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Gamma-irradiation effects on poly(ethylene-co-vinyl acetate) (EVA)

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Abstract

Polymer materials (plastics and elastomers) are widely used in applications involving ionizing radiation environmental exposure. Such rush in service conditions might promote significant material degradation. Here, we investigated gamma irradiation effects on poly(ethylene-co-vinyl acetate) (EVA) (25 and 40 wt% vinyl acetate - VA) in the dose range of 5 – 30 kGy. This range is suitable for applications in food preservation and matches expected absorbed doses for nuclear power plants electrical cables and wires. EVA copolymers with 40 or 25 wt% VA predominantly underwent crosslinking effects promoted by gamma irradiation at dose of 10 kGy. Additional irradiation of EVA (25% VA) up to 30 kGy did not promote further alterations. Refractive index or thermal degradation under nitrogen atmosphere remained practically unaltered after gamma irradiation. Our findings suggest that EVA is a suitable material for irradiated food packaging films, and in electrical cable jacketing materials exposed to gamma radiation.

Keywords: *EVA, gamma radiation, thermal analysis, FTIR, refractive index.*

Data Availability: Research data is available upon request from the corresponding author.

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1. Introduction

Polymer materials (plastics and elastomers) are widely used in applications involving ionizing radiation environmental exposure (gamma, electron beam, etc.)[1]. Polymer material irradiation might significantly promote changes in their physicochemical and mechanical properties[2]. The interaction of the radiation with polymer structure is a complex and random process, which results in formation of ionizing and excited molecules. Free radicals produced by these processes might modify physical properties of the material. In high-energy radiation environments, polymer materials should withstand ionizing radiation for long time and yet, retaining important features, such as strength, extensibility, degradation stability, dimensional stability, electrical insulation, etc[3-5].

Poly(ethylene-co-vinyl acetate) (EVA) has a broad range of industrial applications[6]. EVA is a copolymer made up of polyethylene and poly(vinyl acetate) segments. The random incorporation of the vinyl acetate (VA) units in EVA progressively hinders the ability of the polymer to crystallize, thus, in a vinyl acetate level of 50 wt% EVA copolymers are amorphous materials[6]. In fact, all properties of EVA are strongly influenced by the percentage of VA. EVA has been widely used as a material of the high-barrier family due to its low permeability to gases and organic vapors[7]. EVA is used in green-houses covering films[8], food packaging applications[9], controlled drug release[10], electrical cable jacketing materials[11], among other applications. Some EVA industrial applications can result in exposition to ionizing irradiation, such as in packages of food irradiated for preservation[9], or in electrical cable jacketing used in nuclear power plants (NPPs)[11]. In general, EVA is eligible for uses in ionizing radiation environments up to absorbed dose of 100 kGy without significant alterations in its physical properties[1,12].

In this work, we investigated radiolytic effects on EVA (25 and 40 wt% VA). The samples were gamma irradiated in dose range of 5 – 30 kGy. This range is suitable for applications in food preservation and matches expected absorbed doses for NNPs electrical cables and wires. Also, EVA was gamma irradiated in higher doses of 500 and 1000 kGy in order to investigate the influence of the irradiation on oxidative process at thermal properties.

2. Materials and Methods

2.1 Material

In this work were used poly(ethylene-co-vinyl acetate) (EVA) commercial (analytical grade, Sigma Aldrich, 40 wt% VA; average-number molar mass, Mn, of ~18 kg/

mol; average-weight molar mass, Mw, of ~ 62 kg/mol, and density of ~ 0.965 g/mL (EVA40), or 25 wt% VA; Mn ~ 17 kg/mol, and density of ~ 0.948 g/mL (EVA25). EVA films (~ 0.1 mm in thickness) were solvent cast in concentration of 0.1 g/mL using methyl ethyl ketone (MEK, analytical grade Merk) as solvent, by slow evaporation in air at room temperature.

2.2 Gamma irradiation of samples

The samples were gamma irradiated by using a non-attenuated Co-60 source (Gammacell GC220 Excel irradiator - MDS Nordion, Canada). Irradiation doses were of 5, 10, 15, 20, 30, 500 and 1000 kGy in air, dose rate of ~ 2.96 kGy/h (dose rate uncertainty = 0.018×10^{-6} kGy/h, with k = 1 coverage factor) at room temperature (~ 300 K).

2.3 Viscosity-average molecular mass (Mv) determination

Samples viscosity was calculated from the relative viscosity ($\eta_{rel} = \nu/\nu_0 \sim t/t_0$), where ν and ν_0 are the cinematic viscosities of the polymer solution and the solvent, respectively, and t and t_0 are the solution and solvent tetrahydrofuran (THF) flow times, respectively, which result in the cinematic viscosity measurement. These measurements were carried out with an Ostwald-type capillary (75 mm) viscometer immersed in a thermal bath at 20.0 ± 0.1 °C. After obtaining the relative viscosity, the specific viscosity ($\eta_{sp} = \eta_{rel} - 1$), and the reduced viscosity ($\eta_{red} = \eta_{sp}/C$) were calculated. *C* is the solutions concentration of the (0.2 g/dL). The intrinsic viscosity was determined by the Solomon-Ciuta Equation 1[13], which has validity to Huggins constant $K_H \leq 0.5$[13].

$$[\eta] = \left(\frac{1}{C}\right)\sqrt{2\left(\eta_{sp} - \ln \eta_{rel}\right)} \quad (1)$$

The viscosity-average molecular mass, Mv, was obtained by means of Mark-Houwink relation[13]:

$$[\eta] = K.M_v^a \quad (2)$$

where the constants *K* and *a* are 7.78×10^{-3} (dL/g) and 0.44, respectively for THF-EVA system at 20 °C[14]. All viscosity experiments were performed in quintuplicate.

2.4 Refractive index measurements (RI)

RI was evaluated by an Abbe Hedwig-Dransfeld Allce (40-d-80637, OPTECH) refractometer at ~ 22 °C with alpha-bromonaphthalene as contact liquid.

2.5 Thermogravimetry analysis (TGA)

Termogravimetry Analysis (TGA) (Simultaneous TGA/DSC2 STARe thermoanalyzer- Mettler Toledo-Switzerland) on samples was carried out in 70 microliter aluminum oxide crucibles, under N_2 (~99.5%) atmosphere (20 mL.min^{-1} flux), heating rate of 10 °C.min^{-1} in the 30-600 °C temperature range.

2.6 Fourier transform infrared spectroscopy analysis (FTIR)

FTIR analyses were performed in a FTIR-4600 Jasco Spectrometer (Japan) equipped with an ZnSe crystal Attenuated Total Reflection (ATR ProOne) accessory. Experiments were run in 32 scans, at 4 cm^{-1} resolution, in the 4000 - 400 cm^{-1} wavenumber range, under normal atmosphere.

2.7 Contact angle measurement

Sessile drop water contact angle measurements were carried out using a pocket goniometer (model PG-2, Fibro System AB), in quintuplicate, with 10 µL of distilled water at room temperature (~ 300 K).

3. Results and Discussions

3.1 Viscosity-average molecular mass (Mv)

The viscosity-average molecular mass (Mv) was determined through the Mark-Houwink relationship (Equation 2). Here, $K_H \sim 0.4$ was determined for both copolymers EVA40 and EVA25, by using Huggins method[13], allowing to use the Solomon-Ciuta Equation 1 to calculate the intrinsic viscosity [η]. Figure 1 shows viscosity-average molecular mass (Mv) versus absorbed dose for EVA40 and EVA25. When EVA is gamma irradiated in 10 kGy dose, Mv increases significantly for both EVA40 and EVA25, indicating crosslinking effect in the molecular structure of EVA, according to mechanism shown in Figure 2. At

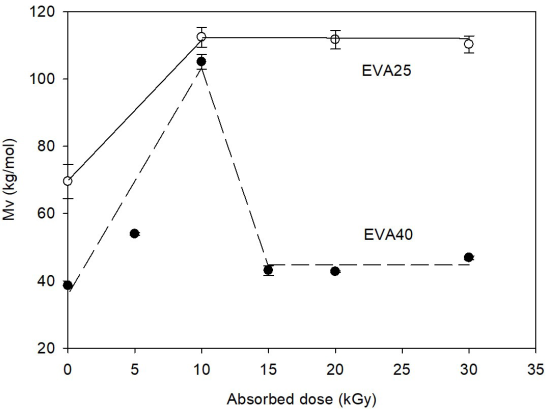

Figure 1. Relationship viscosity-average molecular mass (Mv) with absorbed dose on EVA40 and EVA25.

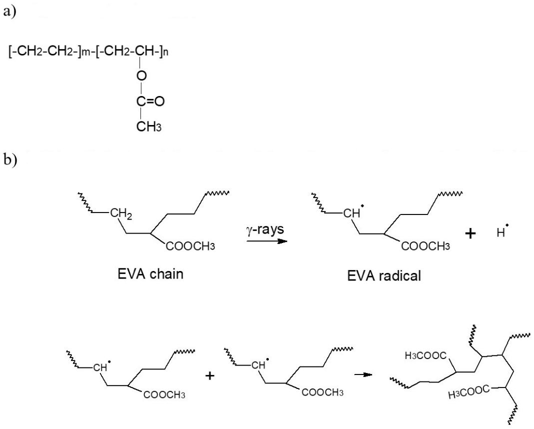

Figure 2. EVA: (a) chemical structure, (b) EVA radiolysis and formation of three-dimensional network (crosslinking).

first step hydrogen bond scissions take place, following by hydrogen abstraction of a very close segment of another PE molecule from EVA, finalized by combination of two very large molecules. However, above 15 kGy, EVA40 molar mass decreases to original value. Here, at 15 – 30 kGy dose range, there is no evidence of predominance between main chain scission and crosslinking induced by ionizing radiation, since no significant modification occur on the molar mass. On the other hand, EVA25 maintain the molar mass 60% above the original molar mass. EVA25 presents higher ethylene content that contribute for predominance of crosslinking against main chain scissions effect, even at air atmosphere under gamma irradiation. It is worth mentioning that gamma-irradiated polyethylene (PE) undergoes predominantly crosslinking at inert atmosphere, however, oxygen degradation take place at air atmosphere[15].

3.2 Thermogravimetry analysis (TGA)

Figure 3 shows the thermograms of EVA40 and EVA25 at different gamma irradiation doses and atmosphere conditions. Gamma irradiated (1000 kGy) and unirradiated (0 kGy) EVA40 and EVA25, under N_2, thermally degradation in two steps: a) mass loss in the range of 300 – 370 °C is assigned to the degradation of vinyl acetate and formation of acetic acid, and b) mass loss in the range of 380 – 500 °C corresponds to the degradation of the polymer main chain , also observed by Mai and Yu[16].

Table 1 shows the thermal degradation parameters (Tonset, Tmax) for EVA40 and EVA 25 at different gamma irradiation doses and atmosphere conditions. The maximum-rate thermal degradation temperature (Tmax) was obtained by the inflexion point of TGA plot for each thermal degradation step. Tonset is the initial thermal degradation point of the copolymers. It can be noted that gamma irradiation did not influence these thermal parameters on both copolymers, EVA40 and EVA25, under N_2, even at high gamma irradiation (1000 kGy). Çopuroğlu and Şen[17] also did not observe significantly chance on thermogravimetry properties in gamma-irradiated EVA (VA 13 wt%) at range doses of 25 – 400 kGy. On the other hand, oxygen exerts a strong influence on the behavior of the thermal degradation of the copolymers, promoting decrease in Tonset and Tmax parameters of EVA40 and EVA25. In addition, a combined effect of oxidative degradation and gamma irradiation was identified when gamma irradiated (500 kGy) EVA (40 and 25) was thermally degraded under O_2 atmosphere, see Figure 2. Results indicate that radiolysis accelerate copolymers oxidative processes.

3.3 Fourier transform infrared (FTIR) spectroscopy analysis

FTIR spectrum of gamma-irradiated EVA40 (Figure 4) shows the absorption bands associated to ethylene and acetate groups existing into polymer structure. The bands 2918 cm^{-1} and 2850 cm^{-1} were assigned to C-H stretch

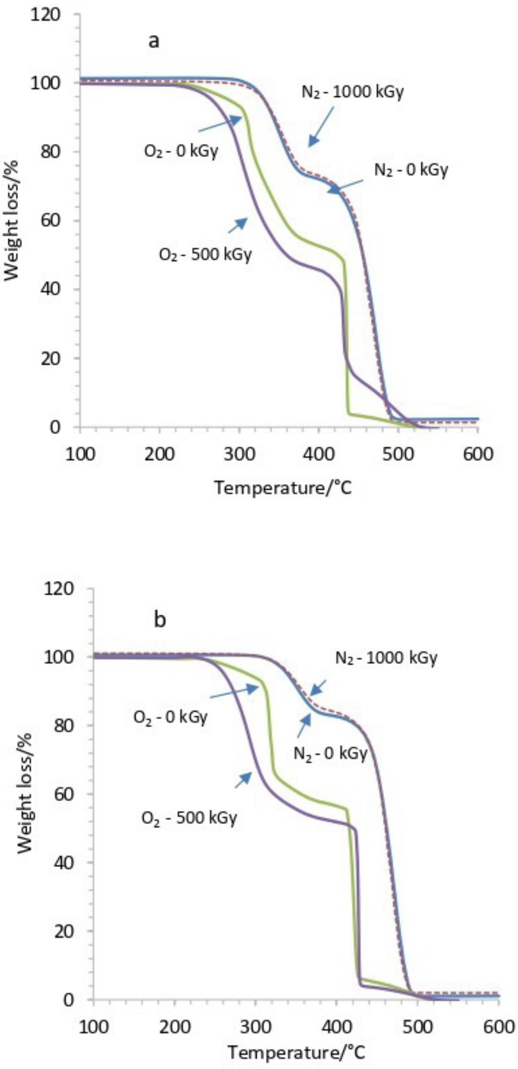

Figure 3. Thermograms of (a) EVA40 and (b) EVA25. At gamma irradiation and atmosphere conditions of N_2 (0 and 1000 kGy) and O_2 (0 and 500 kGy).

Table 1. Thermal degradation parameters (Tonset, Tmax) for EVA40 and EVA25 at different gamma irradiation doses and atmosphere conditions.

Dose (kGy)	Atmosp.	Tonset (°C)		Tmax (°C)			
				EVA40		EVA25	
		EVA40	EVA25	1^a Step	2^a Step	1^a Step	2^a Step
0	N_2	325.59	327.69	350.83	472.26	353.87	468.01
	O_2	310.63	320.65	322.51	558.11	340.52	464.03
500	O_2	284.08	275.49	310.53	459.52	307.04	562.78
1000	N_2	327.65	330.29	356.31	468.95	354.84	462.68

in methylene, and methyl groups, respectively, while the carbonyl group C=O stretching was present in the 1733 cm^{-1} band The bands at 1233 cm^{-1} and 1020 cm^{-1} were assigned to acetate C-O groups stretching , and the 1463 cm^{-1} band was assigned to CH_2 and CH_3 stretching vibrations[18,19].

The radiolysis of EVA40 at doses of 5 and 10 kGy promotes observable changes in the CH_2 stretching band at 1463 cm^{-1} (Figure 4), which is indicative of alterations in the CH_2 group chemical environment. Additionally, molar mass changes (Figure 1) suggest radiation-induced crosslinking in the polymer.

Table 2 shows methylene index, which represents an indicative of alterations in the CH_2 group induced by gamma-irradiation on EVA40. This parameter was calculated by the ratio between CH_2 (1463 cm^{-1}) and CO (1233 cm^{-1}) bands maximum transmittance values. This last did not undergo any significant changes promoted by gamma irradiation.

EVA25 spectra showed alterations on transmittance bands only at absorbed dose of 30 kGy, as displayed on Figure 5. These results corroborate changes observed in viscosity experiments, in which the molar mass increased in dose range of 10 - 30 kGy (Figure 1) due to the crosslinking effects on molecular structure.

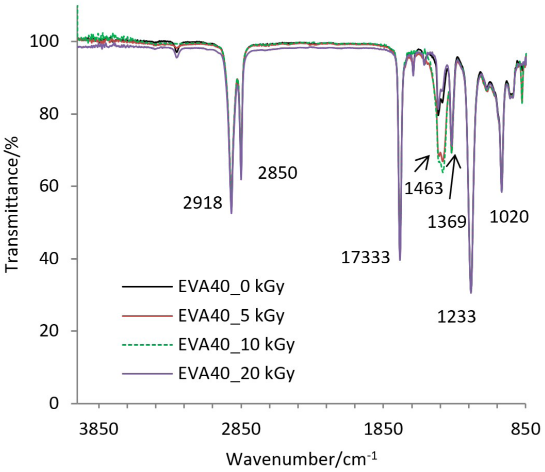

Figure 4. FTIR spectra of EVA40 in different absorbed doses.

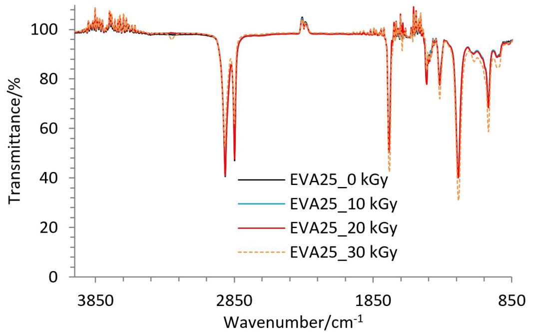

Figure 5. FTIR spectra of EVA25 in different absorbed doses.

3.4 Contact angle measurements

Table 3 shows contact angle results of gamma-irradiated EVA40 and EVA25. Gamma-irradiated EVA40 presented similar values of contact angles on range of 87° – 89° at dose of 0 – 30 kGy, featuring EVA40 as a hydrophobic material (contact angle < 90°). Gamma-irradiated EVA25 also showed hydrophobic features at all absorbed doses. However, it is also worth noting that contact angle increased at ~10° at 10 kGy and 30 kGy. Nevertheless, it can be observed that gamma irradiation did not significantly change the hydrophobic features of EVA. It is important to highlight that materials used in applications of food packaging and electrical-cable jackets, as EVA, need to have hydrophobic properties.

3.5 Refractive index measurements (RI)

By analyzing the refractive index data from Table 4 can be observed that significant changes did not take place in both gamma-irradiated EVA40 and EVA25 copolymers. In contrast, Mandani and El-Sayed[20] observed crosslinking effects on EVA9 (vinyl acetate of 9 wt%) that promoted significant alterations on refractive index in dose range of 10 – 50 kGy. Likely, vinyl-acetate content above 25 wt% into EVA promotes stabilization on this optical property.

Table 2. Methylene index for EVA40 in different doses.

Dose (kGy)	$CH_{2(1463)}/CO_{(1233)}$
0	0.28
5	0.41
10	0.47
20	0.25

Table 3. Contact angles for EVA25 and EVA40 in different doses.

Copolymer	Dose (kGy)	Contact angle (°)
EVA25	0	76.98 ± 1.64
	10	85.82 ± 1.47
	20	77.85 ± 1.76
	30	86.55 ± 1.68
EVA40	0	87.18 ± 0.23
	10	86.47 ± 1.84
	15	88.03 ± 0,92
	20	81.52 ± 2.90
	30	89.34 ± 0.17

Table 4. Refractive index for EVA25 and EVA40 in different doses.

Copolymer	Dose (kGy)	Refractive index
EVA25	0	1.652 ± 0.005
	10	1.654 ± 0.005
	20	1.655 ± 0.002
	30	1.656 ± 0.001
EVA40	0	1.653 ± 0.002
	5	1.645 ± 0.003
	15	1.654 ± 0.003
	20	1.642 ± 0.003
	30	1.656 ± 0.001

4. Conclusions

Poly(ethylene-co-vinyl acetate) (EVA) copolymer with 40 or 25 wt% of vinyl acetate (EVA40, and EVA25, respectively) predominantly underwent crosslinking effects promoted by gamma irradiation at dose of 10 kGy. EVA40 viscometry molar mass (Mv) increased from ~ 40 to ~ 105 kg/mol, while EVA25 Mv increased from ~70 to ~110 kg/ml. Gamma irradiation EVA40, in 15 - 20 kGy doses, remains the original molar mass.

Thermal degradation under N_2 and refractive index properties of EVA did not undergo significant radiation-induced changes. Gamma irradiation did not significantly change the hydrophobic features of EVA. Combined effect of oxidative degradation and gamma irradiation was observed when gamma-irradiated (500 kGy) EVA (40 and 25) was thermally degraded under O_2 atmosphere. Thus, radiolysis accelerates oxidative processes in the copolymers.

Our findings suggest that EVA40 or EVA25 are eligible copolymers for uses in suitable material for irradiated food packaging films, and in electrical cable jacketing materials installed in nuclear facilities.

5. Author's Contribution

- **Conceptualization** – Maria Thalita Siqueira de Medeiros; Patricia Araújo; Elmo Silvano de Araújo.
- **Data curation** – Maria Thalita Siqueira de Medeiros; Thaíses Lima; Patricia Araújo; Elmo Silvano de Araújo.
- **Formal analysis** – Maria Thalita Siqueira de Medeiros; Thaíses Lima; Elmo Silvano de Araújo.
- **Funding acquisition -** Patricia Araújo; Elmo Silvano de Araújo.
- **Investigation** – Maria Thalita Siqueira de Medeiros; Patricia Araújo; Elmo Silvano de Araújo.
- **Methodology** – Maria Thalita Siqueira de Medeiros; Thaíses Lima; Patricia Araújo; Elmo Silvano de Araújo.
- **Project administration** – Patricia Araújo; Elmo Silvano de Araújo.
- **Resources** – Maria Thalita Siqueira de Medeiros; Patricia Araújo; Elmo Silvano de Araújo.
- **Software** – NA.
- **Supervision** – Patricia Araújo; Elmo Silvano de Araújo.
- **Validation** – NA.
- **Visualization** – NA.
- **Writing – original draft** – Maria Thalita Siqueira de Medeiros; Patricia Araújo; Elmo Silvano de Araújo.
- **Writing – review & editing** – Maria Thalita Siqueira de Medeiros; Thaíses Lima; Patricia Araújo; Elmo Silvano de Araújo.

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