1. Introduction

Recently, the production of bioethanol, mainly intended as a partial or total substitute for gasoline, was the object of much discussion regarding the use of lignocellulosic biomass (Sánchez and Cardona, 2008). Despite a strong demand in this area, it is important to point out that lignocellulosic materials have a large number of applications (Keshwani and Cheng, 2009). However, it is important that all the steps involved in the production of bioethanol must also benefit other applications of these materials, such as the ones we consider here. For example, the production of lignocellulosic fibers will probably have to be closely overseen, from plantation to cropping, so that lignocellulosic materials are produced with better reproducibility of properties in even larger quantities to meet the market demand and the requirements of the several sectors.

The use of fibers from renewable resources can be both a positive contribution to the environment as well as to the petroleum supply problem. Agricultural products and by-products have gained attention as sources of fibers for further use as reinforcement of thermoplastic matrices (Megiatto et al., 2007; Trindade et al., 2004), since the hydrophilic and polar natures of the lignocellulosic fibers will probably have to be closely overseen, from plantation to cropping, so that lignocellulosic materials are produced with better reproducibility of properties in even larger quantities to meet the market demand and the requirements of the several sectors.

With the growing global energy crisis and current environmental problems, much research aimed at the production and use of agricultural products as a source of fibers to reinforce polymeric matrices for composites (Megiatto et al., 2007) has been carried out. Lignocellulosic fibers are biodegradable, resistant, and non-abrasive. Furthermore, they exhibit low specific density, which brings important advantages for composite applications where the use of lightweight materials is very important due to the fuel consumption (Zini et al., 2004). Hence, they are excellent candidates to replace traditional synthetic fibers (Satyanarayana et al., 2007; Frollini et al., 2004). Among the lignocellulosic fibers, sisal is one of the most used, owing to its high mechanical strength and physical characteristics related to its high cellulose content (Paiva and Frollini, 2006; Megiatto et al., 2008; Oliveira et al., 2008).

The hydrophilic and polar natures of the lignocellulosic fibers and the non-polar characteristics of many thermoplastic matrices could alter composite properties, owing to the lack-of-adhesion and non-uniform dispersion of the fibers in the matrix (Paul et al., 2008). When phenolic resins are used as matrices and lignocellulosic fibers are used as reinforcement materials, the lack-of-adhesion problem can be considerably minimized by favorable interactions between polar hydroxyl groups of the phenolic matrix and the hydrophilic fibers. This represents an important advantage of this matrix as compared to the hydrophobic thermoplastic matrices (Megiatto et al., 2007; Trindade et al., 2004), since the intensity of the intermolecular interactions through the interface controls various properties of the composites (Jacob and Berg, 1994). Another advantage of using phenolic matrices is their low processing temperature (<200 °C), which is below the thermal
decomposition temperature of the lignocellulosic fibers (Oliveira et al., 2008).

In previous work, methods of modifying the lignocellulosic fibers were developed to improve fiber/matrix interactions in composites made with phenolic or lignophenolic resins. The properties of natural and/or modified non-wood fibers such as sugarcane bagasse, curaua (Ananas ericifolius), sisal and phenolic matrices using formaldehyde or furfural as a substitute for formaldehyde were reported (Trindade et al., 2004, 2005; Megiatto et al., 2007, 2008; Oliveira et al., 2008).

These studies intended to use the materials obtained from biomass to modify the matrix or the surface of the fibers. The phenolic thermoset resins are widely known and used, owing to their excellent properties such as dimensional and thermal stability, and chemical resistance (Achary and Ramaswamy, 1998; Trindade et al., 2005; Ku et al., 2008). The raw materials used in the production of phenolic resins (phenol and formaldehyde) are obtained on a large-scale from non-renewable sources. Therefore, the substitution of these reagents by equivalents obtained from non-fossil sources is an interesting alternative from both the economical and environmental perspectives (Razera and Froolini, 2004; Hoareau et al., 2006; Paiva and Froolini, 2006). Moreover, substituting formaldehyde with other aldehydes obtained from renewable sources could also eliminate the potential emission of formaldehyde during the use of phenolic resins (Oliveira et al., 2008).

Glyoxal (OHC–CHO) is a dialdehyde that can be obtained from several natural sources, such as from the fermentation of lipids or as a by-product of biological processes (Hirayama et al., 1984). The two adjacent carbonyl groups make glyoxal highly reactive. The low vapor tension of the glyoxal solution and its low toxicity constitute some of the advantages of using glyoxal instead of formaldehyde (Mattioda et al., 1982). Glyoxal is already used as a substitute of formaldehyde in wood adhesive applications (Ballestri et al., 2005; El Mansouri et al., 2007a,b).

In continuation of our research on renewable resources as reinforcement of polymeric matrices (Megiatto et al., 2007), we describe a study on biobased composites from glyoxal–phenolic matrices reinforced by sisal fibers. As in previous work (Trindade et al., 2004, 2005; Megiatto et al., 2007, 2008; Oliveira et al., 2008), resorcinol was used as an accelerator for curing the glyoxal–phenol resins. Glyoxal was used as substitute for formaldehyde, and we intended to reach two goals with this substitution: (a) to use a material obtained from non-fossil sources – the glyoxal; and (b) to evaluate the effects of the presence of the two aldehyde groups, which can lead to the production of pre-polymer chains (glyoxal–phenol) and thermosets with properties considerably different from those of phenol–formaldehyde.

2. Methods

2.1. Materials

Sisal fibers were kindly supplied by Lwarcel (Lençóis Paulista, SP, Brazil). The fibers were Soxhlet-extracted with a cyclohexane/ethanol mixture (1:1, v/v) for 50 h to remove the soluble extractives (waxes, terpenes, fatty acids). Then, the fibers were washed with distilled water and dried in an air-circulated stove at 70 °C, until a constant weight was reached. The properties of these sisal fibers are presented in Table 1. The characterization was carried out according to the procedures described elsewhere (Trindade et al., 2005).

2.1.1. Glyoxal–phenol resin synthesis

The synthesis of the glyoxal–phenol resin was carried out using aqueous glyoxal (Vetec, 40%), phenol (Synth, 99%), and potassium hydroxide (Synth, 97%) in the molar proportion of 1.6:1.0:0.136. Phenol and potassium hydroxide were added to the reaction flask and the glyoxal was gradually added with constant mechanical stirring. After mixing, the system was heated to 100 °C and maintained at this temperature for 2 h. The resulting pre-polymer was cooled to room temperature and neutralized with hydrochloric acid (Synth, 37%). Water was then eliminated under reduced pressure.

2.1.2. Glyoxal–phenol resin characterization

Before analysis, the crude glyoxal–phenol resin was washed with chloroform in order to remove most of the unreacted products. Nuclear Magnetic Resonance spectra (1H, 13C, DEPT and 2D) were recorded on a Bruker Avance 300 spectrometer at 300 K in methanol. The 31P NMR spectra were registered on a Bruker DPX-200 spectrometer operating at 81 MHz. The glyoxal–phenol resin was derivatized prior to the 31P NMR analysis (Argyropoulos, 1994; Granata and Argyropoulos, 1995). A solvent mixture comprising pyridine and CDCl3 (1.6:1, v/v), dried with molecular sieves, was used as stock solution. Then, a solution of chromium (III) acetylacetonate in pyridine/CDCl3 (5 mg mL\(^{-1}\)) was added to act as a relaxation agent in the stock solution. The pre-polymer was phos- phitylated with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphos- pholane. Cholesterol (Sigma–Aldrich) (43 mg mL\(^{-1}\)) was used as an internal standard. A sample of 30 mg of pre-polymer was dissolved in 0.5 mL of DMF in a 2 mL flask and sealed with a Teflon-faced septum. Subsequently, 0.3 mL of pyridine/CDCl3 stock solution was added, followed by the addition of 0.1 mL of both the internal standard and the relaxation reagent solution. The phosphitylation reagent (0.1 mL) was added to this mixture, and the flask was tightly closed and stirred for 30 min to ensure thorough mixing. After derivatization, the mixture was transferred to a 5 mm tube for 31P NMR analysis. The chemical shifts were relative to the reaction product of water with the phosphitylating reagent, giving a sharp signal at 132.2 ppm.

Thermogravimetric analysis (TGA) of the glyoxal–phenol resin was carried out using Shimadzu equipment, model TGA-50. The samples (8–10 mg) were placed in platinum pans and heated from 25 °C to 800 °C at 10 °C min\(^{-1}\) under a synthetic air atmosphere (flow of 20 mL min\(^{-1}\)). Differential scanning calorimetry (DSC) analysis was performed using a Shimadzu instrument, model DSC-50. The samples (6–8 mg) were placed in sealed aluminum pans and heated from 50 °C to 400 °C at 10 °C min\(^{-1}\) under a synthetic air atmosphere (flow of 20 mL min\(^{-1}\)).

2.1.3. Biobased composites preparation

Glyoxal–phenol resin was mixed with resorcinol (10%, w/w), which is used as an accelerator for further curing the glyoxal–phenol resins, under mechanical stirring at 40 °C for 20 min. Subsequently, the sisal fibers (30%, w/w, 3 cm length, and randomly oriented) were impregnated using this mixture (glyoxal–phenol resin and resorcinol) for 20 min, using a mechanical mixer especially developed for this process (JY mixer, Pardinho, SP, Brazil). The compression molding was carried out in a metallic mold under pressure. The molding was carried out in two different cure cycles:

<table>
<thead>
<tr>
<th>Components</th>
<th>Cellulose</th>
<th>Hemicellulose</th>
<th>Lignin</th>
<th>Ash</th>
<th>Crystallinity index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (%)</td>
<td>64.4 ± 1.1</td>
<td>23.9 ± 0.4</td>
<td>9.7 ± 0.2</td>
<td>1.3 ± 0.1</td>
<td>60.6</td>
</tr>
</tbody>
</table>

\(^{a}\) Free from humidity. \(^{b}\) Determined as difference between holocellulose (cellulose + hemicellulose) and cellulose content.
Cure cycle 1: 75 °C/1 h/0 ton; 85 °C/1 h/0 ton; 100 °C/1 h/2 ton; 115 °C/1.5 h/10 ton; 125 °C/2 h/16 ton; and 150 °C/2 h/16 ton.

Cure cycle 2: 75 °C/0.5 h/0 ton; 85 °C/1 h/0 ton; 100 °C/1.5 h/2 ton; 115 °C/2 h/10 ton; 150 °C/2 h/16 ton; and 180 °C/2 h/16 ton.

2.1.4. Biobased composites characterization
For the Izod impact test, 20 unnotched samples were cut from each plate and shaped according to ASTM D256: 63.5 mm of length × 12.7 mm of width × 4.5 mm of thickness. Impact strength was assessed using Izod impact equipment (CEAST Resil 25). The impact tests were carried out at room temperature with an impact speed of 4 m s⁻¹ and an incident energy of 5.5 J. Data were expressed as their arithmetic mean values ± standard deviation.

Scanning electron microscopy (SEM) images were taken with a Zeiss-Leica apparatus model 440, with an electron acceleration of 20 kV. Fractured samples were covered with a thin layer of gold in a sputter coating system prior to analysis.

Water absorption analyses were performed according to the ASTM D570. The dimensions of the samples for the water absorption experiments were 76.2 mm × 25.4 mm × 3.2 mm. The samples were immersed in distilled water at room temperature. After certain time intervals, the samples were removed from water, put on a piece of dry cloth (to remove the excess of water), and weighed on a high-precision balance. The percentage mass increase (water content) was calculated by the weight difference. Data were expressed as their arithmetic mean values.

Dynamic mechanical thermoanalysis (DMTA) was carried out using a DMA thermal analyzer, model 2980 from TA Instruments, operating with the 3-point bending clamp (flexural mode). The dimensions of the samples were 64 mm long × 12 mm wide × 3.2 mm thick. The equipment was calibrated with a metallic standard. The experimental conditions were: oscillation amplitude of 20 μm, 1 Hz frequency, heating rate of 2 °C min⁻¹, and temperature range of 30–230 °C.

Thermogravimetry (TG) and differential scanning calorimetry (DSC) analyses of the composites were carried out in the same conditions described previously for the glyoxal–phenol resin.

3. Results and discussion
3.1. Glyoxal–phenol resin characterization

³¹P NMR (Fig. 1a) showed signals belonging to carboxylic acid (134.9–135.2 ppm) and aliphatic alcohol (147.1–148.8 ppm) hydroxyl groups. These signals suggested the presence of both residual glycolic acid and glycolic ester derivatives. This hypothesis was confirmed by signals at 3.9 ppm (Hₐ) in the ¹H NMR spectrum (Fig. 1b) and at 178.8 ppm (Cₚ) and 62.2 ppm (Cₐ) in the ¹³C NMR spectrum (Fig. 1c). These assignments were supported by DEPT (Fig. 1d), HMOC and HMBC (spectra not shown) correlation signals. Moreover, the ³¹P NMR spectrum showed various phenolic groups between 137.0 and 140.9 ppm. ¹H, ¹³C DEPT (Fig. 1d), HMOC and HMBC (not shown) NMR spectra revealed a ketone/carbonyl signal (198.8 ppm, Cₙ) associated with a methylene signal (δ¹H: 4.8 ppm, Hₜ; δ¹³C: 65.8 ppm, Cₜ). After treating the resin with sodium borohydride, the ketone signal disappeared in the ¹³C NMR spectrum, though the glycolic carbonyl signal remained. The particularly low field of the methylene chemical shift observed in the ¹H NMR spectrum indicated that this group was between a phenolic nucleus and the ketone. The signals at 8.4 ppm (¹H, Hₜ) and at 169.4 ppm (¹³C, Cₜ) are assigned to a same C–H bond (DEPT and HMOC spectra) without any neighboring proton (HMBC). It was probable that the carbon atom was linked to a quaternary carbon and the unusual low field chemical shifts were likely due to a completely conjugated structure. The ¹³C spectrum complexity could not allow an easy assignment of this quaternary atom. Nevertheless, an enolic structure might be formed, leading to a glycolic enol ester, which could be locked by hydrogen bonding into a six-membered ring. Considering that phenolate anions are mainly involved in a C-centered reactive center in ortho and para positions of the phenol group when reacting with aldehydes (Oliveira et al., 2008), the reaction with glyoxal generated a mixture of oligomers like (A) and (B) proposed in Scheme 1, which are compatible with the previous spectra (Fig. 1 and Table 2).
The TGA curve of the glyoxal–phenol resin is presented in Fig. 2a. The small mass loss that occurred in the beginning is related to the water vaporization that was not totally eliminated during the roto-evaporation stage of the pre-polymer. Between 150 °C and 200 °C, the mass loss probably occurred owing to the cure reactions that took place during scanning, releasing water that vaporized. However, at temperatures higher than 200 °C, an accentuated mass loss was observed, which could correspond to more complex cure reactions that occurred during scanning. At higher temperatures, decomposition of the polymer began. Furthermore, at 800 °C, the material was practically decomposed.

In the DSC curve of the glyoxal–phenol resin (Fig. 2b), an endothermic peak was observed at 125 °C that corresponded to the thermal cure process of the resin. This thermal cure occurred with the release of water during scanning. Volatilization of this water generated endothermic peaks. At 236 °C and 278 °C, two exothermic peaks were observed, which were related to the more complex cure reactions that occurred during the analysis, and the decomposition reactions of the glyoxal–phenol thermoset polymeric chains that formed during scanning. The events observed in the DSC curve were in agreement with those of the TGA curve.

### 3.2. Biobased composites characterization

The results obtained in the Izod impact-strength test, with respect to the composites of the glyoxal–phenol matrix, obtained using resorcinol as a cure accelerator, reinforced with 30% (w/w) sisal fibers, are presented in Table 3.

Regardless of the cure cycle used, the impact-strength value obtained was practically identical. The impact-strength value of the phenolic thermoset without the reinforcement of fibers was close to 12 J m⁻¹ (Trindade et al., 2004). The results of the Izod impact-strength test (Table 3) demonstrated that the presence of
fibers greatly improved this property. The fibers were able to efficiently distribute the tension along the matrix, thus improving the impact strength. The composites of glyoxal–phenol matrix reinforced with sisal fibers had an impact strength 10-times higher than that of the phenolic thermoset.

Fig. 3 shows the SEM images of the composites with cure cycles 1 and 2 (see Section 2).

The SEM images of the composite with cure cycle 1 showed that the fibers were more adhered to the matrix and also more recovered by the matrix (Fig. 3a), when compared to the composite with cure cycle 2 (Figs. 3c and 3d). In addition, it was possible to observe the presence of the matrix inside the fiber (Fig. 3b). In the composite with cure cycle 2, a higher contact among the fibers (Fig. 3c) and a lower fiber/matrix adhesion (Fig. 3d) were observed. Thus, cure cycle 2, which reached higher temperatures, could lead to a larger production of volatile components, generating “voids” in the matrix. Hence, sisal fibers were less protected by the matrix, which made easier the interaction of the fibers with water molecules, and consequently increased the composite water absorption.

Fig. 4 presents the water absorption curves of glyoxal–phenol composites reinforced with 30% (w/w) sisal fibers, cured either with cycle 1 or 2. The composite prepared using the cure cycle 1 had the lowest water absorption, confirming observations from SEM images. With the experimental data obtained in the water absorption test, it was possible to evaluate the diffusion mechanism based on Fick’s theory (Espert et al., 2004). The experimental values can be expressed with Eq. (1), where $M_t$ corresponds to the water content at time $t$ and $M_e$ corresponds to the water content at equilibrium. When the log $M_t/M_e$ was plotted as a function of time, the linear part of the obtained curve could be used to determine the linear coefficient “$k$”

$$\log\left(\frac{M_t}{M_e}\right) = \log(k) + n \log(t)$$

The parameter $k$ (Table 3) is related to the affinity between the composite and water molecules. Though the increase in the final molding temperature caused a large increase in the amount of absorbed water, it did not alter the composite’s affinity to water molecules. The higher amount of absorbed water was related to imperfections and voids in the matrix, as mentioned earlier.

Linearity presented by the curves of log $M_t/M_e$ versus time (figures not shown) allowed us to consider water diffusion in composites to be similar to the Fickian regime (Comyn, 1985). The diffusion rate of water molecules that penetrated the composite was lower than the mobility of the polymer segments. Equilibrium inside the composite was quickly reached and was maintained independent of time. In Fick’s model, the ability of water molecules to penetrate composites can be evaluated through analyses of the diffusion coefficient $D$ (Eq. (2)), where $L$ is the thickness of the sample

$$\left(\frac{M_t}{M_e}\right) = \frac{4}{L} \frac{D}{\pi} t^{0.5}$$

The composite with cure cycle 1 had a higher diffusion coefficient ($D$) than those with cure cycle 2 (Table 3). The higher the value of $D$, the quicker the diffusion of water molecules was in the

<table>
<thead>
<tr>
<th>Glyoxal–phenol composites reinforced with sisal fibers</th>
<th>Izod impact strength (J m$^{-1}$)</th>
<th>$k$ (h$^2$)</th>
<th>$D$ (mm$^2$ h$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cure cycle 1</td>
<td>118 ± 13$^a$</td>
<td>0.5</td>
<td>10.7</td>
</tr>
<tr>
<td>Cure cycle 2</td>
<td>113 ± 18$^b$</td>
<td>0.5</td>
<td>3.8</td>
</tr>
</tbody>
</table>

$^a$ Standard deviation.

$^b$ Standard error – angular coefficient (Eq. (2)): $3 \times 10^{-5}$ and $1 \times 10^{-5}$ for cure cycles 1 and 2, respectively.

Table 3 Izod impact-strength of glyoxal–phenol–resorcinol composites reinforced with sisal fibers and values of water affinity “$k$” and diffusion coefficient ($D$) calculated from water absorption experiments according to Fick’s model (Eq. (2), see text).

Fig. 3. SEM images of the impact fracture surface of glyoxal–phenol–resorcinol composites reinforced by sisal fibers with cure cycle 1 [(a) × 300; (b) × 1000] and cycle 2 [(c) × 500]; (d) ×500.

composite. The fibers were better covered by the matrix in composites cured by cycle 1 owing to a better fiber/matrix adhesion (as observed in the SEM images). The establishment of hydrogen bonding between the fiber and water slowed down the water molecules, decreasing the value of $D$. Since, in the composite with cure cycle 1, hydrogen bonding occurred less frequently, the value of $D$ increased as compared with the composite with cure cycle 2 in which the fibers were more exposed and interacted more with the water molecules.

Evaluation of the thermal stability of the material is also of great importance for composite applications. Hence, thermogravimetric analyses of the composites were carried out (Fig. 5a and b). Up to 100 °C, a small mass loss was observed, which was related to humidity, mainly owing to the presence of cellulosic fibers that are hygroscopic in nature. Between 100 °C and 250 °C the mass was practically constant, demonstrating that the material is very stable for applications at this temperature range.

Above 300 °C, a significant mass loss occurred owing to (a) thermal decomposition of the cellulose and hemicellulose present in the sisal fibers that were used as reinforcement; (b) oxidation reactions (followed by decomposition) involving aliphatic bridges that bonded the aromatic rings of the matrix; and (c) homolytic breaks of bonds between rings and aliphatic bridges, and between rings and phenolic hydroxyl groups, with the generation of radical entities (Paiva and Frollini, 2006).

The decomposition of lignin present in the sisal fibers began at 400 °C. Another stage of mass loss occurred at 450 °C for the composites molded with cure cycle 1, and at 600 °C for the composites molded with cure cycle 2. As previously explained, the composite cured with cycle 2 was more cross-linked than that cured with cycle 1. The increase of cross-linking resulted in the increase in thermal energy necessary to degrade the material.

An exothermic peak around 220 °C related to residual cure reactions was observed in DSC curves of the composites (Fig. 5c and d).
Another exothermic peak was observed at 300 °C, which was related to the decomposition of cellulose present in the sisal fibers. Thermal degradation of cellulose led to depolymerization and generation of anhydrocellulose (Scheirs et al., 2001). One last exothermic peak was observed around 390 °C, which was related to the decomposition of lignin present in the sisal fibers as well as related to the decomposition of the phenolic matrix.

By considering the parameters obtained by the DMTA technique (storage modulus $E'$; loss modulus $E''$; internal friction $\tan \delta$), it was possible to extract information about the molecular mobility of the material. When the considered polymer corresponded to a thermoset, the mobility was mainly related to the segments located at cross-linking points. When the thermoset was a part of a composite, then other characteristics were considered. The dynamical–mechanical properties of the composites were determined from the properties of their components, system morphology, and the nature of the interface between the components. The layers of the matrix that were around the fiber immediately posterior to the interface, could have different properties when compared with the rest of the material (Paiva and Frollini, 2002; Trindade et al., 2005).

The curves of the storage modulus, loss modulus, and $\tan \delta$ versus temperature for the glyoxal–phenol composites reinforced with 30% (w/w) sisal fibers are presented in Fig. 6a–c, respectively.

The storage modulus was higher for composites molded with cure cycle 1 (see experimental), demonstrating that this composite was more rigid than the one with cure cycle 2. For the fiber/matrix interface, the value of $E'$ decreased owing to the energy dissipation during stress transfer, and a higher dissipation of this energy occurred for composites with a weak interface (Ray et al., 2001). The composite molded with cure cycle 2, which presented the lowest storage modulus, demonstrated a lower fiber/matrix interaction caused by imperfections in the matrix, as previously mentioned. Additionally, fibers that were less covered by the matrix caused higher humidity absorption (as it was observed in the water absorption test). Water molecules could have a plasticizing effect, decreasing the storage modulus.

Composites molded with cure cycle 1 had a lower loss modulus from approximately 150 °C and $\tan \delta$, as compared with the composite molded with cure cycle 2. Smaller values of $E''$ and $\tan \delta$ could indicate better interaction in the fiber/matrix interface because the improvement in the composite interface might lead to a more efficient stress transfer between the fibers and matrix, and a lower energy dissipation, consequently decreasing $E''$ (Trindade et al., 2005).

The global maximum in curves of $\tan \delta$ versus temperature, which could indicate the temperature of the glass transition ($T_g$) of the composites, appeared around 165 °C for composites molded with cure cycle 1, and 200 °C for composites molded with cure cycle 2. Composites with cure cycle 2 were more cross-linked because this cure cycle reached higher temperatures. Higher cross-linking led to greater difficulty in the movement of chain segments, which made the glass transition to occur at higher temperature (Paiva and Frollini, 2006). However, it is not necessary that a totally cured matrix be obtained because it could lead to a more brittle material with loss of some properties (Trindade et al., 2005).

![Fig. 6. DMTA curves obtained for the glyoxal–phenol–resorcinol composites reinforced by sisal fibers. (a) $E'$ versus temperature; (b) $E''$ versus temperature; (c) $\tan \delta$ versus temperature. ▲ Composite–cure cycle 1, ● Composite-cure cycle 2.](image)
Scheme 2. Schematic representation of the interactions between the polar groups of the lignocellulosic fiber (sial) and of the phenolic type matrix using an SEM image.

4. Conclusion

The polar and the non-polar characteristics of lignocellulosic fibers and many polymeric matrices could result in composites without the appropriate properties, mainly owing to the lack-of-adhesion at the interface.

If phenolic type resins are used as matrices, as in the present work, the obtained results show that this problem can be considerably minimized, due to the interactions between polar groups present in their chemical structures (Scheme 2).

In addition, for the first time, a glyoxal–phenolic resin was developed in alkaline conditions and was characterized using 1H, 13C, 2D, and 31P NMR spectrometries. Glyoxal is a dialdehyde obtained from several natural resources that exhibits low vapor tension and low toxicity. These properties make glyoxal a very suitable candidate for the preparation of thermosets by at least partially replacing formaldehyde in the phenolic resins. The glyoxal–phenol thermoset resin was reinforced by sisal fibers (30%, w/w) owing to their excellent mechanical properties. Two different cure cycles were used: cycle 1 limited the curing temperature to 150 °C, whereas cycle 2 limited the temperature to 180 °C. Furthermore, cycle 1 displayed the best adhesion between the resin and the sisal fibers, along with excellent dynamical–mechanical properties. These results are promising and demonstrate that biobased composites with good properties can be prepared using high proportions of materials obtained from biomass, such as sisal fibers and glyoxal.

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