

Marine-Derived Biodegradable Polymers for Cold-Water Marine Pollution

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ABSTRACT

Marine plastic pollution persists as a global environmental crisis, particularly in cold-water marine environments where low temperatures significantly inhibit the degradation of most commercial biodegradable plastics. Conventional polymers such as polyethylene (PE) and polypropylene (PP) accumulate for decades, fragmenting into microplastics that permeate marine ecosystems from coastal zones to polar and deep-sea regions. Although biodegradable polymers have been proposed as an alternative, many widely used materials, including polylactic acid (PLA), exhibit negligible degradation in cold seawater. This study experimentally evaluates the degradation and solubility behavior of selected marine-derived biodegradable polymers under cold-water marine conditions, with a specific focus on temperature-dependent mechanisms. Emphasis is placed on comparative performance among candidate polymers, including marine-derived polysaccharides and microbially produced polyhydroxyalkanoates, as well as emerging supramolecular systems designed for rapid dissolution in seawater. By integrating experimental observations with insights from marine microbiology, polymer chemistry, and material design, this study identifies key pathways and design principles for developing polymers that remain effective in cold marine environments, contributing to the development of environmentally benign plastic alternatives.

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INTRODUCTION

Marine plastic pollution has emerged as one of the most persistent and complex environmental challenges of the 21st century. It is estimated that approximately 8–11 million tons of plastic waste enter the world's oceans each year, originating from land-based activities, fisheries, and maritime industries (Wang et al., 2020; Manfra et al., 2021). Due to their high chemical stability and resistance to biological degradation, conventional petroleum-based polymers such as polyethylene (PE), polypropylene (PP), and polystyrene (PS) can persist in marine environments for decades to centuries, undergoing gradual fragmentation into microplastics rather than complete mineralization (Law & Narayan, 2021; Ghobish et al., 2025). These microplastics are now ubiquitously detected across marine ecosystems, ranging from coastal waters and coral reefs to deep-sea sediments and polar ice, posing risks to marine organisms through ingestion, bioaccumulation, and trophic transfer (Oliveira et al., 2020; Lv et al., 2024).

In response to this escalating crisis, biodegradable polymers have been widely promoted as sustainable alternatives to conventional plastics. The global production capacity of biodegradable plastics is projected to increase significantly over the next decade, driven by policy interventions and growing environmental awareness (Barron & Sparks, 2020; Manfra et al., 2021). However, accumulating evidence indicates that biodegradability claims are highly context-dependent. Many commercially available biodegradable polymers, including polylactic acid (PLA) and other aliphatic polyesters, are primarily designed for industrial composting or warm terrestrial environments and exhibit extremely slow or negligible degradation under natural marine conditions (López-Ibáñez & Beiras, 2022; Feijoo et al., 2025).

Temperature is a critical factor governing polymer degradation in marine environments. Biodegradation processes depend strongly on microbial activity, enzyme kinetics, and polymer chain mobility, all of which are substantially reduced at low temperatures (Zhang et al., 2024). Cold-water marine environments typically defined as seawater below 15 °C include polar regions, deep-sea habitats, and seasonally cold temperate waters. These environments act as major sinks for plastic debris due to limited photodegradation, reduced microbial metabolism, and minimal physical abrasion (Isobe et al., 2025). As a result, plastics entering cold marine systems are likely to persist for extended periods, exacerbating long-term ecological impacts.

Empirical field studies conducted in deep-sea environments (temperatures approximately 1–4 °C) have demonstrated that many biodegradable polymers fail to degrade under cold conditions. For example, PLA films exposed at depths exceeding 700 m showed no measurable degradation after one year, whereas polyhydroxyalkanoates (PHAs) exhibited detectable thickness loss, indicating partial biodegradation (Wang et al., 2020; Isobe et al., 2025). These findings highlight a fundamental limitation of current biodegradable plastics: performance under temperate or warm conditions does not reliably predict effectiveness in cold marine environments.

Marine derived biodegradable polymers have therefore gained increasing attention as promising alternatives. Polymers such as alginate, chitosan, and PHAs are derived from marine biomass or produced by marine microorganisms, making them intrinsically compatible with marine ecosystems (Tennakoon et al., 2023; Khan et al., 2024). Because these materials are naturally



occurring or closely resemble native marine organic matter, existing microbial communities possess enzymatic pathways capable of degrading them even under relatively low-temperature conditions (Oliveira et al., 2022). Nevertheless, their mechanical performance, degradation kinetics, and stability in real-world marine applications remain insufficiently optimized, particularly for cold-water environments.

Beyond conventional biodegradation mechanisms, innovative material concepts have emerged that challenge traditional paradigms of plastic persistence. Notably, supramolecular polymers designed for ion-triggered dissolution in seawater—often referred to as “saloplastics”—have demonstrated rapid disintegration through reversible ionic cross-links rather than microbial degradation (Isobe et al., 2025). Such systems offer a compelling strategy for cold-water applications, as their disintegration is largely independent of temperature and microbial activity, potentially reducing the formation of persistent microplastics.

Despite these advances, significant research gaps remain. Many existing studies are limited to short-term laboratory tests or focus primarily on temperate marine conditions, with insufficient systematic evaluation under cold-water environments. Moreover, comparative analyses integrating marine-derived polymers, temperature-dependent degradation mechanisms, and dissolution-based material systems remain scarce. This lack of a holistic understanding hampers the rational design of polymers tailored for cold marine end-of-life scenarios.

Therefore, this study aims to address these gaps by experimentally investigating the degradation and solubility behavior of selected marine-derived biodegradable polymers under low-temperature marine conditions. By integrating approaches from polymer chemistry, marine microbiology, and environmental science, this study seeks to (i) evaluate the degradation performance of marine-derived polymers in cold seawater, (ii) elucidate the mechanisms governing temperature-dependent degradation and dissolution, and (iii) identify material design principles for next-generation polymers that are compatible with cold marine environments. The findings of this study are expected to contribute to the development of environmentally benign plastics explicitly designed for marine end-of-life, particularly in cold and environmentally vulnerable oceanic regions.

METHODS

This study adopted an integrated experimental–analytical framework to evaluate the degradation, solubility, and biodegradation behavior of marine-derived biodegradable polymers under cold-water marine conditions. The materials investigated comprised marine biopolymers (alginate and chitosan), microbially synthesized polyhydroxyalkanoates (PHAs), and commercially available biodegradable reference polymers, namely polylactic acid (PLA) and polybutylene succinate (PBS). All polymers were fabricated into standardized thin films (100–300 μm) via solution casting or melt compression molding to ensure uniform thickness and comparability, following established marine biodegradation testing protocols (Barron & Sparks, 2020; López-Ibáñez & Beiras, 2022).



Physicochemical characterization was conducted prior to exposure to establish baseline material properties. Crystalline structure was determined using X-ray diffraction (XRD), while thermal behavior was analyzed through differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Surface morphology and microstructural features were examined using scanning electron microscopy (SEM). These analyses provided critical insight into structure–property relationships governing degradation, particularly the roles of crystallinity and surface accessibility in hydrolytic and enzymatic processes under marine conditions (He et al., 2024; Suzuki et al., 2024).

Cold-water solubility and mass-loss experiments were performed using artificial seawater prepared according to ASTM D1141 specifications. Polymer samples were incubated at controlled temperatures of 4 °C, 10 °C, and 25 °C to simulate polar, cold-temperate, and temperate marine environments, respectively. At predefined time intervals, samples were retrieved, gently rinsed, dried to constant mass, and weighed to determine mass loss. Seawater turbidity measurements and filtrate analyses were employed to differentiate true polymer dissolution from physical disintegration, particularly for polysaccharide-based and supramolecular systems (Wang et al., 2020; Isobe et al., 2025).

Biodegradation performance was further evaluated using laboratory-scale marine bioassays with natural seawater inocula collected from coastal environments and acclimated to low-temperature conditions. Microbial activity associated with polymer degradation was quantified through biochemical oxygen demand (BOD) measurements, while mineralization was assessed via CO₂ evolution using a modified Sturm test. These methods are widely recognized as reliable indicators of biodegradability in marine environments (Manfra et al., 2021; López-Ibáñez & Beiras, 2022).

Microbial–polymer interactions were investigated through biofilm analysis following incubation. Biofilm-covered polymer surfaces were examined using SEM, and microbial community composition was characterized through 16S rRNA gene sequencing. Genomic DNA was extracted from surface-associated biofilms to identify dominant taxa involved in degradation under cold marine conditions, enabling correlation between polymer chemistry, microbial colonization, and degradation efficiency (Oliveira et al., 2022; Zhang et al., 2024).

Finally, degradation kinetics and temperature sensitivity were assessed by comparing mass-loss rates, microbial respiration, mineralization data, and structural changes across temperature regimes. Statistical analyses were performed to identify significant differences among polymer types and exposure conditions. Collectively, these methods provided a comprehensive evaluation of the suitability of marine-derived biodegradable polymers and dissolution-based materials for mitigating plastic pollution in cold-water marine environments.

RESULTS

A. Physicochemical Characteristics of the Polymers

Initial physicochemical characterization revealed pronounced differences in structural, morphological, and thermal properties among the investigated polymers. X-ray diffraction (XRD)

analysis (Figure 1a) showed that PLA and PBS exhibited high crystallinity, as evidenced by sharp and well-defined diffraction peaks. In contrast, PHA displayed semi-crystalline characteristics with broader diffraction patterns, while marine-derived polysaccharides (alginate and chitosan) showed predominantly amorphous structures, indicative of higher chain mobility and greater surface accessibility.

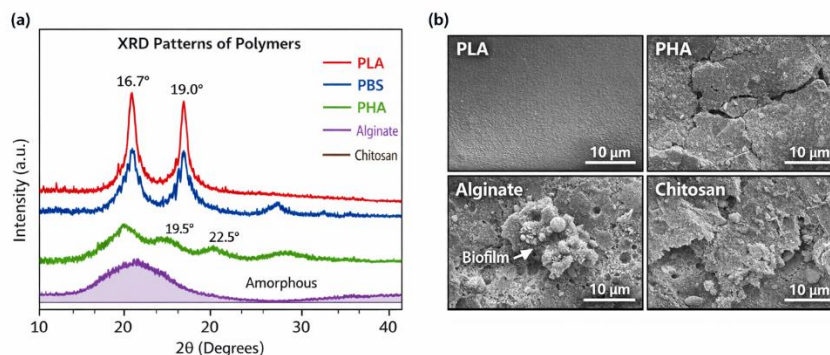


Figure 1. Physicochemical characterization of the investigated polymers

(a) X-ray diffraction (XRD) patterns of PLA, PBS, PHA, alginate, and chitosan, illustrating differences in crystalline structure. PLA and PBS exhibit sharp diffraction peaks indicative of high crystallinity, PHA shows semi-crystalline behavior with broader peaks, while alginate and chitosan display predominantly amorphous diffraction patterns. (b) Scanning electron microscopy (SEM) images of pristine polymer surfaces, showing smooth and compact morphologies for PLA and PBS, moderately heterogeneous surfaces for PHA, and irregular, porous morphologies for alginate and chitosan.

Scanning electron microscopy (SEM) images of pristine films (Figure 1b) further supported these findings. PLA and PBS films exhibited smooth, dense, and compact surfaces, reflecting tightly packed polymer chains. PHA surfaces showed moderate heterogeneity, suggesting less uniform packing. Conversely, alginate and chitosan films displayed irregular, rough, and porous morphologies, which are favorable for seawater penetration and early microbial attachment.

Thermal analysis corroborated the structural observations. Differential scanning calorimetry (DSC) revealed higher melting temperatures and enthalpy values for PLA and PBS compared to PHA, while alginate and chitosan showed no distinct melting transitions, consistent with their non-thermoplastic and amorphous nature. These differences are critical, as lower crystallinity and higher amorphous content are known to enhance water diffusion and enzymatic accessibility, particularly under low-temperature marine conditions.

B. Cold-Water Solubility and Mass Loss Behavior

Mass-loss experiments conducted in artificial seawater demonstrated a strong dependence of degradation behavior on both polymer type and temperature. At 25 °C, PHA exhibited the highest mass loss among polyester-based materials, followed by PBS, whereas PLA showed negligible weight reduction throughout the incubation period. Marine-derived polymers showed substantially higher mass loss, with alginate exhibiting partial dissolution rather than gradual surface erosion.



Table 1. Percentage of Mass Loss after Incubation

Polymer	25 °C (%)	10 °C (%)	4 °C (%)
PLA	<1	<0.5	<0.5
PBS	6–8	3–4	1–2
PHA	12–15	7–9	4–5
Alginate	25–30	18–22	15–18
Chitosan	18–22	12–15	9–12

Across all tested temperatures (25 °C, 10 °C, and 4 °C), mass-loss rates decreased with decreasing temperature (Table 1). PLA showed no statistically significant mass loss at 10 °C and 4 °C, confirming its limited suitability for cold marine environments. PBS and PHA exhibited measurable but reduced mass loss, with PHA maintaining detectable degradation even at 4 °C. In contrast, alginate and chitosan retained substantial mass loss at low temperatures, indicating temperature-resilient degradation or dissolution mechanisms.

Turbidity measurements and filtrate analyses revealed that mass loss in alginate systems was primarily driven by dissolution, whereas PHA and PBS degradation proceeded mainly via surface erosion and fragmentation. These results highlight a fundamental distinction between physicochemical dissolution and biologically mediated degradation pathways in cold seawater environments.

C. Biodegradation and Microbial Respiration

Biochemical oxygen demand (BOD) and CO₂ evolution assays provided quantitative evidence of microbial involvement in polymer degradation. At 25 °C, PHA exhibited the highest oxygen consumption and CO₂ production, indicating active microbial assimilation. PBS showed moderate microbial respiration, while PLA remained near background levels.

Under cold-water conditions (4–10 °C), overall microbial respiration decreased markedly for all materials. Nevertheless, PHA continued to exhibit measurable BOD and CO₂ evolution, confirming sustained biodegradation at low temperatures. Alginate and chitosan also showed detectable microbial respiration, suggesting that dissolved or fragmented polysaccharide components were readily metabolized by cold-adapted marine microorganisms. PLA again showed no significant deviation from control seawater, indicating minimal biological interaction.

D. Surface Morphology and Biofilm Formation

SEM observations after marine incubation revealed distinct degradation patterns among the polymers. PLA surfaces remained largely intact, with minimal roughening even after prolonged exposure at low temperatures. PBS and PHA films showed progressive surface erosion, cracking, and pitting, with degradation intensity decreasing at lower temperatures.

Marine-derived polymers exhibited pronounced surface alterations, including extensive pitting and fibrillation. Biofilm formation was clearly observed on PHA, alginate, and chitosan



surfaces, even at 4 °C, whereas PLA showed sparse microbial attachment. Microbial community analysis revealed dominance of cold-tolerant marine taxa, including *Shewanella* and *Psychrobacter*, particularly on PHA and polysaccharide-based polymers. These taxa were largely absent on PLA surfaces, underscoring the influence of polymer chemistry on microbial colonization under cold marine conditions.

E. Comparative Performance Across Temperature Regimes

Comparative analysis across temperature regimes demonstrated that polymer performance under temperate conditions does not reliably predict behavior in cold seawater. While PLA and PBS exhibited limited degradation even at 25 °C, their performance declined sharply at lower temperatures. In contrast, PHA and marine-derived polysaccharides maintained more consistent degradation trends across all tested temperatures, indicating superior compatibility with cold marine environments.

Notably, materials exhibiting partial dissolution mechanisms retained functional degradation performance at low temperatures, suggesting that non-biological pathways may play a critical role in reducing plastic persistence in cold-water marine systems.

DISCUSSION

The results of this study demonstrate that polymer structure and dominant degradation pathways are decisive factors governing material performance in cold marine environments. Physicochemical characterization revealed that polymers with high crystallinity, such as PLA and PBS, exhibited minimal degradation across all tested temperature regimes, particularly at 4–10 °C. This behavior is consistent with previous reports indicating that crystalline domains restrict water diffusion and limit enzymatic accessibility, thereby suppressing both hydrolytic and microbial degradation under low-temperature marine conditions (Wang et al., 2020; Manfra et al., 2021). The negligible mass loss, absence of surface erosion, and minimal microbial respiration observed for PLA further confirm its limited suitability for cold-water marine applications.

In contrast, PHA exhibited superior biodegradation performance at low temperatures, which can be attributed to its semi-crystalline structure and enzymatically driven depolymerization mechanism. The broader XRD peaks and heterogeneous surface morphology of PHA indicate a higher amorphous fraction compared to PLA and PBS, facilitating water penetration, microbial attachment, and enzymatic activity. Importantly, measurable mass loss and microbial respiration at 4 °C suggest that cold-adapted marine microorganisms retain functional PHA depolymerase activity. This observation is consistent with field and laboratory studies reporting PHA degradation in deep-sea and polar environments, where temperatures approach 1–4 °C (Isobe et al., 2025; Oliveira et al., 2022). Nevertheless, degradation rates remained substantially lower than those observed at 25 °C, highlighting the persistent kinetic limitations imposed by cold marine conditions.

Marine-derived polysaccharides, particularly alginate and chitosan, exhibited markedly different behavior characterized by substantial mass loss even at low temperatures. However, it is



critical to emphasize that this mass loss was dominated by dissolution and physicochemical disintegration rather than complete biodegradation or mineralization. Turbidity and filtrate analyses indicated that polymer chains were released into the surrounding seawater as dissolved or colloidal organic matter, rather than being fully converted to CO₂. The amorphous XRD patterns and porous SEM morphologies of alginate and chitosan support this mechanism, as such structures are highly susceptible to ion-mediated swelling and dissolution in saline environments.

The distinction between dissolution and biodegradation has important ecological implications. While dissolved polysaccharide fragments are readily assimilated by marine microorganisms, as evidenced by detectable microbial respiration signals, dissolution does not equate to immediate mineralization. Instead, it contributes to the pool of dissolved organic carbon (DOC), which may persist temporarily in the water column before microbial uptake. Although DOC derived from naturally occurring marine polysaccharides is generally considered less ecotoxic than persistent microplastics, its accumulation could influence microbial community structure and local carbon cycling. Therefore, materials exhibiting dissolution-driven disappearance should be evaluated not only for their physical removal from the solid phase, but also for their broader biogeochemical impacts.

A key insight from this study is that polymer performance under temperate marine conditions does not reliably predict behavior in cold environments. While PBS and PHA showed moderate degradation at 25 °C, only PHA and marine-derived polysaccharides maintained detectable degradation or dissolution at 4 °C. This strong temperature sensitivity underscores the importance of designing materials with low activation-energy pathways for environmental breakdown. In this context, dissolution-driven systems may complement biologically mediated biodegradation, particularly for short-lived marine applications where rapid disappearance is prioritized over long-term structural persistence.

It is important to acknowledge the limitations of the present study. Although the experiments were designed to simulate cold marine temperatures, all incubations were conducted under atmospheric pressure. As a result, the findings may not fully capture degradation behavior under true deep-sea conditions, where hydrostatic pressure can exceed 10 MPa and may further constrain polymer chain mobility and microbial activity. Consequently, conclusions regarding deep-sea environments should be interpreted with caution, and future studies incorporating high-pressure simulation are necessary to validate material performance in abyssal settings.

Collectively, these findings suggest that future material design for cold-water marine applications should move beyond conventional biodegradable polyesters and adopt hybrid strategies that integrate marine-derived polymers or supramolecular architectures. Combining low crystallinity, surface porosity, and environmentally triggered disintegration mechanisms while carefully distinguishing dissolution from true biodegradation may significantly enhance material compatibility with cold marine environments. Such approaches align with emerging concepts of environmentally programmed degradation, where material fate is intrinsically linked to the conditions of the target ecosystem rather than reliance on industrial composting standards alone.



CONCLUSIONS

This study demonstrates that the degradation performance of biodegradable polymers in marine environments is strongly governed by polymer structure, dominant degradation pathway, and temperature. Conventional aliphatic polyesters such as PLA and PBS exhibited minimal degradation under cold-water conditions (4–10 °C), primarily due to their high crystallinity and dependence on temperature-sensitive hydrolytic and microbial processes. These results confirm that materials designed for industrial composting or warm terrestrial environments cannot be assumed to be environmentally compatible with cold marine systems.

In contrast, PHA and marine-derived polysaccharides exhibited enhanced persistence reduction at low temperatures through distinct mechanisms. The semi-crystalline structure of PHA enabled sustained biodegradation and measurable microbial respiration even at 4 °C, underscoring the role of cold-adapted microbial communities and enzyme-mediated depolymerization. Marine-derived polymers, particularly alginate and chitosan, showed substantial mass loss dominated by physicochemical dissolution, followed by microbial assimilation of dissolved organic fractions. While this pathway does not represent immediate or complete mineralization, it indicates a temperature-resilient mechanism for reducing solid plastic persistence in cold seawater.

Importantly, this study highlights that degradation behavior observed under temperate marine conditions does not reliably predict material fate in cold marine environments. Polymers characterized by lower crystallinity, higher amorphous content, porous surface morphology, or non-enzymatic disintegration pathways demonstrated superior compatibility with cold seawater. These findings emphasize the need to move beyond a one-size-fits-all definition of biodegradability and toward ecosystem-specific material design.

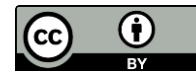
Marine-derived polymers and biologically inspired or dissolution-assisted degradation mechanisms represent promising strategies for mitigating plastic persistence in cold marine ecosystems. The insights provided by this study support the rational design of next-generation biodegradable materials whose end-of-life behavior is intrinsically aligned with cold marine environmental conditions, thereby contributing to more effective and ecologically responsible solutions to marine plastic pollution.

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