

## CONTRIBUTION OF BRAZIL NUT SHELL FIBER AND ELECTRON-BEAM IRRADIATION IN THERMO-MECHANICAL PROPERTIES OF HDPE

Pamella Polato<sup>1</sup>, Leandro Alex Lorusso<sup>1</sup>, Clécia de Moura Souza<sup>1</sup>, Anne Chinellato<sup>2</sup>, Ricardo de Rosa<sup>3</sup> and Esperidiana Augusta Barretos de Moura<sup>1</sup>

### ABSTRACT

In the present work, the influence of electron-beam irradiation on thermo-mechanical properties of HDPE and HDPE/Brazil nut shell fiber composite was investigated. The materials were irradiated at radiation dose 50 kGy using a 1.5 MeV electron beam accelerator, at room temperature in presence of air. The irradiated and non-irradiated samples were submitted to thermo-mechanical tests and the correlation between their properties was discussed. The results showed that the incorporation of Brazil nut shell fiber represented a significant gain ( $p < 0,05$ ) in tensile strength at break, flexural strength, flexural module, Vicat softening temperature and heat distortion temperature (HDT) properties of the HDPE. In addition, the irradiated HDPE/Brazil nut shell fiber composite presented a significant increase ( $p < 0.05$ ) in this properties compared with irradiated HDPE.

Keywords: Brazil nut shell fiber, mechanical properties, electron-beam irradiation.

First TMS-ABM International Materials Congress, 26-30 July, 2010.

<sup>1</sup> Instituto de Pesquisas Energéticas e Nucleares, IPEN - CNEN/SP, Av. Prof. Lineu Prestes, 2242, 05508-000, São Paulo, SP, pamella.polato@ipen.br, +55 11 3133-9883

<sup>2</sup> Mash: Tecnologia em Compostos e Masters, Av. Marechal Tito, 6829, 08115100 São Paulo, SP.

<sup>3</sup> Amazon Brazil Nuts, Rua Heliópolis, 262 B, 05318-010 São Paulo, SP

### 1. Introduction

The use of natural fiber in thermoplastic polymer composites is continuously increasing, because the composite materials obtained are both economically sound and environmentally friendly. Natural fibers are replacing the synthetic fibers in thermoplastic composites because these are not biodegradable. Other important advantages are that natural fibers are quite cheap, available, and recyclable and show good mechanical properties, low energy demand and an environmental appeal compared to synthetic ones. Furthermore, natural fibers are much less abrasive and, therefore, the manufacture of natural fiber composites has the benefit of causing less wear and deterioration of machine parts. So the use of natural fibers with thermoplastics has drawn industry's attention, especially for high volume and low cost applications [1-3].

Brazil nuts are the seed of *Bertholletia excelsa* tree. *B.excelsa* belongs to Lecythidaceae family and is native to the Amazon rain forest. Their fruits, Brazil-nuts, have high caloric and protein content. Additionally, they contain selenium which reduces the effects of free radicals. Besides being an appreciated aliment because of its flavor, the Brazil nut has a considerable nutritional value [4, 5].

Brazil nuts are one of the main products collected and sold by extractivists. A significant part of the nut harvest is exported to developed countries where they are added, for instance, to ice-cream, chocolates and other sweets [5, 6]. Brazil-nut products advertisements imply that some of the profit is used to improve the life quality of extractivists. It represents about 30 million reais in local economy with a direct impact on the livelihoods of local communities, smallholders and indigenous populations. In Acre state itself there are over 15 thousand families having Brazil nuts as their main source of income. The Brazil nut has a high economic importance in the majority of Amazonian states. About 60% is being exported *in natura* to Europe, Japan and United States of America and only about 5% is being domestically consumed. The nuts are dried and sold either inside or without their shells [6-9]. Due to a higher consumption increasing, a large amount of shells has been discarded as residue in sanitary landfills and / or incinerated.

The high density polyethylene (HDPE) is a thermoplastic used for several industrial applications such as blow molding, injection molding, and extrusion, due to its low cost, desired mechanical properties, low temperature resistance, impermeability to water and processing facility [10-12].

A promising approach to the controllable modification of the properties of the polymer materials is based on treatment with ionizing radiation, particularly, electron-beam irradiation [13]. The electron-beam irradiation can affect the polymeric materials leading to a production of free radicals. These free radicals can in turn lead to degradation and/or cross-linking phenomena, with release of gases, discoloration, changes in mechanical, thermal and barrier properties [12-15]. In recent years electron-beam irradiation has been efficiently applied to promote cross-linking and scission of the polymeric chains to modify the properties of the different polymers for versatile applications, and improve polymeric materials composites [16]. In this study, the influence of electron-beam irradiation on thermo-mechanical properties of HDPE and HDPE/Brazil nut shell fiber composite was investigated.

## 2. Experimental

### 2.1. Materials

The materials used in this study were HDPE resin (HDPE JV060U – commercial grade by Braskem S/A), with MFI = 7,0 g/10 min at 190 °C/2,16 Kg, specific density = 0,957 g/cm<sup>3</sup> and Brazil nut shell fiber residues disposed by Brazil nuts industries.

### 2.2. Preparation of HDPE/Brazil nut shell fiber composite

In order to remove the impurities, the Brazil nut shell fiber residues were scraped, washed, and kept in distilled water for 24 h. The fiber was then dried at 80 ± 2 °C for 24 h in an air-circulating oven. The dry fiber was reduced to fine powder, with particle

sizes equal or smaller than 250  $\mu\text{m}$  by using ball mills and dried again at  $80 \pm 2 \text{ }^\circ\text{C}$  for 24 h to reduce the moisture content to less than 2 %. The HDPE resin reinforced with 40% Brazil nut shell fiber was obtained by mixing 40 parts of dry fiber with 60 parts of HDPE resin (in weight), using a double screw extruder machine made by Indústrias Romi S.A.

### 2.3. Electron-beam Irradiation

HDPE resin and HDPE/Brazil nut shell fiber composite were irradiated at radiation dose of 50 kGy using a electrostatic 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 14 kGy/s. Irradiation doses were measured using cellulose triacetate film dosimeters “CTA-FTR-125” from Fuji Photo Film Co. Ltd. The irradiated and non-irradiated samples were submitted to thermo-mechanical tests and the correlation between their properties was discussed.

### 2.4. Thermo-mechanical tests

The thermo-mechanical tests were carried out on the materials eight days after irradiation, in order to consider post irradiation effects. The tensile tests were performed according to ASTM D 638 [17] and the flexural tests were based on ASTM D 790 [18]. Vicat softening temperature tests were done according to ASTM D 1525 [19] and those of heat distortion temperature (HDT) were based on ASTM D 648 [20]. 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  $p < 0.05$ .

## 3. Results and Discussion

The results of the tensile strength at break tests for both, irradiated and non-irradiated HDPE and HDPE/Brazil nut shell fiber composite, are given in Fig. 1.

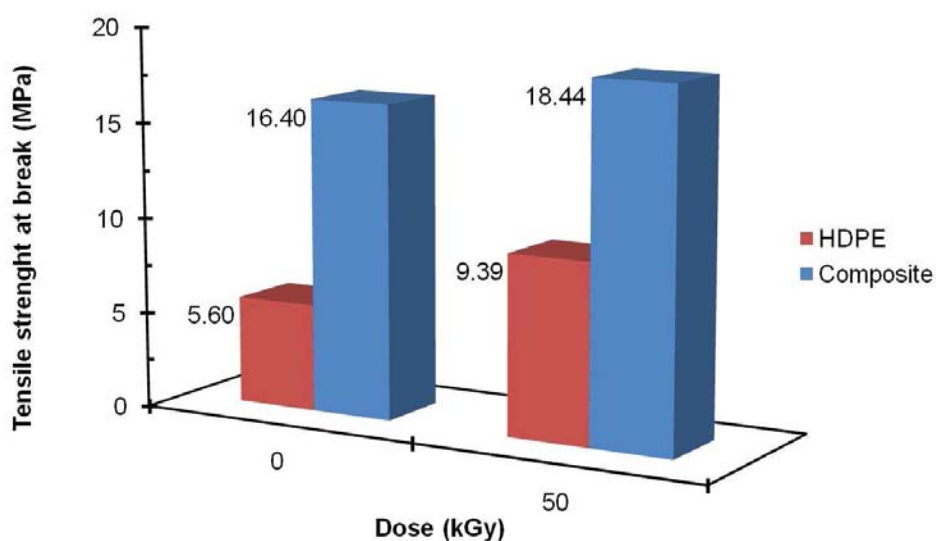


Figure 1. Tensile strength at break as a function of the electron-beam radiation dose for the HDPE and HDPE/Brazil nut shell fiber composite.

The results presented in Fig. 1 represent the average values calculated from the data obtained by tensile tests. The standard deviation for results of the tensile strength at break was less than 10% for all tests. As it can be seen, there were significant increases ( $p < 0.05$ ) in the tensile strength at break of the HDPE and of the HDPE/Brazil nut shell fiber composite, for all ranges of radiation doses studied. The values for HDPE/Brazil nut shell fiber composite tensile strength at break were around 193 % higher than for non-irradiated HDPE samples and ca. 96 % higher for irradiated samples. These results showed a significant gain of ca. 68 % ( $p < 0.05$ ) at irradiated HDPE tensile strength at break compared to original HDPE (non-irradiated) and around 12 % for the HDPE/Brazil nut shell fiber composite after electron-beam irradiation.

The flexural strength average data for both irradiated and non-irradiated HDPE and HDPE/Brazil nut shell fiber composite are given in Fig. 2.

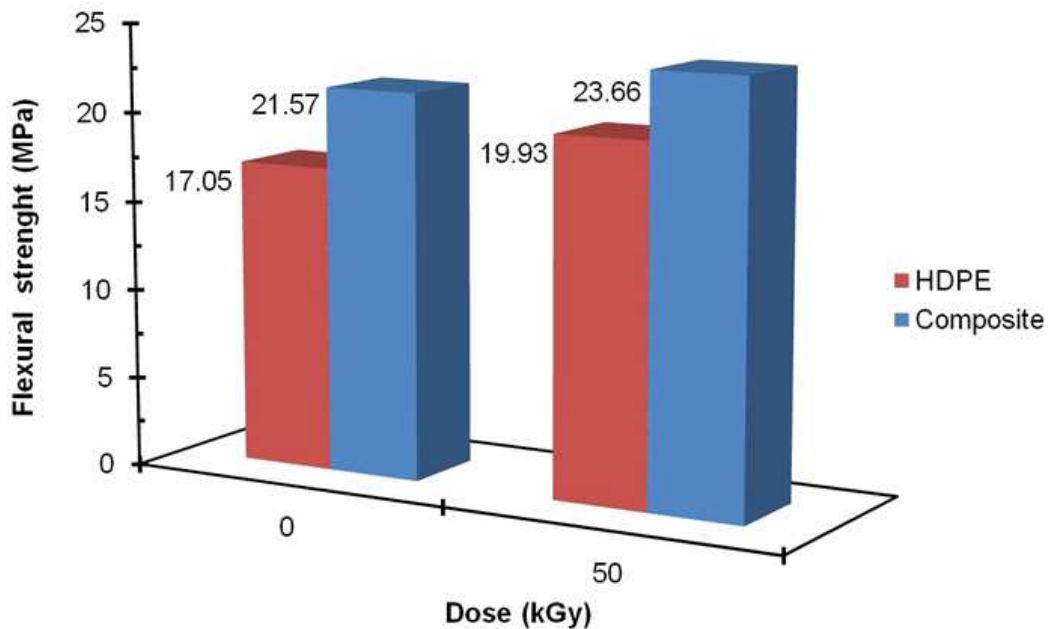


Figure 2. Flexural strength as a function of electron-beam radiation dose for the HDPE and HDPE/Brazil nut shell fiber composite.

As it can be observed at Fig.2, the HDPE/Brazil nut shell fiber composite flexural strength was, significantly, ca. 27 % higher ( $p < 0.05$ ) than for non-irradiated HDPE samples and around 19 % higher for irradiated samples. This Figure also shows an increase by 17 % at flexural strength of the HDPE after electron-beam irradiation and ca. 10 % for irradiated HDPE/Brazil nut shell fiber composite compared with the non-irradiated composite.

Figure 3 shows the results of the flexural module tests for both irradiated and non-irradiated HDPE and HDPE/Brazil nut shell fiber composite. A significant gain ( $p < 0.05$ ), concerning flexural module of HDPE, can also be observed in this figure, due to the incorporation of Brazil nut shell fiber. Significantly, for the non-irradiated samples, the composite showed a gain by 129 % ( $p < 0.05$ ) and a gain by 130 % for irradiated samples. As a result of the irradiation dose applied, the flexural module

increased around 8.0 % for HDPE and 9.0 % for HDPE/Brazil nut shell fiber composite.

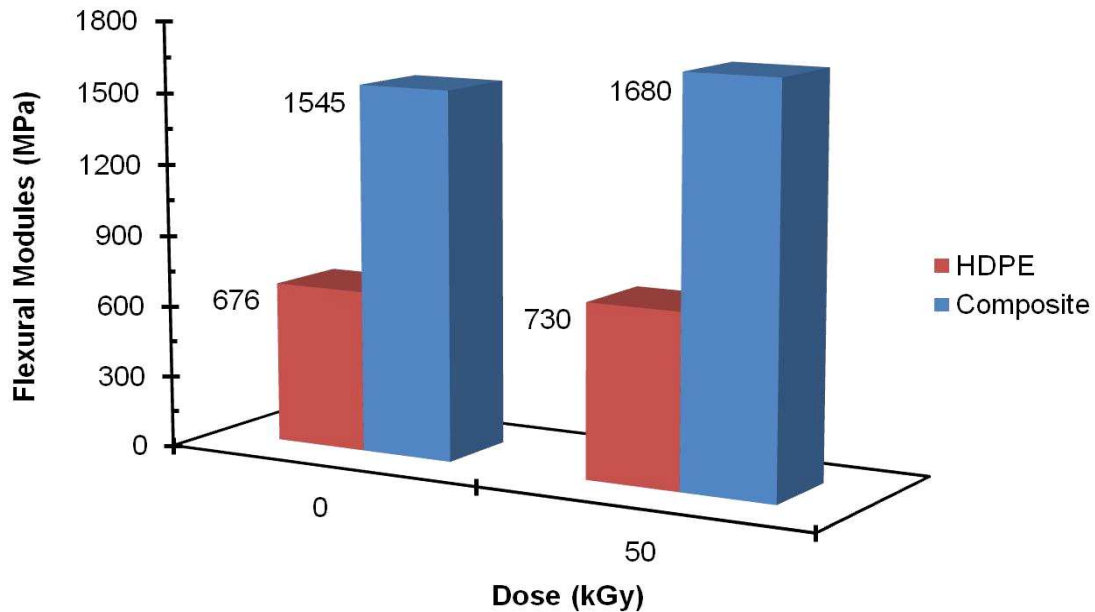


Figure 3. Flexural module as a function of electron-beam radiation dose for the HDPE and HDPE/Brazil nut shell fiber composite.

In figures 4 and 5, the results of the heat distortion temperature (HDT) and the Vicat tests, respectively, can be seen, for both irradiated and non-irradiated HDPE and HDPE/Brazil nut shell fiber composite. Fig. 4 shows a gain, concerning HDT, of around 20 % ( $p < 0.05$ ) for the HDPE, due to the incorporation of Brazil nut shell fiber and a gain of 16 % for irradiated samples.

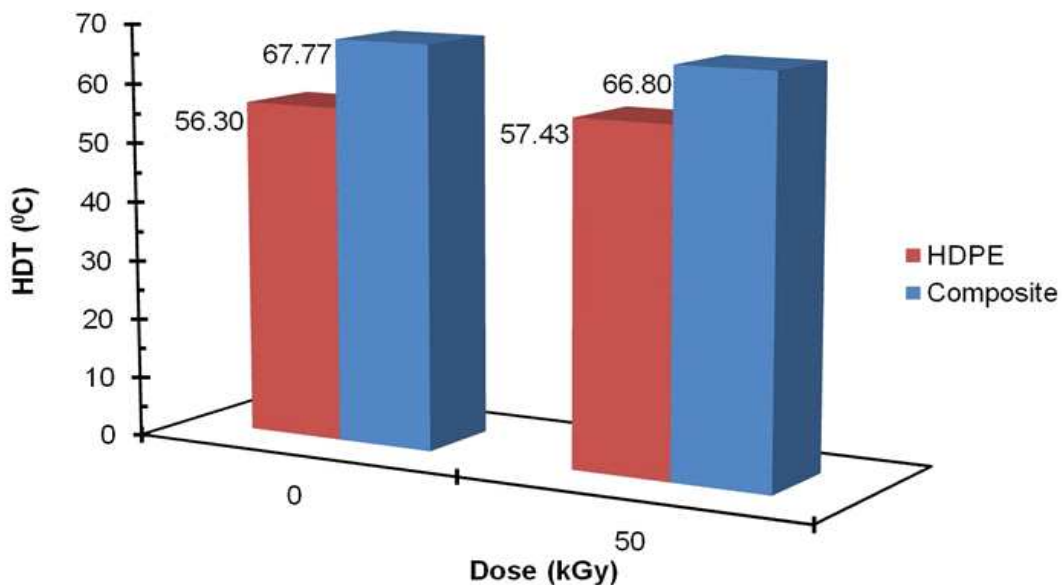


Figure 4. HDT as a function of electron-beam radiation dose for the HDPE and HDPE/Brazil nut shell fiber composite.

As it can be seen in this figure, there were no observed improvement of the HDT at the irradiation dose applied for both materials.



The Vicat tests results presented in Fig. 5 demonstrated that the incorporation of Brazil nut shell fiber tends to Vicat reduction.

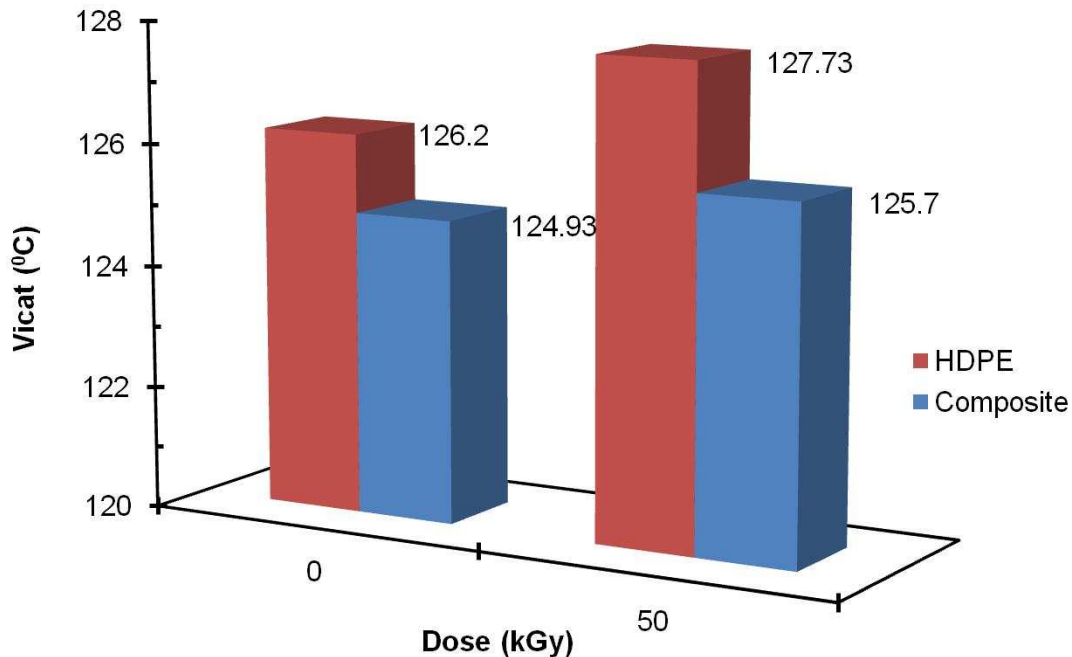


Figure 5. Vicat as a function of electron-beam radiation dose for the HDPE and HDPE/Brazil nut shell fiber composite.

As it is known, ionizing radiation promotes preferential HDPE cross-linking, which improves its properties [21]. The results of mechanical properties tests show a gain ranging from 9 to 12 % for HDPE/Brazil nut shell fiber composite after electron-beam irradiation. This indicates that the irradiation process led to a production of free radicals in which cross-linking prevailed over degradation.

#### 4. Conclusion

The objective of the present study was to evaluate the contribution of Brazil nut shell fiber and electron-beam irradiation in thermo-mechanical properties of HDPE. The results showed that the incorporation of Brazil nut shell fiber represented a significant gain ( $p < 0,05$ ) in tensile strength at break, flexural strength, flexural module, Vicat softening temperature and heat distortion temperature (HDT) properties of the HDPE. In addition, the irradiated HDPE/Brazil nut shell fiber composite presented a significant increase ( $p < 0.05$ ) in this properties compared with irradiated HDPE. In other words, when the fiber is added, there is a higher gain and, when both processes are combined, that is, irradiation is applied and the fiber is added, the gains are even greater. Therefore, this operation is highly recommended for applications in which a better performance is required.

#### Acknowledgements

The authors wish to thank Carlos Gaia da Silva and Elizabeth S. R. Somessari for performing the EB irradiation.

## References

1. KHAN, M.A.; KHAN, R.A.; HAYDARUZZAMAN, A.H.; KHAN, A.H. Effect of gamma radiation on the physico-mechanical and electrical properties of jute fiber-reinforced polypropylene composites. *Journal of Reinforced Plastics and Composites*, Jul 2009; vol. 28: pp. 1651 - 1660.
2. D'ALMEIDA, J.R.M.; AQUINO, R.C.M.P.; MONTEIRO, S.N. Tensile mechanical properties, morphological aspects and chemical characterization of piassava (*Attalea funifera*) fibers. *Composites: Part A* 37, p.1473–1479, 2006.
3. BONELLI, C.M.C.; ELZUBAIR, A.; MIGUEZ SUAREZ, J.C.; 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
4. CONTINHO, V.F. Efeito da suplementação com castanha-do-Brasil (*Bertholletia excelsa* H.B.K.) no estado nutricional de praticante de capoeira em Relação ao Selênio. 2003. 176 f. Tese (Doutorado em Ciências dos Alimentos) Universidade de São Paulo, São Paulo, 2003.
5. GLÓRIA, M.M. AND REGITANO D'ARCE, M.A.B. Concentrado e isolado protéico de torta de castanha-do-pará: obtenção e caracterização química e funcional. *Ciência e Tecnologia de Alimentos*, Campinas, v. 20, n. 2, p. 240. (2000).
6. YANG, J. Brazil nuts and associated health benefits: A review. *LWT - Food Science and Technology*. v. 42, p. 573-1580, 2009.
7. FELBERG, L.; ANTONIASSI, R.; DELIZA, R.; FREITAS, S.C.; MODESTA, R. C. D. Soy and Brazil nut beverage: processing, composition, sensory, and color evaluation. *Ciênc. Tecnol. Aliment.* vol.29, n.3, pp. 609-617. 2009.
8. CAMARGO, P.B.; SALOMÃO, R.P.; TRUMBORE, S. ; MARTINELLI, L.A. How old are large Brazil-nut trees (*Bertholletia excelsa*) in the Amazon? *Sci. Agric.*, 51 (2), p.389-391, 1994.
9. SOUZA, I.F. Cadeia produtiva de castanha-do-brasil (*Bertholletia excelsa*) no estado de mato grosso. Mato Grosso do Sul, 2006, 141 p. Dissertação (Mestrado) Campo Grande: Departamento de Economia e Administração, Universidade Federal de Mato Grosso do Sul.
10. CANEVAROLO JR., S.V. *Ciência dos Polímeros*. São Paulo: Artliber Editora Ltda. 2a edição, 2006.
11. MULINARI, D.R.; VOORWALD, H.J.C.; CIOFFI, M.O.H.; SILVA, M.L.C.P.; GOUVÊA DA CRUZ, T.; SARON, C. Sugarcane bagasse cellulose/HDPE composites obtained by extrusion. *Composites Science and Technology*, v. 69, p. 214–219, 2009.

12. LIU, H.; FANG, Z.; PENG, M.; SHEN, L.; WANG, Y. The effects of irradiation cross-linking on the thermal degradation and flame-retardant properties of the HDPE/EVA/magnesium hydroxide composites. *Radiation Physics and Chemistry*, v. 78, p. 922–926, 2009.
13. 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.
14. CHARLESBY A, ROSS M. Effect of high-energy radiation on long chain polymers. *Nature*, p.171:167, 1953.
15. CLEGG, D.W.; COLLYER, A.A. *Irradiation effects on polymers*. Elsevier Science. Publishers Ltd. England, p. 68-69, 1991.
16. RAGHAVAN, J. Evolution of cure, mechanical properties, and residual stress during electron beam curing of a polymer composite. *Composites: Part A*, v. 40, p.300–308, 2009.
17. American Society for Testing and Materials - ASTM, D 638-01. *Standard Test Method for Tensile Properties of Plastics*, 2001.
18. American Society for Testing and Materials - ASTM, D 790 – 00, *Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials*, 2000.
19. American Society for Testing and Materials - ASTM, D 1525 – 00, *Standard Test Method Vicat Softening Temperature of Plastics*, 2000.
20. American Society for Testing and Materials - ASTM, D 648 – 01, *Standard Test Method for Deflection Temperature of Plastics Under Flexural Load in the Edgewise Position*, 2001.
21. ZIAIE, F.; BORHANI, M.; MIRJALILI, G.; BOLOURIZADEH, M.A. Effect of crystallinity on electrical properties of electron beam irradiated LDPE and HDPE. *Radiation Physics and Chemistry* v.76, p.1684–1687, 2007.