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CHARACTERIZATION OF HDPE/BRAZIL NUT SHELL FIBER COMPOSITE TREATED BY ELECTRON-BEAM RADIATION

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ABSTRACT

Nowadays, many studies have been carried out in order to improve the HDPE properties. One of them is the incorporation of some vegetal fibers. In this work Brazil nut shell fibers were incorporated into the HDPE matrix using a twin screw extruder machine. After extrusion processing, the HDPE/Brazil nut shell fibers (60:40 w/w) composite (***Composite***) was pelletized and fed into injection molding machine and specimens test samples were obtained. Part of the specimens test samples were irradiated up to 250 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 thermo-mechanical tests, melt flow index (MFI) tests and sol-gel analysis and the correlation between their properties was discussed. The results showed significant changes in HDPE thermo-mechanical properties due to Brazil nut shell fibers addition and electron-beam irradiation. Significant increases of around 200 % in tensile strength at break, 27 % in flexural strength and 130 % in flexural modules of the HDPE were observed because Brazil nut shell fibers alone. However, the elongation at break, Izod impact and the MFI presented a large reduction. Concerning electron-beam irradiation, the thermo-mechanical properties for both, HDPE and ***Composite***, presented significant increase as a function of radiation dose applied, except in relation to elongation at break properties. The sol-gel analysis results suggested a gain in the degree of radiation cross-linking for both, HDPE and ***Composite*** irradiated samples. The SEM micrographs showed the better interfacial adhesion between fiber and HDPE after irradiation and under the MFI test conditions the both, HDPE and ***Composite*** samples irradiated could not be determined because irradiated samples did not show any flow.

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

1. INTRODUCTION

The use of vegetal fiber in thermoplastic polymer composites is continuously increasing and has drawn industry´s attention, especially for high volume and low cost applications [1-3].

Nowadays, vegetal fibers are replacing the synthetic fibers in thermoplastic composites because these are not biodegradable. Other important advantages are that vegetal fibers are quite cheap, available, and recyclable and show good mechanical properties, low energy demand and an environmental appeal compared to synthetic ones.

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 [4, 5].

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 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 [6-9].

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].

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].

Melt flow index (MFI) is a measure of melt viscosity. The viscosity of a melt is dependent on its speed of flow as well as temperature and basic molecular characteristics.

Knowing the MFI of a polymer is vital to anticipating and controlling its processing. Generally, higher MFI polymers are used in injection molding, and lower MFI polymers are used with blow molding or extrusion process. [17, 18].

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. 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 = 0.951 g/cm³ and Brazil nut shell fiber residues disposed by Brazil nuts industries.

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 24h. 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 r educe 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 and 60 parts of HDPE resin (in weight) using a twin-screw extruder machine "ZSK 18 MEGAlab extruder" made by Coperion Werner & Pfleiderer GmbH & Co. KG. The compounded materials passed through the different zones of the extruder and were finally extruded. The extrudates coming out of the extruder were cooled down by using cold water for a better dimensional stability and wound up manually, pelletized by a pelletizer and fed into injection molding machine to obtain specimens test samples of HDPE/Brazil nut shell fiber composites (60:40 wt %) Composite.

2.3. Electron-beam irradiation

HDPE resin and **Composite** 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 thermo-mechanical tests and the correlation between their properties and radiation dose applied was discussed. Irradiation doses were measured using cellulose triacetate film dosimeters ''CTA-FTR-125'' from Fuji Photo Film Co. Ltd.

2.4. Thermo – mechanical tests

The thermo-mechanical tests were carried out eight days after irradiation, in order to consider post irradiation effects. The tensile tests were performed according to ASTM D 638 [19] and the flexural tests were based on ASTM D 790 [20]; the Vicat softening temperature tests were done according to ASTM D 1525 [21] and those of heat distortion temperature (HDT) were based on ASTM D 648 [22].

2.5. Melt flow index (MFI) measurements

The melt flow index (MFI) for each composition was determined with a Microtest extruder plastometer in the conditions specified for HDPE (ASTM 1238-04). [23]

2.5. Sol- Gel analysis

The sol-gel analyses of the materials were performed on four weighed 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:

$$\text{Gel fraction } \% = WdWi\ .100\% \qquad (1)$$

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

2.6. Statistical analysis

The difference between the results for irradiated and non-irradiated samples were then statistically assessed 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

3.1. Thermo - mechanical tests

The thermo-mechanical tests results presented at following figures represent the average values calculated from the data obtained by tests for both, irradiated and non-irradiated HDPE and ***Composite***, except for the Figs.5 and 6. The standard deviation 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 HDPE/Brazil nut shell fiber composite (***Composite***) are given in Fig. 1.

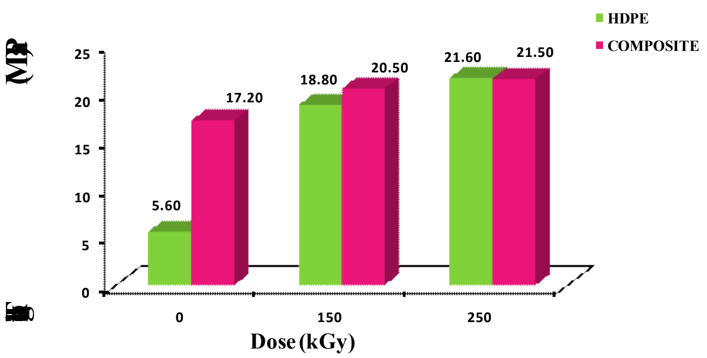

Figure 1. Tensile strength at break, as a function of the electron-beam radiation dose, for the HDPE and HDPE/Brazil nut shell fiber composite.

This figure shows an increase of around 210% in tensile strength at break of HDPE due to Brazil nut shell fiber addition alone ($p < 0.05$). Concerning electron-beam irradiation there were significant increases in tensile strength at break for both, HDPE and ***Composite***; however, 150 kGy the ***Composite*** presented a better performance than HDPE, but above this dose, HDPE and ***Composite*** tends to present similar values.

Figure 2 shows the results of the percentage elongation at break for both, irradiated and non irradiated HDPE and HDPE/Brazil nut shell fiber composite. As it can be observed, there were significant decreases ($p < 0.05$) in elongation at break of the HDPE due the incorporation of Brazil nut shell fiber.

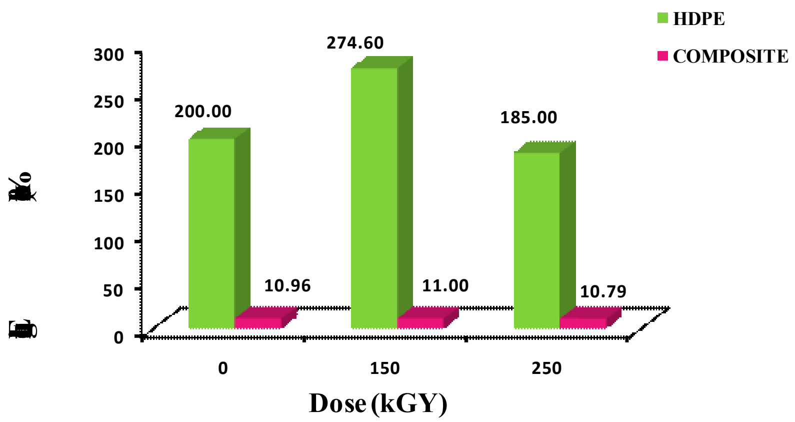

Figure 2. Elongation at break (%), as a function of the electron-beam radiation dose, for the HDPE and HDPE/Brazil nut shell fiber Composite.

However, both irradiated HDPE and ***Composite*** reached its highest values at 150 kGy, showing that higher radiation doses leads to reduction in elongation at break.

The flexural strength tests results for both irradiated and non-irradiated HDPE and HDPE/Brazil nut shell fiber composite are given in Fig.3.

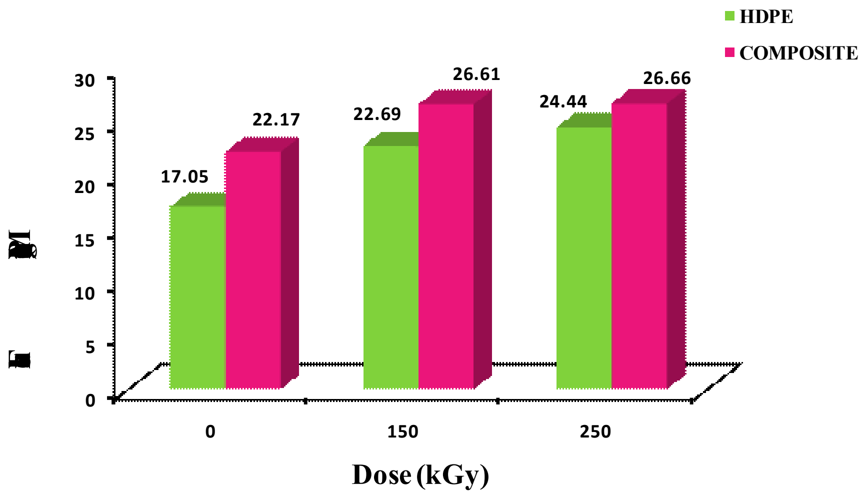

Figure 3. Flexural strength, as a function of the electron-beam radiation dose for HDPE and HDPE/Brazil nut shell fiber composite.

As it can be observed, the ***Composite*** flexural strength was ca. 30% higher than neat HDPE ($p < 0.05$). This increase in Composite flexural strength may be a consequence of the use of smaller particles of Brazil nut shell fiber. The incorporation of this smaller particles implies in increase of its surface area, increasing the interfacial area available for close Brazil nut shell/HDPE contact and, consequently, increasing in flexural strength. It can also be observed that the electron-beam irradiation causes an increase in HDPE flexural strength by 18-38 % and 8-18 % for ***Composite*** when compared with non-irradiated samples.

The flexural modulus average data for HDPE and HDPE/Brazil nut shell fiber composite are given in Fig.4.

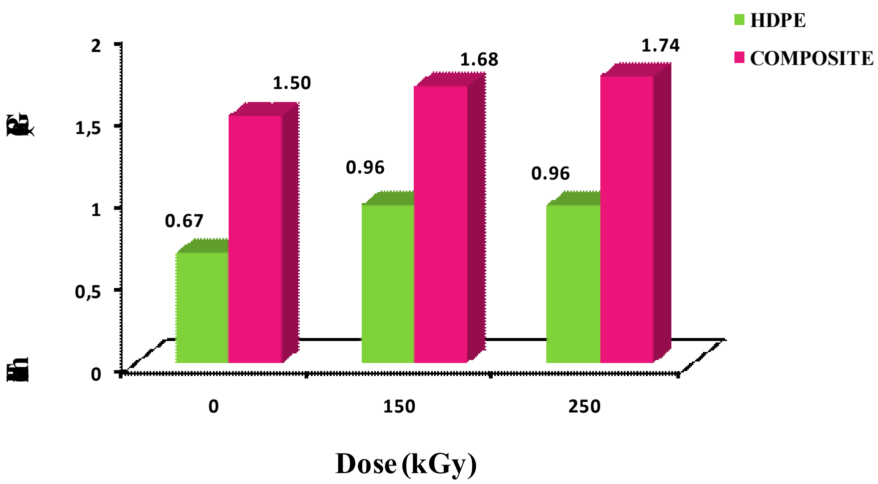

Figure 4. Flexural modulus, as a function of the electron-beam radiation dose, for HDPE and HDPE/Brazil nut shell fiber composite.

A significant gain ($p < 0.05$), concerning flexural modulus of HDPE, can also be observed in this figure, due the incorporation of Brazil nut shell fiber. Significantly, for the non-irradiated samples, the flexural modulus of ***Composite*** samples was around 118% higher than HDPE samples ($p < 0.05$). Recent studies on the mechanical behavior of reinforcement fibers in polymers have reported that fibers insertion can contribute to the modulus increase, because the Young's modulus of the fibers is higher than the thermoplastic modulus. Considering that the tensile and flexural modulus are related to the material rigidity, and, the Young's modulus was higher for the fibers than for thermoplastics, if the fibers are distributed and aggregated to the matrix, a higher flexural modulus for the material can be resulted [24-28.]. On the other hand, the flexural modulus for the irradiated ***Composite*** showed a gain by 90 % and ca. 80 % when compared with irradiated HDPE, for radiation dose of 150 and 250 kGy, respectively.

In Figure 5, heat distortion temperature (HDT) tests results are shown for both irradiated and non-irradiated HDPE and HDPE/Brazil nut shell fiber composite. This figure shows a gain around 15 % ($p < 0.05$) for the HDPE, due to the incorporation of Brazil nut shell fibers. In relation to electron-beam processing, both HDPE and ***Composite*** presented significant increases as a function of radiation dose applied; nevertheless, the ***Composite*** presents better performance than HDPE.

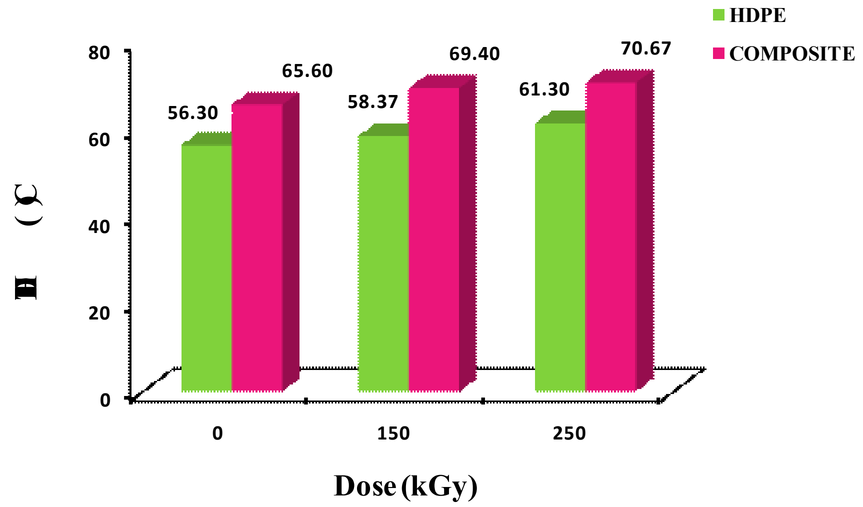

Figure 5. HDT as a function of electron-beam radiation dose for the HDPE and HDPE/Brazil nut shell fiber composite.

In Figure 6, Vicat tests results for both, irradiated and non-irradiated HDPE and HDPE/Brazil nut shell fiber composite are showed. This figure shows a little tendency for reduction in Vicat softening temperature of HDPE due to Brazil nut shell fibers incorporation. On the other hand, both irradiated HDPE and ***Composite*** presented a higher Vicat softening temperature than non-irradiated samples.

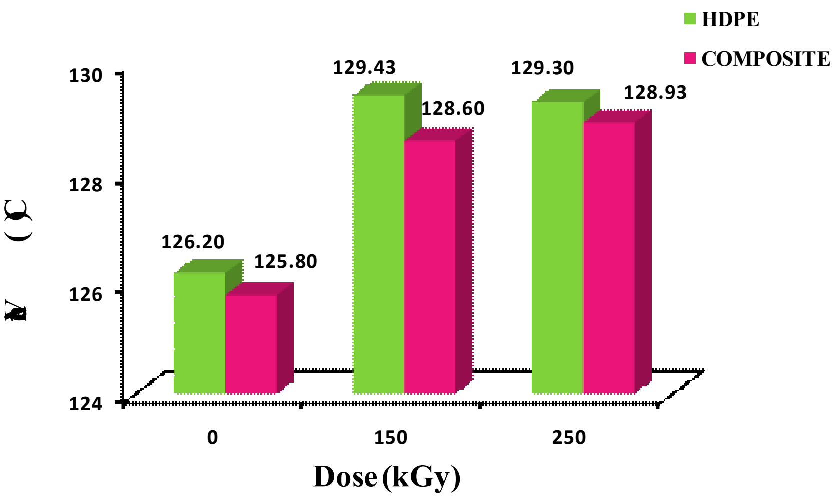

Figure 6. Vicat as a function of electron-beam radiation dose for the HDPE and HDPE/Brazil nut shell fiber composite.

Figure 7 presents the impact strength tests results for both irradiated and non-irradiated HDPE and HDPE/Brazil nut shell fiber composite. This figure shows a significant reduction, of around 93.86 % in original HDPE impact strength due to Brazil nut shell fiber addition ($p < 0.05$). After electron-beam irradiation can be observed a significant gain in impact strength for the HDPE of around 97.13 % at 150 kGy and 97.45 % at 250 kGy. Concerning HDPE/Brazil nut shell fiber composite the electron-beam radiation treatment caused a large reduction in their impact strength properties.

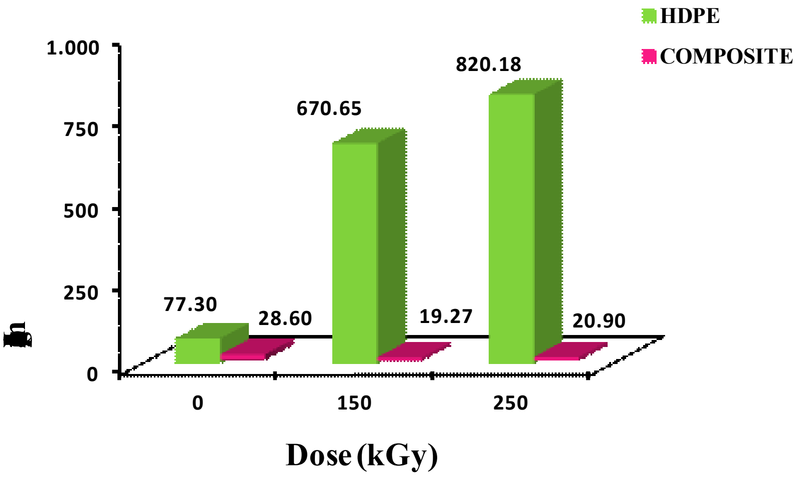

Figure 7. Impact strength as a function of electron-beam radiation dose for the HDPE and HDPE/Brazil nut shell fiber composite.

3.2. Sol – Gel analysis

Figure 8 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 29 % probably the fiber particles added that should be insoluble in the solvent. After electron-beam irradiation, the HDPE at 150 and 250 kGy presented gel content of around 84 % and 88 % respectively, while the irradiated ***Composite*** presented gel content of about 95 %. The gel content in ***Composites*** is slightly greater than 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 thermo-mechanical properties of the HDPE resin and HDPE/Brazil nut shell fiber composite. As seen in this figure, there was a small increase in gel content due to Brazil nut shell fiber incorporation.

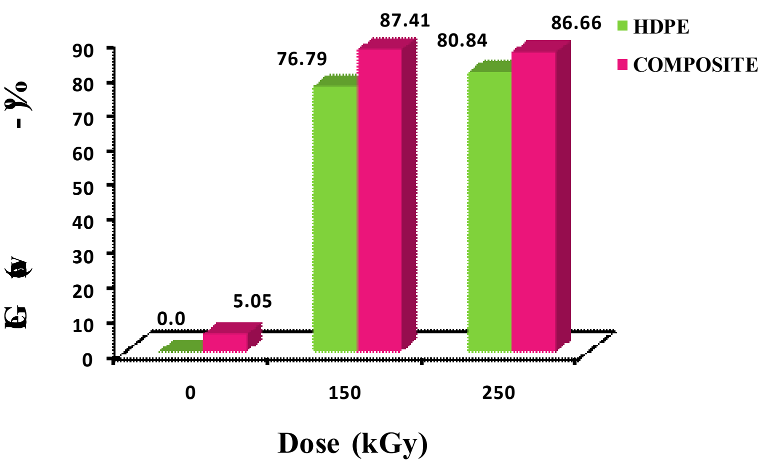

Figure 8. Sol-Gel process as a function of electron-beam radiation dose for the HDPE and HDPE/Brazil nut shell fiber composite.

3.3. Melt flow index (MFI) measurements

The results for the MFI measurements showed that the Brazil nut shell fiber addition promoted a significant loss of around 45 % in melt flow index of HDPE, which decreased from 6.41 g/10 min at 190 °C/2.16 Kg to 3.52 g/10 at 190 °C/2.16 Kg. These results confirm that fiber addition significantly ***affects*** the dynamic viscoelastic melt of polymer, since they could reduce molecular mobility and, consequently, the flow. Under the MFI test conditions, both irradiated HDPE and Composite did not show any flow, and, consequently the MFI could not be determined.

4. CONCLUSION

The objective of the present study was to investigate the changes in thermo - mechanical properties of HDPE with due to Brazil nut shell incorporation and electron-beam radiation treatment. The results showed that the fiber addition contributed to a significant gain ($p < 0.05$) in tensile strength at break, flexural strength, flexural modulus and HDT which may be mainly attributed to the good compatibility between hydrophilic Brazil nut shell fiber and the hydrophobic HDPE polymer phases due to use of smaller size fiber particles. The small size of the particles material implies an increase of its surface area, increasing the interfacial area available for close fiber/HDPE contact, thus increasing the mechanical strength and modulus and, consequently, decreasing the elongation at break and impact strength of the neat HDPE. The improvement of these 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, consequently improving the mechanical properties of the HDPE and HDPE/Brazil nut shell fiber composite.

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