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CONGRESSO INTERNACIONAL DE CIÊNCIA, TECNOLOGIA E DESENVOLVIMENTO

UVC-INDUCED PHOTOOXIDATIVE DEGRADATION OF LDPE MICROPLASTICS: STRUCTURAL AND THERMAL ALTERATIONS
SDG (6, 12, 14)

Summary
This work investigates the effects of UVC-induced photooxidation on low-density polyethylene (MP-LDPE) microplastics using Fourier transform infrared spectroscopy with attenuated total reflectance (FTIR-ATR) and thermogravimetric analysis (TGA). Chemical modifications were evidenced by the appearance of carbonyl and hydroxyl absorption bands in the FTIR spectra. The degree of oxidation was evaluated semiquantitatively by calculating the carbonyl index (CI), which increased progressively up to 120 days of exposure, showing a linear correlation with exposure time ($R^2 = 0.92$). Thermal degradation behavior, evaluated by TGA, revealed a marked reduction in the initial degradation temperature (from 347 °C to 117 °C after 150 days), as well as the appearance of a second stage of degradation and a slight increase in the final residue. These findings confirm that prolonged UVC radiation promotes significant oxidative degradation of MD-LDPE, detectable through chemical and thermal analyses.

Palavras-chave: microplastics; low-density polyethylene; photoaging; infrared; thermogravimetry.

Introduction

Microplastics are defined as plastic particles smaller than 5 mm. Among them, low-density polyethylene (LDPE) particles are frequently found in the environment, whether of primary (e.g., cosmetic microspheres) or secondary (e.g., plastic bag fragments) origin (Yu et al., 2019). Prolonged exposure to ultraviolet radiation, especially UVC radiation, promotes aging processes that cause physical and chemical changes in polymers, such as increased roughness, oxidation, and the formation of polar groups, which alter their environmental behavior (Yu et al., 2019; Ainali et al., 2021).

FTIR-ATR is a widely used technique to monitor the oxidation of polyolefins, allowing the identification of functional groups formed during aging (Zhu and Li, 2024). The CI, calculated from the ratio between the absorbance of the C=O stretching band (~1715 cm^{-1}) and a reference band (usually ~1465 cm^{-1}), is a semi-quantitative metric used to assess the degree of polymer oxidation (Ainali et al., 2021; Campanale et al., 2023). Although the CI is a widely used method for this purpose, it is essential to

understand that there is no standardization for its calculation (Zhu and Li, 2024). Many studies employ different methods to determine the CI, such as using the maximum intensity or the area under the band, which leads to inconsistencies in the results, especially when the methods for obtaining the baseline and smoothing the curve are not presented; and difficulty in comparing with other studies (Campanale et al., 2023; Gomes et al., 2024; Zhu & Li, 2024;).

This study aims to investigate the effects of UVC radiation-induced aging on MP-LDPE, using FTIR-ATR and TGA techniques to monitor the chemical and thermal changes resulting from oxidation. The combination of these techniques allows a comprehensive understanding of the degradation mechanisms of MP-LDPE under simulated environmental conditions. Furthermore, this study presents the parameters used to calculate the CI, including those used to obtain the baseline and smooth the curve, making it reproducible. Furthermore, TGA detects changes in degradation temperature associated with aging, complementing the analysis and discussion of the results. This study directly contributes to SDG 14 (target 14.1) by providing reproducible metrics (FTIR-ATR and TGA) to monitor microplastic degradation, and supports SDGs 6 and 12 (12.4, 12.5) by strengthening the technical basis for water quality surveillance and plastic waste management.

Literature review

Context and relevance of MP-PEBD

LDPE plastic represents approximately 20% of global plastic waste (Geyer et al., 2017). This is due to the fact that this polymer is used in the manufacture of various types of packaging (plastic bags, food packaging, hygiene product containers), electrical cable and wire coverings, geomembranes, agricultural films for soil cover, toys, and single-use plastics such as sanitary pads, diapers, and hospital supplies. It is noteworthy that agricultural films made from this polymer are currently the largest source of microplastics in soils (Huang et al., 2020). The durability, low density, and low cost that make it useful also make it a persistent pollutant (Richard et al., 2019).

When exposed to various biotic and abiotic aging factors, MPs undergo weathering conditions that induce the formation or modification of surface functional

groups; decreasing its hydrophobicity, molecular weight, density, and ductility through chain scission, which consequently increases its contaminant sorption capacity (Torres et al., 2021). Furthermore, due to its low density (lower than that of water), transport to different ecosystems occurs more easily, making it ubiquitous even in the most remote environments (Zhang et al., 2019).

Photodegradation mechanisms of MP-LDPE

The photooxidation mechanism of LDPE promotes radical reactions that lead to crosslinking or chain scission, the latter of which introduces oxygen-containing functional groups, starting with peroxides, followed by the generation of alcohols, ketones, or aldehydes and carboxylic acids. After weathering, the long, nonpolar chains gradually transform into increasingly polar oligomers that eventually become soluble (Menzel et al, 2022).

The three stages of LDPE degradation by photoirradiation are also considered: (i) surface abrasion, (ii) crack formation, and (iii) generation and agglomeration of nanoparticles. During these stages, polymer chain scission and crosslinking reactions occur predominantly in the amorphous regions, leading to a reduction in particle size and molar mass, as well as an increase in crystallinity, the size of crystalline domains, and the presence of oxygenated groups in the structure. The loss of mechanical strength and ductility, combined with chemicrystallization and internal stresses, accelerates the rupture and release of micro and nanoparticles.

Environmental effects and impacts of LDPE on different environments and living beings

Photooxidation and fragmentation of LDPE result in smaller, more polar particles with a higher specific surface area, favoring the adsorption of persistent organic contaminants (POCs), heavy metals, and pharmaceuticals (Wang et al., 2021). These particles act as mobile vectors for pollutants, transporting toxic substances between aquatic and terrestrial compartments. The increased crystallinity and roughness of degraded surfaces further enhances the affinity for hydrophobic compounds, promoting bioaccumulation at higher trophic levels (Koelmans et al.,

2019). LDPE's lightness and buoyancy allow its atmospheric and marine dispersion, contributing to its global presence.

Studies have shown that oxidized microplastics trigger inflammatory responses, oxidative stress, and cytotoxic effects in living beings (Choi et al., 2021; Park et al., 2020). In fish and invertebrates, the accumulation of these particles in the digestive tract alters metabolism and reproduction (Senousy et al., 2023; Bobori et al., 2022), while in agricultural soils, fragmented LDPE can modify microbial structure and soil permeability, affecting plant productivity (Rillig et al., 2019; Lian et al., 2022). Although the mechanisms of toxicity are not yet fully understood, there is consensus that surface oxidation and the release of additives (such as antioxidants and plasticizers) intensify biological impacts.

The lack of specific regulations for secondary microplastics – as indicated by the European Commission (2018) – reinforces the importance of experimental studies that identify degradation mechanisms, spectroscopic and thermal indicators, and their relationship to environmental toxicity. Although the WHO does not yet recommend routine monitoring of MPs in drinking water, the growing evidence of adverse effects on human and ecosystem health justifies the development of standardized detection and risk assessment methods.

Method

Chemicals and instruments

MP-LDPE were purchased from Bianquímica Comercial LTDA. For the photoaging experiments, a darkroom with a UV transilluminator made of 1020 stainless steel was used, equipped with two 8W lamps (UV 254 nm and UV 365 nm) that cannot be turned on simultaneously.

Photoagins experiments

MP-LDPE in the form of fragments with approximately 2 mm particle size were exposed to UVC irradiation (254 nm, 8 W) in a darkroom with dimensions of 355 mm x 240 mm x 190 mm, resulting in a radiant flux of 93.9 W/m^2 (Figure 1.a) The

experiments were conducted at room temperature (25°C) for 180 days without power interruption. The microplastics were placed in 12 cm diameter petri dishes containing 6 g (Figure 1.b). For a more homogeneous irradiation, the plastics were reconditioned in the dishes weekly. For characterizations, 10 mg of microplastics were removed after 30, 60, 90, 120 and 150 days. For comparison purposes, virgin plastics were characterized, i.e., with 0 days of aging.

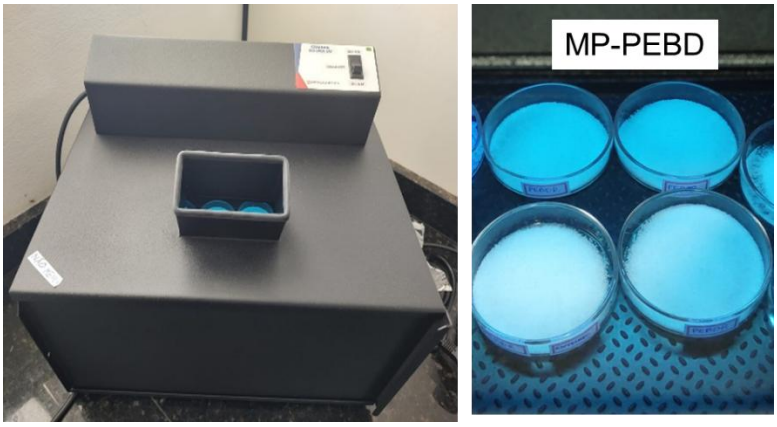

Figure 1 – (a) Dark chamber used in the photoaging experiment. (b) MP-LDPE samples placed in a petri dish and subjected to UVC photoirradiation.

Characterization of aged microplastics

FTIR analyses were conducted using a Thermo Nicolet iS10 FTIR spectrometer (Thermo Scientific, Waltham, MA, USA) equipped with an ATR accessory. Spectra were acquired in the wavenumber range of 600 to 4000 cm^{-1} using 32 scans with a spectral resolution of 4 cm^{-1}. TGA was performed based on ASTM E1131 and E2250 for PE samples. TGA analyses were carried out on Q500 from TA Instruments and the following parameters were used: heating rate of 10°C.min^{-1}, sample weight of approximately 5 mg, temperature range from 30 to 800°C, a nitrogen atmosphere with a flow rate of 100 mL.min^{-1} and platinum pan.

Results and discussion

Análise por espectroscopia de infravermelho (FTIR-ATR)

Regarding the chemical changes caused by UVC photoaging, a study was carried out using spectra obtained by FTIR-ATR analysis. In the virgin microplastic (day 0), it is possible to identify an asymmetric and symmetric stretching of the –CH_2–

group (characteristic of saturated polymers (2915 and 2849 cm^{-1}) and a bending of the $–CH_2–$ (1463 and 719 cm^{-1}), which corresponds to the main bands of MP-LDPE (Figure 2.a). After 30-60 days of aging, it was possible to identify the emergence of new bands, such as the formation of carbonyl groups (ketones, aldehydes or carboxylic acids) at 1709 cm^{-1}, indicating oxidation of the polymer chain; in addition to alkoxyl groups at 1180 cm^{-1}, indicating advanced oxidative degradation (Yu *et al*., 2019; Campanale *et al*., 2023). This evolution indicates that UVC photoaging promoted chemical changes in the polymer structure. A tool commonly used as a quantitative analysis of the oxidation of aged polyolefin plastics (such as polyethylene) is based on the calculation of carbonyl or vinyl indices performed either by the height of the peaks or by the area of the peaks presented in the FTIR spectra (Zhu *et al*., 2024). In the present work, the height of the peaks was used as a method to calculate the carbonyl index (CI), where the FTIR spectra were processed to remove baseline artifacts using the Savitzky-Golay smoothing method (polynomial order 3 and smoothing window of 101 points). After baseline correction, the carbonyl index was calculated using Equation 1:

$$CI = \frac{A_{1700-1780}}{A_{1463}} \qquad (1)$$

Where, $A_{1700–1780}$ corresponds to the maximum height of the peaks between 1700 and 1780 cm^{-1} (carbonyls) and A_{1463} to the reference band. The values of A1700−1780 were used based on the peak height of the samples collected from 0 to 150 days. The carbonyl indices obtained were, respectively, 0.0012; 0.0057; 0.0072; 0.0264; 0.0262 and 0.0363. To determine the evolution of the carbonyl index as a function of time, a linear regression study was performed using the Origin 22b software. From the linear regression, the straight-line equation (Equation 2) and the coefficient of determination R^2 = 0.92 and adjusted R^2 = 0.90 were obtained, which indicates a good correlation between the increase in oxidation and the time of exposure to UVC radiation (Figure 2.b).

$$CI = 0.000244 * t - 0.00113 \qquad (2)$$

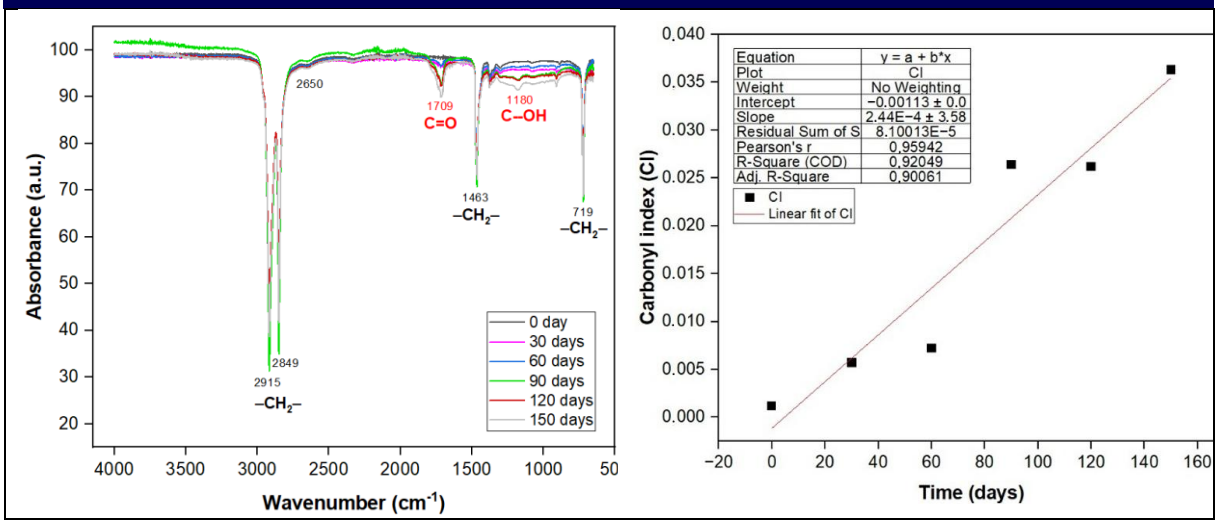

Figure 2 – (a) FTIR-ATR spectra of microplastic samples with 0, 30, 60, 90, 120 and 150 days of UVC photoaging. (b) Linear regression fit of carbonyl indices obtained by Origin 22b software.

The thermal stability of MP-LDPE powder samples subjected to UVC exposure for different periods was evaluated by TGA (Figure 2 and Table 1). The results reveal a clear trend of decreasing initial degradation temperature ($T_{1\_initial}$) with increased exposure time, dropping from 347 °C for the unaged sample (0 days) to only 117 °C after 150 days of exposure. This behavior indicates a progressive photoinduced oxidative degradation process that compromises the polymer's structural integrity and thermal resistance. From 60 days onward, a second mass loss stage (T_2) appears, beginning between 529–542 °C and extending up to approximately 790 °C. This suggests the formation of intermediate degradation products or thermally stable structures induced by aging. Additionally, the residual mass at 800 °C slightly increases after 60 days (from 0.22% to up to 0.32%), which may be associated with the formation of carbonized fractions or crosslinked structures resistant to thermal decomposition. These findings confirm that sunlight exposure leads to significant structural changes in LDPE, reducing its thermal stability and inducing new thermal degradation pathways.

Table 1 – Initial degradation temperature (T1), mass losses (Mass Loss 1 and 2), corresponding degradation temperatures (T1 and T2), and final residue at 800 °C

obtained by TGA for MP-LDPE powder samples exposed to UVC for different durations. The data highlight the evolution of thermal stability and the emergence of multistep degradation behavior with aging.

Sample	$T_{1\_initial}$ (°C)	T_{1_final} (°C)	Mass loss 1 (%)	$T_{2\_initial}$ (°C)	T_{2_final} (°C)	Mass loss 2 (%)	Residue at 800°C
0 day	347	528	99.78	-	-	-	0.22
30 days	323	529	99.75	-	-	-	0.25
60 days	300	529	98.68	529	790	0.855	0.32
90 days	158	534	99.58	534	790	0.166	0.25
120 days	130	539	99.74	-	-	-	0.26
150 days	117	542	99.70	542	790	0.049	0.25

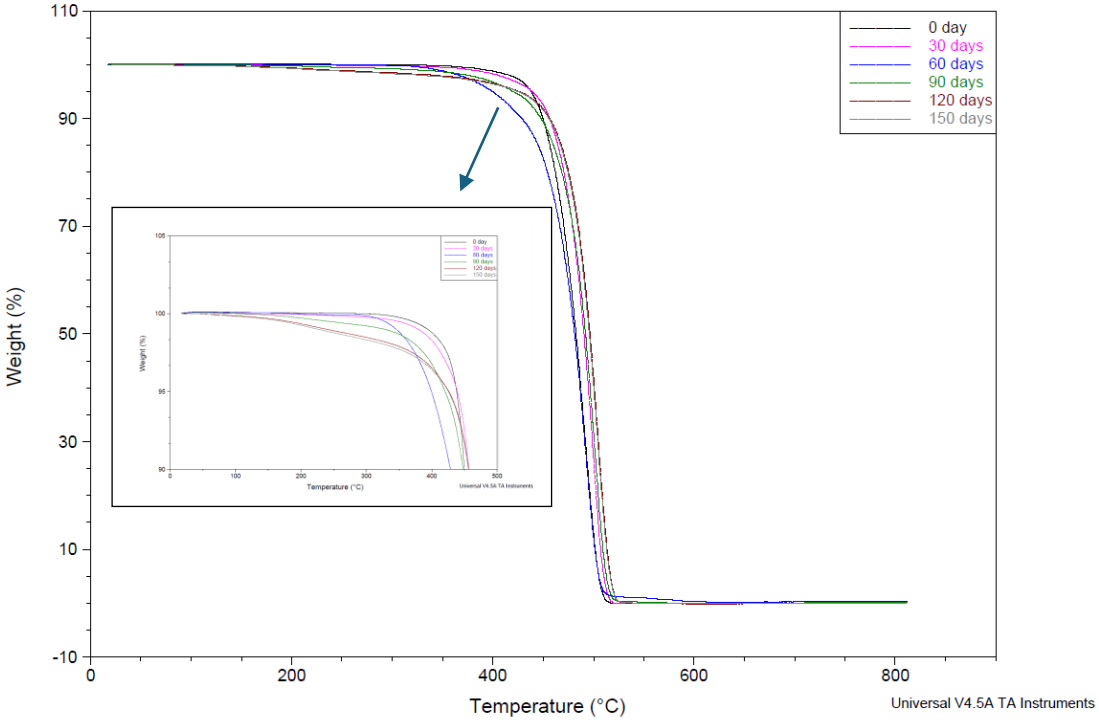

Figure 3 – TGA curves of MP-LDPE powder samples exposed to UVC for different durations. The inset highlights the region of initial mass loss.

Conclusion

The results demonstrate that UVC radiation induces significant chemical and thermal changes in MP-LDPE. FTIR-ATR analyses revealed the progressive formation of

oxygenated groups, such as carbonyls and hydroxyls, indicating a photoinduced oxidative degradation process. The carbonyl index increased continuously with exposure time, reflecting the intensification of polymer oxidation. TGA data corroborated these findings, showing a sharp decrease in the degradation onset temperature, the emergence of a second degradation stage, and a slight increase in the final residue. These findings confirm that UVC-induced photooxidative aging compromises the thermal stability of MP-LDPE and can be effectively monitored using spectroscopic and thermal analysis techniques.

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