

## ADDING VALUE TO BRAZILIAN FIBERS: BIO-BASED MATRICES REINFORCED WITH SISAL

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### Abstract

*The aim of this study was to prepare phenolic and polyurethanic composites, using matrices derived from renewable sources and sisal fibers, a lignocellulosic fiber largely available in Brazil. Sugarcane organosolv lignin and Pinus sodium lignosulfonate were used as a substitute for phenol in the preparation of phenolic resin. Sodium lignosulfonate and castor oil were used as a substitute for polyols in the preparation of polyurethanes. Results indicated that phenolic-type composites with superior impact strength were produced when phenol was substituted for lignin or sodium lignosulfonate, as well as when formaldehyde was replaced for glutaraldehyde. Good results of impact strength have also been obtained for composites based on polyurethane-type matrices. Overall, from high content of raw material deriving from renewable sources, it has been possible to prepare composites with good properties.*

### 1 Introduction

The use of renewable raw materials obtained from diverse processes, has attracted worldwide interest. This issue has assumed even greater importance in recent years due to large expansion that can be envisioned for biorefineries that produce bioethanol. It may be expected that diverse lignocellulosic fibers will be grown to a greater extent than currently, particularly in Brazil due to the availability of land [1]. Lignocellulosic fibers obtained from plants with short growth cycles, as sisal, have been preferentially considered in our studies, with the objective of adding value to these fibers, as, for example, Brazil is the world's largest producer of sisal, but exports most of its production. Sisal lignocellulosic fibers have several advantages such as excellent mechanical properties, and they can be considered good reinforcements for polymeric matrices [2].

Sugarcane organosolv lignin (OL) and Pinus sodium lignosulfonate (SL) are obtained as byproduct in biorefineries, and they were used as substitute for phenol in the synthesis of phenolic resins. The phenolic hydroxyl groups in their structure increase the reactivity of lignin toward to formaldehyde in reactions to obtain phenolic resins [3]. Glutaraldehyde (GLU) is a dialdehyde that can be obtained by the oxidation of compounds from biomass and it was used to replace formaldehyde (FOR) in some

resins syntheses. The presence of the alcoholic hydroxyl groups in the SL and SL-GLU prepolymer allows their use as a partial substitute of polyols in the synthesis of polyurethanic matrices [4]. Castor oil (CO), obtained from renewable source, can be used directly as a raw material for the polyurethanes preparation [5].

Lignocellulosic fibers are compatible with both lignophenolic and lignopolyurethane matrices, owing to their structural similarities. The presence of polar hydroxyl groups in both matrices and main components of the lignocellulosic fibers (cellulose and lignin) favors the fiber/matrix adhesion. Besides, hydroxyl groups present in the lignocellulosic fibers can react with the isocyanate groups of MDI, leading to the chemical bonding between matrix and reinforcement [6].

## 2 Experimental

Phenol was completely replaced by OL (kindly supplied by Dedini SA-Piracicaba, São Paulo, Brazil) and SL (kindly supplied by Lignotech Brasil, São Paulo-SP, Brazil) in the synthesis of lignophenolic prepolymers (OL-FOR, SL-FOR, OL-GLU, and SL-GLU) performed as described elsewhere [7]. The lignophenolic composites were obtained by adding the sisal fibers (3 cm in length, 30 wt%, randomly distributed) to the prepolymer. Lignopolyurethanes composites were prepared by adding diphenylmethane diisocyanate (MDI), CO, SL or SL-GLU to the sisal fibers (30 wt%). In both cases, fibers were impregnated by the resins through mechanical stirring. Lignophenolic and lignopolyurethane composites were compression molded under conditions established in previous studies [8, 9]. The impact strength and flexural tests were carried out as recommended in ASTM D 256 [10] and ASTM D 790 [11], respectively.

## 3 Results and discussion

Table 1 shows the mechanical properties of all composites prepared in this study. The set of results indicated that phenolic-type composites with superior impact strength were produced when phenol was substituted for OL or SL, as well as when formaldehyde was replaced for glutaraldehyde. The good interaction of the phenolic-type resins with the sisal fibers, which has a surface with hydroxyl groups available to interact with the resin, intensified the fiber/matrix adhesion at the interface, improving the mechanical properties of the obtained composites.

Phenolic-type composites	Impact strength (J m <sup>-1</sup> )	Flexural strength (MPa)	Polyurethanic-type Composites	Impact strength (J m <sup>-1</sup> )	Flexural strength (MPa)
Phenol-FOR/Sisal	373 ± 27	63.7 ± 5.7	CO/MDI/Sisal	813 ± 58	10.9 ± 0.9
OL-FOR/Sisal	426 ± 31	21.1 ± 4.5	CO/SL/MDI/Sisal	342 ± 22	59.8 ± 3.9
SL-FOR/Sisal	1030 ± 75	34.1 ± 5.3	CO/SL-GLU/MDI/Sisal	785 ± 69	25.8 ± 2.5
OL-GLU/Sisal	329 ± 0.5	5.8 ± 1.5	SL-GLU/MDI/Sisal	779 ± 103	23.0 ± 1.2
SL-GLU/Sisal	766 ± 72	9.9 ± 3.0			

**Table 1.** Impact and flexural strength of phenolic, lignophenolic, polyurethanic and lignopolyurethanic composites.

Good results of impact strength have also been obtained for composites based on polyurethane-type matrices (Table 1). Polyurethanic composite based on castor oil (CO/MDI/Sisal: 813 J m<sup>-1</sup>) and those based on castor oil associated to sodium lignosulfonate-glutaraldehyde (CO/SL-GLU/MDI: 785 J m<sup>-1</sup>), and only based on sodium lignosulfonate-glutaraldehyde (SL-GLU/MDI/Sisal: 779 J m<sup>-1</sup>) showed impact strength very similar.

The low viscosity of the pre-polymers allowed good wettability of the sisal fiber and the presence of hydroxyl groups, as well as moieties of lignin, in matrices and fibers, led to strong interactions at the interface and allowed efficient load transfer from the matrices to the fibers. After the impact test, the *fiber bridging* phenomenon was observed in many samples of both composites (phenolic-and polyurethane-type matrices), indicating good adhesion at the fiber-matrix interface. Images of scanning electron microscopy (figures not shown) revealed a strong adhesion between fiber and matrix for all composites, this was possibly due to both the similarity of structures in the fiber and matrix, and possible reactions between hydroxyl groups of sisal fibers with isocyanate groups present in the polyurethanic matrices.

#### 4 Conclusions

The substitution of phenol by sugarcane organosolv lignin and pinus sodium lignosulfonate in the synthesis of phenolic resins resulted in composites with improved mechanical properties compared to traditional phenol-formaldehyde resins. The presence of lignin moieties in both fiber and matrix greatly improved the adhesion at fiber/matrix interface. Besides, the use of castor oil and sodium lignosulfonate-glutaraldehyde to prepare polyurethanic-type composites also resulted in composites with high impact strength. Overall, this study demonstrated that it is possible to prepare composites with good properties using high content of raw material derived from renewable resources.

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