

Polyhydroxybutyrate Composites with Random Mats of Sisal and Coconut Fibers

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Biodegradable polymeric composites using natural fibers have been investigated aiming to mitigate environmental impacts. In this paper, polyhydroxybutyrate (PHB) composites obtained using random mats of sisal and coconut fibers by compression molding in a hydraulic press, and the fiber content varied between 10% and 15% relative to the weight of the polymer. Thermal analyses were performed such as Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). Flexural and tensile tests were performed before and after conditioning in climate chamber with temperature and moisture. The results of thermal analysis show that the thermal stability of the materials remained, both PHB without fiber as for composites with natural fibers mats. The results of mechanical tests indicated that the PHB without fibers and composites showed similar flexural strength values, while the results of the tensile test PHB without fibers showed resistance to higher tensile composite.

Keywords: PHB, natural fibers mats, thermal properties, mechanical properties

1. Introduction

A few years ago, researchers have focused on the development of polymer composites using natural raw material replacing those synthetically produced aiming at reducing environmental impacts¹⁻³. Studies using biodegradable polymers such as PHB has attracted attention since it can be applied in industries such as packaging^{4,5}, agriculture³ and biomedical because they are biocompatible and provide adequate mechanical properties for application^{6,7}.

The polyhydroxybutyrate (PHB) is natural thermoplastic polyester belonging to the class of polyhydroxyalkanoates, completely biodegradable, decomposed into water and carbon dioxide by the action of microorganisms in natural environments⁸. Generally, the PHB is produced by anaerobic fermentation of sucrose from sugarcane by natural microorganisms and purified by natural solvent^{9,10}. In addition, PHB also can be produced under aerobic conditions¹¹ and other carbon sources, e.g, sugars such as glucose and xylose¹², carbohydrates sources as sugarbeet juice¹³, agricultural residues¹⁴ and even fatty acids¹⁵.

It is a polymer having hydrophobic and highly crystalline feature¹⁶, with mechanical properties comparable to a conventional thermoplastic^{17,18}. However, application on an industrial scale is limited due to low strain rate, rapid thermal degradation and mainly the high cost compared to

conventional thermoplastic polymers^{16,19,20}. In addition, the high stiffness and mechanical brittleness difficult processing of PHB. To achieve greater flexibility, a plasticizer can be added to increase the free volume between the polymer chains^{21,22} or a copolymer of PHB, for example, polyhydroxybutyrate-co-hydroxyvalerate (PHBV) can be used²³⁻²⁵. Another possibility to improve the performance of PHB is to use natural or synthetic fibers as reinforcing the polymeric matrix obtaining a composite²⁶⁻²⁸.

Natural fibers can be an alternative to improve polymer properties. Despite having low processing temperatures, high sensitivity to environmental effects, mechanical properties variable and modest when compared to the high-performance fibers (glass, carbon and aramid)^{29,30}, natural fibers provide low-density materials, less abrasion and wear of equipment and molds when processed^{29,31,32}. Among the natural fibers can include fibers extracted from the sisal plant and coconut husk.

Sisal fiber as reinforcement in polymer matrix can provide good mechanical properties due to their high cellulose content and stiffness^{33,34}. In relation to coconut fibers, their main characteristics relates to its availability as waste in many tropical countries, durability combined with the mechanical performance of wear resistance³⁶⁻³⁸. The use of this fiber has economic importance such as obtaining products with high aggregate value and contributes to the reduction of coconut husk residues in the environment³⁸.

In this context, the aim of this work was to develop PHB composites using random mats of sisal and coconut fibers

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studying their thermal properties and mechanical behavior in flexural and tensile tests. The use of natural fiber in mat form was intended because it is lower price than fabric and also this type of mat facilitates the molding process of the composites with polymeric matrix PHB.

2. Experimental

2.1. Materials

The polymer matrix used was polyhydroxybutyrate (PHB) given by the company PHB Industrial S/A (Biocycle)³⁹ with a density of 1.20 g.cm⁻³; molar mass of approximately 600,000 g.mol⁻¹; and softening temperature (Vicat) of about 135 °C.

As plasticizer was used the purified glycerol (VETEC Fine Chemicals, Brazil) with the addition of 10% (w/w), which was selected due to low cost and generally can be obtained as a by-product of soap manufacturing and biodiesel after purification.

Sisal and coconut fibers were used in random mats for compression molding processes. Twelve samples of sisal and coconut fibers were taken randomly from mats to measure the length and diameter of the fibers using an optical microscope, Leica, Model DM2700P.

2.2 Preparation of the composites

Before processing, it was necessary to dry the polyhydroxybutyrate (PHB) in an oven at 103°C for 1 hour to remove moisture. Thereafter, the composites were molded in a laboratory hydraulic press containing heating plates, Marconi brand, model MA 098/A. For this press molding, it was used an aluminum alloy mold which was previously cleaned with acetone and applied to a product release agent containing carnauba wax and some oil derivatives.

For the molding of composites were used random mat of sisal fibers with yarn weight of approximately 370.0 g.m⁻², and mat of coconut fibers with yarn weight of approximately 567.0 g.m⁻². The sisal and coco mats were not subjected to chemical treatment or drying before use, to prevent a further step in the molding process. Thus, the mats were cut into the dimensions of the mold, for use in the composite molding with PHB polymer matrix.

PHB and the plasticizer glycerol were mixed, placed in the mold along with the fibers and pressed with 5 ton molding force, resulting in a pressure of 17.4 Kgf.cm⁻², and temperature of 180°C for 5 minutes. After cooling, the plate was demolded in ambient temperature. The mass fraction was 92.4% of matrix (PHB and glycerol) in the case of composite sisal fibers, and 90.1% of matrix for the composite mat of coconut fibers.

Plates containing only the PHB matrix with the plasticizer glycerol obtained using similar procedure for comparison. Each molded was cut and tested from 8 to 10 test specimens, for which the composite fiber varied between 10% and 15% relative to the weight of the polymer.

The specimens cut with miter saw and sanded to size (127 x 12.7 x 5) mm and (250 x 25 x 3) mm for the flexural and tensile tests, respectively. In the case of specimens for tensile, the ends were sanded to paste the “tabs” of epoxy resin containing glass fiber fabric to reduce the grip of the tension in the specimen. The “tabs” were bonded with cyanoacrylate adhesive, Loctite brand.

2.3 Thermal analysis

For analyzes by Differential Scanning Calorimetry (DSC) of samples were used approximately 5 mg in an aluminum capsule. The conditions involved an initial program in a nitrogen atmosphere (flow 50 mL.min⁻¹) at a heating rate 10 °C. min⁻¹ to 400 °C, with an initial isotherm of 2 minutes. All analyzes were performed in duplicate. The analyses were performed at the Materials Research Laboratory (UFSCar/Campus Sorocaba, Brazil), in equipment brand TA Instruments, USA, model Q20.

For Thermogravimetry Analysis (TGA) samples were analyzed approximately 8 mg of platinum crucible. The analysis conditions were: heating rate 10 °C. min⁻¹ in an inert atmosphere of nitrogen 50 mL.min⁻¹, analysis range 30 to 700 °C. Analyses were performed in University of São Paulo (IQSC/ USP/ São Carlos, Brazil), in equipment of brand Shimadzu, Japan, model TGA-50.

2.4. Water absorption

The water absorption or conditioning in climate chamber was achieved by adapting the ASTM D5229M-92⁴⁰. PHB specimens and their composites were weighed and placed directly into the cooling chamber (brand EQUILAM, KEQUN 300 model) at a temperature of 60 °C in saturated moisture for 7 days. After the test of water absorption, the specimens were weighed again obtaining the result the average moisture of each material.

2.5. Mechanical testing

The flexural testing of the polymeric matrix and the composites were performed in a universal testing machine EMIC brand, model DL 10000 with a schedule of the flexural testing at three points in accordance with ASTM D790-02, Procedure A⁴¹. For tests were used a 500 Kg load cell and a test speed of about 2.2 mm/min. The specimens were cut in the dimensions of 127 mm length and 12.7 mm of width, in accordance with ASTM D790 standard.

Tensile testing were performed using the universal testing machine, EMIC brand, model DL 10000, with load cell of 500 kgf and 2 mm/min test speed. For testing, specimens were cut in dimensions of 250mm length and 25mm of width in accordance with ASTM D3039/D3039M-08⁴² for rectangular specimens.

3. Results and Discussion

3.1. DSC of the fibers and polymeric matrix

To identify the temperature to which the natural fibers could be used DSC analyzes were performed. Figure 1 shows the degradation curves for the coconut fibers and sisal fibers.

The DSC curves of the coconut fibers and sisal fibers in Figure 1, showed similar profiles. In both analyzes it was possible to see a curve around 100 °C which is related to the elimination of water due to the hydrophilic character of the fibers. It is also noted in those same curves (Figure 1), two degradation peaks at around 290°C and 360°C, which temperatures cause the decomposition of cellulose and hemicellulose. Lignin remains in this temperature range because its decomposition generally starts from 370 °C^{43,44,45}. TGA analyzes were also performed to verify the thermal events of the analyzed fibers.

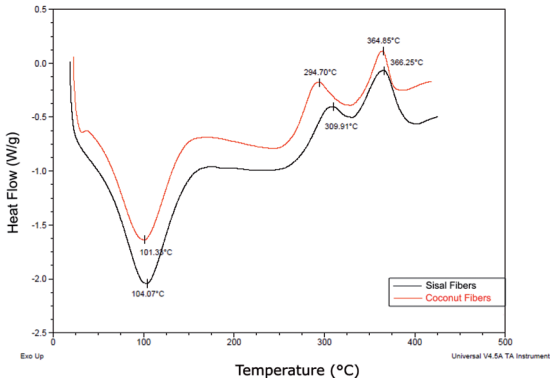


Figure 1: DSC curve of sisal and coconut fibers

By the DSC analysis of the fibers was possible to estimate that up to near 200 °C, it is feasible to use natural fibers without thermal degradation. Thus, these sisal and coconut fibers can be used for molding composites with polymeric matrix PHB, which has melting temperature around 170 °C.

Figure 2 shows the DSC curve of the polymer matrix of polyhydroxybutyrate (PHB). The analysis was performed with a heating rate of 10 °C min⁻¹ to 185 °C with isothermal for 2 minutes and the same rate cooling. In Figure 2 can be seen a crystallization temperature (T_c) at about 86 °C, which is in accordance with the literature⁴⁶.

In order to study the polymer behavior at higher temperatures, PHB degradation curve was performed (Figure 3) with a heating rate of 10°C.min⁻¹ to 400 °C.

In the curve of Figure 2 the endotherms peaks showing at 142°C and 169°C are double melting temperatures, which are usually seen in PHB. Some studies have indicated this multiple melting behavior of PHB is contributed to different crystalline structure in PHB during DSC melting scan⁴⁷⁻⁴⁹. Hong et al.⁴⁹ refer to the smaller peak as a melting

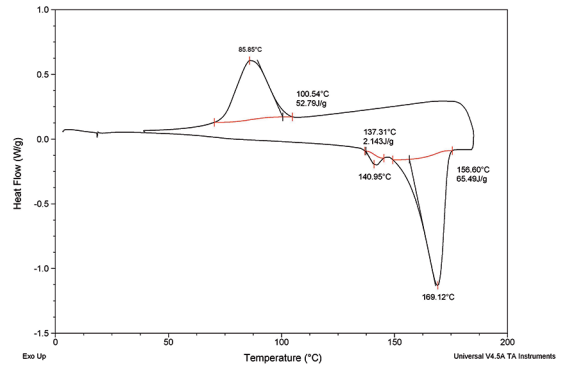


Figure 2: DSC curve of PHB before processing

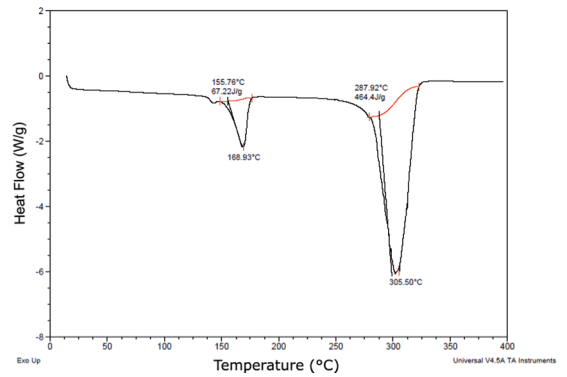


Figure 3: DSC curve of PHB up to 400 °C, before processing

temperature of small and imperfect crystallites that formed during evaporation of the solvent. In addition, the peak of 141°C is also referred as Vicat softening temperature in according with data sheet of PHB³⁹.

In Figure 3 other endothermic peak is observed at 305°C, probably due to degradation of the polymer, which occurs the breaking of ester bonds (chemical bond more susceptible to breakage), and thus decreasing the molar mass.

3.2. Crystallinity Degree

By the DSC analysis, it was calculated the degree of crystallinity (X_c (%)) of PHB according to the equation (1):

$$X_c(\%) = \frac{\Delta H_m}{\Delta H_0} \times 100 \quad (1)$$

which ΔH_0 is the melting enthalpy per unit mass of PHB 100% crystalline, wherein the reference value is 146 J/g^{16,50-52} and ΔH_m is melting enthalpy per unit mass of the PHB obtained from the integral of the peak melting temperatures.

The crystallinity calculated for the analyzed PHB was 46.3% for two peaks of melting temperatures, which is according with 45% of crystallinity for PHB cited in literature⁵³. Another paper⁵⁴ reports that the crystallinity of PHB can vary 35 to

45% depending on the experimental parameters. However, these results are considered relatively low compared with other published studies^{16,51}. This difference may be explained due to different molar mass values of PHB used in the referenced papers. Different companies currently produce bacterial PHB, e.g., PHB Industrial (Brazil) produces PHB 45% crystalline approximately, from sugar cane molasses⁵³.

As the value of crystallinity had been lower than expected for this polymer, it was decided to add a plasticizer to facilitate the moulding. According to Quental⁵⁵, the thermal degradation of PHB begins to occur at temperatures close to its melting temperature (between 170-200°C) and this effect may reflect the thermal and mechanical properties of the polymer and reduce the processing temperature range.

DSC analyzes were also performed for PHB and molded composites. The results can be seen in Figure 4 and Table 1. The crystallinity of composites was calculated according to the equation (2):

$$X_c(\%) = \frac{\Delta H_m}{\Delta H_0 W_m} \times 100 \quad (2)$$

which W_m is the weight fraction of PHB in composite, ΔH_0 is the melting enthalpy per unit mass of PHB and ΔH_m is melting enthalpy per unit mass of the composite obtained from the integral of the peak melting temperature⁵⁶.

In Table 1, the crystallinity calculated for PHB after molding was 31.7%, considering two peaks of melting temperatures. This value was lower than crystallinity of PHB before compression molding that was 46.7% of crystallinity.

Also the Table 1 shows that the incorporation of sisal and coconut fibers caused an increase in crystallinity compared to PHB composite matrix. This increase in crystallinity of composites may possibly be related to the action of the fibers as nucleating agents. These agents may be particulates or fibers dispersed in the matrix, thus the large number of small crystals are formed around them^{57,58}.

This type of behavior also occurred in the work presented here, which explains the increase in crystallinity of the composite compared to PHB matrix after compression molding. Thus the higher crystallinity value occurred for the composite containing the mats of coconut fibers that have value greater weight in relation to the mats of sisal fiber (Table 1), allowing greater number of nucleation crystals and increasing the degree of crystallinity of the PHB matrix in the composite.

Considering Figure 4, it is observed that there were small decreases in relation to the melting temperature (T_m) of composite PHB/Coconut fibers and PHB/Sisal fibers compared to PHB without fibers.

In Figure 4 and Table 1, the crystallization temperature (T_c) of PHB was approximately 62°C and the composites PHB/fibers showed values near 74°C. Thus, the crystallization temperatures of these molded materials containing glycerol

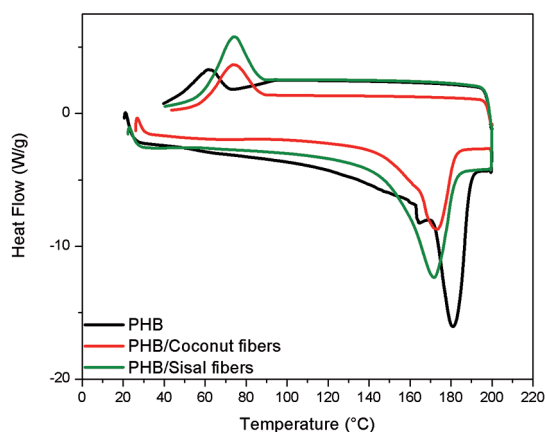


Figure 4: DSC curves of the post-molding PHB and composites PHB/coconut fibers and PHB/Sisal fibers.

(Figure 4) showed a decrease compared to PHB before processing, which showed a value of approximately 86°C (Figure 2). The DSC curves for temperatures up to approximately 325 °C (Figure 5) were carried out for the post-molding PHB and composites.

In figure 5 it is observed that the peak temperature associated degradation of PHB was decreased before processing from 305 °C (in Figure 3) to 296 °C (in Figure 5) for the post-molding PHB (Figure 5). There was a greater reduction in the composites, i.e., for PHB/coconut fiber (286 °C) and PHB/sisal fiber (281 °C), probably due to natural fibers that exhibit the start of degradation around 260 °C (Figure 1).

3.4. TGA of the fibers and matrix of PHB

In Figure 6 (A and B) are shown TGA and its derivative (DTG) of coconut fibers and sisal fibers, which presented similar profiles. Temperatures values of these analyze are shown in Table 2.

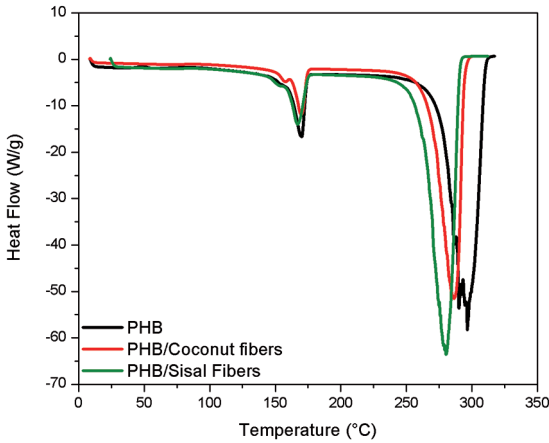
The first event is a result of mass loss due to evaporation of adsorbed water molecules (25-105 °C temperature range), which corresponds to 8.1% to the coconut fibers and 5.9% for sisal fibers.

According to Figure 6 and Table 2, the beginning of the degradation occurred at around 251 °C for coconut fiber and 267 °C for sisal fibers. Thus, the second event showed range of 251-363 °C for coconut fiber and between 267-393 °C for sisal fibers, with a mass loss of 51.5% and 55.5%, respectively. Probably, these intervals are related to the decomposition of cellulose and hemicellulose of natural fibers that are between 200-370 °C^{44,59}.

The third event occurred between 401-502 °C and 431-502 °C for coconut fibers and sisal fibers, respectively. This range suggests the degradation of lignin, since due to its complex structure is more difficult to be decomposed. According to Campos⁴⁴ the temperature range for the decomposition of lignin is between 370-500 °C^{43,45}.

Table 1: Thermal properties of PHB and composites after molding. Maximum melting temperature (T_m peak); variation melting enthalpy (ΔH); crystallinity (X_c).

Material	T_m peak ($^{\circ}\text{C}$)	T_c peak ($^{\circ}\text{C}$)	ΔH (J/g)	X_c (%)
PHB	163.5 and 181.96	61.90	0.87 and 45.36	31.7
PHB/sisal fiber	171.77	73.50	56.78	42.10
PHB/coconut fiber	173.45	73.76	58.98	44.82

**Figure 5:** DSC curves up to 325 $^{\circ}\text{C}$ of PHB post-molding and composites PHB/coconut fibers and PHB/sisal fibers

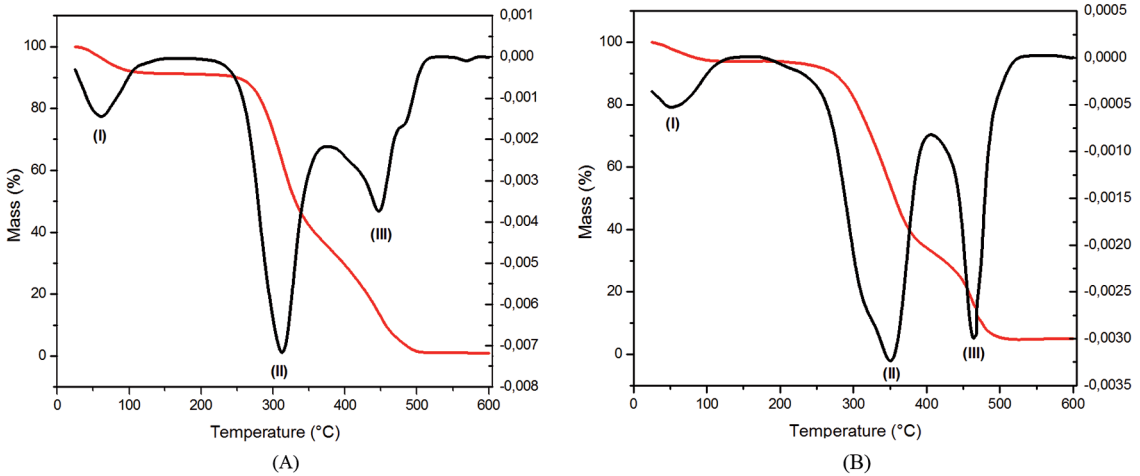
3.5. TGA of PHB and composites

Figures 7 and 8 show the PHB stability curves before processing and post-molding PHB containing 10% (w/w) glycerol, respectively.

In the TGA and DTG analysis of PHB before processing (Figure 7) it was observed only one thermal event which started at 246 $^{\circ}\text{C}$ and up to 320 $^{\circ}\text{C}$ with a mass loss of 97.7%.

PHB plasticized with 10% (w/w) of glycerol after molding had a curve with two thermal events for mass loss (Figure 8). The first event with onset of degradation at 126 $^{\circ}\text{C}$ to 180 $^{\circ}\text{C}$ and a mass loss of 5.9%, probably related to the beginning of the glycerol degradation as plasticizer and the hydration water evaporation.

In the second event (Figure 8), degradation began at a temperature of approximately 235 $^{\circ}\text{C}$, which is below that

**Figure 6:** TGA and DTG curves of coconut fibers (A) and sisal fibers (B), heating rate: 10 $^{\circ}\text{C} \cdot \text{min}^{-1}$ under nitrogen atmosphere flow of 50 $\text{mL} \cdot \text{min}^{-1}$ **Table 2:** Values of the initial temperature (T_i), final temperature (T_f), peak temperature (T_{peak}) and the percentage mass loss of the events I, II and III of coconut fibers and sisal fibers.

Event	Coconut fibers			
	T_i ($^{\circ}\text{C}$)	T_f ($^{\circ}\text{C}$)	T_{peak} ($^{\circ}\text{C}$)	Mass loss (%)
I	25	105	59	8,1
II	251	363	312	51.5
III	401	502	445	27.5
Sisal fibers				
	T_i ($^{\circ}\text{C}$)	T_f ($^{\circ}\text{C}$)	T_{peak} ($^{\circ}\text{C}$)	Mass loss (%)
	25	106	53	5.9
	267	393	349	55.5
	431	502	464	23.2

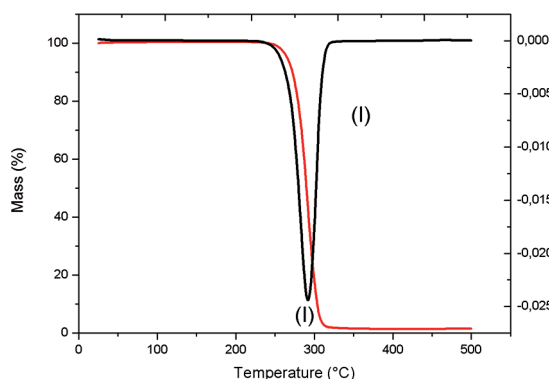


Figure 7: TGA and DTG curves of PHB before processing. Heating rate: $10^{\circ}\text{C}\cdot\text{min}^{-1}$ under nitrogen atmosphere flow of $50\text{ mL}\cdot\text{min}^{-1}$

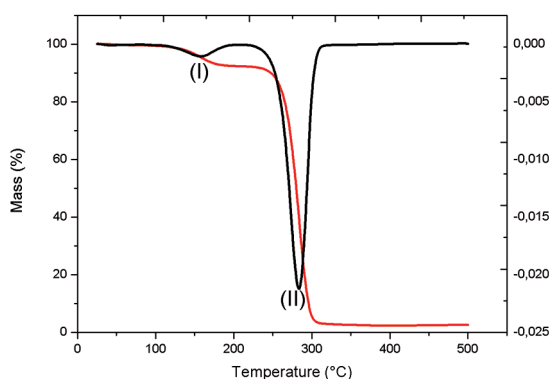


Figure 8: TGA and DTG curves of PHB plasticized with 10% glycerol. Heating rate: $10^{\circ}\text{C}\cdot\text{min}^{-1}$ under nitrogen atmosphere flow of $50\text{ mL}\cdot\text{min}^{-1}$

obtained for PHB before processing, whose temperature was 246°C (Figure 7). This decrease can be attributed due to the addition of plasticizer, which have low molar mass allocates between the polymer chains, increasing distance between them which may reduce the viscosity of the polymer, also contributing to increasing the flexibility of the material⁶⁰. In degradation range ($235\text{--}311^{\circ}\text{C}$) of Figure 8, the mass loss was 88.5%.

Wang et al.⁶¹ used adding plasticizer ATBC (acetyl tributyl citrate) at 0, 10, 20, 25 and 30% PHB. In this case, the author found that increasing plasticizer content there was a decrease in initial degradation temperature of 224°C (neat PHB) to 188°C (30% ATBC). Erceg et al.¹³ studied the degradation of the PHB plasticized with ATBC which confirms the reduction in thermal stability with ATBC content.

In Figure 9 and Table 3 the results are shown of TG/DTG analysis of PHB and composites reinforced with sisal and coconut fibers mats. The initial values of temperature degradation (T_i), final degradation temperature (T_f), peak degradation temperature (T_{peak}) and mass loss (%) for PHB, PHB/10% glycerol and composites containing sisal and coconut fibers mats can be observed in Table 3.

PHB analysis in Figure 9 also reveals the peak related to the beginning of glycerol degradation at about 150°C and the end of degradation at 300°C .

Regarding TGA and DTG curves of the composite (Figure 9 (A) and (B)), the composite PHB/coconut fibers showed thermal degradation range of $237\text{--}311^{\circ}\text{C}$ with a mass loss of 84.5%. As for the composite PHB/Sisal fibers is showed degradation range in $244\text{--}309^{\circ}\text{C}$, with a mass loss of 86.5%. Thus, the incorporation of natural fibers yielded no significant change and the thermal stability maintained to about 235°C , both PHB without fiber and composites.

3.6. Conditioning test

Flexural and tensile specimens of the polymeric matrix and molded composites were tested at room temperature and after their conditioning in climate chamber.

The PHB and its composites were placed directly in the climate chamber at 60°C for 7 days. After conditioning, the specimens were superficially dried as described in ASTM D5229M-92⁴⁰ to remove excess water and then weighed. Thus, it was possible to determine the total percentage of water absorbed by the equation (3):

$$M(\%) = \frac{W_i - W_0}{W_0} \times 100 \quad (3)$$

in which W_i is the specimen weight after conditioning and W_0 is the mass of dry sample in oven.

The moisture content after-conditioning of specimens (containing PHB) for flexural and tensile tests are presented in Table 4.

The PHB/10% (w/w) glycerol, presented relatively high moisture absorption due to ester bonds of the PHB chains and especially because of the hydrophilicity of the plasticizer glycerol which has facility to form hydrogen bonds with water.

For flexural and tensile specimens, PHB without fiber presented moisture content of 2.6% and 1.7%, respectively; PHB/coconut fiber 6.1% and 4.6%, respectively; and PHB/sisal fibers of 3.3% and 2.4%, respectively. In this case, the natural fibers have different moisture absorbing capacity and this capacity is associated with the chemical composition of cellulose, lignin and hemicellulose⁶².

3.7. Flexural properties

The flexural tests were performed for composites PHB with coconut and sisal fibers at room temperature and after conditioning in climate chamber. The results were compared with those obtained from the PHB matrix without fibers. The obtained average curves are shown in Figure 10 and Figure 11.

The maximum strength (MPa), maximum deflection (mm) and flexural modulus (MPa) data of the obtained average curves of the flexural tests at room temperature

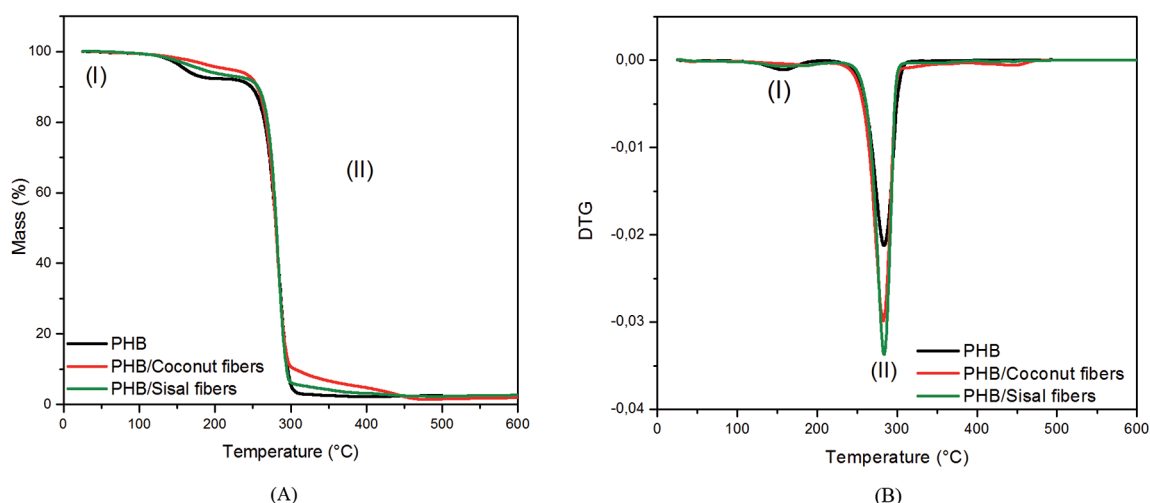


Figure 9: TGA curves (A) and DTG curves (B) of PHB plasticized with glycerol and composite PHB/coconut fibers and PHB/sisal fibers. Heating rate: 10 °C.min⁻¹ under inert atmosphere flow of nitrogen 50 mL.min⁻¹

Table 3: Values of the initial temperature (T_i) final temperature (T_f), peak temperature (T_{peak}) and the percentage loss of mass of events related to PHB and post-molding composites reinforced with coconut and sisal fibers mats.

Event	T_i (°C)	PHB		Mass Loss (%)
		T_i (°C)	T_{peak} (°C)	
I	246	320	292	97.7
PHB/10% Glycerol				
I	126	180	155	5.9
II	235	311	284	88.5
PHB/Coconut fibers				
I	237	311	282	84.5
PHB/Sisal fibers				
I	244	309	283	86.5

Table 4: Content of moisture from flexural and tensile specimens of PHB without reinforcement and composites with coconut and sisal fibers mats after conditioning in a humid chamber.

Molded Materials	Moisture content (%)	
	After conditioning in a humid chamber	
	Flexural test	Tensile test
PHB/10% glycerol	2.6	1.7
PHB/Coconut fibers	6.1	4.6
PHB/Sisal fibers	3.3	2.4

and after conditioning of the PHB and its composites are shown in Table 5.

According Figure 10 and Table 5, with the standard deviation values can be considered that PHB without fibers and composites showed flexural strength (maximum) with close values. After the flexural tests, it was observed that none of the materials suffered brittle fracture.

In the study by Gunning et al.²⁸, it is reported that natural fibers cause an increase in flexural strength showing that the materials containing jute fiber was an improvement compared to PHB without fibers, while composites with hemp fibers

exhibit lower increase of the jute fibers as reinforcement. In contrast, Melo et al.⁶³ found that the incorporation of carnauba fiber causes a decrease in the flexural strength may improve by up to 14% after chemical treatment with peroxide. This suggests that the increase in flexural strength is associated with good interfacial adhesion between the fiber and the polymer matrix.

For PHB/Coconut fibers composite there was a greater deformation (Table 5) showing a behavior of a more ductile material, which is related to the mechanical properties of the fiber type⁶⁴.

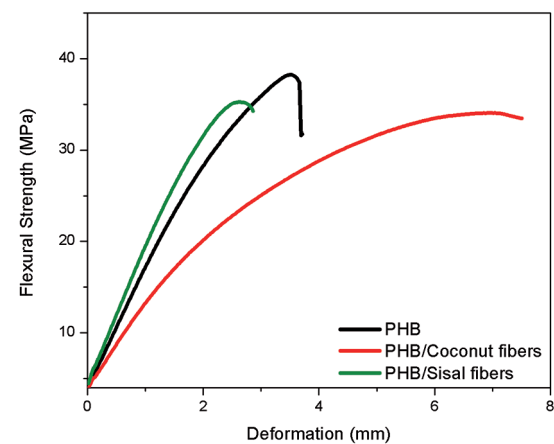


Figure 10: Representative mean curves from flexural tests of PHB composites and PHB without fibers tested at room temperature

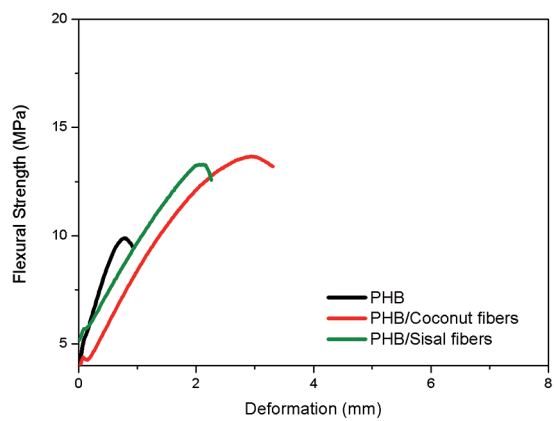


Figure 11: Representative mean curves from flexural test of PHB composites and the PHB without fibers after conditioning a humid chamber

In tests conducted after-conditioning (Figure 11), the maximum flexural strength values had a significant decline that results from the absorption of water by the material. The decrease in mechanical properties was more pronounced for the PHB without fibers, showing a decline of around 74% compared to PHB without conditioning in climate chamber.

Dittenber and GangRao⁶⁵ discuss in their work on the challenge in the development of structural components utilizing natural fibers, limiting their application due to their lower mechanical properties and poor moisture resistance, as the

fibers of natural origin, being hydrophilic, have high water absorption and incompatible with hydrophobic polymeric matrices. Additionally, the biodegradable polymers also tend to absorb more moisture than polymers synthetically produced, so the decrease in resistance after conditioning can be related to water absorption by PHB matrix and the glycerol present, which also has hydrophilic nature.

The coconut fibers and sisal fibers composites showed a decrease in strength of about 60% and 62%, respectively, due to diffusion of water by the fiber after conditioning. In this study, the samples were not sealed on the sides after cutting and the fibers were highly exposed to moisture. Therefore, the simulated conditions were the most drastic possible, which explains the decrease in the values of mechanical resistance properties.

The flexural modulus had a large decline for the composites analyzed after conditioning. Thus, it can be stated that the PHB and composites did not have a good flexural strength in these conditions and even the physical appearance of the specimens were visibly affected. Because it is a biodegradable material^{1,38}, probably the PHB suffered degradation during the climate test.

However, the results of flexural tests suggest what is expected from a biodegradable material; when in contact with moisture and temperature, degradation in the polymer structure cause reduction in properties. Therefore, the feasibility of using these composites depends on application.

3.8 Tensile properties

Tensile tests were performed to PHB without fibers and composites with coconut and sisal fibers mats.

Table 6 shows maximum tensile strength (MPa), maximum deformation (mm) and modulus of elasticity (MPa) data of the obtained average curves of the tensile test at room temperature and after conditioning of PHB and their composites. The obtained average curves are shown in Figure 12 and Figure 13.

Analyzing the data in Table 6 and the curves in Figure 12 it is observed that the PHB without fibers had tensile strength and deformation higher when compared to composites.

PHB unreinforced tested at room temperature had tensile strength average 22.2 MPa. PHB/coconut fibers and PHB/sisal fibers composite showed the values 11.9 MPa and 18.2

Table 5: Data of flexural strength (MPa), maximum deformation (mm) and modulus (MPa) obtained by the average curve of the flexural test PHB unreinforced and reinforced composites with coconut fibers and sisal fibers.

Materials	Room temperature			After conditioning		
	Flexural Strength (MPa)	Maximum deformation (mm)	Flexural Modulus (MPa)	Flexural Strength (MPa)	Maximum deformation (mm)	Flexural Modulus (MPa)
PHB	38.3 ± 2.5	3.5	2683 ± 244	9.9 ± 1.1	0.8	2098 ± 181
PHB/Coconut	34.0 ± 2.0	7.0	2045 ± 124	13.6 ± 2.8	2.9	999 ± 265
PHB/Sisal	35.3 ± 5.5	2.6	2898 ± 324	13.3 ± 2.1	2.1	661 ± 260

Table 6: Maximum tensile strength (MPa), maximum deflection (mm) and the modulus of elasticity (MPa) data obtained by the average curve of the tensile test of PHB unreinforced and reinforced composites with coconut fibers and sisal fibers.

Materials	Room temperature			After conditioning		
	Tensile Strength (MPa)	Maximum deformation (mm)	Modulus of elasticity (MPa)	Tensile Strength (MPa)	Maximum deformation (mm)	Modulus of elasticity (MPa)
PHB	22.2 ± 0.5	10.4	1005 ± 43	19.0 ± 1.6	9.2	582 ± 79
PHB/Coconut	11.9 ± 1.0	4.0	828 ± 45	8.4 ± 1.0	4.3	457 ± 23
PHB/Sisal	18.2 ± 1.5	6.5	958 ± 43	12.2 ± 1.0	5.7	579 ± 26

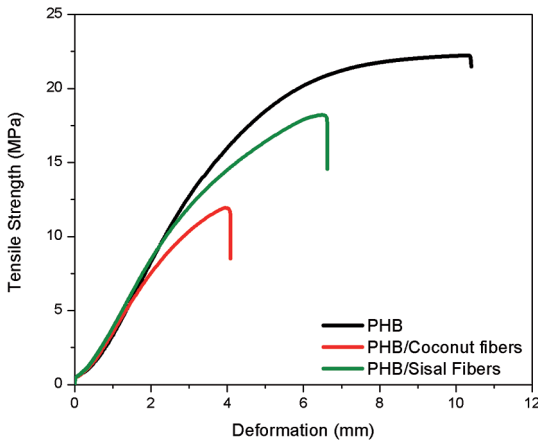


Figure 12: Representative mean curves from tensile test of PHB composites and PHB without fibers tested at room temperature

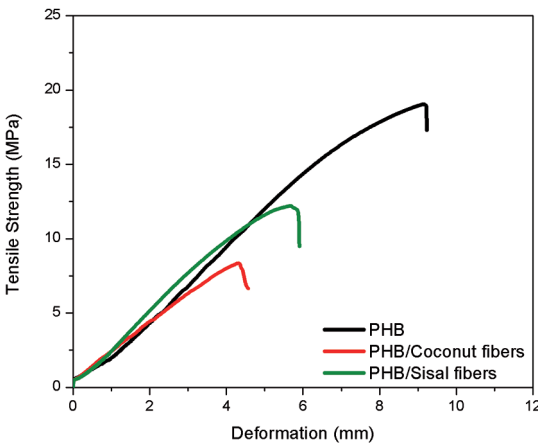


Figure 13: Representative mean curves from tensile test of PHB composites and PHB without fibers after conditioning in a humid chamber

MPa, respectively. The PHB/sisal fibers had a tensile strength similar to PHB without fibers, while for PHB/ coconut fibers there was a more significant decline in resistance values.

The decrease in tensile strength suggests a low interfacial interaction between the polymer matrix and the fibers, since PHB has a hydrophobic characteristic and the fibers are hydrophilics. This result corroborate with the results obtained by Gunning et al²⁸ that evaluated the mechanical properties of PHB composites with three different natural fibers; jute, hemp and lyocell.

Furthermore, existing high moisture content of the fibers, which is higher for the composite with coconut fibers, has further weakened the bonds at the interface. This can be confirmed by tests carried out after conditioning shown in Figure 13, where the PHB unreinforced declined in strength around 14% compared to the tensile test at room temperature and the composite of coconut fibers and sisal fibers that decreased by 29% and 33%, respectively.

In this work, the values of the diameter of the sisal fibers were measured and are in the range from 150.7 to 428.6 μm with an average of $261.6 \mu\text{m} \pm 92.4$. For coconut fiber diameters were observed in a range from 195.3 to 501.8 μm with an average of $339.7 \mu\text{m} \pm 76.5$. Some studies show that the coconut fibers have a larger diameter than sisal fibers. By Lima et al⁶⁶, it was found that the average diameter of the sisal fibers was $280 \mu\text{m} \pm 27$ which is close to the value found in this study. Verma et al⁶⁷ showed that the diameter of the sisal fibers is a range of 50 to 200 μm , whereas the diameter of coconut fibers is in a range of 100–450 μm .

In relation to the aspect ratio (length to diameter or L/D) of sisal and coconut fibers, the calculated average values were 266.3 μm and 300.5 μm respectively, characteristic of long fibers. Monteiro et al⁶⁸ also calculated the aspect ratio of coconut fibers resulting a value of 572 μm much higher than that found in this study. Thus, it can be seen that the diameter and the aspect ratio of natural fibers such as coconut and sisal vary due to different crops species, soil, climate, and others parameters⁶⁹ that explain the variation of the results.

At first idea, due to the aspect ratio values calculated for the fibers, it was expected an increase in the mechanical properties of the composite in tensile test. However, this behavior was not observed. Probably, in the case of this study, the low adhesion at the interface between the natural fibers and the matrix PHB is predominating on the aspect ratio (L/D) of fibers in composites. Furthermore, the sisal and coconut fibers are randomly distributed in the mats which cause a decrease in resistance to longitudinal stress which occurs in the tensile test.

4. Conclusions

The results of thermal analysis of TG showed that the incorporation of natural fibers did not cause significant change

in the material properties up to approximately 235 °C, ie, the thermal stability was maintained to the PHB without fiber and to the composites.

The results of flexural tests of PHB composites with sisal fibers mat showed flexural strength and modulus close to that of PHB polymer without fibers, when tested at room temperature. However, considering the set of mechanical test results of flexural and tensile strength of composites containing coconut fiber mats were observed decrease in the mechanical properties of composites.

The insertion of natural fibers in mat form is an alternative to reuse these agricultural residues reducing disposal. Moreover, the decline in relation to the flexural properties after conditioning at elevated temperature and humidity of composites containing PHB is interesting when it is necessary to use materials that have biodegradable characteristics. The incorporation of natural fibers in composites permits the use of smaller amount of PHB polymer matrix, which is more expensive than natural fiber.

Potential applications for the biocomposites could be little tubes and plastic bags for planting seedlings of vegetables and fruits in agriculture. These biocomposites also can be applied in the manufacture of disposable type packaging trays substituting for example expanded polystyrene.

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6. References

- Caraschi JC, Ramos UM, Leão AL. Compósitos biodegradáveis de polihidroxibutirato (PHB) reforçado com farinha de madeira: propriedades e degradação. *Acta Scientiarum*. 2002;24:1609-1614.
- Jia W, Gong RH, Hogg PJ. Poly (lactic acid) fibre reinforced biodegradable composite. *Composites: Part B: Engineering*. 2014;62:104-112.
- Touchaleaume F, Martin-Closas L, Angellier-Coussy H, Chevillard A, Cesar G, Gontard N, et al. Performance and environmental impact of biodegradable polymers as agricultural mulching films. *Chemosphere*. 2016;144:433-439.
- Dhar P, Bhardwaj U, Kumar A, Katiyar, V. Poly(3-hydroxybutyrate)/cellulose nanocrystal films for food packaging applications: Barrier and Migration studies. *Polymer Engineering & Science*. 2015;55(10):2388-2395.
- Arrieta MP, López J, López D, Kenny JM, Peponi L. Development of flexible materials based on plasticized electrospun PLA-PHB blends: Structural, thermal, mechanical and disintegration properties. *European Polymer Journal*. 2015;73:433-446.
- Ni J, Wang M. In vitro evaluation of hydroxyapatite reinforced polyhydroxybutyrate composite. *Materials Science and Engineering: C*. 2002;20(1-2):101-109.
- Meischel M, Eichler J, Martinelli E, Karr U, Weigel J, Schmöller G, et al. Adhesive strength of bone-implant interfaces and in-vivo degradation of PHB composites for load-bearing applications. *Journal of the Mechanical Behavior of Biomedical Materials*. 2016;53:104-118.
- Reddy CSK, Ghai R, Rashmi, Kalia VC. Polyhydroxyalkanoates: an overview. *Bioresource Technology*. 2003;87(2):137-146.
- Shanks RA, Hodzic A, Wong S. Thermoplastic biopolyester natural fiber composites. *Journal of Applied Polymer Science*. 2004;91(4):2114-2121.
- Thipathi AD, Srivastava SK, Singh RP. Statistical optimization of physical process variables for bio-plastic (PHB) production by *Alcaligenes* sp. *Biomass and Bioenergy*. 2013;55:243-250.
- Rodgers M, Wu G. Production of polyhydroxybutyrate by activated sludge performing enhanced biological phosphorus removal. *Bioresource Technology*. 2010;101(3):1049-1053.
- Zhang Y, Sun W, Wang H, Gen A. Polyhydroxybutyrate production from oil palm empty fruit bunch using *Bacillus megaterium* R11. *Bioresource Technology*. 2013;147:307-314.
- Wang B, Sharma-Shivappa RR, Olson JW, Khan SA. Production of polyhydroxybutyrate (PHB) by *Alcaligenes latus* using sugarbeet juice. *Industrial Crops and Products*. 2013;43:802-811.
- Corneli E, Adessi A, Dragoni F, Regolini G, Bonari R, de Philippis R. Agroindustrial residues and energy crops for the production of hydrogen and poly-β-hydroxybutyrate via photofermentation. *Bioresource Technology*. 2016;216:941-947.
- Shen L, Hu H, Ji H, Cai J, He N, Li Q, et al. Production of poly(hydroxybutyrate-hydroxyvalerate) from waste organics by the two-stage process: Focus on the intermediate volatile fatty acids. *Bioresource Technology*. 2014;166:194-200.
- Erceg M, Kovačić T, Klarić I. Thermal degradation of poly(3-hydroxybutyrate) plasticized with acetyl tributyl citrate. *Polymer Degradation and Stability*. 2005;90(2):313-318.
- Bucci DZ, Tavares LBB, Sell I. PHB packaging for the storage of food products. *Polymer Testing*. 2005;24(5):564-571.
- Ahankari SS, Mohanty AK, Misra M. Mechanical behaviour of agro-residue reinforced poly(3-hydroxybutyrate-co-3-hydroxyvalerate), (PHBV) green composites: A comparison with traditional polypropylene composites. *Composites Science and Technology*. 2011;71(5):653-657.
- Janigová I, Lacík I, Chodák I. Thermal degradation of plasticized poly(3-hydroxybutyrate) investigated by DSC. *Polymer Degradation and Stability*. 2002;77(1):35-41.
- Choi JS, Park WH. Effect of biodegradable plasticizers and mechanical properties of poly(3-hydroxybutyrate). *Polymer Testing*. 2004;23(4):455-460.
- Satyanarayana KG, Arizaga GGC, Wypych F. Biodegradable composites based on lignocellulosic fibers – An overview. *Progress in Polymer Science*. 2009;34(9):982-1021.
- Callister WD Jr. *Ciência e Engenharia de Materiais: Uma Introdução*. Rio de Janeiro: LTC Editora; 2008.
- Modi S, Koelling K, Vodovotz Y. Assessment of PHB with varying hydroxyvalerate content for potential packaging applications. *European Polymer Journal*. 2011;47(2):179-186.

24. Brunel DG, Pachekoski WM, Dalmolin C, Agnelli JAM. Natural additives for poly (hydroxybutyrate – CO – hydroxyvalerate) – PHBV: effect on mechanical properties and biodegradation. *Materials Research*. 2014;17(5):1145-1156.
25. Jost V, Langowski HC. Effect of different plasticisers on the mechanical and barrier properties of extruded cast PHBV films. *European Polymer Journal*. 2015;68:302-312.
26. Guo J, Zhang Q, Cai Z, Zhao K. Preparation and dye filtration property of electrospun polyhydroxybutyrate–calcium alginate/carbon nanotubes composite nanofibrous filtration membrane. *Separation and Purification Technology*. 2016;161:69-79.
27. Soane IT, Manfredi LB, Cyras VP. Properties and processing relationship of polyhydroxybutyrate and cellulose biocomposites. *Procedia Materials Science*. 2015;8:807-813.
28. Gunning MA, Geever LM, Killion JA, Lyons JG, Higginbotham CL. Mechanical and biodegradation performance of short natural fibre polyhydroxybutyrate composites. *Polymer Testing*. 2013;32(8):1603-1611.
29. Levy Neto P, Pardini LC. *Compósitos Estruturais - Ciência e Tecnologia*. São Paulo: Edgard Blucher; 2006.
30. Sanjay MR, Arpitha GR, Yogesha B. Study on Mechanical Properties of Natural - Glass Fibre Reinforced Polymer hybrid Composites: A Review. *Materials Today: Proceedings*. 2015;2(4-5):2959-2967.
31. Malkapuram R, Kumar V, Singh Y. Recent Development in Natural Fiber Reinforced Polypropylene Composites. *Journal of Reinforced Plastics and Composites*. 2009;28(10):1169-1189.
32. Ku H, Wang H, Pattarachaiyakoo N, Trada M. A review on the tensile properties of natural fiber reinforced polymer composites. *Composites Part B: Engineering*. 2011;42(4):856-873.
33. Rong MZ, Zhang MQ, Liu Y, Yang GC, Zeng HM. The effect of fiber treatment on the mechanical properties of unidirectional sisal-reinforced epoxy composites. *Composites Science and Technology*. 2001;61(10):1437-1447.
34. Maries I, Kuruvila J, Sabu T. Mechanical performance of short banana/sisal hybrid fiber reinforced polyester composites. *Journal of Reinforced Polyester Plastics and Composites*. 2010;29(1):12-29.
35. Thomas S, Paul SA, Pothan LA, Deepa B. Natural Fibers: Structure, Properties and Applications. In: Kalia S, Kaith BS, Kaur I, eds. *Cellulose Fibers: Bio- and Nano-Polymer Composites – Green chemistry and technology*. Berlin, Heidelberg: Springer; 2011. p. 3-42.
36. Salazar VLP, Caraschi JC, Leão AL. Avaliação dos produtos de emissão a partir da pirólise de assentos automotivos feitos de fibra de coco e de espuma de poliuretano. *Engenharia Sanitária e Ambiental*. 2005;10(2):162-166.
37. Mir SS, Nafsin N, Hasan M, Hasan N, Hassan A. Improvement of physico-mechanical properties of coir-polypropylene biocomposites by fiber chemical treatment. *Materials & Design*. 2013;52:251-257.
38. Essabir H, Bensalah MO, Rodrigue D, Bouhfid R, Qaiss A. Structural, mechanical and thermal properties of bio-based hybrid composites from waste coir residues: Fibers and shell particles. *Mechanics of Materials*. 2016;93:134-144.
39. PHB Industrial S/A. *Material Safety Data Sheet*. Available from: <http://www.biocycle.com.br/images/msds.pdf> Access in: 02/12/2015.
40. American Society for Testing and Materials (ASTM). *ASTM D5229/D5229M – 92. Standard Test Method for Moisture Absorption Properties and Equilibrium Conditioning of Polymer Matrix Composite Materials*. West Conshohocken: ASTM; 2010.
41. American Society for Testing and Materials (ASTM). *ASTM D790 – 02. Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials*. West Conshohocken: ASTM; 2002.
42. American Society for Testing and Materials (ASTM). *ASTM D3039/D3039M – 08. Standard Test Method for Tensile Properties of Polymer Matrix Composite Materials*. West Conshohocken: ASTM; 2008.
43. Sharma RK, Wooten JB, Baliga VL, Lin X, Chan WG, Hajaligol MR. Characterization of chars from pyrolysis of lignin. *Fuel*. 2004;83(11-12):1469-1482.
44. Campos A, Teodoro KBR, Marconcini JM, Mattoso LHC, Martins-Franchetti SM. Efeito do tratamento das fibras nas propriedades do biocompósito de amido termoplástico/policaprolactona/sisal. *Polímeros*. 2011;21(3):217-222.
45. Fiore V, Scalici T, Nicoletti F, Vitale G, Prestipino M, Valenza A. A new eco-friendly chemical treatment of natural fibres: Effect of sodium bicarbonate on properties of sisal fibre and its epoxy composites. *Composites Part B: Engineering*. 2016;85:150-160.
46. Forster PL, Martins NA, Parra DF, Egute NS, Lugão AB. Influence of gamma radiation on thermal properties and water vapor transmission of Poly(3-hydroxybutyrate) (PHB) in blends. In: *International Nuclear Atlantic Conference – INAC*. 2009, Sep 27-Oct 2; Rio de Janeiro, RJ, Brazil. Rio de Janeiro: Associação Brasileira de Energia Nuclear; 2009.
47. Zhao H, Cui Z, Sun X, Turng LS, Peng X. Morphology and Properties of Injection Molded Solid and Microcellular Poly(lactic Acid)/Polyhydroxybutyrate-Valerate (PLA/PHBV) Blends. *Industrial & Engineering Chemistry Research*. 2013;52(7):2569-2581.
48. Wellen RMR, Rabelo MS, Araújo Júnior IC, Fecine GJM, Canedo EL. Melting and crystallization of poly(3-hydroxybutyrate): effect of heating/cooling rates on phase transformation. *Polímeros*. 2015;25(3):296-304.
49. Hong SG, Lin YC, Lin CH. Crystallization and degradation behaviors of treated polyhydroxybutyrates. *Reactive & Functional Polymers*. 2008;68(11):1516-1523.
50. Baltiere RC, Mei LHI, Bartoli J. Study of the influence of plasticizers on the thermal and mechanical properties of poly(3-hydroxybutyrate) compounds. *Macromolecular Symposia*. 2003;197(1):33-44.
51. Rosa DS, Chui QSH, Pantano Filho R, Agnelli JAM. Avaliação da Biodegradação de Poli-β-(Hidroxibutirato), Poli-β-(Hidroxibutirato-co-valerato) e Poli-ε-(caprolactona) em Solo Compostado. *Polímeros*. 2002;12(4):311-317.
52. Parra DF, Fusaro J, Gaboardi F, Rosa DS. Influence of poly (ethylene glycol) on the thermal, mechanical, morphological, physical-chemical and biodegradation properties of poly (3-hydroxybutyrate). *Polymer Degradation and Stability*. 2006;91(9):1954-1959.

53. Bordes P, Pollet E, Avérous L. Nano-biocomposites: Biodegradable polyester/nanoclay systems. *Progress in Polymer Science*. 2009;34(2):125-55.
54. Porter M, Yu J. Crystallization Kinetics of Poly(3-hydroxybutyrate) Granules in Different Environmental Conditions. *Journal of Biomaterials and Nanobiotechnology*. 2011;2(3):301-310.
55. Quental AC, Carvalho FP, Tada ES, Felisberti MI. Blendas de PHB e seus copolímeros: miscibilidade e compatibilidade. *Química Nova*. 2010;33(2):438-446.
56. Iggui K, le Moigne N, Kaci M, Cambe S, Degorce-Dumas JR, Bergeret A. A biodegradation study of poly(3-hydroxybutyrate-co-3-hydroxyvalerate)/organoclay nanocomposites in various environmental conditions. *Polymer Degradation and Stability*. 2015;119:77-86.
57. Gomes TS, Visconte LLY, Pacheco EBAV. Substituição da fibra de vidro por fibra de bananeira em compósitos de polietileno de alta densidade. Parte 1. Avaliação mecânica e térmica. *Polímeros*. 2013;23(2):206-211.
58. Ghaffar AMEHA. *Development of a biodegradable material based on Poly (3-hydroxybutyrate) PHB*. [Dissertation]. Halle: Martin-Luther Universität Halle-Wittenberg; 2002.
59. Martin AR, Martins MA, Mattoso LHC, Silva ORRF. Caracterização química e estrutural de fibra de sisal da variedade *Agave sisalana*. *Polímeros*. 2009;19(1):40-46.
60. Schlemmer D, Sales MJA, Resck IS. Preparação, caracterização e degradação de blendas PS/TPS usando glicerol e óleo de buriti como plastificantes. *Polímeros*. 2010;20(1):6-13.
61. Wang L, Zhu W, Wang X, Chen X, Chen GQ, Xu K. Processability modifications of poly(3-hydroxybutyrate) by plasticizing, blending, and stabilizing. *Journal of Applied Polymer Science*. 2008;107(1):166-173.
62. Mohanty AK, Misra M, Hinrichsen G. Biofibres, biodegradable polymers and biocomposites: An overview. *Macromolecular Materials and Engineering*. 2000;276-277(1):1-24.
63. Melo JDD, Carvalho LFM, Medeiros AM, Souto CRO, Paskocimas CA. A biodegradable composite material based on polyhydroxybutyrate (PHB) and carnauba fibers. *Composites Part B: Engineering*. 2012;43(7):2827-2835.
64. Ishizaki MH, Visconte LLY, Furtado CRG, Leite MCAM, Lesblanc JL. Caracterização mecânica e morfológica de compósitos de polipropileno e fibras de coco verde: influência do teor de fibra e das condições de mistura. *Polímeros*. 2006;16(3):182-186.
65. Dittenber DB, GangaRao HVS. Critical review of recent publications on use of natural composites in infrastructure. *Composites Part A: Applied Science and Manufacturing*. 2012;43(8):1419-1429.
66. Lima PRL, Santos RJ, Ferreira SR, Toledo Filho TR. Characterization and treatment of sisal fiber residues for cement-based composite application. *Engenharia Agrícola*. 2014;34(5):812-825.
67. Verma D, Gope PC, Shandilya A, Gupta A, Maheshwari MK. Coir Fibre Reinforcement and Application in Polymer Composites: A Review. *Journal of Materials and Environmental Science*. 2013;4(2):263-276.
68. Monteiro SN, Terrones LAH, Carvalho EA, d'Almeida JRM. Efeito da interface fibra/matriz sobre a resistência de compósitos poliméricos reforçados com fibras de coco. *Matéria (Rio de Janeiro)*. 2006;11(4):395-402.
69. Faruk O, Bledzki AK, Fink HP, Sain M. Progress Report on Natural Fiber Reinforced Composites. *Macromolecular Materials and Engineering*. 2013;299(1):9-26. DOI: 10.1002/mame.201300008