

More than PHB – the PHAmily of Copolymers: Justifications for Broader Use and Summary of Biodegradation Facts on Polyhydroxyalkanoates (PHA) – A Review



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Review

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Globally, a significant portion of plastics are mismanaged, ultimately ending up in the environment. While reducing, reusing, and recycling plastics should be the preferred end-of-life scenarios, biodegradable plastics are compatible with all of these routes and represent a promising alternative. Polyhydroxyalkanoates (PHAs), a family of polyesters synthesized by various microorganisms, stand out in this regard. The most common type of PHA, poly(3-hydroxybutyrate) (PHB), is particularly relevant as it is both biobased and biodegradable. Additionally, there is substantial knowledge about this thermoplastic polyester, its applications, and its commercial availability. However, over 150 other PHA building blocks have been identified, with some having been tested and developed for various promising applications. Despite this, not all PHA copolymers have been fully evaluated for their biodegradability across diverse environmental conditions. Nevertheless, due to their biosynthesis in living microorganisms, a good degree of biodegradability is expected. Moreover, PHAs can also be chemically recycled into valuable chemicals, positioning them as the biobased polymer with the most versatile end-of-life options. This review summarizes the current state of knowledge on PHA copolymers, their current end-of-life pathways, the most relevant biodegradability standards, and their degradability by depolymerase enzymes.

Keywords

biodegradation, polyhydroxyalkanoates (PHAs), mismanagement, plastic waste, microplastics, circularity

Introduction

Plastics are engineering materials composed of at least one polymer and various additives, such as nucleating agents, colorants, fillers, processing aids, plasticizers, and stabilizers. They can be grouped into thermoplastics, elastomers, and thermosets. Traditional plastics, primarily derived from fossil resources, have been valued for their durability

since their mass market introduction 75 years ago. Plastics play a vital role in everyday life, serving essential functions across a multitude of settings. They are abundantly used in industrialized and emerging countries, with per capita consumption exceeding 100 kg annually in some countries. Despite significant efforts, the global recycling rate of plastics remains low, hovering around 10 % (according to current data published by Plastics Europe, see Fig. 1)¹. This is in spite of continued efforts by the plastics industry to considerably increase that rate. The diversity of plastic materials

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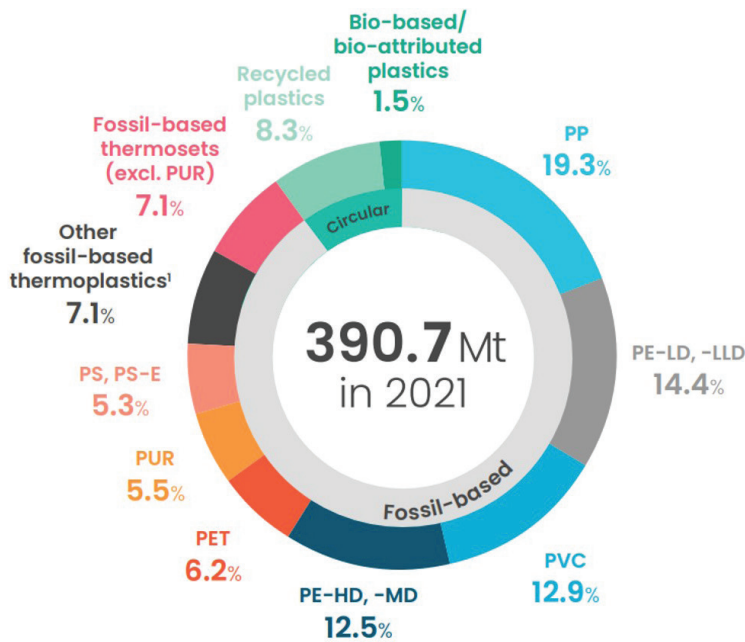


Fig. 1 – Out of the 390.7 million tons of plastics covered in the *Plastics Europe 2022 dataset for global plastics production in 2021* (thermoplastics & thermosets), the fractions of post-consumer recycled plastics and bioplastics are only 8.3 % and 1.5 %, respectively¹. Reproduced with permission from *PlasticsEurope*.

– ranging from compounds to composites – and the wide variety of products pose significant challenges for effective and efficient recycling. Additional barriers include scant motivation and incentives for recycling, and the low value of recycled materials.

From 1950 to 2015, the annual growth rate of plastics production increased from 2 million tons/year to 380 million tons/year, representing an annual growth rate of 8.4 %, which is 2.5 times faster than the increase in global gross domestic product over the same period². During this time, the properties of plastics improved and diversified through copolymerization, compounding, and processing. These developments enabled plastics, particularly polyolefins, to replace traditional, heavier, more expensive materials such as glass and metals. Plastics are remarkably cost-effective, characterized by low price per kilogram, low density, low-cost mass production, and ease of use. For example, plastics can be colored throughout, directly injection-molded into final complex shapes without machining, and joined through mechanisms like snapfit connections, eliminating the need for fasteners typically required with other materials. In addition, plastics offer valuable properties such as electrical and thermal insulation, as well as resistance to water, diluted acids and bases, solvents, and various other agents.

Due to their low cost and density (significantly reducing the cost of transportation), plastics have increasingly been used for single-use items, driven by the absence of material scarcity or economic necessity to reuse or recycle these products. However, the externalized costs of this approach are immense, although they are not currently borne by the plastics value chain, creating little incentive for change. The externalized costs of fossil-based plastics use in packaging are estimated at 3.17 trillion US\$/year³. These costs include plastic waste management and healthcare related to diseases caused by exposure to plastics. This corresponds to 18.5 US\$/kg (17.3 €/kg) of plastics, or 1.7 Eurocents for a single plastic bag! In other words, the true costs of fossil-based, non-degradable plastics exceed their current market price by far. Even carbon credits priced at 100 €/ton would only account for a fraction of the actual costs when considering the full life cycle of plastics. It is clear that sustainable solutions are urgently needed.

Currently, the packaging industry globally consumes approximately half the plastics materials produced per year. Geyer *et al.* estimated that, out of the 8.3 billion tons of cumulative plastics production up to 2015, only 2.5 billion tons remain in use, while 4.9 billion tons have been discarded (see Fig. 2)².

A significant portion of discarded plastics is now found in landfills, in the open environment, in basically all ecosystems. Despite society's progress and in recognizing and addressing unsustainable production and disposal practices for many materials, the issue of plastic waste has seen little fundamental change. Plastic waste can be considered hazardous due to its potential to generate persistent microplastics and release harmful additives into the food chain. However, it is neither classified nor managed like other types of hazardous waste, which is a fundamental problem in the continued mismanagement of 90 % of plastic waste.

Linear economy

The linear economy “take-make-use-dispose” model exerts significant strain on the environment. Fossil resources are being depleted, and waste accumulates in landfills and ecosystems when not incinerated – releasing CO₂ and contributing to greenhouse gas emissions and climate change. Since the largest portion of plastic materials is used in short-lived products, these items become waste after a few days (packaging), several years (consumer goods), or a couple of decades (building and construction). It is estimated that approximately 8 % of crude oil is consumed by the plastics industry, with half of that embodied in plastic products and the other half used in their manufacturing. At the end of

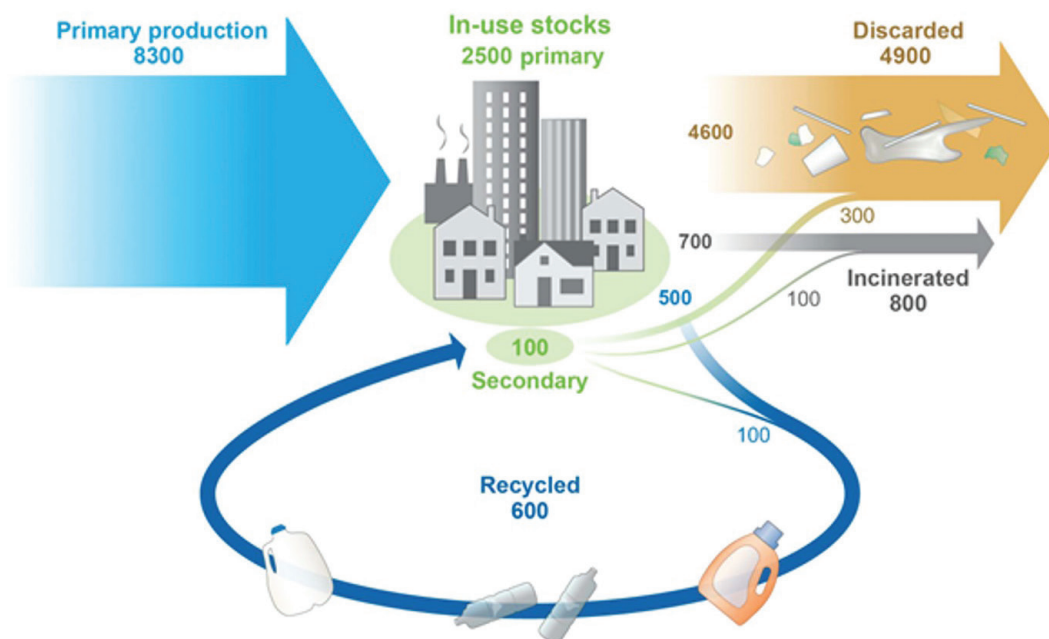


Fig. 2 – The mass flow of all plastics ever produced shows that the benefits of the largest part of it are long gone, but waste persists². Reproduced with permission.

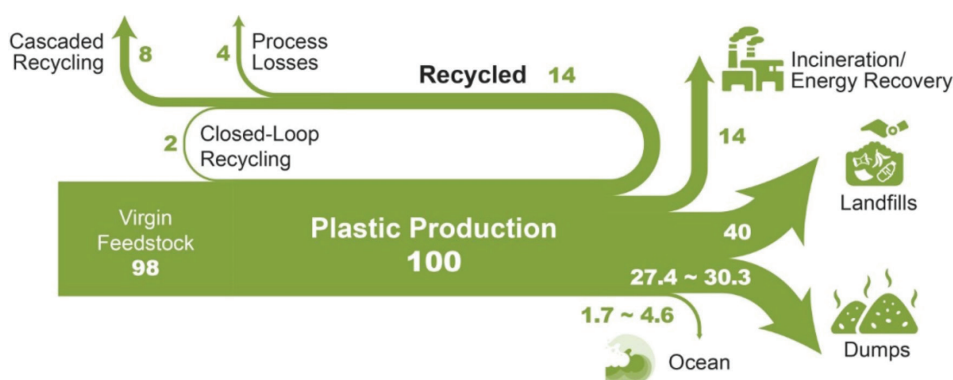


Fig. 3 – Source: Material flow of plastics packaging today, globally. A textbook example of “linear economy”⁵. Licensed under a Creative Commons Attribution 3.0.

their life cycle, a large fraction of plastics is incinerated for energy recovery (misleadingly termed “thermal recycling”), generating additional fossil carbon emissions⁴.

This linear use of plastics is further illustrated in the Sankey diagram (Fig. 3), which highlights the material flow of plastics for packaging — both the largest-volume and the shortest-lived application⁵.

There is little incentive to recycle plastics, and the majority is discarded after use. Unfavorable end-of-life scenarios arise not only from mismanagement but also from product design. Furthermore, the inherent properties of plastics can lead to unfavorable outcomes, such as the shedding of persistent micro- and nanoplastics throughout various phases of their life cycle. In other words, even with complete collection and recycling, the problems caused

by persistent plastics cannot be fully resolved. Addressing the root cause is essential. Given the vast amount of annual plastics output, even a small fraction of leakage into the environment cannot be neglected. Over the past decade, as attention has shifted toward plastic littering, increasing number of reports have documented plastic waste in all types of ecosystems at all levels, from macroplastics to meso-, micro-, and nanoplastics.

Circular economy

The polymer industry is in urgent need of a paradigm shift to become more circular in the very near future. While the industry has long been recognized for its contributions to job creation, economic growth, convenience, along with other benefits, the public’s perception in recent years has shifted due

to the escalating issue of plastic waste. The widespread presence of microplastics and macroplastics across virtually all ecosystems — despite increasing environmental awareness, health concerns, evolving regulations, and technological advances — has highlighted our inability to manage plastic waste effectively.

Concepts or blueprints for a circular economy of plastics, such as those developed by the Ellen MacArthur Foundation⁶, emphasize the need for both technological advancements and behavioral changes. However, transitioning to this model would impact the cost of plastics. Numerous local, regional, national, and global incentives and initiatives have been introduced to promote recycling, such as bottle deposit systems, school-based education programs, public awareness campaigns, and public (co-)funding for recycling technology development. Additionally, regulations like the EU's Single-Use Plastics Directive (EU 2019/904)⁷, have been enacted to curb the wasteful use of plastic.

Sustainability has become increasingly important in recent years in the communication of several market players, partly driven by voluntary action and to some extent in response to sustainability reporting requirements, particularly within the EU⁸. Consumers are now presented with more products made from recycled materials, ranging from recycled polyethylene (rPE) and recycled polypropylene (rPP) shopping bags to recycled poly(ethylene terephthalate) (rPET) bottles and casings for appliances like coffee machines, and many more. However, the recycling process is often exploited for marketing purposes, even though current plastics recycling technologies contribute significantly to microplastic pollution¹². Bioplastic products remain less common and are heavily dependent on local laws and initia-

tives. Still, 90.2 % of plastics are virgin materials derived from fossil sources¹, a stark contrast to the high levels of circularity achieved already decades ago for other materials such as steel and paper. Steel and paper are efficiently recycled due to their higher market value per unit volume, established collection systems, and relatively low material variability, unlike the complex assortment of plastic products. Steel scrap and waste paper have long been effectively reclaimed and recycled, whereas plastic recycling has lagged behind. More than a decade ago, Plastics Europe reported the post-consumer plastic waste (PC waste) recycling rate of 22.5 % (Fig. 4):

As shown in Fig. 4, already 15 years ago the industry praised its recycling initiatives. As shown further, the facts depict a disappointing picture: the actual recycling rates remain far from making the industry truly “green”. Fig. 5 compares the post-consumer (PC) waste treatment data from 2009 and 2020 on a country-by-country basis.

Comparing the two charts in Fig. 5 shows improvements in the recycling rates of several countries, and energy recovery (waste incineration) has increased due to bans on landfilling organic waste (e.g., “Council Directive 1999/31/EC on the landfill of waste” in the EU of 26 April 1999). However, the plastics industry remains predominantly linear. As Li *et al.* aptly summarized, “Less than 10 % of the plastics generated globally are recycled, while the rest are incinerated, accumulated in landfills, or leak into the environment⁵.”

Currently, the plastics recycling rates within the EU vary, from 21 % in Finland to 45 % in the Netherlands, with Norway (non-EU country), Spain, and Germany achieving recycling rates above 40 %¹. The EU's targets for plastic recycling are 50 % by 2025 and 60 % by 2030¹¹⁹.

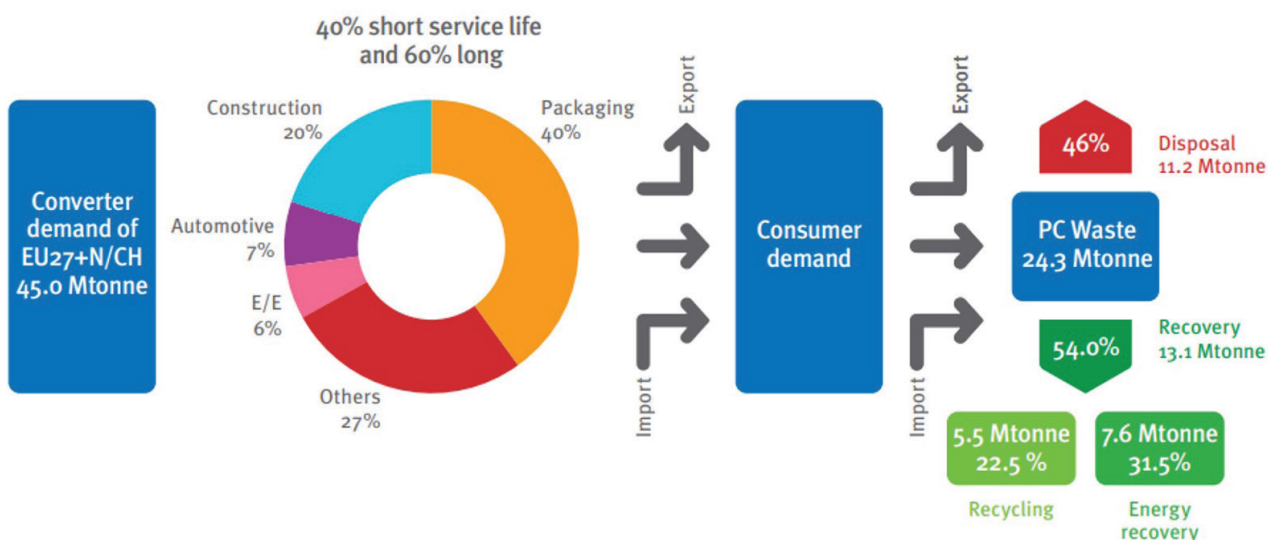
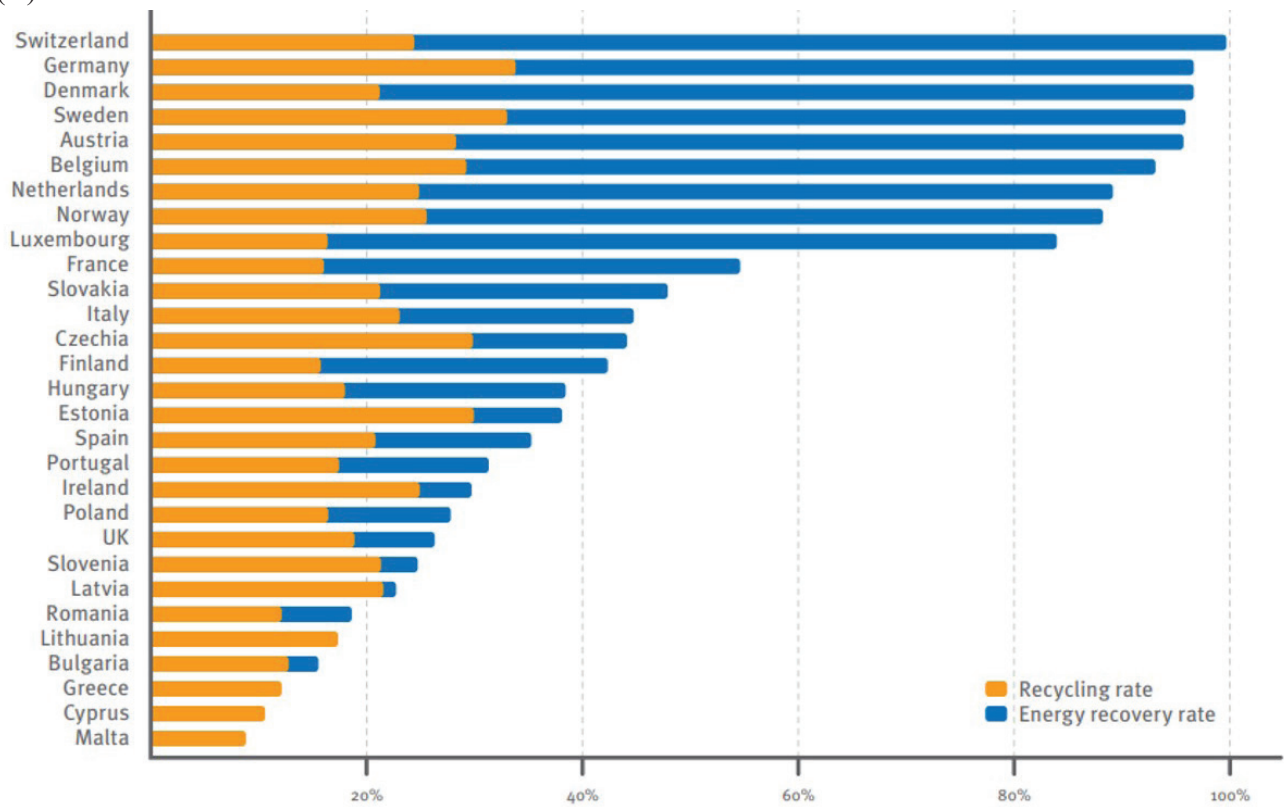


Fig. 4 – In 2009, Europe's plastics recycling rate was reported at 22.5 %⁹. In 2024, despite 15 years of ongoing efforts, the rate has only slightly improved. PC = post-consumer; E/E = electric/electronic.

(A)



(B)

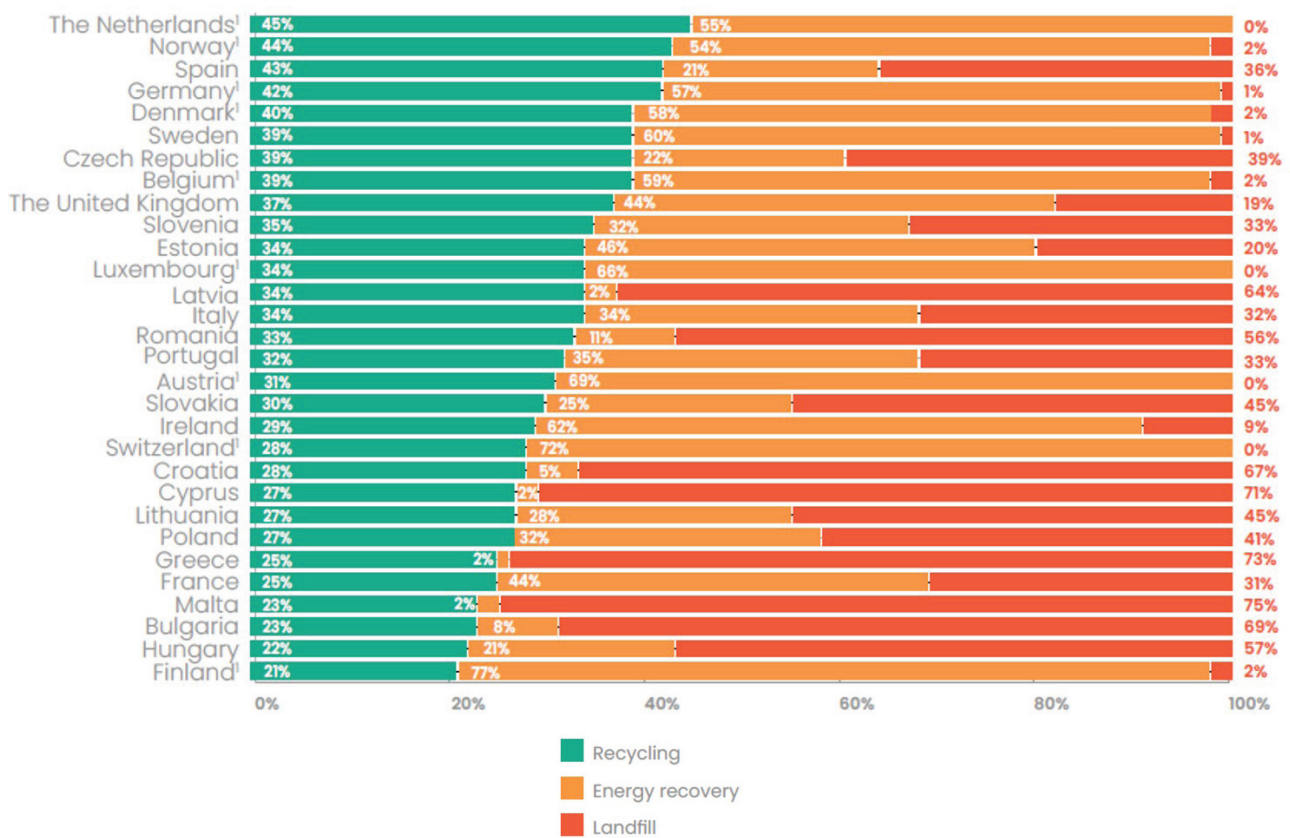


Fig. 5 – Comparison of plastics recycling rates across European countries in 2009 (A) and 2020 (B). Source: Plastics Europe (2022)¹: Countries with landfill restrictions.

Overall, the incremental increases in recycling rates have not kept pace with the ever-growing demand for plastics. In fact, the total volume of plastic waste continues to rise annually. High plastic recycling rates can be achieved when specific materials are separately collected, as seen in packaging (e.g., PET bottles). In agriculture and the construction sector, high recycling rates have also been achieved¹ due to the limited variety of materials. However, the increasing trend toward composite materials and complex, multi-material products poses significant challenges to post-consumer plastic recycling. In-process recycling, such as reworking defective batches or sprues in injection molding, is only a second best solution, as it still consumes energy and could be avoided by using more efficient processes, such as hot runner systems.

Waste incineration (“thermal recycling”) has been considered a viable end-of-life option for contaminated plastics items or composites. When reuse and recycling are prioritized before incineration, a cascaded use is achieved. However, it is essential to recognize that incineration generates additional fossil-based CO₂ emissions, contributing to global warming, even if the materials can replace other fuels. Incineration also produces toxic gases, such as hydrochloric acid¹⁰ and dioxins¹¹, which are only captured in modern waste incineration facilities. Waste incineration may also be considered for biobased and biodegradable plastics that do not degrade into valuable compost. In such cases, the same mineralization products are produced as in traditional incineration, but with the added benefit of energy recovery, which can be used for applications such as combined heat and power. This approach might be advantageous for contaminated products or packaging materials.

Recycling options for thermosets and elastomers are more limited than for thermoplastics, where remelting (mechanical recycling) offers a more straightforward route, typically resulting in lower-quality end products when post-consumer waste is used. Due to the crosslinked nature of thermosets and elastomers, they need to be disposed of after their (first) use, as mature technologies for feedstock recycling do not yet exist. It is clear that the recycling rate of plastics needs to increase significantly. Currently, global recycling averages only 9 %, with the best-performing European countries achieving 40–45 %. However, the target has to approach 100 %, as seen with materials like glass, paper, and scrap metals. Society can certainly do much better in collecting, sorting, and reusing plastics through upcycling or downcycling processes, while also managing possible micro- and nanoplastics emissions. Even with optimized plastic collection

and recycling systems, some plastic leakage into the environment will remain unavoidable¹². “Leakage” refers to plastics that inadvertently end up in nature, whether in terrestrial or aquatic ecosystems, often through unintended means such as floods or natural disasters. Plastics used in emergency situations, such as humanitarian aid, can also tend to be discarded in nature. These materials should be inherently degradable to mitigate environmental damage, similar to the challenges posed by PFAS (per- and polyfluoroalkyl substances), which persist in the environment globally, creating issues that are not yet fully understood¹³.

A recent OECD (Organisation for Economic Co-operation and Development) report, entitled “Global Plastics Outlook: Policy Scenarios to 2060” states the following based on 460 million tons of plastics produced in 2019¹⁴:

- Plastics are not circular: globally, only 9 % of plastics were recycled, 19 % were incinerated, 50 % went to sanitary landfills, and 22 % ended up in “uncontrolled dumpsites, [were] burned in open pits, or leaked into the environment”. Plastics leakage into the environment: Of the 22 million tons of plastic that entered the environment, 88 % were macroplastics. Microplastics (particles smaller than 5 mm) primarily came from tire abrasion, textile washing, and brake wear.

- Accumulated plastics in the environment: Rivers hold an estimated 109 million tons of plastic waste, while oceans contain 30 million tons. In 2019 alone, an additional 6.1 million tons of plastic waste entered the oceans.

- Carbon footprint of plastics: Plastic production accounts for 3.4 % of global anthropogenic greenhouse gas emissions, largely due to its fossil-based origins.

The sources of plastic outflow into the environment are presented in Fig. 6.

Even if all plastic littering were to stop immediately, rivers would continue to transport plastic waste from their reservoirs into the oceans, where the resulting microplastics can cause significant harm to wildlife and human health¹⁶. One major concern is that floating plastic debris, such as unfilled polyolefins or foamed products can adsorb environmental toxins like hormone residues or hormone-like substances, pesticides, and even pathogenic, antibiotic-resistant microbes. These plastics are then ingested by marine species, entering the food chain and potentially reaching humans¹⁷. Without new policies, the OECD estimates that by 2060, the plastics lifecycle will remain 86 % linear¹⁸, as shown in Fig. 7.

22 million tonnes of plastic leaked in the environment in 2019, and this estimate is projected to double by 2060

Distribution of leakages by type and source

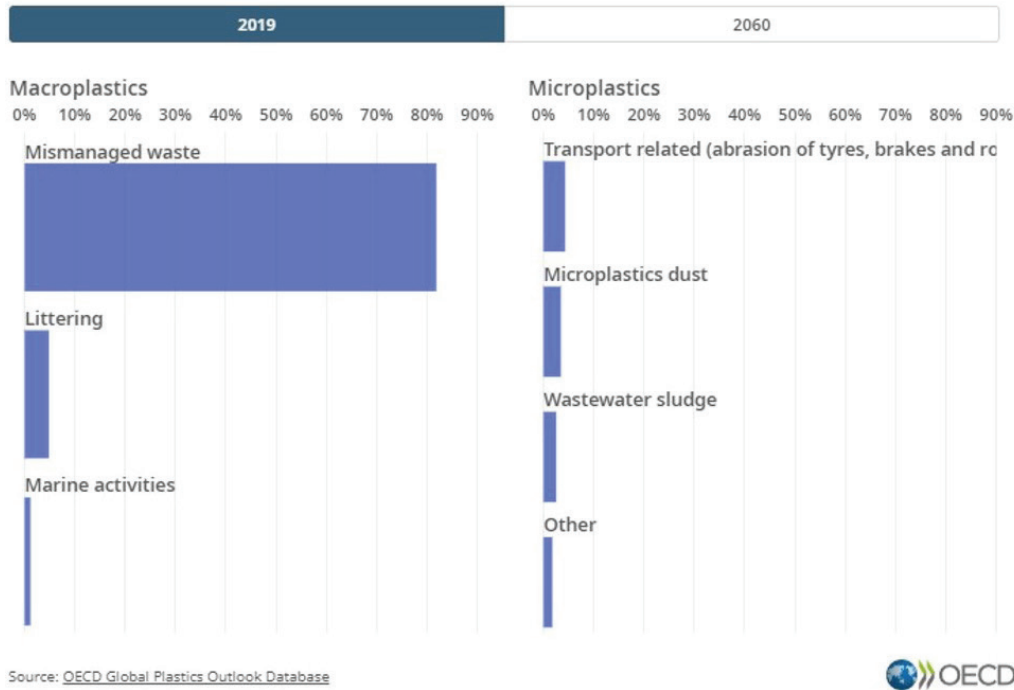


Fig. 6 – OECD estimate of plastics leakages into the environment in 2019¹⁵. Reproduced with permission.

This projection is not optimistic, especially considering the global climate neutrality targets for 2040 and 2050 addressed in various government and organizations' documents. A shift from 9 % to only 14 % circularity within the next 36 years is far from ambitious. The plastics industry should definitely be able to achieve far better progress. If the current rate of littering persists, there might soon be more plastics than fish in the ocean by mass in the near future¹⁹, as a result of increasing plastic load and declining fish population.

Lebreton and Andrady estimated global mismanaged plastic waste (MPW) at “between 60 and 99 million metric tons (Mt) in 2015. In a business-as-usual scenario, this figure could triple to 155–265 Mt/y by 2060”.²⁰ The authors highlight significant geographic differences, as shown in Fig. 8.

With a strong drive towards a sustainable-by-design principle, it can be expected that the *per capita* plastics consumption will decrease in future. However, with a growing global population and ongoing economic development, there will still be a strong net increase in total plastics use on a global level.

As Fig. 8 shows, the projected MPW inflow into the environment is estimated to be particularly

high in Africa and Asia. The authors estimate that “between 1.15 and 2.41 million tons of plastic waste enter the oceans annually via rivers, with over 74 % of emissions occurring between May and October. The top 20 polluting rivers, mostly located in Asia, account for 67 % of the global total”²¹. Various online platforms visualize the impact of plastic pollution, *e.g.*,^{22–24}. For instance, images of the “Great Pacific Garbage Patch” and wildlife entangled in plastic debris are widely available. Plastics are highly persistent, and their estimated lifetimes in marine environments, especially oceans, can extend over several hundred years²⁵ (Table 1). This long-term persistence is now common knowledge.

The lifetime of plastic waste in the environment depends on factors such as light availability, oxygen (including oxygen radicals), and temperature. Clearly, effective solutions are needed to address the persistent issue of plastic waste.

Solutions

We cannot eliminate plastics from modern life; consumption itself can never be fully sustainable. However, its detrimental side effects can and need to be minimized. Therefore, the focus should be on identifying, qualifying, scaling, and managing sub-

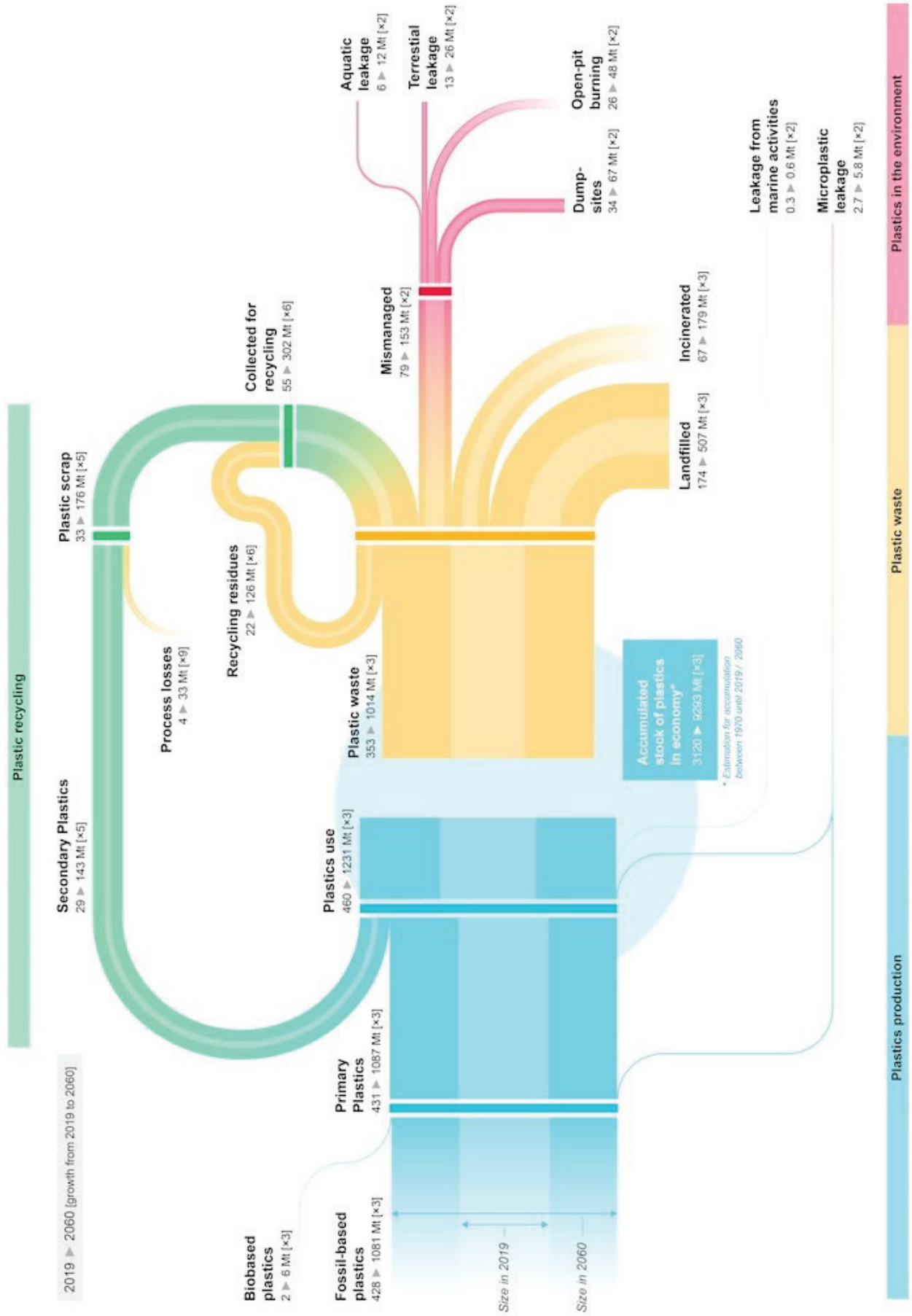


Fig. 7 – OECD projections for 2060 foresee only 14 % circularity in plastics¹⁸. Reproduced with permission.

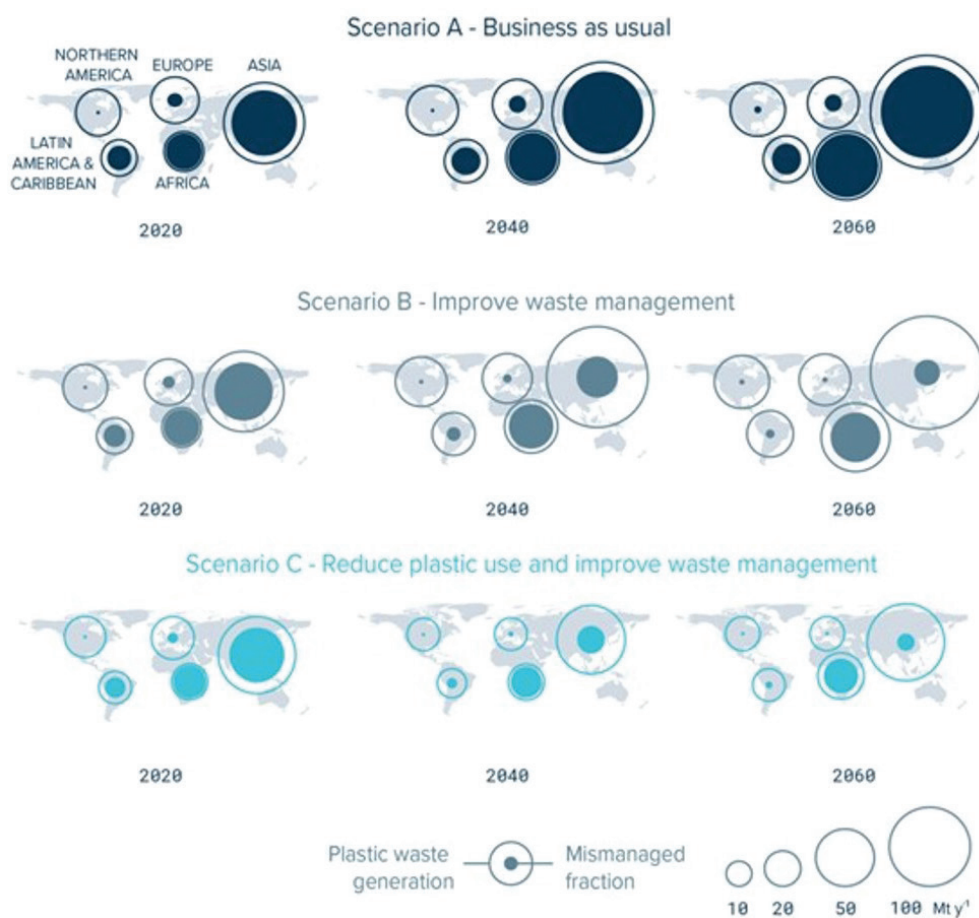


Fig. 8 – Estimated distribution of mismanaged plastic waste in 2020, 2040, and 2060 for three different cases by the OECD²⁰. Reproduced with permission.

Table 1 – Estimated lifetime of man-made articles (and leaves/orange peels as reference) in nature²⁶. Reproduced with permission.

Type of material	Duration ²⁶ (typical, depending on the environment)	Comments
Vegetables	5 days–1 month	
Paper	2–5 months	
Cotton T-shirt	6 months	
Orange peels	6 months	
Tree leaves	1 year	
Wool socks	1–5 years	
Plastic-coated paper milk cartons	5 years	Complete disintegration time for microplastics from PE-liner not considered.
Leather shoes	25–40 years	
Nylon fabric	30–40 years	Complete disintegration time for microplastics from the polyamide not considered.
Tin cans	50–100 years	
Aluminium cans	80–100 years	
Glass bottles	1 million years	
Styrofoam cup	500 years to forever	“Forever” is an overestimation.
Plastic bags	500 years to forever	“Forever” is an overestimation.

stitutes for today's plastic materials over their entire life cycle, ensuring they remain affordable for the consumer while minimizing environmental impacts for both current and future generations. To put this into perspective, the 500-year lifetime of plastic waste spans over 16 generations. This is almost twice the time since Hans Carl von Carlowitz introduced the concept of sustainability in 1713 through his work *Sylvicultura oeconomica*. Interestingly, 500 years is also approximately the time it takes for land, without intervention, to regenerate into a forest. Bioplastics in general can enhance the sustainability of the polymer industry through three key aspects:

Biobased raw materials (feedstock): These materials can reduce the carbon footprint and promote local value creation. This process is referred to as “defossilization”. **Recyclability:** Bioplastics can be recycled in the same way as conventional fossil-based plastics, contributing to a circular system. Mechanical recycling for thermoplastics is well established, while feedstock recycling (which involves recovering monomers) is still in its early stages. For all types of plastic more research is needed. **Biodegradability:** Compostable bioplastics can also degrade in nature, which reduces their accumulation in the environment, particularly reducing the presence of persistent micro- and nanoplastics. This intrinsic property is well-established for many biopolymers in various environments. However, it is important to approach the concepts of biobased, recyclable, and degradable plastics with nuance, as assumptions and environmental conditions play crucial roles. Clear definitions and well-controlled reference materials are essential for making polymers/blends/compounds as well as their products and life cycles comparable, ensuring decision-makers and consumers are not misled. For instance, “biobased” can be defined by the biobased carbon content as per ASTM D6866, a standard method for determining the biobased content of various materials.

For example, PET is produced from two monomers: monoethylene glycol ($C_2H_6O_2$, 62 g mol⁻¹) and terephthalic acid ($C_6H_4(COOH)_2$, 166 g mol⁻¹). If only the alcohol is biobased, (as in Plantbottle™), the organic carbon fraction in the pure material is $2/(2+8)=20\%$ according to ASTM D6866. However, marketing may cite a $62/(62+166-18)=30\%$ biobased content on the mass of the polycondensated constituents, inflating the figure by 50% compared to the standard used in technical discussions, since water after esterification is not part of the final polyester material.

It is critical that bioplastics contain only “harmless” additives, a standard that should also apply to all existing fossil-based plastics. Since micro- and nanoplastics can enter the food chain and eventually

end up on our plates, no toxic additives should be allowed in any plastic items. Currently, there are no appropriate standards in this regard, as plastics are generally underregulated in chemicals legislation, but we should advocate for transparency regarding the additives used, and develop a precise “positive list” of allowed additives for all plastic formulations. Today, the recipes for plastic materials remain trade secrets, and little public information is available on model formulations for common applications that use only biobased, biodegradable, and safe additives.

One promising solution is polyhydroxyalkanoates (PHAs), a class of biopolyesters made from renewable raw materials. These include first-generation feedstocks like sugars and lipids²⁷, and second-generation feedstocks such as waste materials²⁸. The latter is particularly advantageous as it avoids competition with feed and food production for land resources, and saves expenditures on fertilizer and water. For instance, when using sugar for producing poly(3-hydroxybutyrate) (PHB) under aerobic conditions, 2.8 tons of glucose is required for 1 ton of bioplastics, primarily due to considerable loss of the carbon source as CO₂²⁹. However, through gas fermentation, PHAs can also be obtained from C₁ waste materials (CH₄ from biogas, power-2-gas or synthetic natural gas (SNG) from, e.g., methanation of wood- or waste-derived syngas from gasification)³⁰. This approach significantly broadens the feedstock base and eliminates the need for complex purification of sugar-containing lignocellulosic hydrolysates.

Biodegradation of bioplastics

“Biodegradable” plastics are materials that can be decomposed in nature by microorganisms. The rate of degradation depends on environmental conditions: warm, humid composting environments will enable faster biodegradation of polymers than cold seawater. The microorganisms secrete enzymes that ultimately “mineralize” the bioplastics, breaking the polymers down into smaller units, which can then be further metabolized by the microorganisms. Understanding the end products of this enzymatic degradation is essential. For example, the water-soluble material poly(vinyl alcohol) (PVA), used in 3D printing filaments and as a wrapping material for detergents, first breaks down into ketones, fatty acids, and alcohols during anaerobic biodegradation³¹. Typically, polyesters can be hydrolyzed by hydrolytic enzymes like lipases, whereas specialized enzymes (depolymerases) tend to achieve higher degradation rates than broad-spectrum enzymes. In 1963, A. Chowdhury was the first to report enzymes capable of degrading PHB. PHA/B depolymerases (EC 3.1.1.75 and EC 3.1.1.76), and lipase

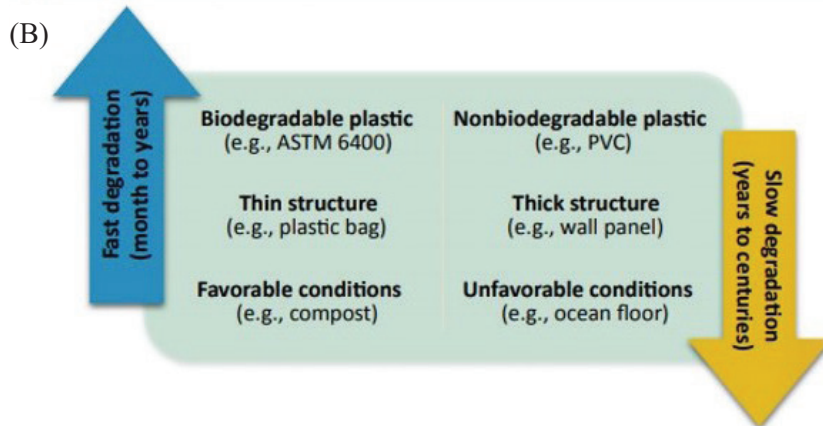
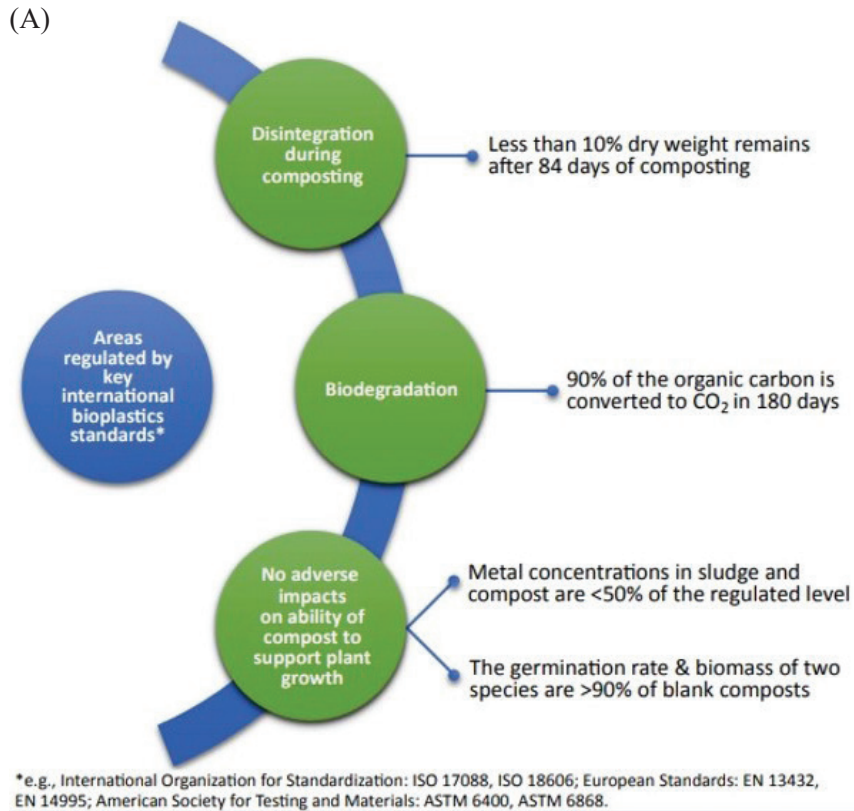


Fig. 9 – Degradability tests and their context. Source:³⁶

	WORLDWIDE ISO	EUROPE CEN	US ASTM	AUSTRALIA STANDARDS Australia
PLASTICS	ISO 17088	EN 14995	ASTM D6400	AS 4736
PACKAGING	ISO 18606	EN 13432		
PAPER COATING			ASTM D6868	

Fig. 10 – Standards for degradability of plastics. Source:²⁶

(EC 3.1.13), from *Paucimonas (Pseudomonas) lem-oignei* were found to depolymerize PHA efficiently³². Building upon the concept of the grossly unsustainable practice of oxo-degradable plastics, several researchers have been exploring ways to incorporate enzymes into bioplastic formulations to control degradability rates^{33,34}.

A common misconception about bioplastics and biopolymers is that they will decompose on their own, even in dry conditions. This is not true — compare it to wood in old artworks and furniture that has lasted for centuries. Bioplastics, like fossil-based plastics, can be damaged when exposed to UV light, but will begin degrading only when in contact with microorganisms/enzymes in a humid environment. Auto-fragmentation can be observed in oxo-degradable plastics, and under intense UV exposure in all types of plastics.

Several standards for degradability have been developed (Figs. 9 and 10). One of the most widely recognized is EN 13432 “Requirements for packaging recoverable through composting and biodegradation — Test scheme and evaluation criteria for the final acceptance of packaging materials”³⁵. It is important to note that “degradability” and “compostability” are not synonymous. Compostability refers to conditions under which the material will degrade, such as those found in industrial composting or home composting, where typically lower temperatures are achieved. For instance, poly(lactic acid) (PLA) will readily degrade under industrial composting conditions but will not break down in a typical backyard compost heap, where temperatures do not reach above the glass transition temperature of 55 °C for PLA degradation³⁹. EN 13432 specifies the following requirements for “*Aerobic biodegradation tests*”:

A.2.2.1 The period of application for the test specified in the test methods shall be a maximum of 6 months.

A.2.2.2 For the test material, the percentage of biodegradation shall be at least 90 % in total or 90 % of the maximum degradation of a suitable reference substance after a plateau has been reached for both test material and reference substance.”

The standard also requires that, after 12 weeks, no more than 10 % of the sample’s initial weight may be larger than the pores present in a 2-mm sieve, meaning that full degradability is not expected within this timeframe. Due to varying activity levels of composts, it is recommended to integrate a positive reference material (e.g., cellulose or starch) in biodegradability tests. As a negative reference, commercial polyethylene (PE) is often used for comparison. Fig. 9 provides an overview of degradability tests.

Standards for biodegradability of plastics are summarized in Fig. 10.

Several testing institutes offer certificates and labels of “biodegradability”. For instance, the “OK compost home” standard³⁷ establishes a maximum film thickness of 109 µm for e.g., AONILEX® 151C (a commercial PHA grade produced by Kaneka) to meet this standard. This implies that a thicker, injection-molded part made from the same material as a thin film, will also degrade in a home compost setting, but over a longer period than stipulated by EN13432. Consequently, such a product would not fall under this standard. Some bioplastic-based products on the market claim to be biodegradable and/or compostable. However, without reference to a clear standard, such claims are, at best, incomplete.

For an overview of biodegradability standards (and misuses by some market players), refer to³⁸. Renewable Carbon has compiled a comprehensive visual overview of biodegradability of common bioplastics³⁹ (Fig. 11).

As Fig. 11 illustrates, natural polymers like starch, cellulose, and PHB (and its copolymers) are fully biodegradable, in contrast to other materials. However, claiming a material as “biodegradable” in absolute terms can be misleading. For example, PLA will also degrade in the shaded grey cases in Fig. 11, but it will take significantly longer compared to PHB or starch, although still much faster than fossil-based plastics. It is important to note that the marine environment is a heterogeneous ecosystem. Tropical surface water cannot be compared to cold, deep waters with low light and oxygen levels. An analogy can be drawn to wood: under oxygen-poor water, logs can survive for hundreds of years, as evidenced by old shipwrecks. It is clear that lab-based biodegradability tests are more reproducible than field trials, as they cannot cover all environmental conditions in which plastic waste might end up. Additionally, the potential formation of methane (CH₄) under anaerobic conditions, with its detrimental impact on climate change must not be neglected. Therefore, degradability in practical settings should always be reported in relation to reference materials.

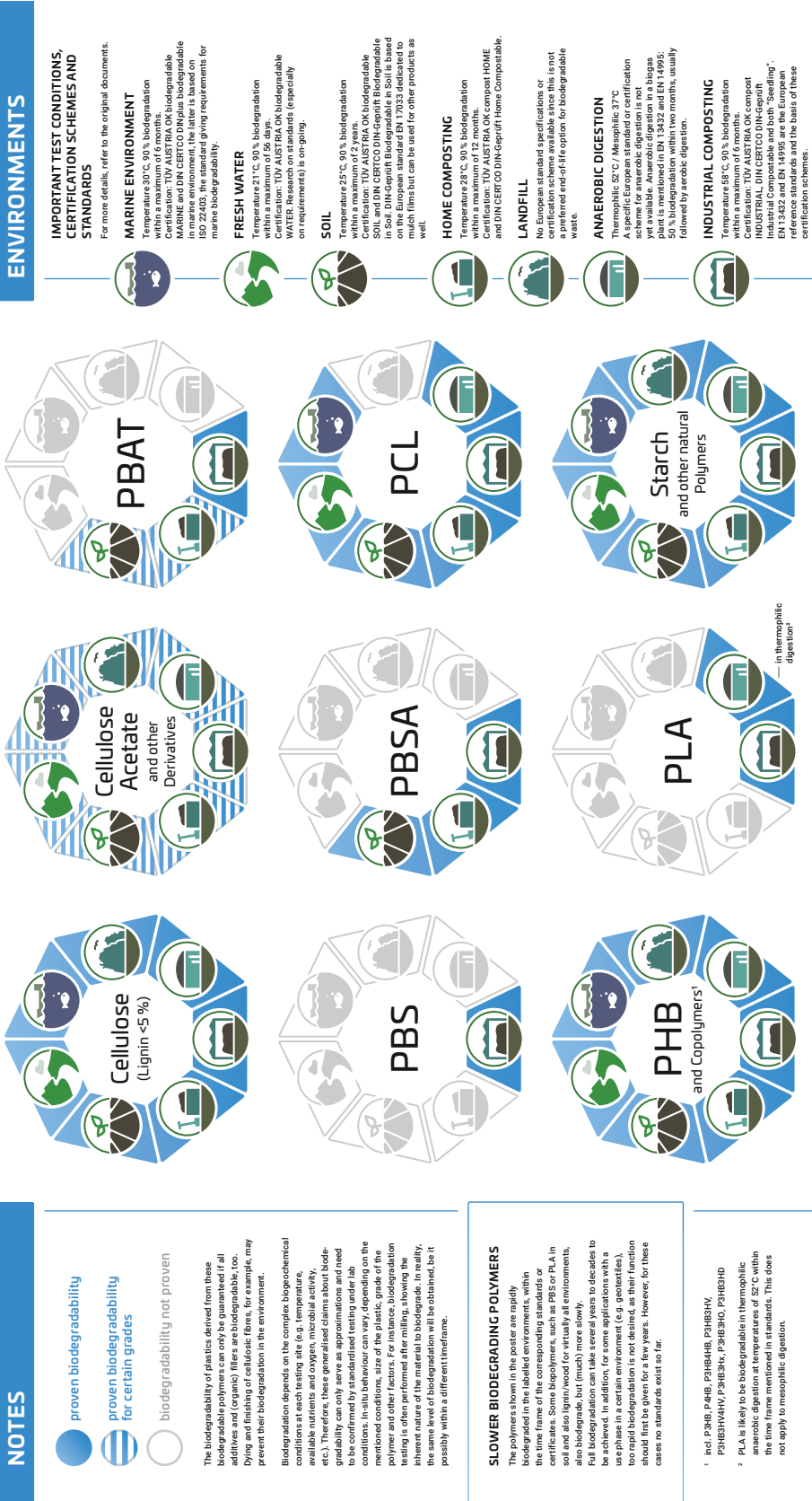
Polyhydroxyalkanoates (PHAs)

Natural polymers (biopolymers), such as cellulose, starch, proteins, and DNA (deoxyribonucleic acid), are built by living organisms from simple monomers of varying chain lengths. As natural compounds, they are all completely biodegradable through microbial enzymatic activity. Aliphatic polyesters comprise hydroxycarboxylates, including polyhydroxyalkanoates (PHAs), as well as chemically polymerized polylactic acid (PLA) (which is not found in nature), and fossil-based poly(ε-caprolactone) (PCL), which is also not a natural com-

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Fig. 11 – Nine biopolymers and seven settings: Full green stands for proven biodegradability for all grades, and shaded green stands for “biodegradability for some grades”.
Comments: ¹(for PHB) incl. P3HB: Poly(3-hydroxybutyrate), P4HB: Poly(4-hydroxybutyrate), P3HB4H: Poly(3-hydroxybutyrate-co-4-hydroxybutyrate), P3HB3HV: Poly(3-hydroxybutyrate-co-3-hydroxyvalerate), P3HB3HV4HV: Poly(3-hydroxybutyrate-co-3-hydroxyvalerate-co-4-hydroxyvalerate), P3HB3Hx: Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate), P3HB3HD: Poly(3-hydroxybutyrate-co-3-hydroxydecanoate); ²(for PLA): “PLA is likely to be biodegradable in thermophilic anaerobic digestion at temperatures of 52 °C within the time frame mentioned in standards. This does not apply to mesophilic digestion”.³⁹

pound⁴⁰. Hydroxy acids are organic acids containing both a carboxyl (–COOH) and a hydroxyl (–OH) group. Depending on the location of the OH group on the carbon backbone of the (fatty) acid, hydroxy acids are categorized as α -, β -, γ -, ... ω -hydroxy acids. For α -hydroxy acids (AHA), the OH group is located on the second carbon atom (adjacent to the carboxyl group). These compounds are termed “2-hydroxy”. Well-known examples of AHA are lactic acid and citric acid. β -hydroxy acids (BHA), have the OH-group on the third carbon atom, counting from the COOH group, and these compounds are called “3-hydroxy-”. Examples are salicylic acid and 3-hydroxybutyric acid (BHB, 3HB). For ω -hydroxy acids (OHA), the OH-group is attached to the carbon atom farthest from the COOH-group. Said BHB (or β -hydroxybutyric acid = 3-hydroxybutyric acid) is also found as its conjugate base β -hydroxybutyrate (3-hydroxybutyrate). BHB is a chiral compound with two enantiomers: D- β -hydroxybutyric acid (=R(-)-3-hydroxybutyric) and L- β -hydroxybutyric acid (=S(+)-3-hydroxybutyric acid), with the D-form being the naturally occurring one. BHB plays several roles in living organisms. It is the most abundant ketone body in mammals, formed during fatty acid metabolism in the liver. Cells can gain their energy from ketone bodies *via* acetyl-CoA in the Krebs (citric acid) cycle. Nearly 100 years ago, French scientist Maurice Lemoigne⁴¹ discovered the polymer poly(3-hydroxybutyrate) (PHB) in the bacterium *Bacillus megaterium* (now known as *Priestia megaterium*). This PHB was the first PHA (polyhydroxyalkanoate) identified. The atactic polymer synthesized from L- β -hydroxybutyric acid via chemical reactions is not biodegradable by depolymerase enzymes, which exhibit high stereospecificity⁴².

Beyond PHB – the PHA class of biopolymers

The polymers of 3-hydroxy acids = 3-hydroxyalkanoates are called poly(3-hydroxyalkanoates), or simply polyhydroxyalkanoates (PHAs). While 4-hydroxy acids and 5-hydroxy acids can also occur, these are less common but still classified as PHAs. For instance, P(4HB) and P(3HB-co-4HB) are frequently researched representatives of this group¹²⁰.

To date, more than 150 natural PHA monomer constituents have been identified^{43–45} (compare also Table 1), and more than 300 genera of archaea and bacteria (both Gram-positive and Gram-negative) are known to produce PHAs with varying compositions^{46–48}. In theory, an infinite number of PHA molecules are possible. PHAs can be grouped into short-chain-length PHAs (scl-PHA, with C3-C5 monomers), medium-chain-length PHAs (mcl-PHA, with C6-C14 monomers)⁴⁹, and long-chain-length PHAs (lcl-PHA, with more than 14 carbon atoms in their monomers)⁵⁰. PHB is the most commonly oc-

curing and extensively studied PHA. The simplest PHA, P(3HP) (poly(3-hydroxypropionate)), is characterized by its low melting temperature, high flexibility, good degradability, and high stability, though it is only produced by genetically engineered strains⁹⁰. The term poly(hydroxy acid) (PHA) was introduced by Findlay and White in 1983, after discovering that homopolymeric poly((R)-3-hydroxybutyrate) (PHB) was not always encountered; instead mixed polymers of different short- and medium chain (they also found 3-hydroxyhexanoate) β -hydroxy fatty acids were often present. Thus, PHA came to stand for poly(hydroxyalkanoates) or poly(hydroxy fatty acids)⁵¹.

Following Lemoigne’s discovery of PHB granules in *B. megaterium*⁴¹, similar PHB-containing granules were found in other bacteria and archaea. Table 2 summarizes the monomers that can be identified in PHA⁴⁶. It is essential to specify the exact type of PHA in research, as the literature often erroneously uses PHA and PHB interchangeably, which is clearly incorrect.

The broad range of monomers accounts for the diverse property spectrum of PHAs⁵². In 1993, Hans-Martin Müller and Dieter Seebach recognized PHAs as a “fifth class of physiologically important organic biopolymers”, alongside polyisoprenoids, polypeptides, polysaccharides, and polynucleotides, which highlights their significance. Today, PHAs are an interesting field of research, with several dozen companies scaling up PHA production. Global production of PHAs is currently estimated between 30 to 100 kt/y, though the industry is still in its early stages compared to the volumes of commodity polymers. Even materials like PFTE (Teflon™), which reaches production of approx. 250,000 tons annually, by far surpass PHA production⁵⁴. Nonetheless, a “new wave” of PHA commercialization is emerging. For a review of the current industrial status of PHA, refer to⁵⁵.

Degradability of PHAs

PHAs are highly versatile and are used today in applications such as 3D printing filaments, injection-molded products, and paper coatings.

Given the diverse potential end-of-life scenarios for PHA products, the environmental conditions where PHA waste ends up will dictate the biodegradation dynamics. Marine and soil environments are, in general terms, the most common habitats where PHA ends up. PHA can be degraded by different microbes in various environments, see Table 3.

A significant number of studies have focused on identifying the microbial species and enzyme depolymerases involved in environmental biodegradation of PHAs. Bacterial PHA depolymerases are

Table 2 – Selected monomers that can be identified in polyhydroxyalkanoates⁴⁶. Reproduced with permission.

3-hydroxy acids	3-hydroxy acids (unsaturated)	3-hydroxy acids (branched)	3-hydroxy acids (substituted side-chain)	Other than 3-hydroxy acids
Propionic	2-butenoic	2-methylbutyric	Cyclohexylbutyric	4-Hydroxybutyric
Butyric	4-pentenoic	2-methylvaleric	5-Phenylvaleric	
Valeric	4-hexenoic	2,6-dimethyl-5-heptenoic	7-Fluoroheptanoic	4-Hydroxyvaleric
Hexanoic	5-hexenoic	4-methylhexanoic	9-Fluorononanoic	4-Hydroxyhexanoic
Nonanoic	6-heptenoic	5-methylhexanoic	6-Chlorohexanoic	4-Hydroxyheptanoic
Decanoic	7-octenoic	6-methyloctanoic	8-Chlorooctanoic	4-Hydroxyoctanoic
Undecanoic	8-nonenoic	7-methyloctanoic	3-Bromhexanoic	5-Hydroxyvaleric
Tetradodecanoic	9-decenoic	6-methylnonanoic	8-Bromooctanoic	5-Hydroxyhexanoic
	10-undecanoic	7-methylnonanoic	11-Bromoundecanoic	Malic
	6-dodecenoic	8-methylnonanoic	7-Cyanoheptanoic	
	5-tetradecenoic	7-methyldecanoic	9-Cyanononaic	
	5,8-tetradeca-dienoic	9-methyldecanoic	12-Hydroxy-dodecanoic	
	5,8,11-tetradeca-trienoic		Succinic acid methylester	
	4-hexadecenoic		Adipic acid methylester	
	4,7-hexadeca-dienoic		Suberic acid methylester	
			Pimelic acid propylester	
			Sebacic acid benzylester	

Table 3 – Examples of poly(hydroxyalkanoates)-degrading microbes⁵⁶. Licensed under a Creative Commons Attribution-NonCommercial 4.0 International License (CC BY-NC 4.0).

Environment	PHA-degrading microbe
Soil	<i>Acidovorax facilis</i> , <i>Aspergillus fumigatus</i> , <i>Comamonas</i> sp., <i>Pseudomonas lemoignei</i> , <i>Variovorax paradoxus</i>
Activated sludge	<i>Alcaligenes faecalis</i> , <i>Pseudomonas</i> sp.
Seawater	<i>Comamonas testosteroni</i>
Anaerobic sludge	<i>Ilyobacter delafieldii</i>
Lake water	<i>Pseudomonas stutzeri</i>

commonly found in genera such as *Cupriavidus*, *Alcaligenes*, *Comamonas*, and *Pseudomonas*^{24,57}. A notable 27-month study revealed that the majority of species colonizing PHA surfaces and creating a biofilm in seawater derived from sediment⁵⁸. Regarding soil environments, a large-scale study of Chinese landfills identified mcl-PHA depolymerase from *Pseudomonas caeni* and 3-hydroxyvalerate (3HV) dehydrogenase from *Fermentimonas caenicola* as key enzymes for PHA degradation⁵⁹.

Guérin *et al.* demonstrated that PHB and its copolymers are biodegradable in all studied natural environments: soil, sludge, freshwater, and seawater⁶⁰. They found that PHB serves as a carbon source for various fungi and bacteria, which secrete extra-

cellular PHA depolymerases. These carboxylesterases, specific to polyoxoesters bonds, do not attack related polythioester bonds⁶¹.

Jendrossek found that PHA depolymerases which he had isolated were specific for either scl-PHAs or mcl-PHAs⁶². Key reviews in this field, such as Koller and Mukherjee⁶³, praise biodegradability as the most beneficial attribute of PHAs. Another notable review by Meereboer *et al.*⁶⁴, discusses test regimes and provides an overview of PHA and PHA composite materials degradation in different environments.

Generally, the longer the alkyl chain of a PHA, the slower its degradation rate⁶⁵. Additionally, increased wettability of a compound tends to accelerate degradation. However, whether PHA can biodegrade in humans and animals remains inconclusive⁶⁵. While PHB was quickly degraded in the rumen due to the presence of an adequate microflora⁶⁶, *in vivo* PHA implants in a rat model showed low degradability⁶⁷. According to Volova *et al.*: “Degradation of different types of PHA is strongly influenced by the temperature, humidity, type of soil, amount of precipitation, and the density of microbial populations. Myxomycetes are considered to be the most efficient soil PHA degraders, and *Penicillium* is the most typical genus. But many bacterial species also participate in biodegradation. In all environments, most PHA-degrading soil microorganisms degrade

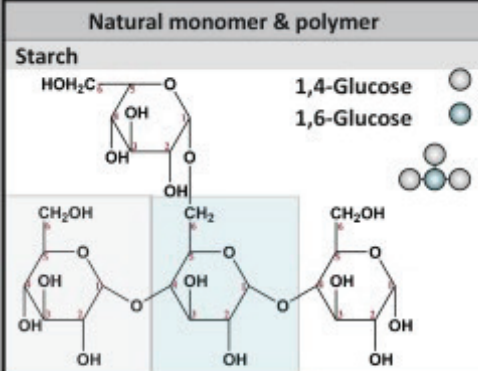

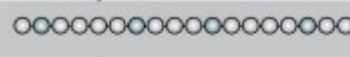

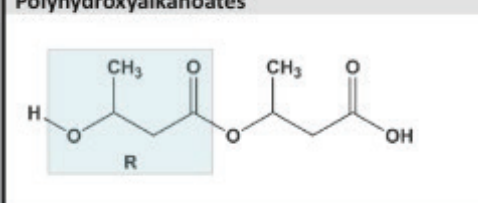
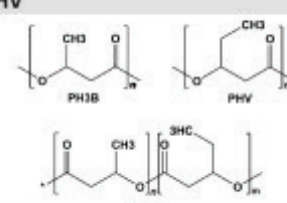
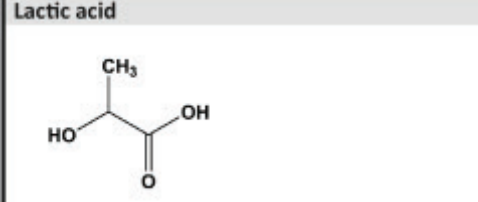
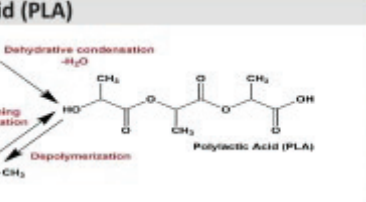
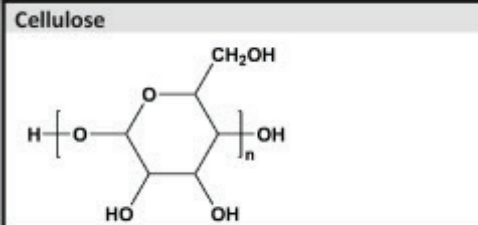
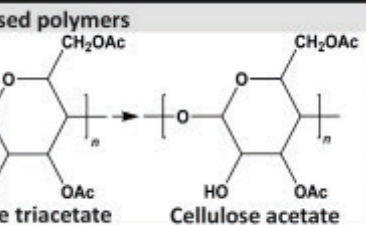
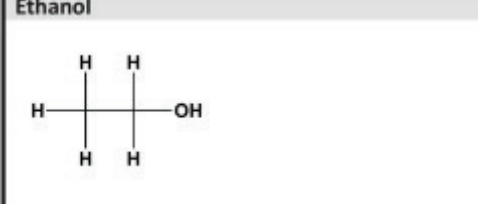
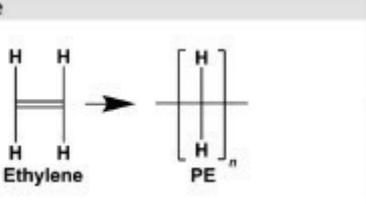
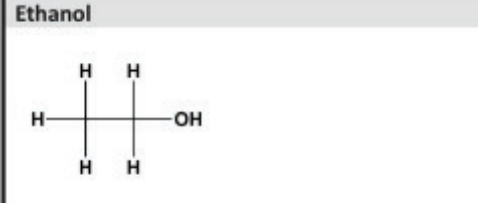
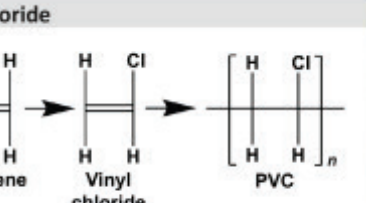
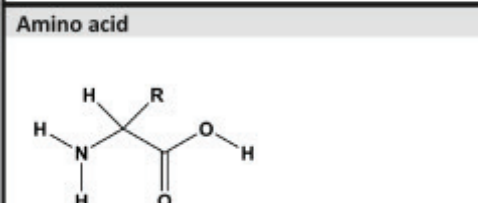
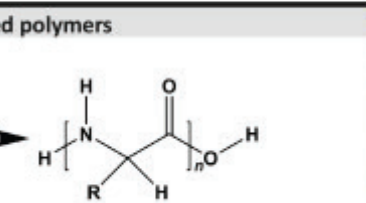
Natural monomer & polymer	Polymer processing
<p>Starch</p>  <p>1,4-Glucose 1,6-Glucose</p>	<p>Starch-based polymers</p> <p>Hydrolyzed Starch</p>  <p>Bioplastic polymer</p>  <p>Bioplastic plasticizer crosslinkers</p> 
<p>Polyhydroxyalkanoates</p>  <p>R</p>	<p>PHA, PHB, PHV</p>  <p>PHB PHV PHBV</p>
<p>Lactic acid</p> 	<p>Poly(lactic acid) (PLA)</p>  <p>Dehydrative condensation $-H_2O$ Lactic acid Ring opening polymerization Depolymerization Lactide Poly(lactic acid) (PLA)</p>
<p>Cellulose</p> 	<p>Cellulose-based polymers</p>  <p>Cellulose triacetate Cellulose acetate</p>
<p>Ethanol</p> 	<p>Polyethylene</p>  <p>Ethylene PE</p>
<p>Ethanol</p> 	<p>Poly(vinyl chloride)</p>  <p>Ethylene Vinyl chloride PVC</p>
<p>Amino acid</p> 	<p>Protein-based polymers</p> 

Fig. 12 – Excerpt from the work of Karan et al. on the degradability of poly(hydroxyalkanoates) compared to starch and poly(lactic acid) (PLA)³⁶.

short-chain PHAs only. Increasing the degrees of crystallinity of degrading PHA suggests preferential disintegration of their amorphous phase in the soil as compared with [the] crystalline phase⁶⁸.

Fig. 12 provides an excerpt from the work of Karan *et al.*³⁶

As shown in Fig. 12, PHAs (notably PHB and the co-polymer poly([*R*]-3-hydroxybutyrate-*co*-3-hydroxyvalerate)(PHBV)) are described as biodegradable in water, soil, and industrial composting conditions. The rate of PHA biodegradation in marine environments is discussed by Dilkes-Hoffman *et al.*⁶⁹ (Fig. 13).

The authors concluded: “It was determined that the mean rate of biodegradation of PHA in the marine environment is $0.04\text{--}0.09\text{ mg day}^{-1}\text{ cm}^{-2}$ ($p=0.05$) and that, for example, a PHA water bottle could be expected to take between 1.5 and 3.5 years to completely biodegrade.” In comparison, own measurements from one of the authors of the present paper indicated that the maximum degradation rate of PHB in warm, humid compost was up to $20\text{ }\mu\text{m}$ (film thickness of test specimen) per day, while in $5\text{ }^{\circ}\text{C}$ seawater, only up to $1\text{ }\mu\text{m}$ per day was lost.

Several studies have attempted to elucidate and standardize how PHAs biodegrade in soil, although debris and the degree of pollution often hinder the recovery of samples from the soil at the end of the experiments. As expected, results are contradictory due to differences in soils parameters, including oxygen levels, light exposure, pH-value, temperature, C/N ratio, moisture, and microbial composition⁷⁰. The effect of temperature was investigated by Gil-Castell and colleagues, who observed that high-

er temperatures under non-mesophilic conditions increased both the degree of PHA degradation and the loss of molecular weight, reducing the polymer’s physical properties⁷¹.

On the other hand, multiple studies have consistently shown that lower levels of PHA crystallinity correspond to higher biodegradation rates in soil environments¹⁴. Indeed, in soil, amorphous structures decompose faster than crystalline ones, which first require fragmentation⁷². However, a study conducted in the South China Sea, after X-ray measurements, found no significant differences in degradation levels between the amorphous and crystalline portions of P(3HB-*co*-3HV). The study also elucidated how the geometry of the material plays a key role. Specifically, films (due to the presence of more pinholes) degrade more easily than pellets⁷³. Similarly, foamed material will degrade faster than solid items due to increased surface area and wettability. In a noteworthy finding, Derippe and colleagues measured cumulative oxygen consumption as a parameter to monitor PHA biodegradation in seawater. They concluded that mcl-PHA degraded at a significantly lower rate compared to scl-PHA, which exhibited degradation levels comparable to cellulose⁷⁴. Opening new unexplored scenarios, this observation contrasts the concept that incorporating different monomers (as in the case of mcl-PHA) decreases polymer crystallinity and facilitates biological depolymerization.

In Fig. 14, the marine degradation of poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) and poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) is compared to cellulose and PLA⁷⁵.

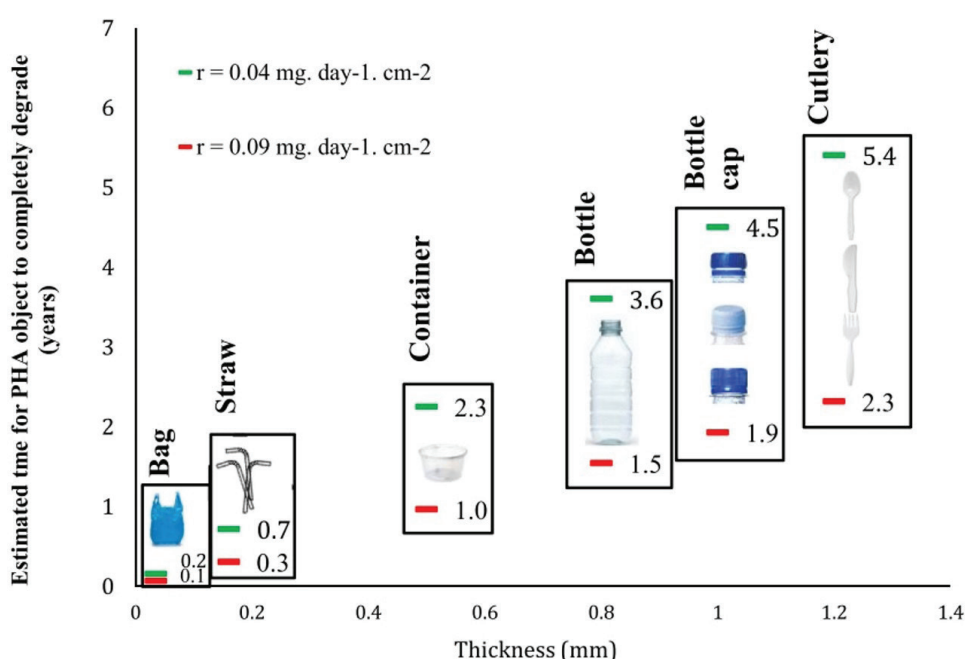


Fig. 13 – Estimated degradation time of poly(hydroxyalkanoates)-based products in marine environments⁶⁹.

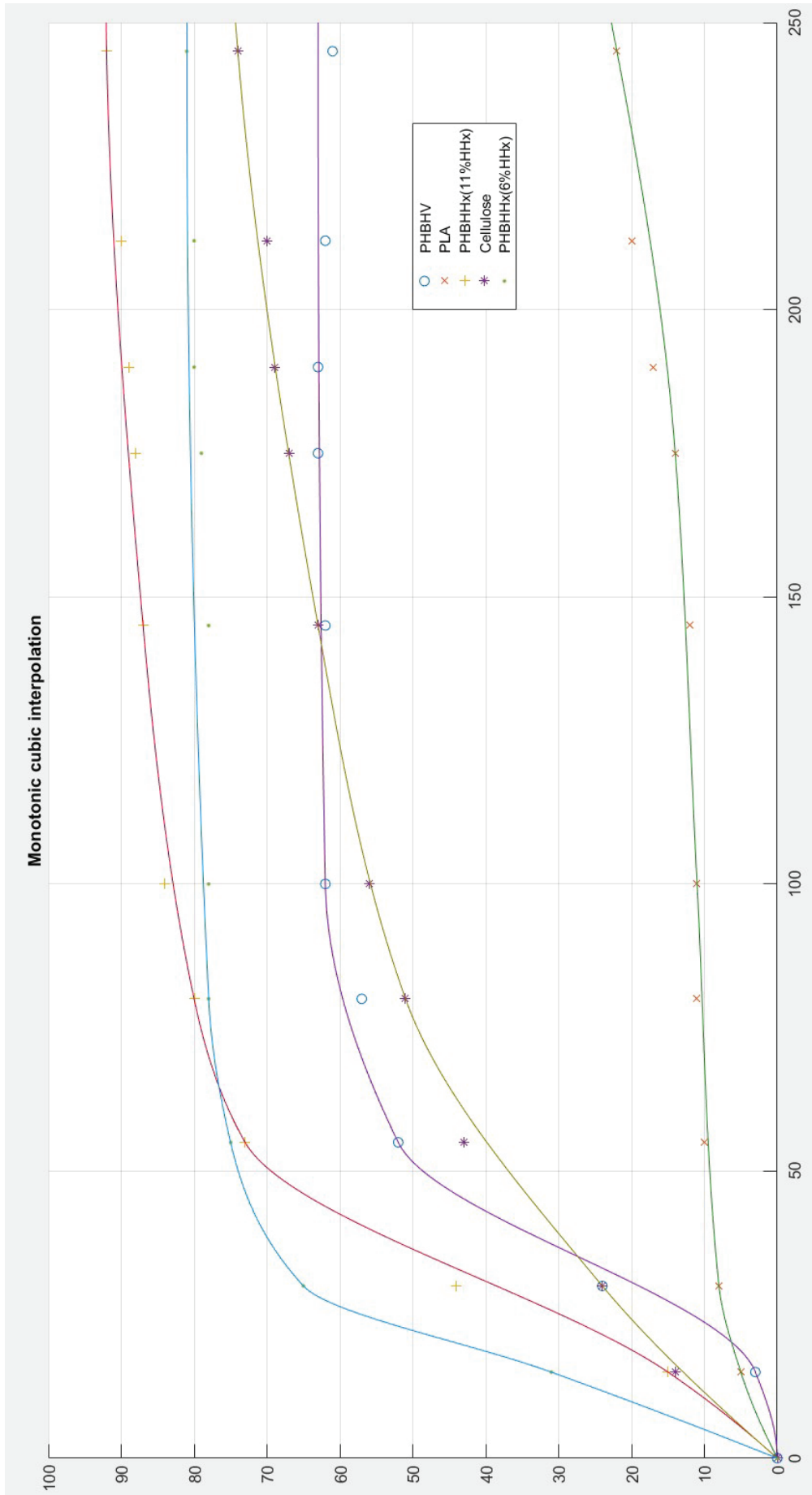


Fig. 14 – Marine degradation of the materials PHBV (Poly-3-hydroxybutyrate-co-3-hydroxyvalerate), PHBHHx (Poly-3-hydroxybutyrate-co-3-hydroxyhexanoate) (6 % HHx and 11 % HHx), and PLA, determined by NF EN ISO 19679 standard⁷⁵. x-axis = days, y-axis = % degradation.

Table 4 summarizes the findings from the literature on PHA degradability.

Regarding aerobic versus anaerobic digestion, it is important to note that PHAs have a density >1 , causing them to sink in water bodies unless they are foamed. Additives and blend partners also influence degradability, with cross-linking reducing and prolonging the degradation process. Anaerobic digestion may lead to the formation of CH_4 in addition to CO_2 and water, which might be undesirable in the open environment since it is more climate-potent than CO_2 . Various studies have compared PLAs' end-of-life scenarios with other bioplastics⁷⁶.

Concerning the mechanisms of PHA degradation, Dilkes-Hoffman *et al.*⁶⁹ wrote: "The biodegradation of PHA is known to primarily occur through surface erosion *via* enzyme catalysed hydrolysis"^{60,77}.

PHA can degrade both biotically and abiotically⁵⁷. It was found that the incorporation of monomers other than 3HB into a PHB matrix reduces crystallinity, which lowers the melting temperature, increases flexibility, and accelerates the polymers' degradation rate⁵⁶.

Non-natural PHAs

Through chemocatalysis, it is possible to synthesize uncommon or unnatural PHAs with different/novel monomers exhibiting side chains with special functionalities. Such lab-made PHAs can be customized for desired crystallinity and chain length. Homopolymers, random or block copolymers are feasible. Westlie *et al.* demonstrated such an activity⁷⁸ by catalytically carbonylating epoxides, producing several synthetic β -lactones, including β -lactones with fluorinated substituents. These β -lactones were then polymerized into fluorinated PHA, which are not found in nature. Such polymers complement the list shown in Table 1²⁶, where exemplary 3-hydroxyacids with aliphatic, unsaturated, branched, and substituted side-chains, and other hydroxy acids, are shown. Unusual PHA biosynthesis is also discussed by Olivera *et al.*⁷⁹

Closing remarks

Biodegradability is a nuanced concept. Common compostability standards like EN13432 require 90 % mineralization (i.e., organic carbon \rightarrow CO_2) within 180 days, which is feasible only for films under standardized testing conditions. On the other hand, nucleating agents and additives do not need to be degradable to meet compostability standards or qualify for recognized labels. As polyesters, PHAs

by theory are susceptible to hydrolysis (cleavage of ester bonds) by acids, alkalis, and enzymes. This has been demonstrated in various environments and with various PHAs. Natural PHAs, predominantly PHB, are fully degradable in all relevant conditions. However, with the synthesis of exotic PHA types, with PHAs being polymers of 3-hydroxy acids, as well as polymers of 4-hydroxy acids and 5-hydroxy acids, the question arose: Are all PHAs degradable in all environments? The 2021 article by Renewable Carbon already summarized this statement as "positive" for the commercially relevant types of PHAs, i.e., PHB, P(4HB), P(3HB-*co*-4HB), P(3HB-*co*-3HV), P(3HB-*co*-3HV-*co*-4HB), P(3HB-*co*-3Hx), P(3HB-*co*-3HO) and P(3HB-*co*-3HD)³⁹.

To address the plastics crisis, further exploration of PHA applications is essential, such as:

- Manufacturing textiles from PHA to prevent microplastics pollution.
- Manufacturing tires from PHA (mcl-PHA) to enable degradation of tire wear particles. Producing marine-use plastic parts and components from PHA.
- Developing PHA-based packaging and other short-lived products prone to environmental leakage.
- Work on PHA recycling investigating chemical leasing models (prioritizing value-added products over mass productions of traditional chemicals)⁸⁰ and its extendibility towards plastics.

It can be reasonably postulated that all naturally occurring and unmodified PHAs (*i.e.*, without cross-linking) are biodegradable both in controlled and uncontrolled environments. This also applies to copolymers in the PHA class. Crystallinity slows down degradation, while wettability and porosity increase degradation. In general, scl-PHAs degrade faster than their mcl- and lcl-PHA counterparts. However, at least 0.3 mm/year (or 1 $\mu\text{m}/\text{day}$) will be mineralized in the presence of moisture and microorganisms. When they are present, degradation will occur. While not all grades and products will meet classic standards like EN 13432, it is fair to assume that the degradability rate of PHAs will surpass that of most other bioplastics. Thus, leaked PHA particles will have a shorter lifetime in the environment. Composting (controlled) or "littering" (uncontrolled) degradation should not be encouraged as end-of-life options for PHA-based materials, except for special cases. However, when they occur, environmental harm will be minimal.

The degradability of PHA, from the body of literature studied, is summarized in the following chart (Fig. 15).

Table 4 – Summary of (successful) PHA degradability studies.

Type of PHA	Formula	Chain length	“general” degradability	Mostly aerobic, partly anaerobic		Anaerobic			Aerobic			Laboratory or other	Comment
				Industrial composting, thermophilic	Home composting, mesophilic	Soil	Fresh water	Sea water	Interface Seabed**	Soil	Fresh water		
PHA (“all”) or several	R	Type***	[25] ^a [30], [37] ^e , [88]	[81]	[92]	[82]	[83]	[25] [83]				[84] ^m [87] ⁿ [94] ^d	
poly(3HP)	H	scl										[52], [53] ^h , [112]	poly(3-hydroxypropionate)
PHB, P3HB	CH ₃	scl	[28] ^b , [27], [110]	[81], [93]	[92], [99], [111]	[82] [92]	[92]	[83]		[101]		[31] [50] [94] ^d	poly[(R)-3-hydroxybutyrate]
synthetic poly[(R,S)-3-hydroxybutyrate] ((R,S)-PHB)	CH ₃	scl		[40]								[58]	Steerable rate of degradability
P(4HB)	CH ₃	scl	[84]									[48] ^j [84]	P(4HB)
PHBV		scl	[28], [27], [98], [102], [110]	[81], [99]	[86], [104], [111]	[82]	[97]	[83]		[97], [101]		[38]	P(3HB-co-3HV)
PHV	CH ₂ CH ₃	scl	[28], [27]	[93]								[64] [93]	poly(3-hydroxyvalerate) (P(3HV))
PHHx	propyl	mcl			[89] ^o							[42] ^f	poly(3-hydroxyhexanoate) (P(3HHx))
PHH, P3HHp	butyl	mcl		[116]								[118] ^q	poly(3-hydroxyheptanoate) (P(3HHp))
PHO	pentyl	mcl	[106], [109], [113], [114], [117]		[89] ^o [90] ^p	[90] [90] [96]	[90]					[42] ^f , [45], [48], [49], [50] [63] [91] [95] [96]	poly(3-hydroxyoctanoate) (P(3HO))

Table 4 – continued

Type of PHA	Formula	Chain length	“general” degradability	Mostly aerobic, partly anaerobic		Anaerobic			Aerobic			Laboratory or other	Comment
				Industrial composting, thermophilic	Home composting, mesophilic	Soil	Fresh water	Sea water	Interfaced**	Soil	Fresh water		
PHN	R hexyl	Type*** mcl	[109]									[42] ^f [91]	poly(3-hydroxynonanoate)
PHD	R heptyl	Type*** mcl	[106]									[42] ^f	poly(3-hydroxydecanoate)
PHUD	R octyl	Type*** mcl										[59]	poly(3-hydroxyundecanoate)
PHDD	R nonyl	Type*** mcl	[106]										poly(3-hydroxydodecanoate)
PHTD	R undecyl	Type*** mcl	[106]										poly(3-hydroxytetradecanoate)
PHBHV	R scl	Type*** scl	[27]	[81]			[83]	[83]	[47]			[61]	poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (P(3HB-co-3HV))
PHBHHx, PHBH	R scl	Type*** scl	[27]			[82]		[47]				[94] ^d	poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBHHx) at 6 and 11 mol% in HHx
P(3HB-co-4HB)	R scl	Type*** scl	[99], [100]	[81]		[82]				[103]		[31] ^d , [43] ^e [57] ^f [61]	
PHPV	R scl	Type*** scl										[45] ^h	poly(3-hydroxyphenylvalerate)
PHOU	R scl	Type*** scl										[45] ^h , ⁱ	poly(3-hydroxyoctanoate-co-b-hydroxyundecanoate)
P(3HB-co-3HP-co-5HV)	R scl	Type*** scl	[105]										poly[(R)-3-hydroxybutyrate-co-3-hydroxypropionate-co-5-hydroxyvalerate]s
PHBO	R scl	Type*** scl				[108]	[108]	[108]	[108]				Poly(3-hydroxybutyrate-co-3-hydroxyoctanoate)
Undefined PHA grade (single material)	R scl	Type*** scl	[107], [115]			[32]						[29] ^c	

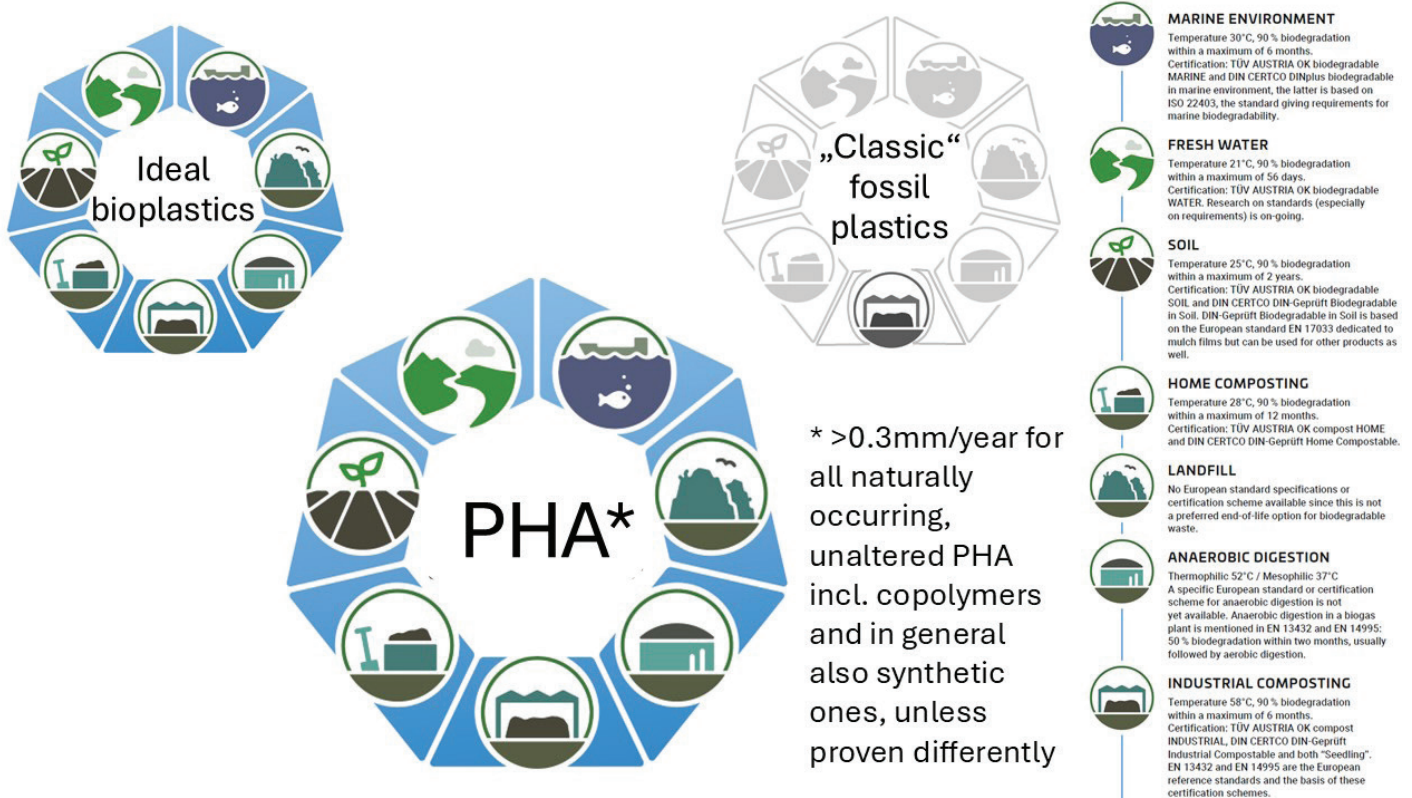


Fig. 15 – In a nutshell, it is fair to assume complete degradability of all poly(hydroxyalkanoates) in controlled and uncontrolled environments, not always according to established standards, but faster than most other bioplastics and, of course, much faster than fossil-based polymers³⁹.

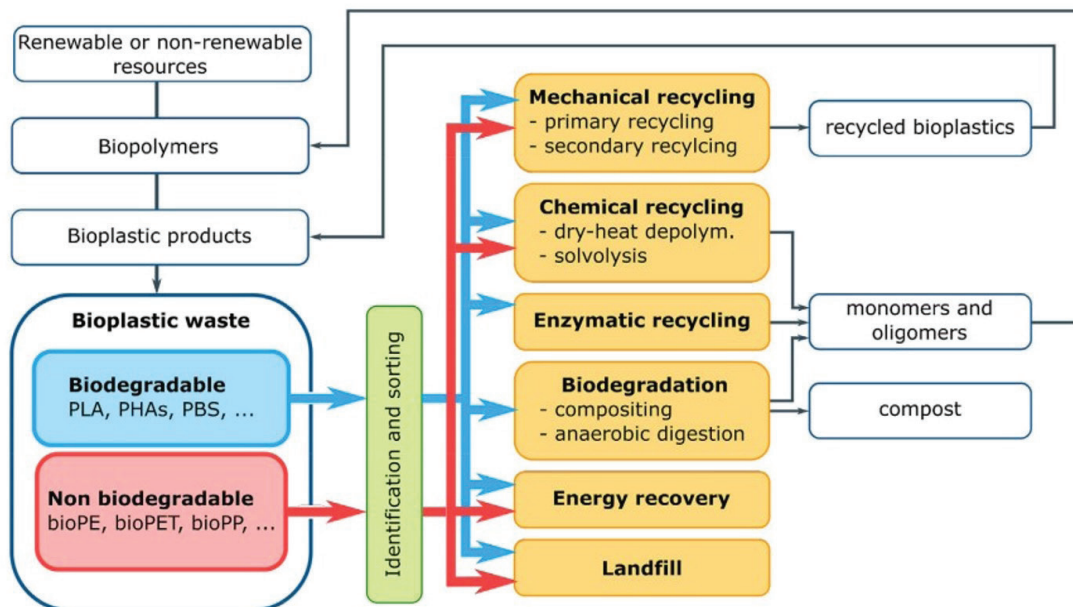


Fig. 16 – End-of-life routes for biodegradable and non-biodegradable bioplastic waste²⁷. Note: Though landfills should be obsolete, they are still common in many countries for organic material. PBS = poly(butylene succinate).

Conclusions

Plastics, after metals, are arguably the most important class of wood and concrete materials by production volume. However, the polymer industry today is largely linear, with significant quantities of plastics mismanaged at the end of their lifecycle. Biobased and biodegradable plastics can offer a partial solution by reducing the environmental harm from leaked plastics. Fig. 16 summarizes various end-of-life options for biodegradable and non-biodegradable bioplastic waste.

Biodegradable thermoplastics can not only be recycled but also mineralized under uncontrolled conditions, preventing accumulation of microplastics with its associated detrimental effects. For bioplastics formulations and products that are likely to degrade in nature, or produce microplastics (primary and secondary) and/or be leaked into the environment, it is essential to ensure they contain additives and fillers that are also degradable. Further work is required in compounding, processing, and application development of bioplastics. PHA can play a key role, particularly as the major types of PHA are fully degradable, even in marine environments.

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