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Ionizing radiation influence on the morphological and thermal characteristics of a biocomposite prepared with gelatin and Brazil nut wastes as fiber source

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ABSTRACT

Composites of acrylamide, glycerin, gelatin and Brazil nuts shell fiber have been prepared by the solution/suspension casting technique. The effect of two doses of electron beam (EB) irradiation on the structural properties of the polymeric composites has been investigated by X-ray diffraction, thermogravimetric analysis (TG), scanning electron microscope (SEM), gel content and the swelling behavior. Gel content increased with the radiation dose. The results obtained by X-ray diffraction analysis suggest that crystallinity decreases with increasing dose. The gelatin/fiber composites, before and after irradiation, showed to be poorly stable against thermal decomposition.

1. Introduction

Natural fibers can be classified as vegetables, animals and minerals materials. All the vegetal fibers have cellulose in composition, while the fibers of animal origin consist basically of proteins (Saheb and Jog, 1999).

The structure and properties of biodegradable polymer were studied at several laboratories, using natural proteins or other compounds (Qiu et al., 2004; Jo et al., 2005; Ciesla et al., 2006; Mishra et al., 2008). There are also examples from the literature of the development of new composites materials from biodegradable polymers and lignocellulosic materials Mortain et al. (2004).

Although the Brazil nuts market growths continuously the nut shell fiber residues have no further application. The search for alternative technologies is crucial for the utilization of by-products from Brazil nuts processing, with the aim of developing new products with higher added value. Primary organic components of any nutshells are cellulose, hemicellulose and lignin. This sort of material could be used as reinforcement to enhance polymer mechanical properties, as other natural fibers, piassava fiber for instance, employed with the same objective showed encouraging results (Schuchardt et al., 1995; Moura et al., 2010).

Gelatin is the partially renatured collagen, which consists of triple helical superstructure of extended polypeptide chains. It has been widely used as binder or coating materials in the pharmaceutical, biomedical and photographic industries. Gelatin is an interesting material because when dehydrated it is a partially crystalline polymer and has a relatively low melting point (Daí and Liu, 2006). At approximately 40 °C, gelatin aqueous solutions are in the sol state and form physical, thermoreversible gels on cooling. During gelation, the chains undergo a conformational disorder–order transition and tend to recover the collagen triple-helix structure (Ross-Murphy, 1992; Sobral and Habitante, 2001). Gelatin films with plasticizer have sufficient stability, strength and flexibility to allow them to be used as support and packaging materials.

The radiation induced ionization of a material gives rise to radicals and the subsequent alteration of the structure of the material via radical chemical action. High energy ionizing radiation cannot only cause alterations to the chemical structure of a polymer through mechanisms like cross-linking, chain scission, oxidation, change in the number and nature of double bonds but can also give rise to the presence of trapped charge within the material, the trapping characteristics of which may be influenced by the radiation-induced structural alterations (Kacarevic-Popovic et al., 2004)

Ionizing radiation is able to induce cross-linking of collagen gelatin (Cataldo et al., 2008). Some authors found that the thermal and functional properties of gelatin-based films depend on the type and concentration of the plasticizers being employed (Vanin et al., 2005).

The sol–gel analysis of irradiated polymers allows to estimate important radiation parameters as yield of cross-linking and degradation, gelation dose, etc., and to correlate these with some physical–chemical properties (Rosiak, 1998).

The acknowledged versatility of polymeric materials, which are widely used in the form of plastics, films, coatings and fibers,

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arises from the complex structural organization in these materials. X-ray diffraction (XRD) has long been successfully used to study various aspects of these structures in semicrystalline polymers, which includes thermoplastics, thermoplastic elastomers and liquid crystalline polymers (Murthy, 2004).

The objective of this work was to prepare a hybrid composite using gelatin and waste lignocellulosic Brazil nut fiber and to study the ionizing radiation influence on some characteristics like morphology, sol–gel and thermal behavior.

2. Experimental

2.1. Material

Bovine skin gelatin was kindly donated by GELITA do Brasil Ltda, 240Bloom/6 mesh, lot: LF21658 05 and Art Mono Acrylamide H, from Aratrop Industrial. Glycerin PA ACS, cod. 15375 were provided by Casa Americana de Art. Lab. Ltda (CAAL). Brazil nut shell fiber from the residues disposed by the processing industries of Brazil nuts was provided by Amazon Brazil Nuts.

2.2. Preparation and incorporation of Brazil nut shell fiber in gelatin

Brazil nut shell fiber was washed in distilled water for 24 h and oven dried at 80 ± 2 °C. The dried fiber was reduced to fine powder in a ball mill, with particle sizes ≤ 250 μm. The specimens of gelatin reinforced with 10% of Brazil nut shell fiber were prepared by dissolving glycerin as plasticizer (20% w/w), acrylamide as copolymer (25% w/w) and gelatin (25% w/w) in distilled water in a water bath at 80 °C. After homogenization, the fibers were added under stirring for 30 min.

2.3. Electron-beam irradiation

The prepared samples were irradiated using an electron beam (EB) accelerator (Dynamitron II, Radiation Dynamics Inc.), at room temperature, in the presence of air, dose rate 2.81 kGy/s, energy 1.202 MeV, beam current 0.62 mA, tray speed 6.72 m/min, being 20 and 40 kGy the applied doses. Cellulose triacetate film dosimeters "CTA-FTR-125" from Fuji Photo Film Co. Ltd. were employed. After irradiation, samples were kept in plastic bags and stored in a dry ambiance in the dark.

2.4. Thermogravimetric analysis (TG)

Thermal stability of composites was evaluated using a thermogravimetric analyzer TGA-50 (Shimadzu, Japan). Sample with 5.0 ± 1.0 mg was placed in a platinum cell, under air atmosphere with a flow rate of 50 mL/min. Experiments were conducted from ambient temperature (25 °C) to 600 °C at a heating rate of 10 °C/min.

2.5. X-ray diffraction

Wide-angle X-ray diffraction (XRD) patterns were obtained using a diffractometer Rigaku Denki Co. Ltd., Multiflex model, Cu Kα radiation ($\lambda = 1.5406$ Å), with tube voltage 40 kV; tube current 20 mA; step counter 0.02°; counting time 4 sec (first measurements) and 1 sec (subsequent ones); slits DS ½°, SS ½°, KS 0.3 mm; monochromator graphite. Each diffraction pattern was normalized to make possible the samples comparison from results obtained by using different counting times.

2.6. Sol–gel analysis

The non-irradiated and irradiated composites sol–gel analyses were performed on four weighed samples with 300 ± 10 mg. The gel content of the cross-linked samples was estimated by measuring the insoluble part in dried sample after immersion in solvent (water) for 12 h at boiling point (100 °C). The gel fraction was calculated as follows:

$$\text{GelFraction}\ (\%) = \frac{Wd}{Wi} \times 100\%$$

where Wi = initial weight of the dried sample. Wd = weight of the dried insoluble part of sample after extraction with water.

2.7. Water absorption

The fiber water absorption was determined in accordance with ASTM D 570. Samples were kept in water for a period of 316 h, and the absorption of water was measured every hour for the first 12 h and then every 24 h until constant weight.

2.8. Scanning electron microscopy (SEM)

Observation of morphology was performed using a Philips, XL 30 scanning electron microscope. The samples were freeze fractured under liquid nitrogen; the fractured surface was fixed with carbon, introduced into a vacuum sputter coater until reach the critical point drying and then coated with gold. The analysis was performed on gold sputtered samples using secondary electrons, and with a beam voltage of 15–20 kV.

3. Results and discussion

Mechanical properties improvement due to electron beam treatment was observed in different polymeric systems (Youssef, 2009; Inamura et al., 2010). In the present work, non irradiated sample presented an adhesive, opaque and elastic aspect. By increasing the radiation dose, the adhesive, elastic consistency aspects decreased, and the brightness was intensified.

Gel content by extraction with water (Table 1) was determined. The increase of swelling and gel fraction with the radiation dose suggests a crosslinking arrangement and, consequently hydrogel formation as a result of water absorption, as mentioned elsewhere (Vijayabaskar et al., 2008).

It has been suggested that changes in sorption properties are related to the crystallinity of the material (Chapiro, 1988). Crosslinking and or degradation reactions occurring during irradiation may explain results presented in Table 1.

An attempt of morphological characterization of the composites was done by scanning electron microscopy (Fig. 1). The micrographs show good dispersion of the fiber in the polymeric matrix. Previous work Inamura et al. (2010) showed that the adhesion between lignocellulosic fiber and matrix resulted in a higher tensile strength produce by irradiation. Ismail and Nurdin (1998) showed mechanical properties improvement with the

Table 1
Soluble fraction (Fs), Gel fraction (Fg) content and swelling (%) after EB irradiation.

Dose	Fs (%)	Fg (%)	Swelling (%)
0 kGy	94.3 ± 0,7	5.7 ± 0,7	93.1 ± 10.6
20 kGy	72.3 ± 0.9	27.7 ± 0.9	213.9 ± 9.3
40 kGy	66.1 ± 1.6	33.9 ± 1.6	283.9 ± 3.2

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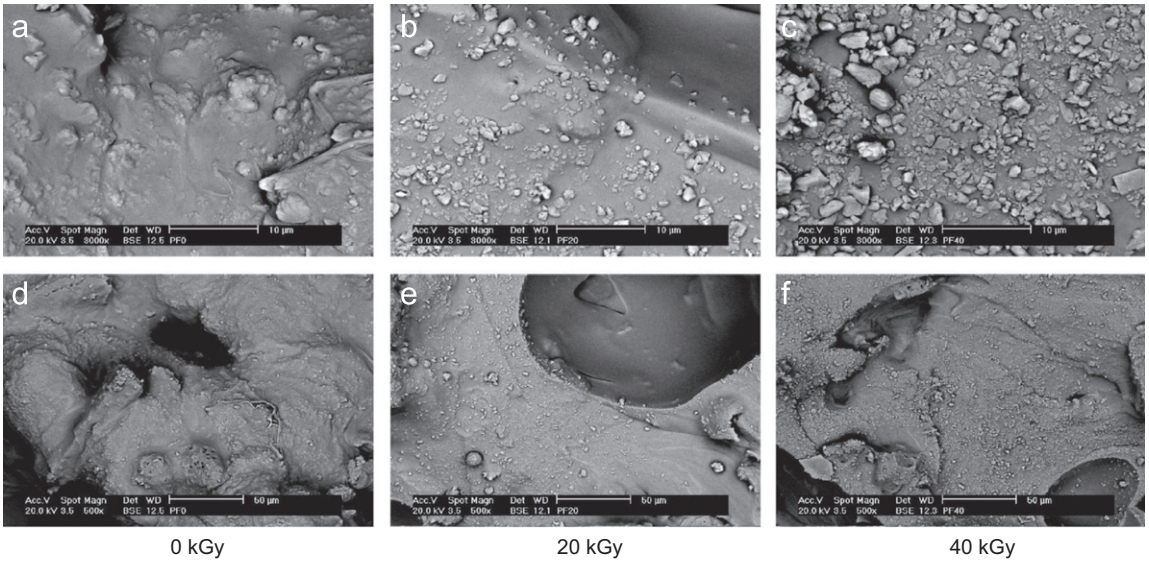

Fig. 1. SEM images for gelatin–Brazil nut shell fiber composite at different radiation doses: (a) non-irradiated (3000 ×); (b) 20 kGy (3000 ×); (c) 40 kGy (3000 ×); (d) non-irradiated (500 ×); (e) 20 kGy (500 ×) and (f) 40 kGy (500 ×).

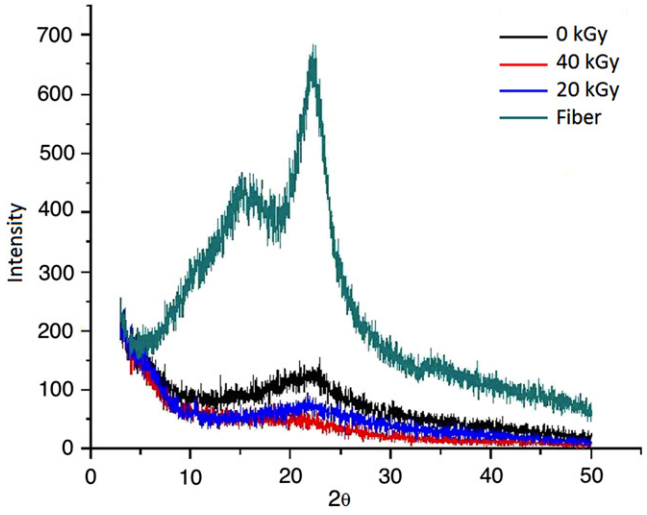

Fig. 2. X-ray Diffraction of Brazil nut shell fiber alone and their composites EB-irradiated at 0, 20 and 40 kGy.

strong adhesion between fiber and matrix. Also Moura et al. (2010) presented a smooth and better interfacial adhesion between EVOH and piassava composite as a consequence of EB irradiation. The applied doses were not sufficient to show strong differences among the irradiated and non-irradiated samples.

The versatility of polymeric materials, widely used in various forms, arises from their complex structural organization. Kantoglu and Guven (2002) had cited that the crystallization of a polymer depends on the ability of the polymer molecules to align themselves to form regular ordered regions and this is achieved to a greater extent with shorter chain molecules where there are less chain entanglements. X-ray diffraction has been successfully used to study various aspects of these structures in semicrystalline polymers. Diffraction patterns of non-irradiated and EB irradiated Brazil nut fiber composites were obtained. Fig. 2 shows the X-ray diffraction intensity of nut shell fiber as a function of diffraction angle, for the control and EB irradiated samples. It is possible to observe that the fiber alone presents the two strongest peaks in the 2θ around 15° and 23° that have been attributed in the

Table 2
TGA of Brazil nut shell fiber composites EB-irradiated at 0, 20 and 40 kGy.

Dose (kGy)	1st transformation region			2nd transformation region		
	0	20	40	0	20	40
Td[a] (°C)	46	44	75	191	180	206
Tmax[b] (°C)	91	86	90	247	240	246
Tf[c] (°C)	141	140	118	288	290	300
WL[d] (%)	28.34	25.93	11.84	56.33	63.97	71.30

[a] Onset degradation temperature.
[b] Temperature of maximum degradation rate.
[c] End degradation temperature.
[d] Peak weight loss.

literature to the presence of lignin, cellulose and hemicellulose (Reddy et al., 2010). Irradiated composites presented very small peaks intensities in the 2θ around 23° in a dispersed scattering characteristic of an amorphous phase. Cited authors observed that high amount of amorphous materials are tarnished and appearing as a broad peak. As already established, radiation cleaves the amorphous region of the cellulose more easily than the crystalline region, together with a reduction in the molecular mass (Driscoll et al., 2009). Structural change from semicrystalline to amorphous, indicating that cross-linking has been achieved with irradiation has been observed in other materials as well (Saion and Teridi, 2006).

The thermal stability or degradation pattern of the products was evaluated by thermogravimetric analysis (TGA). The results (Table 2) show the decomposition profiles of the material characterized basically by two main distinct transformation region of mass loss. The first one is attributed to the loss of adsorbed and bound water, and volatiles evaporation that occurs between ambience temperature and 140 °C, corresponding to a weight loss ranging from 11.8 to 28.3%. Present results are in agreement with Barreto et al. (2003), which observed similar behavior with gelatin products in the first stage, up to ca. 200 °C.

The second transformation region described in Table 2, corresponds to maximum degradation rate which start about 180 °C until 300 °C, corresponding to the greatest weight loss between 56 and 71%, depending of radiation doses. This strong loss until 246 °C, where the loss is maximum pointed to unnoticeable cross-

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linking. Some authors associated the second step with the gelatin chain breakage (helical structure) and peptide bonds rupture in the range of 250–400 °C (Barreto et al., 2003; Peña et al., 2010).

The composite irradiated at 40 kGy presented a gain of about 7.9% in onset degradation temperature compared with control.

4. Conclusion

The results suggest that EB radiation treatment lead to a decrease in the crystallinity of the gelatine–lignocellulosic composites. On the other hand, the sol–gel and TG analyses of the irradiated composites allow us to estimate that crosslinking and degradation took place. Controlling structure and texture by appropriate means and conditions of processing, is mandatory for providing polymer blend or composites with desired physical and mechanical properties.

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