

Mechanical and Thermal Characterization of Native Brazilian Coir Fiber

G. GOULART SILVA,¹ D. A. DE SOUZA,¹ J. C. MACHADO,¹ D. J. HOURSTON²

¹ Depto de Química/ICEx/UFMG, CP 702, Belo Horizonte, 31270-901, MG, Brazil

² IPTME, Loughborough University, Loughborough, LE11 3TU, Leics, United Kingdom

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ABSTRACT: Coir fiber native to the Brazilian northeast coast has been characterized by mechanical, thermal, and microscopy techniques. The tensile strength, initial modulus, and elongation at break were evaluated for untreated and alkaline-treated fibers. The results showed an enhancement of mechanical properties after 48-h soaking in 5 wt % NaOH. The thermal stability slightly decreased after this alkaline treatment. A thermal event was observed between 28 and 38°C. The heat capacity, C_p , as a function of temperature curves between -70 and 150°C, were obtained for the untreated and alkaline-treated coir fibers. The morphologies of the coir-fiber surfaces and cross sections were observed by scanning electron microscopy. The properties and the morphologies were discussed, comparing the native Brazilian coir fiber with the more extensively studied native Indian coir fiber. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1197-1206, 2000

Key words: coir fiber; mechanical characterization; thermal characterization; morphology

INTRODUCTION

Raw materials from renewable resources,¹ including natural fibers,² have lately been the objects of great interest. The coir fiber is extracted from the external portion of the fruit of the coconut palm (*Cocos nucifera* L.),³ which is a by-product of the copra-extraction process and is generally considered a waste material. A better understanding of these fiber properties will help in the development of new products. Uses of coir fiber in domestic (mats, carpets, rope), building (thermal insulation), and automotive (cushions, seat covers, etc.) applications have been reported.⁴ Possible

applications for fibers from other parts of the coconut tree have been also mentioned.⁵

Coir consists of cellulose fibers with hemicellulose and lignin as the bonding material. Therefore, in a sense the coir fiber is itself a fibrous-composite material. Table I summarizes some of the relevant properties of coir fiber compared with sisal, which is a typical natural fiber. The data shown in Table I^{4,6} were obtained mainly for the coir varieties grown in India.³ The fibers are reported to be polygonal to round in cross section.⁴ However, it seems that the diameter is generally considered to be round in the coir-fiber literature.⁴⁻⁷ Natural products present, in general, a wide range of physical and chemical properties depending on the locality in which they were grown, the climate, the method of extraction, etc.⁴ The Indian varieties of coconut palm were extensively studied, whereas for the South American varieties, only a small amount of infor-

Correspondence to: G. Silva. E-mail: glaura@dedalus.lcc.ufmg.br

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Table I Main Properties of Coir and Sisal Fibers^{4,6}

	Coir	Sisal
Diameter (μm)	100–460	50–200
Cellulose content (%)	32–43	66–72
Lignin content (%)	40–45	10–14
Microfibrillar angle ($^{\circ}$)	30–49	10–22
Density (g cm^{-3})	1.15	1.45
Initial modulus (GPa)	4–6	9–12
Tensile strength (MPa)	131–175	568–640
Elongation (%)	15–40	3–7
Electrical resistivity ($\Omega \text{ cm}$)	$9\text{--}14 \times 10^5$	$4.7\text{--}5.0 \times 10^5$

mation is available.³ It may be the case that there are local differences, which are not negligible, in Brazilian coir fibers. The Brazilian coast is so large that several different climatic regions are involved. These conditions are likely capable of producing differences in plant characteristics such as fiber chemical composition and certain morphological features.

Cellulose content, microfibrillar angle, and other structural variables, such as cell dimensions and defects, are likely to be the most important parameters controlling structure–property relationships in natural fibers.⁸ Cells in natural fibers such as coir consist of the crystalline cellulose arranged helically in a noncrystalline cellulose–lignin complex matrix. The microfibrillar angle is the angle that the helical spirals of cellulose crystallites form with the fiber axis.⁹

Coir fiber has low cellulose content and a high microfibrillar angle (Table I) when compared to other natural fibers.^{4,6} Tensile strength and Young's modulus (initial or elastic modulus) increase with cellulose content in plant fibers,^{8,9} which can explain the relatively poor mechanical properties of coir fiber (Table I). On the other hand, the moduli also are low for fibers with high microfibrillar angle (θ)⁹ such as coir. The elongation at break increases with increasing θ .⁹ The microfibrillar angle for coir fiber is almost three times higher than that for other natural fibers. Therefore, the elongation at break of coir is the highest known for typical natural fibers.^{4,6} This property is certainly useful in cushion applications. The high lignin content of coir is responsible for other

useful properties,⁴ such as weather, fungal, and bacterial resistance. As the lignin content increases, the fiber becomes stiffer and tougher.

The well-known commercial process called mercerization, an alkaline treatment, is used to improve wettability and bonding of natural fibers such as cotton with polymers. Parameters such as NaOH concentration and soaking time and temperature have been extensively studied^{10–12} in the treatment of coir fibers. A decrease in mass and increase in superficial roughness by the removal of the cuticle layer are observed. The mechanical properties are improved by alkaline treatment under moderate conditions.

As already mentioned, the native Indian varieties of coir fiber have been extensively studied.^{3–8,10–12} Mechanical properties including initial modulus, strength, and elongation have been carefully evaluated as functions of treatment, fiber diameter, gauge length, and strain rate.^{7,12} This article reports the mechanical and thermal properties of coir fiber native to the northeast Brazilian coast. The effect of alkali treatment was evaluated and morphologic changes were studied by using scanning electron microscopy.

EXPERIMENTAL

Coconut shells, from the northeast Brazilian coast, were obtained from local sources that trade the liquid content of the fruit. The shells were soaked in water for 4 months to facilitate the removal of fibers (retting). After air drying for more than 1 week, the raw fibers used in this work were separated from the rest of the shell. Sodium hydroxide treatment (mercerization) was carried out by soaking the coir fibers in 5 wt % NaOH solutions for 48 and 72 h. Fibers were then taken out, washed thoroughly with water, and air-dried.

There was a considerable amount of variation in the thickness between fibers and also in the thickness uniformity of individual fibers. The native Brazilian coir fibers are typically oval in cross section. For each 50-mm length of fiber, measurements were made at five different points of each of the two oval diameters and the average of these values was used.

Stress–strain behavior was examined by using a Lloyd 2000R instrument. The gauge length of the fibers was kept constant at 50 mm and strain rate was 20 mm/min. These are typical conditions for

coir-fiber measurements.^{7,12} Mean breaking load (tensile strength), breaking elongation, and initial modulus were obtained at room temperature by testing fibers with various diameters and typical results related to a large number of tests are reported. The procedure to select fibers for the mechanical tests took into account the distribution of diameters. For each one of six typical average diameter of fibers untreated and treated, approximately four or five fibers were measured. Therefore, a total of approximately 60 fibers were tested. The accuracy of the mechanical data for each diameter and globally for the set of untreated and treated fibers was also evaluated.

A Leica Cambridge Stereoscan S360 scanning electron microscope was used to study the surface and cross sections of coir fiber. The samples were mounted on special stubs and gold-coated by sputtering to avoid electrostatic charge and to improve image resolution. To study the cross sections, the fibers were fractured after holding them with forceps in liquid nitrogen for a few moments.

Thermogravimetry (TG) and modulated-temperature differential scanning calorimetry (MTDSC) were performed. For TG measurements, the fibers were ground in a ball mill and sieved to standard size fractions ranging from 325 to 400 mesh. TG was carried out by using a Shimadzu TGA-50 thermobalance and by using a dynamic air flow at a rate of 150 mL/min. The mass of the samples was between 5 and 6 mg; the heating rate was of 10°C/min; the temperature range covered was between room temperature and 600°C, and platinum crucibles were used. The weight loss as a function of temperature (TG) and the differential of the TG curves (DTG) were analyzed.

For the MTDSC experiments, a TA MTDSC 2920 was used. The fibers were cut into small pieces and hot-pressed at 180°C by using a 5-ton load for 10 min. The MTDSC procedure consisted of different annealing steps. The first annealing was at 150°C for 20 min and the second one was at 160°C for 6 h. Following the annealing procedures, the samples were quenched to -100°C (at 40°C/min) in the DSC pan and then heated at 3°C/min with modulation amplitude of 1.0°C and a period of 60 s. A nitrogen flux (150 mL/min) and aluminum crucibles were used. The heat-capacity measurements were performed after calibration with an empty pan and sapphire standard. After each annealing experiment, the MTDSC curve was checked in relation to the presence of the

remaining water. This was done by observing if there are thermal events at 0°C.

RESULTS AND DISCUSSION

Morphologic and Mechanical Characterization

Figure 1 shows SEM micrographs of untreated coir-fiber surface and the fiber after soaking in NaOH for 72 h. In Figure 1(c,d), a higher magnification of the samples in Figure 1(a,b) are presented. As is well known, alkali treatment dissolves and leaches out the fatty acids and their condensation products that form the waxy cuticle layer. This treatment^{10,13} induces a loss of mass among other changes and a rough fiber surface with regularly spaced pits is obtained [Fig. 1(b)]. The treatment for 48 h produces the same effect, but is less extensive, and was reported^{6,12} to provide the best conditions for improvement in mechanical properties of native Indian varieties of coir fiber. Therefore, a soaking time of 48 h was maintained in the study of mechanical properties.

The surprising oval cross section of the native Brazilian coir fibers are shown in the SEM micrographs in Figure 2. In Figure 2(a), a fiber treated for 48 h in NaOH is shown for which the central lacuna was observed in higher magnification in Figure 2(b). In Figure 2(c), the cellulose helical spirals emerging from the fractured cross section are shown.

Figure 3 shows typical stress-strain diagrams for the untreated and treated (48 h) native Brazilian coir fibers. These curves are similar in shape for the majority of natural fibers.⁷ Initially, a linear portion due to elastic deformation is observed. This is followed by a nonlinear region in which the strain value increases rapidly and finally an approximately linear region is again observed.

Tables II and III show typical results obtained for the coir fibers in this program. The average results for the sets of six fibers with typical diameters are shown. With the five fibers tested, to each average diameter we could estimate the accuracy of each measurement and the total accuracy, which is also shown in Tables II and III.

The elongation at break was in the range expected for coir fibers (Table I). This parameter does not seem to be correlated with the fiber diameter in any way. An increase of approximately 10% after alkaline treatment was observed.

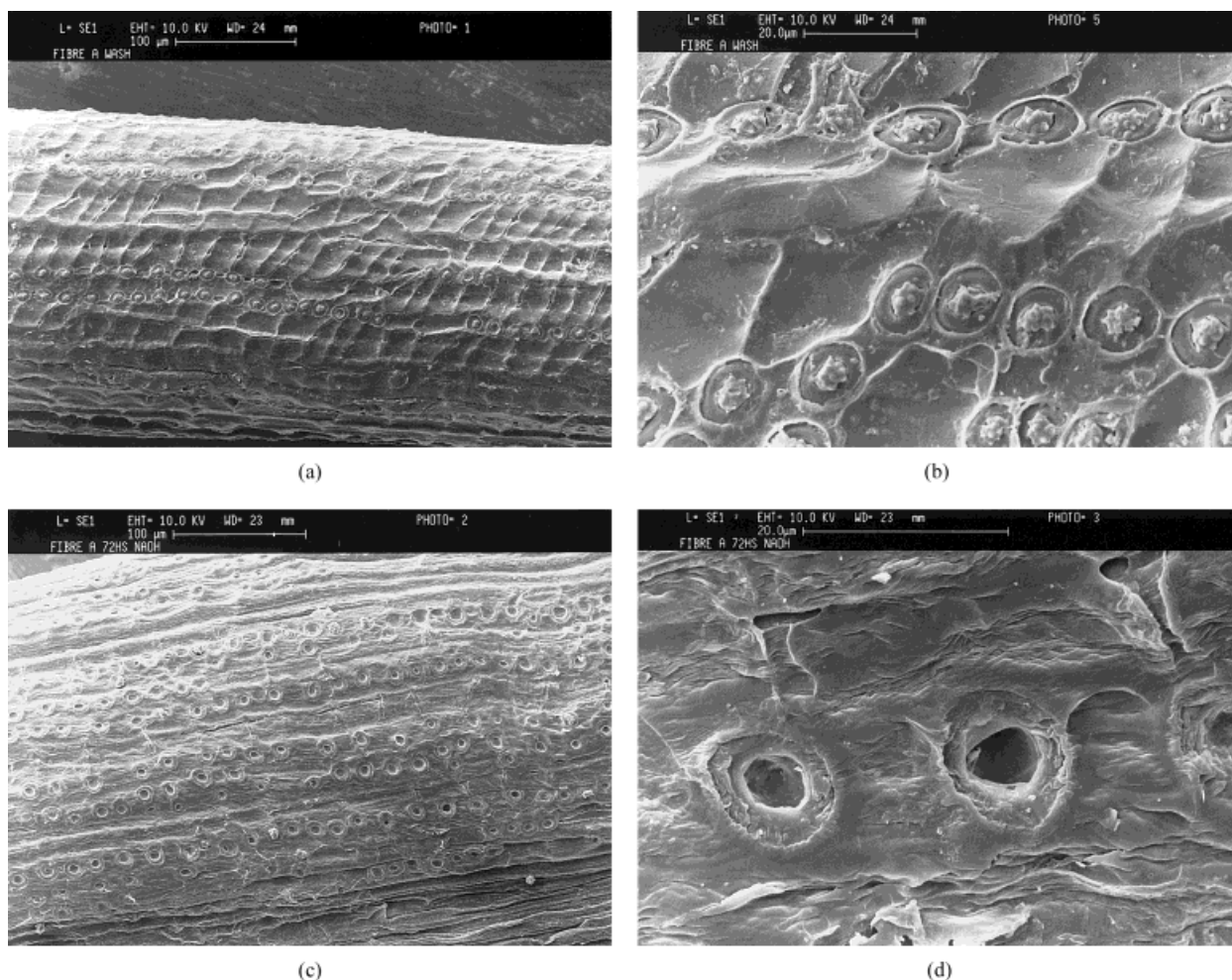


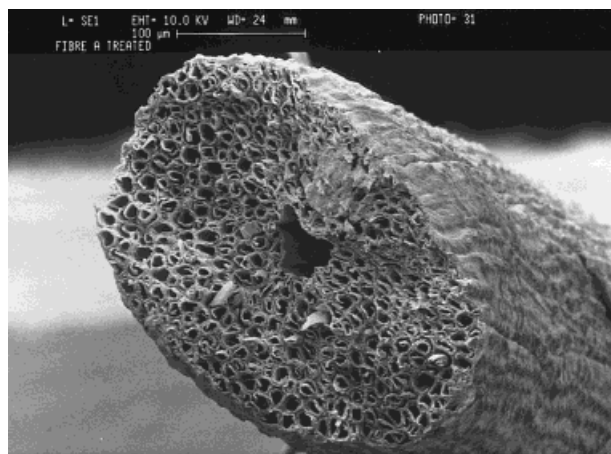
Figure 1 Scanning electron micrographs at two magnifications. (a) and (b): raw coir fiber, and (c) and (d): coir treated for 72 h in 5 wt % NaOH.

The two oval diameters were used to calculate an average round diameter (d), which was used in the calculation of tensile strength (UTS) and initial modulus (IM). If the oval cross section is used to carry out these calculations, small increases of the moduli are obtained. Nevertheless, the results obtained for the native Brazilian coir fiber are lower than expected for coir fibers (see Table I). The effect of this different cross-sectional shape seems to be very important. When a calculation is performed by using the lower diameter (d_2) as a pseudo-round diameter for our fibers, the mechanical properties UTS and IM increase, attaining the range expected for other coir fibers. Therefore, it should be pointed out that the mechanical performance of these fibers, in use, is not necessarily inferior to the other coir fibers, the results of UTS and IM in Tables II and III being probably masked by geometric features. This means that

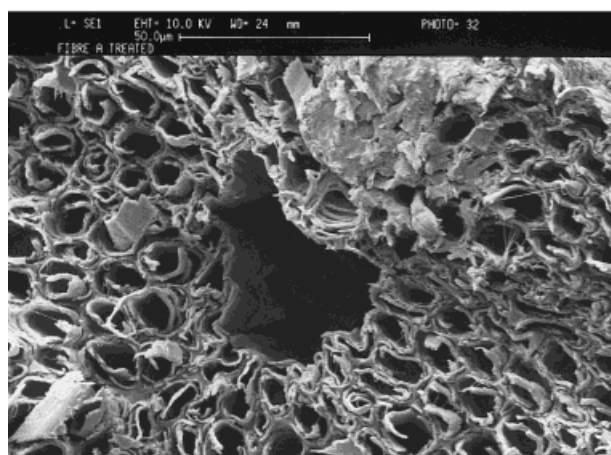
the application of a stress through a round or oval fiber should be analyzed more carefully in relation to the distribution of stress on the cross section. This question needs to be evaluated by further studies of Brazilian fibers.

The increase in UTS after alkaline treatment is about 24%, and in IM, the increase is 42%. The enhancement of mechanical properties after alkaline treatment is a result typically obtained for coir fibers.^{7,12,14} These changes in mechanical properties have been recently correlated elegantly with structural changes observed by analyzing X-ray parameters such as coupling constants and mean square displacements.¹³

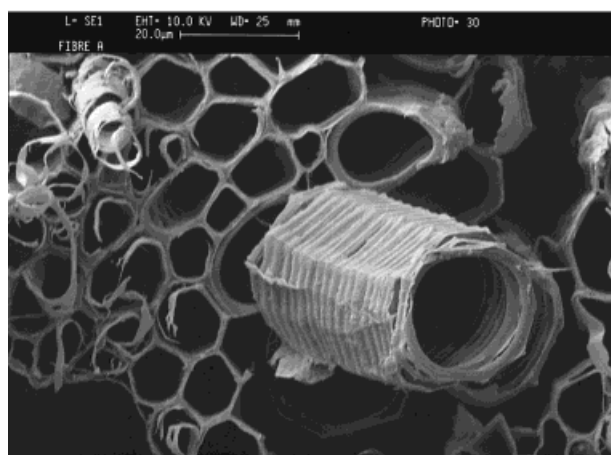
There is also no appreciable variation in UTS and IM with increase in fiber diameter (Tables II and III). Values in Table II seem to show a tendency toward decreasing UTS with fiber-diameter increase. However, if we consider the accuracy



(a)



(b)



(c)

Figure 2 Scanning electron micrographs (a) and (b) of typical cross sections of treated-coir fiber at two magnifications; (c) a cellulose helical spiral in a fractured cross section.

range (see Tables II and III) of the mechanical data, the values do not indicate a clear trend.

Thermal Characterization

Thermogravimetric curves for untreated and alkaline-treated coir fibers in air are shown in Figure 4. Table IV summarizes the data obtained for untreated and treated fibers after three different soaking periods.

The first weight loss is associated with the moisture loss with a peak at 39°C for all samples. The treated coir fibers show a range of dehydration prolonged to temperatures > 100°C. The water content also increases after alkaline treatment. An average water loss increase of 4% was observed (Table IV) after alkaline treatment (first weight loss) and this is also approximately the level of water content increase reported by other authors.¹⁵ These results indicate a stronger interaction between water and the coir fiber components after the removal of the cuticle layer and other chemical modifications produced by the alkaline treatment.

Two decompositions are observed after dehydration in an air atmosphere as shown in Figure 4, and previously reported in the literature¹⁵ for coir fibers. The thermal degradation in a N₂ atmosphere is characterized by the overlap of these two weight-loss processes as has been reported by Varma et al.¹⁶ for coir fibers. In general, for the native Brazilian coir fibers in air, the first coir degradation appears with a maximum near 300°C, and the second stage exhibits a peak after 400°C, as shown in Table IV. A decrease in the thermal stability after alkaline treatment is observed in our samples in Table IV. The untreated fibers show the first peak at 334°C and the treated samples show peaks near 290°C. The opposite behavior, an increase in thermal stability with alkaline treatment, has been reported in the literature by Mahato et al.¹⁵ and Varma et al.¹⁶ However, very small soaking periods (2 and 4 h, respectively) and different concentrations were used in these works.

Differential scanning calorimetry (DSC) studies of coir fiber to detect thermal transitions and heat capacity changes have not yet been reported. The major difficulty is to overcome the problems associated with water evaporation during the measurements and the overlap of transitions involving cellulose and lignin components and their complexes.¹³ The melting temperature of cellulose compounds is reported to be located near

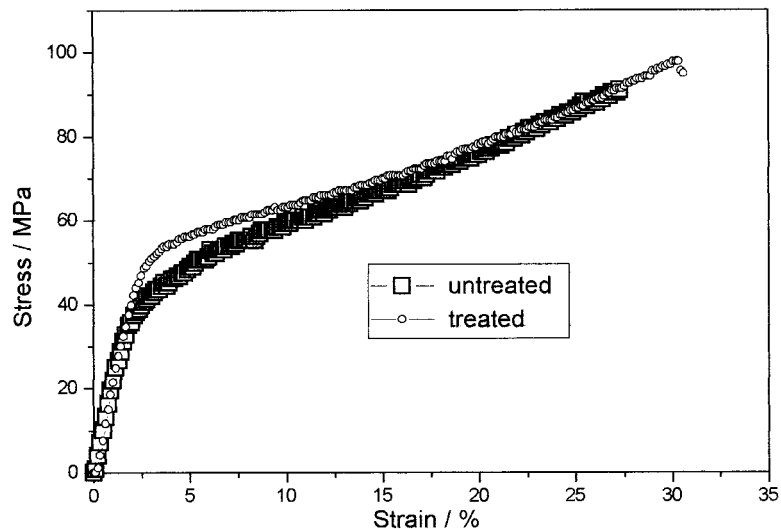


Figure 3 Typical stress–strain curves for untreated and treated (48 h/5 wt % NaOH) coir fiber.

300°C,¹⁷ which overlaps with the temperature-degradation range. The glass transition temperature (T_g) of cellulose itself, both in extracted cellulose and in natural fibers, is the object of significant controversy in the literature.^{18,19} Values between -30 and 160°C have been cited.¹⁸ Other second-order transitions are reported¹⁹ for cellulose and lignin compounds around room temperature. Lignin, a commercial product from the Kraft pulping process, shows a T_g of approximately 135°C as measured by DSC.²⁰ Lignin samples extracted from coconut husk were characterized by DSC and a T_g range between 147 and 172°C was reported.²¹

The weight loss associated with water can be observed from 25 to $> 160^\circ\text{C}$ (Table IV), depend-

ing on the degree of hydrogen bonding interaction. This weight loss may manifest itself in a DSC experiment by changes in the baseline, which produce most of the wrong interpretations. Besides water evaporation, differences in the extraction processing, leading to chemical differences in the wood components, and the different methods of thermal characterization, are likely to be the major causes of the conflicting data on the thermal transitions of such materials.

Nevertheless, Ramiah and Goring,¹⁹ carrying out a detailed study of the thermal expansion of cellulose and lignin compounds in the dry and the water-swollen states, established, in our opinion, a clear basis for the discussion of the thermal transitions associated with these materials near

Table II Mechanical Properties of Untreated Coir Fibers

Sample	d_1 (mm) ^a (± 0.005)	d_2 (mm) ^a (± 0.005)	$d_{(d_1+d_2)/2}$ (mm) (± 0.005)	UTS ^b (MPa)	EB ^c (%)	IM ^d (GPa)
1	0.270	0.230	0.250	91	27	2.3
2	0.360	0.254	0.307	84	34	2.1
3	0.370	0.310	0.340	82	31	1.9
4	0.419	0.269	0.344	71	28	2.1
5	0.431	0.306	0.369	67	28	1.9
6	0.493	0.328	0.411	59	25	2.0
			Average:	76 ± 15	29 ± 5	2.1 ± 0.3

^a Average length was approximately 50 mm. d_1 and d_2 are the two oval diameters. d was used to calculate UTS and IM.

^b Ultimate tensile strength.

^c Elongation at break.

^d Initial modulus.

Table III Mechanical Properties of Treated Coir Fibers (48 h 5 wt % NaOH)

Sample	d_1 (mm) ^a (± 0.005)	d_2 (mm) ^a (± 0.005)	$d_{(d_1+d_2)/2}$ (mm) (± 0.005)	UTS ^b (MPa)	EB ^c (%)	IM ^d (GPa)
1	0.350	0.220	0.290	98	30	2.7
2	0.330	0.270	0.300	92	32	3.2
3	0.367	0.255	0.311	87	34	3.0
4	0.410	0.230	0.320	102	36	2.8
5	0.360	0.290	0.330	99	33	2.8
6	0.420	0.260	0.340	85	32	3.0
Average:				94 \pm 12	33 \pm 5	2.9 \pm 0.3

^a Average length was approximately 50 mm. d_1 and d_2 are the two oval diameters. d was used to calculate UTS and IM.

^b Ultimate tensile strength.

^c Elongation at break.

^d Initial modulus.

room temperature. In their work, drying procedures, in some cases at temperatures $> 150^\circ\text{C}$ and for > 9 h, were applied. Their results pointed to a second-order transition, a maximum in the second differential of volume with respect to tem-

perature versus temperature curve, in the range $19\text{--}33^\circ\text{C}$ for various cellulose and lignin compounds in the dry state. They also observed a further transition between 80 and 110°C for some samples. For water-swollen wood compounds, the secondary transition appearing near 20°C showed an expansion decreasing above the transition temperature. Ramiah and Goring¹⁹ proposed that the breaking of weak hydrogen bonds produces the second-order transition observed in the plot of specific volume versus temperature for various dry cellulose and lignin compounds between 19 and 33°C .

The MTDSC technique is a development of conventional DSC.²² MTDSC was recently largely used to overcome the difficulties associated with the study of transitions, in general T_g , in multi-component and multiphase materials.^{23–25} The modulation of temperature provides the easy extraction of other signals, besides the conventional heat flow, from the modulated heat-flow response. The heat capacity associated with reversible events can be easily deconvoluted from the response of irreversible events.²³

MTDSC analysis of Brazilian coir fibers, after careful preparation (see Experimental), was performed in an attempt to observe the thermal transitions involving cellulose, lignin, and cellulose–lignin complex¹³ in this natural composite material. The MTDSC results expressed in terms of the heat flow and heat capacity signals are shown in Figure 5. As already discussed, the main difficulty is the water content and the transitions associated with water-bound complexes of the fiber constituents. Hatakeyama et al.²⁶ studied the C_p behavior of cellulose and lignin by conven-

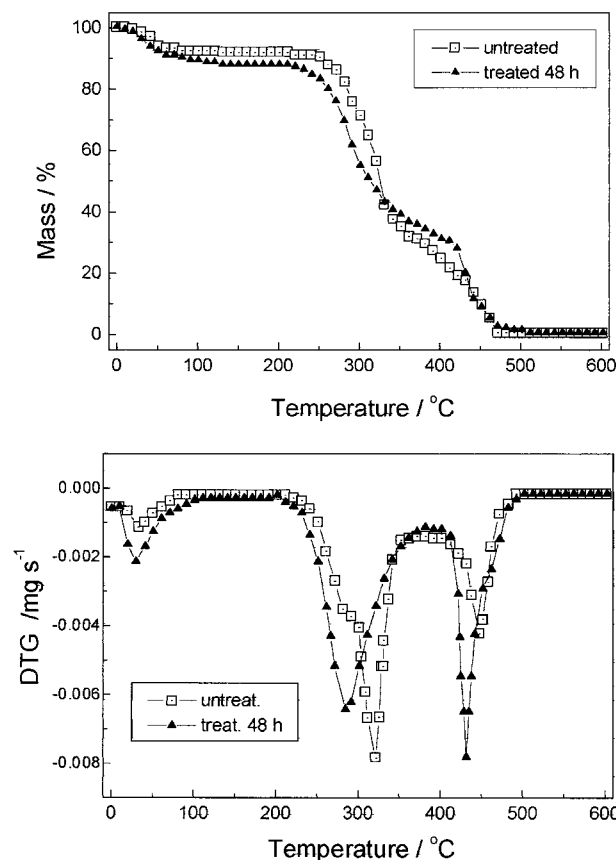


Figure 4 TG and DTG curves for coir fiber untreated and treated with 5 wt % NaOH/48 h.

Table IV Thermogravimetric Results for Coir Fiber Subjected to Different Periods of Alkali Treatment

Coir Fiber	Transition Temperature Range (°C)	Transition Peak (°C)	Weight Loss (%)	Residue ^a (%)
Untreated	28–93	39	6	
	215–388	334	58	
	388–510	476	34	1
NaOH-treated 24 h	25–161	39	9	
	161–388	289	53	
	388–566	447	37	1
48 h	25–167	39	12	
	167–405	291	57	
	405–510	439	30	0.4
72 h	28–130	39	9	
	209–405	297	63	
	405–484	418	24	3

^a After heating to 600°C.

tional DSC. They annealed the samples at 150°C for 5 min before each measurement. In Figure 5(a), the heat-flow signal is shown for untreated and treated coir fibers after annealing for 20 min at 150°C and after annealing for 6 h at 160°C. Table V shows some of the MTDSC results obtained. For all samples, a thermal event was observed between 28 and 38°C, which can be associated with the second-order transitions reported by Ramiah and Goring¹⁹ in cellulose and lignin compounds. No clear evidence was seen of the lignin T_g between 130 and 150°C,²⁰ which may indicate a strong association between the lignin and cellulose in these fibers.

The significant differences observed in Figure 5(a) between the untreated and treated samples is the more pronounced exothermic nature of the process at 32–38°C for treated samples. This exothermic event is probably associated with the stronger water interaction in the alkaline-treated fiber. The annealing at 160°C for 6 h was not able to change this feature significantly. This event continues to be exothermic after annealing at 160°C. Therefore, it was also performed over several periods (3–12 h) annealing at 180°C. These experiments were an attempt to obtain a heat-flow signal without an exothermic event. However, in all subsequent MTDSC experiments, the same feature in the heat-flow signal was registered for alkaline-treated coir fibers. Higher temperatures for thermal annealing were not used, because they can cause degradation in the material, as observed by the TG study (Table IV).

The problem of interaction between water and hydrophilic polymers has been recently studied by Hatakeyama and Hatakeyama.²⁷ They pointed to the existence of three types of water: free water, freezing bound water, and nonfreezing water. The degree of interaction increases between the three types. In our data, the free or absorbed water is eliminated on the first weight loss reported in Table IV. The freezing bound water is reported to leave hydrophilic polymers at around 150°C²⁷ and the nonfreezing water later. However, temperatures > 160°C are unlikely to limit the degradation of cellulose and lignin. To guarantee that the drying procedures used before our MTDSC experiments have removed all the water accessible to these temperatures and, at the same time, did not produce thermal degradation of the other components, Figure 6 shows the isothermal treatments performed in this work. Figure 6(a) shows the annealing at 150°C for 20 min and Figure 6(b) the annealing at 160°C for 6 h for both untreated and treated (48 h/5 wt % NaOH) fibers. Considering that the accuracy of thermogravimetric measurements is of approximately 1 wt %, Figure 6 shows that no changes in mass were observed after the first minutes of annealing. It should be noted that a slight increase on the dry condition is obtained when the temperature is raised to 160°C. This result confirms the heat-flow indications in Figure 5(a).

The C_p results obtained for untreated and treated coir fibers dried at 150°C and annealed at 160°C for 6 h are shown in Figure 5(b).

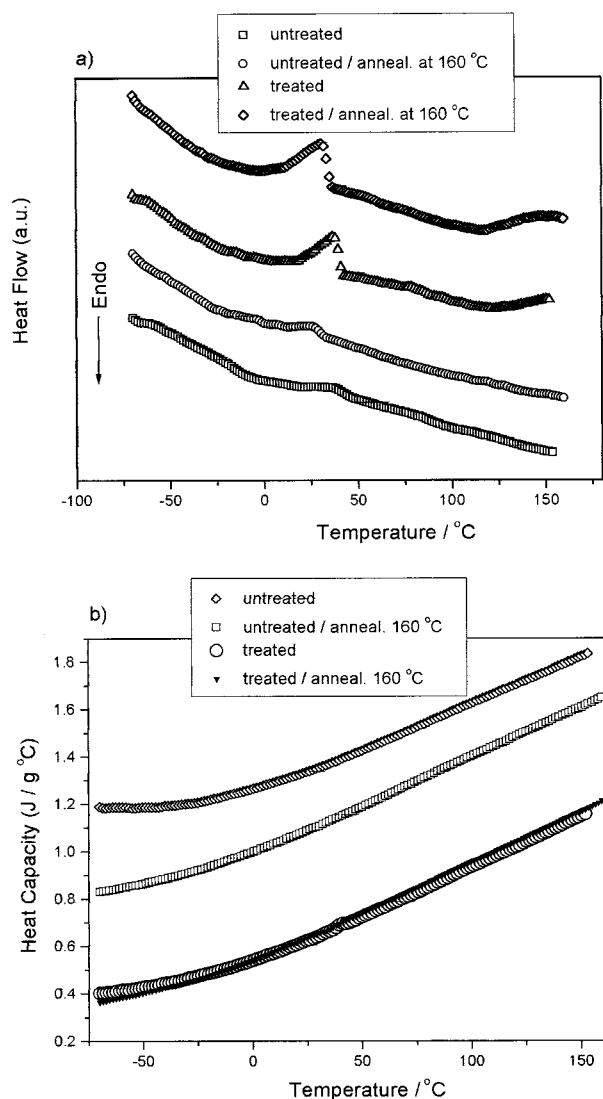


Figure 5 MTDSC results for coir fiber untreated and treated (48 h/5 wt % NaOH) after 20 min annealing at 150°C and after 6 h annealing at 160°C. (a) Heat flow versus temperature. (b) Heat capacity versus temperature.

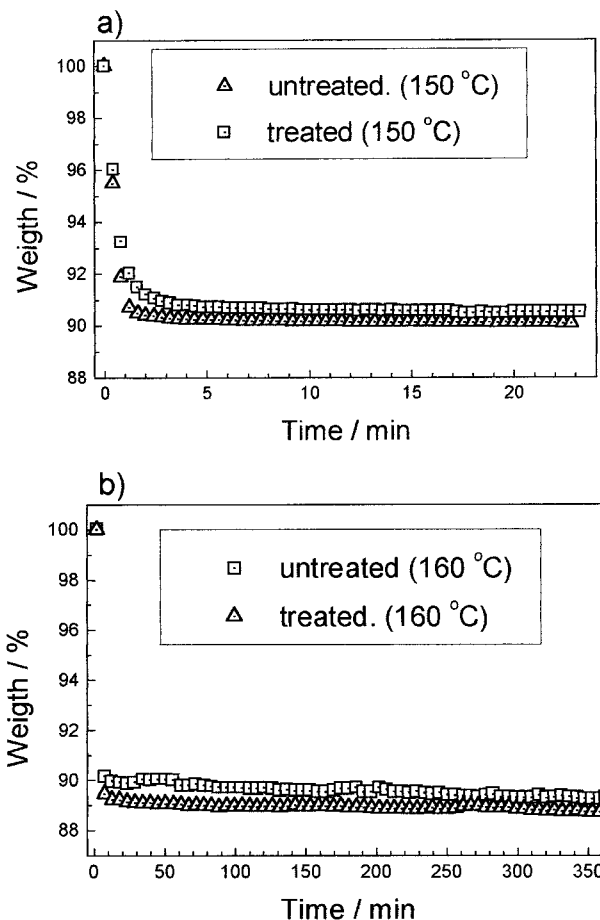


Figure 6 TG isotherms for coir fiber untreated and treated (48 h/5 wt % NaOH). (a) 20 min annealing at 150°C and (b) 6 h annealing at 160°C.

Hatakeyama et al.²⁶ reported that the C_p of lignin and amorphous cellulose are similar despite their completely different chemical structures. The results obtained for C_p at 25 and 100°C are shown in Table V. The values for untreated coir after annealing for 20 min at 150°C are similar to other natural fibers^{18,26} and for cellulose and lignin

Table V MTDSC Results for Untreated and Alkaline-Treated Coir Fiber

Sample	Temperature of the Thermal Event (°C)	C_p at 25°C (J g ⁻¹ deg ⁻¹)	C_p at 100°C (J g ⁻¹ deg ⁻¹)
Untreated			
Anneal. 20 min at 150°C	38	1.34	1.63
Anneal. 6 h at 160°C	28	1.09	1.40
NaOH treated, 48 h			
Anneal. 20 min at 150°C	38	0.63	0.94
Anneal. 6 h at 160°C	32	0.63	0.96

compounds.²⁶ After annealing for 6 h at 160°C, a decrease in C_p was observed, which could be associated with an increase in the cellulose crystallinity,²⁶ structural rearrangements of the lignin–cellulose complex, or other effects. For the alkaline-treated coir fiber, the initial C_p values are significantly lower than for the raw fiber and did not change after annealing.

CONCLUSIONS

Morphologic and mechanical results show that the native Brazilian coir fibers, which have an oval cross section, have ultimate tensile strength and initial modulus significantly improved by alkaline treatment. The elongation at break was also increased by 10% by the alkaline treatment. The results of elongation at break are approximately 33% for treated fibers. SEM results showed that the removal of superficial cuticle produces higher surface roughness.

The thermogravimetric results show an increase in water content and a slight decrease in thermal stability with alkaline treatment. The MTDSC experiments show an exothermic event (28–38°C) for all coir fiber samples. The C_p values for raw coir fiber are similar to other natural fibers (C_p value at 25°C of 1.34 J g⁻² deg⁻²) and there was a significant decrease in C_p after annealing treatment and the alkaline treatment.

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