



Abiotic and biotic degradations of a LDPE blend in soil of South Brazil landfill

Gabriela Miranda¹ · Jéssica Pires¹ · Gabriela Souza² · Flávia Fraga² · Carla Azevedo² · Rogério Lourega^{1,2} · Jeane Lima^{1,2} · Rosane Ligabue^{1,2}

Received: 16 March 2020 / Accepted: 9 September 2020 / Published online: 20 September 2020
© Iran Polymer and Petrochemical Institute 2020

Abstract

Polyethylene degrades slowly when discarded in the environment and exposed to natural weathering. A solution to this problem is the incorporation of additives to accelerate its biodegradation. In the present study, a biodegradable low-density polyethylene (LDPE) blend was obtained by the mixture of LDPE with a biodegrading additive (8% w/w) and the effect of accelerated weathering on biodegradation process was assessed. Chemical, mechanical, thermal, and morphological properties of non-aged and aged samples were studied. Results showed that aging process caused changes on structural characteristics (insertion of functional groups), morphological (appearance of micro-cracks and increased roughness), mechanical (greater stiffness and loss of plasticity) and thermal (lower degree of crystallinity and thermal stability) properties. The presence of biodegrading additive contributed to aging process, since polar functional groups were inserted into additive exposed to soil underwent greater degradation than their non-aged counterparts. CO₂ production of aged LDPE blend demonstrated that accelerated weathering influences biodegradation process. In this work, due to availability of O₂ gas, aerobic microorganisms can be the main responsible by the material deterioration, leading to production of microbial biomass, CO₂ and H₂O. Thus, the results of biodegradation (166 days) obtained in this work are promising, once it was reached a natural soil from South Brazil landfill.

Keywords LDPE · Biodegrading additive · Accelerated weathering · Biodeterioration · Biodegradation

Introduction

Polyethylene (PE) is one of the most widely used plastics in the world for a variety of several applications, mainly packaging, due to its low cost and excellent properties, including low strength, hardness and rigidity, as well as ductility and impact strength [1, 2]. PE types used commercially were high-density polyethylene (HDPE), low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), ultra-high molar weight polyethylene (UHMWPE), and ultra-low-density polyethylene (ULDPE) [3]. LDPE films are light and easy to use, making them attractive for

industrial applications. They are odor-free, non-toxic and show good ductility and low water permeability, allowing their use in food packaging [4, 5]. Their degree of crystallinity influences properties such as tensile and impact strength, stiffness, and chemical resistance [5]. However, their linear chain and lack of functional groups lead a very slow degradation under natural conditions [1, 2]. Additionally, when discarded these materials occupy large areas, and when mechanically recycled require a significant amount of water for rinsing purposes [6–8]. In this context, there is a crucial environmental need to develop new methods and technologies that can make this polymer more degradable or biodegradable.

In general, polymer degradation or biodegradation is influenced by both abiotic and biotic factors. Abiotic term is referred to parameters such as mechanical stress, light and temperature, and biotic term is referred to the involvement of naturally microorganisms such bacteria, fungi and algae [9, 10]. Some studies report that chemical, thermal, or photo-oxidative treatment can facilitate LDPE biodegradation.

✉ Jeane Lima
jeane.lima@puers.br

¹ Graduate Program in Materials Engineering and Technology, School of Technology, Pontifical Catholic University of Rio Grande do Sul, Porto Alegre, Brazil

² School of Technology, Pontifical Catholic University of Rio Grande do Sul, Porto Alegre, Brazil

These processes are capable of reducing the hydrophobicity and molar weight of LDPE, favoring degradation by microorganisms [11–13]. According to the literature, biodegradation can be considered as a secondary process where microorganisms use these oxidized products for conversion of H_2O , CO_2 , and CH_4 or energy storage products, such as polyhydroxy alkanates [14, 15]. However, natural weathering caused by solar radiation, moisture, and wind leads to a slow oxidative degradation due to the formation of free radicals [16].

Considering biodegradation process of biodegradable polymers it can be divided in four steps: biodeterioration, depolymerization, bioassimilation, and mineralization. In biodeterioration step, there is microbial biofilm formation, which leads to polymer surface degradation, and consequently, its fragmentation into smaller particles. After that, microorganisms release extracellular enzymes, which catalyze the depolymerization of polymer chain into oligomers, dimers, or monomers. Bioassimilation occurs when these small particles and depolymerized compounds are absorbed by microbial cells producing primary and second metabolites. Finally, all these metabolites are degraded and mineralized into CO_2 , CH_4 , H_2O , and N_2 [9]. Many techniques can be used in combination to measure or quantify biodegradation process, such as: TGA, which measures thermal stability of a polymer, and a decrease in this parameter can be an indicator of polymer degradation; GPC, which measure molar weights of polymers (M_n and M_w), and a decrease in M_n can indicate chain scission; FTIR, which is normally used to evaluate and monitor chemical modifications in polymer structure; SEM, which can be used to observe formation of cracks and holes or biofilm formation (demonstrate microbial colonization); and standards methods, for the production of CO_2 and/or CH_4 measurements [17].

Another way of promoting LDPE biodegradation is by adding substances such as natural macromolecules, pro-oxidants compounds, or biomolecules to the matrix [18–20]. Pro-oxidants additives are organometallic which need oxidative degradation (ultraviolet radiation and/or heat) to be activated. After that, it allows molecular weight decrease and addition of oxygenated groups on PE surface, which are easily metabolized by microorganisms [17]. Biodegrading additives are composed since natural substances (enzymes or natural polymer) to synthetic polymers containing ester, hydroxyl or ether groups, which are prone to hydrolytic cleavage by microorganisms [19, 21]. In our group's previous work [22] degradation process in soil of polypropylene (PP) blends with 2–8% (w/w) of two biodegrading additives (organic and enzymatic) was evaluated over 6 months. Both additives had influence on PP degradation with 2% of additive (low percentage), indicating acceleration of this process by their action. Authors highlighted the need for further studies with enzymatic additive because it never has been

reported in literature before. Moreover, in other work of our research group [23], the degradation process in natural fresh water of the same PP blends was evaluated over 6 months. PP degradation also was favored by the use of enzymatic additive in fresh water, showing that blends could have less durability after use, which may lead to environmental benefits, since it is an alternative to minimize the effects caused by plastic waste. The main aim of all these additives is induce deterioration of PE structure after discard, to allow more access of microorganisms and their extracellular enzymes during the biodegradation process. Thus, this study aims to investigate and evaluate the changes in the chemical, thermal, mechanical and morphological properties of abiotically degradable LDPE blend prepared with an biodegrading additive (without metals) related to pure LDPE, after exposition to accelerated aging (abiotic degradation) and inoculation in soil (biodegradation).

Experimental

Materials

Low-density polyethylene (LDPE) was obtained in pellet form by Braskem (Brazil, product code PB608, MFI 30 g/10 min and density 0.915 g/cm^3). Biodegrading additive was used in pellet form and it contained 95% LDPE and 5% of enzymatic compounds (India). Soil used in biodegradation assays (pH 8.03, 37.7% dry basis moisture content, 59.3% water holding capacity and C/N ratio of 22.7) was obtained from a landfill located in Porto Alegre city (Rio Grande do Sul state, Brazil). Commercial corn starch (~25% amylose and ~75% amylopectin) was purchased from Unilever Company (Brazil). Potassium hydroxide (KOH) and hydrochloric acid (HCl, 37%) were supplied by Vetec and Neon (Brazil), respectively. Glutaraldehyde and osmium tetroxide (OsO_4) were supplied by EMS Company (USA). Phosphate buffer solution and acetone were supplied by Merck (Germany).

Biodegradable LDPE film preparation

LDPE/biodegrading additive blend (8% w/w) was prepared by injection, using a thermoplastic injector (Wittmann Battelfield, Austria) with a single screw speed of 350 mm/s and a temperature profile of 175 °C in the first zone, 170 °C in the middle, 165 °C in the last zone and 180 °C in the nozzle. Pure LDPE (M_n 10.0 kg/mol and M_w 96.0 kg/mol) and LDPE/additive blend (M_n 7.2 kg/mol and M_w 93.1 kg/mol) were denominated as PE0 and PE8, respectively. Films were prepared by hot-pressing at 110 °C under three tons for 2 min in a hydraulic press model MA098 (Marconi, Brazil).

It presented approximately 0.20 mm of thickness, which was measured using a digital caliper ruler.

Abiotic degradation (accelerated weathering test)

A QUV/spray/240 accelerated weathering chamber (QLAB, USA) was used for abiotic degradation study (Fig. 1a), in accordance with ASTM G154-16. PE0 and PE8 films (95 × 65 mm, independent triplicate) were exposed to alternating cycles of 8 h of UV light (UVA lamps at 0.89 W/cm² and 340 nm with an incident radiation beam at 90° and temperature of 60 °C) and 4 h of water spray (tap water) over 1000 h (42 days), at 40 °C and 50% relative humidity. To assess the effect of exposure over time, the aged samples were removed from the chamber every 200 h (8 days). Films were identified using the acronym PEX-YYY, where X designated the additive amount in the blend and YYY as the exposure time (h), e.g., PE0-600 (pure LDPE with 600 h exposure).

Biodegradation assays

Biodegradation tests were carried out by two different methods (Fig. 1b, c) described below:

Soil exposition assay (biodeterioration evaluation)

Non-aged and aged (600 and 1000 h) PE0 and PE8 samples were exposed to soil for 60 days (composting conditions:

58 °C; 50% moisture), at a sample/soil ratio of 0.5 g/30 g, in a microbiological incubator (Brazil) according to ISO 14855-12.

Carbon mineralization assay (aerobic biodegradation evaluation)

Aerobic biodegradation test of non-aged and aged (800 h) PE8 samples was performed in accordance with ISO 17,556 and ASTM D5988-18 for 166 days (22 ± 1 °C) in soil (sample/soil ratio of 1 g/500 g), respectively. Commercial corn starch was used as positive control, and the system which contained only soil was used as blank. KOH solution was used to trap the produced CO₂ and a 0.25 M HCl solution was used for the titration to quantify this production. For each system, it was used 20 mL of 0.5 M KOH solution and 50 mL of distilled water. KOH solutions of the systems were removed each 1 week, titrated with HCl and it was replaced by a new KOH solution and distilled water. According to the stoichiometry (Eqs. 1 and 3), produced CO₂ was calculated (Eq. 4), where V_{HCl} is the spent volume of HCl solution in the acid–base titration. Elemental analysis was performed for both materials to quantify C content, which was used to calculate theoretical CO₂ (Eq. 5) based on stoichiometry of Eq. 2. Produced and theoretical CO₂ were used to calculate carbon mineralization percentage (Eq. 6) for all samples.

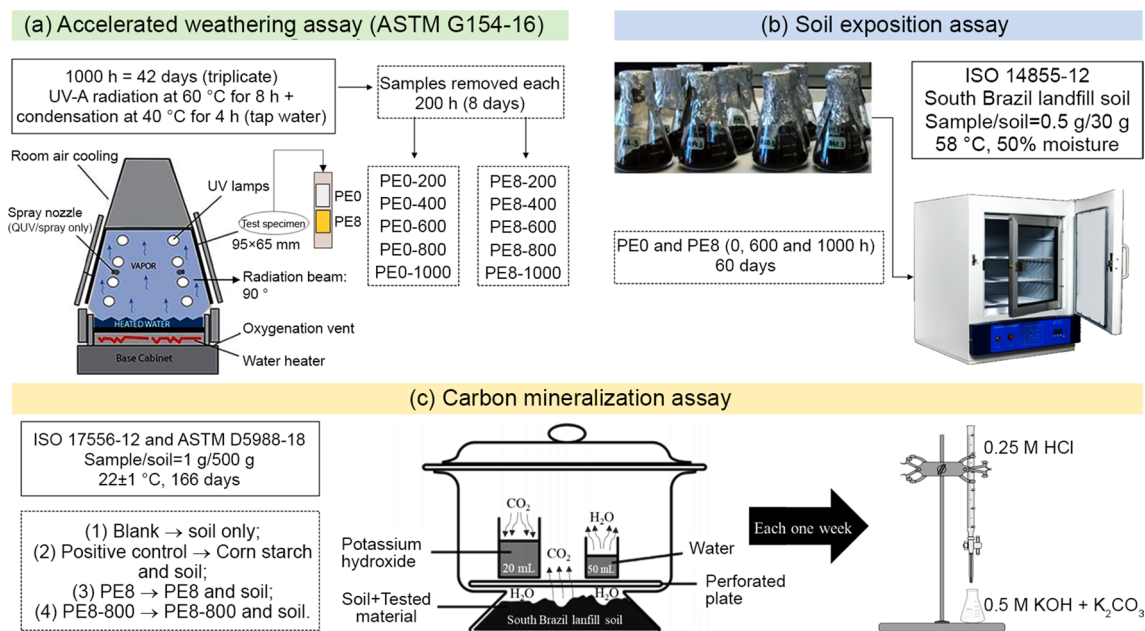
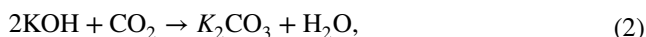
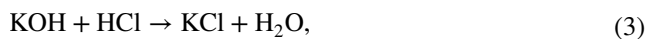


Fig. 1 Scheme of accelerated weathering (a), soil exposition (b) and carbon mineralization assays



$$\text{mgCO}_2\text{produced} = \left(\frac{0.5\text{M} \times 20\text{mL}}{0.25\text{M}} - V_{\text{HCl}} \right) \times \frac{0.25\text{M}}{2} \times 44 \frac{\text{g}}{\text{mol}}, \quad (4)$$

$$\text{mgCO}_2\text{theoretical} = \frac{mc \times 44 \frac{\text{g}}{\text{mol}}}{12 \frac{\text{g}}{\text{mol}}}, \quad (5)$$

$$\text{Carbon mineralization(\%)} = \frac{\text{mgCO}_2\text{produced}_{\text{test material}} - \text{mgCO}_2\text{produced}_{\text{Blank}}}{\text{mgCO}_2\text{theoretical}} \times 100. \quad (6)$$

Characterizations

Thermal, mechanical, morphological, and spectroscopic characterizations were performed on the non-aged and aged PEO and PE8 films.

Differential scanning calorimetry (DSC)

Thermal behavior analysis of the specimens was carried out in a calorimeter (TA Instruments, model Q20, USA) in the heat/cool/heat mode from -90 to 200 °C, at rate of 10 °C/min, under nitrogen atmosphere (flow rate at 50 mL/min). Melting temperature was determined in the second heating step (in triplicate). Degree of crystallinity was calculated using melting enthalpy (ΔH_m) of 286.6 J/g as reference, corresponding to 100% crystalline LDPE [24].

Thermogravimetric analysis (TGA)

Thermal stability was determined in an SDT Q600 device (TA Instruments, USA). Specimens were heated from room temperature to 600 °C under nitrogen atmosphere (flow rate at 100 mL/min) with heating rate 10 °C/min (in triplicate).

Fourier transformed infrared spectroscopy (FTIR)

FTIR spectra were obtained at room temperature in UATR mode, in the range of 4000 – 650 cm^{-1} , on a Perkin Elmer spectrometer (Spectrum One model). The carbonyl index (CI) (in triplicate) was calculated according to the method described in literature, before and after the aging test, using formula shown in Eq. 7 [25].

$$\text{CI} = \frac{A_{1715}}{A_{2870}}, \quad (7)$$

where A_{1715} is the absorbance of the carbonyl group ($\text{C}=\text{O}$ of acids, aldehydes, ketones) and A_{2870} is the symmetric stretching of methylene group ($-\text{CH}_2-$).

Tensile test

Tensile tests were performed in a Q800 DMTA apparatus (TA Instruments, USA), cell load of 18 N, film tension mode at 25 °C and rate of 3 N/min, using samples measuring 0.20 mm (thickness) \times 7 mm (length) \times 3 mm (width). Young's modulus of the specimens was determined at triplicate according to ASTM D638-14. Biodegraded samples could not be evaluated due the deterioration level after soil exposition.

Dynamic mechanical properties

Dynamic mechanical properties of specimens (7 mm \times 3 mm \times 0.2 mm) were analyzed in a Q800 DMTA apparatus (TA instruments, USA), in the multi-frequency mode. Samples were heated from -100 to 90 °C, at rate of 3 °C/min, under an oscillating frequency of 1 Hz (in duplicate).

Field emission scanning electronic microscopy (FEG-SEM)

Surface morphology of the specimens coated with a thin layer of gold was assessed by FEG-SEM, using an FEI Inspect F50 scanning electron microscope (Japan) in secondary electron mode (SE). Biodeterioration (biofilm formation and microorganism morphology) on the sample surface was also evaluated and required sample preparation. To that purpose, samples were fixed with 25% glutaraldehyde in 0.2 M phosphate buffer solution for 24 h and then immersed in a solution content 2% of OsO_4 in 0.2 M phosphate buffer (pH 7.0) for 30 min, followed by sequential dehydration in increasing concentrations of acetone, for 30 min each. Finally, the samples were left in 100% acetone for 1 h, and then air-dried at room temperature.

Elemental analysis

Carbon, hydrogen, and nitrogen contents of the non-aged and aged specimens were determined by elemental analysis in a TruSpec CHNS elemental analyzer (LECO, USA), equipped with infrared and thermal conductivity detectors. Films were analyzed in an O_2 atmosphere at 950 °C.

Gel permeation chromatography

Number average molar weight (M_n) and weight average molar weight (M_w) and molar weight distribution were determined by GPC (in triplicate) in a Viscotek 350A HT—GPG system (Malvern Instruments, UK), equipped with columns set PLgel

20 mm Mixed-A 300×7.5 mm (Polymer Laboratories, UK). 1,2,4-Trichlorobenzene was used as eluent, with a flow rate of 0.8 mL/min at 135 °C. Polystyrene (Pressure Chemical, USA) with a molar weight of 2450 to 44.8×10^6 g/mol was used as calibration standard. The following Mark–Houwink constants were used in the calculations: K (PS)=0.000121; α (PS)=0.707; K (PE)=0.000406; α (PE)=0.725.

Statistical analysis

DSC and tensile test were assessed applying two-way repeated-measures ANOVA followed by Bonferroni post hoc test (Statistical Package for the Social Science, software version 20.0; SPSS, v.20.0). The significance level established in the present study was $p < 0.05$.

Results and discussion

Influence of accelerated weathering on the properties of LDPE blend

Structural characteristics

Incorporation of additive did not change the structural characteristics of pure LDPE based in FTIR analyses. The changes in structural characteristics of PE0 and PE8 during accelerated weathering test were evaluated by FTIR. Figure 2 shows the FTIR spectra of the non-aged and aged PE0 and PE8 films. The bands at 1373 and 910 cm^{-1} are assigned, respectively, to vibrations of the alkyl (CH_3) and vinyl bending ($\text{HC}=\text{CH}_2$) groups associated to PE structure. The appearance of bands at 1714 and 1176–1018 cm^{-1} assigned to vibrations of C=O stretching (carboxylic acid) and C–O stretching (alcohols), respectively, is due polymer photodegradation (Norrish type I and II reactions) in accelerated weathering conditions [2]. Moreover, an increase in band intensity was observed related to these groups with the increase of exposure time (600 and 1000 h), confirming the strong time effect on the photodegradation process. According to the literature, the exposition to abiotic factors contributes to biodegradation, since carbonyl group formation may occur due to polymer chain oxidation by exposure to UV light, leading to increase carbonyl index [26–28]. Similar behavior was observed in this work for both samples (Table 1). These surface changes have led to biofilm formation [29].

Thermal properties

Table 1 shows melting temperatures (T_m) and crystallinity values (X) of non-aged and aged PE0 and PE8 films. Incorporation of the biodegrading additive in polymeric matrix

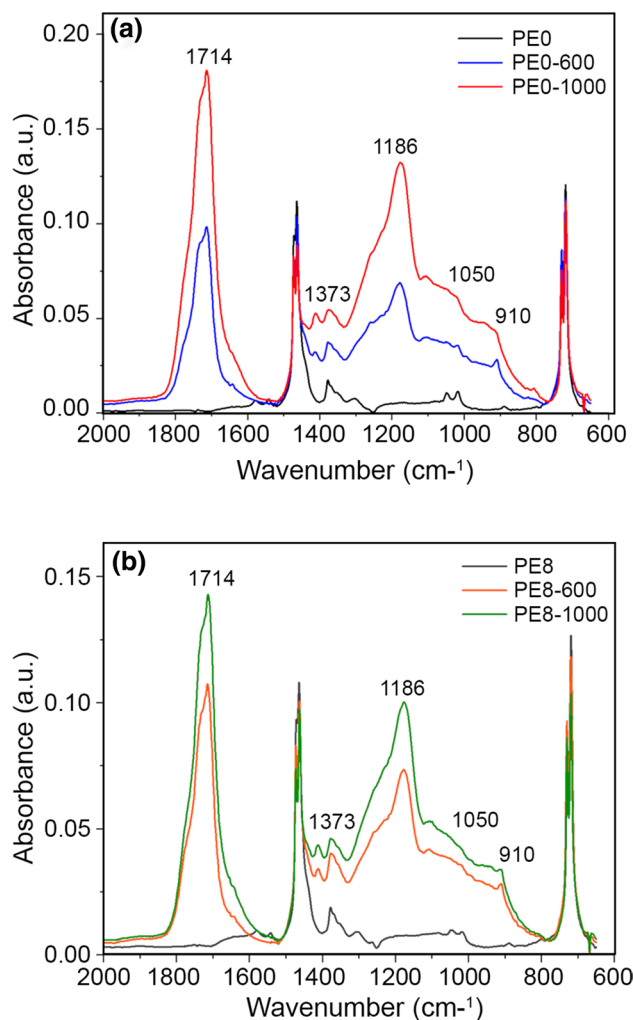


Fig. 2 FTIR spectra in 2000 to 650 cm^{-1} wavenumber: **a** PE0 films and **b** PE8 films

did not alter significantly their thermal properties (PE0 and PE8, Table 1). In general, there was no significant interaction between the independent factors exposition times and the presence of additive ($F=2.19$; $p=0.09$). Considering independent variables, there was significant interaction only at 600 h when PE8 and PE0 groups were compared ($\Delta T=2.06^\circ\text{C}$; standard error = 0.46, $p=0.01$; $F=20.03$). Regarding the influence of exposure time, statistical analysis demonstrated that T_m did not vary significantly for isolated PE0 group. However, for PE8 groups, when 0 h is compared with the other exposition times, there were significant differences at 800 h ($\Delta T=2.92^\circ\text{C}$; $p=0.026$) and 1000 h ($\Delta T=3.20^\circ\text{C}$; $p=0.03$). Moreover, comparing exposition times as 600 h ($\Delta T=2.30^\circ\text{C}$; $p=0.02$), there was significant variation. T_m data showed parametric distribution. Regarding the $X\%$ values, statistical analysis indicated that when PE0 group was evaluated individually, it did not exhibit significant variation over time. For PE8 group, it was observed a

Table 1 Melting temperature (T_m), crystallinity degree ($X\%$), Young's modulus, stress and strain values at break for PE0 and PE8 films before and after accelerated aging

Sample	Time (h)	T_m (°C)	X (%)	Young's modulus (MPa)	Stress-at-break (MPa)	Strain-at-break (%)
PE0	0	104.2±0.2	35.0±2.0	58.8±1.0	8.5±0.1	138.7±1.2
	600	104.6±0.4	39.4±0.9	112.3±1.7	7.1±0.2	20.7±2.0
	800	106.1±0.2	37.2±0.1	121.9±1.8	5.7±0.2	11.7±2.1
	1000	106.4±0.1	37.9±1.1	–	–	–
PE8	0	104.3±0.1	32.4±3.8	67.1±0.5	8.6±0.1	159.2±0.7
	600	106.7±0.7	40.5±0.9	120.8±3.9	7.9±0.4	19.6±4.4
	800	107.8±1.0	40.6±0.3	136.7±1.9	5.4±0.2	8.3±2.2
	1000	107.6±0.6	40.7±0.5	–	–	–

tendency of increasing crystallinity comparing 0 h and 800 h ($\Delta X = 1.25\%$; $p = 0.07$). A comparison of the groups (PE0 x PE8) showed significant difference between values in 800 h ($\Delta X = 3.09\%$; $F = 229.59$; $p < 0.001$). $X\%$ data also showed parametric distribution.

Ojeda et al. [16] evaluated the thermal behavior of HDPE/LLDPE commercial blend containing a pro-oxidant additive over 1 year of natural weathering. They observed an increasing trend of the blend crystallinity and proposed that this increase results in decreasing molecular size, and thus decreasing chain mobility, dominating in the blend. Gulmine et al. [27] studied the accelerated weathering of PE samples in the Weather-Ometer and QUV machines (ASTM G53-96) for 800 h. It was observed an increase in the crystallinity, density and hardness, as well as a broadening of the melting peak of the PE samples degraded by accelerated aging. They attributed it to changes in crystallite sizes, molecular weight differences that are brought about by chain breaking and secondary recrystallization.

Thermogravimetric analysis was performed to evaluate the thermal degradation behavior of samples after exposure to accelerated weathering. Figure 3 shows the TG and DTG curves for non-aged and aged (600 and 1000 h) specimens. Non-aged PE0 (Fig. 3a, b) and PE8 (Fig. 3c, d) films displayed similar thermal behavior with only one step in the degradation process. The Table 2 presents the temperature at 10% weight loss (T_{10}) values of PE0 and PE8 samples. This parameter was used to evaluate the beginning of the thermal event. For non-aged PE0 and PE8 samples, T_{10} values were similar, while it was lower in aged (600 and 1000 h) PE0 and PE8 samples. Thermal behavior changes in the aged films can be attributed to photodegradation that alters polymer structural characteristics, as shown in FTIR analysis. Oxidative degradation of materials as polyethylene occurs due to chain scission by free radicals, generating compounds with shorter chains [30]. During the accelerated degradation, these degradation processes can lead to formation of smaller molecules lowering the initial degradation temperature in

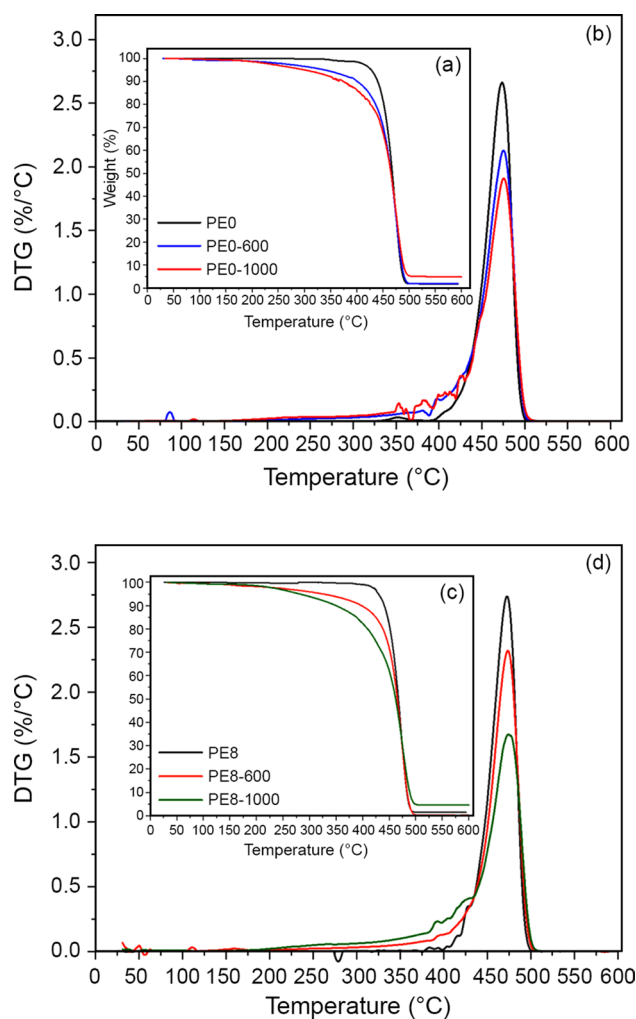


Fig. 3 TG and DTG curves of non-aged and aged PE0 and PE8 films: **a** TG curve of PE0, **b** DTG curve of PE0, **c** TG curve of PE8, and **d** DTG of PE8

the thermal degradation. Corti et al. [20] reported lower degradation temperature values for LLDPE samples with pro-oxidant additives exposed to outdoor weathering.

Table 2 Carbonyl index (CI), temperature at 10% weight loss (T_{10}), M_n and M_w values, and melting temperature (T_m) of non-aged and aged samples before and after soil exposure

Sample	Time		CI	T_{10} (°C)	M_n (kg/mol)	M_w (kg/mol)	T_m (°C)
	Aging (h)	Bio (days)					
PE0	0	0	0.1±0.0	439.0±1.1	9.5±1.4	89.4±1.9	104.2±0.2
		60	0.1±0.1	440.8±0.5	8.5±2.1	83.8±1.8	104.6±0.6
	600	0	1.3±0.1	398.6±3.2	1.9±0.2	17.3±4.8	104.6±0.4
		60	0.9±0.1	411.7±17.4	2.8±1.2	32.0±6.7	105.3±0.6
	1000	0	2.5±0.3	358.5±18.3	1.4±0.5	22.5±12.0	106.4±0.1
		60	0.6±0.2	392.2±25.1	2.5±0.3	31.9±9.9	106.6±0.1
PE8	0	0	0.1±0.0	439.6±1.5	10.7±1.0	83.6±1.1	104.3±0.1
		60	0.4±0.1	440.3±1.5	10.0±1.5	83.8±2.2	105.3±0.7
	600	0	1.5±0.2	401.7±9.7	1.3±0.6	17.1±9.7	106.7±0.7
		60	0.5±0.1	428.8±12.8	2.4±0.4	25.1±11.2	106.8±0.7
	1000	0	1.9±0.2	337.2±13.9	2.3±0.5	47.1±6.1	107.6±0.6
		60	0.8±0.2	385.5±3.4	2.7±0.4	44.8±10.8	108.4±0.4

Mechanical properties

Mechanical tests were performed to assess the mechanical behavior of samples after accelerated weathering (Table 1) to determine whether the material becomes stiffer or flexible with exposure time. After 1000 h of exposure, films were disintegrated and, therefore, could not be evaluated. Thus, only the 600 and 800 h exposure specimens were used. For PE0 and PE8 samples (non-aged and aged), Young's modulus rose as exposure time increased, i.e., films became stiffer over time. This behavior is corroborated for decrease in the strain values (Table 1). A similar increase of Young's modulus was observed for both specimens (approximately 100% over 800 h) when compared with non-aged samples. Besides that, PE8 samples exhibited higher Young's modulus when compared to PE0 samples, indicating that the biodegrading additive modified the elastic behavior of the material. Statistical analysis was only performed for Young's modulus (E) values, confirming the effect of exposure time of accelerated aging for PE0 and PE8. When PE0 and PE8 films were compared, there was a significant difference over the time ($\Delta E = 16.317$ MPa; $F = 425.105$; standard error = 0.791; $p < 0.001$). In an intra-group analysis, either for PE0 or PE8 groups, there were significant differences considering the comparison among 0 h and other exposition times ($F = 1557.381$; $p = 0.019$; and $F = 1660.317$; $p = 0.018$, respectively). Young's modulus data also showed parametric distribution.

According to literature, from $\tan \delta$ curves, it is possible to identify the transitions temperatures related to β -relaxation (branch relaxation) and α -transition, which are associated with molecular mobility and lamellar slip of the crystalline phase, respectively [28, 31]. Storage modulus (Fig. 4a) and loss modulus curves (Fig. 4b) indicate the effect of aging time the polymer chains, since these chains lose their ability of absorb and dissipate the energy during aging, leading to smaller displaced peaks. So, when these curves are evaluated,

it is possible to observe that the incorporation of the additive reduced the PE chain mobility once there was a shift in β -relaxation value to a higher temperature [32]. The $\tan \delta$ curves of PE0 (Fig. 4c) show peaks at -21.9 °C (shoulder) and 64.6 °C (strong peak) corresponding to β -relaxation and α -transition, respectively. The same behavior was observed for non-aged PE8 (-17.9 and 62.8 °C, related to β -relaxation and α -transition, respectively). The peaks for aged PE0 and PE8 films occurred at higher temperatures (2.2 and 72.8 °C for PE0; -11.7 and 83.2 °C for PE8), indicating that aging reduces chain mobility due to changes in the amorphous phase of the material and increases crystallinity [32].

Morphology

FESEM images (Fig. 5) show changes on the surface of PE0 and PE8 films over time during the aging process, with severe cracks in PE0-1000 and minor cracks in PE8-1000. This surface behavior (cracking) has been reported for LDPE samples after 800 h exposure in a QUV chamber [26, 27]. According to the literature, abiotic degradation occurs primarily in amorphous regions and reduces strain values, which is considered the main parameter for detecting chain scission and crosslinking during abiotic degradation [4, 16, 33–36]. Moreover, this behavior also was evidenced by the increase of crystallinity degree and Young's modulus, as well as the decrease of loss modulus of PE8 samples after aging exposition times.

Soil exposition assay (biodegradation evaluation)

Morphology

FESEM images of PE0 and PE8 samples (Fig. 5) were obtained to assess biofilm formation after 60 days of soil exposure. Microorganism adhesion was observed on the

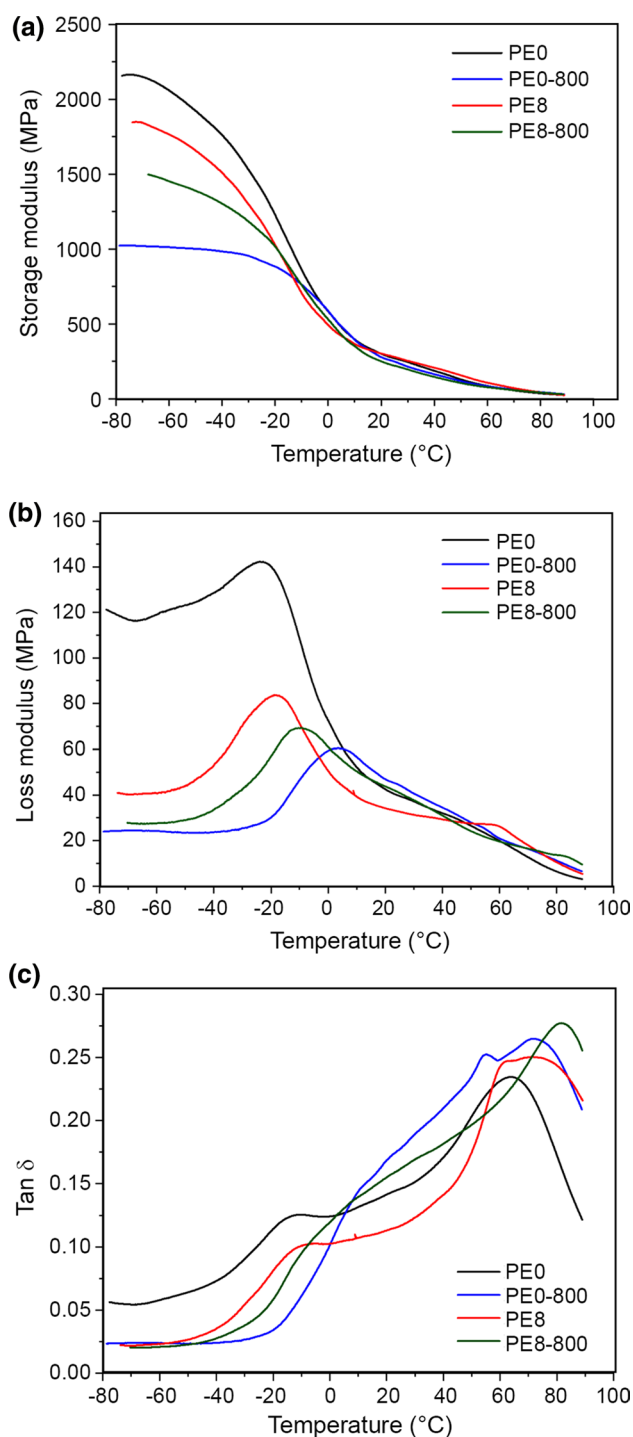


Fig. 4 Storage modulus (a), loss modulus (b), and Tan δ (c) versus temperature curves for non-aged and aged PE0 and PE8 films

surface of all samples (0, 600, and 1000 h). PE0 films (non-aged and aged) present similar microorganisms (*coccus*, *hyphae*, and *spores*). Besides these microorganisms, it was also observed the presence of *bacillus* in samples of PE8 (non-aged and aged). Additionally, the microbial community began to enter the micro-cracks present in aged

films, invading the bulk polymer. Filamentous microorganisms develop their mycelia framework within the materials. The mechanical action of apices penetrating in the materials increases the pores size, which provokes cracks and due to this, the material resistance and durability are weakened [36].

Structural characteristics

FTIR analyses of PE0 and PE8 films after 60 days of soil exposure showed changes in structural characteristics (Fig. 6). Spectra of PE0 and PE8 films exhibited bands at $3697\text{--}3290\text{ cm}^{-1}$ (OH stretching), 1641 cm^{-1} (C=O stretching of secondary amides), 1556 cm^{-1} (N–H bending of secondary amides), $1100\text{--}1007\text{ cm}^{-1}$ (C–O bond and N–O stretching) and 910 cm^{-1} ($\text{H}_2\text{C}=\text{CH}_2$ group). PE0- and PE8-aged samples spectra showed two bands in the $1650\text{--}1500\text{ cm}^{-1}$ range, corresponding to C=O stretching and N–H bending of secondary amides and C=C stretching of the aromatic ring. Structural changes after exposure to microorganisms have also been reported in the literature and are related to consumption of oxygenated groups present in the polymer by the microorganisms [2, 37]. Table 2 shows the carbonyl indexes (CIs) for these samples after 60 days of soil exposure. In non-aged films, only PE8 displayed an increase in the carbonyl index (sixfold), reinforcing the finding that the additive facilitates the surface degradation. However, the CI declined in aged films. Comparison of the CIs of aged PE0 and PE8 films after 60 days' soil exposure showed a sharper decline in 600 h in PE8, and 1000 h for PE0. A previous study also reported the decrease of CI in a microbiologic assay with HDPE and LDPE [38].

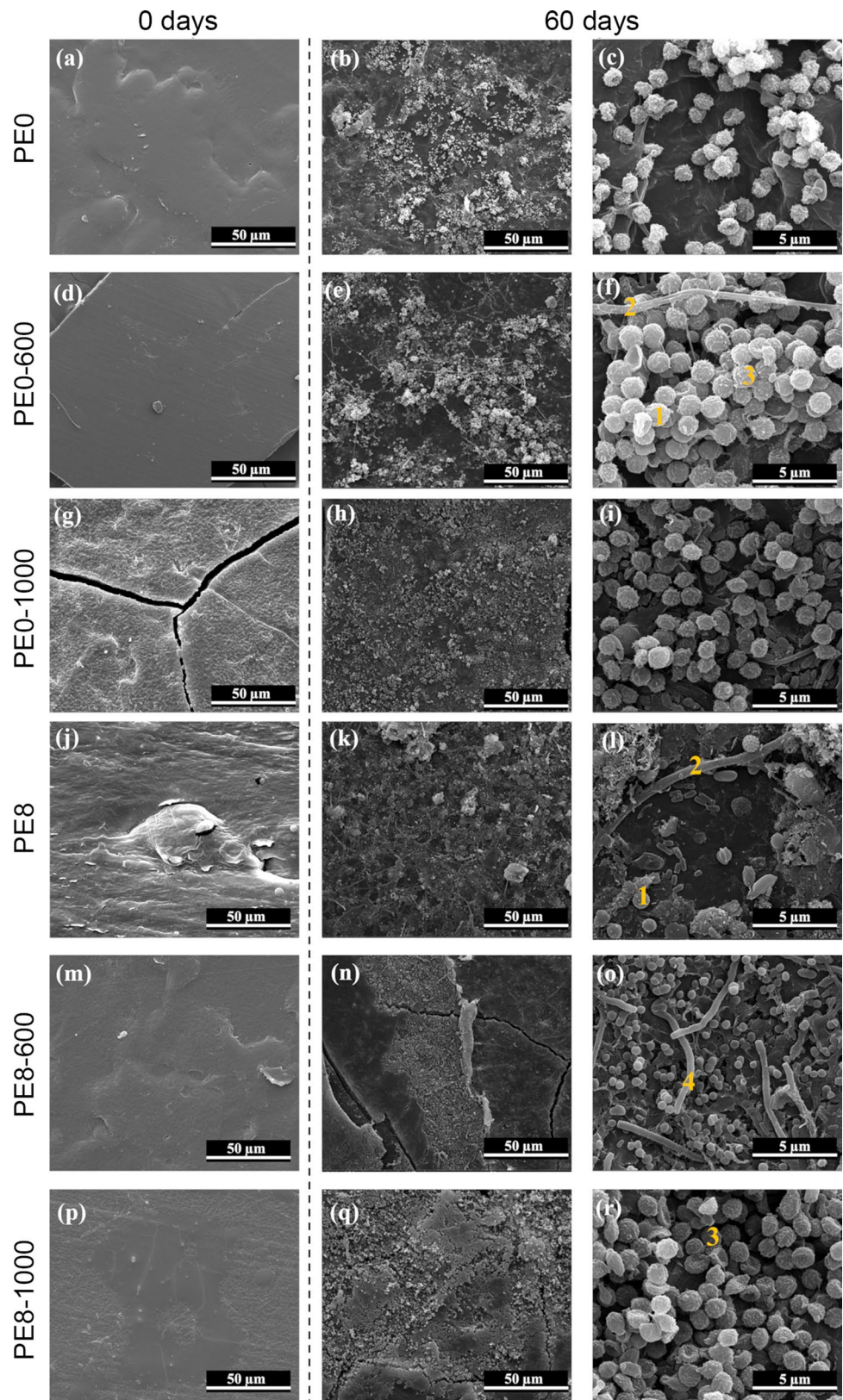
Thermal properties

TGA analysis was performed on non-aged and aged PE0 and PE8 films after 60 days' exposure to soil (Table 2). Non-aged PE0 and PE8 films obtained similar T_{10} values ($\approx 440\text{ }^\circ\text{C}$) before and after soil exposure. Similar thermal behavior was observed for all the aged samples after soil exposure and both groups displayed a slight upward trend in T_{10} . There were not changes in T_m values of the samples after soil exposition.

Molar weight evaluation

In the present study, molar weight of PE0 and PE8 samples declined with aging time related to non-aged samples (Table 2). However, when aging times were compared between them, there was no difference (PE0-600 and PE0-1000), with exception of PE8-600 and PE8-1000 that presented different values, being molar weight value of PE8-1000 greater. Even values seemed to be dissimilar and it

Fig. 5 FE-SEM images of non-aged and aged samples before and after exposition to soil: **a** PE0 non-aged, **b, c** PE0 non-aged 60 days, **d** PE0-600, **e, f** PE0-600 60 days, **g** PE0-1000, **h, i** PE0-1000 60 days, **j** PE8 non-aged, **k, l** PE8 non-aged 60 days, **m** PE8-600, **n, o** PE8-600 60 days, **p** PE8-1000 and **q, r** PE8-1000 60 days. PE0 films present coccus (1), hyphae (2) and spores (3) morphology. Besides, PE8 films present bacillus (4) morphology. Figures a, b, d, e, g, h, j, k, m, n, p (mag. $\times 2000$). Figures c, f, i, l, o and r (mag. $\times 10,000$)



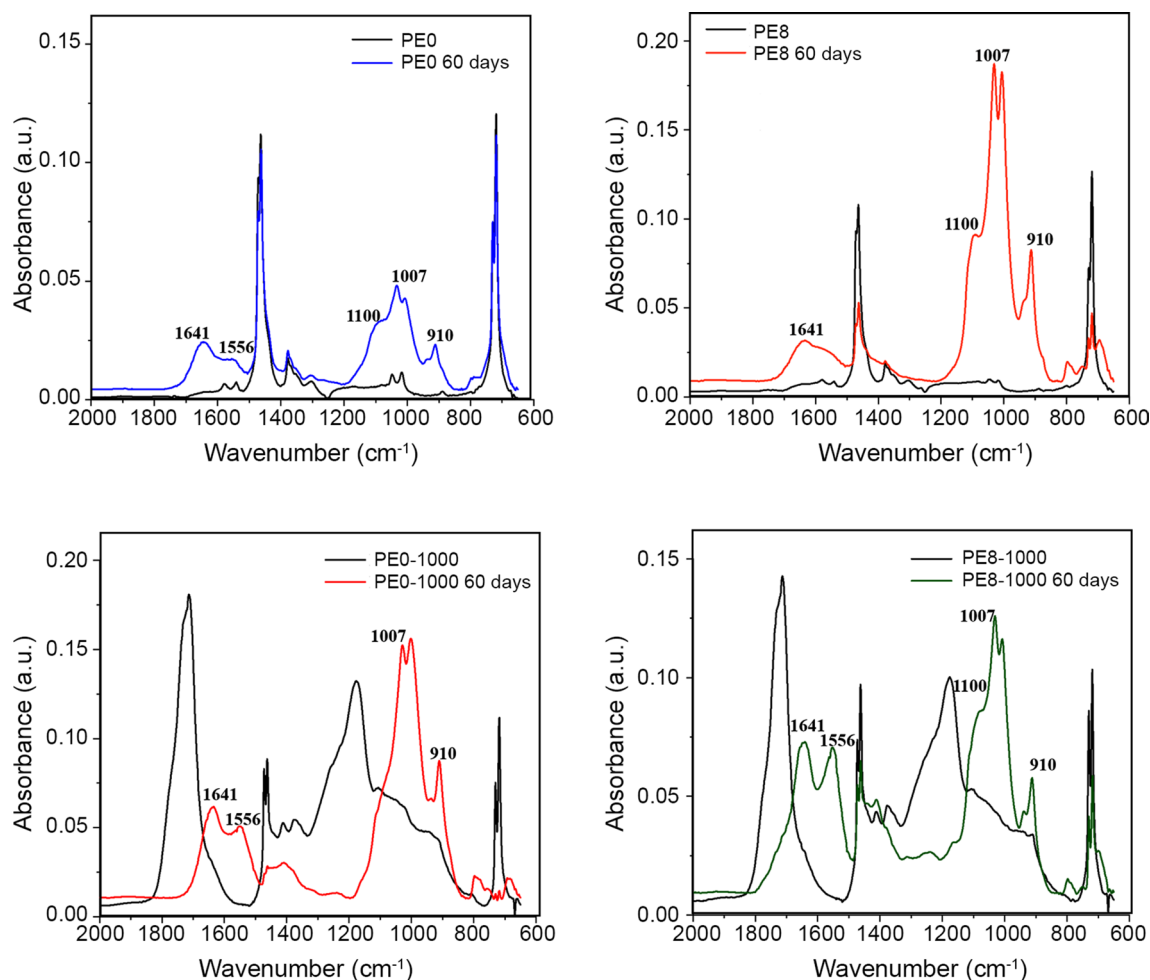


Fig. 6 FTIR spectra of PE0 and PE8 samples (0 and 1000 h) before and after 60 days of soil exposure in the interval of wavenumber 2000 to 650 cm^{-1} : **a** PE0, **b** PE0-1000, **c** PE8, and **d** PE8-1000

should be reminded that assays were performed in independent triplicate. Albertsson and Karlsson [14] studied the degradation behavior of LDPE (M_n 37.2 kg/mol and M_w 196.5 kg/mol) and LDPE/pro-oxidant additive (M_n 37.5 kg/mol and M_w 192.9 kg/mol) in water medium at 95 °C for 45 days. The researchers observed a decrease in M_n and M_w values for LDPE (M_n 8.0 kg/mol and M_w 54.0 kg/mol) and LDPE/additive (M_n 3.2 kg/mol and M_w 19.4 kg/mol). They identified that low molar weight products (carboxylic acids, hydrocarbons, ketones, aldehydes, and alcohols) formed after the degradation were responsible for the molar weight decrease. Teymori et al. [39] studied the thermal aging at 80 °C of LDPE (M_n 22.3 kg/mol and M_w 257.8 kg/mol) over 42 days and found that M_n and M_w values decreased with longer exposure times, with M_n and M_w values of 9.1 and 33.8 kg/mol, respectively. Ojeda et al. [16] evaluated changes in molar weight of LDPE before (143 kg/mol) and after 280 days (42.9 kg/mol) of natural weathering exposition and also observed a decrease in M_w values. Related to

soil exposition samples, it was possible observe an increase in molar weight values only for PE0-600. Santo et al. [1] exposed a LDPE previously UV-irradiated to a crude extracellular laccase from a bacterial strain *Rhodococcus ruber* and observed a decrease in molar weight values before (M_n 40.4 kg/mol and M_w 116.5 kg/mol) and after exposition (M_n 34.2 kg/mol and M_w 93.6 kg/mol). Yang et al. [13] exposed PE to a two bacterial strains from the guts of plastic-eating wax worms and observed that M_n values did not change but M_w decreased, which M_w value was 90.0 kg/mol before, 82.5 kg/mol (strain 1) and 78.2 kg/mol (strain 2).

Carbon mineralization assay (aerobic biodegradation evaluation)

Carbon dioxide production and carbon mineralization

The results of elemental analysis showed a C content of 37.73% for positive reference material (starch), 90.62% for

PE8 sample and 78.32% for PE8-800 samples, showing that aging process decreased C content in PE8 samples. Therefore, the accelerated weathering can alter the carbon amount available to microorganisms, since random chain scission and crosslinking reactions occur during this process [15].

Figure 7 shows the mg CO_2 produced and mineralization percentage results for the blank (soil only), positive control (corn starch), PE8 and PE8-800. The amount of cumulative CO_2 produced after 166 days.

(Fig. 7a) was higher in the aged sample with additive (5144.5 mg) compared to positive control (4825.9 mg) and non-aged PE8 (4740.5 mg). Final values of C mineralization (%) for positive control, PE8 and PE8-800 were 21.3, 6.7 and 20.3%, respectively. A trend of faster biodegradation was observed for the positive control when compared to the other samples (until 40 days, Fig. 7b). This result is important, since the positive control can be used to evaluate soil quality. A comparison of the amount of cumulative CO_2 produced by PE8 and PE8-800 films at the end (166 days) indicated that accelerated weathering facilitated microbial attack, according to the literature [2, 40]. Moreover, PE8-800 sample showed a percentage of mineralization final value very similar to positive control, which is a biodegradable material and from renewable source. These results clearly demonstrate the effect of accelerated weathering on the LDPE biodegradation, as reported in the literature. Esmaeli et al. [12] studied CO_2 evolution for LDPE in soil over 125 days (ASTM D5988-12). The authors found that samples that were in contact with the soil/selected microorganisms (*Lysinibacillus xylanilyticus* and *Aspergillus niger*) exhibited mineralization of 15.8% (non-aged) and 29.5% (aged), whereas those in contact with the soil alone displayed only 7.6% (non-aged) and 8.6% (aged). According to literature, these mineralization values may be attributed to the microbial assimilation of carbon present in the UV-modified samples or abiotic

oxidation products [41]. Castro-Aguirre et al. [40] also obtained lower mineralization percentage values in non-aged and pure LDPE samples ($6.8 \pm 4.8\%$), as well as, for this sample in powder form ($3.7 \pm 2.5\%$) after exposing it to a compost at 58°C during 60 days.

Structural characteristics

FTIR analysis of the PE8 and PE8-800 films after 166 days of aerobic biodegradation indicated changes in structural characteristics. For PE8 sample, bands were observed at $3697\text{--}3290\text{ cm}^{-1}$, attributed to --OH stretching, and at $1100\text{--}1007\text{ cm}^{-1}$ corresponding to the C--O bond and N--O stretching. Similar bands were found for the PE8-800 film, in addition to $1650\text{--}1500\text{ cm}^{-1}$, attributed to C=O stretching and N--H bending of secondary amides, and C=C stretching of the aromatic ring. These bands are associated with N and C mineralization. Under aerobic conditions, organic nitrogen can be transformed into NH_3 or NH_4^+ during ammonification and then into nitrites (NO_2^-). Nitrites formed at the end of mineralization are converted into nitrates [15].

Molar weight evaluation

On the biodegradation process, changes in the material molar weight occur due to depolymerization and bioassimilation steps. As previously mentioned, in the soil exposition test, aging time influences the decline in molar weight. M_n values obtained after the aerobic biodegradation were 10.3 ± 1.0 and 3.1 ± 0.4 kg/mol for PE8 and PE8-800, respectively. M_w values obtained after the aerobic biodegradation were 82.9 ± 0.7 and 49.8 ± 4.4 kg/mol for PE8 and PE8-800, respectively. It showed the effects of aging exposure and soil microbiome. Fontanella et al. [18] evaluated

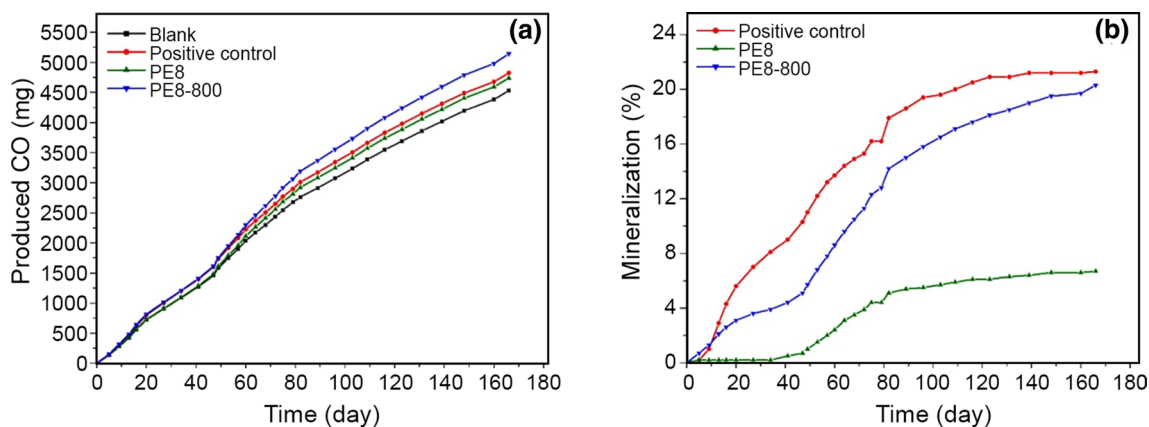


Fig. 7 Produced CO_2 (mg) curve for the blank (soil only), positive control (corn starch), PE8 and PE8-800 **a**, and mineralization percentage curve **b** for the positive control, PE8 and PE8-800 over 166 days

abiotic degradation for 300 h thermal oxidation and biodegradation (*Rhodococcus ruber*) of pure LDPE and mixed with pro-oxidants additive. Although, they observed a decrease in molar weight after abiotic exposure, and the values did not change after biodegradation.

According to Morro et al. [10] the biodegradation process can complement the photodegradation. However, its efficacy depends on several factors, such as material composition, physical and chemical surface properties, and native microbiota. In addition, very small changes in these factors can result in large differences in material biodegradation behavior [10]. Likewise, changes in the biodegradation tests conditions (temperature, pH and moisture, as well as nutrition composition) can modify the material biodegradation behavior, due the change of amount and predominance of the microorganism species [42]. Gu [41] proposed that dominant group of microorganisms and degradation pathways associated to polymer degradation process generally are determined by environment conditions. Also, the biodeterioration and degradation of polymeric substrate rarely reach 100% and a little portion of this can be incorporated to microbial biomass, humus and others natural products.

Conclusion

Abiotic and biotic degradations of a LDPE blend in soil of South Brazil landfill were indications of the changes in chemical, thermal, mechanical and morphological properties of a biodegradable LDPE blend prepared with a biodegrading additive (without metals), after exposition to accelerated aging and inoculation in soil. The presence of additive favored degradation process, given that polar functional groups were incorporated into the chemical structure of LDPE. Biotic degradation was more accentuated in the aged films (with/without additive) exposed to soil when compared to their non-aged counterparts. Results obtained in the biodegradation assay are promising, once that it was reached in a natural soil from South Brazil landfill, which has its origin from the composting of urban solid waste and due to this, its composition and characteristics are the closest to reality. Moreover, aged material exhibits biodegradable behavior, once that reached the greater values of carbon mineralization. Combination of biodegrading additive and abiotic factors showed that LDPE blends became more attractive for soil microbiota adhesion, surface material biodeterioration and carbon mineralization. Therefore, biodegradable LDPE blends obtained in this work can be considered as an alternative for plastic packaging industry, reducing the effects caused by plastic waste on the environment.

Acknowledgements The authors thank CAPES (Financial Code—001) for scholarships, as well as PUCRS and Brasilata Company for

technical and financial support, Laboratório Central de Microscopia e Microanálise (LabCEMM/PUCRS) for morphological analyzes and Laboratory of Dr. Marcelo Villar (PLAPIQUI/CONICET) for the GPC analyses.

References

1. Santo M, Weitsman R, Sivan A (2013) The role of the copper-binding enzyme—laccase—in the biodegradation of polyethylene by the actinomycete *Rhodococcus ruber*. *Int Biodeter Biodeg* 84:204–210
2. Peixoto J SL, Krüger R (2017) Brazilian Cerrado soil reveals an untapped microbial potential for untreated polyethylene biodegradation. *J Hazard Mater* 324B:634–644
3. Silva E, Neto J (2016) Impactos Ambientais da produção de garrafas de polietileno numa indústria de Teresina. *Polimeros* 26:49–54
4. Adelhafidi A, Babaghayou I, Chabira S, Sebaa M (2015) Spectroscopic analysis of weathering effects on low density polyethylene. *J Chem Eng Chem Res* 2:529–535
5. Sen S, Raut S (2015) Microbial degradation of low density polyethylene (LDPE): a review. *J Environ Chem Eng* 3:462–473
6. Scott G (2000) Green polymers. *Polym Degrad Stabil* 68:1–7
7. Ojeda T, Dalmolin E, Forte M, Jacques R, Bento F, Camargo F (2009) Abiotic and biotic degradation of oxo-biodegradable polyethylenes. *Polym Degrad Stabil* 94:965–970
8. Martínez-Romo A, González-Mota R, Soto-Bernal J, Rosales-Candelas I (2015) Investigating the degradability of HDPE, LDPE, PE-BIO, and PE-OXO films under UV-B radiation. *J Spectrosc* 10:1–6
9. Haider T, Völker C, Kramm J, Landfester K, Wurm F (2019) Plastics of the future? The impact of biodegradable polymers on the environment and on society. *Angew Chem Int Ed* 58:50–62
10. Morro A, Catalina F, Sanchez-León E, Abrusci C (2019) Photodegradation and biodegradation under thermophile conditions of mulching films based on poly (butylene adipate-coterephthalate) and its blend with poly (lactic acid). *J Polym Environ* 27:352–363
11. Shah A, Hasan F, Hameed A, Ahmed S (2008) Biological degradation of plastics: a comprehensive review. *Biotechnol Adv* 26:246–265
12. Esmaeli A, Pourbabae A, Alikhani H, Shabani F, Esmaeli E (2013) Biodegradation of low-density polyethylene (LDPE) by mixed culture of *Lysinibacillus xylanilyticus* and *Aspergillus niger* in soil. *PLoS ONE* 8:e71720
13. Yang J, Yang Y, Wu W, Zhao J, Jiang L (2014) Evidence of polyethylene biodegradation by bacterial strains from the guts of plastic-eating wax worms. *Environ Sci Technol* 48:13776–13784
14. Ojeda T, Freitas A, Birck K, Dalmolin E, Jacques R, Bento F, Camargo F (2011) Degradability of linear polyolefins under natural weathering. *Polym Degrad Stabil* 96:703–707
15. Albertsson A, Kalrsson S (1994) Environment-adaptable polymers. *Polym Degrad Stabil* 41:345–349
16. Gewert B, Plassmann M, Macleod M (2015) Pathways for degradation of plastic polymers floating in the marine environment. *Environ Sci Proc Imp* 17:1513–1521
17. Raddadi N, Fava F (2019) Biodegradation of oil-based plastics in the environment: existing knowledge and needs of research and innovation. *Sci Total Environ* 679:148–158
18. Fontanella S, Bonhomme S, Kounty M, Husarova L, Brusson JM, Courdavault JP, Pitterif S, Samuel G, Pichonh G, Lemairea J, Delort AM (2010) Comparison of the biodegradability of various polyethylene films containing pro-oxidant additives. *Polym Degrad Stabil* 95:1011–1021

19. Nowak B, Pajak J, Drozd-Brarkowicz M, Rymarz G (2011) Microorganisms participating in the biodegradation of modified polyethylene films in different soils under laboratory conditions. *Int Biodeter Biodeg* 65:757–767
20. Corti A, Sudhakar M, Chiellini E (2012) Assessment of the whole environment degradation of oxo-biodegradable linear low density polyethylene (LLDPE) films designed for mulching applications. *J Polym Environ* 20:1007–1018
21. Richter M, Schulenburg C, Jankowska D, Heck T, Faccio G (2015) Novel materials through nature's catalysts. *Mater Today* 18:459–467
22. Pires J, Miranda G, de Souza G, Fraga F, Ramos A, de Araújo G, Ligabue R, Azevedo C, Lourega R, de Lima J (2019) Investigation of degradation of polypropylene in soil from enzymatic additive. *Iran Polym J* 28:1045–1055
23. Pires J, Ramos A, Miranda G, de Souza G, Fraga F, Azevedo C, Ligabue R, de Lima J, Lourega R (2020) Natural freshwater degradation of polypropylene blends with additives of a distinct nature. *Polym Bull* published online
24. Dartora P, Santana R, Moreira A (2015) The influence of the long chain branches of LLDPE on processability and physical properties. *Polimeros* 25:531–539
25. Barbeş L, Rădulescu C, Stihl C (2014) Spectrometry characterization of polymeric materials. *Rom Rep Phys* 66:765–777
26. Tavares C, Gulmine J, Lepienski C, Akcelrud L (2003) The effect of accelerated aging on the surface mechanical properties of polyethylene. *Polym Degrad Stabil* 81:367–373
27. Gulmine J, Janissek P, Heise H, Akcelrud L (2003) Degradation profile of polyethylene after artificial accelerated weathering. *Polym Degrad Stabil* 79:385–397
28. Ndlovu S, Van Reenen A, Luyt A (2013) LDPE-wood composites utilizing degraded LDPE as compatibilizer. *Compos A* 51:80–88
29. Restrepo-Flórez JM, Bassi A, Thompson M (2014) Microbial degradation and deterioration of polyethylene—a review. *Int Biodeter Biodeg* 88:83–90
30. Reddy M, Gupta R, Bhattacharya S, Parthasarathy R (2008) Abiotic oxidation studies of oxi-degradable polyethylene. *J Polym Environ* 16:27–34
31. Lucas E, Soares B, Monteiro E (2001) Caracterização de polímeros—determinação de peso molecular e análise térmica. E-papers, Rio de Janeiro
32. Pedrosa A, Rosa D (2005) Mechanical, thermal and morphological characterization of recycled LDPE/corn starch blends. *Carbohydr Polym* 59:1–9
33. Vogt N, Kleppe E (2009) Oxo-biodegradable polyolefins show continued and increased thermal oxidative degradation after exposure to light. *Polym Degrad Stabil* 94:659–663
34. Benítez A, Sánchez J, Arnal M, Müller A (2013) Monitoring abiotic degradation of branched polyethylenes formulated with pro-oxidant through different mechanical tests. *Polym Degrad Stabil* 98:1705–1716
35. Benítez A, Sánchez J, Arnal M, Müller A, Rodríguez O, Morales G (2013) Abiotic degradation of LDPE and LLDPE formulated with pro-oxidant additive. *Polym Degrad Stabil* 98:490–501
36. Lucas N, Bienaime C, Belloy C, Queneudec M, Silvestre F, Nava-Saucedo JE (2008) Polymer biodegradation: mechanisms and estimation techniques—a review. *Chemosphere* 73:429–444
37. Albertsson A, Barenstedt C, Karlsson S, Lindberg T (1995) Degradation product pattern and morphology changes as means to differentiate abiotically and biotically aged degradable polyethylene. *Polymer* 36:3075–3083
38. Ojha N, Pradhan N, Singh S, Barla A, Shrivastava A, Khatua P, Rai V, Bose S (2017) Evaluation of HDPE and LDPE degradation by fungus, implemented by statistical optimization. *Sci Rep-UK* 7:1–13
39. Teymouri Y, Kwamen R, Blümich B (2015) Aging and degradation of LDPE by compact NMR. *Macromol Mater Eng* 300:1063–1070
40. Castro-Aguirre E, Auras R, Selke S, Rubino M, Marsh T (2017) Insights on the aerobic biodegradation of polymers by analysis of evolved carbon dioxide in simulated composting conditions. *Polym Degrad Stabil* 137:251–271
41. Gu JD (2003) Microbiological deterioration and biodegradation of synthetic polymeric materials: recent research advances. *Int Biodeter Biodeg* 52:69–91
42. Nguyen DM, Do TVV, Grillet AC, Thuc HH, Nhan C, Thuc H (2016) Biodegradability of polymer film based on low density polyethylene and cassava starch. *Int Biodeterior Biodegradation* 115:257–265