End-of-life biodegradation? how to assess the composting of polyesters in the lab and the field

Rakine Mouhoubi, Merel Lasschuijt, Salma Ramon Carrasco, Hubert Gojzewski, Frederik R. Wurm

Sustainable Polymer Chemistry Group, MESA+ Institute for Nanotechnology, Faculty of Science and Technology, Universiteit Twente, PO Box 217, 7500 AE Enschede, the Netherlands

ARTICLE INFO

Keywords:
Biodegradation
Polymer
Polyester
Polylactide
Compost
Bioplastic

ABSTRACT

The aerobic composting of biodegradable plastics can be a promising solution to the growing issue of waste accumulation. Therefore, this article offers a review of papers investigating the biodegradability of polyesters (PLA, PHB, PBS and PCL) in home- and industrial composting. Not only the thermal and biodegradation properties are discussed, but also a comparison is made between the different polyesters under the same composting conditions. From this review, it becomes clear that composting shows promise for polyester waste management. However, although several methods for assessing the composting properties of polyester have been developed, the fact that they rarely follow the same standards does not allow for a comparative analysis that would clearly define composting as the most viable solution.

1. Introduction

With the increased use of plastics, the accumulation and management of waste has become a growing issue despite several approaches to solve the problem worldwide according to different waste management strategies (Rigamonti et al., 2014; Wurm et al., 2020). Therefore, one possible end-of-life options for polymeric materials is biodegradation, which makes the design of polymers that break down under certain conditions necessary, e.g. seawater, soil, compost, etc (Haider et al., 2019; Lim and Thian, 2022; Wang et al., 2021). Biodegradation refers to the breakdown of organic materials by the action of aerobic or anaerobic microorganisms such as bacteria and fungi converting them into CO₂ or methane and water. When biodegradation proceeds under a set of controlled conditions, it is referred to as composting. Through composting, the aerobic degradation process is accelerated without producing hazardous products (Samantaray et al., 2021). Unlike anaerobic biodegradation, composting requires less artificial heating since it releases heat itself, and occurs faster, being an exothermic bio-oxidation process. Biodegradation and composting cannot be used interchangeably, not all biodegradable materials can be composted (Lim and Thian, 2022). According to ISO 17088:2012 and 2021, composting is “the autothermic and thermophilic biological decomposition of biowaste in the presence of oxygen and under controlled conditions by the action of micro-organisms and macro-organisms in order to produce compost” (Berger and Laurent, 2019). This implies that composting requires to control the temperature and to supply water, oxygen, and organic matter such as leaves and food scraps continuously. Composting cannot be used for all biodegradable polymers (Kijchavengkul and Auras, 2008; Samantaray et al., 2021). Furthermore, composting conditions may vary, e.g. industrial composting or home composting have distinctively different conditions (Rudnik, 2019a). These environmental conditions make it difficult to decide whether composting can be a viable solution for treating waste from materials that should combine reasonable degradation rates with useful properties of the initial material, e.g. packaging with a certain lifetime and barrier properties and complete degradation in a conventional industrial composting plant (Kijchavengkul and Auras, 2008; Samantaray et al., 2021). Therefore, compostable polymers must fulfill criteria such as compatibility with the composting process, no negative effect on quality of compost, and a consistent degradation rate with other known composting materials (Rudnik, 2019a).

In this review different polyesters were selected, either of renewable or petrochemical origin and their properties and composting performance were compared. Since these polyesters are considered as “bioplastics”, which are labelled as biodegradable and are either based on biomass or petroleum, their stability in compost has been evaluated...
This is believed to be the first report on a comparison of polyesters with respect to their composting properties in relation with different international standards. With an increasing market share of bioplastics, composting is expected to become a more important end-of-life-option for various plastic products even though the commercial adoption is still in its infancy (Lim and Thian, 2022). Thus, this review aims to investigate how the composting properties of polyesters are assessed under different conditions and whether composting can be already considered as a viable solution in the treatment of polyester waste. Here, composting performances studied by different protocols of 4 different polyesters that have a commercial use or are currently being researched for commercial use or are currently being researched for commercial use are shown. The bio-based polyesters polylactide (PLA), poly(hydroxy butyrate) (PHB), and poly(butyl succinate) (PBS), and the petroleum-based polycaprolactone (PCL) (Fig. 1) were chosen in this article and their composting properties were compared.

1.1. Composting

Industrial composting is conducted at elevated temperatures (of around 60 °C) at high relative humidity and in the presence of oxygen. These biodegradation conditions are more optimal compared to other biodegradation conditions, e.g. in soil or waters (Haider et al., 2019). At home, in the garden, the composting conditions are milder, i.e., with lower and less constant temperatures compared to the industrial composting plants, mainly due to the smaller size of compostable materials. With lower temperatures, also the biodegradation rates are reduced compared to industrial composting; however, it has to be stated that this reduction depends strongly on the chemical nature of the considered material or processing parameters or additives present (Kijchavengkul and Auras, 2008).

In general, the composting process follows a specific temperature pattern that defines its phases (Rudnik, 2019b), starting with the mesophilic phase at a range of 25–40 °C, lasting from a few hours to a few days, where bacteria and fungi exothermically degrade organic compounds such as monosaccharides, starch, or lipids. Then it goes through the thermophilic phase from 35 to 65 °C, where bio-oxidation occurs, which can last from a few days to several months in which the action of thermophilic bacteria and fungi increases the degradation rate. It is followed by the cooling phase. After the consumption of the organic compounds, the compost cools and becomes stable; it finally reaches the maturation or curing phase (Fig. 2) (Sikorska et al., 2021).

Temperature is a key parameter in regulating microbial activity but also influences polymer properties depending on glass transition or melting temperatures of the considered polymer. The optimum temperature range for open windrow composting is 40–65 °C, industrial in-vessel composting operates at a temperature higher than 60 °C, and home composting takes place in a domestic setting with lower temperatures (Rudnik, 2019a, b). Composting requires an appropriate chemical composition with optimal amounts of carbon, nitrogen, and oxygen on the starting waste. The microorganisms that break down organic waste use carbon as an energy source, and the nitrogen is built into their cell structure with simultaneous energy releasing. Almost all energy is released as heat, which can raise the temperature of the compost to 60–70 °C. In the composted material, the pH is considered optimal between 6.5 and 7.5, and the most favorable relative humidity in the range of 40–50% should also be kept (Sikorska et al., 2021). The temperature of the composting process and the rate of oxidation strongly depend on the temperature, composted mass humidity, and substrate porosity, which ensures aeration, as well as on the presence of nitrogen in an available form (Nozhevnikova et al., 2019).

Therefore, before studying the degradation of different polymers in compost in detail, it is important to study their thermal properties and stability. Then, a comparison of these different polyesters under the same composting conditions can be made to find out which one would be the most promising.

1.2. Thermal properties of biodegradable polyesters

PLA. PLA is a thermoplastic polyester synthesized from condensation of lactic acid or by ring-opening polymerization of lactide, with both monomers coming from fermented starch. PLA products have many applications, including packaging, paper coating, fibres, films, etc (Casalini et al., 2019). PLA ranges from being an amorphous glassy polymer, with a glass transition temperature of about 50–60 °C, to a semi-crystalline polymer with a melting point of 170–180 °C, depending on the sequence of enantiomeric repeating units (L and D) in the polymer backbone (Vouyiouka and Papaspyrides, 2012). It has a limited thermal stability at temperatures above 190 °C (Casalini et al., 2019). It is only degradable at elevated temperature over 60 °C making it not home compostable (Al Hosni et al., 2019). Temperature and ambient humidity can influence its resistance to hydrolysis (Endres and Siebert-Raths, 2012). The thermal decomposition of PLA was studied in the literature by using thermoanalytical techniques (Kopinke et al., 1996). It was shown that the dominant thermal decomposition pathway at the maximum decomposition rate temperature for pure PLA (360 °C) is intramolecular transesterification, resulting in the formation of cyclic oligomers (Ozdemir and Hacaloglu, 2016). Thermal decomposition also includes other reaction pathways with for example acrylic acid from cis-elimination as well as carbon oxides and acetaldehyde from fragmentation reactions that were detected but they have not been identified.
during composting (Fig. 3).

The thermo-oxidative degradation of polylactide as shown in Fig. 4 was also studied between 70 and 150 °C. It was shown that the oxidative degradation of PLA under these temperature conditions leads to a random chain scission resulting in a reduction of the molar mass, processes which probably also happen during the composting of PLA. A proposed closed-loop oxidation mechanism involving hydroperoxides (POOH) is shown in Fig. 4, completed by the decomposition of the PO-
radical by three possible \( \beta \)-scissions (Rasselet et al., 2014).

PHB. Poly(hydroxy alkanoate)s (PHA) are a broad class of bio-based materials, of which especially poly-3-hydroxybutyrate (P3HB) is of current interest with the biggest market share (Alves Mariane et al., 2017). PHB is a semi-crystalline, thermoplastic polymer produced from microorganisms by fermentation. It has a glass transition temperature of 5 °C and a high melting point ranging between 173 and 180 °C (Czerwiecka-Kubicka et al., 2017). Due to its biodegradability and biocompatibility, PHB is used for biomedical, pharmacological, environmental, and packaging applications (Amada et al., 2021). P3HB is very crystalline making it stiff and brittle. The copolymerization with 3-hydroxyvalerate (3HV) was for example performed to reduce the crystallinity (VanderHart et al., 1995). The thermal decomposition of P3HB at 170 °C was investigated (Aoyagi et al., 2002; Erceg et al., 2005). It was shown with the analysis of volatile products of P3HB by pyrolysis gas chromatography that the thermal decomposition involves a random chain scission (\( \text{cis}-\text{elimination} \)) reaction of the ester groups forming crotonic acids and its oligomers (Fig. 5). By studying the thermo-oxidative degradation of P3HB and the P3HB3HV it was shown that the addition of 3-hydroxyvalerate in the P3HB led to higher thermal stability (Rudnik, 2019b).

PBS. Polybutylene succinate (PBS) is a semi-crystalline thermoplastic polyester predominantly produced from petrochemical sources (also bio-based feedstocks can be used) and mainly used in agriculture and packaging. PBS has a melting point between 90 and 120 °C and a low glass transition temperature of –40 to –10 °C (Aliotta et al., 2022). The thermal degradation of PBS was investigated by thermogravimetric analysis, and it was shown that this aliphatic polyester presents a high thermal stability. Its degradation takes place in two stages at around 400 °C. It was assumed that the first stage of decomposition is due to degradation of the oligomer leading to a small loss of mass. The second step is the predominant mechanism with random cleavage of the ester bond (random chain scission) leading to the formation of carboxyl end groups and vinyl groups (Chrissafis et al., 2005).

PCL. Polycaprolactone (PCL) is a semi-crystalline thermoplastic polyester derived from the chemical synthesis of petroleum-based caprolactone. It has a glass transition temperature of –60 °C and a low melting point of around 60 °C (McKeen, 2021). It is used in biomedical applications such as controlled drug delivery or in thermoplastic polyurethanes for surface coatings, adhesives and synthetic leather and fabrics (Guarino et al., 2017). The mechanisms of thermal decomposi-
tion of PCL have been debated. It was suggested that PCL undergoes both random chain scission and specific chain end scission at the same time on non-isothermal heating and degrades only by unzipping of the monomer from the hydroxyl end of the polymer chain on isothermal heating (Aoyagi et al., 2002). Under aerobic conditions, PCL also hydrolyses to capronic acid (6-hydroxyhexanoic acid) that further oxidizes to adipic acid. Then, after intermediate steps, decomposition of citric acid leads to the formation of water and CO2 (Aoyagi et al., 2002; Endres and Siebert-Raths, 2012).

1.3. Biodegradation mechanisms of PLA, PHB, PBS, and PCL.

The biodegradability of the polyesters depends on their chemical structure and the nature of the hydrolyzable ester bonds in the main chain. Kinetics of biodegradation are dependent on hydrophilicity, crystallinity, additives, purity, molar mass, enzymatic selectivity, solubility and solubility of the degradation products or oligomers, and others (Becker and Wurm, 2018). Biodegradation of PLA occurs via a two-stage mechanism. The first step is the hydrolysis of ester linkage that can be accelerated by acids or bases and/or affected by both temperature and moisture levels. In a second step, microorganisms that are involved digest the lower molecular weight lactic acid oligomers, producing carbon dioxide and water. It is worth noting that PLA degrades in compost in both high humidity and temperature (Hakkarainen, 2002). PCL is easily degradable because microorganisms secrete PHB depoly-
merases, which are specific enzymes that hydrolyse the ester bonds into oligomers and water-soluble monomers. PHB is quite resistant to mois-
ture with the enzymatic degradation being from two to three orders of magnitude faster than the rate of simple hydrolytic degradation (Roohi et al., 2018). PBS degraded by microbial hydrolysis using fungi shows that films composed of high molar mass polymers retained their crystallinity longer than similar films of low molar mass PBS (Song and Sung, 1995). PCL is fully biodegradable when composted because of its low melting point close the industrial composting temperature. If composted below the melting point, the microscopic changes of PCL surface and crystallinity after incubation in natural environments suggest that the enzymatic degradation of PCL is a two-step process. The amorphous phase is degraded, which is accompanied by an increase of crystallinity and then the crystalline phase is degraded (Krasowska et al., 2016).

Under these conditions, PCL degrades both by enzymatic and chemical hydrolysis of the ester bonds of PCL. Hydrolysis of PCL produces 6-
hydroxyhexanoic acid which is subsequently metabolised. A summary of the thermal degradation and biodegradation properties is shown in Table 1: the lower the \( T_g \) or \( T_m \) of the polymer, the more easily it bio-
degrades. However, it is necessary to test the biodegradation of these polyesters under the same standard experimental conditions to effec-
tively compare their biodegradation properties and determine the best way to manage the resulting polyesters waste.

1.4. Cost of biodegradable polyesters

The cost of manufacturing biodegradable plastics is mostly more than double compared to that of conventional plastics (Yusoff et al., 2016). Therefore, it is important to consider the price of the polyesters as well when considering how the best way to manage their end of life. From the polyesters selected herein, PLA is the cheapest per kg, followed
by PCL, PBS, and as last PHB (Naser et al., 2021). PLA is approximately half-price (~1.80 €/kg) of PBS (~3.50 €/kg) and PHB (~4.00 €/kg) (Rudnik, 2019c). PBS and PHB have a multi-step and relatively complex manufacturing process, which at the same time is expensive, increasing the price as a raw material (Sasimowski et al., 2021). It was estimated that the production cost for PHB is four to nine times higher than the price of polyethylene (Amadu et al., 2021). Costs can be reduced by formation of composites or blends with cheap biopolymers, such as starch or biowaste. Considering the production capacity of bioplastics, it is expected to reach 1.86 million tons in 2022 (Rudnik, 2019c). The production capacity of PLA is expected to grow by 50 % by 2022 compared to 2017. Additionally, ranking the polyesters based on annual production, the order is PLA > PBS > PCL > PHB (Jeremic et al., 2020; Naser et al., 2021; Shaikh et al., 2021).

1.5. Testing protocols, standards, and reactors for composting

The disintegration of the polyester into fragments is the first phase of degradation. The result of the whole process is the production of carbon dioxide, which is the consequence of aerobic degradation (Hakkarainen, 2002). Standard test methods to characterize biodegradability and compostability often measure the CO₂ concentration or the O₂ depletion during the process (Starnecker and Menner, 1996). The composting of polymers is studied in the laboratory by different setups mimicking the environmental conditions during an industrial or a home composting scenario (Haider et al., 2019; Starnecker and Menner, 1996). It should be noted that little information is available on the degradation of compostable polyesters in a large-scale composting facility under outdoor conditions.

Internationally recognized standardization bodies proposed systems to certify materials compostable, i.e. the International Organization for Standardization (ISO), the American Standard Testing Methods Reference (ASTM), the European Committee for Standardization (CEN), and the Japanese Industrial Standards (JIS) (Kale et al., 2007c). Probably the mostly referred standards are the ISO 14855, EN 13,432 and ASTM D6400/5338 that can be used as a basis to describe the requirements of a certain material as “compostable” based on its biodegradability. The US Composting Council uses the label “compostable” based on data of the ASTM D6400 standard, while in Germany “DIN CERTCO” by the Deutsches Institut für Normung (DIN) is based on data following EN 13,432 (Song et al., 2009). In general, compliance with the European standard EN 13,432 is a reasonable measure for compostability under industrial composting conditions. A packaging polymer can be called compostable following the EN13432 standard, if its organic components (>1 wt%) are naturally biodegradable; its disintegration in the (industrial) composting process happens in a certain time; no negative effect on the composting process and compost quality occurs. Further, EN 13,432 also requires that all components in the product have to be compostable, such as dyes, glue, etc. (Rujnić-Sokele and Pilipović, 2017). Two ISO standards have been developed (Kjeldsen et al., 2018);
ISO 14855–1 is a common test method that measures evolved carbon dioxide and the degree of disintegration of the material using infrared analysis, gas chromatography or titration. This method, that does not exceed 6 months, simulates aerobic composting with the test material exposed to an inoculum derived from compost in an environment wherein temperature, aeration and humidity are controlled. The second standard ISO 14855–2 involves a method with a standard duration of 45 days that enables the measurement of evolved carbon dioxide in the test vessel by using gravimetric analysis of carbon dioxide absorbent. An example of a laboratory system developed for biodegradation studies under composting conditions based on ISO 14855–1 standards is given (Fig. 6). The carbon dioxide produced from the reaction vessels by the studied compostable material is trapped in alkaline solution bottles. Then the amount of trapped carbon dioxide is determined by titration with an acid solution (the Japanese JISK6953 is identical to the ISO-14855) (Funabashi et al., 2009; Kale et al., 2007c).

2. Composting performance of polyesters: Selected literature examples

Representative examples of papers that studied the biodegradation of polyesters under different conditions in compost over the past 20 years from all over the world were selected. Several modes of composting and types of samples have been used and investigated to elucidate the degradation of these polyesters. A visual overview of all the selected literature can be found in Fig. 12.

### 2.1. Biodegradation of PLA in compost

Kale et al. (2006, 2007a, 2007b) studied the biodegradability of PLA bottles and other single-use products in three similar reports. The biodegradability study of PLA bottles made of 96 % l-lactide was carried out under real composting conditions (Fig. 7. B.). Additionally, PLA trays and deli containers were also studied, both made of 94 % l-lactide and 6 % d-lactide under the same conditions.

The deli containers had a higher molecular weight compared to the other specimen; the compost used consists of cow manure, wood shavings and waste feed. The study was carried out over a period of 30 days with a temperature of 65 °C, a relative humidity of 63 ± 5 %, and a pH of 8.5 ± 0.5. Molar mass analysis was conducted via Gel Permeation Chromatography. In the first few days, the shape of the materials changed, which was attributed to the higher temperature of the compost, which was higher that the glass transition temperature of PLA. A decrease of molar mass and mass dispersity (PDI) was reported (Fig. 7. A.). The molar mass decrease of the bottles in the first 15 days was much lower than for the trays and deli containers. At day 30, it was not possible to locate any pieces of the trays or deli containers for analysis (which does not mean that smaller particles might have been present). After 57 days, the molar mass values for the bottles were below 5 kDa, but no complete degradation was measured (Kale et al., 2007b). The lower degradation rate of the bottles is mainly due to its higher crystallinity given by a higher amount of l-lactide. Additionally, the changes in the glass transition temperature were measured: the bottles showed a decrease of 0.97 °C/day, the trays showed a decrease of 0.7 °C/day and the deli containers showed a decrease of 0.53 °C/day as the glass transition temperature decreases with the molar mass decreases, indicating a first-order degradation kinetics.

Karamanlioglu and Robson (2013) also studied the biodegradability of PLA and used samples in the shape of coupons, which were composted. They used different temperatures (i.e., 25, 37, 45 and 50 °C) and a moisture content of 30–35 % with a pH of 7.2. They found that at a temperature higher than 37 °C, signs of perforations, fungal growth and physical disintegration on the specimen were visible. The tensile strength decreased more with an increase in temperature, as did the weight loss. No significant weight loss was found at 25 °C, but at 37 °C, 20 % weight loss was obtained after 12 months. At 45 °C a weight loss of 57 ± 4 % was obtained after 9 weeks and at 50 °C a weight loss of 44 ± 6 % was determined after 5 weeks. After this period, no further measurements could be done due to physical disintegration of the samples (Fig. 7. C.). The different results due to differences in temperature highlight the important role temperature plays in the aerobic biodegradation process.

### 2.2. Biodegradation of PHB in compost

Weng et al. (2011) studied the degradation of different PHAs, including PHB, under controlled composting conditions. They tested the biodegradation according to the method described in ISO 14855–1. The compost consisted of inulin, dry and volatile solids with a pH of 8.2 and temperature of 58 °C. The authors found a systematic trend for different PHAs with different chemical structures. The order of biodegradability under the controlled composting conditions was P(3HB, 4HB) > (40 %mol 4HB) > PHBV(40 %mol HV) > PHBV(20 %mol HV) > PHBV(3 %mol HV) > (P(3HB, 4HB)) with (poly)hydroxybutyrate-co-hydroxyvalerate = PHBV, hydroxyvalerate = HV, which correlated well with the HV and 4HB content in the samples. The biodegradation of the investigated PHAs occurred by enzyme-catalyzed, microbial, surface erosion. HBV-20 showed the fastest biodegradation rate after 15 days; however, all samples had a similar extent of biodegradation after 15 days (around 15–25 %). After 70 days of the measurement, no further increase of the biodegradation was detected for all samples, including the reference material cellulose, which reached around 83 %. After 70
Fig. 6. Examples of composting evaluation using different setups of different complexity. A. Method based on ISO 14855–1. B. Respirometric biodegradation flask system according to the ASTM D6400 standard. C. Scheme of the Microbial Oxidative Degradation Analyzer (MODA) according to ISO 14855–2. Sources: A. Kunioka et al., 2006. B. Anstey et al., 2014. C. Funabashi et al., 2009.
days, all PHAs biodegraded between 80 and 90 %, depending on the comonomer composition (with PHBV-40: 90.5 %, PHBV-20 = 89.3 %, PHBV-3 = 80.2 %, P(3HB,4HB) = 90.3 %, PHB = 79.7 %) according to ISO 14855–1. An over-time overview of the film degradation is shown in Fig. 8.

Gutierrez-Wing et al. (2011) used ASTM standards to study the degradation of PHB and PHB plasticized with tributyl citrate (TBC) under composting conditions in an especially designed reactor. For the ASTM 5338–98, 2003 standard, the compost consisted of horse bedding, tree trimmings, wood shavings and bark with a C:N ratio of 30:1 (30 parts carbon for each part nitrogen by weight). Degradation of three different plates with thicknesses of 0.24, 1.2 and 5 mm were studied at 58 °C and a moisture content of 55 %. Complete degradation of the 0.24 and 1.2 mm thick plates was detected after 16 weeks. However, the 1.2 mm thick plate degraded slightly faster, which is unusual. The 5 mm thick plate did not reach complete degradation after 16 weeks. Additionally, with ASTM 5929–96, 2004 standard, the compost consisted of shredded virgin newsprint, pine bark, corn starch, corn oil, bovine casein, urea and a buffer/nutrient solution with a C:N ratio of 35:1. The study was performed with 0.5, 1.2 and 3.5 mm thick plates, a lower temperature (40 °C) and the same moisture content as above. Findings showed the 0.5 and 1.2 mm thick plates degraded completely after 26 weeks. The 3.5 mm thick plate did not reach complete degradation after 16 weeks. A lag time of 84 days was found.

Fig. 7. A. Photos of the PLA bottles exposed at 30 day of compost conditions. B. Weight change (●) over time of d) PLA bottles, e) trays and f) deli containers under real composting conditions. C. Physical changes to PLA coupons buried in compost. A) before burial; B) after 1 year burial at 25 °C; C) after 1 year burial at 37 °C; D) after 10 weeks of burial at 45 °C; E) after 2 months of burial at 50 °C; F) after 1 month of burial at 55 °C in compost. Scale bar represents 2 cm. Sources: A. & B. Kale et al., 2006. C. Karamanlioglu and Robson, 2013.
results of this study indicate that an initial mass:initial surface area ratio lower than 67 mg cm\(^{-2}\) allows complete degradation in compost in less than 4 months. When the plates become thicker, the initial mass:initial surface area ratio increases and complete degradation takes longer. Interestingly, the additive TBC slowed down the degradation rates of PHB significantly, indicating that additive-use in bioplastics needs to be screened and carefully considered.

2.3. Biodegradation of PBS in compost.

Zhao et al. (2005) studied the composting of PBS using compost of the municipal solid waste facilities by Nangong Compost Factory (Beijing, China) as the inoculum. Three PBS samples (powder, film, granules) were mixed with the compost. Composting was performed according to ISO 14,855 at 58 °C. With increasing the surface of the PBS sample, the biodegradation rates increased, reaching around 72 % biodegradation for powder after 90 days (61 % for films, 14 % for granules, respectively).

Sasimowski et al. (2021) studied the biodegradability of PBS in bioreactors filled with compost from a local waste management facility. Degradation was measured in a bioreactor with a temperature of 58 °C and a humidity of 60 % for 70 days. They found a weight loss of 0.06 % per day, with 4.5 % after 70 days.

Anstey et al. (2014) studied the biodegradation under composting conditions of PBS and PBS composites with biobased fillers by a respirometric biodegradation flask system (Fig. 9. A.). Their 3-month-old compost consisted of 48 % of dry solids and 52 % of volatile solids with a pH of 7.5 and a C:N ratio of 8.5. Temperatures of 58 ± 2 °C and moisture content of 50–55 % were used. These conditions are suitable for mesophilic and thermophilic microorganisms in organic mature compost environments. The pure PBS reached 90 % biodegradability in 160 days, the mixing of different biofillers affected the composting kinetics significantly. Compared to the results obtained by Sasimowski et al. (2021) after 70 days, this study found a much higher degree of biodegradation (4.5 % vs 20 %): different environmental test conditions have a strong influence on the overall biodegradation.

Puchalski et al. (2018) studied the biodegradability of commercially available PBS and polybutylene succinate adipate (PBSA) copolymers in...
compost under laboratory conditions (ISO 20200:2016) for 24 weeks. The compost had a pH of 7, a temperature of 58 ± 2 °C, a moisture content of 53.1 % and contained 3.2 × 10^7 cfu/g (colony forming unit) microorganisms. What is interesting about this study compared to the other two is that the authors did not only consider the weight loss but also investigated the mechanical properties during the biodegradation process. They found that the sample began to fragment after 6 weeks and the stress and elongation at breakpoint of PBS after 4 weeks decreased from 34.8 MPa to 12.7 MPa (tested via ISO-527–2-1A). After 24 weeks, the PBS sample showed a weight loss of 30 %, with a degree of crystallinity that increased making the sample more brittle, attributed to degradation of the glassy parts of the sample. The increase of crystallinity is a result of the hydrolysis and enzymatic degradation (Fig. 9. B shows photographs of the investigated sample varying with time).

2.4. Biodegradability of PCL in compost.

Krasowska et. al (2016) studied the biodegradability of PCL in compost over a period of 3 months. The compost pile consisted of dehydrated sewage sludge, burnt lime and straw and had a temperature ranging between 16.6 and 19.2 °C, a pH ranging between 5.8 and 7.8 and moisture content ranging from 42.4 to 45.8 %. The values differ because natural conditions are used and therefore fungi could play the main role in the degradation process. The results showed a weight loss of 5.6 % after 2 weeks and 86.3 % after 4 weeks. Disintegration of PCL in the compost was observed faster (after 5 weeks) than in studied aqueous environments because of more favorable biotic and abiotic conditions in compost.

Kalita et al. (2020) studied the biodegradation of PCL under composting conditions. Their compost contained vegetable waste, cow dung, sawdust and dried tree leaves; incubation was done at 58 ± 5 °C at around 60 % relative humidity. Here, after 4 weeks, a weight loss of around 55 % was obtained. After 90 days, a weight loss of 81 % was obtained. In the same paper, also the biodegradation of PLA and PLA-PCL blends was investigated. The PLA samples showed a weight loss of 86 % indicating a higher percentage of biodegradation compared to PCL. SEM images of the two polyester samples after different times are shown in Fig. 10 indicating a significant degree of degradation. Also, Richert and Dąbrowska (2021) compared the biodegradation of PLA with PCL under composting conditions at 20 °C for 7 days. However under these conditions, the opposite trend was found: they concluded that PCL showed faster degradation based on biological oxygen demand as indicator of the intensity of organic matter transformation. In general, these two examples show clearly how important the experimental conditions are and that drawing conclusions is difficult. Relative statements concerning how fast a certain polymer biodegrades have to be carefully evaluated.

2.5. Comparison of the composting performance between PLA, PHB, PBS and PCL

Several studies reported individually on the biodegradation of different polymers; however, to compare the performances between the different polymers, degradation tests need to be studied under the same composting conditions. The composting of PLA and PCL (of different suppliers) was investigated following ISO 14855–2 standard using a Microbial Oxidative Degradation Analyzer (at 58 °C) (Funabashi et al., 2009). Powders (around 125–250 µm) and pellets of both polymers were analysed, indicating different composting kinetics dependent on the supplier and an overall faster composting of PLA compared to PCL in this study. The anaerobic degradation of PCL and PLA at 55 °C for biogas production showed 54–60 % of the theoretical biogas production for PCL, while PLA gave higher values between 56 and 80 % (Smějkalová et al., 2016). A comparison for all polymers was conducted by Hosni et. al who studied the biodegradation of polymer discs under controlled compost conditions over a period of 10 months with varying temperature (i.e., 25, 37, 50 °C) (Al Hosni et al., 2019). This study reported the changes in the mechanical properties and the weight loss of the specimen to evaluate biodegradation. The compost used had a moisture content of 35 %, a water holding capacity of 75 % and a pH of 7.1. To measure the weight loss, discs were weighed and reburied every week. Fungal growth was evaluated via scanning electron microscopy (SEM). The discs had an average thickness of 3 mm and diameter of 1 cm. As shown below, all polymers degraded in compost at 50 °C with PCL having the fastest rate of degradation showing a complete degradation after 91 days under these conditions. The tensile strength was already

![Fig. 10. SEM images representing the test sample before biodegradation and after biodegradation under composting conditions. Source: Kalita et al., 2020](image_url)
significantly reduced after 2 weeks. Under the same conditions, PLA showed complete degradation after 269 days, while PHB and PBS did not show complete degradation in the 10 months of the study; weight loss of 95.4 ± 2 % (for PHB) and 56.6 ± 5.03 % (for PBS) were reported. When the temperatures were reduced to 25 or 37 °C, degradation rates decreased only slightly for PHB, but significantly for PCL. Even more pronounced, no degradation was detected for PLA and PBS at 25 and 37 °C. These results underline the importance of temperature during composting for different polymers, related to their thermal properties. From this study, it can be concluded that there is a trend for biodegradation at 50 °C under composting conditions such as PBS < PHB < PLA < PCL (Fig. 11).

Al Hosni et al. (2019) further identified fungal strains present on the respective polymer specimen; a summary is shown in Table 2. PCL and PHB proved the greatest diversity of fungal taxa, which can explain their most pronounced weight loss at all temperatures. In contrast, for PLA and PBS, fungal strains were detected on the sample surfaces only at 50 °C. These differences can be due to molar mass, hydrophobicity or crystallinity which influence the microbial attachment. In addition, a higher degree in hydrophilicity will lead to higher degrees of hydrolysis. A summary of all the different studies above is shown in Table 3 and Fig. 12.

From the comparison of the different studies regarding the 4 polyesters (Fig. 12), it is obvious that the testing conditions play a crucial role to evaluate the stability or the degradation rates during composting.

ISO 14,855 and ASTM D6400/5338 contain criteria to certify a material as compostable by determining its biodegradability. Above, several findings are discussed and every paper uses different testing conditions, even though some meet the same ISO and ASTM standards. This is because requirements by most standards only broadly stipulate the use of municipal sewage sludge or mature compost that are subject to biases such as pH, humidity, and microbial strains (Lim and Thian, 2022). Therefore, further comparison of the stability polyesters is hard or even impossible. Weng et al. (2011) and Zhao et al. (2005) for example both used ISO 14,855 but different pH, sizes and shapes of the specimen. The same occurred for the studies following the ASTM 5338 standards: Kalita et al. (2020) and Gutierrez-Wing et al. (2011) both used this standard but differed in moisture content and compost composition.

It has become clear that apart from polymer characteristics (e.g., molar mass, degree of crystallinity, tacticity), environmental conditions are extremely important for the degradation kinetics. From the papers discussed in this review article, it can be concluded that the degradation is more effective at high temperatures, e.g. in industrial composting facilities and under aerobic conditions. At higher temperature, multiple activities are elevated such as polymer chains with a higher mobility, microbial enzymatic activity rate which is higher, and oxygen diffusion and hydrolysis which are also faster compared to lower temperatures.

### Table 2

| Polyester | 25 °C | 37 °C | 50 °C |
|-----------|-------|-------|-------|
| PCL       | 3     | 2     | 2     |
| PHB       | 2     | 1     | 2     |
| PLA       | None  | None  | 3     |
| PBS       | None  | None  | 1     |

Fig. 11. Weight change over time of polymer discs buried in compost at different temperatures.

Source: Al Hosni et al., 2019
Especially, at temperatures above the $T_p$, the polymer transitions from the glassy to the rubbery phase and becomes more flexible and therefore experiences a higher rate of degradation. Second, mature solid compost is mostly used containing a high water content (around 50%). Presence of moisture supports microbial activities and enables the acceleration of biodegradation and is a mandatory component in the hydrolytic process for fracturing of polymer chains (Lim and Thian, 2022). Size and shape of the specimen also influence the degradation speed (Funabashi et al., 2009; Weng et al., 2011; Zhao et al., 2005). Large polymers with high molar mass or with shapes that offer large surface area for exposure to moisture and microbes will undergo faster rate of degradation (Lim and Thian, 2022). At last, thermophilic microorganisms (inoculum) are important: microorganisms play a role in the biodegradation of the polymers and is a non-discretionary factor in biodegradation and microbial enzyme is substrate specific. Therefore, one microorganism can support the degradation of one polymer but not of another. Streptomyces, for example, degrade PHB but do not degrade PBS and PLA at all; Bacillus is able to reach 100 % degradation of PCL but almost no degradation for PBS, PHB, and PLA occurs (Tokiwa and Calabia, 2004). Therefore, identification of polymer-degrading microbes and their metabolic pathways are necessary for the development of microbial and genetic engineering strategies to improve efficacy of biodegradation of polymer waste (Lim and Thian, 2022).

### Table 3
Summary of selected composting studies of PLA, PCL, PHB and PBS.

| Polyester | Degradation method | Findings | References |
|-----------|--------------------|----------|------------|
| PLA bottles | No ASTM – Compost containing cow manure, wood shavings and waste feed that cows do not eat. | $T_p$ decreases of 0.97 °C/day | Kale et al., 2006, 2007a; Kale et al., 2007b |
| PLA trays | No ASTM – Compost containing cow manure, wood shavings and waste feed that cows do not eat. | No significant weight loss | Kazamanioglu and Robson, 2013 |
| PLA deli containers | No ASTM – Mature green compost from the Compost Shop UK at 25 °C | 37 °C: 20 % weight loss after 12 months; 45 °C: 57 ± 4 % weight loss after 9 weeks; 50 °C: 44 ± 6 % weight loss after 5 weeks | Richert and Dąbrowska, 2021 |
| PLA coupons | No ASTM – Mature green compost from the Compost Shop UK at 25 °C | 37 °C: 122 mg O$_2$/L oxygen consumption after 7 days of incubation; 50 °C: 100 % weight loss after 275 days | Al Hosni et al., 2019 |
| PLA | ASTM D5338-15 | 86.3 % degradation after 4 weeks | Krasowska et al., 2016 |
| PLA sheets | No ASTM – Commercial compost from the Compost Shop UK at 25 °C | 37 °C: 140 mg O$_2$/L oxygen consumption after 7 days of incubation | Richert and Dąbrowska, 2021 |
| PCL films | No ASTM – Municipal waste treatment plant in Glyfada containing dehydrated sewage sludge, burnt line and straw at ~ 18 °C | 86.3 % degradation after 4 weeks | Krasowska et al., 2016 |
| PCL films | No ASTM – Compost extract of microorganisms and Ringer’s solution | 50 °C: 140 mg O$_2$/L oxygen consumption after 7 days of incubation | Richert and Dąbrowska, 2021 |
| PCL | ASTM D5338-15 | 81 % weight loss in 90 days | Al Hosni et al., 2019 |
| PCL sheets | No ASTM – Commercial compost from the Compost Shop UK at 25 °C | 37 °C: 79.6 ± 3.3 % weight loss after 10 months | Al Hosni et al., 2019 |
| PHB films | No ASTM – Compost extract of microorganisms and Ringer’s solution | 50 °C: 100 % weight loss after 91 days | Al Hosni et al., 2019 |
| PHB 0.24 mm plate | ISO 14855-1:2005, compost factory organic waste | 99-100 % weight loss after 112-140 days | Gutierrez-Wing et al., 2011 |
| 1.2 mm plate | ASTM D5338-98 (2003) | 1.2 mm plate: 98-100 % weight loss after 84-112 days | |
| 5 mm plate | ASTM D5929-96 (2004) | 5 mm plate: 45 % weight loss after 210 days | |
| 0.5 mm plate | ASTM D5929-96 (2004) | 0.5 mm plate: 100 % weight loss after 26 weeks | |
| 1.2 mm plate | ASTM D5929-96 (2004) | 1.2 mm plate: 100 % weight loss after 26 weeks | |
| 3.5 mm plate | ASTM D5929-96 (2004) | 3.5 mm plate: 96 % weight loss after 50 weeks | |
| PHB sheets | No ASTM – Commercial compost from the Compost Shop UK at 25 °C | 37 °C: 59.4 ± 4.0 % weight loss after 10 months | Al Hosni et al., 2019 |
| PBS | ASTM D6400 – organic mature compost | 37 °C: 1.5 % weight loss after 10 months | Al Hosni et al., 2019 |
| PBS sheets | ISO 20200:2016 | 50 °C: 95.4 ± 2.0 % weight loss after 10 months | |
| PBS (and wheat bran biocomposites) | ISO 20200:2015 | 4.5 % weight loss after 70 days | Sasimowski et al., 2021 |
| PBS (and composites) | ASTM D6400 – organic mature compost | 90 % degradation in 160 days | Anstey et al., 2014 |
| PBS | ISO 20200:2016 | 30 % weight loss after 24 weeks | Puchalski et al., 2018 |
| PBS sheets | No ASTM – Commercial compost from the Compost Shop UK at 25 °C | 37 °C: 3.5 ± 1.5 % weight loss after 10 months | Al Hosni et al., 2019 |

3. Conclusions and outlook

Due to the longterm effects of petroleum-based plastics on the environment and the scarcity and increasing price of oil, compostable (and bio-based) polymers have gained more interest over the past decades with composting as a possible end-of-life scenario in waste management. Compostable polymers, especially bio-based polymers, have attracted a lot of interest in both research and industry. The global demand for renewable polymers is growing steadily as improved processing technologies and the effect of scaling up have driven down the price of compostable polymers. Further studies are needed to extend the use of compostable polymers. Ensuring that bioplastics are compostable is important in the food packaging sector. Correct certification with composting standards would address the problems of contamination of
plastics by food residues, which leads to their rejection in sorting centres and the poor management of food waste. Nevertheless, as often for the biodegradation field, every study uses their own conditions, such as compost ingredients, water-content, pH, temperature, sample size, sample composition (additives, molar mass, molar mass dispersity, crystallinity, thermal history, etc.) making it complicated or impossible to compare data between different papers. Therefore, it is recommended to replicate some of the studies with different polyesters but under the same conditions to assemble a general matrix on polymer composting properties. For this, also each polymer needs to be characterized in detail to report crystallinity, molar mass characteristics and possible additives or impurities. Additionally, not many academic studies performed tests under ISO/ASTM standards in compost, which makes it even harder to replicate the study; thus, it would be a large contribution to literature to extent this database. Therefore, development of new approaches to polymer chemistry and macromolecular design, improved recycling infrastructure and consumer awareness, standardisation of regulations and policies, will contribute to the implementation of biodegradable and compostable polymers in a variety of areas.

Declaration of Competing Interest

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

Data availability

No data was used for the research described in the article.

References:

Al Hosni, A.S., Pittman, J.K., Robson, G.D., 2019. Microbial degradation of four biodegradable polymers in soil and compost demonstrating polycaprolactone as an ideal compostable plastic. Waste Manage. 97, 105-114.

Allotta, L., Seggiani, M., Lanzeri, A., Gigante, V., Cinelli, P., 2022. A brief review of poly (Butylene Succinate) (PBS) and Its Main copolymers: synthesis, blends, composites, biodegradability, and applications. Polymers 14, 844.

Alves Mariane, I., Macagnan Karine, L., Rodrigues Amanda, A., de Assis Dener, A., Torres Matheus, M., de Oliveira Patrícia, D., Lígia, F., Vendruscolo Claire, T., Moreira Angelita da, S., 2017. Poly(3-hydroxybutyrate)-P(3HB): Review of Production Process Technology. Industrial Biotechnology 13, 192-208.

Amadu, A.A., Qiu, S., Ge, S., Addico, G.N.D., Ameke, G.K., Yu, Z., Xia, W., Abbew, A.-W., Shao, D., Champagne, P., Wang, S., 2021. A review of biopolymer (Poly-β-hydroxybutyrate) synthesis in microbes cultivated on wastewater. Sci. Total Environ. 756, 143729.

Anstey, A., Muniyasamy, S., Reddy, M.M., Misra, M., Mohanty, A., 2014. Processability and biodegradability evaluation of composites from Poly(butylene succinate) (PBS) Bioplastic and Biofuel Co-products from Ontario. J. Polym. Environ. 22, 209-218.

Aoyagi, Y., Yamashita, K., Doi, Y., 2002. Thermal degradation of poly [(R)-3-hydroxybutyrate], poly [ε-caprolactone], and poly [(S)-lactide]. Polym. Degrad. Stab. 76, 53-59.

Becker, G., Wurm, F.R., 2018. Functional biodegradable polymers via ring-opening polymerization of monomers without protective groups. Chem. Soc. Rev. 47, 7739-7792.

Berger, C., Laurent, F., 2019. Trunk injection of plant protection products to protect trees from pests and diseases. Crop Prot. 124, 104831.

Chrissafis, K., Paraskevopoulos, K.M., Bikaris, D.N., 2005. Thermal degradation mechanism of poly(ethylene succinate) and poly(butylene succinate): comparative study. Thermochim Acta 435, 142-150.

Czerniecka-Kubińska, A., Fracz, W., Jasiorski, M., Blazażewski, W., Pilch-Pitera, B., Pyda, M., Zarzycka, I., 2017. Thermal properties of poly(3-hydroxybutyrate) modified by nanoclay. J. Therm. Anal. Calorim. 128, 1513-1526.

Endres, H.J., Siebert-Raths, A., 2012. 10.19 - Performance profile of biopolymers compared to conventional plastics. In: Matyjaszewski, K., Möller, M. (Eds.), Polymer Science: A Comprehensive Reference. Elsevier, Amsterdam, pp. 317-353.
