2013 International Nuclear Atlantic Conference - INAC 2013
Recife, PE, Brazil, November 24-29, 2013
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR - ABEN
ISBN: 978-85-99141-05-2

BIODEGRADABLE ALIPHATIC-AROMATIC COPOLYESTER/CORN STARCH BLEND COMPOSITE REINFORCED WITH COFFEE PARCHMENT HUSK

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Keywords: Composite, coffee parchment husk, biodegradable polymer, mechanical properties, SEM

ABSTRACT

In recent years, studies have shown that the addition of natural fiber or proper filler is an effective strategy for achieving improved properties in biodegradable polymer materials. Moreover, is especially important if such fibers are residues of agro-industrial processes. In this work, a promising technique to develop biodegradable polymer matrix composite based on aliphatic-aromatic copolyester/corn starch blend (Evela™) and coffee parchment husk, which is residue from coffee processing is described. The biodegradable polymeric blend (Evela™) with 5 % (w/w) of ball-milled coffee parchment husk fiber powder, with size ≤ 250 μm, without any modification was prepared by melt-mixing processing, using a twin screw extruder machine and then pelletized. In a second step, the pelletized Evela™/coffee parchment (Composite) was then dried at 70 ± 2 º C for 24 h in a circulating air oven, fed into injection molding machine and test specimens were obtained. The Composite specimen samples were irradiated using an electron beam accelerator, at radiation dose of 20 and 40 kGy, at room temperature in presence of air. The irradiated and non-irradiated samples were characterized by means of scanning electron microscopy (SEM), X-Ray diffraction (XRD), tensile tests and sol-gel analysis and the correlation between their properties was discussed. In addition, coffee parchment husk fiber characterization by SEM, EDS, XRD and WDXRF have also been carried out with a view to evaluate its importance in determining the end-use properties of the composite.

1. INTRODUCTION

Polymers have replaced many conventional materials such as metals, ceramics among others in various applications. The most important advantages of using polymers are: easy processing, high productivity and low cost in combination with its versatility [1].

Despite the polymers and their derivatives have historically contributed immensely to the global technological development, by enhancing the quality of life of modern man, the continue use of these materials has brought concerns to society. Mostly because of its, low recyclability and great cumulative power in the biosphere, particularly due to its low biodegradability and non-renewable origin (Petroleum) [2].

The concern with the environment is leading society to search for new products that have the least environmental impact possible. Within this context, the discovery of materials that serve as a basis for polymeric compounds which are less harmful to the environment, is of great importance. A wide variety of polymers derived from renewable resources (natural) has the potential to perform various functions, such as: adhesives, coatings, gels, foams, films, thermoplastic and thermoset resins [3].

One of the most promising raw materials studied for the production of biodegradable polymer is starch, which is a renewable natural carbohydrate obtained from a great variety of corns. Starch is a low cost material compared to most synthetic polymers and is highly available. It has been studied for manufacturing products such as water-soluble bottles for detergents and insecticides, bags, controlled release systems of drugs, among others. The native starch has, in general, one granular structure with about 15-45% crystallinity. Under the action of high temperature and pressure, starch can be converted into a thermoplastic starch (TPS) [4].

The aliphatic-aromatic copolyester/corn starch blend has in its composition approximately 52% of corn starch. And unlike synthetic polymers, starch is a renewable and biodegradable compound that can be processed by industrial techniques similar to the polyolefin, mainly involving extrusion and injection [5].

In Brazil, the production of polymer composites reinforced with vegetable fibers is of utmost importance. The transformation of these fibers in products leads to higher added value , contributes to the preservation of the environment, enables the sustainable use and generates social benefits such as the creation of direct jobs, improving the quality of life of the communities involved, which has these fibers as their main, if not only, source of income, They usually live in poverty, with minimal health, housing and sanitation conditions.

The main disadvantage of the incorporation of natural vegetable fibers in polymeric materials is associated with the development of a weak interface between the fibers and the polymer. Natural fibers are highly hydrophobic and polar due to the presence of hydroxyl groups (OH-) and thus have weak chemical affinity with polymers featuring low polarity, such as unsaturated polyester. Thus, these fibers should be subjected to physical or chemical treatments to modify properties and surface morphology, enabling greater chemical interaction with the matrix chosen. Best interfaces can be obtained from the fiber surface treatments to increase surface tension either by the incorporation of coupling agents or interfacial adhesion agents, but the type of treatment used should be analyzed for each case [6-8].

Growing coffee results in a high volume of waste, mainly coffee husk (epicarp), which use has been studied, pulp or mucilage (mesocarp), parchment (endocarp) and silver skin. The peel, pulp or mucilage, parchment and silver skin are different forms of waste from the coffee processing after harvest. In Brazil, the most common form of coffee processing is drying the whole fruit, resulting in waste from peel and parchment and a yield of 50% of the harvested weight[7].
One way of improving the fiber-polymer interaction can be the use of ionizing radiation. Ionizing radiation can be considered an alternative to several traditional ways of modifying the physical and chemical properties of the polymeric materials. When a polymer is irradiated two different reactions occur simultaneously: a main polymer chain scission and the chemical bonding between

different polymeric molecules (cross-linking). These reactions happen simultaneously and the predominance of one over the other depends on the chemical structure of the polymer, the conditions of irradiation and specific factors of the material that will absorb the energy. Studies performed in the last decades have shown that the improvement of material properties by irradiation is the result of scission and crosslinking processes and simultaneous alignment and stabilization of the morphology of the material [10-11].

The introduction of natural fibers in the manufacturing of composite materials has received great attention by researchers and industry. Plant fibers have low cost, are biodegradable, nontoxic, possess excellent mechanical properties and are not abrasive, thus causing less environmental impact when used [8].

2. MATERIALS AND METHODS

2.1. Material

In this study we used the commercial aliphatic-aromatic copolyester/corn starch blend (Evela™) with MFI between 2.7 and 4.9 g/10 min at 190°C / 2.16 Kg, density 1.32 g/cm³ and melting point of 116-122 ° C; and coffee crop residues (parchment) provided by the Experimental Farm of EPAMIG in Machado, MG, Brazil.

2.2. Coffee Parchment Husk Fiber Preparation

Coffee parchment husk 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 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 %.

2.3. Coffee Parchment Husk Fiber Characterization

The coffee parchment husk fiber characterization by Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), X-Rays Diffraction (XRD) and Wavelength Dispersive X-ray Fluorescence (WDXRF) has also been carried out with a view to evaluate its importance in determining the end-use properties of the composite.

2.4. Composites Preparation

Composites were prepared by melting extrusion process, using a twin screw extrusion machine "extruder AX 16LD40" made by AX Plásticos Máquinas Técnicas Ltda. The polymeric matrix (Evela™) was reinforced with 5% parchment fiber , using 95 parts of polymer and 5 parts of fiber (95:5 wt%). The material coming out of the extruder was cooled down by using cold water for a better dimensional stability,then pelletized, and dried again at 80 ± 2 ºC for 24 h in a circulating air oven and fed into injection molding machine to obtain specimens test samples.

2.5. Electron-Beam Irradiation

Samples of neat Evela™ and composites were irradiated at 20 kGy and 40 kGy using a 1.5 MeV electron beam 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 22.37 kGy/s. Irradiation doses were measured using cellulose triacetate film dosimeters ‘‘CTA-FTR-125’’ from Fuji Photo Film Co. Ltd.

2.6. Scanning Electron Microscopy (SEM)

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

2.7. X-Rays Diffraction (XDR)

XRD patterns of neat Evela™ and composites were obtained using a diffractometer by 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°.

2.8. Tensile Tests

The tensile tests (ASTM D 638) were performed in this work in order to evaluate the mechanical behavior of the materials studied. Each value obtained represented the average of five samples

2.9. Sol-Gel Analysis

The percentage of gel is an effective measure for evaluating the degree of crosslinking of a material. Neat samples of Evela™ and the irradiated and not irradiated composite were weighed (300 mg ±10 mg), and placed in round bottom flasks with 250 ml of chloroform. Chloroform is the ideal solvent for Evela. The flask was connected to a condenser and the samples were kept under reflux at 130 °C (±2 °C) for 12 hours. After 12 hours of reflux with hot chloroform, the samples were dried in a circulating air oven at 70 °C (±2 °C) and weighed until presenting constant weight. The crosslinking percentage of the samples is determined by Equation 1:

$$\% \text{ of crosslinking: } 100 - [(\mathbf{B}\text{-}\mathbf{C}) / \mathbf{A}] \times 100 \quad (1)$$

where:
A is initial mass of the sample;
B is initial mass of the sample along with a support;
C is final weight of the sample together with a support;

3. RESULTS AND DISCUSSION

3.1. Coffee Parchment Husk Fiber Characterization

3.1.1. Scanning Electron Microscopy (SEM) of fiber

SEM micrographs of coffee parchment and of the powder obtained after parchment ball-milling are shown in Fig. 1.

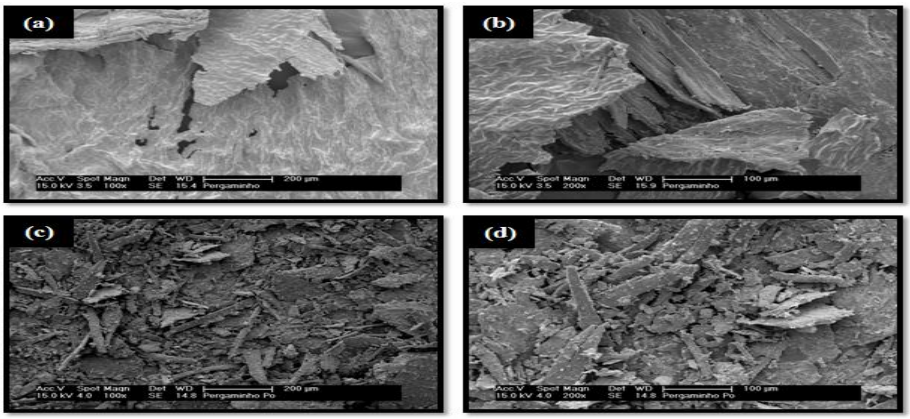

Figure 1: SEM micrographs (100 X and 200X) of coffee parchment (1a) and (1b), and of ball-milled coffee parchment (1c) and (1d).

Micrographs 1a and 1b show the morphology of parchment and the fiber disposition in it. The effects of ball milling can be seen in 1c and 1d, which show smaller broken fibers in disorder.

3.1.2. Energy Dispersive Spectroscopy (EDS)

Fig. 2 shows X-ray spectrometry of the parchment surface.

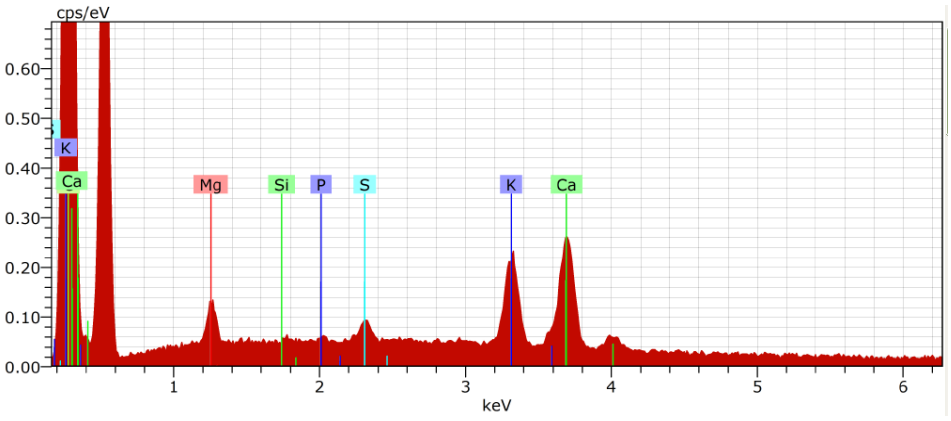

Figure 2: X-ray spectrometry of the parchment surface .

Table 1: Percent composition (%wt.) of coffee parchment.

Element	Carbon (C)	Calcium (Ca)	Potassium (K)	Magnesium (Mg)	Sulfur (S)
Wt (%)	87,52	6,41	3,90	1,60	0,56

As any material obtained from living organisms, carbon is the main component. Besides carbon it is important to point out the presence of calcium, potassium , magnesium and sulfur.

3.1.3. X-Ray Diffraction (XRD)

The XRD pattern of coffee parchment is shown in Fig. 3.

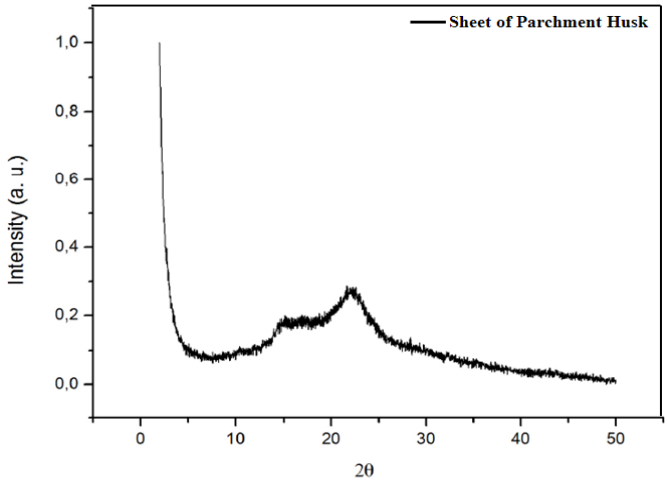

Figure 3: XRD pattern of coffee parchment.

The obtained curve follows the cellulose XRD pattern, basically an amorphous material with small main crystalline peaks at around 2Θ = 14.3°and 2Θ = 22.6° .

3.1.4. Wavelength Dispersive X-ray Fluorescence (WDXRF)

The results of coffee parchment fiber inorganic composition and loss on fire obtained by wavelength dispersive X-ray fluorescence are presented in table 2:

Table 2: Results of coffee parchment fiber obtained by wavelength dispersive X-ray fluorescence.

Elements	Percentage
Loss on Fire	96,0
K	2,0
Ca	1,80
Mg	0,36
S	0,18

P	0,04
Cl	0,02
Fe	0,019
Cu	0,010
Mn	0,010
Zn	< 0,005
Sr	< 0,005

As previously seen in the EDS analysis, this analysis also show calcium, potassium, magnesium and sulfur as the main inorganic components of the tested material.

3.2. Scanning Electron Microscopy (SEM)

SEM micrographs of cryo-fractured neat Evela and of the irradiated and non-irradiated (N.I.)* composites are shown in figures 4 and 5.

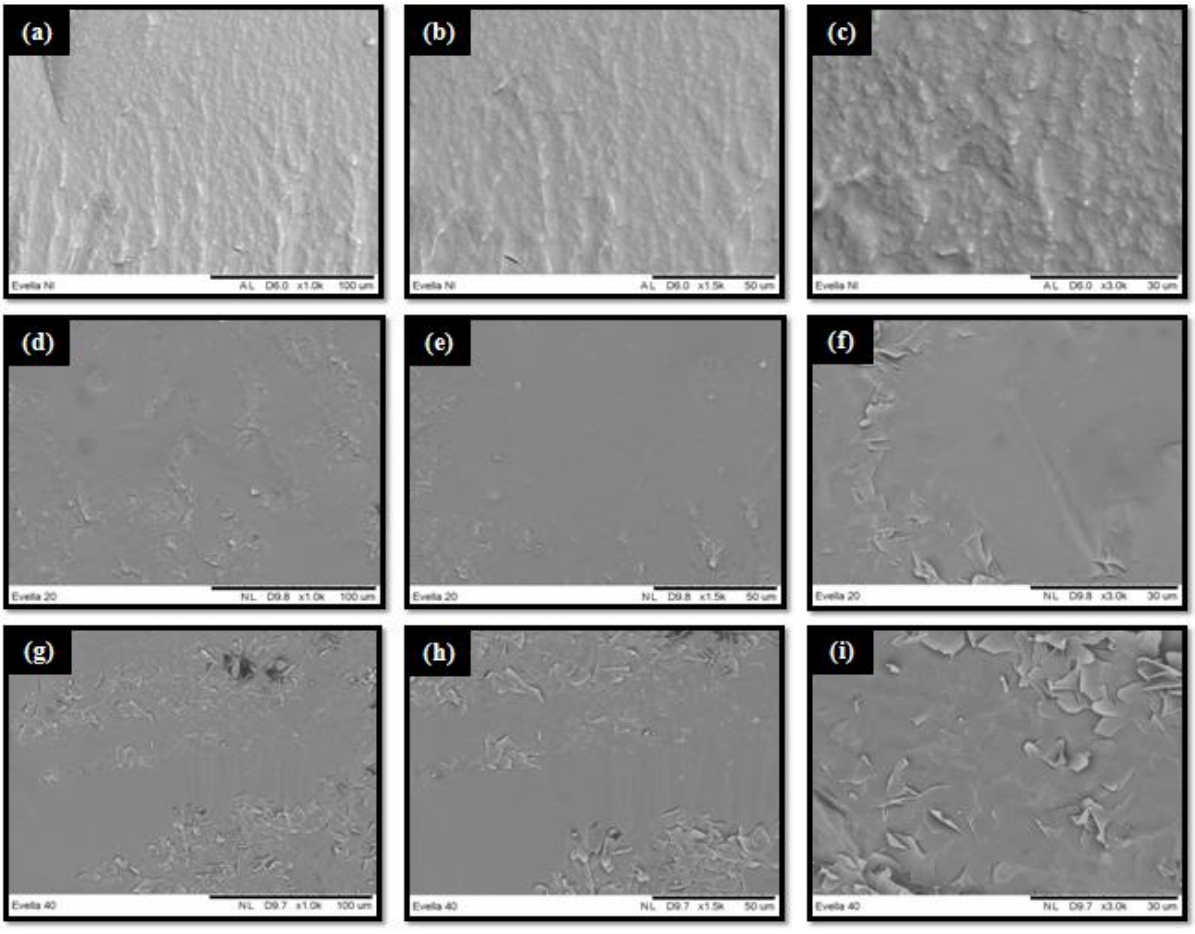

Figure 4: (a),(b), (c) SEM micrographs of neat Evela N.I.* at different magnifications ; (d), (e),(f) SEM micrographs of neat Evela irradiated with 20 kGy dose at different magnifications ;(g),(h),(i) SEM micrographs of neat Evela irradiated with40 kGy dose at different magnifications.

As it can be seen in Figure 4, the non-irradiated neat Evela showed a rough and wrinkled surface while the samples of neat Evela irradiated at 20 kGy and 40 kGy present less rough surfaces.

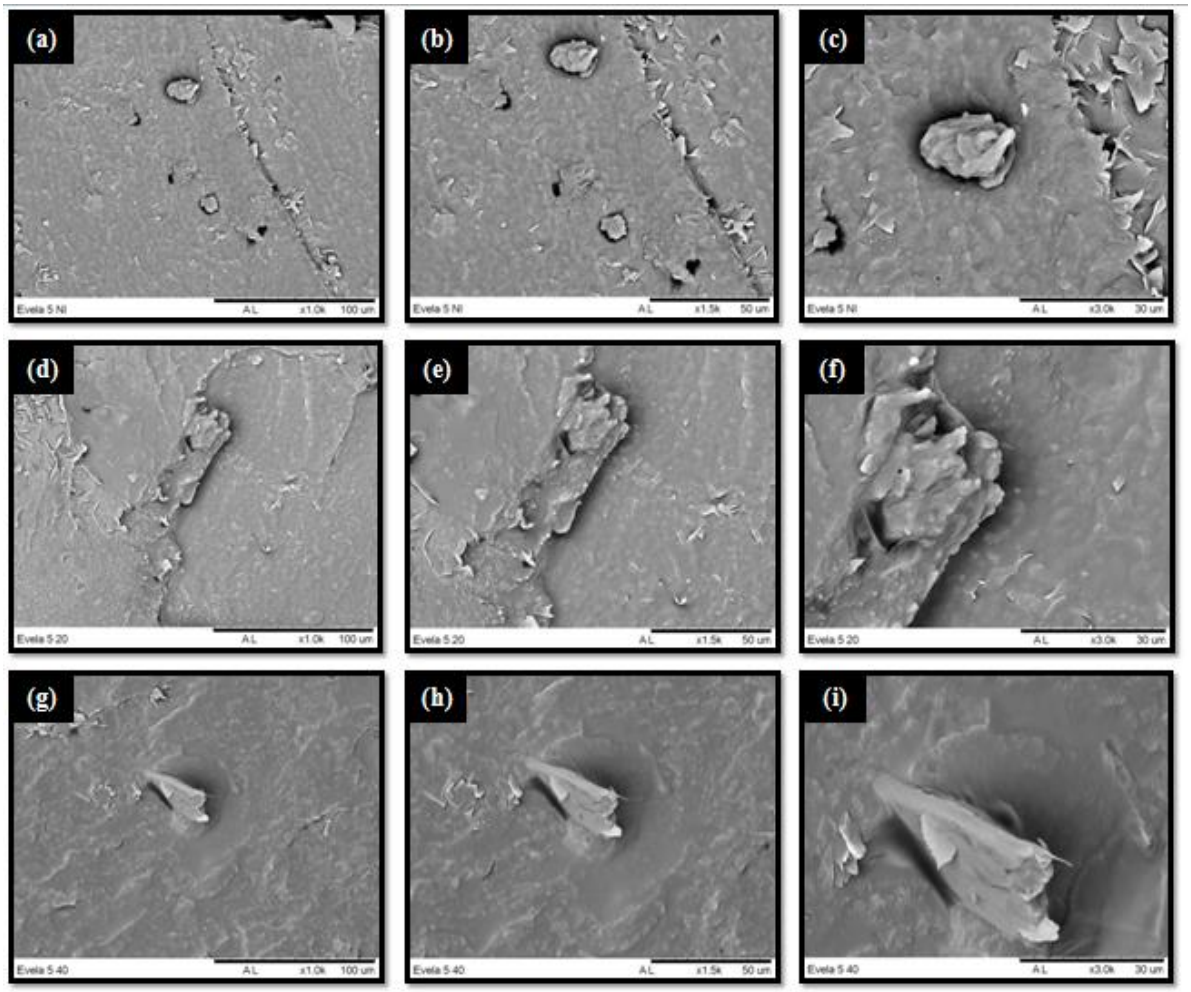

Figure 5: (a),(b) (c) SEM micrographs of Composite N.I.* at different magnifications ; (d), (e),(f) SEM micrographs of Composite irradiated with 20 kGy dose at different magnifications ;(g),(h),(i) SEM micrographs of Composite irradiated with40 kGy dose at different magnifications.

As it can be seen in Figure 5, both the irradiated and the non-irradiated composite showed rough wrinkled surfaces when cryo-fractured. In all cases it was observed some voids between fibers and matrices.

3.3. X-Ray Diffraction (XRD)

The XRD patterns of neat Evela™ and its irradiated and non-irradiated composites are shown in Fig.6.

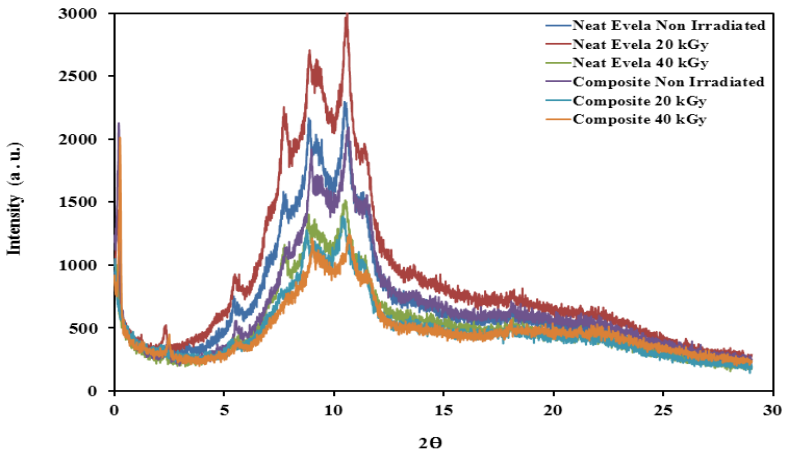

Figure 6: XRD patterns of neat Evela and its composites: Neat Evela Non Irradiated; Neat Evela 20 kGy; Neat Evela 40 kGy; Composite Non Irradiated; Composite 20 kGy; Composite 40 kGy

It can be seen that all materials follow similar patterns showing basically the same peeks of cristalinity.

3.4. Tensile Tests

Figure 7 shows the diagram for tensile strength versus elongation of neat Evela™ and its irradiated and non-irradiated composites.

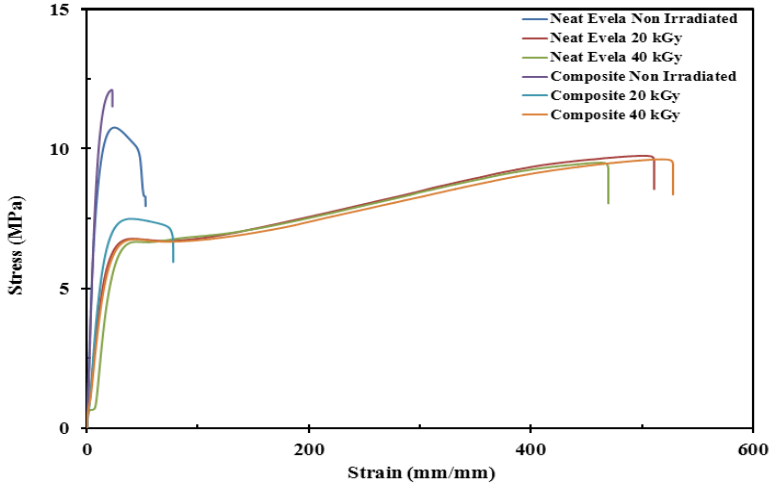

Figure 7: Diagram Stress (MPa) X Strain (mm/mm) for neat Evela and its composites: Neat Evela Non Irradiated; Neat Evela 20 kGy; Neat Evela 40 kGy; Composite Non Irradiated; Composite 20 kGy; Composite 40 kGy

Table 3 presents the results of mechanical tests of neat Evela™ and its irradiated and non-irradiated composites. The results presented are the average values calculated from data obtained for five specimens. These results showed that the addition of 5 % of coffee parchment husk fiber in Evela™ improved the tensile strength at break and its Young modulus. However, when the composite is subjected to radiation its mechanical behavior is worse than the one presented by neat Evela™. The gain in tensile strength at break was around 51% for the N.I composite when compared with the neat N.I. Evela. Results also presented a Young modulus for the N.I. composite with a gain of approximately 380 % when compared with neat Evela N.I.

Table 3: Mechanical test results of neat Evela and its irradiated e non –irradiated composites.

Properties	Neat Evela N.I*	Neat Evela 20 kGy	Neat Evela 40 kGy	Composite N.I*	Composite 20 kGy	Composite 40 kGy
Tensile strength at break (MPa)	6,64 ± 0,44	8,10 ±0,23	8,01 ±0,15	10,03 ±0,22	5,67 ±0,12	5,61 ±0,10
Elongation at break (%)	83,22 ±21,55	517,33 ±19,61	533,51 ±35,87	25,9 ±5,13	59,01 ±14,87	73,94 ±14,41
Young modulus (MPa)	8,00 ±2,04	1,56 ±1,17	1,50 ±0,42	38,73 ±4,30	9,60 ±0,81	7,60 ±0,69

3.5. Sol-Gel Analysis

Table 4 shows the results of sol-gel analysis for the different materials that were studied.

Table 4: Sol-gel analysis for non- irradiated neat Evela; neat Evela 20 kGy; neat Evela 40 kGy; non-irradiated Composite; Composite 20 kGy; Composite 40 kGy

Degree of crosslinking	Neat Evela N.I*	Neat Evela 20 kGy	Neat Evela 40 kGy	Composite N.I*	Composite 20 kGy	Composite 40 kGy
% of crosslinking	18,41±0,08	14,15±0,08	13,53±0,08	17,66±0,02	19,28±0,06	19,31±0,06

4. CONCLUSIONS

The objective of the present work was to evaluate changes in morphological and mechanical properties of a biodegradable of a polymer composite presenting a matrix based on aliphatic-aromatic copolyester/corn starch blend (Evela™) and coffee parchment husk treated with electron-beam radiation. Results showed that the incorporation of 5 % (wt %) of parchment fiber in the polymer matrix resulted in a gain of 51% in tensile strength and approximately 380% for Young modulus. However, when the composites were irradiated mechanical behavior is worse than the neat Evela behavior. Such behavior can be justified because of the low degree of

crosslinking shown by the irradiated samples. Changes in surface morphology were observed indicating the effects of irradiation doses on the material structure. The addition of parchment fiber in the polymer matrix resulted in a rough surface with voids between fiber and matrix. In one hand the addition of fiber resulted in a material with improved tensile strength and its Young modulus, in the other hand irradiation was not able to improve the material mechanical properties studied in this work.

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