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REVIEW

Biodegradability of poly(3-hydroxyalkanoate) and poly(ε-caprolactone) via biological carbon cycles in marine environments

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Abstract

Approximately 4.8–12.7 million tons of plastic waste has been estimated to be discharged into marine environments annually by wind and river currents. The Ellen MacArthur Foundation warns that the total weight of plastic waste in the oceans will exceed the total weight of fish in 2050 if the environmental runoff of plastic continues at the current rate. Hence, biodegradable plastics are attracting attention as a solution to the problems caused by plastic waste. Among biodegradable plastics, polyhydroxyalkanoates (PHAs) and poly(ε-caprolactone) (PCL) are particularly noteworthy because of their excellent marine biodegradability. In this review, the biosynthesis of PHA and cutin, a natural analog of PCL, and the biodegradation of PHA and PCL in carbon cycles in marine ecosystems are discussed. PHA is biosynthesized and biodegraded by various marine microbes in a wide range of marine environments, including coastal, shallow-water, and deep-sea environments. Marine cutin is biosynthesized by marine plants or obtained from terrestrial environments, and PCL and cutin are biodegraded by cutin hydrolytic enzyme-producing microbes in broad marine environments. Thus, biological carbon cycles for PHA and PCL exist in the marine environment, which would allow materials made of PHA and PCL to be quickly mineralized in marine environments.

Marine environments are likely to be filled with plastics

Plastics are used in various aspects of our lives and are indispensable. In 2018, the global production of plastics reached 359 million ton [1]. Compared to when the industrial production of plastics began in 1950, there are currently ~200 times as many plastic products produced every year [2]. It has also been estimated that 300 million tons of plastic waste is generated annually, of which 79% is disposed of in landfills or discharged into the environment [3, 4]. In addition, 4.8–12.7 million tons of plastic waste, equivalent to 1.7–4.6% of that generated by coastal countries, is estimated to be discharged annually into the marine environment by wind and river currents [5]. Moreover, ~70% of the garbage at 37 ocean sampling points around the world have been found to be made up of plastics [6]. The Ellen MacArthur Foundation warns that the total weight of plastic waste in the oceans will exceed the total weight of fish in 2050 if the environmental runoff of plastic continues at this rate [7]. Large pieces of plastic debris spilled into the marine environment can be inadvertently ingested by or entangled with wildlife, causing their populations to decline and ultimately destroying the ecosystem. In particular, lost and found fishing gear (abandoned, lost, or otherwise discarded fishing gear: ALDFG), which is estimated to account for ~10% of marine plastic debris, continue to drift and entrap organisms in the ocean (ghost fishing), leading to significant economic problems [8]. In addition, persistent organic pollutants (POPs), which exist at low concentrations in the ocean, are concentrated on the surfaces of plastics discharged into the marine environment due to the hydrophobic properties of the plastic surface [9]. Plastic beads or pieces of plastic with a size of <5 mm spilled into the environment are called microplastics. There are concerns that if POPs present on microplastics are ingested by wildlife, they could be concentrated and stored in cells and tissues [10], eventually

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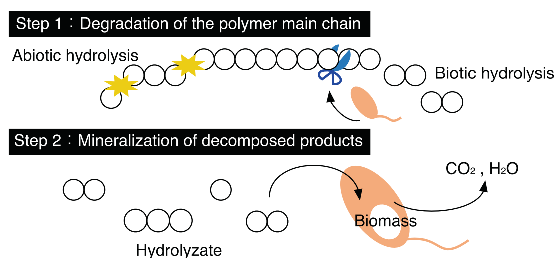


Fig. 1 Biodegradation process of biodegradable plastics. The process consists of steps 1 and 2

entering the human body through the food chain and resulting in adverse health effects [11].

Definition of biodegradable plastics

Biodegradable plastics are attracting attention as one of the solutions to the problems caused by plastic waste. Biodegradable plastics are materials degraded by the actions of microorganisms in the environment that are finally converted into inorganic substances. In general, the conversion rate of a material from an organic to an inorganic substance determines whether the material is a biodegradable plastic.

The degradation of biodegradable plastics proceeds in two stages (Fig. 1). The first stage is the degradation of the main chain of the polymer by microbial hydrolytic enzymes or nonbiological hydrolysis and the consequent formation of molecules of a size that can be taken up by microorganisms. The second stage is the mineralization of the decomposed products during catabolism, i.e., their conversion into carbon dioxide, nitrogen oxide, methane, and water [12]. Most of the international methods for evaluating the biodegradability of plastics are based on the quantification of carbon dioxide production or biochemical oxygen demand during the decomposition process [13].

Enzymatic and environmental degradability of biodegradable plastics

Table 1 [14–19] shows the properties of biodegradable plastics. Biodegradable plastics are obtained by microbial synthesis and chemical synthesis (Fig. 2).

Poly(3-hydroxyalkanoate) (PHA) is produced by microorganisms as an energy storage material. In contrast, poly(ε-caprolactone) (PCL), poly(ethylene succinate) (PESu), poly(butylene succinate) (PBSu), poly(butylene succinate-*co*-adipate) (PBSA), poly(butylene adipate-*co*-terephthalate) (PBAT), and poly(lactic acid) (PLA) are produced from petroleum or biomass via chemical synthesis. Biodegradable plastics are hydrolyzed by enzymes produced by microorganisms [20]. However, chemically synthesized biodegradable plastics do not have a dedicated degradation enzyme, unlike PHA [21]. Chemically synthesized biodegradable plastics are recognized and hydrolyzed in the environment as substrate analogs by lipases, which use fat as a substrate, and by cutinases, which uses the polyester cutin (present in the cuticular layer of plants), as a substrate [22–29] (Table 2).

Due to its structural similarity to polyalanine, PLA can also be degraded by some types of proteolytic enzymes, such as Proteinase K [30, 31] (Table 2).

Biodegradable plastics have different degradation rates in different environments, depending on their type (Table 3) [32–39].

With the exception of PHA and PCL, the biodegradation rate of such plastics in a marine environment is generally low. This means that many products currently available as biodegradable plastics cannot be readily degraded in marine environments. Therefore, there is a concern that they may damage the marine ecosystem in a manner similar to the damage caused by commodity plastics. In addition to the aliphatic polyesters PHA and PCL, several polymers, such as cellulose [40–42], agarose [43, 44], proteins [45], and poly(vinyl alcohol) (PVA) [46], have been suggested to exhibit relatively high biodegradability in marine environments.

This review focuses on two biodegradable polyesters, PHA and PCL, because they have clear carbon cycles in marine ecosystems and could be used as thermoplastics. The biosynthesis of PHA and cutin as a natural analog of PCL, as well as the biodegradation of PHA and PCL in carbon cycles, are described in a marine ecosystem.

What is PHA?

Some bacteria and archaea produce PHA, a type of aliphatic polyester, as an energy storage material when nutrient sources such as nitrogen and phosphate are suppressed due to the presence of excessive carbon sources in the environment [14]. In PHA-producing bacteria, PHA exists in an amorphous state as native PHA granules [47]. Once these granules are extracted from the cells with solvent, they are partially crystallized and used as a biodegradable thermoplastic. A variety of PHAs with different structures are produced depending on the type of bacterial species and carbon source provided [48]. Based on the number of carbons present in a monomer, PHA can be classified into three groups: short-chain PHA (≤5 carbons), medium-chain PHA (6–14 carbons), and long-chain PHA (more than 15 carbons). Among them, a homopolyester composed of *R*-3-hydroxybutanoic acid, known as poly(3-hydroxybutanoic

Table 1 Properties of biodegradable and commodity plastics

Plastic	Synthetic method	Biodegradability	Melting point (°C)	Tensile strength (MPa)	Elongation at break (%)	Reference
P(3HB)	Microbial synthesis	+[a]	180	43	5	[14]
PCL	Chemical synthesis	+[a]	56–65	4–785	20–1000	[15]
PBSu		+[a]	114	19.3	375	[16]
PBSA		+[a]	45.4–97.2	8.1–17.3	310–450	[16]
PBAT		+[a]	110–115	32/36	580/820	[17]
PLA		+[a]	120–170	53–70	10–100	[18]
HDPE[b]		–[c]	120–140	14.5–38	2–130	[19]
LDPE[d]		–[c]	105–116	40–78	90–800	[19]
PP[e]		–[c]	160–176	26–41.1	15–700	[19]

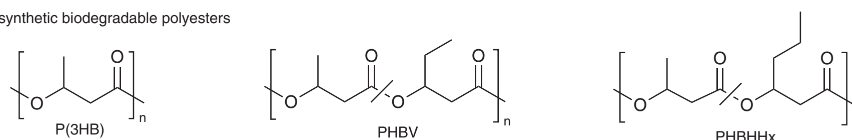
[a]Biodegradable or compostable plastics

[b]*HDPE* high density polyethylene

[c]Nonbiodegradable commodity plastics

[d]*LDPE* low density polyethylene

[e]*PP* polypropylene



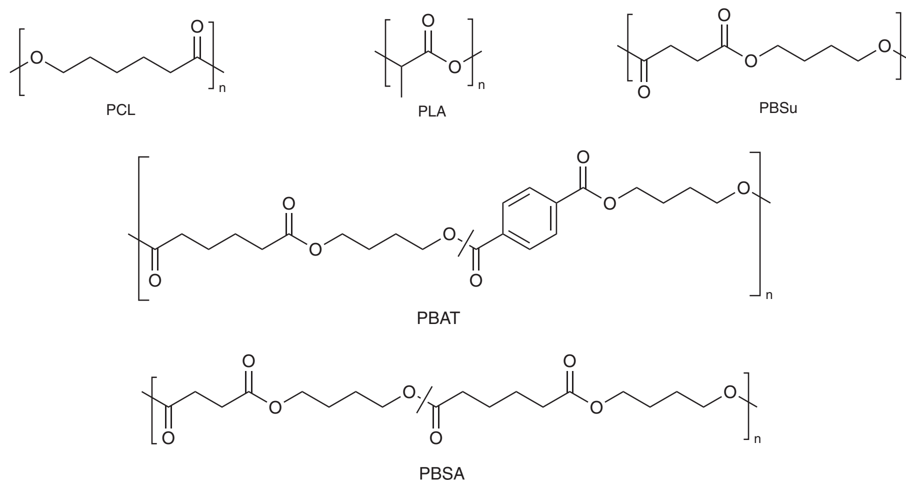


Fig. 2 Chemical structures of biodegradable plastics

Table 2 Relationship between biodegradable plastics and the enzymes that degrade them

Biodegradable plastic(s)	Degrading enzymes	Original substrates	Reference(s)
P(3HB)	P(3HB) depolymerases	P(3HB)	[20, 21]
PCL, PBSu, PBSA, PBAT	Cutinases lipases	Cutin triacylglycerols	[22, 23–29, 157]
PLA	Proteases	Proteins	[30, 31]

Table 3 Environmental biodegradability of biodegradable plastics

Plastic	Soil	Freshwater	Seawater	Reference(s)
P(3HB)	+	+	+	[32–34]
PCL	+	+	+	[32, 34–36]
PBSu	+	±	–	[32, 34, 35, 37]
PBSA	+	+	±	[32, 37]
PBAT	±	±	–	[32, 38, 39]
PLA	–	–	–	[32, 35, 39]

+ high biodegradability in various environments, ± low biodegradability, – very little or no biodegradability

Table 4 PHA-producing bacteria isolated from marine environments

Strain	Phylum	Isolated point	PHA produced	Reference
Afifella marina	Proteobacteria	Seawater	P(3HB)	[63]
Alcanivorax borkumensis	Proteobacteria	Seawater sediment	PHA	[64]
Alteromonas lipolytica	Proteobacteria	Seawater	P(3HB)	[65]
Alteromonas macleodii MCCB 278	Proteobacteria	Seawater	PHA	[66]
Bacillus cereus MCCB 281	Firmicutes	Seawater	PHBV	[66]
Bacillus licheniformis MSBN12	Firmicutes	Marine sponge *Callyspongia diffusa*	P(3HB)	[67]
Bacillus megaterium	Firmicutes	Sediment	PHA	[68]
Bacillus sp. strain NQ-11/A2,	Firmicutes	Sediment	P(3HB)	[69]
Bacillus thuringiensis	Firmicutes	Seashore	P(3HB), PHBV	[70]
Brevibacterium casei MSI04	Actinobacteria	Marine sponge *Dendrilla nigra*	P(3HB)	[71]
Burkholderia sp. AIU M5M02	Proteobacteria	Shallow sea mud	P(3HB)	[72]
Colwellia psychrerythraea	Proteobacteria	Arctic marine sediments	PHA	[73]
Colwellia sp. JAMM-0421	Proteobacteria	Deep sea	P(3HB), PHBV	[74]
Desulfobacterium autotrophicum	Proteobacteria	Sediment	P(3HB), PHBV	[75]
Desulfobotulus sapovorans	Proteobacteria	Sediment	P(3HB), PHBV	[75]
Desulfococcus multivorans	Proteobacteria	Sediment	P(3HB), PHBV	[75]
Desulfonema magnum	Proteobacteria	Sediment	P(3HB), PHBV	[75]
Desulfosarcina variabilis	Proteobacteria	Sediment	P(3HB), PHBV	[75]
Dinoroseobacter shibae DFL 12^T	Proteobacteria	*Prorocentrum lima*	PHA	[76, 77]
Dinoroseobacter sp. JL1447	Proteobacteria	*Phaeodactylum tricornutum* Bohlin	P(3HB)	[77]
Erythrobacter citreus MCCB 277	Proteobacteria	Seawater	PHA	[66]
Erythrobacter longus DSMZ 6997	Proteobacteria	*Enteromorpha linza*	PHA	[77]
Gordonia bronchialis MCCB 280	Actinobacteria	Seawater	PHA	[66]
Halomonas hydrothermalis	Proteobacteria	Seawater	P(3HB)	[78]
Halomonas meridiana MCCB 282	Proteobacteria	Seawater	PHA	[66]
Halomonas profundus	Proteobacteria	Deep sea shrimp	P(3HB), PHBV	[79]
Halomonas sp. SF2003	Proteobacteria	Seawater	PHBV	[80]
Labrenzia alexandrii DFL 11^T	Proteobacteria	*Alexandrium lusitanicum*	PHA	[77]
Marinobacter guineae	Proteobacteria	Seawater	PHA	[63]
Massilia sp. UMI-21	Proteobacteria	Seaweed	PHA	[81]
Methylarcula marina	Proteobacteria	Coastal seawater	P(3HB)	[82]
Methylarcula terricola	Proteobacteria	Coastal sediment	P(3HB)	[82]
Methylobacterium sp.	Proteobacteria	Sediment	PHA	[68]
Moritella sp. JCM21335	Proteobacteria	Deep sea	PHBV, PHBV-*co*-PHA	[74]
Neptunomonas antarctica	Proteobacteria	Sediment	P(3HB)	[83]
Oceanicola granulosus	Proteobacteria	Seawater	P(3HB)	[84]
Oceanimonas doudoroffii	Proteobacteria	Seawater	P(3HB)	[85]
Paracoccus homiensis	Proteobacteria	Sediment	PHA	[68]
Paracoccus seriniphilus	Proteobacteria	Sediment	PHA	[68]
Photobacterium leiognathi 208	Proteobacteria	Seawater	P(3HB)	[86]

Table 4 (continued)

Strain	Phylum	Isolated point	PHA produced	Reference
Photobacterium leiognathi 683	Proteobacteria	Fish	PHBV	[86]
Photobacterium phosphoreum 1883	Proteobacteria	Fish	P(3HB)	[86]
Pseudoalteromonas sp. SM9913	Proteobacteria	Deep sea sediment	Poly(3-hydroxydodecanoate-*co*-3-hydroxydecanoate)	[87]
Pseudomonas guezennei	Proteobacteria	Marine microbial mat	PHA mainly composed of 3-hydroxydecanoate (64 mol%) and 3-hydroxyoctanoate (24 mol%)	[88]
Pseudomonas sp. CMG607w	Proteobacteria	Sediment	Blend of scl-PHA and mcl-PHA	[89]
Rhodovulum euryhalinum	Proteobacteria	Seawater	PHA	[90]
Rhodovulum sulfidophilum	Proteobacteria	Mud from intertidal flats	PHA	[91]
Rhodovulum visakhapatnamense	Proteobacteria	Seawater	PHBV	[91]
Roseobacter denitrificans OCh 114	Proteobacteria	*Enteromorpha linza*	PHA	[77]
Roseobacter litoralis OCh 149	Proteobacteria	Seeweed	PHA	[77]
Roseospira goensis	Proteobacteria	Sediment	PHBV	[91]
Saccharophagus degradans ATCC 43961	Proteobacteria	Salt marsh grass	P(3HB)	[92]
Shewanella basaltis	Proteobacteria	Seawater	PHA	[63]
Shewanella surugensis JAMM-0036	Proteobacteria	Deep sea	Oligo PHA	[74]
Sphingopyxis alaskensis	Proteobacteria	Seawater	P(3HB)	[93]
Spirulina subsalsa	Cyanobacteria	Coast	P(3HB)	[94]
Staphylococcus arlettae	Firmicutes	Sediment	PHA	[68]
Staphylococcus cohnii	Firmicutes	Sediment	PHA	[68]
Thiohalocapsa marina	Proteobacteria	Seawater	P(3HB)	[91]
Vibrio azureus BTKB33	Proteobacteria	Sediment	P(3HB)	[95]
Vibrio harveyi	Proteobacteria	Seawater	P(3HB), PHBV	[86]
Vibrio harveyi MCCB 284	Proteobacteria	Tunicate *Phallusia nigra*	P(3HB)	[96]
Vibrio parahaemolyticus	Proteobacteria	Seashore	P(3HB)	[70]
Vibrio proteolyticus	Proteobacteria	Seashore	P(3HB), PHBV	[70]
Vibrio sp. BM-1	Proteobacteria	Marine environments	P(3HB)	[97]
Vibrio sp. KN01	Proteobacteria	Seawater	P(3HB), P(3HB-*co*-5-hydroxyvalerate-*co*-3-hydroxypropionate)	[98]

acid) [P(3HB)], is the most common PHA produced by many microorganisms.

P(3HB) is a thermoplastic biodegradable polymer with a melting point of ~180 °C and thermal and mechanical properties similar to those of isotactic polypropylene (PP). P(3HB) is a hard and brittle material with high crystallinity and low elongation at break (~5%) [49]. Copolymerization with another hydroxyalkanoate (HA) unit as a second component can change the thermal and mechanical properties of P(3HB), as the second component can act as a defective factor in its crystal structure, thus reducing the degree of crystallinity [50–52]. For example, in the case of poly(3-hydroxybutanoic-*co*-17 mol% 3-hydroxyhexanoic acid) (PHBHHx), in which P(3HB) is copolymerized with 3-hydroxyhexanoic acid (3HHx) as the second component, the melting point of PHBHHx decreases from ~180 to 130 °C, and the crystallinity decreases from 60 + 5% to 29 + 5% compared to the P(3HB) homopolymer. At the same time, the tensile strength decreases from 43 to 20 MPa, and the elongation at break changes from 6 to 850% [51, 53]. Thus, P(3HB) can be changed from a hard and brittle material to a flexible material by copolymerization with a second component.

Mechanism of PHA biosynthesis

The synthesis of P(3HB) begins with the conversion of 2 molecules of acetyl-CoA to acetoacetyl-CoA catalyzed by β-ketothiolase (PhaA, EC 2.3.1.9). Next, NADPH-dependent acetoacetyl-CoA reductase (PhaB, EC 1.1.1.36) converts acetoacetyl-CoA into the P(3HB) monomer (*R*)-3-hydroxybutyryl-CoA (3HB-CoA), which is polymerized by PHB polymerase (PhaC, EC 2.3.1-), resulting in the formation of P(3HB) [54]. In addition, the intermediate produced in the fatty acid biosynthetic pathway, (*R*)-3-hydroxyacyl ACP ((*R*)-3HA-ACP), is converted to (*R*)-3HA-CoA by (*R*)-3HA-ACP transferase (PhaG, EC 2.4.1-) to provide a PHA monomer [55, 56]. In *Aeromonas caviae*, also known as a PHBHHx-synthesizing bacteria and a type of *Pseudomonas* species, (*R*)-specific enoyl-CoA hydratase (PhaJ, EC 4.2.1.119) hydrates enoyl-CoA, which is an intermediate in the β-oxidation pathway, to produce 3HA-CoA as a PHA monomer [57]. PHA synthase is classified into four classes (I, II, III, and IV). The class I PHA polymerase (EC 2.3.1.B2) from *Cupriavidus necator*, which shows specificity for (*R*)-3HA-CoA, a monomer having 3–5 carbons, consists of a homodimeric protein comprising a single subunit (PhaC) with a molecular weight of ~60 kDa [58]. The class II PHA polymerase (EC 2.3.1.B3) from *Pseudomonas* spp., which shows specificity for (*R*)-3HA-CoA with 6–14 carbons, is a homodimeric protein consisting of a single subunit (PhaC) with a molecular weight of ~60 kDa [59]. The class III PHA polymerase (EC 2.3.1.B4) from *Allochromatium vinosum* is a heterodimeric enzyme composed of a 40 kDa PhaC subunit and a PhaE subunit of ~40 kDa, which shows a specificity for (*R*)-3HA-CoA with 3–5 carbons. The class IV PHA polymerase present in *Bacillus megaterium* is a heterodimeric enzyme composed of a PhaC subunit of ~40 kDa and a PhaR subunit of ~20 kDa, which has specificity for (*R*)-3-hydroxyacyl-CoA with 3–5 carbons. However, other PHA monomeric components (3HHx, 3HO, 4HB, 6HHx) are also available as substrates [60, 61].

PHA-producing bacteria in marine environments

Since the discovery by Lemoigne in 1925 that *B. megaterium* stores P(3HB), several microbes have been found to synthesize PHA in a variety of environments [62]. As listed in Table 4, various species of PHA-synthesizing microorganisms have also been isolated from a wide range of marine environments—from shallow to deep seawater [63–98].

PHA-synthesizing bacteria belonging to the phyla Proteobacteria, Firmicutes, and Actinobacteria have been isolated from shallow water and surrounding marine sediments below a depth of 200 m. *Burkholderia* sp. AIU M5M02, isolated from shallow sea mud, can synthesize P(3HB) using mannitol from seaweed as a carbon source [72]. Sulfate-reducing bacteria (SRBs), such as the *Desulfococcus–Desulfosarcina* group, *Desulfococcus multivorans* DSM 2059 strain, *Desulfobotulus sapovorans* DSM 2055 strain, *Desulfosarcina variabilis* DSM 2060, *Desulfonema magnum* DSM 2077, and *Desulfobacterium autotrophicum* HRM2 strain, which have contributed to carbon and sulfur cycling in the marine environment, have synthesized P(3HB) and PHBV [75]. *Halomonas hydrothermalis* isolated from coastal waters synthesizes P(3HB) using crude glycerol, a *Jatropha* biodiesel byproduct, as a carbon source [78]. *Massilia* sp. UMI-21 isolated from seaweed synthesizes PHA using starch, maltotriose, and maltose as carbon sources [81]. *Pseudomonas guezennei* isolated from atoll microbial mats uses glucose as a single carbon source to synthesize a medium-chain 3HA copolymer consisting of 3HB, 3HHx, 3-hydroxyoctanoate (3HO), 3-hydroxydecanoate (3HD), 3-hydroxydodecenoate (3Hdde), and 3-hydroxydodecanoate (3HDd) [88]. The *Vibrio* sp. KN01 strain isolated from seawater was found to synthesize P(3HB) using glucose, fructose, gluconic acid, and soybean oil as carbon sources [98]. Thus, PHA-producing bacteria that inhabit shallow waters can synthesize various forms of PHA from carbon sources such as polysaccharides, sugars, organic acids, fatty acids, and glycerol that are derived from either marine plants or from fats/oils and their degradation products.

An oxygen-evolving photosynthetic cyanobacteria, *Spirulina subsalsa*, has been isolated from shallow seawater as a PHA producer. This strain biosynthesized 5.9% P(3HB) per dry cell weight from carbon dioxide in a marine medium [94]. In addition, aerobic nonoxygenic photosynthetic bacteria (aerobic anoxygenic phototrophic bacteria: AAPB) are widely distributed in marine environments and are known to be PHA producers. Bacteria classified in the genera *Dinoroseobacter*, *Roseobacter*, *Labrenzia*, and *Erythrobacter*, which are marine AAPBs isolated from marine microalgae, synthesize PHA in the presence of sugars or organic acids. Among them, PHA production by *Dinoroseobacter* sp. JL1447 increased with light irradiation [77]. Three species of purple sulfur bacteria (*Thiohalocapsa marina*, *Thiophaeococcus mangrovi*, and *Marichromatium bheemlicum*) and nine species of red nonsulfur bacteria (purple nonsulfur bacteria) (*Afifella marina*, five species of *Rhodovulum* and three species of *Roseospira*) were isolated [91]. Likewise, various PHA producers have been found in marine organisms. *Photobacterium phosphoreum* is present in the luminescent organs and intestines of fish [86], and bacteria belonging to the genera *Vibrio* [99], *Bacillus* [67], and *Brevibacterium*

[71] that cohabitate with sponges have the ability to synthesize PHA.

PHA-producing bacteria have also been isolated from the deep sea, organisms living in the deep sea, and deep seafloor soils, although the numbers of such bacteria are fewer than those found in the shallow sea. *Colwellia* sp. JAMM-0421 and *Moritella* sp. strain JCM21335, isolated from deep seawater, synthesize PHA from sugars and fats [74]. *Pseudoalteromonas* sp. SM9913 isolated from deep sea bottom soil synthesized copolymers of 3HD and 3HDD using either glucose, decanoic acid, or olive oil as a single carbon source [87]. *Halomonas profundus* AT1214, isolated from deep sea hydrothermal vent shrimp, synthesizes P(3HB) from sugars and organic acids [79].

The diversity of the PHA synthase gene, *phaC*, in seawater from seven sampling sites at a depth of 24–5373 m was assessed by *phaC* amplicon analysis. A PhaC amino acid sequence fragment encoded by the gene obtained from the marine amplicon analysis revealed that in marine environments, the known class I PhaC homologs from *Chromobacterium, Marinobacter, Rhodospirillum, Acetobacteraceae bacterium, Oceanibaculum*, and *Oceanicaulis* were the most dominant, followed by the class I PhaC homolog of betaproteobacteria and class I and class II PhaC homologs of gammaproteobacteria [100].

In addition to reports on microbial PHA synthesis in marine environments, marine metagenomic analysis thus suggests that PHA-synthesizing bacteria inhabit a wide range of marine environments, from shallow waters to deep waters, thereby contributing to the production of PHA in the ocean.

Degradation of PHA in marine environments

PHA is known to be highly biodegradable in various marine environments. Microbes that produce extracellular PHA-degrading enzymes [such as P(3HB) depolymerase (EC 3.1.1.75)] are widespread in the ocean. Enzymatic degradation products of PHA are metabolized and mineralized by marine microorganisms. PHA is also produced in the ocean, as mentioned above, and is also degraded and mineralized in the ocean. Therefore, PHA can be regarded as a polymer in which the carbon cycle is established not only in the terrestrial environment but also in the marine environment. Some studies on the biodegradation of PHA in the ocean are given below.

P(3HB), PHBV, and P(3HB-*co*-4HB) films were installed in a seawater circulation tank in the waters around Jogashima Island, Kanagawa, Japan; the thickness of the films was observed to decrease by 13–22 μm after 3 weeks, and the thickness of the PHBV films was observed to decrease by 100–140 μm after 17 weeks. After 8 weeks of environmental exposure, the weight of the PHBV film decreased by 65% compared to the initial weight, and the elongation at break and the stress at break were zero [101]. However, the molecular weight of the specimens did not change before or after exposure. A P(3HB) film was installed in Akabane Port, Aichi, Japan, and after one week, several craters had appeared. Two weeks later, the weight of the P(3HB) film was reduced by ~60% from the initial weight [102]. When a P(3HB) film was incubated at 25 °C in seawater collected from the Pacific Ocean in Aichi, Japan, 9% of the initial weight was lost after 10 weeks, but the molecular weight and crystallinity of the specimens did not change before and after incubation. Moreover, after 3 weeks of immersion in seawater, the tensile strength of P(3HB) decreased to ~60% of the initial value [103]. After 6 weeks of PHBV film immersion in Baltic Seawater, it was observed that the film weight decreased by 60% compared to the initial weight, and its surface became rougher [104]. When P(3HB) and PHBV films (73 ± 5 mg, 30 mm in diameter, 0.1 mm thick) and injection-molded products (330 ± 25 mg, 10 mm in diameter) were immersed in the South China Sea the weights of the films decreased by 42% and 46%, respectively, after 160 days compared to the initial weights, and the weights of injection-molded parts decreased by 38% and 13%, respectively [105]. After P(3HB), PHBV, and P(3HB-*co*-4HB) were added to seawater collected from Tokyo Bay and Oarai Beach, Ibaraki, Japan at 25 °C under aerobic conditions for 28 days, the weight of each film decreased by 23–41%, 100%, and 59–70%, respectively, compared to the initial weights. According to the MITI method, the BOD biodegradability of P(3HB), PHBV and P(3HB-*co*-4HB) reached 14–27%, 78–84%, and 43–51%, respectively, after incubation for 28 days at 25 °C in seawater [34]. When P(3HB) and PHBV were incubated at 30 °C in artificial seawater with 13 marine microbial inoculum sources in accordance with the active standard, ASTM D6691, all samples showed more than 70% degradation after incubation for 40 days. When P(3HB) and PHBV films were incubated in seawater and submarine soil collected from Woods Hole Harbor at 21 °C for 49 days, their weights reduced by ~90% compared to their initial weights. Moreover, after P(3HB) and PHBV films were incubated in a seawater circulation tank in Woods Hole Harbor (12–22 °C, pH 7.9–8.1) for 90 days, their weights decreased by 33–70% compared to their initial weight [106]. BOD biodegradation testing of P(3HB) and its copolymers of seawater samples suggests that there is a positive correlation between biodegradability and temperatures in the range of 10–27 °C [32]. The degradability of PHBV in seawater with submarine soil collected from Lorient harbor in the Atlantic Ocean, France was 90% after 210 days [107].

PHBV fibers were immersed in deep seawater collected from Rausu, Toyama, and Kume, Japan for 12 months, and their tensile strength was measured every 3 months. On the one hand, the tensile strength of PHBV fibers immersed in seawater collected from Kume was completely lost after 3 months. On the other hand, after 3 months of immersion in seawater collected from Toyama, ~80% of the initial tensile strength of PHBV fibers was retained, and ~30% was retained after 12 months. Holes and cracks were found on the surface of the PHBV fibers after immersion in seawater [36]. Thus, PHA was shown to be biodegradable in a wide range of marine environments, including coastal, shallow-water, and deep-sea environments.

Environmental exposure tests of PHBV at four coastal sites in Puerto Rico suggested that the period when PHBV degradation begins is positively correlated to both viable cell counts and PHBV-degrading microbial counts [108]. However, there was no significant difference in the ratio of P(3HB)-degrading microbial counts to viable cell counts in soil, freshwater, or seawater [soil: 0.003–33% (median 4.4, average 9.3); freshwater: 0.59–25% (median 15, average 13); and seawater: 0.24–43.8% (median 2.5, average 9.7)]. The viable cell counts decreased in the following order: soil [1.3×10^5–1.6×10^8 c.f.u./g (median 5.3×10^6, average 1.1×10^7)], freshwater [2.3×10^2–3.2×10^5 c.f.u./g (median 9.6×10^3, average 6.9×10^4)], and seawater [1.6×10^2–3.1×10^5 c.f.u./g (median 7.9×10^2, average 5.4×10^3)] [109]. The time required for 1 mm thick PHBV films to be fully biodegraded was generally shorter in soil and freshwater environments [anaerobic sludge (6 weeks), estuarine sediment (40 weeks), activated sludge (60 weeks), and soil (75 weeks)] and was longer in marine environments [seawater (350 weeks)] [33]. Considering these data, it is highly likely that both microbial density and the total number of degrading microbes in the environment determine the lag time for the initiation of PHA degradation in the environment and the subsequent rate of degradation. Based on previously reported data regarding PHA degradation in shallow-water marine environments, coastal areas, and estuaries, Dilkes-Hoffma et al. estimated that the average degradation rate of PHA would be 0.04–0.09 mg/day/cm^2. Employing the estimated degradation rate, they predicted that it would take 1.5–3.5 years for a 800 μm thick PHBV bottle to be fully biodegraded [110].

Recent studies have revealed that the surfaces of plastic materials spilled into natural environments create an ecosystem that is completely different than that of natural environments. The microbiota that form on such a plastic surface has been designated a "plastisphere" by the marine ecologist Zettler et al. [111]. Recently, it has become clear that the plastisphere plays an important role in the degradation of biodegradable plastics in marine environments. When PHBHHx was aerobically incubated at 23 °C in seawater collected from Takasago Port, Japan, a plastisphere was found to be formed on the surface, which contained PHA-degrading bacteria [112]. Shotgun metagenomic analysis of microflora formed on PHA, PET, and ceramic surfaces showed that the abundance of the P(3HB) depolymerase protein included in the plastisphere on the PHA surface was more than 20 times higher than those on PET, ceramic surfaces, or seawater [113]. Thus, it is presumed that when PHA is exposed to the marine environment, PHA-degrading microbial species are enriched in the plastispheres, and the enzymes produced by these microbes degrade PHA to compounds with a low molecular mass, followed by mineralization by the surrounding microorganisms.

Taken together, the environmental degradation of PHA is influenced by interrelated factors, such as biological factors (microbiota structure, abundance of degrading microbes, biofilm formation capacity, etc.), environmental factors (location, temperature, nutrients, sunlight and UV light, dissolved oxygen, salinity, pH, etc.), and characteristic features of the polymers (primary structure, shape, crystallinity, thermal properties, etc.).

PHA-degrading bacteria in marine environments

As described in the previous section, the biodegradation of PHA has been demonstrated in a wide range of marine environments. PHA-degrading bacteria have also been isolated from various marine environments in which PHA is degraded (Table 5) [112, 114–125].

Hence, the high biodegradability of PHA in a particular marine environment can be correlated with the ubiquity of its degrading microorganisms.

Three PHA-degrading bacteria, classified in the phylum gammaproteobacteria and isolated from marine environments [*Pseudomonas stutzeri* YM1006 (coastal seawater, Jogashima, Japan) [123], *Shewanella* sp. JKCM-AJ-6,1α (coastal seawater, Yaizu Port, Japan) [124], and *Marinobacter* sp. NK-1 (deep seawater, Sagami Bay, Japan) [120]] have been studied in detail. These strains grew well in 0.5 M NaCl, which is similar to seawater. When *P. stutzeri* YM1006 was cultured in the presence of P(3HB) and (*R*)-3HB, it secreted and produced P(3HB) depolymerase in the culture supernatant. Although it grew well in the presence of (*S*)-3HB, this enzyme was not produced. *Shewanella* sp. JKCM-AJ-6,1α produced P(3HB) depolymerase in the presence of P(3HB) and (*R*)-3HB; however, it did not produce this enzyme in the presence of (*S*)-3HB. *Marinobacter* sp. NK-1 strains grew well using several organic acids and amino acids, in addition to P(3HB), (*R*)-3HB, and (*S*)-3HB. This strain secreted P(3HB)

Table 5 PHA-degrading bacteria isolated from marine environments

Strain	Phylum	Class	Isolated point	Reference
Marisediminitalea aggregata (basionym: *Aestuariibacter aggregatus*) WH169	Proteobacteria	Gammaproteobacteria	Seawater	[114]
Aestuariibacter halophilus S23	Proteobacteria	Gammaproteobacteria	Plastisphere on PHBHHx	[112]
Alcanivorax dieselolei B-5	Proteobacteria	Gammaproteobacteria	Seawater	[114]
Alcanivorax sp. 24	Proteobacteria	Gammaproteobacteria	Marine plastic debris	[114]
Alcaligenes faecalis AE122	Proteobacteria	Betaproteobacteria	Seawater	[115]
Pseudoalteromonas haloplanktis (homotypic synonym: *Alteromonas haloplanktis*)	Proteobacteria	Gammaproteobacteria	Seawater	[116]
Alteromonas sp. MH53	Proteobacteria	Gammaproteobacteria	Deep sea sediment	[117]
Bacillus sp.	Firmicutes	Bacilli	Plastisphere on PHBV	[118]
Bacillus sp. strain NRRL B-14911	Firmicutes	Bacilli	Seawater	[119]
Bacillus sp. MH10	Firmicutes	Bacilli	Deep sea sediment	[117]
Comamonas testosteroni YM1004	Proteobacteria	Betaproteobacteria	Seawater	[162]
Enterobacter sp.	Proteobacteria	Gammaproteobacteria	Plastisphere on PHBV	[118]
Aliiglaciecola lipolytica (homotypic synonym: *Glaciecola lipolytica*) E11	Proteobacteria	Betaproteobacteria	Plastisphere on PHBH	[112]
Gracilibacillus sp.	Firmicutes	Bacilli	Plastisphere on PHBV	[118]
Marinobacter sp. NK-1	Proteobacteria	Gammaproteobacteria	Deep sea	[120]
Nocardiopsis aegyptia	Actinobacteria	Actinobacteria	Marine seashore sediments	[121]
Pseudoalteromonas sp. NRRL B-30083	Proteobacteria	Gammaproteobacteria	Seawater	[122]
Pseudoalteromonas gelatinilytica NH153	Proteobacteria	Gammaproteobacteria	Seawater	[114]
Pseudoalteromonas shioyasakiensis S35	Proteobacteria	Gammaproteobacteria	Plastisphere on PHBHHx	[112]
Pseudomonas stutzeri YM1006	Proteobacteria	Gammaproteobacteria	Seawater	[123]
Psychrobacillus sp. PL87	Firmicutes	Bacilli	Deep sea sediment	[117]
Rheinheimera sp. PL100	Proteobacteria	Gammaproteobacteria	Deep sea sediment	[117]
Shewanella sp. JKCM-AJ-6,1α	Proteobacteria	Gammaproteobacteria	Seawater	[124]
Streptomyces sp. SNG9	Actinobacteria	Actinobacteria	Sediment	[125]

depolymerase in the presence of P(3HB) and (*S*)-3HB. *Streptomyces* sp. SNG9 isolated from marine sediment expressed only weak P(3HB) depolymerase activity in the copresence of easy-to-use carbon sources, in addition to P (3HB). These data suggest that P(3HB) and its degradation products are likely candidates that act as inducers of the production of P(3HB) depolymerase, while easy-to-use carbon sources may repress its production [125].

Structure and function of marine P(3HB) depolymerases

Extracellular P(3HB) depolymerases (EC 3.1.1.75) are a group of enzymes that hydrolyze PHA composed of short-chain length hydroxyalkanoic acids (C3-C5): poly(3-hydroxypropionate) [P(3HP)], P(3HB), poly(3-hydroxyvalerate) (P(3HV)), and poly(4-hydroxybutyrate) [P (4HB)]. Although some of the enzymes that have the same EC numbers have hydrolytic activity against amorphous PHA in cells [intracellular P(3HB) depolymerases], they are different from extracellular P(3HB) depolymerases. Here, we describe extracellular P(3HB) depolymerases that hydrolyze crystalline PHA and are associated with the environmental degradation of plastics composed of PHAs.

Since P(3HB), the substrate for extracellular P(3HB) depolymerases, is a solid substance, the enzymatic reaction of P(3HB) depolymerase is a heterogeneous system that occurs at the solid–liquid interface. For efficient enzymatic reactions in such a heterogeneous system, P(3HB) depolymerases consist of a catalytic domain (CD) containing an active site, a substrate binding domain (SBD) for binding enzyme molecules to the surface of P(3HB), and a linker domain (LD) connecting these two functional domains. This multidomain structure (CD+SBD) is also commonly found in insoluble polymer hydrolytic enzymes such as cellulase and chitinase. The CDs of P(3HB) depolymerases contain three catalytic residues (Ser-His-Asp), of which the serine

Table 6 Domain structures and properties of marine P(3HB) depolymerases

(a) Domain structures

Strain	Accession number	CD	LD	SBDs	Molecular mass (kDa)	Reference(s)
Alcaligenes faecalis AE122	AAB40611	Type A	Fn(III)	SBDI, SBDII	90 (SDS-PAGE) 65 (Predicted)	[115, 126]
Alcanivorax sp. 24	WP_133493510	Type A	Fn(III)	SBDI, SBDII	65 (Predicted)	[114]
Bacillus sp. NRRL B-14911	ZP_01169502	Type A	Unclassified LD1, LD2	SBDI, SBDII	63 (Predicted)	[119]
Marinobacter sp. NK-1	BAC15574	Type A	Cad	SBDI, SBDII	62	[120, 127]
Pseudomonas stutzeri YM1006	BAA32541	Type A	Cad	SBDI, SBDII	58	[123, 128]
Shewanella sp. AJ-6,1α	BAU59415	Type A	Fn(III)	SBDI, SBDII	47	[131]

(b) Properties

Strain	K (ml/μg)[a]	Thermostability (°C)	Optimum temperature (°C)	pH stability	Optimum pH	Sodium demand	Reference(s)
Alcaligenes faecalis AE122	ND[b]	ND[b]	55	ND[b]	9.0	Yes	[115, 126]
Marinobacter sp. NK-1	0.20 ± 0.02[c]	4–37	37	7.5–10.0	8.0	No	[120, 127]
Pseudomonas stutzeri YM1006	0.22 ± 0.02[c]	4–50	37	6–12	7.4	ND[b]	[123, 128]
Shewanella sp. AJ-6,1α	0.18 ± 0.01[d]	4–15	ND[b]	7–10.5	7.5	Yes	[124]

[a] *K* value indicates the binding constant between an enzyme and the surface of P(3HB)

[b] ND means not determined

[c] Determined by means of the UV method with a P(3HB) film [122]

[d] Determined by means of the optical density method with P(3HB) granules [126]

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residue is the active center that cleaves the ester bond. The CDs of the enzyme are classified as serine hydrolases belonging to the α/β hydrolase superfamily [23].

Homologs of P(3HB) depolymerase genes have been found in the genomic DNA of various marine bacteria. To date, several P(3HB) depolymerase proteins from marine bacteria have been characterized (Table 6a, b) [114, 115, 119, 120, 123, 124, 126–128].

The CDs of P(3HB) depolymerases are classified into types A and B based on the position of the lipase box (Gly-X-Ser-X-Gly) contained within the CD. Both of these types are in a circular permutation relationship with each other, and both are presumed to have higher order structures that are made up of α/β hydrolase folds [129]. All of the marine P(3HB) depolymerases characterized to date are only of type A, in which the lipase box is located at the center (Fig. 3).

There are three types of LDs in P(3HB) depolymerases: fibronectin type III [Fn(III)], and cadherin (Cad), and threonine (Thr) types. Among them, Fn(III)- and Cad-type sequences were found in the LD of marine P(3HB) depolymerases. As an exception, the P(3HB) depolymerase from *Bacillus* sp. NRRL B-14911 consists of two types of LDs, LD1 and LD2, both of which did not show homology with any of the known LDs [119].

P(3HB) depolymerases of terrestrial microbes are composed of one CD, one LD, and one SBD, whereas all marine P(3HB) depolymerases have two SBDs in addition to one CD and one LD. Therefore, the molecular masses of marine P(3HB) depolymerases (60–70 kDa) are larger than those of terrestrial enzymes (40–50 kDa) [21, 128, 130]. Compared with the average substrate binding constant between the P(3HB) surface and the SBD of terrestrial P(3HB) depolymerase ($K = 1.0$ ml/μg) [21], those of marine P(3HB) depolymerases were as small as 0.2 ml/μg. In other words, this feature of the domain structure of marine P(3HB) depolymerases (i.e., having two SBDs) may compensate for its weak binding. Although the P(3HB) depolymerase produced by the marine bacterium *Shewanella* sp. JKCM-AJ-6,1α encodes two SBDs (SBDI and SBDII) at the locus, both were proteolytically cleaved during the secretion and production of the enzyme. The substrate binding constant of this enzyme that lacks two SBDs was the lowest among all the marine P(3HB) depolymerases (0.18 ± 0.01 ml/μg, Table 6b). This low binding constant is presumed to be complemented by a relative increase in hydrophobic interactions caused by a decrease in the dielectric constant due to the action of salt in seawater [131]. Thus, some characteristics of marine P(3HB) depolymerases differ from their terrestrial counterparts.

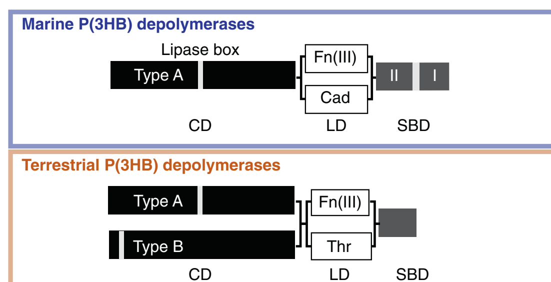

Fig. 3 Schematic representative of marine and terrestrial P(3HB) depolymerases. CD catalytic domain, LD linker domain, SBD substrate binding domain. Fn(III), Cad, Thr indicate fibronectin type III-, cadherin-like-, and threonine-rich linker domains, respectively. In type A, the lipase box is located at the center of the CD, while in type B, it is located near the amino terminus of the CD

Marine P(3HB) depolymerases produced by marine species, such as *Alcaligenes faecalis* AE122, *Shewanella* sp. JKCM-AJ-6, 1α, *Marinobacter* sp. NK-1, and *P. stutzeri* YM1006 were characterized (Table 6b). Except for the enzyme from *Shewanella* sp. JKCM-AJ-6, 1α, those from the other species showed thermostability in the same temperature range as the sea temperature (−2 to 35 °C) [132]. On the other hand, the P(3HB) depolymerase from *Shewanella* sp. JKCM-AJ-6, 1α showed similar thermolability to most of the general enzymes active in marine environments. All marine P(3HB) depolymerases are stable in the marine pH range of 7.8–8.2 [133]. The P(3HB) depolymerase from *Shewanella* sp. JKCM-AJ-6, 1α was found to have no enzymatic activity at low salinity; however, the activity of the enzyme was enhanced at a NaCl concentration of 0.5 M, which is similar to that of seawater. By contrast, the addition of 0.5 M NaCl did not alter the activity of P(3HB) depolymerase from *Marinobacter* sp. NK-1. These results indicate that these P(3HB) depolymerases have an effect on the hydrolytic activity of P(3HB) in the marine environment.

What is PCL?

PCL is a linear aliphatic polyester composed of 6-hydroxyhexanoic acid as its constituent, which can be chemically synthesized by the ring-opening polymerization of ε-caprolactone. The glass transition temperature and melting points of PCL are −65 to −60 and 56–65 °C, respectively [15]. PCL is used as an impact-modifying additive for plastics, a ceramic binder, a binder for metal molds, a hot-melt adhesive, a heat-transfer ink, a flow modifier for resin molding, and a refractive index modifier. Although PCL is a chemically produced synthetic polymer, unlike PHA, PCL is known to be biodegradable in a variety of environments because it is recognized by microorganisms as an analog of the natural polymeric compound cutin [24].

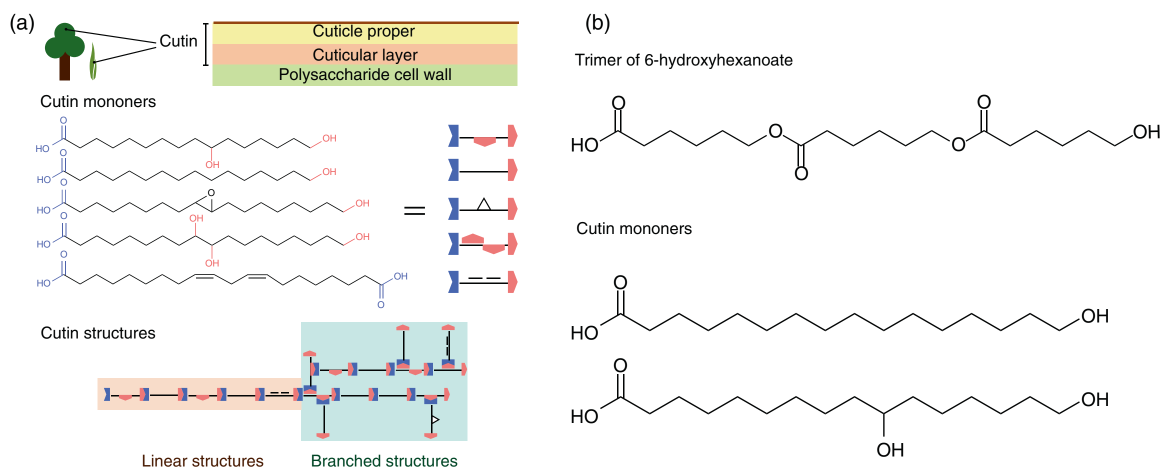

Fig. 4 **a** Cutin domain structure and **b** comparison of the chemical structures of cutin monomers with the PCL trimer [24]

The carbon cycle of cutin in the ocean

The cuticular layer on the surface of plants (mosses, gymnosperms, and angiosperms) functions as an extracellular hydrophobic layer to protect these plants from external environmental stresses and desiccation [134]. The cuticular layer contains mainly C16 and C18 hydroxy fatty acid condensed polyesters, known as cutins. Typical cutin monomers are composed of 10,16-dihydroxyhexadecanoic acid, 16-hydroxyhexadecanoic acid, 18-hydroxy-9,10-epoxyoctadecanoic acid, 9,10,18-trihydroxyoctadecanoic acid, and 18-hydroxyoctadec-9-enoic acid; the composition of which depends on the plant species. These monomers are linked to each other and to glycerol by an ester bond, resulting in cutin consisting of a straight chain and branched domain structure (Fig. 4a). Cutin biosynthesis in plants starts with de novo C16 or C18 fatty acid synthesis in the plastid of epidermal cells. Fatty acids are transported to the endoplasmic reticulum, where acyl-CoA is synthesized by the catalytic activity of the long-chain fatty acid CoA ligase (EC 6.2.1.3). ω-Hydroxylase, midchain hydroxylase, and epoxidase belonging to the cytochrome P450 family 77 subfamily A (EC 1.14.-) oxidize the ends and midchain carbons of cutin monomer-CoA, which is then converted into monoacylglycerol after its transfer to glycerol 3-phosphate by acyltransferase (EC 2.3.1.-). Next, monoacylglycerol is transported to the cuticular layer via the ABC transporter. In the cuticular layer, monoacylglycerol is polymerized by GDSL-motif lipase/hydrolase (EC 3.1.1.3-) to form cutin [135, 136].

Cutin also exists in the marine environment. Marine cutin has two main origins. One is associated with the influx of terrestrial environmental plants into the ocean, and the other is derived from marine plants. C16 and C18 hydroxy fatty acids, characteristic of terrestrial higher plants, have been detected in seabed sediments, providing evidence for the influx of cutin from a terrestrial environment to the sea [137–140]. The cutin content of marine sediments was observed to decrease from areas near an estuary to the deep sea to the seafloor below 1000 m, where 99.4% was found to be lost. This suggests that terrestrial cutin entering the ocean is almost completely degraded in the ocean [137]. The leaf surfaces of marine plants, such as *Thalassia testudinum*, *Posidonia australis*, and *Zostera marina* L., also have a cuticular layer, which contains cutin as a constituent in its interior [141–144].

Through this mechanism, a carbon cycle is formed in which cutin is biosynthesized in marine environments or transported from terrestrial environments and subsequently biodegraded in the marine environment.

Marine degradability of PCL

PCL, a biodegradable plastic, exhibits high biodegradability in a variety of environments. It is known to show high biodegradability similar to that exhibited by PHA in marine environments. The reason for this is presumably due to the structural similarity of PCL to cutin, where PCL enters the carbon cycle of cutin and is biodegraded in the ocean.

Exposure of PCL specimens to water collected from Bohai Bay for 52 weeks resulted in numerous depressions on the surface of the specimens and a decrease in their mechanical strength. The weights of the specimens were reduced by 29.8% compared to the initial weight [145]. After the PCL specimens were immersed in water obtained from Akabane Port, Aichi, Japan for 5 weeks, the tensile strength was completely lost, the elongation at break was 0%, the Young's modulus was reduced to ~50% of the initial value, and the weight was reduced by ~34% of the initial weight [102]. When PCL was incubated in a buffer containing seawater collected from Tokyo Bay and the

Pacific Ocean for 28 days at 25 °C under aerobic conditions, PCL reached a BOD biodegradation of 56–79% [34]. When PCL was incubated in a buffer containing seawater collected from Osaka Bay for 17 days at 27 °C under aerobic conditions, PCL showed a BOD biodegradation of 14.5–40.9% [32]. After 12 months of PCL specimens exposure to deep seawater drawn from Rausu, Toyama, and Kume, many pores and cracks were found on the surface of the specimens, and their tensile strength was completely lost [36].

PCL-degrading bacteria in the marine environment

PCL shows good degradability in various marine environments, and PCL-degrading microorganisms have been found in a wide range of marine environments. Bacteria belonging to the genus *Pseudomonas* isolated from marine environments, such as *P. litoralis*, *P. oceani*, and *P. pelagia*, demonstrated the ability to degrade PCL [146]. A PCL-degrading bacterium closely related to *Pseudomonas pachastrellae* was isolated from a plastic debris surface in a coastal environment. The strain grew well under NaCl concentrations similar to those of seawater (specific growth rate at 0.5 M NaCl: 0.3 h^{-1}), suggesting that this strain is a typical marine bacterium. In the presence of PCL and its degradation product, 6-hydroxyhexanoic acid, PCL-degrading enzymatic activity was expressed in the culture supernatant by this strain in a marine medium [147]. *Streptomyces* sp. SM14 isolated from marine sponges degraded PCL [148]. Marine species of the genus *Alcanivorax*, including *Alcanivorax* sp. 24, *A. xenomutans* JC109, and *A. dieselolei* B-5 formed clear zones on PCL-containing plates [114]. *Shewanella* sp., *Moritella* sp., *Psychrobacter* sp., and *Pseudomonas* sp. were isolated as PCL-degrading bacteria from deep sea sediments of the Kurile and Japan Trenches. Among them, *Shewanella* sp. CT01 and *Moritella* spp. CT12 and JT01 are psychrophilic and piezophilic bacteria adapted to deep sea environments [149].

PCL-degrading enzymes: cutinases and lipases

Cutinases (E.C.3.1.1.74) are enzymes that hydrolyze the carboxy ester bonds of cutins, while lipases (E.C. 3.1.1.3) are enzymes that hydrolyze triacylglycerols. Both enzymes belong to the α/β hydrolase superfamily and contain three catalytic residues (Ser-His-Asp) and two amino acid residues that form an oxyanion hole to stabilize the transition state of the substrate. Nucleophilic attack by the hydroxyl group of the catalytic serine on the carbon of the substrate carbonyl group forms an acyl intermediate, and nucleophilic attack of this intermediate by water molecules results in hydrolysis of the ester bond [150–152]. Cutinases and lipases tend to have an affinity for short-chain ester substrates and long-chain ester substrates, respectively. However, it is difficult to classify both of these enzymes on the basis of substrate specificity alone, since there are cutinases that degrade long-chain triacylglycerols and lipases that degrade cutin [153, 154]. It is also known that both enzymes differ in their structure around the active site. There are two types of lipases, one that retains the lid domain covering the active site and the other that does not [150]. However, almost all cutinases do not have a lid domain [152]. Binding of the micelle surface of a fat substrate to the lid domain changes its structure and increases the area of the hydrophobic surface around the active site, thus increasing the interaction between the substrate and active site. This phenomenon is referred to as "interfacial activation" and helps to increase the enzymatic activity at the liquid–liquid interface of oil and water. By contrast, the interfacial activation effect of the lid domain is small at the solid–liquid interface, such as polyester and water, while the lid domain can physically inhibit the hydrolytic activity of an enzyme at the solid–liquid interface [155]. The effect of the presence or absence of the lid domain on the hydrolysis of polyesters was investigated using lipase from *Rhizopus oryzae* and cutinase from *Fusarium solani*, and it was found that easy access to the active site of the enzyme due to the absence of the lid domain enhanced the rate of polyester hydrolysis [156]. The lipases from *Bacillus pumilus* [29] and *Moesziomyces antarcticus* (homotypic synonym: *Candida antarctica* [157, 158]), which have PCL hydrolysis activity, lack a lid domain. These findings suggest that lipases and cutinases that do not retain the lid domain may be involved in the hydrolysis of PCL and other polyester substrates.

Marine PCL hydrolytic enzyme candidates

The α/β-hydrolase (CDS: ABO2449) of *Alcanivorax borkumensis*, which was expressed in *Escherichia coli*, was found to have the ability to hydrolyze a variety of aliphatic polyesters, such as PLA, PBSA, and PESu in addition to PCL. The gene for this enzyme is homologous (identity level 42–90%) to genes encoding putative proteins of hydrocarbon-degrading microorganisms, including *Alcanivorax* spp., *Hoyosella subflava* (homotypic synonym: *Amycolicicoccus subflavus*), *Marinobacter nanhaiticus*, and *Hydrocarboniphaga effusa*. This enzyme displayed high specificity for a short acyl chain of C2–C4. It was active in the pH range of 7–11 and in the temperature range of 4–70 °C and was also active in the

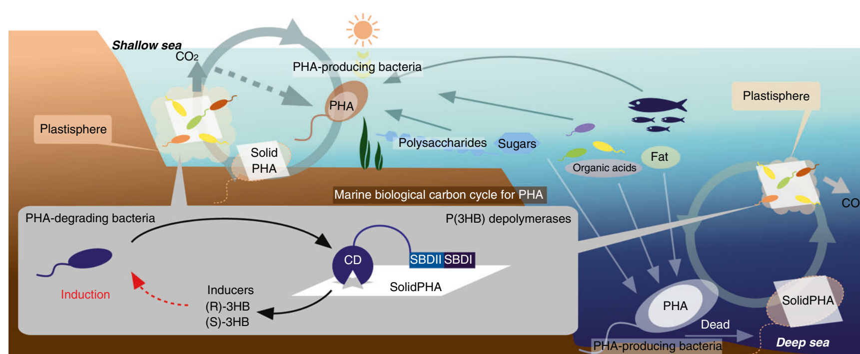

Fig. 5 Ocean biological carbon cycle model where PHA would be incorporated

presence of 3 M NaCl. Considering that the pH of the marine environment is 7.8–8.2 [133] and the water temperature ranges from −2 to 35 °C [132], this enzyme may be involved in PCL hydrolysis in the marine environment [159]. A PCL-degrading enzyme, Esterase SM14est, which is produced by the marine bacterium *Streptomyces* sp. SM14, possesses a conserved lipase box (Gly-X1-Ser-X2-Gly) and catalytic triad. This enzyme has 9 β-sheet and 7 α-helix structures and belongs to the α/β- hydrolase superfamily [148].

Compared to studies on cutinases or lipases with PCL-degrading activity from terrestrial microorganisms, there are very few studies related to marine microorganisms. Nevertheless, recent marine genomic analysis suggests that PCL-degrading enzymes are generally found in marine environments. For example, 349 homologs of cutinase-like enzyme genes were detected in 31 marine metagenomes and 11 terrestrial metagenomes from 108 marine water samples and 25 terrestrial samples. An enzyme with PET hydrolytic activity, PET 2, which was cloned from a marine metagenomics data set, could degrade PCL [160]. Cutinase-like enzyme (PE-H) produced by the marine bacterium *Pseudomonas aestusnigri* VGXO, which possesses PCL-hydrolytic activity, exhibited 48–51% homology with polyester hydrolases from the terrestrial species *Streptomyces viridis*, *Thermobifida* sp., and *Ideonella sakaiensis* [161]. These findings indicate that cutinase-like enzymes, which catalyze PCL hydrolysis, are present in the marine environment as well as in the terrestrial environment.

Induction of PCL degradation activity by PCL

The expression of cutinases produced by *Fusarium vanettenii* (homotypic synonym: *F. solani* f. sp. pisi) and *F. verticillioides* (heterotypic synonym: *F. moniliforme)* require the hydrolysates of PCL, which function as inducers. This could be due to structural homology with a trimer of PCL and the cutin constituent, 10,16-dihydroxy C16 acid, in the structure of 9,10,18-trihydroxy C18 acid [24] (Fig. 4b). Although the cutinase of *Aspergillus oryzae* degrades PBSu, the constituents of PBSu, succinate, and 1,4-butanediol induce the enzyme [25].

A marine bacterium, *Pseudomonas* sp. TKCM64, isolated from marine debris, not only exhibited PCL-hydrolytic activity but also had PESu hydrolytic activity. In the presence of PCL, its degradation products or cutin monomers, this strain expressed both PCL and PESu degradation activity. However, this strain showed relatively low polyester degradation activity in the presence of succinic acid and ethylene glycol, which are components of PESu. From these data, it can be inferred that chemically synthesized polyesters other than PCL and their constituents do not function as inducers of the said degradative enzymes in this strain [147]. This may provide insight into the low marine degradability of chemically synthesized polyesters other than PCL.

Conclusion

To date, biodegradable plastics that degrade in soil and compost have been developed, but most of them show negligible degradation in the ocean. Among them, the biodegradable polyesters PHA and PCL showed good biodegradability in marine environments where biological carbon cycles exist for both polyesters. This allows the materials made of PHA and PCL to be taken up into these carbon cycles and quickly mineralized. Consequently, such materials showed good biodegradability in marine environments. The marine environment has a low density of microorganisms compared to other environments, which makes it difficult to rapidly degrade biodegradable plastics. However, from the viewpoint of utilizing the biological carbon cycles inherently present in the ocean, it is possible to sufficiently increase the biodegradation rate of biodegradable plastics in the ocean (Figs. 5 and 6). A great deal of information is still needed to understand the biological carbon cycle in the ocean if we aim to develop plastics that are fully biodegrade at a sufficient rate in the ocean. We hope that this review provides a starting point for more research on this subject in the future.

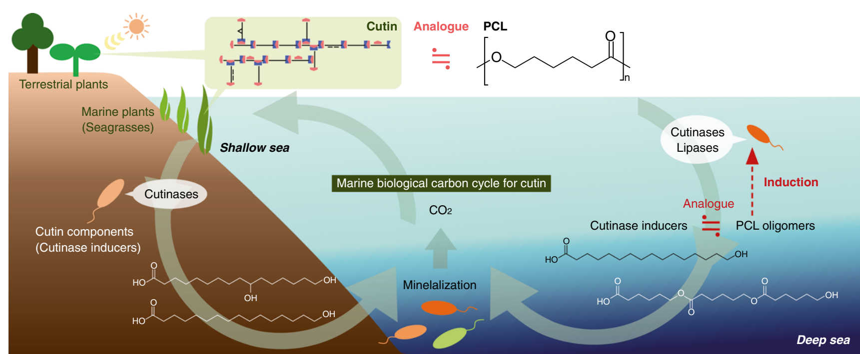

Fig. 6 Ocean biological carbon cycle model where PCL and cutin would be incorporated

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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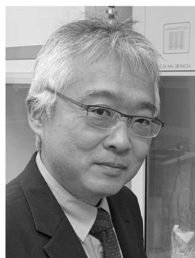

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