Carnauba Straw: Characterization and Chemical Treatments

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ABSTRACT: The influence of chemical modifications, such as dewaxing with hexane and carbon tetrachloride, and alkaline treatment, on the mechanical, thermal, and sorption properties of carnauba straw was investigated for the first time. Scanning electron microscopy showed that the solvent treatments removed the wax layer, exposing the straw fibrils. The straw water sorption capacity was very high, and the treatments turned it from Fickian to non-Fickian. The results show that the solvents used were very effective in removing the surface wax layer, whereas alkali, on the other hand, promoted a more marked change in the chemical structure of the straw. The chemical treatments demonstrated that the wax surface layer

INTRODUCTION

Cellulose-based natural fibers, such as sisal, jute, coconut, and pineapple, have a great potential for replacing more traditional materials, such as glass fibers, in composites.^{1–4} These fibers are characterized by their hardness, impact resistance, flexibility, and high modulus. They are abundant, biodegradable, and renewable. Furthermore, these inexpensive, low-density fibers cause less skin and lung irritation.

In recent years, the concern with CO_2 emissions and other environmental factors has stimulated interest in natural materials. Efforts have been made to use natural-fiber composites instead of glass-fiber ones, especially in nonstructural applications. Several fields have started to use reinforced composites with natural fibers, such as the automotive industry, which uses them in the interior door and roof panels, seat backs, knobs, and internal parts of the luggage compartment. Compared with glass fibers, natural fibers are very efficient in sound absorption, have low cost, are lightweight, and do not split into was very important in determining the final properties of this material and that its removal reduced the thermal stability and Young's modulus from 143 to 48 MPa and increased its hydrophilicity, changing the contact angle from 90 to 60°. As a result, carnauba straw is a potentially promising material to be used, for example, as a natural fiber with polymer matrices for the manufacture of lowcost, ecofriendly composite materials. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 1614–1621, 2011

Key words: biomaterials; fibers; hydrophilic polymers; infrared spectroscopy; modification

fragments during an accident.⁵⁻⁸ Researchers in this field are in agreement that such renewable and plentifully available materials still present a number of disadvantages, such as wettability, incompatibility with some polymeric matrices, and a high water absorption capacity. The fiber-matrix surface adhesion issue is the most widely investigated point. The hydrophilic characteristics of natural fibers are in contrast with the usual hydrophobic characteristics of polymeric materials; this results in composites with poor mechanical properties. In an attempt to overcome this restriction, several physical surface (cold plasma and corona discharge) and chemical [with maleic anhydride, organosilanes, isocyanates, sodium hydroxide (NaOH), permanganate, and peroxide] treatments have been suggested.9-13

In Brazil, several natural fibers are produced by local communities, especially in the north and northeast. The country has extensive plantation areas, and there are a large number of projects that take into account environmental and economical sustainability. Therefore, a further advantage to the use of these fibers, beyond all those previously cited, is the fact that they represent a new source of income for the rural population and add a social function to their cultivation.¹⁴ One of these projects, which motivated this study, is supported by Petrobras S. A with the objective of testing the use carnauba straw

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in place of aluminum foil for the protection of the thermal insulation of steam pipes.

Although very extensive, no natural fiber literature reports the use of carnauba straw or fiber in polymeric compounds or any other application. Most carnauba studies are related to the use of carnauba wax^{15,16} in areas such as pharmaceutical products, cosmetics, plastics, photographic films, coatings, impermealizers, lubricants, varnish, and in the food industry. Therefore, the potentiality and industrial applications of this material should be investigated. The carnauba tree (Copernicia prunifera) is a typical Brazilian plant. There are other Copernicias in South America, Copernicia in Venezuela and Copernicia alba in Bolivia and Paraguay; however, only the prunifera leaves produce wax. In general, plants produce wax to prevent moisture loss through their leaves. The wax powder on the surface prevents the excessive transpiration that occurs in environments with extended dry seasons and low relative humidities. Like other vegetable fibers, carnauba straw is composed mainly of cellulose and lignin, in addition to smaller amounts of other substances.^T

The aim of this study was to characterize the main properties of this new material (thermal stability, hydrophilicity, and mechanical resistance) in untreated form and after three different chemical treatments for possible future commercial applications as a biocomposite filler.

EXPERIMENTAL

Carnauba straw, usually used to make hats, bags, and baskets, was obtained from a small handcraftmaking community in the northeast of Brazil. NaOH, carbon tetrachloride (CCl_4), and hexane (Reagen Ltd., São Paulo, Brazil) were analytical grade and were used as received.

Carnauba straw chemical treatments

Treatment with NaOH

Straw samples ($7.0 \times 1.0 \text{ cm}^2$) were placed in test tubes containing a 0.1*M* NaOH aqueous solution at 40°C for 30 min. The samples were then exhaustively washed with distilled water until they reached neutral pH and were dried at room temperature. The straw/alkali ratio (m/v) was 1.0 g of straw per 10 mL of alkaline solution.

Treatments with CCl_4 and hexane (C_6H_{12})

Straw samples (7.0 \times 1.0 cm²) were placed in test tubes containing 10 mL of CCl₄ or hexane. The treatments were carried out at 60 and 65°C for CCl₄ and hexane, respectively. The treatment times ranged from 5 to 120 min. The straw/solvent ratio (m/v) was 1.0 g of straw for 10 mL of solvent.

Characterization

Spectroscopic analysis [Fourier transform infrared (FTIR)–attenuated total reflectance (ATR)]

Infrared analyses were carried out in a Thermo Nicolet Nexus 470 spectrometer. The spectra were obtained by the ATR technique with an SeZn crystal and incidence angles of 30, 45, and 60°. A small piece of straw was cut with dimensions similar to the SeZn crystal ($50 \times 10 \text{ mm}^2$), put in contact with the crystal, and pressed.

Scanning electron microscopy (SEM)

Electron micrographs were obtained with a Philips XL-30 scanning electron microscope with a tungsten filament, a voltage of 25.0 kV, and a secondary electron detector. Before SEM evaluation, the samples, consisting of small pieces of straw, were coated with gold using a plasma sputtering apparatus.

Water sorption measurements

Straw samples (7.0 \times 1.0 cm²) were weighed and placed in test tubes with distilled water at room temperature. Increases in the sample weight were recorded at 5, 15, 30, and 60 min; 2, 3, 4, 5, 6, 7, 8, and 9 h; and afterward, daily for the next 9 days, for a total of 240 h. Each experiment was run in quintuplicate for each treatment, in addition to the untreated sample. The molar percentage uptake (*Q*) of water per 100 g of straw was calculated as

$$Q_t = \frac{M_e(w)/M_r(w)}{M_i(s)} \times 100 \tag{1}$$

and was plotted against the square root of time. Here, $M_e(w)$ is the mass of water at equilibrium; $M_r(w)$ is the relative molecular mass of water, that is, 18.0 g/mol; and $M_i(s)$ is the initial mass of the sample. When equilibrium was reached, Q_t was defined as the molar percentage uptake at infinite time, that is, Q_{∞} . The values of the kinetic parameters *n* and *k* for water sorption by carnauba straw were calculated with eq. (2):¹⁸

$$\ln\left(\frac{Q_t}{Q_\infty}\right) = \ln k + n \ln t \tag{2}$$

where Q_t is the molar percentage water uptake at time t, Q_{∞} is the molar percentage water uptake at equilibrium, k is a constant, and t is time. Linear regression was used to calculate values of k and n. The value of n classified the sorption mechanism,

0.8 0.6 0.4 · CCI. 0.2 Hexan NaOH Untreated 0.0 4000 3000 2000 1000 Wavenumbers (cm⁻¹)

Figure 1 FTIR-ATR spectra for untreated carnauba straw and straw chemically treated with hexane, CCl₄, and NaOH.

whereas k indicated the interactions between the penetrant and the straw.

Contact angle measurements

Tilting-plate goniometry was performed with a commercial automated DSA 100 Krüs, goniometer. The tilting-plate goniometer employed a liquid-handing robot to aspirate 0.5 mL of water and dispense 6-µL drops onto the surface of the test substrate held within the focal plane of a magnifying camera. These and all other aspects of tilting-plate goniometry were performed under computer control. Proprietary algorithms were used to deduce the contact angles from drop images captured at a programmed rate by a frame grabber. The experiment time was 10 min. The measurements were done at four different points of each sample (two points at each side). The results presented are the average of these four measurements.

Thermal analysis [thermogravimetry (TG)/ differential thermogravimetry (DTG)]

TG curves were obtained with a Shimadzu DTG-60H thermoanalyzer balance at temperatures between 25 and 800°C with a heating rate of 10°C/min in a nitrogen atmosphere.

Mechanical properties

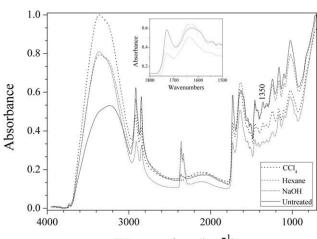
The mechanical tests were performed with a Shimadzu Autograph AG-I universal test machine with a load cell of 100 kN and a speed of 5 mm/ min. The test samples measured 9.0 cm in length and 1.0 cm in width. However, only 60% of this length (5.4 cm) was available to be loaded. The remaining 40% was covered with several layers of paper and a cyanoacrylate-based adhesive to protect the straw edges and also to prevent the sample from flowing out of the grips. The results represent the average of three analyzed samples.

RESULTS AND DISCUSSION

Carnauba straw chemical treatments

The alkaline treatment was chosen because it is a conventional treatment for natural fibers defined as *mercerization*.^{19,20} Hexane (bp = 69° C) and CCl₄ (bp $= 76.6^{\circ}$ C) treatments were performed to remove any amount of carnauba wax present on the straw surface because the solvents used were compatible with carnauba wax.

Initially, the FTIR-ATR spectra of the untreated carnauba straw were obtained with incidence angles of 30, 45, and 60°. The purpose of using different angles and consequently different penetration depths was to obtain a more representative surface (60°) or bulk (30°) spectra. However, the results did not show significant differences among the spectra obtained at different penetration depths. However, it was possible to observe that the spectrum obtained at an incident angle of 30° exhibited much better quality, certainly because as the incidence angle decreased, the number of reflections increased and so did the peak intensities. Therefore, it was decided that such an incidence angle should be chosen to obtain all spectra. Figure 1 shows the carnauba straw spectra after treatments with hexane, CCl₄, and NaOH and the spectrum for untreated straw for comparison purposes. The results show a typical cellulosic fiber spectrum^{11,19,21–25} with OH stretching of water, alcohols, and phenols at about 3400 cm⁻¹ (from hemicellulose and lignin); CH₂ stretching at 2920 cm⁻¹ (from cellulose); C=O stretching at 1720 cm⁻¹; adsorbed water at 1635 cm⁻¹; a shoulder at 1600 cm⁻¹, attributed to the C=C stretching vibration of the aromatic groups present in the lignin structure;^{19,26} H-O-C bending at 1452 cm⁻¹; O-H in-plane deformation at 1350 cm⁻¹, referred to by some authors as the *lignin band;*²¹ O–H in-plane deformation at C(6) at 1240 cm⁻¹; C–O–C asymmetric stretching from the β -glycosidic link at 1155 cm⁻¹; and C-O vibration at 1020 cm⁻¹. A comparison of spectra showed that the OH stretching band became more intense for all of the treated samples and even more so for the sample treated with CCl₄. One possible explanation is that the solvents used removed the wax surface layer, exposing the OH groups and causing the fiber to become more hydrophilic. According to the results, CCl₄ seemed to be the most effective solvent. It was also possible to observe a reduction in the shoulder located at 1600 cm⁻¹



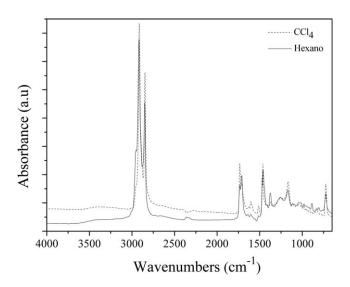


Figure 2 FTIR spectra of the residues from treatments with hexane and CCl₄.

(in detail) and in the absorption band at 1350 cm^{-1} , especially with alkaline treatment. Because both bands were lignin-related, the results suggest that lignin concentration decreased with this treatment.

After treatment, the solvent used was concentrated by evaporation, and the spectra of this residue were obtained. The results are shown in Figure 2. As shown, only hexane and CCl₄ residues were shown because, in the case of NaOH, the solution was clear at the end of treatment. The main absorption bands present in Figure 2 were compared with those reported in the literature²⁷ for carnauba wax. From that, it was possible to identify the symmetric and asymmetric CH₂ stretching at 2915 and 2850 cm⁻¹, respectively; the C=O vibration at 1730 cm^{-1} ; $-CH_2$ -scissoring vibrations at 1460 cm⁻¹; angular deformation of the C-H bond of alkane (umbrella motion) at 1376 cm⁻¹; C–O stretching vibration at 1160 cm⁻¹; and CH₂ rocking vibration at 720 cm⁻¹. The results confirm that the residue was composed basically of carnauba wax, which was removed from the straw surface.

SEM

Figure 3 shows the electron micrographs obtained for the untreated straw surface [Fig. 3(a,b)] and those treated with hexane [Fig. 3(c,d)], CCl₄ [Fig. 3(e,f)], and NaOH [Fig. 3(g,h)]. The presence of fibrils and globular marks became more evident for the treatments with hexane and CCl₄ and indicated that the thin carnauba wax layer was removed from the surface of the straw; this exposed its fibrils. As a result, these treatments seemed to roughen the straw surface. On the other hand, the micrographs of the samples treated with NaOH were not drastically changed, compared with the untreated fiber. This result is in good agreement with the previous one, where no residue was found in the alkaline solution after the treatment. On the other hand, it differs from the results found for many other natural fibers, where it was shown that alkaline treatment always leaves the surface cleaner and removes certain amounts of lignin, wax, and oils.9,10,28 It is also different from the FTIR-ATR results, which showed a more significant change in the spectrum of the alkali-treated straw. It is important to point out that this vegetable material has not been studied before and that alkaline treatment results are very dependent on the experimental conditions, such as alkali concentration, time, and temperature. Besides, SEM is a surface technique, whereas FTIR is a bulk technique.

Water sorption

The results of the water sorption experiments for the untreated sample for a period of 240 h (data not shown) indicate that the sorption process occurred very rapidly, and after about 50 h, the amount of absorbed water tended toward an equilibrium value of about 10 mol %. On the basis of this result, the experimental time was reduced to 48 h to optimize the subsequent experiments. Figure 4 shows the results for the straws treated with hexane, CCl₄, and NaOH. With treatments based on hexane and CCl₄, the water sorption process became faster at short times, although the equilibrium values remained practically unchanged (with the experimental errors considered). This result is in good agreement with previous findings obtained by SEM and FTIR. Considering that solvent treatments were the most effective in removing the surface wax layer (nonpolar), it would be expected that (1) the surface became more polar and, therefore, more hydrophilic and (2) the surface morphology was modified, exposing the fibrils and globular marks, increasing the surface roughness, and creating voids that accelerated water sorption. Comparing the equilibrium water sorption values for carnauba straw ($\sim 180\%$) with other natural materials, such as linseed, sisal, and coir, which range from 20 to 40%,^{6,20} we observed that the former were much higher. This characteristic, which initially could be considered a disadvantage over other materials, could easily be overcome with water-based waterproofing agents, such as acrylic resins (this subject is under investigation, and the results will be published soon). Table I shows the values of n and kfor carnauba straw in water obtained from the angular and linear coefficients of curves shown in Figure 4, respectively. The value of n for untreated straw was close to 0.5, characterizing a Fickian diffusion process, whereas the value of k was very low, indicating low interaction between the straw and

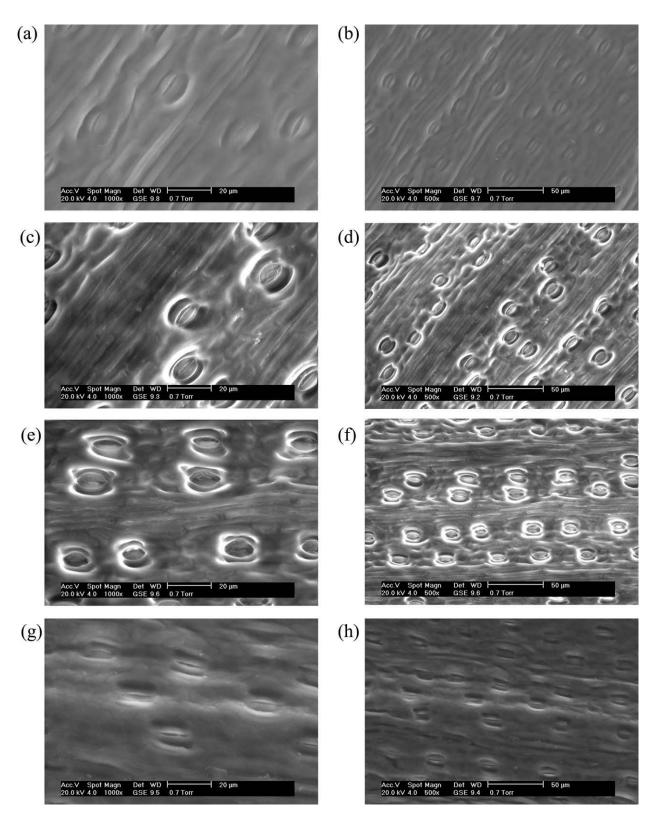


Figure 3 SEM micrographs for (a,b) untreated straw, (c,d) straw treated with hexane, (e,f) straw treated with CCl₄, and (g,h) straw treated with NaOH.

water. After the treatments, the n values decreased to around 0.3, indicating a non-Fickian diffusion process, whereas the k values increased, indicating a stronger straw–water interaction. These results are

supported by those previously obtained by SEM. In summary, the solvent treatments changed the surface morphology and led to a larger initial water uptake. Surface wax layer removal made the surface more

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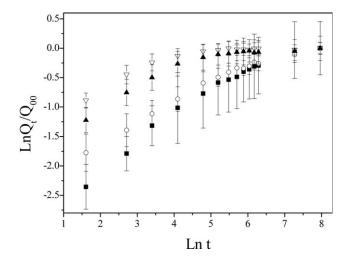


Figure 4 Sorption curves for (\blacksquare) untreated carnauba straw and samples treated with (\blacktriangle) hexane, (\bigtriangledown) CCl₄, and (\bigcirc) NaOH.

hydrophilic, increasing the k values. This is also an important result from the application point of view because it shows that the treatments used accelerated water uptake. Because this high water affinity usually is not desirable, we concluded that for many applications the straw could be used without any previous treatment, reducing its production cost and preventing the use of organic solvents.

Contact angle measurements

One of the main potential applications of carnauba straw is its use as a natural filler in composites. In this case, properties such as wettability, adhesion, and compatibility must be determined. All these physicochemical properties are related to contact angle measurements. Therefore, the technique has been widely used to monitor the surface properties. The behavior of a drop placed over the surface indicates different wettability situations: contact angle $(\theta) = 0$ shows that the surface presents a high wettability or that it is a hydrophilic surface; when $0^{\circ} <$ $\theta < 90^{\circ}$, the surface is predominantly hydrophilic; and when $90^{\circ} < \theta < 180^{\circ}$, the surface is predominantly hydrophobic. Figure 5 shows the results. The untreated straw had an initial contact angle of 98°, and even at longer times, the value remained above 90°; this characterized the surface as predominantly hydrophobic. Such a characteristic was probably due

TABLE IValues of n and k for Carnauba Straw in Distilled Water

Treatment	п	k
Untreated	0.49 ± 0.03	0.05
Hexane	0.38 ± 0.02	0.,16
CCl ₄	0.26 ± 0.04	0.29
NaOH	0.28 ± 0.01	0.10

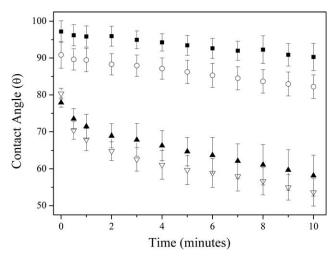


Figure 5 Contact angle as a function of $\ln t$ for (\blacksquare) untreated carnauba straw and samples treated with (\blacktriangle) hexane, (\bigtriangledown) CCl₄, and (\bigcirc) NaOH.

to the presence of a wax layer on the straw surface. It was also possible to observe that alkaline treatment caused only a slight change in the hydrophobic character. On the other hand, the treatments with solvents, especially hexane, caused a dramatic decrease in the contact angle and made the surface predominantly hydrophilic. It could, therefore, be concluded that with removal of the surface wax layer, the solvents made the straw surface more hydrophilic. It was also possible to observe that for the solvent-treated samples, the time-dependent contact angle variations were more evident, which was probably due to the increase in rugosity caused by wax removal. These results corroborate those previously obtained by SEM and water sorption tests.

Thermal analysis

The thermal stability of carnauba straw was measured with TG/DTG. Figure 6 shows DTG curves for untreated and chemically treated carnauba straw, whereas Table II lists the main results. The weight loss at low temperatures, between ambient and 150°C, with a maximum at 60°C, could have been related to the presence of absorbed or combined water released during the dehydration process because carnauba straw is quite hydrophilic. A weight loss of 7-9% was found for all of the samples analyzed; with the highest value occurring for the alkali-treated sample. The amount of water present in carnauba straw is comparable to other lignocellulosic materials, such as cotton, jute, and sisal fibers.^{29,30} However, the release temperature ($60^{\circ}C$) found for carnauba was higher than those obtained for other materials, which are usually around 40°C. This result indicates that in the case of carnauba straw, water is more strongly bound to the material;

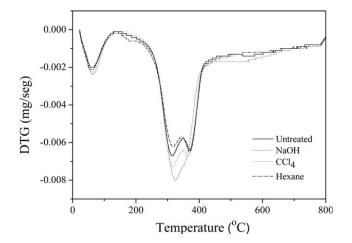


Figure 6 DTG curves for untreated carnauba straw and samples treated with hexane, CCl₄, and NaOH.

therefore, higher temperatures are required to eliminate it. For the untreated sample, after dehydration, one doublet peak was observed, starting at 200°C, with maxima at 314 and 370°C, representing the decomposition process of the carnauba straw constituents. As already stated, to the best of our knowledge, there are no studies on the characterization of carnauba straw. However, the literature about other lignocellulosic materials also describes the presence of two peaks. Tomaczak et al.31 and Hourston et al.²² reported the first peak at 259°C and the second at 313°C for coir fibers. For sisal fiber, the reported values are about 270°C for the first peak.²⁰ The results for carnauba straw show a higher thermal stability than those shown for other vegetable materials. According to the literature, the first peak is due to the decomposition of hemicellulose components, whereas the second corresponds to cellulose degradation between 330 and 420°C. The final residue of about 20% was possibly related to the condensation of lignin components and straw ash. Thermograms of untreated and treated straw demonstrate that the most significant change was caused by the alkaline treatment. In this case, the two peaks were now condensed into one. The first, related to hemicellulose, became more intense and showed a higher decomposition temperature (from 314 to 325°C), whereas the second, related to cellulose, was

present only as a small shoulder on the right side of the main peak. The alkaline treatment is an industrial process, known as mercerization. It is the most widely used method for improving wettability and adhesion.³² Parameters such as NaOH concentration, time, and temperature have been exhaustively studied and have yielded very different results. However, it is generally accepted that such treatment increases the fiber–matrix adhesion by removing impurities, such as fatty acids, from the surface; increases the rugosity; and modifies the crystalline structure of cellulose. This results indicate that the

treatment could have destroyed part of the crystaline

Mechanical properties

structure of cellulose.

The test results are shown in Table III. Compared with other lignocellulosic-based materials, carnauba straw is in the same range as cotton and sisal in terms of modulus and as cotton, sisal, and flax in terms of tensile strength.^{8,31} It was also observed that all treatments caused a decrease in the modulus and tensile strength. Once again, alterations were more marked with alkaline treatment. The literature shows that mercerization may or may not improve the parameters analyzed, depending on experimental conditions. Improvement usually occurs when the process causes structural changes, such as fiber shrinkage and/or increases in cellulose crystallinity.24,33 In our case, alkaline treatment seemed to destroy the cellulose crystaline structure and, therefore, reduced the mechanical resistance of the material.

CONCLUSIONS

Untreated carnauba straw and straw submitted to chemical treatments with hexane, CCl₄, and NaOH were, to the best of our knowledge, physicochemically characterized for the first time. SEM results show that the solvent treatments (hexane and CCl₄) produced the most significant changes on the straw surface because of the removal of the carnauba wax layer, whereas changes resulting from the alkaline treatment were less marked. Although water

TABLE II

DTG Results for Untreated Carnauba Straw and Straw Chemically Treated with CCl₄, Hexane, and NaOH

	First stage		Second stage		Third stage	
Treatment	T (°C)	Weight loss (%)	T (°C)	Weight loss (%)	T (°C)	Weight loss (%)
Untreated	59.4	7.23	314.6	30.43	370.8	22.24
Hexane	59.9	7.22	317.8	28.39	370.1	22.20
CCl ₄	61.9	7.40	316.4	28.17	365.4	23.03
NaOH	63.3	8.34	325.0	49.5	—	—

T =temperature.

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TABLE III
Mechanical Properties of the Untreated Carnauba Straw
and Straw Chemically Treated with CCl ₄ , Hexane, and
NaOH

Treatment	Young's	Tensile	Elongation at
	modulus (GPa)	strength (MPa)	break (%)
Untreated	4.91 ± 0.24	84.5 ± 20.7	2.93 ± 0.38
NaOH	2.00 ± 0.35	48.1 ± 4.9	2.50 ± 0.50
CCl ₄	3.10 ± 0.27	73.6 ± 14.3	$\begin{array}{r} 2.38 \pm 0.43 \\ 2.22 \pm 0.17 \end{array}$
Hexane	3.02 ± 0.85	67.6 ± 22.2	

sorption experiments showed that the chemical treatment did not change the final amount of sorbed water, they did accelerate the process; this indicated a higher water-straw affinity. Contact angle measurements also corroborated our analysis, indicating that the treatments made the predominantly hydrophobic surface of the untreated straw become predominantly hydrophilic. Thermograms showed event characteristics of water elimination, followed by hemicellulose and cellulose degradation. Thermal analysis demonstrated that alkaline treatment induced a number of changes in the chemical structure of straw, probably related to cellulose crystaline structure modification. By contrast, the solvent treatments only removed the surface layer wax. We concluded from the mechanical test that both solvent alkaline treatments decreased the tensile and strength and modulus values. Furthermore, it was found that the chemical treatments did not improve any property that could be important in industrial application or in polymeric composites. This may be an advantage, given that the use of untreated straw prevents the use of organic solvents and, therefore, drastically reduces the production costs.

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References

- 1. Antich, P.; Vazquez, A.; Mondragon, I.; Bernal, C. Compos A 2006, 37, 139.
- Acha, B. A.; Reboredo, M. M.; Marcovich, N. E. Compos A 2007, 38, 1507.
- 3. Brahmakumar, M.; Pavithran, C.; Pillai, R. M. Compos Sci Technol 2005, 65, 563.

- Threepopnatkul, P.; Kaerkitcha, N.; Athipongarporn, N. Compos B 2009, 40, 628.
- 5. John, M. J.; Anandjiwala, R. D. Polym Compos 2008, 29, 187.
- 6. John, M. J.; Thomas, S. Carbohydr Polym 2008, 71, 343.
- Mohanty, A. K.; Misra, M.; Drzal, L. T. J Polym Environ 2002, 10, 19.
- 8. Wambua, P.; Ivens, J.; Verpoest, I. Compos Sci Technol 2003, 63, 1259.
- 9. Alix, S.; Philippe, E.; Bessadok, A.; Lebrun, L.; Morvan, C.; Marais, S. Bioresour Technol 2009, 100, 4742.
- 10. Belgacem, M. N.; Gandini, A. Compos Interfaces 2005, 12, 41.
- Bessadok, A.; Langevin, D.; Gouanve, F.; Chappey, C.; Roudesli, S.; Marais, S. Carbohydr Polym 2009, 76, 74.
- 12. Bismarck, A.; Springer, J.; Mohanty, A. K.; Hinrichsen, G.; Khan, M. A. Colloid Polym Sci 2000, 278, 229.
- 13. Gassan, J.; Bledzki, A. K. J Appl Polym Sci 1999, 71, 623.
- Luz, S. M.; Goncalves, A. R.; Del'arco, A. P.; Ferrao, P. M. C. Compos Interfaces 2008, 15, 841.
- 15. Huang, W. Petrol Sci Technol 2010, 28, 1.
- da Silva, F. D. B.; Medeiros, S.; Bezerra, A. M. E.; de Freitas, J. B. S.; Assuncao, M. V. Rev Cienc Agron 2009, 40, 272.
- Gomes, J. A. F.; Leite, E. R.; Cavalcante, A. C. R.; Candido, M. J. D.; Lempp, B.; Bomfim, M. A. D.; Rogerio, M. C. P. Pesqui Agropecu Bras 2009, 44, 58.
- Crank, J. The Mathematics of Diffusion; Clarendon: Oxford, 1975.
- 19. Bertoti, A. R.; Luporini, S.; Esperidiao, M. C. A. Carbohydr Polym 2009, 77, 20.
- Bismarck, A.; Mohanty, A. K.; Aranberri-Askargorta, I.; Czapla, S.; Misra, M.; Hinrichsen, G.; Springer, J. Green Chem 2001, 3, 100.
- 21. Mwaikambo, L. Y.; Ansell, M. P. J Appl Polym Sci 2002, 84, 2222.
- Silva, G. G.; De Souza, D. A.; Machado, J. C.; Hourston, D. J. J Appl Polym Sci 2000, 76, 1197.
- 23. Sgriccia, N.; Hawley, M. C.; Misra, M. Compos A 2008, 39, 1632.
- 24. Siroky, J.; Blackburn, R. S.; Bechtold, T.; Taylor, J.; White, P. Cellulose 2010, 17, 103.
- Schwanninger, M.; Rodrigues, J. C.; Pereira, H.; Hinterstoisser, B. Vib Spectrosc 2004, 36, 23.
- Mohanty, A. K.; Misra, M.; Drzal, L. T. Compos Interfaces 2001, 8, 313.
- Salaun, F.; Vroman, I.; Aubry, C. Powder Technol 2009, 192, 375.
- 28. Gassan, J.; Bledzki, A. K. Compos Sci Technol 1999, 59, 1303.
- 29. Gassan, J.; Bledzki, A. K. Angew Makromol Chem 1999, 268, 22.
- Mishra, S.; Misra, M.; Tripathy, S. S.; Nayak, S. K.; Mohanty, A. K. Polym Compos 2002, 23, 164.
- Tomczak, F.; Satyanarayana, K. G.; Demetrio Sydenstricker, T. H. Compos A 2007, 38, 2227.
- 32. Corrales, F.; Vilaseca, F.; Llop, M.; Girones, J.; Mendez, J. A.; Mutje, P. J Hazard Mater 2007, 144, 730.
- Lopattananon, N.; Payae, Y.; Seadan, M. J Appl Polym Sci 2008, 110, 433.