

# Phenol–Furfural Resins to Elaborate Composites Reinforced with Sisal Fibers—Molecular Analysis of Resin and Properties of Composites

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**ABSTRACT:** Resol type resins were prepared in alkaline conditions (potassium hydroxide or potassium carbonate) using furfural obtained by acid hydrolysis of abundant renewable resources from agricultural and forestry waste residues. The structures of the resins were fully determined by <sup>1</sup>H, <sup>13</sup>C, and 2D NMR spectrometries with the help of four models compounds synthesized specially for this study. MALDI-Tof mass spectrometry experiments indicated that a majority of linear oligomers and a minority of cyclic ones constituted them. Composites were prepared with furfural–phenol resins and sisal fibers. These fibers were chosen mainly because they came from natural ligno-cellulosic material and they presented excellent mechanical

properties. Thermal analyses (dTG and DSC) and electron microscopy images indicated that the composites displayed excellent adhesion between resin and fibers. Impact strength measurement showed that mild conditions were more suitable to prepare thermosets. Nevertheless, mild conditions induced a high-diffusion coefficient for water absorption by composites. Composites with good properties could be prepared using high proportion of materials obtained from biomass without formaldehyde. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2291–2303, 2008

**Key words:** phenol–furfural resin; sisal; composites; MALDI; NMR

## INTRODUCTION

Over 75% of all polymeric matrices in composites are thermoset polymers in which the resins are crosslinked by heat, pressure, and addition of catalyst during the curing.<sup>1</sup> Phenolic resins made with phenolic derivatives and formaldehyde (PF) are often used in plastic and automotive industries, and because of versatile properties their applications in the aerospace industry are growing. They exhibit superior fire resistance as compared to other thermosetting polymers such as polyesters and epoxides, excellent dimensional stability, thermal stability, chemical resistance, and low-bearing capability at elevated temperature. The thermomechanical properties of phenolic resins are related to their high cross-linking density after curing, giving them low impact strength, partially compensated when composites

are made.<sup>2</sup> To decrease the dependence of PF resins on formaldehyde, and hence their dangerous formaldehyde emissions, phenolic–furfural (PFu) resins have been developed.<sup>3</sup> They present good flow properties and the cured products have superior electrical properties.<sup>4</sup> Furfural is a slower reacting aldehyde than formaldehyde but it is obtained from natural resources by acid hydrolysis of abundant agricultural and forestry waste residues.<sup>5</sup> PFu resins have mainly been used as exterior-grade structural wood adhesives<sup>6</sup> and also for cold-setting binders for foundry core sand.<sup>7</sup> Until now, to the best of our knowledge, they were not used as thermoset matrices reinforced by fibers to make composites.

Our laboratories have been already involved on the valorization of biomass by the elaboration of composite materials made with phenolic polymers and annual plant fibers.<sup>8–13</sup> Among natural fibers, sisal is one of the most widely used. It shows great potential because of its high mechanical and physical characteristics<sup>14</sup> due to a high cellulosic content.<sup>15</sup> Recently, we reported on the isolation and characterization of lignin and hemicelluloses from sisal fibers;

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we studied the properties of oxidized lignin and fibers after reaction with furfuryl and polyfurfuryl alcohols and also the properties of composites made with the chemically modified fibers and phenolic thermoset matrices.<sup>16,17</sup>

In this article, structures of phenol–furfural resins are completely described and the properties of composites made with furfural–phenolic prepolymers and sisal fibers are presented.

## EXPERIMENTAL

### General

Starting materials and solvents of appropriate grade were obtained from Aldrich and used without further purification.

Sisal fibers used in the preparation of the composites were pretreated (Soxhlet) with cyclohexane/ethanol (1 : 1, v/v) for a period of 48 h to extract low-molecular weight substances such as waxes and terpenes (natural impurities), and then with water for 24 h to extract inorganic contaminants. The fibers were dried in a circulating-air stove (60°C) up to constant weight. The properties of sisal fibers (chemical composition: cellulose 65%; hemicellulose 20%; total Klason lignin 12%; ash 1%) used were described in a previous work.<sup>16</sup> A crystallinity index of 66% was found from X-ray diffraction curves.<sup>16</sup>

Synthesized compounds were purified on Merck silica gel 60. TLC analyses of the synthesized compounds were carried out on Fluka silica gel 60 F<sub>254</sub> plates (thickness 0.20 mm). Melting points were measured on a heating microscope Electrothermal 9100 Reichert (Fisher Bioblock Scientific, Illkirch, France).

Studies by <sup>1</sup>H and <sup>13</sup>C NMR were registered using Bruker Avance 300 Fourier transform spectrometer (Bruker SA, Wissembourg, France). FTIR and UV/Vis spectra were obtained respectively, with a Paragon 1000 PC and a Lambda 18 Perkin-Elmer spectrometers (Perkin-Elmer France, Courtaboeuf, France). GC-MS analyses were performed with a Finnigan Trace mass spectrometer (Thermo Fisher Scientific, Courtaboeuf, France) interfaced with a Finnigan Trace GC Ultra gas apparatus (line transfer temperature, 250°C) equipped with a PTV injector (splitless mode) using helium as carrier gas. A fused silica capillary RTX-5MS column, 15 m, 0.25 mm i.d., film thickness 0.25 μm was selected. The oven temperature was programmed from 40°C (initial hold time: 1 min) to 320°C at a rate of 15°C min<sup>-1</sup>; this final temperature was maintained for 15 min. The electron energy was fixed at 70 eV. Only the most significant peaks were given. Liquid secondary ion mass spectrometry (LSIMS) and high-resolution

mass spectrum (HRLSIMS) analyses were performed using a VG Micromass AutoSpec Q (Micromass UK, Manchester, England) operating with a positive LSIMS ionization mode (Cs<sup>+</sup>, ion bombardment energy: 35 keV; matrix: magic bullet) after dissolution of the sample in methanol. MALDI-Tof mass spectra were recorded on an Ultraflex instrument (Bruker Daltonics, Wissembourg, France) equipped with a pulsed nitrogen laser of 20 Hz at a wavelength of 337 nm. Data were acquired with the Flex Control software under the following conditions. The source was operated in the positive mode with an acceleration voltage of 25.0 kV, and a delayed extraction time of 40 ns was applied. The reflectron mode was used for the Tof analyzer (voltages of 26.3 kV and 14.1 kV). Ions were detected over a mass range from *m/z* 300 to 5000, the matrix ions being deflected up to *m/z* 300 to avoid detector saturation. The laser fluence and the number of shots were adjusted for each studied sample. External calibration was performed with commercial polyethylene glycol possessing an average mass of 2000 g mol<sup>-1</sup> (Aldrich, France). The mass spectra were obtained from the recorded raw data using Flex Analysis software by applying external calibration protocol aforementioned. For MALDI-Tof analyses, among all matrices that were tested, the best results were obtained with 2,5-dihydroxybenzoic acid (DHB) that was purchased from Acros Organics (Halluin, France). A solution of the DHB matrix (10 mg mL<sup>-1</sup>) in water/ acetonitrile (1/1, v/v) was mixed with the resin sample, dissolved in methanol at the same concentration. This solution (0.5 μL) was deposited onto the MALDI target according to the dried droplet procedure, and after evaporation of the solvent, the MALDI target was introduced into the mass spectrometer ion source. Cationization experiments were performed by adding a solution of NaI (10<sup>-2</sup> mol L<sup>-1</sup>), as cationizing agent, to the resin methanol solution (1/1, v/v) prior to MALDI analyses, as described earlier. ESI mass spectra were recorded on a Quattro Micro triple quadrupole mass spectrometer (Micromass UK, Manchester, England) fitted with an electrospray ion source. The mass spectrometer was calibrated in the positive ion mode using a mixture of NaI and CsI. Voltages were set at +3.5 kV for the capillary and +0.5 kV for the skimmer lens. The source was heated at 120°C. Nitrogen was used as nebulizing and drying gas at 15 L h<sup>-1</sup> and 250 L h<sup>-1</sup>, respectively. Data were acquired in the scan mode from *m/z* 50 to *m/z* 1500 in 2 s. Fifteen scans were summed to produce the final spectrum. MS/MS experiments were conducted with a collision energy of 15 eV using argon as the collision gas. The resin sample was dissolved in a solution of acetonitrile/water (1/1, v/v) and infused at 10 μL min<sup>-1</sup> into the ESI source.

### Preparation and properties of resins and composites

#### Phenol-furfural resin for chemical analyses

Phenol-furfural resin was prepared according to Patel et al.<sup>4</sup> To molten phenol (4.0 g, 42.5 mmol), potassium carbonate (0.8 g) or potassium hydroxide (0.35 g) dissolved in water (2 mL) were added and the reaction mixture was raised to 135°C. Furfural (4.08 g, 42.5 mmol) was added dropwise while the temperature was maintained at 135°C for 3.25 h. Most of the unreacted materials was removed under vacuum at temperature under 135°C. The solid residue was treated with hot water ( $\approx 70^\circ\text{C}$ ) to remove the residual phenol. The dark resin was dissolved in acetone and precipitated in diethyl ether. After centrifugation (6000 rpm, 5 min,  $10^\circ\text{C}$ ), the resin was obtained as a brown solid, which was dried at  $25^\circ\text{C}$  (6 g, yield 68%). The structure of the resin was established by NMR spectrometry ( $^1\text{H}$ ,  $^{13}\text{C}$ , DEPT135, HMQC) and mass spectrometry (MALDI-Tof, LSIMS and ESI).

#### Prepolymers to prepare composites PC1-PC4

Prepolymers were prepared as described previously using the following conditions: phenol-furfural- $\text{K}_2\text{CO}_3$  heated at  $130^\circ\text{C}$  for 3.25 h for composite PC1; phenol-furfural-KOH heated at  $130^\circ\text{C}$  for 3.25 h for composite PC2; phenol-furfural-KOH heated at  $70^\circ\text{C}$  for 1 h for composite PC3; phenol-formaldehyde-furfural-KOH heated at  $70^\circ\text{C}$  for 1 h for composite PC4. The purification step of the resin to remove unreacted materials was omitted. Preparation of prepolymers for composites PC3 and PC4 used milder conditions: reaction time, 1 h; temperature,  $70^\circ\text{C}$ . In prepolymer for composite PC4, part of furfural (20% w/w) was replaced by formaldehyde.

#### Composite preparations

Composites were obtained by mixing the prepolymers, resorcinol (10% w/w), as curing accelerator, and sisal fibers (fiber length: 3.0 cm; 30% w/w) randomly oriented by mechanical stirring (JVJ mixer, Pardiniho, SP, Brazil) at  $50^\circ\text{C}$  for 0.5 h to obtain an optimum impregnation of sisal fibers by the resins. Compression molding was carried out in molds measuring  $220\text{ mm} \times 99.5\text{ mm} \times 5\text{ mm}$  at  $50\text{ kgf cm}^{-2}$ . Cure cycle parameters ( $40^\circ\text{C}/0.25\text{ h}$ ;  $50^\circ\text{C}/1\text{ h}$ ;  $85^\circ\text{C}/1\text{ h}$ ;  $125^\circ\text{C}/1.5\text{ h}$ ) were previously determined by DSC measurements.<sup>10,16</sup>

Differential scanning calorimetry, thermogravimetric analyses, and scanning electron microscopy measurements

Differential scanning calorimetry (DSC) analyses were carried out on a Shimadzu DSC equipment, model 50 (Shimadzu do Brasil, São Paulo, Brazil) in the temper-

ature range from 20 to  $500^\circ\text{C}$ , at  $10^\circ\text{C min}^{-1}$ , under nitrogen atmosphere ( $20\text{ mL min}^{-1}$ ). Thermogravimetric analyses (TGA) were performed using a Shimadzu model TGA-50TA apparatus (Shimadzu do Brasil, São Paulo, Brazil) in the temperature range from 20 to  $800^\circ\text{C}$  at  $10^\circ\text{C min}^{-1}$  under nitrogen atmosphere ( $20\text{ mL min}^{-1}$ ). The results were presented in form of the first derivative (dTG). Scanning electron microscopy (SEM) images were taken with a Zeiss-Leica apparatus model 440 (Zeiss Microscopia Comercio, Representação e Serviços Ltda, Rio de Janeiro, Brazil) and an electron acceleration 20 kV. Fractured samples were covered with a thin layer of gold in a sputter coating system prior to analysis.

#### Impact strength

Ten unnotched samples were cut from each plate and shaped according to ASTM D256 ( $63.5\text{ mm} \times 12.7\text{ mm} \times 4.0\text{ mm}$ ). Impact strength was assessed using an Akron Ceast Resil 25 (Polimate LTDA, São Paulo, Brazil) Izod impact testor. Impact tests were carried out at room temperature with an impact speed of  $4\text{ m s}^{-1}$  and incident energy of 5.5 J. As established in ASTM D256, at least five measures in each experiment were used to calculate the average values reported in the next section.

#### Water absorption

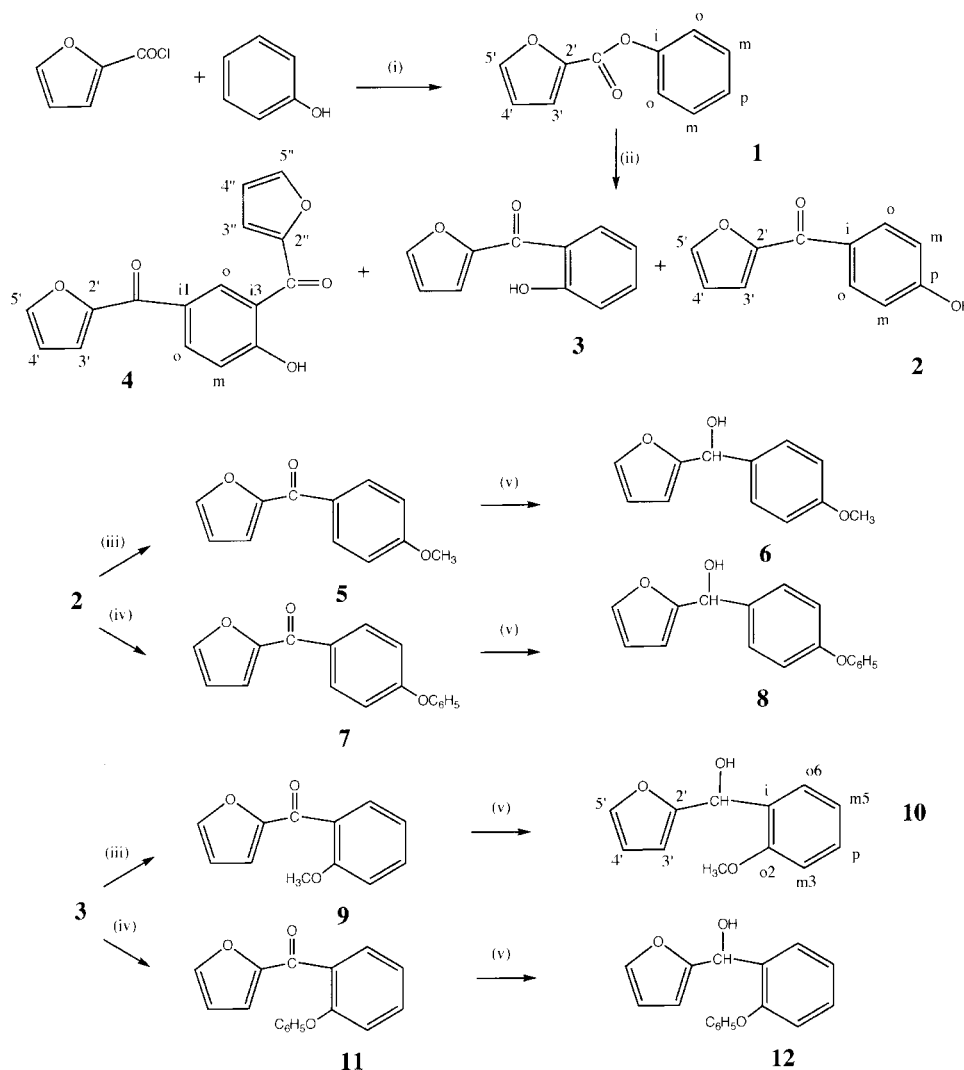
Water absorption studies were performed according to ASTM D 570-98 standard. The dimensions of the specimens for water uptake experiments were  $76.2\text{ mm} \times 25.4\text{ mm} \times 3.2\text{ mm}$ . Three specimens of each sample were dipped in distilled water at  $25^\circ\text{C}$ . The specimens were removed from water after certain periods of time, wiped with a cloth, and weighed in a high-precision balance before they were dipped again in water. The content of water was calculated by the weight difference.

#### Synthesis of model molecules for NMR signal assignments

A synthetic scheme of model preparations was given in Scheme 1 with the numbering of compounds for NMR assignments.

#### Furan-2-carboxylic acid phenyl ester 1

Furoyl chloride (0.091 mol) was added dropwise at  $0^\circ\text{C}$  to a solution of phenol (0.1 mol) and triethylamine in dichloromethane (100 mL) under magnetic stirring and nitrogen atmosphere; the stirring was continued at room temperature for 2 h. Hydrochloric acid (0.1M) was added to the organic mixture and then the organic phase was washed with water to neutrality. After drying over sodium sulfate, the or-



**Scheme 1** Syntheses of models for phenol–furfural resin analyses. (i)  $\text{CH}_2\text{Cl}_2$ ,  $\text{NEt}_3$ , room temperature, 2 h. (ii)  $\text{AlCl}_3$ ;  $120^\circ\text{C}$ , 30 min;  $160^\circ\text{C}$ , 2 h. (iii)  $\text{KOH}$ ;  $\text{THF}/\text{H}_2\text{O}$ ; reflux 24 h. (iv)  $\text{K}_2\text{CO}_3$ ;  $\text{BnBr}$ ; acetone; reflux 24 h. (v)  $\text{NaBH}_4$ ; ethanol;  $70^\circ\text{C}$ , 20 h. Atom numbering was indicated for NMR assignments.

ganic phase was filtered and evaporated under vacuum. The residue was purified by column chromatography on silicagel (eluent, dichloromethane) affording compound 1 after crystallization in methanol (12.8 g, yield 75%, mp  $38.6^\circ\text{C}$  literature<sup>18</sup>:  $37\text{--}40^\circ\text{C}$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  ppm: 6.51–6.53 (m,  $\text{H}_{4'}$ , 1H); 7.12–7.22 (m,  $\text{H}_{3'}+\text{H}_{p'}+\text{H}_{o'}$ , 3H); 7.30–7.38 (m,  $\text{H}_m+\text{H}_{o'}$ , 2H); 7.60 (m,  $\text{H}_{5'}$ , 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  ppm: 113.23 ( $\text{C}_{4'}$ ); 118.30 ( $\text{C}_{3'}$ ); 122.67 ( $\text{C}_o$ ); 126.08 ( $\text{C}_p$ ); 129.54 ( $\text{C}_m$ ); 144.01 ( $\text{C}_2$ ); 147.19 ( $\text{C}_5$ ); 150.27 ( $\text{C}_i$ ); 156.93 ( $\text{C}=\text{O}$ ). MS  $m/z$  188 ( $\text{M}^+$ , 4%); 171 (14%); 131 (44%); 121 (44%); 120 (100%); 95 (30%); 92 (60%); 65 (30%); 39 (30%).

#### Preparation of compounds 2, 3, and 4 by Fries reaction of compound 1

The hydroxyfurophenones 2 and 3 were prepared from compound 1, by Fries reaction; minor amount

of compound 4 were also formed. A mixture of compound 1 (5 g, 26.6 mmol) and aluminum chloride (4.5 g, 34 mmol) was heated at  $120^\circ\text{C}$  for 30 min, under magnetic stirring and nitrogen atmosphere, and then at  $160^\circ\text{C}$  for 2 h. The solid mixture was cooled to room temperature and hydrolyzed with a mixture of concentrated hydrochloric acid and ice. The aqueous phase was treated with dichloromethane (100 mL) to extract the organic compounds (ester and phenols). The phenols were obtained by treating the organic phase with an aqueous sodium hydroxide solution (0.5M, 100 mL), the latter being extracted twice with dichloromethane (75 mL). After drying over sodium sulfate, the dichloromethane phase was filtered and evaporated under vacuum yielding an oily residue (4.7 g) containing phenols 2, 3, and 4. The phenols were separated by column chromatography on silicagel (eluent, dichloromethane/ethyl acetate 9/1 v/v) giving compound 2

(1.4 g, yield 31%, mp 161–162°C literature<sup>19</sup> 163–164°C), compound **3** (oil, 2.35 g, yield 47%), and compound **4** (oil, 0.7 g, yield 9%).

#### Furan-2-yl-(4-hydroxyphenyl)methanone **2** (Scheme 1)

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ ppm: 6.68–6.69 (m, H<sub>4'</sub>, 1H); 7.08–7.10 (m, H<sub>m</sub>, 2H); 7.39–7.40 (m, H<sub>3'</sub>, 1H); 8.00–8.01 (m, H<sub>5'</sub>, 1H); 8.07–8.09 (m, H<sub>o</sub>, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ ppm: 111.6 (C<sub>4'</sub>); 114.7 (C<sub>m</sub>); 118.6 (C<sub>3'</sub>); 128.5 (C<sub>i</sub>); 131.3 (C<sub>o</sub>); 146.4 (C<sub>5'</sub>); 152.3 (C<sub>2'</sub>); 161.2 (C<sub>p</sub>); 179.6 (C=O). Assignments were established using HMBC and HMQC NMR experiments. MS *m/z* 188 (M<sup>+</sup>, 90%); 160 (28%); 131 (16%); 121 (100%); 93 (30%); 65 (34%); 39 (20%).

#### Furan-2-yl-(2-hydroxyphenyl)methanone **3** (Scheme 1)

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ ppm: 6.68–6.69 (m, H<sub>4'</sub>, 1H); 6.97–7.05 (m, H<sub>m</sub>, 1H); 7.09–7.13 (m, H<sub>m</sub>, 1H); 7.45–7.48 (m, H<sub>3'</sub>, 1H); 7.53–7.60 (m, H<sub>p</sub>, 1H); 7.76–7.81 (m, H<sub>o</sub>, 1H); 8.30–8.35 (m, H<sub>5'</sub>, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ ppm: 112.0 (C<sub>4'</sub>); 117.9 (C<sub>i</sub>); 118.2 (C<sub>m</sub>); 118.6 (C<sub>m</sub>); 120.7 (C<sub>3'</sub>); 131.1 (C<sub>5'</sub>); 135.7 (C<sub>p</sub>); 146.9 (C<sub>o</sub>); 151.5 (C<sub>2'</sub>); 162.9 (C<sub>o</sub>); 184.4 (C=O). Assignments were established using DEPT135, HMBC and HMQC NMR experiments. MS *m/z* 188 (M<sup>+</sup>, 90%); 160 (34%); 131 (30%); 121 (30%); 120 (100%); 95 (22%); 92 (51%); 65 (24%); 39 (21%).

#### [3-(Furan-2-carbonyl)-4-hydroxyphenyl]-furan-2-yl-methanone **4** (Scheme 1)

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ ppm: 6.72–6.74 (m, H<sub>4'</sub>, 1H); 6.76–6.77 (m, H<sub>4''</sub>, 1H); 7.20–7.25 (m, H<sub>m</sub>, 1H); 7.40–7.44 (m, H<sub>3'</sub>, 1H); 7.59–7.63 (m, H<sub>3''</sub>, 1H); 7.80–7.83 (m, H<sub>5'</sub>, 1H); 7.84–7.87 (m, H<sub>5''</sub>, 1H); 8.32–8.36 (m, H<sub>o</sub>, 1H); 9.23 (s, H<sub>o</sub>, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ ppm: 112.0 (C<sub>4'</sub>); 112.4 (C<sub>4''</sub>); 118.0 (C<sub>i3</sub>); 118.6 (C<sub>m</sub>); 119.6 (C<sub>3'</sub>); 121.4 (C<sub>3''</sub>); 127.7 (C<sub>i1</sub>); 133.9 (C<sub>o</sub>); 136.5 (C<sub>o</sub>); 146.4 (C<sub>5'</sub>); 147.4 (C<sub>5''</sub>); 151.3 (C<sub>2''</sub>); 152.1 (C<sub>2'</sub>); 166.5 (C<sub>OH</sub>); 179.7 (C=O); 183.9 (C=O). Assignments were established using DEPT135, HMBC, and HMQC NMR experiments. MS *m/z* 282 (M<sup>+</sup>, 100%); 254 (11%); 214 (69%); 187 (19%); 186 (59%); 158 (33%); 147 (51%); 95 (69%); 39 (14%).

#### Preparation of compounds **5**, **9** by methylation of the phenols **2** and **3**

A mixture of the phenolic compounds, **2** or **3** (0.3 g, 1.61 mmol), potassium hydroxide (3.2 mmol) and methyl iodide (3.5 mol), dissolved in a tetrahydrofuran–water mixture (25 mL/5 mL), was refluxed for 24 h under magnetic stirring and nitrogen atmosphere. Dichloromethane (100 mL) was added to the

mixture and the organic phase was successively washed with a dilute sodium hydroxide solution to eliminate the unreacted phenol, and water. After drying over sodium sulfate, the dichloromethane phase was filtered and evaporated under vacuum yielding the methoxy derivatives **5** (0.26 g, yield 80%) or **9** (0.24 g, yield 75%), giving one spot in TLC.

#### Furan-2-yl-(4-methoxyphenyl)methanone **5** (Scheme 1)

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ ppm: 3.81 (s, OCH<sub>3</sub>, 3H); 6.85–6.92 (m, H<sub>4'</sub>, 1H); 7.24–7.32 (m, H<sub>m</sub>, 2H); 7.50–7.56 (m, H<sub>3'</sub>, 1H); 7.96–8.01 (m, H<sub>5'</sub>, 1H); 8.30–8.37 (m, H<sub>o</sub>, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ ppm: 55.8 (OCH<sub>3</sub>); 112.5 (C<sub>4'</sub>); 114.1 (C<sub>m</sub>); 120.1 (C<sub>3'</sub>); 130.1 (C<sub>i</sub>); 132.1 (C<sub>o</sub>); 146.9 (C<sub>5'</sub>); 152.8 (C<sub>2'</sub>); 163.5 (C<sub>p</sub>); 181.2 (C=O). MS *m/z* 202 (M<sup>+</sup>, 82%); 174 (29%); 159 (12%); 135 (100%); 131 (20%); 107 (23%); 95 (24%); 92 (25%); 77 (33%).

#### Furan-2-yl-(2-methoxyphenyl)methanone **9** (Scheme 1)

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ ppm: 3.70 (s, OCH<sub>3</sub>, 3H); 6.41–6.46 (m, H<sub>4'</sub>, 1H); 6.87–6.96 (m, H<sub>m</sub>+H<sub>o</sub>, 3H); 7.29–7.41 (m, H<sub>3'</sub>+H<sub>p</sub>, 2H); 7.55 (s large, H<sub>5'</sub>, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ ppm: 56.1 (OCH<sub>3</sub>); 112.0 (C<sub>4'</sub>); 112.6 (C<sub>m</sub>); 120.6 (C<sub>m</sub>); 121.0 (C<sub>3'</sub>); 128.2 (C<sub>i</sub>); 129.8 (C<sub>5'</sub>); 132.7 (C<sub>p</sub>); 147.6 (C<sub>o</sub>); 153.3 (C<sub>2'</sub>); 157.8 (C<sub>o</sub>); 183.4 (C=O). MS *m/z* 202 (M<sup>+</sup>, 59%); 185 (58%); 174 (28%); 173 (100%); 171 (14%); 157 (40%); 135 (82%); 131 (21%); 115 (20%); 105 (23%); 95 (47%); 92 (36%); 77 (62%); 51 (14%); 39 (17%).

#### Preparation of compounds **7**, **11** by benzylation of the phenols **2** and **3**

A mixture of the phenolic compounds, **2** or **3** (0.45 g, 2.4 mmol), potassium carbonate (3.4 mmol) and benzyl bromide (3.5 mol) in acetone (25 mL), was refluxed for 24 h under magnetic stirring and nitrogen atmosphere. Dichloromethane (100 mL) was added to the mixture and the organic phase was successively washed with a dilute sodium hydroxide solution to eliminate the unreacted phenol, and water. After drying over sodium sulfate, the dichloromethane phase was filtered and evaporated under vacuum. The residue was chromatographed on silicagel (eluent, dichloromethane/ethyl acetate 9.5/0.5 v/v) giving compound **7** (0.55 g, yield 82%, mp 80–81°C) or compound **11** (oil, 0.6 g, yield 90%).

#### Furan-2-yl-(4-benzyloxyphenyl)methanone **7** (Scheme 1)

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ ppm: 5.0 (s, CH<sub>2</sub>—O, 2H), 6.43–6.50 (m, H<sub>4'</sub>, 1H); 6.9–7.0 (m, H<sub>m</sub>, 2H); 7.1–7.15 (m,

H<sub>3</sub>, 1H); 7.25–7.4 (m, C<sub>6</sub>H<sub>5</sub>, 5H); 7.55–7.65 (m, H<sub>5</sub>, 1H); 7.85–7.95 (m, H<sub>o</sub>, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ ppm: 70.2 (OCH<sub>2</sub>); 112.1 (C<sub>4</sub>); 114.6 (C<sub>m</sub>); 119.7 (C<sub>3</sub>); 127.5 (*ortho* C<sub>6</sub>H<sub>5</sub>); 128.2 (*para* C<sub>6</sub>H<sub>5</sub>); 128.7 (*meta* C<sub>6</sub>H<sub>5</sub>); 130.1 (C<sub>i</sub>); 131.8 (C<sub>o</sub>); 136.2 (ipso C<sub>6</sub>H<sub>5</sub>); 146.6 (C<sub>5</sub>); 152.6 (C<sub>2</sub>); 162.5 (C<sub>p</sub>); 181.1 (C=O). LSIMS: *m/z* 301 (M+Na)<sup>+</sup>; HR-LSIMS: calculated for C<sub>18</sub>H<sub>14</sub>O<sub>3</sub>Na 301.08406, measured 301.08398.

#### Furan-2-yl-(2-benzyloxyphenyl)methanone **11** (Scheme 1)

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ ppm: 5.1 (s, CH<sub>2</sub>—O, 2H); 6.45–6.55 (m, H<sub>4</sub>, 1H); 7.0–7.1 (m, H<sub>m</sub>+H<sub>o</sub>, 3H); 7.2–7.3 (m, C<sub>6</sub>H<sub>5</sub>, 5H); 7.4–7.5 (m, H<sub>3</sub>+H<sub>p</sub>, 2H); 7.6–7.7 (m, H<sub>5</sub>, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ ppm: 70.4 (OCH<sub>2</sub>); 112.2 (C<sub>4</sub>); 113.2 (C<sub>m</sub>); 120.2 (C<sub>3</sub>); 120.7 (C<sub>m</sub>); 126.8 (*ortho* C<sub>6</sub>H<sub>5</sub>); 127.5 (*para* C<sub>6</sub>H<sub>5</sub>); 128.4 (*meta* C<sub>6</sub>H<sub>5</sub>); 128.6 (C<sub>i</sub>); 129.6 (C<sub>o</sub>); 132.3 (C<sub>p</sub>); 136.5 (ipso C<sub>6</sub>H<sub>5</sub>); 147.0 (C<sub>5</sub>); 153.1 (C<sub>2</sub>); 156.5 (C<sub>o</sub>); 183.2 (C=O). LSIMS: *m/z* 301 (M+Na)<sup>+</sup>; HR-LSIMS: calculated for C<sub>18</sub>H<sub>14</sub>O<sub>3</sub>Na 301.08406, measured 301.08398.

#### Preparation of compounds **6**, **8**, **10**, **12** by reduction of the carbonyl derivatives **5**, **7**, **9**, and **11**

A mixture of the carbonyl derivative (1.8 mmol) and sodium borohydride (4 mmol) in ethanol (30 mL) was heated at 70°C for 20 h under magnetic stirring and nitrogen atmosphere. Hydrochloric acid (10%) was added to the organic mixture to reach pH = 1. Dichloromethane (100 mL) was added and the organic phase was decanted, washed with water to neutrality, dried over sodium sulfate, filtered and evaporated under vacuum. The residue was purified by column chromatography on silicagel (eluent, dichloromethane/ethyl acetate 9.5/0.5 v/v), giving the corresponding alcohol as an oil with a yield at about 85%.

#### Furan-2-yl-(4-methoxyphenyl)methanol **6** (Scheme 1)

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ ppm: 3.2 (broad s, OH, 1H); 3.90 (s, OCH<sub>3</sub>, 3H); 5.84 (broad singlet, CHOH, 1H); 6.21–6.23 (m, H<sub>4</sub>, 1H); 6.41–6.45 (m, H<sub>3</sub>, 1H); 6.97–7.02 (m, H<sub>o</sub>, 2H); 7.42–7.46 (m, H<sub>m</sub>, 2H); 7.47–7.49 (m, H<sub>5</sub>, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ ppm: 54.8 (OCH<sub>3</sub>); 69.3 (CHOH); 106.8 (C<sub>4</sub>); 109.8 (C<sub>3</sub>); 113.4 (C<sub>o</sub>); 127.6 (C<sub>m</sub>); 132.8 (C<sub>i</sub>); 142.0 (C<sub>5</sub>); 155.9 (C<sub>2</sub>); 158.9 (C<sub>p</sub>). Assignments were established using DEPT135, HMBC, and HMQC NMR experiments. MS *m/z* 204 (M<sup>+</sup>, 82%); 187 (100%); 159 (22%); 144 (49%); 135 (95%); 115 (53%); 109 (91%); 95 (83%); 77 (46%).

#### Furan-2-yl-(2-methoxyphenyl)methanol **10** (Scheme 1)

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ ppm: 3.7 (broad s, OH, 1H); 3.89 (s, OCH<sub>3</sub>, 3H); 6.18 (broad singlet, CHOH, 1H); 6.20–

6.22 (m, H<sub>4</sub>, 1H); 6.41–6.44 (m, H<sub>3</sub>, 1H); 6.97–7.03 (m, H<sub>m3</sub>, 1H); 7.06–7.12 (m, H<sub>m5</sub>, 1H); 7.38–7.43 (m, H<sub>p</sub>, 1H); 7.45–7.48 (m, H<sub>o6</sub>, 1H); 7.50–7.51 (m, H<sub>5</sub>, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ ppm: 55.1 (OCH<sub>3</sub>); 65.7 (CHOH); 106.5 (C<sub>4</sub>); 109.8 (C<sub>3</sub>); 110.4 (C<sub>m3</sub>); 120.3 (C<sub>m5</sub>); 127.5 (C<sub>p</sub>); 128.7 (C<sub>o6</sub>); 131.9 (C<sub>i</sub>); 141.7 (C<sub>5</sub>); 155.5 (C<sub>2</sub>); 156.3 (C<sub>o2</sub>). Assignments were established using DEPT135, HMBC, and HMQC NMR experiments. MS *m/z* 204 (M<sup>+</sup>, 100%); 176 (42%); 157 (53%); 135 (75%); 115 (50%); 81 (36%); 77 (45%).

#### Furan-2-yl-(4-benzyloxyphenyl)methanol **8** (Scheme 1)

<sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>CO) δ ppm: 5.20 (s, CH<sub>2</sub>O, 2H); 5.50 (s, CHOH, 1H); 6.24–6.26 (m, H<sub>4</sub>, 1H); 6.43–6.45 (m, H<sub>3</sub>, 1H); 7.11–7.14 (m, H<sub>o</sub>, 2H); 7.45–7.62 (m, H<sub>m</sub>+H<sub>5</sub>+C<sub>6</sub>H<sub>5</sub>, 7H). <sup>13</sup>C NMR ((CD<sub>3</sub>)<sub>2</sub>CO) δ ppm: 69.6 (OCH<sub>2</sub>); 76.4 (CHOH); 107.6 (C<sub>4</sub>); 109.6 (C<sub>3</sub>); 114.3 (C<sub>o</sub>); 127.1, 127.5, 128.0, 128.2 (C<sub>m</sub>+C<sub>6</sub>H<sub>5</sub>); 131.6 (C<sub>i</sub>); 136.6 (Cipso C<sub>6</sub>H<sub>5</sub>); 142.1 (C<sub>5</sub>); 154.6 (C<sub>2</sub>); 158.2 (C<sub>p</sub>). Assignments were established using DEPT135, HMBC and HMQC NMR experiments. MS *m/z* 280 (M<sup>+</sup>, <1%); 263 (23%); 91 (100%); 65 (16%).

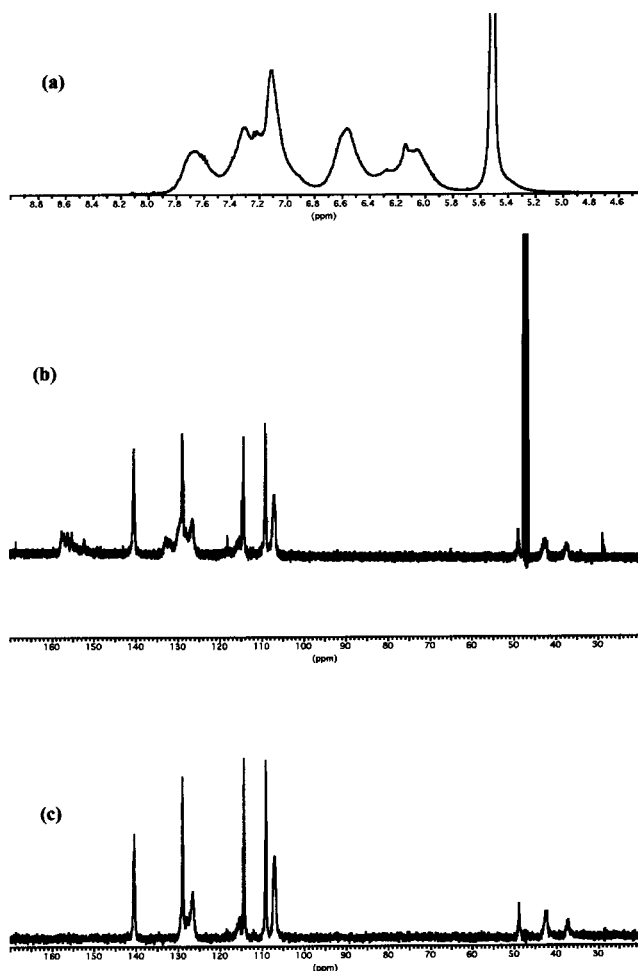
#### Furan-2-yl-(2-benzyloxyphenyl)methanol **12** (Scheme 1)

<sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>CO) δ ppm: 5.20–5.22 (m, CH<sub>2</sub>O, 2H); 5.26 (s, CHOH, 1H); 6.26–6.27 (m, H<sub>4</sub>, 1H); 6.44–6.48 (m, H<sub>3</sub>, 1H); 7.08–7.11 (m, H<sub>m3</sub>, 1H); 7.21–7.25 (m, H<sub>m5</sub>, 1H); 7.44–7.62 (m, H<sub>o6</sub>+H<sub>p</sub>+H<sub>5</sub>+C<sub>6</sub>H<sub>5</sub>, 8H). <sup>13</sup>C NMR ((CD<sub>3</sub>)<sub>2</sub>CO) δ ppm: 70.0 (OCH<sub>2</sub>); 70.4 (CHOH); 107.6 (C<sub>4</sub>); 109.5 (C<sub>3</sub>); 111.6 (C<sub>m3</sub>); 120.7 (C<sub>m5</sub>); 125.0 (C<sub>i</sub>); 126.6–131.0 (C<sub>o6</sub>+C<sub>p</sub>+C<sub>6</sub>H<sub>5</sub>); 136.7 (Cipso C<sub>6</sub>H<sub>5</sub>); 141.9 (C<sub>5</sub>); 154.5 (C<sub>2</sub>); 155.5 (C<sub>o2</sub>). Assignments were established using DEPT135, HMBC, and HMQC NMR experiments. MS *m/z* 280 (M<sup>+</sup>, <1%); 189 (20%); 172 (20%); 91 (100%); 65 (16%); 39 (6%).

## RESULTS AND DISCUSSION

### Structural analysis of phenol–furfural resins

Phenol–furfural resins (PFu's) used in this study were prepared according to a classical procedure given by Patel et al.<sup>4</sup> Though an infrared characterization of PFu's was published by Bermello et al.,<sup>20</sup> the main structural analysis of this type of materials was performed by Pizzi et al.<sup>6</sup> on resorcinol-phenol-furfural resins using MALDI-Tof and <sup>13</sup>C NMR spectrometries. The main assignments of the <sup>13</sup>C NMR spectra referred to 2-furyl-hydroxyphenylcarbinol units, but some of them were not described in the literature. Our objective was to establish unambiguously the structure of a phenol–furfural resin



**Figure 1** NMR spectra of phenol-furfural resins (solvent: DMSO  $d_6$ ). (a)  $^1\text{H}$  NMR, (b)  $^{13}\text{C}$  NMR, (c) DEPT-135  $^{13}\text{C}$ -NMR.

obtained using either sodium carbonate or sodium hydroxide as alkaline source, the  $^{13}\text{C}$  NMR spectra of both resins being very similar.

#### NMR analysis of phenol-furfural resin and model molecules

Analyses of  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra of the PFu resins were based on the NMR assignments established on four model compounds (**6**, **8**, **10**, **12**) synthesized for the purpose (Scheme 1). To limit the instability of benzylic alcohols, very easily transformed into quinone-methides, *ortho*- and *para*-phenol hydroxyl groups were protected by methyl or benzyl groups. Alcohols **6**, **8**, **10**, **12** were characterized unambiguously by mass spectrometry and  $^1\text{H}$ ,  $^{13}\text{C}$ , HMQC, and HMBC NMR experiments (see experimental part).

The  $^1\text{H}$ ,  $^{13}\text{C}$ , and DEPT-135  $^{13}\text{C}$  NMR spectra of a phenol-furfural resin prepared with potassium carbonate are presented in Figure 1. The assignments of signals were indicated in Table I.

A structure of PFu oligomers in accordance with the NMR spectra was proposed in Table I. The mechanism of their formation (Scheme 2), classical for this type of resin, started by a *para* attack of the phenolate ion on furfural. The quinone-methide formed (FQM) was attacked by a second phenolate anion to give a furfuryl diphenol methane in its anionic form. The *ortho* carbon anion was able to react with the quinone-methide FQM to give by polycondensation the oligomers, as schematized in Table I. The NMR data confirmed previous assignments given by Pizzi et al.<sup>6</sup> on resorcinol-phenol-furfural resins. Nevertheless, signals due to  $-\text{CHF}_u-\text{OH}$  carbons as terminal groups between 70 and 75 ppm were difficult to detect.<sup>6</sup>

The proposed structure was confirmed by mass spectrometry experiments.

#### Mass spectrometry analysis of phenol-furfural resin

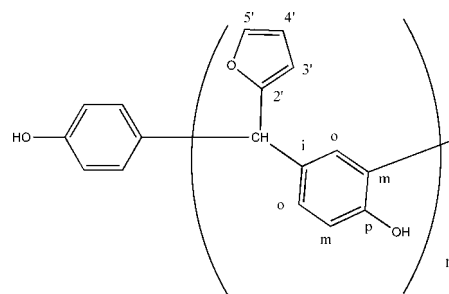
MALDI-ToF was shown to be a method of choice for polymer analyses.<sup>21</sup> Among various matrices usually used, the best results in terms of ionization efficiency were obtained with 2,5-dihydroxybenzoic acid (DHB), in agreement with reported MALDI analyses of phenol-based resins by Pizzi et al.<sup>6</sup> This matrix provided the most populated polymeric distributions with ions recorded over a large mass range (from  $m/z$  400 up to 3500) as displayed in Figure 2.

Indeed, two different ion populations were clearly detected but with different relative abundances. According to the ion signal relative intensities, provided that there is no discrimination during the competitive ionization processes, a major product polluted by one side-product constituted the studied resin. For both detected polymers, the mass difference between two consecutive ions belonging to the same polymeric distribution equaled 172 Da, indicating a phenol substituted by a furan moiety as monomer units. The major compound exhibited ions starting at  $m/z$  477 up to  $m/z$  3230, the most abundant ions being detected around 800–1000 Da. The ionization process by protonation or cationization was then questioned. Although potassium adducts were clearly seen on the mass spectra whatever the nature of the matrix (for instance, the ion at  $m/z$  1165 was accompanied by the ion at  $m/z$  1203), the nature of the most abundant ions was not defined. To assess the formation of protonated versus cationized species, a cationization agent (NaI) was added to the resin solution during sample preparation with DHB matrix. The detected ion distributions were all shifted downwards by a measured mass increment of 16 Da indicating the substitution of potassium by sodium.

Thus, it was established that the detected ions were potassium adducts. Indeed, the exclusive formation of potassium adducts could be easily

**TABLE I**  
**Chemical Shifts and Assignments of Carbons and Protons of Phenol–Furfural Resin**  
 (see Scheme 1 and Experimental Section)

Hypothetical formula of PF resin and atom numbering



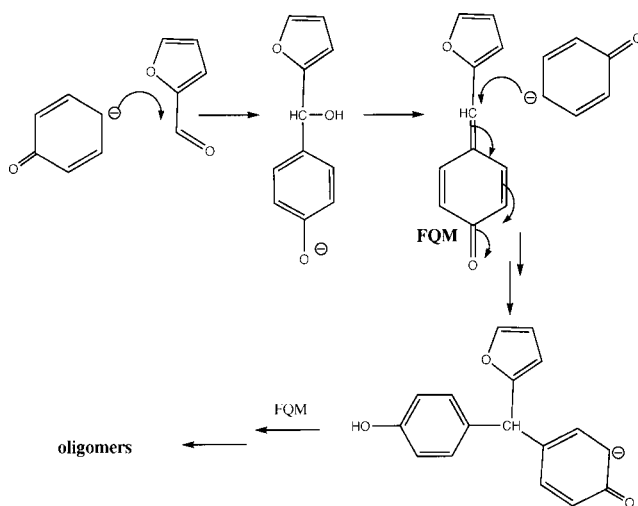
Chemical shift (ppm)	Assignment
Tertiary carbons <sup>a,b</sup>	
37.5	CH-Fu
42.5	CH-Fu
49.1	CH-Fu
106.9–107.3	C <sub>4'</sub>
109.2	C <sub>3'</sub>
114.4–114.8	C <sub>o</sub> for phenol in para position
115.4–115.6	Unknown
126.4–127.0	C <sub>m</sub> for phenol in para position
128.6–129.3	C <sub>o</sub> and C <sub>p</sub> for phenol in ortho position
140.5–140.9	C <sub>5'</sub>
Quaternary carbons <sup>a,b</sup>	
129.0–133.0	C <sub>i</sub> for phenols in ortho and para positions
152.0–158.0	C <sub>2'</sub> , C <sub>o'</sub> , and C <sub>p</sub> for phenols in ortho and para positions
Protons <sup>c,d</sup>	
5.8–6.3	H <sub>4'</sub>
6.4–6.7	H <sub>3'</sub>
6.8–7.5	H <sub>o</sub> + H <sub>m</sub> + H <sub>p</sub>
7.5–7.9	H <sub>5'</sub>

<sup>a</sup> Assigned by DEPT-135.

<sup>b</sup> Assigned by comparison of <sup>13</sup>C chemical shifts of models.

<sup>c</sup> Assigned by comparison of <sup>1</sup>H chemical shifts of models.

<sup>d</sup> Assignments confirmed by HMQC experiments.



**Scheme 2** Formation mechanism of phenol–furfural oligomers.

explained when considering the use of potassium carbonate during the polymerization process.

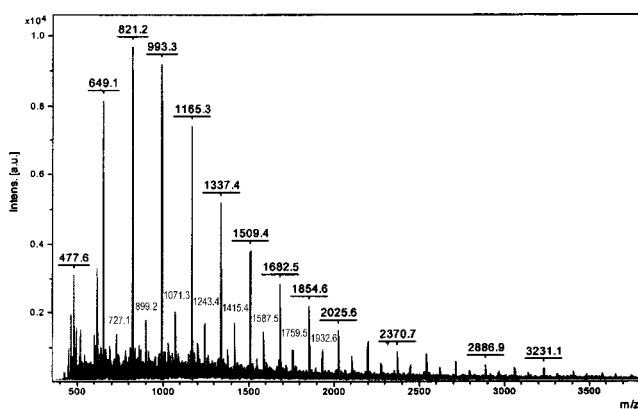
Two series of (M+K)<sup>+</sup> ions were evidenced in Maldi:

The major product exhibited (M+K)<sup>+</sup> ions at  $m/z$  477 → 649 → 821 → 993 → 1165 → 1337 → 1509, ...

A side-product was detected through (M+K)<sup>+</sup> ions at  $m/z$  555 → 727 → 899 → 1071 → 1243 → 1415 → 1587, ...

Both ion series were separated by a mass difference of 94 Da corresponding to a phenol moiety. Besides, end group calculations in these two series gave masses of 94 Da easily attributed to a phenol molecule. So, it could be envisaged that the major polymer components (first series) were issued from a polymerization process initiated by a phenol molecule ( $m/z$  477 = 94 + 2 × 172 + 39) like in Scheme



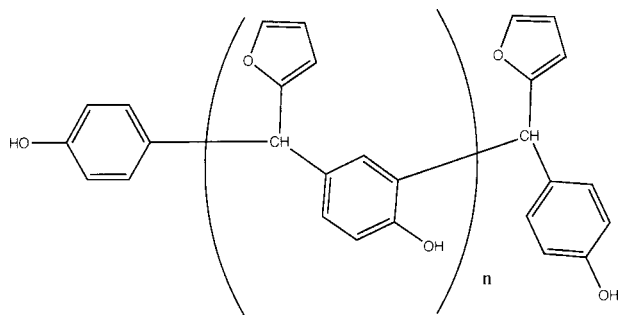


**Figure 2** MALDI-ToF analysis (positive mode, DHB matrix) of phenol-furfural resins.

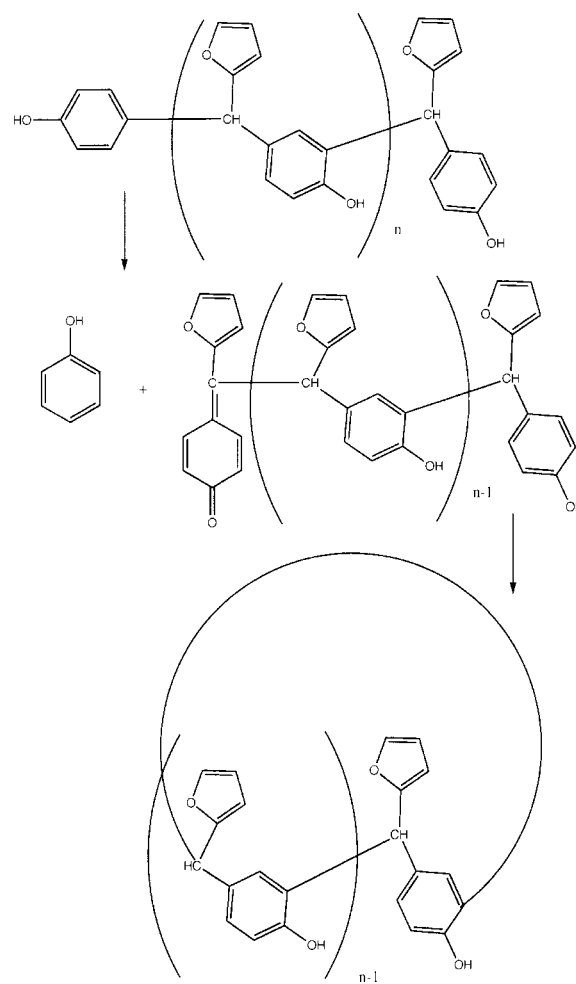
2, giving oligomers displaying structures described in Scheme 3.

The minor polymer components (second series) displayed peaks at mass of the first series minus 94 Da, corresponding to a loss of a phenol molecule ( $649 \rightarrow 555$ ;  $821 \rightarrow 727$ ; ...). These fragments were likely cyclic molecules (as shown in Scheme 4) obtained from the linear fragment forming phenol and quinone-methide followed by intramolecular nucleophilic attack by the *ortho* carbon of the phenol from the other end of the molecule (Scheme 4). With positive LSIMS, a series of ions was detected at  $m/z$  345, 517, 689, 861, 1033, 1205, 1377 corresponding likely to protonated molecules  $(M+H)^+$ . These ions belong to the same series as the minor one obtained with MALDI-ToF, but in the latter case they are cationized.

MALDI-ToF analyses were completed by ESI experiments. ESI analyses conducted in the positive mode allowed to detect only ions of the major product in the low molecular mass range ( $m/z$  305  $\rightarrow$  477  $\rightarrow$  649  $\rightarrow$  821). It should be noted that the first ion at  $m/z$  305 was not observed in MALDI better suited for high molecular weight ion detection. Tandem mass spectrometry was attempted to gather structural information, but the low energy collision acti-



**Scheme 3** Structure of main phenol-furfural oligomers in accordance with MALDI-ToF mass spectrum.



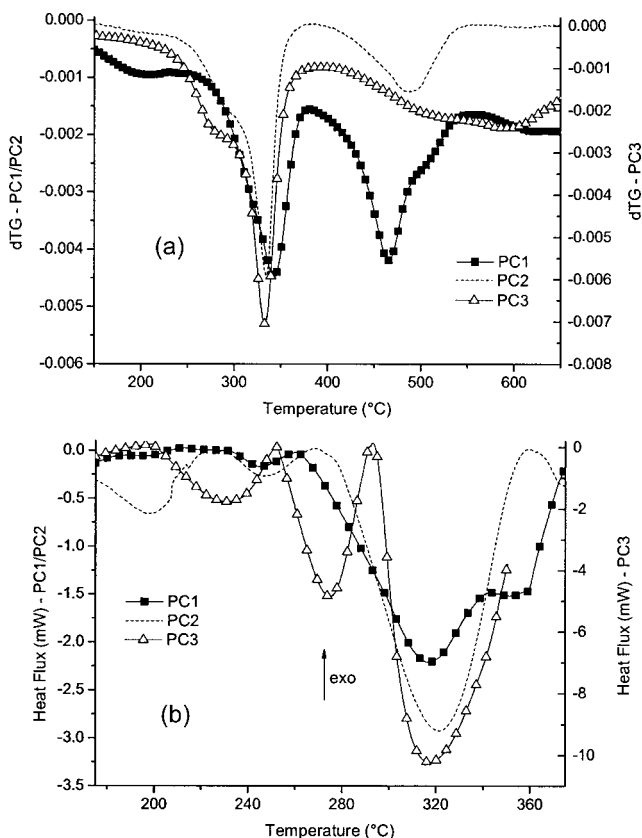
**Scheme 4** Hypothetical formation of minor phenol-furfural oligomers in accordance with MALDI-ToF mass spectrum.

vated dissociations (CAD) of the two selected parent ions ( $m/z$  305 and 477) did not provide informative data. Only one loss of water was observed. The difficulties encountered to fragment these ions were certainly due to the nature of the parent ions i.e., a cationized species less prone to fragment than a protonated ion.

Mass spectrometry analyses were in favor of a predominant linear structure of the oligomeric chain in the studied phenol-furfural resins.

#### Composites based on phenol-furfural thermosets and sisal fibers

Several phenol-furfural composites reinforced with sisal fibers (PC1-PC4) were prepared (see experimental part). Prepolymer resins for composites PC1 (phenol-furfural- $K_2CO_3$ /3.25 h/130°C) and PC2 (phenol-furfural-KOH/3.25 h/130°C) were obtained using similar conditions except the alkaline catalyst. Prepolymer resin for composite PC3 (phenol-furfu-



**Figure 3** Thermal analyses of composites PC1, PC2, and PC3 (see experimental). (a) dTG, (b) DSC.

ral-KOH/1 h/70°C) was made to verify whether phenol-furfural/KOH resin could be prepared using milder conditions than for preparation of prepolymer for composite PC2 by lowering reaction time (1 h instead of 3 h 15), and temperature (70°C instead of 135°C). To verify the influence of substituting formaldehyde (20% w/w) to furfural, a composite (PC4) with a phenol-formaldehyde-furfural resin (phenol-formaldehyde-furfural-KOH/1 h/70°C) was prepared using the mild conditions leading to PC3 resin.

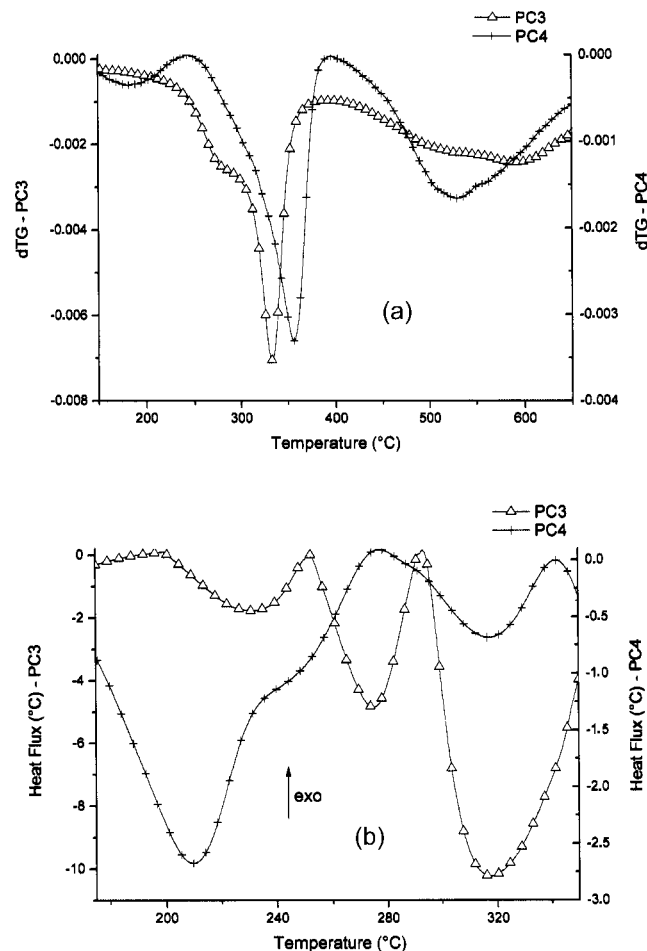
#### Thermal analyses

Composites were characterized by thermal analyses: Figure 3 for PC1, PC2, and PC3 and Figure 4 for PC4 by comparison to PC3 (milder conditions). According to previous studies,<sup>10,16,17</sup> dTG and DSC curves of sisal reinforced composites showed peaks related to thermal degradation first of carbohydrates (hemicelluloses and cellulose), from 270 to 300°C to higher temperatures, and then of lignin at 450°C and higher values. Thermal decomposition of the polymeric matrices was observed in the same domains. The thermal decompositions were exothermic, but as volatiles are liberated as decomposition byproducts,

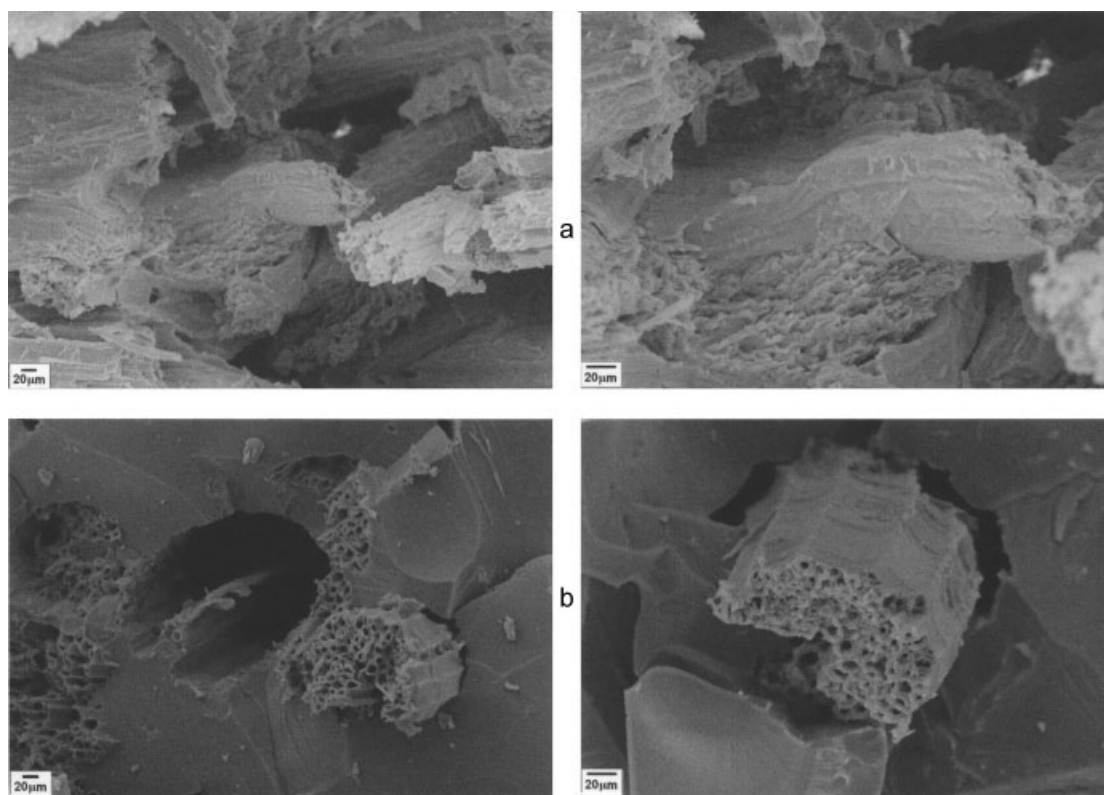
depending on the balance of the two events (decomposition/volatilization of byproducts), endothermic or exothermic peaks could be observed in DSC curves.

Specific comparisons of PC1 versus PC2 composites, indicated (Fig. 3) that the profiles of dTG and DSC curves from 300°C to higher temperatures are similar. Nevertheless, DSC curves of PC2 and PC3 displayed some shifts, mainly related to the first two endothermic peaks (near 200 and 250°C for PC2 and 230, 270°C for PC3) and the dTG curve of PC3 showed a wider interval of thermal decomposition, from 420°C to higher, when compared with PC2.

DSC curve of PC4 (Fig. 4) displayed an endothermic peak near 210°C, not observed with PC3 and likely related to a residual cure occurring during the scanning.<sup>10</sup> It could indicate that, when formaldehyde and furfural were mixed, the crosslinking step occurred in a less intensive extension during the composite preparation. The residual cure occurring during scanning seemed to protect the fibers, because dTG curves showed that the peak related to the decomposition of cellulose/hemicellulose was



**Figure 4** Thermal analyses of composite PC4 by comparison to PC3 (milder conditions, see experimental). (a) dTG, (b) DSC.



**Figure 5** SEM images of fractured surface of phenol-furfural composites made with sisal fibers and phenol-furfural prepolymers prepared using different catalysts: (a) KOH (PC2), (b) K<sub>2</sub>CO<sub>3</sub> (PC1) (left side, magnification ×500; right side, magnification ×1000; see discussion).

shifted to higher temperature for PC4, when compared to PC3.

#### Scanning electron microscopy

SEM images of PC1 and PC2 (Fig. 5) at low magnification (left side) showed that adhesion between matrix and fiber was better when KOH was used [Fig. 5(a) left side vs. Fig. 5(b) left side]. Also, some microcavities around the fiber were present when carbonate potassium was used [Fig. 5(b) left side]. The interface between fiber and matrix, examined at higher magnification (right side), showed some debonding of the fiber from the matrix with potassium carbonate [Fig. 5(b) right side]. A good adhesion at matrix-fiber interface was observed when sodium hydroxide was used [Fig. 5(b) right side]. The less homogeneous material observed when potassium carbonate was used was likely due to release of CO<sub>2</sub> decreasing interactions at the interface.

SEM images of composite PC3 showed an efficient impregnation of the fiber by the matrix [Fig. 6(a)] and a reasonable fiber-matrix adhesion at interface [Fig. 6(b)].

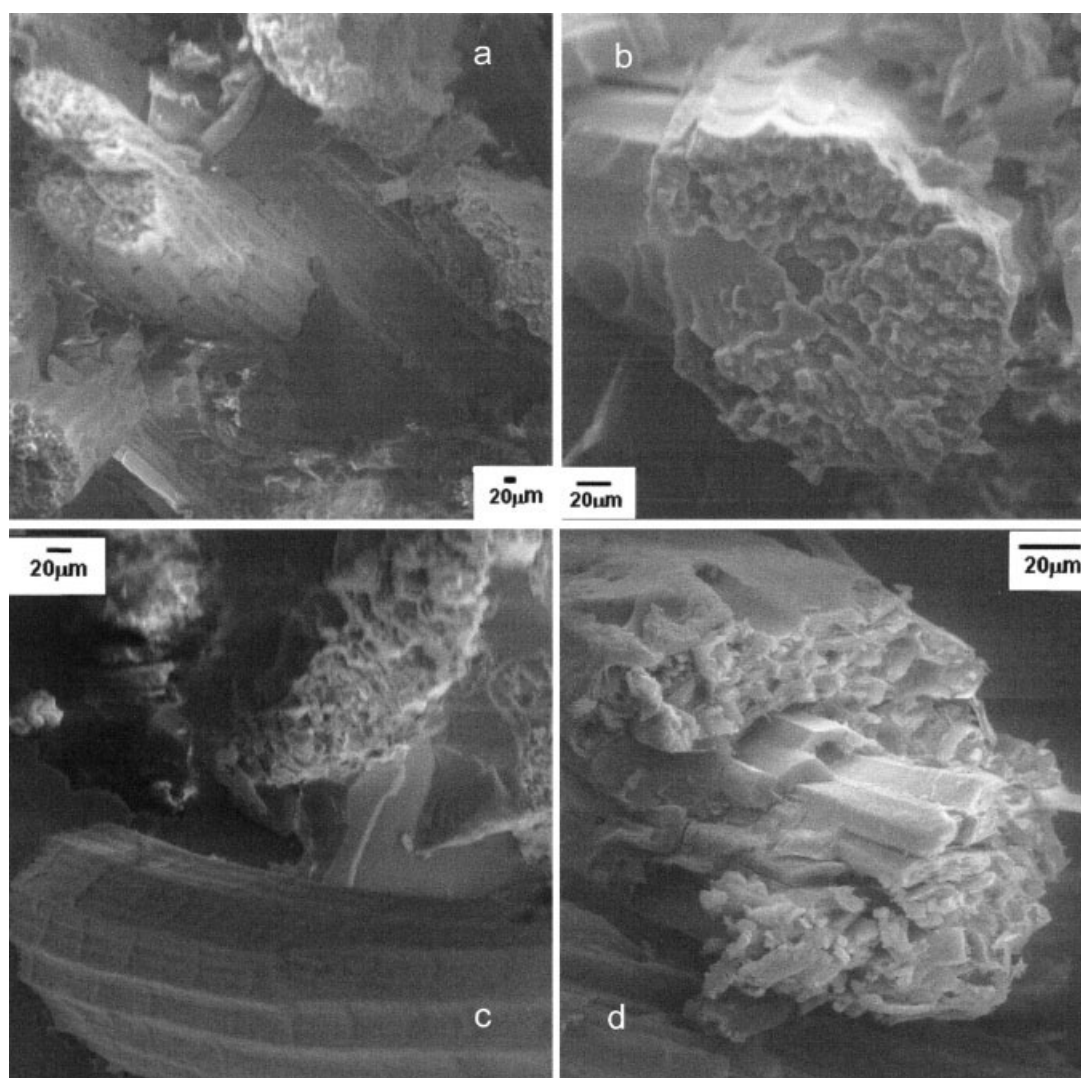
SEM images of composite PC4 showed both a good impregnation of the inner parts of the fiber by the resin phenol-formaldehyde-furfural [Fig. 6(c)]

and a good adhesion at fiber-matrix interface [Fig. 6(d)].

Viscosity of resins used to prepare PC3 and PC4 were lower than those used for PC1 and PC2, because of the lower time interval and temperature used to prepare the former resins, when compared with the latter. This lower viscosity favored the diffusion of the resins into the inner part of sisal fibers.

#### Impact strength

Impact strength of the phenolic thermosets without fibers reinforcement was usually found near 12 J m<sup>-1</sup>.<sup>9</sup> Impact strength values for composites PC1-PC4 (Table II) showed that the presence of sisal fibers improved this property. When the composite is submitted to an impact effort, a weak interface might conduce to a crack in the matrix or at the interface before the load transfer mechanism from matrix to fiber has occurred in all directions, leading then to lower impact strength. This effect seemed to act in composites made with resins based on K<sub>2</sub>CO<sub>3</sub> (PC1) instead of KOH (PC2): the impact strength of the former was almost half of the latter (Table II). Then, a composite with higher impact strength and more homogeneous (lower standard deviation) was obtained, when KOH was substituted to K<sub>2</sub>CO<sub>3</sub>, as



**Figure 6** SEM images of fractured surface of composites made with sisal fibers and prepolymers prepared under mild conditions: using phenol–furfural mixture **PC3** (a) (magnification  $\times 100$ ) and (b) (magnification  $\times 300$ ); using phenol–formaldehyde–furfural mixture **PC4** (c) (magnification  $\times 200$ ) and (d) (magnification  $\times 500$ ).

catalyst. The impact strength of **PC3** proved that composites with good properties could be obtained when resins were prepared in mild conditions.

Although the impact strength of **PC4** was somewhat higher than that of **PC3** (Table II), the high standard deviation could be taken as an indication that a less homogeneous material was obtained. Probably, the

matrix network had area containing aromatic rings linked mainly through bridges of furfural type structures, and others with methylene bridges, originating from the reaction between formaldehyde and aromatic rings. Mixing formaldehyde and furfural to prepare phenolic thermosets was not compensatory, when these resins were used to prepare composites.

**TABLE II**  
Izod Impact Strength of Sisal Reinforced Phenol–Furfural Matrices Composites (**PC1–PC3**) and Sisal Reinforced Phenol–Formaldehyde–Furfural Matrix Composite (**PC4**) (unnotched samples)

Sample	Impact strength ( $\text{J m}^{-1}$ )
PC1	$53 \pm 10$
PC2	$113 \pm 8$
PC3	$136 \pm 8$
PC4	$182 \pm 23$

**TABLE III**  
Water Diffusion Coefficient,  $D$ , for Sisal Reinforced Phenol–Furfural Matrices Composites (**PC1–PC3**) and Sisal Reinforced Phenol–Formaldehyde–Furfural Matrix Composite (**PC4**)

Sample	$D$ ( $\text{mm}^2 \text{h}^{-1}$ ) $\times 10^3$
PC1	36
PC2	49
PC3	98
PC4	116

### Water absorption

Composites **PC1-PC4** were also characterized with respect to water absorption. The experimental values were well fitted using the eq. (1)<sup>22</sup>:

$$\log M_t/M_\infty = \log(k) - n \log(t) \quad (1)$$

where  $M_t$  and  $M_\infty$  correspond to water content at time “ $t$ ” and at equilibrium, respectively.

For all experiments the value of “ $n$ ” was found near 0.5; so, the water diffusion through the composites followed Fick’s law. Then, it was possible to calculate the water diffusion coefficient  $D$  for each composite using eq. (2) (Table III):

$$(M_t/M_\infty) = (4/L)(D/\pi)^{0.5} t^{0.5} \quad (2)$$

where  $L$  corresponds to the thickness of the composite.

Water diffusion in the bulk of a composite depended on the formation of hydrogen bonds between water and both polymeric matrix and fibers. Higher were the numbers and intensity of these bonds, lower was the mobility of water molecules, spending more time in the bulk of the material and consequently decreasing their diffusion coefficient.

**PC3** and **PC4** displayed higher water diffusion coefficients than **PC1** and **PC2** (Table III), as a probable main consequence of the more extensive filling of the inner parts of fibers by the resins in **PC3** and **PC4**, when compared with **PC1** and **PC2**, as already mentioned during the discussions of SEM images. The hydrophilic character of fibers led to intense hydrogen bonds with water molecules. If the ducts are intensively filled and the surfaces of fibers are covered by the less polar phenolic type polymer, as occurring in **PC3** and **PC4**, the interaction with water will be less intense, decreasing the residence time of this molecule in the bulk of the composite, increasing then the values of water diffusion coefficients (Table III).

### CONCLUSIONS

Synthesis of appropriate models combined with <sup>13</sup>C NMR and MALDI-T of spectrometries were used for a detailed molecular characterization of PFu resins. They showed the presence of a majority of linear oligomers and a minority of cyclic ones. Composites made with these resins reinforced by sisal fibers were prepared. Thermal analyses (dTG and DSC) and electron microscopy images indicate that the composites display excellent adhesion between the resin and the sisal fibers. Impact strength measurement showed that mild conditions were more suitable

to prepare thermosets. They induced higher diffusion coefficient for water absorption. These promising results showed that composites with good properties could be prepared using high proportions of materials obtained from biomass, such as sisal fibers and furfural.

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