

Mechanical Properties of Polypropylene Composites Reinforced with Macadamia Nutshell Fibers

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Abstract: The use of natural fibers as an additive in polymeric matrices has attracted interest of the automotive industries, for its low cost, mechanical properties, biodegradability and lightness. However, the hydrophilic nature of the fiber makes polymer compatibility difficult. Fiber surface treatments can be used to enhance the fiber/matrix interface. In the present work, polypropylene (PP) composites reinforced with fibers from macadamia nutshell were obtained and characterized. Macadamia nutshell fibers were treated by an alkaline treatment with sodium hydroxide (NaOH 4%) to improve adhesion between fibers and matrix. Fibers were characterized by techniques of Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD). The PP was mixed with the macadamia fibers (treated and untreated), in proportions of 5 and 10% (wt/wt) using a thermokinetic mixer. Furthermore tensile, flexural and impact specimens (Pure PP and composites) were prepared by an injection molding process and tested for evaluation of mechanical properties. The results showed that the insertion of treated fibers in the PP matrix increased the stiffness of the composites. However, the composites reinforced with untreated fibers presented higher impact energy absorption when compared to composites reinforced with treated fibers.

Keywords: Macadamia nutshell; polypropylene; alkaline treatment; mechanical properties

1 Introduction

In recent years, natural fibers such pineapple, flax, jute, coconut, sugarcane bagasse, palm, and others have been extensively studied as an alternative to reinforce polymer matrix due to their advantages such as sustainable, low cost, low density and biodegradable features [1-3]. However, the incompatibility with non-polar matrices, moisture adsorption and vulnerability to thermal degradation are the main disadvantages for the use of natural fibers in composites [4-7]. Thus, to improve interfacial contact is necessary a superficial change. Many treatments have been used in order to improve compatibility of natural fibers, which can be physical or chemical, with the goal of modifying the surface of the fibers [8-11].

The alkaline treatment applied to natural fibers has been used. This treatment decreases the amount of hemicellulose, lignin, waxes, and oils soluble in alkaline solution, and therefore reduces the level of fiber aggregation, making a surface rougher. In others words, the alkaline treatment of natural fibers changes the orientation of highly packed crystalline cellulose and forms an amorphous region, which makes the interior of the fiber more accessible for chemical action. Furthermore, treatment reduces the diameter and increases the aspect ratio of the fiber [12-14].

Natural fibers from macadamia nutshell (*Macadamia integrifolia*) are a cellulosic material readily available and can be used as reinforcement in a thermoplastic-based composite [15]. Macadamias are native to Australia's rainforests. Its almond is highly valued, and can be consumed raw or toasted, being widely used in confectionery and ice creams. The kilo of macadamia nut varies from US\$ 0.91 to

US\$ 1.17 to the producer and gives a good economic return when the productivities are superior to three tons per hectare [17].

The technological development of macadamia crops occurred in the Hawaii Agricultural Experiment Station (HAES), where the main cultivars planted in the world were selected. Due to its climatic conditions, Brazil is among the countries with the highest potential for macadamia nut production in the world. Currently in Brazil, macadamia cultivation is concentrated in regions that traditionally produce coffee [17-20].

The great production of macadamia has to do with its high international market value, thus generating a lot of waste. For each ton of macadamia, 70 to 77% of its grains produced are considered residues [21].

The density of the macadamia epicarp is about 0.680 g.cm^{-3} , which configures a fiber with low density when compared to synthetic fibers (2.55 g.cm^{-3}). This fact guarantees the lightness of parts injected for automotive purposes (aerodynamics). Macadamia epicarp main components are: lignin (47.6%), cellulose (25.8%), hemicellulose (11.7%), (0-2%) ash and 10% moisture [22].

As an alternative for the redirection of residues from a factory near the region where this research is being developed, we chose the bark fiber as reinforcement in the composite. In this work it was evaluated the potential of macadamia nutshell fibers as reinforce in composites using polypropylene (PP) as matrix and also an alternative surface treatment, in order to improve interfacial fiber/matrix adhesion.

2 Experimental

2.1 Materials

Macadamia nutshell fibers were obtained by Tribeca, located at Fazenda Santa Marta in Pirai-RJ. Polypropylene (PP) obtained from Braskem was used as matrix.

2.2 Treatment of the Macadamia Nutshell Fibers

First, the fibers were ground, oven dried at 100°C to constant weight, then sieved in a 35 mesh sieve. Fibers were washed with warm water at 100°C until the wash water did not display any further color change. Fibers were again oven dried for 24 hours at 100°C . Subsequently the fibers were submitted to alkaline treatment with NaOH (4% w/v) for an hour under constant stirring at 70°C . After that process, the fibers were washed with distilled water until they reached neutral pH, and dried. The chemical modification provides more dimensional stability, reduce water absorption capacity and give resistance to fiber against fungal decay [23].

2.3 Fibers Characterization

Micrographs were obtained in a scanning electron microscope HITACHI with tungsten filament operating at 10kV, employing low-vacuum technique and secondary electron detector. Samples were dispersed on a brass support and fixed with a double face 3M tape. Macadamia nutshell fibers untreated and treated were characterized by X-Ray Diffractometry (XRD) and Scanning Electron Microscopy (SEM). X-ray diffractograms were obtained in a Shimadzu diffractometer, model XDR-6100. The measuring conditions were: CuK α radiation with graphite monochromator, 30 kV voltage and 40 mA electric current. The patterns were obtained in 10-502 θ angular intervals with 0.05 step and 1s of counting time. The crystallinity index (CI) was calculated by Segal's empirical method, by Eq. (1):

$$CI = \frac{I_{(002)} - I_{(am)}}{I_{(002)}} \times 100 \quad (1)$$

CI → Crystallinity index [%]

$I_{(002)}$ → Peak diffraction intensity representing the crystalline material near $2\theta = 22^\circ$;

$I_{(am)}$ → Peak diffraction intensity representing amorphous material near $2\theta = 16^\circ$.

2.4 Composites Processing

The treated and untreated macadamia nutshell fibers were mixed with the polypropylene (PP) in a thermokinetic mixer model MH-50H, with the speed rate kept at 5250 rpm, in which fibers were responsible for 5 and 10 wt% of the composition. After mixing, composites were ground and injected directly in a mold with specific dimensions for tensile, flexural and impact specimens.

2.5 Mechanical Tests

The tensile and flexure tests were performed on an EMIC brand equipment with a load cell of 5 kN. The dimensions of tensile and flexural test specimens were in accordance with ASTM D 638-14 and ASTM D 790-15, respectively. Impact tests were performed on an EMIC brand Izod type equipment with a 4 Joules pendulum.

Composites were analyzed in an EMIC testing machine (model DL2000), equipped with pneumatic claws with a load cell of 5 kN. In the tensile tests, five specimens of composites were analyzed, with dimensions in agreement with the ASTM D 638 standard. In the flexural tests, a load was applied on the specimen at 1.3 mm min^{-1} crosshead motion rate. Five specimens were analyzed with dimensions in agreement with the ASTM D 790 standard. Impact tests were performed on an EMIC brand Izod type equipment with a 4J pendulum.

3 Results and Discussions

3.1 Fibers Characterization

The micrographs of the untreated macadamia nutshell fibers presented a homogeneous surface (Fig. 1(a)), similar surfaces were observed on palm fibers and sugarcane bagasse [24, 25]. On the other hand, the treated fibers were less agglomerated and rough (Fig. 1(b)). It was observed a rough surface along with the presence of pores and pits (which carry water and nutrients to different plant locations) [26,27].

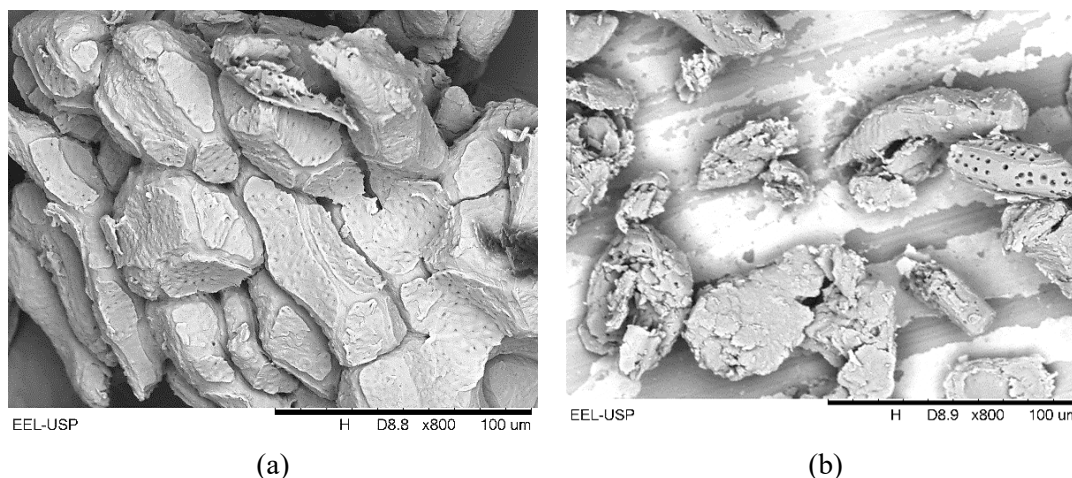


Figure 1: SEM of the nutshell macadamia fibers: untreated (a), treated (b)

Fig. 2 shows the XRD of macadamia nutshell fibers in natural condition and after the alkaline treatment. It can be seen a diffraction pattern of lignocellulosic fibers with 2 theta peaks at 10° and 22° related to (101) and (002) lattice planes, respectively. Apparently, the diffractograms of both fibers are similar. However, when the crystallinity degree of each fiber was calculated, it was noticed that there was a difference, as shown in the Tab. 1. This fact can be explained due to partial removal of amorphous components, such as lignin and hemicelluloses, causing an increasing in the crystalline degree [26].

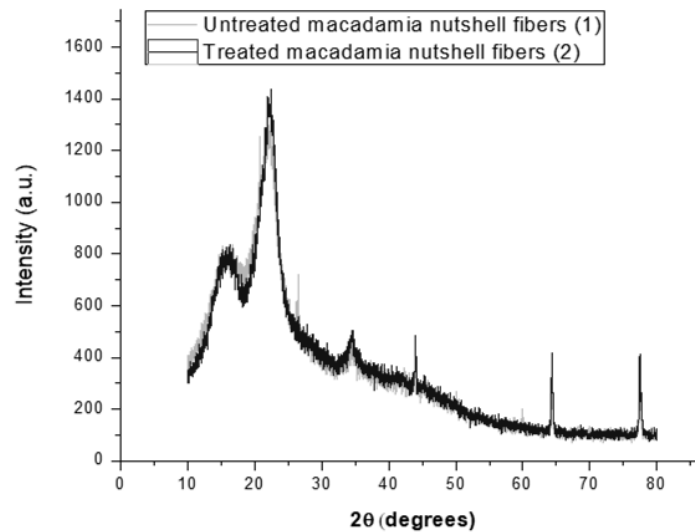


Figure 2: XRD of the nutshell macadamia untreated and treated fibers

Table 1: Crystallinity indexes (CI) of the nutshell macadamia fibers (untreated and treated)

Samples	I_{am}	$I_{(002)}$	CI
Untreated fibers	831.33	1291.92	35.7%
Treated fibers	822.97	1430.62	42.5%

3.2 Mechanical Tests

The tensile strength and modulus of untreated and treated macadamia nutshell polypropylene composites are shown in Tab. 2. It was observed a tensile modulus increase for treated fiber when compared to untreated fiber composite. Alkaline treatment improves fiber/matrix adhesion due to the removal of impurities. Thus, mechanical properties of natural fibers depend on its surface. When the fibers are treated, their length and diameter decrease [28]. The same material in different granulometry has distinct densities and mechanical properties, as noted in a study considering pine fibers sieved in a 28 and 35 mesh sieve [29]. Costa et al. observed that untreated fiber with larger size has higher density, but decreasing its size and adding the alkaline surface treatment, the density decreases, contributing to the lightness of the composite [29].

Moreover, the use of short fibers favors the processing of the composite (in the case of this work by mixing in homogenizer and subsequent injection in molds), and avoids the length breaks due to processing, as seen in jute fibers in a PP matrix [30]. Therefore, many papers choose to use a short granulometry, including with fibers sieved in 35 mesh sieves, in order to obtain a better interaction fiber/matrix [31]. Because of this, in this work was used macadamia nutshell fibers sieved in 35 mesh sieve as reinforce in PP matrix composite.

Table 2: Mechanical properties of the composites and pure PP obtained in the tensile test

Samples	Elongation at break (%)	Tensile Strength (MPa)	Tensile Modulus (MPa)
PP	8.2 ± 0.5	30.6 ± 0.0	1803.9 ± 393.2
CP 5%	7.7 ± 0.3	27.6 ± 0.1	1737.5 ± 278.6
CP 10%	6.4 ± 0.3	25.6 ± 1.4	1634.4 ± 196.9
CPM 5%	6.4 ± 0.6	32.5 ± 0.1	2093.9 ± 492.7
CPM 10%	5.6 ± 0.5	28.5 ± 0.5	2567.2 ± 1008.6

Composites reinforced with treated fibers presented an increase of 42% in stiffness when compared to the pure PP and 47% compared to the composites reinforced with untreated fibers (Tab. 2). The superficial treatment fibers and the percentage of fibers inserted in the matrix influenced directly in the mechanical properties of the composites. A similar behavior was studied with rice husk fibers [32].

The flexural strength and modulus of the composites were influenced by concentration fibers inserted in the matrix when compared to pure PP (Tab. 3). It was observed that flexural strength of the treated fiber composites was higher than untreated fiber composites because alkali treatment of the macadamia nutshell fibers helped to reduce the hydrophilic character of the fiber's surface resulting in increasing interfacial bonding between the fiber and polypropylene matrix in the composites [34]. Through the impact test it was shown that the insertion of macadamia fibers into the matrix improved the strength of the composites was due to the increase of energy absorbed in the impact, it was observed an increase of 103% (CP 10%) when compared to the pure polymer. Results similar were observed with hemp fibers [28,29]. The amount of fibers in the matrix also contributes to improve impact strength. The treatment performed on the fibers improved the adhesion between fiber/matrix, facilitating the transference of energy from the matrix impact, which is one of the factors influencing this property. The insertion of fibers in the matrix also increased the impact resistance due to the mechanism of energy dissipation. The fibers dissipated energy during the mechanical friction process

Table 3: Results of the flexural test and impact test with different conditions

Samples	Flexural Strength (MPa)	Flexural Modulus (MPa)	Impact Strength (kJ. m ⁻²)
PP	45.0 ± 0.9	1212.5 ± 130.6	36.1 ± 0.3
CP 5%	41.3 ± 0.6	1271.8 ± 79.0	69.2 ± 0.9
CP 10%	42.6 ± 0.8	1449.4 ± 42.0	73.3 ± 0.6
CPM 5%	59.0 ± 6.9	1925.7 ± 302.4	43.5 ± 0.2
CPM 10%	46.6 ± 0.2	1454.9 ± 67.7	70.0 ± 0.7

4 Conclusion

Alkaline treatment with sodium hydroxide alters the fiber morphology and crystallinity degree. This resulted in an increase in the mechanical properties in composites. It was observed also that the percentage of fiber directly interfered in the properties of the composites when compared to PP pure. This fact can be explained due to reaction between hydroxyl groups of macadamia nutshell fiber and the chemical agents causing an increase of the interfacial bonding fiber/matrix in the composites.

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References

1. Durkin, D. P., Ye, T., Choi, J., Livi, K. J. T., Shuai, D. (2018). Sustainable and scalable natural fiber welded palladium-indium catalysts for nitrate reduction. *Applied Catalysis B: Environmental*, 221, 290-301.
2. Chegiani, F., El Mansori, M. (2018). Friction scale effect in drilling natural fiber composites. *Tribology International*, 119, 622-630.
3. Pappu, A., Thakur, V. K. (2017). Towards sustainable micro and nano composites from fly ash and natural fibers for multifunctional applications. *Vacuum*, 146, 375-385.
4. Adekomaya, O., Jamiru, T., Sadiku, R., Huan, Z. (2017). Negative impact from the application of natural fibers. *Journal of Cleaner Production*, 143, 843-846.
5. AL-Oqla, F. M., Salit, M. S. (2017). 2: Natural fiber composites. *Materials Selection for Natural Fiber Composites*, 23-48.
6. Väisänen, T., Das, O., Tomppo, L. (2017). A review on new bio-based constituents for natural fiber polymer composites. *Journal of Cleaner Production*, 149, 582-596.

7. Lau, K., Hung, P., Zhu, M., Hui, D. (2018). Properties of natural fibre composites for structural engineering applications. *Composites Part B: Engineering*, 136, 222-233.
8. Varghese, A. M., Mittal, V. (2018). 5: Surface modification of natural fibers. *Biodegradable and Biocompatible Polymer Composites*, 115-155.
9. Sood, M., Dwivedi, G. (2018). Effect of fiber treatment on flexural properties of natural fiber reinforced composites: A review. *Egyptian Journal of Petroleum*, 27(4), 138-144.
10. Bakri, M. K. B., Jayamani, E., Hamdan, S. (2017). Processing and characterization of banana fiber/epoxy composites: effect of alkaline treatment. *Materials Today: Proceedings*, 4(2), 2871-2878.
11. Sepe, R., Bollino, F., Boccarusso, L., Caputo, F. (2018). Influence of chemical treatments on mechanical properties of hemp fiber reinforced composites. *Composites Part B: Engineering*, 133, 210-217.
12. de Farias J. G. G., Cavalcante, R. C., Canabarro, B. R., Viana, H. M., Simão, R. A. (2018). Surface lignin removal on coir fibers by plasma treatment for improved adhesion in thermoplastic starch composites. *Carbohydrate Polymers*, 165, 429-436.
13. Zukowski, B., Silva, F. A., Toledo, R. D. (2018). Design of strain hardening cement-based composites with alkali treated natural curauá fiber. *Cement and Concrete Composites*, 89, 150-159.
14. Bakri, M. K. B., Jayamani, E., Hamdan, S. (2017). Processing and characterization of banana fiber/epoxy composites: effect of alkaline treatment. *Materials Today: Proceedings*, 4(2), 2871-2878.
15. Bae, J., Su, S. (2013). Macadamia nut shell-derived carbon composites for post combustion CO₂ capture. *International Journal of Greenhouse Gas Control*, 19, 174-182.
16. Sipião, B. L. S., Paiva, R. L. M., Goulart, S. A. S., Mulinari, D. R. (2011). Effect of chemical modification on mechanical behavior of polypropylene reinforced pineapple crown fibers composites. *Procedia Engineering*, 10, 2028-2033.
17. Lima, E. A., Silveira, L. S., Masi, L. N., Crisma, A. R., Davanzo, M. R. et al. (2014). Macadamia oil supplementation attenuates inflammation and adipocyte hypertrophy in obese mice. *Mediators Inflamm.*
18. Perdoná, M. J. (2013). Cultivo Consorciado De Café E Macadâmia. *Pesquisa & Tecnologia*, 10(2), 1-6.
19. Perdoná, M. J., Martins, A. M., Suguino, E., Soratto, R. P. (2012). Crescimento e produtividade de macadâmia em consórcio com cafeeiro arábica irrigado. *Agropecuária Brasileira*, 47(11), 1613-1620.
20. Sobierajski, G. da R., Dos, S., Francisco, V. L. F., Rocha, P., Ghilardi, A. A. et al. (2006). Noz-macadâmia: produção, mercado e situação no Estado de São Paulo. *Informações Econômicas*, 36(5), 25-36.
21. Marshall, C. A., Johns, M. M. (1998). Phosphoric acid activation of nutshells for metals and organic remediation: process optimization. *Journal of Chemical Technology and Biotechnology*, 72, 255-263.
22. Maia, C. M. B. F., Araújo, L. F., Madari, B. E., Gaioso, F. L., Guiotoku, M. et al. (2012). Casca de macadâmia (*Macadamia integrifolia*) e seu potencial para a produção de biocarvões. *Comunicado Técnico-Embrapa*, 301, 1-3.
23. Xie, Y., Xiao, Z. (2010). Effects of chemical modification of wood particles with glutaraldehyde and 1,3-dimethylol-4,5-dihydroxyethyleneurea on properties of the resulting polypropylene composites. *Composites Science and Technology*, 70(13), 2003-2011.
24. Goulart, S. A. S., Oliveira, T. A., Teixeira, A., Miléo, P. C., Mulinari, D. R. (2011). Mechanical behavior of polypropylene reinforced palm fibers composite. *Procedia Engineering*, 10, 2034-2039.
25. Pereira, P. H. F., Voorwald, H. C. J., Cioffi, M. O. H., Mulinari, D. R. (2011). Sugarcane bagasse pulping and bleaching: thermal and chemical characterization. *BioResources*, 6(3), 2471-2482.
26. Carvalho, K. C. C., Mulinari, D. M., Voorwald, H. J., Cioffi, M. O. (2010). Chemical modification effect on the mechanical properties of HIPS/coconut fiber composites. *BioResources*, 5(2), 1143-1155.
27. Mulinari, D. R., Marina, A. J. F., Lopes, G. S. (2015). Mechanical properties of the palm fibers reinforced HDPE composites. *International Journal of Chemical and Molecular Engineering*, 9(7), 903-906.
28. Mulinari, D. R., Voorwald, H. J. C., Cioffi, M. O. H., Silva, M. L. C. P. (2009). Preparation and properties of HDPE/sugarcane bagasse cellulose composites obtained for thermokinetic mixer. *Carbohydrate Polymer*, 75(2), 317-321.
29. Costa, I. L. M., Alves, A. R. R., Mulinari, D. R. (2017). Surface treatment of *Pinus Elliottii* fiber and its application in composite materials for reinforcement of polyurethane. *Procedia Engineering*, 200, 341-348.

30. Doan, T. T. L., Gao, S. L., Mäder, E. (2006). Jute/polypropylene composites I. Effect of matrix modification. *Composites Science and Technology*, 66(7-8), 952-963.
31. Paula, G. P. (2014). *Formulação e Caracterização de Compósitos com Fibras Vegetais e Matriz Termoplástica*, (Dissertation for the Master's Degree in Materials Engineering and Science). Universidade Estadual do Norte Fluminense Darcy Ribeiro, Brazil.
32. Yang, H. S., Kim, H. J., Son, J., Park, H. J., Lee, B. J. et al. (2004). Rice-husk flour filled polypropylene composites; mechanical and morphological study. *Composite Structures*, 63(3-4), 305-312.
33. Wu, Y., Xia, C., Cai, L., Garcia, A. C., Shi, S. Q. (2018). Development of natural fiber-reinforced composite with comparable mechanical properties and reduced energy consumption and environmental impacts for replacing automotive glass-fiber sheet molding compound. *Journal of Cleaner Production*, 184, 92-100.
34. Venkateshwarana, N., Elaya Peruma, A., Arunsundaranayagam, D. (2013). Fiber surface treatment and its effect on mechanical and visco-elastic behaviour of banana/epoxy composite. *Materials & Design*, 47, 151-159.