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Research Article

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Posted Date: November 24th, 2026

DOI: https://doi.org/10.21203/rs.3.rs-11621519/v1

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Mechanistic Insights into Fluid Polarity-Driven Environmental Ageing and Structural Failure of High-Density Polyethylene Containers

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Funding: This work was supported by Marico India Limited, Mumbai, India.

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Abstract

High-density polyethylene (HDPE) is widely used for packaging containers because of its excellent chemical resistance and mechanical durability. However, prolonged outdoor exposure of oil-filled HDPE containers often causes panelling, an inward deformation that compromises structural integrity and service performance. In this study, commercial HDPE bottles are exposed to natural outdoor weathering for 40-45 days under three conditions: empty (control), filled with a mid-polar oil, and filled with a high-polar synthetic ester. Pronounced panelling occurs in both oil-filled systems, with the high-polar ester producing the greatest deformation. A multiscale characterization using attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR), Brunauer-Emmett-Teller (BET) surface analysis, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and atomic force microscopy (AFM) reveals the degradation mechanism. ATR-FTIR confirms progressive photo-oxidation with increasing fluid polarity, while TGA and DSC demonstrate reduced thermal stability and changes in crystalline organization. BET and AFM reveal polarity-dependent surface modification and nanoscale morphological evolution. These findings establish that increasing fluid polarity accelerates environmental ageing through enhanced fluid–polymer interactions, promoting stress localization and macroscopic panelling. This work provides mechanistic insight into fluid-assisted degradation of HDPE and offers guidance for designing more durable polymer packaging for prolonged outdoor applications.

1. Introduction

High-density polyethylene (HDPE) is one of the most extensively used semicrystalline polyolefins because of its excellent balance of chemical resistance, mechanical strength, low density, ease of processing, and cost-effectiveness[1–3]. Owing to these attributes, HDPE has become the material of choice for manufacturing packaging containers, industrial storage vessels, pipelines, automotive components, and household products[4]. In the packaging industry, blow-moulded HDPE containers are widely employed for storing edible oils, lubricants, personal-care formulations, and chemically aggressive liquids because of their excellent barrier properties and resistance to environmental stress cracking[5]. Despite these advantages, the long-term durability of HDPE remains a significant concern when containers are exposed to outdoor environments, where simultaneous exposure to solar radiation, oxygen, temperature fluctuations, and atmospheric moisture progressively alters the polymer structure[6,7]. Unlike instantaneous mechanical failure, environmental ageing of HDPE is a multiscale physicochemical process that begins at the molecular level and gradually propagates to the microstructure before ultimately manifesting as macroscopic structural deformation[8,9] One of the most common manifestations of this degradation in industrial packaging is panelling, an inward collapse of container walls that occurs during prolonged storage under outdoor conditions[7,10]. Panelling not only compromises the aesthetic appearance of the package but also reduces dimensional stability, structural integrity, and service reliability. Although panelling is frequently encountered in commercial HDPE packaging, its underlying degradation mechanism remains incompletely understood because it results from the simultaneous interaction of chemical ageing, polymer morphology, fluid sorption, and mechanical stress development[11–13].

1.1 Environmental ageing of HDPE under natural weathering

Environmental ageing of polyethylene is governed primarily by photo-oxidative and thermo-oxidative degradation initiated through free-radical reactions[7,14–17]. Upon prolonged exposure to ultraviolet (UV) radiation, chromophoric impurities, hydroperoxides, catalyst residues, and structural defects absorb incident photons, generating alkyl (R$^{\bullet}$), alkoxy (RO$^{\bullet}$), and peroxy (ROO$^{\bullet}$) radicals[18,19]. These radicals initiate an autocatalytic oxidation process consisting of initiation, propagation, and termination reactions. Hydrogen abstraction by peroxy radicals produces hydroperoxide species, which subsequently undergo homolytic decomposition to generate additional radicals, thereby accelerating oxidation. Repeated propagation cycles ultimately result in β-scission of the polyethylene backbone, producing lower molecular weight fragments terminated by oxygen-containing functional groups such as ketones, aldehydes, carboxylic acids, alcohols, and esters[20]. The accumulation of these oxidation products progressively alters the physicochemical properties of HDPE. Oxidative chain scission decreases molecular weight, disrupts tie molecules connecting crystalline lamellae, modifies the amorphous phase, and reduces the ability of the polymer network to redistribute mechanical stresses[21]. Simultaneously, thermal exposure enhances oxygen diffusion and molecular mobility, further accelerating oxidative degradation. Consequently, environmental ageing produces measurable changes in chemical composition, crystallinity, thermal stability, surface morphology, and mechanical performance. The degradation process is further influenced by the presence of antioxidants, stabilizers, catalyst residues, and transition-metal impurities, which either retard or catalyse hydroperoxide decomposition depending on their chemical nature[6].

1.2 Fluid-polymer interactions and the role of fluid polarity

Although environmental ageing of polyethylene has been investigated extensively, considerably less attention has been devoted to the role of the contacting fluid in governing degradation kinetics[7,22]. In practical applications, HDPE containers rarely remain empty; instead, they are continuously in contact with oils, lubricants, cosmetic formulations, edible oils, or synthetic esters throughout their service life. These fluids interact primarily with the amorphous regions of the semicrystalline polymer, where molecular mobility is greatest and diffusion pathways are readily accessible. The extent of fluid sorption and the resulting physicochemical changes depend strongly on fluid polarity. Relatively non-polar or mid-polar fluids generally interact with polyethylene through weak van der Waals forces, producing limited sorption, moderate plasticization, and increased chain mobility without substantially modifying the chemical structure of the polymer[23]. In contrast, polar fluids, particularly oxygen-containing synthetic esters, possess stronger intermolecular affinity for oxidized polymer surfaces and exhibit greater compatibility with the amorphous phase. This behaviour can facilitate oxygen transport, alter local free volume, and accelerate photo-oxidative reactions occurring at the polymer–fluid interface[9]. From a polymer physics perspective, fluid-assisted ageing represents the combined influence of diffusion, oxidation, and structural rearrangement. Sorption-induced changes within the amorphous regions modify chain mobility, while oxidative reactions progressively alter the surrounding semicrystalline morphology. Consequently, fluid polarity is expected to influence not only the rate of chemical oxidation but also the evolution of crystalline organization, thermal stability, nanoscale morphology, and ultimately the mechanical integrity of the polymer[24].

1.3 Multiscale evolution of HDPE during environmental ageing

Environmental degradation of semicrystalline polyethylene occurs over multiple length scales, extending from molecular chemistry to macroscopic structural failure[11]. At the molecular level, oxidation generates oxygen-containing functional groups that can be detected by ATR-FTIR spectroscopy. At the microstructural level, oxidative chain scission modifies the organization of crystalline lamellae and amorphous domains, influencing melting behaviour, crystallization kinetics, and thermal stability, which are readily evaluated using DSC and TGA. Simultaneously, changes in surface morphology and local viscoelastic heterogeneity develop through progressive surface restructuring, providing nanoscale evidence of degradation that can be examined using atomic force microscopy. These molecular and microstructural changes ultimately determine the macroscopic mechanical response of the polymer. Oxidative embrittlement weakens the network of tie molecules connecting crystalline lamellae, reducing the capacity of the material to accommodate stresses generated by fluid diffusion, temperature cycling, and internal pressure variations. As degradation progresses, localized deformation accumulates, eventually producing irreversible wall collapse in the form of panelling. Therefore, panelling should not be regarded as an isolated mechanical phenomenon but rather as the final manifestation of a multiscale environmental ageing process involving coupled chemical, structural, thermal, and mechanical transformations[14,16].

1.4 Knowledge gap and objectives of the present work

Although previous investigations have significantly advanced the understanding of polyethylene weathering, most studies have examined either environmental degradation or polymer-fluid interactions independently. The synergistic influence of fluid polarity and natural outdoor weathering on the complete degradation pathway of HDPE has received comparatively little attention. In particular, the relationship between oxidative chemistry,

surface evolution, crystalline reorganization, thermal destabilization, and the subsequent development of panelling remain poorly understood. Furthermore, the mechanistic role of fluid polarity in governing these interconnected processes has not been systematically established.

In the present work, we investigate the environmental ageing behaviour of commercial HDPE packaging containers exposed to natural sunlight for 40-45 days under three representative conditions: (i) empty HDPE (control), (ii) HDPE filled with a mid-polar oil, and (iii) HDPE filled with a high-polar synthetic ester[16,17]. By integrating ATR-FTIR spectroscopy, BET surface analysis, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and atomic force microscopy (AFM), we establish a direct structure-property-mechanism relationship linking fluid polarity to chemical oxidation, surface evolution, crystalline morphology, thermal stability, and nanoscale mechanical heterogeneity. Based on these complementary observations, a comprehensive degradation mechanism is proposed to explain how fluid polarity governs the progression of environmental ageing and ultimately controls the susceptibility of HDPE containers to macroscopic panelling under realistic outdoor service conditions[18,25].

2. Experimental Methodology

2.1 Materials

Commercial high-density polyethylene (HDPE) bottles supplied by Marico India Ltd. were used as the model packaging system in this investigation. The bottles, representative of commercially manufactured oil-packaging containers, were produced by injection blow moulding and possessed an average wall thickness of approximately 1.2 mm and a density of 0.96 g cm^{-3}. To investigate the influence of fluid polarity on the environmental ageing behaviour of HDPE, three groups of bottle samples were examined: (i) Sample A (Control, empty HDPE bottles without any liquid content), (ii) Sample B (HDPE bottles filled with a

mid-polar oil, representative of conventional hydrocarbon or vegetable oil-based formulations commonly employed in consumer packaging), and (iii) Sample C (HDPE bottles filled with a high-polar synthetic ester, selected to represent lubricant formulations possessing stronger intermolecular polarity and greater affinity for polymer surfaces). All bottle samples were exposed simultaneously to natural outdoor weathering for 40-45 days under identical environmental conditions. Exposure included natural solar irradiation, ambient atmospheric oxygen, relative humidity, and diurnal temperature fluctuations characteristic of the local climate. During the exposure period, the ambient temperature varied between approximately 30 and 45 °C. Although the incident ultraviolet (UV) irradiance was not monitored quantitatively, all samples were positioned under identical exposure conditions throughout the study to ensure a consistent comparative assessment of fluid-assisted environmental ageing. Consequently, differences observed among the samples are attributed primarily to the nature of the contacting fluid rather than variations in the external exposure environment.

2.2 Sample Preparation

Following 40-45 days of natural outdoor weathering, the HDPE bottles were sectioned into specimens measuring approximately 1 × 1 cm^2. To investigate the regions most susceptible to environmental ageing, the specimens were primarily collected from areas exhibiting visible panelling or surface deformation. Residual oils and surface contaminants were removed by sequential washing with n-hexane to dissolve absorbed organic residues, followed by rinsing with ethanol to eliminate residual solvent and low-molecular-weight surface contaminants. The cleaned specimens were subsequently air-dried under ambient laboratory conditions and stored in a desiccator prior to characterization to minimize moisture uptake and prevent further environmental ageing before analysis.

2.3 Characterization

To elucidate the influence of fluid polarity on the environmental ageing and physicochemical evolution of HDPE, a combination of complementary spectroscopic, thermal, surface, and morphological characterization techniques was employed. Attenuated Total Reflectance Fourier-Transform Infrared (ATR-FTIR) spectroscopy was used to investigate oxidative chemical modifications occurring within the polymer matrix. Spectra were recorded using a Nicolet 6700 Fourier-transform infrared spectrometer (Thermo Scientific, USA) equipped with a diamond ATR accessory over the range of 4000–400 cm^{-1} at a spectral resolution of 2 cm^{-1}, with 32 scans collected for each specimen. The evolution of characteristic oxidation-related functional groups, including carbonyl and hydroxyl species, was monitored to assess the extent of photo-oxidative degradation. Changes in accessible surface characteristics resulting from fluid–polymer interactions were evaluated by nitrogen adsorption-desorption analysis using a Quantachrome Autosorb iQ-XR surface area analyzer. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method, while pore size distribution was determined using the Barrett–Joyner–Halenda (BJH) model. Thermal stability was investigated using a TGA Q500 thermogravimetric analyzer (TA Instruments, USA). Approximately 10 mg of each specimen was heated up to 600 °C at a heating rate of 10 °C min^{-1} under a continuous nitrogen atmosphere. The onset degradation temperature (Tonset) and the temperature corresponding to the maximum degradation rate (Tmax) were used to evaluate changes in the thermal stability of environmentally aged HDPE. The influence of environmental ageing on crystalline structure and thermal transitions was examined using a DSC Q2000 differential scanning calorimeter (TA Instruments, USA) under a nitrogen atmosphere. Samples weighing 5-7 mg were heated from 30 to 180 °C at 10 °C min^{-1}, maintained isothermally for 3 min to eliminate previous thermal history, and subsequently cooled at the same rate. The degree of crystallinity (Xc) was calculated from the melting enthalpy (ΔHm) according to[26,27]:

$$Xc(\%) = \frac{\Delta \mathrm{Hm}}{\Delta \mathrm{Hm}^0} \times 100$$

where ΔHm is the experimentally measured melting enthalpy and ΔHm° = 293 J g^{-1} is the theoretical melting enthalpy of 100% crystalline polyethylene. Nanoscale surface morphology was characterized using a Nanosurf Drive atomic force microscope operating in tapping mode. Images were acquired over a scan area of 10 × 10 μm^2 under ambient laboratory conditions. Surface roughness parameters, including the arithmetic average roughness (Ra) and root-mean-square roughness (Rq), were determined using Gwyddion image analysis software to evaluate morphology evolution associated with fluid-assisted environmental ageing. Unless otherwise stated, all characterization experiments were performed on multiple specimens under identical experimental conditions. Consistent trends were observed across replicate measurements, and representative datasets are presented throughout this study for clarity.

3. Results and Discussion

3.1 FTIR Analysis

The chemical evolution of HDPE following natural environmental ageing under different fluid environments was investigated by ATR–FTIR spectroscopy (Figure 1)[1,26]. The spectrum of the control HDPE exhibited the characteristic absorption bands of polyethylene, including the asymmetric and symmetric stretching vibrations of methylene groups at 2915 and 2848 cm^{-1}, respectively, together with the CH_2 bending vibration at 1460 cm^{-1}. No discernible absorption was observed within the carbonyl (1700 - 1750 cm^{-1}) or hydroxyl (3200 - 3600 cm^{-1}) regions, indicating that the unexposed polymer retained its original chemical structure with negligible oxidative modification. Following outdoor exposure, distinct changes in the FTIR spectra became evident, reflecting the progressive oxidation of the polymer matrix.

The HDPE specimens containing the mid-polar oil exhibited the emergence of a weak and broad carbonyl absorption centred near 1748 cm^{-1}, accompanied by a low-intensity hydroxyl

band around 3400 cm^{-1}. These features are characteristic of oxygen-containing degradation products generated during photo-oxidative ageing, including ketones, aldehydes, carboxylic acids, and hydroperoxide-derived species. The relatively low intensity of these bands suggests that oxidation was limited and primarily confined to the near-surface region. Such behaviour is consistent with mild fluid sorption and partial oxidation of the amorphous phase, while the overall polyethylene backbone remained largely preserved.

In contrast, the high-polar ester-filled HDPE exhibited substantially stronger oxidation-related spectral features. A pronounced carbonyl band appeared at 1736–1737 cm^{-1}, together with distinct absorptions at 1176 and 1110 cm^{-1}, corresponding to C-O stretching vibrations associated with oxygen-containing functional groups and ester-related species. The slight shift of the carbonyl absorption toward lower wavenumbers indicates a modified chemical environment around the carbonyl functionality, which is consistent with stronger interfacial interactions between the absorbed polar fluid and the oxidatively modified polymer surface. Although ATR-FTIR alone cannot unequivocally establish the formation of new covalent linkages, the observed spectral evolution clearly demonstrates a greater extent of oxidative modification in the presence of the high-polar ester. The oxidation behaviour observed in Figure 1 can be interpreted within the framework of the classical free-radical photo-oxidation mechanism of polyethylene. Under prolonged solar irradiation, hydroperoxide species generated during the early stages of ageing undergo homolytic cleavage, producing alkyl and alkoxy radicals that react rapidly with atmospheric oxygen to form peroxy radicals. Subsequent hydrogen abstraction and β-scission reactions generate progressively lower molecular weight polymer fragments terminated by oxygen-containing functional groups, giving rise to the carbonyl and hydroxyl absorptions observed in the FTIR spectra. The presence of a polar fluid is expected to enhance molecular mobility within the amorphous regions and facilitate oxygen transport to the polymer surface, thereby accelerating oxidative degradation. Consistent with

these spectral observations, both the carbonyl index and hydroxyl index increased progressively in the order:

Control HDPE < Mid-polar oil-filled HDPE < High-polar ester-filled HDPE.

This systematic increase indicates that the susceptibility of HDPE to environmental ageing increases with fluid polarity. Collectively, the FTIR results demonstrate that prolonged natural weathering promotes oxidative modification of the polyethylene matrix, while the presence of high-polar fluids intensifies this process through enhanced fluid-polymer interactions, thereby establishing the chemical basis for the subsequent thermal, morphological, and mechanical changes discussed in the following sections.

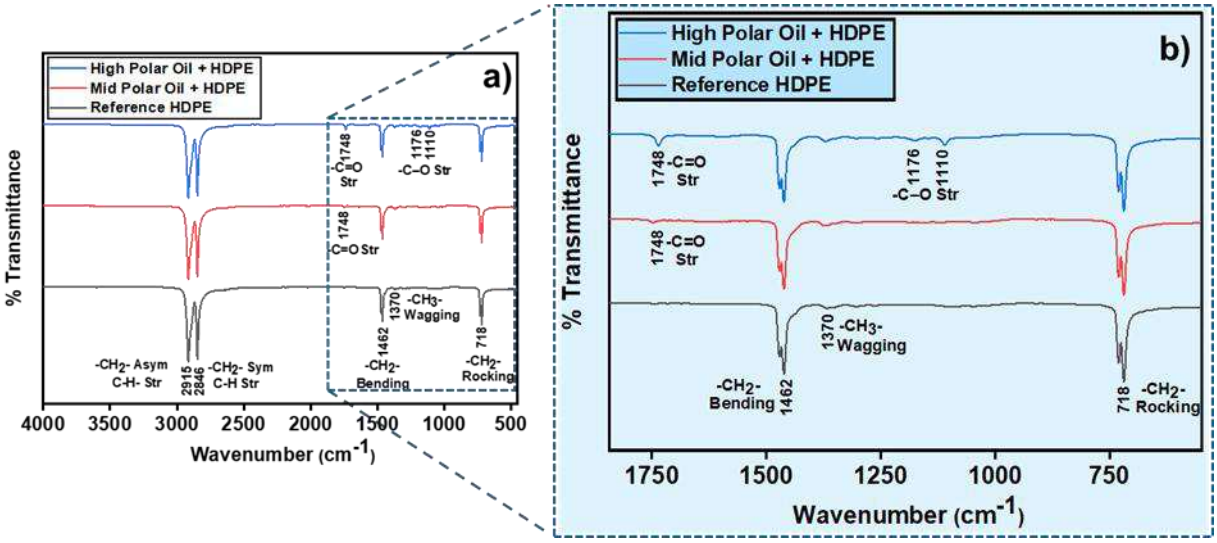

Figure 1. ATR–FTIR spectra of HDPE after natural environmental ageing under different fluid environments. (a) The control HDPE, mid-polar oil-filled HDPE, and high-polar ester-filled HDPE, illustrating the progressive evolution of oxidation-related absorption bands following outdoor exposure. (b) Enlarged view of the development of absorption bands, which are consistent with progressive oxidative modification of the polyethylene matrix.

3.2 BET Analysis

Nitrogen adsorption-desorption measurements were performed to evaluate changes in the accessible surface characteristics of HDPE following environmental ageing under different

fluid environments (Figure 2). The control HDPE exhibited the highest nitrogen uptake, corresponding to a BET specific surface area of 38.79 m^2 g^{-1}, indicating a relatively accessible surface with heterogeneous mesostructural features. Following outdoor exposure in the presence of the mid-polar oil, the BET surface area decreased markedly to 17.63 m^2 g^{-1}, accompanied by a reduction in the adsorption capacity throughout the measured relative pressure range. A further, although less pronounced, decrease was observed for the high-polar ester-filled HDPE, which exhibited a surface area of 17.16 m^2 g^{-1}. The systematic reduction in nitrogen uptake indicates a progressive decrease in the accessible surface available for adsorption following prolonged fluid exposure. The corresponding BJH pore-size distribution exhibits a similar trend (Figure 2b). The control specimen displays a comparatively broad distribution of accessible mesostructural features, whereas both fluid-exposed specimens exhibit lower pore-volume intensity and a narrower distribution. These observations are consistent with modification of the near-surface microstructure following prolonged environmental ageing. The reduction in accessible surface area can be attributed to the combined influence of fluid sorption, surface restructuring, and oxidative ageing occurring within the amorphous regions of HDPE. Sorbed fluid molecules may occupy accessible free-volume elements and alter the local packing of polymer chains, thereby reducing the quantity of nitrogen-accessible adsorption sites. Because polar esters possess greater affinity for oxidized polymer surfaces than mid-polar fluids, the high-polar ester system exhibits the lowest accessible surface area, suggesting a greater extent of interfacial modification.

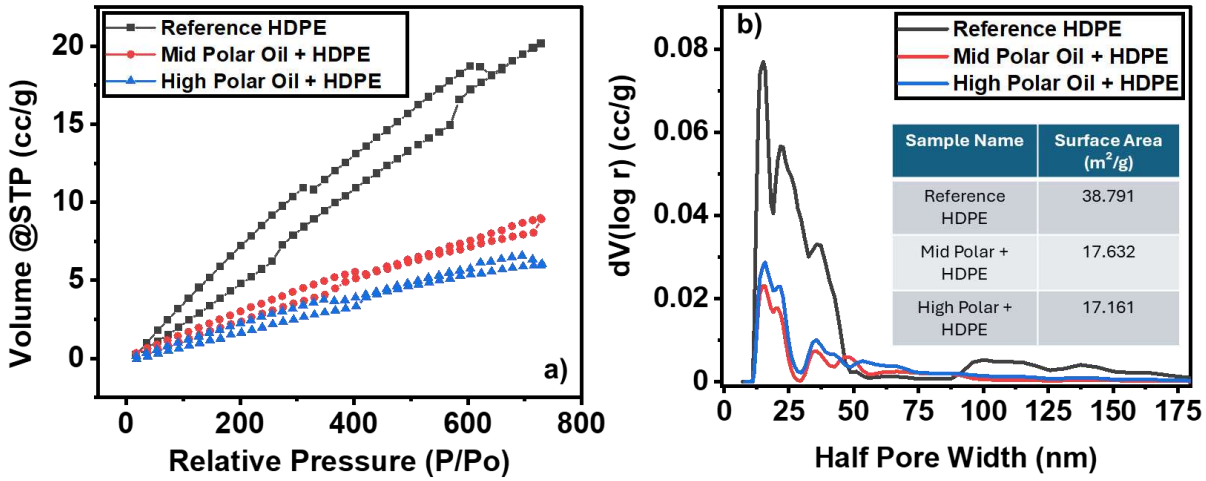

Figure 2. Nitrogen adsorption-desorption analysis of HDPE following natural environmental ageing under different fluid environments. (a) Nitrogen adsorption-desorption isotherms showing a progressive reduction in adsorption capacity after exposure to mid-polar oil and high-polar ester. (b) BJH pore-size distribution illustrating corresponding changes in accessible mesostructural features.

Although BET analysis does not directly identify pore filling or chemical interactions, the observed reduction in nitrogen accessibility is consistent with enhanced fluid-polymer interactions and microstructural evolution during environmental ageing. When considered together with the ATR-FTIR results, these findings suggest that increasing fluid polarity promotes more extensive oxidative modification of the HDPE surface, which subsequently influences its thermal behaviour and nanoscale morphology discussed in the following sections.

3.3 TGA analysis

Thermogravimetric analysis was performed to investigate the influence of fluid polarity on the thermal stability of HDPE following prolonged environmental ageing (Figure 3). All specimens exhibited the characteristic single-step thermal decomposition behaviour of polyethylene, indicating that environmental exposure did not alter the fundamental degradation mechanism

of the polymer. Nevertheless, distinct differences in the onset of thermal degradation and decomposition profiles were observed among the three specimens. The control HDPE exhibited the highest thermal stability, with the onset of significant mass loss occurring at the highest temperature. This behaviour is characteristic of relatively intact polyethylene chains possessing high molecular integrity and limited oxidative modification.

Following environmental exposure in the presence of the mid-polar oil, the thermogravimetric profile shifted towards lower temperatures, indicating a measurable reduction in thermal stability. Such behaviour is consistent with partial oxidative ageing of the polymer matrix. The formation of oxygen-containing functional groups during photo-oxidation introduces chemically weaker bonds than the original carbon–carbon backbone, thereby increasing the susceptibility of the polymer to thermally induced degradation. In addition, limited fluid sorption within the amorphous regions may increase local chain mobility, contributing to earlier thermal decomposition.

The high-polar ester-filled HDPE exhibited the greatest reduction in thermal stability, with the onset of rapid degradation occurring at approximately 430 °C, together with a steeper mass-loss profile. These observations are consistent with more extensive oxidative modification of the polymer matrix, as indicated by the ATR-FTIR analysis. During prolonged environmental ageing, hydroperoxide decomposition and subsequent β-scission reactions progressively reduce the average molecular weight of polyethylene, generating oxidized chain ends that are thermally less stable than the original polymer backbone. Consequently, decomposition is initiated at lower temperatures despite the overall degradation remaining a single-step process. It is noteworthy that the environmental exposure temperature (30-45 °C) is substantially lower than the decomposition temperatures observed by TGA. However, prolonged exposure to elevated ambient temperatures, in combination with solar irradiation and atmospheric oxygen, promotes chain mobility and oxygen diffusion within the amorphous phase of HDPE, thereby

accelerating thermo-oxidative ageing prior to thermal analysis. The reduced thermal stability observed in TGA therefore reflects the cumulative molecular changes induced during natural weathering rather than degradation occurring directly at ambient temperature. The thermal stability follows the order [Control HDPE > Mid-polar oil-filled HDPE > High-polar ester-filled HDPE] demonstrating that increasing fluid polarity is associated with progressively greater thermal destabilization of environmentally aged HDPE. When considered together with the ATR–FTIR results, the TGA data indicate that fluid polarity accelerates oxidative modification of the polymer, producing molecular structures that exhibit lower resistance to subsequent thermal degradation while preserving the intrinsic decomposition pathway characteristic of polyethylene.

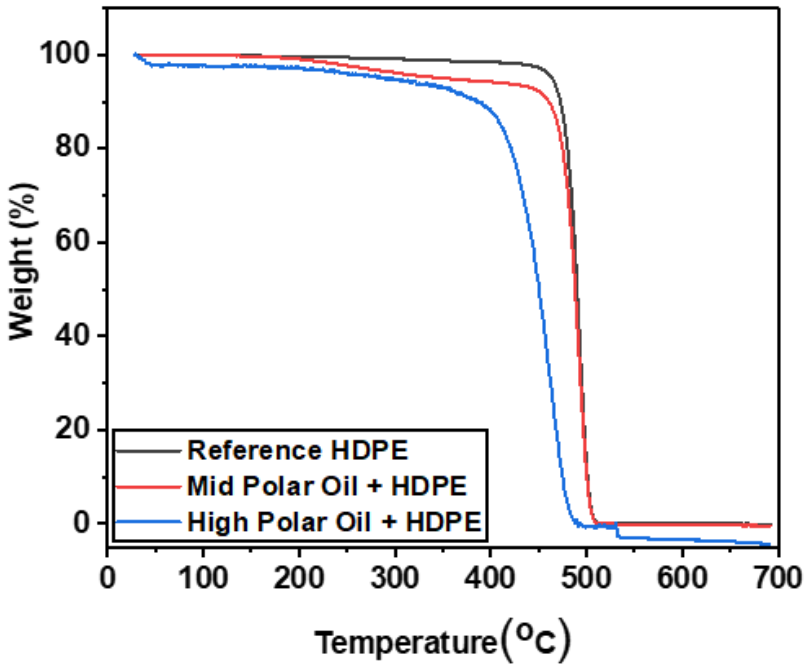

Figure 3. Thermogravimetric (TGA) curves of reference HDPE, HDPE filled with mid-polar oil, and HDPE filled with high-polar oil, illustrating the effect of oil polarity on thermal degradation behaviour.

3.4 DSC Analysis

Differential scanning calorimetry (DSC) was employed to investigate the influence of fluid polarity on the crystalline structure and thermal transitions of HDPE following natural environmental ageing (Figure 4). The heating and cooling thermograms of all specimens exhibit the characteristic melting and crystallization behaviour of semicrystalline polyethylene, indicating that environmental ageing modifies the degree of structural order without altering the fundamental thermal transition mechanism. The control HDPE displays a sharp crystallization exotherm during cooling together with a well-defined melting endotherm centred at approximately 131–132 °C during the subsequent heating cycle (Figure 4a-c). The narrow and intense thermal transitions are characteristic of well-organized lamellar crystals and an intact semicrystalline microstructure with efficient chain packing. Following exposure to the mid-polar oil, both the crystallization and melting peaks become broader and decrease in intensity relative to the control specimen. This behaviour indicates a reduction in crystalline order and melting enthalpy, suggesting disruption of the regular lamellar arrangement. Such changes are consistent with partial sorption of the fluid within the amorphous regions of HDPE, where increased chain mobility reduces the efficiency of molecular packing during recrystallization. Consequently, the formation of well-developed crystalline lamellae is partially suppressed, producing a lower overall degree of crystallinity.

The high-polar ester-filled HDPE also exhibits a reduction in both crystallization and melting peak intensity compared with the control polymer; however, the decrease is less pronounced than that observed for the mid-polar oil. This behaviour suggests that although environmental ageing modifies the crystalline morphology, the dominant effect of the high-polar fluid is not extensive plasticization but rather oxidative modification of the polymer matrix. As demonstrated by the ATR-FTIR analysis, the high-polar ester promotes greater formation of oxygen-containing functional groups, while the TGA results indicate a corresponding reduction

in thermal stability. Under such conditions, oxidative chain scission occurring primarily within the amorphous regions may generate shorter polymer segments capable of limited recrystallization during thermal cycling, partially compensating for the loss of crystalline order. Consequently, the apparent crystallinity remains higher than that of the mid-polar system despite more extensive chemical degradation. The degree of crystallinity therefore follows the order: Control HDPE > High-polar ester-filled HDPE > Mid-polar oil-filled HDPE. This trend highlights the coexistence of two distinct ageing mechanisms. The mid-polar oil predominantly influences the physical organization of the semicrystalline structure through fluid-induced plasticization and disruption of chain packing, whereas the high-polar ester primarily accelerates oxidative degradation through enhanced fluid-polymer interactions. These competing processes influence the crystalline morphology in different ways, demonstrating that the extent of chemical degradation is not necessarily directly proportional to the reduction in crystallinity. Collectively, the DSC results complement the FTIR and TGA observations by demonstrating that environmental ageing influences not only the chemical composition of HDPE but also its semicrystalline microstructure. The evolution of crystalline order plays a

critical role in determining the subsequent mechanical response of the polymer and ultimately contributes to the development of macroscopic panelling during prolonged outdoor exposure.

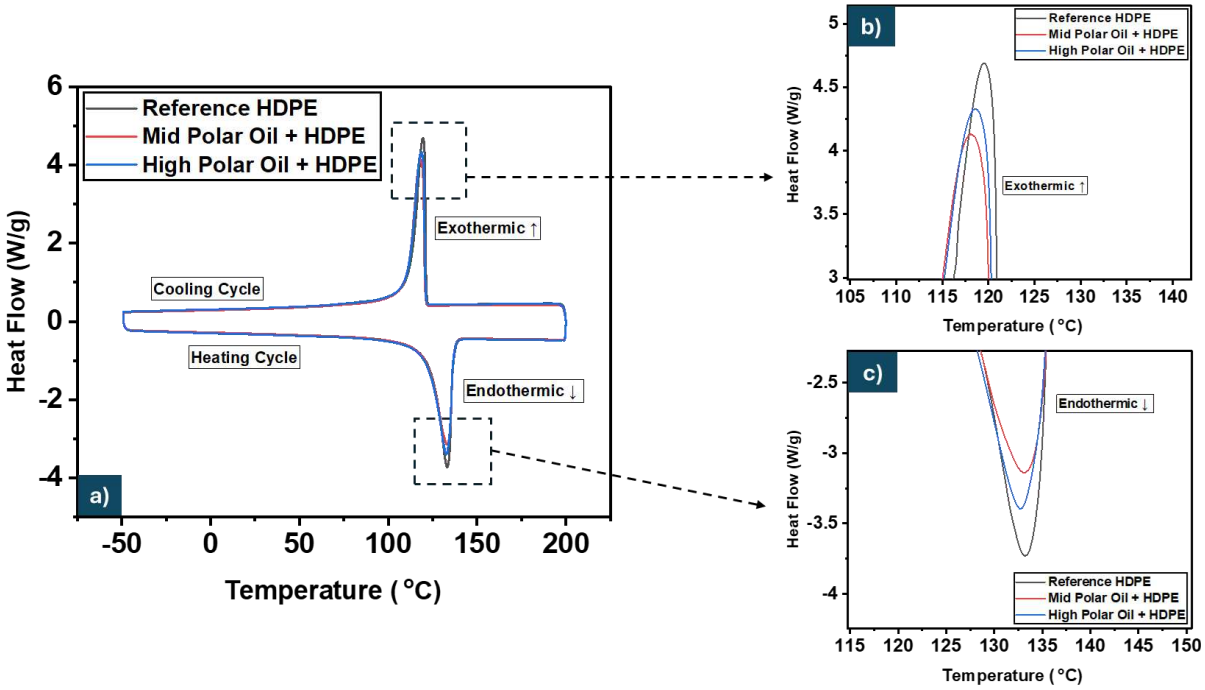

Figure 4. Differential scanning calorimetry (DSC) thermograms of HDPE following natural environmental ageing under different fluid environments. (a) Heating and cooling thermograms of the control HDPE, mid-polar oil-filled HDPE, and high-polar ester-filled HDPE. (b) Enlarged view of the crystallization exotherms obtained during the cooling cycle. (c) Enlarged view of the melting endotherms obtained during the heating cycle.

3.5 AFM Analysis

Atomic force microscopy (AFM) was employed to investigate the nanoscale morphological evolution of HDPE following prolonged environmental ageing under different fluid environments[27,28]. Both topographical and phase-contrast imaging were used to evaluate changes in surface morphology and local viscoelastic heterogeneity associated with fluid-assisted degradation. The control HDPE exhibits a relatively homogeneous surface morphology with an average surface roughness of approximately 43.7 nm (Figure 5a). The

topographical image displays a continuous surface characterized by uniformly distributed nanoscale features, indicative of an intact semicrystalline morphology. The corresponding phase image (Figure 5b) shows minimal phase contrast, suggesting relatively uniform mechanical behaviour across the scanned region with limited nanoscale heterogeneity.

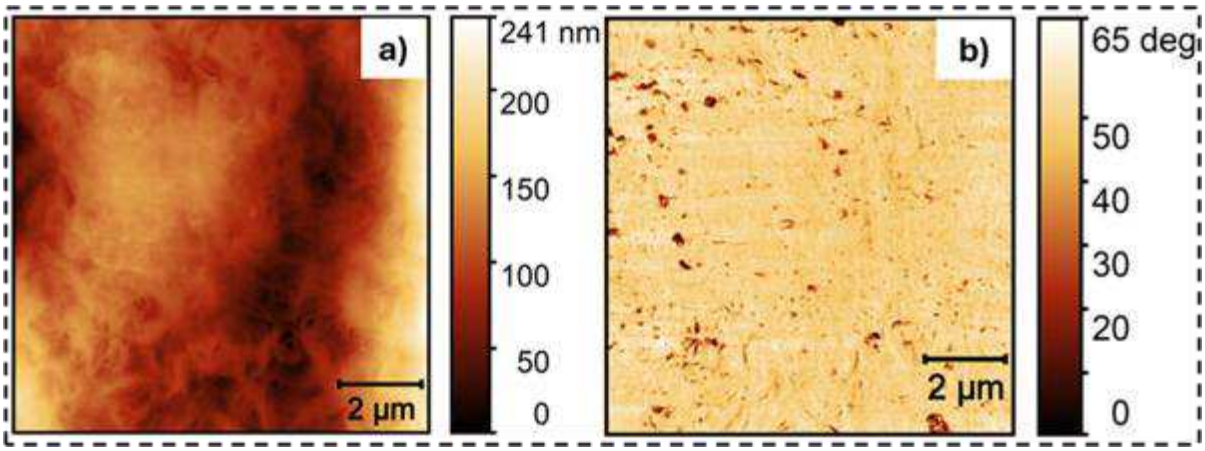

Figure 5. AFM topographical (a) and phase-contrast (b) images of the control HDPE following natural environmental exposure. The surface exhibits relatively uniform nanoscale morphology and homogeneous phase contrast, indicative of an intact semicrystalline structure with limited mechanical heterogeneity.

Following exposure to the mid-polar oil, pronounced modifications in surface morphology become evident (Figure 6a). The average surface roughness increases substantially to approximately 70-80 nm, accompanied by irregular ridges, depressions, and heterogeneous surface features. Such morphological changes are consistent with localized disruption of the near-surface microstructure arising from fluid-assisted environmental ageing. The corresponding phase image (Figure 6b) exhibits increased spatial variation in phase contrast, indicating the development of mechanically heterogeneous regions possessing different local viscoelastic responses. This behaviour is consistent with localized plasticization and heterogeneous structural rearrangement within the amorphous phase of HDPE.

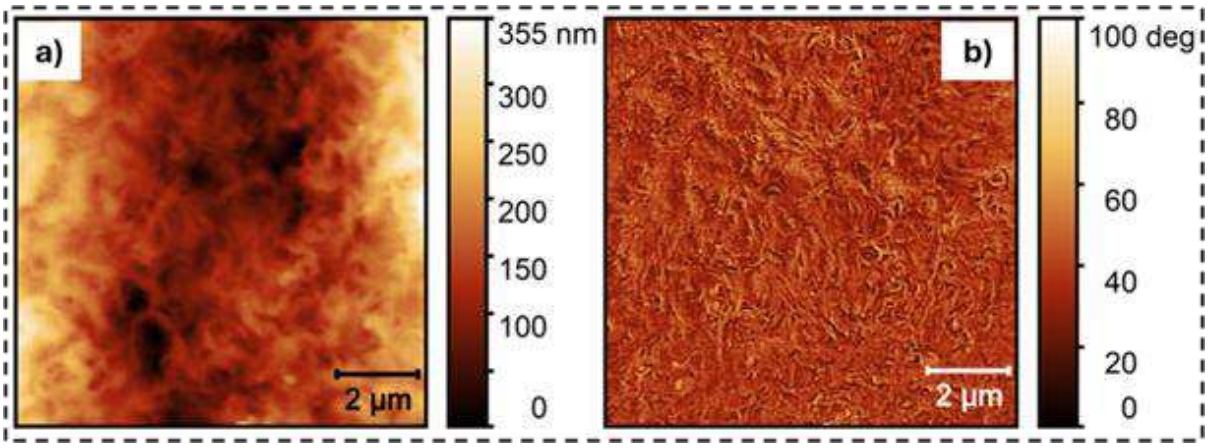

Figure 6. AFM topographical (a) and phase-contrast (b) images of the mid-polar oil-filled HDPE after environmental ageing. Increased surface roughness together with heterogeneous phase contrast indicates localized morphological restructuring and spatial variations in near-surface viscoelastic behaviour.

A markedly different surface morphology is observed for the high-polar ester-filled HDPE (Figure 7a). Although the measured surface roughness decreases to approximately 25 - 34 nm, the surface does not become uniformly smooth. Instead, AFM reveals compact, domain-like surface features together with localized raised regions distributed across the polymer surface. The reduction in roughness therefore reflects nanoscale surface reorganization rather than recovery of the original polymer morphology. The corresponding phase image (Figure 7b) displays pronounced phase separation with well-defined domains exhibiting distinct phase contrast. Because AFM phase imaging is sensitive to variations in local energy dissipation and mechanical properties, these observations indicate substantial heterogeneity in the near-surface viscoelastic behaviour of the environmentally aged polymer. When interpreted together with the FTIR and TGA results, this heterogeneous phase response is consistent with extensive oxidative modification and microstructural reorganization promoted by the high-polar ester.

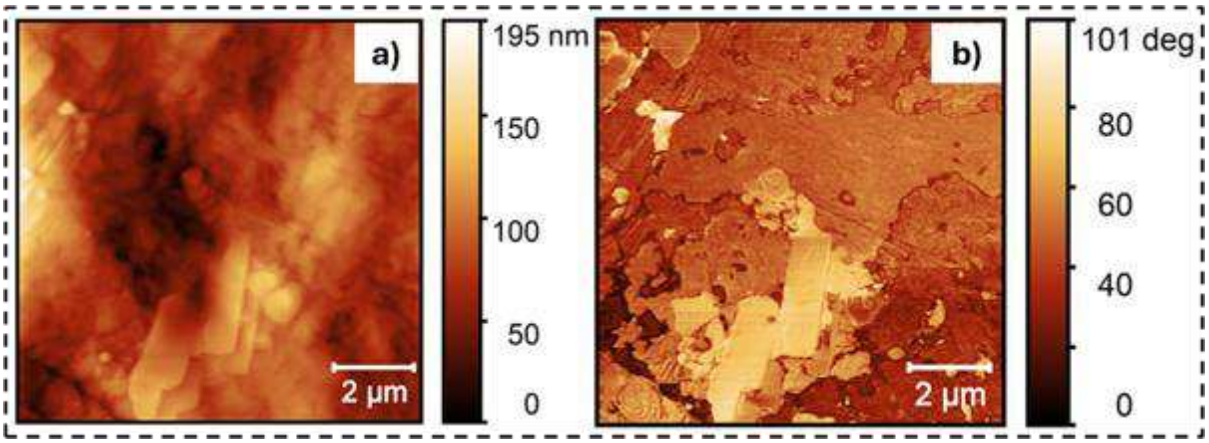

Figure 7. AFM topographical (a) and phase-contrast (b) images of the high-polar ester-filled HDPE after environmental ageing. The development of compact domain-like surface features and pronounced phase heterogeneity is consistent with extensive microstructural reorganization associated with fluid-assisted oxidative ageing.

Collectively, the AFM observations demonstrate that increasing fluid polarity modifies the surface morphology of HDPE through two distinct mechanisms. The mid-polar oil primarily induces physical restructuring characterized by increased surface roughness and localized morphological irregularities, whereas the high-polar ester promotes more extensive chemical ageing, leading to the formation of compact but mechanically heterogeneous surface domains. These nanoscale structural changes complement the spectroscopic and thermal analyses and provide direct morphological evidence linking fluid-assisted environmental ageing to the progressive loss of structural integrity preceding macroscopic panelling[23].

3.6 Structure-Property Relationship and Proposed Mechanism of Fluid Polarity-Driven Environmental Ageing

The collective experimental results establish a direct structure-property relationship linking fluid polarity to the progressive environmental ageing and mechanical instability of HDPE during prolonged outdoor exposure (Figure 8). Rather than arising from a single degradation process, panelling develops through the combined influence of photo-oxidative chemistry,

microstructural evolution, and mechanically induced stress redistribution within the polymer container. Environmental ageing of HDPE is initiated at the polymer surface through the combined action of ultraviolet radiation, atmospheric oxygen, and elevated ambient temperature. Solar irradiation promotes the formation of hydroperoxide species within the amorphous regions of polyethylene, which subsequently undergo homolytic decomposition to generate alkyl and alkoxy radicals. These radicals participate in autocatalytic oxidation through hydrogen abstraction and peroxy radical formation, ultimately producing oxygen-containing functional groups and oxidized chain ends via β-scission reactions. The progressive development of carbonyl and hydroxyl functionalities observed in the ATR-FTIR spectra provides clear evidence of this oxidative ageing process.

The presence of fluids significantly modifies the kinetics of environmental ageing. The mid-polar oil primarily affects the physical organization of the polymer by diffusing into the amorphous regions, where it increases local chain mobility and perturbs intermolecular packing. Consequently, DSC reveals the greatest reduction in crystalline order, while AFM demonstrates pronounced increases in surface roughness and localized mechanical heterogeneity. Because oxidation remains comparatively limited, the polymer largely retains its molecular integrity despite experiencing moderate physical softening. These combined effects result in gradual reduction of structural rigidity and moderate panelling during outdoor exposure. In contrast, the high-polar ester follows a fundamentally different degradation pathway. Owing to its greater polarity, the ester exhibits stronger affinity for the oxidized polymer surface, promoting more extensive fluid sorption and interfacial modification. Although BET primarily indicates a reduction in nitrogen-accessible surface characteristics rather than direct pore filling, the collective observations from BET, FTIR, TGA, DSC, and AFM consistently demonstrate that the high-polar fluid produces the greatest extent of molecular and microstructural alteration. Enhanced oxidative modification generates a higher

concentration of oxygen-containing functional groups, while progressive chain scission lowers molecular integrity and thermal stability. Simultaneously, localized reorganization of the semicrystalline morphology produces mechanically heterogeneous surface domains, as revealed by AFM phase imaging.

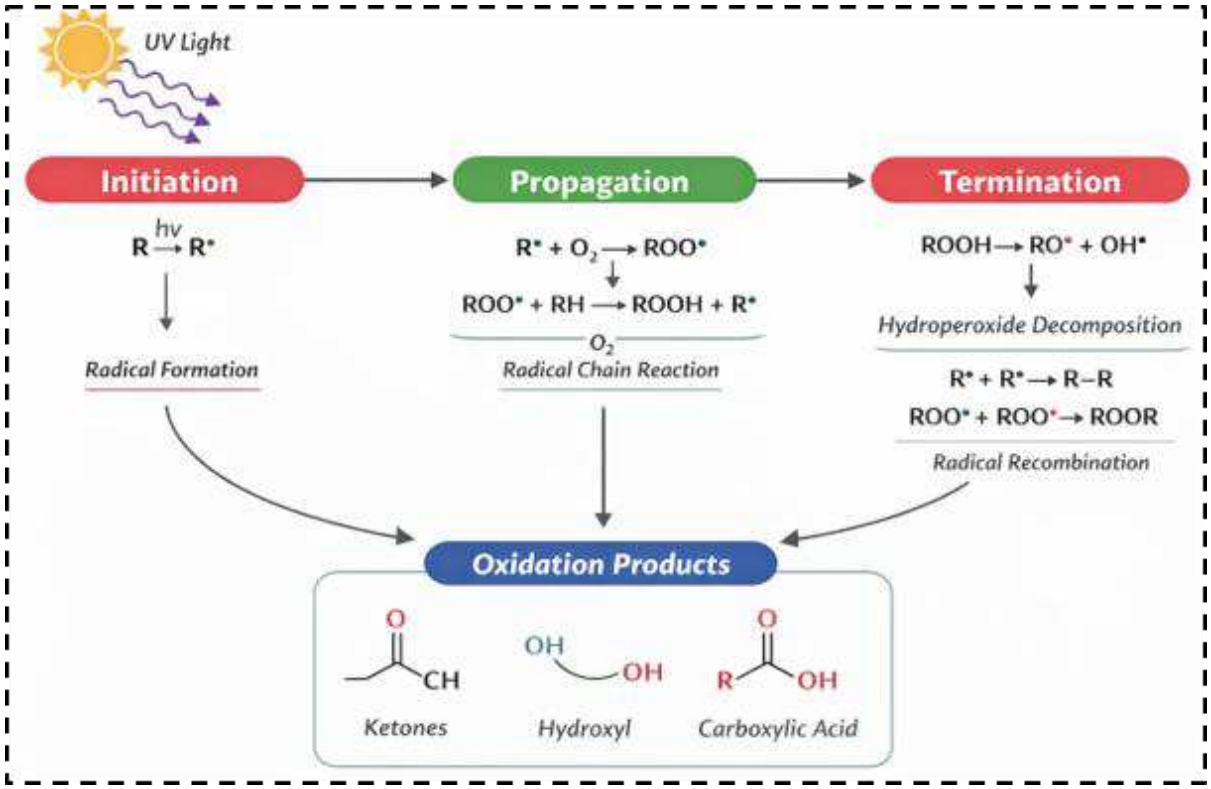

Figure 8. Schematic representation of the photo-oxidative degradation mechanism of HDPE under UV exposure, showing initiation, propagation, and termination steps leading to chain scission and formation of oxygenated products.

The evolution from molecular oxidation to macroscopic deformation is governed by the interplay between chemical degradation and mechanical stress development. Oxidative chain scission progressively reduces molecular weight and weakens the network of tie molecules connecting crystalline lamellae, thereby diminishing the ability of the polymer to redistribute applied stresses. Simultaneously, fluid sorption generates concentration gradients across the wall thickness of the container, while repeated day–night thermal cycling induces cyclic dimensional changes and internal pressure fluctuations. As the polymer becomes progressively

embrittled, these stresses can no longer be accommodated elastically, resulting in localized deformation, wall instability, and ultimately inward collapse of the container, commonly referred to as panelling.

Conclusion

This study systematically investigated the influence of fluid polarity on the environmental ageing behaviour of commercial HDPE packaging containers exposed to natural outdoor weathering. By integrating spectroscopic, thermal, surface, and nanoscale morphological characterization, a comprehensive structure–property relationship was established linking fluid polarity to the progressive physicochemical evolution and structural instability of HDPE. ATR-FTIR analysis demonstrated progressive formation of oxygen-containing functional groups, indicating that increasing fluid polarity accelerates photo-oxidative modification of the polyethylene matrix. Thermal analyses further revealed that environmentally aged HDPE exhibits reduced thermal stability and altered crystalline organization, reflecting the combined influence of oxidative chain scission and microstructural evolution. BET measurements showed a substantial reduction in nitrogen-accessible surface area following fluid exposure, consistent with fluid sorption and near-surface structural modification, while AFM revealed pronounced polarity-dependent changes in surface morphology and local mechanical heterogeneity. The collective experimental evidence demonstrates that the degradation pathway of HDPE is strongly governed by the polarity of the contacting fluid. Mid-polar fluids primarily induce physical restructuring through localized plasticization and disruption of chain packing, whereas high-polar synthetic esters promote more extensive oxidative modification, thermal destabilization, and nanoscale microstructural reorganization. These molecular and microstructural changes progressively reduce the ability of the polymer to accommodate stresses generated during natural weathering, ultimately leading to localized deformation and

macroscopic panelling. This work demonstrates that panelling is not simply a consequence of fluid sorption, but rather the final manifestation of a multiscale environmental ageing process involving coupled oxidative chemistry, semicrystalline structural evolution, thermal degradation, and mechanical stress localization. The mechanistic framework proposed in this study provides new insight into the degradation behaviour of polyethylene under realistic service conditions and highlights the importance of fluid-polymer compatibility in the design of durable HDPE packaging intended for prolonged outdoor applications.

Acknowledgements

The authors sincerely acknowledge Marico India Limited for financial support of this research. The authors are also grateful to the Central Research Facility (CRF), Indian Institute of Technology Delhi, for providing access to the advanced characterization facilities utilized in this work. Vishal Bhaskar gratefully acknowledges the Ministry of Education (MoE), Government of India, for providing financial support through an Institute Fellowship.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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