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Impact of Electron Beam on PBAT/PLA (Ecovio) Bags by Raman spectroscopy and Thermogravimetry

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Abstract: Biodegradable polymers are compounds derived from renewable sources, such as biomass and organic components. They emerge as a promising alternative to reduce the environmental impact of traditional petroleum-derived polymers. These polymers have physico-chemical characteristics that allow faster degradation compared to conventional polymers, significantly reducing the time of residence in the soil and its negative impacts on the environment. Ecovio®, a sustainable and advantageous alternative, is composed of an aliphatic-aromatic copolymer Ecoflex® and polylactic acid (PLA), both biodegradable. Its formulation includes non-stick and slip agents to facilitate the processing of extrusion films. Romapack produces biodegradable bags with 55% PBAT (poly (butylenoadipate co-terephthalate)) and 45% PLA (polylactic acid) (Ecovio). In partnership with IPEN, these bags were irradiated with ionizing radiation of electron beams at absorbed doses of 25, 50 and 100 kGy to investigate possible improvements in their structure and time of degradation. Raman and thermogravimetric spectroscopy analyses were performed to observe possible changes in the polymeric chains of Ecovio bags at different doses. Thermogravimetry showed the variation of mass loss in relation to temperature and/or time, revealing improvements in relation to thermal stability. The results indicate that PLA(polylactic acid) is more susceptible to degradation compared with PBAT(poly(butylene adipate co-terephthalate)). Ionizing radiation has modified the properties of Ecovio® and expanded its range of applications, this contributes to the creation of more environmentally friendly products, as degradation contributes to their biodegradability.

Keywords: Ecovio®, biodegradable polymers, ionizing radiation, biodegradation.

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Impactos da irradiação por feixe de elétrons em sacolas de PBAT/PLA (Ecovio) observados por espectroscopia Raman e Termogravimetria

Resumo: Os polímeros biodegradáveis são compostos derivados de fontes renováveis, como biomassa e componentes orgânicos. Eles surgem como uma alternativa promissora para reduzir o impacto ambiental dos polímeros tradicionais derivados do petróleo. Esses polímeros possuem características físico-químicas que permitem degradação mais rápida em comparação com os polímeros convencionais, reduzindo significativamente o tempo de permanência no solo e seus impactos negativos no meio ambiente. O Ecovio®, alternativa sustentável e vantajosa, é composto por um copolímero alifático-aromático Ecoflex® e ácido polilático (PLA), ambos biodegradáveis. Sua formulação inclui agentes antiaderentes e deslizantes para facilitar o processamento de extrusão de filmes. A Romapack, produz sacolas biodegradáveis com 55% de PBAT (poli (butilenoadipato co-tereftalato)) e 45% de PLA (ácido polilático) (Ecovio). Em parceria com o IPEN, essas sacolas foram irradiadas com radição ionizante de feixes de elétrons nas doses absorvidas de radiação de 25, 50 e 100 kGy para investigar possíveis melhorias na sua estrutura e no tempo de degração. As análises por espectroscopia Raman e Termogravimetria foram realizadas para observar possíveis mudanças nas cadeias poliméricas das sacolas de Ecovio em diferentes doses. A termogravimetria mostrou a variação de perda de massa em relação à temperatura e/ou tempo, revelando melhorias em relação à estabilidade térmica. Os resultados indicam que o PLA(ácido polilático) é mais suscetível a degradação em comparação com o PBAT(poli (butilenoadipato co-tereftalato)). A radiação ionizante modificou as propriedades do Ecovio® e expandiu a sua gama de aplicações, isso contribui para a criação de produtos mais ecológicos, pois a degradação contribui para a sua biodegradabilidade.

Palavras-chave: Ecovio®, polímeros biodegradáveis, radiação ionizante, biodegradação.

1. INTRODUCTION

For many years plastics bags have been produced with petroleum derivatives films, such as, polyethylene, polystyrene, polypropylene. In order to reduce plastic discharge, it had been developed a series of additives to improve properties like durability, mechanical and thermal resistance of plastics products, that gives longer life due to several ways for reuse. On the hand, taking into account environmental issues, these polymers need long time for degradation [1]. Then, alternative technologies have been developed to decrease degradation time and to produce polymers from renewable sources [1].

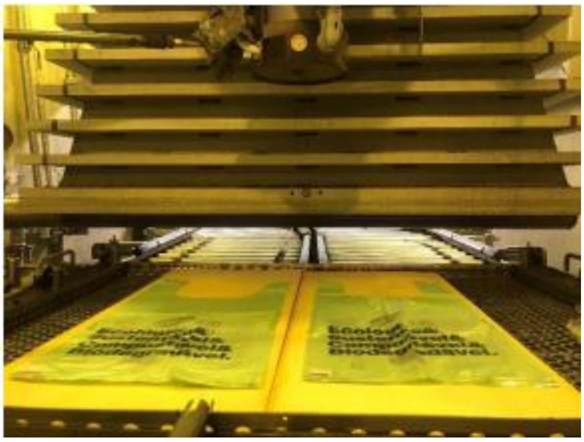
Biodegradable polymers are compounds derived from renewable sources such as biomass and organic components [2]. Biodegradable polymers have physicochemical characteristics that allow a faster degradation compared to conventional polymers. They are able to suffer decomposition by microorganisms under natural conditions, such as composting or aquatic environments, reducing significantly the time of permanence in the environment and its negative impacts to the soil [2]. This differentiates them from conventional polymers, which can persist for hundreds of years in the environment. Therefore, they appear as a promising alternative to reduce the environmental impact of traditional polymers derived from petroleum. Ecovio®, being a sustainable and advantageous alternative, is composed of biodegradable aliphatic-aromatic Ecoflex® copolymer and polylactic acid (PLA). Ecovio presents characteristics similar to olefins in biodegradable material. Its formulation includes anti-lock and sliding agents to facilitate film extrusion processing [3]. Its composition consists of 55% PBAT (Poly (butylene adipate co-terephthalate)) and 45% PLA (polylactic acid) [4]. It was mentioned by Yaming, C., Jungang, L., and Jimin, F. (2012) [5] that PLA has good mechanical, thermal and biodegradable properties that meet the requirements for various end-use applications. On the other side, they cited that the major problem for their commercialization and applications is the high brittleness and cost of PLA. They mentioned that a worldwide commercially available and widely used biodegradable polymer is PBAT. It has many advantages amongst all the biodegradable materials, with high flexibility, excellent impact strength and melt processibility. In addition, PBAT has very fast biodegradation rate. It was reported that whether in the form of films or molded objects, PBAT has exhibited significant biodegradation within 1 year in soil, water with activated sludge, and seawater.

Eventhough these materials have the potential to reduce plastic pollution the effectiveness of biodegradation depends on environmental conditions and the presence of suitable microorganisms. Advanced research has shown that through irradiation in several different dose ranges, mechanical properties of these polymers and efficiency in the degradability process can be improved. Ionizing radiation is a type of radiation that has energy capable of ionizing atoms and molecules, displacing electrons from atoms. The use of electron accelerators to modify materials is a viable option that does not result in increased waste. These changes, induced by radiation doses, alter the structure of Ecovio® bags, thus modifying their degradation time while improving properties during needed time for farming [6], [7]. Raman spectroscopy requires small sample size, minimal sample preparation, high-quality spectra can be obtained in few seconds the analysis. The structures information can be obtained by optical observation of the spectral characteristics [5]. Thermogravimetric Analysis (TGA) is a thermoanalytical technique that allows us to monitor the variation of sample mass in a controlled atmosphere of nitrogen or synthetic air. With this technique it is possible to observe the loss and/or gain of mass as a function of temperature or time [8]. So, in this research we investigated the effect of EB irradiation on Ecovio bags by Raman spectroscopy and thermal gravimetry.

2. MATERIALS AND METHODS

The plastic bags (Ecovio®, with 55% PBAT and 45% PLA) supplied by Romapck were stacked in sets of 10 bags for each radiation absorbed dose and irradiated with absorbed doses of 25, 50 and 100 kGy in the Dynamitron electron accelerator, Figure 1. Some preliminar characterization were performed and there were no significant differences between 1st and 10th bags, so, just 1st bag of each radiation absorbed dose are presented in this study.

Figure 1: Experimental arrangement for EB irradiation at IPEN.



Source : Author, 2024.

2.1. Raman Spectroscopy

The Raman spectra were obtained using the Raman microscope (model: Xplora Plus) with 785 nm wavelength, 85 mW laser power, with the SyncerityTM CCD detector model, 1200 grid (750 nm) and 50 X objective lens. Before every sample measure- ment, crystal silicon with fixed peak position at 520 cm^{-1} was used to calibrate the Raman shifts.

The analyses were performed in the Raman region of 2000 cm^{-1} to 400 cm^{-1}. The analyzes were performed on 1st and 10th bag, from top to bottom of the pile, using EB horn as zero reference direction of penetration. Maximum energy of this EB facility is 1.5 MeV, so this experimental choice was to verify if it was observable by Raman spectroscopy the dose differences between two samples for various absorbed doses due to penetration of electron. Furthermore, samples were taken from two different locations, one with a printed stamp and the other without, with dimensions of 1 cm x 1 cm and bags' thickness is 0.4 mm.

2.2. Thermogravimetry (TGA)

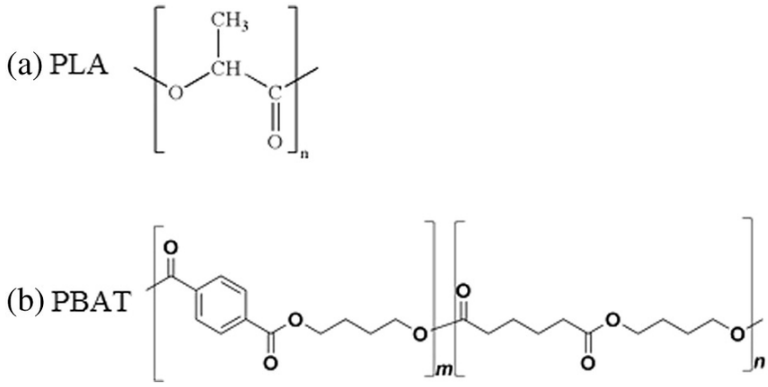
For the thermogravimetric analysis, TA Instruments SDTQ600 was used. The number 1 and 10 bags were cut in dimensions of 4x1 cm^2, in the regions with printing and without printing. The samples were heated from 20 °C to 800 °C, with a heating rate of 20 °C min^{-1}. in synthetic air atmosphere at a flow rate of 100 mL min^{-1}.

3. RESULTS AND DISCUSSIONS

3.1. Raman Spectroscopy

For the interpretation of Raman, literature findings [7], [9]–[11] of PBAT and PLA raman shift were used. Spectra there were obtained in the range from 800 to 2000 cm^{-1}, regions where there are peaks of PBAT and PLA (chemical structures shown in Figures 2(b) and (a) [5] in the composition of biodegradable bags Ecovio®, as presented in Table 1 [5]–[7].

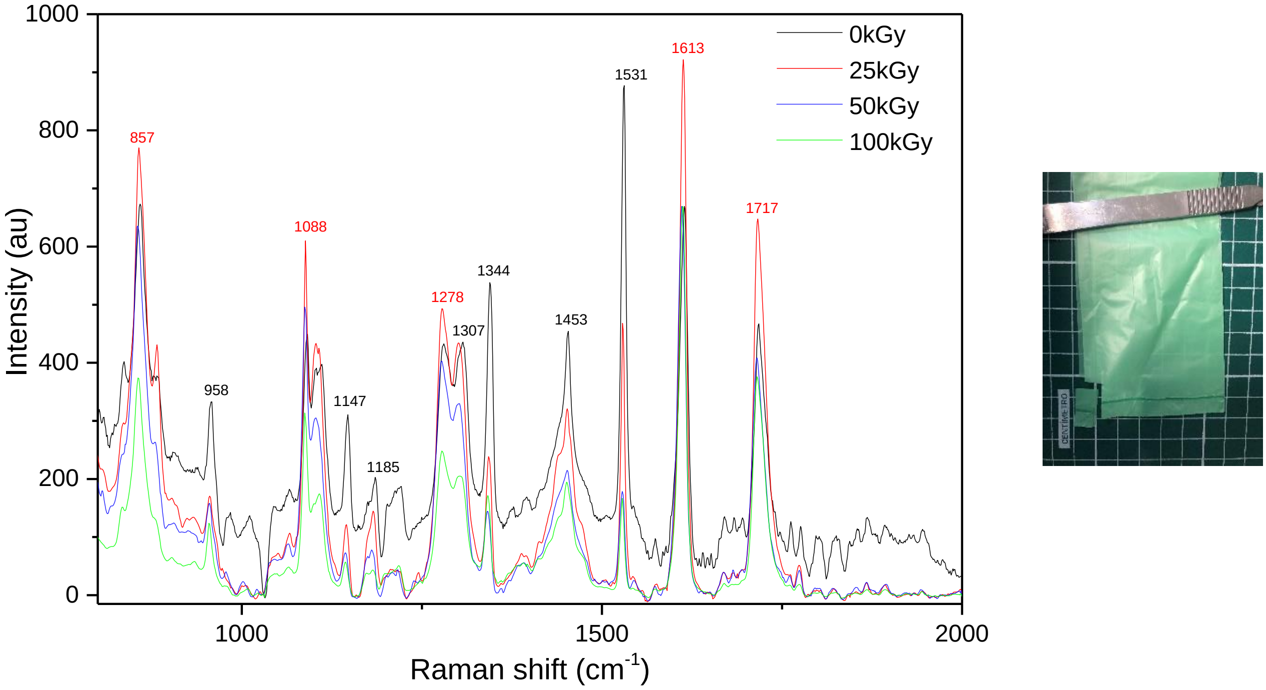
Figure 2: Chemical structure of (a) PLA and (b) PBAT.



Source Yanming Cai • Jungang Lv • Jimin Feng, 2013 [5]

It was possible to observe the influence of radiation absorbed doses (25, 50 and 100 kGy) on the intensities of Raman displacements compared to 0 kGy in Figures 3 to 6.

Figure 3: Raman spectra of non irradiated and EB irradiated with 25, 50 and 100kGy) samples taken from a location that has no printed stamp of Ecovio ® bags.



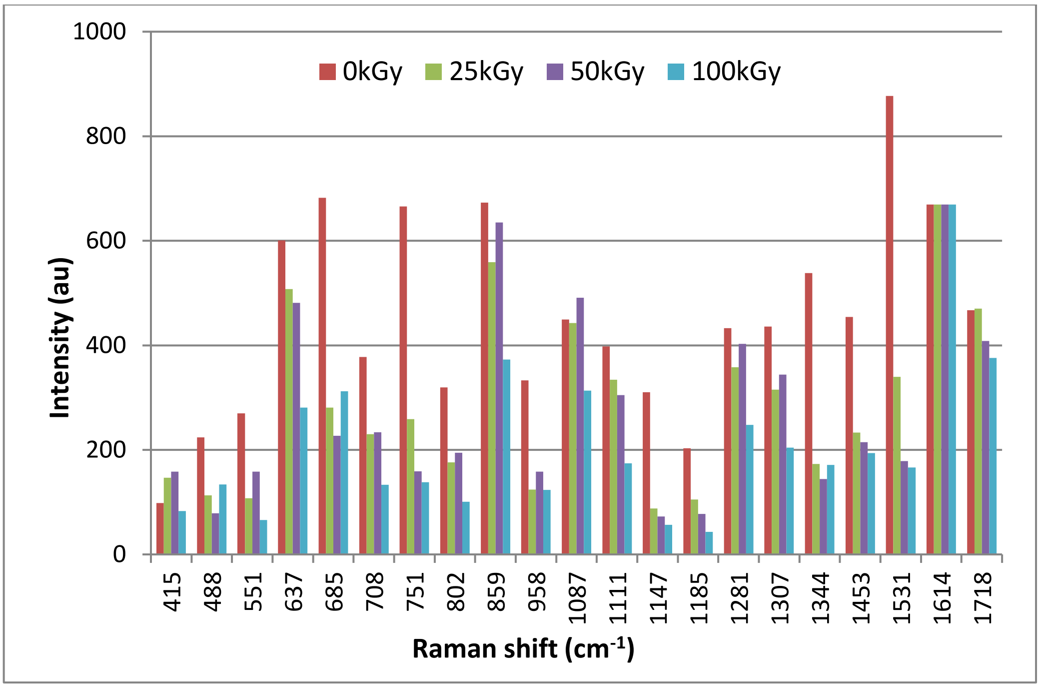
Source : Author, 2024.

The Raman spectra observed of pure PLA with main bands and wavenumbers are shown in Figure 3 and Table 1. The peak of pristine PLA was C=O stretching at 1774 cm^{-1} in the literature, 1454, and 1385 cm^{-1} asymmetric and symmetric deformations modes of the CH_3 groups. The peak at 1297 cm^{-1} could be due to the CH deformation vibration peak (βC-H PLA and PBAT) that is usually found at 1299–1305 cm^{-1}. The peak at 1127 cm^{-1} can be assigned to the CH_3 group rocking vibration, the peak at 1050 cm^{-1} to the stretching of C–CH_3 bond (ν C–C PLA), the peaks at 874 cm^{-1} and 408 cm^{-1} to the vibrational states of the C–COO and C–CO groups, respectively. The peak at 308 cm^{-1} was characteristic of the vibration of two different groups: C–O–C and C–CH_3 [6], [7], [11]. Small differences observed of the Raman shifts reported by the authors could be due to samples processing as PLA filaments or filler presence of their study, compared to films of bags. Then, in Figure 3, Raman shift peaks that can be attributed for PLA are: 415 cm^{-1} C-CO, 637 cm^{-1}, 859 cm^{-1} ν C-COO, 1087 cm^{-1} ν C-CH_3, 1111 cm^{-1} ν C–O (PBAT+PLA), 1147 cm^{-1} r_{as} CH_3, 1281 cm^{-}

[1] δs CH, 1307 cm^{-1}, 1453 cm^{-1} δas CH_3, 1614 cm^{-1} ν (C=C) 1718 cm^{-1} v (C=O), that was observed at of 1772 cm^{-1} using approximate values of the literature [11].

Peaks at 731, 1121 and 1169 cm^{-1} were characteristic and can be used as indicative peaks in the identification of PBAT.

Figure 4: Raman intensity of samples without printed stamp on Ecovio ® bags.

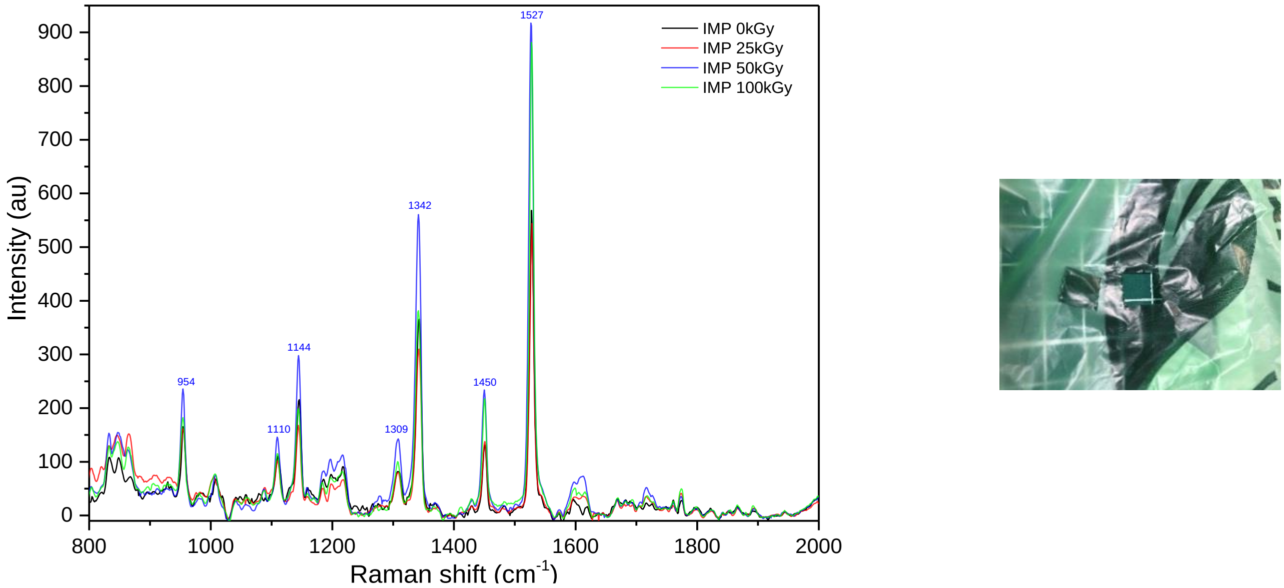


Source: Author, 2024.

From Figure 5, the main peaks in the Raman spectrum of PBAT included: 119, 206, 273, 632, 704, 797, 856, 878, 1024, 1043, 1105, 1177, 1280, 1300, 1396, 1449, 1577, 1613, 1673 and 1718 cm^{-1} [6], [7], [11]. This indicates that some scission due to ionizing radiation interaction with Ecovio may have occurred in the carbonyl group, associated with the displacement of its stretch deformation at 1717 cm^{-1} [7], in Figure 3, observed in Figure 5 at 1527 cm^{-1} [11]

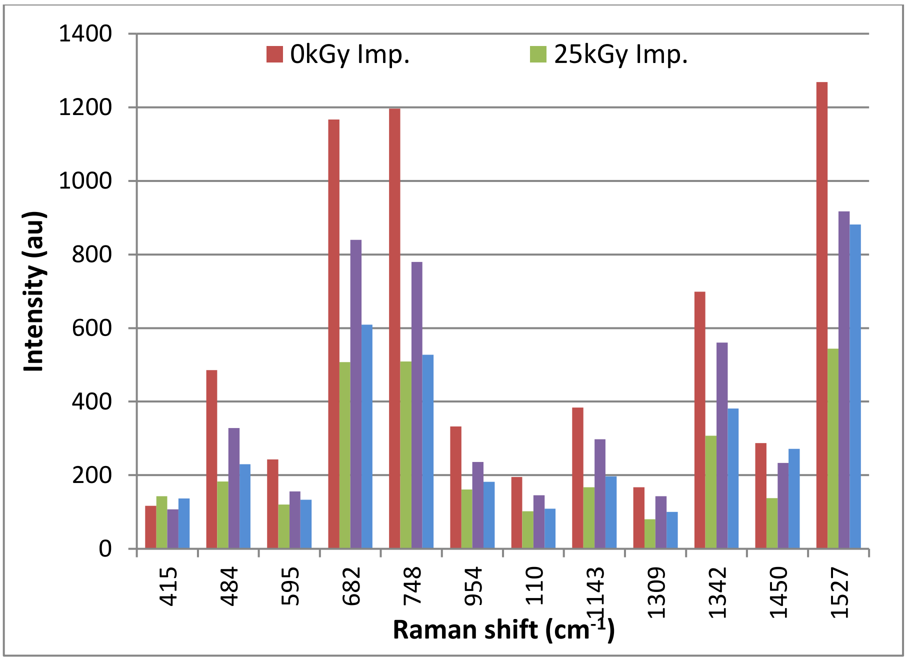
The Raman shift in 1453 and 1450 cm^{-1} can be attributed to the assimetric deformation of CH_3.

Figure 5: Raman spectra of samples taken from a site that has printed stamp on Ecovio ® bags.



Source: Author, 2024.

Figure 6: Raman spectra of samples with printed stamp on Ecovio ® bags.



Source: Author, 2024.

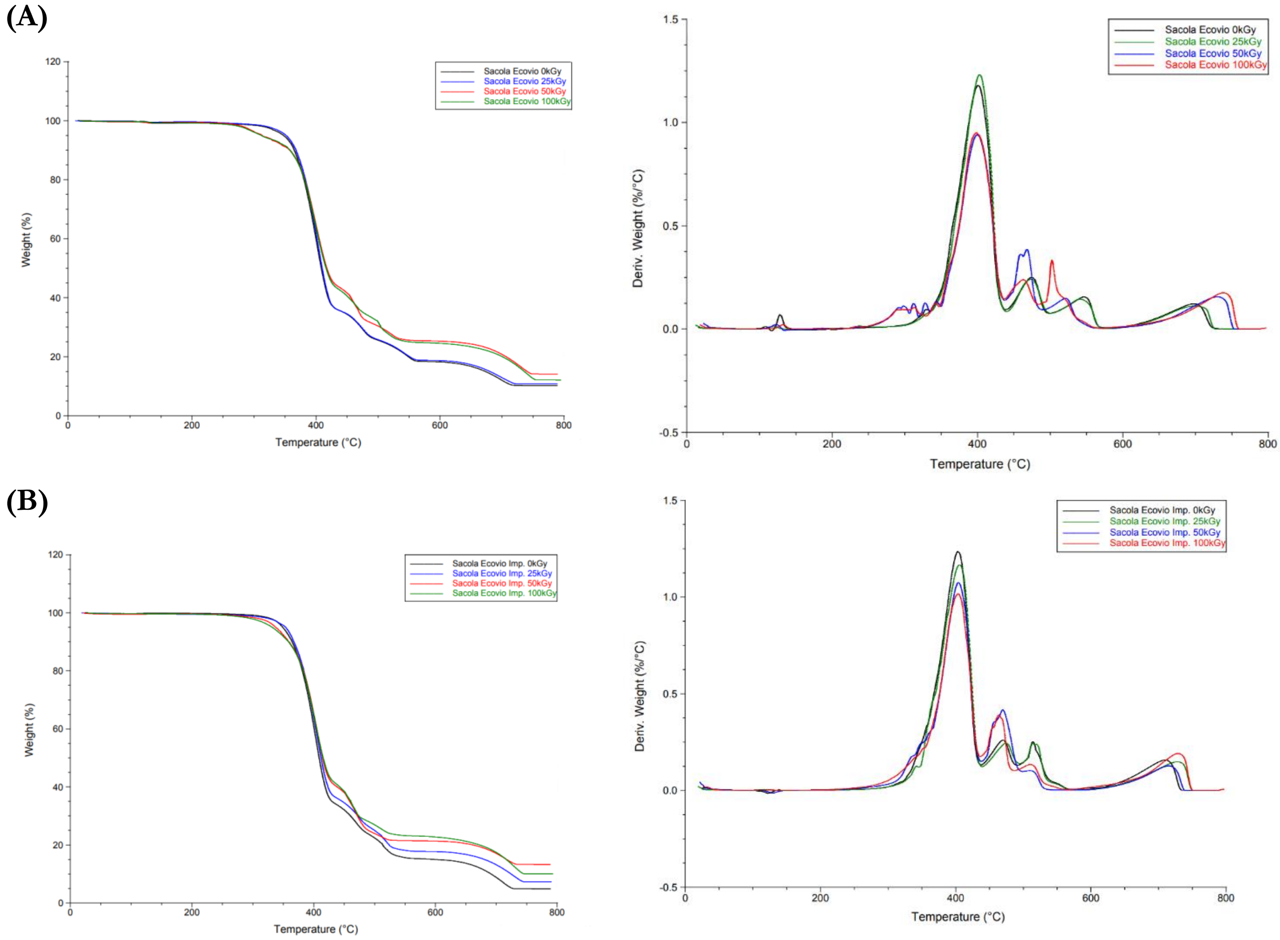
Table 1: Interpretation of vibrational modes found in Raman spectra for PBAT-PLA samples

Raman shift (cm^{-1})	Interpretation [7]	Interpretation [5]
802	Vibrational states of the C–COO ···· PLA	
958	Stretching of C–CH_3**PLA	
1088	ν C–C PLA*	stretching absorption of C–O–C PLA
1111	ν C–O (PBAT+PLA)*	C–O stretching mode PBAT
1147	C=O stretching** ?PLA	
1185	C=O stretching** PLA	stretching absorption of C–O–C PLA
1307	βC-H (PLA)*	PBAT
1344	δ sim CH_3 PLA**	symmetric bending absorption of CH_3, CH PLA
1453	δ assim CH_3 PLA**	asymmetric bending absorption of CH_3 PLA
1614	ν C=O (PBAT)*	strong absorption of C = C in benzene ring PLA and C=O PBAT
1717	ν C=O (PBAT+PLA)	C = O stretching (PLA+PBAT)

3.2. Thermogravimetry (TGA) results

The thermograms of the EB irradiated and non irradiated Ecovio bags films are graphically presented in Figure 7 (A and B) and the thermal parameters summarized in Table 2 (no printed) and 3 (printed portion). Ecovio® bags films showed four steps decomposition processes under air atmosphere, eventhough del Campo et al [6] had observed three main weight loss steps. the first step associated with the PLA phase [6]. In our study we observed in ECOVIO® bag no printed area that the first weight loss (WL) occurred at T d_{max} 1=400 °C WL= 63 %, second at T d_{max} 2=474 °C WL= 10 %, our third and fourth steps can be assigned to the decomposition of PBAT. T d_{max} 3=547 °C WL= 8 %, T d_{max} 4=700 °C WL= 8 %. Irradiated samples presented decreasing temperatures with variances of 2.3 °C, 4.5 °C, 5.4 °C for the 1st, 2nd and 3rd events, respectively, and increasing temperature and variance of 17.8 °C for the 4th event with increasing radiation absorbed dose. Indicating that PLA sufffered some scission on polymeric chain, affecting the maximum degradation temperatures. On the other hand, PBAT seems to have suffered slight crosslinking with increasing radiation absorbed dose. Furthermore, concerning thermal stability, reduction temperature tendency of 6.1 °C variance of initial temperature of degradation observed, reinforces that some scission occurred in PLA with increasing radiation absorbed dose.

Figure 5: TG/DTG curves of 0, 25, 50 and 100kGy EB irradiated Ecovio(R) bags : A) no print ; B) printed



Source: Author, 2024.

Table 2: Ecovio irradiated Bags (no printed part)

Initial Temp.(°C)	1st Temp. (°C)	Weight Loss (%)	2nd Temp. (°C)	Weight Loss (%)	3rd Temp. (°C)	Weight Loss (%)	4th Temp. (°C)	Weight Loss (%)	Weight Loss TOTAL (%)
236.6	400.4	63.5	474.5	10.0	547.3	7.8	200.2	8.1	88.9
225.2	402.7	64.1	474.1	9.9	543.7	6.9	704.7	8.0	88.8
225.1	398.5	55.9	467.5	12.1	521.4	5.9	724.2	11.3	85.2
223.4	397.6	56.3	463.3	8.9	501.2	9.1	738.6	12.7	87.0
6.1	2.3	4.5	5.4	1.4	21.5	1.4	17.8	2,4	1.7

Table 3: Irradiated Ecovio bags printed part

Initial Temp.(°C)	1st Temp. (°C)	Weight Loss (%)	2nd Temp. (°C)	Weight Loss (%)	3rd Temp. (°C)	Weight Loss (%)	4th Temp. (°C)	Weight Loss (%)	Weight Loss TOTAL (%)
245.4	403.1	65.8	470.4	10.4	513.6	8.3	710.3	10.4	94.8
230.5	406.1	63.5	475.1	10.2	513.0	7.9	728.5	10.5	91.6
231.8	403.5	59.6	469.2	15.9	515.5	2.5	715.8	8.2	86.2
225.9	403.5	58.5	464.1	12.7	513.8	5.2	729.3	13.1	89.4
8.4	1.4	3.4	4.5	2.7	1.1	2.7	9.4	2.0	3.6

When print is added to ECOVIO® bag film the first weight loss (WL) occurred at T d_{max} 1=403 °C WL= 66 %, second at T d_{max} 2=470 °C WL= 10 %, our third and fourth steps can be assigned to the decomposition of PBAT T d_{max} 3=514 °C WL= 8 %, T d_{max} 4=700 °C WL= 10 %. There was no significant temperatures interference by the ink presence on 1^{st} and 2^{nd} events, but promoted a small increase in the 3^{rd} event degradation temperature maximum WL. Irradiated samples presented decreasing variance of 1.4 °C, 4.5 °C, 1.1 °C for the 1^{st}, 2^{nd} and 3^{rd} events, respectively, and increasing variance of 9 °C for the 4^{th} event with increasing radiation absorbed dose. This indicates that PLA sufffered some scission on polymeric chain affected the maximum degradation temperatures even with print presence. On the other hand, PBAT seems to have suffered slight crosslinking with increasing radiation absorbed dose. Additionally, print affected temperatures in reducing T d_{max} 3, and increasing T d_{max} 4, compared to non printed films. Furthermore, concerning thermal stability, decrease tendency with variance of 8.4 °C f initial temperature of degradation is observed, that reinforces that some scission occurred in PLA with increasing radiation absorbed dose even with print presence.

4. CONCLUSIONS

The application of ionizing radiation in Ecovio® bags allowed modifying their properties and expanding its applications, contributing to the creation of more ecological and efficient products due to degradation that would favor biodegradability. From Raman results it suggests that PLA is more prone to degradation than PBAT. That is corroborated by TGA results that indicate slight PLA scission and PBAT crosslinking with increasing radiation absorbed doses up to 100 kGy. Future work will be on field composting tests.

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CONFLICT OF INTEREST

The authors declare that there are no known competing personal, professional, financial, and work-related issues that could appear as a negative influence in future before and after publication.

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