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## Mechanical behavior of natural fiber composites

Andressa Cecília Milanese\*, Maria Odila Hilário Cioffi and Herman Jacobus Cornelis Voorwald

*UNESP – Univ Estadual Paulista, FEG – Faculdade de Eng de Guaratinguetá,  
Fatigue and Aeronautics Materials Research Group, Av Dr Ariberto Pereira da Cunha n°333  
12516-410 – Guaratinguetá/SP – Brazil*

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### Abstract

The use of natural fibers as reinforcement in polymeric composites for technical applications has been a research subject of scientists during the last decade. There is a great interest in the application of sisal fiber as substitutes for glass fibers, motivated by potential advantages of weight saving, lower raw material price, and ecological advantages of using green resources which are renewable and biodegradable.

Castor oil, a triglyceride vegetable that has hydroxyl groups, was reacted with 4,4' diphenylmethane diisocyanate (MDI) to produce the polyurethane matrix. Woven sisal fibers were used untreated and thermal treated at 60°C for 72h, and the composites were processed by compression molding.

The present work study tensile behavior at four composites: dry sisal/polyurethane, humid sisal/polyurethane, dry sisal/phenolic and humid sisal/phenolic resin. The moisture content influences of sisal fibers on the mechanical behaviors were analyzed.

Experimental results showed a higher tensile strength for the sisal/phenolic composites followed by sisal/polyurethane, respectively. In this research, sisal composites were also characterized by scanning electron microscopy.

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*Keywords:* sisal fiber; castor oil based polyurethane resin; phenolic resin; tensile strength; scanning electron microscopy

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### 1. Introduction

Natural fibers, classified as lignocellulosic materials, have been used as reinforcement material once present innumerable advantages, such as: low specific mass, easy handle, biodegradability and renewable

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\* Andressa C. Milanese. Tel.: +55-12-31232865; fax: +55-12-31232852.

E-mail address: [pos06001@feg.unesp.br](mailto:pos06001@feg.unesp.br); [andressa.cm@ig.com.br](mailto:andressa.cm@ig.com.br).

resource, insulator thermal, electric and acoustic, aesthetic aspects, non-toxic, beyond low cost [1-3].

Brazil has a great production of sisal and export for the entire world, with a yearly production of 111.900 tons, in 2005. It is also responsible for 56% of the worldwide production [4]. The main producer's states are Bahia - 93.5%, Paraíba - 3.5% and Rio Grande do Norte - 3%, semiarid region [4].

Sisal fibers are extracted from *Agave sisalana perrine* leaves, monocotyledon originated from Mexico [1,5,6]. Each leaf of sisal provides, in weight, 4% of staple fibers, 0.75% cuticle, 8% dry matter and 87.25% water [1,7]. The microstructure of the natural fibers are constituted from cellulose fiber reinforced an amorphous matrix of the hemicellulose and lignin. These celluloses consist of microfibrils dispersed all along the length of the sisal fiber. Natural fibers moisture content in general is placed between 5 to 20% and due to the hydrophilic characteristic cellulosic fiber, once this characteristic affects the mechanical properties of the composites because the moisture can lead to poor processability and porous products during processing of composites [7,8].

According Li, Mai and Ye [7], to modify the fiber surface structure in order to enhance the bond strength between fiber and matrix and reduce water absorption of sisal fiber chemical and thermal treatment are used. There are many reports about sisal fibers composites, Paiva and Frollini [9] studied unmodified and modified surface sisal fibers by mercerization (alkali treatment) using NaOH 10%, esterification (succinic anhydride) and ionized air treatment on phenolic and lignophenolic matrixes. The study showed an improvement on fiber/matrix interfacial adhesion by mercerization and esterification when compared to ionized air treatment. Mwaikambo and Ansell [10,11] and Rong et al. [12] also observed the fiber surface topography and crystallographic index changes with mercerization treatment. However they observed yet that depending on the NaOH concentration a reduction of fiber thermal resistance is promote. Bismarck et al. [13] reported that the sisal fibers thermal stability is not affected by dewaxing treatment while the mercerization and methyl methacrylate grafting increases the maximum decomposition temperature by 10°C as compared to untreated fibers. Jacob et al. [6] investigated the influence of mercerization (NaOH 4%), silane and thermal (150°C for 8h) treatments on the tensile strength in woven sisal fabric reinforced natural rubber composites. The study shows that the highest values are exhibited by thermally treated composites besides provide better adhesion and a stronger interface than other chemical modifications.

Castor oil is a vegetable triglyceride, not employed for feeding. The molecule is, characteristically, formed by hydroxyl groups and applied as a polyol in the synthesis of cross-linked polyurethane (PU) [14]. Viscous liquid castor oil is obtained from expressing or extracting with solvent from *Ricinus communis* plant seeds, which belong to the *Eurphorbiaceae* family [15,16]. Main producers of castor plants are India, China and Brazil, which were responsible for 92% of the worldwide production, in 2001 [17]. There are different varieties of castor seeds, but in average it is possible to obtain 46 to 55wt% of oil [16]. This oil is a natural resource where 87-90% of the fatty acid presents in their constitution is the ricinoleic acid [14]. The use of this oil on the synthesis of PU produces a polymer less aggressive to humans and environment [18].

Silva [3] studied the behavior of slabs from castor oil based polyurethane resin with coconut and sisal as plain weaves; unidirectional short fibers (10 mm of length) and unidirectional long fibers. Results show sisal fibers present the best results when compared to coconut fibers. The raise of fibers content fraction increase tensile strength, stiffness and water absorption but decrease the flexural strength.

Polymeric laminates of epoxy and castor oil based polyurethane resins reinforced unidirectional sisal fibers were studied by Carvalho [19] as reinforce of timber wood. It was observed that the use of these composites is technically viable to application as reinforce. Mercerization treatment (NaOH 10%) on the sisal woven fabric for an hour reduces the composites variability on tensile behavior, however decreases stiffness and tensile strength.

The study of sisal fiber and castor oil based polyurethane as raw material in the production of composites contribute to environmental preservation once these materials are derived from natural, biodegradable and renewable resources. The objective of the present study is to characterize tensile properties of natural composites manufactured by compressing molding. The main purpose of using a thermal treatment in the sisal fibers is to promote the fiber surface modification and improve fiber/matrix adhesion.

## 2. Experimental

Woven sisal fabric was obtained from the Northeast region of Brazil and received in form of plain weave. The fabric presents two millimeters of thickness and a fiber diameter of 100-200 $\mu$ m.

Fibres in natural condition, denominated “humid”, and fibers thermally treated in the oven at 60°C for 72 hours, denominated “dry”, were used as reinforcement. Determination of moisture regain (*h*) in the sisal fibers was calculated according to the ASTM D1348 standard [20], method A.

As matrixes the castor oil based polyurethane and the phenolic resins were used. The castor oil based polyurethane is cured at room temperature. Kehl Industry Ltda from Brazil provides these reagents and has its patent. It is a bi-component formed by a polyol and a pre-polymer. The polyol has yellow colour and density at 1.0-1.2 g/cm<sup>3</sup>. The polyol components can be available as bio-based materials [21], it is soluble in water and produces biodegradable residue [22]. The pre-polymer IC201 is composed by 4,4'-methylenediphenyl diisocyanate (MDI) with a density at 1.24 g/cm<sup>3</sup>.

Cascophen RS216M is a synthetic phenolic resin based-water with room temperature cure and manufactured by Alba Adhesives Ind. Com. Ltda. It is formed from a liquid resin and its hardener (formaldehyde) that presents dynamic viscosity of 0.53-0.65 Pa.s and gel time around 3.5-6.0 hours at 21°C [23].

Reagents were mixed according to the stoichiometric quantity of 2:1 in mass of polyol and isocyanate, respectively and 5:1 in mass of phenolic and catalyzer, respectively. The components were manually mixed about five minutes, followed by deposition on silicon mold with 3.3 millimetres of thickness.

Woven sisal fabric composites with 33-44 wt% of reinforcement were prepared by compress molding at room temperature. The components of resins were manually mixed and shed upon fibers. Laminate thickness is the equivalent of a fabric layer and samples were removed from the mold after 4-8 days processed. The fibers were arranged between flat plates of glass pressed after extraction of the bubbles with a metal roller. Plastic sheets were used as release agent to polyurethane laminates.

Tensile specimens of composites were prepared in agreement to the ASTM D3039 [24] and resin specimens according to ASTM D638 [25]. Tensile specimens of PU resin and phenolic/sisal fibers were tested at a rate of 10 mm/min. Phenolic resin and PU/sisal fibers composites were tested at a rate of 0.2 mm/min and 5 mm/min, respectively. Minimums of six specimens per test condition were tested.

Tensile tests were performed using a universal machine, INSTRON, model 8801. All tests were carried out at room temperature. Samples fracture surface used in the tensile tests of resins and laminates were analyzed by scanning electron microscopy (SEM).

## 3. Results and Discussion

Table 1 shows on the tensile strength and its respective elongation for polyurethane and phenolic resins and laminates specimens tested.

The tensile strength of polyurethane (PU) resin is 2.5 MPa and its elongation at maximum load and break are 29.4% and 31.2%, respectively. Results show low precision on the tensile strength, which is observed by the high coefficient of variation produced. The PU resin presents high elongation until the

rupture showing to be a ductile-fragile material. Low tensile strength values are consequence a lot of voids that are formed during the cure process. These voids act as stress concentration and are responsible to the propagation of cracks during tensile tests. Voids presence shows a great influence on the tensile strength, which can be confirmed by the decreasing in this property according to the increase in the voids content. However, the influence on the elongation in not significant to the data indicated in Table 1.

Table 1. Tensile data of resins and laminates

Materials	PU resin	Phenolic resin	PU/humid sisal $h=17.3\%$	PU/dry sisal $h=4.1\%$	Phenolic/humid sisal $h=16.5\%$	Phenolic/dry sisal $h=6.7\%$
<b>Properties</b>						
Tensile strength at yield (MPa)	2.5	4.9	17.0	16.9	25.2	24.9
Standard deviation	0.4	1.8	2.0	1.0	2.5	1.3
Coefficient of variation (%)	17.8	36.5	11.9	5.86	9.98	5.32
Elongation at yield (%)	29.4	0.14	8.0	6.2	7.9	8.7
Standard deviation	2.2	0.06	0.4	0.3	0.4	0.5
Coefficient of variation (%)	7.62	41.3	4.8	5.52	5.26	5.29
Elongation at break (%)	31.2	0.16	11.3	8.0	8.5	9.1
Standard deviation	3.9	0.05	2.2	1.2	0.8	0.5
Coefficient of variation (%)	12.4	34.0	19.3	15.2	9.65	5.75

Tensile strength of phenolic resin is 4.9 MPa and its elongation at maximum load and break are 0.14% and 0.16%, respectively. Results show low precision on the tensile strength values considering that the values scattering produce a high coefficient of variation. Phenolic resin presents low elongation at break, which is associated to the brittleness characteristic of this material. During the cure process the resin shows the presence of discontinuities like microvoids or microbubbles.

The tensile strength of PU/humid sisal is 17.0 MPa and its elongation at maximum load and break are 8.0% and 11.3%, respectively. PU/humid sisal laminate presents elongation at break higher than 11%, characteristic of ductile material. Tensile strength of PU/humid sisal laminate shows an increase about 7 times with the addition of humid sisal fibers when compared to the PU resin. Fig. 1 shows the fracture surface to the PU/humid sisal laminate. In Figs. 1(a) and 1(b) the presence of voids in the resin that were formed during polymerization process is effective. Pull-out fibers of laminate is observed in the Fig. 1(b). Regarding fiber surfaces, Figs. 1(a) and 1(c), was not observed the presence of matrix adhered to the fibers, showing the low adhesion between fiber/matrix.

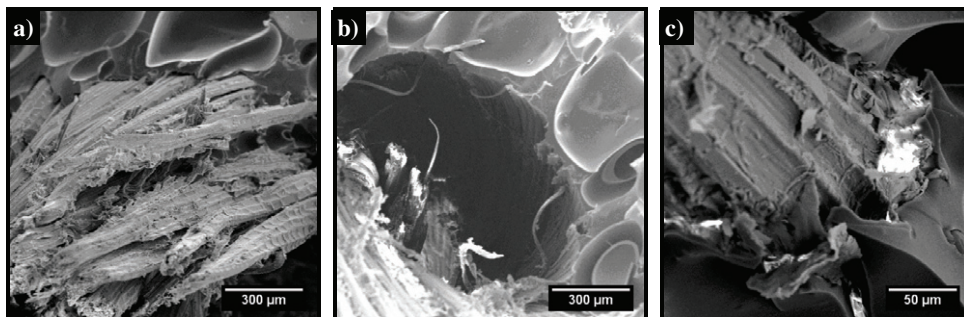


Fig. 1. SEM of fracture surface on the PU/humid sisal. (a) absence of matrix on the sisal fibers (100x); (b) pull-out and voids on the resin (100x); (c) adhesion fiber/matrix (500x)

Tensile strength of PU/dry sisal is 16.9 MPa and its elongation at maximum load and break are 6.2%

and 8.0%, respectively. Polyurethane/dry sisal laminate presents elongation at break higher than 8%, characteristic of ductile material. Tensile strength value of PU/dry sisal laminate shows an increase about 7 times when compared to the PU resin, which can be associated to the reinforcement by dry sisal fiber exposed at 60°C to 72 h. It is important to visualize on Figs. 2(a) and 2(b) the presence of matrix adhered on fibers surface, phenomena attributed to the fibers drying process. Due to this fact, it was concluded that the absence of water in the fibers collaborates to sisal fiber polyurethane matrix interface. A combination of interlaminar and intralaminar fractures and large amount of resin adhered on to the fibres surface can be observed in both SEM pictures, indicating high fibre/matrix adhesion.

The tensile strength of PU/humid sisal and PU/dry sisal laminates present similar values. Moisture decreasing proves, in consequence, a reduction in the elongation, which was not considered suitable to application as PU/sisal composite in structures, otherwise, can be observed a reduction in the standard deviation for tensile strength, favorable factor to this material.

Average tensile strength of phenolic/humid sisal laminate is 25.2 MPa and its elongation at maximum load and break are 7.9% and 8.5%, respectively. Phenolic/humid sisal laminate presents elongation at break higher than 8%, characteristic of ductile material. Tensile strength of phenolic/humid sisal laminate shows an increase about 5 times in comparison to the phenolic resin, which is associated to the humid sisal fibers reinforcement. Results show high precision by the tensile strength and elongation values considering that these values show low standard deviation and low coefficient of variation.

Tensile strength of phenolic/dry sisal laminate is 24.9 MPa and average elongation at maximum load and break are 8.7% and 9.1%, respectively. Phenolic/dry sisal laminate presents elongation at break higher than 9%, characteristic of ductile material. Tensile strength of phenolic/dry sisal laminate shows an increase about 5 times with the addition of dry sisal fibers in the oven for 72 hours when compared to the phenolic resin. Figs. 2(c) e 2(d) shows the fracture surface to the phenolic/dry sisal laminate. In Fig. 2(c) presents a large amount of resin adhered on to the fibres surface and Fig. 2(d) shows the fiber broken end from transversal fracture of dry sisal, delamination occurred in this case, explained by step formation.

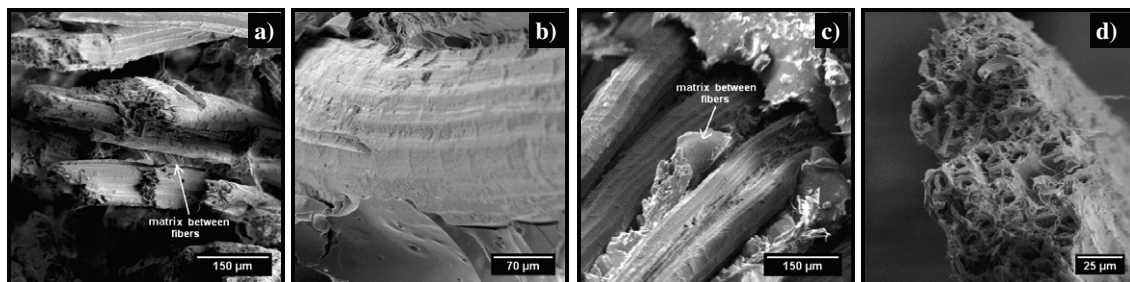


Fig. 2. SEM of fractures surface. (a) PU/dry sisal: matrix between fibers (200x); (b) PU/dry sisal: adhesion fiber/matrix (350x); (c) phenolic/dry sisal: matrix between fibers (200x); (d) phenolic/dry sisal: fiber broken end of dry sisal (750x)

The tensile strength values of phenolic/humid sisal fibers and phenolic/dry sisal fibers laminates vary at 25 MPa. The influence of moisture reduction for sisal fiber properties was observed by the increase of standard deviation on the tensile strength and in the elongation of laminate, favorable factors to phenolic/sisal laminate application as structures components.

The absence of moisture in the sisal fibers collaborates with fiber/matrix adhesion, showing the requirement of thermal treatment. Regarding to the application of sisal fibers as reinforcement on the phenolic matrix is important to show that laminates specimen present low values of variation coefficient for the tensile strength and the elongation. In opposite, of the phenolic resin that presents high values of variation coefficient, attributed to manufacturing process.



#### 4. Conclusions

Tensile strength at yield of polyurethane based on castor oil is 2.5 MPa with a correspondent elongation at 29%, which characterize a ductile behavior. Phenolic resin behaves as a fragile material. This material presents a tensile strength at yield of 4.9 MPa and an elongation of 0.13%. After polymerization, it was observed a great volumetric retraction on the specimens. It was possible to verify the existence of heterogeneity into the sample by scanning electron microscopy.

Thermal treatment on the PU/sisal laminates it was not suitable to application of this material as structural reinforce when is considering its tensile behavior, but thermal treatment of sisal is indicated to phenolic/sisal laminates because the treatment causes a decrease to standard deviation on the tensile strength and increases this elongation. Phenolic/sisal fiber laminate presents the biggest tensile strength (25MPa) followed by PU/sisal laminates (17MPa).

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