



UvA-DARE (Digital Academic Repository)

Biodegradability of novel high T_g poly(isosorbide-co-1,6-hexanediol) oxalate polyester in soil and marine environments

Wang, Y.; Davey, C.J.E.; van der Maas, K.; van Putten, R.-J.; Tietema, A.; Parsons, J.R.; Gruter, G.-J.M.

DOI

[10.1016/j.scitotenv.2021.152781](https://doi.org/10.1016/j.scitotenv.2021.152781)

Publication date

2022

Document Version

Final published version

Published in

Science of the Total Environment

License

CC BY

[Link to publication](#)

Citation for published version (APA):

Wang, Y., Davey, C. J. E., van der Maas, K., van Putten, R.-J., Tietema, A., Parsons, J. R., & Gruter, G.-JM. (2022). Biodegradability of novel high T_g poly(isosorbide-co-1,6-hexanediol) oxalate polyester in soil and marine environments. *Science of the Total Environment*, 815, Article 152781. <https://doi.org/10.1016/j.scitotenv.2021.152781>

General rights

It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations

If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: <https://uba.uva.nl/en/contact>, or a letter to: Library of the University of Amsterdam, Secretariat, P.O. Box 19185, 1000 GD Amsterdam, The Netherlands. You will be contacted as soon as possible.
UvA-DARE is a service provided by the library of the University of Amsterdam (<https://dare.uva.nl>)



Biodegradability of novel high T_g poly(isosorbide-co-1,6-hexanediol) oxalate polyester in soil and marine environments



Yue Wang^{a,b}, Charlie J.E. Davey^{a,b}, Kevin van der Maas^a, Robert-Jan van Putten^c, Albert Tietema^b, John R. Parsons^b, Gert-Jan M. Gruter^{a,c,*}

^a van 't Hoff Institute for Molecular Sciences (HIMS), University of Amsterdam, Science Park 904, 1098 XH Amsterdam, the Netherlands

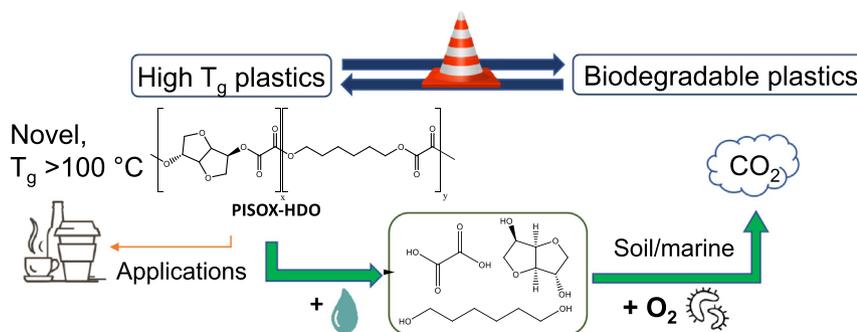
^b Institute for Biodiversity and Ecosystem Dynamics (IBED), University of Amsterdam, Science Park 904, 1098 XH Amsterdam, the Netherlands

^c Avantium Support BV, Zekeringstraat 29, 1014 BV Amsterdam, the Netherlands

HIGHLIGHTS

- Biodegradability and non-enzymatic hydrolysis of PISOX-HDO (poly(isosorbide oxalate copolyester with 1,6-hexanediol as third monomer; isosorbide / 1,6-hexanediol ratio = 3/1); a representative of a new class of high T_g renewable polyesters
- Unique combination of High T_g (103 °C), very good mechanical- and gas barrier properties and fast degradability in soil and marine environment
- Fast degradability results from facile non-enzymatic hydrolysis of oxalate ester bonds.
- Good application potential due to unique combination of excellent mechanical and thermal properties and fast biodegradability

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 12 October 2021

Received in revised form 5 December 2021

Accepted 26 December 2021

Available online 4 January 2022

Editor: Daniel CW Tsang

Keywords:

Bio-based plastic
Renewable plastic
Biodegradable plastic
Marine-degradable plastics
Polyoxalates

ABSTRACT

In order to reduce the plastic accumulation in the environment, biodegradable plastics are attracting interest in the plastics market. However, the low thermal stability of most amorphous biodegradable polymers limits their application. With the aim of combining high glass transition temperature (T_g), with good (marine) biodegradation a family of novel fully renewable poly(isosorbide-co-diol) oxalate (PISOX-diol) copolyesters was recently developed. In this study, the biodegradability of a representative copolyester, poly(isosorbide-co-1,6-hexanediol) oxalate (PISOX-HDO), with 75/25 mol ratio IS/HDO was evaluated at ambient temperature (25 °C) in soil and marine environment by using a Respicond system with 95 parallel reactors, based on the principle of frequently monitoring CO_2 evolution. During 50 days incubation in soil and seawater, PISOX-HDO mineralised faster than cellulose. The ready biodegradability of PISOX-HDO is related to the relatively fast non-enzymatic hydrolysis of polyoxalates. To study the underlying mechanism of PISOX-HDO biodegradation, the non-enzymatic hydrolysis of PISOX-HDO and the biodegradation of the monomers in soil were also investigated. Complete hydrolysis was obtained in approximately 120 days (tracking the formation of hydrolysis products via ^1H NMR). It was also shown that (enzymatic) hydrolysis to the constituting monomers is the rate-determining step in this biodegradation mechanism. These monomers can subsequently be consumed

* Corresponding author at: van 't Hoff Institute for Molecular Sciences (HIMS), University of Amsterdam, Science Park 904, 1098 XH Amsterdam, the Netherlands.

E-mail addresses: y.wang6@uva.nl (Y. Wang), c.j.e.davey@uva.nl (C.J.E. Davey), k.vandermaas@uva.nl (K. van der Maas), robert-Jan.vanputten@avantium.com (R.-J. van Putten), a.tietema@uva.nl (A. Tietema), j.r.parsons@uva.nl (J.R. Parsons), g.j.m.gruter@uva.nl (G.-J.M. Gruter).

and mineralised by (micro)organisms in the environment much faster than the polyesters. The combination of high T_g ($>100^\circ\text{C}$) and fast biodegradability is quite unique and makes this PISOX-HDO copolyester ideal for short term applications that demand strong mechanical and physical properties.

1. Introduction

The annual production of plastics worldwide was close to 370 million tons in 2019 and 2020 (Global Plastic Production, 1950–2020 | Statista; PlasticsEurope, 2020). The annual plastic production is predicted to increase to 1 billion tons by 2050 (De Smet, 2016). Plastics are used for many applications and play an important role in industry, transportation and our daily lives. Plastics are also cheap and lightweight, which makes it difficult to replace them with other materials. Because bulk plastics are very cheap, their main applications are short term, meaning that they are used only once or a few times before being discarded. This leads to enormous amounts of plastic waste, which is not always disposed of properly and causes environmental pollution. This has been widely reported both for terrestrial and marine ecosystems (Chae and An, 2018; Li et al., 2016). Their resistance to (bio)degradation causes plastic materials to remain in the environment and interact with other pollutants (as carrier). Especially for micro- and nanoplastics, this facilitates global migration and accumulation in the food chain (Li et al., 2020). A change in mentality and improved infrastructure regarding plastic use and waste-management is therefore required, but even highly advanced systems cannot completely prevent littering, which requires materials to break down over time to avoid accumulation in the environment. Therefore, environmental biodegradability (fate-in-nature) will be required to be considered a design feature for plastics.

As our plastics today are essentially all fossil based, plastic waste disposal by incineration causes large amounts of CO_2 emissions. Fossil based biodegradable plastics can still lead to CO_2 emissions which ultimately originate from fossil fuels. Spierling et al. (2018) suggested that switching around 66% (around 220 Mt. by 2017 estimates) of plastic production to biobased could potentially save 241–316 Mt. of CO_2 -eq. annually.

Biodegradation of plastics in the environment typically takes place in three steps: disintegration, depolymerisation, and assimilation and mineralization by microorganisms. Abiotic factors (heat, light, mechanical stress, moisture/water) directly affect the first two steps and indirectly affect the third step, whereas biotic factors (microorganisms by enzymatic actions) could directly influence all three steps (Badia et al., 2017; Krueger et al., 2015; Krzan et al., 2006). In short, plastics break down to oligomers and monomers, so that microorganisms can take them up and utilize them as substrates for metabolism and growth.

Poly(lactic acid) (PLA), poly(hydroxyalkanoates) (PHA), starch blends, polybutylene adipate terephthalate (PBAT), polybutylene succinate (PBS) and polycaprolactone (PCL) are typically considered as biodegradable thermoplastics which are produced on industrial scale (Lambert and Wagner, 2017; Satti and Shah, 2020). However, their commodity applications are limited by their poor physical properties, a low glass transition temperature (T_g) being one of these, especially, for the replacement of fossil based counterparts, such as poly(ethylene terephthalate) (PET) and polystyrene (PS

(Scholz and Gross, 2001). Therefore biobased thermoplastics with increased T_g are attracting attention (Nguyen et al., 2018). Aiming for high T_g , a novel type of biorenewable copolyesters, poly(isosorbide-co-1,6-hexanediol) oxalates (PISOX-HDO) (Figure 1) was recently synthesised in our group (Wang and Gruter, 2018). Potential applications could be (single-use) coffee cups/straws, or even paper coating. One of the drivers for this research is our ongoing development of technology to obtain oxalic acid via electrocatalytic reduction of CO_2 (Schuler et al., 2021a, 2021b).

Often, plastics claimed to be biodegradable are tested under industrial composting conditions, such as those described in ISO 14855-1 (2012), ASTM D6400 (2019), EN 13432 (2000). Their biodegradation in nature is, however, likely to be not as fast as consumers would expect based on these tests (Nazareth et al., 2019). PLA, for instance, is compostable, yet minimal degradation has been observed at ambient temperature in seawater and soil. These different results can easily be explained by the fact that, compared to in the natural environment, industrial composting provides more favourable conditions for PLA biodegradation, most importantly due to higher temperature (i.e. close to PLA T_g), total concentration of microorganisms and a higher moisture content than present in soil (Haider et al., 2019). Napper and Thompson (2019) reported that a commercially compostable carrier bag completely disappeared within 3 months in a marine environment, yet no measurable surface area loss was observed after 27 months in the soil. Therefore, testing novel plastics in both soil and marine environments at ambient temperature is important to evaluate their environmental biodegradability and thus their fate-in-nature. Additionally, ISO 17556 (2019), ASTM D5988 (2018) and ISO 19679 (2020) are related standard methods. Briassoulis et al. (2019a, 2020, 2019b) discussed these standard methods and also methods of plastic biodegradation under natural marine environment.

Polyoxalates (oxalic acid based polymers) and their copolymers have been reported to hydrolyze easily (Table S.1). Garcia and Miller (2014) even observed that poly-(decylene-co-resorcinol bis(hydroxyethyl)ether) oxalate (50% aromatic) was hydrolysed by the humidity in the air. Polyoxalates have been mainly considered for medical applications, such as drug carriers, so most studies have focused on non-enzymatic hydrolysis under physiological conditions (Table S.1). However, Yoshikawa et al. (2011) claimed food containers had intermediate layers containing poly(ethylene oxalate) which was environmentally biodegradable. Polyoxalate applications for packaging and agriculture have been scarcely reported. Given that hydrolysis is considered the rate limiting step for polyesters biodegradation (Sander, 2019; Wang et al., 2022), PISOX-HDO is expected to be biodegradable in both marine and soil environments because its sensitivity to hydrolysis (moisture).

Annually, over 8 million tons of plastic is estimated to end up in the sea (Jambeck et al., 2015). When plastics end up in the sea, those with low density will float, while plastics with higher density will sink and deposit on the seafloor. In contrast to polyolefins, polyesters and nylons have a higher

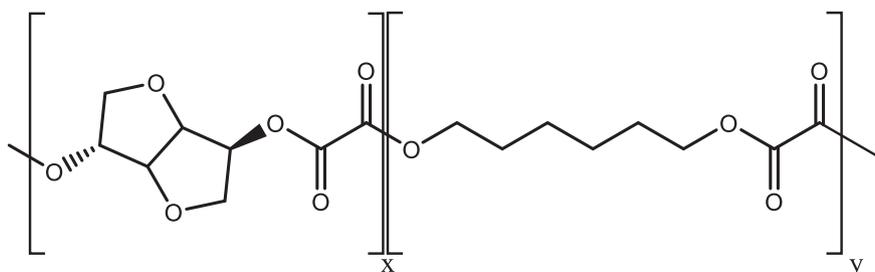


Fig. 1. Poly(isosorbide-co-1,6-hexanediol) oxalate (PISOX-HDO).

density than seawater, however, limited research has been conducted on plastic ending up on the seawater/sediment interface, which is a biologically active zone (Tosin et al., 2012). PISOX-HDO has a density of 1.38 g ml^{-1} , which means it will sink in water. It is therefore important to see how it behaves in aquatic environments, both from a hydrolysis and a biodegradation point of view. When marine degradability within a reasonable time is required, polyesters (which typically all have densities $>1 \text{ g ml}^{-1}$ and as a consequence do not float) will really benefit from non-enzymatic hydrolysis as a mechanism towards full (bio)degradation. In this light it is also interesting to consider a “use before date” not only for food products but also for certain types of (hydrolysable) packaging. Solving the problems with current plastics without compromising on convenience may be as obtainable as a “carrot on a stick”.

The aim of this research is to assess the biodegradability of PISOX-HDO in soil and marine (seawater and marine sediment) environments. In order to understand the underlying mechanisms, the biodegradation of the monomers in soil and non-enzymatic hydrolysis of the PISOX-HDO polymer in water was also studied.

2. Materials and methods

2.1. Test materials

Oxalic acid (99.0%) and 1,6-hexanediol (99%) were purchased from Sigma–Aldrich and Aldrich respectively. Isosorbide was obtained from Carbonsynth and was further purified by distillation and crystallization in house. Cellulose (powder, $20 \mu\text{m}$ average particle size) and sodium oxalate (99.5%) were purchased from Sigma–Aldrich and Alfa Aesar respectively. Dimethyl sulfoxide (DMSO, 99.9%) was purchased from Fisher Scientific.

PISOX-HDO (25% of 1,6-hexanediol and 75% of isosorbide) was synthesised in our group (Wang and Gruter, 2018). Two separate batches of PISOX-HDO were used for the experiments, both with similar T_g around $103 \text{ }^\circ\text{C}$ and density of 1.38 g ml^{-1} . Their number average molecular weights (M_n) are 21,000 and 28,600 g mol^{-1} respectively, and butyltin hydroxide oxide hydrate (catalyst, 120 ppm) was only used (for synthesis) in the first batch. No catalyst was used in the synthesis of the second batch. The first batch of PISOX-HDO was used for polymer biodegradation in soil and hydrolysis at room temperature. The second batch of PISOX-HDO, with the same 1,6-hexanediol/isosorbide ratio, was used in the seawater, pre-exposure and heat-shock experiments.

2.2. Soil, seawater and sediment

Soil was collected from an active agricultural field at Vredepeel, Limburg province, in the Netherlands and previously described by Schlemper et al. (2017). It was sieved through a 4 mm mesh, and stored in air-dry conditions. Soil was dried at $40 \text{ }^\circ\text{C}$ for 70 h before experiments. Related properties of soil were listed in Table S.2.

Seawater and sediment was collected at Zandvoort in the Netherlands, at low tide. Seawater was filtered with coarse filter paper and sediment was sieved through a 4 mm mesh filter. They were used at the same day of sampling.

2.3. Biodegradation testing method

A Respicond respirometer was used for execution of the biodegradation tests and details of the methods were described by us before (Wang et al., 2022). Briefly, biodegradation tests were performed in the dark, in closed 250 ml vessels which were maintained at $25 \text{ }^\circ\text{C}$. Three to five replicates were carried out for each test material or media (blank). CO_2 evolved from the test medium was trapped by a potassium hydroxide solution inside the vessel. Then the amount of trapped CO_2 was calculated based on the decrease in the conductivity of the KOH solution. Conductance in the KOH solution was measured hourly and the solution was refreshed regularly, before the absorption of CO_2 reached its limit. The incubation experiments lasted around 50 days.

2.3.1. Environment

2.3.1.1. Soil. To each of the Respicond vessels, 15 g of wet soil (or $\sim 12.5 \text{ g}$ dry soil), was added. The moisture level of soil was adjusted to about 50% of the field capacity by slowly adding a mineral salt solution (Table S.3). After this moisture adjustment, the pH of the soil was 5.9, which was determined after adding a 0.01 M CaCl_2 solution (Hendershot et al., 1993). Typically, the amount of organic carbon introduced by the polymer or monomer test substance to the dry soil was kept at around 5 mg C g^{-1} dry soil. This means that approximately 63 mg of carbon was added per vessel. The resulting carbon to nitrogen ratio (C:N) in the soil containing test material, was around 12.5. The test materials were added to the dry soil as solution (monomers dissolved in mineral salt solution combined with the step of adding moisture) or ground powder (polymers), respectively. Monomers were studied individually and also in a mixture (corresponding to the monomer composition of PISOX-HDO, i.e. 50 mol% oxalic acid, 12.5 mol% 1,6-hexanediol and 37.5 mol% isosorbide). Sodium oxalate was also tested.

Oxalic acid and 1,6-hexanediol were additionally tested at lower concentrations, which corresponded with their molar proportion in polymers (50% and 12.5%). This resulted in approximately 1.1 and 0.8 mg C g^{-1} dry soil respectively.

For PISOX-HDO, 6 pre-exposure experiments were performed by first adding 50% of the carbon loading in the form of PISOX-HDO (2.5 mg C g^{-1} dry soil). After 80 days, the second 50% of carbon loading (2.5 mg C g^{-1} dry soil of isosorbide or PISOX-HDO) was added to these pre-exposed vessels separately in triplicates. This second addition is considered as the starting point of incubation. One of the vessels containing the isosorbide test was excluded due to leakage.

2.3.1.2. Marine environment. About 50 g filtered seawater was used in all experiments. In the sediment experiments 20 g of drip-dried sediment was added to the seawater. Subsequently test materials equivalent to about 75 mg carbon were added directly to each vessel, except for the blanks.

2.3.2. Calculation

The degree of biodegradation (percentage of added substrate-carbon converted into CO_2 , Dt, %) of a test material at time t was calculated according to Eq. (1):

$$\text{Dt} = \frac{\text{CO}_{2,\text{sample}} - \text{CO}_{2,\text{blank}}}{\text{ThCO}_2} * 100 \quad (1)$$

Here $\text{CO}_{2,\text{sample}}$ (mg) represents the amount of accumulated CO_2 evolved from a vessel containing media and test material at time t. $\text{CO}_{2,\text{blank}}$ (mg) is the average amount of accumulated CO_2 of the blanks (soil, seawater or and sediment) at time t. ThCO_2 (mg) is the maximum amount of CO_2 that could theoretically evolve from the test material, based on the amount carbon added. Failures due to malfunction of the Respicond and outliers were removed.

2.4. Hydrolysis

In an NMR tube approximately 10 mg polymer powder ($<425 \mu\text{m}$) was added to 1 ml D_2O , containing 2.0 mg ml^{-1} dimethyl sulfoxide (DMSO) as a standard. The tubes were subsequently sealed by melting and stored at a controlled temperature of $25 \text{ }^\circ\text{C}$. A Bruker Avance III 400 MHz NMR spectrometer was used to measure (^1H NMR) soluble hydrolysis products. ^1H NMR was measured once or twice a week over a period of 160 days. The hydrolysis experiments were performed in triplicate. This method allows for tracking hydrolysis without invasive sampling, making it convenient for long term experiments.

To test if a paper cup coated with PISOX-HDO would release monomers upon multiple fills with hot liquid (such as water/tea or coffee), an NMR tube filled with PISOX-HDO powder as described above was placed in a cup filled with hot water from a coffee machine. ^1H NMR was measured

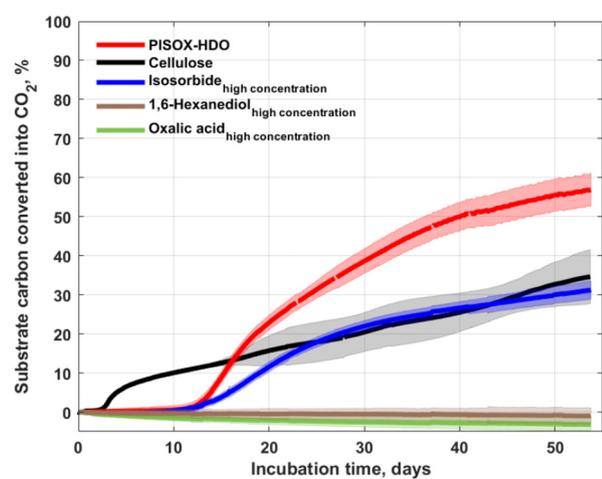
after the NMR tube in the cup had cooled down at room temperature for approximately 30 min. This was repeated for a total of four times with the same NMR tube.

3. Results and discussion

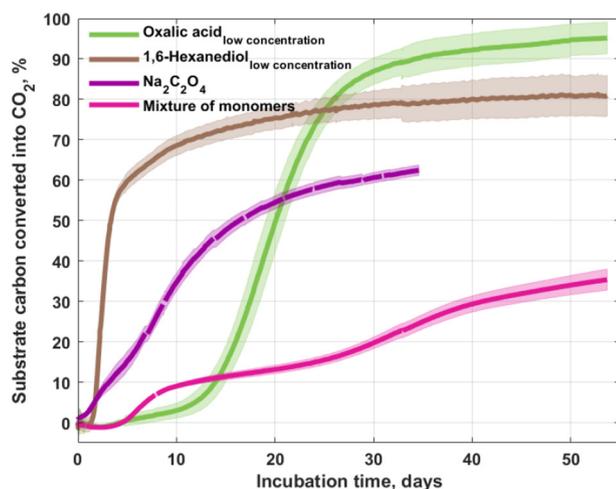
3.1. Biodegradation of PISOX-HDO and its monomers in soil

The biodegradability of PISOX-HDO and its monomers was tested in soil at 25 °C. Under the same conditions we tested the biodegradation of cellulose as a reference. Within the 53 day window, PISOX-HDO showed a much higher level of degradation than cellulose, despite it having a significantly longer lag phase (Figure 2). The fact that PISOX-HDO with a T_g of 103 °C is quite surprising as high T_g synthetic polyesters, such as poly(ethylene terephthalate) (PET), are typically not degradable (Chiellini et al., 1996; Nguyen et al., 2018; Polman et al., 2021).

After 53 days incubation time, 57 (± 4)% of the PISOX-HDO polyester was converted into CO₂. After these 53 days the curve still has an upward trend (substrate carbon conversion rate after 53 days was close to 0.5%



(a)



(b)

Fig. 2. 53 day biodegradation curves of (a) PISOX-HDO and its monomers, and cellulose (reference) with approximately 5 mg (substrate) carbon per gram of dry soil and (b) oxalic acid and 1,6-hexanediol with low concentration (1.1 and 0.8 mg C g⁻¹ dry soil), sodium oxalate and the mixture of monomers at 25 °C. Mean biodegradation (lines) were plotted. The shaded area represents the standard deviation of at least three replicates, except for 1,6-hexanediol and oxalic acid (in (a)), in which case it represents the range of duplicates.

per day). As a result, it is likely that PISOX-HDO will biodegrade completely to CO₂ and biomass in a matter of months in soil, depending on parameters such as temperature, sunlight, water content and soil type. This shows its competitive biodegradability with other biobased and biodegradable plastics. For instance, PLA is compostable, but shows very slow degradation at ambient temperature in soil (Karamanlioglu et al., 2017; Kunioka et al., 2006). Barragán et al. (2016) observed that buried Mater-Bi films, a commercial product consisting of thermoplastic starch-vegetable oil-copolyesters, lost less than 20% of its total mass after 60 days in soil at 25 °C. Furthermore, buried films and pellets of commercially available polyhydroxybutyrate (PHB) and polyhydroxybutyrate-co-hydroxyvalerate (PHBV) showed losses of 5%–50% of the initial mass within 50 days under natural tropical conditions (Boyandin et al., 2013). With comparable or even better biodegradability than these much lower T_g commercial polymers, the higher T_g of PISOX-HDO allows for a wide range of single use applications, such as packaging for hot foods and drinks.

Generally, biodegradable building blocks (monomers) are a prerequisite for biodegradation of their polymers, because breaking polymers down to oligomers and monomers is a precondition for the final step of biodegradation (mineralization). Therefore, the biodegradation of PISOX-HDO monomers was also tested (Figure 2a). Unexpectedly, PISOX-HDO reached a higher biodegradation percentage than that of all of its monomers when they were measured individually. Specifically, the biodegradation percentage of isosorbide was approximately half that of PISOX-HDO while the degradation percentages of oxalic acid and 1,6-hexanediol were zero or even negative. The low level of biodegradation of oxalic acid and 1,6-hexanediol in soil are not in line with the literature and the fast biodegradation of PISOX-HDO indicates that its monomers should also be biodegradable (Evans, 1998; Siotto et al., 2011). It is therefore likely that the biodegradation may have been limited by the apparently high and potentially toxic concentration of the monomers (5 mg C g⁻¹ dry soil) added to soil.

To check possible toxicity of/inhibition by oxalic acid and 1,6-hexanediol, they were tested at reduced concentrations (Figure 2b). At these reduced loadings the monomers all showed clear degradation over a 53 day period. Oxalic acid exhibits a significant lag phase, whereas 1,6-hexanediol at this loading started degrading after only a few days. These observations show that the lack of biodegradation observed earlier (Figure 2a) was indeed caused by the high concentrations of oxalic acid and 1,6-hexanediol, which apparently inhibited microbial activity in soil. In order to better understand the reason for the relatively long lag phase of oxalic acid, an experiment with sodium oxalate was also performed (Figure 2b), which showed essentially no lag phase. This suggests that the toxicity and lag phase regarding oxalic acid are caused by its strong acidity rather than by the oxalate itself. This is furthermore supported by the pH of soil (3.8) after adding oxalic acid solution, which increased to 6.7 after incubation.

Remarkably, the lag phases of isosorbide, oxalic acid with low concentration, and PISOX-HDO were similar (Figure 2). This would suggest that the lag phase of PISOX-HDO resulted from microbial adaption (to monomers) instead of the time required for hydrolysis. The latter is commonly considered as the rate-limiting step for polyester biodegradation in soil. In order to test this, the biodegradation rate of a mixture of monomers corresponding to the monomer composition of PISOX-HDO (50 mol% oxalic acid, 12.5 mol% 1,6-hexanediol and 37.5 mol% isosorbide) was studied (Figure 2). Clearly the lag phase of this mixture was much shorter than that of PISOX-HDO. This is in line with the lack of hydrolysis being the main cause of PISOX-HDOs lag phase. These samples contain the same amount of oxalic acid as the experiments in which only oxalic acid was used, showing a similar initial pH value of 3.6, yet biodegradation starts already within 5 days. This discrepancy could be explained by the addition of other carbon sources, which may facilitate the adaptation of microorganisms. Similarly, Loh and Tan (2000) reported that the presence of glucose enhanced the biodegradation rate of phenol. They suggested that adding a more readily degradable carbon source could support cell growth and increase the tolerance of microorganisms to high

phenol concentrations. It is also possible that different organisms are responsible for the breakdown of the various monomers, and that they have a different sensitivity towards the acidity. No conclusive statement can be made on this, as this method does not allow for distinguishing between the degradation of different carbon sources within the same sample. In order to test this, in future research labeled monomers could be used to distinguish carbon sources.

Pre-exposure, i.e. adding the test material to activate the inoculum before repeating the addition and starting the biodegradation test, a way to decrease the lag phase of biodegradation due to microbial adaptation. In this way PISOX-HDO and isosorbide were added to vessels containing soil that had been pre-exposed with PISOX-HDO and the day of this addition was defined as the starting point of incubation. The biodegradation rates of PISOX-HDO and isosorbide in these incubations are shown in Figure 3. The biodegradation rate of isosorbide in pre-exposed soil increased immediately from 0.5 to 2.4 mg CO₂ day⁻¹ within 4 days. This indicates that the lag phase of isosorbide in the earlier experiments resulted from microbial adaptation. On the other hand, the increase in biodegradation rate of PISOX-HDO with pre-exposure started after 14 days (Figure 3). It indicates that the lag phase of PISOX-HDO (regardless of pre-exposure or not) mainly resulted from the lack of depolymerization (hydrolysis) instead of microbial adaptation. This is a different result than reported for the effect of pre-exposure on PLA compostability, which was significantly accelerated after pre-exposure (Kunioka et al., 2006).

In short, it appears that the rate determining step for PISOX-HDO biodegradation in soil is the hydrolysis to its monomers. These monomers can subsequently be consumed by microorganisms in the soil. As was observed, some of these monomers can inhibit biodegradation at high concentrations, but the hydrolysis of these polymers leads to a gradual release of the monomers, which limits their concentrations and therefore their inhibition/toxicity. Apart from this, the addition of mixtures of carbon sources may facilitate the microbial adaptation and even the biodegradation rate of our polymers.

3.2. PISOX-HDO degradation in the marine environment

The biodegradability of PISOX-HDO in the marine environment was assessed by using a Respirometry system with 95 parallel reactors to monitor CO₂ conversion. Figure 4 shows the biodegradation curves of PISOX-HDO and cellulose in seawater, with and without sediment, at 25 °C. After incubation with seawater and sediment for around 50 days, 17% (± 2%) of PISOX-HDO was converted into CO₂, which was more than three times as much as for cellulose (around 5%). The degradation rate of PISOX-HDO

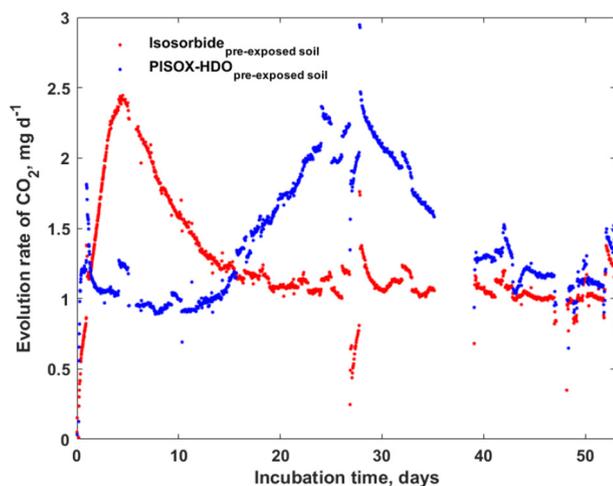


Fig. 3. The evolution rate of CO₂ (per vessel) from isosorbide and PISOX-HDO biodegradation in PISOX-HDO pre-exposed soil. Average of 2–3 replicates were plotted in dots.

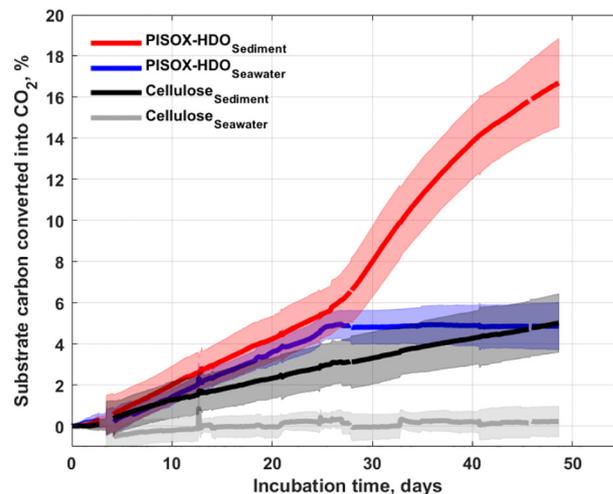


Fig. 4. Biodegradation curves of PISOX-HDO and cellulose in seawater and on the interface of seawater and sediment. Mean biodegradation percentages (lines) were plotted. The shaded area represents the standard deviation of at least three replicates. The data between 2 and 4 days was excluded due to an unintentional temperature decrease of the water bath of the Respirometry to 20.3 °C.

in seawater only was initially not much slower than with sediment and seawater, but CO₂ evolution stopped after around 25 days. In this case cellulose degradation was very slow and the difference in rate with the PISOX-HDO was thus much more pronounced than in the presence of sediment.

The pH of the seawater (with PISOX-HDO, without sediment present) was measured after 76 days and the pH had dropped from the initial value of 7.7 to 1.7. The decrease in pH indicates an increase in oxalic acid concentration, which means that the hydrolysis to the monomers is faster than the mineralization of these monomers, as is the case for the oxalic acid biodegradation in soil. This very low pH likely inhibited microbial activity. In sediment (with PISOX-HDO) this drop in microbial activity was not observed, likely because of the higher amount of microbes preventing the build-up of oxalic acid and also the buffering effect of the sediment. In the actual environment, the inhibition of biodegradation by acidification due to oxalic acid release is not expected, because of concentrations of oxalic acid released would be much lower.

In other studies concerning the biodegradation of polymers in seawater with sediment, the biodegradation (mineralization) of PHB and Mater-Bi films was reported to be around 50% and 20%, respectively, in a similar time frame as we used at room temperature, which is in the same range as observed for PISOX-HDO (Briassoulis et al., 2020a, 2020b; Tosin et al., 2012).

Interestingly Bagheri et al. (2017) studied the mass loss of so-called biodegradable plastic films poly(D,L-lactide-co-glycolide) (PLGA, lactide:glycolide 50:50), PHB, and PLA in seawater for 1 year. They observed 100%, 5% and 0% mass loss, respectively. They attributed the complete degradation of PLGA in seawater to non-enzymatic hydrolysis.

3.3. PISOX-HDO hydrolysis

The results of the biodegradation experiments in both soil and seawater show that hydrolysis of the polyester is the rate-determining step and main depolymerisation route in the conversion to CO₂. In principle, hydrolysis in nature can occur in two ways: non-enzymatic and enzymatic hydrolysis. Enzymatic hydrolysis requires specific hydrolases that are typically present in fungi and bacteria. Although non-enzymatic hydrolysis is expected to be slower at ambient temperature and neutral pH, as hydrolysis is typically base and/or acid catalysed, it is likely to still take place. Therefore the evaluation of non-enzymatic hydrolysis is necessary to fully investigate the environmental fate of PISOX, especially taking into account that the relatively fast (non-enzymatic) hydrolysis of polyoxalates is known.

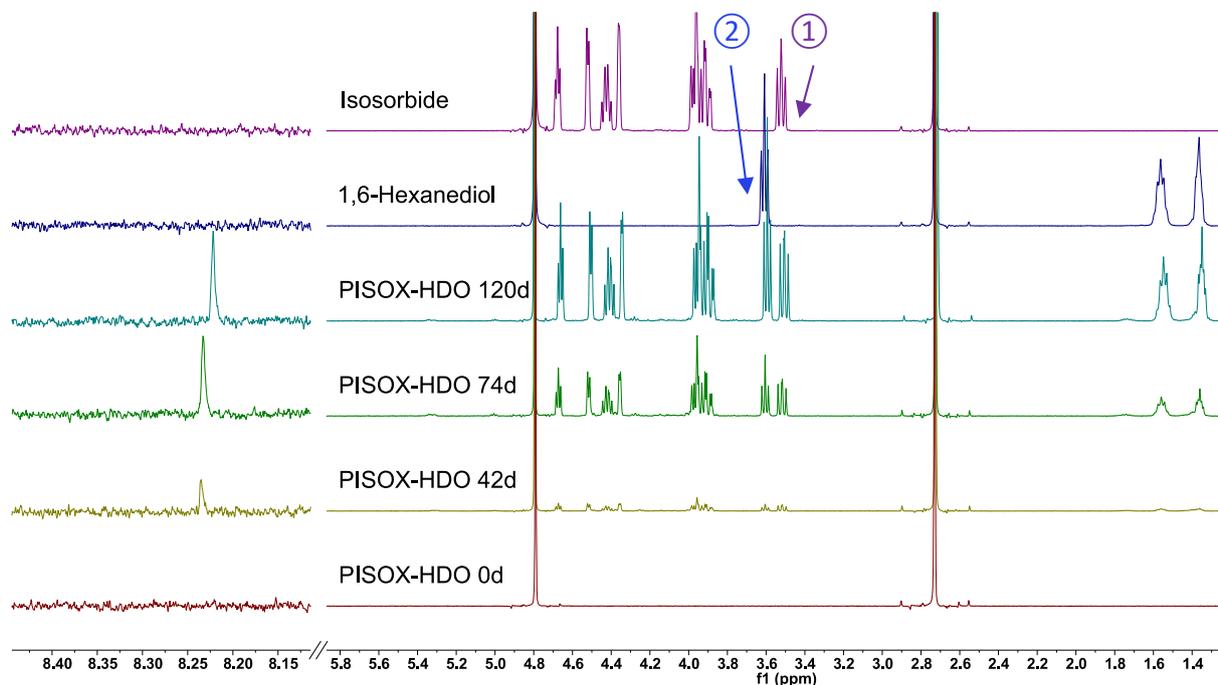


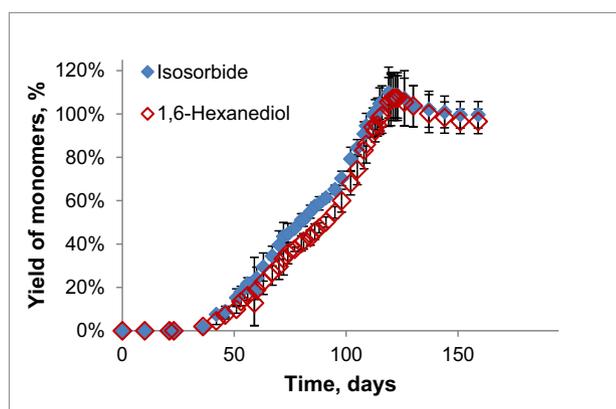
Fig. 5. ^1H NMR spectra of isosorbide, 1,6-hexanediol and hydrolysis of PISOX-HDO in 1 mL D_2O with 2.0 mg dimethyl sulfoxide as internal standard: measurements after 0 d, 42 d, 74 d and 120 d reaction time are shown. The excerpt on the left shows an expansion of the area around 8.2 ppm.

Figure 5 shows the ^1H NMR spectra of PISOX, isosorbide and 1,6-hexanediol in D_2O . Strong signals observed at approximately 2.73 ppm correspond to the methyl groups of DMSO. Triplets at 3.49–3.54 and 3.58–3.62 ppm represent a single CHO proton of isosorbide (position 1) and 4 CH_2O protons of 1,6-hexanediol (position 2), respectively, the areas of which, relative to the DMSO, were used to quantify the level of hydrolysis. Very weak resonances started appearing after 5 weeks in the ^1H NMR spectra of PISOX, indicating the process of non-enzymatic hydrolysis and the subsequent release of soluble monomers had started. Their intensity increased gradually over time. Oxalic acid cannot be observed via ^1H NMR, because both protons of oxalic acid are exchanged with D_2O .

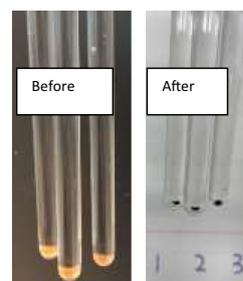
A small peak at 8.22 ppm was also formed over time, observed first in one of the triplicates after 5 weeks. This peak can be assigned to formic acid, which is one of the end groups of PISOX, formed by decarboxylation of oxalic acid end groups. Its intensity was generally too low to quantify (<1% of DMSO peak integral) till the end of hydrolysis, while an increase

over time was observed (Figure 5, expansion). Nevertheless the low pH of the solution ($\text{pH} < 2$) after complete hydrolysis indicates the presence of oxalic acid. No other significant peaks were present in the NMR spectra, which shows that oxalic acid, 1,6-hexanediol and isosorbide are the soluble end products of PISOX-HDO hydrolysis, together with a small amount of formic acid.

The hydrolysis of PISOX was demonstrated in Figure 6 (a), which shows the individual yields in time of hydrolysis products, isosorbide and 1,6-hexanediol, at 25 °C in D_2O . Traces of monomers were first observed after 5 weeks and hydrolysis was complete after approximately 120 days, which was also confirmed visually (Figure 6 (b)). The lag phase and exponential increase in the yields of hydrolysis products indicate random scission of ester bonds along the polyester backbone was predominant (*endo*-wise attack), which resulted in a decrease in molecular weight, but minimal release of monomers in the initial phase of hydrolysis (Gigli et al., 2019). As hydrolysis proceeded, the amount of end-groups increased and with it the



(a)



(b)

Fig. 6. (a) Individual yield of monomers (isosorbide and 1,6-hexanediol) during 6-month hydrolysis at 25 °C in D_2O as percentage of their theoretical maximum release. Error bars represent standard deviation of triplicate hydrolysis experiments. (b) Photos of PISOX-HDO (brownish particles) before and after hydrolysis in NMR tube. Dark brown particles left was catalyst.

amount of end-groups released. A linear increase in yield of monomers would have been expected if chain-end scission were dominant, as in that case the amount of end-groups would remain constant. Additionally, there is the matter of autocatalysis, a phenomenon which is also observed in the hydrolysis of PLGA and PLA (Ford Versypt et al., 2013; Grizzi et al., 1995; Li, 1999; Siparsky et al., 1998). Esterification and ester hydrolysis reactions are acid-catalysed and as hydrolysis proceeds, more oxalic acid will be released, which results in increased acidity of the solution and therefore faster hydrolysis. In a natural environment, this effect would be absent due to the lower concentrations of this oxalic acid.

After about 114 days the measured yields exceed 100%, yet in time these decreased again to a stable value of approximately 100%, even after 820 days (Fig. S.1). It is conceivable that DMSO could interact with polymers and oligomers of PISOX, the consequence of which would be a slightly reduced DMSO concentration. This would lead to an overestimation of the monomer concentrations in the initial part of the graph. Eventually PISOX-HDO completely hydrolysed to soluble monomers, consequently releasing all DMSO into solution, normalising the yields at 100%.

A short NMR relaxation delay ($d_1 = 1$ s) could result in less accuracy (around 10%) between experimental and theoretical ratios (Fig. S.2). Because insufficient delay times will lead to lower signal intensity. If not all ^1H nuclei are fully relaxed, this will result in less accurate integrations (relative to DMSO). However, a good correlation between monomers concentration and integral ratio to fixed concentration of DMSO was determined (Fig. S.3) and used for quantification in this study.

Nevertheless, in terms of determining the complete hydrolysis of PISOX-HDO, the overall trend and the consistency of the trend and triplicates support the hypothesis that PISOX-HDO can (non-enzymatically) fully hydrolyse in a relatively short time (around 5 months). Especially, compared to the hydrolysis of PLA, which only yielded 4% of lactic acid under the same conditions and timeline, the hydrolysis rate of PISOX-HDO is very high (Fig. S.4). Additionally, the fact that the isosorbide and 1,6-hexanediol curves show essentially the same trend suggests that they are distributed randomly within the PISOX-HDO structure.

The combination of PISOX's high T_g and high level of degradability make it quite a unique material, and it could prove valuable for short lifetime applications, especially in combination with high temperatures. A potential application could be single-use coffee cups, or even paper coating. Of course in that case it would be important to assess its suitability for high temperature applications. Therefore, PISOX's resistance to hydrolysis after a high temperature shock, was tested via ^1H NMR. An NMR tube with PISOX-HDO powder and D_2O was placed in a cup filled with hot water (directly from a coffee machine), which cooled down to room temperature in about 30 min. Furthermore, in order to take into account reuse of a disposable paper cup with plastic film, shocks were applied four times. No soluble monomer was observed in any of the ^1H NMR spectra. This simple test suggests PISOX-HDO has a good resistance to hot water in single-use applications.

3.4. The role of hydrolysis in biodegradation of PISOX-HDO

Depolymerization is a precondition for mineralization, i.e. microbial utilization of polymer carbon, which for polyesters typically means hydrolysis of ester bonds at room temperature in the soil in the dark. Generally, non-enzymatic hydrolysis is supposed to be slower than enzymatic hydrolysis, considering relatively neutral pH in soil. However, non-enzymatic hydrolysis of PISOX-HDO released soluble monomers, which were first observed in NMR after 5 weeks (Figure 6) in water (D_2O). This was later than mineralization started in soil (2 weeks), even though less water was available in soil. Moreover, after 7 weeks over half of PISOX-HDO was biodegraded while only 20% of PISOX-HDO hydrolysed after 8 weeks. Therefore, this slower non-enzymatic hydrolysis rate indicates enzymatic hydrolysis was dominant in soil in our study.

Release of monomers from PISOX-HDO hydrolysis was not observed before 5 weeks while biodegradation of PISOX-HDO started within a week in seawater with sediment, as well as in just seawater. It is relevant to note

that the polymer used in the marine experiments had a higher molecular weight and did not contain catalyst, two factors that should decrease the amount of released oligomers and monomers. However, hydrolysis (yield of monomers, 10–20%) and biodegradation (CO_2 yield around 15%) of PISOX-HDO were similar after 7 weeks. Although it is not clear whether enzymatic hydrolysis of PISOX-HDO occurred in seawater, complete hydrolysis of PISOX-HDO is expected within a relatively short time (around 5 months at 25 °C). Since hydrolysis is the predominant mechanism for the degradation of PISOX-HDO in seawater and its monomers are reported readily biodegradable in water (ECHA, 2021). PISOX-HDO is therefore biodegradable in the marine environment.

In conclusion, the non-enzymatic hydrolysis of PISOX-HDO demonstrates its potential to degrade (hydrolyse) relatively rapidly in the marine environment, even under unfavorable conditions for biodegradation, such as the deep sea where it is dark and cold with low biological activity.

4. Conclusions

The biodegradability of copolyester poly(isosorbide oxalate) -*co*-1,6-hexanediol (PISOX-HDO) in soil and marine environments was assessed by monitoring CO_2 formation in time at ambient temperature (25 °C) using a respirometer (Respicond). PISOX-HDO was shown to be significantly more biodegradable than cellulose in both media around 7 weeks. In soil it will degrade completely to CO_2 and biomass in a matter of months, whereas in seawater with sediment this would be close to a year. This is extremely fast when compared to the majority of plastics that are currently mass-produced and littered. Especially its degradation in the marine environment stands out when taking into account that plastic litter often ends up there. Furthermore, it was shown that (enzymatic) hydrolysis to its monomers is the rate-determining step in this biodegradation mechanism. It was also shown that PISOX-HDO can hydrolyse non-enzymatically. The combination of high T_g (>100 °C) and high level of biodegradability is quite unique and makes it suitable for short term applications that demand strong mechanical and physical properties. One such application would be disposable plastic (coated) coffee cups. The initial heat shock tests showed no measurable release of monomer, which appears to make this an ideal material for such applications. Other potential applications would be agriculture (mulching films, fertilizer coating) or packaging.

Funding

This work was supported by Netherlands Organisation for Scientific Research (NWO) [grant number 731.017.203].

CRediT authorship contribution statement

Yue Wang: Biodegradation and hydrolysis experiments, methodology, formal analysis, visualization, original draft; review & editing. **Charlie J. E. Davey:** Biodegradation experiments, review & editing. **Kevin van der Maas:** Polymer synthesis and characterization, review & editing. **Robert-Jan van Putten:** Hydrolysis methodology, project administration; resources, original draft, review & editing. **Albert Tietema:** Biodegradation methodology, review & editing. **John R. Parsons:** Biodegradation methodology, review & editing. **Gert-Jan M. Gruter:** Conceptualization, funding acquisition, review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that they could have appeared to influence the work reported in this paper.

Acknowledgments

We thank the following people for their contribution to this research: Dr. E. de Rijke, R.L. van Hall (MSc) and J.C. Schoorl for guidance and help

on the Respicond setup and for other related measures; L. Lövdahl, D. Sgarioni Santos and Dr. Z. Zong for help on the visualization of the biodegradation data.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2021.152781>.

References

- ASTM D5988, 2018. Standard test method for determining aerobic biodegradation of plastic materials in soil, 2018. ASTM International, ASTM International, West Conshohocken, PA. www.astm.org.
- ASTM D6400, 2019. Standard specification for labeling of plastics designed to be aerobically composted in municipal or industrial facilities. ASTM International, West Conshohocken, PA. www.astm.org.
- Badia, J.D., Gil-Castell, O., Ribes-Greus, A., 2017. Long-term properties and end-of-life of polymers from renewable resources. *Polym. Degrad. Stab.* 137, 35–57. [10.1016/j.polydegradstab.2017.01.002](https://doi.org/10.1016/j.polydegradstab.2017.01.002).
- Bagheri, A.R., Laforsch, C., Greiner, A., Agarwal, S., 2017. Fate of so-called biodegradable polymers in seawater and freshwater. *Global Chall.* 1, 1700048. <https://doi.org/10.1002/gch2.201700048>.
- Barragán, D., Pelacho, A., Martín-Closas, L., 2016. Degradation of agricultural biodegradable plastics in the soil under laboratory conditions. *Soil Res.* 54, 216–224.
- Boyandin, A.N., Prudnikova, S.V., Karpov, V.A., Ivinon, V.N., Dđ, N.L., Nguyễn, T.H., Lê, T.M.H., Filichev, N.L., Levin, A.L., Filipenko, M.L., Volova, T.G., Gitelson, I.I., 2013. Microbial degradation of polyhydroxyalkanoates in tropical soils. *Int. Biodeterior. Biodegradation* 83, 77–84. <https://doi.org/10.1016/j.ibiod.2013.04.014>.
- Briassoulis, D., Pikasi, A., Briassoulis, Chr, Mistriotis, A., 2019. Disintegration behaviour of bio-based plastics in coastal zone marine environments: a field experiment under natural conditions. *Sci. Total Environ.* 688, 208–223. <https://doi.org/10.1016/j.scitotenv.2019.06.129>.
- Briassoulis, D., Pikasi, A., Papardaki, N.G., Mistriotis, A., 2020b. Aerobic biodegradation of bio-based plastics in the seawater/sediment interface (sublittoral) marine environment of the coastal zone – test method under controlled laboratory conditions. *Sci. Total Environ.* 722, 137748. <https://doi.org/10.1016/j.scitotenv.2020.137748>.
- Briassoulis, Demetres, Mistriotis, A., Mortier, N., Tosin, M., 2020a. A horizontal test method for biodegradation in soil of bio-based and conventional plastics and lubricants. *J. Clean. Prod.* 242, 118392. <https://doi.org/10.1016/j.jclepro.2019.118392>.
- Chae, Y., An, Y.-J., 2018. Current research trends on plastic pollution and ecological impacts on the soil ecosystem: a review. *Environ. Pollut.* 240, 387–395. <https://doi.org/10.1016/j.envpol.2018.05.008>.
- Chiellini, E., Corti, A., Giovannini, A., Narducci, P., Paparella, A.M., Solaro, R., 1996. Evaluation of biodegradability of poly(ϵ -caprolactone)/poly(ethylene terephthalate) blends. *J. Environ. Polym. Degrad.* 4, 37–50. <https://doi.org/10.1007/BF02083881>.
- De Smet, M., 2016. The New Plastics Economy—Rethinking the Future of Plastics & Catalysing Action. Ellen MacArthur Foundation, Cowes, Isle of Wight, UK.
- ECHA, 2021. ECHA. <https://echa.europa.eu/registration-dossier/-/registered-dossier/5661/5/3/2> <https://echa.europa.eu/registration-dossier/-/registered-dossier/15109/5/3/2> <https://echa.europa.eu/registration-dossier/-/registered-dossier/14786/5/3/4> (accessed 8.23.21).
- EN 13432, 2000. Packaging – Requirements for Packaging Recoverable Through Composting and Biodegradation – Test Scheme and Evaluation criteria for the Final Acceptance of Packaging n.d.
- Evans, A., 1998. Biodegradation of ¹⁴C-labeled low molecular organic acids using three biometer methods. *J. Geochem. Explor.* 65, 17–25. [https://doi.org/10.1016/S0375-6742\(98\)00058-2](https://doi.org/10.1016/S0375-6742(98)00058-2).
- Ford Versypt, A.N., Pack, D.W., Braatz, R.D., 2013. Mathematical modeling of drug delivery from autocatalytically degradable PLGA microspheres — a review. *J. Control. Release* 165, 29–37. <https://doi.org/10.1016/j.jconrel.2012.10.015>.
- Garcia, J.J., Miller, S.A., 2014. Polyoxalates from biorenewable diols via oxalate metathesis polymerization. *Polym. Chem.* 5, 955–961.
- Gigli, M., Quartinello, F., Soccio, M., Pellis, A., Lotti, N., Guebitz, G.M., Licocchia, S., Munari, A., 2019. Enzymatic hydrolysis of poly(1,4-butylene 2,5-thiophenedicarboxylate) (PBTF) and poly(1,4-butylene 2,5-furandicarboxylate) (PBF) films: a comparison of mechanisms. *Environ. Int.* 130, 104852. <https://doi.org/10.1016/j.envint.2019.05.046>.
- Global Plastic Production 1950-2020, Global plastic production 1950-2020|Statista. <https://www.statista.com/statistics/282732/global-production-of-plastics-since-1950/> (accessed 8.22.21).
- Grizzi, I., Garreau, H., Li, S., Vert, M., 1995. Hydrolytic degradation of devices based on poly(DL-lactic acid) size-dependence. *Biomaterials* 16, 305–311. [https://doi.org/10.1016/0142-9612\(95\)93258-F](https://doi.org/10.1016/0142-9612(95)93258-F).
- Haider, T.P., Völker, C., Kramm, J., Landfester, K., Wurm, F.R., 2019. Plastics of the future? The impact of biodegradable polymers on the environment and on society. *Angew. Chem. Int. Ed.* 58, 50–62. <https://doi.org/10.1002/anie.201805766>.
- Hendershot, W.H., Lalonde, H., Duquette, M., 1993. Soil reaction and exchangeable acidity. *Soil Sampling and Methods of Analysis*, p. 2.
- ISO 14855-1, 2012. Determination of the Ultimate Aerobic Biodegradability of Plastic Materials Under Controlled Composting Conditions — Method by Analysis of Evolved Carbon Dioxide — Part 1: General Method. The International Organization for Standardization.
- ISO 17556, 2019. Plastics — Determination of the Ultimate Aerobic Biodegradability of Plastic Materials in Soil by Measuring the Oxygen Demand in a Respirometer or the Amount of Carbon Dioxide Evolved. The International Organization for Standardization.
- ISO 19679, 2020. Plastics — Determination of Aerobic Biodegradation of Non-floating Plastic Materials in a Seawater/sediment Interface — Method by Analysis of Evolved Carbon Dioxide. The International Organization for Standardization.
- Jambeck, J.R., Geyer, R., Wilcox, C., Siegler, T.R., Perryman, M., Andrady, A., Narayan, R., Law, K.L., 2015. Plastic waste inputs from land into the ocean. *Science* 347, 768–771. <https://doi.org/10.1126/science.1260352>.
- Karamanlioglu, M., Preziosi, R., Robson, G.D., 2017. Abiotic and biotic environmental degradation of the bioplastic polymer poly(lactic acid): a review. *Polym. Degrad. Stab.* 137, 122–130. [10.1016/j.polydegradstab.2017.01.009](https://doi.org/10.1016/j.polydegradstab.2017.01.009).
- Krueger, M.C., Harms, H., Schlosser, D., 2015. Prospects for microbiological solutions to environmental pollution with plastics. *Appl. Microbiol. Biotechnol.* 99, 8857–8874.
- Krzan, A., Hemjinda, S., Miertus, S., Corti, A., Chiellini, E., 2006. Standardization and certification in the area of environmentally degradable plastics. *Polym. Degrad. Stab.* 91, 2819–2833. [10.1016/j.polydegradstab.2006.04.034](https://doi.org/10.1016/j.polydegradstab.2006.04.034).
- Kunioka, M., Ninomiya, F., Funabashi, M., 2006. Biodegradation of poly(lactic acid) powders proposed as the reference test materials for the international standard of biodegradation evaluation methods. *Polym. Degrad. Stab.* 91, 1919–1928. [10.1016/j.polydegradstab.2006.03.003](https://doi.org/10.1016/j.polydegradstab.2006.03.003).
- Lambert, S., Wagner, M., 2017. Environmental performance of bio-based and biodegradable plastics: the road ahead. *Chem. Soc. Rev.* 46, 6855–6871.
- Li, P., Wang, X., Su, M., Zou, X., Duan, L., Zhang, H., 2020. Characteristics of plastic pollution in the environment: a review. *Bull. Environ. Contam. Toxicol.* <https://doi.org/10.1007/s00128-020-02820-1>.
- Li, S., 1999. Hydrolytic degradation characteristics of aliphatic polyesters derived from lactic and glycolic acids. *J. Biomed. Mater. Res.* 48, 342–353.
- Li, W.C., Tse, H.F., Fok, L., 2016. Plastic waste in the marine environment: a review of sources, occurrence and effects. *Sci. Total Environ.* 566–567, 333–349. <https://doi.org/10.1016/j.scitotenv.2016.05.084>.
- Loh, K.-C., Tan, C.P.-P., 2000. Effect of additional carbon sources on biodegradation of phenol. *Bull. Environ. Contam. Toxicol.* 64, 756–763. <https://doi.org/10.1007/s0012800068>.
- Napper, I.E., Thompson, R.C., 2019. Environmental deterioration of biodegradable, oxo-biodegradable, compostable, and conventional plastic carrier bags in the sea, soil, and open-air over a 3-year period. *Environ. Sci. Technol.* 53, 4775–4783. <https://doi.org/10.1021/acs.est.8b06984>.
- Nazareth, M., Marques, M.R.C., Leite, M.C.A., Castro, Í.B., 2019. Commercial plastics claiming biodegradable status: is this also accurate for marine environments? *J. Hazard. Mater.* 366, 714–722. <https://doi.org/10.1016/j.jhazmat.2018.12.052>.
- Nguyen, H.T.H., Qi, P., Rostagno, M., Feteha, A., Miller, S.A., 2018. The quest for high glass transition temperature bioplastics. *J. Mater. Chem. A* 6, 9298–9331.
- PlasticsEurope, 2020. Plastics – the Facts 2020. <https://www.plasticseurope.org/en/resources/publications/4312-plastics-facts-2020> (accessed 2.21.21).
- Polman, E.M.N., Gruter, G.-J.M., Parsons, J.R., Tietema, A., 2021. Comparison of the aerobic biodegradation of biopolymers and the corresponding bioplastics: a review. *Sci. Total Environ.* 753, 141953. <https://doi.org/10.1016/j.scitotenv.2020.141953>.
- Sander, M., 2019. Biodegradation of polymeric mulch films in agricultural soils: concepts, knowledge gaps, and future research directions. *Environ. Sci. Technol.* 53, 2304–2315. <https://doi.org/10.1021/acs.est.8b05208>.
- Satti, S.M., Shah, A.A., 2020. Polyester-based biodegradable plastics: an approach towards sustainable development. *Lett. Appl. Microbiol.* <https://doi.org/10.1111/lam.13287> n/a.
- Schlemper, T.R., Leite, M.F.A., Lucheta, A.R., Shimels, M., Bouwmeester, H.J., van Veen, J.A., Kuramae, E.E., 2017. Rhizobacterial community structure differences among sorghum cultivars in different growth stages and soils. *FEMS Microbiology Ecology* 93. <https://doi.org/10.1093/femsec/fix096>.
- Scholz, C., Gross, R.A., 2001. *Polymers From Renewable Resources: Biopolyesters and Biocatalysis*. ACS Symposium Series. American Chemical Society, Washington, DC <https://doi.org/10.1021/bk-2000-0764>.
- Schuler, E., Demetriou, M., Shiju, N.R., Gruter, G.-J.M., 2021a. Towards sustainable oxalic acid from CO₂ and biomass. *ChemSusChem* 14, 3636–3664. <https://doi.org/10.1002/cssc.202101272>.
- Schuler, E., Ermolich, P.A., Shiju, N.R., Gruter, G.-J.M., 2021b. Monomers from CO₂: superbases as catalysts for formate-to-oxalate coupling. *ChemSusChem* 14, 1517–1523. <https://doi.org/10.1002/cssc.202002725>.
- Siotto, M., Tosin, M., Degli Innocenti, F., Mezzanotte, V., 2011. Mineralization of monomeric components of biodegradable plastics in preconditioned and enriched sandy loam soil under laboratory conditions. *Water Air Soil Pollut.* 221, 245. <https://doi.org/10.1007/s11270-011-0787-8>.
- Siparsky, G.L., Voorhees, K.J., Miao, F., 1998. Hydrolysis of polylactic acid (PLA) and polycaprolactone (PCL) in aqueous acetonitrile solutions: autocatalysis. *J. Environ. Polym. Degrad.* 6, 31–41. <https://doi.org/10.1023/A:1022826528673>.
- Spielering, S., Knüpfner, E., Behnsen, H., Mundersbach, M., Krieg, H., Springer, S., Albrecht, S., Herrmann, C., Endres, H.-J., 2018. Bio-based plastics - a review of environmental, social and economic impact assessments. *J. Clean. Prod.* 185, 476–491. <https://doi.org/10.1016/j.jclepro.2018.03.014>.
- Tosin, M., Weber, M., Siotto, M., Lott, C., Degli-Innocenti, F., 2012. Laboratory test methods to determine the degradation of plastics in marine environmental conditions. *Front. Microbiol.* 3, 225.
- Wang, B., Gruter, G.J.M., 2018. Polyester Copolymer. WO201821132A1.
- Wang, Y., Murcia Valderrama, M.A., van Putten, R.-J., Davey, C.J.E., Tietema, A., Parsons, J.R., Wang, B., Gruter, G.-J.M., 2022. Biodegradation and Non-Enzymatic Hydrolysis of Poly(Lactic-co-Glycolic Acid) (PLGA12/88 and PLGA6/94). *Polymers* 14, 15. <https://doi.org/10.3390/polym14010015>.
- Yoshikawa, S., Katayama, T., Kogure, M., 2011. Environmentally Friendly Biodegradable Multilayer Containers. JP2011213374A.