International Journal of Materials Engineering and Technology

Published Online: December 2014
Available online at http://pphmj.com/journals/ijmet.htm
Volume 12, Number 2, 2014, Pages 151-176

USE OF SPONGE-GOURD (*Luffa cylindrica*) AGRO-RESIDUE AS FILLER FOR RENEWABLE HIGH DENSITY POLYETHYLENE: DEVELOPMENT AND CHARACTERIZATION OF COMPOSITES

Viviane A. Escócio[1], **Elen B. A. V. Pacheco**[1], **Ana Maria F. de Sousa**[2], **André de P. Cavalcante**[2] **and Leila L. Y. Visconte**[1]

[1]Universidade Federal do Rio de Janeiro
Instituto de Macromoléculas Professora Eloisa Mano
Avenida Horácio Macedo, 2030, Prédio do Bloco J - CT
Cidade Universitária, Ilha do Fundão
CEP 21941-598 Rio de Janeiro, Brasil
e-mail: vivi75@ima.ufrj.br

[2]Universidade do Estado do Rio de Janeiro - Instituto de Química
Brasil

Abstract

The availability of raw materials obtained from natural resources in Brazil has motivated their use in the development of more sustainable technologies to obtain novel materials. In this regard, the combination of renewable high density polyethylene (HDPE), obtained from ethanol produced from sugarcane, with residues generated from the production of sponge-gourds, which are generally burnt, was investigated. The residues were characterized according to their moisture, lignin, soluble extractives, ash contents and density, and thermogravimetric analysis was also carried out. The milled waste material was then blended (10-40%wt/wt) with renewable HDPE by

Received: June 25, 2014; Accepted: August 13, 2014
Keywords and phrases: agrofiber residue, sponge-gourds, bio-based HDPE, composites, renewable materials.

extrusion. Specimens were injection-molded for the assessment of properties such as tensile, flexural and Izod impact strengths. The morphological and thermal properties were also investigated. The results show that the addition of the waste material affected all of the properties studied, which were similar to those reported in the literature for composites produced with HDPE obtained from a fossil source. It was found that the sponge-gourd waste has good potential for application as a cellulosic filler, aimed at providing a totally renewable composite with improved tensile modulus and tensile and flexural strength properties compared with the pure renewable HDPE, without altering the thermal properties.

1. Introduction

The sponge-gourd belongs to the botanical family Cucurbitaceae and the gender *Luffa*. The most well known and cultivated species in Brazil is *Luffa cylindrica*, comprised of a lignocellulosic material. In Brazil, the sponge-gourd is cultivated on family farms in most areas of the country. In the last ten years, production has increased and the farming practice is becoming commercialized. The highest production of sponge-gourd in Brazil is in Minas Gerais, with a planted area of over 100 hectares. The ripe fruit is principally used for cleaning and personal hygiene purposes [1]. In Minas Gerais, the sponge-gourd is mainly produced to supply the sponge market. Data supplied by the producers of this region indicate that the waste material generated during sponge production represents around 30% (by weight) of the total amount processed. This residue is generally discarded and burnt. For this reason, the research group of the Center for Excellence in Recycling and Sustainable Development (in Portuguese *Núcleo de Excelência em Reciclagem e Desenvolvimento Sustentável* - NERDES) located at the *Instituto de Macromoléculas Professora Eloisa Mano* (IMA) of *Universidade Federal do Rio de Janeiro* (UFRJ), Brazil, has studied the use of sponge-gourd residue as a lignocellulosic filler in composites. The use of natural lignocellulosic fillers, principally those from agricultural residues, in polymers is an attractive option due to their low cost and good mechanical and non-abrasive properties. These natural fillers offer a potential substitute

for conventional fibers such as glass, aramid and carbon [2] and can provide artifacts of low weight.

In order to achieve the goal of sustainability, in this study a polymeric matrix obtained from a renewable source, that is, ethanol from sugarcane, was used. Brazil is the largest producer of sugarcane in the world, with around 490 million tons being produced per year [3, 4] and it has the second largest ethanol production globally [3, 4]. Sugarcane is an example of a renewable raw material which can be used as a clean energy source and a basic raw material for products [3, 4].

Brazil has gained global recognition for its use of renewable energy, which represents more than 44% of the sources for the national energy matrix. Sugarcane products are responsible for 16% of Brazil's total energy supply [3, 4]. The potential of Brazil in terms of natural resources has motivated their use in recent years in the development of new, more sustainable, technologies.

In Brazil industrial polyethylenes are produced from two raw material sources: ethanol extracted from sugarcane, herein referred to as 'renewable polyethylene', and petroleum, herein referred to as 'conventional polymer'. According to the supplier, due to its characteristics, renewable polyethylene sequesters atmospheric carbon dioxide during processing, reducing the greenhouse effect [3, 4].

No reports of studies on composites with polyolefin produced from ethanol and a filler could be found in the scientific literature. However, some research studies on composites comprised of polyethylene produced from a fossil source and sponge-gourds [5-7] and some lignocellulosic fillers from agricultural practices [8-16] have been published. In the latter case, the agricultural residues did not receive any treatment to increase the interfacial adhesion.

Sousa and collaborators [5] studied the influence of different processing conditions for mixtures of high density polyethylene (HDPE), from a fossil source, with *Luffa cylindrical*. The following parameters were studied:

processing temperature, extruder rotation, fiber content and particle size. The results showed that the parameters that most affected the mechanical properties were lignocellulosic filler content and particle size. Other polymers obtained with this type of fiber have also been studied. There are reports on the extraction of nanocrystals from sponge-gourd cellulose to strengthen polycaprolactone [6] as well as the superficial treatment of the sponge-gourd fiber prior to its addition to the ester vinyl resin [7].

Other agricultural fibers obtained from rice husk have been used as a reinforcement agent for post-consumer HPDE originating from a fossil source [8] and it was verified that the tensile modulus, flexural modulus and flexural strength increased with the incorporation of 5 and 10%wt of rice husk fiber. However, in relation to pure polyethylene, with the addition of modified rice husk the values for impact strength decreased with the addition of 5%wt while they increased by 35% with the addition of 10%wt. Also, there was an increase of approximately 11% in the tensile modulus with the addition of 10%wt of modified rice husk.

In other studies on polyethylene composites banana-tree fibers have been used [10-13]. Gomes and collaborators [10, 11] studied high density polyethylene composites and their results showed that the addition of banana-tree fibers increased the values for the elastic modulus under tensile stress, elastic modulus under flexural stress and impact strength by approximately 732%, 164% and 135%, respectively, in relation to the pure polymer, demonstrating that this fiber represents a potential substitute for glass fibers in polymers. Coconut fiber [14] can also be used as a filler in polyolefin composites.

Lei and collaborators [15] investigated composites comprised of recycled HDPE (R-HDPE) and natural fibers (pine and sugarcane bagasse). The fiber to R-HDPE ratio was fixed at 30:70 (%wt/wt). The results showed lower tensile and impact strengths for R-HDPE/bagasse and R-HDPE/pine composites compared with the pure R-HDPE, although the storage modulus values were 48% and 44% higher for the composites with bagasse and pine, respectively, in relation to R-HDPE.

Panthapulakkal and Sain [16] studied the potential of agro-residues such as wheat straw, cornstalk and corncob as reinforcements for polyethylene, in the search for alternatives to the use of wood fiber, by investigating their mechanical properties (tensile modulus, tensile strength, flexural strength and impact strength). They prepared HDPE composites with a high content of agro-residues (65%wt). The wheat straw showed the highest reinforcement potential and the trend observed was corncob < corn stalk < wood flour < wheat straw.

In this context, the objective of this study was to develop totally renewable composites comprised of polyethylene obtained from ethanol and different contents of vegetal sponge-gourd residue (10, 20, 30, and 40%wt/wt). The influence of this residue on the melt flow index (MFI), mechanical properties and thermogravimetric analysis was investigated through comparison with the pure polyethylene.

2. Materials and Methods

2.1. Raw materials

The high density polyethylene (HDPE) SHC 7260 (Braskem, Brazil) used to obtain the composites in this study was obtained from ethanol produced from sugarcane. It had a density of 0.959g/cm^3 and melt flow index of 7.2g/10min (190°C; 2.16g). The sponge-gourd residue (cellulosic filler) was provided by the company Bushings Bonfim (Minas Gerais State, Brazil).

2.2. Characterization of sponge-gourd residue

The sponge-gourd residue was milled for processing and then separated according to particle size in a Produtest electromagnetic vibration sifter. Two particle sizes were used in the study: <0.15 and 0.21-0.42mm. These two filler samples were characterized to evaluate the moisture content [17], density [18], ash content [19], soluble extracts [20] and lignin content by the Klason method [21]. Also, thermogravimetric analysis (TGA) was carried out on a TA Instruments TG analyzer (model Q500) with a nitrogen flow of 60mL/min, heating rate of 10°C/min and temperature range of 25 to 700°C.

The particles sizes (<0.15 and 0.21-0.42mm) were verified by scanning electron microscopy (SEM) (Jeol SEM microscope, model JSM-6510LV).

2.3. Mixing procedure

The renewable HDPE composites with 10, 20, 30 and 40%wt/wt of sponge-gourd residue were processed in a twin-screw co-rotating interpenetrating extruder (Tecktril, model DCT-2). Prior to processing, the cellulosic filler was conditioned in an oven with air circulation for 24h at 60°C. The polymer and filler were premixed before being placed in the extruder. The extrusion conditions were: extruder rotation 300rpm; feeder rotation 15rpm; and temperature in processing zone 1 90°C, zones 2 to 5 140°C, zones 6 to 9 160°C and head 180ºC. The pellets obtained in processing were dried at 60°C to remove the moisture.

2.4. Characterization of the polymer and the composites

The samples, under pellet form, were dried in an oven with air circulation for 24h at 60°C before injection molding. The specimens used for the evaluation of the tensile [22], flexural [23] and impact [24] properties were prepared by injection molding (Arburg Allrounder 270S-400-170) using the following conditions: temperatures of zone 1 160°C, zone 2 170°C, zone 3 175°C and zone 4 180°C; nozzle temperature 195°C; injection pressure 800 to 1100bar; and cooling time 30s at room temperature. The data for the tensile strength, tensile modulus, flexural strength and impact strength were treated using the software Statgraphics Centurion.

The melt flow index (MFI) [25] was determined in a Dynisco Kayeness polymer test system (model LMI4003). Before performing this test, the samples, in the form of pellets, were dried in an oven with air circulation for 24h at 60°C.

Tension and flexural testes were carried out in a universal testing machine (EMIC DL-3000). The Izod impact strength test was performed in a CEAST Resil impact tester using a hammer with an energy of 2J and an angle of 60°. The specimens were conditioned for 48h at 23°C and 48% moisture, as recommended in the standard [26].

The thermogravimetric analysis (TGA) of the composites was performed under the same conditions used for the characterization of the sponge-gourd reside.

The morphology of the samples was examined by SEM using a Jeol SEM microscope (model JSM-6510LV). Gold sputtering of the specimen fractured in the impact test was carried out using a Denton vacuum (model Desk V).

3. Results and Discussion

3.1. Characterization of sponge-gourd residue

Table 1 shows the results for the characterization of the sponge-gourd residue used as cellulosic filler, which had a fibrillar form. The density value obtained was 1.25g/cm^3, which is lower than those reported for traditional additives used for the reinforcement of polymers, for example, the density of glass fiber is 2.55g/cm^3 [27, 28]. A lower density contributes to obtaining a lighter composite.

The moisture content of the sponge-gourd residue was 10.7%wt, which is similar to the amounts normally found in wood, that is, between 10 and 18%wt [29].

Table 1. Characterization of sponge-gourd residue originating from Minas Gerais State, Brazil

Properties	Mean
Density, g/cm^3	1.25 ± 0.05
Moisture, %wt	10.7 ± 0.6
Ash, %wt	0.9 ± 0.3
Extractives, %wt	2.7 ± 0.7
Lignin, %wt	14.7 ± 0.5

The average value obtained experimentally for the ash content of the sponge-gourd residue was 0.9%wt, as shown in Table 1. According to the

literature [30-32], silicate, oxalate, sulfate and carbonate ash of Ca, Na, K, and Mn are commonly present and adhered to the surface of cellulosic fibers in the form of their respective salts.

The content of soluble extractives was 2.7%wt, while in the literature a value of 3.2%wt is reported for sponge-gourd residue [31] This analysis was carried out in order to quantify the percentage of soluble extractives, such as polysaccharides of low molar weight and inorganic impurities, in hot water.

Similar values for the ash, lignin and moisture contents of cellulosic residues were found in the literature [33] for a vegetal Brazilian sponge-gourd (ash content = 0.7%wt and lignin content = 15.5%wt) [33] and for other fibers, for instance, banana-tree fiber (moisture content=8.6%wt) [33]. The composition of the lignocellulosic materials is dependent on various factors, such as the plant species and variety, plant age, soil type and climatic conditions [31, 33, 34].

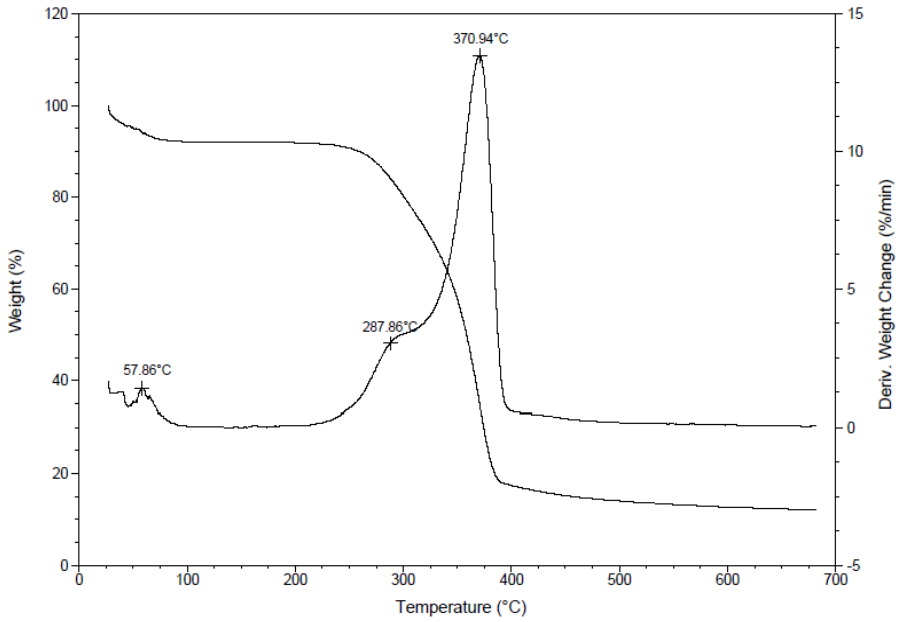

Figure 1. Curves for the thermal degradation values and their derivative obtained for the sponge-gourd residue in N_2.

The thermogravimetric analysis results for the sponge-gourd residue are shown in Figure 1. In the derivative thermogravimetric (DTG) curves, a small peak was observed at ~58ºC, probably related to the loss of moisture, although the residue had been dried before the analysis. However, its hydrophilicity hinders the water total removal. This weight loss was of approximately 7%wt. Another two peaks were observed as follows: a second peak at 288ºC, attributed to hemicellulose degradation, with a loss of 15%wt and a third peak at 371°C with a loss of 60%wt, related to cellulose degradation. Similar values in relation to sisal fiber are reported in the literature [34].

3.2. Evaluation of the mechanical properties of the composite

Tables 2 and 3 show the descriptive statistics related to the mechanical properties of the pure HDPE and the composites with different contents of sponge-gourd residue for the two samples with different particles sizes. The effect of the sponge-gourd residue content on the renewable HDPE mechanical properties was investigated using one-way analysis of variance (ANOVA). In this study, a p value of <0.05 was considered to indicate that the specific experimental factor and/or its interactions has a significant influence on the response variable, meaning that the residue content had an effect on the mechanical properties evaluated. For all of the mechanical properties investigated in this study the p value was <0.05, indicating that the sponge-gourd residue content does significantly affect the mechanical properties.

Table 2. Tensile properties of renewable HDPE and the composites with sponge-gourd residue

Renewable HDPE: Sponge-gourd residue (%wt/wt)	**Tensile strength**			**Tensile modulus**		
	Mean, MPa	SD, MPa	CV, %	Mean, MPa	SD, MPa	CV, %
100:0	19.2	0.2	1	679	41	6

Sponge-gourd residue with a particle size of < 0.15 mm						
90:10	20.2	0.6	3	1032	82	8
80:20	19.9	0.3	2	1289	81	6
70:30	21.2	0.4	2	1682	158	9
60:40	20.8	0.3	1	2082	237	11
Sponge-gourd residue with a particle size of 0.21-0.42mm						
90:10	17.9	0.3	2	897	18	2
80:20	18.7	0.3	2	1280	63	5
70:30	19.9	0.2	1	1819	90	5

Table 3. Flexural and impact properties of renewable HDPE and the composites with sponge-gourd residue

Renewable HDPE: Sponge-gourd residue (%wt/wt)	**Flexural strength (MPa)**			**Impact strength (J/m)**		
	Mean, MPa	SD, MPa	CV, %	Mean, MPa	SD, MPa	CV, %
100:0	28.4	0.5	2	34.7	1.0	3
Sponge-gourd residue with a particle size of <0.15mm						
90:10	30.2	0.6	2	33.3	1.6	5
80:20	33.5	0.5	1	31.3	0.9	3
70:30	37.7	0.5	2	26.9	2.4	9
60:40	35.8	0.3	1	25.5	1.0	4
Sponge-gourd residue with a particle size of 0.21-0.42mm						
90:10	25.6	0.6	2	38.2	4.7	12
80:20	28.9	1.2	4	41.4	4.2	10
70:30	33.9	0.5	2	37.4	7.5	20

The renewable HDPE mechanical properties were affected by the content of sponge-gourd residue. Figures 2-8 present, respectively, a comparison of the average projection (confidence interval of 95%) for the maximum tensile strength, tensile modulus, flexural strength and impact strength.

Considering the property of tensile strength, as shown in Figures 2 and 3, the results show that the addition of 30%wt of sponge-gourd residue with a particle size <0.15mm produced an increase of 11% in relation to the pure renewable HDPE. Despite being a relatively small increase, this is an important result considering that the composites contained no additives to improve the polymer-cellulosic residue interaction. It is known that the interaction between the matrix and the cellulosic filler is not favored, considering that lignocellulosic residues have a hydrophilic nature while HDPE has a hydrophobic nature. This low level of interaction tends to hinder the adhesion among the phases which, in general, leads to a reduction in the mechanical properties [35].

However, with the addition the sponge-gourd residue with a particle size of 0.21-0.42mm it was observed that the values for the tensile strength of the composites with 10 and 20%wt of cellulosic residue were 6.8% and 2.6% lower, respectively, in relation to the pure renewable HDPE. However, with the addition of 30%wt of this sponge-gourd residue the same property increased by 3.6% in relation to the pure renewable HDPE. These results suggest that the limit of reinforcement for these composites is around 30%wt of cellulosic filler, considering the composition ranges studied.

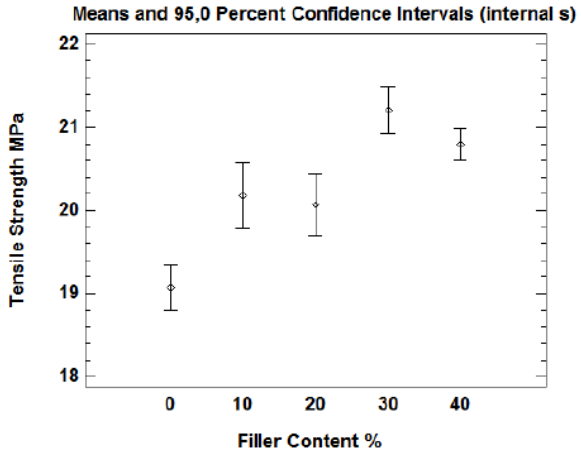

Figure 2. Average projection obtained for maximum tensile strength of renewable HDPE and sponge-gourd residue composites with filler particle size <0.15mm (software Statgraphics Centurion).

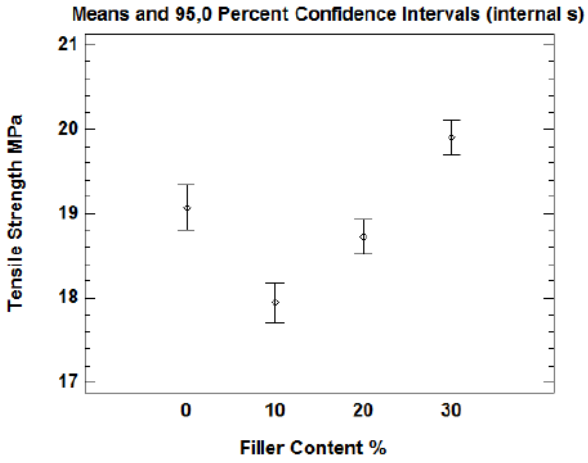

Figure 3. Average projection obtained for maximum tensile strength of renewable HDPE and sponge-gourd residue composites with particle size 0.21-0.42mm (software Statgraphics Centurion).

The elasticity modulus for the renewable HDPE also increased considerably with the addition of the sponge-gourd residue (Figures 4 and 5) reaching 207% in relation to the pure polymer when 40%wt of cellulosic filler with a particle size of <0.15mm was added.

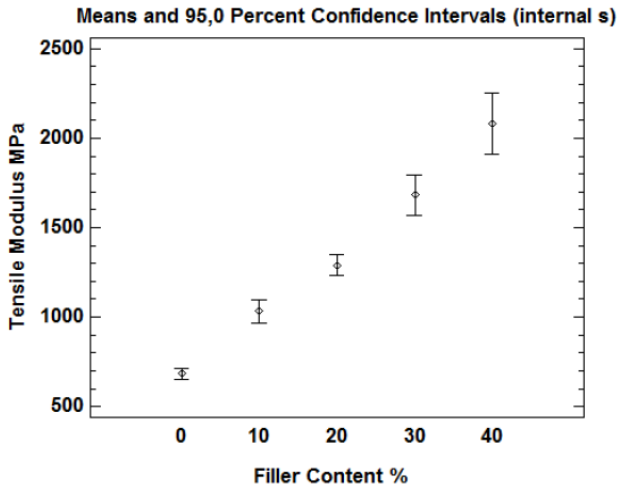

Figure 4. Average projection obtained for elasticity modulus of renewable HDPE and sponge-gourd residue composites with filler particle size <0.15mm (software Statgraphics Centurion).

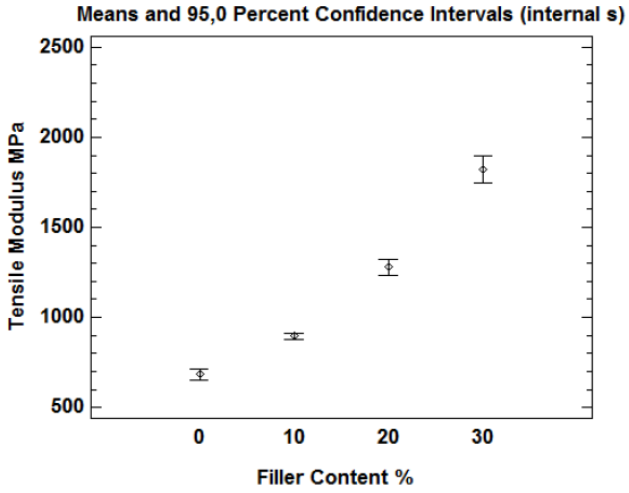

Figure 5. Average projection obtained for elasticity modulus of renewable HDPE and sponge-gourd residue composites with filler particle size 0.21-0.42mm (software Statgraphics Centurion).

Figures 6 and 7 show the results for the flexural strength. It can be observed that with increasing residue content there is an increase in the values for this property, reaching a maximum of 37.5MPa with 30%wt of

lignocellulosic material, representing a 35% increase in relation to the pure polymer, for the smaller particle size. The flexural strength value for the composites containing the residue with the larger particle size decreased with the addition of 10%wt of sponge-gourd residue and increased with 20 and 30%wt. In this case, the addition of a low content of cellulosic filler also affected this property. In the content range studied, it was verified that the tensile and flexural strengths reached maximum values for the composite containing 30%wt of the residue.

The impact strength of the composites (Figure 8) decreased with the addition of the lignocellulosic residue of the smaller particle size (<0.15). Once again, it is important to note that the sponge-gourd residue was used without any kind of treatment to enhance the interfacial adhesion between the polar cellulosic residue and the nonpolar matrix (HDPE). In the results for the impact strength of the composites containing 10, 20 and 30%wt of filler with the larger particle size (0.21 to 0.42mm), relatively high values were observed for the standard deviation (10-20%). Thus, no conclusions could be drawn regarding the influence of the residue with this particle size on the impact strength (Figure 9).

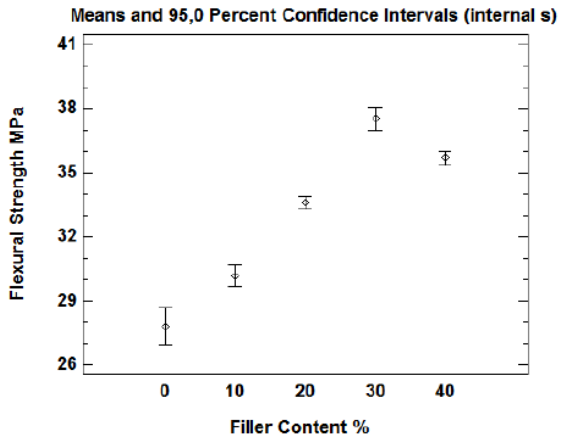

Figure 6. Average projection obtained for flexural strength of renewable HDPE and sponge-gourd residue composites with filler particle size < 0.15mm (software Statgraphics Centurion).

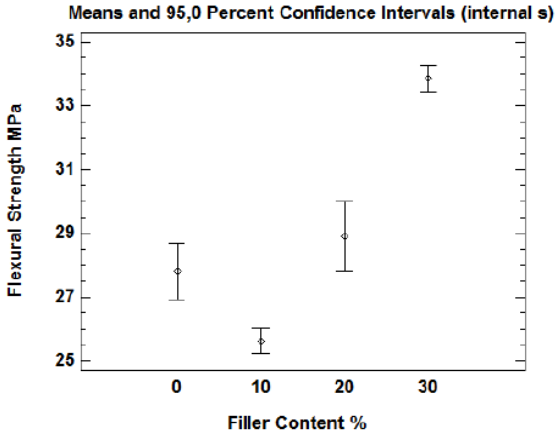

Figure 7. Average projection obtained for flexural strength of renewable HDPE and sponge-gourd residue composites with filler particle size 0.21-0.42mm (software Statgraphics Centurion).

According to the literature [36, 37], fiber can support tensile stress up to a maximum amount which is transferred to the matrix and for this to occur there is a critical length. The critical length is dependent on the diameter and maximum load resistance, and the interfacial resistance between the filler and the matrix [38] which explains the behavior of composites with different particle sizes in the tensile and flexural tests. The two particles sizes (< 0.15 and 0.21-0.42mm) used to produce the composites favored their tensile and flexural strength with the addition of 30%wt filler. When 40%wt filler was added the limit for obtaining good properties is surpassed, probably because the incompatibility of the cellulose filler with the matrix surpassed the reinforcement effect which the filler provided at 30%wt. However, according to the literature [36], the presence of filler generally decreases the impact strength of the composite and often contributes to higher crack propagation. This behavior was observed for the filler with the smaller particle size. The impact strength values for the composites produced with the larger particle size presented high standard deviations and thus conclusions could not be drawn.

Similar behaviors for the tensile strength, tensile modulus, flexural and impact strength have been described in the literature [39] for high density polyethylene obtained from fossil material and bamboo fiber. For composites

of HDPE/bamboo fiber (70/30%wt/wt) the authors reported increases of up to 19% and 49% for the tensile and flexural strengths, respectively, and an increase of 1.700% in the tensile modulus with the addition of 40%wt bamboo fiber.

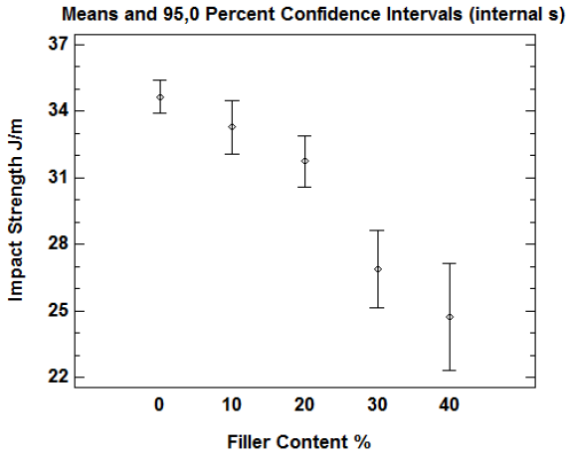

Figure 8. Average projection obtained for impact strength of renewable HDPE and sponge-gourd residue composites with filler size particle <0.15mm (software Statgraphics Centurion).

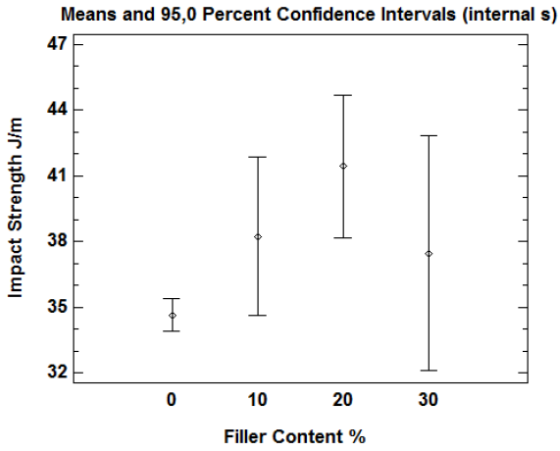

Figure 9. Average projection obtained for impact strength of renewable HDPE and sponge-gourd residue composites with filler size particle 0.21-0.42mm (software Statgraphics Centurion).

Table 4 summarizes a comparison between results found in the literature for composites based on HDPE of fossil origin and those reported herein for HDPE obtained from a renewable source material. It can be observed that the values for the tensile strength, tensile modulus and flexural strength are similar. The composite obtained with only renewable materials provided very promising results.

Table 4. Comparison of results for composites produced using renewable HDPE and conventional HDPE

Properties	Renewable HDPE with 30%wt sponge-gourd (this study)	Conventional HDPE 30%wt fiber bamboo [39]	Conventional HDPE with 30%wt sponge-gourd [5]	Conventional HDPE with 10%wt rice husk [8]
Tensile strength (MPa)	21	26	17	~ 20
Tensile modulus (MPa)	1682	2675	1410	-
Flexural strength (MPa)	38	28	35	~ 19
Impact strength (J/m)	28	57	53	~43

The melt flow index (MFI) is an important physical parameter for the processing of plastic. It is a representative parameter in relation to rheology information and is widely used commercially to evaluate polymers. Table 5 shows the results for the MFI where a decrease in the MFI value can be noted as the sponge-gourd residue content in the composite increases, which is due to the increasing viscosity of the HDPE/filler system. This result suggests that the filler imposed a barrier to the polymer flow. With the addition of 20%wt of sponge-gourd residue the decrease in the value for this property was 43% and with the addition of 40%wt the decrease was 83% in relation to pure HDPE. The same behavior was observed for the two particle sizes.

Table 5. Melt flow index for renewable HDPE and sponge-gourd residue composites

Renewable HDPE: Sponge-gourd residue (%wt/wt)	**Flow index** (g/10min)	
	Sponge-gourd particle size	
	< 0.15 mm	**0.21-0.42 mm**
100:0	8.4 ± 0.3	8.4 ± 0.3
90:10	6.8 ± 0.2	6.4 ± 0.5
80:20	4.8 ± 0.4	5.1 ± 0.4
70:30	3.0 ± 0.2	3.1 ± 0.6
60:40	1.4 ± 0.2	-

3.3. Morphological analysis of composites

Figure 10(a) shows the micrograph of the cellulosic filler sponge-gourd with a particle size of <0.15mm, where an irregular surface can be observed. Figure 10(b) shows the impact-fractured surface of the HDPE, which is smoother than those of the composites (Figures 10(c)-(f)). In general, the composites show rough fracture surfaces, particularly those with 40%wt of cellulosic filler.

From the SEM results it can be observed that the filler particles were pulled out due to the force applied during the impact strength test. In Figures 10(c) and 10(d) this particle removal can be verified. This behavior is due to the low adhesion at the polymer/filler interface which increased with the filler content. The high degree of roughness observed on the surface of the composite with 40%wt of filler hindered the observation of the fracture mechanism. Voids were also observed, which may be related to the evaporation of the water present, mainly, in the composites with a higher cellulosic filler. During the injection, which was carried out at 195°C, the moisture evaporated and voids were formed as the specimens cooled.

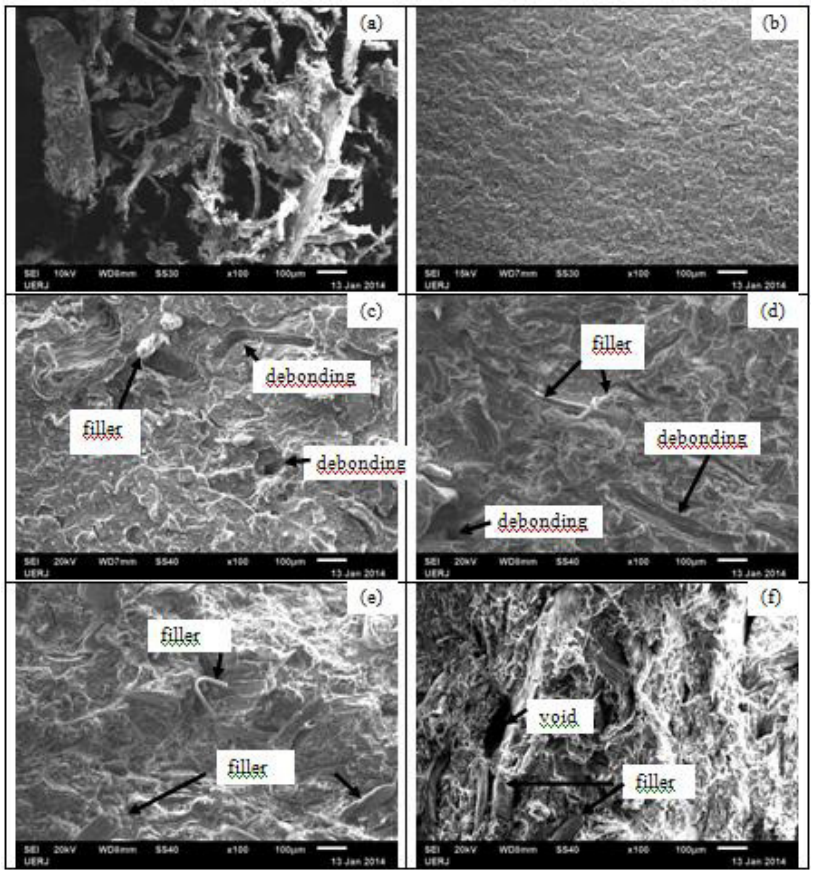

Figure 10. SEM micrographs of fracture surfaces for the following samples: sponge-gourd residue with particle size <0.15mm (a), renewable HDPE (b) and renewable HDPE/cellulosic filler composites: (c) 90/10%wt/wt, (d) 80/20%wt/wt, (e) 70/30%wt/wt and (f) 60/40%wt/wt.

Figure 11(a) shows the micrograph of the cellulosic filler with a particle size of 0.21-0.42mm. Figures 11(b)-(d) show the fractured surfaces of the HDPE composites with cellulosic filler and some delaminated fibers. Delamination occurs since the lignin, present in the fiber, is weak and separates between the cellulose fibers [40]. Although this may also have occurred in the case of the composites produced with smaller filler particles (Figure 10), it is more evident for those obtained with larger filler particles.

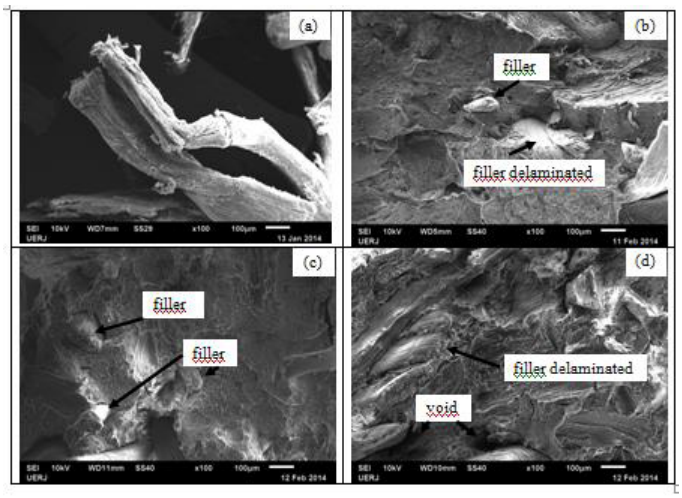

Figure 11. SEM micrographs of sponge-gourd residue of particle size 0.21-0.42mm (a), and renewable HDPE/cellulosic filler composites: (b) 90/10%wt/wt, (c) 20/80%wt/wt, (d) 70/30%wt/wt.

3.4. Thermogravimetric analysis of composites

The results for the thermogravimetric analysis of the samples are shown in Table 6 and the curves for the thermal degradation in the presence of nitrogen can be seen in Figures 12 and 13. It can be observed that with the addition of sponge-gourd residue to the HDPE two additional degradation events occur compared with the HDPE. The degradation stages related to the sponge-gourd residue can be more clearly observed with an increase in its content in the composites.

Table 6 shows the degradation onset temperatures (T*onset*). It can be observed that the T*onset* values show a significant difference in function of the presence of the filler. The T*onset* values shift toward lower temperatures with an increase in the composite filler due to the presence of fiber, which degrades at lower temperatures compared with polyolefin. The addition of up to 20%wt/wt filler had almost no effect on the maximum degradation temperature of the HDPE, as can be seen in Table 5. With the addition of the sponge-gourd residue a shoulder appears at lower temperatures (258 to 268°C), which becomes more evident as the filler content is increased, being

most pronounced with 40%wt/wt (258°C). This may be due to the hemicellulose content of the fiber being lower than the cellulose content, which has a greater effect in this composition.

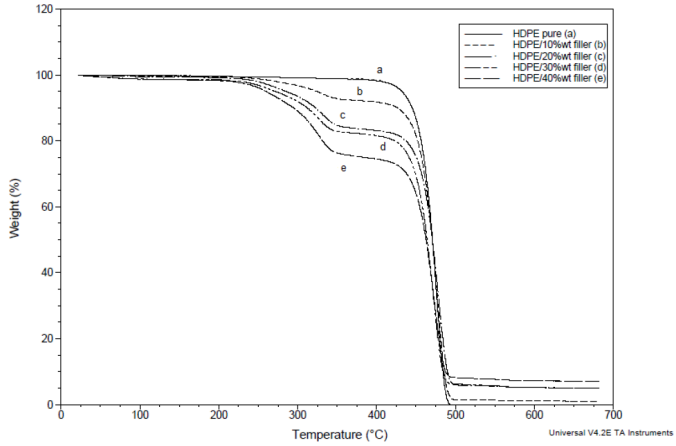

Figure 12. Curves for the weight loss (determined by TG) of the renewable HDPE and sponge-gourd composites with filler particle size of <0.15mm: 90/10%wt/wt, 80/20%wt/wt, 70/30%wt/wt, 60/40%wt/wt in nitrogen.

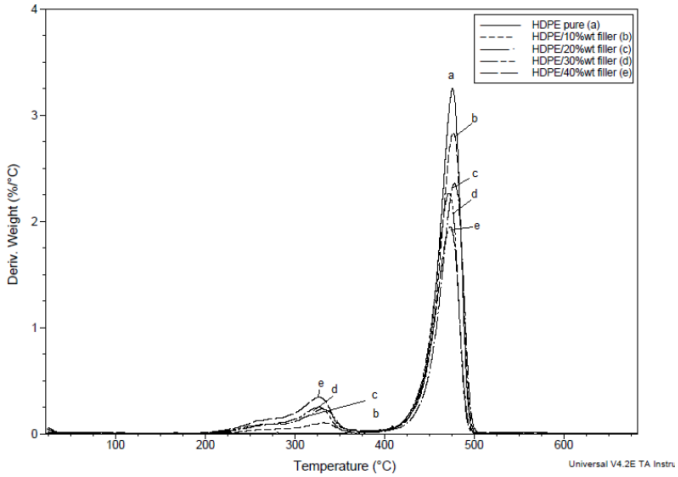

Figure 13. Curves for the derivative of the weight loss (determined by TG) of pure renewable HDPE and renewable HDPE/cellulosic filler composites with filler particle size <0.15mm: 90/10%wt/wt, 80/20%wt/wt, 70/30%wt/wt, 60/40%wt/wt in nitrogen.

Table 6. Results for the thermal gravimetric analysis of pure renewable HDPE and its composites with sponge-gourd residue

Renewable **HDPE/sponge-gourd (%wt/wt)**	**Tonset (°C)**	**Residue (%wt)**	**Maximum degradation temperature in the range of 300-350°C (°C)**	**Maximum degradation temperature in the range 400-500°C (°C)**
100:0	456	0.0	-	475
90:10	320	1.4	333	477
80:20	292	5.7	331	478
70:30	279	5.2	328	472
60:40	233	7.3	258*/329	474

4. Conclusions

The results show that the addition of sponge-gourd residue to renewable HDPE had a significant influence on all of the properties studied (tensile strength, elasticity modulus, flexural strength, impact strength and melt flow index) in relation to the pure HDPE, and in most cases the affect was positive.

It was also observed that the filler samples with different particle sizes showed distinct behaviors in the case of some properties. In relation to the micrographs, it was observed that the surface of the pure polymer fracture is smooth and those of the composites had a higher degree of roughness, which was most evident in the case of the composite with a filler content of 40%wt/wt. The presence of voids, the pull-out of particles and, most clearly, the delamination of cellulosic filler could be observed on the surface of the composites. The latter feature was mainly evident in the composites with a larger particle size.

The melt flow index decreased with the addition of filler, which was to be expected considering that there was an increase in the system viscosity. In relation to the thermal stability of the composites, the degradation

temperatures were shifted to lower temperatures due to the presence of the cellulose and hemicellulose which degrade at lower temperatures than polyethylene.

Thus, it can be concluded that totally renewable HDPE composites which have similar performance as conventional HDPE composites can be obtained, with good mechanical and thermal properties, enabling a decrease in the environmental impact associated with the disposal of sponge-gourd residue via its reuse.

Acknowledgment

We would like to thank *Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro* (FAPERJ), *Banco Nacional de Desenvolvimento* (BNDES), *Financiadora de Estudos e Projetos* (FINEP), *Conselho Nacional de Desenvolvimento Científico e Tecnológico* (CNPq), *Coordenação de Aperfeiçoamento de Pessoal de Nível Superior* (CAPES), *Núcleo de Excelência e Reciclagem e Desenvolvimento Sustentável* (NERDES) and BRASKEM for supplying the renewable HDPE.

References

[1] J. F. Lopes, W. A. Marouelli and H. R. da Silva, Irrigação na cultura da bucha vegetal, Embrapa Brasília, 2013.

[2] H. Ku, H. Wang, N. Pattarachaiyakoop and M. Trada, A review on the tensile properties of natural fiber reinforced polymer composites, Compos. Part. B-Eng. 42 (2011), 856-873.

[3] R. Belloli, Polietileno verde do etanol da cana-de-áçucar brasileira: biopolímero da classe mundial, (Trabalho de conclusão de Curso submetido a Universidade Federal do Rio Grande do Sul, Porto Alegre, Brasil), 2010.

[4] L. Shen, J. Haufe and M. K. Patel, Product overview and market projection of emerging bio-based plastics (Group Science, Technology and Society, Utrecht), 2009.

[5] A. M. F. Sousa, V. A. Escócio, E. B. A. V. Pacheco, L. L. Y. Visconte, A. de P. Cavalcante, A. G. Soares, M. F. Junior, L. C. C. Motta and G. F. C. Brito, Experimental Design as a Tool for the Processing and Characterization of HDPE

Composites with Sponge-gourds (*Luffa-Cylindrica*) Agrofiber residue, J. Sustain. Development 6 (2013), 106-117.

[6] G. Siqueira, J. Bras, N. Follain, S. Belbekhouche, S. Marais and A. Dufresne, Thermal and mechanical properties of bio-nanocomposites reinforced by Luffa cylindrica cellulose nanocrystals, Carbohyd. Polym. 91 (2013), 711-717.

[7] E. J. Siqueira and V. R. Botaro, Luffa cylindrica fibres/vinylester matrix composites: Effects of 1, 2, 4, 5-benzenetetracarboxylic dianhydride surface modification of the fibres and aluminum hydroxide addition on the properties of the composites, Compos. Sci. Technol. 82 (2013), 76-83.

[8] S. L. Fávaro, M. S. Lopes, A. G. V. de Carvalho Neto, R. R. de Santana and E. Radovanovic, Chemical, morphological, and mechanical analysis of rice husk/post-consumer polyethylene composites, Compos. Part A 41 (2010), 154-160.

[9] D. R. Mulinari, H. J. C. Voorwald, M. O. H. Cioffi, M. L. C. P. Silva, T. G. Cruz and C. Saron, Sugarcane bagasse cellulose/HDPE composites obtained by extrusion, Compos. Sci. Technol. 69 (2009), 214-219.

[10] T. S. Gomes, L. L. Y. Visconte and E. B. A. V. Pacheco, Substituição da Fibra de vidro por Fibra de Bananeira em Compósitos de Polietileno de Alta Densidade. Parte 1, Avaliação Mecânica e Térmica, Polímeros: Ciência e Tecnologia 23 (2013), 206-211.

[11] E. B. A. V. Pacheco, L. L. Y. Visconte and T. S. Gomes, Assessment of glass fiber replacement with banana tree fiber in high density polyethylene composites, In book by Jeremy C. Culleri, Recycling: Technological Systems, Management Practices and Environmental Impact, Nova Science, 2013.

[12] S. A. Paul, K. Joseph, G. D. G. Mathew and L. A. Pothen, Influence of polarity parameters on the mechanical properties of composites from polypropylene fiber and short banana fiber Compos. Part A 41 (2010), 1380-1387.

[13] M. Biswal, S. Mohanty and S. K. Nayak, Banana fiber-reinforced polypropylene nanocomposites: Effect of fiber treatment on mechanical, thermal, and dynamic-mechanical properties, J. Thermoplast. Compos. 25 (2012), 765-790.

[14] M. H. Ishizaki, L. L. Y. Visconte, C. R. G. Furtado, M. C. A. M. Leite and J. L. Leblanc, Caracterização mecânica e morfológica de compósitos de polipropileno e fibras de coco verde: influência do teor de fibra e das condições de mistura, Polímeros: Ciência e Tecnologia. 16 (2006), 182-186.

[15] Y. Lei, Q. Wu, F. Yao and Y. Xu, Preparation and properties of recycled HDPE/natural fiber composites, Compos. Part A 38 (2007), 1664-1674.

[16] S. Panthapulakkal and M. Sain, Agro-residue reinforced high-density polyethylene composites: Fiber characterization and analysis of composite properties, Compos. Part A 38 (2007), 1445-1454.

[17] American Society for Testing and Materials-ASTM D 1348-94, Standard Test Methods for Moisture in cellulose, USA, 2008.

[18] International Organization for Standardization ISO 8962, Plastics-Polymer Dispersions-Determination of Density, 1987.

[19] Technical Association of Pulp and Paper Industry (TAPPI), Standard Method T211 om-93, 1993.

[20] Technical Association of Pulp and Paper Industry (TAPPI), Standard Method T212 om-98, 1998.

[21] E.de O. S. Saliba, N. M. Rodriguez, S. A. L. de Morais, D. Piló-Veloso, Ligninas -Métodos de obtenção e caracterização química, Ciência Rural. 31 (2001), 917-928.

[22] American Society for Testing and Materials - ASTM D638-03, Standard Test Methods for Tensile properties of plastics, Annual Book of ASTM Standards, Philadelphia, Plastics 08.01, 2007.

[23] American Society for Testing and Materials - ASTM D790-03, Standard Test Methods for Flexural properties of Unreinforced and Reinforced Plastics and reinforced plastics and electrical insulating materials, Annual Book of ASTM Standards, Philadelphia, Plastics 08.01 (2007), 150-160.

[24] American Society for Testing and Materials - ASTM D256-06a, Standard Test Methods for Determining the Izod Pendulum Impact Resistence of plastics and electrical insulating materials, Annual Book of ASTM Standards, Philadelphia, Plastics 08.01 (2007), 1-20.

[25] American Society for Testing and Materials - ASTM D1238-10, Standard Test Method for Melt Flow Rates of Thermoplastics by Extrusion Plastometer, Annual Book of ASTM Standards, Philadelphia, Plastics, 08.01, 2007.

[26] American Society for Testing and Materials – ASTM D618-08, Standard Practice for Conditioning Plastics for Testing, Annual Book of ASTM Standards, Philadelphia, Plastics, 08.01.

[27] A. Bismarck, A. Baltazar-Y-Jimenez, K. Sarikakis, Green composites as panacea? socioeconomic aspects of green materials, Environment, Development and Sustainability 8 (2006), 445-463.

[28] J. Gassan, V. S. Gutowski and A. K. Bledzki, About the surface characteristics of natural fibres, Macromol. Mater. Eng. 283 (2000), 132-139.

[29] F. M. Yamaji and A. Bonduelle, Utilização da serragem na produção de compósitos plástico-Madeira, Revista Floresta 34 (2004), 59-66.

[30] T. H. D. Sydenstricker, S. Mochnaz and S. C. Aminco, Pull-out and other evaluations in sisal-reinforced polyester biocomposites, Polym. Test. 22 (2003), 375-380.

[31] V. O. A. Tanobe, T. H. D. Sydenstricker, M. Munaro and S. C. Amico, A comprehensive characterization of chemically treated Brazilian sponge-gourds (*Luffa cylindrica*), Polym. Test. 24 (2005), 474-482.

[32] E. J. Siqueira, Compósitos de resina estervínica reforçados com fibras da Luffa cylindrica modificada superficialmente, Dissertação de mestrado da Engenharia de Materiais da REDEMAT, Ouro Preto, 2008.

[33] J. L. Guimarães, E. Frollini, C. G. da Silva, F. Wypych and K. G. Satyanarayana, Characterization of banana, sugarcane bagasse and sponge gourd fibers of Brazil, Ind. Crop. Prod. 30 (2009), 407-415.

[34] A. R. Martin, M. A. Martins, L. H. C. Mattoso and O. R. R. F. Silva, Caracterização química e estrutural de fibra de sisal da variedade Agave sisalana, Polímeros: Ciência e Tecnologia. 19 (2009), 40-46.

[35] W. F. Smith, Princípios de Ciência e Engenharia de Materiais, 3rd ed., McGraw-Hill, Lisbon, c. 13, 2003.

[36] M. Rabello, Aditivação de Polímeros, Artliber, São Paulo, Brazil, 2000.

[37] S. Joseph, M. S. Sreekala, Z. Oommen, P. Koshy and S. Thomas, A comparison of the mechanical properties of phenol formaldehyde composites reinforced with banana fibre and glass fibres, Compos. Sci. Technol. 62 (2002), 1857-1868.

[38] J. R. Callister and D. William, Ciência e engenharia de materiais uma introdução, 5th. ed., LTC, Rio de Janeiro, 2002.

[39] S. Mohanty and S. K. Nayak, Short Bamboo Fiber-reinforced HDPE Composites: Influence of Fiber Content and Modification on Strength of the Composite, J. Thermoplast. Compos. 29 (2010), 2199-2210.

[40] G. Scott, Polymers and the Environment, The Royal Society of Chemistry, Cambridge, UK, 1999.