Degradability of Epoxy/Sisal Fiber Composites via Simulated Soil

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Abstract: The increase in the disposal of new polymeric materials is growing considerably in recent years, causing a major environmental impact. In view of this factor, many researchers have been studying and producing biodegradable composites whose shorter time to degradation reduces the volume of waste in landfills. Reinforcements made from natural fibers, especially sisal, has been much used in these new composites due to their low density, because they are derived from renewable source, are not toxic and their low cost compared to synthetic fibers. In view of this need, this study evaluated an epoxy/sisal composite via TGA (Thermogravimetric Analysis), DSC (Differential Scanning Calorimetry), the impact resistance and the mass variation evaluation before and after exposure in simulated soil for a period of 8 weeks.

Keywords: Biodegradation, epoxy resin/sisal composite, simulated soil, impact resistance, thermal analysis.

1. INTRODUCTION

Researchers around the world seek to study and produce composite materials that are biodegradable, with good properties and low cost and whose waste is minimal, polluting the environment as little as possible with disposal in landfills [1].

Thus, polymeric composites reinforced with natural fibers have been widely used as a viable and inexpensive way to substitute fibers originated from petrochemical derivatives. Among the natural fibers, sisal has distinguished itself by presenting characteristics such as low density, easy to use, come from renewable source that contribute to environmental preservation and good resistance that reaches 38% of fiber glass strength. In addition, the cultivation of this fiber helps to generate income in poor rural regions in Brazil [2, 3].

The produced composites will be evaluated before and after buried in simulated soil via TGA (Thermogravimetric Analysis) that studies the mass change as a function of temperature or time. Another way used to evaluate this compound is the method known as DSC (Differential Scanning Calorimetry) that through the energy absorbed or released with respect to a reference considered thermally inert with respect to time or temperature, when they are subjected to a controlled programming [3,4] will evaluate the glass transition temperature for amorphous or semicrystalline composites. This temperature corresponds to the point at which a substance changes its behavior from a glassy state to an elastomeric state by moving the amorphous parts of the polymer and determines the operating temperature. The weight loss and the consequent degradation of the samples will be evaluated daily for a period of 15 days and after this period were weighed every week until the eighth week of exposure [3-5].

Also was teste the determination of impact strength are used to evaluate the fragile fractures in this materials, being a simple test with small and low cost specimens [6-7].

2. MATERIALS AND METHODS

2.1. Composite

To carry out this work, a polymer composite manufactured from a type sisal plain weave fabric with a thickness average of 2.4 mm used as reinforcement and the epoxy resin was used as the matrix. The curing process was made by hand mixing the epoxy and hardener in a stoichiometric ratio of 1: 0.35 by weight [3].

This process took about 10 minutes, being this mixture subsequently subjected to a vacuum (pressure of -600 mm / Hg) at room temperature for about 20 min to reduce the amount of bubbles in the composite. After this process, the mixture was injected into molds. This composite was kindly provided by the research group on Fatigue and Aeronautical Materials of São Paulo University (UNESP), Guaratinguetá – SP and present approximately 40% of its volume in fiber.

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2.2. Prepare of the Simulated Soil

The preparation of the simulated soil was made based on the ASTM G-160-03, where equal parts of sand beach, horse manure and fertile soil with low clay content were mixed. The soil after preparation was packed in PET containers to start the biodegradability tests [6-12].

2.3. Degradability Evaluation

To evaluate the degradability of epoxy/sisal fiber compound, specimens of about 1 g were immersed in simulated soil and evaluated daily for 15 days and after this period was assessed weekly until the eighth week of exposure. The sample size and mass were based on literati data [8-12]. For this evaluation, samples were removed from the ground, cleaned and weighed on an analytical balance Sartorius accurately to the tenth milligram available on Laboratory of Polymers of Oswaldo Aranha Foundation University (UNIFOA) – Volta Redonda.

The system consists of PET bottles cut into 15 cm high and placed in light and temperature isolated ambient. All the weighing process was done to minimize the time of exposure of the samples to air during the weighing process, which might cause measurement errors.

2.4. Differential Scanning Calorimetry (DSC)

The thermal characterization by DSC was performed on a PerkinElmer Inc. equipment Model DSC 8000 available in São Paulo University (UNESP) - Guaratinguetá at Thermal Analysis Laboratory. It was done in the composite before (virgin) and after exposure to degradation in soil (eight weeks), using a heating rate of 20°C/min for the first heating, for the first cooling a rate of 50°C/min and a second heating rate of 20°C/min according to the recommendations of ASTM D3418 in the range -30°C to 150°C under constant flow of nitrogen (20ml/min) and using as sample containers a standard aluminum capsules with sample mass of approximately 8.5 mg [9].

2.5. Thermogravimetry (TGA)

The thermogravimetric curves or TGA were evaluated according to ASTM E2550 that determines the initial degradation temperature as the immediately previous temperature of the first deflection on the baseline of the TGA curve or DTG, final degradation temperature as the immediately subsequent temperature at last deflection on the baseline TGA and DTG curve, the onset temperature and the extrapolated temperature of onset of specific weight change from the inflection point of the TGA curve and the weight change as the change in dimension in a given event you want to evaluate [3,4,10].

The test samples were taken from specimens before exposure in soil (virgin sample) and after eight weeks exposed in soil and have been tested in the laboratory of Thermal Analysis in the Department of Materials and Technology of São Paulo University (UNESP) in TG/DTA 6200 equipment brand SII Nano Technology INC, EXSTAR 6000 series, using the following parameters: temperatures between 30 and 850°C, constant flow of nitrogen (100ml / min), heating rate 10°C/min platinum sample holder and sample mass of approximately 17,0 mg. These tests were compared with pure epoxy resin (virgin) under the same analysis conditions.

2.6. Impact Resistance

This dynamic test is made with test pieces in the form of a square cross bar, with U or V shaped notches that are fixed horizontally and are struck by a pendulum. The response indicates the energy required to break the notched specimens under standard conditions without, however, providing a quantitative value of the material's tenacity and is proportional to the difference between the hammer height before and after the impact multiplied by the weight of the hammer. This energy is smaller the more fragile the material. In this work was used the Izod type machine of the Pantec brand, Canti Lever XJU-22 model with capacity of 5,5J, which is available in the Mechanical Tests Laboratory of the São Paulo University (EEL/USP) and the tests were made in accordance with ASTM D 6110-06 [6,7,13].

3. RESULTS AND DISCUSSION

3.1. Degradability Evaluation

To evaluate the biodegradability of the epoxy/sisal fiber composite, samples were exposed for 8 weeks at room temperature in a simulated soil. During this period, it could be seeing that there was an intense gain of weight in the first 24 hours (approximated 2% in mass). Furthermore, it can be observed a linear behavior in the first week, until a pseudo-steady stage being reached where the mass remains almost the same (Figure **1**). This process may be due to

absorption of water which penetrates into the polymer matrix by diffusion processes which leads to a hydrolyzing the bonds between the coating and the fiber surface causing degradation of the fiber/matrix adhesion and consequently worsening the mechanical properties of the composite [4,5].

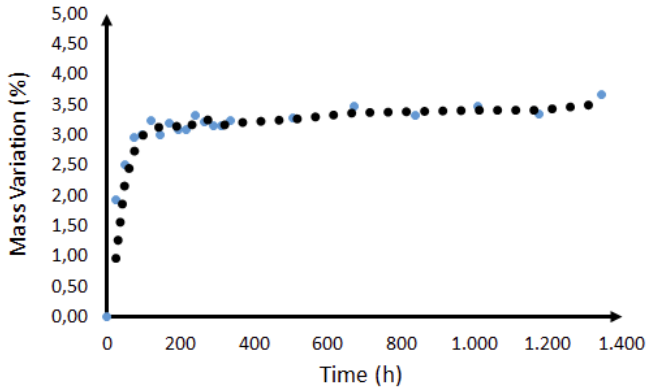

Figure 1: Exposure graph of the composite to the simulated soil (blue points - measured values and black points - trend curve).

This mechanism can be enhanced by factors such as: temperature increase, types of reinforcements used in the manufacture of the composite, the amount of voids which shows this laminate and polarity of the matrix. This process takes place until the equilibrium and can be attributed to the relaxation process of the polymer chain and hygrothermal fill existing voids [3-5].

3.2. Termogravimetry (TGA)

The graph of the thermal decomposition of the sample (Figure **2**) shows the mass variation of the epoxy resin/sisal polymer composites under nitrogen atmosphere.

The results demonstrate that the pure resin decomposes in one step (348°C), with a final average residue of approximately 9.2% corresponding to the resin fixed carbon which is not degraded by burning under an inert atmosphere to temperatures used [4].

However, the epoxy resin/sisal composites decomposes in two stages. The first step corresponds to the loss of moisture and the second related to the degradation of the polymer and fiber. This second step also indicates that there was good compatibility between the resin and the fiber, since the composite breaks down as a homogeneous sample [4,5].

It is also observed that the epoxy/sisal virgin composite has a lower moisture content (3.8%) compared to the same composite after 8 weeks of exposure in simulated soil (5.8%). Confirming the mass gain observed in the biodegradation test.

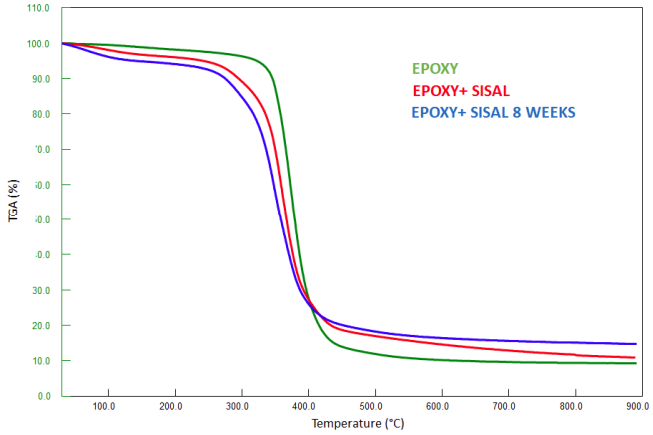

Figure 2: TGA graph of pure epoxy resin and epoxy resin/sisal virgin composites and after exposure for 8 weeks in simulated soil.

The residues observed at 850°C in virgin samples and after exposure to the simulated soil (11% and 15% respectively) are in agreement with that expected due to the increased fiber content in the composition and consequently higher fixed carbon from the resin and fiber [3-5].

Residues observed at 850°C on virgin samples and after exposure to the simulated soil (11% and 15%, respectively) are according expectations due to the increase of the fiber content in the composition and consequent increase in the fixed carbon content from the resin and from the fiber.

Samples of the epoxy/sisal virgin composite presents onset temperature about 330°C, while the samples after exposure to simulated soil, has a decreased onset temperature of about 5% (314,2°C) and both have a lower onset temperature than the pure resin (348°C), indicating that the presence of fiber, as well as exposure time in simulated soil (for samples with fiber) affect the degradation temperature of the studied composites.

3.3. Differential Scanning Calorimetry (DSC)

The glass transition temperature (Tg) is obtained from the baseline deviation of the average temperature. These data shows an increase of epoxy/sisal virgin composite Tg of about 3.3% compared to pure epoxy and about 4.8% for the epoxy/sisal composite after 8 weeks of exposure simulated soil compared to the same virgin composite (Figures **3**, **4** and **5**).

One of the several mechanisms explaining this increase in Tg is the permeation of water through the fiber matrix interface which promotes bonding type hydrogen bridges, increasing energy, and hence the temperature needed to drive the system molecules [3-5].

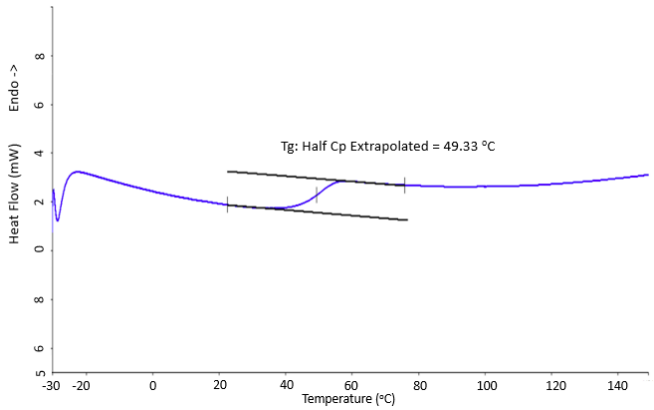

Figure 3: DSC curve of pure epoxy resin.

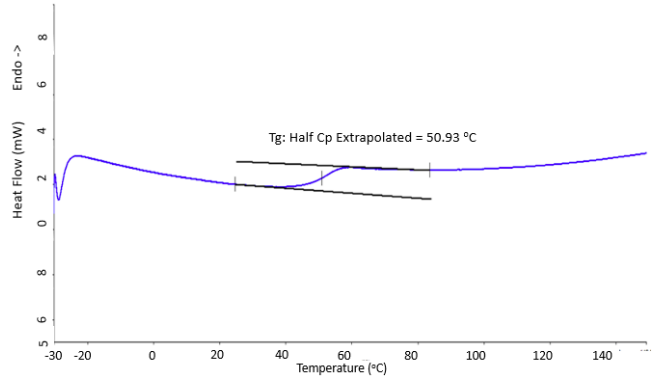

Figure 4: DSC curve of the resin epoxy/sisal virgin composite.

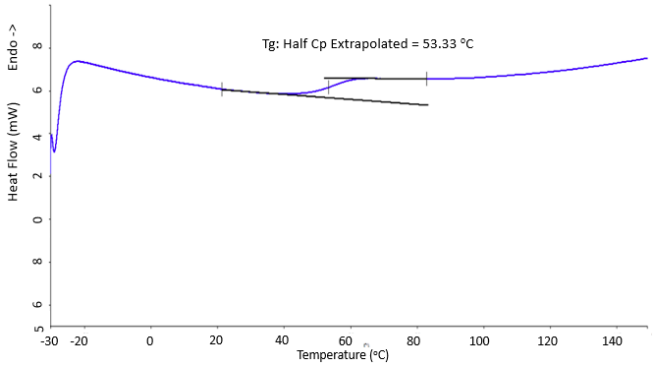

Figure 5: DSC curve epoxy/sisal composite after exposure for 8 weeks in simulated soil (AUTHOR, 2016).

3.4. Impact Resistance

The average of the results of the impact test show a decrease in composite material strength with simulated soil exposure as observed in Table **1**.

Table 1: Epoxy Resin/Sisal Fiber Composite Impact Strength during the 8 Week Exposure Period on Simulated Soil

Week	Impact resistance (kJ/m^2)
1	43.91
2	40.90
3	37.8
4	34.86
5	31.85
6	30.34
7	27.32
8	25.82

4. CONCLUSION

The results demonstrate that in a short exposure period, the composite present a significant degradability that can be confirmed by the biodegradation and impact resistance testing. In these, the epoxy resin/sisal fiber composite suffered partial degradation along the study period due to the diffusion process of this soil water between the interface matrix/resin which leads to a hydrolyzing of the connections, so that the mechanical properties of the composite becomes worse. This water uptake was confirmed by the level of water loss observed in the TGA method and the change in glass transition temperature observed in the DSC.

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