

1 Identification of Commercial Oxo-Biodegradable Plastics: Study of UV Induced Degradation in an Effort 2 to Combat Plastic Waste Accumulation

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13 Abstract

14 About 50% of plastics is discarded after only single use which creates major environmental burdens. End of life
15 single-use items such as carrier bags constitute a large proportion of the litter found in marine and terrestrial
16 environments alike. The main objective of the current work was to investigate the response of an oxo-
17 biodegradable commercial plastic film product to photo-degradation using accelerated weathering, verifying the
18 claim of its biodegradability and suitability as an eco-friendly product. The test specimens used were white to
19 transparent commercial grade plastic bags of PE origin acquired from an international franchise of household
20 goods, which were claimed to be of oxo-biodegradable nature. This study is also geared towards the
21 appropriateness of such products to reduce plastic waste accumulation in urban environments. The film samples
22 were exposed to weathering up to 20 continuous days to determine their degradability and assess their thermal
23 properties as a means to determine impact of UV induced oxo-biodegradation. Haze (%), light transmission (%)
24 and the total change in colour (ΔE) were measured as indicators to the degradation profile of the polymeric
25 materials, in addition to tensile pull mechanical properties and thermal stability. The melting peak indicates the
26 melting point (T_m) of the polymer and with exposure to weathering it showed a slight decrease from 105 to
27 102°C indicating that biodegradation mechanism was triggered. The reduction in strain at rupture was also
28 indicative of a loss in crystalline structure, coupled with Young's modulus increase throughout weathering
29 exposure tests.

30 **Keywords:** Plastic Film, Oxo-biodegradable, Colour, Haze, TGA.

31

32 1. Introduction

33 Plastics are an appealing versatile material associated with low production cost when compared to other classical
34 materials (e.g. cement, wood and metal). Their beneficial properties have resulted in a worldwide annual
35 production rate that exceeds 335 million tonnes [1]. About 50% of plastics are discarded after single use which
36 creates major environmental burdens associated with accumulation and pollution [2]. Plastic carrier bags are one
37 example of a single-use item and were first introduced on the market back in the 1970s and quickly became an
38 essential item to our daily lives. Carrier bags typically consist of polyethylene (PE) which orients the
39 petrochemical market towards polyolefin (PO) plastic film production. End of life single-use items such as
40 carrier bags are frequently thrown away in the environment by consumers and contribute significantly to marine
41 and terrestrial pollution. It was estimated that 98.6 billion carrier bags were introduced in the European Union
42 (EU) market in 2010 and about 100 billion plastic bags were added ever since on an annual basis. Plastic bags
43 are usually provided free of charge or for a very low charge when consumer products are purchased at outlets.
44 However, few countries have started implementing stringent regulations against their use even if a consumer
45 charge is applied. Within an EU context, the annual per capita usage of plastic bags exceeds 450 bags per person
46 [3]. It is estimated that about 8 billion plastic shopping bags are used per annum in the United Kingdom, 4.3
47 billion in Australia, 9.8 billion in Hong Kong, 3.3 billion in Bangladesh, 100 billion in the United States and 300
48 billion to 1 trillion in China [4-5].

49 The majority of single use plastics is still disposed of in a non-sustainable way, i.e. without the recovery of
50 energy or their recycling to useful products [6]. Uncontrolled incineration or mechanical tillage in the field have
51 high environmental impacts and generate air and soil pollution [7]. The accumulation of plastic waste in the
52 environment, the growing awareness for global warming and the environment in general have significantly
53 boosted the consumer's interest in using biodegradable materials, forcing industries to make available
54 biodegradable alternatives. Various types of plastic materials can be designed to be biodegradable, including
55 polyesters, which typically possess a poor water-solubility. They are not directly bioavailable to organisms but
56 can be degraded via an extracellular enzymatic process. Enzymes secreted by microorganisms initiate the first
57 step in degradation by catalysing the hydrolysis of the ester bonds and degrading the polymer into oligomers and
58 monomers. These lower molecular weight intermediates ($\approx 500 \text{ g mol}^{-1}$) show a much higher water solubility
59 and can pass through the cell membrane for further intracellular metabolization by microorganisms [7].

60 Biodegradable plastics are subdivided in two categories depending on the manufacturing process and
61 degradation mechanism. The first type are hydro-biodegradable plastics which are mainly produced from
62 renewable raw materials such as starch, but could still contain up to 50% of plastics derived from crude oil or
63 aliphatic polyesters [8]. The second type of biodegradable polymers are oxo-biodegradables, which are based on
64 petrochemical naphtha blends mixed with pro-oxidant additives. The latter have become popular nowadays for
65 packaging and film applications [9]. Their degradation can be initiated by different factors such as UV light,
66 moisture, heat and microorganisms in processes classified as photo-oxidative degradation, thermal degradation
67 and biodegradation. The degradation of polymers can be assessed by measuring changes in physical properties,

68 loss in molecular weight (MW), amount of carbon-dioxide evolved and by calculating microbial growth on the
69 surface of the polymer after exposure to the natural conditions. To monitor this chemical reaction, evolution of
70 certain products is typically monitored such as carbon dioxide [10]. Controversy exists as to the impact of
71 products from oxo-biodegradation, on the environment due to their release of metals and chemicals [8]. In
72 contrast, hydro-biodegradables divert feedstock from natural food resources in their manufacturing process and
73 are quite costly to produce.

74 There are several testing methods to assess degradation by measuring MW, tensile properties, weight loss, extent
75 of fragmentation, enzyme assays, biochemical oxygen demand and carbon dioxide production. To confirm that
76 degradation has occurred, the combination of multiple tests is employed. The combination of the test procedure
77 has to be selected according to the potential fields of polymer application and its way of disposal, such as
78 compost, soil, marine and so on. Appendix A presents a review of the main studied that encompass testing
79 procedure of biodegradability and impact of surrounding environment.

80 Accumulation of plastic waste in environment forces many industries to generate biodegradable products.
81 Municipal solid waste (MSW) management through composting and replacement of conventional plastics with
82 biodegradable ones is an environmentally friendly process because it decreases the output of waste to landfills,
83 while saving energy and yielding valuable organic compounds and nutrients that can be used in agriculture [11].
84 Degradation of plastic is a complicated process as it is associated with release of large quantities of carbon
85 dioxide into environment together with other toxic compounds. It is estimated that 2.8 kg of carbon dioxide
86 (CO₂) is released by incineration of 1 kg of plastic [12]. The introduction of biodegradable films, therefore,
87 requires an assessment of their biodegradability within both managed and natural environments using
88 harmonized assessment criteria [13]. Nazareth et al. [14] experimentally evaluated alteration and chemical and
89 structural composition of selected plastic products marketed in Canada, USA and Brazil as biodegradable. The
90 aging experiments carried out by seawater immersion for 180 days showed no evidence of degradation for 4 out
91 of the 6 studied samples. This finding denotes unequivocal green-washing practices: the inadequate adoption of
92 green marketing is deceiving to consumers and may lead to improper disposal of these materials.

93 The main objectives of the current work are to investigate the response of an oxo-biodegradable plastic product
94 to photo degradation using accelerated weathering testing. The test specimens used in this work were white to
95 transparent commercial grade plastic bags acquired from an international franchise of household goods, which
96 were claimed to be of oxo-biodegradable nature and also declared to be of PE origin. The work provides a
97 realistic evaluation on the applicability of commercial plastic grades available on the market and their true nature
98 in terms of biodegradability and environmental friendliness. Additionally, information is generated on the
99 appropriateness of this class of materials to reduce PSW accumulation in urban environments. The film samples
100 were exposed to weathering conditions to determine their degradability and assess their thermal properties as a
101 means to determine the impact of UV induced oxo-biodegradation. Haze (%), light transmission (%) and the

102 total change in colour (ΔE) were measured as indicators to the degradation profile of the polymeric materials, in
103 addition to tensile pull mechanical properties.

104

105 **2. Materials & Methods**

106 *2.1. Acquisition of Materials*

107 White to transparent commercial grade plastic bags acquired from a household goods franchise were used as test
108 specimens. The plastic bags were claimed to be of oxo-biodegradable nature of PE origin. The bags were cut
109 into standard test specimens with a size of 20 x 1 cm as described in previous works [9,15]. The thickness of the
110 test specimens was measured and reported to be as 200 μm . Pigmentation of the bags due to store logo stamp
111 was avoided in all test specimens used in this work as presented in [Figure S1](#) of the [Supplementary Materials](#)
112 [File](#).

113

114 *2.2. Fourier Transformed infrared spectrometry (FTIR)*

115 A JASCO FTIR 4700 unit equipped with an attenuated reflectance (diamond) infrared spectroscopy (ATR)
116 attachment was used for the analysis and the identification of material's chemical fingerprint before exposure to
117 accelerated weathering (irradiation). The test was conducted in accordance with ISO 10640. Samples were tested
118 using 32 scans for the background and each individual spectrum in the range of 4000 to 400 cm^{-1} [16]. Storage
119 and transportation of samples was done using a sealed hygienic plastic PE bag which was always kept in dark
120 room conditions (approximately 22-23°C/50% relative humidity) as previously conducted in Al-Salem et al. [9].

121

122 *2.3. X-Ray Fluorescence (XRF) Workflow*

123 The control (unexposed) samples were subjected to x-ray fluorescence (XRF) analysis in emission mode for
124 possible heavy metal detection using a VANTA (M series) - Olympos Company make XRF gun calibrated at
125 laboratory conditions. Reported results are an average of three random experimental runs as recommended by
126 manufacturer to evaluate possible inclusion of typically oxo-biodegradable additives.

127

128 *2.4. Accelerated Exposure (Aging) of Plastic Films*

129 The test specimens were exposed to accelerated (ageing) weathering tests as per ASTM D 4329 to simulate the
130 outdoor conditions and exposure of such materials to natural environment [17]. The tests were conducted using
131 a Q-lab QUV model machine equipped with solar radiation mimicking technology utilising UVA fluorescent
132 bulbs which is responsible for majority of solar degradation of polymeric materials. The protocol was used to
133 set the exposure cycles for 8 continuous hours of UV exposure at 60°C, followed by 4 hours of condensation at
134 50°C. A minimum of four replicates were used in each exposure rack with an irradiance of the lamp equal to
135 0.68 W m^{-2} and calibrated every 400 h of continuous operation. The tests were terminated after 20 days of

136 continuous exposure, at which time about 40% of materials showed breakages in several places rendering them
137 as out of service and detecting the materials threshold limit.

138

139 *2.5. Thermal Response and Stability*

140 Thermal degradation of the samples was investigated using a Mettler-Toledo TGA 3+ Model coupled with StarE
141 data acquisition/analysis software set to record the data every second under a heating rate (β) of $15^{\circ}\text{C min}^{-1}$. A
142 constant flow of pure (99.99%) dry nitrogen gas (N_2) with a flow rate of 50 ml min^{-1} was maintained throughout
143 the experiments. The measurements were conducted using $1 \pm 0.1 \text{ mg}$ samples from RT to 600°C made with at
144 least triplicates showing high repeatability with standard deviation (std) not exceeding 1% in accordance with
145 the International Confederation for Thermal Analysis and Calorimetry (ICTAC) recommendations [18-19] for
146 non-isothermal (dynamic) thermogravimetry; to diminish sample size influences on the kinetics. The crucibles
147 used in all experimental runs were made of alumina oxide (Al_2O_3) with a $70 \mu\text{L}$ size. Weight loss (%) and first
148 derivative (DTG, $\% \text{ }^{\circ}\text{C}^{-1}$) were recorded constantly, and the onset (T_{os}), midset (T_{md}), inflection point (T_{if}) and
149 maximum degradation temperatures (T_f) were recorded based on the thermogravimetric analysis conducted.

150

151 *2.6. Crystallinity Estimation Using Differential Scanning Calorimetry (DSC)*

152 A Netzsch DSC (Model 60 Plus Series) was used to test control and exposed specimens using approximately
153 $3 \pm 0.1 \text{ mg}$ samples taken from the middle section of the film specimens. Al_2O_3 crucibles were used for both
154 samples and reference materials (no weight) experimental runs. The heat flow was recorded against actual time
155 of experimental runs. Crystallinity measurements were determined using scans of the first and second heating
156 cycle between 50 to 230°C based on the peak area of the heat flow curve between 60°C and 130°C with a N_2 gas
157 flowrate of 20 ml min^{-1} and a heating rate of $10^{\circ}\text{C min}^{-1}$. Cooling rate was set at $15^{\circ}\text{C min}^{-1}$ in similar conditions
158 in accordance with ISO 11357-1 and ISO 11357-3. The analysis in this work includes the second heating cycle,
159 in order to determine the actual behaviour after eliminating the inherited effect of weathering on the samples.
160 The degree of crystallinity (%) was calculated by dividing the melting enthalpy over the melting enthalpy of a
161 100% crystalline PE (293.6 g J^{-1}) for both the first and second heating cycle, respectively [20].

162

163 *2.7. Scanning Electron Microscopy (SEM)/Energy Dispersive Elemental Spectroscopy (EDS)*

164 Scanning Electron Microscopy (SEM) was conducted to determine the extent of degradation and investigate
165 micro-cracks on the surface of test specimens before and after exposure to accelerated weathering. The analysis
166 was performed after coating the samples with pure gold (Au) to condition the plastic to a charging state
167 appropriate for SEM imaging. A Jeol JSM 6010LA Model sputter coater was used with a 15 mA sputter current
168 (60 seconds, approximately 3 nm thickness), was used. Argon (Ar) gas was used to purge the sputter coater
169 system. A TESCAN - VEGA 3 model microscope equipped with a Bruker Energy Dispersive Elemental
170 Spectroscopy (EDS) analysis system and software, was utilised in this study. Imaging was conducted using a

171 voltage of 15 kV and EDS analysis was done on uncoated polymeric articles to avoid over charging the samples
172 and obtaining realistic experimental results (see [Figure S2 in the Supplementary Materials File](#)).

173

174 *2.8. Mechanical Properties Evaluation*

175 The mechanical properties were evaluated at room temperature to determine the impact of exposing the samples
176 to various degradation media following ASTM D 882. Experiments were conducted using a Tinuis Olsen (UK)
177 50 ST Model - Universal Testing Machine (50 kN load cell) set to a 500 mm min⁻¹ test speed. The width and
178 thickness of the film specimens were measured using an internally calibrated Vernier callipers to the nearest 0.1
179 mm. Processing and cutting variation was minimal between the width and the thickness over the length of some
180 samples accounting for less than 1% for the total number of samples measured. The variation not being more
181 than ±0.02 mm for width and ±0.01 mm for thickness with a constant width of 10 mm and thickness as depicted
182 previously. The maximum extension available was 1065 mm equivalent to a strain of 900%. Strain at break
183 (elongation at break) was measured based on cross head displacement and a gauge of 100 mm. For yield strength,
184 it was observed that some specimens showed multiple yield points and some had a distinct yield. To standardize
185 the results for easy comparison between all specimens, it was decided to consider the first yield point as the yield
186 strength of the specimen. The measurement values obtained are the average of the replicate specimens stored
187 directly from the machine's software (Horizon 10.2.5.0). The tests were conducted with a gauge grip separation
188 of 100 mm as suggested by the experimental protocol followed and was also set to terminate at 75% of ultimate
189 force. The threshold of detection was input in the test program at 3 N. To assure accurate readings that reflects
190 the true modulus of elasticity determined from the stress and strain curves, the grip separation was reduced to
191 25 mm for the accelerated weathering specimens at threshold limit of weathering exposure. This was done due
192 to the fact that samples were shorter due to exposure to UV for prolonged periods of time in the weathering
193 chamber similar to our previous work [9].

194

195 *2.9. Haze and Light Transmission Measurements*

196 A Diffusion System MF709 (spherical) haze meter (model BS 2782) was employed to measure the haze (%) and
197 light transmission (%) at the midpoint of the studied samples, in accordance with ASTM D1003-13 for samples
198 exposed to the degradation media. Replicates of the tested specimens were tested for haze (%) and light
199 transmission (%) and the average of the readings were reported. The average readings of the replicates for each
200 formulation were measured and all experimental results conducted resulted from taking a minimum of two
201 readings (runs), having a ±5% error for each data point (replicate).

202

203

204 *2.10. Measurement of Colour Parameters and Total Change in Colour (ΔE)*

205 Standard colour parameters for light/dark (L^*), red/green (a^*), and yellow/blue (b^*) post degradation were
206 measured using a Shenzhen Technology 3NH Model colorimeter according to ASTM D 2244-11. Parameters
207 measured were used to calculate the total change in colour (ΔE) between control samples and each formulation
208 thus [15]:

$$209 \quad \Delta E = \sqrt{((\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2)} \quad (3)$$

210 Where ΔL , Δa and Δb are the values of the difference between the control specimen measurements (control
211 samples with no exposure) and those of each tested batch.

212 **3. Results and discussion**

213 *3.1. Identification of plastic material*

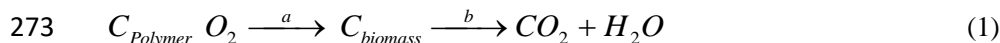
214 The test specimens in this work were white to transparent commercial grade plastic bags claimed to be of oxo-
215 biodegradable nature. To determine the exact polymer and additive content, ATR analysis was conducted on the
216 specimens. ATR is a technique used for detecting the absorption in the range of mid-infrared region and was
217 used to detect distinctive adsorption peaks of the plastic films studied. Several prominent peaks were identified.
218 **Figure 1** shows spectra obtained for control (pre-weathered) specimen. The prominent peaks identified in the
219 range between 700 to 760 cm^{-1} corresponds to the rocking vibration associated to the crystallinity of the polymer.
220 The peak between 1460-1480 cm^{-1} relates to CH_2 bending vibration, while the band between 2850-2950 cm^{-1}
221 associated with the asymmetric and symmetric CH stretching [16]. The major peak was around 1470 cm^{-1} which
222 is a distinctive PE band [21]. The overall spectra of the sample and the aforementioned bands are also associated
223 with oxo-biodegradable PE spectra as confirmed by previous authors [22-23]. Oxo-prodegradant additive peaks
224 were also identified at 850 cm^{-1} , and 2800 to 3000 cm^{-1} and 1200 cm^{-1} to 1500 cm^{-1} which is typically associated
225 with calcium carbonate (CaCO_3) additive for PE commercial grades [14,24]. Küpper et al. [25] analysed PE
226 sample's ATR-spectrum, and in addition to the main 1470 cm^{-1} PE band, bands in the interval between 3400 and
227 3200 cm^{-1} and around 1600 cm^{-1} were also observed assigned to UV-stabilisers of the hindered amine stabiliser
228 (HAS)-type. In the studied oxo-biodegradable PE sample, none of these bands were observed. The sample
229 studied in this work is classified to be of PE origin as claimed by the manufacturer, and was confirmed to be so
230 based on the peaks detected.

231 In order to detect possible inclusion of typical oxo-biodegradable additives, the test samples were subjected to
232 XRF analysis in emission mode for possible metal and additives detection (**Table 1**). Analysis of the control PE
233 bags specimens (0 days' exposure) indicated that metals from the first transition series were present in the
234 polymer. Transition metal ions are the most widely reported pro-degradant additives used. They are added into
235 the polymer matrix in order to weaken the carbon-carbon backbone and make it more degradable [26]. These
236 additives catalyse the decomposition of hydro peroxides into free radicals. The most used transition metals
237 include iron, cobalt and manganese. Iron accelerates photo-degradation while manganese and cobalt render the
238

239 plastic more sensitive to thermal degradation. These metal ions are generally introduced at trace levels in the
240 form of an organic complex [27]. In the present samples manganese (10 ppm) and iron (314 ppm) were detected.
241 Apart from transition metals also high levels of calcium were identified. The presence of calcium is related with
242 common fillers and additives, such as calcium carbonate and calcium stearate [27]. One of the commercially
243 available thermo-oxidative additive is the patented AddiFlex which works in synergy with CaCO₃. The presence
244 of CaCO₃ increases UV degradation by up to 66%, hence less additive is required. It has been claimed to be
245 biodegradable, forming water, carbon dioxide and biomass [28]. Titanium was detected at 240 ppm which is
246 usually found in a form of the titanium dioxide pigment and as catalytic residue from Ziegler–Natta catalysts
247 and pigmentation used for PE bags by various manufacturers [27]. According to the 94/62/EC regulation for
248 packaging materials, the sum of concentration levels of lead, cadmium, mercury and hexavalent chromium
249 present in packaging or packaging components shall not exceed 100 ppm by weight [29]. Furthermore,
250 chromium and lead are not to exceed 60 ppm [24]. From the regulated chemicals, only chromium was present
251 in the studied PE bag at a level of 7 ppm which is below the permissible limit, which means that it adheres to
252 the regulation. Table 1 also reveals the evolution of the samples exposed to accelerated weathering as a function
253 of exposure days. A decreasing trend was noticed with majority of the samples as a function of weathering time
254 (20 days). This shows that the UV irradiation took affect and triggered the degradation mechanism of the oxo-
255 biodegradable samples. Nonetheless, iron, potassium and calcium were evidently at slightly higher concentration
256 to the control samples post 20 days of weathering. This shows that iron was the prevailing transition metal used
257 in the oxo-prodegradant additive used on the commercial bags which was also increasing as a residue after the
258 carbon-carbon cleavage takes place due to biodegradation. This phenomenon was also previously observed by
259 other authors using similar analytical surface techniques [9] indicating filler residues post biodegradation (e.g.
260 calcium and potassium). Therefore, it can be stated that the plastic film has experienced the degradation
261 mechanism and based on the moderate losses of the metals; the mechanism was not drastically severe with
262 respect to 20 days of accelerated UV exposure. This accelerated weathering duration should also be noted to be
263 equivalent to over 1 year and three months in arid climatic conditions [9,15,17].

264 3.2. *Effect of weathering on thermal stability*

265 Polymer weathering leads to free radicals' formation, which are combined with oxygen to form peroxides and
266 hydroperoxide radicals. Additionally, alkanes, alkenes, ketones, aldehydes, alcohols, carboxylic acids, keto-
267 acids, linear-esters and lactones are formed, which decrease the polymer's molar mass and hydrophobicity,
268 leading to increased bioavailability for degradation. Abiotic degradation can be accelerated by the addition of
269 certain organic salts of transition metals which generate free radicals during redox reaction. These radicals
270 decompose previously generated hydroperoxide or generate hydrocarbon chains. Biodegradable plastics are a
271 source of carbon and energy for micro-organisms. The biodegradation under aerobic conditions can be best
272 described as per the following reaction [10]:



274 Where the carbon of the polymer is assimilated by microorganisms into biomass and then it is mineralized into
275 carbon dioxide and water. Reaction *a* is the core biodegradation one whilst reaction *b* is the mineralisation
276 pathway. UV accelerated weathering as per ASTM D 4329 was used on the plastic bag specimens to simulate
277 the exposure to the natural environment. After the accelerated weathering the thermal response and stability were
278 investigated. Weight loss (%), midset (T_{md}), inflection point (T_{if}) were recorded based on the thermogravimetric
279 analysis conducted and are presented in Table 2.

280 According to the TGA thermograms (presented in the Supplementary Materials File within Figures S3 to S9),
281 the materials exhibited single step weight loss. Table 2 presents the onset temperature (T_{md}), midset temperature
282 (T_{md}) (which is the temperature on the thermogram where 50% of weight loss occurs), inflection point (T_{if}), final
283 maximum temperature (T_{f}), and weight loss before and after accelerated weathering. The midset temperature
284 also decreased with weathering duration by some 10°C. The decrease in the degradation temperature indicates a
285 lower thermal stability of these materials [15]. The shift in the midset temperatures also points towards the fact
286 that samples exposed to weathering by 20 days (480 continuous hours) are more brittle and have started to lose
287 their amorphous region within the PE matrix which is a semi-crystalline polymer. A similar observation was
288 also made previously by other authors [24]. Although the thermal decomposition of un-weathered (control)
289 samples occurs with almost little residue remaining (≈ 19 wt%), the amount of residue is higher for samples that
290 have undergone weathering. As can be seen from the table, the pre-exposure weight loss was 80% but after 20
291 days of accelerated weathering this value decreased to 38%. This suggests that the origin of the residue of these
292 samples is mainly the additive, which may not completely decompose in the temperature range of these
293 experiments due to its inorganic components [30]. It also indicates that samples are more brittle with weathering
294 making them more susceptible to thermal degradation under thermogravimetry. This also confirms that the
295 samples have underwent the desired UV triggered degradation mechanism due to prodegradants presence.

296 The degree of crystallinity was estimated using differential scanning calorimetry (DSC) by dividing the melting
297 enthalpy over the melting enthalpy of a 100% crystalline PE (293.6 g J^{-1}) for both the first and second heating
298 cycle, respectively [20]. The values obtained are presented in the Table 3, and the thermograms are presented in
299 Figures S10 to S14. As it can be seen from the table with the accelerated weathering duration the crystallinity
300 decreases from 82% to 35% as calculated from the 2nd heating cycle. Guadagno et al. [31] has observed an
301 increase in crystallinity for LLDPE from 37.9% to 53.8% over 300 hours. The chain scission due to the photo-
302 oxidation makes the amorphous chains more mobile and free to crystallise further, and this happens mainly when
303 the degradation occurs simultaneously in many chains. Corti et al. [32] observed the increase in crystallinity was
304 observed after both the first and the second heating, but the increase was much more pronounced after the first
305 heating. Ojeda et al. [27] has also observed that the reduction in molar mass was followed by an increase in
306 crystallinity due to the higher freedom of motion of smaller polymer chains, which could be rearranged in more

307 crystalline structures while mechanical properties fell to zero in about 3 to 4 months of sun exposure. The pre-
308 exposed PE sample showed a melting endothermic peak at 105°C (as shown in DSC graphs in the [Supplementary](#)
309 [Material File](#)). The melting peak indicates the melting point (T_m) of the polymer and with exposure to weathering
310 it showed a slight decrease from 105 to 102°C. Overall, the thermal properties and stability of the plastic films
311 showed a high resistance to thermal degradation. This also indicates that the film samples are stable due to the
312 presence of the additive within the polymer matrix. The incremental decrease in the tested specimens ([Table 3](#))
313 shows that the samples are losing the crystalline region of the polymeric matrix but without a clear effect on the
314 thermal stability.

315 *3.3. Mechanical properties*

316 To determine their integrity and durability, the studied materials were exposed to weathering conditions and the
317 mechanical properties were assessed before and after weathering. The mechanical profile of the samples
318 conforms with commercial plastic film specifications, in terms of tensile pull properties [9]. This shows that the
319 composition of the PE with the additives presents is suitable to be marketed as a crier bag for consumer demand.
320 [Figure 2](#) shows the Young's modulus and ultimate strain measured for the studied samples with respect to the
321 different weathering times. By comparative assessment, the sample that was not exposed to weathering had the
322 lowest Young's modulus compared to samples exposed to weathering. This shows that the products'
323 deformability and elasticity decrease with exposure time [15]. The Young's modulus for the studied samples is
324 between 439 and 975 MPa, while the ultimate strain decreased from 618.75% to 13.89% over the 20 days
325 weathering exposure. The Young's modulus and strain at break values are depicted in [Table 4](#). Young's modulus
326 is related to lower crystalline content of materials [33] which indicates that samples in this work have started to
327 lose their structure with exposure time due to photo-degradation. Ojeda et al. [27] evaluated abiotic and biotic
328 degradation of plastic bags of high-density polyethylene (HDPE) and linear low-density polyethylene (LLDPE)
329 formulated with pro-oxidant additives. The studied materials were exposed to natural weathering and were
330 analysed with respect to changes in mechanical and structural properties. In the study, the strain at fracture of
331 the oxo-biodegradable PE decreased from 400% to 60% over the duration of 80-day natural weathering exposure.
332 While the stress at fracture decreased from 52 MPa to 16 MPa over the 20 days weathering period. Based on the
333 mechanical properties studies, it can be noted that the material conforms with typical HDPE commercial grade
334 resins used in formulating oxo-biodegradable PE bags [9,24], and that there is a clear loss of plastic integrity as
335 a function of weathering duration which is in direct relation to the biodegradation mechanism the samples were
336 subjected to.

337

338 *3.4 Physical properties with respect to UV degradation*

339 The haze and light transmission (%) were measured to determine the loss of properties after exposure to
340 weathering. Haze (%) is one of the main physical properties that indicate polymer degradation. As the plastic is
341 being degraded, its surface roughness increases hence increasing the haze. [Figure 3](#) shows estimated haze and

342 light transmission at different weathering durations. The sample that was not exposed to weathering showed a
343 haze of 89.62% and after 20 days of weathering this value decreased slightly to 88.65%. Table 5 shows the
344 estimated values of haze and light transmission at different weathering times. Increase in haze also indicates
345 sever cross-linking in the polymeric matrix. This was previously observed in past studies. Al-Salem et al. [9,34]
346 studied the abiotic and biotic degradation of pro-oxidant filled PE films, haze increased with respect to soil burial
347 time where an increase of 63% was estimated by the twelfth month of field testing. While the inverse effect was
348 noticed with light transmission as it decreased due to less light being scattered in samples that suffered loss of
349 amorphous regions. The light transmission in this study did not change significantly, it showed an increase from
350 67.67% to 70.68%.

351 Standard colour parameters for light/dark (L^*), red/green (a^*), and yellow/blue (b^*) post degradation were
352 measured according to ASTM D 2244-11 to calculate the total change in colour (ΔE) between the control samples
353 and samples exposed to weathering. Al-Salem et al. [9] reported the degradation of pro-oxidant filled PE films
354 and the total change in colour was assessed for white plastic bags of PE origin containing pro-oxidant filler. The
355 total change in colour for the material studied after 19 days of UV exposure was 23, while in this study the total
356 change in colour (ΔE) increased from 0.75 to 1.05 after 5 days and 20 days of weathering respectively. The
357 values for different weathering durations are presented in Table 6. This indicates that a bleaching effect started
358 to take place to a minimal degree in this work.

359 *3.5. Micro-graph analysis and EDS elemental analysis*

360 One of the methods to evaluate extent of biodegradation is to evaluate the micrographs produced with SEM.
361 SEM was conducted to determine the extent of degradation and investigate micro-cracks on the surface of test
362 specimens before and after exposure to accelerated weathering. Figure 4 depicts the micrographs obtained from
363 the microscopic evaluation of the tested materials. A presence of the CaCO_3 filler and inorganic additives can
364 be observed in the form of disunity zones in the matrix. After 15 days of exposure dark spots were noticed on
365 the sample, that could possibly be a biofilm formation on the surface. After 20 days of weathering exposure
366 some micro cavities can be noticed. Ojeda et al. [27] exposed oxo-biodegradable films to open environments
367 and noted biofilm formation on the surfaces of the materials tested. A similar observation was noticed by both
368 Bonhomme et al. [35]. The EDS analysis of the control samples and accelerated weathering ones are shown in
369 Figure 5. The samples' surfaces showed the presence of the inorganic ion of elemental calcium. A similar
370 observation was previously made by other researchers in the field [14,27]. As indicated previously by XRF
371 analysis, the tested samples contained calcium, which can likely be attributed to inorganic filler in the form of
372 CaCO_3 . The metal elements were also observed to start diminishing and were not easily detected on the surface
373 by the EDS. This is in direct relation to the biodegradation phenomena taking place due to the oxo-prodegradant
374 taking affect and transition metals being less prominent in the analysis. This was previously observed by Al-
375 Salem et al. [9] on oxo-biodegradable films.

376 **4. Environmental Implications of Plastic Solid Waste Accumulation**

377 Plastics accumulate in the environment at a rate of 25 million metric tons per annum. PE represents 64% of
378 plastic materials produced as packaging and bottles, which are usually discarded after single use [36]. The major
379 problem is that large portion of plastics produced is used to make disposable packaging items or other short-
380 lived products that are permanently discarded within a year of manufacture [37]. Single use plastic bags are one
381 of the packaging materials that accumulate in the environment due to low biodegradability. Their accumulation
382 generates plastic pollution and takes up landfill space. Plastic pollution is a recognised international problem
383 that is associated with environmental and health concerns. The 80% of the waste that accumulates on the
384 shorelines, the ocean surface and seabed is plastic [38]. Plastic bags have small mass and are usually
385 contaminated rendering their recycling economically not feasible [39]. Replacing plastic bags with
386 biodegradable materials could help solve the plastic pollution problem.

387 Due to plastic's resilience against degradation and its increased use and production in industry, the issue of
388 plastic pollution has become a risk to global ecology. Plastic pollution arises from both terrestrial and marine
389 sources. There is a continuous stream of pollutant plastic via: inappropriate dumping of domestic and industrial
390 refuse and unintentional dumping through poorly contained and transported waste. Plastic accumulation in the
391 marine environment poses a large threat to wildlife, the main dangers are associated with it are entanglement
392 and ingestion of pollutants. Conventional plastics do not naturally degrade when released to the environment.
393 This is not unexpected, as the main reasons for the widespread use of many polymers is their high stability and
394 durability [40]. One of the attractive alternatives of dealing with accumulation problems is its degradation.
395 Various polymer absorbs UV and undergo photolytic, photo-oxidative, and thermo-oxidative reactions that result
396 in their degradation however depending on the application, product needs controlled stability as for example
397 packaging products need durability instead of degradation. To increase the resistance and durability, the plastic
398 products are produced so to increase their resistance to UV and thermal exposure Synthetic polymers are stable
399 and are commonly used in packaging, food industry and etc. However, their stability is counterbalanced by
400 polymers contributing to the demand for oil and resistance to biodegradation that leads to accumulation in the
401 environment. The alternative to synthetic polymers are biodegradable polymers such as starch-based blends but
402 their cost is higher and there is a lack of waste management infrastructure for such wastes. Further research is
403 required to make the biodegradable polymers cost effective [41].

404 One production method of biodegradable plastics is to produce them based on conventional plastics with
405 enhanced degradability, without compromising the material properties. Polymers with additional functional
406 groups have been produced. The motivation behind this is to make material more susceptible to attack from
407 microbial enzymes. However, biodegradation of such polymers is still relatively limited. There is still a
408 requirement for substantial energy input in order for the degradation to initiate and it is uncertain whether these
409 polymers are biodegraded or whether they disintegrate into smaller pieces [41]. There are limited scientific
410 studies on oxo-biodegradable polymers and their degradability. They have to be validated as more environmental

411 alternatives to conventional plastics. Based on these needs, this study aimed to assess the degradation of
412 commercial PE bags claiming to be oxo-biodegradable. The findings of the study presented herein also indicate
413 that the film samples have started to decompose and deteriorate with time equivalent to over one year in natural
414 weathering [9]. However, judging by the fact that the samples were still showing mechanical integrity post 20
415 days of exposure, and did not appear to be deteriorated to a powdery or residue like form even after accelerated
416 weathering, it could be well stated that the materials formulation can't perform as a waste accumulation or
417 mitigation material. On the other hand, the samples were also within standards for metal content and could be
418 classed as a safe plastic product based on eth European standards we have depicted. Nonetheless, further leaching
419 tests mimicking samples deterioration in the environment and possible metal contamination is also a must. This
420 also puts an argument based on eth oxo-biodegradable plastic characterised here, that hydro-biodegradable
421 materials could be more effective due to having a more soluble material (e.g. starch) within the polymer matrix
422 itself. The readers are also referred to our review annexed in [Appendix A](#) for a comparative assessment to recent
423 cases with starch based polymers response in open environments.

424 **5. Conclusion**

425 The main objective of the work was to investigate the response of an oxo-biodegradable plastic product to photo
426 degradation using accelerated weathering testing. The test specimens were white to transparent commercial
427 grade plastic bags claimed to be of oxo-biodegradable nature. To determine the exact polymer and additive
428 content, ATR analysis was conducted on the specimens. Several prominent peaks were identified around 1470
429 cm^{-1} which is a distinctive PE band. The material was classified to be PE as claimed by the manufacturer. In
430 order to detect inclusion of metal additives the XRF analysis was used and metals from the first transition series
431 were identified. From the regulated chemicals according to 94/62/EC, only chromium was present in the studied
432 PE bag at a level of 7 ppm, which means that it adheres to the regulation. UVA accelerated weathering as per
433 ASTM D 4329 was used on the plastic bag specimens to simulate the exposure to natural environment. After the
434 accelerated weathering the thermal response and stability were investigated. According to the TGA thermograms
435 the materials exhibited single step weight loss and the decrease in the degradation temperature in respect with
436 weathering was identified that indicated a lower thermal stability of these materials. The thermal decomposition
437 of un-weathered samples occurred with little residue remaining (19 wt%), the amount of residue was higher for
438 samples that have undergone weathering. This suggests that the origin of the residue of these samples is mainly
439 the additive, which may not completely decompose in the temperature range of these experiments due to its
440 inorganic components. To determine the integrity and durability of the studied material the mechanical properties
441 were assessed before and after weathering. By comparative assessment the sample that was not exposed to
442 weathering had the lowest Young's modulus. This shows that the products deformability and elasticity decreased
443 with exposure time. The young's modulus for studied samples was between 439 and 975 MPa while the ultimate
444 strain decreased from 618.75% to 13.89% over the 20 days weathering. The haze and light transmission (%)
445 were measured to determine the loss of properties after exposure to weathering. The control sample showed the

446 haze of 89.62% and after 20 days of weathering this value decreased slightly to 88.65%. The light transmission
447 in this study did not change significantly, it showed an increase from 67.67% to 70.68% while the total change
448 in colour (ΔE) increased from 0.75 to 1.05 after 5 days and 20 days of weathering respectively. SEM was
449 conducted to determine the extent of degradation and investigate micro-cracks on the surface of test specimens
450 before and after exposure to accelerated weathering. After 20 days of weathering exposure some micro cavities
451 could be noticed. The current study showed that the commercial PE bag claiming to be oxo-biodegradable started
452 to show signs of degradation after accelerated weathering. However, biodegradation of such polymers is still
453 relatively limited. There is still a requirement for substantial energy input in order for the degradation to initiate
454 and it is uncertain whether these polymers are biodegraded or whether they disintegrate into smaller pieces.
455 There are limited scientific studies on oxo-biodegradable polymers and their degradability. They still have to be
456 validated as more environmental alternatives to conventional plastics. Based on these needs, this study aimed to
457 assess the degradation of commercial oxo-biodegradable PE bags.

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461 **Conflict of Interest**

462 The authors declare that the work presented in this study does not represent a conflict of interest in any shape or
463 form.

464 **Author Contribution Statement**

465 Ana Antelava, Data Analysis and Original Draft Preparation; Achilleas Constantinou, Draft Review; Ali
466 Bumajdad; Draft Review, George Manos; Draft Review, Raf Dewil; Draft Review, Sultan Al-Salem;
467 Conceptualization, Data Analysis and Draft Review.

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