

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

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Introduction

Microplastic fibers (MPFs) derived from synthetic textiles and other sources represent a significant proportion of the microplastic (MP) load in many environmental matrices¹⁻³ and have been shown to have negative impacts on aquatic organisms^{4,5}. However, the majority of studies investigating the fate and effects of MP particles have employed commercially available pristine spherical reference materials, limiting the relevance of the data produced^{6,7}. Recent studies have explored ways to produce more environmentally relevant MP reference materials^{1-3,8}, but they do not reflect the partially degraded nature of MPs and MPFs in the natural environment.

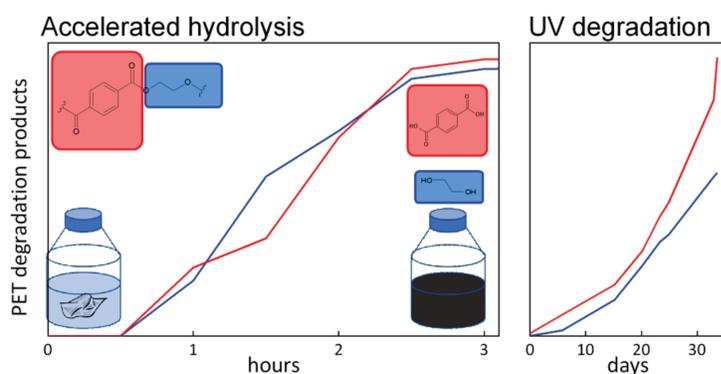
UV-induced oxidation (photodegradation) is the most effective degradation mechanism for many plastic materials released into the natural environment^{9,10}. These physicochemical changes are important when trying to assess the risks associated with MP pollution, as they may influence MPF environmental fate, bioavailability and effects on organisms^{6,11-13}. However, photodegradation of polymers is still very slow (weeks to months) under typical environmental conditions^{9,14-16}. There is,

therefore, a need for accelerated degradation methods that allow rapid and controlled simulation of environmental degradation mechanisms for the production of partially degraded MP and MPF reference materials^{6,17}.

Here we demonstrate a fast and cheap hydrolytic degradation method for producing environmentally relevant, partially degraded polyester (PET) MPFs reference materials for use in fate and effects studies. The degree of degradation was quantitatively determined by measuring the PET degradation products terephthalic acid (TA) and ethylene glycol (EG), allowing specific levels of degradation to be achieved. Scanning electron microscopy (SEM) imaging was used to visualize the degree of physical modification resulting from degradation process. Finally, the environmental relevance of the accelerated hydrolysis method was verified by comparing the hydrolysed PET and degradation products to PET MPFs exposed to UV irradiation in seawater.

Take-home message

- developed a cheap and fast method to degrade PET microfibers to use as reference material
- the extent of hydrolysis can be monitored by LC-UV and/or LC-MS analysis of PET degradation products (ethylene glycol and terephthalic acid)
- the same degradation products generated by photodegradation
- **our method generates reference material that resembles weathered PET microfibres**, although there are slight differences



Methods

Accelerated hydrolysis

200 mg of PET MPFs were introduced in glass bottles containing 25 mL aqueous solution of NaOH (10 % NaOH; pH 14) and hydrolysis was conducted at 90 °C using an oil bath.

UV degradation

UV degradation of PET fibers was performed using a Suntest CPS+ (Atlas Material Testing Solutions) equipped with a xenon UV lamp (1500 W) and fitted with a natural daylight filter. PET fibers were mixed into MilliQ or seawater at a concentration of 8 mg mL⁻¹ and placed into 35 mL quartz tubes with glass stoppers. Irradiation was conducted at 65 W/m² and the temperature in the exposure chamber was maintained at 24 ± 3 °C.

LC-UV-MS/MS analysis of degradation products

EG was derivatized by adding 50 µL sample, 100 µL 4 M NaOH and 50 µL benzoyl chloride to 250 µL with deionized water. The reaction was vortexed and incubated at room temperature for 5 min. Next, the reaction was quenched by adding 50 µL 10% glycine and incubating for 3 min at room temperature. The dibenzoyl derivate was then extracted with 1 mL pentane. Phase separation was accomplished by centrifugation at 10 000 xg for 5 min, and the organic phase was evaporated under nitrogen at 50 °C. The dried extract was dissolved in 800 µL 10 mM ammonium formate (pH 2.8) in 50% acetonitrile. Derivatized samples were diluted 500-fold prior to analysis. TA was analysed without derivatization by diluting samples 100-fold prior to analysis. Samples were analysed on an Agilent 1260 LC coupled to a 4670 mass spectrometer using a ZORBAX Eclipse Plus C18 column (2.1x50 mm, 1.7 µm) with 10 mM ammonium formate and acetonitrile as the mobile phase.

Scanning electron microscopy

MPFs were mounted on double sided tape and coated in a thin layer of evaporated gold to make them conductive. MPF imaging was performed (1000x magnification) using a FEI Nova Nano SEM 650 scanning electron microscope (SEM), operated in high vacuum mode at accelerating voltages of 5 kV, with an emission current of 90 pA and at a working distance of 8 mm.

Results and discussion

TA and EG assay

Accelerated hydrolytic degradation method development

PET fibers were subjected to alkaline hydrolysis over time to determine whether they are suitable for use as partially degraded MPF reference materials. Physical and chemical degradation was studied using a combination of SEM, gravimetry and LC-UV-MS/MS. SEM analysis showed superficial fiber degradation occurs after 30 min, with significant structural damage observable after 1 h. After 6 h, substantial structural degradation had occurred, and no material was detected after 24 h (Figure 2A). LC-MS/MS analysis of PET degradation products similarly showed a linear time-dependent increase in both TA and EG degradation products that plateaued after 2.5 to 3 h, increasing slightly at 24 h (Figure 2B). This was inversely mirrored when measuring undissolved PET gravimetrically (Figure 2B).

We suggest that by 6 h, the fibers are degraded into a mixture of monomers (i.e. EG and TA) and short water-soluble polymers. At this point, the PET fibers are almost undetectable by SEM. Full hydrolysis of the water-soluble polymers into the final degradation products occurs by 24 h. Thus, alkaline hydrolysis of PET fibers can be used to generate reference material of partially degraded MPF by attenuating hydrolysis time.

Comparison of hydrolysis and UV degradation

We confirmed whether PET degradation by alkaline hydrolysis resembles UV-degradation that occurs in the environment. To this end, we exposed PET fibers in seawater to simulated sunlight and measured the generation of EG and TA as described above. Small holes were observed in the fibers exposed to UV after ~33 days (Figure 3A), suggesting the onset of physical changes to

the PET MPFs. Both TA and EG were measured after only 6 days and steadily increased throughout the experiment (Figure 3B). Controls incubated in the dark at room temperature over the same amount of time contained no measurable EG or TA.

We conclude that PET degradation can be measured by TA and EG, and by extension that the degree of fiber degradation in our reference material is a valid benchmark for environmental fate studies. As hydrolysis occurs mainly in polymers that have water-sensitive groups in the polymer backbone, such as polyesters (including polyethylene terephthalate), polyanhydrides, polyamides, polyethers and polycarbonates, the method described above has potential application for producing a broad range of partially degraded plastic reference materials.

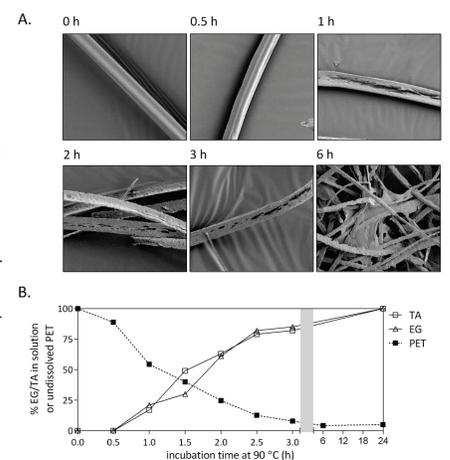


Figure 2: Accelerated hydrolysis fully degrades PET. A) SEM images of PET subjected to accelerated hydrolysis (1000x magnification). B) TA and EG measured by LC-UV-MS/MS plotted with undissolved PET determined gravimetrically during accelerated hydrolysis.

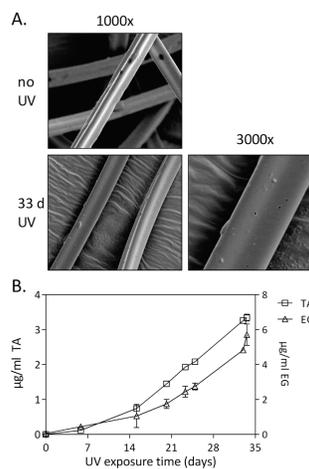


Figure 3: UV-irradiated PET releases terephthalic acid and ethylene glycol. A) SEM images of UV irradiated PET fibers. B) TA and EG measured by LC-UV-MS/MS.

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