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Sisal Fibers: Surface Chemical Modification Using Reagent Obtained from a Renewable Source; Characterization of Hemicellulose and Lignin as Model Study

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Sisal fibers have one of the greatest potentials among other lignocellulosic fibers to reinforce polymer matrices in composites. Sisal fibers have been modified to improve their compatibility with phenolic polymer matrices using furfuryl alcohol (FA) and polyfurfuryl alcohols (PFA) that can be obtained from renewable sources. The modification corresponded first to oxidation with ClO_2, which reacts mainly with guaiacyl and syringyl units of lignin, generating *o*- and *p*-quinones and muconic derivatives, followed by reaction with FA or PFA. The FA and PFA modified fibers presented a thin similar layer, indicating the polymer character of the coating. The untreated and treated sisal fibers were characterized by ^{13}C CP-MAS NMR spectrometry, thermal analysis, and scanning electron microscopy. Furthermore, for a better understanding of the reactions involved in the FA and PFA modifications, the sisal lignin previously extracted was also submitted to those reactions and characterized. The characterization of isolated lignin and hemicellulose provides some information on the chemical structure of the main constitutive macrocomponents of sisal fibers, such information being scarce in the literature.

KEYWORDS: Sisal; chemical modification; furfuryl alcohol; polyfurfuryl alcohol; sisal hemicellulose; sisal lignin; ^{31}P NMR; ^{13}C CP-MAS NMR; thermal analysis; SEM

INTRODUCTION

In the field of polymer composites, lignocellulosic materials exhibit many attractive features including low density, low requirements on processing equipment, no abrasion during processing abundance and biodegradability (*1, 2*). The main advantage of lignocellulosic fibers upon their mineral counterpart is their environmental friendliness, due, for instance, to the CO_2 neutral life cycle and possibility of incineration for energy recovery after disposal (*3*). The use of lignocellulosic materials to replace synthetic fibers in the production of composites has gained significant importance in technical applications, such as in the automotive industry, as well as in the packaging industry (*4–6*).

Among several lignocellulosic materials, sisal fiber shows great potential. It is very easily cultivated and has short renewal times. Brazil and Tanzania are the two main producing countries (*7*). At the present time, sisal fibers are mainly used as ropes for boats and in the agricultural industry. Sisal rope has excellent resistance to sunlight, little stretch, and good knot-holding ability. The sisal fibers might be considered as a good material to reinforce polymeric matrices (*8, 9*) due to their higher mechanical and physical characteristics (*10*) in relation with a high cellulosic content (*11*). However, the main difficulty in introducing these fibers in polymeric matrices, which are usually hydrophobic, resides in the hydrophilic character of the fibers, as a consequence of the presence of a large number of hydroxyl groups at their surface. To produce composites with higher mechanical properties, it is necessary to promote improvements in the interface area.

In previous studies (*12–15*), we have reported a new way to chemically modify the surface of sugar cane and curaua fibers. This method involves a preferential modification of the lignin polymer, partly preserving the cellulose. The modification of the fibers concerned a preferential oxidation by sodium periodate and/or chlorine dioxide of guaiacyl and syringyl units of lignin, generating *o*- and *p*-quinones and muconic derivatives to react with furfuryl alcohol (FA). This latter substance can be easily obtained by reduction of furfural, which is isolated from

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renewable sources (*16*). The mechanism involved in the grafting of furfuryl alcohol to the oxidized lignin structures remains unknown. The FA-modified sugar cane and curaua fibers had a thin coating of polyfurfuryl alcohol (PFA), indicating that the FA polymerization reaction had occurred. When this thin coating of PFA is formed, the fiber/phenolic matrix interaction is favored at the interface, which increased the adhesion between fibers and matrix polymer. However, the chemical treatments also caused some fiber degradation, which affected their mechanical properties and decreased the impact strength of the corresponding composites (*14*).

In our continuous interest in both the development of new valorized application areas for sisal fibers and the design of natural composites with superior properties, chemical modification with FA was applied to sisal fibers. This paper concerns our first effort to carry out the FA chemical modification in the sisal fibers. The goal of the study was to submit sisal fibers to softer chemical conditions than those used in the sugar cane and curaua fiber, aiming to improve fiber/matrix interactions in the composite without excessive degradation of the fibers and, consequently, a decrease in their mechanical properties. The use of PFA, previously prepared, was also considered to investigate the polymer character of the furfuryl coating layer of the fibers. Lignin isolated from sisal using a mild acidolysis technique was characterized and taken as a model to approach the reactivity of hydroxyl groups involved in the reactions. In a complementary study, sisal hemicellulose was isolated and characterized.

EXPERIMENTAL PROCEDURES

General. Prior to the isolation of lignin and hemicellulose, sisal fibers (kindly given by Incomar SP, Brazil) were Soxhlet extracted with a mixture of cyclohexane/ethanol (1:1, v/v) for 48 h and subsequently with water for 24 h. The fibers were dried in an air-circulating oven (60 °C) and then ground to a powder (1 mm diameter) with a Forplex grinder. The sugar composition of the hemicellulose was determined according to the procedure described by Ruiz and Ehrman, which is based on acidic hydrolysis of hemicellulose and quantitative determination of free sugar content by HPLC (*17*).

Macrocomponent Extraction. The procedure for extracting the hemicellulose was adapted from that of Sun (*18*). The yield of isolated hemicellulose was typically 60% of the total hemicellulose (*18*). The isolation procedure for lignin was adapted from that of Gellerstedt and Lindfors (*19*) and was similar to that described elsewhere (*12–14*). The yield of extracted lignin, based on fiber lignin content, was at about 10%. The purity of the sisal lignin was 90%, estimated by Klason lignin determination and corrected for soluble lignin contribution. This result indicates that the isolated lignin has some residual carbohydrates, despite our effort to purify the material by alkaline dissolution and precipitation in acidic aqueous medium.

Lignin Oxidation with Chlorine Dioxide. An aqueous chlorine dioxide solution was prepared according to a procedure described elsewhere (*20*). A suspension of lignin (200 mg) in water (30 mL) was treated with a ClO_2 aqueous solution (0.17 mmol) and acetic acid (50 μL) at 55 °C. After 30 min, the solution was centrifuged and washed several times with water. The oxidized lignin was dried under vacuum over phosphorous pentoxide.

Lignin Modification with Furfuryl Alcohol. The procedure for the modification of lignin with FA was adapted from the one used for sugar cane bagasse fibers (*12*). After reaction, the mixture was centrifuged and washed with toluene. The modified lignin was dried under vacuum over phosphorous anhydride. After chemical treatment with FA, a mass increase of about 10% was observed.

Lignin Modification with Polyfurfuryl Alcohol. PFA was prepared according to a classical procedure (*21, 22*). The FTIR and ^{1}H NMR spectra were in accordance with those published by Choura et al. (*22*). The oxidized lignin (30 mg), placed in a vial reactor in suspension with toluene (0.2 mL) and 0.3 mL of the PFA–toluene solution (5 mg/mL), was stirred at 100 °C for 2 h. Subsequently, the reaction mixture was centrifuged and extensively washed with toluene. The modified lignin was dried under vacuum over phosphorous anhydride. A mass increase of about 12% was observed.

Characterization of Lignin and Hemicellulose. The ^{1}H and ^{13}C NMR spectra were recorded using a 1 cm diameter tube on a Bruker Avance DPX-400 spectrometer at 300 K. The solvents were DMSO-d_6 for lignin and D_2O for hemicellulose. Chemical shifts were referenced to residual signals of DMSO (^{1}H, 2.50 ppm; ^{13}C, 39.52 ppm) for the runs on lignin and from signals of small amounts of DMSO added to the D_2O (^{1}H, 2.71 ppm; ^{13}C, 39.39 ppm) for the runs on hemicellulose. The ^{13}C NMR spectra were recorded from 200 mg of sample/mL of solvent, after 20000 scans for lignin and 10000 scans for hemicellulose. A 90° pulse flipping angle (9.5 μs pulse width) and 2.5 s delay time between scans were used. Quantitative ^{31}P NMR spectra were registered on a Bruker Avance DPX-200 spectrometer operating at 81 MHz. An inverse gated decoupling sequence was used with a pulse-flipping angle of 90° and a relaxation delay between pulses of 25 s. About 1000 transients were acquired to ensure a high signal/noise ratio. Prior to ^{31}P NMR analysis, the lignins were derivatized according to a method published by Argyropoulos (*23, 24*). For each lignin sample, at least two spectra were recorded to decrease standard error. The maximum standard deviation of the reported data was 2×10^{-2} mmol g^{-1}, whereas the maximum standard error was 1×10^{-2} mmol g^{-1}. The accuracy of syringyl and condensed hydroxyl groups is lower due to overlapping of their signals. The contamination of lignin by carbohydrate induced an overestimated value for aliphatic hydroxyl groups. Thus, their variation after chemical modification was only relative. FT-IR spectra were obtained using a Perkin-Elmer Paragon 1000 PC spectrometer. The compound was mixed with KBr (sample/KBr, 2/200 mg) and pressed under vacuum to form pellets.

Oxidation of Sisal Fibers and Reaction with Furfuryl and Polyfurfuryl Alcohols. Soxhlet extracted sisal fibers (2 g) were oxidized by a ClO_2 water solution (1.6 mmol) and acetic acid (0.5 mL) at 55 °C. After reaction, the fibers, which turned yellow-red, were washed with water until neutrality. The oxidized fibers (2 g), impregnated with 11 g of FA or PFA, were heated at 55 °C for 45 min. The excess of FA or PFA was removed by Soxhlet extraction for 16 h using ethanol or acetone, respectively. Subsequently, the fibers were dried in an air-circulating oven at 85 °C, until constant weight. The weight percent gain (WPG) due to reaction was determined on the basis of the original and final oven-dried fiber weights.

Fiber Characterization. Contents of humidity, ash, Klason lignin, holocellulose (cellulose + hemicellulose), α-cellulose (pure cellulose), and hemicellulose were determined as described elsewhere (*14*). Averages were calculated based on a minimum of three samples for all of the mentioned analyses. The content of humidity determined for the sisal fibers was equal to 9% (w/w). The values obtained for chemical composition of sisal fibers were as follows: cellulose, 65%; hemicellulose, 20%; total

Table 1. Composition of Hemicellulose Fraction

component	relative percentage[a]
residual lignin	4.6
xylose	68.5
galactose	16.6
arabinose	2.5
glucose	2.2
cellobiose	1.8
mannose	1.4
nonidentified	2.4

[a] Expressed as mg/100 mg of dry extracted hemicellulose fraction; the relative margin of error is ±1%.

Klason lignin, 12%; and ash content, 1%. These values were in accordance with literature reports (*9, 10*), despite large variations with respect to sources, age of plants, and measurement methods.

The crystallinity index was determined by X-ray diffraction using a Rigaku Rotaflex model RU-200B diffractometer operating at 40 kV, 20 mA, and l (Cu Ka) = 1540 Å. The crystallinity index of sisal fibers was calculated as described by Buschle-Diller and Zeronian (*25*), and the value found was equal to 66%. Solid-state ^{13}C CP-MAS (cross polarization magic angle spinning) NMR spectra of unmodified and modified sisal fibers were performed at room temperature on a Bruker Avance DPX-400 NMR spectrometer at a frequency of 100.61 MHz and a spinning rate of 8 kHz. Samples were packed in MAS 4 mm diameter zircon rotors. Chemical shifts were related to tetramethylsilane (TMS), which was used as an external standard. The acquisition time for all spectra was set to 16 h (30000 scans). DSC analyses were carried out on Shimadzu DSC equipment, model 50, in the temperature range from 20 to 500 °C, at 10 °C/min, under a nitrogen atmosphere (20 mL/min). Thermogravimetric analyses were carried out using a Shimadzu model TGA-50TA apparatus in the temperature range from 20 to 800 °C at 10 °C/min under a nitrogen atmosphere (20 mL/min). Scanning electron microscopy (SEM) was carried out in a Zeiss-Leica apparatus model 440, electron acceleration = 20 kV. The samples were covered with a thin layer of gold in a sputter coating system prior to analysis.

RESULTS AND DISCUSSION

Analysis of Isolated Macrocomponents of Sisal Fibers. *Hemicellulose Fraction Analysis.* Individual, well-identified, neutral sugars and residual lignin contents of extracted hemicellulose are shown in **Table 1**. Not surprisingly, xylose was the most important free sugar, suggesting high proportions of xylans, which are the most abundant of the hemicellulose structures found in the cell walls of nonwood plants. They can constitute >30% of the dry weight for total hemicellulose (*18*). Appreciable levels of galactose were measured, and minor quantities of arabinose, glucose, and mannose were also identified in this fraction. The presence of cellobiose was due to degradation of cellulose.

The ^{1}H NMR spectrum presented the typical signal pattern expected for hemicellulose (*18, 26*) (figure not shown). The signals between 3.3 and ppm were due to equatorial protons and other protons of the anhydroxylose units of hemicellulose. The acetyl groups gave signals at 2.53 and 2.22 ppm. The weak signal at 5.0 ppm was due to protons of galactopyranosyl units. The protons of the α-linked glucuronic acid units gave rise to signals at 5.58 and 5.39 ppm.

The assignment of the ^{13}C NMR spectrum (**Figure 1**) was based on available literature data on other nonwood plants (*26–34*). The main 1,4-linked β-D-xylopyranose units were

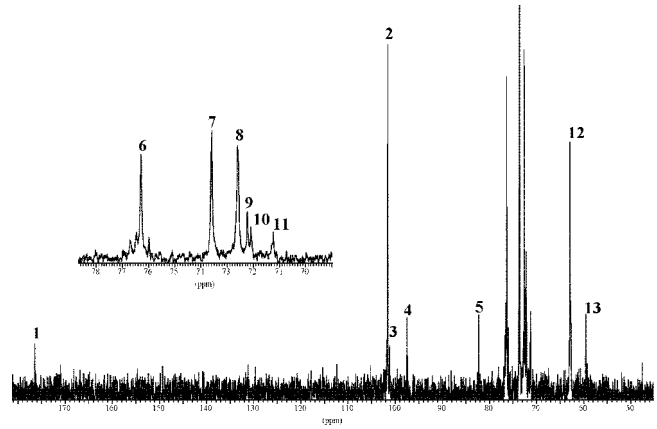

Figure 1. ^{13}C NMR spectrum of isolated hemicellulose from sisal (solvent D_2O).

characterized by five strong signals at 101.5 (signal 2), 76.3 (signal 6), 73.6 (signal 7), 72.6 (signal 8), and 62.8 ppm (signal 12) corresponding to chemical shifts of C1/C5 carbons. The signals at 101.1 (signal 3), 72.2 (signal 9), 72.1 (signal 10),and 71.2 ppm (signal 11) were assigned to C-1, C-4, C-3,and C-2 of galactopyranosyl residues linked to the β-D-xylopyranose chain. The signal at 59.6 ppm (signal 13) was due to the 4-*O*-methoxyl group of glucuronic acid residue in xylans. The carbonyl resonances from uronic acids contributed to a signal at 176.4 ppm (signal 1), which was indicative of the C-6 in methyl uronic acids. The C-1 and C-4 of the 4-*O*-methylglucuronic acid residues in the hemicellulose displayed signals at 97.5 (signal 4) and 82.2 ppm (signal 5), respectively. The absence of important signals between 110 and 170 ppm indicated that the hemicelluloses were relatively free from aromatic residues. This result confirmed the analyses of neutral sugars previously mentioned. The molecular information obtained on hemicellulose from sisal fibers was considered to be interesting data for further studies on sisal fibers (*35*). In addition, structural information on both sisal hemicellulose and lignin is scarce.

Lignin Analysis. The isolated lignin from sisal using mild acidolysis technique was considered only as a model of sisal lignin.

The FT-IR spectrum (not shown) presents the characteristic bands of the aromatic skeleton of a lignin macromolecule (*17, 36*) at 1595, 1510, and 1422 cm^{-1}. It was observed that the intensity of the band at 1328 cm^{-1}, associated with syringyl units (S), was higher than that for the band at 1275 cm^{-1}, representing the guaiacyl units (G), which appeared only as a shoulder. Moreover, the intensity of the band at 1460 cm^{-1} was higher than the one at 1510 cm^{-1}. All of these observations were indicative of GS type lignin (*37*). A small band observed at 835 cm^{-1} corresponded to small amounts of *p*-hydroxyphenyl units (H). These results were confirmed by ^{31}P NMR spectroscopy (vide supra).

The ^{1}H NMR spectrum of isolated lignin (**Figure 2**) shows the presence of typical lignin signals (*38, 39*). Signals 3 (3.8 ppm) and 1 (6.8 ppm) were assigned to methoxy and aromatic protons, respectively. Signals 4 (3.4 ppm) and 5 (2.6 ppm) were due to residual water and DMSO, respectively. Signals 2, between 5.0 and 5.5 ppm, were assigned to H_α, H_β, and H_γ of aryl-ether units, and the signals 8 between 0.8 and 1.4 ppm were due to methyl and methylene protons in saturated aliphatic side chains. These were more intense than signals 6 and 7 between 1.9 and 2.1 ppm due to methyl or methylene protons adjacent to either a double bond or carbonyl group. This suggests that a large part of the side chains in the C_9 units was saturated in the

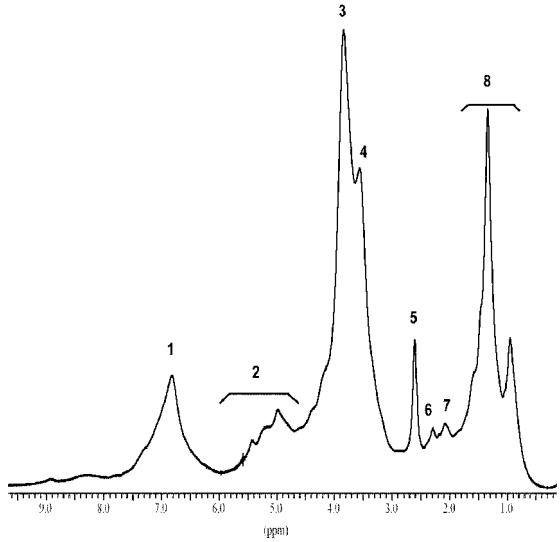

Figure 2. ^{1}H NMR spectrum of acidolysis lignin isolated from sisal fibers (solvent DMSO).

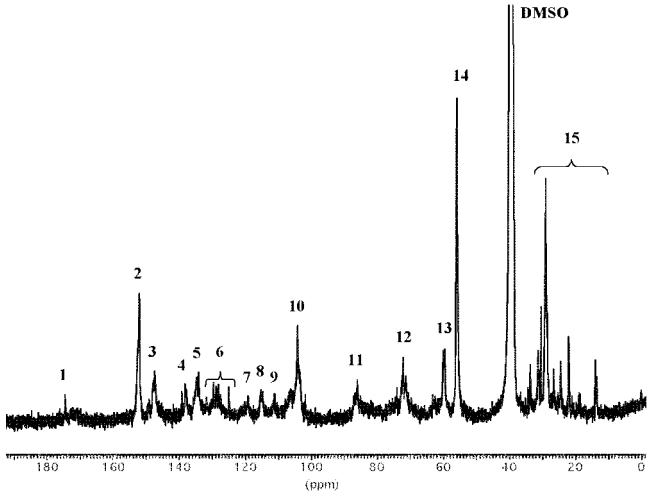

Figure 3. ^{13}C- NMR spectrum of acidolysis lignin isolated from sisal fibers (solvent DMSO).

lignin sample, extracted from sisal fibers. A similar observation has been made for isolated sugar cane bagasse lignin (*12*, *40*).

The ^{13}C NMR spectrum of isolated lignin is presented in **Figure 3**. Most of the observed signals have previously been assigned in straw and wood lignin spectra (*17*, *28*, *40*). Signal 1 at 175 ppm was due to aliphatic acid groups. The syringyl units were characterized by signals 2, 4, and 10 at, respectively, 152.4, 139.5, and 104.5 ppm. The guaiacyl units were also identified by signals 7 and 9 at 119.6 and 111.6 ppm. Signals 3 and 5 at 147.7 and 134.7 ppm were attributed to both units. The signals between 130 and 125 ppm (signal 6) and 115.5 ppm (signal 8) were due to *p*-coumaric acids. The C_β, C_α, and C_γ in β-*O*-aryl units showed signals 11, 12, and 13 at, respectively, 86.4, 74.3, and 63.9 ppm. The absence of signals at 161.8, 131.7, and 121.5 ppm, due to *p*-hydroxyphenyl units, confirmed that the isolated lignin from sisal was of GS type, which agreed with the results obtained by FT-IR and ^{31}P NMR (vide supra). The signals for the γ-methyl and α- and β-methylene groups in *n*-propyl side chains of the lignin occurred between 13.9 and 34.0 ppm in the spectra (signal 15). Some of these peaks in this region could also be attributed to aliphatic contaminants, even though a purification step was carried out on the lignin sample.

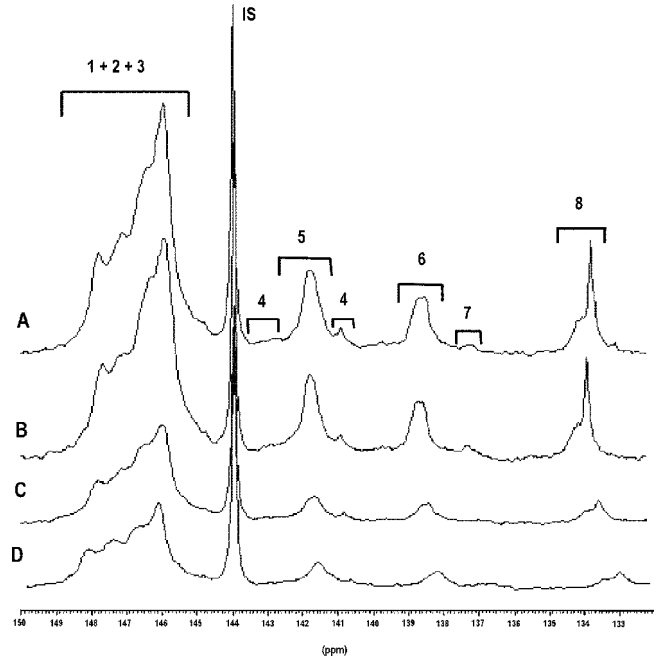

Figure 4. ^{31}P NMR spectra of lignins isolated from sisal fibers: (**A**) unmodified; (**B**) ClO_2 oxidized; (**C**) ClO_2 oxidized and FA treated; (**D**) ClO_2 oxidized and PFA treated. 1+2+3, α-OH in β-O-4 units (erythro and threo forms), primary OH, and residual carbohydrate; 4, phenolic OH in condensed units; 5, OH in syringyl units; 6, OH in guaiacyl units; 7, OH in *p*-hydroxyphenyl units; 8, carboxylic acids; IS, internal standard, cholesterol.

Chemical Modification of Lignin Extracted from Sisal Fibers. Previous studies on sugar cane bagasse and curaua fibers (*12–15*) have shown that lignin was the main polymer involved in the reaction with ClO_2 and grafting FA. Similar experiments were performed on sisal fibers in the present work. To get a better understanding of the chemical modification involved, previously the reaction was performed on lignin extracted from sisal fibers. The chemical modification was mainly studied by ^{31}P NMR spectroscopy. The thermal stability of lignin polymers modified by FA and PFA was also examined.

Spectroscopy. To quantify the various hydroxyl groups present in the lignin samples, ^{31}P NMR spectra of the phosphitylated polymers were recorded (*23*). The lignin samples were derivatized with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane before and after the chemical modification (*24*). The spectra showed signals for the different hydroxyl groups of the studied lignins. The signals were integrated by reference to cholesterol, allowing quantification of the various hydroxyl groups. Phenolic hydroxyl groups define the reactivity during the oxidation process and the treatments with FA and PFA, so any information related to the modified lignin is valued. The ^{31}P NMR spectra of phosphitylated lignins are shown in **Figure 4**, and the quantitative data on the distribution of the various hydroxyl groups are presented in **Table 2**, even though the accuracy of syringyl and condensed hydroxyl groups is lower due to overlapping of their signals (see Experimental Procedures). Signal assignments and details of the integration can be found elsewhere (*23*, *25*).

The spectrum for isolated lignin, shown in **Figure 4**, was in accordance with the GS type lignin classification established by FT-IR spectrometry. As seen in **Figure 4**, the oxidation reaction induced a reduction of both aliphatic and phenolic

Table 2. Quantification of Several Hydroxyl Groups in Isolated and Chemically Modified Lignins from ^{31}P NMR Analyses of Their Phosphitylated Derivatives

	OH (mmol/g) in lignin				
	nonmodified	oxidized	oxidized and FA treated	oxidized and PFA treated	PFA
aliphatics[a]	2.38	2.12	1.52	1.20	0.35
syringyl units[a]	0.36	0.33	0.17	0.17	
guaiacyl units	0.24	0.21	0.14	0.12	
p-hydroxyphenyl units	0.05	0.05			
condensed units[a]	0.28	0.05	0.04	0.03	
total phenol	0.93	0.64	0.35	0.29	
acid units	0.27	0.22	0.14	0.10	
H/G/S	1/4.8/7.2	1/4.2/6.6			

[a] Due to overlapping of signal the values were determined only for comparative analysis (see Experimental Procedures).

hydroxyl groups (11 and 31%, respectively). These results reflected the ClO_2 efficiency in the degradation of the lignin macromolecule. The decrease of aliphatic hydroxyl groups is likely due to lignin component instead of carbohydrate contaminants, these structures being less reactive. Among the various phenolic units, the syringyl (S) and guaiacyl (G) decreased similarly, that is, 0.03 mmol/g (8%), whereas the *p*-hydroxyphenyl moieties (H) remained unchanged after oxidation. It is known that the H component is less susceptible to oxidation, as compared to G and S structures (*41*). Crestini et al. (*42*) found, using a methyltrioxorhenium/H_2O_2 oxidative system for lignin model compounds, that the decrease in aliphatic hydroxyls was indicative of side-chain oxidation processes and the reduction of the noncondensed phenolic hydroxyl groups could be explained either by aromatic ring cleavage, by oxidative coupling reactions, or by the formation of unsaturated units (quinones and muconic derivatives). Side-chain oxidation processes and aromatic ring cleavage result in the yield formation of carboxylic acid groups, whereas the coupling reactions increase the amount of condensed hydroxyl groups, resulting in more condensed insoluble structures (*41*). The results presented in **Table 2** indicate that the main products formed by the ClO_2 oxidation reaction of lignin are unsaturated units, likely quinones and muconic derivatives (mainly esters). This conclusion was based on the decrease of both condensed hydroxyl and carboxylic contents. The aliphatic/aromatic hydroxyl ratio increased after treatment with ClO_2, suggesting a preferential degradation of the aromatic units with respect to aliphatic units.

The ^{31}P NMR spectrum of PFA (not shown) displayed only aliphatic hydroxyl groups (**Table 2**). This was in accordance with a nonlinear structure of the polymer where the hydroxyl groups were at the end of the polymer chain (*22*). After chemical modification of oxidized lignin with FA or PFA, the content of aliphatic and aromatic hydroxyl groups was lower than for oxidized lignin (**Figure 4**; **Table 2**). This was most likely an indication of the involvement of the hydroxyl groups of lignin, or even of FA and PFA, in the polymerization reaction (*12*). This hypothesis is under current investigation on lignin models.

Thermal Analysis. The thermal properties of the unmodified and modified lignins were studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (**Figure 5**). The curves shown in **Figure 5** are typical of lignins isolated from annual plants, such as sisal and sugar cane (*12*).

The initial weight loss demonstrated in the TGA curves (**Figure 5a**) was caused by volatilization of moisture and other volatile products present in all samples. The weight-loss profile depended both on the lignin isolation method and on the nature of the species (*42*). The occurrence of thermal degradation of lignin over a wide range of temperatures has been described by several authors (*43–46*). Formic acid, formaldehyde, carbon dioxide, and water can be identified among the volatile compounds released during the first decomposition step. The second degradation step leads to saturation and decomposition of aromatic rings, rupture of lignin C–C bonds, and release of water, CO_2, and CO and causes structural rearrangements. Methane and methanol are also formed (*44*). Other degradation mechanisms of lignin occur through dehydration, thus yielding derivatives with lateral unsaturated chains (*12*, *47*, *48*). Some residual hemicellulose might be present in the lignin samples (*12*). The thermal degradation of this polysaccharide takes place near 275 °C (**Figure 5b**). The thermolysis reactions occur by disintegration of intramolecular interaction, cleavage of glycoside bonds, and decomposition of polymer chains (*18*).

The first derivative of the TGA curves (**Figure 5b**) shows two peaks representing unmodified and modified lignin. The first one (250–275 °C) was likely due to decomposition of associated hemicellulose (*18*, *44*, *45*), as previously mentioned, and the second one (temperatures > 350 °C) to the decomposition of the lignin macromolecule. The partial oxidation of lignin to quinones and muconic derivatives and the posterior reaction with FA and PFA displaced the second peak to lower temperatures, when compared to unmodified lignin (**Figure 5b**).

The DSC curves in **Figure 5c** show endothermic peaks (near 240 °C) for the oxidized and PFA-modified lignins and an exothermic peak for the unmodified lignin, probably due to the decomposition of hemicellulose. For the modified lignins, the evaporation of volatile byproducts (endothermic process) prevailed over the decomposition process (exothermic), whereas the latter process predominated for the unmodified lignin sample (**Figure 5c**). The two peaks observed above 300 °C are related to the decomposition of lignin. The first one, near 350 °C, endothermic, probably is related to the thermal decomposition of the aliphatic moiety, and the second one, near 430 °C, exothermic, is probably related to the decomposition of aromatic rings of that macromolecule. Confirming the TGA results, the reactions with FA and PFA displaced those peaks to lower temperature, indicating that the chemical modifications slightly diminished the thermal stability of this material.

Chemical Modification of Sisal Fibers. The chemical modification was based on a preferential oxidation of the guaiacyl and syringyl phenols of lignin into *o*- and *p*-quinones and muconic derivatives. The oxidation was carried out with ClO_2 in aqueous solution and was followed by a reaction with FA and PFA. After extensive Soxhlet extraction, with appropriate solvent, and careful drying of the modified fibers (see Experimental Procedures), the experimental conditions led to a weight percent gain of about 4% for the FA and 5% for the PFA modifications, indicating that both FA and PFA were likely grafted onto the sisal fiber surfaces.

In a recent work (*49*), the FA- and PFA-modified sisal fibers were analyzed by inverse gas chromatograph (IGC) and biodegradation measurements to evaluate the changes occurring at the sisal fiber surface. The IGC analysis showed that the FA and PFA chemical treatments considerably increased the dispersive component of the free energy surface of sisal fibers (γ_S^D), indicating a decrease of the polar character of fiber surface. The enzymatic degradation results, performed with cellulase, revealed that the PFA coating layer in the sisal fiber surface was able to prevent the diffusion of the enzyme to the polysaccharide matrix, protecting the fibers against enzymatic

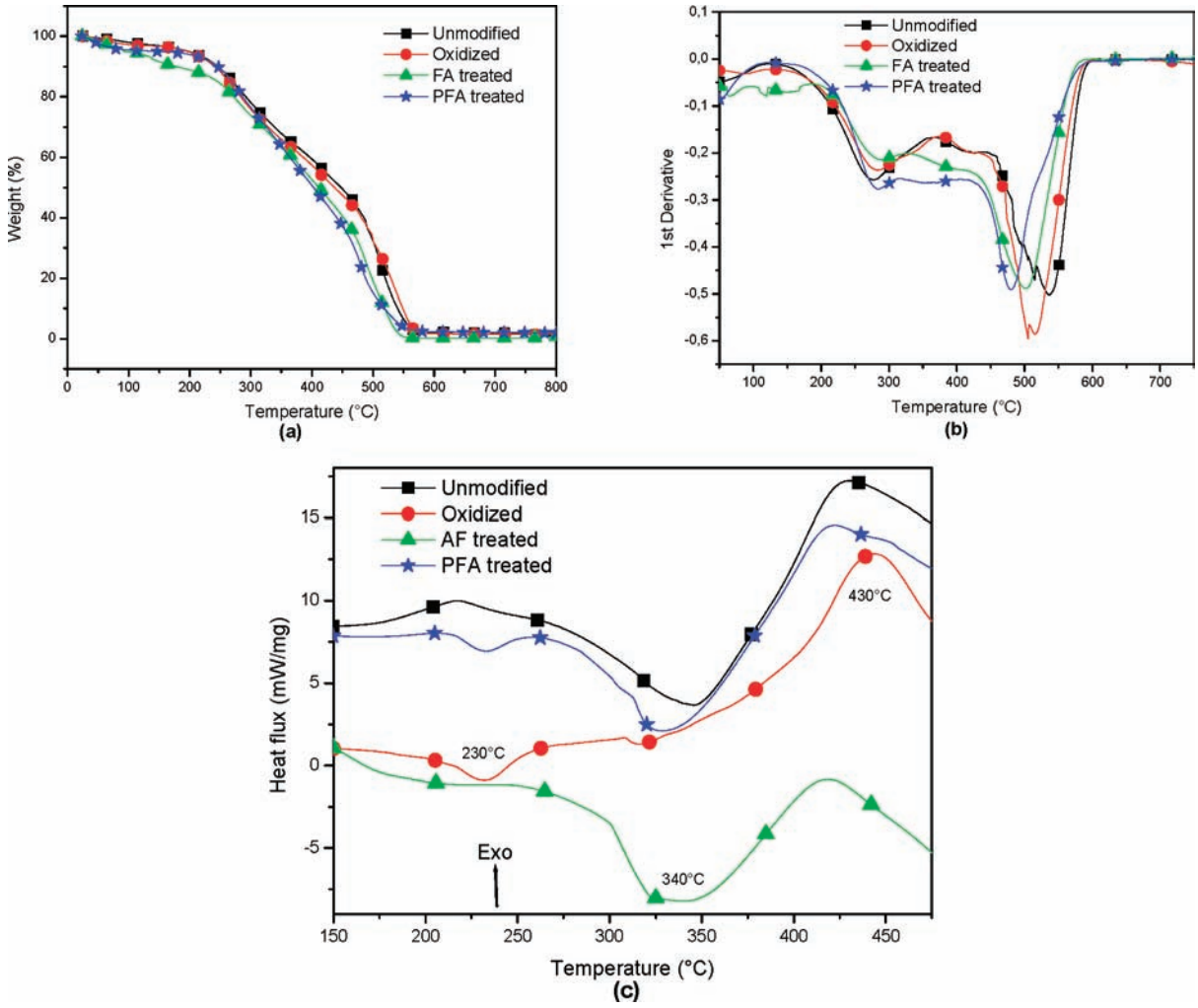

Figure 5. Thermal analysis of unmodified and modified lignins isolated from sisal: (**a**) TG curves; (**b**) first derivative TG curves; (**c**) DSC curves.

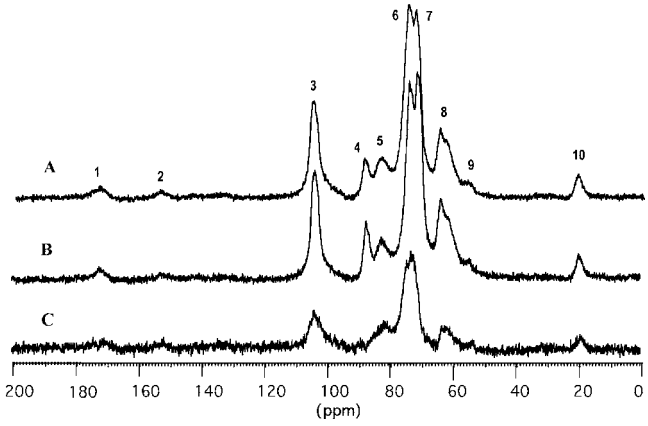

Figure 6. ^{13}C CP-MAS (7000 rpm): (**A**) unmodified sisal fibers; (**B**) ClO_2 oxidized + FA grafted sisal fibers; (**C**) difference (**A** − **B**).

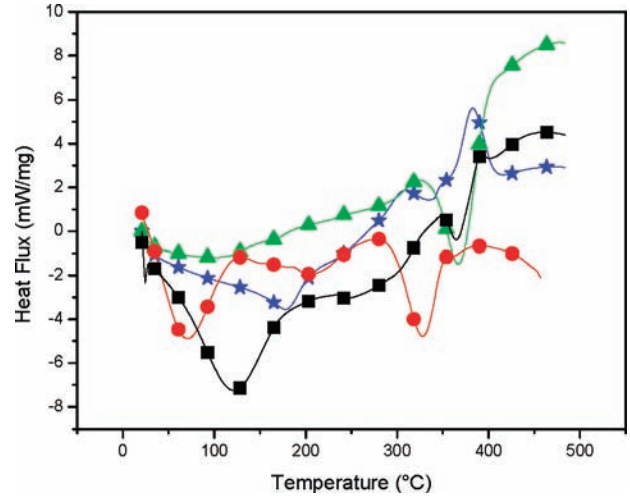

Figure 7. DSC curves of sisal fibers: (black) unmodified; (red) ClO_2 oxidized; (green) modified with ClO_2 + FA; (blue) modified with ClO_2 + PFA.

degradation during the time considered. These studies reinforce the idea that the PFA coating layer formed after both chemical treatments is probably grafted onto the sisal fiber surface.

Spectroscopy. The solid-state ^{13}C CP-MAS NMR spectrum of the fibers is presented in **Figure 6** . It shows characteristic signals of lignocellulosic fibers (*50*). The spectrum displays a signal at 22 ppm, assigned to the methyl carbon of the acetyl group in hemicellulose (signal 10). The region between 60 and 110 ppm was dominated by strong signals, which were assigned mostly to the various cellulosic carbons, namely, C1 (signal 3), C4 crystalline (signal 4), C4 amorphous (signal 5), C2, C3, C5 (signals 6 and 7), and C6 (signal 8). The hemicellulose also gave signals in this region. Only signal 9 in this part of the spectrum could be assigned to lignin (methoxy groups of aromatic moieties). The region between 110 and 160 ppm (main signal 2), which is specific for aromatic carbons of lignin, did not present strong signals. This was in accordance with the lower

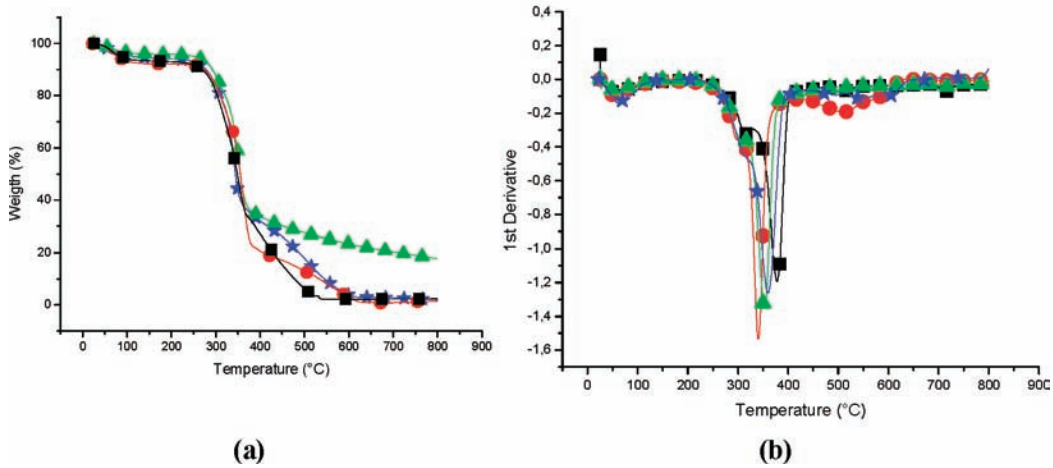

Figure 8. TG curves for unmodified and modified sisal fibers: (black) unmodified; (red) ClO_2 oxidized; (green) modified with ClO_2 + FA; (blue) modified with ClO_2 + PFA; (**a**) weight loss; (**b**) first derivative.

lignin content of sisal fibers when compared to sugar cane fibers (*14*, *15*). Carbonyl groups of acetoxy and other ester functions in hemicellulose were observed at 173 ppm (signal 1).

Chemical modification of sisal fibers with chlorine dioxide (ClO_2) and FA should mainly affect the lignin polymer component. In fact, spectra **B** and **C** of **Figure 6** indicate that the carbohydrate matrix was also affected. The peaks due to carbohydrates (60–110 ppm) were less intense, and this was probably due to partial oxidation of both hemicellulose and the amorphous region of cellulose. A similar behavior was observed for sisal fibers oxidized with ClO_2 and subsequently reacted with PFA instead of FA. This is an indication that the carbohydrate matrix was accessed and degraded by both modifications, with FA and PFA. In contrast to sugar cane bagasse (*14*), the grafting of FA was not observed by CP-MAS ^{13}C NMR spectrometry, maybe due to lower FA content grafted onto sisal fibers. The weight gain percent (WPG) for sisal, at about 4%, should be compared to 18% observed for sugar cane bagasse (*14*). This difference between FA content grafted onto sisal and sugar cane fibers can be explained by the softer reaction conditions selected in this study to obtain fibers with enhanced strength properties.

Thermal Analysis. **Figure 7** shows DSC curves for unmodified and modified sisal fibers. Considering the curve corresponding to unmodified fibers, the peaks related to the thermal degradation of hemicellulose and cellulose appeared near 300 and 350 °C, respectively, and those related to the degradation of lignin appeared from 500 °C to higher temperatures (**Figure 7**). The thermal decomposition is an exothermic event, but as a result of volatiles being liberated as decomposition byproducts, and depending on the balance of the two events (decomposition/volatilization of byproducts), both endothermic and exothermic peaks can be observed. The peaks related to the decomposition of lignin were of low intensity, due to the small content of this macromolecule in sisal fibers. Some differences could be noted between the curves of chemically modified fibers and those of unmodified fibers (**Figure 7**). Exothermic peaks near 325 °C were found for PFA (*51*), and then the thermal decomposition of PFA probably interfered with the thermal processes that occur between 300 and 350 °C related to polysaccharides. Moreover, the modification of the lignin fraction, due to its reaction with PFA, shifted the peak related to its decomposition to a lower temperature, when compared to unmodified fiber. This supports

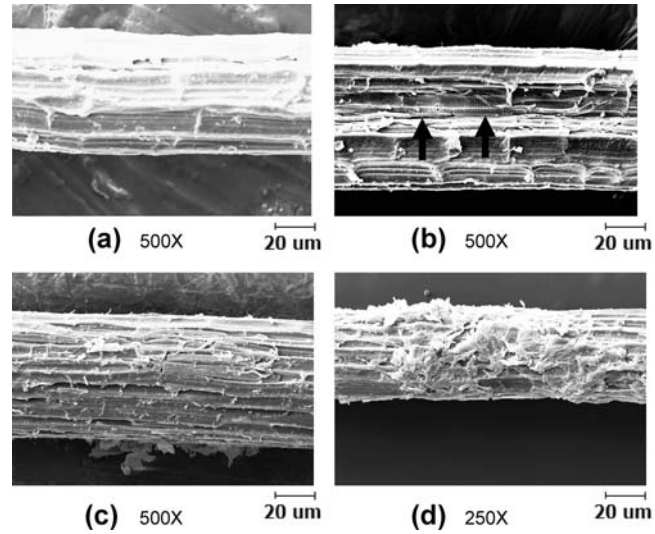

Figure 9. SEM images of sisal fibers: (**a**) unmodified; (**b**) ClO_2 oxidized; (**c**) treated with FA; (**d**) treated with PFA.

the results already observed for the thermal decomposition of the PFA-modified lignin by TGA (**Figure 5**).

On the whole, the TG curves obtained for the fibers (**Figures 8**) confirmed the previous discussion regarding the DSC results. It can be inferred that the peak related to the thermal decomposition of lignin (near 500 °C) had a very low intensity in the case of the unmodified fibers, and the partial oxidation of lignin increased the intensity and enlarged this peak (**Figure 8**). The enlargement of the peak related to the lignin can be perceived as an indication that the modifications with FA and PFA made the lignin structure more heterogeneous.

Scanning Electron Microscopy. To evaluate possible changes in the morphology of the sisal fibers after the chemical modifications, untreated and treated fibers were characterized by SEM (**Figure 9**).

In **Figure 9a**, it is possible to observe the presence of some fragments at the surface of untreated sisal fiber. These fragments probably correspond to residues of parenquimal cells, in which the fiber was previously linked. After ClO_2 oxidation (**Figure 9b**), it is possible to observe that the fragments were removed by this treatment. Moreover, the oxidation of fibers with ClO_2 withdraws several layers of cells, revealing some internal structures of the sisal fibers, such as spiral vases (see arrows). By comparing the SEM images of the FA and PFA treated sisal

fibers (**Figure 9c**,**d**, respectively), it can be seen that both chemical modifications introduced a coating at the surface of the lignocellulosic fiber, which is more evident for PFA-treated sisal fiber. This reveals that the PFA, previously synthesized, is also grafted at the sisal fiber surface.

Conclusion. A recently developed process was for the first time utilized to chemically modify sisal fibers in an aqueous medium, using raw materials from renewable resources such nonwood fibers and FA. This was in agreement with the current tendency to prioritize developing processes under environmentally friendly conditions. The results showed that both FA and PFA modifications introduced a thin coating of PFA at the sisal fiber surface. This polymeric thin coating can decrease the intrinsic hygroscopic character of sisal fibers and increase the interactions between these modified fibers and polymeric matrices, as phenolic resins, in composite preparations. Reactions performed on lignin extracted from sisal fibers have shown the reactivity of phenolic groups in the chemical process. The application of the FA- and PFA-modified fibers as reinforcement material in phenolic-based composites is reported in a companion paper (*49*); the results are in full accordance with the presented studies. Moreover, hemicellulose and lignin extracted from sisal fibers were characterized. These results contributed to complementing the information on the macromolecular components of sisal fibers, which, to the best of our knowledge, has been very scarce until now.

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