



Phenolic and lignosulfonate-based matrices reinforced with untreated and lignosulfonate-treated sisal fibers



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ABSTRACT

The present investigation addressed the use of treated and untreated sisal fibers (3 cm, 30 wt%, randomly distributed) as a reinforcement in bio-based composites. Sodium lignosulfonate (NaLS) was used to physically treat the sisal fibers and also as a *macromonomer* to prepare phenolic-type thermosets, namely, the matrices (LCs). The introduction of NaLS moieties on the surface of the fibers and in the chemical structure of the matrix aimed to increase the affinity of the fiber-matrix interface in addition to increasing the bio-sourced character of the final material. Sisal fibers were treated (and subsequently characterized) with aqueous 5 wt% NaLS solutions *via* heating (70 °C/1 h, SFT1), ultrasound irradiation (1 and 2 h, SFT2 and SFT3, respectively), and room temperature treatment at 24 h followed by ultrasound (1 h, SFT4). Briefly, considering only some properties of the composites, the following results can be highlighted: all the phenolic composites (PC, control samples) exhibited impact and flexural strengths considerably greater than the unreinforced phenolic thermoset (PT). The phenolic composite reinforced with untreated sisal fiber (PC-UF) and PC-SFT4 exhibited an impact strength of approximately 435 Jm⁻¹, and the others, PC-SFT1 and PC-SFT2, had a tendency to have a greater impact strength, with the exception of PC-SFT3 when compared with PC-UF. Based on the results exhibited by the PC-treated fibers, only LC-SFT1 and LC-SFT2 were prepared among the LC-treated fibers besides LC-UF. The set of PCs exhibited a lower impact strength than their LC composite counterparts. For example, the impact strength of LC-UF was approximately 1000 Jm⁻¹ (compared to approximately 435 Jm⁻¹ for PC-UF). This is a very good result for a thermoset matrix reinforced with natural fibers and clearly shows that the fiber-matrix interaction at the interface was favored when the thermoset was prepared from NaLS, and then, the load received during the impact was more efficiently transferred to the sisal fibers. SEM images showed good adhesion at the fiber-matrix interface of LC-treated fibers due to the similarity of the chemical structure of the matrix and treated sisal fiber. Concerning the assessment of the thermal conductivity (at 10, 25 and 50 °C), only the thermosets (phenolic, PT, lignosulfonate-based, and LT), the composites reinforced with untreated fibers (PC-UF and LC-UF), and PC-SFT2 (due to its high impact strength) were evaluated. The results showed no significant variation in the thermal conductivity as a function of temperature. There was no significant variation in the thermal conductivity of both thermosets (the thermal conductivity of PT and LT at 25 °C, for instance, were 0.30 and 0.28 Wm⁻¹K⁻¹, respectively) to their respective composites (at 25 °C, the thermal conductivity was 0.40 and 0.36 Wm⁻¹K⁻¹ for PC-UF and PC-SFT2, respectively, and 0.24 Wm⁻¹K⁻¹ for LC-UF). A tendency towards lower conductivities (at 10, 25 and 50 °C) was observed for LC-UF when compared with PC-UF. Overall, these results meet the current expectations concerning the production of materials prepared from a high percentage of raw materials from renewable sources with good properties.

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1. Introduction

Sisal, which grows in Brazil, is an *Agave sisalana* species and, as a tropical plant resistant to dry and hot climates, is well adapted to the semi-arid climate of Northeast Brazil (Brasfibra, 2016). Brazil is the largest world producer of sisal and practically defines the worldwide production, as shown in Fig. 1.

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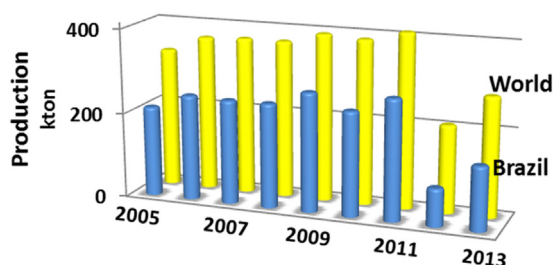


Fig. 1. Production of sisal from 2005 to 2013 (Faostat, 2016).

In 2012, due to some local problems, mainly a prolonged drought, the Brazilian production of sisal decreased considerably, and in 2013, there was an increase in production compared to the previous year both of which impacted world production (Fig. 1).

The main products marketed are biodegradable yarns used in handcrafted applications, ropes, carpets, and other products. Our goal is to add value to sisal through the development of research in diverse areas (Lacerda et al., 2015; Rodrigues et al., 2014; Santos et al., 2015), including the use of lignocellulosic sisal fiber as reinforcement in polymeric matrices (de Oliveira et al., 2015; Santos et al., 2014; Santos et al., 2014), such as phenolic matrices. In this context, in the present study, treated and untreated sisal fibers were used as reinforcements in phenolic type polymeric matrices.

Composites reinforced with lignocellulosic fibers have been shown to be viable alternatives in many applications for replacing polymers reinforced with glass or other fibers (La Mantia and Morreale, 2011; Mahendran et al., 2013; Terzopoulou et al., 2015).

Lignocellulosic fibers (such as sugarcane bagasse, sisal, coir, hemp, flax, jute) have been used in several applications for a long time, and their use as reinforcements in polymeric matrices have been technologically relevant, as a result of their application in various industrial sectors, such as the automotive (Salazar et al., 2011; Xia et al., 2016), construction (Kulma et al., 2015), packaging (Berthet et al., 2015), aerospace (Scarponi, 2015) and interior design sectors (Zandvliet et al., 2014).

Phenolic resins result from the polycondensation of phenol and aldehydes and are among the most common synthetic thermosets and are used in a wide variety of applications (Feng et al., 2016; Liang et al., 2016; Thakur and Thakur, 2014). These thermosets have desirable properties, such as outstanding mechanical performance, dimensional stability, and wear resistance even at high temperatures (Alonso et al., 2011; Frollini et al., 2013b; Frollini and Castellan, 2012; Liu and Laborie, 2011; Zhang et al., 2016).

The characteristics of the composite fiber/matrix interface play an important role in its mechanical properties as the load transfer from the matrix to the fibers occurs through the interface. The material properties may be improved if the interactions at the fiber/matrix interface are intensified. Several treatments are suggested in the literature to modify the fiber surface and intensify the fiber/matrix adhesion (Khanam, 2010; Kushwaha and Kumar, 2010; Lin and Renneckar, 2011; Paul et al., 2008; Zhu et al., 2015). However, the modifications must involve, at least partially, reagents obtained from renewable sources to not invalidate the use of vegetable fibers as reinforcement.

In prior studies, lignocellulosic fibers were modified with different chemicals for use as reinforcements in phenolic composites (Botaro et al., 2010; Megiatto et al., 2010, 2008, 2007). Sugarcane bagasse and curaua fibers were oxidized using chlorine dioxide (ClO_2) followed by grafting furfuryl alcohol (FA) (Trindade et al., 2005). Sisal fibers were modified by $\text{K}_2\text{Cr}_2\text{O}_7$ or ClO_2 oxidation followed by treatment with FA or poly(furfuryl alcohol) (PFA) (Megiatto et al., 2007). In another study, sisal fibers were modified through a reaction with hydroxymethylated lignins (Megiatto et al.,

2008). Additionally, mercerization treatment (NaOH 2%) and esterification with benzophenone tetracarboxylic dianhydride (BTDA) have been applied to sisal fibers (Botaro et al., 2010). Overall, these treatments led to an improvement in the interactions between the fiber and the matrix at the interface, which could be observed through improvements in the properties of water absorption of the phenolic composites reinforced with these fibers. Nevertheless, the treatments mentioned are aggressive to the fiber, and there was some fiber degradation affecting the fiber's action as a reinforcement and leading to a decrease in the impact strength of these materials compared with unmodified fiber reinforced composites.

Due to the reasons mentioned previously, treatments that do not involve the chemical modification of the fibers, such as adsorption of compatibilizing agents on the fiber surface, were considered in this work. Therefore, seeking to improve the fiber/matrix interfacial adhesion, sodium lignosulfonate (NaLS), which is a macromolecule obtained from a renewable source, was used as an agent of fiber modification through adsorption on the fiber surfaces combined with heating and ultrasound irradiation.

Wood refinery has been an important resource in obtaining the major components of lignocellulosic materials (cellulose, hemicellulose and lignin) allowing the separated use of these materials to develop alternative chemicals based on renewable sources (Cherubini and Strømman, 2011; Romaní et al., 2011). Lignosulfonates (Fig. 2b) can be obtained as the product of the sulfite pulping of wood. Unlike lignin, the lignosulfonates are water soluble due to the introduction of sulfonate groups (Fig. 2b) (Fredheim and Christensen, 2003).

The presence of polar hydroxyl groups in both the phenolic matrix (Fig. 2a) and in the main components of the lignocellulosic fibers (cellulose and lignin, Fig. 2c and b, respectively) favors the fiber/matrix adhesion compared with hydrophobic thermoplastic matrix composites, such as those based on polyolefins. Lignins are complex macromolecules with phenolic-type aromatic rings in their structures, Fig. 2d. This characteristic, which is common to lignosulfonates and also to phenolic matrices, as outlined in Fig. 2a and b, represents another possibility to improve the interaction between the fiber and the phenolic polymer matrix (Fig. 2a) if lignosulfonate is present on the fiber surface.

With respect to phenolic-type matrices, several studies have been carried using lignin extracted using an organosolv process from sugarcane bagasse as a total or partial replacement for phenol in the preparation of phenolic resins (Hoareau et al., 2006; Ramires et al., 2010a) because in its complex structure there are phenolic aromatic rings, Fig. 1d. Within this context, it is also expected that NaLS will be a potential replacement for phenol in phenolic resins (Da Silva et al., 2012). In the present study, NaLS was also used to prepare the matrices as well as to modify the surface of the fibers, which, in turn, reinforced the matrices leading to an intensification of the interactions at the fiber/matrix interface and obtaining composites prepared from a high content of renewable raw materials.

In summary, in the present study, phenolic-type matrices were first reinforced with untreated sisal lignocellulosic fibers and treated fibers that were, previously modified physically through the adsorption of lignosulphonate on the surfaces. Subsequently, lignosulphonate replaced phenol in the preparation of the phenolic-type resins with the goal to use these resins in the production of matrices reinforced by untreated and treated sisal lignocellulosic fibers.

The use of composites reinforced with lignocellulosic fibers in the automotive among other industries places importance on studies related to the thermal conductivity of these materials. This property is relevant, for instance, in the maintenance of air conditioning inside (Kim et al., 2006). In the present study, the thermal conductivity were determined for some composites.

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