Materials Research. 2010; 13(2): 159-163

Production and Evaluation of Recycled Polymers from Açaí Fibers

***Clívia Danúbia Pinho da Costa Castro*[a], *Carmen Gilda Barroso Tavares Dias*[b], *José de Assis Fonseca Faria*[a,*]**

[a]*Faculdade de Engenharia de Alimentos, Universidade de Campinas – UNICAMP, Campinas, SP, Brazil*
[b]*Faculdade de Engenharia Mecânica, Universidade Federal do Pará – UFPA, Belém, PA, Brazil*

Received: August 5, 2009; Revised: March 17, 2010

The possibility of recycling and the favorable mechanical properties of the products have encouraged the study and production of thermoplastic composites from natural fibrous waste. Açaí (cabbage palm) fiber, which is removed from the seed, has been slightly investigated, as compared to what is already known about the fruit pulp. In this study, the influence of açaí fiber as an element of reinforcement in recycled everyday usage thermoplastics using simple, low cost methodology was evaluated. Recycled matrixes of high impact polystyrene and polypropylene were molded by hot compression from which the fiber composites were obtained. The FTIR technique showed that the process was efficient in preventing degradation of the açaí fibers. The influence of the fiber on the mechanical behavior of the recycled matrixes was investigated by microscopic images of compression and impact tests. The results showed better impact performance for the fiber combined with the polymeric matrixes.

Keywords: *recycling, açaí fiber, polypropylene, polystyrene*

1. Introduction

The trend to add value to products and that are environmentally friend has encouraged transformation industries to work with waste recovery. Discarded post-consumer plastics are generally considered a problem due to the damage they cause to the environment. Most come from disposable food packages, which, after being discarded in landfills, pile up and increase the volume of waste and the visual pollution[1-3].

In 2007 the use of polymeric resins in packages accounted for 14. 5% of the Brazilian market of processed plastics, consuming 25% of the polypropylene (PP) and 7% of the polystyrene (PS) produced in Brazil[4]. One of the alternatives to reduce the amount of material currently treated as urban solid waste is to recycle it[5]. The traditional process for producing thermoplastic materials is the mechanical one[6], involving the use of relatively simple equipments.

Recycling plastic waste with vegetable fibers, plentiful in the Amazon region, would increase its value, and this process has aroused interest in studying the production and application of such composites[7].

In general, vegetable fibers, when adequately combined with polymers, can provide better flexibility and improve mechanical resistance and toughness[8-10]. However composites reinforced with natural fibers tend to show low mechanical resistance due to poor interfacial adhesion caused by the low chemical interaction of the fibers[11].

Açaí (*Euterpe oleracea*, Mart.) is a plant originating from the Amazon region. The pulp is highly consumed[12] and the waste is removed from the nut. The fruit of this palm tree shows the potential for consumption as a new product throughout the world, inserting itself in market niches for functional and nutraceutical products[13].

Due to the extensive consumption of the fruit, much research has been carried out on the pulp, but almost none on the waste[14]. According to Rogez[15], in Belém, the capital of the State of Pará, the largest producer and consumer of açaí in Brazil, the açaí pulp trade produces about 300 t of organic waste per day. In the Amazon region in general, most of this waste consists of seeds, which are thrown into the streets and into landfills with no treatment, and just a small portion is used as organic fertilizer or in local handcrafts.

Reis et al.[14] carried out a study on the potential of using açaí seeds for the production of briquettes, and also suggested the use of the nuts as an energy source for the State of Pará, taking into account factors such as their calorific power and the easy acquisition of this waste. For use in the development of new materials, the study of seed fiber is still recent. The results regarding the thermal behavior, for instance, show there are similarities between coconut seed and sisal fibers, with satisfactory thermal stability at 230 °C[16]. The fiber exhibited good adhesion in cementitious matrixes, and the composites demonstrating the best mechanical properties were those containing lower contents (0.3%) of in nature fiber, since the fiber content increased water absorption and apparent porosity[17].

This study investigated the influence of fiber as an element of reinforcement for post consumption package materials, using simplified and low cost methodology.

2. Experimental

2.1. Materials

For the production of the composites, post-consumer packages were used as well as the waste from açaí pulp processing, high impact polystyrene cups (HIPS) and PP bottles were obtained from schools and universities in the city of Belém-Brazil. The company Amazon Dry Ltda in Belém-Brazil provided the fibers, which had already been mechanically extracted from the seed.

*e-mail: assis@fea.unicamp.br.

2.2. Methods

2.2.1. Preparation of fiber mats from the seeds

Açaí fibers are naturally short and were used as they were received, with no chemical or physical treatment.

To facilitate random scattering in the polymeric matrix, the fibers were previously collected in molds, forming mats, which were dried in an incubator at 70 °C for half an hour.

2.2.2. Production of recycled materials

The urban waste was submitted to basic mechanical recycling treatments such as: collection, cleaning, grinding, washing and drying.

The HIPS and PP were molded by hot compression according to ASTM D 695-08, obtaining recycled matrixes in the shape of flat panel, shaped on a galvanized steel mold consisted of three-plate frame. The external dimensions of the plates were 200 × 150 × 6 mm and the internal ones were 180 × 130 × 6 mm. The HIPS and PP fragments were placed individually between the plates, pressed in a hand press at 1.26 MPa and heated in a domestic electric oven up to softening of the PP (148 °C) and HIPS (147 °C). A thermoelectric sensor was inserted into the center of the material to control the temperature. Cooling was produced by forced air convection at room temperature, and the pressure was maintained until the material had cooled to room temperature. The composites were formed using the same process of mechanical matrix conformation and under the same pressure; however, alternate layers of recycled blades and açaí fiber mats were placed inside the mold and heated at 206 °C for the composite with PP and at 167 °C for HIPS. The materials produced by this process were composites consisting of polypropylene with açaí fibers (PPA) and of high impact polystyrene with açaí fibers (HIPSA), both with 11% of fiber (mass/mass). In order to compare the results, recycled polypropylene (PP) and high impact polystyrene (HIPS) materials were produced without the addition of fiber.

2.2.3. Mechanical tests

The following tests were carried out according to ASTM standards: tensile strength (ASTM D 638-90), tensile compression (ASTM D 695-90) and tensile impact (ASTM D 256-90b), as well as standardization of the proofs of PP, PPA, HIPS and HIPSA taken from the molded plates. In all these tests the composites, consisting of alternating layers of fiber and polymer, were tested as a flat isostrain configuration so that the tension applied would provoke a uniform strain on every layer of the composites[18].

The tensile strength test was carried out up to material rupture using a NTS apparatus with a strain rate of 1 mm/min. The compressive strength was determined using the simple axial compression test with an EMIC machine with load cell of 500 N. For impact strength, an impact test machine (Charpy® GUNT HAMBURG WP 410) equipped with a 300 Nm pendulum was used with notched samples.

2.2.4. Spectroscopy

The Fourier Transformed Infrared (FTIR) technique was used to quantitatively assess possible degradation in the reprocessed polymers. HIPS and PP samples after recycling, and samples of the composites, were prepared using the pressed disk technique[19] and characterized in a Perkin Elmer® 1760X FTIR Fourier transformed infrared spectrometer. The spectra were analyzed per unit of transmittance using 4 scans at intervals of 2 cm^{-1}, ranging from a band at 4000 to 400 cm^{-1}, obtained from the absorption intensities of the molecule bands expressed in percent transmittance.

2.2.5. Scanning electron microscopy (SEM)

The interface between the fiber and the matrix in the ruptured region was investigated, but only the impact and compression proofs obtained using LEO, a model 1450 VP scanning electronic microscope, were evaluated at an accelerating voltage of 10 kV. The magnification level was studied at 300X. After the tests, the notched samples were sectioned below the rupture surface, fixed on metal supports and coated with gold so that they would turn into conductors[19].

3. Results and Discussion

3.1. Evaluating the molding process

The materials showed a satisfactory molding level since they maintained the shape of the mold when submitted to the polymer fusion temperature. The samples of HIPS, PP and PPA were flat with no signs of deterioration, and apparently with no major defects such as bubbles or voids, although the HIPSA composites showed small cavities throughout the material.

To analyze the influence of fiber on the recycled products, variations in the spectra were compared by observing the behavior of the peaks. In the spectrum of the recycled PP and reinforced PP (Figure 1), the presence of nitrogen-containing groups can be seen at 1645 and 1378 cm^{-1} and halogen-containing groups at 1455 and 564 cm^{-1}, suggesting the presence of additives. Furthermore, there was strong interaction between the fiber and the recycled product at the peaks shown at 1645 and at 1043 cm^{-1}, related to oxygen-containing groups, probably due to hydrogen bonds or a possible polymer degradation. In order to minimize polymer oxidation during the processing the temperature can be reduced but the molding pressure has to be increased.

The FTIR technique showed a good state of preservation of the discarded, recycled polymer during processing, with no significant changes in the polymer spectra after recycling when compared with the spectra of commercial resins[20].

The spectra of the reinforced and non-reinforced HIPS presented almost identical absorption bands (Figure 2) and there was no evidence of strong interaction with the recycled fiber. The minimum peak at 1601 cm^{-1} was probably due to the occurrence of amines and amides. Preservation of the polymer characteristics after reprocessing can be explained by the short-time consumption during packaging

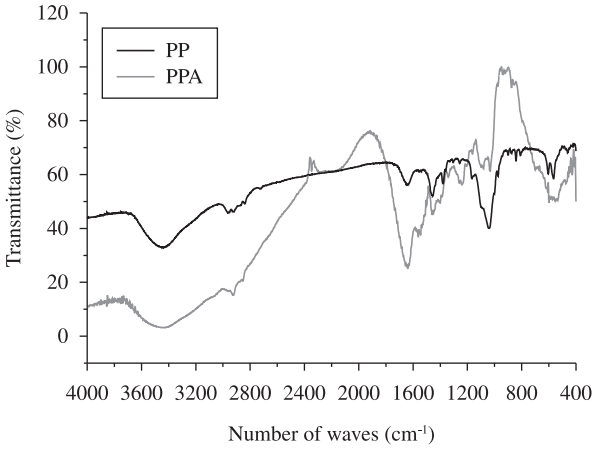

Figure 1. FTIR spectrum of polypropylene (PP) and polypropylene/açaí fiber composite (PPA).

and by the thermal processing, which was not aggressive to the materials. A study of snack-bar disposables, for example, showed that the original features of post-consumer polystyrene cups were much better preserved than other plastics present in urban waste, due to the small post-cycle consumption time and reduced influence of weather or any other variants[1]. With respect to the way the samples were obtained, it can be seen that the temperature range of 147–167 °C was sufficient to wet the fiber in the matrix and did not exceed the degradation temperature of the açaí fiber, which is around 230 °C[16]. The hot molding process has the advantage of reducing the possibility of plant fiber degradation, providing the fibers are only subjected to one temperature cycle during the composite molding process[23].

In the spectrum of the recycled PP, no carbonyl groups were found in the absorption range from (1750 to 1700 cm^{-1}). Absorption of oxygen-containing substances was observed at 1645 and 1043 cm^{-1}, probably related to amine and alcohol groups, respectively. The incidence of hydroperoxides was lower than commonly formed during the use of virgin resin without additive. The expected decomposition of hydroperoxides in the recycled waste may have been avoided by the presence of residual additives from the processing of the virgin resin.

Generally polymer degradation results in the formation of free radicals that can lead to branches, crosslinks and/or chain scission due to the reaction with atmospheric oxygen[21]. Also in a study on PP reprocessed after use[22] carbonyl absorption (1712, 1750 and 1775 cm^{-1}) continued increasing, showing that the hydroperoxides formed during consumption, split into carbonyl groups at the high reprocessing temperatures. Based on such research, an evaluation was carried out in a search for possible chemical degradation of the recycled polymers, as shown by the appearance of peaks with absorption values corresponding to decomposition products of the hydroperoxides, such as carbonyl (1750 – 1700 cm^{-1}) and alcohol (1300 – 1000 cm^{-1}) groups.

3.2. Mechanical characteristics of the composites

The recycled polymers showed lower tensile strength at rupture when combined with fiber. The values for tensile strength at rupture of the PP (22.27 ± 0.73 MPa) and HIPS (12.75 ± 0.78 MPa) composites did not surpass the values of the recycled polymers without fiber.

Reports in the literature show that, in general, the tensile strength of pure PP is higher than that of PP containing natural fibers, except when coupling agents that improve interfacial adhesion and consequently, the tensile mechanical results, are used[24-26]. In the present study, the results of the tensile test with the HIPS/açaí fiber composites were in agreement with similar work carried out with HIPS/sisal fibers produced using a similar process, in which the tensile strength at rupture decreased from 21.66 to 11.41 MPa when combined with short sisal fibers at 20% by volume. This behavior was attributed to weak interfacial adhesion due to the difference in polarity between the constituents of the composite, and also due to the restriction to matrix flow, imposed by the sisal fiber[27].

The results of the compression test also showed that the fiber did not improve the strength of the recycled polymers. The average values for the compressive strength of the PP and HIPS were 39.74 ± 8.55 and 42.88 ± 7.61 MPa, respectively. From the SEM images, it can be seen that adherence of the fibrous layers to the recycled material was not sufficient to avoid the occurrence of delamination and fiber displacement, which were both favored by the longitudinal organization of the layers in relation to the tensile application. This behavior was more frequent in the HIPS composites. The image in Figure 3 shows details of the weak interfacial adhesion between the matrix of HIPS and the fiber, which consequently resulted in low compression resistance of the tested composite.

In the impact test, the seed fiber increased the resistance of the recycled polymers by about 44% for PP and 12% for HIPS. Such increase of impact resistance was also observed in a study using PP reinforced with chemically treated short sisal fibers[28]. Taking into consideration that the chemical treatment of the fiber reduces its hydrophilic nature and thus favors adhesion with the hydrophobic matrix[29], the use of this fiber proved to be more advantageous since it does not demand chemical or physical treatment of the fiber surface to allow for adhesion.

The images obtained by SEM showed the fracture, starting and fiber displacement mechanisms of the açaí fiber, showing higher incidences of interfacial adhesion between the constituents of the PPA composites. In some of these areas, the açaí fibers had been pulled out, leaving globular vestiges in the matrix (Figure 4). This behavior indicates strong interactions between the globular particles on the surface of the fiber and the polymeric matrix. On the other hand, removing these globular vestiges would cause greater exposure of the fibrils and globular particles, providing a larger contact adhesion area for the matrix and promoting tensile transfer. An alternative way of removing the globular vestiges would be treatment of the surface

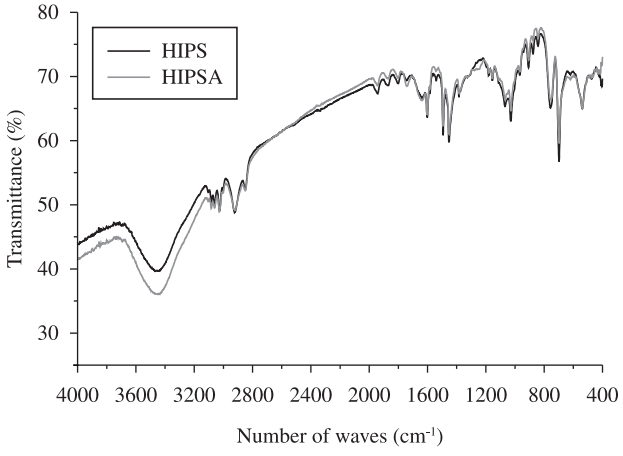

Figure 2. FTIR spectrum of polystyrene (HIPS) and polystyrene/açaí fiber composite (HIPSA).

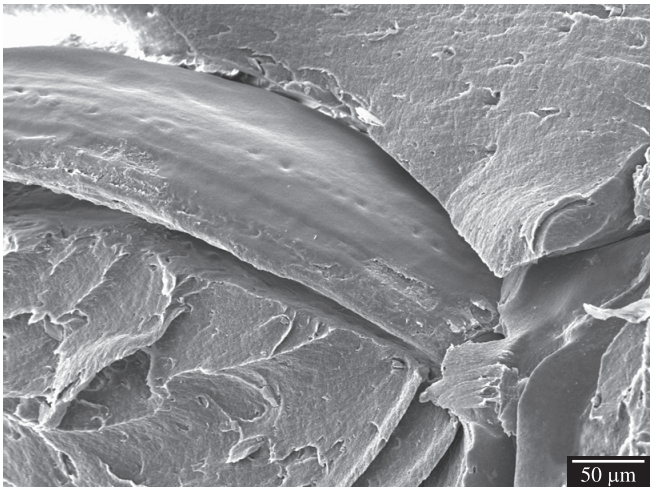

Figure 3. Detail of interfacial weak adhesion between açaí fibers and polystyrene (HIPS) under compression.

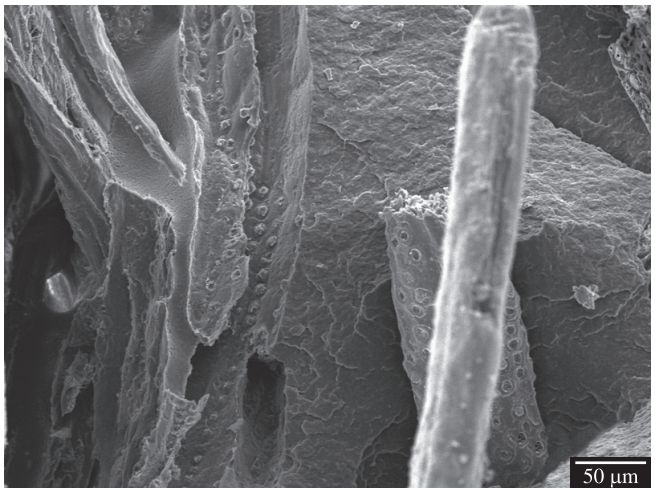

Figure 4. Detail of fiber vestiges in polypropylene/açaí fibers composite (PPA) under impact.

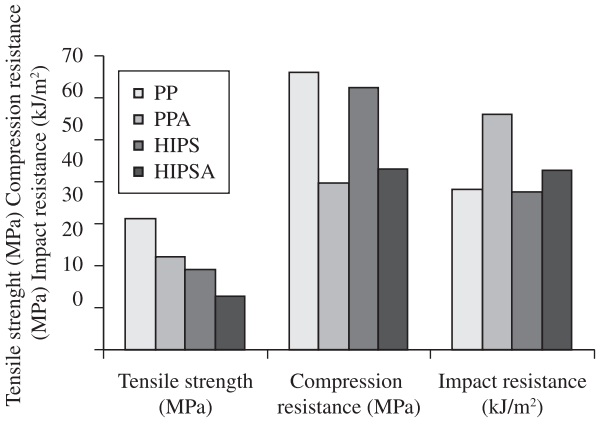

Figure 5. Comparison of mechanical trial results: polypropylene (PP), polystyrene (HIPS), polypropylene/açaí fiber composite (PPA) and polystyrene/açaí fiber composite (HIPSA).

with heated water and agitation, promoting greater roughness of the fiber without removing its internal components, such as lignin and hemicelluloses[30], since removal of the latter components could compromise adhesion and mechanical behavior[10]. Figure 5 shows the results of mechanical test for the polymeric materials with and without açaí fiber. It can be observed that the tensile strength and the compression resistance of the polymers decrease when the açaí fiber was used, however the impact resistance for both polymer increased and mainly for the composite containing PP. The better impact performance of the PPA was probably because of the higher interfacial adhesion between the fiber and this polymer as already discussed.

4. Conclusions

Hot compression molding proved to be a good alternative for the reprocessing of PP and HIPS used packages to obtain composites with açaí fiber. The tested process condition was sufficient to produce the composite without fiber degradation. It was concluded that the fiber increased the impact resistance of both polymer. Such result represents a new alternative for the reinforcement of thermoplastic material with açaí fiber for the production of composites.

Acknowledgements

The authors are grateful to Amazon Dry® Ltda. for providing the seed fibers and to the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) for the research scholarship.

References

1. Carvalho GA. *Aspectos tecnológicos e mercadológicos da reciclagem de plásticos descartados de lanchonetes*. [dissertation]. Rio de Janeiro: University of Rio de Janeiro; 1997.
2. Manrich S, Frattini G and Rosalini AC. *Identificação de plásticos*: uma ferramenta para reciclagem. São Carlos: EDUFSCar; 1997.
3. Albuquerque JAC. *O plástico na prática*. Porto Alegre: Sagra Luzzatto; 1999.
4. Associação Brasileira da Indústria do Plástico. *Perfil da indústria brasileira de transformação de material plástico*. São Paulo: ABIPLAST; 2007.
5. Garcia EEC. Desenvolvimento de embalagem e meio ambiente. In: Centro de Tecnologia De Embalagem. *Brasil pack trends 2005*: embalagem distribuição e consumo. Campinas: CETEA/ITAL; 2000.
6. Rodrigues FL and Cavinatto VM. *Lixo:* de onde vem? Para onde vai? São Paulo: Moderna; 1997.
7. Marinelli AL, Monteiro MR, Ambrósio JD and Branciforti MC, Kobayashi M, Nobre AD. Desenvolvimento de compósitos poliméricos com fibras vegetais naturais da biodiversidade: uma contribuição para a sustentabilidade amazônica. *Polímeros Ciência e Tecnologia*. 2008; 18(2):92-99.
8. Lee BH, Kim HJ and Yu WR. Fabrication of long and discontinuous natural fiber reinforced polypropylene biocomposites and their mechanical properties. *Fibers and Polymers*. 2009; 10(1):83-90.
9. Hu R and Lim JK. Fabrication and mechanical properties of completely biodegradable hemp fiber reinforced polylactic acid composites. *Journal of Composite Materials*. 2007; 41(13):1655-1699.
10. Soleimani M, Tabil L, Panigrahi S and Opoku, A. The effect of fiber pretreatment and compatibilizer on mechanical and physical properties of flax fiber-polypropylene composites. *Journal of Polymers and the Enviroment*. 2008; 16:74-82.
11. Thwe MM and Liao K. Durability of bamboo-glass fiber reinforced polymer matrix hybrid composites. *Composites Science and Technology*. 2003; 63:75-387.
12. Homma AKO. *Sistema de produção do açaí*. Belém: Embrapa Amazônia Oriental; 2006.
13. Homma AKO, Nogueira OL, Menezes AJEA, Carvalho JEU, Nicoli CML and Matos GB. *Açaí*: novos desafios e tendências. Amazônia: Ciência & Desenvolvimento. 2006; 1(2):7-23.
14. Reis BO, Silva IT, Silva IMO and Rocha BRP. Produção de briquetes energéticos a partir de caroços de açaí. In: Anais of AGRENER; 2002, Out.; Campinas, Brazil; 2002. p. 85-89.
15. Rogez H. *Açaí*: preparo, composição e melhoramento da conservação. Belém: EDFPA; 2000.
16. Martins MA, Mattoso LHC and Pessoa JDC. *Comportamento térmico da fibra do açaí*. São Carlos: Embrapa Instrumentação Agropecuária; 2005. (Comunicado Técnico, 68).
17. Lima Júnior UM. *Fibras da semente do açaizeiro (Euterpe oleracea mart.):* avaliação quanto ao uso como reforço de compósitos fibrocimentícios [dissertação]. Porto Alegre: University of Rio Grande do Sul; 2007.
18. Smith WF. *Princípios de ciência e engenharia dos materiais*. Lisboa: McGraw-Hill; 1998.
19. García-Hernández E, Licea-Claveríe A, Zizumbo A, Alvarez-Castillo A and Herrera-Franco PJ. Improvement of the interfacial compatibility between sugar cane bagasse fibers and polystyrene for composites. *Polymer Composites.* 2004; 25(2):134-145.
20. Haslam J, Willis HA and Squirrell DCM. *Identification and analysis of plastics*. Londres: Butterworth; 1972.

21. Teixeira VG, Coutinho FMB and Gomes AS. Síntese e caracterização de copolímeros de estireno e divinilbenzeno clorometilados. *Polímeros: Ciência e Tecnologia*. 2004; 14(4):267-273.

22. Sellin N and Campos JSC. Surface analysis of PP films treated by corona discharge. *Materials Research.* 2003; 6(2):163-166.

23. Bodros E, Pillin I, Montrelay N and Baley C. Could biopolymers reinforced by randomly scattered flax fibre be used in structural applications? *Composites Science and Technology*. 2007; 67:462-470.

24. Hristov VN and Vasileva ST. Deformation mechanisms and mechanical properties of modified polypropylene/wood fiber composites. *Polymer Composites*. 2004; 25(5):521-526.

25. Sombatsompop N, Yotinwattanakumtorn C and Thongpin C. Influence of type and concentration of maleic anhydride grafted polypropylene and impact modifiers on mechanical properties of PP/wood sawdust composites. *Journal of Applied Polymer Science*. 2005; 97:475-484.

26. Doan T-T-L, Gao S-L and Mäder E. Jute/polypropylene composites I. Effect of matrix modification. *Composites Science and Technology*. 2006; 66:952-963.

27. Antich P, Vázquez A, Mondragon I and Bernal C. Mechanical behavior of high impact polystyrene reinforced with short sisal fibers. *Composites Part A: Applied Science and Manufacturing*. 2006; 37:139-150.

28. Mukhopadhyay S and Srikanta R. Effect of ageing of sisal fibres on properties of sisal: polypropylene composites. *Polymer Degradation and Stability*. 2008; 93:2048-2051.

29. Mohanty S and Nayak SK. Effect of MAPP as a coupling agent on the performance of jute-PP composites. *Reinforced Plastics and Composites*. 2004; 23(6):625-637.

30. Santiago BH and Selvam PVP. Tratamento superficial da fibra de coco: estudo de caso baseado numa alternativa econômica para fabricação de materiais compósitos. *Revista analítica*. 2007; (26):42-45.