# Comparison between irradiated HDPE/piassava fiber/nanoclay and HDPE/piassava fiber/nanoclay/PP blend

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## Abstract

In the present work, the changes in physicochemical, morphological and thermal properties of HDPE/Piassava fiber/nanoclay and HDPE/Piassava fiber/nanoclay/PP blend electron-beam irradiated were evaluated. The samples were irradiated with 100 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, thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and the correlation between their properties was discussed. The results showed that the incorporation of Piassava (Attalea funifera Mart) fiber and nanoclay followed by electron-beam irradiation represented a significant gain ($p < 0.05$) in thermo-mechanical properties, changes in surface morphology and reduction in MFI. After irradiation, the nanocomposite showed a gain in the degree of cross-linking, and a better interfacial adhesion between fiber, nanoclay and HDPE. In addition, the HDPE/Piassava fiber/nanoclay/PP blend presented better properties behavior than HDPE/Piassava fiber/nanoclay. In conclusion, based on these results, it may be claimed that incorporation of piassava fiber in small size particles and nanoclay followed by electron-beam irradiation effectively improved the properties of HDPE and led to the obtaining of a HDPE/Piassava fiber/nanoclay/PP blend with superior properties for several industrial applications.

***Keywords:*** nanoclay, nanocomposites, piassava fiber, polymer-nanocomposite, electron-beam irradiation, HDPE/nanoclay

## 1. Introduction

Lately, many researchers have experimented with the addition of polymer fibers in order to modify and improve their properties, which has shown positive results by the obtaining of end products with better performance than the original thermoplastic (Neto, 2006). Basically, the thermoplastic matrices available, such as polypropylene (PP) and polyethylene (PE) show the most potential benefits when combined with vegetal fibers to make composites for industrial applications (Bonelli, 2005; Joseph, 1999; Santos, 2003). However, both thermoplastic and thermoset materials can be reinforced with

vegetal fibers and made into composite materials, 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, 2009).

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. The main use of these fibers is for industrial and domestic brooms, industrial brushes, ropes, baskets, carpets and roofs. It is estimated that around 50% of the fiber is discarded during the cut, cleaning and baling and as residue by the transformation industries (Aquino, 2000; Moura, 2009).

The use of clay in polymeric nanocomposites has shown good results, contributing to remarkable improvement in material compared with virgin polymers or conventional micro- and macro-composites. Recently, much effort has been made to develop polymer-clay nanocomposites and to understand the enhancement in properties upon addition and dispersion of organoclay in polymers (Filippi, 2008; Varlot, 2002). High density polyethylene (HDPE) is a thermoplastic polyolefin widely used for several applications due to its good mechanical properties, chemical resistance, impermeability to water, low cost and easy processing (Raghavan, 2009). Polyolefins are difficult to intercalate into the interlayer space of swelling hydrophilic clay without chemical modification of one of the two components. Since HDPE is a polyolefin, a solution found in this work to the lack of interfacial adhesion between HDPE and PP nonpolar and polar clays for HDPE/Piassava fiber/nanoclay and HDPE/Piassava fiber/nanoclay/PP blend was the addition of polyethylene grafted with maleic anhydride to polyethylene matrix that has been established for the intercalation / exfoliation process, with important improvements in the material rigidity, keeping the shearing stress and tension with acceptable results (Neto, 2006).

Nowadays, electron beam 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. Under irradiation with high energy beams, HDPE predominantly undergoes cross-linking in the amorphous regions; the cross-linking effectively increases intermolecular bonds in this region of HDPE, resulting in an improvement in material properties, such as better mechanical, thermal and chemical properties (Bengtsson, 2006; Clegg, 1991; Gheysari, 2001; Lei, 2007a).

This work studied the influence of electron-beam radiation processing and the incorporation of a Brazilian smectitic clay (bentonite chocolate clay) and Piassava fiber (*Attalea Funifera* Mart.), which is also typical from Brazil, in HDPE and HDPE/PP blends.

## 2. Material and Methods

### *2.1. Material*

The materials used in this study were HDPE resin (HDPE JV060U) a commercial grade by Braskem S/A, with MFI = 6.4 g/10 min at 190 0C/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 0C/2.16 Kg, specific density = 0.893 g/cm$^3$, 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 (Piassava), with particle sizes equal to or smaller than 250 μm by using ball mills and then it was dried again at 80 ± 2 ºC for 24 h to reduce its moisture content to less than 2 %.

*2.1.2 Nanoclay preparation*

Before the bentonite chocolate clay becomes ready to be incorporated as a nanoparticle in the composite, clay should be modified by quaternary ammonium compounds, for example, to make an intercalated nanocomposite exfoliate. In this work, the clay was modified by the addition of a quaternary salt and sodium carbonate and underwent the processes of dispersion into water, stirring and heating for a determinate time, and just then was it filtered and dried for the disaggregation of one particle in another, and finally characterized as a nanoclay.

*2.1.3 Nanocomposites preparation*

Preparation of nanocomposites was carried out in two steps. Firstly, the composite of 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. The extrudates coming out of the extruder were cooled down by using cold water for a better dimensional stability and wound up manually. Finally, the HDPE/Piassava/nanoclay (67:30:3 wt %) was pelletized by a pelletizer. In a second step, part of the pelletized HDPE/Piassava/nanoclay was then dried at 80 ± 2 º C for 24 h in a circulating air oven, fed into injection molding machine and specimens test samples were obtained. Part (50 %) of the pelletized HDPE/Piassava/nanoclay 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/nanoclay/PP blend (33.5:15:1.5:50 wt %).

*2.2 Electron-beam irradiation*

Part of the materials obtained were irradiated with 100 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*

Tensile tests (ASTM D 638), flexural tests (ASTM D 790) and heat distortion temperature (HDT) (ASTM D 648), were performed in this work in order to evaluate the thermo-mechanical behavior of the materials studied.

*2.3.3 Thermogravimetric analysis*

Thermogravimetric analyses (TG) were carried out using a TGA 50 (Shimadzu, Japan). TGA analyses of the materials were performed on four weighed samples with $3.0 \pm 1.0$ mg of the irradiated and non-irradiated materials. Samples were heated from 25 to 500 ºC, at a heating rate of 10 ºC/min (in an oxygen atmosphere).

*2.3.4 MFI measurements*

MFI measurements were determined with a Microtest extruder plastometer (ASTM 1238-04) in the conditions specified for polyethylene and polypropylene.

*2.3.5 Scanning Electron Microscopy (SEM)*

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

## 3 Results and Discussion

*3.1 Thermo-mechanical tests*

The results of the average values obtained at the tensile strength at break tests for HDPE, HDPE/Piassava/nanoclay and HDPE/Piassava/nanoclay/PP blend are shown in figure 1. As it can be seen, there was a significant increase ($p < 0.05$) of about 280 % for non-irradiated HDPE/Piassava/nanoclay and HDPE/Piassava/nanoclay/PP blend in comparison with HDPE samples. After irradiation treatment, a significant increase ($p < 0.05$) of 280 % for HDPE and 40 % for HDPE/Piassava/nanoclay/PP blend was observed.

Figure 1. Tensile strength at break for HDPE, HDPE/Piassava/nanoclay and HDPE/Piassava/nanoclay/PP blend.

The results of the flexural strength average data are represented in figure 2.

As it can be seen, the flexural strength of the non-irradiated composites showed a significant increase ($p < 0.05$) of 30% for HDPE/Piassava/nanoclay and 88% for HDPE/Piassava/nanoclay/PP blend when compared with non-irradiated HDPE. These results showed that the addition of the fiber and nanoclay represented important gains in original HDPE flexural strength and when the composites obtained are blended with the PP polymer the gains in this property can reach even higher values. Concerning the electron-beam radiation treatment, only the irradiated HDPE presented a small gain of 6 % compared with the original HDPE flexural strength.

Figure 2. The flexural strength for HDPE, HDPE/Piassava/nanoclay and HDPE/Piassava/nanoclay/PP blend.

Figure 3 shows the results of the flexural modulus average data for HDPE, HDPE/Piassava/nanoclay and HDPE/Piassava/nanoclay/PP blend. Concerning non-irradiated samples, figure 3 shows that, in comparison with HDPE flexural modulus, a significant decrease ($p < 0.05$) of 32 % can be observed for HDPE/Piassava/nanoclay. On the other hand, a significant increase ($p < 0.05$) in this property, of about 118 %, can be observed for HDPE/Piassava/nanoclay/PP blend. After electron-beam irradiation, both, HDPE and its nanocomposites presented a significant increase ($p < 0.05$). The sharpest increase (204 %) can be observed for the irradiated HDPE/Piassava/nanoclay samples, while the irradiated HDPE/Piassava/nanoclay/PP blend samples increased only ca. 7 % and HDPE increased about 6 %.

Figure 3. The flexural modulus for HDPE, HDPE/Piassava/nanoclay and HDPE/Piassava/nanoclay/PP blend.

Lei *et all* (2007) studied the influence of the addition of 1 – 3 % Cloisite® 15A, a commercial natural montmorillonite modified on mechanical properties of HDPE/Wood Composites with 2 % maleated polyethylene (MAPE) with 1.0 wt % maleic anhydride as compatibilizer. They observed a higher gain in tensile and flexural strength (24.2 %; 19.6 %) for the addition of 1% nanoclay, and a gain of 11 % in flexural modulus for the addition of 3 % nanoclay. In our previous works, the effects of electron-beam irradiation on mechanical properties of HDPE/Piassava composite (60:40 wt %) was studied (Souza, 2010).The results showed significant increases of around 200 % in tensile strength at break, 30 % in flexural strength and 110 % in flexural modules of the HDPE because of piassava fibers addition alone. Concerning electron-beam irradiation, the thermo-mechanical properties for both, HDPE and HDPE/Piassava composite, presented significant increase as a function of the radiation dose applied, except in relation to the composite `s elongation at break properties.

Table I shows HDT results for HDPE, HDPE/Piassava/nanoclay and HDPE/Piassava /nanoclay/PP blend. The results presented a gain of about 14 % for both non-irradiated nanocomposites when compared with HDPE samples. After electron-beam irradiation, HDT for nanocomposite increased ca. 11 % for

HDPE/Piassava/nanoclay and ca. 19 % for HDPE/Piassava/nanoclay/PP compared with irradiated HDPE, On the other hand, the addition of PP in nanocomposite promoted a higher increase in HDT, of about 6 %.

Table I - HDT results for HDPE, PP and their nanocomposites

*3.2 Melt flow index (MFI) measurements*

The results for MFI measurements carried out at 190 0C/2.16 kg conditions for non-irradiated HDPE, PP and their nanocomposites were 6.41 g/10 min for HDPE, 12.27 g/10 min for PP, for HDPE/Piassava/nanoclay was 5.85 g/10 min, and 8.30 g/10 min for HDPE/Piassava/nanoclay/PP blend. These results showed a significant reduction in nanocomposites `MFI values when compared with those of the HDPE and PP resins. It seems that piassava fibers and nanoclay affect the dynamic viscoelastic melt of polymer, since they could reduce molecular mobility and, consequently, the flow. Under MFI test conditions, none irradiated samples of HDPE, PP and nanocomposites showed any flow and, therefore, MFI could not be determined. In fact, the samples showed a rubber-like behavior with no flow. This indicates that the level of radiation doses used for cross-linking was quite sufficient to cross-link HDPE and PP chains and to convert their plastic nature to a more rubber - like material.

*3.3 Thermogravimetric analysis*

The results of the thermogravimetric analyses (TG) are presented in Table II. They represent the average values calculated from the data obtained by TG analysis. The standard deviation for TG analysis was less than 10% for all tests. As it can be seen, there was a slight decrease ($p < 0.05$) in weight loss, after the samples heated up to 500 ºC, for HDPE/Piassava/nanoclay (ca. 3 % at 0 kGy and 1.6 % at 100 kGy) and HDPE/Piassava/nanoclay/PP blend (ca. 1 % at 0 kGy and 2 % at 100 kGy) when compared with HDPE. This drop can also be observed in relation to onset degradation temperature for non-irradiated HDPE/Piassava/nanoclay/PP blend that decreased ca. 20 % in comparison with HDPE, while a slight gain of about 6 % may be observed for non-irradiated HDPE/Piassava/nanoclay. After irradiation with 100 kGy, a reduction in thermal stability for HDPE/Piassava/nanoclay (ca.10 %), and an increase for HDPE/Piassava/nanoclay/PP (ca. 3 %) were also observed (Table II).

Table II - Onset degradation temperature and weight loss for HDPE and their nanocomposites

*3.4 Scanning Electron Microscopy (SEM)*

Figure 4 shows SEM surface micrographs (magnification 100 X) for HDPE/Piassava/nanoclay/PP blend and HDPE/Piassava/nanoclay, non-irradiated and irradiated samples. As it can be seen, non-irradiated HDPE/Piassava/nanoclay revealed a rough, dense and compact cryofractured surface with a large number of cavities in the matrix phase, which can indicate a poor interfacial adhesion between piassava fiber and

matrix. In contrast, the irradiated HDPE/Piassava/nanoclay revealed a slightly smoother cryofractured surface without the presence of cavities. That can indicate that, as a consequence of the electron-beam irradiation, this nanocomposite became smooth and with a better fiber-matrix interfacial adhesion. Comparing the irradiated and non-irradiated HDPE/Piassava/nanoclay/PP blend, it is clear that there are some cavities on the irradiated sample and small differences between the samples which can mean that, in this case, the radiation dose used was not enough to cause a large modification.

Figure 4. Scanning electron microscopy (SEM) surfaces micrographs (magnification 100 X). (A) non-irradiated HDPE/Piassava/nanoclay, (B) HDPE/Piassava/nanoclay with 100 kGy; (C) non-irradiated HDPE/Piassava/nanoclay/PP blend, and (D) HDPE/Piassava fiber/nanoclay/PP blend with 100 kGy.

## 4 Conclusion

The mechanical tests showed that the incorporation of Piassava fiber and nanoclay was very beneficial for mechanical properties when compared with HDPE for both composites. HDPE/Piassava fiber/nanoclay/PP blend also showed gains when compared with HDPE/Piassava fiber/nanoclay. These results might mean that the adition of PP was also good for the improvement of these properties. Thermogravimetric analysis showed that non-irradiated HDPE/Piassava fiber/nanoclay had higher temperature of decomposition, which means that this material has a higher thermal stability than the others. The micrographies revealed that radiation causes a better interfacial adhesion for HDPE/Piassava fiber/nanoclay. These results are very important because they can contribute to the obtaining of better materials in order to expand the application fields of these materials.

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## References

Aquino, R.C.M.P; D´Almeida, J.R.M & Monteiro, S.N. 2000. Propriedades de compósitos de piaçava com matriz polimérica. 55º Congresso Anual da ABM, 2898.

Bengtsson, M.; Oksman, K.; Stark, N.M. 2006. Profile Extrusion and Mechanical Properties of Crosslinked Wood-Thermoplastic Composites. Polymer Composites, 184-194.

Bonelli, C.M.C.; Elzubair, A.; Suarez, J.C.M.; Mano, E.B. 2005. Comportamento térmico, mecânico e morfológico de compósitos de polietileno de alta densidade reciclado com fibra de piaçava. Polímeros: Ciência e Tecnologia, 15-4, 256-260.

Clegg, D.W.; Collyer, A.A. 1991. Irradiation effects on polymers. Elsevier Science. Publishers Ltd. England, 68-69.

Filippi, S.; Marazzato, C.; Magagnini, P.; Famulari, A.; Arosio, P.; Meille, S. V. 2008. Structure and morphology of HDPE-g-MA/organoclay nanocomposites: Effects of the preparation procedures. European Polymer Journal - Macromolecular Nanotechnology, 44, 987–1002.

Gheysari, D.; Behjat, A.; Haji-Saeid, M. 2001. The effect of high-energy electron beam on mechanical and thermal properties of LDPE and HDPE. European Polymer Journal, 37-2, 295–302.

Joseph, P.V.; Joseph, K.; Thomas, S. 1999. Effect of processing variables on the mechanical properties of sisal-fiber-reinforced polypropylene composites. Composites Science and Technology, 59, 625-1640.

Kilttinaovarat, S.; Suthamnoi, W. 2009. Physical properties of polyolefin / bamboo charcoal composites." Journal of metals, materials and minerals, 19-1, 9-15.

Lei, Yong; Wu, Q.; Clemons, C.M.; Yao, F.; Xu, Y. 2007a. Influence of Nanoclay on Properties of HDPE/Wood Composites. Journal of Applied Polymer Science, 106, 3958–3966.

Lei, Y.; Wu, Q.; Yao, F.; Xu, Y. 2007b. Preparation and properties of recycled HDPE/natural fiber composites. Composites: Part A, 38, 1664–1674.

Moura, E. A. B.; Nogueira, B. R.; Ortiz, A. V. 2009. 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.

Neto, F. L.; Pardini, L. C. 2006. Compósitos estruturados: Ciência e tecnologia. Ed. Edgard Blucher.

Raghavan, J. 2009. Evolution of cure, mechanical properties, and residual stress during electron beam curing of a polymer composite. Composites: Part A, 40, 300–308.

Santos, P.; Pezzin, S.H. 2003. Mechanical properties of polypropylene reinforced with recycled-pet fibers. Journal of Materials Processing Technology 143–144.

Souza, T.L.S.; Chinellato, A; Moura, E.A.B. 2010. Effects of radiation doses on thermo-mechanical and viscoelastic behavior of HDP/Piassava fiber composite. In: 9th meeting of the Ionizing Radiation and Polymers Symposium.

Varlot, K.; Reynaud, E.; Vigier, G.; Varlet, J. 2002. Mechanical properties of clay-reinforced polyamide, J Polym Sci Part B: Polym Phys, 40, 272-283.

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