Effects of environmental conditions on latex degradation in aquatic systems

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HIGHLIGHTS

► We characterised the degradation of latex in outdoor aquatic microcosms.
► Degradation rate was dependent on light and material thickness.
► Photooxidation is shown to be the primary degradation pathway.
► Degradation products include the formation of nanosized particles.
► Mass balance indicates that loses to the atmosphere occur.

ABSTRACT

Following use polymer materials may be released to the natural environment distributed to various environmental compartments and may undergo a variety of mechanical and chemical weathering processes. This study characterised the degradation of a latex polymer of different thicknesses under a range of environmental conditions in outdoor microcosms. Samples were immersed in either demineralised water, artificial freshwater and marine water media and exposed for a period of 200–250 days with exposure starting at different times of the year. Effects of pH, agitation and the exclusion of light on degradation were also studied. At the end of the exposure period, recovery of polymer material ≥ 1.6 μm ranged from a low of 22.04% (± 16.35, for the freshwater treatment at pH 5.5) to a high of 97.73% (± 0.38, for the exclusion of light treatment). The disappearance of the bulk material corresponded to an increase in nanoparticles and dissolved organic material in the test media. Modelled degradation kinetics were characterised by multi-phasic degradation patterns and the results indicated degradation rate is affected by light intensity and polymer thickness. Mass balance analysis indicates that losses of volatile materials to the air compartment may also be occurring.

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1. Introduction

The release of polymer materials (PMs) into the environment is recognised as an issue of worldwide concern (Barnes et al., 2009). A number of studies have demonstrated PMs to be a major component of litter on the ocean surface (Barnes and Milner, 2005; Barnes et al., 2010), on the seafloor (Galgani et al., 2000; Oigman-Pszczol and Creed, 2007; Stefatos et al., 1999) and on coastlines around the world (Bravo et al., 2009; Santos et al., 2009). Once in the environment PMs may be degraded by abiotic or biotic factors working together or in sequence (Agamuthu and Faizura, 2005; Krzan et al., 2006). Degradation of PMs could involve disintegration of the PM into increasingly smaller polymer fragments, including microscopic and nanosized particles; chemical transformation of the PM and polymer fragments; degradation of the PM and polymer fragments into non-polymer organic molecules; transformation/degradation of these non-polymer

molecules into other compounds; and ultimate mineralisation to carbon dioxide and water. Due to the many degradation processes that occur, environmental systems receiving PMs will potentially be exposed to a complex mixture of the parent material, polymer fragments of different sizes and polymer degradation and transformation products. Each of these could be taken up by and affect aquatic and terrestrial organisms. For example, there is increasing concern over the impacts of nanoparticles on organisms as particle size is recognised as an important property in determining their interaction with living systems. Desai et al. (1997) showed that 100 nm sized particles of a polylactic polyglycolic acid co-polymer had a 10-fold higher intracellular uptake in an in-vitro cell culture when compared to 10 μm sized particles made of the same material. Nanoparticles have also been shown to produce cytotoxic, genotoxic, inflammatory and oxidative stress responses in mammalian and fish systems (Dhawan et al., 2011).

The majority of our current understanding on the processes influencing polymer degradation has been derived from artificial laboratory studies that investigate a single mechanism of degradation such as photodegradation (N. Nagai et al., 2005; Y. Nagai et al., 2005),

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thermal degradation (Agostini et al., 2008; Cit et al., 2010), and biodegradation using microbial cultures (Cherian and Jayachandran, 2009; Cosgrove et al., 2007; Linos et al., 2000; Saad et al., 2010; Tsuchii et al., 1997). There is limited information on the degradation of polymers under environmentally relevant conditions where a number of degradation mechanisms occur at once and where information is available, the focus has been on understanding degradation in marine systems (O'Brine and Thompson, 2010; Rutkowska et al., 2002a,b; Sudhakar et al., 2007). These studies have tended to focus on weight loss, changes in tensile strength, breakdown of molecular structure and identification of specific microbial strains to utilise specific polymer types. The potential for PMs to form other chemical compounds and nano-sized particles has received little attention.

The aim of this work was therefore to characterise the degradation of a case study polymeric latex film under realistic conditions. To do this, outdoor microcosms were used so that the formation and subsequent degradation of the polymer transformation products could be monitored over time under natural cycles of sunlight and temperature. Experiments were initiated at different times of the year to cover different seasons and freshwater was used as the basic degradation medium. The specific objectives were to: i) explore the effects of season on the degradation rate of the latex film, ii) explore differences in degradation rates in freshwater and marine water, iii) investigate the importance of temperature and light for polymer degradation, iv) characterise molecular changes to the latex film during the degradation process, and v) characterise to what extent particles in the nanometer size range are formed following degradation of a polymer.

2. Methods

2.1. General study design

The degradation studies were undertaken using a latex film which is used in the manufacture of medical devices (0.08 mm thickness, provided by a leading UK manufacturer). For all studies, latex samples (approximately 25 cm^2) were placed individually into clear glass vessels (volume 250 ml) and spread out in 200 ml of test media. For each time point individual samples were established in triplicate and control samples, without latex, were also established. To expose the latex to natural cycles of sunlight and temperature, test vessels were then placed outdoors on a platform, under non-sterile conditions, and covered with a non ultra-violet filtering perspex sheet (B&Q, UK) to prevent flooding by rainfall. Evaporation was dealt with by regularly replacing lost water with the respective media, except for the marine water experiment where demineralised water was used to prevent the build-up of salts. Weather conditions for the entire study were recorded using a weather station located next to the experimental site (Delta-T Devices Ltd., UK).

2.1.1. Semi-field degradation over different seasons

To understand the effects of season on the degradation of latex, two experiments were initiated at different times of the year: one in August 2010 and one in November 2010. The degradation medium used was demineralised water. For the summer study, samples were removed for analysis after 10, 20, 35, 50, 90, 120 and 250 days of exposure and for the winter study, samples were removed after 30, 60, 90, 120, 150 and 200 days. A water/sediment system was also investigated during these time periods but the results were inconclusive so will not be reported here.

2.1.2. Importance of selected environmental variables and thickness on latex degradation

To assess the effects of different environmental variables on latex degradation, a series of studies were undertaken in June 2011 using an artificial freshwater media (pH 7.9; containing $CaCl_2$ 294 mg/l; $MgSO_4$ 123.25 mg/l; $NaHCO_3$ 64.75 mg/l and KCl 5.75 mg/l). The variables investigated were; an additional pH value (pH 5.5); presence/absence of sunlight; and water movement. Studies were also performed using artificial marine water (Red Sea Salt mix, Red Sea Aquatics Ltd., UK, batch number 26 04 0915; pH 8.4), and a thicker latex film (1.5 mm). Media pH was adjusted using either NaOH or HCl accordingly. The exclusion of light was achieved by covering the test vessels with foil and the effect of water movement was simulated by shaking the relevant vessels once a week for 16 h at 80 rpm. For all of these manipulations a more rigorous sampling regime was applied with samples being removed and taken for analysis after 1, 3, 7, 14, 28, 56, 112 and 200 days of exposure. Throughout the study pH was recorded (see Supporting information Table 1).

2.2. Analytical methods

2.2.1. Weight loss

Upon collection, samples were filtered under vacuum using pre-dried and weighed, 1.6 μm pore diameter, glass fibre filter papers (Whatman, UK). The filter papers were then dried at 40 °C to a constant weight and the weight recorded. A sample (20 ml) of the filtered test media was taken at this stage and stored at 5 °C for characterization in terms of nanoparticle concentration and size distribution and dissolved organic carbon (DOC) concentration. For material from the marine media, it was necessary to wash the salts off the filtered sample. To do this, samples were immersed in demineralised water for 24 h and filtered. This process was repeated until a constant weight was measured. After weighing, latex samples were kept in the fridge until the chemical functionality of the latex sample could be assessed.

2.2.2. Changes in chemical functionality

Changes in chemical functionality of the latex samples were characterised using Fourier Transform Infra-Red spectroscopy (FTIR). The infra-red absorption spectra of the filtered latex samples were measured using an ATR (Attenuated Total Reflection)-FTIR. ATR makes use of an evanescent wave to collect the absorption spectrum of a studied sample as radiation is passed through a crystal at an angle in which total reflection occurs on the top surface where the sample is located. The FTIR spectra were recorded using a Bruker spectrometer model Vertex 70 (Bruker, Germany) in the 400–4000 cm^{-1} wave number range. All spectra were the average of 16 scans recorded at a resolution of 4 cm^{-1} and peak height was used to represent the IR intensity, which is expressed as absorbance.

2.2.3. Particle analysis

Nanoparticle tracking analysis (NTA) was used to determine the number and size distribution of particles in the size range 30 nm to 2000 nm. Analysis was performed using a NanoSight LM 10 (NanoSight Ltd., UK). To characterise each individual sample and control in a representative manner, nine video images of each sample were taken. The focus of the camera was judged by eye and was adjusted so the majority of particles on the screen were in focus at the start of video capturing. Video image length was set at 60 s and all images were taken at room temperature. The processing of video images was performed using NTA 2.2 software. The detection threshold was set to automatic; this determines the minimum grey scale value of any particle in the image necessary for it to qualify as a particle to be tracked. A blur (smoothing setting) of 5×5 was then used following the recommendation in the operating manual that if automatic threshold detection is used, the blur setting should be increased by one level higher than normally used. The minimum expected particle size was set at 30 nm for all samples due to the unknown nature of the samples being analysed. The minimum track length, which defines the minimum number of steps a particle must take before its size is calculated and included in the analysis, was set to automatic allowing the software to calculate this based on the particles in the video. To verify that the filtering process was not affecting the distribution profiles, a mixture of mono-dispersed