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Influence of Electron Beam Irradiation on PP/Piassava Fiber Composite Prepared by Melt Extrusion Process

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ABSTRACT

In the latest years, the interest for the use of natural fibers in materials composites polymeric has increased significantly due to their environmental and technological advantages. Piassava fibers (*Attalea funifera*) have been used as reinforcement in the matrix of thermoplastic and thermoset polymers. In the present work (20%, in mass), piassava fibers with particle sizes equal or smaller than 250 µm were incorporated in the polypropylene matrix (PP) no irradiated and polypropylene matrix containing 10 % and 30 % of polypropylene treated by electron-beam radiation at 40 kGy (PP/PPi/Piassava). The composites PP/Piassava and PP/PPi/Piassava were prepared by using a twin screw extruder, followed by injection molding. The composite material samples obtained were treated by electron-beam radiation at 40 kGy, using a 1.5 MeV electron beam accelerator, at room temperature, in presence of air. After irradiation treatment, the irradiated and non-irradiated specimens tests samples were submitted to thermo-mechanical tests, melt flow index (MFI), sol-gel analysis, X-Ray diffraction (XRD) and scanning electron microscopy (SEM).

Keywords: Piassava fiber, composites, thermo-mechanical properties, electron-beam radiation, XRD.

1. INTRODUCTION

The enormous variety of vegetal fibers from plants of the Brazilian biodiversity and residues from agroindustry has been a great motivation factor for the progress that is observed at the country concerning the research and development fields based on polymeric composites with vegetal fibers (SATYANARAYANA, K.G. et al., 2007). These researches has led to the characterization of a diversity of fibers with desirable properties for the obtaining of materials composites with exceptional mechanical and thermal properties and chemical stability to applications of great importance both from the economic point of view as environmental, for the different segments of the Brazilian industry (MARINELLI, A. L. et al, 2008; D´ALMEIDA, J. R. M. et al., 2003). Basically, the thermoplastic matrices available, such as polypropylene (PP) and polyethylene (PE) show the potential benefits when combined with vegetal fibers to make composites for industrial applications (BONELLI, 2005). However, both thermoplastic and thermoset polymers can be reinforced with vegetal fibers but composites with very short fibers tend to have thermoplastic matrices. This is because fibers must be able to go through small clearances, such as the gap between the extruder screw and the extruder wall or the gate that connects the mold cavity with the runner system in both injection molding and transfer molding when being extruded or injection molded. Moreover, thermoplastics often need the additional strength or additional stiffness gained from reinforcement with short fibers (KILTTINAOVARAT et al., 2009).

Regarding polymeric composites with vegetable fibers the major disadvantage is that vegetal fibers begin to degrade at temperatures that are concurrent with processing temperatures typically experienced by commodity thermoplastic polymers. Therefore, novel techniques processing or modification in current techniques must be employed to retain the intrinsic properties of the vegetable fibers and prevent their degradation (BARONE, et al. 2005).

Piassava (Attalea funifera Mart) is a Brazilian lignocellulosic fiber extracted from the leaves of a palm tree of natural occurrence in the Atlantic rain forest and its exploitation is an extractive activity that represents the main source of income to approximately 2000 small-scale farmers, processors and their families. At present, over 10.000 tons of this fiber are extracted from the Atlantic Forest annually. Piassava fibers have been described as harder than other lignocelulosic fibers and have higher lignin content (around 48%) than any of the other common lignocellulosic fibers (AQUINO et al., 2001; D'ALMEIDA et al., 2006; SCHUCHARDT et al., 1995). This could be responsible for its inherent flexural rigidity and water proof resistance. The main use of these fibers is for industrial and domestic brooms, industrial brushes, ropes and baskets, carpets and roofs. It is estimated that around 30 % of the fiber is discarded during the cut, cleaning and baling and around 20 % is disposed as residue by the transformation industry, before production (SCHUCHARDT et al., 1995, MOURA et al., 2009). Recently, Brazilian researchers have been investigating the use of fibers as a possible reinforcement of polymeric-based composites. Their research has showed that the residue from piassava can be an important alternative to the reinforcement of thermoplastic (AQUINO et al., 2001; D'ALMEIDA et al., 2006; MOURA et al., 2009).

Nowadays, ionizing radiation has been efficiently applied for controllable modification in polymers. In general, irradiation of polymers causes two simultaneous and concurrent processes: cross-linking and degradation (NAGASAWA, N. et al, 2005; MOURA, 2006; CHOI, H. Y. et al, 2008; KHAN, F. et al, 1999; ALESSI, S. et al, 2007; KIM, H.S. et al, 2008). The main advantages of the use of the ionizing radiation for the modification of materials are: the process can be carried out at room temperature, without use of chemical initiators; reactions free from solvents and, therefore, no pollutant (BUCHALLA, R. et al, 1993). Besides, for many materials treated by the radiation processes, the improvement of the properties is superior those obtained by conventional processes.

Polypropylene (PP) is one of the polymeric materials more used due to a good balance between price and properties. PP exhibits improves resistance thermo-mechanics and rigidity due to its high melting temperature and higher crystallinity Under irradiation with high energy beams, Polypropylene predominantly undergoes degradation by chain scission. Studies have reported that the melt index of PP could decrease significantly in the course of irradiation treatment using electron beam or gamma rays because a degradation process could occur at surface boundaries between crystalline and amorphous regions (CLEGG, 1991; THAKUR et al. 2010). Studies have reported that PP degraded/oxidized by ionizing radiation can be used as a compatibilizer between the PP matrix and unmodified montmorillonite nanoclay composites, enhancing the compatibility between nonpolar polymer and hydrophilic nanoclay (THAKUR et al. 2010; GÜVEN, et al., 2011). In the present work the changes in morphological and mechanical properties of neat PP due to addition of Piassava fiber and PP irradiated with electron-beam are studied.

2. Material and Methods

2.1. Material

In this work the polypropylene (PP) was used H 301 (PP - BraskemS\A), with MFI to 10g\10 min to 230 ºC\2.16Kg, density specifies of 0,905 g/cm³ and piassava (*Attalea funifera Mart*) fiber residues disposed by some brooms and brushes manufacturers.

2.2. Preparation of the Fiber of Piassava

In order to remove the impurities, the piassava fiber residues were scraped, washed, and kept in distilled water for 24 h. The fiber was then dried at 80 ± 2 ºC for 24 h in an air-circulating oven. The dry fiber was reduced to fine powder, with particle sizes equals or smaller than 250 μm by using ball mills and then it was dried again at 80 ± 2 ºC for 24 h to reduce the moisture content to less than 2 %.

2.3. Irradiation treatment

Part of polypropylene resin (iPP *) was irradiated at 40 kGy using a 1.5 MeV electron beam accelerator (Dynamitron II, Radiation Dynamics Inc., 1.5 MeV energy, 25 mA current and 37.5 kW power), at room temperature, in air, dose rate 28.02 kGy/s. Irradiation doses were measured using cellulose triacetate film dosimeters ‘‘CTA-FTR-125’’ from Fuji Photo Film Co. Ltd..

2.4. Composites Preparation

Composites were prepared by melting extrusion process, using an extrusion machine twin screw extruder “AX 16LD40”. Neat PP were blended with irradiated PP (iPP*) (0, 10, 30 %) and with 20 % of piassava fibers, based on the percentage weight ratio (wt %). The extrudates were pelletizer, dried at 80 ± 2 ºC for 24 h in a circulating air oven and fed into injection molding machine (Sandreto model 430/110) to obtain specimens test samples.

2.5. Mechanical tests

The tensile tests were performed according to ASTM D 638, the flexural tests were based on ASTM D 790, and Izod impact (J/m) based on ASTM D 256. The differences between the results for irradiated and non-irradiated materials were then statistically evaluated by ANOVA using BioEstat software (version 5.0, 2007, Windows 95, Manaus, AM, Brazil). Significance was defined at $p < 0.05$.

2.6. Melt flow index (MFI) measurements

The evaluation of the index of fluidity of the samples neat PP, PP/iPP*10/Piassava20 and PP/iPP*30/Piassava20 were accomplished according to the norm ASTM D1238.

2.7. X-Rays Diffraction (XRD)

XRD patterns of neat PP, PP* and its composite samples were obtained using a diffractometer Rigaku Denki Co. Ltd., Multiflex model, CuKα radiation ($\lambda = 1.5406$ Å) at 40 kV and 20 mA. With this procedure, the angles (2θ) of diffraction of all the samples were measured from 2° to 50°.

2.8. Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) analyses were carried out using a LX 30 (Philips). The samples were cryofractured under liquid nitrogen, and then the fractured surface was coated with a fine layer of gold and observed by SEM.

3. Results and Discussion

3.1. Mechanical tests results

Figure 1shows the diagram stress (MPa) X strain (mm/mm) for neat PP and its composites.

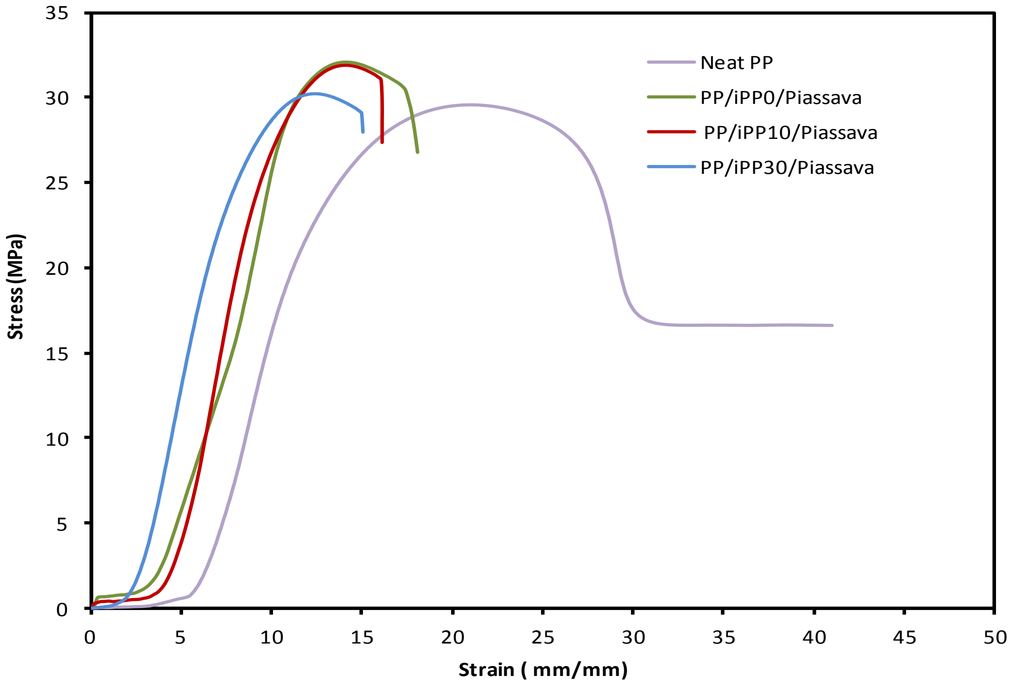

Figure I. Diagram Stress X Strain for neat PP and its composites: PP/iPP*0/Piassava; PP/iPP*10/Piassava; PP/iPP*30/Piassava.

Table I present the results of the mechanical tests for neat PP and its composites. The results showed that the addition of iPP * in composites improved the tensile strength at break and Young's modulus of composites, but reduced the impact resistance. However, when 30 % of iPP* was added, the tensile resistance behavior of the composite was lower than that shown by PP/ iPP*0/Piassava and PP/iPP*10/Piassava composites, except on the Young's modulus.

Table I. Mechanical and thermo-mechanical tests results of neat PP and its composites

Properties	Neat PP	PP/iPP*0/ Piassava	PP/iPP*10/ Piassava	PP/iPP*30/ Piassava
Young's modulus (MPa)	167.61 ± 17.02	177.2 ±47.68	199.66 ± 29.93	208,25±7,17
Izod impact (J/m)	56.66 ± 0,01	50 ± 0	43,33 ± 0,04	36,66 ± 0,01
Elongation at break (%)	215.09±113.94	22.34 ± 7.49	18.25 ± 0.98	18,52 ± 2,66
Tensile strength at break (MPa)	16.14 ± 0.45	28.23 ± 0.24	30.53 ± 0.39	29,31 ± 0,84

3.2. Melt flow index (MFI) measurements

The MFI values of neat PP, iPP* and their composites are presented in Table II. The MFI value of iPP* increased and was greater than twice compared with neat PP and their composites.

Table II. MFI values of neat PP, iPP* and their composites

Materials	MFI (at 230 °C/2.16 kg) (g/10min)
Neat PP	21.70
iPP*	58.64
PP/iPP*0/Piassava	11.84
PP/iPP*10/Piassava	11.62
PP/iPP*30/Piassava	23.38

* ***irradiated polypropylene***

3.3. Sol-gel analyses results

Table III presents the results of the sol-gel of neat PP and its composites. There was a significant change in the sol-gel percentage of neat PP compared with composites due to iPP* addition. The PP/iPP*10/Piassava presented the better cross-linking degree when compared with the others materials

Table III: Sol-gel analysis of Neat PP; PP/iPP*0/Piassava; PP/iPP*10/Piassava; PP/iPP*30/Piassava.

	Neat PP	**PP/iPP*0/Piassava**	**PP/iPP*10/Piassava**	**PP/iPP*30/Piassava**
Cross-linking Degree %	*0.5±0*	3.59±0.89	21.37±10.32	7.97±7.97

3.4. X-Rays Diffraction (XRD)

The XRD patterns of neat PP and its composites are shown in Figure 2. It can be seen, the XRD spectrum of neat PP showed characteristics α-monoclinic crystal structure with a prominent 2θ peak at around 13.8^0, 16.5^0, 18.2^0 and 20.5^0. For both PP/iPP*10/Piassava, PP/iPP*30/Piassava composites, the diffraction intensity of the PP matrix peaks presented a large increase when compared with that of neat PP.

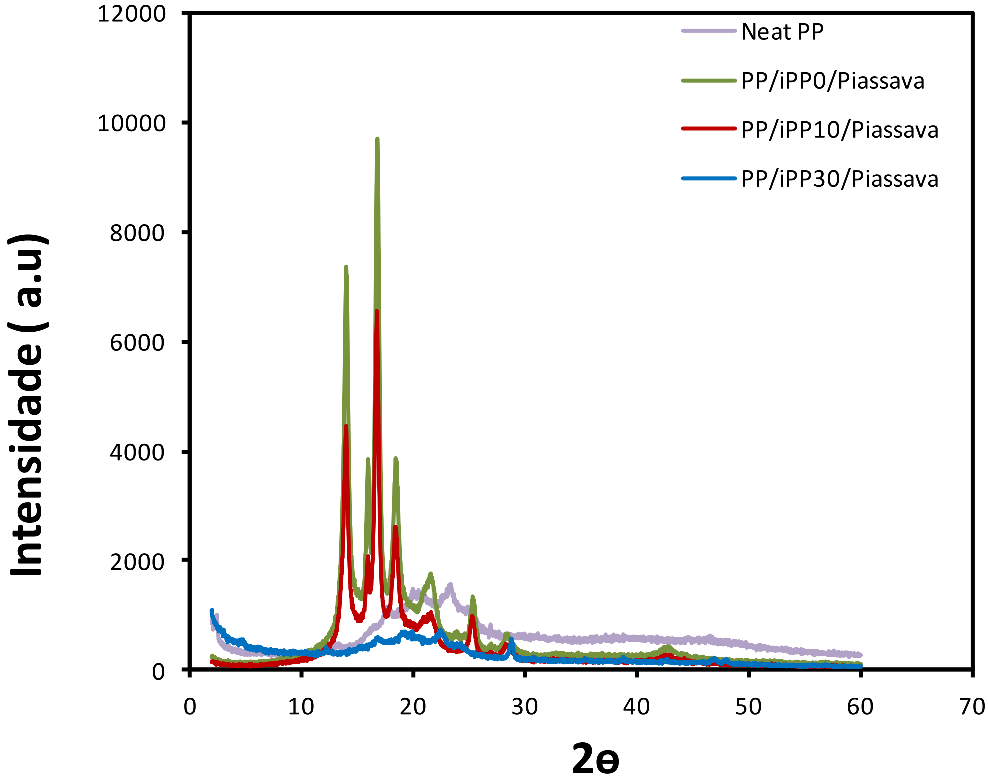

Figure 2. XRD patterns of neat PP and its composites

3.5. Scanning Electron Microscopy (SEM)

SEM micrographs of cryo-fractured surfaces of neat PP and its composites are shown in Figures 3 and 4.

As it can be seen in Fig.3 and 4, neat PP showed a rough, dense and compact cryo-fractured surface. The micrographs surface of PP/iPP*30/Piassava revealed several cracks and voids between fiber and matrix. In contrast, the PP/iPP*10/Piassava composites revealed a rough, dense and compact cryo-fractured surface without presence of cracks and voids or cavities. This suggested that the 10 % addition of iPP* led to a better interfacial adhesion between piassava fibers and PP.

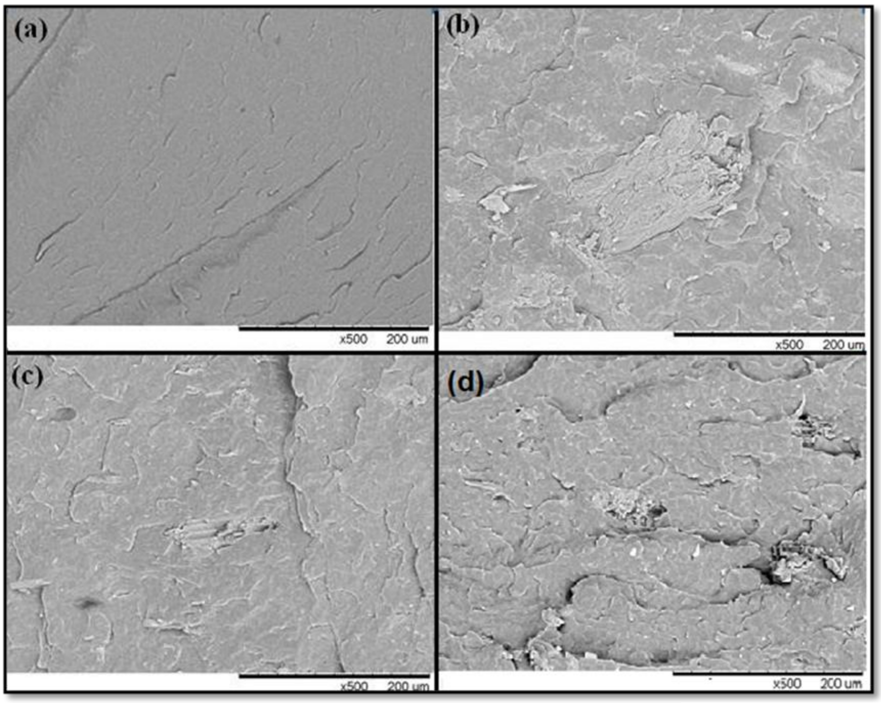

Figure 3 SEM micrographs (500 X) for surfaces of Neat PP (3a); PP/iPP*0/Piassava20 (3b); PP/iPP*10/Piassava20 (3c) and PP/iPP*30/Piassava20 (3d).

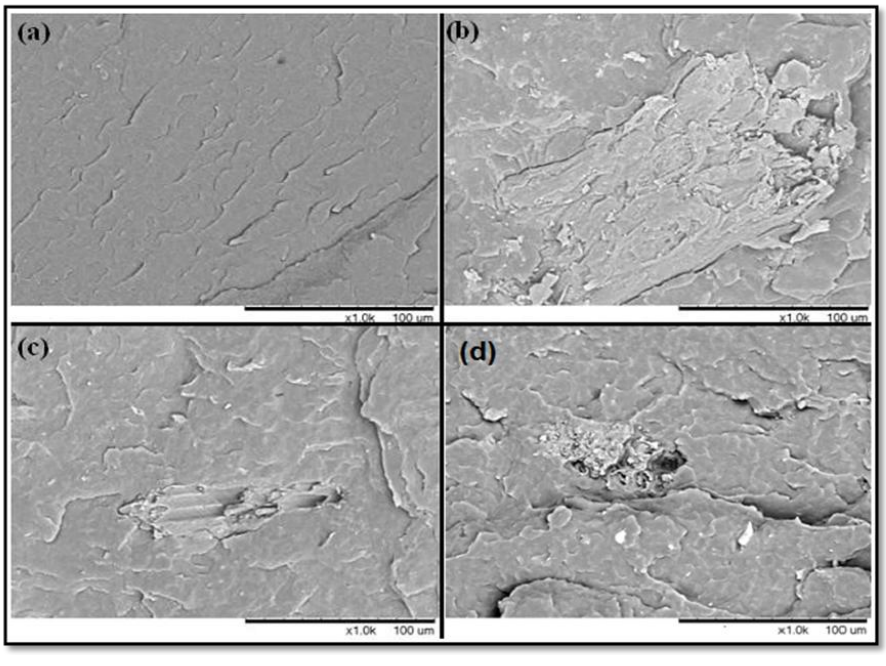

Figure 4. SEM micrographs (1000 X) for surfaces of Neat PP (4a); PP/iPP*0/Piassava20 (4b); PP/iPP*10/Piassava20 (4c) and PP/iPP*30/Piassava20 (4d).

4. Conclusions

The objective of the present work was to evaluate the changes in morphological and mechanical properties of neat PP due to addition of Piassava fiber and irradiated PP with electron-beam radiation. The results showed that the incorporation of 10% (% in weight) of irradiated PP in PP /piassava composite led to the significant changes in mechanical morphological properties of composite when compared with composite without iPP* addition. The results showed that the incorporation of 10 % (in wt) of iPP* in composite effectively improved the composite properties and led to obtaining materials with superior properties suitable for several industrial applications.

REFERENCES

1. ALESSI, S.; DISPENZA, C.; FUOCHI, P.G.; CORDA, U.; LAVALLE, M.; SPADARO, G. E-beam curing of epoxy-based blends in order to produce high-performance composites Radiation Physics and Chemistry 76 (2007) 1308–1311.
2. AQUINO, R.C.M.P., D´ALMEIDA, J.R.M., MONTEIRO, S.N., "Flexural mechanical properties of piassava fibres (Attalea funifera)-resin matrix". Composites. Journal of Materials Science Letters, v.20, p.1017-1019 (2001)
3. AMERICAN SOCIETY FOR TESTING AND MATERIALS. – ASTM. Standard Test Methods for Tensile Properties of Plastics. D 638 - 99. ASTM, 1999.
4. AMERICAN SOCIETY FOR TESTING AND MATERIALS. – ASTM. Standard Test Meth. for Detemining the Izod Pendulum Impact Resistance of Plastics. D 256-97. ASTM, 1997.
5. BARONE, J.R..; SCHMIDT, W. F.; LIEBNER, C.F.E. Compounding and molding of polyethylene composites reinforced with keratin feather fiber. Composites Science and Technology, v. 65 p. 683–692, 2005.
6. BONELLI, C.M.C.; ELZUBAIR, A.; SUAREZ, J.C.M.; MANO, E.B. Comportamento térmico, mecânico e morfológico de compósitos de polietileno de alta densidade reciclado com fibra de piaçava. Polímeros: Ciência e Tecnologia, vol.15, n.4, p. 256-260 (2005).
7. BOURBAN, C.;KARAMUK, E.; DE FONDAUMIERE, M. J.; RUFFIEX, K.; MAYER, J. WINTERMANTEL, E. Processing and characterization of a new biodegradable composite made of a PHB/V matrix and regenerated cellulosic fibers. J. Envirom. Polym. Degrad. v.5 p.159-166, 1997.
8. BUCHALLA, R., SCHUTTLER, C., BOGL, K.W., Effect of ionizing radiation on plastic food packaging materials: a review, Part 1. Chemical and physical changes, J. Food Prot. v. 56, p. 991–997 (1993).
9. CARRADO, K.A., BERGAYA, F. (editores). Clay Minerals Society Workshop Titles. Clay-based Polymer Nanocomposites (CPN). Volume 15, 2007. Chantilly, VA, USA.
10. CHOI, H. Y.; HAN, S. O.; LEE, J. S.Surface morphological, mechanical and thermal characterization of electron beam irradiated fibers. App. Surf. Sci., 255, p.2466–2473, 2008.
11. CLEGG, D.W.; COLLYER, A.A. Irradiation effects on polymers. Elsevier Science. Publishers Ltd. England, p. 68-69, 1991.
12. D´ALMEIDA, J. R. M.; MONTEIRO, S. N. Compósitos reforçados por fibras naturais – oportunidades e desafios. In: 58o CONGRESSO ANUAL DA ASSOCIAÇÃO BRASILEIRA DE METALURGIA E MATERIAIS, Rio de Janeiro, 2003. Anais ... São Paulo: ABM, 2003. p. 1725-1734.
13. GÜVEN, O; ZENGIN, F. Preparation of polypropylene/montmorillonite nanocomposites using ionizing radiation. In: *Report of the 1st RCM on Radiation Curing of Composites for Enhancing the Features and Utility in Health Care and Industry,*Vienna, 18-22 July 2011.
14. KHAN, F.; AHMAD, S. R.; KRONFLI, E. Stability of jute fibres on exposure to ionising radiation. Polymer Degradation and Stability 63, p.79-84, 1999.
15. KILTTINAOVARAT, S. and SUTHAMNOI, W. Physical properties of polyolefin / bamboo charcoal composites. Journal of metals, materials and minerals, vol.19 no.1 pp.9-15, (2009).
16. KIM, H. S.; KIM, H. J. Enhanced hydrolysis resistance of biodegradable polymers and bio-composites. Polymer Degradation and Stability, v. 93, p. 1544–1553, 2008.

17. MARINELLI, A. L.; MONTEIRO, M. R.; AMBRÓSIO, J. D.; BRANCIFORTI, M. C.; MARTINS, G. S.; IOZZI, M. A.; MARTINS, M. A.; MATTOSO, L. H. C.; FERREIRA; F. C. Caracterização mecânica e térmica de compósitos de poli (cloreto de vinila) reforçados com fibras de sisal. Pol. Ciência Tecn., vol. 14, n° 5, p. 326-333, 2004.
18. MAYA, J. J.; SABU, T. Review biofibres and biocomposites. Carbohydrate Polymers, v.71
19. MOURA, E.A.B. Avaliação do desempenho de embalagens para alimentos quando submetidas a tratamento por radiação ionizante. 2006. Tese (Doutorado) – Instituto de Pesquisas Energéticas e Nucleares, São Paulo.
20. MOURA, E.A.B.; NOGUEIRA, B.R.; ORTIZ, A.V. “Changes in Physicochemical, Morphological and Thermal Properties of Electron-Beam Irradiated Ethylene–Vinyl Alcohol Copolymer (EVOH) as a Function of Radiation Dose” - International Topical Meeting on Nuclear Research Applications and Utilization of Accelerators, Proceedings Series, IAEA – International Atomic Energy Agency, May, 2009. In: http://www-pub.iaea.org/MTCD/publications/PDF/P1433_CD/datasets/abstracts/sm_eb-16.html>
21. NAGASAWA, N.; KANEDA, A.; KANAZAWA, S.; YAGI, T.; MITOMO, H.; YOSHII, F.; TAMADA, M. Application of poly(lactic acid) modified by radiation crosslinking. Nuclear Instruments and Methods in Physics Research B 236 (2005) 611–616.
22. PAIVA, L.B., MORALES, A.R., VALENZUELA-DÍAZ, F.R. Organoclays: Properties, preparation and applications. Applied Clay Science, vol.42, p. 8-24, 2008.
23. SATYANARAYANA, K. G.; GUIMARÃES, J. L.; WYPYCH, F. Studies on lignocellulosic fibers of Brazil. Part I: Source, production, morphology, properties and applications. Composites: Part A, vol. 38 p.1694–1709, 2007.
24. SCHUCHARDT U.; BIANCHI M.L.; GONÇALVES, A.R.; CURVELO, A.A.S.; BISCOLLA, F.C.; PERES, L.O., “Piassava fibers (Attalea funifera). I. Chemical analysis, extraction and reactivity of its lignin”, Cellulose Chem. Technol. 29, p.705–712 (1995).
25. THAKUR, V.; LEUTERITZ, A.; GOHS, U.; KRETZSCHMAR, B.; WAGENKNECHT, U.; BHOWMICK, A. K.; HEINRICH, G. Montmorillonite nanocomposites with electron-beam modified atactic polypropylene. Applied Clay Science, v. 49, p. 200–204, 2010, ISSN 01691317.