

PHOTOCHEMICAL DEGRADATION PATHWAYS OF LINEAR LOW DENSITY POLYETHYLENE REVEALED BY INTEGRATED FTIR, RAMAN, AND AI-ASSISTED SEM ANALYSIS

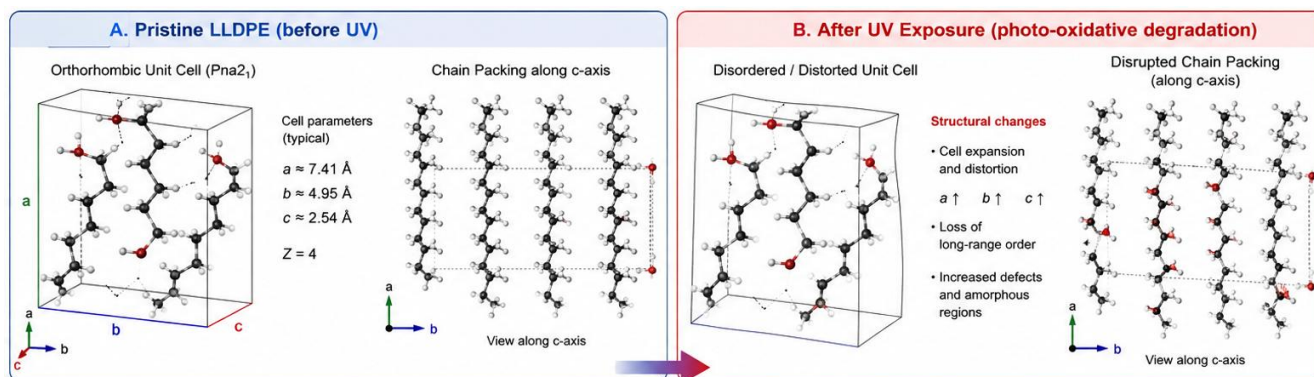
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Graphical Abstract



Schematic overview of LLDPE photochemical degradation from UV-induced oxidation, supported by complementary FTIR, Raman, and SEM characterization

ABSTRACT

Linear low-density polyethylene (LLDPE) is the dominant polymer in agricultural films, mulch covers, and packaging throughout Ecuador and Latin America, where intensive agricultural economies drive high per-capita consumption. Its prolonged outdoor use under intense equatorial UV radiation accelerates photooxidative degradation, generating microplastic particles that have been detected in remote ecosystems including the Antarctic region, underscoring the global reach of local plastic degradation. LLDPE films were subjected to two parallel exposure regimes: (i) natural weathering on the rooftop of Yachay Tech University, Urcuquí, Ecuador, for up to 342 days, and (ii) accelerated UV irradiation in a laboratory chamber equipped with a 50 W LED source at 365 nm for up to 579 hours (~97 equivalent days, based on 6 active sunlight hours per day). Chemical and structural evolution was monitored by ATR-FTIR spectroscopy, Raman spectroscopy, and scanning electron microscopy (SEM). Carbonyl index ($CI = A_{1715}/A_{1463}$), crystallinity ratio (I_{729}/I_{730}), and Raman-derived conformational indices were calculated. AI-assisted image analysis was applied to SEM micrographs to quantify surface defect area fraction. Spectroscopic identification was supported by a polymer reference library of 18 pellet standards created in collaboration with the IAEA Marine Environment Laboratory, Monaco. Environmental weathering produced a carbonyl index of ~0.22 after 342 days, with strong linear kinetics ($R^2 = 0.992$), whereas 400 h (~67 equivalent days) of controlled UV irradiation yielded a maximum CI of ~0.08 ($R^2 = 0.859$). The crystallinity-related I_{729}/I_{730} ratio declined from ~1.70 to ~1.45, consistent with progressive disruption of crystalline domains. Raman spectroscopy confirmed conformational reorganization toward trans conformers and orthorhombic ordering. AI-assisted SEM analysis quantified defect area fractions increasing from 0.32% to 3.37% under ambient weathering and from 0.31% to 5.29% under UV irradiation. LLDPE photodegradation is a coupled oxidation–reorganization process involving carbonyl accumulation, chemi-crystallization, and progressive surface embrittlement that ultimately generates microplastic particles. Integrated ATR-FTIR, Raman, and AI-assisted SEM analysis provides a comprehensive multi-scale framework for predicting polymer service lifetimes and informing mitigation strategies.

Keywords: LLDPE, photochemical degradation, UV and ambient aging, orthorhombic crystallinity, AI image analysis; agricultural plastic; Ecuador; microplastic.

Rutas de degradación fotoquímica del polietileno lineal de baja densidad reveladas mediante un análisis integrado por FTIR, Raman y SEM asistido por inteligencia artificial

RESUMEN

El polietileno lineal de baja densidad (LLDPE) constituye el polímero predominante en películas agrícolas, acolchados plásticos y materiales de embalaje en Ecuador y Latinoamérica, donde las economías agrícolas intensivas impulsan un elevado consumo per cápita. Su prolongada exposición a la intemperie bajo la intensa radiación ultravioleta (UV) característica de la región ecuatorial acelera los procesos de degradación foto-oxidativa, favoreciendo la generación de partículas de microplásticos que han sido detectadas incluso en ecosistemas remotos, como la región Antártica, lo que evidencia el alcance global de la degradación local de los materiales plásticos. En este estudio, películas de LLDPE fueron sometidas a dos regímenes de exposición paralelos: (i) envejecimiento ambiental natural sobre la azotea de la Universidad Yachay Tech, Urcuquí, Ecuador, durante un período de hasta 342 días, y (ii) irradiación ultravioleta acelerada en una cámara de laboratorio equipada con una fuente LED de 50 W a 365 nm, durante un máximo de 579 horas (equivalente a aproximadamente 97 días de exposición ambiental, considerando seis horas efectivas de radiación solar por día). La evolución química y estructural del polímero se evaluó mediante espectroscopía infrarroja por transformada de Fourier con reflectancia total atenuada (ATR-FTIR), espectroscopía Raman y microscopía electrónica de barrido (SEM). Se determinaron el índice de carbonilo ($CI = A_{1715}/A_{1463}$), la relación de cristalinidad (I_{729}/I_{730}) y diversos índices conformacionales derivados de los espectros Raman. Adicionalmente, se implementó un análisis asistido por inteligencia artificial sobre las micrografías SEM para cuantificar la fracción superficial ocupada por defectos. La identificación espectroscópica fue respaldada por una biblioteca de referencia compuesta por 18 estándares poliméricos en forma de pellets, desarrollada en colaboración con el Laboratorio del Medio Marino del Organismo Internacional de Energía Atómica (OIEA), Mónaco. El envejecimiento ambiental produjo un índice de carbonilo cercano a 0.22 después de 342 días, mostrando una cinética prácticamente lineal ($R^2 = 0.992$), mientras que 400 horas de irradiación UV controlada (equivalentes a aproximadamente 67 días de exposición ambiental) alcanzaron un valor máximo de $CI \approx 0.08$ ($R^2 = 0.859$). Paralelamente, la relación de cristalinidad I_{729}/I_{730} disminuyó de aproximadamente 1.70 a 1.45, indicando una pérdida progresiva del orden cristalino y la alteración de los dominios cristalinos. La espectroscopía Raman evidenció una reorganización conformacional caracterizada por un incremento en la fracción de conformaciones trans y un mayor ordenamiento de la fase cristalina ortorrómbica, consistente con procesos de quimio-cristalización inducidos por la degradación. El análisis de imágenes SEM asistido por inteligencia artificial cuantificó un incremento de la fracción superficial de defectos desde 0.32 % hasta 3.37 % durante el envejecimiento ambiental y desde 0.31 % hasta 5.29 % bajo irradiación UV controlada. En conjunto, los resultados demuestran que la fotodegradación del LLDPE constituye un proceso acoplado de oxidación química y reorganización estructural, caracterizado por la acumulación progresiva de grupos carbonilo, la reorganización conformacional mediante quimi-cristalización y el aumento gradual de la fragilidad superficial, procesos que finalmente conducen a la generación de microplásticos. La exposición en condiciones ecuatoriales intensifica significativamente la severidad de la degradación, mientras que la detección de microplásticos derivados de estos materiales en sedimentos antárticos confirma el transporte ambiental de alcance global de los productos de degradación. La integración de ATR-FTIR, espectroscopía Raman y análisis SEM asistido por inteligencia artificial constituye una metodología multiescala robusta para comprender los mecanismos de degradación fotoquímica del LLDPE, predecir la vida útil de materiales poliméricos expuestos al ambiente y contribuir al diseño de estrategias orientadas a mitigar la contaminación por microplásticos.

Palabras claves: polietileno lineal de baja densidad (LLDPE); degradación fotoquímica; envejecimiento ambiental y por radiación ultravioleta; estructura cristalina ortorrómbica; análisis de imágenes asistido por inteligencia artificial; plásticos de uso agrícola; Ecuador; microplásticos.

1. INTRODUCTION

Linear low-density polyethylene (LLDPE) is one of the most extensively produced polyolefins globally, owing to its favorable combination of mechanical resistance, flexibility, impact toughness, and processability [1,2]. Global plastics production reached 413.8 Mt in 2023, with polyethylene and polypropylene accounting for 26.2% and 19.0%, respectively, or 45.2% combined. PE-LD/LLD represented 14.0%, while PE-HD/MD

accounted for 12.2%. [2,3,4]. In Ecuador and across Latin America, LLDPE is the material of choice for agricultural mulch films, greenhouse covers, irrigation tubing, and food packaging applications in which the polymer is deployed directly under intense equatorial solar radiation for extended periods. This pattern of use, combined with inadequate end-of-life management infrastructure, makes the region a significant source of environmental microplastic contamination. Polyethylene

microplastics have been reported in remote environments, including Antarctic sediments and surface waters, demonstrating the capacity of plastic-derived particles to undergo long-range environmental transport. These observations provide an important global context for understanding degradation and fragmentation of polyethylene materials. [5,15].

Despite their versatility, polyolefins present considerable environmental concerns because of their persistence in natural ecosystems and susceptibility to secondary microplastic formation through prolonged weathering [5,6]. Among conventional degradation mechanisms, photochemical degradation induced by ultraviolet (UV) radiation represents the dominant environmental aging pathway for polyethylene [8,9]. Solar UV initiates oxidative reactions that modify the polymer backbone through chain scission, branching, crosslinking, and oxidation, progressively altering mechanical, thermal, and optical properties [10,11]. Although pristine polyethylene exhibits limited intrinsic UV absorption, catalyst residues, hydroperoxides, and structural defects introduced during polymerization act as photoactive centers that initiate radical reactions [12]. Under atmospheric oxygen, radical propagation generates ketones, aldehydes, esters, alcohols, and carboxylic groups that accumulate progressively during exposure [13].

LLDPE exhibits distinctive degradation behavior reflecting its molecular architecture. Synthesized by copolymerization of ethylene with α -olefin comonomers (butene, hexene, or octene), LLDPE possesses a predominantly linear backbone with uniformly distributed short-chain branching [14]. This intermediate morphology between LDPE and HDPE governs oxygen diffusion, molecular mobility, and crystalline organization, thereby influencing susceptibility to UV-induced oxidation and fragmentation [15]. Critically, photochemical degradation preferentially initiates within

amorphous domains where molecular mobility facilitates oxygen penetration and radical propagation [16].

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) is the established technique for evaluating polyethylene photooxidation, with the carbonyl stretching region near $1710\text{--}1730\text{ cm}^{-1}$ providing one of the most reliable indicators of oxidation [17,18]. However, FTIR offers limited insight into simultaneous supramolecular structural rearrangements. Raman spectroscopy provides complementary information by probing molecular conformation, chain ordering, and crystalline organization [19]. Importantly, the absence of a pronounced Raman signal near $\sim 1700\text{ cm}^{-1}$ should not be interpreted as a lack of oxidation, since C=O stretching is predominantly infrared-active rather than Raman-active [20,22]. Instead, Raman spectroscopy is particularly valuable for monitoring conformational evolution involving trans chain formation and crystallinity changes. Polyethylene crystals exhibit predominantly orthorhombic structure, whose characteristic Raman band near 1418 cm^{-1} is associated with crystalline trans conformers [21,22]. UV-induced chain scission within amorphous domains increases chain mobility, enabling molecular rearrangement toward energetically favorable trans conformations, ultimately resulting in chemi-crystallization [23,24].

The present study investigates the photochemical degradation of LLDPE films under environmental exposure and controlled UV irradiation using ATR-FTIR, Raman spectroscopy, and scanning electron microscopy (SEM) with AI-assisted image analysis. Spectroscopic identification was supported by a reference library of 18 polymer pellet standards developed within the same laboratory through a collaboration with the IAEA Marine Environment Laboratory of Monaco, which donated the polymer collection for this purpose. Special emphasis is placed on understanding the coexistence of oxidative chemistry and supramolecular reorganization, and on the implications of progressive LLDPE degradation for

microplastic generation in the context of intensive plastic use in Ecuador and Latin America.

2. MATERIALS AND METHODS

2.1 Materials

LLDPE pellets were employed as the sole polymeric material. LLDPE was selected because of its extensive application in packaging, agricultural films, and outdoor polymeric structures across Ecuador and Latin America, as well as its recognized susceptibility to environmental weathering and microplastic generation [1–7]. Structurally, LLDPE consists of a predominantly linear polyethylene backbone with uniformly distributed short-chain branches derived from α -olefin comonomers, which influence molecular mobility, oxygen diffusion, and crystalline organization [14,23,25].

2.2 Preparation of LLDPE Films

LLDPE was supplied in pellet form by NUTEC. Films were fabricated by compression moulding in a twelve-ton, two-column manual hydraulic laboratory press fitted with electrically heated platens under independent digital temperature control. For each film, [7.3] g of LLDPE pellets were placed between Kapton® polyimide release sheets within stainless steel moulds and processed at a platen temperature of 137.8 °C (280 °F).

A degassing protocol was applied to eliminate entrapped air and volatile species from the melt, comprising four consecutive cycles of three stages: (i) preheating at the target temperature for 3 min without applied pressure, allowing thermal equilibration and the onset of melting; (ii) application of 1000 psi for 3 min at constant temperature, promoting uniform polymer flow and consolidation within the mould; and (iii) rapid single-motion pressure release, permitting the escape of trapped gases and volatiles. Kapton® was selected as the release layer for its thermal stability and non-adherent character, and was verified not to introduce surface contamination or modification during hot pressing. After the fourth cycle, moulds were removed from the press and allowed to cool freely to room temperature on a marble surface.

This protocol was established through systematic optimization against gas-bubble formation within the polymer matrix, a defect that compromised the surface uniformity required for spectrophotometric analysis. Increasing the initial pellet mass and increasing the processing temperature were each evaluated independently and neither fully eliminated the defects; the introduction of the degassing cycle, combined with the Kapton® release layer, yielded optically clear and structurally uniform films suitable for photodegradation testing..

2.3 Photochemical Degradation Experiments

2.3.1 Environmental Weathering Exposure

Natural weathering was performed at the rooftop of Yachay Tech University, Urcuquí, Ecuador (0.406278° N, 78.169889° W), an equatorial location characterized by elevated UV intensity and strong solar irradiance. Films (~5 × 5 cm) were mounted on weather-resistant aluminium supports built specifically for this study. Samples were maintained under outdoor exposure for up to 342 days and collected at predetermined intervals; collected fragments were wrapped in aluminium foil and stored under dark conditions until characterization. To contextualize UV dose, peak solar irradiance in Urcuquí occurs between 10:00 and 16:00, providing approximately 6 effective UV hours per day. Accounting for an estimated 10% rainy-day fraction that reduces intense UV, approximately 342 outdoor days corresponds to roughly through an interpolation of 1,620 UV exposure hours under natural conditions.

2.3.2 Controlled Ultraviolet Exposure

Accelerated UV aging was conducted in a laboratory-built chamber internally coated with aluminium foil to maximize irradiation homogeneity. A 50 W LED source at 365 nm wavelength was positioned 10 cm above specimens. This UVA wavelength induces photooxidative degradation via hydroperoxide decomposition and radical propagation in polyethylene [8–13]. Specimens were exposed continuously for up to

579 h, collected at ~80 h intervals, and immediately protected from light (by cover then inside of aluminium foil) prior to characterization.

Because peak solar UV exposure in Urcuquí spans approximately 6 hours per day (10:00–16:00), each 6 hours of continuous irradiation in the UV chamber is considered equivalent to one representative outdoor day as an interpolated approach knowing that the real weathering is more complex. Therefore, 342 h of controlled UV exposure corresponds to approximately 57 equivalent or interpolated value in days, 400 h to ~67 interpolated outdoor time in days, and 579 h to ~97 interpolated outdoor time in days. This equivalency framework allows direct comparison between controlled-chamber and environmental-weathering datasets and is consistent with the carbonyl index crossover observed between the two exposure systems.

2.4 ATR-FTIR Characterization and Carbonyl Index Determination

ATR-FTIR spectra were collected using a PerkinElmer Spectrum Two spectrometer, equipped with a diamond ATR accessory (4000–650 cm^{-1} , 6 scans). Spectra were collected in triplicate at multiple regions per sample to account for heterogeneity. Identification of specific carbonyl and structural bands was supported by a polymer reference spectral library of 18 pellet standards developed in the same laboratory through a collaboration with the IAEA Marine Environment Laboratory of Monaco, which donated the polymer collection for library construction. Spectral processing was performed in OriginPro. A linear baseline was applied across the carbonyl region using fixed anchor points at 1760 and 1690 cm^{-1} , held constant for all spectra in the series. Both CI and the crystallinity ratio were calculated from peak height (absorbance maximum) rather than integrated band area, with the carbonyl band taken at its maximum near ~1715 cm^{-1} and the reference band at ~1463 cm^{-1} . Photooxidative degradation was quantified through the carbonyl index (CI),

$$\text{CI} = I_{1715} / I_{1463}$$

where I_{1715} is the carbonyl stretching band absorbance (ketones, aldehydes, esters, carboxylic species) and I_{1463} is the methylene scissoring band serving as an internal normalization reference [11,17,18]. A crystallinity-sensitive index was also calculated from the FTIR split ratio between the 730 and 719 cm^{-1} methylene rocking doublet: the 730 cm^{-1} band is preferentially associated with crystalline orthorhombic regions, whereas the 719–720 cm^{-1} band contains significant amorphous character [23,25], providing a morphological indicator of structural reorganization during degradation. Peak extraction and band fitting were performed using OriginPro.

2.5 Raman Spectroscopy and Conformational Analysis

Raman measurements were acquired using a HORIBA LabRAM HR Evolution spectrometer with 633 nm excitation, selected to minimize fluorescence in the polymer. The Raman probe spot diameter (~5–10 μm) provides substantially higher spatial resolution than ATR-FTIR (~3 mm sampling area), enabling localized structural interrogation. Spectroscopic assignments were cross-referenced against the 18-standard polymer library developed in collaboration with the IAEA Marine Environment Laboratory of Monaco. Key LLDPE-relevant Raman bands monitored included: 1130 cm^{-1} (symmetric C–C stretching of long trans sequences), 1298 cm^{-1} (CH_2 twisting, trans conformers), 1305 cm^{-1} (CH_2 twisting, amorphous conformers), and 1418 cm^{-1} (orthorhombic crystalline conformers) [16,17].

Raman-derived conformational indices were defined following the framework of Hiejima, Nitta, and co-workers [16,17]:

$$\varphi_{tr} = \frac{I_{1296}}{I_{1296} + I_{1305}}$$

(all-trans conformer fraction)

$$\varphi_{ctr} = \frac{I_{1418}}{0.46 (I_{1296} + I_{1305})}$$

(orthorhombic crystalline fraction)

$$\varphi_{NCCT} = \varphi_{tr} - \varphi_{ctr}$$

(non-crystalline consecutive trans chains)

The NCCT fraction (ϕ_{NCCT}) is proposed as a key structural indicator of conformational disorder and molecular rearrangement preceding chemi-crystallization. Future quantitative extraction of these indices through Gaussian–Lorentzian deconvolution of the 1130, 1298, 1305, and 1418 cm^{-1} bands is recommended for complete mechanistic validation.

2.6 Morphological Characterization by SEM with AI-Assisted Analysis

SEM imaging and quantitative surface-defect analysis. Surface morphology was investigated by scanning electron microscopy (SEM) by using the Thermofisher Apreochem-S SEM in low vacuum protocol to characterize morphological changes associated with LLDPE surface degradation under ambient environmental weathering and controlled UV irradiation. Quantitative analysis of surface defects was performed using the open-source ImageJ software (Fiji distribution). Each SEM micrograph was spatially calibrated according to its corresponding scale bar and converted to 8-bit grayscale. The images were then processed using the Find Edges function to enhance morphological features, followed by threshold adjustment to distinguish defective regions from the polymer matrix. The same image-processing and thresholding parameters were maintained for all micrographs within each comparative analysis to ensure consistent determination of the defect area fraction. For morphological classification, three defect categories were considered: (i) microvoids, (ii) debris-like fragments, and (iii) elongated grooves or crack-like features. AI-assisted visual analysis using ChatGPT-based vision tools was applied to the thresholded SEM micrographs to assist in identifying and delineating these morphological features. In the corresponding segmentation maps, magenta outlines represent microvoids, yellow outlines represent debris-like fragments, and blue outlines represent elongated grooves or crack-like features, consistent with Figures 6 and 7.

The total defect area fraction was calculated as the percentage of the analyzed surface area occupied by the identified defects. ImageJ was used for the quantitative area-fraction measurement, while the AI-assisted analysis was used as a complementary tool for defect identification and morphological classification. This standardized workflow enabled comparative evaluation of surface-defect development as a function of exposure condition and aging time.

3. Results

3.1 General Degradation Overview and Exposure Equivalency

LLDPE was evaluated under two distinct degradation regimes: environmental weathering for up to 342 days and accelerated UV irradiation for up to 579 h (~97 equivalent or interpolated value in days). In both cases, progressive physicochemical modifications were detected; however, substantial differences in degradation intensity were observed. Environmental weathering produced markedly more pronounced oxidation than controlled UV irradiation, reflecting the multifactorial nature of natural exposure, which combines broad-spectrum solar radiation with atmospheric oxygen, humidity fluctuations, thermal cycling, and environmental contaminants.

Visual inspection revealed progressive loss of transparency under environmental conditions, with films transitioning from initially transparent to progressively hazy morphology, indicating alterations in light scattering associated with surface roughness and structural heterogeneity. Increased rigidity and reduced flexibility were evident at advanced exposure times, indicating progressive embrittlement. Under controlled irradiation, similar but less severe changes were observed.

The UV interpolated outdoor time framework (6 h chamber exposure = 1 equivalent outdoor day) is internally consistent with the carbonyl index data: 400 h (~67 interpolated outdoor time in days) of controlled UV

yielded CI ~ 0.08 , comparable to the CI observed at ~ 90 days of environmental weathering, suggesting that this approximation is internally consistent with carbonyl

index trends, although chamber exposure cannot fully replicate natural weathering complexity for this equatorial deployment context.

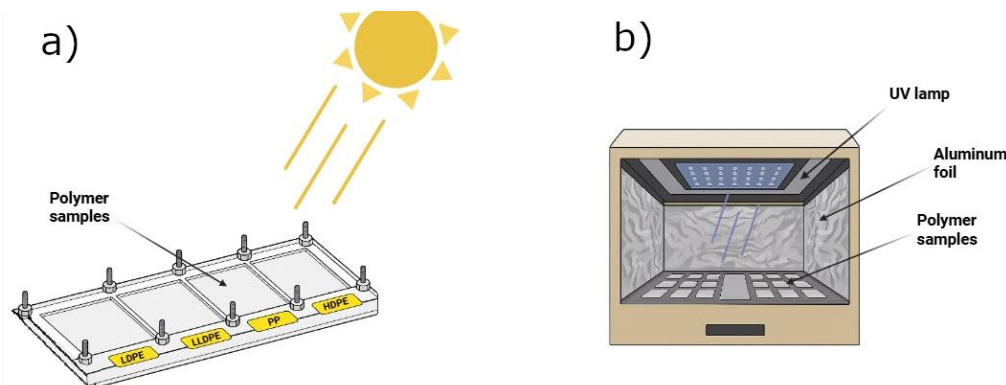


Figure 1. Overview of the LLDPE photodegradation experimental design. (a) Aluminium support structure used for outdoor rooftop weathering at Yachay Tech University, Urcuquí, Ecuador (0.41° N, 78.17° W), an equatorial site with ~ 6 effective UV hours per day (10:00–16:00). (b) Laboratory-built UV irradiation chamber (50 W, 365 nm LED, aluminium-foil-lined interior).

3.2 ATR-FTIR Characterization and Carbonyl Index

Evolution

ATR-FTIR analysis revealed clear evidence of photooxidative degradation in LLDPE under both exposure conditions (Figure 2). The characteristic polyethylene vibrational bands remained visible throughout degradation: asymmetric and symmetric CH_2 stretching at ~ 2918 and ~ 2848 cm^{-1} , CH_2 bending at ~ 1462 cm^{-1} , and rocking mode at ~ 720 cm^{-1} , confirming preservation of the polyethylene backbone. Progressive development of absorption features in the carbonyl region (1760 – 1690 cm^{-1}) was evident under both exposure

conditions, indicating formation of ketones, aldehydes, esters, and carboxyl-containing oxidation products. Increasing C–O stretching at ~ 1100 cm^{-1} , growing carbonyl C=O absorbance at ~ 1715 cm^{-1} , and progressive hydroxyl (O–H) band intensification were observed, collectively representing progressive oxidation and moisture-related processes. The methyl deformation at ~ 1370 cm^{-1} and the crystalline methylene rocking at 730 cm^{-1} provided additional structural markers.

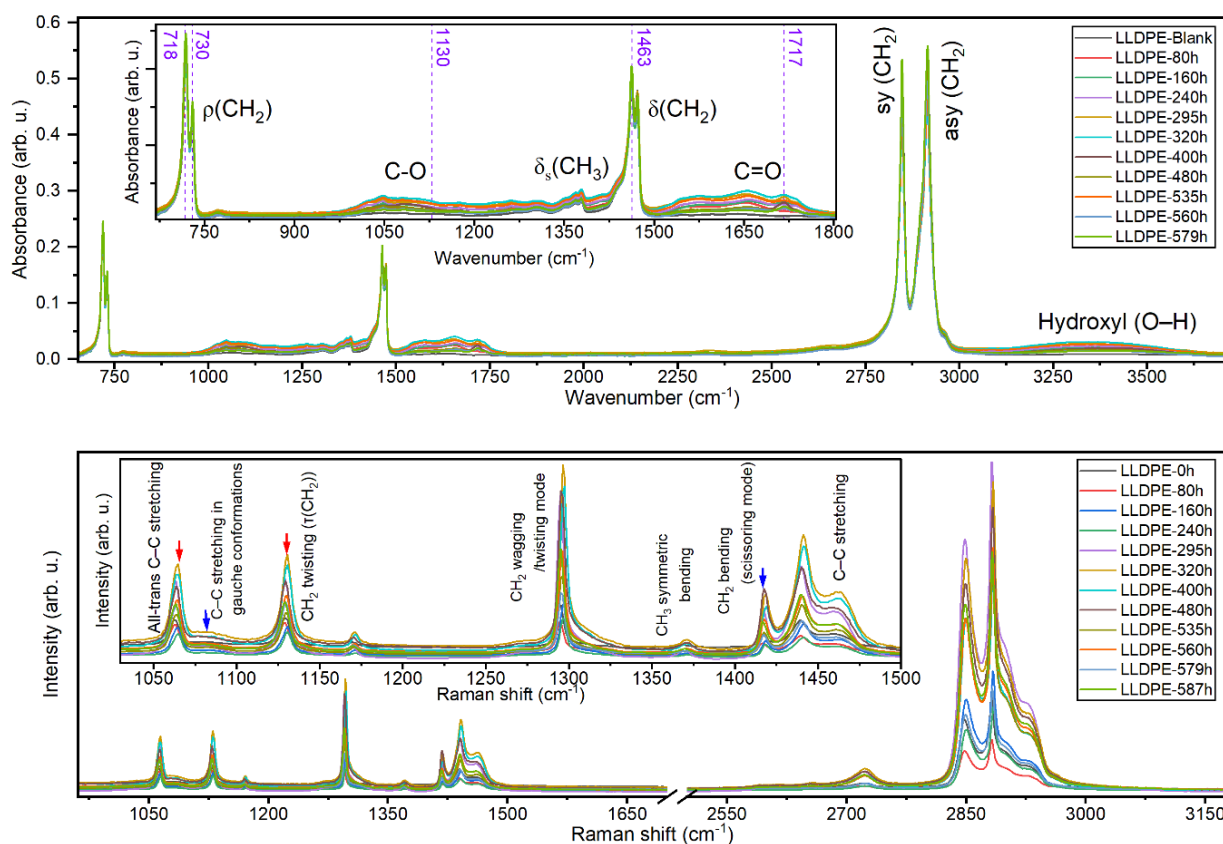


Figure 2. Stacked vibrational spectra of LLDPE films at progressive exposure stages. Upper panel; ATR-FTIR spectra (4000–650 cm^{-1}) for the UV irradiation series (0–579 h). Lower panel; Raman spectra for the controlled UV irradiation series (0–579 h, interpolated outdoor time to 0–97 outdoor days). Annotated bands; 2918/2848 cm^{-1} (CH_2 asymmetric/symmetric stretching, backbone reference), 1715 cm^{-1} (C=O carbonyl stretching; ketones, aldehydes, esters), 1462 cm^{-1} (CH_2 scissoring, internal normalization reference), 1370 cm^{-1} (CH_3 deformation), 1100 cm^{-1} (C–O stretching of secondary oxidation products), 730/720 cm^{-1} (orthorhombic crystalline/amorphous CH_2 rocking doublet). Progressive carbonyl and hydroxyl band intensification under both conditions confirms advancing photooxidation.

Quantification through the carbonyl index (CI) demonstrated progressive increase throughout environmental exposure, rising from ~ 0.03 in pristine material to ~ 0.22 after 342 days, with highly linear kinetics (slope = 6.90×10^{-4} ; $R^2 = 0.992$). A plateau in CI began around 220–250 days, where values stabilized between 0.20 and 0.22, indicating approach to a diffusion-limited oxidation regime in which surface oxidation layers retard further UV penetration and oxygen transport into the polymer bulk [20, 6]. Under controlled UV irradiation, similar polyethylene vibrational features remained detectable after 400 h (~ 67 interpolated outdoor time days), but carbonyl bands were considerably weaker. The maximum CI reached ~ 0.08

after 400 h, interpolated outdoor time to approximately 90 days of environmental weathering. Linear fitting yielded a slope of $\sim 2.408 \times 10^{-4}$ ($R^2 = 0.859$), confirming lower but reproducible oxidation kinetics.

The crystallinity-sensitive ratio (I_{729}/I_{730}) declined gradually from ~ 1.65 – 1.75 in pristine and early-stage samples to ~ 1.44 – 1.47 after prolonged weathering, indicating progressive disruption of orthorhombic crystalline ordering and increasing structural disorder. This trend continued beyond the CI plateau, suggesting that structural reorganization persists into advanced degradation stages even after oxidation kinetics begin to saturate.

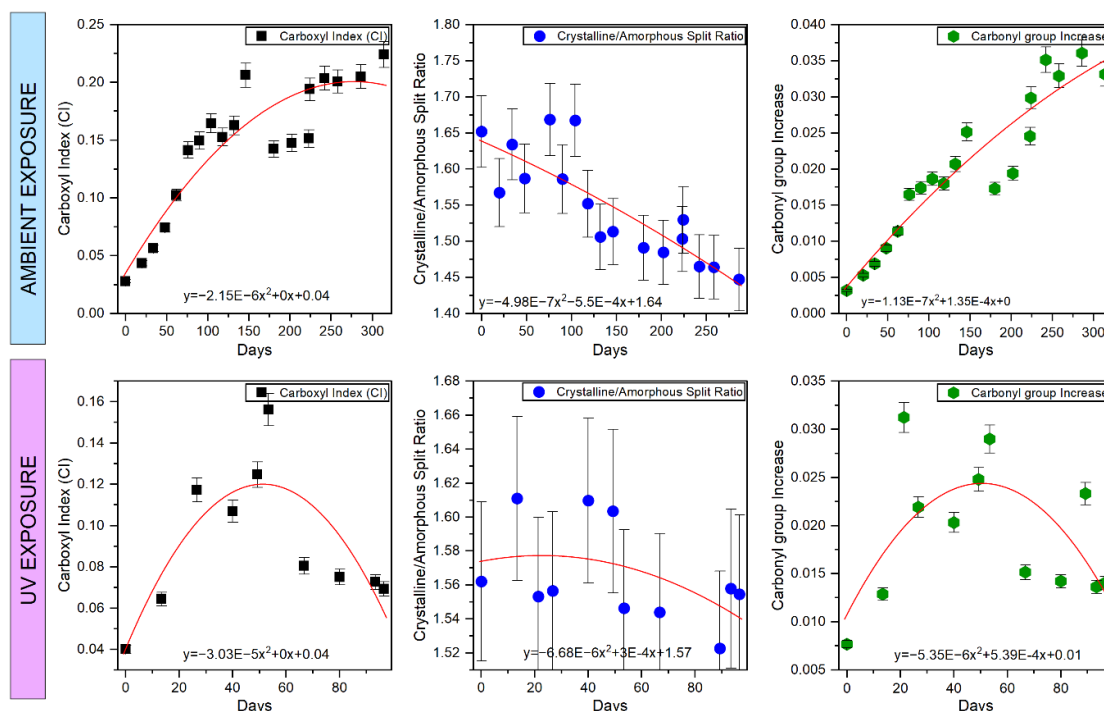


Figure 3. Quantitative degradation indices as a function of exposure duration. Upper set (environmental weathering, 0–342 days): (a) carbonyl index ($CI = A_{1715}/A_{1463}$) vs. time with linear fit ($R^2 = 0.992$), (b) crystallinity ratio (I_{729}/I_{730}) vs. time, (c) carbonyl absorbance at 1715 cm^{-1} vs. time. Lower set (controlled UV, 0–579 h / 0–97 equivalent days); corresponding indices with linear fits. The CI plateau at ~220–250 days (ambient) and the continued decrease in crystallinity ratio indicate that oxidation approaches a diffusion-limited regime while structural reorganization continues at advanced degradation stages. Error bars represent triplicate measurement standard deviation.

3.3 Raman Spectroscopic Evolution and Conformational Analysis

Raman spectroscopy confirmed preservation of the characteristic polyethylene spectral profile throughout degradation while revealing temporal changes in vibrational intensity and fluorescence behavior (Figure 4). Under both conditions, LLDPE displayed characteristic bands at ~ 1062 , 1130 , 1298 , 1418 , 1441 , 2852 , and 2884 cm^{-1} . Spectral evolution is consistent with LLDPE's structural position between highly linear HDPE and highly branched LDPE, consistent with the structural position of LLDPE between highly linear and highly branched polyethylene variants. Spectral assignments were cross-validated using the 18-standard polymer reference library created in collaboration with the IAEA Marine Environment Laboratory of Monaco. The Raman-derived carbonyl index exhibited substantial variability ($R^2 = 0.46$ for environmental exposure),

without the monotonic increase expected for progressive oxidation. This behavior is mechanistically expected: C=O stretching vibrations are predominantly infrared-active and exhibit inherently weak Raman activity [19,22]. Consequently, the absence of a systematic Raman carbonyl trend does not indicate limited oxidation, but rather reflects an intrinsic spectroscopic complementarity between the two techniques. Under controlled UV irradiation, bands at ~ 2852 and $\sim 2884\text{ cm}^{-1}$ exhibited a marked transient intensity reduction at approximately 160 h (~ 27 equivalent/interpolated days), followed by partial recovery at later times, consistent with intermediate structural transitions previously reported in UV-degraded polyethylene systems [17,26]. Fluorescence background progressively decreased under controlled irradiation, suggesting photobleaching of fluorescent impurities or additives initially present in the virgin polymer.

The key diagnostic value of Raman spectroscopy lies in monitoring conformational evolution. The 1298/1305 cm^{-1} band ratio tracks the progressive conversion of amorphous to trans conformers, while growth of the 1418 cm^{-1} band relative to the 1296/1305 pair indicates increasing orthorhombic crystalline ordering. Although full peak deconvolution was not completed in this study,

spectral evolution trends are consistent with progressive accumulation of trans conformers and chemicrystallization during UV exposure, particularly at advanced degradation stages where the CI plateau suggests that structural reorganization becomes the dominant degradation mode.

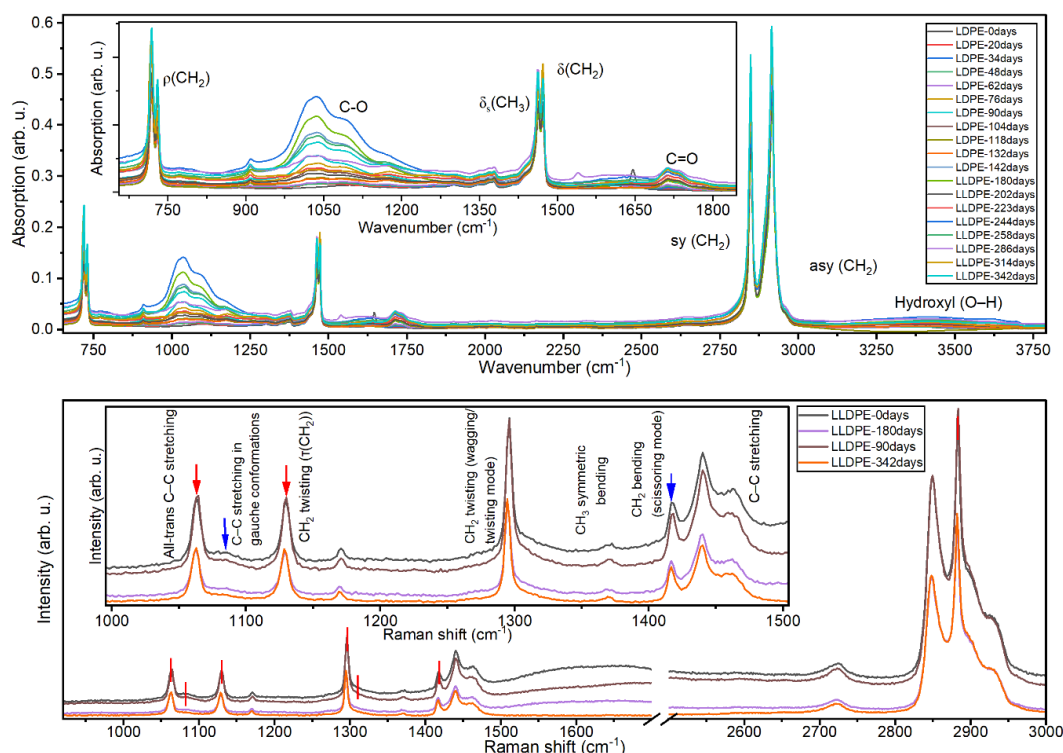


Figure 4. FTIR and Raman spectroscopic evolution of LLDPE films at progressive exposure stages of environmental weathering series (0–342 days). Upper panel; Stacked ATR-FTIR spectra (4000–650 cm^{-1}) with fingerprint region as inset with annotated bands; 1130 cm^{-1} (symmetric C–C stretching, long trans sequences), 1298 cm^{-1} (CH_2 twisting, trans conformers). Lower panel; Stacked Raman spectra (700–3100 cm^{-1}) for environmental weathering (0–342 days) and controlled UV irradiation (0–579 h / 0–97 equivalent days) peaks used to calculate All-trans conformer fraction (red arrows), Orthorhombic Crystalline fraction (blue arrows).

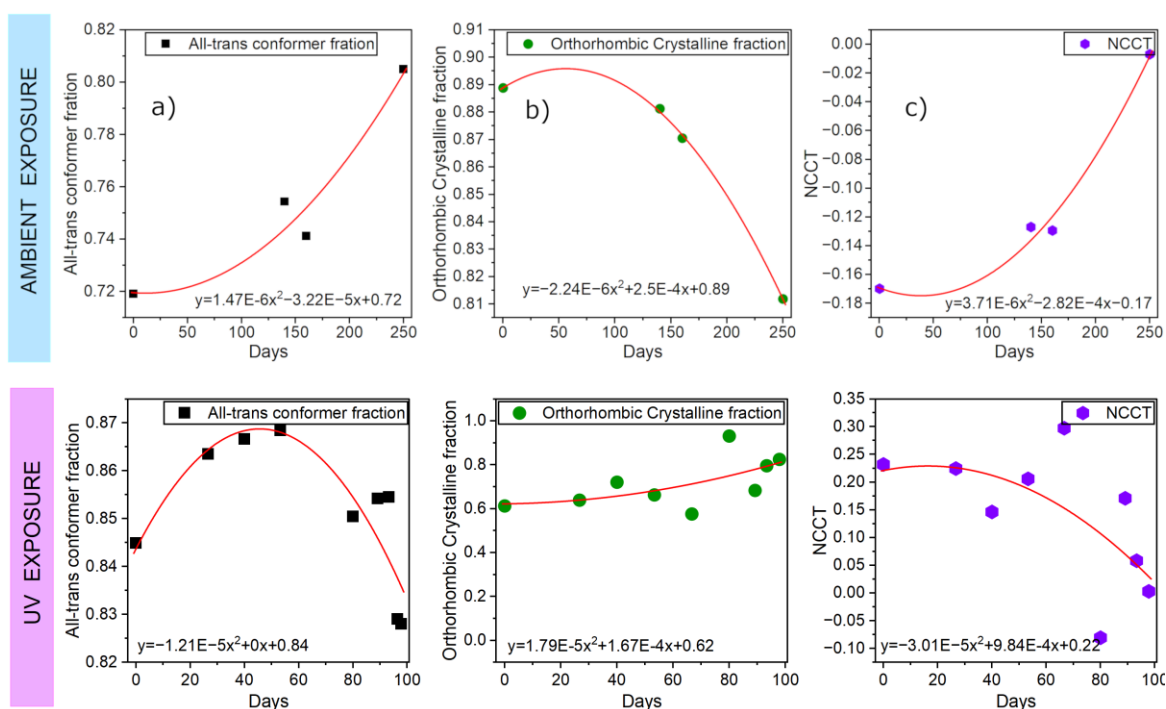


Figure 5. Raman Indexes as 1305 cm^{-1} (CH_2 twisting, amorphous conformers), 1418 cm^{-1} (orthorhombic crystalline conformers), $2852/2884\text{ cm}^{-1}$ (CH_2 symmetric/asymmetric stretching). (b) Evolution of Raman carbonyl index showing high variability ($R^2 = 0.46$), consistent with the inherently weak Raman activity of $\text{C}=\text{O}$ vibrations.

3.4 Morphological Evolution by SEM with AI-Assisted Defect Quantification

Figure 6 presents SEM micrographs of LLDPE surfaces exposed to natural ambient conditions for 0, 104, and 342 days were acquired using the ChemiSEM-S Scanning Electron Microscope from Thermofisher. The pristine sample (0 days) exhibits a relatively smooth and homogeneous morphology with only isolated superficial imperfections attributable to manufacturing or handling. After 104 days (~616 effective UV hours equivalent), the surface becomes noticeably rougher with the emergence

of shallow linear defects and micro-scratches distributed across the exposed face, indicating the onset of surface deterioration driven by combined environmental stressors. After 342 days, a dense network of grooves, scratches, and irregular defects covers a large fraction of the observed area, consistent with progressive chain scission and embrittlement promoting microstructural discontinuities that serve as precursors for crack propagation and fragmentation.

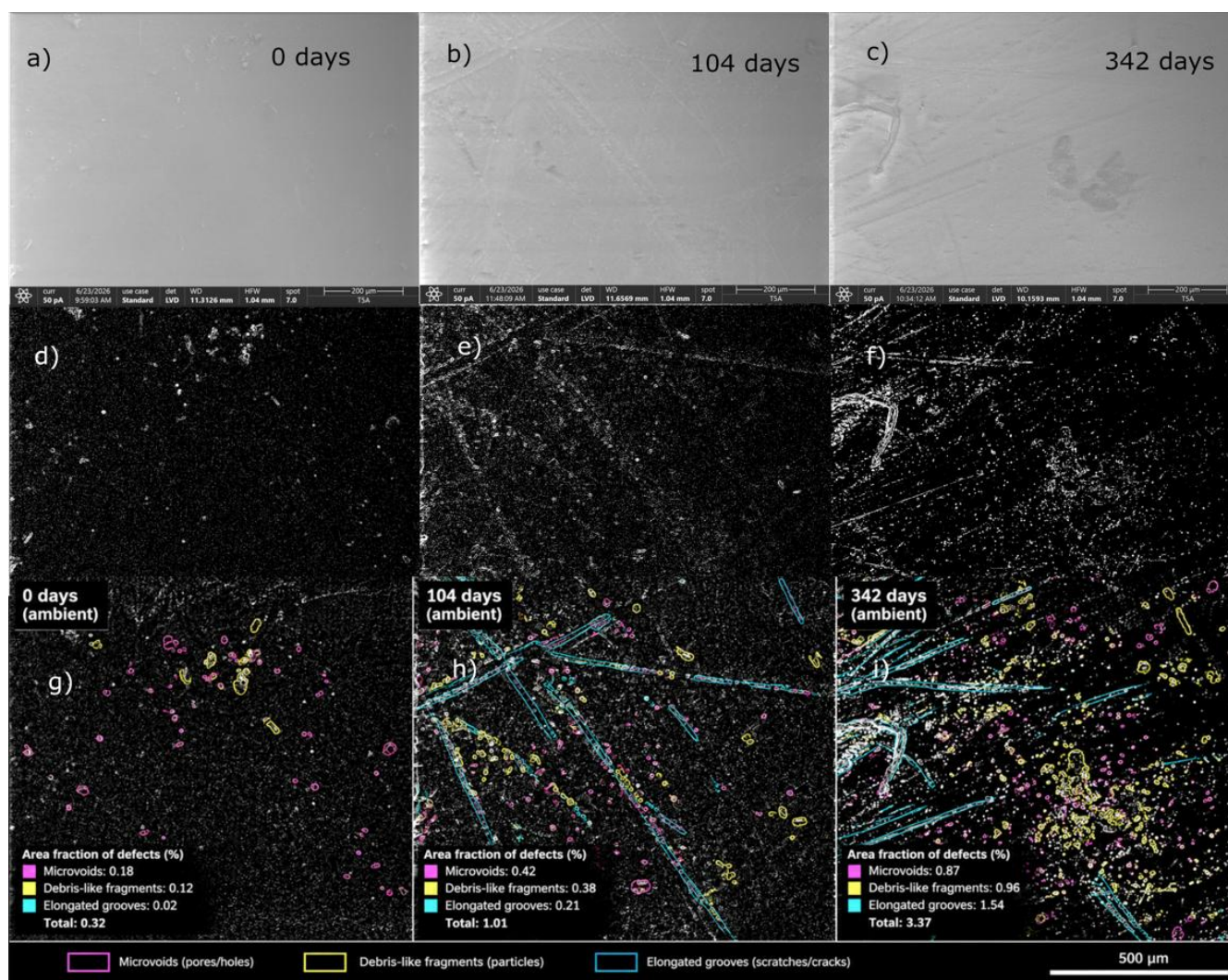


Figure 6. SEM micrographs and quantitative surface-defect analysis of LLDPE during ambient environmental weathering. (a) Pristine LLDPE (0 days), showing a relatively smooth and homogeneous surface with isolated imperfections attributed to sample handling. (b) LLDPE after 104 days of outdoor exposure, showing increased surface heterogeneity and the appearance of shallow linear features. (c) LLDPE after 342 days of outdoor exposure, exhibiting a greater density of grooves, cracks, and irregular surface features. (d–f) Corresponding edge-detection and thresholded images generated using ImageJ. Identical image-processing and thresholding parameters were maintained for the three exposure conditions to ensure consistency in the determination of defect area fractions. (g–i) AI-assisted segmentation maps corresponding to 0, 104, and 342 days, respectively. The processed image from imagen-J was provided to the AI to be processed. Magenta outlines represent microvoids, yellow outlines represent debris-like fragments, and blue outlines represent elongated grooves/crack-like features. The resulting defect area fractions for each exposure condition are reported in Table 1.

Figure 7 shows the LLDPE surface evolution during controlled UV irradiation at 0, 320 h (~50 equivalent days), and 560 h (~93 equivalent days). Similar to the environmental series, the pristine sample exhibits a smooth surface with minor imperfections. After 320 h, numerous particulate features, cavities, and localized defects become visible with increased surface roughness, consistent with photo-oxidative degradation generating

oxidized regions with altered mechanical properties. At 560 h, the surface exhibits substantially higher defect density including cavities, debris-like fragments, microvoids, and elongated grooves, indicating advanced photo-degradation where repeated chain scission and oxidation weaken the polymer matrix and facilitate material loss from the surface.

Each micrograph was spatially calibrated using Imagen-J from fiji using its corresponding scale bar and converted to 8-bit grayscale. Edge detection was subsequently applied to enhance morphological features, followed by threshold adjustment to segment the defective regions from the polymer matrix and using the same parameters to make it comparative the defect area fraction from the polymer surface. AI-Assisted Defect Quantification was used to obtain objective and reproducible surface damage metrics, AI-assisted image analysis (ChatGPT vision model) was applied to all SEM micrographs provided from previously process by Imagen-J. The AI systematically identified and color-coded surface defects;

scratches, cracks, and grooves (red); pits and voids (yellow); and adhered particles and debris (green). Defect area fractions were quantified for each image, yielding the progressive increases summarized in Table 1. The monotonic increase in defect area under both conditions is fully consistent with FTIR-derived carbonyl index evolution and the proposed coupled oxidation–chemicrystallization degradation mechanism. The accumulation of cracks, cavities, and fragmented surface regions ultimately generates microplastic particles that enter terrestrial, freshwater, and marine environments—particle.

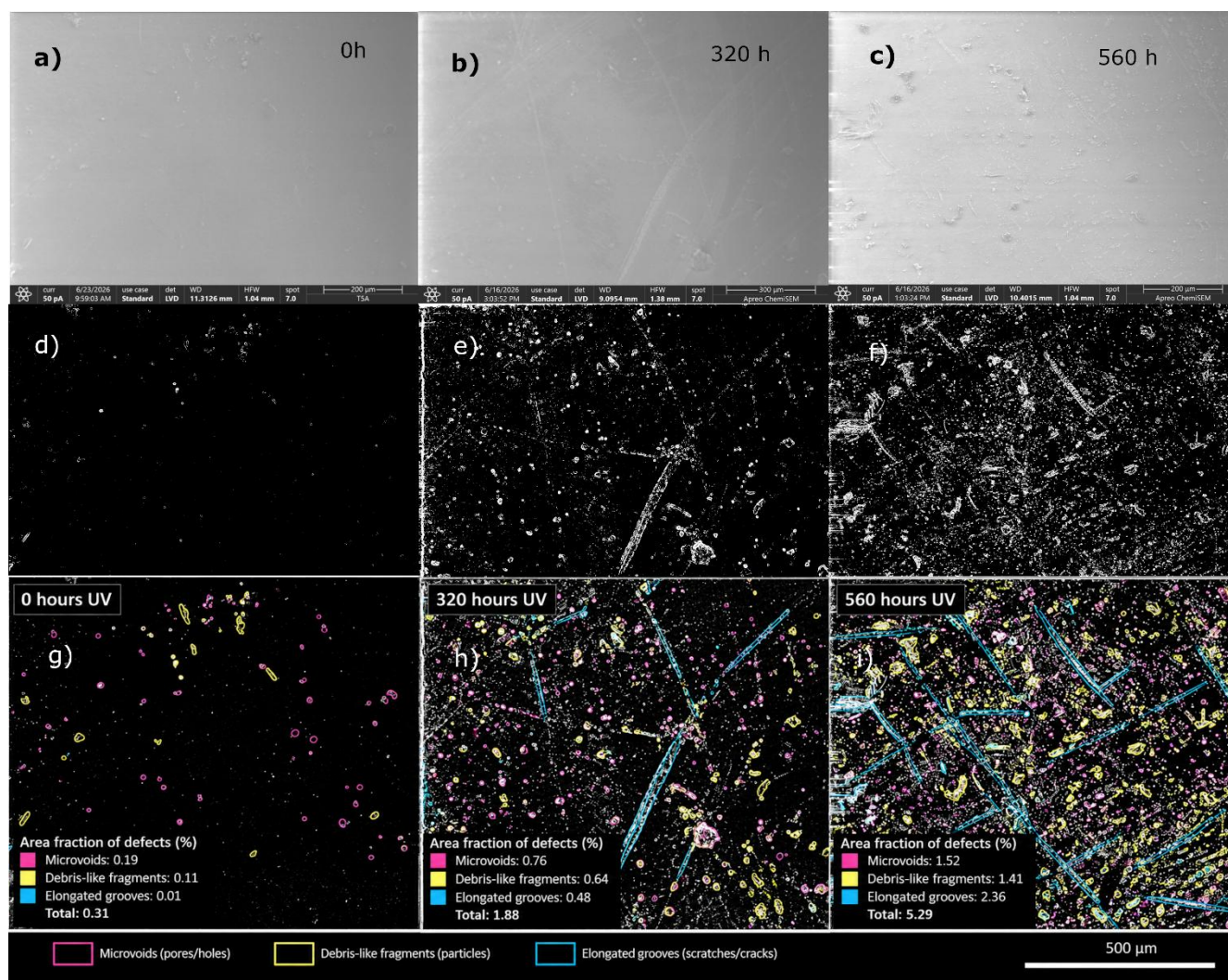


Figure 7. SEM micrographs and quantitative surface-defect analysis of LLDPE during controlled UV irradiation (50 W, 365 nm). (a) Pristine LLDPE (0 h), showing a relatively smooth and homogeneous surface with minor imperfections. (b) LLDPE after 320 h of UV irradiation (~50 equivalent/interpolated days), showing increased surface heterogeneity, localized cavities, and particulate features. (c) LLDPE after 560 h (~93 equivalent/interpolated days), exhibiting a higher

density of microvoids, elongated grooves, and debris-like surface features. (d–f) Corresponding edge-detection and thresholded images processed in ImageJ using identical parameters to enable consistent defect-area determination. (g–i) AI-assisted segmentation maps for 0, 320, and 560 h, respectively; magenta, yellow, and blue outlines indicate microvoids, debris-like fragments, and elongated grooves, respectively. Defect area fraction are shown in Table 1

Table 1. AI-assisted SEM defect area quantification (%) for LLDPE under ambient weathering (Figure 6) and controlled UV irradiation (Figure 7). Values represent the percentage of analyzed surface area classified as defective. UV hours are expressed alongside outdoor equivalent days (1 day $\approx$ 6 UV chamber hours).

Figure	Image #	Exposure Time	Defect fraction by Imagen-J (%)	Defect fraction by AI (%)
Figure 6	1	0 days	0.22	0.32
	2	104 days	2.87	1.01
	3	342 days	4.62	3.37
Figure 7	1	0 h (0 days equiv.)	0.43	0.31
	2	320 h (~50 days equiv.)	3.45	1.88
	3	560 h (~93 days equiv.)	4.42	5.29

4. Discussion

The degradation behavior of LLDPE documented in this study demonstrates that prolonged UV exposure induces a coupled process of oxidative chemistry and supramolecular structural reorganization. While ATR-FTIR clearly revealed progressive oxidation through carbonyl formation, Raman spectroscopy indicated simultaneous conformational evolution. The combined FTIR, Raman, and SEM evidence shows that LLDPE degradation is not limited to simple oxidation but involves a dynamic interplay among chain scission, conformational rearrangement, crystallinity evolution, and localized embrittlement. This mechanistic complexity has direct implications for predicting microplastic generation from LLDPE films used extensively in agriculture and outdoor applications throughout Ecuador and Latin America.

A primary finding is the substantially stronger degradation observed under environmental weathering compared with controlled UV irradiation. After 342 days of outdoor aging, LLDPE reached CI $\sim$ 0.22, whereas 400 h ($\sim$ 67 equivalent days) of controlled 365 nm irradiation yielded CI $\sim$ 0.08, equivalent to approximately 90 days of environmental exposure. Environmental degradation involves simultaneous exposure to broad-spectrum solar radiation, atmospheric oxygen, humidity fluctuations, thermal cycling, and environmental contaminants, all of which synergistically intensify photooxidation [6–13]. The incorporation of rainwater further accelerates oxidative processes by increasing the local concentration of dissolved oxygen available to react with nascent radical species at the polymer surface. These findings confirm that monochromatic accelerated UV exposure cannot fully replicate natural degradation complexity, a limitation with important implications for accelerated aging protocols used in material certification.

The carbonyl index increased systematically during environmental weathering, but its temporal evolution was better represented by a nonlinear empirical fit than by a strictly linear relationship. The curvature of the CI response indicates that the apparent oxidation rate changed with exposure time rather than remaining constant. This behavior is consistent with the progressive evolution of the oxidized surface layer and changing transport and reaction conditions within the polymer. The polynomial fits shown in Figure 3 are used as empirical descriptions of the measured temporal trends and should not be interpreted as evidence that the underlying degradation mechanism is intrinsically quadratic. The plateau at $\sim$ 220–250 days (CI $\sim$ 0.20–0.22) reflects a diffusion-limited regime in which heavily oxidized surface layers retard UV penetration and oxygen transport, in agreement with established polyethylene

photooxidation models [6, 20]. The continued decrease of the I_{729}/I_{730} crystallinity ratio beyond this plateau indicates that structural reorganization and morphological deterioration persist even after oxidation kinetics begin to saturate, suggesting a mechanistic shift from chemistry-dominated to structure-dominated degradation at advanced stages.

The apparent failure of Raman spectroscopy to provide a consistent monotonic carbonyl trend ($R^2 = 0.46$) constitutes a mechanistically important finding rather than an analytical shortcoming. C=O stretching vibrations near $1700\text{--}1730\text{ cm}^{-1}$ are predominantly infrared-active because the C=O bond exhibits strong dipole moment change but limited polarizability variation [19,22]. Consequently, Raman spectroscopy should not be used as a primary oxidation monitoring tool in polyethylene systems. Instead, its strength lies in probing conformational evolution and crystalline ordering. The $1298/1305\text{ cm}^{-1}$ intensity ratio provides a direct measure of trans versus amorphous conformer populations, while the 1418 cm^{-1} band tracks orthorhombic crystalline accumulation. This complementarity between the two techniques is one of the principal methodological contributions of this work.

UV-induced chain scission within amorphous domains is the likely initiating event for conformational reorganization. As chains are cleaved, shorter and more mobile segments can rearrange into energetically favorable trans conformations. Progressive accumulation of trans conformers can lead to chemi-crystallization: the incorporation of previously amorphous trans-rich segments into ordered orthorhombic domains [17,23]. In LLDPE, the substantial amorphous fraction created by short-chain branching makes this mechanism particularly significant. Chemi-crystallization initially appears as an increase in apparent crystallinity despite ongoing chemical degradation, but at advanced stages the propagation of oxidation toward crystalline interfaces and tie molecules disrupts lamellar order, consistent with the

observed decrease in I_{729}/I_{730} ratio at prolonged exposures.

The NCCT concept provides an important mechanistic bridge. Non-crystalline consecutive trans chains represent trans conformers not yet incorporated into orthorhombic crystals; during degradation, reduction in the NCCT fraction accompanied by increasing ϕ_{Ctr} would indicate progressive ordering. Future Raman deconvolution studies quantifying ϕ_{tr} , ϕ_{Ctr} , and ϕ_{NCCT} as functions of exposure time will allow direct testing of this chemi-crystallization hypothesis and may reveal whether a critical NCCT threshold correlates with the onset of macroscopic embrittlement and crack propagation.

AI-assisted SEM defect quantification provides a semi-quantitative approach for multi-timepoint surface damage metric for LLDPE under these exposure conditions. The monotonic increase in defect area fraction under both ambient ($0.22\% \rightarrow 4.62\%$ over 342 days) and UV-irradiated ($0.43\% \rightarrow 4.42\%$ over 560 h / ~ 93 equivalent days) conditions is fully consistent with progressive chain scission and embrittlement. The higher defect area at equivalent timepoints under ambient conditions reflects the greater chemical complexity and multi-stressor nature of outdoor weathering. Crucially, the formation of surface cracks, microvoids, and fragmented regions directly generates microplastic particles. Given the intensive use of LLDPE agricultural films in Ecuador, Colombia, Peru, and across Latin America, this degradation pathways represent a significant and ongoing source of environmental microplastic contamination one whose global reach is confirmed by detection of polyethylene microplastics including Antarctic ecosystems [5,15].

Photobleaching of Raman fluorescence under controlled UV irradiation, rather than the fluorescence increase reported in some oxidation studies, likely reflects differences in additive package composition, irradiation wavelength, or the dominance of physical photobleaching of impurities over chemical generation of conjugated

oxidation products. Environmental exposure produced more heterogeneous Raman responses, attributable to fluctuating climatic conditions and deposition of atmospheric particulates on sample surfaces.

Taken together, the results support a coupled degradation model in which oxidation-driven chain scission (monitored by CI), conformational reorganization (monitored by Raman), and surface embrittlement (quantified by AI-assisted SEM) operate in parallel and feedback loops. FTIR oxidation indices reach saturation at advanced stages, but structural evolution continues, making Raman-derived crystallinity and conformational parameters essential for characterizing late-stage degradation. The integration of these complementary techniques with AI-assisted image quantification offers a powerful multi-scale framework for predicting polyethylene service lifetimes and designing evidence-based strategies to mitigate microplastic generation from agricultural and packaging applications.

5. Conclusions

This study demonstrated that the photochemical degradation of LLDPE under both environmental weathering (up to 342 days) and controlled UV irradiation (up to 579 h, ~97 equivalent outdoor days) involves a coupled process of oxidative chemistry and supramolecular structural reorganization rather than simple surface oxidation alone.

ATR-FTIR analysis confirmed progressive photooxidation through carbonyl formation near 1715 cm^{-1} . Environmental weathering produced CI ~0.22 after 342 days ($R^2 = 0.992$), while controlled 365 nm irradiation reached CI ~0.08 at 400 h (~67 equivalent days), confirming that monochromatic accelerated UV cannot fully reproduce natural weathering complexity. The CI plateau at ~220–250 days signals the onset of diffusion-limited oxidation. The concurrent decrease in the I_{729}/I_{730} crystallinity ratio indicates continuing structural disruption beyond this plateau.

Raman spectroscopy provided mechanistically essential conformational information. Its weak correlation with carbonyl formation ($R^2 = 0.46$) reflects the inherently limited Raman activity of C=O vibrations—not an absence of oxidation—and underscores the importance of using FTIR and Raman as complementary rather than redundant techniques. Spectral evolution of the 1298, 1305, and 1418 cm^{-1} bands are consistent with progressive accumulation of trans conformers and orthorhombic crystalline ordering through chemi-crystallization.

Manual defect fraction analysis by Imagen-J and defect detection fraction was powered by AI-assisted SEM analysis provided the first objective quantification of LLDPE surface defect evolution, with defect area fractions increasing from ~0.22% in pristine material to ~4.62% after 342 days of ambient weathering and ~4.42% after 560 h (~93 equivalent days) of UV irradiation. This progressive surface damage provides microstructural precursors conducive to microplastic release and particle generation.

The equatorial deployment context is critical: in Ecuador and across Latin America, LLDPE dominates agricultural film applications where it is exposed to some of the world's highest UV fluences.

The carbonyl index plateau after ~250 days indicates that late-stage LLDPE degradation is increasingly governed by conformational reorganization rather than net oxidation, making Raman-derived parameters (ϕ_{Ctr} , ϕ_{tr} , ϕ_{NCCT}) will be essential in future work aimed at quantifying advanced degradation. Future work should complete Gaussian–Lorentzian deconvolution of the 1130, 1298, 1305, and 1418 cm^{-1} Raman bands and correlate extracted structural indices with carbonyl index evolution to fully validate the proposed chemi-crystallization mechanism.

The integrated ATR-FTIR, Raman, and AI-assisted SEM methodology presented here constitutes a multi-scale analytical framework that can support future efforts to

predict long-term service lifetimes and design strategies to reduce microplastic generation from polyethylene-based materials in agricultural and packaging applications globally.

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Author Contributions

C. Reinoso (CR): Conceptualization and experimental design; spectroscopic measurements (ATR-FTIR, Raman, SEM); data curation; original manuscript writing and revision (corresponding author).

D. Cherrez (DCh): Experimental execution; preparation of LLDPE films; UV chamber and outdoor weathering exposure operations; spectroscopic data acquisition; data curation and organization.

C. Loyo (CL): Peer review of manuscript; data curation; contribution to scientific discussion and interpretation.

A. Diaz (AD): Peer review of manuscript; data curation; contribution to scientific discussion and interpretation.

M. Bosquez (MB): Peer review of manuscript; data curation; contribution to scientific discussion and interpretation.

All authors have read and approved the final manuscript.

References

- [1] Ammala, A., Bateman, S., Dean, K., Petinakis, E., Sangwan, P., Wong, S., Yuan, Q., Yu, L., Patrick, C., & Leong, K. H. (2011). An overview of degradable and biodegradable polyolefins. *Progress in Polymer Science*, 36(8), 1015–1049.
<https://doi.org/10.1016/j.progpolymsci.2010.12.002>
- [2] Plastics Europe. (2024). *Plastics – The fast facts 2024: An analysis of European plastics production, demand and waste data*. Plastics Europe.
- [3] Statista Research Department. (2024). *Global plastics production from 1950 to 2023*. Statista.
- [4] Yousif, E., & Haddad, R. (2013). Photodegradation and photostabilization of polymers, especially polystyrene: Review. *SpringerPlus*, 2, 398.
<https://doi.org/10.1186/2193-1801-2-398>
- [5] Ranjan, V. P., & Goel, A. (2019). Degradation of low-density polyethylene under different environmental conditions. *Journal of Polymers and the Environment*, 27, 1931–1940.
- [6] White, J. R., & Turnbull, A. (1994). Weathering of polymers: Mechanisms of degradation and stabilization, testing strategies and modelling. *Journal of Materials Science*, 29, 584–613.
- [7] Gardette, J. L., Mailhot, B., Lemaire, J., & Therias, S. (2005). Basic aspects of polymer degradation. *Macromolecular Symposia*, 225(1), 129–146.
- [8] Allen, N. S., & Edge, M. (1992). *Fundamentals of polymer degradation and stabilization*. Springer.

- [9] Rabek, J. F. (1995). Polymer photodegradation: Mechanisms and experimental methods. Chapman & Hall.
- [10] Hamid, S. H. (2000). Handbook of polymer degradation (2nd ed.). Marcel Dekker.
- [11] Rivaton, A., Gardette, J. L., Mailhot, B., & Therias, S. (2005). Photooxidation of polymers. *Comptes Rendus Chimie*, 9(11–12), 1396–1408.
- [12] Lee, H., Kim, J., & Park, S. (2023). Surface oxidation and carbonyl index evolution of low-density polyethylene subjected to dielectric barrier discharge treatment. *Polymer Degradation and Stability*, 214, 110467.
- [13] Benítez, A., Sánchez, J. J., Arnal, M. L., Müller, A. J., Rodríguez, O., & Morales, G. (2013). Abiotic degradation of LDPE and LLDPE films formulated with pro-oxidants. *Polymer Degradation and Stability*, 98(2), 490–501.
- [14] Peacock, A. J. (2000). Handbook of polyethylene: Structures, properties, and applications. Marcel Dekker.
- [15] Gao, Y., Zhang, X., & Wang, J. (2025). Photoaging behavior of polyethylene and polypropylene microplastics under UVA irradiation and seawater conditions. *Polymer Degradation and Stability*, 232, 111145.
<https://doi.org/10.1016/j.polymdegradstab.2024.111152>
- [16] Hiejima, Y., Kawada, H., Kida, T., & Nitta, K. (2025). Raman spectroscopic observation of conformational changes during thermal exposure and its effects on melting and crystallization behavior of high-density polyethylene. *Polymer Degradation and Stability*, 232, 111152.
<https://doi.org/10.1016/j.polymdegradstab.2024.111152>
- [17] Hiejima, Y., Kida, T., Takeda, K., Igarashi, T., & Nitta, K. (2018). Microscopic structural changes during photodegradation of low-density polyethylene detected by Raman spectroscopy. *Polymer Degradation and Stability*, 150, 67–72.
<https://doi.org/10.1016/j.polymdegradstab.2018.02.010>
- [18] Hiejima, Y., Kida, T., & Nitta, K. H. (2021). In situ Raman spectroscopic observation of polymer chains in semi-crystalline polyethylene solids. *Zeitschrift für Physikalische Chemie*, 235(1-2), 59-79.
<https://doi.org/10.1515/zpch-2020-1618>
- [19] Gugumus, F. (1990). Thermooxidative degradation of polyethylene and polypropylene. *Polymer Degradation and Stability*, 27(1), 19–34.
- [20] Celina, M. (2013). Review of polymer oxidation and its relationship with materials performance and lifetime prediction. *Polymer Degradation and Stability*, 98(12), 2419–2429.
- [21] Carlsson, D. J., & Wiles, D. M. (1976). The photodegradation of polypropylene films. *Journal of Macromolecular Science, Part C*, 14(1), 65–106.
- [22] Bower, D. I., & Maddams, W. F. (1992). The vibrational spectroscopy of polymers. Cambridge University Press.
- [23] Strobl, G. (2007). The physics of polymers: Concepts for understanding their structures and behavior (3rd ed.). Springer.
- [24] Wunderlich, B. (2005). Thermal analysis of polymeric materials. Springer.
- [25] Zerbi, G., Gallino, G., Del Fanti, N., & Baini, L. (1989). Morphological defects in polyethylene by vibrational spectroscopy. *Polymer*, 30(12), 2324–2327.
- [26] Thompson, R. C., Swan, S. H., Moore, C. J., & vom Saal, F. S. (2009). Our plastic age. *Philosophical Transactions of the Royal Society B: Biological Sciences*, 364(1526), 1973–1976.
<https://doi.org/10.1098/rstb.2009.0054>
- [27] Bergmann, M., Mützel, S., Primpke, S., Tekman, M. B., Trachsel, J., & Gerdt, G. (2019). White and wonderful? Microplastics prevail in snow from the Alps to the Arctic. *Science Advances*, 5(8), eaax1157.
<https://doi.org/10.1126/sciadv.aax1157>