Comparative assessment of marine weathering of ROP-derived biopolymers against conventional plastics

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Keywords: Plastic, bio-based, bioplastic, weathering, leaching, seawater

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Abstract: Bio-based plastics were designed to replace single-use plastics and to cause less post-consumer environmental damage. This paper assesses the weathering of four bio-based polymers created by ring opening polymerization (ROP) promoted by a previously reported Ti-based catalyst, to detect any problems before production was scaled up. Samples were aged in seawater to identify degradation products and monitor structural changes. Surfaces evidenced degradation and a range of leaching products was observed. Aside from compounds used in the preparation of the plastics (i.e. residual monomers and benzyl alcohol), the degradation products included carboxylic acids (often found in plastic leachate), oxacyclohexadecan-2-one (potentially toxic to aquatic life) and triphenylmethane (potential carcinogen). Overall, there were fewer structural changes in the fossil fuel based polymer (PS) and in the commercially available bio-based plastic studied for comparison purposes than the lab based bio-based polymers.

1. Introduction

Growing public awareness of plastic pollution has led businesses and researchers to seek new, more eco-friendly polymers. In particular, avoidance of petroleum-based feedstocks has been key. Focus has switched to plant-based/natural feedstocks, which could reduce the environmental impact of plastic particularly when synthesised from responsibly sourced crops that use renewable energy (Urbanek *et al.*, 2018; Álvarez-Chávez *et al.*, 2012). While many biopolymers can hold environmental advantages over conventional plastics in terms of sustainability of raw materials and energy requirements (and embodied carbon) in production processes, there has been much less attention on the environmental impact of degradation products when leaked into the environment as waste, compared to the relatively better known impacts of conventional plastics (Álvarez-Chávez *et al.*, 2012). For example, biopolymers can release degradation products. that may have been used in the polymerization process (e.g. additives or catalysts) or that may be part of the polymer (Galloway *et al.*, 2017). Knowing the identity of these degradation products and source of them in the synthesis process is an important step towards ensuring that potential environmental concerns can be identified and mitigated early in the biopolymer development process. However, relatively few studies have assessed degradation in plastic polymers without additives or at different points in the design and development process (Gewert *et al.*, 2018).

Four bio-based polymers polycaprolactone (PCL), polypentadecalactone (PDL), polylactic acid (PLA) and polyvalerolactone (PVL) were created using ring opening polymerization (ROP) of the corresponding cyclic esters and a Ti-based catalyst recently reported by us (Supplement: Table 1). The laboratory-created polymers were compared to two commercially available plastics, both used in the food industry. When polymers are made for commercial purposes, they will include additives such as plasticizers, which add flexibility and reduce brittleness (Vieira *et al.*, 2010). The current experiment focuses on the polymers themselves and so does not include potential additives.

This paper aims to assess the degradability of the in-house laboratory-prepared biopolymers against a commercially produced PLA straw and a commercially produced polystyrene (PS) coffee cup lid in a rapid simulated marine weathering test. Seawater was chosen for the tests because the marine environment is often a sink for plastic. Evidence of surface weathering was assessed and identification of weathering products was undertaken to help remediate potential environmental releases associated with biopolymers.

2. Materials and Methods

The catalyst employed for the ROP procedure was [Ti(NCMe)Cl(L(O)$_3$(OMe)] (L = monomethoxycalix[4]arene), prepared as in Sun *et al.* (2020). A toluene solution of pre-catalyst (0.010 mmol, 1.0 mL toluene) was added into a Schlenk tube at room temperature. The solution was stirred for 2 min, and then monomer (2.5 mmol) along with 1.5 mL toluene was added. The reaction mixture was placed into an oil/sand bath pre-heated at 130 °C, and the solution was stirred for 24 h. The polymerization mixture was quenched by addition of an excess of glacial acetic acid (0.2 mL) and the resultant solution was poured into methanol (200 mL). The resultant polymer was collected on filter paper and dried *in-vacuo* (Supplement: Table 1).

Approximately 500 mg of each biopolymer and two commercially available plastics, a biodegradable straw and a polystyrene coffee cup lid collected from local businesses were used. Seawater was collected from the North Sea near Scarborough, Yorkshire (Lat: N54:16:34; Long: W0:23:41). Half of the seawater was filtered and acidified (pH 1.9) to remove microbes and to accelerate mechanical weathering. A pH of 3 or lower increases the rate of degradation of PCL (Bartnikowski *et al.*, 2019). Letting plastics age at a natural rate is impractical in a short experiment (Andrade *et al.*, 2019). While the low pH did not reflect realistic environmental conditions, it provided a useful reference of degradation products compared to the subtler effects at ambient marine pH.

Small portions of each sample were set aside in dry containers with no UV light exposure for comparison to weathered plastics. Samples were divided in two, one to be aged in natural seawater and one in acidified. Samples were weighed and placed in beakers in 200ml of acidified or natural seawater. One beaker of seawater and one of acidified seawater were used as blanks as it was important that the blanks be as similar as possible to the experimental samples. Because the amount of plastic available was so small, no replicates could be created. Samples were aged for 1, 2, 3, and 4 weeks at room temperature and consistently shaken at 110 rpm in a temperature-controlled room. Turbulence is positively correlated with degradation of plastics (Suhrhoff and Schoz-Böttcher, 2016; Andrade *et al.*, 2019). Lights were set to a 12-hour day/night cycle. The light spectrum showed no signal below 400 nm, the upper limit of UV light and so the plastic was not exposed to UV light (Supplement: Figure 1). The temperature of the water during the experiment was set at 26°C given that increases in temperature increase the rate of degradation (Bartnikowski *et al.*, 2019).

At the end of each week, 25 ml from each beaker including blanks was collected by pipette and frozen for subsequent analysis. 25 ml of seawater or acidified seawater was added back to the beakers to keep the volume consistent. The seawater and acidified seawater were stored at the same temperature in a controlled room and so were the same temperature as the samples.

Gas chromatography-mass spectrometry (GC-MS) and Inductively-Coupled Plasma Mass Spectrometry (ICP-MS) were used to assess organic and inorganic leaching products respectively (see Supporting Information).

The physical breakdown of the plastics was recorded using two methods. A scanning electron microscope (SEM) was used to photograph surface changes. Fourier transform infrared (FTIR) spectroscopy was used to measure alterations in the chemical structures of the plastics and to identify breakdown products. Other researchers have used FTIR to determine changes in plastic due to weathering (Zbyszewski and Corcoran, 2011; Brandon *et al*., 2016).

3. Results and Discussion

Biodegradation involves: i) bio-deterioration, the modification of surfaces; ii) bio-fragmentation, the conversion of polymers to oligomers and monomers; iii) assimilation, where microbes convert polymers to CO_2, water and biomass (Eubeler *et al*., 2009; Emadian *et al*., 2017). Although the degradation period was short, there was some evidence of bio-fragmentation and of the conversion of polymers to oligomers and monomers. Over one month, the plastics released degradation products and exhibited signs of surface bio-fouling which may indicate biologically-mediated weathering in the seawater experiments (Figure 1).

Surface Structure

The degradation process begins with mechanical weathering, which allows other chemical methods of weathering to occur (Cooper and Corcoran, 2010). Break down of plastics occurs on the surface, where microbes and enzymes have access. As cracks and pits appear on the surface, more of the interior of the plastic becomes available for degradation. SEM pictures were used to look for cracks and pits or the presence of microbial communities, which could indicate the beginning of degradation.

Under SEM, the surface textures of PDL and PVL were complex, which made evidence of weathering difficult to access. Physically, PCL did not show signs of weathering under SEM.

PDL samples weathered in acidified seawater were more visibly degraded than those in natural seawater (Figure 1). Acidified samples showed more areas that appeared dried and cracked (Figure 1, c and d). There may have been some holes in weathered PVL samples, particularly in the acidified sample (Figure 1, e and f). Under SEM, the unweathered PLA had two distinct types of surface, one filled with air bubbles and one without. Samples aged in acidified seawater exhibited signs of cracking in areas where bubbles were present. Since bubbles were also present in unweathered samples and probably occurred during the slow solvent evaporation process (Tong and Ouano, 1985). In other areas of PLA, no signs of aging were visible (Figure 1, g and h). The PLA straw had a very simple surface structure that did not show many signs of weathering in the acidified seawater. Mineral deposits such as sodium chloride crystals were visible on the surface of all weathered samples. The polystyrene had a simple surface structure. Signs of pitting and cracking were visible in the samples weathered in acidified seawater (Figure 1 k).

For polymers to degrade, first a biofilm, primarily of bacteria and diatoms must form on the surface (Balasubramanian *et al*., 2010; Urbanek *et al*., 2018). Diatoms are one of the most common groups of microbes found on plastic and while their presence does not provide conclusive evidence of weathering, they are widely documented to play an important role in plastic degradation processes (Avio *et al*., 2017). Several of the plastics showed some microbial growth (Figure 1). Of all the plastic samples, the PCL, one of the plastics with the most complex surface structure, showed the most microbial growth. Benthic diatoms, possibly *Amphora*, *Navicula* or *Achnanthes* species (Molino and Wetherbee, 2008) were visible on the surface and a biofilm appeared to form (Figure 1, a and b). *Phormidium*, a genus of filamentous cyanobacteria that can degrade hydrocarbons, may also be present on some of the weathered plastics (Avio *et al*., 2017). Some genera produce pads or stalks to aid in adhesion, which can be seen in Figure 1 (j) (Molino and Wetherbee, 2008).

Samples of the PLA straw and coffee cup lid weathered in natural seawater showed signs of cracking and also some microbial growth (Figure 1, i, j and l). There were no visible microbes on the surface of the PDL or PVL.

FTIR results

The monomers of the lab-produced plastics were cyclic esters that vary in the number of carbons and in their molecular weight. The lightest was δ-valerolactone, with a molecular weight 100.12 g/mol, followed by ε-caprolactone at 114.14 g/mol, *rac*-lactide at 144.12 g/mol and ω-pentadecalactone at 240.38 g/mol (https://pubchem.ncbi.nlm.nih.gov/). Most samples had a small double peak in the CH_2/CH_3 region between around 2850 and 3000 cm^{-1} and a large peak representing a carbonyl group at approximately 1700 cm^{-1}. The exception was the polystyrene coffee cup lid which did not contain a carbonyl group There were lower CH_2, CH_3 and carbonyl peaks for PLA than for the other plastics (Figure 2).

Because this was a preliminary experiment, the results are used to indicate a change in the plastics over time but are not quantifying the changes.

A difference in height of FTIR spectra indicates a change in chemical bonds from weathering (Brandon *et al.*, 2016). Increases in some functional groups can indicate some degradation of the polymer. For some polymers, there were differences between samples acidified and natural samples, which may have indicated faster weathering in acidified samples. End chain scission reactions may have been the mechanism if the presence of oxygen allowed for the formation of free radicals (Gewert *et al.*, 2015). New groups such as CH_2 or CH_3 can be formed as old bonds are broken. For example, auto-oxidation caused by abiotic factors can lead to the formation of new functional groups such as esters and keto groups (Artham *et al.*, 2009).

There were few differences between the weathered and unweathered PCL samples with more changes in the acidified than non-acidified samples. A C-O stretch peak around 1160 cm^{-1} was lower for acidified samples than the other samples. This peak might represent an ester. There was a peak at around 1000 cm^{-1} or slightly higher that might also be a C-O stretch and a primary alcohol. This peak was higher for the acidified samples than the others. There was a peak at around 800 cm^{-1} that might represent C-H bending and is higher for the acidified samples than the unweather samples. Samples weathered in natural seawater were lower than both the other treatments.

For PDL there were few differences between the different weathering treatments. At about 1160 cm^{-1} C-O stretch that was higher for acidified samples may represent an ester. A small peak between 1080-1100 cm^{-1} may be a C-O stretch, representing alcohol and was higher for the natural samples, lower for unweathered samples and not present for acidified samples.

PLA is in the polyester family with characteristic peaks at 1,096 cm^{-1} and 1,186 cm^{-1} representing the C-O stretching vibration and around 1,747 cm^{-1} representing the C=O stretching vibration. There are peaks around 1,453 cm^{-1} and 1,360 cm^{-1} representing C-H bending vibration peaks (Zuo *et al.*, 2017). Zuo *et al.* (2017) observed that as PLA aged, the intensities of the C-O, C=O and C-H peaks were gradually weakened. The effects of heat, water and oxygen fractured the C-O bond in starch, hydrolysed the C=O bonds and reduced the number of C-H bonds (Zuo *et al.*, 2017).

There were many small differences in the PLA peaks from the unweathered to the weathered samples The carbonyl peak at around 1700 cm^{-1} was higher for the acidified samples. A peak at around 1640 cm^{-1} representing C=C stretching was only present in the samples weathered in natural seawater. A peak in the unweathered samples at 1480 cm^{-1} was lower in the natural samples and absent in acidified samples. 1450 cm^{-1} and 1465 cm^{-1} both represented C-H bending. Between about 1400 cm^{-1} and 1440 cm^{-1}, the sample weathered in natural seawater was highest, the unweathered sample was lower and the acidified sample was the lowest. Between 1395 cm^{-1} and 1440 cm^{-1}, there was O-H bending that represents carboxylic acid. At about 1190 cm^{-1}, there was a possible C-O stretch, which was higher for the acidified samples than for the other samples and could represent an aliphatic ether. At about 1120 cm^{-1}, there was a peak in the sample weathered in natural seawater that was higher than the other samples. At about 1060 cm^{-1}, there was a peak that was higher for the unweathered samples, lower for the acidified samples and lowest for natural seawater samples. Both peaks could represent C-O stretches and could represent alcohols.

For PVL, the carbonyl peak at about 1700 cm^{-1} was slightly higher for acidified samples. A possible C-O stretch between 1120-1160 cm^{-1} was higher for acidified samples than unweathered samples and lowest for samples weathered in natural seawater. There were two peaks between about 1040 cm^{-1} and 1090 cm^{-1}. Both were higher for samples weathered in natural seawater than unweathered samples and lower for acidified samples than unweathered samples. These peaks could have represented C-O stretching and alcohol. There was higher peak for samples weathered in natural seawater than unweathered samples at 800 cm^{-1}, which could have represented C-H bending. The same peak was much lower for acidified samples.

The commercially available products changed little during the weathering period. There were few differences in the peaks for the PLA Straw samples. A peak from 1600-1680 cm^{-1} that could be a C=O bond and represent an amide was higher for acidified samples than the others. A peak at 800 cm^{-1} that could represent C-H bending was only present in unweathered samples. There were fewer changes in the PS Lid than in the other plastic types.

At around 1400 cm^{-1} a C-H peak representing a methyl group was present in was absent in the acidified samples but present in the others.

Degradation Products

Degradation products were compared to the GC-MS library and rated by confidence of how accurate the identifications were. Only compounds identified with a confidence of ≥ 95%, a standard when identifying unknown compounds (Schymanski *et al.*, 2008) were included. Twenty-six degradation products were identified in total, some associated with only one plastic, some with more (Table 1). All the plastics except the polystyrene coffee cup lid in natural seawater leached some identifiable degradation products that were not present in equivalent blank treatments. More different degradation products were identified in acidified than natural seawater. The plastic that leached the most degradation products was PVL (31) followed by PDL (29), PCL (24), PLA (16), lid (12), and straw (10). The most common group of compounds present in the leachate were carboxylic acids including saturated fatty acids such as pentadecanoic acid, hexadecanoic acid, heptadecanoic acid and octadecanoic acid. In a 15-day exposure of conventional plastics to seawater, Andrade *et al.* (2019) also found degradation products such as carboxylic acids. Abiotic degradation results in carbonyl groups that are hydrophilic and increase degradability (Gewert *et al.*, 2015).

Other identified chemical groups included plasticizers (1,2-benzenedicarboxylic acid, diisooctyl ester, bis(2-ethylhexyl) phthalate and dibutyl phthalate) and plant metabolites (such as hexacosane, nonanoic acid and squalene; Table 1). Since the monomers are made from plants, the presence of plant metabolites could indicate that the monomers were breaking down further. Plastic degradation products can include polymer fragments such as monomers and oligomer and can result in the formation of new end groups such as carboxylic acids (Gewert *et al.*, 2015). Some samples contained benzyl alcohol, which was used as an initiator (converts the Ti-Cl to a Ti-OR species) in the polymerization process. Degradation products can include residual chemicals from the polymerization process (Gewert *et al.*, 2018).

PCL samples in natural seawater released different lengths of long chain unsaturated fatty acids as well as triphenyl methane. Samples in acidified seawater contained saturated fatty acids but also contained a wider variety of leachates. The only degradation products they had in common were octadecanoic acid and triphenyl methane. The acidified water contained δ-valerolactone, the monomer of polyvalerolactone.

Polypentadecalactone was the largest of the biopolymers. Samples in natural seawater contained unsaturated fatty acids, the monomer δ-valerolactone and benzyl alcohol. Only two leachates were identified in both natural and acidified seawater, δ-valerolactone and oxacyclohexadecane. Acidified seawater contained fewer leachates. Chemicals only appearing in acidified seawater were 13-Methyloxacyclotetradecane-2,11-dione and 2-hydroxy-cyclopentadecanone.

There were only three identifiable degradation products in PLA weathered in natural seawater all carboxylic acids. Acidified seawater contained saturated fatty acids but also chemicals such as triphenylmethane and dibutyl phthalate, which could raise issues of toxicity (Tkaczyk *et al.*, 2020; Staples *et al.*, 1997), although it must be stressed that the acidified samples do not represent ambient environmental conditions.

The straw released fewer degradation products into both acidified and natural seawaters than lab-created PLA. The plasticizer diethyl phthalate was identified in seawater and the antioxidant breakdown product 7,9-di-*tert*-butyl-1-oxaspiro(4,5)deca-6,9-dience-2,8-dione was identified in acidified seawater. Saturated fatty acids and squalene were also identified. Pieces of coffee cup lid weathered in natural seawater did not leach any identifiable degradation products. Samples in acidified seawater included saturated fatty acids and squalene.

It is unclear how degradation products such as 7,9-di-*tert*-butyl-1-oxaspiro(4,5)deca-6,9-dience-2,8-dione, triphenylmethane and dibutyl phthalate were present in the ROP-derived plastics. 7,9-Di-*tert*-butyl-1-oxaspiro(4,5)deca-6,9-dience-2,8-dione is a breakdown product of an antioxidant and dibutyl phthalate is a common plasticizer (Rani *et al.*, 2015). These degradation products could be expected in the breakdown of plastics with additives but not in plastics such as the laboratory created PLA, which did not contain plasticizers. As plasticizers were not used in the laboratory, cross-contamination can be ruled out. Future experiments, may be able to determine whether the plasticizers derive from the catalyst or from the polymer degradation. It is unlikely that they come from the GC-MS process, as the GC-MS is cleaned and unlikely to carry plasticizers from previous runs or from one sample to another.

The metal used in the catalyst, titanium, was found in the samples by ICP-MS. Although titanium is ubiquitous in plastic, the bio-based plastics do not contain any additives and the titanium could, therefore, only come from the catalyst. There is relatively little in the literature on the leaching of catalysts into the marine environment from plastics. One study investigated the presence of antimony, which is used as a catalyst for the manufacture of polyethylene terephthalate (PET). It was found to leach readily into the water from PET water bottle (Westerhoff *et al.*, 2008).

Conclusions

The data presented suggest that even in short term exposure experiments, there is evidence of degradation of novel biopolymers in simulated marine environments. The integration of a range of analytical methods is effective in tracing both physical degradation and chemical degradation products. SEM showed physical damage and evidence of rapid fouling in the natural seawater treatments, while FTIR showed bonds breaking and reforming on the surface of the plastics that may indicate structural changes to the polymers. Analysis of degradation products are consistent with this in showing hydrocarbons such as triphenylmethane, which could indicate some polymer breaking in the bioplastics. Other degradation products found in the water included long chain fatty acids which could have resulted from the breaking of bonds shown by FTIR.

Commercial plastics, which likely included additives such as antioxidants to slow their degradation, did not leach as much as the in-house prepared bio-polymers. The bio-polymers contained no additives, which simplified the experiment. Commercial plastics were also physically shaped into products and smoothed to remove any cracks and surface structures that would allow weathering to start more rapidly as cracks and pits in the surface of a plastic often begin the degradation process (Cooper and Corcoran, 2010; Sivan, 2011). This might indicate that in the natural environment plastics do not degrade as much as they may in the laboratory and this needs to be taken into account.

The plastics tested here are promising in that there are relatively few degradation products that pose particular toxicity concerns. This could be useful in food packaging where it is long known that substances can migrate from packaging to food (Arvanitoyannis and Bosnea, 2004). It could also benefit the marine environment since a large portion of waste plastic in the ocean comes from food and drink packaging (De Frond *et al.*, 2019). However, seven of the 27 degradation products were listed in PubChem (https://pubchem.ncbi.nlm.nih.gov/) as harmful or toxic to aquatic life. Four (1,2-benzenedicarboxylic acid, diisooctyl ester, benzophenone, dibutyl phthalate, nonanoic acid) were only associated with one of the plastics tested. Three were associated with multiple plastic types so may be of more cause for concern. Future research will need to be conducted to assess the concentrations of these degradation products for a clearer view of the damage that they may cause to aquatic life. The majority of the degradation products are expected to break down further over time in ambient environmental conditions. The presence of catalysts in breakdown products, highlights the need to use low toxicity transition metals such as Ti in synthesis.

There were limitations to this study that can be addressed in future research. The ROP derived polymers were not compared to polymers created with the standard industry catalyst, tin octoate. While the data are revealing in showing short term degradation products of biopolymers, future studies should prioritise longer term exposure under a range of ambient environmental conditions (freshwater, saltwater and transitional waters), experiments to trace the ultimate fate of degradation products and the role of biological processes in mediating the degradation. Toxicology tests for bio-polymers are also needed before the plastics are put into mass production. If the plastics prove to be better for the environment and the public accepts them, then an increase in production could lower the cost of the bio-polymers, which is currently prohibitive.

Acknowledgements

This work was funded by the UK Engineering and Physical Sciences Research Council (EPSRC) under grant EP/S025537/1 (Evolving a Circular Plastics Economy). We thank Kevin Welham, Bob Knight, Mike Thompson, Timothy Dunstan, Kim Rosewell, Dean Moore for their assistance with the laboratory analysis.

Conflicts of interest

There are no conflicts to declare.

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