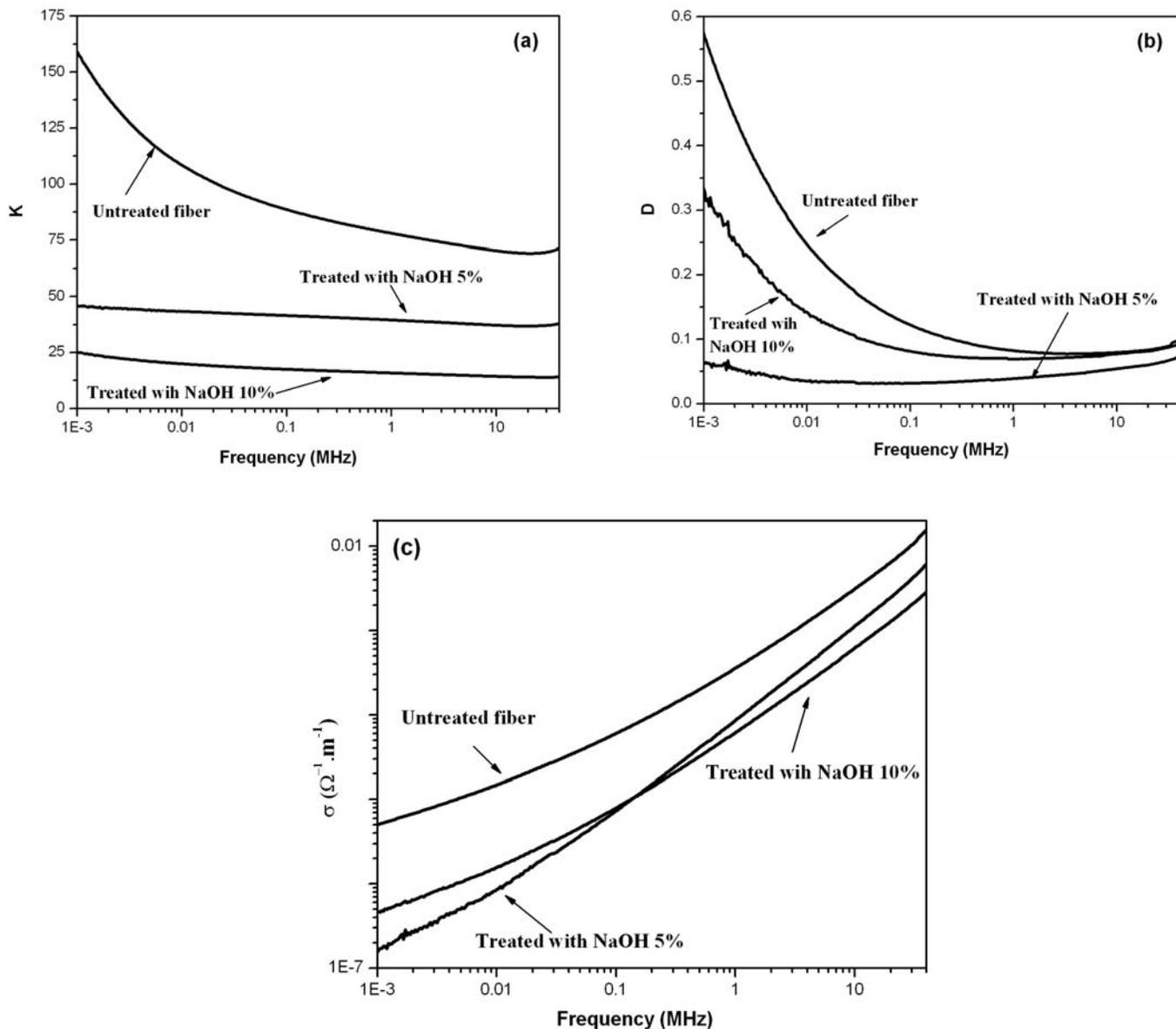
Fig. 9. Dielectric parameters for the dwarf-green coir fibers: (a) permittivity, (b) dielectric loss, and (c) dielectric conductivity

The dielectric loss values for untreated fiber were higher than those for the treated ones. This could be due to the higher dissipation characteristic associated with a larger amount of amorphous phase in untreated fibers. At higher frequencies, the relaxation in all samples was approaching a saturation regime in response to the external field. At these frequencies, small dipoles such as OH, which are responsible for the losses, present a similar behavior in the three phases; i.e. cellulose, lignin, and hemicellulose. However, the dielectric loss values of the fiber treated with NaOH 10% was higher than for the one treated with NaOH 5% and the conductivity (Fig. 9c) was higher for the treated fibers when compared with those without chemical treatment. This happens due to the large

number of interfaces between the fibers and air pores that constitute the cellulose network. Therefore, due to the alkaline treatment, there was a modification of these dielectric features, as a result of a mutual influence (not necessarily linear).

The electrical conductivity of the cellulose and other polysaccharides can be changed drastically by adding small amounts of water. The presence of hemicelluloses, lignin, and wax contributes to a homogeneous morphology of the natural fiber and a reasonable impermeability. However, the fiber lost part of its character after alkaline treatment. The water molecules produce a bridge parallel to the glucosidic linkage along the chain and between adjacents chains, which increases the stiffness of the polymer chain.

Cellulose is utilized by the electric industry in the form of paper to fabricate cord coverings, capacitors, bobbins, transformer spacers, and other equipment. The paper sometimes should be combined with other isolating materials to improve its dielectric features. For instance, paper has a dielectric permittivity of approximately 1.6-2.6, and when it is combined with mineral oil that value increases by as much as six times. As dwarf-green coir fibers presented permittivity values between 25 and 158, this kind of fiber has a good potential as a renewable material to be used as a dielectric component.

CONCLUSIONS

1. The thermal, mechanical, and dielectric properties before and after alkali treatment of dwarf-green coir fibers were investigated. The chemical and morphological data indicated that treatment with 10% NaOH solution resulted in strong surface modifications.
2. In this work the dwarf-green coir fibers, as a renewable and recyclable by-product of food consumption, showed some promising properties for their use as reinforcement in composite materials. Another possibility of application is reflected by the dielectric properties of these fibers, which can be classified as an insulating material, which has potential use as insulation of cables, small capacitors, support for energy transformers station, and electric motor wiring isolation, etc.

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