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# Biodegradable plastics in the marine environment: a potential source of risk?

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## Abstract

The marine environment is facing the threat of increasing plastic pollution, especially from disposable plastics. Presently, governments worldwide are promoting policies to restrict or prohibit conventional plastics. As one hopeful alternative to conventional disposable/non-durable plastics, biodegradable plastics have attracted much attention and controversy in terms of their definition, environmental impact, and environmental significance, as they may be widely used. Therefore, it is necessary to clarify the facts about biodegradable plastics, understand the current knowledge gaps, and identify promising fields of relevant research. This review briefly introduces some common biodegradable plastics, their mechanisms of biodegradation, indicators for the biodegradation process, and factors concerning biodegradability and summarizes studies on the biodegradation of biodegradable plastics in the marine environment. The lifespan of biodegradable plastics varies greatly due to their compositions/properties as well as significant differences in the marine environment. Then, the potential risks of biodegradable plastics, including the release of pollutants (micro/nanoplastics, degradation products, and additives), adsorption-desorption of pollutants (pesticide, etc.), and their impact on biomes and biogeochemical cycles are discussed, fully revealing their possible impacts on the marine environment. It is believed that, in addition to the waste of resources, a high abundance of microplastics, toxic leachates, and complex effects on habitats and the environment may also cause problems for the marine environment as a result of the widespread and inappropriate use of biodegradable plastics. Based on the discussion, some constructive suggestions on how to use



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biodegradable plastics reasonably and prudently in the future are put forward.

**Keywords:** Biodegradable plastics, marine environment, microplastics, hydrolysis, plastic additives, ecological risks, microbial community

## INTRODUCTION

Since the last century, human life has been deeply affected by artificial polymers, such as plastic and rubber, as well as the pollutants from their products<sup>[1]</sup> (marine plastic litter, microplastics, plasticizers, *etc.*). With the widespread concerns and appeals of various sectors of society<sup>[1]</sup>, new solutions are emerging to reduce artificial polymer pollution<sup>[2]</sup>. As one of the most promising options, biodegradable plastics (BPs) are widely considered an alternative to conventional plastics in Europe, the USA, and China<sup>[3]</sup>. BPs are artificially synthesized or chemically modified polymers that can be completely mineralized<sup>[4]</sup>, i.e., eventually converted into carbon dioxide and water, by biological activity<sup>[5]</sup> or, in a narrow sense, naturally occurring microorganisms<sup>[6]</sup>. Similar and confusing nouns include “bioplastics” and “bio-based plastics”. Different from bio-based plastics, which are wholly or partially made from biological materials and not necessarily compostable or biodegradable, BPs could be made from fossil fuel-based materials. As a less formal term, “bioplastics” is sometimes used as a collective term to cover both bio-based plastics and BPs<sup>[7]</sup> or specifically to refer to bio-based plastics<sup>[8]</sup> [Table 1].

BPs are primarily used as disposable or non-durable plastic products, such as packaging, mulching film, and tableware<sup>[16]</sup>. These items accounted for 49% of global plastic production in 2019<sup>[17]</sup>. As early as 2018, before the COVID-19 pandemic, 5% of annual municipal solid waste and 40% of plastic waste in the United States were containers and packaging plastics, as estimated by USEPA (by weight)<sup>[18,19]</sup>. It is notable that only 14.5% of this waste was recycled in the United States<sup>[18]</sup>. For these products, the short service time greatly increases the frequency of their discovery in the environment. For example, disposable or non-durable plastic products are common in marine litter globally<sup>[20]</sup>. Moreover, the pandemic has led to increased demand for single-use plastics, including plastic bags, electronic packaging, food delivery and takeout packaging, and personal protective equipment<sup>[21]</sup>. The International Solid Waste Association shows that consumption of single-use plastics has increased by 250%-300% since the pandemic began<sup>[17]</sup>, accompanied by secondary pollutants, such as ubiquitous microplastics in the marine environment, from abandoned personal protective equipment<sup>[22]</sup>. Although the pandemic will end one day, its impact on consumption habits (such as online shopping and express delivery, in which plastic packaging is widely used) might continue for a long time; meanwhile, it reminds us that disposable plastic products cannot be completely replaced<sup>[21]</sup>. Especially in recent years, the successive restrictions or bans on the use of single-use plastics put forward by a variety of countries have aroused a huge demand for BPs<sup>[2,3]</sup>. Considering that BPs accounted for only 0.3% and 0.6% of plastic production in 2019<sup>[23]</sup> and 2020<sup>[24]</sup>, respectively, the consumption of BPs should increase greatly in the near future, as predicted. The consumption of “biodegradable and compostable plastic products” in Europe was estimated to be beyond 300,000 tons in 2020, three times the consumption in 2015<sup>[25]</sup>.

This does not mean that there is no controversy in novel polymer materials known as “biodegradable plastics”. One of the most common questions is whether BPs can degrade efficiently in the real and complex natural environment<sup>[9]</sup>, including the aquatic environment. Firstly, the definition of “biodegradable” is vague<sup>[23]</sup>. Actually, it should be expressed as “biodegradable under certain conditions”<sup>[3]</sup>. According to the retrieval of American Standard for Testing and Materials (ASTM) standards of test methods [Table 2], BPs could be divided into several categories, including “industrial compostable”, “marine biodegradable”, and

**Table 1. Common BPs: their sources, properties, and usage**

| Composition                                  | Abbreviation | Source*           | Material density (g/mL) <sup>†</sup> | Usage <sup>§</sup>  |
|--|--------------|-------------------|--------------------------------------|---|
| Poly(lactic acid)                            | PLA          | Bio-based         | 1.25                                 | Packaging, paper coatings, mulch films, compost bags, etc.  |
| Polyhydroxyalkanoate                         | PHA          | Bio-based         | 1.20-1.25                            | Disposable drinking cups, cutlery, trays, food plates and food containers; soil retention sheathing and other agricultural films; garbage bags, shopping bags, etc. |
| Polyhydroxybutyrate                          | PHB          | Bio-based         | 1.18-1.26                            | Bottles, bags, packaging film and disposable nappies, etc.  |
| Poly(hydroxybutyrate-co-valerate)            | PHBV         | Bio-based         | 1.25                                 | Films and paper coatings, biomedical applications, etc.   |
| Starch blends                                | -            | Bio-based         | 1.25-1.35                            | Food packaging, bottles, cutlery, straws, disposable bags, etc.   |
| Polyglycolic acid                            | PGA          | Bio-based         | 1.53                                 | Packaging films for oxygen-sensitive products, shale gas mining and other industrial processes, and synthetic fast absorbable sutures for surgery                   |
| Cellulose acetate                            | CA           | Bio-based         | 1.20-1.30                            | Textiles, optical film for LCD technology, antifog goggles, filters, etc.   |
| Poly( $\epsilon$ -caprolactone)              | PCL          | Fossil-based      | 1.12                                 | Mulch and other agricultural films, etc.  |
| Poly(butylene Succinate)                     | PBS          | Bio-/fossil-based | 1.23-1.26                            | Food packaging, mulch film, plant pots, hygiene products, fishing nets, fishing lines, etc.   |
| Poly(butylene succinate-co-butylene adipate) | PBSA         | Bio-/fossil-based | 1.23                                 | Ditto   |
| Poly(butylene adipate)                       | PBA          | Fossil-based      | 1.02-1.12                            | Injection molding for automotive, mechanical and electronic industries, etc.  |
| Poly(butylene adipate-co-terephthalate)      | PBAT         | Fossil-based      | 1.25                                 | Food packaging, agricultural film, etc.   |

\*It was provided by Kjeldsen *et al.*<sup>[9]</sup>. <sup>†</sup>The data were obtained at 25 °C and provided by Ki and Ok Park<sup>[10]</sup>, Van den Oever *et al.*<sup>[11]</sup>, Rafiqah *et al.*<sup>[12]</sup>, Rivera-Briso *et al.*<sup>[13]</sup>, or Chemical Retrieval on the Web<sup>[14]</sup>. <sup>§</sup>It was provided by Shah *et al.*<sup>[15]</sup> or Chemical Retrieval on the Web<sup>[14]</sup>.

“soil biodegradable”, which are also certified in the European certification scheme<sup>[3]</sup>. There is also another relatively sound standard system for BPs, the International Organization for Standardization (ISO) standard system [Table 2]. Most certified “biodegradable plastics” could only be efficiently biodegraded in aerobic or industrial anaerobic conditions. The relatively high temperature and ideal moisture content in industrial composting could accelerate the biodegradation process; it is also suggested that the aquatic environment has fewer microbes per unit than compost and soil environments<sup>[27]</sup>. Consequently, the average biodegradation level of BPs in industrial composting is 72.3% over 75 days, based on the data obtained from comprehensive data analysis, while that in the marine environment is 47.1% over 155 days<sup>[27]</sup>. In addition, there are unignorable differences between laboratory test conditions and the natural environment<sup>[28]</sup>. Therefore, the degradability of BPs might be overestimated. For example, the material densities of most BPs [Table 1] are higher than that of surface water (including seawater); thus, immediately after entering the aquatic environment, they could sink to the bottom<sup>[29]</sup>, where the environment may be dark with anoxic or anaerobic conditions and maintain a relatively low temperature. There must be deviations and uncertainties between the supposed biodegradation rate and the actual rate in the environment.

The longer (than expected) environmental degradation term might greatly reduce the difference between BPs and conventional plastics, for example, in some risks<sup>[30]</sup>, while the shorter lifespan might bring different environmental impacts than conventional plastics. Hence, the question is: In what way will BPs, which are expected to be used widely, affect the marine environment? Could they become potential sources of pollutants or carriers of harmful microorganisms in the marine environment? During degradation, will they cause secondary ecological risks, via the release of toxics to or other unpredictable impacts on the environment or ecological equilibrium, especially in the context of large-scale disposable use? This review

**Table 2. Active American Standard for Testing and Materials (ASTM) and International Organization for Standardization (ISO) standards of test methods concerning "biodegradable plastics"<sup>[26]</sup>**

| Classification            | Environment  | Degradation pattern        | Standard number  | Standard name  |
|---------------------------|--|----------------------------|--|--|
| <b>ASTM standards</b>     |  |                            |  |  |
| Solid waste disposal site | Landfill   | Anaerobic                  | D5526-18   | Standard test method for determining anaerobic biodegradation of plastic materials under accelerated landfill conditions   |
|                           |  | Aerobic and/or anaerobic   | D7475-20   | Standard test method for determining the aerobic degradation and anaerobic biodegradation of plastic materials under accelerated bioreactor landfill conditions  |
|                           | High-solids anaerobic digester or biologically active landfill | Anaerobic                  | D5511-18   | Standard test method for determining anaerobic biodegradation of plastic materials under high-solids anaerobic-digestion conditions  |
|                           | Composting   | Aerobic                    | D5338-15(2021)   | Standard test method for determining aerobic biodegradation of plastic materials under controlled composting conditions, incorporating thermophilic temperatures   |
| Aerobic                   |  | D6400-21                   | Standard specification for labeling of plastics designed to be aerobically composted in municipal or industrial facilities |  |
| Natural environment       | Soil   | Aerobic                    | D5988-18   | Standard test method for determining aerobic biodegradation of plastic materials in soil   |
|                           | Marine environment   | Aerobic                    | D6691-17   | Standard test method for determining aerobic biodegradation of plastic materials in the marine environment by a defined microbial consortium or natural sea water inoculum   |
|                           |  | Aerobic                    | D7991-15   | Standard test method for determining aerobic biodegradation of plastics buried in sandy marine sediment under controlled laboratory conditions   |
| Either                    | Soil, landfill, compost, land cover and agricultural use       | Abiotic+ Aerobic/anaerobic | D6954-18   | Standard guide for exposing and testing plastics that degrade in the environment by a combination of oxidation and biodegradation  |
| <b>ISO standards</b>      |  |                            |  |  |
| Solid waste disposal site | High-solids anaerobic digester                                 | Anaerobic                  | 15985:2014   | Plastics - Determination of the ultimate anaerobic biodegradation under high-solids anaerobic-digestion conditions - Method by analysis of released biogas   |
|                           |  | Composting                 | Aerobic  | 14855-1:2012   |
|                           |  |                            | 14855-2:2018   | Determination of the ultimate aerobic biodegradability of plastic materials under controlled composting conditions - Method by analysis of evolved carbon dioxide - Part 2: Gravimetric measurement of carbon dioxide evolved in a laboratory-scale test |
|                           |  |                            | 16929:2021   | Plastics - Determination of the degree of disintegration of plastic materials under defined composting conditions in a pilot-scale test  |
|                           |  |                            | 20200:2015   | Plastics - Determination of the degree of disintegration of plastic materials under simulated composting conditions in a laboratory-scale test   |
|                           | Natural environment  | Soil                       | Aerobic  | 17556:2019   |
| Aqueous medium            |  |                            | Aerobic  | 14851:2019   |
|                           |  | Aerobic                    | 14852:2021   | Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium - Method by analysis of evolved carbon dioxide  |
|                           |  | Anaerobic                  | 14853:2016   | Plastics - Determination of the ultimate anaerobic biodegradation of plastic materials in an aqueous system - Method by measurement of biogas production   |
| Marine environment        | Aerobic  | 22766:2020                 | Plastics - Determination of the degree of disintegration of  |  |

|         |            |   |
|---------|------------|---|
| Aerobic | 22403:2020 | plastic materials in marine habitats under real field conditions<br>Plastics - Assessment of the intrinsic biodegradability of materials exposed to marine inocula under mesophilic aerobic laboratory conditions - Test methods and requirements |
|---------|------------|---|

These test methods can also be applied to non-biodegradable plastic materials, such as those selected for landfill facilities.

provides some information about BPs and collects studies and views on the degradation of BPs in the marine environment and their ecological effects to deepen the understanding of the environmental impact of BPs. Significantly, some results in other environments (e.g., in soil) are also included to make inferences, since some evidence for BPs in the marine environment is still not sufficient.

## MAIN TEXT

### Biodegradation ability in the marine environment and related factors

#### *Biodegradation process and description indicators*

In general, the biodegradation process of BPs can be divided into three steps [Figure 1]: fragmentation, hydrolysis, and biodegradation of products (such as oligomers and monomers). (I) In the first step, processes dominated by abiotic factors or biotic factors (also named biodeterioration<sup>[31]</sup>) induce fragmentations. Abiotic factors, including mechanical stress (e.g., caused by waving scouring, sand abrasion, or animals<sup>[32]</sup>), light<sup>[33]</sup>, thermal, and chemical factors<sup>[34]</sup>, play their roles in the fragmentation of BPs. (II) Hydrolysis, as a depolymerization reaction, is the rate-limiting step in the biodegradation of BPs<sup>[35]</sup>. The hydrolysis rate of the whole BP could be either approximately uniform (bulk erosion mechanism) or determined by the process on the surface (surface erosion mechanism)<sup>[31]</sup>. Most BPs are aliphatic polyesters or contain glycosidic bonds [Table 1]: PLA, PBAT, and starch-based materials (e.g., Mater-bi<sup>®</sup> and Bioflex<sup>®</sup>) are among the most popular BPs<sup>[36,37]</sup> [Figure 2<sup>[7,38-41]</sup>]. They are “fast” hydrolyzed by extracellular enzymes<sup>[42]</sup>, and some of them could be hydrolyzed in an alkali environment without any enzyme<sup>[43]</sup>. However, it is difficult for most hydrolases to permeate the structure of BPs<sup>[44]</sup>, so bulk hydrolysis rates of BPs are determined by the bulk diffusion rate and migration distance of water molecules<sup>[45]</sup>. (III) The last step is the degradation of hydrolysis products. The products could be taken in and then mineralized by microbial cells. Therefore, this step can be divided into bioassimilation and mineralization<sup>[31]</sup>. The entire process of this step does not need to take place inside microorganisms. For example, anaerobic microorganisms can degrade BPs to CH<sub>4</sub> and then finally mineralize them *in vitro*. It is worth mentioning that some believe that deterioration processes where plastics begin to lose their physical/structural properties should be the first step of biodegradation<sup>[9]</sup>. However, deterioration does not significantly change the environmental behavior of BPs. Considering this process as a part of biodegradation lacks environmental significance.

These three steps do not necessarily need to be performed sequentially; for example, the first step (fragmentation) may be the result of the second step (hydrolysis)<sup>[46]</sup>. Thus, some studies suggest that the biodegradation process can be summarized into two steps, namely, depolymerization and utilization of byproducts<sup>[47]</sup>; fragmentation is regarded as a pre- or simultaneous biotic/abiotic process<sup>[6]</sup>. In any case, the results of the previous step can greatly speed up the next step. For example, the fragmentation of BPs could greatly accelerate the hydrolysis reaction, especially when surface erosion plays a major role.

Several indicators, such as weight loss, molecular weight reduction, decrease in biochemical oxygen demand (BOD), and CO<sub>2</sub>/CH<sub>4</sub> produced, have been used to describe the biodegradation of BPs [Table 3]. It is difficult to accurately describe the entire biodegradation process with a single indicator. Among them, weight loss is the most widely used [Table 3], even though it cannot track the biodegradation of secondary

**Table 3. Test results for biodegradation ability of BPs in the marine environment**

| BPs                     | Shape and size  | Condition                                | Period                 | Indicators for degradation                                   |                        |                          |                          | Refs. |
|-------------------------|---|--|------------------------|--|------------------------|--------------------------|--------------------------|-------|
|                         |   |  |                        | Weight loss  | Decrease in BOD        | Decrease in $M_w^*$      | CO <sub>2</sub> produced |       |
| PLA                     | Spline, 80 × 4 × 2 mm   | Coastal seawater                         | 52 weeks               | 2%   | -                      | -                        | -                        | [35]  |
|                         | Film, 12 × 12 × 0.32 mm                                       | Artificial seawater, 25 °C               | 1 year                 | 0  | -                      | -                        | -                        | [48]  |
|                         | Film, 150 × 150 × 0.05 mm                                     | Artificial seawater                      | 6 months               | < 1%   | -                      | -                        | -                        | [49]  |
|                         | Film, 30 × 3 × 0.05 mm  | Static seawater, 25 °C                   | 10 weeks               | 0  | -                      | 4.5%                     | -                        | [50]  |
|                         | Film, 30 × 3 × 0.05 mm  | Coastal seawater, 19-26 °C               | 5 weeks                | 25%  | -                      | -                        | -                        | [35]  |
|                         | Sheet, 20 × 20 × 0.2 cm                                       | ASTM D6691                               | 56 days                | -  | -                      | -                        | 7% <sup>†</sup>          | [51]  |
|                         | Spline, 25 × 6 × 2 mm   | Natural seawater; static seawater (lab)  | 1 year                 | < 3%   | -                      | 13% (natural); 25% (lab) | -                        | [52]  |
| PLA mixture             | Film, φ50 × 0.02 mm   | On natural sediment                      | 82 days                | 0.2%   | -                      | -                        | -                        | [53]  |
|                         | Film  | Buried in sand                           | 71 days                | 0.15%  | -                      | -                        | -                        | [54]  |
| PHB                     | Film  | Seawater; sediment                       | 365 days               | 5%-29% (seawater); 65%-99% (sediment)                        | -                      | -                        | -                        | [55]  |
|                         | Film, 12 × 12 × 0.32 mm                                       | Artificial seawater, 25 °C               | 1 year                 | 6%   | -                      | -                        | -                        | [48]  |
|                         | Film, 30 × 20 × 0.1 mm  | Coastal seawater                         | 6 weeks                | 40%-100%   | -                      | -                        | -                        | [35]  |
|                         | Film, 0.005 mm thickness; pellet, φ10 × 5 mm                  | Tropic seawater                          | 160 days               | 42% (film); 38% (pellet)                                     | -                      | 26% (film); 20% (pellet) | -                        | [47]  |
|                         | Film, 30 × 3 × 0.05 mm  | Static seawater, 25 °C                   | 10 weeks               | 8%   | -                      | 2.5%                     | -                        | [50]  |
|                         | Film, 30 × 3 × 0.05 mm  | Coastal seawater, 19-26 °C               | 5 weeks                | 65%  | -                      | -                        | -                        | [35]  |
|                         | Film  | Static seawater, 25 °C                   | 2 weeks                | -  | 80%                    | -                        | -                        | [56]  |
| PHBV                    | Film, 0.1 mm thickness  | Seawater in lab (bay and ocean), 25 °C   | 28 days                | 41% (bay); 23% (ocean)                                       | 27% (bay); 14% (ocean) | -                        | -                        | [57]  |
|                         | Film, 0.16 mm thickness                                       | Lab/aquarium incubation; ASTM 6691       | 49 d (lab or aquarium) | Lab: 99%; 86% <sup>§</sup> ; Aquarium: 30%; 72% <sup>§</sup> | -                      | -                        | 80%-90% (100 d)          | [58]  |
|                         | Sheet, 20 × 20 × 0.2 cm                                       | ASTM D6691                               | 43 days                | -  | -                      | -                        | 89% <sup>†</sup>         | [51]  |
|                         | Film, 60 × 80 × 0.085 mm                                      | Marine sediment                          | 356 days               | 81%-97%  | -                      | -                        | -                        | [59]  |
|                         | Film  | Buried in sand                           | 71 days                | 15%  | -                      | -                        | -                        | [54]  |
|                         | Film, 0.005 mm thickness; pellet, 10 mm diameter, 5 mm height | Tropic seawater                          | 160 days               | 46% (film); 13% (pellet)                                     | -                      | 16% (film); 57% (pellet) | -                        | [47]  |
|                         | Fiber, 0.26 mm diameter                                       | Seawater                                 | 8 weeks                | 65%  | -                      | -                        | -                        | [35]  |
| PHB-co-PHV <sup>†</sup> | Film, 0.1 mm thickness, P(3HB-co-14%3HV)                      | Seawater in lab (bay and ocean), 25 °C   | 28 days                | 100%   | 84% (bay); 78% (ocean) | -                        | -                        | [57]  |
|                         | Film, 0.29 mm thickness                                       | Lab/aquarium (aqu) incubation; ASTM 6691 | 49 d (lab/aqu)         | Lab: 99%; 87% <sup>§</sup> . Aqu: 32%; 48% <sup>§</sup>      | -                      | -                        | 85%-95% (100 d)          | [58]  |
|                         | Film, 150 × 150 × 0.05 mm                                     | Artificial seawater                      | 6 months               | < 1%   | -                      | -                        | -                        | [49]  |
| Mater-Bi <sup>†</sup>   | Sheet, 20 × 20 × 0.2 cm                                       | ASTM D6691                               | 56 days                | -  | -                      | -                        | 38% <sup>†</sup>         | [51]  |
|                         | Film, 200 × 20 × 0.025 / 60 × 80 × 0.012 mm                   | Marine sediment                          | 298 d / 356 days       | 5%-99% / 47%-98%   | -                      | -                        | -                        | [59]  |
|                         | Carrier bags  | Littoral marsh                           | 90 days                | 1.5%-1.6%  | -                      | -                        | -                        | [60]  |
| TPS <sup>†</sup>        | Carrier bags  | Seawater                                 | 90 days                | 1.7%-4.5%  | -                      | -                        | -                        | [60]  |
|                         | Sheet, 20 × 20 × 0.2 cm                                       | ASTM D6691                               | 28 days                | -  | -                      | -                        | 92% <sup>†</sup>         | [51]  |
| PCL                     | Film, 12 × 12 × 0.32 mm                                       | Artificial seawater, 25 °C               | 1 year                 | 1%   | -                      | -                        | -                        | [48]  |

|      |                         |   |          |                          |                        |                          |                  |      |
|------|-------------------------|---|----------|--------------------------|------------------------|--------------------------|------------------|------|
|      | Film, 30 × 20 × 0.1 mm  | Seawater                                | 6 weeks  | 98%                      | -                      | -                        | -                | [35] |
|      | Film, 30 × 3 × 0.05 mm  | Static seawater, 25 °C                  | 10 weeks | 24%                      | -                      | 8.5%                     | -                | [50] |
|      | Film, 30 × 3 × 0.05 mm  | Coastal seawater, 19-26 °C              | 5 weeks  | 34%                      | -                      | -                        | -                | [35] |
|      | Film, 0.1 mm thickness  | Seawater in lab (bay and ocean), 25 °C  | 28 days  | 100% (bay); 67% (ocean)  | -                      | -                        | -                | [57] |
|      | Spline, 80 × 4 × 2 mm   | Coastal seawater                        | 52 weeks | 30%                      | -                      | -                        | -                | [35] |
|      | Sheet, 20 × 20 × 0.2 cm | ASTM D6691                              | 56 days  | -                        | -                      | -                        | 80% <sup>†</sup> | [51] |
|      | Spline, 25 × 6 × 2 mm   | Natural seawater; static seawater (lab) | 1 year   | 32% (natural); 12% (lab) | -                      | 1% (natural); 7% (lab)   | -                | [52] |
|      | Film                    | Buried in sand                          | 71 days  | 1.8%                     | -                      | -                        | -                | [54] |
| PBS  | Spline, 80 × 4 × 2 mm   | Coastal seawater                        | 52 weeks | 2%                       | -                      | -                        | -                | [35] |
|      | Film, 30 × 20 × 0.1 mm  | Seawater                                | 6 weeks  | 2%                       | -                      | -                        | -                | [35] |
|      | Film, 0.1 mm thickness  | Seawater in lab (bay and ocean), 25 °C  | 28 days  | 2%                       | 1% (bay); 2% (ocean)   | -                        | -                | [57] |
|      | Sheet, 20 × 20 × 0.2 cm | ASTM D6691                              | 56 days  | -                        | -                      | -                        | 21% <sup>†</sup> | [51] |
|      | Spline, 25 × 6 × 2 mm   | Natural seawater; static seawater (lab) | 1 year   | < 3%                     | -                      | 28% (natural); 46% (lab) | -                | [52] |
| PBSA | Film                    | Buried in sand                          | 71 days  | 6%                       | -                      | -                        | -                | [54] |
| PBA  | Film, 0.1 mm thickness  | Seawater in lab (bay and ocean), 25 °C  | 28 days  | 34% (bay); 11% (ocean)   | 20% (bay); 10% (ocean) | -                        | -                | [57] |
| PBAT | Spline, 80 × 4 × 2 mm   | Coastal seawater                        | 52 weeks | 56%                      | -                      | -                        | -                | [35] |
|      | Film, 30 × 20 × 0.1 mm  | Seawater                                | 6 weeks  | 7%                       | -                      | -                        | -                | [35] |
|      | Spline, 25 × 6 × 2 mm   | Natural seawater; static seawater (lab) | 1 year   | < 3%                     | -                      | 56% (natural); 61% (lab) | -                | [52] |
|      | Film, φ50 × 0.02 mm     | Seawater; on natural sediment           | 82 days  | 1.2%-1.5%                | -                      | -                        | -                | [53] |

\* $M_{w}$ , molar mass. <sup>†</sup>It is expressed as a percentage of biodegradation of reference cellulose. <sup>‡</sup>The results are for sediment. <sup>§</sup>PHB-co-PHV: poly(hydroxybutyrate-co-hydroxyvalerate); PHO: polyhydroxyoctanoate; TPS: thermoplastic starch; Mater-Bi: a commercial product that is a blend of thermoplastic starch and biodegradable polyesters.

microplastics formed in the BP fragmentation, which rapidly disappear in the natural environment<sup>[48]</sup>. Sometimes, the photogrammetric method is used to determine the approximate weight loss<sup>[59]</sup>. Weight loss could occur throughout the biodegradation process<sup>[35]</sup> and is affected by several interference factors, such as the release of soluble additives and the loss of fragments. Molecular weight reduction, mainly caused by the chain shortening, is a representative indicator for the hydrolysis of BPs, since only in hydrolysis can there be a measurable and significant molecular weight reduction. Due to this, a greater weight loss ratio than molecular weight reduction indicates that surface erosion predominates, such as that for PCL<sup>[50,52]</sup> and PHA<sup>[47]</sup>. A contrary situation indicates that bulk erosion is more important than surface erosion at this stage, as happens to PBS, PBAT<sup>[52]</sup>, and PLA<sup>[50]</sup>.

Indicators associated with specific compositions or products, including mechanical properties and highly ordered structures<sup>[50]</sup>, are rarely used in the assessment of the natural biodegradation of BPs. On the one hand, they are not suitable for comparison between different compositions. On the other hand, some of them are too sensitive to the environment<sup>[35]</sup> and vary significantly in the deterioration process before fragmentation<sup>[9]</sup> and during the whole biodegradation process<sup>[35]</sup>.

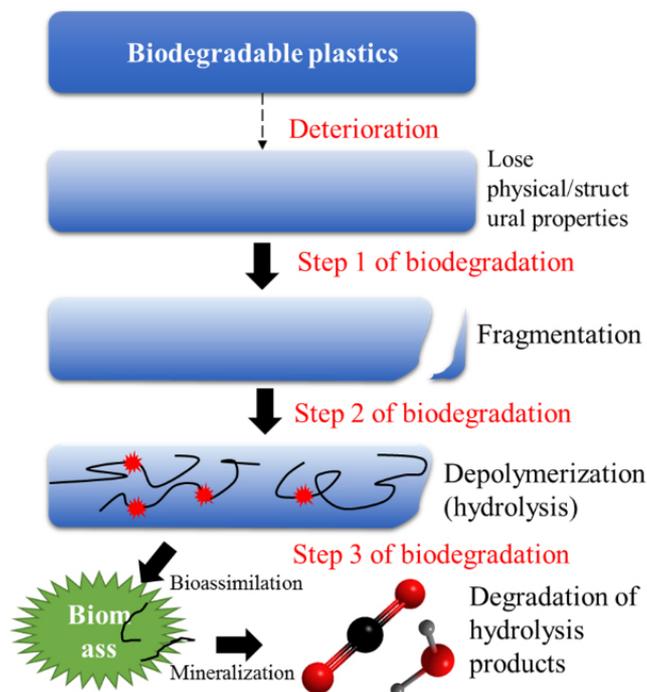


Figure 1. Diagrammatic sketch of biodegradation process of biodegradable plastics.

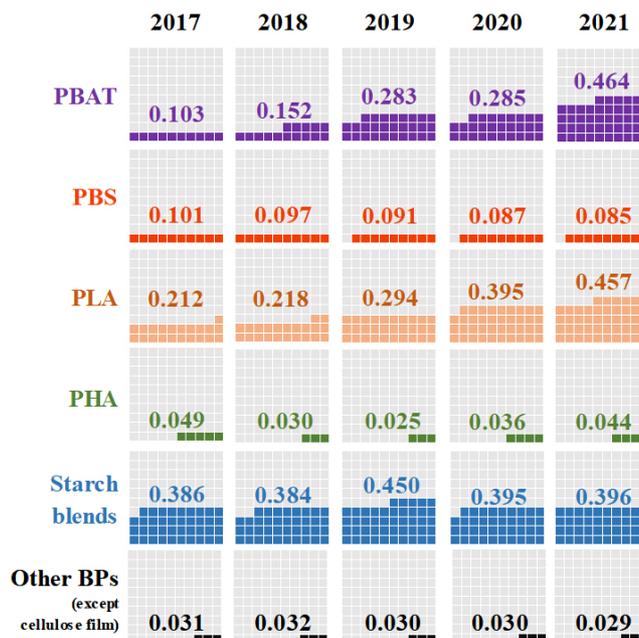


Figure 2. The global production capacities (million tons) of different biodegradable plastic (BP) materials during 2017-2021. Data source: European Bioplastics and nova-Institute, 2017-2021<sup>[7,38-41]</sup>. Only the data from the corresponding annual report are presented.

### Factors affecting biodegradability

#### Properties of BPs

Similar to other organic substances, the biodegradability of BPs first depends on their chemical compositions. Firstly, the properties of BPs affect the adhesion of microorganisms. Properties of polymers,

including surface charge, hydrophilicity/hydrophobicity, roughness, and bioavailability (biodegradability), were supposed to affect surface biofilm formation<sup>[24]</sup>. The positive surface charges on BPs (e.g., PLA) are prone to adhere to microorganisms, since zero charge points of most bacterial cells are between pH of 2 and 4<sup>[24,61]</sup>. The hydrophobicity of plastic surfaces might provide plastics with different microbial compositions from those on glass<sup>[24]</sup>, ceramics<sup>[62]</sup>, or the natural environment<sup>[24]</sup>. Generally, there is stronger adhesion between bacteria and a hydrophobic surface (than a hydrophilic one)<sup>[63]</sup>. The specific surface area of plastics could be affected by their size, shape, and roughness. It takes longer for marine microorganisms to come into contact with and adapt to plastics with small surface areas<sup>[47]</sup>. The specific surface area of BPs increases in the biodegradation process, with the decrease of size and the change of roughness<sup>[24]</sup>.

Secondly, one of the impacts of BPs' properties on their biodegradability, which may be the most important, is that they determine the hydrolysis rate. Some properties that proved important include the following. (i) Hydrolysable bonds and neighboring groups: Typically, hydrolysable bonds and neighboring groups determine the kinetics of bond cleavage<sup>[64]</sup>. For example, it is generally believed that polymers based on cellulose, starch, and proteins (with glycosidic and amide bonds hydrolysable) show better marine biodegradability rates than polyesters (with ester bonds hydrolysable) and could reinforce the biodegradability when combined with polyesters<sup>[44,65]</sup>. On the contrary, the biodegradability of cellulose acetate formed by cellulose acetylation decreases with the increased degree of substitution<sup>[16]</sup>; it might be due to the hindrance of carboxyl bonds during the hydrolysis. Another typical example of the impact of neighboring groups is PET (polyethylene terephthalate), which is persistent in the marine environment due to aromatic rings adjacent to ester bonds. (ii) Chain length: The chain length is related to the number of bonds to be hydrolyzed, the abundance of hydrolysates, and the hindrance of intermolecular contact during the reaction. Lower initial molecular weight (low average chain length) makes the mineralization process progress faster<sup>[58]</sup>. (iii) Structure of BPs: Crystallinity and surface hydrophilicity<sup>[10]</sup> affect the diffusion of water molecules in BPs, hence the hydrolysis. The closely packed crystalline regions are supposed to slow down water molecular diffusion<sup>[64]</sup> and more or less hinder the attack by hydrolase<sup>[66]</sup> (the highly ordered structure of crystalline regions prevents ester bonds within the chains from entering the active site of the hydrolase<sup>[30]</sup>) during biodegradation. Some believe it could be more important for the resistance to nucleophilic attack than the introduction of hydrophobic groups to some extent<sup>[10]</sup>. Several studies suggest that the degree of crystallinity was the dominant factor in the biodegradation rate of a BP product<sup>[66]</sup>. Nevertheless, a study based on the biodegradation of PHA in seawater showed that the amorphous phase and the crystalline phase seemed to degrade synchronously<sup>[47]</sup>. (iv) Specific composition in the blend: Some specific compositions increase the water permeability of the blend, thus accelerating the hydrolysis of BPs<sup>[43]</sup>. (v) Shape of BPs: Specific surface area affects the surface hydrolysis rate, e.g., biodegradation seems slower for PHB pellets than for PHB films [Table 3<sup>[47]</sup>]. Meanwhile, the shape is related to the diffusivity of water in BPs<sup>[45]</sup>. The thickness of BPs dropping down below a so-called critical sample thickness might alter the dominant hydrolysis process from surface erosion to bulk erosion<sup>[31]</sup>.

Finally, some materials (PBAT, PHBV, *etc.*) could act as the sole carbon source for bacteria, while others (PLA and PBS) could not<sup>[67]</sup>, which might be caused by the difference in the uptake ability of microorganisms to hydrolysates.

### Additives

Additives are chemical substances providing plastic desired qualities<sup>[68]</sup>. Plastic additives are complex and diverse; the specific ingredients of plastic additives are often undisclosed as trade secrets. The main essential additives of BPs include crystalline nucleating agents, chain extenders, anti-hydrolysis stabilizers, melt enhancers, plasticizers, *etc.* Inorganic additives such as inorganic nucleating agents might cause the

degradation of plastic products due to their poor compatibility. As the name implies, chain extenders could extend the chain, increase the molecular weight, and increase crosslinking during production, which prolongs the biodegradation time<sup>[44]</sup>. Anti-fouling agents<sup>[69]</sup> and chain extenders<sup>[70]</sup> could inhibit extracellular enzyme activity or prevent the microorganism from producing enzymes. Anti-hydrolysis stabilizers for condensed BPs can significantly improve their aging stability. Therefore, the leaching of plasticizers is supposed to make the plastics brittle and stimulate fragmentation<sup>[71]</sup>. Some other additives, such as colorants<sup>[72]</sup> and photostabilizers<sup>[73]</sup>, could influence the final thermal and UV stability of plastics, which might affect the fragmentation and hydrolysis of BPs.

#### Natural environmental condition

Natural environmental conditions, including habitats and climate zones, could lead to some differences in the degradation of BPs<sup>[74]</sup>. The main environmental factors in the marine environment consist of light, temperature, salinity, pH, nutrients, electron acceptors, grain size of sediments, and microbial population. These factors can not only affect microbial composition, abundance, and activity<sup>[30]</sup> but also cause some abiotic effects on degradation.

UV light accelerates the fragmentation of BPs<sup>[71]</sup> and slowly produces some low molecule weight oxidation products for bioassimilation<sup>[30]</sup>, but the effect of UV light is rapidly attenuated with water depth<sup>[74]</sup>. Light might also decelerate biodegradation, e.g., crosslinks formed during photoirradiation-induced reactions could slow down biodegradation<sup>[30]</sup>. In addition, light can moderate the proportion of photosynthetic autotrophs. Although no significant mineralization effect of plastics is expected due to their metabolic pathways<sup>[75]</sup>, algae are important participants of the “plasticsphere” in the marine environment and affect BPs’ degradation indirectly.

In the marine environment, temperature, pH, and salinity change in a certain range, and ultra-high temperatures could accelerate the oxidative degradation<sup>[76]</sup> and abiotic hydrolysis<sup>[30]</sup> of plastics, while ultra-low temperatures might cause frozen-accelerated degradation<sup>[77]</sup>. However, for biodegradation, a temperature within a suitable range is needed for both the microbial growth on the surface of BPs and the reaction rate of enzymes<sup>[78]</sup>. Different microorganisms (psychrophilic, psychrotrophic, and mesophilic) thrive and are active at various water temperatures<sup>[30]</sup>. Similarly, the effects of pH and salinity on biodegradation indirectly affect the microbial communities, and different microorganisms/enzymes prefer different pH and salinity<sup>[30]</sup>. Specifically, relatively warm and alkali environments are suitable for the enzyme hydrolysis of BPs<sup>[44]</sup>. Additionally, high salinity makes abiotic hydrolysis in seawater slower than in fresh water, possibly due to the slower diffusion of seawater in polyester<sup>[35]</sup>.

The availability of nutrients and electron acceptors is a key factor in the biodegradation of BPs. Essential nutrients and electron acceptors are necessary for the survival and metabolism of microorganisms. Oxygen is an important electron acceptor in the biodegradation (oxidation reaction) of BPs, but it is certainly not sufficient in the marine environment. Given the specific density of BPs, they are more likely to appear under anaerobic or anoxic conditions when offshore. Sunken ships that have not been decayed for hundreds of years can laterally illustrate the impact of the hypoxic environment on biodegradation<sup>[30]</sup>. However, even in this case, biodegradation (hydrolysis and assimilation by anoxic microorganisms) is still proceeding slowly and continuously.

BPs on the surface of sediments were estimated to be biodegraded more quickly than those in the water column, without forceful experimental evidence under similar conditions<sup>[30]</sup>. The properties of sediments, such as grain size and nutrient-related parameters, could affect the biodegradation of BPs placed on or

buried in the sediments<sup>[28]</sup>. Grain size fractions of sediments affect the bacterial abundance, so it also indirectly affects the biodegradation rate of BPs<sup>[59]</sup>, but their effect might be more or less hampered by other factors influencing the microbial community and bioactivity in natural sediments<sup>[59]</sup>.

Enzymatic hydrolysis of BPs needs specific microorganisms which secrete specific extracellular enzymes (hydrolases), as well as oxidation reactions. In contrast, the microorganisms that could be involved in bioassimilation are extensive<sup>[30]</sup>, so the demand for microorganisms in this step is more likely to be satisfied in the natural environment. Furthermore, inhibiting other microorganisms that are not involved in biodegradation may accelerate the biodegradation of BPs, since a broad-spectrum fungicide was found to accelerate the biodegraded rate<sup>[79]</sup>. Classically, hydrolases effective in the hydrolysis of biodegradable polyesters (PLA, PCL, and PBS) belong to cutinases (can hydrolyze ester bonds in cutin), lipases (can hydrolyze ester bonds in lipids), and polyhydroxyalkanoates (can hydrolyze ester bonds in carboxyloesters of bacterial polyesters); they have common features, such as extensive substrate-binding grooves for macromolecular polyesters, catalytic amino acid triad in active sites for binding substrate, and not substrate-specific<sup>[30]</sup>. Some other hydrolases that can be used for biodegradation include amidases and acetyl esterases<sup>[30]</sup>.

In addition, physical shearing caused by currents/waves, wind, fauna, or sediment (especially sands) improves the fragmentation of BPs<sup>[30]</sup>.

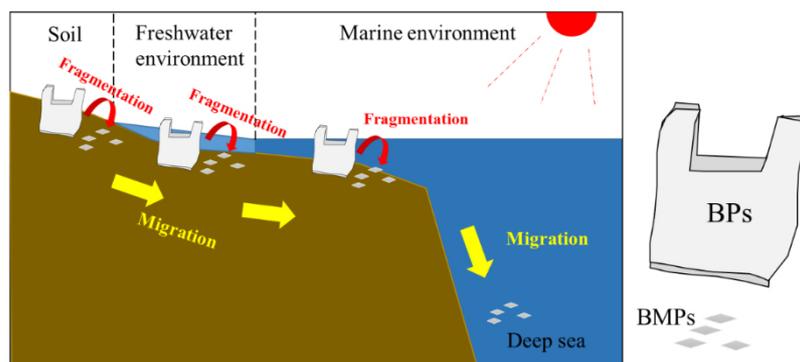
## Sources of potential pollutants

### *Microplastics*

#### Generation and degradation

The fragmentation of plastics in natural environments could produce secondary microplastics (MPs). BPs are supposed to produce even more MPs than conventional plastics in the short term after reaching the natural environment<sup>[80]</sup>. Then, biodegradable microplastics (BMPs) could be degraded. From another perspective, the generation of BMPs can be regarded as one of the stages of BPs' biodegradation. However, in the natural environment, it is difficult to monitor the generation or fate of BMPs. They are even rarely detected in the open environment. As far as we know, the limited data show that PLA and PCL MPs were detected in sediments close to the wastewater outlet<sup>[81]</sup>, seawater<sup>[82]</sup>, and leachate<sup>[83]</sup>. On the one hand, it is related to the low consumption of BP products. On the other hand, it may be due to BPs' high specific densities (which lead to short residence time in water, especially surface water) and shorter lifespan. Abiotic factors (UV radiation and mechanical forces) could produce BMPs from PBAT, PBS, PLA pellets, and PBAT/PLA bags, where the leading factor of BMPs' generation rate is the original shape of BPs<sup>[84]</sup>. Lambert and Wagner also proved the release of BMPs and nanoplastics during weathering of PLA in water<sup>[85]</sup> as well as PBAT in seawater (with/without sediment)<sup>[33]</sup>, PCL during enzymatic hydrolysis<sup>[46]</sup>, and PHB in water under stimulated solar visible light<sup>[86]</sup>, tap water, and drinking water<sup>[87]</sup>. In all the above-mentioned studies, most of the BMPs found were smaller than 50  $\mu\text{m}$ .

The factors affecting the biodegradation rate of BPs also determine the period of stable existence of BMPs; due to higher specific surface areas, BMPs are supposed to be hydrolyzed more rapidly than BPs in the same environment<sup>[30]</sup>. A study supported the faster disappearance of BMPs based on the test results in the soil (ASTM D 5988-12)<sup>[88]</sup>. However, it does not mean that BMPs pose less risk than conventional MPs in the marine environment. On the one hand, a smaller size than BPs could also mean that BMPs are prone to migration on/in marine sediments<sup>[89,90]</sup> and even to depths<sup>[91]</sup> with low microbial activity. It might affect the rate of enzymatic hydrolysis and the existence time of BMPs in the marine environment. Similarly, BMPs formed in other environments could enter the marine environment [Figure 3]. Due to the promotion of UV



**Figure 3.** The generation and migration of marine biodegradable microplastics (BMPs).

light on the fragmentation of BPs<sup>[80]</sup>, the period of BP fragmentation in soil or fresh water might be shorter than that in the marine environment. Therefore, a large proportion of secondary BMPs in the marine environment are supposed to come from other adjacent environments. For BMPs (or nanoplastics) in the marine environment, the exposure time and average abundance during exposure might be key factors for assessing their potential risk. There is no such experimental data at present, but BMPs took tens (polybutylene sebacate)<sup>[92]</sup> to hundreds (Mater-Bi)<sup>[93]</sup> of days to be mineralized in soil, and the biodegradation in the marine environment might take longer. On the other hand, the rapid degradation might pose even higher risks: the toxicity of degradation products is supposed to be stronger than the BMPs that produce them<sup>[94]</sup>.

#### Ecological risks

Among the studies involving BMPs, those concerning ecological risks are the most common [Table 4]. In view of the fact that there are only studies on PLA MPs in the marine environment, the effects of various BMPs on organisms in different environments are also listed in Table 4. It should be noted that most of these results were not obtained when exposed to the environmental abundance of BMPs.

In the marine environment, Green *et al.* suggested that PLA MPs posed weaker effects than a conventional type of plastic (PVC) on the biological activity of a sand-dwelling lugworm<sup>[95]</sup>. A high abundance of PLA MPs (colonized by microalgae) could also elevate the respiration rates of oysters and alter assemblages (decrease species richness, total number, and body size) of benthic fauna<sup>[96]</sup>. Khalid *et al.* suggested that no significant effect could be found on blue mussels exposed to PLA MPs, except for the reduction in glycerophospholipids, which are important structural lipids of biological membranes<sup>[97]</sup>. Green *et al.* adopted a sensitive method (proteomic analysis), which found PLA MPs increased expression of a putative heavy metal binding protein and a putative detoxification enzyme of blue mussels<sup>[98]</sup>. PLA MPs could reduce the fertilization rate of solitary ascidians<sup>[99]</sup>. The response of bivalves and related habitats to the exposure of PLA MPs depend on bivalve species: oysters accelerated filtration, whereas blue mussels chose to slow down filtration; the structure of benthic community changed only in oyster-dominated habits, where the biomass of benthic cyanobacteria and numbers of polychaetes decreased, while oligochaetes increased<sup>[100]</sup>.

In the freshwater environment, PHB MPs led to a weight loss of amphipods, while the biomass increased after being treated with natural or particle-free silica<sup>[101]</sup>. Nanoplastics produced from PHB MPs, instead of their leachate, induce the growth inhibition of cyanobacteria and algae and the immobilization of crustaceans<sup>[86]</sup>. Similar results (negative effects of BMPs instead of leachates) could also be found by PLA MPs on the reproductive output, body length, and mortality of crustaceans<sup>[102]</sup>. PLA MPs could inhabit

**Table 4. Ecotoxicological studies related to BPs in the marine environment, freshwater, and soil**

| Environment                                  | BMPs                                   | Abundance  | Organism involved  | Period (d)  | Adverse effect   | Effect level compared with conventional plastics | Refs. |
|--|--|--|--|---|--|--|-------|
| Marine                                       | PLA (~235.7 μm)                        | 2% of sediment weight  | <i>Arenicola marina</i>  | 31  | Respiration rate, cast production                                  | Weaker than PVC (but PVC MPs are smaller)        | [95]  |
|  | PLA (~65.5 μm)                         | 80 μg/L  | <i>Ostrea edulis</i>   | 60  | Respiration rates  | Similar to HDPE                                  | [96]  |
|  |  |  | <i>Scrobicularia plana</i>                                       |   | Biomasses  | Similar to HDPE                                  |       |
|  |  |  | Juvenile <i>Littorina</i> sp.                                    |   | Abundance  | Similar to HDPE                                  |       |
|  |  |  | Juvenile <i>Idotea balthica</i>                                  |   | Abundance  | Similar to HDPE                                  |       |
|  | PLA (1-10 μm mostly)                   | 10 and 100 μg/L  | <i>Mytilus edulis</i>  | 8   | Glycerophospholipids   | -  | [97]  |
|  | PLA (~65.6 μm)                         | 25 μg/L  | <i>Mytilus edulis</i>  | 52  | Attachment strength, protein expression                            | Weaker than HDPE                                 | [98]  |
|  | PLA (200-500 μm)                       | 100, 200, 400 mg/L   | <i>Microcosmus exasperatus</i>                                   | 1   | Fertilization rates  | Similar to PET                                   | [99]  |
|  | PLA (~65.6 μm)                         | 25 μg/L (Biomass of cyanobacteria, and abundance of polychaetes/ oligochaetes changed at 2.5 μg/L and 25 μg/L) | <i>Mytilus edulis</i><br><i>Ostrea edulis</i>                    | 48  | Filtration rates   | Similar to HDPE                                  | [100] |
|  |  |  |  |   | Filtration rates   | Similar to HDPE                                  |       |
| Biomass of cyanobacteria                     |  |  |  |   | Similar to HDPE  |  |       |
| Abundance of <i>Eteone picta</i> polychaetes |  |  |  |   | Similar to HDPE  |  |       |
| Freshwater                                   | PHB (32-63 μm)                         | 100,000 items/individual   | <i>Gammarus fossarum</i>   | 28  | Assimilation efficiency  | Weaker than PMMA                                 | [101] |
|  |  |  |  |   | Wet weight change  | Similar  |       |
|  | PHB (~200 nm)                          | ~90 mg/L   | <i>Anabaena</i> sp. PCC7120,<br><i>Chlamydomonas reinhardtii</i> | 2   | Growth   | -  | [86]  |
|  |  |  |  |   | Immobilization   | -  |       |
|  | PLA (≤ 59 μm)                          | 500 mg/L (2.08 × 10 <sup>8</sup> items/L)  | <i>Daphnia magna</i>   | 21  | Reproductive output  | Weaker than PVC, stronger than PUR               | [102] |
|  |  |  |  |   | Survival   | Strongest  |       |
|  | PLA (~2.34 μm)                         | 760 and 15,020 μg/L  | <i>Physalaemus cuvieri</i> tadpoles                              | 14  | Body condition indices, caudal development, triglyceride levels    | -  | [103] |
|  | Virgin and UV irradiated PLA (5-50 μm) | 25 mg/L  | <i>Danio rerio</i>   | 11  | Skeletal development, mitochondrial dysfunction, RNA-seq of larvae | -  | [104] |
|  | Mater-Bi® (~41 μm)                     | 1 mg/L   | <i>Dreissena polymorpha</i>                                      | 14  | Glutathione-S-transferase activity                                 | Weaker than PVC                                  | [105] |
| PLA (~2.34 μm)                               | 6 mg/L                                 | <i>Aphylla williamsoni</i> larvae  | 2  | Oxidative stress (nitrite levels, thiobarbituric acid reactive species), antioxidant activity (superoxide dismutase activity, total thiol), acetylcholinesterase activity | Stronger than PE   | [106]  |       |
| PLA (~2.34 μm)                               | 3 and 9 mg/L                           | <i>Danio rerio</i> larvae  | 5  | Swimming distance and speed, acetylcholinesterase activity  | -  | [107]  |       |
| Soil   | Blend of PLA and PBAT (40 μm)          | 1, 10 and 100 mg/L   | <i>Caenorhabditis elegans</i>                                    | 6   | Offspring number   | Similar to LDPE                                  | [108] |

|                            |                       |                             |    |  |   |       |
|----------------------------|-----------------------|-----------------------------|----|--|---|-------|
| PLA (~120 $\mu\text{m}$ )  | 125, 250 and 500 g/kg | <i>Eisenia fetida</i> .     | 2  | Avoidance test   | Similar to PE                                     | [109] |
|                            | 500 g/kg              |                             | 28 | Mortality  | Weaker than PE                                    |       |
|                            | 125, 250 and 500 g/kg |                             |    | Biomass  | Biomass is higher when that lower treated with PE |       |
|                            | 125, 250 and 500 g/kg |                             |    | Offspring number   | Stronger than PE                                  |       |
| PBAT (56.7 $\mu\text{m}$ ) | 20 g/kg               | <i>Arabidopsis thaliana</i> | 49 | Rosette leaf area, plant shoot dry weight, number of fruit per plant | Stronger than LDPE                                | [94]  |
|                            |                       |                             | 28 | Total leaf area, malondialdehyde, reactive oxygen species            |   |       |

tadpoles' growth and development and reduce their lipid reserves<sup>[103]</sup>. After UV photodegradation, the efflux and detoxification rate of PLA MPs from zebrafish larvae decreased, and, accordingly, the oxidative stress effect induced mitochondrial structural damage, dysfunction, and apoptosis<sup>[104]</sup>. Mater-Bi® MPs could induce the glutathione-S-transferase activity of mussels<sup>[105]</sup>, and PLA MPs increased oxidative stress, weakened antioxidant defenses, and showed anticholinergic activity in dragonfly larvae<sup>[106]</sup> and altered moving behavior and inhibited acetylcholinesterase's activity of zebrafish larvae<sup>[107]</sup>; however, these indicators might be too sensitive as a basis for assessing toxicity.

In soil, the reproduction of nematodes could be affected by BMPs<sup>[108]</sup>. The effect of PLA MPs on the avoidance behavior, biomass, and reproduction responses of earthworms is similar to that caused by PE<sup>[109]</sup>. PBAT MPs could more severely inhibit plant growth than HDPE by disrupting the photosynthetic system and increasing the gene expression levels for drug transport<sup>[94]</sup>.

In summary, most test results support the view that a high abundance of BMPs (mainly PLA MPs) could affect organisms, including biomarker contents, oxidative stress, feeding, respiration, behavior, growth, reproduction, abundance, and even mortality. It is not an inconceivable scenario in the context of the widespread use of BPs with improper solid waste management systems. However, the mode and level of these effects are highly dependent on the size and exposure abundance/period/environment of BMPs. Based on limited studies, it is not easy to draw further conclusions.

#### As vectors

It might still be too early to assess the physical/chemical risk of a specific type of BMP on marine organisms with few available data<sup>[87]</sup>. However, another fact to note is that BMPs could sorb toxic pollutants, including PAHs, PFASs, pesticides, pharmaceuticals, and heavy metals, and act as vectors<sup>[110]</sup>. Regarding nonpolar organic chemicals, the sorption capacity of a PAH (phenanthrene) on PBAT MPs is proven to be higher than PE and PS due to a higher proportion of rubbery subfraction, and even higher than some carbonaceous geosorbents (black carbon)<sup>[111]</sup>. The higher (than PS pellets with the larger specific surface area) sorption affinity between BMPs (PBS and PCL) and PAHs (phenanthrene/pyrene) confirmed the effect of rubbery domains; hydrogen bonding between BMPs and the polar derivatives of the above two PAHs also resulted in strong affinity<sup>[112]</sup>. The experiment concerning four chlorophenols (4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, and pentachlorophenol) and PLA found no significant differences between PLA and conventional MPs<sup>[113]</sup>. Regarding polar organic chemicals, the studies on fipronil, tetracycline, and ciprofloxacin supported a higher affinity with BMPs than conventional MPs due to the presence of oxygen-containing functional groups<sup>[110]</sup>. PLA MPs and conventional MPs showed no

significant difference in the sorption of amphiphobic PFAFs<sup>[110]</sup>. BMPs are believed to have weaker adsorption for heavy metals (than conventional MPs), but after degradation for a period of time, their adsorption capacity for heavy metals increases<sup>[110]</sup>.

In addition, the presence of MPs in the marine environment is supposed to improve horizontal gene transfer between bacterial taxa<sup>[114]</sup>. The abundance of antibiotic resistance genes and virulence factors<sup>[115]</sup> in soil treated with PBS films was larger than that of conventional plastics. It seems that conventional MPs and BMPs “choose” different bacterial hosts to spread antibiotic resistance genes and virulence factors<sup>[115]</sup>.

#### *Plastic degradation products or additives*

##### Additives

Additives could release during biodegradation, which is influenced by the biodegradability of BPs<sup>[30]</sup>. One example is the release of carbon black<sup>[116]</sup>, which maintains the mechanical properties of mulching films<sup>[30]</sup> or is used as a pigment or UV absorber<sup>[117]</sup>. Sometimes, the toxicity of plastics depends on the composition and abundance of additives, which causes the different toxicities of different products (with different additives) produced with similar plastic material (such as LDPE, PS, and PP)<sup>[118]</sup>. Moreover, PVC and PUR (which are known to contain a large amount of additives) are considered to be the most toxic with respect to bioluminescence inhibition; meanwhile, all PLA products induced similar bioluminescence inhibition with PVC and PUR in both efficiency and effect level<sup>[118]</sup>, which might also be due to additives. A further study showed that the detected chemical features (possibly related to the numbers of compounds) in the extracts of BPs ranged from 614 (a PHA product) to 20,965 (a starch-based product), and it is suggested that extracts from cellulose- and starch-based BPs posed a strong *in vitro* toxicity<sup>[119]</sup>. It might indicate that BPs contain compounds (including additives) of the same order of magnitude with chemical features, and BPs with the highest chemical features (numbers of compounds) are the most toxic. Another study suggested that additives providing antimicrobial activity could be potentially hazardous<sup>[13]</sup>. Meanwhile, some unclear compositions of additives for proprietary reasons<sup>[30]</sup> might also pose potential risks. For example, the toxicity of MP extracts (from a PLA product) to worms was attributed to undeclared ingredients coumarin and iodocarb (presumably adsorbed) of PLA<sup>[120]</sup>.

##### Degradation products

The degradation products of BPs could also be harmful. Some polyesters (sometimes blended with starch-based BPs), such as PBA<sup>[121]</sup>, PBAT<sup>[94]</sup>, and PLA<sup>[122]</sup>, could release degradation products (e.g., 1,6-dioxacyclododecane-7,12-dione) and related monomers (adipic acid, lactic acid, terephthalic acid, 1,4-butanediol, *etc.*) to the aquatic environment; these leachates might increase proline (a plant stress marker), reduce plant development, inhibit plant growth<sup>[123]</sup>, and lead to plant developmental abnormalities<sup>[121]</sup> in soil. Similar effects could occur in marine plants, such as coastal dune vegetation<sup>[124]</sup>. Moreover, adipic acid is also reported to be slightly to moderately toxic to aquatic organisms<sup>[122]</sup>. In addition to terephthalic acid and butanediol, these products were supposed to be more toxic than parent polymers such as PBAT<sup>[94]</sup>.

#### *Pesticides and other exogenous pollutants*

Beriot *et al.* found that the average sorption percentage of 17 insecticides, 15 fungicides, and 6 herbicides on LDPE and LDPE containing pro-oxidant films was ~23%, whereas that on BP films was ~50%; at the same time, the adsorption of plastic film makes these pollutants difficult to decay in the environment<sup>[125]</sup>.

Some other hazardous substances might be introduced during the production of BPs, such as endotoxins introduced in PHBV produced by Gram-negative bacteria<sup>[13]</sup>.

## Other impacts on the environment

### *Similar effects to conventional plastics*

In a period after entering the natural environment, BPs may pose similar effects on habitats as conventional plastics. It is proven that corn starch-based BP films in the intertidal zone could create anoxic conditions beneath them, reduce primary productivity and organic matter in sediments, and decrease infaunal invertebrate populations, similar to those effects caused by conventional plastics<sup>[126]</sup>.

The risk of entanglement of animals might be influenced by the physical and mechanical properties of BPs<sup>[30]</sup>, where their degradability affects the exposure time and exposure probability indirectly.

### *Additional effects*

The degradation time scale of BPs in the aquatic environment is designed to be shorter than that of conventional plastics. Nevertheless, it also makes the presence of BPs in nature easier to affect the ecological equilibrium and material cycle. At first, microbial communities on the surface of BPs were reported to be different from those on conventional plastics and those in the surrounding environment<sup>[24]</sup>, possibly due to the surface attachment capabilities of microorganisms<sup>[127]</sup> at the beginning of attachment and the ability to utilize BPs as carbon and energy source<sup>[24]</sup> thereafter. For example, during the early stage of plastic surface biofilm formation in the marine environment, the microbial composition of biofilms on conventional plastics and aliphatic polyesters is nearly independent of plastic type<sup>[127]</sup>, but a significant difference in diatom community on the surface of starch-based BP and PE was found<sup>[128]</sup>. Generally speaking, there is more biomass on the surface of BPs than on conventional plastics<sup>[24]</sup>. In the marine environment, higher cell counts and activity of bacteria could be found on PHBV than on PE, with a unique microbial community structure (hydrocarbonoclastic bacteria enriched on the plastic surface)<sup>[129]</sup>. There are differences in specific microbial communities. Pinnell and Turner compared the microbial community composition in benthic seawater of a coastal lagoon and on the surface of ceramic, PET, and PHA: the microorganism compositions on the surface of the latter three are different from that in seawater, and significantly different compositions on PHA surface were found with those of ceramic and PET, dominated by sulfate reducers<sup>[62]</sup>. Kirstein *et al.* suggested that marine biofilm core prokaryotic communities on the plastic substrate (including PLA) were significantly different from that on the glass substrate, but the difference in eukaryotic communities was not significant<sup>[130]</sup>. Although it is believed that the biodiversity on BP surface is lower than that on conventional plastic surfaces<sup>[24]</sup>, whether this conclusion is valid in the marine environment remains to be verified. The different microbial compositions on plastic surfaces could be a hotbed of opportunistic bacteria (pathogen). For example, *Vibrionaceae* and *Pseudoalteromonadaceae*, which are rarely found in seawater and marine sediment, were detected on the surfaces of plastic debris in the seabed<sup>[131]</sup>. However, considering the difference in microbial compositions on the surface of BPs and conventional plastics, a similar conclusion cannot be extended to BPs directly. The enrichment of biomass on plastic surfaces increases the transfer rate of antibiotic resistance genes, which makes plastics hotspots for acquiring and spreading antibiotic resistance<sup>[132]</sup>. BPs and conventional plastics have different capabilities in the enrichment of antibiotic resistance genes, and this difference varies with environmental conditions; the differences in the marine environment remain to be explored<sup>[24]</sup>.

Secondly, the degradation of BPs could change the surrounding environment. BPs could consume more oxygen than PE in the seabed<sup>[30]</sup>. The release of PLA MPs into sediment increases bacterial diversity (alpha diversity) and promotes nitrification and denitrification<sup>[133]</sup>; PLA MPs in lake water could alter the phytoplankton composition (eliminated cryptophytes and increased chrysophytes)<sup>[134]</sup>. A vegetable oil- and starch-based BP bag could even promote root expansion and increase the vegetative recruitment of seagrass (*C. nodosa*)<sup>[135]</sup>. All of the above results support the idea that a large amount of BP deposited on the seafloor can change benthic biogeochemical activities. Considering the high material density of BPs and the current

production of disposable plastic products, it would not be an unimaginable scenario in the seabed of some estuaries or nearshore in the near future.

At the macro level, the widespread use of BPs could indirectly affect the environment. In the marine environment, BPs being mineralized is equivalent to being “burned”, releasing CO<sub>2</sub> or CH<sub>4</sub> slowly; although the whole biodegradation process may take a year or more rather than a few minutes, it does not differ much in carbon emissions calculated by year or decade. Therefore, the substitution of BPs for conventional plastics, in a sense, is to accelerate the carbon emissions from the carbon pool to the atmosphere. Note that BPs are not necessarily bio-based, and the generation of fossil minerals from carbon dioxide is much longer than the mineralization of fossil-based BPs. It is a waste of fossil minerals and accelerates the carbon cycle to use fossil-based BPs. Switching from conventional plastics to bio-based BPs is estimated to cut greenhouse gas emissions<sup>[136]</sup>, but the fate of carbon fixed in plastics and its role in the greenhouse effect are still hard to assess<sup>[11]</sup>. BPs also have a greater impact than conventional plastics on issues including eutrophication and acidification<sup>[11]</sup>. From another perspective, the mass production of bio-based raw materials requires a lot of fertilizers, pesticides, cultivated land, and water resources<sup>[137]</sup>. It may not only cause additional environmental pollution but also occupy the resources required for food production. Some may argue that non-edible parts of crops, such as straw, can still be used as raw materials for BPs. However, the fact is that, by now, most straws will continue to circulate in the agricultural material flow as fertilizer and feed after harvest. Transferring them out of the agricultural sector will greatly increase the opportunity cost of agriculture. Will this demand for food and energy be transferred to marine fishing, mariculture, or offshore oil and combustible ice mining, thereby affecting the marine environment? In the context of the global food and energy shortages caused by conflict this year, it remains a possible scenario.

#### **Limitations of the current research**

At present, most studies on BPs are carried out in soil or freshwater environment. However, there are still many questions about studying BPs in the marine environment: What is the fate of BPs and BMPs in the marine environment, especially in the deep-sea environment? How different is the degradation of various BP materials in the marine environment? Will BPs and BMPs accumulate in the marine environment, and how do they migrate? How do we trace and evaluate the risk of BPs/BMPs in the marine environment?

#### **CONCLUSION**

The previous sections summarize various potential adverse impacts and hazards of BPs on the marine environment and human society, including the release of microplastics, degradation products, additives, and other pollutants, which could entangle animals or alter the material cycles of conventional plastics before decomposition, alter microbial communities on them, and affect biogeochemical activities in the adjacent environment due to their biodegradability. However, one premise of these adverse effects, namely, the large-scale use and improper abandonment of BPs, is not an established fact. Increasing the recycling rate of some plastic products and using durable materials such as metal and ceramic can reduce the proportion of disposable plastics, thus reducing the potential demand for BPs. Additionally, it should be noted that some supposed adverse effects have not been fully confirmed, since studies focusing on ecological risks of BPs in the marine environment are still limited<sup>[30]</sup>. Furthermore, some of BPs' shortcomings can actually be overcome. For example, the application of bio-based BPs could accelerate the regeneration of BPs, making the related carbon cycle more “cost-effective”. Strengthening waste management can directly reduce the impact of BPs on the marine environment. In addition, BPs have unique advantages, such as their superiority in medical applications<sup>[138]</sup> and the ideal material for fishing gear which is often lost in the marine environment<sup>[11]</sup>.

Reducing plastic pollution in the marine environment is an arduous task for human society, so no “weapon” can be given up rashly. Based on the above facts, BPs can and should be used properly: (i) BPs should not be the only option to stop plastic pollution. Comprehensive measures should be taken. In most cases, a lifestyle that reduces material and energy waste should be promoted. For those essential disposable products, proper waste management is a prerequisite for the promotion of BP products. (ii) The widespread use of non-durable organic products such as those produced by BPs should be considered when planning for carbon neutrality and ecological equilibrium. The life cycle of this kind of product may change the carbon cycle and have a long-term impact on the ecosystem in which they end up (such as landfill or marine waste accumulation points). (iii) The use of BP products should be positioned accurately. The provision of “material properties required in the application” or “biodegradability after use”<sup>[30]</sup> is fraught with contradictions. Therefore, it is very important to match the appropriate application for each BP material based on specific properties, including the persistence/exposure time in the marine environment.

To provide practical information for the application of BPs, further studies are necessary. In various marine environments with significant differences, the lifespan and environmental behavior of different biodegradable plastic products need to be correctly evaluated, which is the premise of assessing the contribution of BPs as a carbon source in the ocean. The role of additives and the risks of BMPs/leachates also need more attention. Taking BMPs as an example, the differences in the marine ecotoxicological effects caused by various materials need to be tested and confirmed, especially under the environmental abundance of BMPs. Finally, their impact on the ecosystem and material cycle (including carbon emissions) needs appropriate means or models for a comprehensive assessment.

## DECLARATIONS

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The author contributed solely to the article.

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The author declared that there are no conflicts of interest.

### Ethical approval and consent to participate

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### Consent for publication

Not applicable.

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