2013 International Nuclear Atlantic Conference - INAC 2013
Recife, PE, Brazil, November 24-29, 2013
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR - ABEN
ISBN: **978-85-99141-05-2**

EFFECTS OF ELECTRON-BEAM IRRADIATION ON HDPE/BRAZIL NUT SHELL FIBER COMPOSITE

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ABSTRACT

In recent years, research on the replacement of synthetic fibers by natural fibers as reinforcement in thermoplastic composites has increased dramatically due to the advantages of natural fibers, such as low density, low cost, environmental appeal and recyclability. In the present work, the influence of electron-beam irradiation on mechanical properties of HDPE and HDPE/Brazil Nut Shell (*Bertholletia excelsa*) fiber composite was investigated. The HDPE composite reinforced with 5 % or 10 %, by weight of Brazil nut shell fiber powder with particle sizes equal or smaller than 250 µm were obtained by extrusion, using a twin screw extruder. The materials were irradiated at 200 kGy using a 1.5 MeV electron beam accelerator, at room temperature in presence of air. The irradiated and non-irradiated specimens tests samples were submitted to mechanical and and thermo-mechanical tests, scanning electron microscopy (SEM), X-Ray diffraction (XRD) and sol-gel analysis and the correlation between their properties was discussed.The results showed significant changes in HDPE mechanical and thermo-mechanical properties due to Brazil nut shell fibers addition and electron-beam irradiation. The surface of the cryofractured composite samples irradiated showed important visual changes which suggest a better fiber-matrix interfacial adhesion, due to irradiation treatment. These results showed that it is possible to get interesting property gains by using waste from renewable sources instead of the traditional ones and electron-beam radiation treatment.

Keywords: Brazil nut shell fibers, composite, thermo-mechanical properties, SEM, electron-beam radiation

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. Synthetic fibers are replacing natural fibers in thermoplastic composites because those 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 when compared with synthetic ones. Furthermore, natural fibers are much less abrasive and, therefore, the manufacture of natural fiber composites has the benefit of cause less wear and deterioration of machine parts. So the use of natural fibers with thermoplastics has drawn much attention of the industry, especially, due to high volume of production and low cost of application [1,2].

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. Brazil nuts are one of the main products collected and sold by extractivists [3]. 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 [4, 5]. Brazil-nut products advertisements imply that some of the profit is used to improve the life quality of extractivists. It represents about 17.7 million dollars in local economy with a direct impact on the livelihoods of local communities, smallholders and indigenous populations. The Brazil nut has a high economic importance in the majority of Amazonian states. About 60 % is being exported in nature to Europe, Japan and United States of America and only about 5 % is being domestically consumed. Due to a higher consumption increasing, a large amount of shells, around 2 thousand tons by month, has been discarded as residue in sanitary landfills and / or incinerated [5-8].

High density polyethylene (HDPE) is a linear thermoplastic polymer widely used, presenting balanced mechanical properties, chemical resistance, impermeability to water, low cost and easy processing advantages [9, 10]. The molecular weight, the molecular weight distribution and the amount of branching determine many of the mechanical and chemical properties of the end product. HDPE has been used with natural fibers to prepare composites with good performance [10-12]. A promising approach for the controllable modification of the polymer materials properties is based on ionizing radiation treatment. In general, the cross-linking and degradation processes occur, simultaneously, in amorphous regions of polymers as an effect of ionizing radiation. Cross-linking of HDPE into three-dimensional networks leads to improvement of properties such as tensile strength, chemical resistance and thermal characteristics [13].

Electron beam processing effectively and efficiently creates useful changes in material properties and performance, such as polymer crosslinking and chain scissioning. When HDPE is irradiated with electron-beam (EB), gamma-rays, and other forms of high energy radiation, predominantly undergoes crosslinking. Crosslinked HDPE has become widely adapted for a number of industrial applications, which require withstanding high temperature environments. Crosslinking enhances several key properties of HDPE, including impact strength, barrier properties, in addition to heat resistance. However, because of the chemical nature of PE, this polymer has low stiffness and can be burned easily [14-17].

In this study, the influence of electron-beam irradiation on mechanical and thermo-mechanical properties of HDPE and HDPE/Brazil nut shell fiber composite was investigated.

2. EXPERIMENT / METHODS

2.1. Materials

The materials used in this study were HDPE resin (HDPE JV060U – commercial grade by Brasken S/A), with MFI = 6,41 g/10 min at 190°C/2,16 Kg with specific density = 0,957 g/cm³ and Brazil nut shell fiber residues provided by Amazon Brazil Nuts Ltda.

2.2. Preparation of HDPE/Brazil nut shell fiber composites

In order to eliminate impurities, the fiber was 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 particle sizes equals or smaller than 250 µm by using ball mills and it was dried again at 80 ± 2 °C for 24 h to reduce the moisture content to less than 2%. The HDPE resin reinforced with 5 % and 10 % Brazil nut shell fiber was obtained by mixing 5 parts of dry fiber and 95 parts of HDPE resin (in weight), and 10 parts of dry fiber and 90 parts of HDPE resin (in weight) respectively, using a twin-screw extruder machine “AX 16LD40” made by AX Plásticos Máquinas Técnicas Ltda. The extrudates coming out of the extruder were cooled down by using cold water for a better dimensional stability, pelletized by a pelletizer and fed into injection molding machine to obtain specimens test samples of HDPE/Brazil nut shell fiber composites (95:5 wt % and 90:10 wt %).

2.3. Electron-beam irradiation

HDPE resin and its composites were irradiated at radiation dose of 150 and 250 kGy using an 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. The irradiated and non-irradiated samples were submitted to mechanical and thermo-mechanical tests and the correlation between their properties and the radiation dose applied was discussed.

2.4. Mechanical and thermo-mechanial tests results

The mechanical and thermo-mechanical tests were carried out eight days after irradiation, in order to consider post irradiation effects. Tensile tests (ASTM D 638) and heat distortion temperature (HDT) (ASTM D 648) were performed in this work. Each value obtained represented the average of five samples [18, 19].

2.5. Sol- Gel analysis

The sol-gel analyses of the materials were performed on four weighted samples with 300 ± 10 mg of the irradiated and non-irradiated materials. The gel content of the cross-linked samples was estimated by measuring its insoluble part in dried sample after immersion in solvent (xylol) for 12 hours at boiling point solvent (192°C). The gel fraction was calculated as follows:

$$Gel\ fraction\ (\%) = \frac{W_d}{W_i}\,.100\% \qquad (1)$$

Where:
Wi = initial weight of the dried sample
Wd = weight of the dried insoluble part of sample after extraction with xylol

2.6. Scanning Eletron Microscopy (SEM)

The scanning electron microscopy (SEM) analyses for cryo-fractured under liquid nitrogen samples of the HDPE and HDPE/Brazil nut shell fiber composite were carried out using a LX 30 (Philips). The fractured surface of samples was coated with a fine layer of gold and observed by scanning electron microscopy.

3. RESULTS AND DISCUSSION

3.1. Mechanical and Thermo-mechanical tests results

In figures 1-4 are presented the mechanicaland termo-mechanical tests results for irradiated and non-irradiated HDPE and HDPE/Brazil nut shell fiber composite (Composite). The results presented in these figures represent the average values calculated from the data obtained by tensile tests. The standard deviations for results was less than 10 % for all tests.

The results of the tensile strength at break tests for both, irradiated and non-irradiated HDPE and *Composite* are given in Fig. 1. This figure shows an increase of around 100 % in tensile strength at break of HDPE due to Brazil nut shell fiber addition, for both percentage of the fiber. Concerning electron-beam irradiation it can be observed a gain around 20 % at 150 kGy and 50 % at the dose of 250 kGy. However, HDPE irradiated samples showed a greater gain in tensile strength at break when compared with *Composite* irradiated samples.

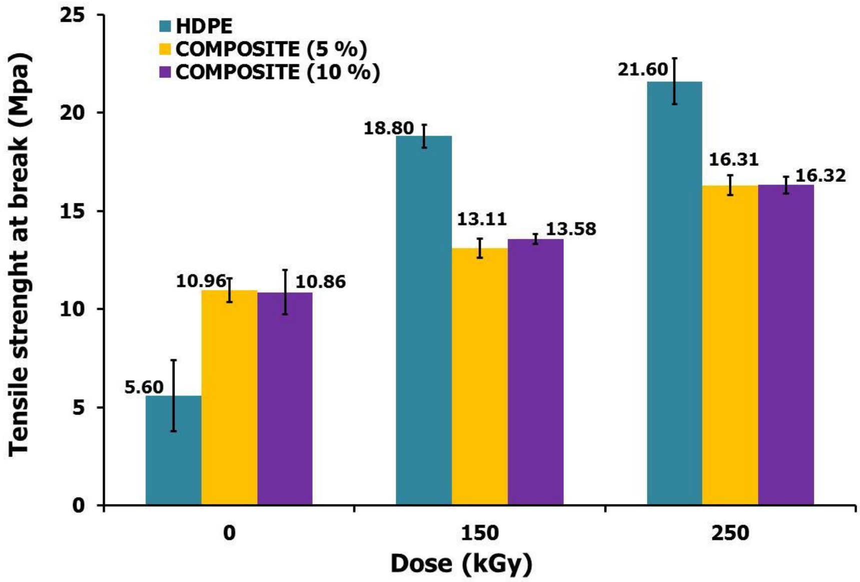

Figure 1: Tensile strength at break, as a function of the electron-beam radiation dose, for the HDPE and HDPE/Brazil nut shell fiber composite.

Figure 2 shows the results of the Young's modulus for both, HDPE and its composites. The *Composite* with 5 % of fiber presented an increase of around 30 % and the *Composite* with 10 % of fiber showed a gain around 80 % in Young's modulus when compared with those of neat HDPE. It can also be observed in this figure that there were significant increases in Young's modulus of the HDPE/Brazil nut shell fiber due the irradiation. The best results were observed for *Composite* with 10 % of fiber addition, at radiation dose of 250 kGy, where the gain was around 65 %.

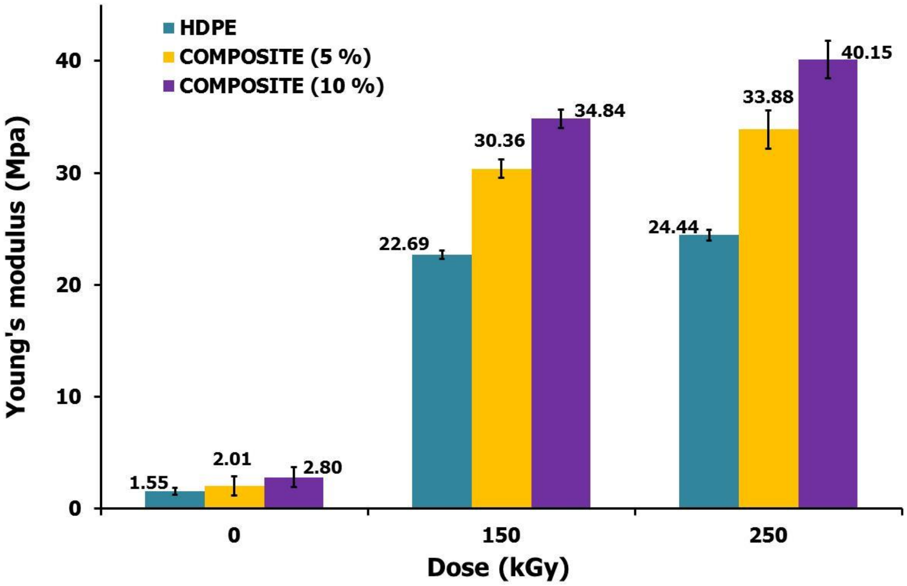

Figure 2: Young's modulus, as a function of the electron-beam radiation dose, for the HDPE and HDPE/Brazil nut shell fiber composite.

The results of the percentage elongation at break for both, irradiated and non irradiated HDPE and HDPE/Brazil nut shell fiber composite are given in Fig.3. As it can be observed, the *Composite* elongation at break was ca. 95 % and 170 % higher than neat HDPE, respectively for 5 and 10 % of fiber addition. It can also be observed that the electron-beam irradiation causes a decrease in *Composites* elongation at break by 80 % when compared with non-irradiated samples.

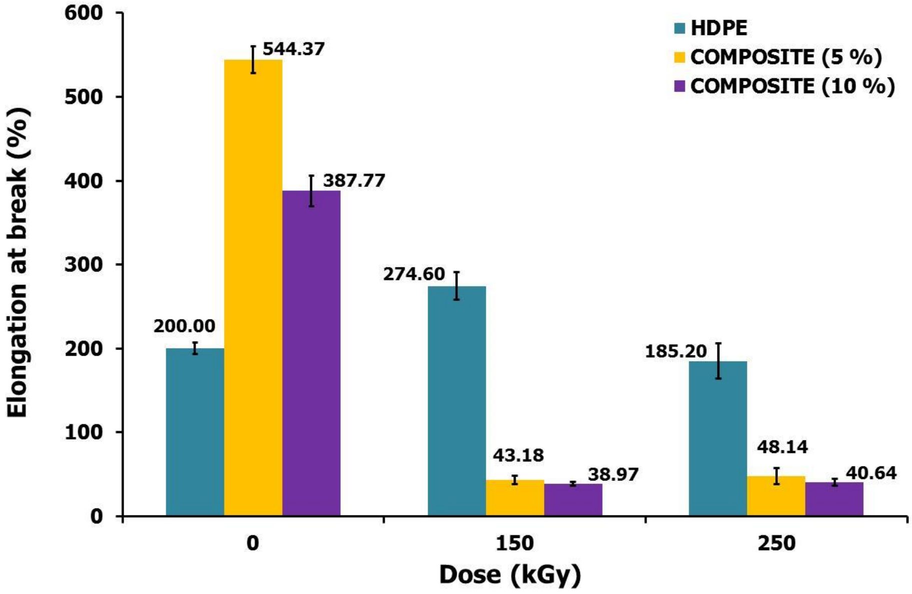

Figure 3: Elongation at break percentage, as a function of the electron-beam radiation dose, for the HDPE and HDPE/Brazil nut shell fiber composite.

The results of heat distortion temperature (HDT) for irradiated and non irradiated HDPE and HDPE/Brazil nut shell fiber composite are given in Fig.4. As it can be observed, the *Composite* HDT with 5 % and 10 % of fiber addition was, respectively, ca. 7 and 12 % higher than those of neat HDPE. It can also be observed that the electron-beam irradiation causes an increase in HDT of *Composite* by 16 % when compared with those of non-irradiated samples and ca. 15 % comparing with neat HDPE samples irradiated with the same radiation dose.

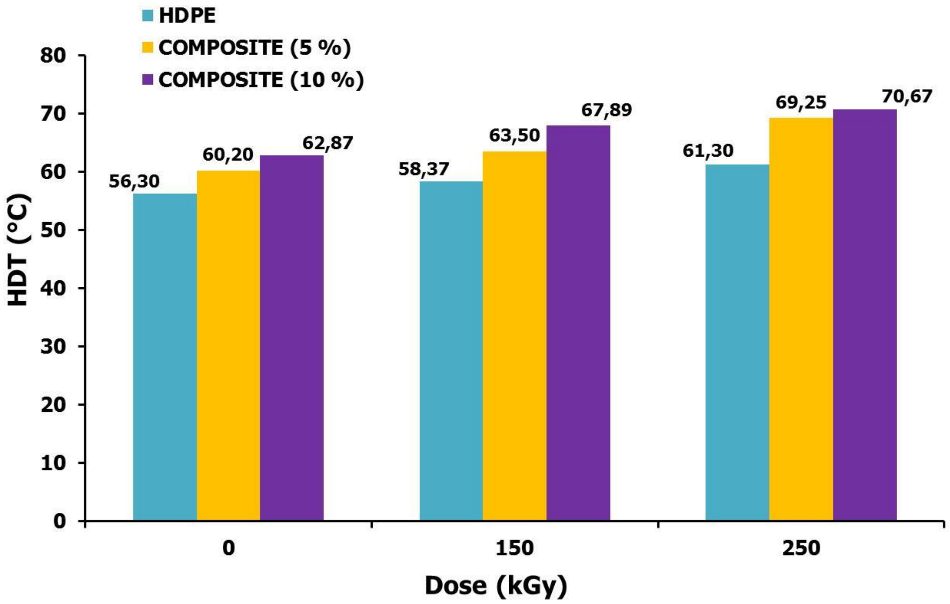

Figure 4: Heat Distortion Temperature, as a function of the electron-beam radiation dose, for the HDPE and HDPE/Brazil nut shell fiber composite.

3.2. Sol - Gel analysis

Figure 5 shows the results of the sol-gel analysis. These results represent the average values calculated from the data obtained by analysis. The standard deviation for results of the gel content was less than 10% for all tests. As it can be seen, non-irradiated *Composite* presented gel content of around 3, 5 % to 5 % of fiber and gel content of 6 % to 10 % of fiber, due to fiber particles that were added to resin HDPE. After electron-beam irradiation, the HDPE at 150 and 250 kGy presented gel content of around 77 % and 85 % respectively. The gel content in *Composites* is slowly greater than those in HDPE at the same radiation dose. The extent of gel formation in the irradiated materials is strongly dependent on the radiation dose applied. The higher gel content corresponds to a higher portion of the structural network formation in the amorphous region of the polymer that makes it insoluble in solvents. These results strongly suggest that electron-beam irradiation leads to significantly higher HDPE molecular chain cross-linking leading to the improvement of the mechanical and thermo-mechanical properties of the HDPE resin and HDPE/Brazil nut shell fiber composite. As seen in this figure, there was a small reduction in gel content due to Brazil nut shell fiber incorporation.

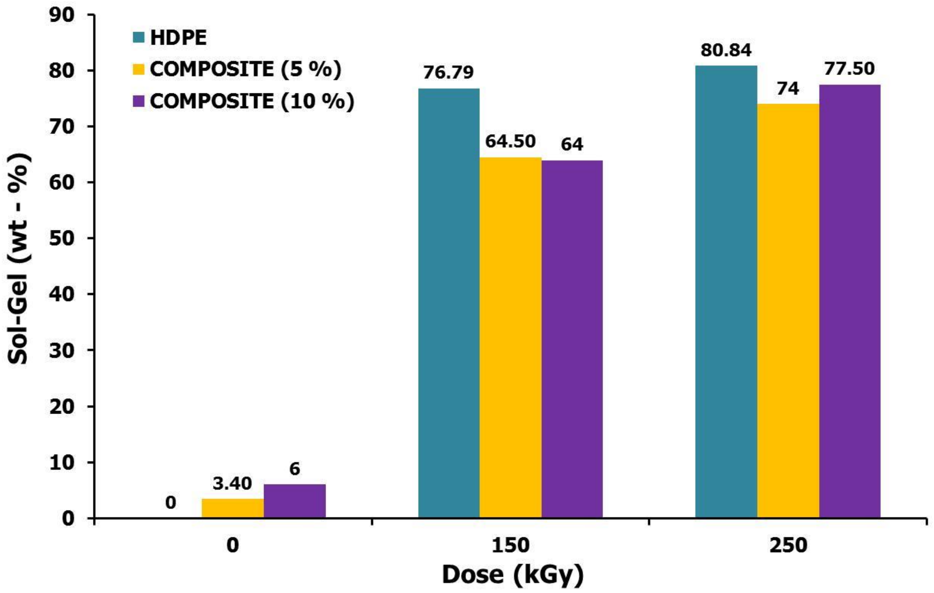

Figure 5: Sol-Gel process as a function of electron-beam radiation dose for the HDPE and HDPE/Brazil nut shell fiber composite.

3.3. Scannin Electron Microscopy (SEM)

Figure 6 shows SEM surface micrographs (magnification 100 X) for HDPE and HDPE/Brazil nut shell fiber composite, non-irradiated and irradiated samples. As it can be seen, non-irradiated HDPE/Brazil nut shell fiber composite revealed a rough, dense and compact cryofractured surface which can indicate a poor interfacial adhesion between Brazil nut shell fiber and matrix. In contrast, the irradiated HDPE/Brazil nut shell fiber composite revealed a cryofractured surface without the presence of cavities. It can indicate that, as a consequence of the electron-beam irradiation, this composite presented a better fiber-matrix interfacial adhesion.

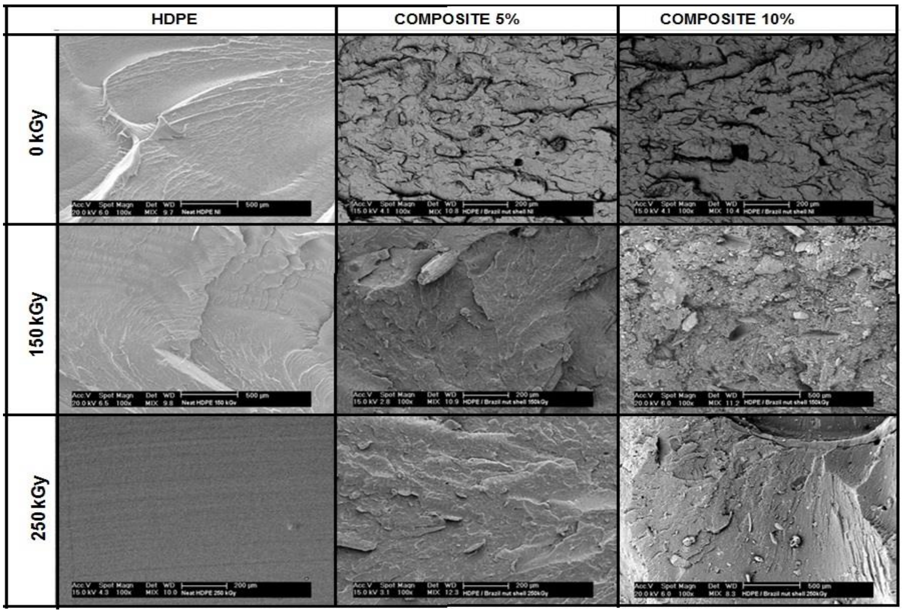

Figure 6: SEM micrographs (100 X) **as a function of electron-beam radiation dose for** surfaces of **the HDPE and HDPE/Brazil nut shell fiber composites.**

4. CONCLUSIONS

The objective of the present study was to investigate the changes in mechanical and thermo-mechanical properties of HDPE due to Brazil nut shell addition and electron-beam radiation treatment. The results showed that the fiber addition contributed to a significant gain in tensile properties, such as tensile strength at break and Young's modulus; as well as at heat distortion temperature (HDT), when compared with mechanical and termo-mechanical properties of neat HDPE. It can also be observed a significant gain in Young's modulus due to radiation treatment, especially at radiation dose of 250 kGy. These results suggest that the small size of the fiber particles used resulted in an increase of the surface area of fiber, increasing the interfacial area available for close fiber/HDPE contact, thus increasing the mechanical strength and modulus and, consequently, decreasing the elongation at break of the neat HDPE. The improvement of these mechanical and thermo-mechanical properties and the large gel content obtained after electron-beam radiation treatment is evidence that cross-linking was introduced between HDPE polymer molecules leading to the formation of a three-dimensional network, and, consequently improving the properties of the HDPE and HDPE/Brazil nut shell fiber composite.

ACKNOWLEDGEMENTS

The authors wish to thank Braskem S.A., Fatec-ZL and Grupo NZ to provide the support for this work.

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