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STUDIES ON THE EFFECTS OF ELECTRON-BEAM RADIATION DOSE ON PROPERTIES OF HDPE/PIASSAVA/CLAY/PP NANOCOMPOSITE

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ABSTRACT

In this work the effects of electron-beam radiation dose on properties of HDPE/Piassava/Clay/PP nanocomposite, prepared by extrusion and injection molding processes are described. The nanocomposite samples were irradiated at 100 and 250 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. The sol-gel analyses were used to determine the degree of cross-linking and the melt flow index (MFI) tests were also carried out. The results showed that the incorporation of Piassava (Attalea funifera Mart) fiber and nanoclay followed by electron-beam irradiation represented significant changes ($p < 0.05$) in their thermo-mechanical properties studied. Under the MFI test conditions, the nanocomposite samples irradiated did not show any flow and, therefore, the MFI could not be determined. The sol-gel analyses showed a reduction in the degree of cross-linking of irradiated nanocomposite, when compared with irradiated neat HDPE at the same radiation dose. As it was expected, these results showed that PP`s degradation effect prevailed over the positive HDPE cross-linking effects, and consequently, the large amount of polypropylene (PP) resin, ca. 50 %, present in HDPE/PP blend, led to obtaining of irradiated nanocomposite with a smaller cross-linking density than those of neat HDPE.

1. INTRODUCTION

The addition of vegetal fibers in polymers has been the focus of research for many years due to their potential to improve the properties of these polymeric materials, leading to a final product with better performance and the use of large amount of residues generated by the fiber industry. The use of thermoplastic matrices such as polypropylene (PP) and polyethylene (PE) shows the most potential benefits when combined with vegetal fibers in making composites of industrial value [1-4].

The techniques for polymeric composites such as extrusion, compression, rotational, and injection molding, are applied into polymers reinforced either with fiber particles or short fibers. Injection molding is an important plastic processing method characterized with rapid production rates. The composite material is heated and pumped into a permanent mold, where it takes shape [5, 6].

Recently, polymer nanocomposite technology, which offers enhanced performance at very low loadings when compared with conventional filler composites, has been on focus. Polymer/clay nanocomposites, which represent a rational alternative to conventional filled polymers, exhibit thermal stability, better mechanical, solvent resistance, flame retardancy, gas barrier and other physicochemical properties in comparison with conventional composites. Another relevant factor to nanocomposites is the synergetic effect between clay and coupling agent to disperse clay particles and optimize nanocomposite properties [7].

The technological application of clay minerals promotes their improvement by decreasing particles size, which results in a much larger surface area per unit volume. Since many important chemical and physical interactions are governed by surfaces, a large surface area can lead to the obtaining of materials with substantially improved properties.

One important consequence of the charged nature of clays is that they are generally hydrophilic species and are, therefore, naturally incompatible with a wide range of polymer types. In order to facilitate clay interaction with a polymer, it is often necessary to make the hydrophilic clay surface become organophilic. Although the modified clay is miscible for polar polymers such as nylon, polystyrene (PS), the organically modified clay does not disperse well in non-polar polymers such as polypropylene (PP) and polyethylene (PE), since such non-polar polymers are still too hydrophobic. Thus, when using polymers such as PE and PP, a compatibilizing agent is required to promote interactions with the clay. Maleic anhydride (MA) grafting turned out to be the most efficient way to make PE and PP sufficiently compatible with organoclays [8, 9].

High density polyethylene (HDPE), aim of this study, is an engineering thermoplastic used for several industrial applications due to low cost, mechanical properties and processing facility. Another material used in this work was polypropylene (PP), which is a commercial plastic with good overall mechanical performance, excellent electrical and insulating properties, chemical inertness, good moisture resistance and low cost, but it shows relatively poor chemical and heat resistance [10, 11].

A polymeric blend is a mixing of polymers, usually of the same chemical family. The purpose of a blend is to obtain a material with combined differentiated physical, chemical and physicochemical properties in order to retain the advantages of each polymer. Although polyethylene and polypropylene blends are commonly immiscible and incompatible, synergistic effects on the properties of these blends have been reported in the literature. Polyethylene and polypropylene blends are commercially very important because of their high impact strength and low temperature toughness. Addition of polyethylene into polypropylene increases the impact strength of polypropylene and addition of polypropylene into polyethylene improves its environmental stress crack resistance. Hence, these blends are technologically very important. The physical, optical and mechanical properties of polymer blends are affected to various degrees by phase morphology. Mechanical properties such as tensile strength, tensile elongation and impact strength for a particular polymer blend vary with the morphology and to a lesser extent with the crystallinity [12, 13].

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. Piassava fibers have been described as harder than other lignocelluloses fibers and have higher lignin content (around 48%) than any of the other common lignocellulosic fibers. Studies from Brazilian researchers have shown that the residues from

piassava can be an important alternative to the reinforcement of thermoplastics and the production of composites with better thermal properties than original polymers [14, 15].

Electron beam radiation has been efficiently applied for controllable modification in polymers and their composites. In general, irradiation of polymers causes two simultaneous and concurrent processes: cross-linking and degradation. Cross-linking increases intermolecular bonds in the amorphous region and makes it resistant to large-strain plastic deformation, resulting in better material properties, such as better impact resistance and thermal-mechanical properties in polymers [16-18]

The main objective of this work was to study the effects of electron-beam radiation dose on properties of HDPE/Piassava/Clay/PP nanocomposite, prepared by extrusion and injection molding processes.

2. EXPERIMENTAL /METHODS

2.1. Materials

The materials used in this study were HDPE resin (HDPE JV060U – commercial grade by Braskem S/A), with MFI = 6.4 g/10 min at 190 ^{0}C/2.16 Kg, specific density = 0. 957 g/cm³, maleic anhydride grafted HDPE (PEGMA) as compatibilizer (1 wt %), PP resin (HP500N), a medium-high fluidity polypropylene homo-polymer manufactured by Arak Petrochemical Corporation, with MFI = 12.27g/10 min at 190 °C/2.16 Kg, specific density = 0.893 g/cm³, and Piassava fiber from agro-industrial residues and bentonite chocolate clay (Pegmatech Especialidades Tecnologicas Ltda.) as a powder with toluene swelling of 8 mL/g.

2.1.1. Piassava fibers preparation

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 %.

2.1.2. Clay preparation

The bentonite chocolate clay was incorporated as a nanoparticle in the composite.The clay has to pass on some processes such as a dispersion in water, stirring and heating for a determinate time, and just then be filtrated and dried for the disaggregation of one particle on another, and finally be characterized as a nanoclay.

2.1.3. Nanocomposites preparation

Preparation of nanocomposites was carried out in two steps. Firstly, the HDPE with 1 % PEgMA/Piassava 30 %/nanoclay 3 %, based on the percentage weight ratio (wt %), was obtained with an extrusion machine twin screw "extruder ZSK 18 Megalab" made by Coperion Werner & Pfleiderer GmbH & Co. KG. The compounded materials passed through the different zones of the extruder and were finally extruded. Finally, the HDPE/Piassava/Clay (67:30:3 wt %) was pelletized by a pelletizer. In a second step, part of the pelletized HDPE/Piassava/Clay (50 %) and PP resin (50 %) were mixed together, then dried at 80 ± 2 º C for 24 h in the circulating air oven and fed into injection molding machine to obtain specimens test samples of HDPE/Piassava/Clay/PP blend (33.5:15:1.5:50 wt %).

2.2 Electron-beam Irradiation

Part of the materials obtained were irradiated up to 250 kGy using a 1.5 MeV 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 28.02 kGy/s. Irradiation doses were measured using cellulose triacetate film dosimeters ‘‘CTA-FTR-125’’ from Fuji Photo Film Co. Ltd.

2.3. Characterization

2.3.1 Statistical Analysis

The difference between the results for irradiated and non-irradiated samples were then statistically evaluated by ANOVA using BioEstat software (version 5.0, 2007, Windows 95, Manaus, AM, Brazil). Significance was defined at $p < 0.05$.

2.3.2. Thermo-mechanical tests

Impact tests [20], tensile tests [21], flexural tests [22], Vicat softening temperature [23] and heat distortion temperature (HDT) [24], were performed in this work in order to observe the thermo-mechanical behavior of the materials studied.

2.3.3. MFI measurements

MFI measurements were determined with a Microtest extruder plastometer [25] in the conditions specified for HDPE and PP.

Melt flow index (MFI) is a measure of the plastic's ability to flow and it is inversely related to melt viscosity and flow qualities. MFI has been used in industry to characterize the flow properties of polymers due to the simplicity and agility of the technique used in its determination. In general, a HDPE resin with a small MFI value has a high molecular weight and long molecular chain. The long molecular chain and high molecular weight help improve the interfacial adhesion between HDPE macromolecules by polymer chain entanglement [2].

2.3.4. 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) at its boiling point (190 ºC) for 12 hours. Gel fraction was calculated as follows:

$$\text{Gel fraction (\%)} = \frac{Wd}{Wi} \cdot 100\% \quad (1)$$

Where,
Wi = represents the initial weight of the dried sample
Wd = weight of the dried insoluble part of sample after extraction.

3. RESULTS AND DISCUSSION

3.1. Thermo-mechanical Tests

These results of the thermo-mechanical tests presented show the average values calculated from the data obtained in tests. The standard deviations for results were less than 10 % for all tests.

The results of the average values obtained in the impact strength tests of HDPE and HDPE/Piassava fiber/Clay/PP (***Nanocomposite***) are presented in Fig. 1. As it can be seen, there was a significant decrease ($p < 0.05$) of about 70 % in impact strength of non-irradiated ***Nanocomposite*** when compared with neat HDPE. These results show that the addition of Piassava fiber and nanoclay in HDPE/PP blend can lead to the obtaining of materials with substantially lower impact strength than neat HDPE. After electron-beam radiation treatment, there was a significant decrease of around 14 % in this property for irradiated ***Nanocomposite*** samples at 100 kGy and a increase of only 140 % at 250 kGy. On the other hand, a significant increase of about 310 % for HDPE at 100 kGy and **960 %** at 250 kGy, respectively, were observed ($p < 0.05$).

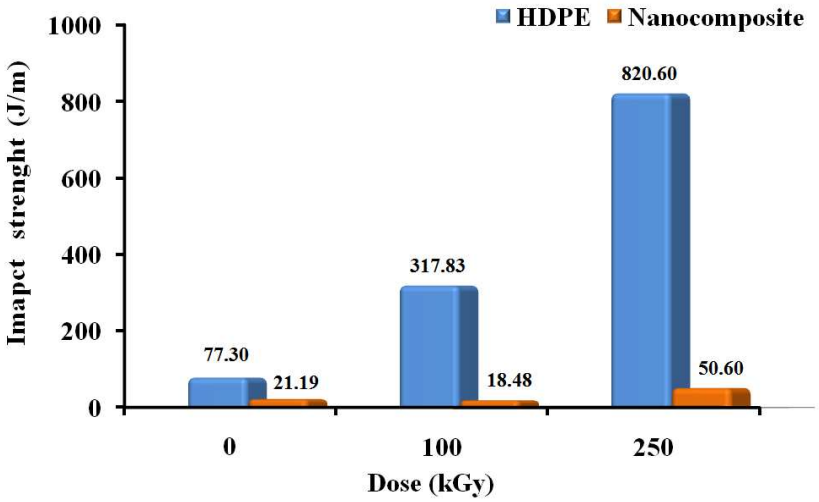

Figure 1. Impact strength for HDPE and Nanocomposite (HDPE/Piassava fiber/Clay/PP).

The results of the average values obtained in the tensile strength at break tests of HDPE and HDPE/Piassava fiber/Clay/PP (***Nanocomposite***) are presented in Fig. 2. As it can be seen, there was a significant increase ($p < 0.05$) of about 370 % for non-irradiated ***Nancomposite*** when compared with neat HDPE. These results show that the addition of Piassava fiber and nanoclay in HDPE/PP blend can lead to the obtaining of materials with higher tensile strength properties than neat HDPE. After electron-beam radiation treatment, the ***Nanocomposite*** presented a significant decrease ($p < 0.05$) up to 30 % in these properties**.** On the other hand, for the irradiated HDPE a significant increase of about 200 % at 100 kGy and 230 % at 250 kGy.was observed.

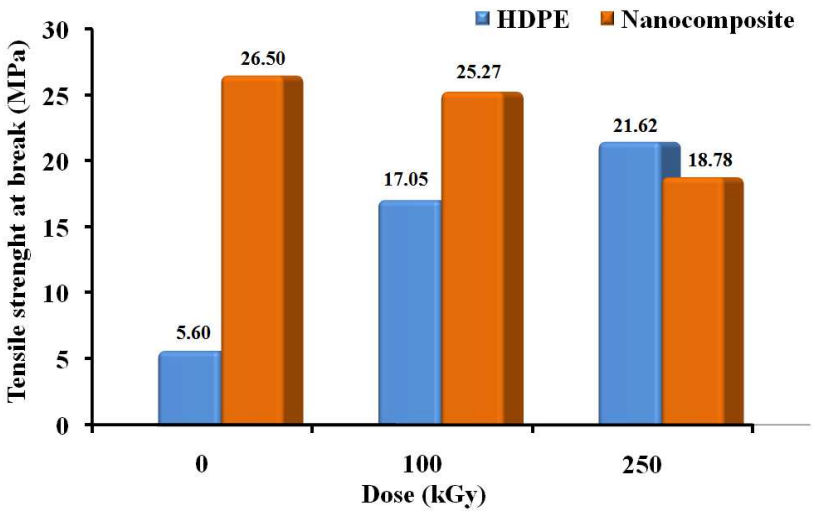

Figure 2. Tensile strength at break for HDPE and Nanocomposite (HDPE/Piassava fiber/Clay/PP).

The Fig. 3 shows the results for flexural strength tests. As it can be seen, the flexural strength of the non-irradiated ***Nanocomposites*** showed a significant increase of ca. 90 % when compared with the neat HDPE. These results show that the addition of the Piassava fiber and nanoclay also represented an important gain in this property when compared with those of neat HDPE. Concerning electron-beam radiation treatment, this figure shows a slight increase in flexural strength of ***Nanocomposite*** at 100 kGy and a significant reduction of around 25 % for the ***Nanocomposite*** at 250 kGy, while the irradiated HDPE showed a slight increase of ca**.** 18 % at 100 kGy and a significant increase of about 40 % at 250 kGy, in comparison with neat HDPE.

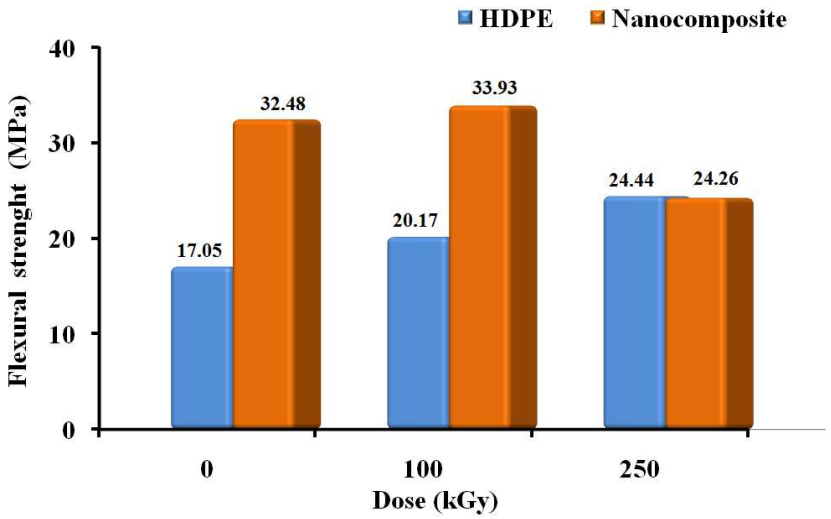

Figure 3. The flexural strength for HDPE and Nanocomposite (HDPE/Piassava/Clay/PP).

The results of the flexural modulus average data for HDPE and ***Nanocomposite*** are presented in Fig. 4. The results showed that flexural modulus of non-irradiated ***Nanocomposite*** was ca. 120 % higher than those of neat HDPE. After electron-beam irradiation, the flexural modulus of ***Nanocomposite*** presented a slight increase up to 7 %. Irradiated HDPE samples showed a significant increase in flexural modulus of around 15 % at 100 kGy and of about 40 % at 250 kGy ($p < 0.05$).

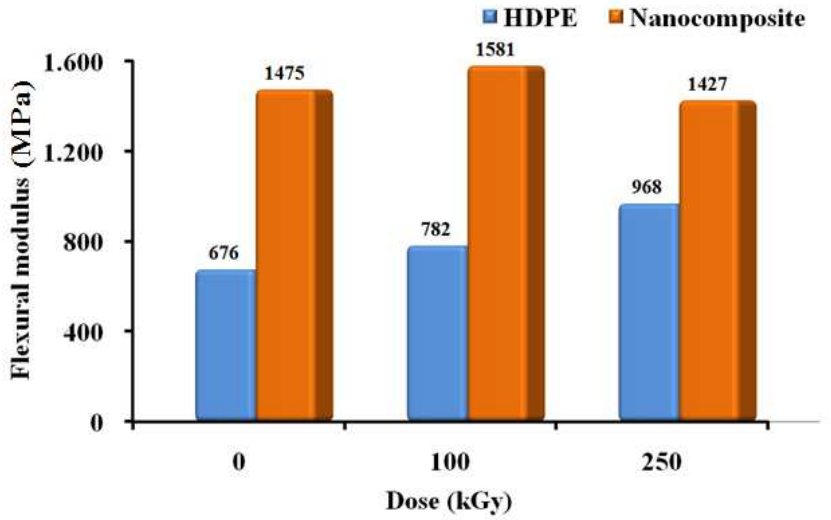

Figure 4. Flexural modulus for HDPE and Nanocomposite (HDPE/Piassava/Clay/PP).

Figure 5 shows the results for elongation at break test. As it can be seen, there was significant decrease of around 90 % in elongation at break of the HDPE due to piassava and nanoclay addition ($p < 0.05$). On the other hand, electron-beam irradiation led to a significant gain in HDPE of around 60 % for the HDPE samples irradiated with 100 kGy elongation at break in comparison with neat HDPE, whereas for irradiated ***Nanocomposite*** a large reduction in this property was observed with radiation dose applied.

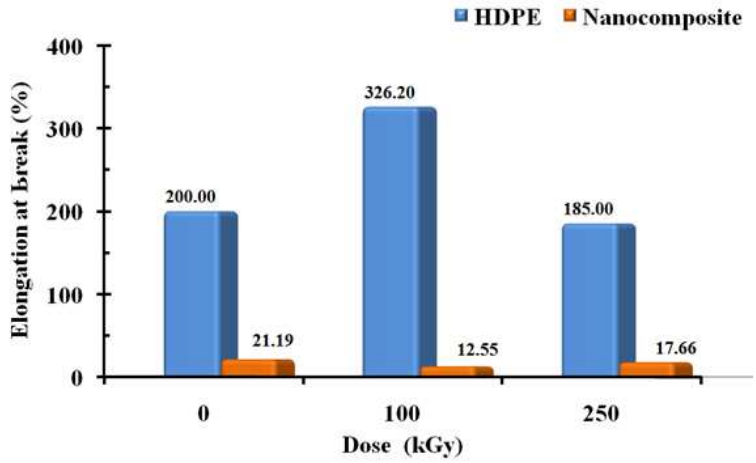

Figure 5. Present the results of the elongation at break for HDPE and Nanocomposite (HDPE/Piassava fiber/clay/PP).

Figure 6 shows the results of the HDT tests for HDPE and ***Nanocomposite***. This figure presents a gain of about 14 ***%*** for HDT of ***Nanocomposite*** when compared with those of neat HDPE. After electron-beam irradiation, After electron-beam irradiation, the HDT for ***Nanocomposite*** increased ca. 5 to 10 **%** in comparison with non-irradiated ***Nanocomposite.*** Figure 6 shows also tha tthere was not significant changes in HDT of irradiated HDPE samples at 100 kGy and an increase of 9 % at 250 kGy when compared with non-irradiated HDPE.

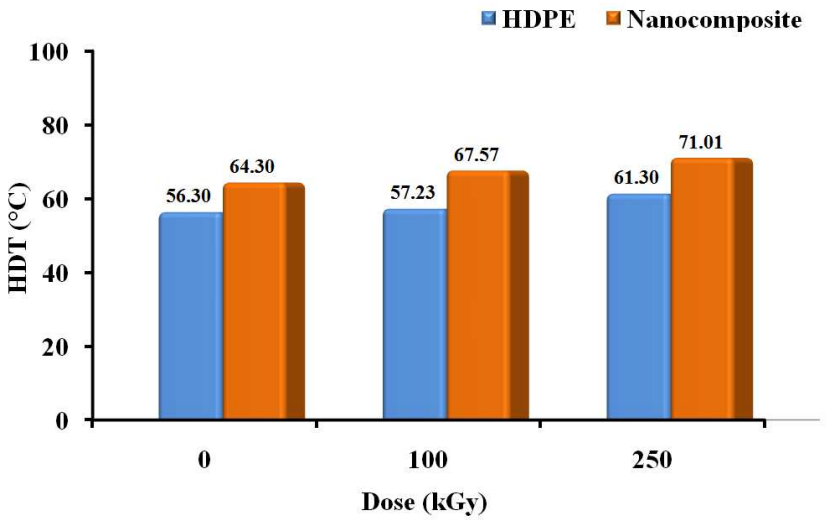

Figure 6. Present the results of HDT for HDPE and Nanocomposite (HDPE/Piassava fiber/clay/PP).

Figure 7 shows the results of Vicat for HDPE and ***Nanocomposite***. This Figure presents a gain of about 7 % for the non-irradiated ***Nanocomposite*** when compared with neat HDPE. After electron-beam irradiation, an increase tendency was observed in Vicat softening temperature of neat HDPE, whereas for the irradiated ***Nanocomposite,*** the Vicat value tended to a reduction with the increase of radiation dose applied.

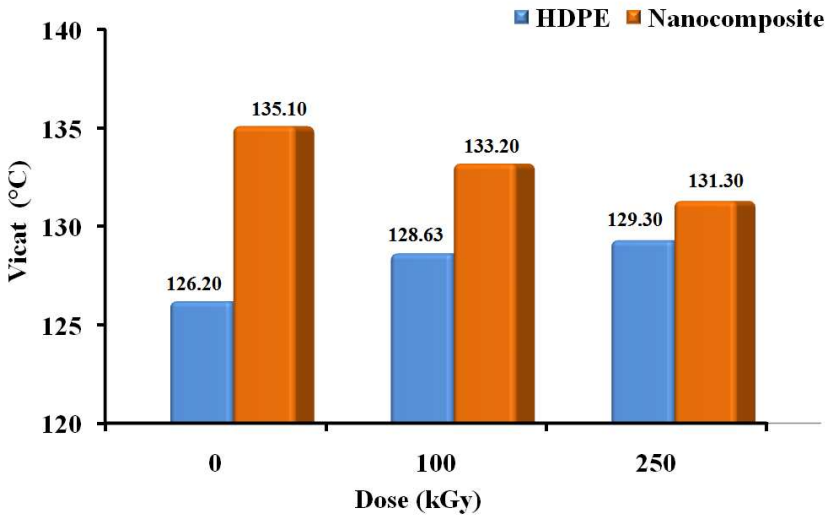

Figure 7. Present the average data results of Vicat for HDPE and the Nanocomposite (HDPE/Piassava fiber/clay/PP).

3.2. Sol Gel analysis

The results of the average values obtained in sol-gel analyses of HDPE and ***Nanocomposite*** are shown in Figure. 6. These results represent the average values calculated from the data obtained by the analysie. The standard deviation for results of the gel content was less than 10 % for all tests. As it can be seen, non-irradiated ***Nanocomposite*** presented gel content of around 7 %, probably due to the fiber particles and nanoclay added, which should be insoluble in the solvent. After electron-beam irradiation, HDPE at 100 and 250 kGy presented gel content of around 80 %, while the irradiated ***Nanocomposite*** presented gel content of about 23 % at 100 kGy and ca. 50 % at 250 kGy. The gel content in ***Nanocomposite*** was smaller than in HDPE for all radiation doses studied in this work. These results strongly suggest that electron-beam irradiation leads to a significantly higher HDPE molecular chain cross-linking leading to the improvement of the thermo-mechanical properties of HDPE resin. On the other hand, the large amount of polypropylene (PP) resin, ca. 50 %, present in HDPE/PP blend, which, preferentially, undergoes degradation by irradiation led to obtaining of irradiated ***Nanocomposite*** with a smaller cross-linking density than those of neat HDPE.

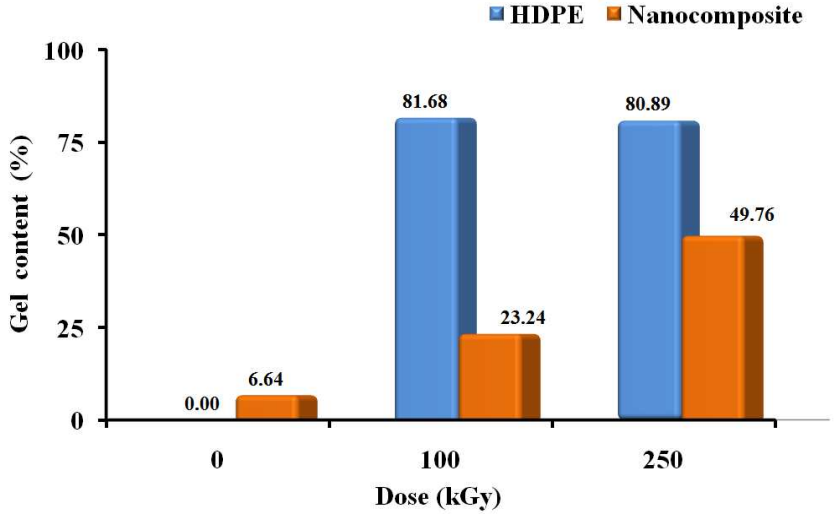

Figure 8. Present the gel content of the electron-beam radiation dose for HDPE and Nanocomposite (HDPE/Piassava fiber/Clay/PP).

3.3. MFI

The results for MFI measurements showed that the incorporation of piassava fiber and clay in HDPE/PP blend lead to the obtaining of ***Nanocomposite*** with MFI of 8.3 g/10 min at 190 °C/2.16 Kg, confirming that fiber addition affects the dynamic viscoelastic melt, since could increase molecular mobility and, consequently, the flow. Under MFI test conditions, both, irradiated

HDPE and ***Nanocomposite*** samples did not show any flow and, therefore, MFI could not be determined. Table 1 shows the results of MFI for HDPE, PP and ***Nanocomposite***

Table 1 of MFI for HDPE, PP and *Nanocomposite*

Material	MFI g/10 min
HDPE	6.41
PP	12.27
Nanocomposite	8.30

4. CONCLUSIONS

The objective of this work was to study the effects of electron-beam radiation dose on properties of HDPE/Piassava/Clay/PP nanocomposite (***Nanocomposite)***, prepared by extrusion and injection molding processes. The results showed that the addition of Piassava fiber and nanoclay in HDPE/PP blend can lead to the obtaining of materials with better thermo-mechanical behavior than neat HDPE. Concerning electron-beam radiation treatment, the results showed a tendency to reduction in thermo-mechanical properties of ***Nanocomposite*** obtained with the radiation dose applied, except for HDT that presented a important gain with increase of radiation dose. As it was expected, these results indicate that PP`s degradation effect prevailed over the positive HDPE cross-linking effects, as it can be observed in the results of the tests for irradiated HDPE in comparison with neat HDPE.

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