1   **Identification of Commercial Oxo-Biodegradable Plastics: Study of UV Induced Degradation in an Effort**

2   **to Combat Plastic Waste Accumulation**

3   Ana Antelava[1#], Achilleas Constantinou[1,2#], Ali Bumajdad[3], George Manos[2], Raf Dewil[4], S.M. Al-Salem[5*]

4   [1]Division of Chemical & Petroleum Engineering, School of Engineering, London South Bank University,

5   London SE1 0AA, UK.

6   [2]Department of Chemical Engineering, University College London, London WCIE 7JE, UK.

7   [3]Chemistry Department, Faculty of Science, Kuwait University, P.O. Box 5969, Safat 13060, Kuwait.

8   [4]Department of Chemical Engineering, KU Leuven, Jan De Nayerlaan 5, 2860, Sint-Katelijne-Waver, Belgium.

9   [5]Environment & Life Sciences Research Centre, Kuwait Institute for Scientific Research, P.O. Box: 24885, Safat

10   13109, Kuwait.

11   #These names share first authorship of the article.

12   *Correspondence to be addressed to: Dr. Sultan Al-Salem (ssalem@kisr.edu.kw)*

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 is 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**

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

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

Biodegradable plastics are subdivided in two categories depending on the manufacturing process and degradation mechanism. The first type are hydro-biodegradable plastics which are mainly produced from renewable raw materials such as starch, but could still contain up to 50% of plastics derived from crude oil or aliphatic polyesters [8]. The second type of biodegradable polymers are oxo-biodegradables, which are based on petrochemical naphtha blends mixed with pro-oxidant additives. The latter have become popular nowadays for packaging and film applications [9]. Their degradation can be initiated by different factors such as UV light, moisture, heat and microorganisms in processes classified as photo-oxidative degradation, thermal degradation 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 (CO_2) 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. Acquirement 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 florescence (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°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±0.1 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 μL size. Weight loss (%) and first

148 derivative (DTG, % °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±0.1 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°C min^{-1}. Cooling rate was set at 15°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     $\Delta E = \sqrt{\left((\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2\right)}$ (3)

210   Where Δ*L,* Δ*a* and Δ*b* are the values of the difference between the control specimen measurements (control

211   samples with no exposure) and those of each tested batch.

212
213   **3. Results and discussion**

214   *3.1. Identification of plastic material*

215   The test specimens in this work were white to transparent commercial grade plastic bags claimed to be of oxo-

216   biodegradable nature. To determine the exact polymer and additive content, ATR analysis was conducted on the

217   specimens. ATR is a technique used for detecting the absorption in the range of mid-infrared region and was

218   used to detect distinctive adsorption peaks of the plastic films studied. Several prominent peaks were identified.

219   Figure 1 shows spectra obtained for control (pre-weathered) specimen. The prominent peaks identified in the

220   range between 700 to 760 cm^{-1} corresponds to the rocking vibration associated to the crystallinity of the polymer.

221   The peak between 1460-1480 cm^{-1} relates to CH$_2$ bending vibration, while the band between 2850-2950 cm^{-1}

222   associated with the asymmetric and symmetric CH stretching [16]. The major peak was around 1470 cm^{-1} which

223   is a distinctive PE band [21]. The overall spectra of the sample and the aforementioned bands are also associated

224   with oxo-biodegradable PE spectra as confirmed by previous authors [22-23]. Oxo-prodegradant additive peaks

225   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

226   with calcium carbonate (CaCO$_3$) additive for PE commercial grades [14,24]. Küpper et al. [25] analysed PE

227   sample's ATR-spectrum, and in addition to the main 1470 cm^{-1} PE band, bands in the interval between 3400 and

228   3200 cm^{-1} and around 1600 cm^{-1} were also observed assigned to UV-stabilisers of the hindered amine stabiliser

229   (HAS)-type. In the studied oxo-biodegradable PE sample, none of these bands were observed. The sample

230   studied in this work is classified to be of PE origin as claimed by the manufacturer, and was confirmed to be so

231   based on the peaks detected.

232   In order to detect possible inclusion of typical oxo-biodegradable additives, the test samples were subjected to

233   XRF analysis in emission mode for possible metal and additives detection (Table 1). Analysis of the control PE

234   bags specimens (0 days' exposure) indicated that metals from the first transition series were present in the

235   polymer. Transition metal ions are the most widely reported pro-degradant additives used. They are added into

236   the polymer matrix in order to weaken the carbon–carbon backbone and make it more degradable [26]. These

237   additives catalyse the decomposition of hydro peroxides into free radicals. The most used transition metals

238   include iron, cobalt and manganese. Iron accelerates photo-degradation while manganese and cobalt render the

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 $CaCO_3$. The presence
244 of $CaCO_3$ 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]:

$$273 \quad C_{Polymer} \; O_2 \xrightarrow{\quad a \quad} C_{biomass} \xrightarrow{\quad b \quad} CO_2 + H_2O \qquad\qquad (1)$$
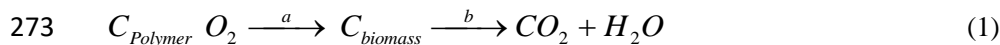
274 Where the carbon of the polymer is assimilated by microorganisms into biomass and then it is mineralized into

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-prodegredant
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.

4. Environmental Implications of Plastic Solid Waste Accumulation

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

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

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

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.

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.

468   **References**

469   1. Plastics Europe (2018). Plastics-The Facts 2017, Belgium.

470   2. UNEP (2018). Single-Use Plastics: A Roadmap for Sustainability; UN Environment Programme.

471   3. Napper I, Thompson R (2019). Environmental Deterioration of Biodegradable, Oxo-biodegradable,

472   Compostable, and Conventional Plastic Carrier Bags in the Sea, Soil, and Open-Air Over a 3-Year

473   Period. Environ Sci Tech 53: 4775-4783.

474   4. Dumas D (2007). Landfill-on-sea, Ecologist, 37: 34-37.

475   5. Clapp J, Swanston L (2009). Doing away with plastic shopping bags: international patterns of norm

476   emergence and policy implementation. Environm Politic 18: 315-332.

477   6. Brems A, Baeyens J, Dewil R (2012). Recycling and recovery of post-consumer plastic waste in a European

478   context. Therm Sci 16: 669-685.

479   7. Siotto M, Sezenna E, Saponaro S, Innocenti F, Tosin M, Bonomo L, Mezzanotte V (2012). Kinetics of
480   monomer biodegradation in soil. J Environ Mange 93: 31-37.

481   8. Oxo-biodegradable plastics association, Types of degradable plastic (2008). Available at:
482   www.biodeg.org/Types%20of% 20Degradable%20Plastic%20(2).pdf

483   9. Al-Salem S, Al-Hazza'a A, Karam H, Al-Wadi M, Al-Dhafeeri A, Al-Rowaih A (2019). Insights into the
484   evaluation of the abiotic and biotic degradation rate of commercial pro-oxidant filled polyethylene (PE) thin
485   films. J Environ Mange 250: 109475.

486   10.Chinaglia S, Tosin M, Degli-Innocenti F (2018). Biodegradation rate of biodegradable plastics at molecular
487   level. Polym Degrad Stab 147: 237-244.

488   11. Anstey A, Muniyasamy S, Reddy M, Misra M, Mohanty A (2014). Processability and Biodegradability
489   Evaluation of Composites from Poly(butylene succinate) (PBS) Bioplastic and Biofuel Co-products from
490   Ontario. J Polym Environ 22: 209-218.

491   12. Burgos N, Valdés A, Jiménez A (2016). Valorization of Agricultural Wastes for the Production of Protein-
492   Based Biopolymers. J Renewable Mater 4: 165-177.

493   13. Harrison J, Boardman C, O'Callaghan K, Delort A, Song J (2018). Biodegradability standards for carrier
494   bags and plastic films in aquatic environments: a critical review. Royal Society Open Science 5: 171792.

495   14. Nazareth M, Marques RC, Leite MCA, Castro IB (2019) Commercial plastics claiming biodegradable status:
496   Is this also accurate for marine environments? J Hazard Mater 366: 714-722.

497   15. Al-Salem SM (2009). Influence of natural and accelerated weathering on various formulations of linear low
498   density polyethylene (LLDPE) films, Mater Des 30, 1729-1736.

499   16. Al-Salem S.M. (2018). The first chemical identification of polyolefin (PO) waste blends using infrared
500   spectroscopy. Waste Management and the Environment IX.

501   17. Al-Salem SM, Abraham G, Al-Qabandi OA, Dashti AM (2015). Investigating the effect of accelerated
502   weathering on the mechanical and physical properties of high content plastic solid waste (PSW) blends with
503   virgin linear low density polyethylene (LLDPE), Polym Test 46: 116-121.

504   18.Vyazovkin S, Burnham AK, Criado JM, Pérez-Maqueda LA, Popescu C, Sbirrazzuoli N (2011). Thermochim
505   Acta 520: 1-19.

506   19.Vyazovkin S, Chrissafis K, Di Lorenzo ML, Koga N, Pijolat M, Roduit B, Sbirrazzuoli N, Suñol JJ (2014).
507   Thermochim Acta 590: 1-23.

508   20.Ojeda T, Freitas A, Birck K, Dalmolin E, Jacques R, Bento F, Camargo F (2011). Degradability of linear
509   polyolefins under natural weathering. Polym Degrad Stab 96: 703-707.

510   21. D'Amelia RP, Gentile S, Nirode WF, Huang L (2016) Quantitative analysis of copolymers and blends of
511   polyvinyl acetate (PVAc) using Fourier transform infrared spectroscopy (FTIR) and elemental analysis (EA).
512   World J Chem Educ 4: 25-31.

22. Abed RMM, Al Khaburi TMM, Al-Senafi F, Munam A, Mahmoud H (2020) Degradability and biofouling of oxo-biodegradable polyethylene in the planktonic and benthic zones of the Arabian Gulf. Marine Pollution Bulletin 150: 110639.

23. Nikolić MAL, Gauthier E, Colwell JM, Halley P, Bottle SE, Laycock B (2017) Rowan Truss. The challenges in lifetime prediction of oxodegradable polyolefin and biodegradable polymer films. Polym Degrad Stab 145: 102-119.

24. Al-Salem SM, Al-Nasser AY, Behbehani MH, Sultan HH, Karam HJ, Al-Wadi MH, Al-Dhafeeri AT, Rasheed Z, Al-Foudaree M (2019) Thermal Response and Degressive Reaction Study of Oxo-Biodegradable Plastic Products Exposed to Various Degradation Media. International Journal of Polymer Science, Article ID 9612813. https://doi.org/10.1155/2019/9612813.

25. Küpper L, Gulmine J, Janissek P, Heise H (2004). Attenuated total reflection infrared spectroscopy for micro-domain analysis of polyethylene samples after accelerated ageing within weathering chambers. Vibrational Spectroscopy, 34(1), 63-72.

26. Davis G (2006). The characterisation of two different degradable polyethylene (PE) sacks. Materials Characterization,57: 314-320.

27. Ojeda T, Dalmolin E, Forte M, Jacques R, Bento F, Camargo F (2009). Abiotic and biotic degradation of oxo-biodegradable polyethylenes. Polym Degrad Stab 94: 965-970.

28. Ammala, A., Bateman, S., Dean, K., Petinakis, E., Sangwan, P., Wong, S., Yuan, Q., Yu, L., Patrick, C. and Leong, K. (2011). An overview of degradable and biodegradable polyolefins. Progress in Polymer Science, 36(8), 1015-1049.

29. European Parliament and Council Directive 94/62/EC (1994) on packaging and packaging waste

30. Contat-Rodrigo L (2013). Thermal characterization of the oxo-degradation of polypropylene containing a pro-oxidant/pro-degradant additive. Polym Degrad Stab, 98: 2117-2124.

31. Guadagno L, Naddeo C, Vittoria V, Camino G, Cagnani C (2001). Chemical and morphological modifications of irradiated linear low density polyethylene (LLDPE). Polym Degrad Stab, 72: 175-186.

32. Corti A, Muniyasamy S, Vitali M, Imam S, Chiellini E (2010). Oxidation and biodegradation of polyethylene films containing pro-oxidant additives: Synergistic effects of sunlight exposure, thermal aging and fungal biodegradation. Polym Degrad Stab, 95: 1106-1114.

33. Mendes LC, Rufino ES, de Paula FOC, Torres AC (2003). Mechanical, thermal and microstructure evaluation of HDPE after weathering in Rio de Janerio city, Polym Degrad Stab, 79: 371-383.

34. Al-Salem, S., Sultan, H., Karam, H. and Al-Dhafeeri, A. (2019). Determination of biodegradation rate of commercial oxo-biodegradable polyethylene film products using ASTM D 5988. J polym Research 26(7).

35. Bonhomme S, Cuer A, Delort A, Lemaire J, Sancelme M, Scott G (2003). Environmental biodegradation of polyethylene. Polym Degrad Stab, 81: 441-452.

36. Sudhakar M, Doble M, Murthy PS, Venkatesan R. (2008). Marine microbe-mediatedbiodegradation of low- and high-density polyethylenes. Int Biodeterior Biodegradation, 61: 203-213

549   37. Hopewell J, Dvorak R, Kosior E (2009). Plastics Recycling: Challenges and Opportunities. Philos. Trans. R.

550   Soc. B 364: 2115−2126.

551   38.Barnes DKA., Galgani F, Thompson RC, Barlaz M (2009). Accumulation and fragmentation of plastic debris

552   in global environments. Philos. Trans. R. Soc. B 364: 1985-1998

553   39. Scott G (2000) Green polymers. Polym Degrad Stab, 68: 1-7.

554   40. Webb H, Arnott J, Crawford R, Ivanova E (2012). Plastic Degradation and Its Environmental Implications

555   with Special Reference to Poly(ethylene terephthalate). Polymers 5: 1-18.

556   41. Singh B. Sharma N (2008). Mechanistic implications of plastic degradation. Polym Degrad Stab, 93: 561-

557   584.