



Research article

Influence of the nature of pro-oxidants on the photooxidation of polyethylene blown films

João Augusto Osório Brandão^{a,*}, Fernando dal Pont Morisso^b, Edson Luiz Francisquetti^c, Ruth Marlene Campomanes Santana^a^a Federal University of Rio Grande do Sul (UFRGS), Engineering School, Laboratory of Polymeric Materials (LAPOL), Bento Gonçalves Ave, 9500, 91501-970, Porto Alegre, Brazil^b Feevale University, Laboratory for Advanced Materials Studies, ERS-239, 2755, 93525-075, Novo Hamburgo, Brazil^c Federal Institute of Rio Grande do Sul, Materials Department, São Vicente Ave, 785, 95174-274, Farroupilha, Brazil

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ABSTRACT

In an attempt to reduce the accumulation of polymeric waste in the environment, such as plastic bags, the use of pro-oxidants has been adopted in polyolefins, including polyethylene (PE), which is one of the most used polymers in film production. The incorporation of this additive to PE film aims to accelerate its oxidation in the process of abiotic degradation, generating oxygenated groups that can facilitate the biotic degradation. Commercial pro-oxidants are commonly organic salts of transition metals. However, their use can lead to a secondary problem, the inappropriate accumulation of transition metals at the site where the polymeric waste was deposited and, for this reason, it has been sought pro-oxidants metals free and that can also be biodegraded. In this context, this work aimed to evaluate the photodegradation of PE blown films obtained by extrusion using a commercial pro-oxidant, d2wTM, an alternative organic pro-oxidant, benzoin, and also a standard film, without pro-oxidant. After undergoing 96 and 144 h of UV light exposure, the blown films were evaluated by dilute solution viscometry, FTIR and SEM analysis. The results showed that the pro-oxidants lead to the formation of more macromolecular fragments containing carbonyl groups than in the standard PE film. The film extruded with benzoin showed greater fragmentation, which may be associated with a greater reduction in the average viscosimetric molar mass, therefore, this additive being a promising organic substance in the induction of photooxidation, as demonstrated by the other results obtained by FTIR and SEM.

1. Introduction

Polymeric materials are indispensable to contemporary life, having infinite applications and, in many cases, replacing other classes of materials, such as glass, ceramics and metals, in several purposes [1, 2, 3, 4]. For this reason, these are research targets in several research centers and universities around the world that also seek to develop new elements that present characteristics such as easy processing, low cost and mechanical properties specific to their use, as well as degradation that prevents them from contributing to a major environmental problem: the accumulation of polymeric waste in the soil, rivers and oceans caused mainly by the incorrect and unconscious disposal of single-use items such as bags, cups and bottles [5, 6, 7, 8]. More recently, polymeric waste, in the form of microplastics, has been investigating in all the environments mentioned [9, 10], including in air [11].

Polyethylene (PE), in its different variants, is one of the most used polymers among petrochemical resins, being a semicrystalline thermoplastic of low cost, easy processing and with excellent mechanical properties, being commonly used to obtain plastic films used as packaging, since it is odorless and non-toxic [6, 12]. However, with a simple structure, containing only carbon (C) and hydrogen (H) atoms, have high chemical inertia and, therefore, presents low degradability, being one of the polymers that most contributes to the environmental problem on a global level [6, 9, 13, 14, 15].

Processing PE with pro-oxidant additives has been an option to favor the abiotic degradation of macromolecules, by photooxidation and thermooxidation, leading to the production of lower molar mass oxygenated fragments. In a second stage of the degradation process, these fragments are assimilated by microorganisms such as fungi, bacteria and algae, constituting the biotic degradation [4, 14, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25]. When processed with such additives, PE is called

* Corresponding author.

E-mail address: jaobrandao@gmail.com (J.A. Osório Brandão).

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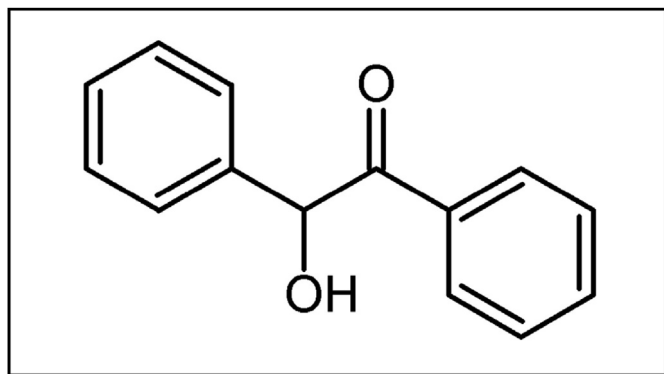
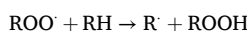
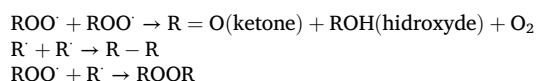


Figure 2. Chemical structure of benzoin.

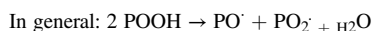
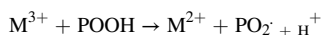
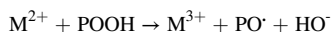


Termination



The photooxidation process of PE is well known and reported in scientific papers. Figure 1 presents a simplified scheme of the PE photooxidation mechanism (showing initiation, propagation and termination), in which it can be seen that the process leads to the formation of oxygenated products such as carboxylic acids, esters, aldehydes, lactones and ketones and hydroxyl-containing fragments [23, 34, 38, 39]. According to the presented scheme, it is also possible to observe that such oxygenated products have their production enhanced by Norrish I and Norrish II reactions [38, 40, 41], characteristic of PE photooxidation. In addition, it is possible to observe the formation of unsaturated fragments, whose unsaturations may or may not be located in the final portion of the carbon chain.

Transition metal-based pro-oxidants act in the propagation phase, accelerating the degradation of hydroperoxides which consequently raises the rate of PE degradation [12, 19, 42, 43]. The d2w™ additive, according to previously published studies, has its composition typically based on manganese stearate [44, 45]. Below is the general reaction of transition metals with hydroperoxides:



However, the use of transition metal-based pro-oxidants, even at low concentrations, can lead to a secondary problem, i.e., their incorrect deposition in the environment. For this reason, the use of transition metal-free organic substances as pro-oxidants has been investigated, which would lead PE, for example, to more accelerated photo-oxidation and thermo-oxidation, but which can also be used as nutrients by microorganisms in biotic degradation. Benzoin, a biodegradable organic compound that has chromophore groups (carbonyl and aromatic rings) in its chemical structure, has been investigated as a pro-oxidant agent for polypropylene [46] and polyethylene [47, 48]. Figure 2 shows the chemical structure of benzoin, containing one carbonyl and two aromatic rings, considered to be chromophore groups.

In this work, the photooxidation of PE additivated with a commercial transition metal-based pro-degradant, d2w™, and benzoin, a fully organic and biodegradable chemical compound, were evaluated. HDPE/LDPE 90/10 films were processed by blown extrusion and subjected to accelerated aging in a UV chamber for 96 and 144 h. The samples were characterized by dilute solution viscometry, to evaluate the change in

Table 1. Percent of power used of motors of Seibt ES-35FR extruder.

Engine	Percentage of power used (%)	Power (kW)
Screw	42.16	5.516
Stretched	55.70	0.37
Winder	14.80	0.37

Table 2. Mass composition of the HDPE/LDPE films.

Sample	HDPE/LDPE (90/10) (%wt)	Benzoin (%wt)	d2w™ (%wt)
PE_Pure	100	-	-
PE_OM	99	-	1
PE_ONM	99	1	-

viscosimetric molar mass; FTIR, to evaluate the formation of functional groups containing carbonyl and other unsaturated products; and SEM, to evaluate the change in surface morphology of the films.

2. Experimental

2.1. Materials

In this work were used two different types of polyethylene produced by Braskem (Brazil): low density polyethylene (LDPE) grade EB-853/72, with MFI of 2.7 g/10 min (190°C/2.16 kg) and high density polyethylene (HDPE) grade HE-150, with MFI of 1.0 g/10 min (190°C/12.6 kg). d2w™ pro-degradant additive, produced by Symphony Enviromental (United Kingdom), in masterbatch. Benzoin powder, produced by Merck KGaG, with a purity of around 99%. Decalin (Decahydronaphthalene) produced by Neon.

2.2. Preparation of PE films without and with pro-oxidant additives

Initially, a mixture of HDPE/LDPE was made in a mass proportion of 90/10, respectively. In this proportion it was easier to control the processing parameters by blown extrusion to obtain the films. Subsequently, the mixture without and with pro-oxidant additives was processed in a Seibt single-screw extruder, model ES 35-FR, with 5 heating zones, 40 mm die diameter, 35 mm screw diameter and L/D ratio of 30:1. The processing of the 3 films was carried out under equal conditions, and the following temperature profile was used: 120/150/175/185/210 °C, from zones 1 (feed) to zone 5 (die). The diameter of the balloon was kept constant during the operation, obtaining films with an average thickness of 30µm. The processing speed was established by the percentage used of the maximum power of each motor (screw, stretched, and winder), according to Table 1.

The names of each of the films evaluated in this work are shown in Table 2, where PE_Pure was assigned to the PE film without addition of a pro-degradant, PE_OM to the PE film obtained with organic metallic pro-degradant (d2w™) and PE_ONM to the film obtained with organic non-metallic pro-degradant (benzoin).

2.3. Accelerated photo-oxidation test

The samples were submitted to accelerated aging in an Adexim Comexim UV chamber, model "C-UV - Hybrid", which operates according to ASTM G-154 recommendations, always in the presence of air. The equipment has eight 40 W lamps, four of which emit UVA radiation ($\lambda = 351 \text{ nm}$) and the other four emit UVB radiation ($\lambda = 313 \text{ nm}$). The samples, with approximate dimensions of $15 \times 15 \text{ cm}$, were exposed to cycles of 4 h of radiation incidence (UVA/UVB) at 50 °C and air humidity equal to the ambient humidity (30%) and 4 h of condensation at 45 °C, performed with distilled water saturated with O₂ and humidity

maintained at 100% in this cycle. The equipment had an automatic temperature control system. The samples were exposed for 96 and 144 h.

2.4. Characterization of PE films before and after photooxidation

2.4.1. Dilute solution viscometry (DSV) and viscosity average molar mass (\overline{M}_v)

HDPE/LDPE films, before and after accelerated aging by exposure UV light, were characterized by dilute solution viscometry (DSV), with determination of intrinsic viscosity ($[\eta]$) and average viscosimetric molar mass (\overline{M}_v) of PE. Five PE solutions were used for each film analyzed, with concentrations of 0.2; 0.4; 0.6; 0.8 and 1.0 g/dL. The sample masses needed to obtain the concentrations mentioned above were diluted in enough decalin to prepare 25 mL of solution. The dissolution process was performed at 140 °C for 1 h. Cannon-Fenske type viscometers (n° 50), with 0.44 mm internal capillary diameter, were used to determine the solution viscosities. The procedures were performed according to ASTM D445 and ASTM D446. Solution viscosities were measured at 135.0 ± 0.1 °C [49] with viscometers immersed in a thermostatic silicone oil bath of the SOLAB brand, model SL 150.

Then, the relative viscosities (η_{rel}), specific (η_{sp}), reduced specific ($\eta_{red.sp}$) and, finally, the inherent ($\ln \eta_{rel/C}$) were determined. Subsequently, plots of the reduced specific viscosities ($\eta_{red.esp}$) and inherent viscosities ($\ln \eta_{rel/C}$) versus concentration were plotted to obtain the intrinsic viscosity ($[\eta]$) of the PE used in the preparation of the solutions, from the extrapolation of the straight lines obtained by linear regression when the concentration tends to zero. Since the values obtained by either curve tend to be the same, the average of both was used as the intrinsic viscosity of the PE. For the determination of the \overline{M}_v , the Makr-Howink-Sakurada equation was used, as presented in Eq. (1):

$$[\eta] = k \cdot (\overline{M}_v)^\alpha \quad (1)$$

The constants α and k were 0.7 and 62×10^{-5} dL/g, respectively [49]. The values of the viscosimetric constants α and k are independent of the type of PE analyzed (whether LDPE, LLDPE or HDPE, for example), according to the literature used as reference.

2.4.2. Fourier transform infrared spectroscopy (FTIR), carbonyl index (COi) and vinyl index (Vi)

The evaluation of the appearance of carbonyl-containing functional groups due to photooxidation of PE was done by FTIR in PerkinElmer equipment, Frontier model, meeting the specifications of ASTM 1131. The analyses were carried out in a controlled environment, with temperature at 25 °C and air humidity at 30%. The films were evaluated in the ATR (Total Attenuated Reflectance) mode, in absorption region from 4000 to 650 cm^{-1} , with 10 scans for each sample. The carbonyl indexes (COi) were calculated from the obtained spectra. The peak at 1463 cm^{-1} was adopted as being poorly variable for PE [39, 49, 50], and the boundaries between 1468 and 1450 cm^{-1} were integrated. The absorption peaks of 1712 cm^{-1} (carboxylic acids), 1723 cm^{-1} (ketones), 1730 cm^{-1} (aldehydes), and 1780 cm^{-1} (lactones) were adopted as the carbonyl absorption peak, and the boundaries between 1780 and 1700 cm^{-1} were integrated [14, 50, 51, 52]. The COi of each sample evaluated was calculated from Eq. (2).

$$\text{COi} = A_{1780-1700} / A_{1468-1450} \quad (2)$$

The calculation of the vinyl index (Vi) was also used to evaluate the appearance of unsaturated fragments. The absorption peak of the double bond between the C atoms (C=C) is located at 1640 cm^{-1} [38] and was integrated between the bands 1680-1620 cm^{-1} . The Vi of each sample was calculated by Eq. (3).

$$\text{Vi} = A_{1680-1620} / A_{1468-1450} \quad (3)$$

Table 3. Intrinsic viscosity ($[\eta]$) of PE in the samples evaluated.

Sample	t exp UV (hours)	$[\eta]_1^*$ (dL/g)	$[\eta]_2^{**}$ (dL/g)	$[\eta]_f^{***}$ (dL/g)
PE_Pure	0	1.5185	1.5651	$1.5418 \pm 0,0329$
	96	1.3219	1.3754	$1.3487 \pm 0,0378$
	144	0.7760	0.7755	$0.7758 \pm 0,0003$
PE_OM	0	1.3812	1.4873	$1.4343 \pm 0,0750$
	96	1.0339	1.1104	$1.0722 \pm 0,0541$
	144	0.7720	0.7585	$0.7653 \pm 0,0095$
PE_ONM	0	1.2376	1.4336	$1.3356 \pm 0,1386$
	96	0.9637	1.0545	$1.0091 \pm 0,0642$
	144	0.5114	0.5086	$0.5100 \pm 0,0020$

* graph ($\eta_{sp,red}$ versus C).

** graph (η_{linehr} versus C).

*** average intrinsic viscosity of $[\eta]_1$ and $[\eta]_2$.

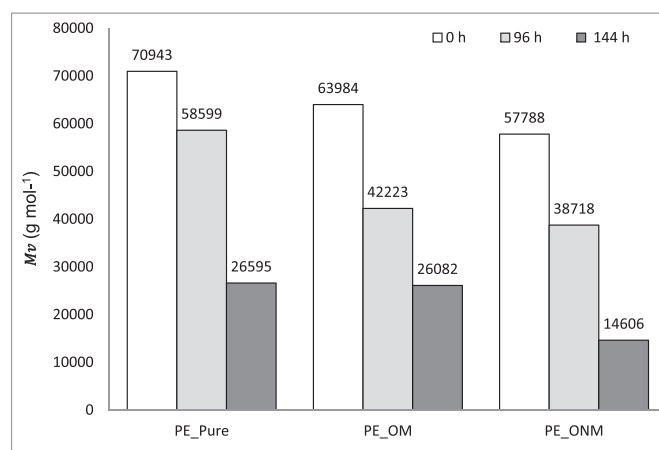


Figure 3. \overline{M}_v of the samples before and after exposure to UV radiation.

2.4.3. Scanning electron microscopy (SEM)

Surface morphologies micrographs of the films were obtained by scanning electron microscopy (SEM) immediately after extrusion processing ($t = 0$) and after the accelerated aging process in a UV chamber. The samples were metallized with gold in the Denton Caccum metallizer, model Desk, according to standard procedures and then evaluated in a Jeol instrument, model JSM6510LV. From electron beams at 10 kV energy, micrographs were obtained with magnifications of 1500x and 5000x.

3. Results and discussion

3.1. Viscosity average molar mass (\overline{M}_v)

Table 3 presents the intrinsic viscosities for PE before and after exposure to UV radiation graphically determined. For the determination of the average viscosimetric molar mass, the value of $[\eta]_f$ was used, i.e., the average value between $[\eta]_1$ and $[\eta]_2$. The small standard deviation values for $[\eta]_f$ reinforce that the concentration range of the PE solutions was ideal for performing the analytical technique. It can be seen that all samples showed a reduction in intrinsic viscosity. The intrinsic viscosity ($[\eta]$) is directly proportional to the average viscosimetric molar mass of the polymer, which therefore indicates degradation with reduction of the PE chain size [53]. It is worth noting that the intrinsic viscosities of the samples with the pro-oxidants, PE_OM and PE_ONM, without exposure to UV radiation ($t = 0$), were lower than the PE_Pure sample, indicating that

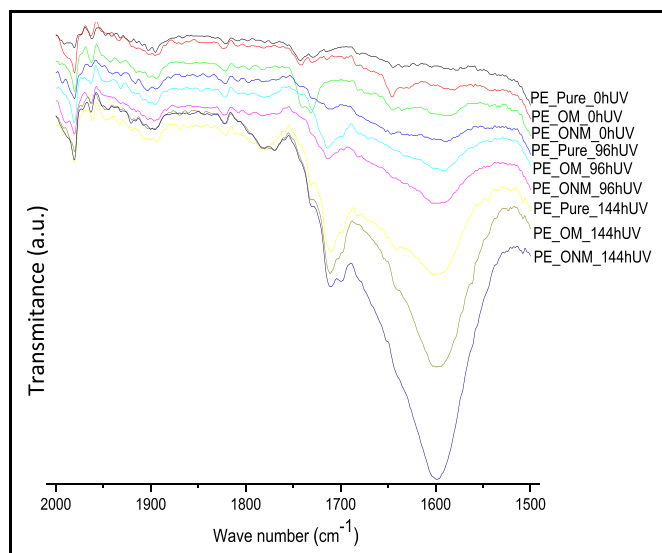


Figure 4. FTIR spectra of the PE samples evaluated.

the additives influenced the scission of the chains during the processing of the films by extrusion, with the PE_ONM film being the lowest of them.

Figure 3 presents the average viscosimetric molar masses of the samples before and after accelerated aging, and the decrease of \bar{M}_v of the PE in the evaluated samples is verified after exposure to UVA/UVB radiation, which proved to be extremely aggressive for the PE in all films.

In the first 96 h, the films containing pro-oxidant additives showed higher reduction of \bar{M}_v , of 34.01% for the PE_OM film and 33.00% for the PE_ONM film, while the PE_Pure film showed 17.40% decrease in molar mass. The results are compatible with those found in another work [54], when the abiotic degradation of PE additivated with commercial pro-oxidant based on metal organic salts was investigated. However, after 144 h and compared to the \bar{M}_v determined for 96 h of exposure, there was 62.27% reduction for the PE_ONM film and of 54.61% for the PE_Pure film, while the PE_OM film showed reduction of only 38.22%. The PE_Pure film showed reduced molar mass, possibly due to the chromophore agents present in the polymer matrix from processing [55], which favored photooxidation. The viscosimetric analysis indicates that benzoin is more efficient in reducing the size of the polymer chains, with a greater decrease in the \bar{M}_v of the PE.

3.2. FTIR

In Figure 4, the FTIR spectra of the samples before and after exposure to UV radiation, between 2000 and 1500 cm^{-1} are presented, plotted using Origin^R. It is observed that there is an increase in the intensity of the carbonyl (1780-1700 cm^{-1}) and unsaturations (1680-1620 cm^{-1}) bands with increasing radiation exposure time, indicating that the PE underwent photooxidation when aged in an accelerated manner in the experiment, with production of fragments containing organic functional groups of the carboxylic acid type, esters, ketones, lactones, and containing vinyl type unsaturations [6, 38].

Subsequently, the COi and Vi were calculated, shown in the graphs in Figure 5, plotted using Origin^R, whose values only reinforce what is observed in the FTIR spectra.

In all films an increase of COi and Vi were observed, indicating an increase in the severity of the photooxidation process by PE. The PE_ONM film shows the highest increase in COi and Vi, especially after 96 up to 144 h of exposure, indicating that the radiation triggers the process that propagates more easily over time and possibly due to the presence of benzoin. The PE_OM film is the second with the highest increase in COi and Vi, indicating that the presence of metal organic salts also accelerate photooxidation, but less effectively than benzoin. Last, with a smaller increase in the indexes, is the PE_Pure film, whose photooxidation, as already mentioned, must have been initiated by contaminants chromophore agents. As shown in Figure 1, the PE photooxidation process leads to the production of macromolecules containing diverse oxygenated functional groups, but with smaller chain sizes than the initial macromolecules. Therefore, the increased COi values are compatible with the reductions in the molar masses of the samples. Furthermore, the results found in these studies are corroborated by those found in another study [28], which evaluated the photooxidation of PE processed with different metal stearates, for which the COi were higher than for PE without additives. In the case of this study, because it is a reaction system with formation of multiple products, Vi only reinforces the oxidation propagation.

3.3. SEM

Figure 6 presents micrographs of the films evaluated, before and after 144 h of UV exposure, at 1500x and 5000x magnification.

The evaluation of the samples shows that all films had different surfaces but intact before exposure to UV radiation. The PE_Pure film is the one presenting the most uniform surface, while the PE_OM film indicates an altered surface, possibly due to the lack of total dissolution of the

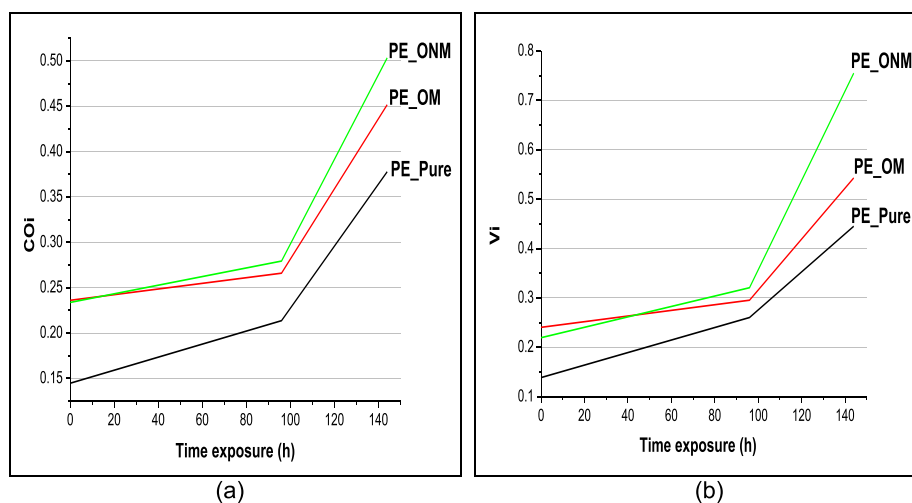


Figure 5. (a) COi and (b) Vi before and after 96 and 144 h of exposure to UV radiation.

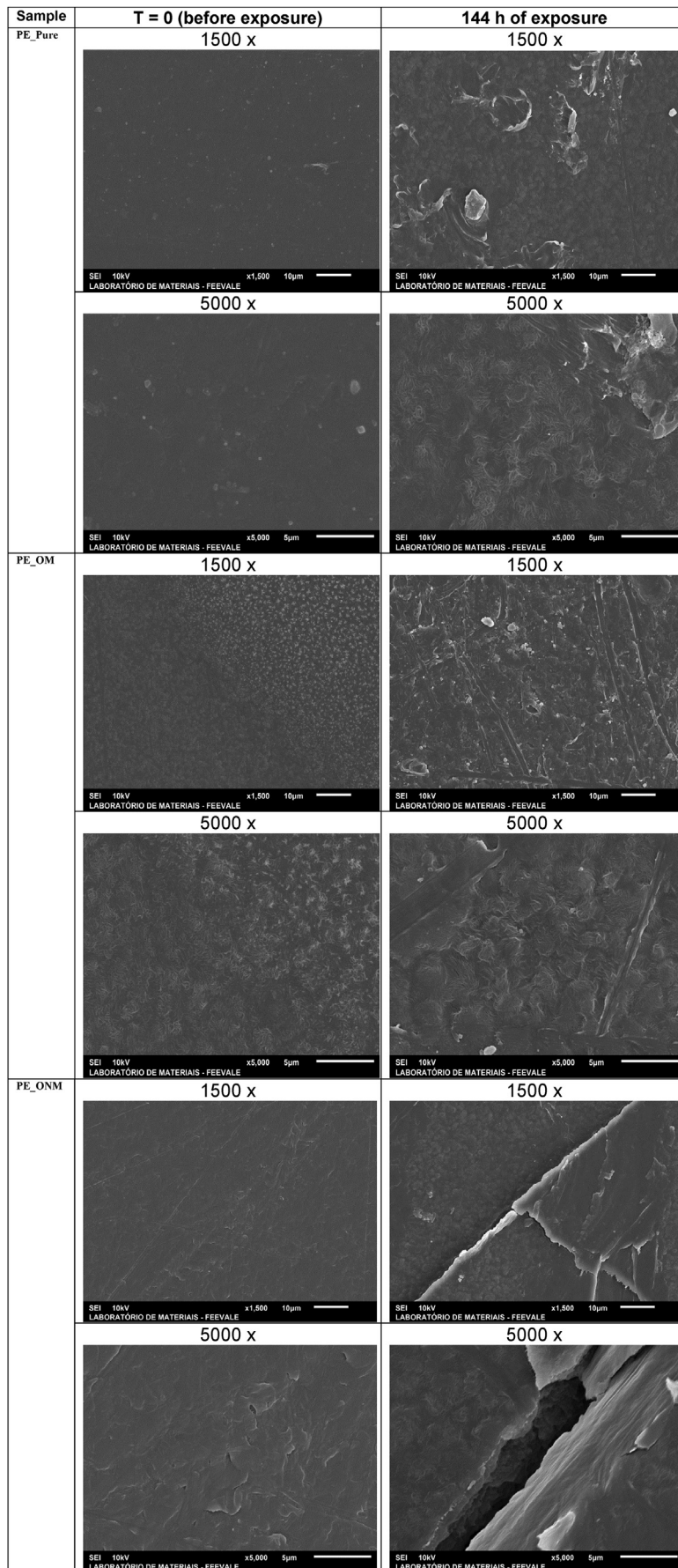


Figure 6. Micrographs of PE films before (t = 0) and after 144 h of UV exposure.

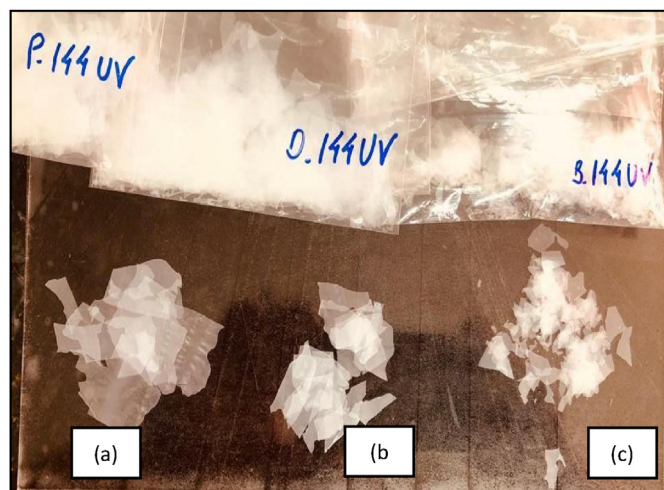


Figure 7. Fragmented films after 144 h of UV exposure: (a) PE_Pure, (b) PE_OM, (c) PE_ONM.

additive in masterbatch. The PE_ONM film, on the other hand, shows some roughness, possibly due to the presence of the polar organic additive. The differences in surface morphology of films processed without and with pro-oxidant additives were also observed in another publication [4].

After 144 h of exposure to UV radiation, the PE suffered photooxidation, with insertion of carbonyl-containing functional groups, appearance of unsaturated fragments and consequent reduction of \overline{M}_v that justify the surface changes observed in all films, which led them to show high fragility. The PE_Pure film was the one that showed less photooxidation effects, with lower molar mass reduction and lower COI increment, reflected in the images obtained by SEM, with visible changes in molecular organization, but containing less erosions and micro-cracks on film surface. The PE_OM film was second with lower molar mass reduction and second higher increment in COI and Vi, indicating that it suffered more photooxidation damage confirmed by the more pronounced micro-cracks than the film without additives. On the other hand, the PE_ONM film, with higher reduction of \overline{M}_v , higher increase in COI and Vi, shows extreme brittleness, clear in micrographic observation after 144 h of exposure. In another work [22], evaluating the photodegradation of PE_ONM with pro-oxidants and photocatalysts, morphological changes compatible with those obtained in this study were found, with changes as clearer the higher the degradation rate observed for the polymer.

The micro-cracks and erosions in the SEM images, which were more clear for the PE_ONM film, justify the fragility of the films that fragmented completely after 144 h of exposure to UVA/UVB radiation, as shown in Figure 7. Note that the fragments of the PE_ONM film are smaller, confirming a higher degree of oxidation of the PE. It can be seen that, naturally, the degradation process of PE films leads to the production of fragments that, with dimensions less than 5 mm, are called microplastics [45]. The PE_ONM film, processed with benzoin, showed higher fragment production. However, smaller polymer chains and containing a greater amount of functional groups [40, 56, 57, 58], in addition to a larger contact surface, according to micrographs, will allow a greater colonization of the material and a higher degree of biodegradation, since it allows a more extensive biofilm formation, indispensable to the process [1, 12, 56].

4. Conclusions

The addition of the evaluated additives favored the photooxidation process of PE. Benzoin acted more strongly as a pro-oxidizing agent of PE than the additive based on organic salts of transition metals, d2w™,

providing a greater reduction of \overline{M}_v , higher carbonyl and vinyl indexes, which led the film to present greater fragility, whose micro-cracks may favor colonization by microorganisms in the biotic phase of oxy-biodegradation, because they increase the contact area of the polymeric material. The benzoin dispersed in the polymeric matrix seems to act as an extrinsic chromophore that favors the absorption of UV radiation and accelerates the photooxidation process of PE. However, the reduction in intrinsic viscosity due to the presence of pro-degradants, which indicates a reduction in the molar mass of the polymer, causes the alteration of several properties, such as transparency, gas barrier properties, and tensile and impact properties. Therefore, the use of these additives needs to be properly evaluated.

Declarations

Author contribution statement

João Augusto Osório Brandão: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Fernando dal Pont Morisso: Performed the experiments.

Edson Luiz Francisquetti: Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Ruth Marlene Campomanes Santana: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

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Data availability statement

Data included in article/supplementary material/referenced in article.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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