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Preparation and characterization of electron-beam treated HDPE composites reinforced with rice husk ash and Brazilian clay

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ABSTRACT

This work evaluates the morphology, mechanical and thermo-mechanical properties of high density polyethylene (HDPE) composites. HDPE reinforced with rice husk ashes (80:20 wt%), HDPE reinforced with clay (97:3 wt%) and HDPE reinforced with both rice husk ashes and clay(77:20:3 wt%) were obtained. The Brazilian bentonite chocolate clay was used in this study. This Brazilian smectitic clay is commonly used to produce nanocomposites. The composites were produced by melting extrusion process and then irradiation was carried out in a 1.5 MeV electron-beam accelerator (room temperature, presence of air). Comparisons using the irradiated and non-irradiated neat polymer, and the irradiated and non-irradiated composites were made. The materials obtained were submitted to tensile, flexural and impact tests. Additionally HDT, SEM and XRD analyses were carried out along with the sol–gel analysis which aimed to assess the cross-linking degree of the irradiated materials. Results showed great improvement in most HDPE properties and a high cross-linking degree of 85% as a result of electron-beam irradiation of the material.

1. Introduction

The objective of this study is to evaluate possible changes in high density polyethylene (HDPE) composite properties when it is reinforced with clay, rice husk ashes, or a combination of both reinforcements, and when the resulting HDPE composites are electron-beam irradiated.

A composite is a material resulting from the combination of two or more materials in order to optimize the properties of each component. Traditional reinforcements used in composites are common materials and do not require high technology, for example, fibers, silica and graphite. The polymer is generally viewed as the weakest link from the mechanical point of view and researchers mostly focused efforts on increasing the content of reinforcement in the final material or improving interaction with reinforcements. Nanoparticles lead to an opposite direction. While a traditional composite may contain up to 40% of reinforcement in weight, the introduction of nanoparticles as reinforcement often shows important gains in material properties in concentrations not exceeding 5% [1].

Currently, one can observe an increasing use of reinforcements coming from renewable resources [2]. Environmental issues have led to the development of biodegradable as well as traditional materials with an increasing level of additives, fillers and reinforcements from vegetable origin as well as renewable polymeric materials [3,4]. The use of agricultural sub-products has been extensively studied as a source of these reinforcements [5,6]. But such organic wastes have also been widely used in energy cogeneration and as a result of burning, large amounts of ash are produced. Because of its characteristics, ash can be used as reinforcement. In addition to its cementitious material nature, studies have shown the capability of adding costless ashes of vegetable origin as a substitute for talc and other mineral fillers [3,5,7].

Among the various natural fibers and ashes that can be used as a dispersed phase in polymer composites is rice husk. The husk is a coating or protective layer formed during the growth of rice grains. Removed during the refining of rice, this shell has low commercial value, since it has little nutritional value and therefore is not used in human or animal food. A few years ago, almost all of this material would end up in the bottom of rivers and fields. Concerned with the growing environmental contamination by this

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waste, some groups have dedicated themselves to the study of its use for power generation. Rice husk ashes may be used as a component in the composition of ceramics and refractory insulation as well as in the construction and rubber industries, and also applied as reinforcement for polymers [9].

Besides the use of green materials and waste, recent research has demonstrated that the addition of little amount of natural clays (less than 10%) may improve mechanical, thermal and barrier properties, and also dimensional stability of a composite when compared with the pure polymer [8–10]. When clay can generate particle sizes at the nanometric level (up to 100 nm) in its processing with the polymer, a nanocomposite is generated. The most common method to obtain a nanocomposite is the processing of a polymer and organoclay mixture in the molten state to allow intercalation of polymer chains between clay lamellae [11–13].

In this study the polymer used was high density polyethylene (HDPE) that is a thermoplastic resulting from the polymerization of ethylene, and is widely used in various industries due to its mechanical properties, chemical resistance, water impermeability, ease of processing and low cost.

HDPE is an inexpensive commodity polymer, but its use in some engineering applications may depend on improving its properties by crosslinking [14]. The use of radiation on the molecules of a polymer, particular for HDPE, is a method often used for modification of its properties, as it promotes a process involving simultaneously crosslinking and scission of the material polymeric chains, leading to greater degrees of compatibility and stabilization. Electron beams applied for radiation processing for crosslinking are usually used within electron energy range 0.5–3 MeV and absorbed dose up to a few hundreds of kGy. Radiation crosslinking involves the formation of three dimensional structures by the abstraction of a hydrogen atom from the PE backbone. The free radical left on the carbon chain then finds another free radical site on a neighboring carbon on another molecule to form a crosslink. Crosslinking is located primarily in the non-crystalline phase and along the lamellar amorphous interphase [15]. Because the cross-linking process changes a linear network into a three-dimensional one, it can produce materials with high thermal stability, better strength, and better resistance to impact [16–19].

2. Experimental methods

The materials used in this study were HDPE JV060U (by Braskem S/A), rice husk ashes disposed by the agroindustry in Uruguay and sodic bentonite chocolate clay powder from the northeast of Brazil (by Pegmatech Especialidades Tecnológicas Ltda.). Rice husk ashes were prepared by first drying them at 130 ± 2 °C for 24 h in an air-circulating oven. Then dry ashes were reduced to fine powder, with particle sizes equal or smaller than 250 μm by using a ball mill, and dried again at 130 ± 2 °C for 24 h to reduce the moisture content. In order to make the sodic clay more organophilic, it was modified by the addition of quaternary ammonium salt and sodium carbonate. Then it underwent dispersion into water and finally it was filtered and dried.

Composites made out of HDPE and one or a combination of the two reinforcements were obtained by hand mixing the materials and then making the final combination undergo melting extrusion in a twin screw extruder. The extruded composites were pelletized, then fed into an injection molding machine and test samples were obtained. Finally, for each composite produced, part of it was submitted to electron-beam radiation. The electron-beam radiation process was carried out at 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.

Table 1
List of materials used in this study.

M1	Non-irradiated composite consisting of 100% HDPE
M2	Non-irradiated composite consisting of 80% HDPE/20% ash (wt%)
M3	Non-irradiated composite consisting of 97% HDPE/3% clay (wt%)
M4	Non-irradiated composite consisting of 77% HDPE/20% Ash/3% clay (wt%)
M5	Composite consisting of 100% HDPE irradiated at 250 kGy
M6	Composite consisting of 80% HDPE/20% ash (wt%) irradiated at 250 kGy
M7	Composite consisting of 97% HDPE/3% clay (wt%) irradiated at 250 kGy
M8	Composite consisting of 77% HDPE/20% Ash/3% clay (wt%) irradiated at 250 kGy

Eight different materials were generated and were available to be analyzed. Table 1 lists the materials produced for this study. The decision on the concentration of ash and clay to be added in the HDPE for this study was based on previous tests comparing different concentrations of each reinforcement in HDPE. No important property improvements were observed in the HDPE/ash composite when the HDPE carried more than 20% of ash. And for the sodic clay, studies evaluating concentrations up to 5% showed that no important improvement in the HDPE/clay composite properties were observed when more than 3% of clay were incorporated in HDPE.

Material characterization was carried out. Characterization involved mechanical and thermo-mechanical testing, scanning electron microscopy, X-ray diffraction and sol–gel analysis. Mechanical and thermo-mechanical properties studied were tensile properties according to ASTM D638 standard [20], flexural strength according to ASTM D790 standard [21], heat distortion temperature according to ASTM D648 standard [22] and Izod impact resistance according to ASTM D256 standard [23]. The results presented in this work are the average for 5 tested specimens and variation between specimens are not greater than 15%. Scanning electron microscopy (SEM) analyses were carried out using a LX30 (Phillips). The samples were cryofractured under liquid nitrogen and then the fractured surface was coated with a fine layer of gold and observed by scanning electron microscopy. X-ray diffraction (XRD) analyses were carried out on a Rigaku Denki Co. Ltd., Multiflex model diffractometer, with CuKα radiation (λ = 1.5406 Å) at 40 kV and 20 mA, with 2θ varying between 2° and 50°. Sol–gel analyses for detecting crosslinking degree was carried out in a system set up with round bottom flasks, Soxhlet extractors, condensers and heating units. Tests were made in triplicate with boiling xylene as solvent and heating for 12 h. Variation between results is not greater than 2%.

3. Results and discussion

Table 2 summarizes the results obtained for the tensile testing. As it can be seen in Table 2, the inclusion of reinforcement in the polymeric matrix greatly increased the tensile strength at break. But the effect in the elongation at break was the opposite. It is also important to notice that the use of irradiation led to superior gains in tensile strength. The irradiated HDPE/clay combination led to a material presenting 23.16 MPa as its tensile strength at break which is 314% greater than the original HDPE property of only 5.60 MPa. The stress–strain curves for the studied materials are shown in Fig. 1.

Table 3 presents the results obtained for the flexural property. As it can be seen from the results in Table 3, for the studied materials most of the time there was loss in the flexural property when the reinforcement was added to the polymeric matrix. Although most of the studied composites presented loss in flexural properties, it

Table 2
Tensile testing results for both irradiated and non-irradiated neat HDPE and its composites.

Material[a]	M1	M2	M3	M4	M5	M6	M7	M8
Tensile strength at break (MPa)	5.60 ± 0.32	19.82 ± 0.92	18.05 ± 0,73	19.34 ± 1.04	21.47 ± 0.89	21.04 ± 0.95	23.16 ± 0.94	22.12 ± 1.27
Elongation at break (%)	200.2 ± 2.2	32.43 ± 0.69	22.39 ± 0.43	20.42 ± 0.52	249.3 ± 3.7	27.09 ± 0.66	17.26 ± 0.92	16.29 ± 0.68

[a] M1 = neat HDPE (NI), M2 = HDPE/Ash (NI), M3 = HDPE/Clay (NI), M4 = HDPE/Ash/Clay (NI), M5 = neat HDPE (250 kGy), M6 = HDPE/Ash (250 kGy), M7 = HDPE/Clay (250 kGy), M8 = HDPE/Ash/Clay (250 kGy).

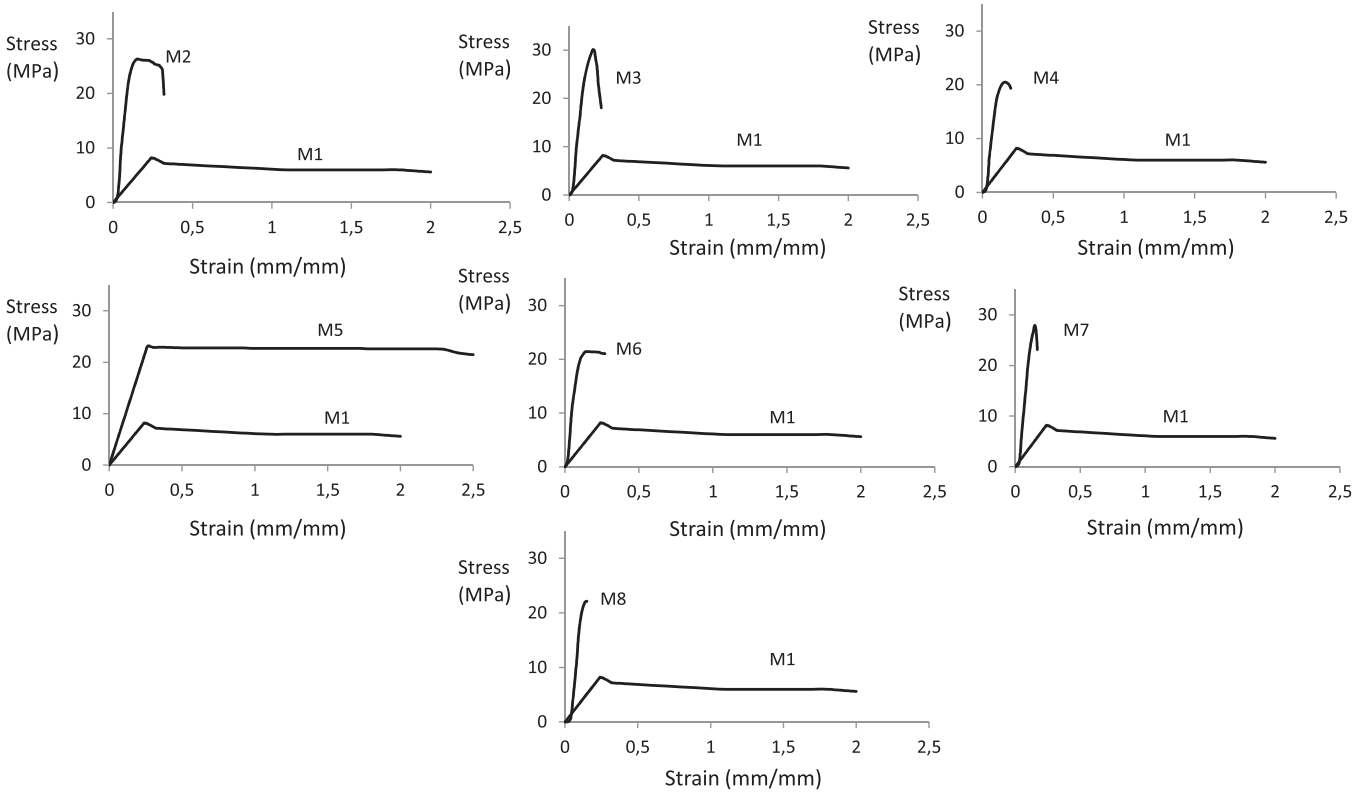

Fig. 1. Stress–strain curves comparing the non-irradiated neat HDPE and the other composites and irradiated materials, where M1 = neat HDPE (NI), M2 = HDPE/Ash (NI), M3 = HDPE/Clay (NI), M4 = HDPE/Ash/Clay (NI), M5 = neat HDPE (250 kGy), M6 = HDPE/Ash (250 kGy), M7 = HDPE/Clay (250 kGy), M8 = HDPE/Ash/Clay (250 kGy).

is important to point out that the irradiated HDPE/clay presented stability in this property.

I

Table 4 summarizes the results obtained for the heat distortion temperature (HDT) and it can be seen that the incorporation of the reinforcement led to an important increase in this thermomechanical property. When irradiated, the composites presented higher gains for this property and it can be featured a 30% in this property for the irradiated HDPE/ash composite. Similarly to the study of Lenza et al. [24], the addition of reinforcements was able to improve HDPE thermo stability.

Table 5 presents the results obtained for the Izod impact test and it can be seen that the incorporation of the reinforcement led to an important increase for this property with a high of 267.3 J/m for the irradiated HDPE/ash combination. It represents an increase of 246% when compared to the non-irradiated neat HDPE.

Scanning electron microscopy (SEM) of the cryofractured materials was carried out for the composites in order to observe reinforcement distribution in the polymeric matrix and changes on the cryofractured surface. Fig. 2 shows the micrographs of the composites obtained for this study. They show a slightly rough HDPE cryo-fractured surface with good reinforcement dispersion in all cases. No important changes on the cryofractured surface of the studied materials were detected.

Fig. 3 shows the results of X-ray diffraction analysis for the neat HDPE and the composites obtained for this study. Neat HDPE presents two characteristic peaks for 2θ between 20° and 25° and these peaks remain in all diffractograms independently of reinforcement addition or irradiation treatment. Although they are not shown in Fig. 2, both the original clay and the quarts modified clay were also analyzed by means of XRD and their characteristic peaks were found at $2\theta = 6.58°$ and $2\theta = 4.58°$, respectively.

Table 3
Flexural strength results for both irradiated and non-irradiated neat HDPE and its composites.

Material[a]	M1	M2	M3	M4	M5	M6	M7	M8
Flexural strength (MPa)	17.05 ± 1.22	14.25 ± 0.96	12.8 ± 1.12	13.51 ± 0.99	23.58 ± 1.54	17.50 ± 1.01	15.03 ± 1.16	16.24 ± 1.58

[a] M1 = neat HDPE (NI), M2 = HDPE/Ash (NI), M3 = HDPE/Clay (NI), M4 = HDPE/Ash/Clay (NI), M5 = neat HDPE (250 kGy), M6 = HDPE/Ash (250 kGy), M7 = HDPE/Clay (250 kGy), M8 = HDPE/Ash/Clay (250 kGy).

Table 4
HDT results for both irradiated and non-irradiated neat HDPE and its composites.

Material[a]	M1	M2	M3	M4	M5	M6	M7	M8
HDT (°C)	56.3 ± 1.7	63.9 ± 2.1	60.2 ± 2.0	61.9 ± 1.8	60.5 ± 1.9	73.4 ± 2.1	63.4 ± 1.4	64.7 ± 1.8

[a] M1 = neat HDPE (NI), M2 = HDPE/Ash (NI), M3 = HDPE/Clay (NI), M4 = HDPE/Ash/Clay (NI), M5 = neat HDPE (250 kGy), M6 = HDPE/Ash (250 kGy), M7 = HDPE/Clay (250 kGy), M8 = HDPE/Ash/Clay (250 kGy).

Table 5
Results Izod impact testing for both irradiated and non-irradiated neat HDPE and its composites.

Material[a]	M1	M2	M3	M4	M5	M6	M7	M8
Izod impact test (J/m)	77.3 ± 6.2	151.0 ± 19.9	93.7 ± 7.1	104.5 ± 0.6	82.9 ± 7.8	267.3 ± 17.4	100.7 ± 9.0	104.2 ± 8.0

[a] M1 = neat HDPE (NI), M2 = HDPE/Ash (NI), M3 = HDPE/Clay (NI), M4 = HDPE/Ash/Clay (NI), M5 = neat HDPE (250 kGy), M6 = HDPE/Ash (250 kGy), M7 = HDPE/Clay (250 kGy), M8 = HDPE/Ash/Clay (250 kGy).

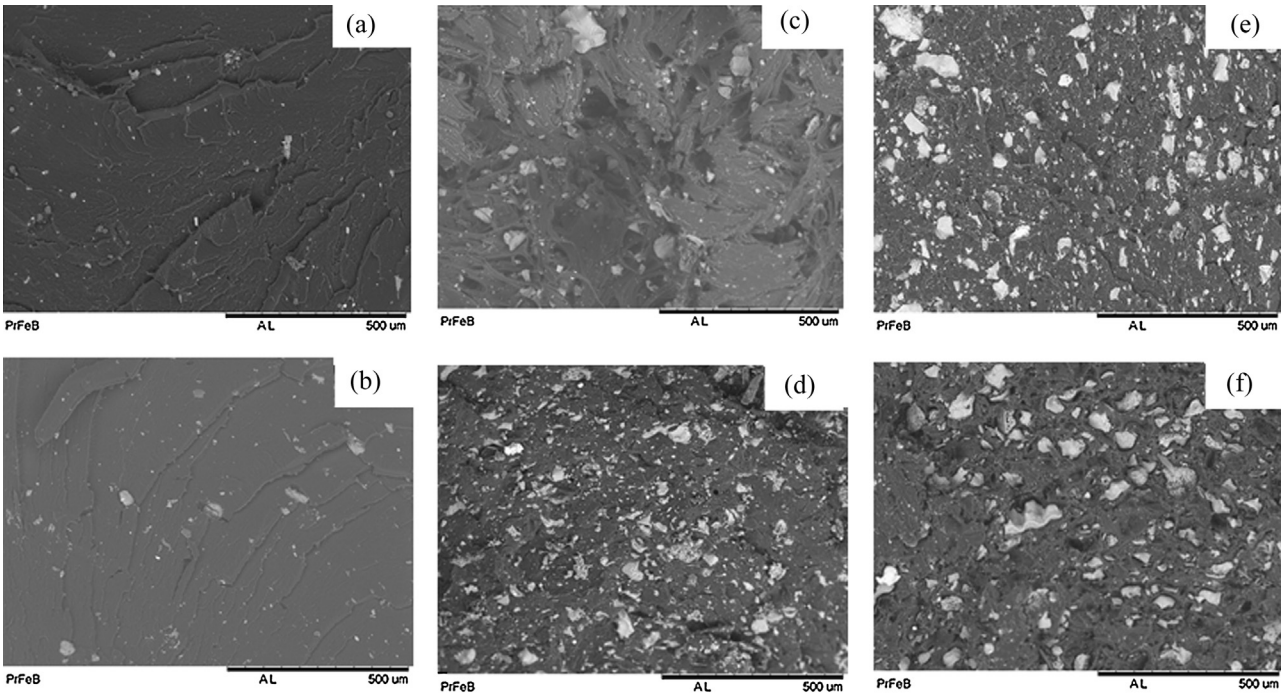

Fig. 2. Micrographs (250×) of the non-irradiated and irradiated composites as follows: (a) HDPE/Clay (non-irradiated), (b) HDPE/Clay (250 kGy), (c) HDPE/Ash (non-irradiated), (d) HDPE/Ash (250 kGy), (e) HDPE/Ash/Clay (non-irradiated), (f) HDPE/Ash/Clay (250 kGy).

In order to evaluate the degree of cross-linking in the HDPE as a result of electron-beam irradiation, the sol–gel analysis was conducted in the non-irradiated and irradiated neat HDPE. The non-irradiated neat HDPE dissolved completely in the xylene. On the other hand, the irradiated HDPE lost only 15% of its original weight dissolved in the organic solvent, and consequently indicating that the other 85% of the material was cross-linked and insoluble in hot xylene. This high cross-linking degree can lead to materials with

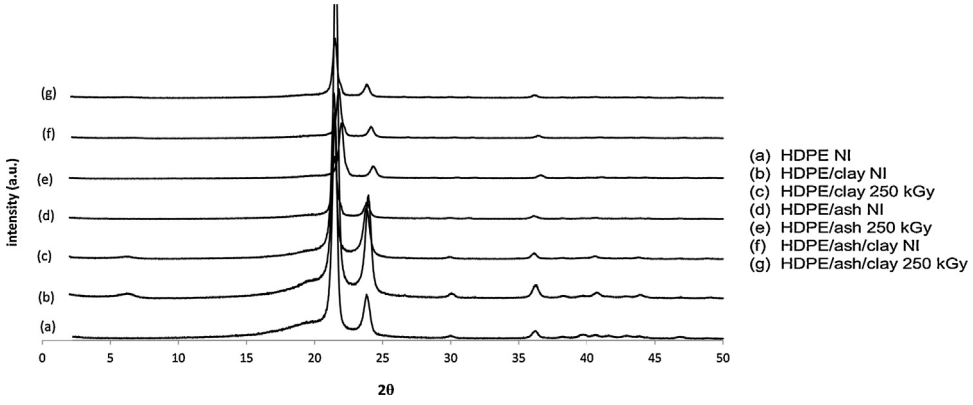

Fig. 3. XRD analysis of the neat HDPE and composites obtained.

improved thermal stability, better strength, and better resistance to impact, as observed in this study.

4. Conclusion

Results showed that the addition of natural clay and residues from the agroindustrial activity is able to lead to great improvement of some polymeric material mechanical and thermo-mechanical properties. The use of electron-beam radiation had a synergetic effect, being able to improve even more such properties and was even able to maintain properties when typical losses are expected for the non-irradiated composite. Sol–gel analysis indicated that cross-linking of the HDPE chains is the main effect of the electron-beam treatment and it explains the synergetic effect of irradiation in the reinforced materials studied.

XRD analysis suggested that the composite extrusion led to an exfoliation of the montmorillonite component of the clay, once the clay typical crystalline peak occurring at $2\theta = 4.58^{\circ}$ for some of composites are not as high as expected when clay itself is analyzed, or they disappear in others. This exfoliation generally results in nanoparticles dissolved in the polymeric matrix and possibly is the main reason why the clay containing composites, even with such little amount of reinforcement, presented outstanding results when comparing to the neat HDPE.

As it was evaluated in this work, when HDPE is both reinforced and irradiated, important property gains occur and its composites tend to behave more similarly to an engineering plastic material. Such results become even more important when composites are generated by the use of waste and environmentally correct materials, as requested by many sustainability projects.

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