Composites from a forest biorefinery byproduct and agrofibers: Lignosulfonate-phenolic type matrices reinforced with sisal fibers

CRISTINA GOMES DA SILVA, FERNANDO OLIVEIRA, ELAINE CRISTINA RAMIRES, ALAIN CASTELLAN, AND ELISABETE FROLLINI

ABSTRACT: The replacement of phenol with sodium lignosulfonate and formaldehyde with glutaraldehyde in the preparation of resins resulted in a new resol-type phenolic resin, sodium lignosulfonate-glutaraldehyde resin, in addition to sodium lignosulfonate-formaldehyde and phenol-formaldehyde resins. These resins were then used to prepare thermosets and composites reinforced with sisal fibers. Different techniques were used to characterize raw materials and/or thermosets and composites, including inverse gas chromatography, thermogravimetric analysis, and mechanical impact and flexural tests. The substitution of phenol by sodium lignosulfonate in the formulation of the composite matrices increased the impact strength of the respective composites from approximately 400 Jm^{-1} to 800 J m^{-1} and 1000 J m^{-1}, showing a considerable enhancement from the replacement of phenol with sodium lignosulfonate. The wettability of the sisal fibers increased when the resins were prepared from sodium lignosulfonate, generating composites in which the adhesion at the fiber-matrix interface was stronger and favored the transference of load from the matrix to the fiber during impact. Results suggested that the composites experienced a different mechanism of load transfer from the matrix to the fiber when a bending load was applied, compared to that experienced during impact. The thermogravimetric analysis results demonstrated that the thermal stability of the composites was not affected by the use of sodium lignosulfonate as a phenolic-type reagent during the preparation of the matrices.

Application: Application of sodium lignosulfonate in the preparation of resins used in the manufacture of composites reinforced with sisal fibers adds value to byproducts generated in forest biorefineries.

The purpose of a biorefinery is to convert wood, agricultural products, byproducts, and agricultural wastes or other biomass into products with added value. This goal is often achieved using different physical, physicochemical, or chemical pretreatment processes. Lignocellulosic biomass and agricultural wastes are appealing as biorefinery feedstock because of their abundance, low cost, and global availability [1,2]. The forest biorefinery combines processes aimed at the recovery and separation of the main components of wood: cellulose, hemicellulose, and lignin. The continuous biomass fractionation process yields a liquid stream rich in hemicellulosic sugars, a solid cellulose stream, and a lignin-rich liquid stream—all of which can be used to produce ethanol fuel, chemicals, and lignin, respectively, for resin production [1,3–5].

Lignin is a biorefinery byproduct produced following the delignification process, which is necessary to refine cellulose and hemicellulose before enzymatic or acid hydrolysis [6,7] that occurs in the production of bioethanol and/or other materials [8]. Due to its high abundance and low cost, lignin has long attracted attention as an alternative to petroleum-derived products [9,10]. Lignin has many functional groups, including aromatic rings, phenolic hydroxyls, carboxyl, and aliphatic hydroxyl groups. Because it is rich in phenolic aromatic rings, lignin has many advantages as a replacement for phenol in the preparation of resol-type phenolic resins, epoxy resins, and other resins [11–15].

The use of lignin as a raw material to produce environmentally friendly products reduces the demand of nonrenewable resources and provides a safe alternative to phenol, a toxic petrochemical [16]. Lignin has other applications, as well. For example, carboxymethyl lignin can be used as a stabilizing agent in aqueous ceramic suspensions; specifically, carboxymethylated lignin derived from sugarcane bagasse has been successfully used as a stabilizing agent for alumina suspensions [17]. Formulations based on lignins have filmogenic properties that, when combined with the hydrophobicity of this macromolecule, have pointed to applications such as slow-release coatings for fertilizers [18]. However, most of the lignin that is produced is burned [19] rather than used to produce value-added materials. Nevertheless, this scenario is changing, due to the increasing presence of biorefineries, including lignocellulosic feedstock biorefineries [4, 20], that aim to use lignin to produce polymers and other materials.

Lignosulfonate is a byproduct of the sulfite pulping process and is water-soluble due to the presence of sulfonic groups. This macromolecule is composed of a hydrophobic aromatic skeleton with hydrophilic sulfonic groups and can be used in applications such as surfactants [21, 22], in polyolefin-lignosulfonate blends [23], and for synthesis of urea-formaldehyde type resins [24]. We focused on the application of lignosulfonates in polymeric materials, specifically addressing the preparation of phenolic-type resins using sodium lignosulfonate (SL) and formaldehyde, or glutaraldehyde, which can be obtained from renewable resources and has low vapor pressure compared to formaldehyde. These two resins, sodium lignosulfonate-formaldehyde (SLF) and sodium lignosulfonate-glutaraldehyde (SLG), were used to prepare thermosets and composites reinforced with sisal fibers (SF). Sisal fiber was used because of its excellent role as a reinforcing agent, as observed in previous studies [13,25], and because of its large-scale availability in Brazil. Phenol-formaldehyde resins and their respective thermoset and composite specimens were prepared as control samples. The prepared thermosets and sisal fibers (the fibers in a prior study [26]) were characterized using inverse gas chromatography (IGC); the results were used to provide information about the interactions that take place at the interface where the thermoset and sisal fiber become constituents of composites. It must be emphasized that the properties of lignocellulosic fibers, besides variety, are affected by factors such as climate, harvesting, and maturity. In addition, their surface properties are influenced by features such as chemical composition, crystallinity, morphology [27], and chemical and mechanical pretreatments [28]. In this context, even for a same type of fiber (e.g., sisal), different parameters can be found through IGC analysis, depending on the history of the lignocellulosic fiber.

EXPERIMENTAL

Sisal fibers were purchased from Sisal Sul Indústria e Comércio Ltda., São Paulo, SP, Brazil. In an attempt to remove additives such as waxes, terpenes, and fatty acids, the fibers were treated with a cyclohexane/ethanol (1:1 v/v) solution for 10 min under reflux. Afterwards, the fibers were washed with distilled water at room temperature and dried in an air-circulating stove at 105°C until the weight stabilized.

Sodium lignosulfonate (SL) Vixilex SD-type, supplied by Borregaard LignoTech (Cambará do Sul, Rio Grande do Sul, Brazil), is a byproduct obtained from the sulfite pulping processing of *Pinus taeda* wood. The SL (Mw approximately 6000 g mol^{-1}, 5.5 wt% sulfur, 1.7% magnesium, 0.2 wt% calcium, and 0.9 wt% sugars, as informed by the supplier) was used to prepare phenolic-type resins (prepolymers).

Prepolymers synthesis (resol-type resins)

Two types of resins were synthesized using SL and formaldehyde (37% solution) or glutaraldehyde (25% solution) in an alkaline medium.

The SLF prepolymer was synthesized using SL, formaldehyde, and solid potassium hydroxide (KOH) (1.0:1.0:0.075 w/w). The SL was added to the aqueous formaldehyde solution and stirred for 15 min. Then, KOH was then added and the solution (total solids content 43.4 wt%) was stirred for 45 min at room temperature (pH approximately 8). Following this step, the system was heated to 70°C for 1 h and then to 97°C for 2 h. The solution was then cooled and neutralized with hydrochloric acid (HCl), and the water was removed under reduced pressure using a rotoevaporator.

The SLG prepolymer was prepared under the same conditions used to prepare the SLF resin, except that the formaldehyde precursor was replaced with glutaraldehyde and the total solids content was 35.0 wt%.

Phenolic resin (phenol-formaldehyde [PF], total solids content 43.4 wt%) was prepared according to the procedure described by Megiatto Jr. et al. [29].

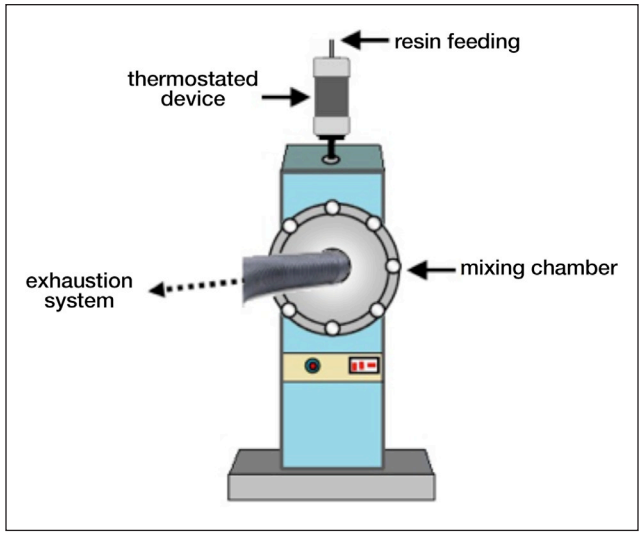
Thermoset preparation

The phenolic-type prepolymers (SLF, SLG, or PF) were heated to 50°C, whereupon resorcinol was added as a curing accelerator (10:1, w/w) and the mixture was stirred for 30 min. At 50°C, prepolymers have lower viscosities than at room temperature, making them easier to mix with resorcinol. The curing reaction was performed in a metallic mold (300 x 140 x 5 mm) using cure cycles determined in prior studies [13,30]:

- **Sodium lignosulfonate-formaldehyde thermoset (SLFT)**
  Heat to 50°C/50 min at ambient pressure, then adjust the pressure to 28.6 kgf cm^{-2} at specified temperature/time intervals: 50°C/10 min, 65°C/60 min, 80°C/60 mi, 95°C/30 min, 105°C/30 min, 115°C/60 min, and 125°C/120 min;
- **Sodium lignosulfonate-glutaraldehyde thermoset (SLGT)**
  Heat to 50°C/90 min at ambient pressure, then adjust the pressure to 28.6 kgf cm^{-2} at specified temperature/time intervals: 50°C/10 min, 65°C/60 min, 80°C/60 min, 95°C/30 min, 110°C/30 min, 125°C/120 min, and 150°C/60 min.

Composite preparation

Composites reinforced with sisal fibers (approximately 3% of moisture, after drying at 105°C for 4 h) were produced by impregnating the fibers (30 wt%, 30-mm length) with the prepolymers/resorcinol (50°C) mixture. The resin was added to the fibers and mechanically stirred for 20 min using a JVJ mixer (Pardinho, São Paulo, Brazil) to efficiently impregnate the fibers (**Fig. 1**). The mixer comprises a fiber/matrix mixing chamber that corresponds to a rotating steel drum with steel forks and a thermostated device in which the polymeric resin is heated. The fibers are distributed in the mixing chamber, and the polymer resin passes through a heated duct (50°C) and then is dripped onto the fibers. Coupled to the steel drum is a pipe connected to an exhaust system for removing volatiles, in case they are released during this step. The fibers



1. Schematic representation of the fiber-resin mixer.

were impregnated with the resin for 20 min, under continuous rotation (20 rpm) of the mixing chamber.

The composites were prepared with randomly distributed fibers in a metallic mold using the thermoset cure cycle previously described, with the exception that pressure was 38.1 kgf cm^{-2} instead of 28.6 kgf cm^{-2}.

Phenol-formaldehyde-type matrices reinforced with SF have been previously studied. By examining variations in the percentages and lengths of the sisal fibers, it was shown that using 30 wt% of SF with fiber lengths of 30 mm resulted in composites with good properties [13, 25]. Therefore, in our study, lignosulfonate matrices were reinforced with 30 wt% sisal fibers that measured 30 mm in length.

Sisal fiber analysis

The crystallinity index of the SF was determined according to the procedure reported by Buschle-Diller and Zeronian [31], and ash content was determined according to a previously described method [26].

Moisture content of the fiber was determined using the method described in ABNT (Brazilian Association for Technical Standards) NBR9656, "Standard test method for moisture content determination by oven drying." The ash content was measured by calculating the percent difference between the initial weight of the dried fiber and the weight of the fiber after calcination at 800°C for 4 h. Klason lignin content was determined as specified in TAPPI Standard Test Method T13m-54, "Lignin in wood," 1991. Holocellulose content was determined according to the description in the TAPPI Standard Test Method T19m-54, "Holocellulose in wood," 1991. The cellulose content was determined by the removal of hemicellulose from the holocellulose with NaOH, as specified in the TAPPI standard T19m-54. The hemicellulose content was then calculated by subtracting the cellulose content from the holocellulose content. Averages for moisture, ash, Klason lignin, holocellulose, and α-cellulose contents were calculated from repeated measurements of three different samples. A minimum of 30 samples were tested.

Tensile testing was carried out using a TA DMA analyzer model 2980 (TA Instruments; New Castle, DE, USA). The experimental testing was carried out at 25°C using a preload of 1.2 N and a ramp force of 1 N min^{-1} up to 18 N, with the operating mode set under control force and a length of approximately 15 mm separating the tension film-type clamps. A minimum of 30 samples were tested.

Inverse gas chromatography

Sisal fiber and thermosets were analyzed by IGC (GC-17A, Shimadzu Corporation; Kyoto, Japan) with a flame ionization detector and stainless steel (316) columns with 5-mm internal diameters. The fibers were cut to nearly 1 mm in length and packed into 2-m columns. The SF column was analyzed with the injector/detector and column temperatures set to 150°C and 30°C, respectively, and an N_2 carrier gas flow rate of 30 mL min^{-1}.

Thermosets were previously triturated, sifted through 150-mesh, and washed with acetone. The thermoset particles then were dried and packed into 2-m long columns. The columns were analyzed with the injector/detector and column temperatures set to 150°C and 50°C, respectively, and an N_2 carrier gas flow rate of 30 mL min^{-1}.

Before the start of each test, the columns were conditioned for 24 h at 150°C with flowing N_2 to remove any possible traces of water or other volatile compounds. Probes were injected at infinite dilution conditions (0.1 mL) using microsyringes (gas-tight Hamilton). Considering a series of n-alkanes (from pentane to decane, Sigma-Aldrich, 99.9%; Sigma-Aldrich, St. Louis, MO, USA) as nonpolar probes and methane serving as a marker, the probes were used to determine the dispersive properties. Chloroform (Sigma-Aldrich, 99.9%) and tetrahydrofuran (Sigma-Aldrich, 99.9%) probes were used to measure the numbers of acceptors and donors, respectively.

To measure the dispersive component of free surface energy (γ^d_S) and the acid/base characteristic of the testing materials, it was necessary to consider the free surface energy dispersive component of the probe in a liquid state (γ^d_L) and superficial area for each probe, which were described by Belgacem et al. [32], Belgacem and Gandini [33], and Gutierrez et al. [34]. The free surface energy and acid/base (AN_S/DN_S) components were calculated according to the procedure reported by Megiatto Jr. et al. [26].

Characterizations of thermosets and composites

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out using a Shimadzu-50 device, under a nitrogen atmosphere (20 mL min^{-1}) at a heating rate of 10°C min^{-1}.

Izod impact testing was conducted as described in ASTM D256, "Standard test method for unnotched Izod impact strength," using a CEAST Resil 25 device (CEAST SpA; Pianezza, Italy). Twenty test pieces (63.5 x 12.7 x 4.0 mm) were cut

and shaped from each plate of thermoset and composite. Flexural testing was conducted according to ASTM-D790 "Standard test method for flexural properties of unreinforced and reinforced plastics and electrical insulating materials," using INSTRON equipment model 5569 (INSTRON; Norwood, MA, USA). Test pieces (127 x 12.7 x 3.2 mm) were cut and shaped from each plate of composite specimen.

Scanning electron microscopy (SEM) was conducted with a Leica Model 440 (Carl Zeiss Microscopy; Jena, Germany) under the same conditions described by Silva et al. [35].

RESULTS AND DISCUSSION

Chemical characterizations—sisal fiber

Table I displays the composition and properties of the sisal fiber. The moisture and ash content values obtained in this study were in agreement with those described in the literature (moisture content 5.0%–10.0%; ash content 0.5%–4.0%) [36–38].

The cellulose, hemicellulose, and lignin contents were in agreement with the results reported by Martin et al. [13] and Ramires et al. [39] for SF grown in Brazil. Sisal fibers have higher values of elongation (Table I) than other lignocellulosic fibers, such as curaua and jute (0.8% and 0.7%, respectively) [30, 40]. In contrast, the tensile strength of the SF used in our study was lower than that of lignocellulosic curaua and jute fibers (636 and 466 MPa, respectively) [30, 40]. The high cellulose content and corresponding high degree of crystallinity, combined with the allowable elongation of SF, resulted in a fiber with excellent potential for use as a reinforcement agent in polymeric matrices.

Property	Content
Moisture (%)	9.9 ± 0.1
Ash (%)	0.49 ± 0.04
Total Klason lignin (%)	9.3 ± 0.1
Holocellulose (%)	85.3 ± 0.9
α-cellulose (%)	64.2 ± 1.0
Hemicellulose (%)	21.1 ± 0.9
Crystallinity index (%)	60
Average diameter (μm)*	316 ± 49
Elongation (%)	1.7 ± 0.2
Tensile strength (MPa)	175 ± 15
*Calculated using SEM (scanning electronic microscopy, figures not shown)	

I. Properties of sisal fiber.

IGC—sisal fibers, sodium lignosulfonate, and thermosets

Inverse gas chromatography results were used to evaluate the dispersive energy and acid/base components of the materials (**Table II**). These components can be an indication of the interactions that occur between SF and the matrix within the interfacial region, which have a strong influence on the mechanical properties of the composite.

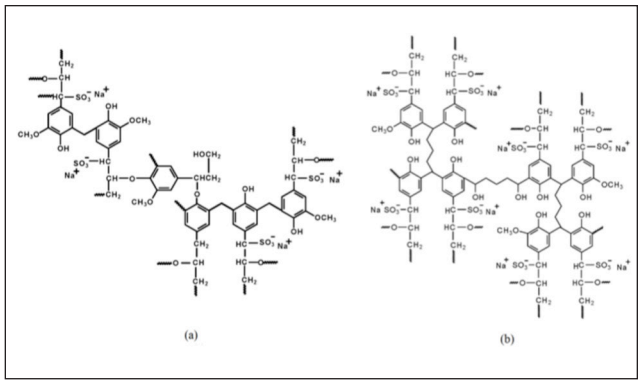
The AN_S/DN_S ratio was equivalent for the three thermosets tested (Table II), indicating a predominance of acidic sites on the surfaces of these materials. However, when the AN_S and DN_S values were considered separately, it was clear that the use of SL increased the AN_S and DN_S values for SLFT compared to phenol-formaldehyde thermoset (PFT) (Table II). The increase of AN_S and DN_S values most likely occurred because of the high proportion of acceptor and donor groups, such as hydroxyl and methoxyl groups present in the SL-based matrix (**Fig. 2**), as indicated by the AN_S (3490 J mol^{-1}) and DN_S (2931 J mol^{-1}) values for isolated SL (Table II). The use of glutaraldehyde, in place of formaldehyde, for the preparation of the thermoset resin precursor resulted in a thermoset (SLGT) with AN_S and DN_S values higher than those of SLFT. These values may be due to the presence of free hydroxyl groups coming from glutaraldehyde that do not react during the crosslinking (Fig. 2) because glutaraldehyde is a dialdehyde.

The replacement of phenol for SL did not alter the free surface energy (γ^d_S) of SLFT compared to PFT (Table II). The value of γ^d_S can be considered as an indication of the density of nonpolar sites on the surface of the material [41]. Thus, the introduction of typical SL moieties did not increase the proportion of nonpolar sites in the matrix. As shown in Table II, isolated SL exhibited a lower value of γ^d_S (31 mJ m^{-2}) than the derived thermosets.

The replacement of formaldehyde for glutaraldehyde in the matrix increased the value of γ^d_S (i.e., the nonpolar character) of SLGT compared to SLFT (Table II). This increase in the free

Samples	γ^d_S (mJ m^{-2})	AN_S (J mol^{-1})	DN_S (J mol^{-1})	AN_S/DN_S	Character
SL	31	3490	2931	1.2	Acid
PFT*	34	3074	2276	1.4	Acid
SLFT	34	4585	3282	1.4	Acid
SLGT	42	4830	3585	1.4	Acid
Sisal fiber*	21	4676	2669	1.8	Acid
*Data from Megiatto Jr. et al. [26].					

II. Free surface energy dispersive component (γ^d_S) and acid-base (AN_S and DN_S) properties of sodium lignosulfonate (SL) and the following thermosets: sodium lignosulfonate-formaldehyde (SLFT), sodium lignosulfonate-glutaraldehyde (SLGT), and phenol-formaldehyde (PFT).



2. Hypothetical structures of (a) sodium lignosulfonate-formaldehyde thermoset (SLFT), and (b) sodium lignosulfonate-glutaraldehyde thermoset (SLGT), based on the general reactivity of aldehydes with phenols in alkaline medium [16].

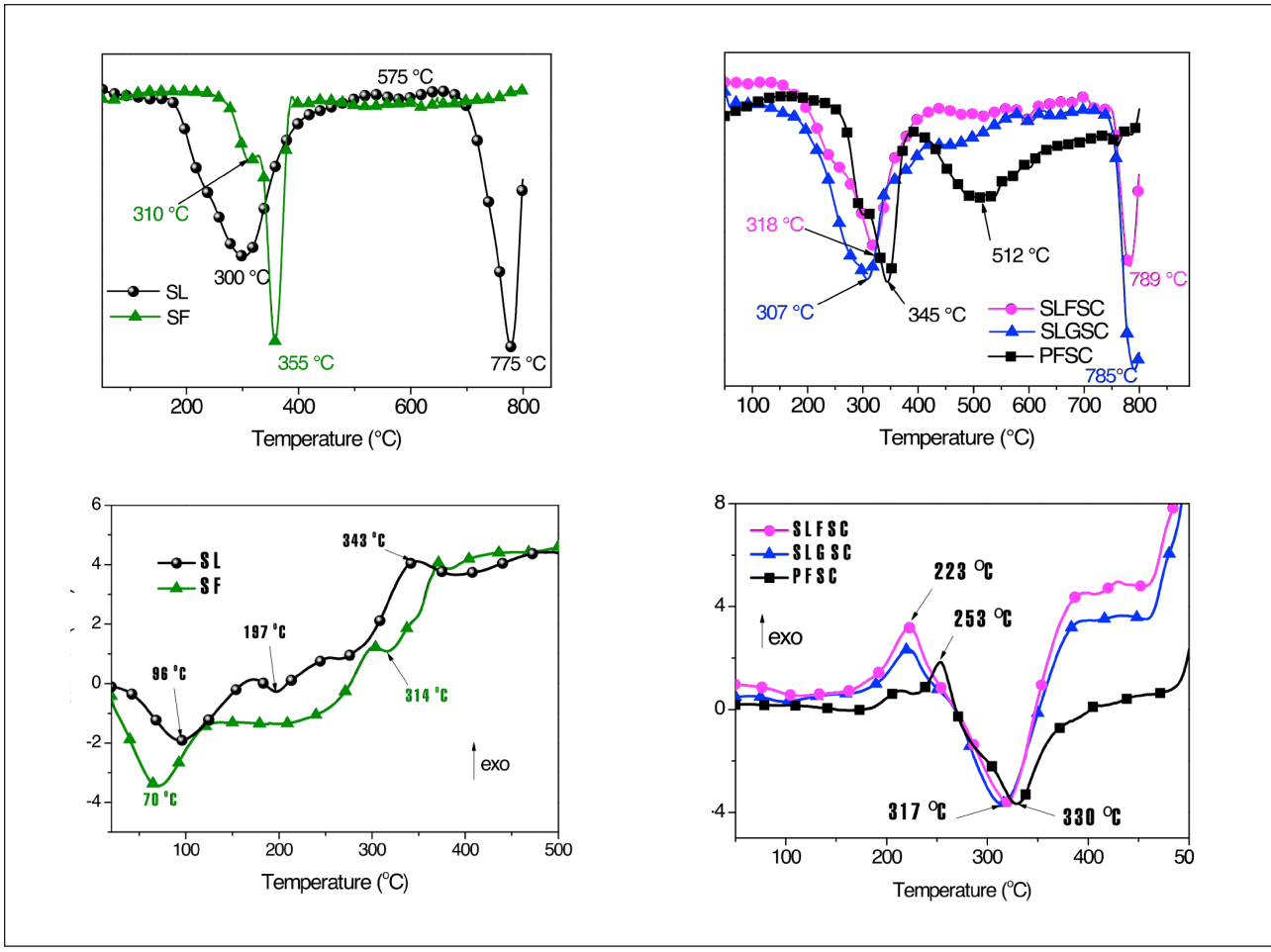
surface energy most likely occurred due to the presence of longer aliphatic chains in SLGT (Fig. 2) compared to those in formaldehyde.

The SLFT exhibited a dispersive component value closer to that of SF than that of SLGT, suggesting that the interactions between regions of low polarity, such as aromatic rings and aliphatic moieties of SF and SLFT, are favored.

Thermal analyses

Phenolic composites can be used in applications as mass transit, marine, offshore and construction materials; all require components that are fire- and high-temperature resistant [42, 43]. In this context, the thermal decomposition of phenolic-type composites has important implications regarding their suitability for some applications. In this study, the thermal stability of the composites was assessed by TGA and DSC.

Figure 3 shows the differential thermogravimetric (dTG) and DSC curves for the sisal fibers, SL, and composites prepared in our present study. Up to 100°C, the thermogravimetric (TG) curve (not shown) indicated that SF experienced a loss in mass of 3.5% related to the release of water (H_2O) molecules (as also indicated by the endothermic peak at 70°C in the DSC curve, Fig. 3c), which were mainly linked to the hemicellulose polar groups. Water preferentially links along the hemicellulose polar groups because the



3. dTG and DSC curves of sisal fiber (SF) and sodium lignosulfonate (SL) (a, c); sodium lignosulfonate-formaldehyde-sisal composite (SLFSC), sodium lignosulfonate-glutaraldehyde-sisal composite (SLGSC), and phenol-formaldehyde-sisal composite (PFSC) (b, d); N_2 atmosphere 20 mL min^{-1} with a heating rate of 10°C min^{-1}.

macromolecule is within the noncrystalline domain, making it more hydrophilic than cellulose, which is located mainly in crystalline domains. The peaks at 310°C and 355°C were indicative of hemicellulose and cellulose decomposition, respectively (Fig. 3a), which led to the exothermic peak observed at 314°C in the DSC curve (Fig. 3c). The TG curve (not shown) indicated that lignin started to thermally decompose above 400°C, a process initiated by dehydration and generation of unsaturated side chains. Another stage of the TG curve involved the decomposition of aromatic rings and the breaking of C-C bonds present throughout the lignin structure accompanied with the loss of water, carbon monoxide (CO), and carbon dioxide (CO_2), followed by structural rearrangement [38, 44]. Due to the low content of lignin in the fibers (Table I), the peak corresponding to the maximum weight loss of the decomposition step of this macromolecule was not observed in the dTG curve (Fig. 3a).

The volatilization of residual moisture led to the endothermic peak at 96°C in the LS-DSC curve (Fig. 3c). The peak in the dTG curve at 300°C (Fig. 3a, SL curve) was related to the maximum weight loss experienced during the first stage of SL decomposition. According to Jakab et al. [45], two steps of SL decomposition take place between 200°C and 400°C that lead to the release of H_2O, CO_2, and sulfur dioxide (SO_2), and the formation of some mercaptans. These steps were most likely represented by the large peak observed at 300°C (Fig. 3a) and are related to the peaks observed from 190°C in the DSC curve (Fig. 3c). The large peak with low intensity at 575°C may be linked to the initiation of the aromatic ring decomposition. During decomposition, a portion of the sodium that is present can form sodium carbonate (Na_2CO_3), which decomposes between 700°C and 800°C while releasing CO_2 [45]. This accompanying release of CO_2 may be indicated by the peak at 775°C (Fig. 3a), along with the final decomposition products of typical lignin moieties.

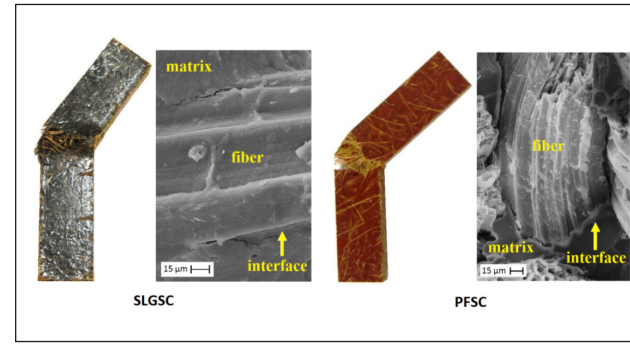
The TG curve (not shown) indicated that the composites experienced a loss in mass up to 100°C (sodium lignosulfonate-glutaraldehyde-sisal composite [SLGSC] and sodium lignosulfonate-formaldehyde-sisal composite [SLFSC] approximately 0.3%; phenol-formaldehyde-sisal composite [PFSC] approximately 2.5%), mainly due to a loss of residual moisture. Above 100°C, water molecules strongly bound to both matrix and fibril polar groups can volatize. The dTG curves indicate a maximum loss in mass at 307°C, 318°C, and 345°C for SLGSC, SLFSC, and PFSC, respectively (Fig. 3b). These peaks corresponded to the decomposition of hemicellulose and cellulose present in the fibers and the initial decomposition of SL moieties present in the matrices of SLGSC and SLFSC, as indicated by the dTG curves of isolated fibers and SL (Fig. 3a). These decompositions led to the peaks observed from approximately 315°C in the respective DSC curves (Fig. 3d). The peaks above 780°C corresponded to other stages in the decomposition process of typical SL moieties present in the matrices of SLGSC and SLFSC, such as the decomposition of aromatic rings. The PFSC composite showed an initial peak at 345°C, a temperature higher than the respective initial peaks of SLGSC and SLFSC. Nevertheless, it should be stressed that in lignocellulosic fiber-reinforced composites, the thermal stability is typically defined by the onset of decomposition of the fibers, i.e., at approximately 250°C. Thus, it can be concluded that the use of SL in the formulation of the matrices did not affect the thermal stability of the respective composites. The exothermic peaks observed from approximately 250°C (Fig. 3d) were probably correlated to residual cure reactions that took place during scanning [14].

It is worth noting that TG and/or endothermic-DSC peaks were not observed up to 100°C and at approximately 190°C; for SLFSC, therefore, this could be an indicator of the absence of formaldehyde trapped inside the composite (present as methylene glycol and/or formaldehyde, with boiling points of 194°C and -19°C, respectively). Similarly, for SLGSC, the absence of peaks between 180°C and 190°C indicated the absence of free glutaraldehyde (boiling point, 187°C).

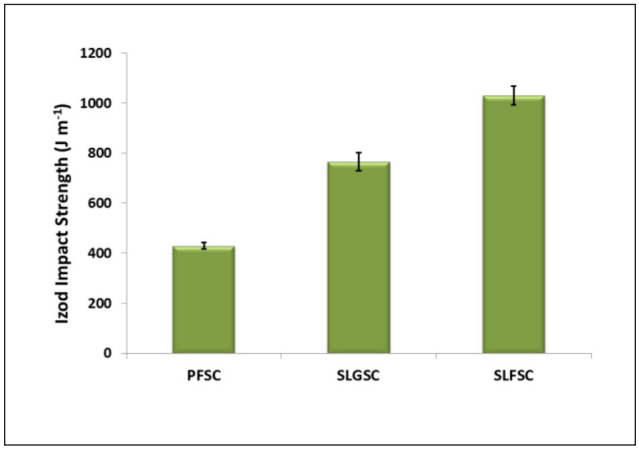
Mechanical tests

Thermosets could not be analyzed using mechanical testing (Izod Impact Strength and Flexural Test by ASTM-D156 and D790, respectively) because they were too fragile to produce samples with the dimensions specified according to testing standards. The efficiency of SF as a reinforcing agent for phenolic-type thermosets was thus demonstrated because the nonreinforced thermosets were too fragile to be analyzed; however, after the addition of fibers there was no problem in performing the mechanical tests. Scanning electron microscopy micrographs (**Fig. 4**) revealed that SF have good ability to absorb energy during mechanical testing, as indicated by the presence of cracks that propagated through the matrix, surrounding the fibers.

Impact strength is an important property of polymeric materials and a decisive parameter leading to the selection of materials for a particular application. In composites, this property is dependent on the characteristics of the matrix, the fiber used as reinforcement, and the quality of the fiber/matrix interface. **Figure 5** shows the impact strength of the composites prepared in the present study.



4. SLGSC and PFSC specimens following impact tests and the respective scanning electron microscopy images of the fractured surfaces.

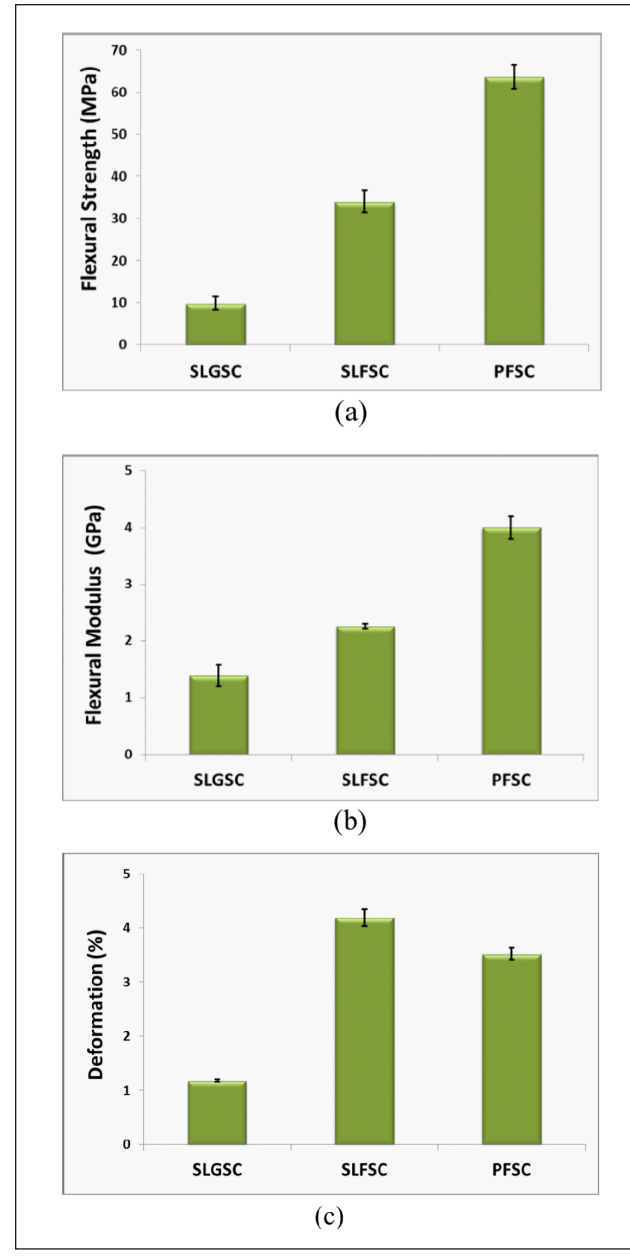


5. Izod impact strength and the standard deviation of the composites reinforced with sisal fibers (30 wt%, 30 mm) within different matrices: PFSC, SLFSC, and SLGSC.

Figure 5 clearly demonstrates that replacing phenol with sodium lignosulfonate effectively increased the impact strength of the (produced) composites (SLGSC and SLFSC) compared to the phenolic composites reinforced with sisal fibers (PFSC). This increase was especially true for SLFSC, which exhibited the highest impact strength value (1029 J m^{-1}). The higher density of basic-character sites (DN_S) in SLFT (3282 J mol^{-1}) and SLGT (3585 J mol^{-1}), when compared to PFT (2276 J mol^{-1}, Table II), resulted from the properties of the thermosets resin precursor (SLF, SLG, and PF). Thus, the high density of basic-character sites in SLF and SLG favored interactions between these resins and the acidic-character sites highly available in sisal fibers, as indicated by the value of its AN_S parameter (4676 J mol^{-1}, Table II). Thus, when SLG and SLF resins were used, the wettability of the SF by the respective resins increased compared to PF resin, leading to composites (SLGSC and SLFSC) with strong interactions at the interface that favor the transference of the load from the matrix to the fiber during impact.

It should be emphasized that the low content of sugar (0.9%, experimental) present in the SL was incorporated into the structure of the matrices because carbohydrates can act as a coreactant with phenol in the preparation of phenolic-type resins [46,47]. Furthermore, the calcium and magnesium compounds that come with the SL (1.7% magnesium, 0.2 wt% calcium, experimental) could have acted as a type of filler that was incorporated into the composites.

We observed that the presence of moieties derived from the use of glutaraldehyde in the preparation of the resin led to a thermoset (SLGT) with a higher free surface energy dispersive component (42 mJ m^{-2}, Table II, γ^d_S) than when formaldehyde was used to prepare the resin (SLFT, 34 mJ m^{-2}, Table II). The greater proximity between the γ^d_S values of SF (21 mJ m^{-2}, Table II) and SLFT, when compared to SLGT, may have benefited the interaction between the nonpolar domains of both fiber and matrix. Thus, it may have resulted in a stronger adhesion at the interface, with increased impact strength



6. (a) Flexural strength, (b) flexural modulus, and (c) deformation of the composites reinforced with sisal fibers (30 wt%, 3 cm) with different matrices: PFSC, SLFSC, and SLGSC.

as a consequence, when the respective composite was prepared (SLFSC) (Fig. 3a).

All the composites displayed the fiber bridging mechanism, as shown in Fig. 3b for SLGSC and PFSC. Fiber bridging typically is an indication of good adhesion at the fiber/matrix interface; it was observed even for PFSC, although to a lesser degree when compared to the composites based on SL. In previous studies, phenolic composites prepared from PF resins and reinforced with SF demonstrated impact strength between 340 J m^{-1} and 512 J m^{-1} [13,25,48]. Thus, the composites we prepared using SL to prepare the matrices are promising because of their high-impact strength between 780 J m^{-1} and 1029 J m^{-1}, approximate-

ly two times higher than other phenolic composites. These results meet the requirements for some automotive parts; for example, the notched impact strength for a body panel roof should be 690 J m^{-1} [49]. In our study, we used unnotched specimens, which usually lead to somewhat higher impact strength compared to notched specimens. Thus, the composites prepared exhibited impact strength comparable to or better than that required for some car parts.

Figure 6 shows the results of flexural testing of the composites. Both the flexural strength and flexural modulus demonstrated the same trend. The SLFSC exhibited higher flexural strength and modulus than SLGSC, but PFSC exhibited the highest value of flexural strength and modulus. However, SLFSC exhibited higher deformation upon breaking (4.7%) when compared to PFSC (3.6%). This set of results suggests that when the composites underwent a bending load, they experienced a different mechanism of load transfer from the matrix to the fiber when compared to the mechanism that acted during impact. In addition, the flexural strength did not appear to be as strongly influenced by the properties of the bulk of the composite as was the impact strength. The flexural and impact tests have distinct characteristics, and the properties of the outer surfaces of the samples may have had more influence on the flexural strength. Thermosets could not be analyzed using mechanical testing, as mentioned previously, but the flexural strength results may be considered as an indicator that the neat thermosets SLGT and SLFT are more fragile than the neat thermoset PFT.

CONCLUSIONS

We reported on an investigation into the use of byproducts produced by forest biorefineries and the agroindustry. Sodium lignosulfonate was used as a substitute for phenol in the preparation of resol resins, and sisal fiber was incorporated as reinforcement in the produced composites. Impact testing results demonstrated the excellent performance of the composites when phenol was replaced by sodium lignosulfonate, and the thermal stability of the composites was not altered. We highlighted the high impact strengths of both composites in which SL replaced phenol due to the importance of this property for such materials and their applications. Also, the values reached in this study indicate that such materials could be used in certain applications (e.g., in some car parts). **TJ**

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ABOUT THE AUTHORS

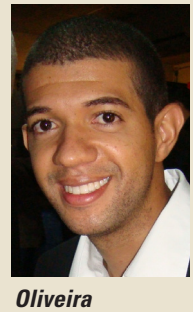
One of our areas of research focuses on the use of raw materials obtained from renewable sources in the preparation of polymeric matrix composites. This study fit well into this area, as lignosulfonate and sisal fibers were used to prepare composites. It complements previous studies where phenol and/or organosolv lignin were used to prepare the matrix, in addition to aldehydes different than glutaraldehyde.

We found it necessary to conduct an exploratory study to achieve the synthesis conditions required to prepare resins from lignosulfonate and glutaraldehyde, as well as to set parameters suitable for curing this type of resin. We found that when phenol was replaced by sodium lignosulfonate, the impact strength reached values never before achieved in our studies on composites based on phenol. This was an interesting finding, as impact strength is a very important property for composites

This research points to another way to enhance the value of lignosulfonates, which are byproducts of forest biorefinery processes. The next step is to conduct studies on the use of lignosulfonate as a macromonomer in the preparation of polyurethanes.

Silva and Ramires are postdoctoral researchers, Oliveira is a doctoral student, and Frollini is professor and head, Macromolecular Materials and Lignocellulosic Fibers Group, Institute of Chemistry of São Carlos, University of São Paulo, Brazil. Castellan is professor emeritus, Laboratoire de Chimie des Polymères Organiques, Université Bordeaux, Bordeaux, France. Email Frollini at elisabete@iqsc.usp.br.


Silva


Oliveira


Ramires


Castellan


Frollini