

1 **Accelerated hydrolysis method for producing partially degraded**
2 **polyester microplastic fiber reference materials**

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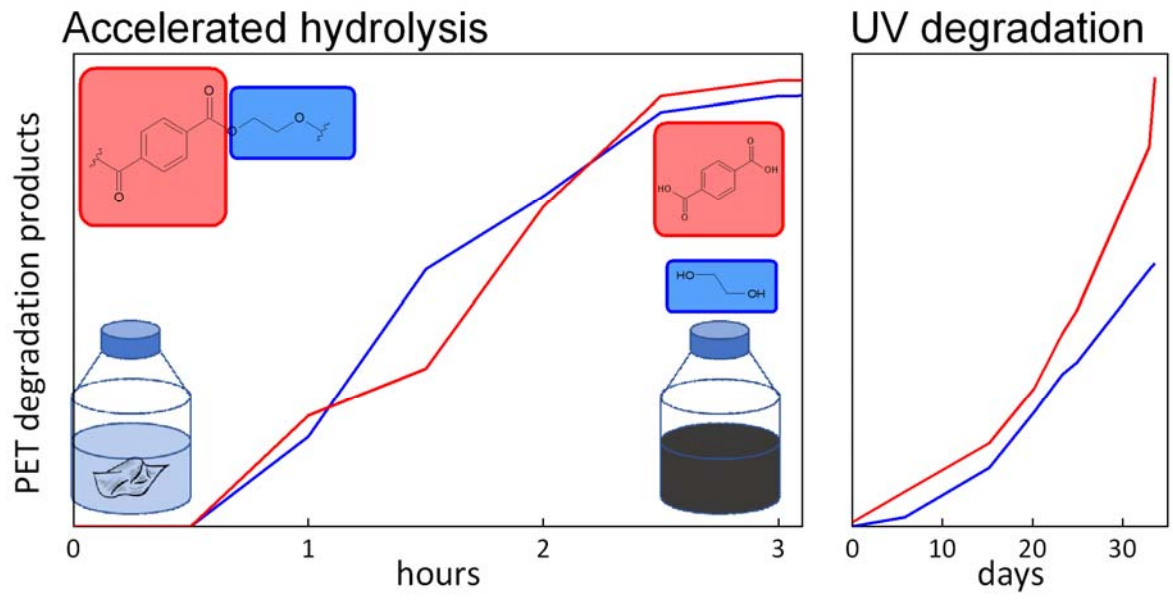
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13



16 ABSTRACT

17 Microplastic fibers (MPFs) from textiles contribute significantly to the microplastic (MP) load
18 in many environmental matrices and have been shown to negatively impact the organisms
19 therein. Most fate and effect studies to date rely on pristine reference MP materials that have
20 limited relevance compared to the partially degraded MP particles and fibers typically present
21 in the natural environment. The current study aimed to develop and validate a rapid method to
22 generate environmentally relevant polyester (PET) MPF reference material with controllable
23 levels of degradation. Importantly, the method produced the same degradation products
24 (terephthalic acid (TA) and ethylene glycol (EG)) as those generated during natural UV
25 (sunlight) exposure of PET. Alkaline hydrolysis provided linearly increasing degrees of
26 degraded PET MPFs over just a few hours, with full decomposition into molecular fragments
27 occurring after 3 hours. The extent of physical degradation was determined by scanning electron
28 microscopy, while chemical degradation was quantified by measuring the production of TA and
29 EG degradation products. The proposed accelerated hydrolysis degradation method is relevant
30 for producing partially degraded PET MPF reference materials for use in fate and effect studies.

31

32 KEYWORDS: microfibers, UV degradation, degradation products, ethylene glycol,
33 terephthalic acid, LC-MS

34

35 INTRODUCTION

36 Microplastic fibers (MPFs) derived from synthetic textiles and other sources represent a
37 significant proportion of the microplastic (MP) load in many environmental matrices¹⁻³ and
38 have been shown to have negative impacts on aquatic organisms^{4,5}. However, the majority of
39 studies investigating the fate and effects of MP particles have employed commercially available
40 pristine spherical reference materials, limiting the relevance of the data produced^{6,7}. As a result,
41 some recent studies have explored ways to produce more environmentally relevant MP
42 reference materials^{1-3,8}. For example, marine litter can be cryomilled to produce irregular
43 shaped fragments with complex surface morphologies and chemistries⁸. As cryomilling of
44 MPFs results in a loss of the fiber shape, techniques such as manual cutting (fibers >1 mm) or
45 microtome (fibers <1 mm) are necessary⁹. However, this still produces reference materials that
46 do not reflect the partially degraded nature of MPs and MPFs in the natural environment. This
47 is important when trying to assess the risks associated with MP pollution, as degradation
48 processes alter both the physical and chemical properties of plastic materials and may influence
49 their environment fate and potential bioavailability and effects on organisms.

50
51 UV-induced oxidation (photodegradation) is the most effective degradation mechanism for
52 many plastic materials released into the natural environment^{10,11}, resulting in the formation of
53 hydroxy, carbonyl, and carboxy groups on the particle surface, as well as cracking and
54 fragmentation¹¹⁻¹⁵. These physicochemical changes are important when trying to assess the risks
55 associated with MP pollution, as they may influence MPF environment fate, bioavailability and
56 effects on organisms^{6,16-18}. However, photodegradation of polymers is still very slow under
57 typical environmental conditions^{10,19-21}. Accelerated degradation using artificial UV exposures
58 in the laboratory, which is a widely accepted approach, can thus take weeks to months for
59 significant degradation to occur, is costly to operate and is not necessarily able to reproduce

60 natural UV degradation process accurately¹⁹. There is, therefore, a need for accelerated
61 degradation methods that allow rapid and controlled simulation of environmental degradation
62 mechanisms for the production of partially degraded MP and MPF reference materials^{6, 22}.
63 These need to be quick, cost effective, reproducible, and with an acceptable degree of
64 environmental relevance in terms of the degradation process and degradation products.

65
66 In this study, we demonstrate a fast and cheap hydrolytic degradation method for producing
67 environmentally relevant, partially degraded polyester (PET) MPFs reference materials for use
68 in fate and effects studies. Temperature and pH were systematically varied to identify conditions
69 resulting in near complete degradation of the polyester MPFs within 3 hours. The degree of
70 degradation was quantitatively determined by measuring the PET degradation products
71 terephthalic acid (TA) and ethylene glycol (EG), allowing specific levels of degradation to be
72 achieved. Scanning electron microscopy (SEM) imaging was used to visualize the degree of
73 physical modification resulting from degradation process. Finally, the environmental relevance
74 of the accelerated hydrolysis method was verified by comparing the hydrolysed PET and
75 degradation products to PET MPFs exposed to UV irradiation in seawater.

76

77 MATERIALS AND METHODS

78 **Materials and chemicals**

79 PET fleece material used to produce consumer clothing products was supplied by a commercial
80 garment producer (Helly Hansen, Norway). All chemicals were purchased from Merck or
81 Sigma-Aldrich. MPFs were carefully removed from the textile using a scalpel and stored in
82 glass vials prior to use. Deionized water was of MilliPore® MilliQ quality. Natural seawater
83 was collected from 90 m depth in Trondheimsfjorden, Norway (63°26'N, 10°24'E), filtered to

84 remove coarse particles and subjected to sterile filtration (0.22 μm Sterivex®) prior to use in
85 the experiments (see SI for more details).

86

87 **Accelerated hydrolytic degradation method development**

88 Two pre-studies investigated the influence of temperature (60-90 °C) and pH (1-14) on the
89 hydrolysis process. Hydrolysis of the PET MPFs was determined gravimetrically in the pre-
90 studies and the method is described in the Supplementary Information (SI). For all exposures,
91 200 mg of PET MPFs were introduced in glass bottles containing 25 mL aqueous solution of
92 NaOH (10 % NaOH; pH 14.4) and hydrolysis was conducted at 90 °C using an oil bath. Samples
93 were collected and subjected to analysis after 0, 0.5, 1, 1.5, 2, 2.5, 3, 6 and 24 h. A full overview
94 of the experimental matrix is presented in Table S1. Upon sampling, the hydrolysis reaction
95 was quenched by transferring the bottles immediately to an ice water bath, as studies showed
96 the reaction rate is significantly reduced at low temperatures (Figure S1). To isolate the fibers
97 for SEM imaging, the samples were filtered using a paper filter with pore size 20-25 μm
98 (Whatman). After the filtration, the fiber samples were left on the filter, rinsed with deionized
99 water, and dried overnight at 80 °C. Samples were stored at -20 °C until analysis.

100

101 **UV degradation validation**

102 UV degradation of PET fibers was performed using a Suntest CPS+ (Atlas Material Testing
103 Solutions) equipped with a xenon UV lamp (1500 W) and fitted with a natural daylight filter.
104 PET fibers were mixed into MilliQ or seawater at a concentration of 8 mg mL⁻¹ and placed into
105 35 mL quartz tubes with glass stoppers. Irradiation was conducted at 65 W/m² and the
106 temperature in the exposure chamber was maintained at 24 \pm 3 °C. Sampling was performed
107 ca. once per week for a period of 32 days and 250 μL aliquots were directly stored at -20 °C in
108 the dark. The 32-day exposure period corresponded to ~304 days (10 months) of UV exposure

109 based on mean European solar irradiance (details in SI). Prior to sampling, the quartz tubes
110 were shaken, after which 250 μ L was removed and filtered through a micropipette tip filter
111 prior to analysis for EG and TA degradation products.

112

113 **Determination of ethylene glycol and terephthalic acid by LC-UV-MS/MS**

114 For analysis, EG was derivatized with benzoyl chloride as previously described²³.
115 Derivatization was accomplished by adding 50 μ L sample, 100 μ L 4 M NaOH and 50 μ L
116 benzoyl chloride to 250 μ L with deionized water. The reaction was vortexed and incubated at
117 room temperature for 5 min. Next, the reaction was quenched by adding 50 μ L 10% glycine
118 and incubating for 3 min at room temperature. The dibenzoyl derivate was then extracted with
119 1 mL pentane. Phase separation was accomplished by centrifugation at 10 000 xg for 5 min,
120 and the organic phase was evaporated under nitrogen at 50 °C. The dried extract was dissolved
121 in 800 μ L 10 mM ammonium formate (pH 2.8) in 50% acetonitrile. Derivatized samples were
122 diluted 500-fold prior to analysis. TA was analyzed without derivatization by diluting samples
123 100-fold prior to analysis.

124

125 Samples were analyzed on an Agilent 1260 HPLC system equipped with a variable wavelength
126 detector coupled to a 4670 triple quadrupole mass spectrometer equipped with an electrospray
127 ion source (Agilent Technologies, Santa Clara, CA, USA). The HPLC column (ZORBAX
128 Eclipse Plus C18 2.1x50 mm, 1.7 μ m particle size, Agilent Technologies) was kept at 25 °C
129 and the injection volume was 10 μ L. The mobile phase consisted of 10 mM ammonium formate
130 pH 2.8 (A) and acetonitrile containing 0.1 % formic acid (B). The 7.5 min HPLC program for
131 EG was as follows: start at 10% B, ramp to 90% B by 3 min, hold until 3.5 min, and ramp to
132 10% B by 3.6 min. The EG derivate was detected by MS using the following mass transitions
133 in positive ionization mode: m/z 271.1 \rightarrow 149 (quantifier) and m/z 271 \rightarrow 105.1 (qualifier).

134 The 6.5 min HPLC program for TA was as follows: start at 10% B, ramp to 90% B by 2 min,
135 hold until 2.5 min, and ramp to 10% B by 2.6 min. TA was detected by UV absorption at 254
136 nm and peak identity was confirmed by MS using the following mass transition in negative
137 mode: m/z 165 \rightarrow 121.1.

138

139 **Scanning electron microscopy**

140 Prior to analysis, MPFs from both the accelerated hydrolysis studies and the UV exposure
141 studies were mounted on double sided tape and coated in a thin layer (5-10 nm) of evaporated
142 gold to make them conductive. MPF imaging was performed (1000x magnification) using a FEI
143 Nova Nano SEM 650 scanning electron microscope (SEM), operated in high vacuum mode at
144 accelerating voltages of 5 kV, with an emission current of 90 pA and at a working distance of
145 8 mm.

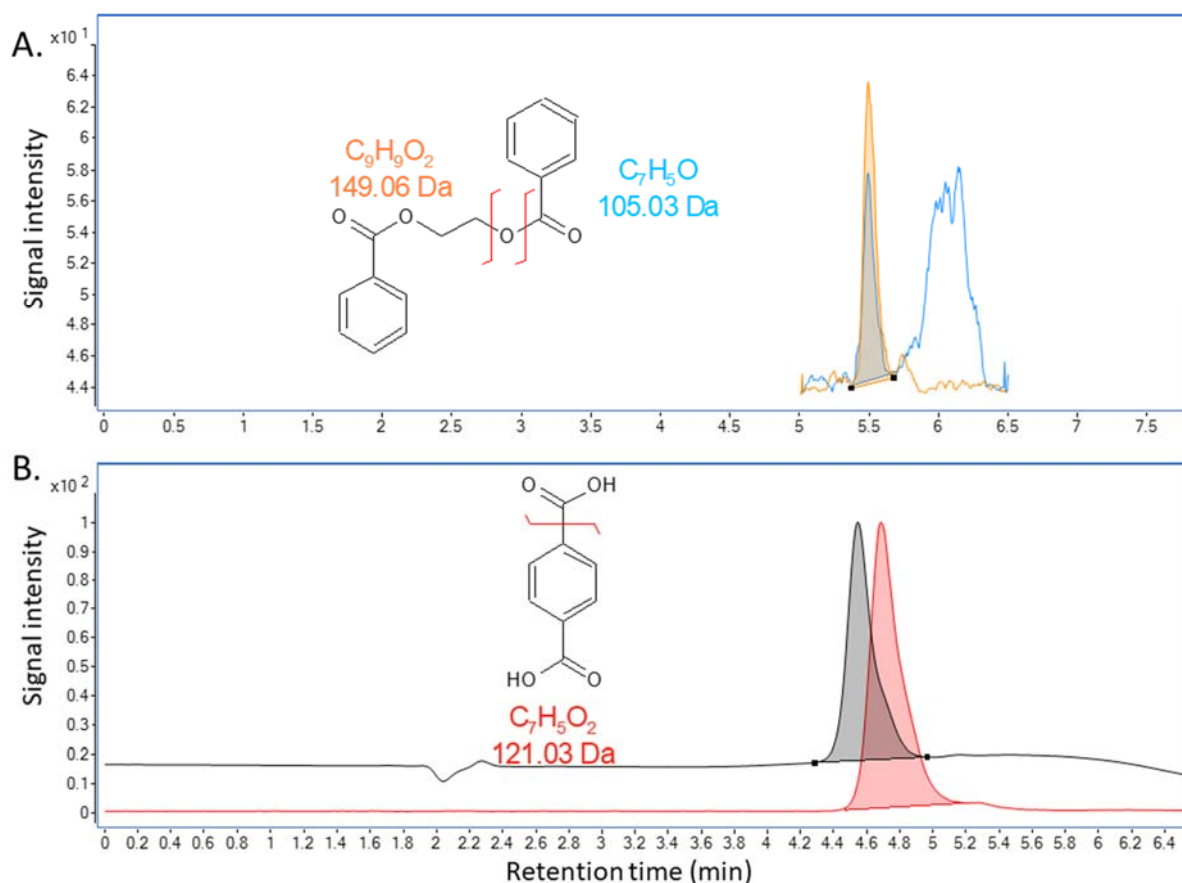
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147 **RESULTS AND DISCUSSION**

148 **TA and EG assay**

149 PET degradation by alkaline hydrolysis leads to the formation of its constitutive components
150 TA and EG (the latter in the form of disodium terephthalate salt)²⁴. Thus, we established
151 protocols to measure both by HPLC with a combination of UV and MS detection. EG detection
152 is potentiated by derivatization using benzoyl chloride (Schotten-Baumann reaction) and
153 extracted with pentane^{23,25}. Two mass transitions were used to detect and quantify EG, and the
154 quantification limit (LoQ) for the assay was 2.5 pg (corresponding to 0.5 ng mL⁻¹, Figure 1A).
155 UV detection was also achievable at 237 nm, but the sensitivity was three orders of magnitude
156 lower and an unidentified co-eluting peak hindered accurate quantification. TA could be
157 quantified directly (*i.e.* without extraction or derivatization) in the water phase. Our experiments
158 were performed in seawater or water containing a high (3.5%) NaCl concentration, neither of

159 which are amenable to electrospray mass spectrometry. We therefore used UV detection at 254
160 nm for TA quantification, using the MS to confirm the identity of the TA peak (Figure 1B). The
161 LoQ for TA detection with UV was 250 pg (corresponding to 50 ng mL⁻¹). More sensitive MS
162 detection can be used if samples are in MilliQ and/or desalted using *e.g.* solid phase extraction
163 columns. For both compounds, a stable-isotope-labelled internal standard can also be used to
164 enable absolute quantification using mass spectrometry, especially when working with low
165 concentrations.
166



167
168 **Figure 1:** Analysis of terephthalic acid and ethylene glycol derivative. A) LC-MS/MS
169 chromatogram of dibenzoyl derivate of EG and benzoyl chloride. The two peaks correspond to
170 mass transitions from the proposed cleavages of the same color shown in the chemical diagram.
171 B) LC-UV-MS/MS chromatogram of TA. The black and red chromatograms correspond to the
172 signals from the UV and MS/MS detectors, respectively, and proposed cleavage is shown.

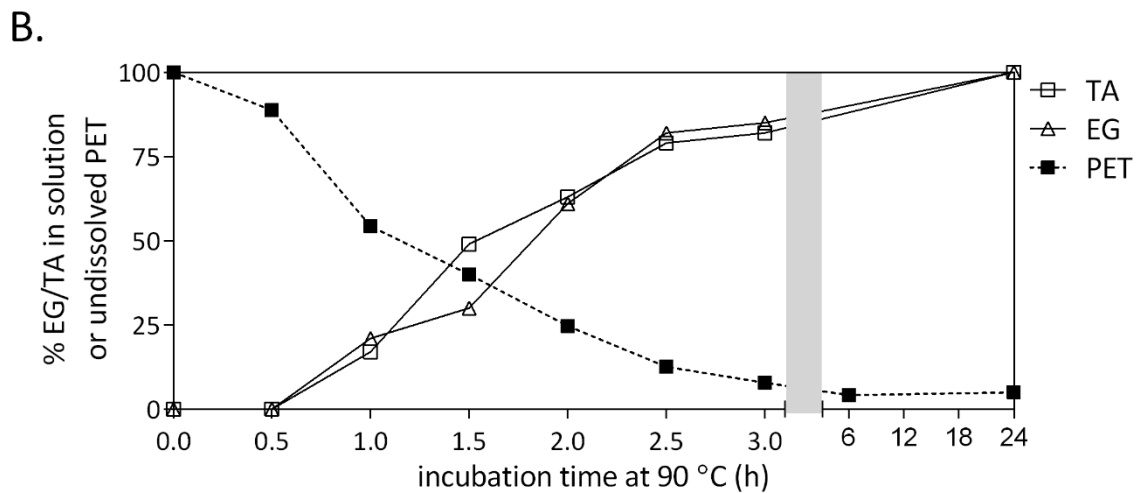
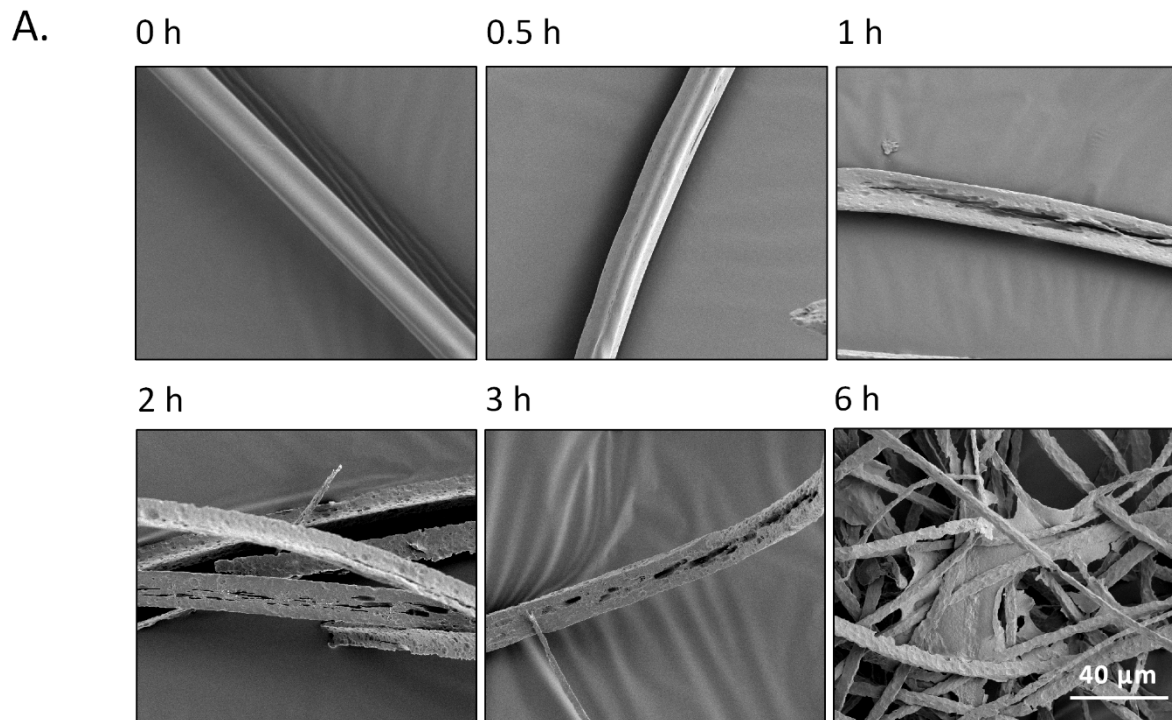
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174 **Accelerated hydrolytic degradation method development**

175 Alkaline hydrolysis is used as a softening process in the production of PET fabrics²⁶ and can
176 also be used in the chemical recycling of PET to its synthetic components TA and EG^{24, 27}. To
177 optimize alkaline hydrolysis, we tested PET degradation at different pH values and
178 temperatures. An aqueous solution at pH 14.4 (10 % NaOH) was found to be most effective at
179 hydrolyzing the PET MPFs, with lower pH values not resulting in any significant hydrolysis. A
180 temperature of 90°C was observed to reduce the hydrolysis time significantly compared to 60
181 and 70°C, with >90% degradation after 3 h (Figure S1) and complete degradation after 24 h.

182

183 Having established a method to rapidly fully degrade PET MPF (24 h), the PET fibers were
184 subjected to alkaline hydrolysis over time to determine whether they are suitable for use as
185 partially degraded MPF reference materials. Physical and chemical degradation was studied
186 using a combination of SEM, gravimetry and LC-UV-MS/MS (Figure 1, Figure S2). SEM
187 analysis showed superficial fiber degradation occurs after 30 min, with significant structural
188 damage observable after 1 h. After 6 h, substantial structural degradation had occurred, and no
189 material was detected after 24 h (Figure 2A). LC-MS/MS analysis of PET degradation products
190 similarly showed a linear time-dependent increase in both TA and EG degradation products that
191 plateaued after 2.5 to 3 h, increasing slightly at 24 h (Figure 2B). This was inversely mirrored
192 when measuring undissolved PET gravimetrically (Figure 2B). We suggest that by 6 h, the
193 fibers are largely degraded into a mixture of monomers (*i.e.* EG and TA) and short water-soluble
194 polymers, although some heavily degraded PET fibers remain detectable by SEM at this point.
195 Full hydrolysis of the water-soluble polymers into the final degradation products occurs by 24
196 h and no fibers are visible by SEM imaging. Thus, alkaline hydrolysis of PET fibers can be
197 used to generate reference material of partially degraded MPF by attenuating hydrolysis time.



199

200 **Figure 2:** Accelerated hydrolysis fully degrades PET. A) SEM images of PET subjected to
 201 accelerated hydrolysis (1000x magnification). B) TA and EG measured by LC-UV-MS/MS
 202 plotted with undissolved PET determined gravimetrically during accelerated hydrolysis. The
 203 grey bar represents a change in the time increment on the x-axis from 0.5 h to 6 h.

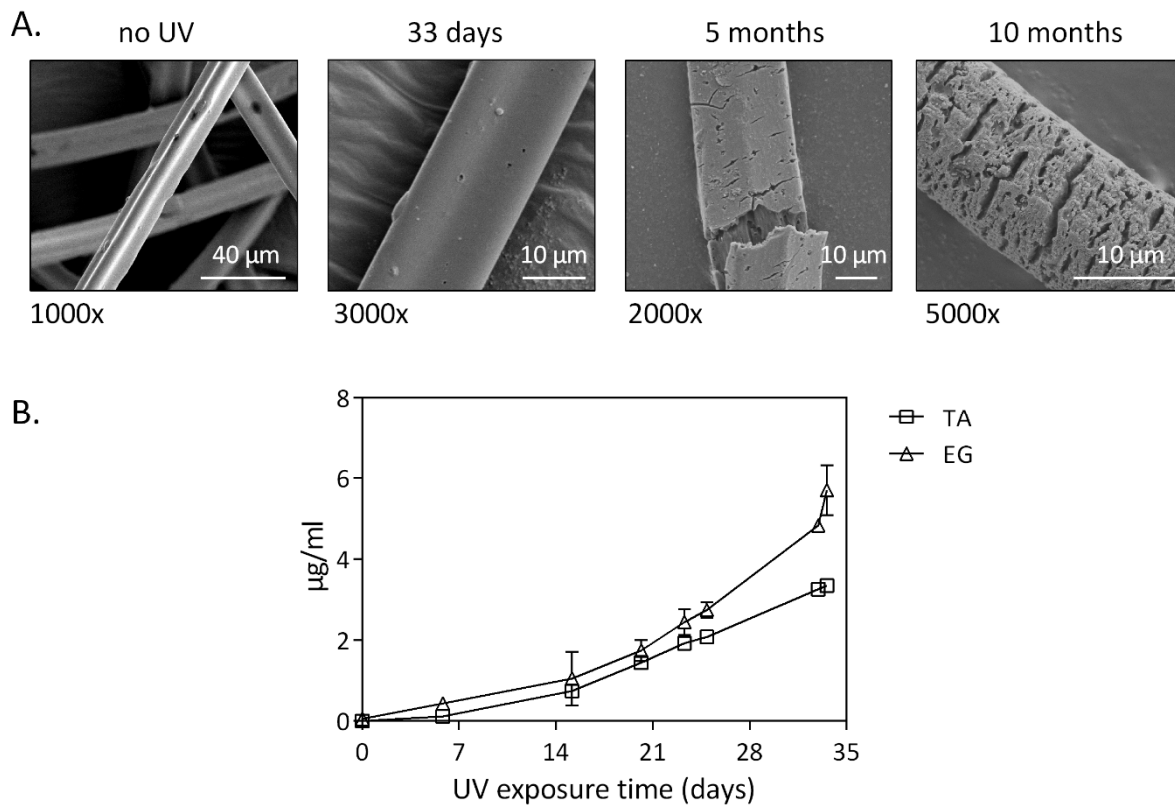
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206 **Comparison of hydrolysis and UV degradation**

207 To determine the environmental relevance of the partially degraded PET MPF reference
208 material, we confirmed whether PET degradation by alkaline hydrolysis resembles UV-
209 degradation that occurs in the environment. To this end, we exposed PET fibers in seawater to
210 simulated sunlight and measured the generation of EG and TA as described above. Small holes
211 were observed in the fibers exposed to UV after ~33 days (Figure 3A), suggesting the onset of
212 physical changes to the PET MPFs. In extended UV exposure studies, the PET fibers exhibited
213 significant changes in their surface morphology after 5 months, which grew even more
214 pronounced after 10 months of UV exposure (corresponding to 7.5 years under natural
215 environmental conditions). These results are consistent with the findings in our recent study
216 investigating the UV degradation of multiple synthetic fiber types.²⁸ Importantly, both the UV
217 exposure and the accelerated hydrolysis approaches yield partially degraded PET fibers that
218 exhibit many physical similarities, including a change from a smooth to an irregular surface and
219 the formation of crack and holes along the fiber length.

220



221
 222
 223 **Figure 3:** UV-irradiated PET releases terephthalic acid and ethylene glycol. A) SEM images of
 224 non-irradiated and UV irradiated PET fibers after 33 days, 5 months and 10 months. B) TA and
 225 EG measured by LC-UV-MS/MS.

226
 227 Pristine, hydrolyzed and UV degraded PET MPFs were also analyzed by FTIR to investigate
 228 changes in the surface chemistry resulting from the two degradation mechanisms (Figure S3).
 229 After 3 h hydrolysis, the PET MPFs were significantly modified physically, but the FTIR
 230 spectrum remained almost identical to that of the pristine material (Figure S3a). Similarly, PET
 231 MPFs subjected to 10 months UV exposure also underwent physical changes, but no significant
 232 differences in surface chemistry were observed (Figure S3b). Although, it could be expected
 233 that UV degradation leads to increased oxidation of the fiber surface, the FTIR spectra do not
 234 support this. It is suggested that the UV degradation mechanism results in products that rapidly

235 fragment from the main fiber or quickly dissolve into the surrounding aqueous media. The
236 photodegradation of PET has been proposed to occur via chain scission leading to the generation
237 of carboxyl end groups followed by the formation of mono- and dihydroxyterephthalates,
238 carboxyl end groups and aldehydes (Norrish Type I reaction)^{29,30}. The likely scenario occurring
239 is that PET fibers are broken down into polymers or oligomers of different lengths with a variety
240 of chemical end-groups that can spontaneously degrade to soluble EG and TA. Although the
241 ultimate degradation products of PET degraded by UV exposure will vary in composition, we
242 propose that TA and EG can be used to estimate PET degradation. Both TA and EG were
243 measured after only 6 days of *in vitro* UV exposure (corresponding to ~2.3 months of sunlight)
244 and steadily increased throughout the experiment (Figure 3B). Controls incubated in the dark
245 at room temperature over the same amount of time contained no measurable EG or TA.

246
247 Importantly, the extent and kinetics of the breakdown reaction from intact fibers to the different
248 degradation products warrants further study to determine exactly which products are formed
249 upon UV exposure. We observed a ratio of 0.5 and 3.5 EG moieties per TA for the alkaline
250 hydrolysis and UV degradation experiments, respectively. The expected ratio for pure PET is
251 1, but it is possible that EG was supplemented with other glycols (e.g. polypropylene glycol) or
252 that EG was degraded during alkaline hydrolysis. During the UV degradation, it is likely that
253 hydroxyterephthalates and polymers are released from the fibers upon UV exposure, which
254 would release EG but not generate a corresponding TA. These terephthalate intermediates
255 would break down much more quickly during the alkaline hydrolysis reactions than during UV
256 degradation experiments, explaining the larger EG-to-TA ratio. Thus, the relationship between
257 TA/EG formation, as well as that between alkaline hydrolysis and UV degradation, should be
258 interpreted as proportional relationships and not direct correlations. Nevertheless, the
259 generation of TA and EG by UV exposure of PET confirms that (1) the two compounds can be

260 used as universal markers of PET degradation and (2) reference materials produced using
261 alkaline hydrolysis can be used to approximate UV degradation. While it is difficult to directly
262 compare the accelerated hydrolysis of the PET fibers with the combination of degradation
263 mechanisms occurring simultaneously under natural environmental conditions (e.g. UV,
264 mechanical and microbial), the method appears to yield comparable physical changes to those
265 caused by UV exposure.

266
267 The current study outlines a fast (<3 h), cheap and reproducible method for producing partially
268 degraded PET MPF reference materials for use in environmental fate studies. Importantly, the
269 reference materials are similar in nature to partially degraded polyester microfibers generated
270 through exposure to UV and the degree of degradation can be accurately controlled depending
271 on the required properties for the final materials. The ability to produce such reference materials
272 is critical for improving our understanding of the fate and impacts of polyester microfibers in
273 the natural environment and represents an important step away from studying pristine reference
274 materials. We conclude that PET degradation can be measured by TA and EG, and by extension
275 that the degree of fiber degradation in our reference material is a valid benchmark for
276 environmental fate studies. As hydrolysis occurs mainly in polymers that have water-sensitive
277 groups in the polymer backbone, such as polyesters (including polyethylene terephthalate),
278 polyanhydrides, polyamides, polyethers and polycarbonates, the method described above has
279 potential application for producing a broad range of partially degraded plastic reference
280 materials.

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285 ASSOCIATED CONTENT

286 **Supporting Information.** Summary of preliminary study, a calculation of total UV irradiance
287 exposure, gravimetric determination of PET dissolution and photographic presentation of
288 hydrolysis are provided in the Supporting Information.

289

290 AUTHOR INFORMATION

291 **Author Contributions**

292 The manuscript was written through contributions of all authors. All authors have given
293 approval to the final version of the manuscript.

294

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302

303 **Notes**

304 The authors declare no competing financial interests.

305

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