Thermal and morphological behavior of EVOH/Piassava fiber composites treated by electron-beam irradiation

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Abstract

Nowadays, treatment with ionizing radiation, particularly, electron-beam irradiation, is a promising approach to the controllable modification of the properties of polymer- based materials. Due to advantages such as low cost, lightweight, possibility of environmental protection and good mechanical properties when compared with fiberglass reinforcement materials, composites reinforced with natural fibers have been investigated several times. This kind of reinforcement is an option to improve polymers and increase the fields of applications of polymeric composite materials. In the present investigation, the changes in physicochemical, morphological and thermal properties of ethylene vinyl alcohol copolymer (EVOH) and Piassava (Attalea funifera Mart) fibers composites treated by electron-beam irradiation were investigated. EVOH and EVOH/Piassava composites were irradiated with doses up to 200 kGy, using a 1.5 MeV electron beam accelerator, at room temperature, in presence of air. The behavior of the materials after irradiation were investigated using differential scanning calorimetry (DSC), thermogravimetric analysis (TG), x-ray diffraction (XRD), scanning electron microscopy (SEM) and sol-gel analysis.

Keywords: composites, piassava fiber, EVOH, polymer composites, electron-beam irradiation

1. Introduction

Treatment with ionizing radiation, particularly electron-beam irradiation, is a promising approach to the controllable modification of the properties of polymer materials. The production of free radicals, as an ionizing irradiation effect on polymers, can lead to degradation and/or cross-linking process, causing changes in their original mechanical, thermal and barrier properties (Buchalla, 1993). In recent years, electron-beam irradiation has been efficiently applied to promote cross-linking and scission of the polymeric chains to modify the properties of different polymers for versatile applications. Ethylene-vinyl alcohol (EVOH) copolymers are a family of resins with excellent gas-barrier properties and

their permeability depends on the copolymerization ratio of ethylene and vinyl alcohol. So EVOH is widely used in various fields such as food packaging and gasoline tanks due to their outstanding gas barrier properties to oxygen and organic compounds (Cabedo, 2006; Kucukpinar, 2004). EVOH presents a considerable chemical resistance, high transparency and easy processability on a wide range of conventional coextrusion processing. However, EVOH is very sensitive to moisture and its gas barrier ability deteriorates in high relative humidity conditions. Besides the increase in the permeability values of EVOH due to water absorption at high relative humidity conditions, its thermal and mechanical properties are also affected (Armstrong, 2004; Kim, 2004; Kucukpinar, 2004; Mokwena, 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. This fiber has higher lignin content (around 48%) than any of the other common lignocellulosic fiber. This could be responsible for its inherent flexural rigidity and waterproof resistance. The main use of these fibers is for industrial and domestic brooms, industrial brushes, ropes and baskets, carpets and roofs. It is estimated that around 30% of the fiber is disposed as residue by the transformation industries, before production (D'Almeida, 2006; Satyanarayna, 2007; Schuchardt, 1995). This study presents the physicochemical, morphological and thermal behavior of EVOH resin due to piassava fiber residues addition and electron-beam radiation treatment.

2. Material and Methods

2.1. Material

The materials used in this study were EVOH resin containing 38 mol % ethylene (commercial grade by EVAL Company of America) and piassava fiber residues disposed by the transformation industry.

2.2. Preparation and incorporation of piassava fiber in EVOH resin

In order to remove impurities, the piassava fiber residues were washed in distilled water for 24 h. The fiber was then dried at 80 ± 2 º C for 24 h in a circulating air oven. The dry fibers were reduced to fine powder, with particle sizes equal to or lower than 125 mm by using ball mills and then were again dried at 80 ± 2 º C for 24 h to reduce the moisture content of less than 2 %. EVOH resin reinforced with 5 % (Composite 5 %) and 10 % (Composite 10 %) piassava fiber was obtained by mixing 5 and 10 parts of fiber with 95 and 90 parts of EVOH resin (in weight), respectively, using a double screw extruder machine "extruder ZSK 18 Megalab" made by Coperion Werner & Pfleiderer GmbH & Co. KG.

2.3. Electron-beam irradiation

EVOH resin and EVOH resin reinforced with piassava fibers (EVOH-Composites) were irradiated up to 200 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 22.4 kGy/s. Irradiation doses were measured using cellulose triacetate film dosimeters ''CTA-FTR-125'' from Fuji Photo Film Co. Ltd.

2.4. Thermogravimetric Analysis (TG)

Thermogravimetric analyses (TG) were carried out using TA Instruments from room temperature to 800 °C at a heating rate of 10 ºC/min (in an oxygen atmosphere). A sample with 3.0 ± 1.0 mg of the irradiated and non-irradiated materials was weighed.

2.5. Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) analyses were carried out using a Mettler Toledo DSC 822e from 30 to 300°C at a heating rate of 5°C/min under nitrogen atmosphere. DSC analyses of the materials were performed on four samples of the irradiated and non-irradiated materials.

2.6. X-Rays Diffraction (XRD)

XRD patterns of non-irradiated and irradiated samples with 100 and 200 kGy 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°. Each diffraction pattern was normalized to enable the samples comparison from results obtained by using different counting times.

2.7. 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.

2.8. Sol-Gel Analysis

The sol-gel analyses of the materials were performed on four weighed samples with 300 ± 10 mg of the irradiated and non-irradiated materials. The gel content of the cross-linked samples was estimated by measuring its insoluble part in dried sample after immersion in solvent (acetic acid) for 12 hours at boiling point solvent (115 ºC) .

3. Results and Discussion

3. 1. Thermogravimetric Analysis (TG)

TG results in Fig. 1 illustrate the decomposition behavior of the non-irradiated materials derivatives. All the materials showed a weight loss of 97 % ± 1 %. EVOH non-irradiated and EVOH at 100 kGy decomposed in two steps, the first step in 382 °C and the other step in 468 °C for both materials. Piassava fiber incorporation increased its decomposition temperature. It is noteworthy to mention that the second decomposition temperature at 468 ^{o}C for EVOH at 100 kGy is drastically decreased in case of composites. This suggests that the composites are more thermally stable then the EVOH alone. TG

results are presented in Table I. It shows the effects of electron-beam radiation doses in the onset degradation temperature and EVOH`s weight loss.

Figure 1. Normalized derivative of TG scan of non-irradiated EVOH and its composites

Table I. Onset degradation temperature of EVOH and EVOH composites as a function of electron-beam radiation dose

3.2. Differential Scanning Calorimetry (DSC)

The results of DSC analysis showed that there were no significant differences ($p < 0.05$) for melting temperature (Tm) for both irradiated and non-irradiated EVOH and composites. The results of DSC analysis for average values of melting enthalpy of the materials studied are given in Table II. The standard deviation for DSC analysis was less than 10 % for all tests. As it can be seen, there were significant increases ($p < 0.05$) at of irradiated Composite 5 % (ca. 9% for 100 kGy; ca. 6 % for 200 kGy) and an increase of Composite 10 % with 200 kGy (ca. 4 %), compared with non-irradiated Composites. On the other hand, there was no significant change on EVOH after irradiation. The crystallinity percentage calculated from the DSC thermograms of EVOH and EVOH composites were calculated by the following equations (Lima, 2008; Dweiri and Azhari, 2004):

i) The crystallinity percentage (X_e) of EVOH samples:

$$X_e = \frac{\Delta\, Hm}{\Delta\, H^0 m} \times 100$$

where:
Δ Hm is the melting enthalpy of the irradiated or non-irradiated EVOH sample
$\Delta\, H^0 m$ is the melting enthalpy of the EVOH sample assuming 100% crystallinity, 169.2 J/g for EVOH 38%

ii) The crystallinity percentage (X_c) of EVOH composites were calculated by the following equation:

$$X_c = \frac{\Delta\, Hm \times 100}{\Delta\, H^0 m \times w}$$

where:
$\Delta\, Hm$ is the melting enthalpy of the EVOH Composites sample
$\Delta\, H^0 m$ is the melting enthalpy of the EVOH sample assuming 100 % crystallinity, 169.2 J/g for EVOH 38 %.
w is the polymer mass fraction in the composite.

The results of crystallinity percentage as a function of electron-beam dose ( ) and crystallinity percentage between composites and EVOH are also shown in Table II. As it can be seen, the crystallinity percentage showed a decrease of ca. 8 % for non-irradiated composite materials when compared with EVOH, and ca. 4 and 7 %, at 100 and 200 kGy, respectively. The differences of piassava concentrations do not present changes between the composites. All irradiated materials had an increase in crystallinity percentage when compared with respective non-irradiated materials.

Table II. Crystallinity percentage of EVOH and its composites as a function of electron-beam radiation dose

These results are very important because the increase in the irradiated materials crystallinity can show a gain in barrier properties and, consequently, a reduction of their water absorption rate at high relative humidity conditions. An increase in crystallinity reduces the mobility of the amorphous chains, leading to more efficient molecular orientation and to significant fall in permeation rates, since a rise in molecular organization makes the diffusivity of the liquid or gas more difficult. Considering that there is a direct influence between EVOH water absorption rate, in its permeability, thermal and mechanical properties (Kucukpinar, 2004), these results can contribute to a better thermal and mechanical response of the materials at high relative humidity conditions when compared with EVOH.

3.3. X-Rays Diffraction (XRD)

X-ray diffractograms of EVOH and its irradiated and non-irradiated composites, are presented in Fig. 2. As it can be seen, there are two main peaks in 2 Theta, 20.54 (101) and 22.30 (200).

Figure 2. XRD patterns of, irradiated and non-irradiated, EVOH and its composites

As it can be seen, there was a slight shift of diffraction peaks with the addition of EVOH fiber, as well as an increase in width and a reduction of the peaks intensities, which suggests that the addition of piassava fiber prevents the crystallization of EVOH, and as result, a decrease in its crystallinity (Hu, 2009; Lei, 2007).

3.4. Scanning Electron Microscopy (SEM)

SEM micrographs for EVOH and its composites at the electron-beam radiation dose range studied in this work are shown in Fig.3. The non-irradiated and irradiated EVOH micrographs revealed rough, dense and compact cryofractured surface morphologies. However, EVOH at 100 and 200 kGy exhibited a more brittle aspect than the non-irradiated EVOH, which can indicate that a more important degradation by irradiation took place. Comparing EVOH with composites 5 and 10 %, it can be seen that there was a large difference between the crystalline form of EVOH and the composites. It means that the order of macromolecules arrangement of EVOH was changed by piassava incorporation.

Figure 3. Scanning Electron Microscopy (SEM) micrographs for non-irradiated (0 kGy) and irradiated (with 100 and 200 kGy) EVOH and its composites.

3.5. Sol-Gel Analysis

At the electron-beam radiation dose range studied in this work and after extraction with solvent, EVOH composite 5 % and composite 10 % samples only presented gel content at 200 kGy (ca. 98 % of gel content). These results show that electron-beam radiation for the doses applied in this work was enough for cross-linking the materials at 200 kGy.

4. Conclusions

The incorporation of piassava fibers promoted a reduction of cristallinity as observed in DSC analysis and confirmed by XRD. However, it was observed that the use of ionizing radiation increased the crystallinity percentage, when compared to non-irradiated materials. The non-irradiated and irradiated EVOH micrographs revealed rough, dense and compact cryofractured surface morphologies, but as the radiation dose increased, the surface exhibited a more brittle aspect, which can indicate that a more important degradation by irradiation took place. The results showed some differences between the crystalline form of EVOH and composites 5 and 10 %. It means that the order of macromolecules arrangement of EVOH was changed by piassava incorporation. These results are very important, since that could lead to the obtaining of materials with better barrier properties, lower water absorption and more stable thermal and mechanical properties in high relative humidity conditions when compared with EVOH resin.

Acknowledgements

The authors wish to thank A. Schulman Brazil to provide the support for this work.

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