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Sugarcane Bagasse Ash Reinforced HDPE Composites: Effects of Electron-Beam Radiation Crosslinking on Tensile and Morphological Properties

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ABSTRACT

Environmental issues have led to the development of polymeric materials reinforced with fibers originated from renewable agricultural sources such as pineapple leaf, sisal, jute, piassava, coir, and sugarcane bagasse. Although sugarcane bagasse fiber residues has been extensively studied and used as a source of reinforcement of polymers, the major portion of these residues is currently burnt for energy supply in the sugar and alcohol industries and as a result of its burning, tons of ashes are produced. Due to the inorganic composition, ashes can be used as reinforcement in polymeric materials. This study presents the preparation and characterization of a composite based on HDPE matrix and sugarcane bagasse ashes as reinforcement cross-linked by electron-beam radiation. The HDPE /Ash composite (95:5 wt %) was obtained by using a twin-screw extruder machine followed by injection molding. After extrusion and injection molding process, the composites were subjected to electron-beam radiation, at radiation doses of 150 kGy and 250 kGy using a Dynamitron electron beam accelerator, at room temperature in the presence of air. The irradiated and non-irradiated composite specimens were characterization by tensile and MFI tests, scanning electron microscopy (SEM), x-ray diffraction (XRD) and sol-gel analysis. In addition, ash from bagasse fiber was characterized by WDXRF.

1. INTRODUCTION

Composites are defined as materials possessing a continuous phase and a discontinuous one, and these two phases being of different nature. Polymeric composites have been studied broadly in the last decades and its main applications are in the automobile , aeronautics and in the building industries, among others; always seeking for economy and sustainability [1].

Thermoplastic composites reinforced with vegetable fibers is of great interest for the industry, especially because natural fibers have low cost when compared to synthetic fiber, and they also present good mechanical properties [2-3].

A great part of the bagasse , a residue from the sugar cane processing is used in its own agribusiness for the co-generation of energy. This residues can be destined to other applications, as reinforcement of polymeric matrices, a smaller cost component once it is an industrial residue, but with good mechanical properties [4-5]. The pyrolysis of the pulp generates ashes rich in inorganic materials, and SiO_2 is the main component [6-7].

Polyethylene is obtained from the ethylene gas or as a byproduct of petroleum and classified according to its density (low, medium, high). Its density is determined by the presence and regularity of the branches, and the polymeric chains may be of 50,000 to 100,000 carbon atoms linked. The molecular weight, molecular weight distribution and number of branches determine many of their chemical and mechanical properties Polyethylene is a semicrystalline polymer, with crystalline domains dispersed in the amorphous regions. The degree of crystallization of the polymer depends on the chemical structure, molecular weight and physical treatment, including temperature and crystallization time and may be changed by forces the material will undergo in the processing and / or throughout its lifetime as a product. The crystallinity of a polymer affects several properties of the final product and can be altered in several ways: reverse-processing, recycling, exposition to the ultraviolet light (exposition to the sun), heating (during use and warehousing), during the production of parts, among others.

It is important to control the degree of crystallinity of the polymer, because the more it becomes crystalline, the higher its melting point and also its mechanical strength are but the lower is its ductility [8-9].

Ionizing radiation (gamma rays or electron beam) is a potential method for modifying polymers, fibers, natural macromolecules as well as the development of new composite materials. Studies performed in the last decades have shown that the improvement of material properties by irradiation is the result of scission and crosslinking processes that occur simultaneously during irradiation and alignment and stabilization of material morphology.[1-4-10-11-12-13-14-15].

MATERIALS AND METHODS

1.1 Materials

High density polyethylene (HDPE JV060U - Braskem S/A), specific density = 0,951 g/cm, MFI (Melt flow index) = 6,41 g/10 min at 190°C/2,16 Kg and sugarcane bagasse ash supplied by Usina Iracemápolis.

1.2 Ash Preparation

Ashes were dried in an oven (Quimis, model Q-317B) at the temperature 150 ± 2º C, ball-milled and classified granumetrically with the aid of sieves so that the ashes used were particles ≤ 250 μm.

1.2.1 Ash characterization

For analyzing the inorganic composition of the ashes from sugarcane bagasse , the method of Wavelength Dispersive X-ray Fluorescence was used (WDXRF). The analyses were accomplished in a spectrometer model RIX 3000, Rigaku, of the Laboratory of Fluorescence of Ray-X in the Center of Chemistry and Environment (CQMA) at IPEN/CNEN.

1.3 Composite Preparation

Ash particles ≤ 250 μm were kept for 4 hours at temperature of 150 ± 2 ºC and the HDPE pellets were dried in an oven (Quimis, model Q-317B) at temperature of 90 ± 2 ºC for 3 hours. Then 5% of sugarcane bagasse ash was incorporated to the polymeric matrix of HDPE (95:5 wt%). The composite was obtained by the extrusion process, in processing temperatures from 160 ºC to 190 ºC, using a twin screw extrusion machine "extruder AX 16LD40" made by AX Plásticos Máquinas Técnicas Ltda. After extrusion the composite HDPE/ash (95:5 wt%) was fed in an injection molding machine model 430/110, for the making specimens for the mechanical tests.

Figure 1: On the left the ''AX 16LD40'' Extruder and on the right the''430/110'' Injection molding machine

1.4 Electron-Beam Irradiation

Samples of neat HDPE and composites were Irradiated at 150 kGy and 250 kGy using an electron beam accelerator (Dynamitron II, Radiation Dynamics Inc., 1.249 MeV energy, 5,05 mA current and 37.5 kW power), at room temperature, in air, dose rate 22.41 kGy/s. Irradiation doses were measured using cellulose triacetate film dosimeters ''CTA-FTR-125'' from Fuji Photo Film Co. Ltd.

1.5 Tensile Tests

The tensile tests (ASTM D 638) were performed in this work in order to evaluate the mechanical resistance of the materials studied. Each value presented here represents the average of five samples.

1.6 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.

1.7 Melt flow index (MFI)

MFI measurements for neat HDPE, and the non-irradiated composite were determined with a microtest extruder plastometer at 190 °C/2.16 kg conditions (ASTM 1238-04)

1.8 X-Ray Diffraction (XRD)

XRD patterns of HDPE irradiated and composites were obtained using a diffractometer Rigaku Denki Co. Ltd., Multiflex model, CuKα radiation (λ = 1.5406 Å) at 40 kV and 20 mA. With this procedure, the angles (2θ) of diffraction of all the samples were measured from 2° to 50°.

1.9 Sol Gel Analysis

Analyses of crosslinking degree was carried out. The system was set up with round bottom flasks, Soxhlet extractors , condensers and heating units. Tests were made in triplicate with xylene as solvent and heating for 12 hours. Final values are obtained by the use of equations 1 and 2.

$$F_S = [(W_i - W_f).W_i^{-1}].100 \quad (1)$$

$$F_G = 100 - F_S \quad (2)$$

Where:

Wi: Initial mass of the sample
Wf: Final mass of the sample
Fs: Soluble fraction of the sample
F_G: Degree of crosslinkig

2. RESULTS AND DISCUSSION

2.1 Ash Characterization

The WDXRF results show that SiO_2 corresponds to 57% of the composition of the sugarcane bagasse ash.

Table 1 : The results of (WDXRF) the Sugarcane bagasse ash

Compounds	***Content (%)***
SiO_2	57±1
Al_2O_3	14±1
Fe_2O_3	13±1
K_2O	5,2±0,1
CaO	3,5±0,1
TiO_2	3,1±0,1
P_2O_5	2,0±0,1
MgO	1,7±0,1
SO_3	0,74±0,05
MnO	0,27±0,05
Na_2O	0,08±0,01
Cr_2O_3	0,04±0,01
Others	< 0,03

2.2 Tensile Tests

Figure 2 shows the diagram tensile strength (MPa) X elongation (mm/mm) for the composites.

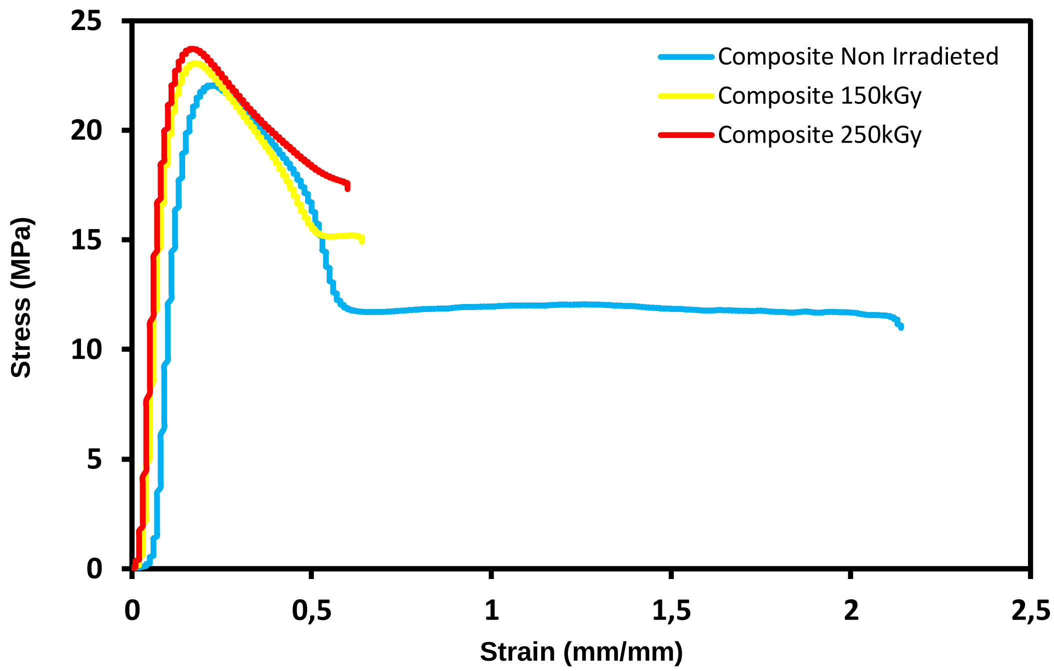

Figure 2: Diagram Stress (MPa) X Strain (mm/mm) for composites: Composite Non Irradiated; Composite 150kGy and Composite 250ky.

Table 2 presents the results of tensile strength for the neat HDPE, irradiated HDPE and for the irradiated and non-irradiated composites. The result presented in this table corresponds to the average results for 5 specimens. It can be seen that the irradiation of the neat HDPE improves tensile strength of the material up to 285%. The addition of ash reinforcement in the HDPE led to an improvement of 95% in tensile strength and when the composite is irradiated an improvement up to 210% was observed. Usually when a material is reinforced to form a composite it presents gains in tensile strength but decreases in elongation. An interesting result in this study is the gain of 8% in elongation of the non-irradiated composite when compared to the non-irradiated neat HDPE.

Table 2: Mechanical Properties for HDPE and Composites.

Materials	Tensile Strenght at Break (MPa)	Elongation at Break (%)	Young modulus (MPa)
Neat HDPE	5,6 ±1,80	200 ±6,87	131,9 ±6,87
HDPE 150kGy	18,6 ±1,15	274 ±17,64	150,1 ±4,11
HDPE 250kGy	21,6 ±0,63	185,2 ±7,13	149,9 ±3,50
Composite Non Irradiated	11 ±2,83	216,2 ±4,47	129,25 ±11,73
Composite 150kGy	14,17 ±0,63	61,4 ±12,61	148,14 ±10,90
Composite 250kGy	17,3 ±0,28	51,3 ±5,16	164,42 ±6,76

2.3 MFI

MFI results are presented in Table 3. The non-irradiated composite presents an increase in MFI of 85% when compared with the neat HDPE, resulting in a less viscous material than neat HDPE.

Table 3: MFI values for neat HDPE and non-irradiated Composite.

Materials	MFI(at 190ºC/ 2.16 Kg)(g/ 10min)
neat HDPE	7.73 ±0,17
Non-irradiated Composite	14,29 ±0,82

2.4 Scanning Electron Microscopy (SEM)

Micrographs in Figure 3 show the slightly rough surface of the cryo-fractured HDPE and the good ash particle dispersion in the HDPE matrix. While the non-irradiated composite shows some voids between matrix and reinforcement, these voids are not observed in the irradiated composites.

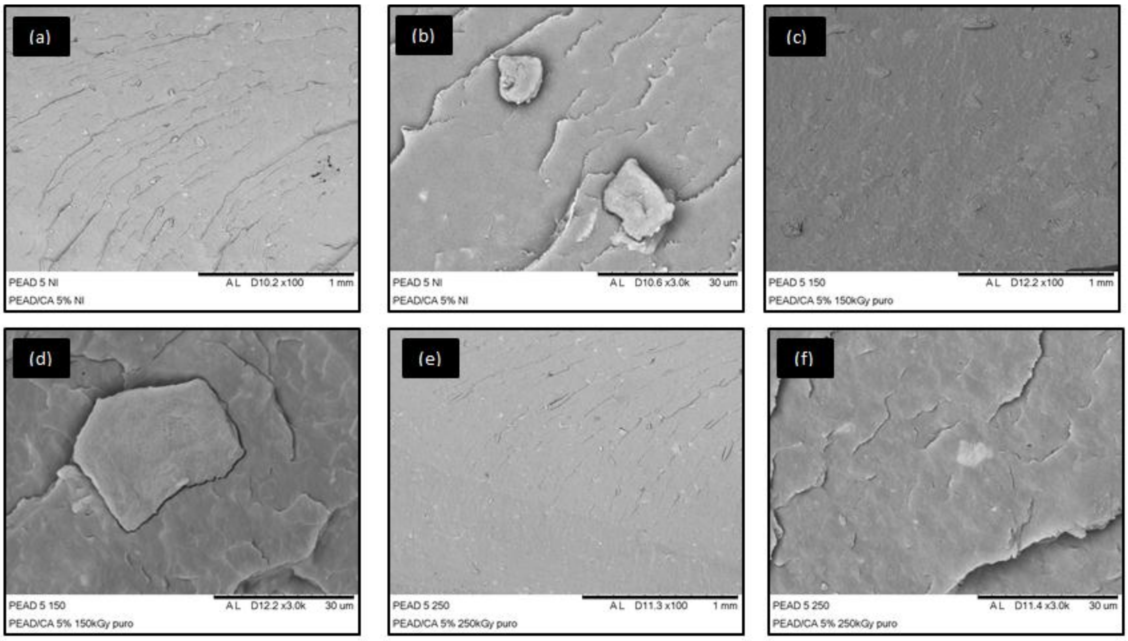

Figure 3: Scanning Electron Microscopy (SEM) for the non-irradiated Composite 100X(a); non-irradiated Composite 3.000X(b); Composite 150kGy 100X (c); Composite 150kGy 3.000X (d); Composite 250kGy 100X (e); Composite 250kGy 3.000X (f).

Micrographs in figure 4 shows how the slightly rough surface of neat HDPE is modified when irradiation doses are applied.

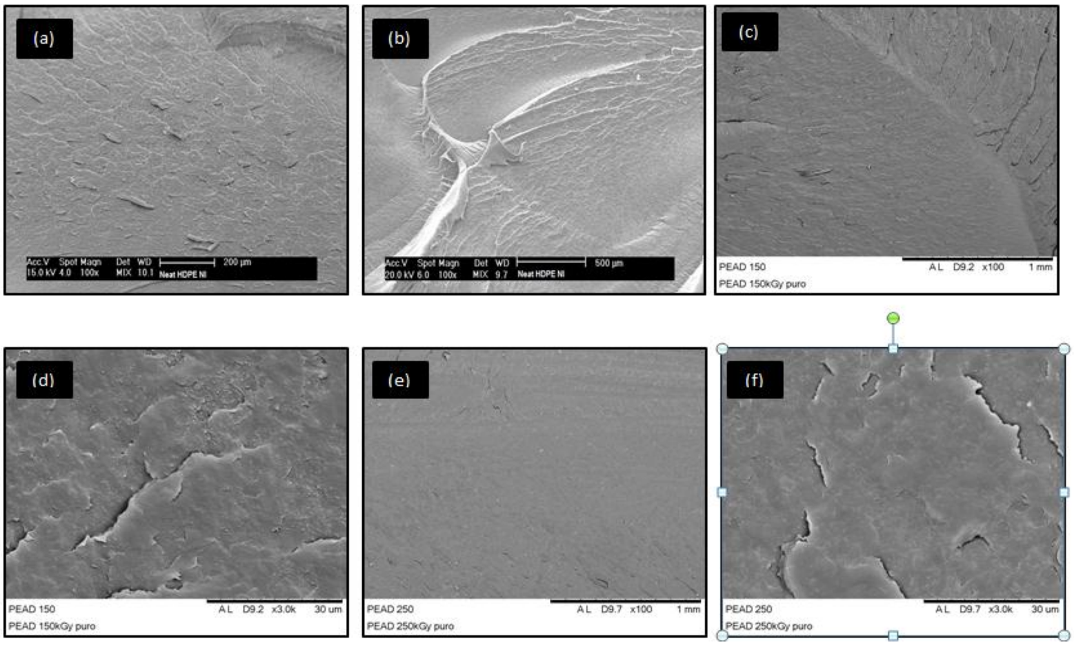

Figure 4: Scanning Electron Microscopy (SEM) of neat HDPE 100X (a); neat HDPE 3000 X (b);HDPE 150kGy X 100 (c); HDPE 150kGy 3000 X (d); HDPE 250kGy 100X (e); HDPE 250kGy 3000X (f).

2.5 X-Ray Diffraction (XRD)

XRD patterns shows that the composite brings new peaks to the material when compared to the neat HDPE . It was not possible to detect changes in crystalinity due to irradiation effects.

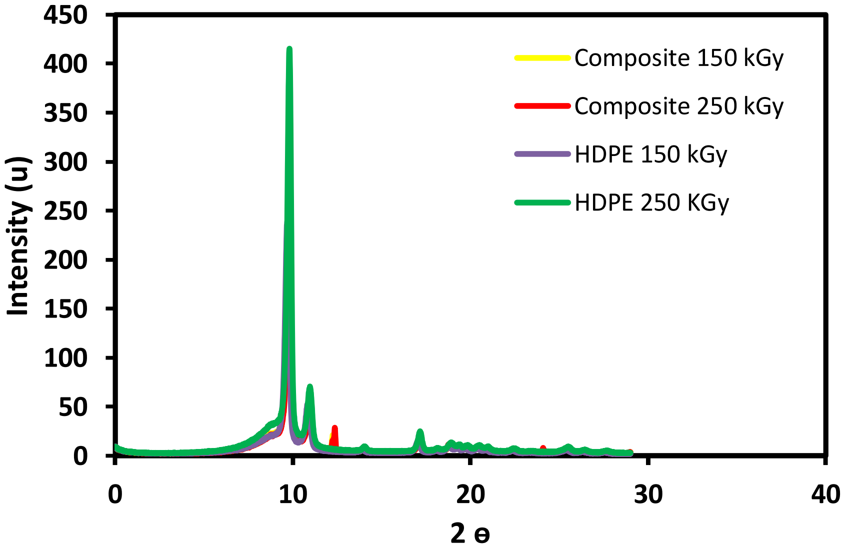

Figure 5: XRD patterns of HDPE 150kGy, HDPE 250kGy and it composite non irradiated (Composite 0kGy), Composite 150kGy and Composite 250kGy.

2.6 Sol Gel Analysis

Figure 6 shows that the higher the irradiation dose, the higher is the crosslinking degree obtained. Results also showed that the composite irradiated not change compared to HDPE irradiated

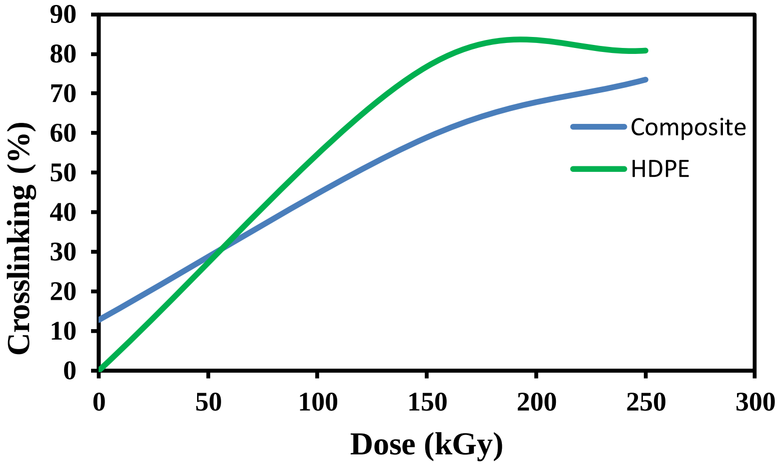

Figure 6: Sol gel analysis for the neat HDPE and the composite at different radiation doses.

3. CONCLUSIONS

Significant gains in tensile strength are verified as irradiation doses are applied to the HDPE. The incorporation of ash reinforcement also led to higher tensile strength. Combining reinforcement and irradiation, higher tensile strengths are obtained but a decrease in elongation was observed. The addition of ashes also led to a less viscous material , shown by the increase of 85% in the MFI. The SEM analysis showed a good dispersion of the ashes in the HDPE matrix and the use of irradiation enhanced the adhesion of ashes and matrix once the voids observed in the non-irradiated composite are no longer observed in the irradiated composites.

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