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Marine biodegradation of otherwise persistent engineering nylons

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Marine biodegradation of otherwise persistent engineering nylons

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Summary

Engineering nylons are generally considered persistent in the environment, including the marine environment. However, some commercially available nylon fishing lines, composed of mass-produced engineering nylon copolymers, unexpectedly exhibit biodegradation in natural seawater, and the mechanisms underlying this behaviour remain unclear. Here, we systematically examined the effect of the composition and structural state of nylon filaments on their marine biodegradation. Accelerated marine biological

oxygen demand (BOD) tests revealed substantial marine biodegradation even in highly crystalline, oriented nylon filaments, with structural disruption further enhancing the process. Long-term in situ seafloor exposure experiments under negligible ultraviolet irradiation revealed progressive surface erosion and mechanical deterioration, suggesting degradation under environmentally relevant marine conditions. Additionally, nylon filament biodegradability strongly correlated with water uptake across compositions and structural states, highlighting hydration-mediated accessibility as a key factor linking polymer structure with microbial biodegradation. Molecular and microbiological analyses further confirmed microbial chain scission and high-molecular-weight nylon assimilation, with a newly isolated *Dasania* species contributing to this process. Therefore, environmental persistence in engineering plastics is not solely determined by polymer chemistry, but also by structure-dependent microbial accessibility, providing new insights into the environmental fate of ghost fishing gear, marine debris, and secondary microplastics.

Main

Marine plastic pollution represents a growing global environmental issue[1-3], and abandoned fishing gear, also known as “ghost gear,” is among the most persistent

pollutants in the marine environment, posing a significant risk of ecological damage[4–6]. These plastic materials can persist for decades and entangle marine organisms[7] and progressively fragment into secondary microplastics that accumulate across marine environments and food webs[1,8].

Engineering polymers such as nylon, are widely used in fishing lines and nets owing to their high mechanical strength and durability under harsh marine conditions[9]. Specifically, nylon 6 (Ny6) and nylon 66 (Ny66) homopolymers, stabilized by dense hydrogen-bonding networks[9,10] that limit water penetration and molecular accessibility[11,12], form semi-crystalline structures. These materials are generally considered environmentally persistent under marine conditions and are regarded as resistant to biodegradation within environmentally relevant timescales[13].

Unexpectedly, however, some commercially available nylon fishing lines exhibit substantial biodegradation in natural seawater despite being composed of engineering nylons long regarded as persistent (Supplementary Fig. 1). This finding challenges the prevailing assumption that the environmental fate of engineering plastics is determined primarily by polymer chemistry alone. Importantly, many commercially available fishing lines are made from mass-produced Ny6/66 random copolymer nylon systems designed for mechanical performance and industrial processability rather than

environmental degradability[9]. Nevertheless, their marine biodegradation behaviour remains largely unexplored.

Previous studies have reported microbial degradation of nylon oligomers[14,15], laboratory enrichment-based degradation of Ny6 and Ny66 homopolymers by marine microorganisms[16–18], and more recent, enzymatic depolymerisation of Ny6 under controlled reaction systems[19]. However, it remains unclear whether commercially relevant high-molecular-weight engineering nylon filaments undergo structure-dependent biodegradation under environmentally relevant marine conditions.

Therefore, motivated by the unexpected degradation behaviour of commercially available fishing lines, we systematically investigated the influence of the composition and structural organization of engineering nylons on their marine biodegradability. Using additive-free nylon filaments prepared via industrially relevant melt-spinning processes, we demonstrated that even highly crystalline, oriented nylon filaments can undergo substantial marine biodegradation depending on the random copolymer composition and structural state, under environmentally relevant marine conditions.

Additionally, by systematically decoupling polymer composition and higher-order crystalline organization, we identified hydration-mediated accessibility as the key governing factor linking polymer structure to biodegradability. Long-term in situ seafloor

exposure experiments under limited ultraviolet irradiation[20], further demonstrated that the polymers degradation process proceeds under environmentally relevant marine conditions. Overall, this study suggested that the environmental persistence of engineering nylons is not an immutable intrinsic material property but is strongly driven by structure-dependent accessibility. It is also worth noting that while persistence can be modulated via copolymerization and structural states, pure homopolymers (e.g., highly oriented Ny66) still exhibit extreme persistence under standard marine conditions unless chemically or physically altered.

Unexpected biodegradation of nylons

During manufacture, commercial nylon fishing lines are often supplemented with industrial additives and subjected to surface treatments that may influence their degradation behaviour. To isolate the intrinsic effects of polymer composition and structure on the biodegradation process, highly oriented nylon filaments with crystallinity and orientation comparable to commercially available nylon fishing lines were prepared using industrially relevant melt-spinning processes without additives or surface coatings. When these prepared highly oriented filaments were subsequently subjected to marine

biodegradation conditions, they unexpectedly exhibited substantial biodegradation, depending on the copolymer composition.

Accelerated marine biological oxygen demand (BOD) tests using marine sediment-enriched natural seawater[21,22] revealed that highly oriented Ny6 and Ny66 homopolymer filaments separately exhibited negligible biodegradation over the measurement period. In contrast, Ny6/66 random copolymer filaments showed substantial oxygen consumption (Fig. 1a). In particular, the biodegradation behaviour of random copolymer 86/14, an industrially relevant composition widely used in commercial monofilament applications was comparable to that of cellulose under these accelerated conditions, although biodegradation rates did not directly reflect timescales in open marine environments. No measurable degradation was observed in sterilized seawater, indicating that the process required microbial activity. Notably, the random copolymer samples exhibited a clear induction period before biodegradation commenced (Fig. 1a, inset), suggesting that microbial colonization or biofilm formation may be necessary prior to depolymerisation[23,24].

To examine the role of structural properties, Ny6 filaments were subjected to cryogenic milling. While as-spun Ny6 filaments showed no detectable biodegradation, cryo-milled Ny6 powders showed obvious oxygen consumption (Fig. 1b), indicating that

structural disruption enabled biodegradation. No significant changes in molecular weight were observed before and after cryogenic milling (Supplementary Fig. 2). X-ray diffraction analysis further confirmed that cryogenic milling reduced the crystallinity and crystal size of the polymers (Fig. 1c, Supplementary Tables 1 and 2).

Systematic comparison of cryo-milled samples further indicated that even under reduced crystallinity conditions, copolymer composition strongly influenced biodegradability (Fig. 1d, e). Using Ny6/66 random copolymers with homogeneous comonomer distribution along the polymer chain[25], biodegradability initially increased with Ny66 content, reaching a maximum at an intermediate composition. However, biodegradability declined, as the content of the Ny66 fraction increased. Thus, optimal biodegradation was only observed within a limited compositional window; it did not increase monotonically with copolymerization.

These findings demonstrated that the marine persistence of engineering nylons is not solely determined by polymer chemistry, but also by higher-order polymer structure and accessibility to microbial degradation.

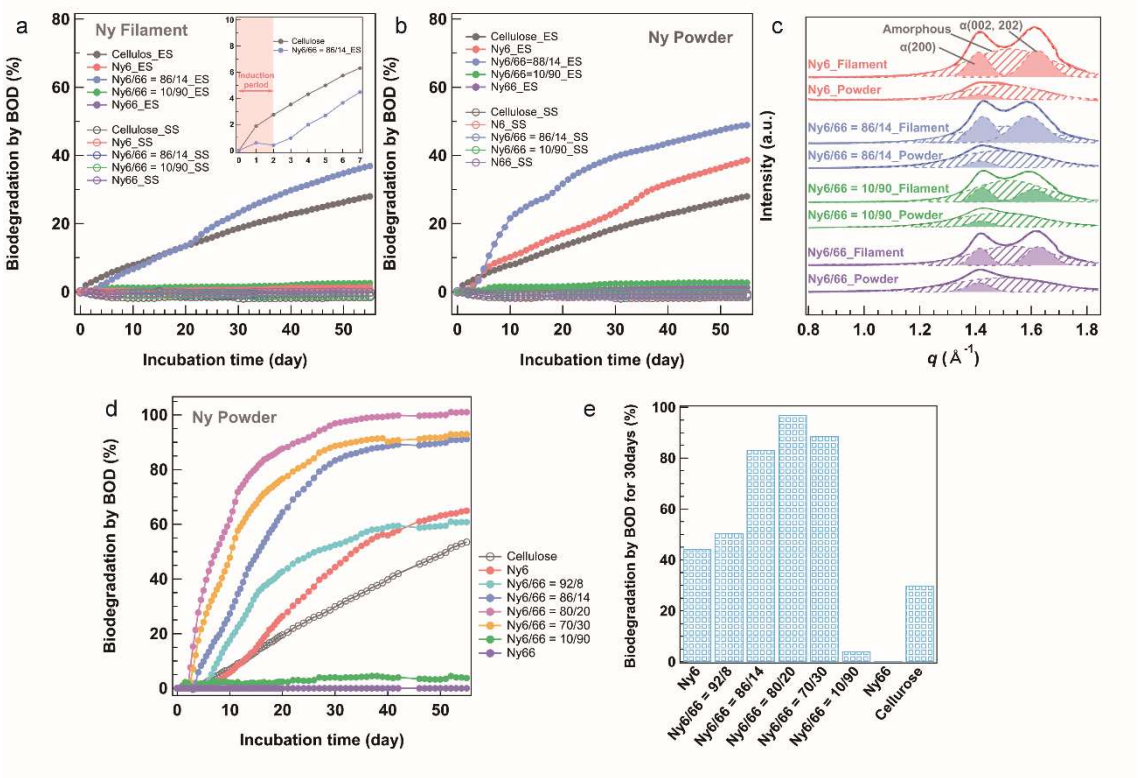


Fig. 1: Unexpected degradation of highly crystalline engineering nylon filaments under marine conditions. **a**, Accelerated marine BOD tests of highly oriented nylon filaments. Cellulose biodegradation served as the positive control, while extracted seawater (ES) and sterilized seawater (SS) served as controls. The copolymer samples exhibited an induction period as shown in the inset. **b**, Effect of cryogenic milling on Ny6 biodegradation. **c,** X-ray diffraction profiles of engineering nylons before and after cryogenic milling. Peak analysis indicated reduced crystallinity and crystal size owing to structural disruption. **d**, Composition dependence of biodegradability under cryo-milled conditions. **e**, Comparison of 30-day biodegradation levels of cryo-milled nylon powders

with different compositions, highlighting the strong composition dependence of marine biodegradability.

Field validation of nylon degradation

To determine whether the observed degradation behaviour of nylon filaments occurs under environmentally relevant conditions and to further isolate the influence of copolymer composition and crystalline organization, a separate series of nylon filaments with low orientation and γ-crystal-rich structures were prepared using different processing conditions across all compositions, without additives or surface treatments. Long-term in-situ marine exposure experiments were conducted at the seafloor, which is characterized by negligible ultraviolet-induced photodegradation.

After exposure to these natural seafloor conditions for 1–6 months, the nylon filaments showed progressive surface whitening, surface deterioration, and mechanical weakening (Fig. 2a). Scanning electron microscopy further revealed surface erosion and pit formation owing to marine exposure (Fig. 2b), and mechanical testing demonstrated a time-dependent decrease in knot strength (Fig. 2c), indicating progressive loss of mechanical integrity under natural marine conditions.

Accelerated marine BOD tests showed measurable Ny6 biodegradation under altered crystalline organization, in contrast to the negligible biodegradation observed for the highly oriented α-crystal-rich polymer (Fig. 2d). Biodegradability further increased systematically with increasing Ny66 content, indicating clear composition dependence (Fig. 2d). This compositional trend is also similar to that observed for the cryo-milled samples (Fig. 1d).

The X-ray diffraction profiles of the marine environment-exposed polymers differed considerably from those of the highly oriented α-crystal-rich filaments and cryo-milled samples (Fig. 2e, Supplementary Table 3), indicating that altered crystalline organization and reduced molecular orientation promoted biodegradability.

Overall, these findings demonstrated that engineering nylon filaments, particularly random copolymers, can undergo degradation under natural marine conditions, with polymer structure and accessibility to microbial degradation playing key regulatory roles in this regard.

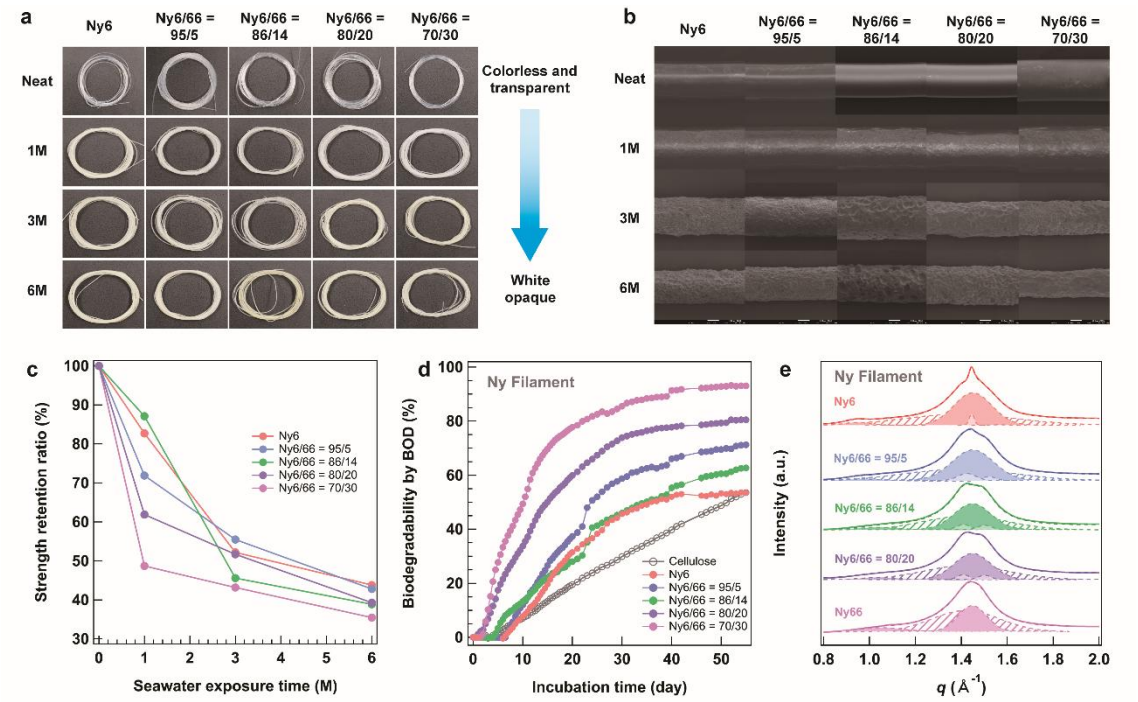


Fig. 2: Field validation of the biodegradation of engineering nylon filaments under natural marine conditions. a, Photographs of nylon filaments after long-term in situ marine exposure at the seafloor at 1, 3, and 6 months. **b,** Scanning electron microscopy images of nylon filaments after field exposure. **c,** Mechanical degradation of nylon filaments owing to field exposure. **d,** Accelerated marine BOD curves of nylon filaments prepared under identical processing conditions to clarify the effect of copolymer composition within structurally distinct filaments. **e,** X-ray diffraction patterns of low-orientation, γ-crystal-rich filaments. The crystalline organization of the filaments is distinct from that of highly oriented α-crystal-rich filaments (Fig. 1c).

Mechanism of nylon biodegradation

Given the strong dependence of engineering nylon biodegradation on polymer composition and structural state, we investigated the physicochemical parameters governing accessibility to microbial degradation.

A strong positive correlation was observed between water uptake and biodegradability in γ-crystal-rich structures with different nylon compositions (Fig. 3a). Similarly, samples with higher water uptake capabilities consistently showed higher biodegradation rates across diverse nylon compositions and crystalline structures, including highly crystalline α-crystal-rich films (Supplementary Fig. 3). These findings further identified hydration-mediated accessibility as a unifying factor that drives biodegradation behaviour.

To examine the molecular mechanisms underlying this hydration behaviour, intermolecular interactions in the amorphous phase were evaluated using high-resolution Fourier transform infrared spectroscopy[26,27]. H-bonding strength in the amorphous phase, quantified as the Equilibrium Enthalpy of H bonds (ΔH) measured in the high-temperature regime and dry state[27], also varied significantly across polymer compositions (Fig. 3b, Supplementary Fig. 4). Notably, the largest ΔH, indicating the strongest intermolecular H bonding, was observed for Ny66, whereas random copolymer Ny6/66 (86/14) showed the lowest ΔH, implying weakened intermolecular interactions. This

trend was also consistent with the observed variation in water uptake (Fig. 3a), where a lower ΔH correlated with higher hydration and enhanced biodegradability.

In contrast, Ny6 and Ny6/66 (10/90) exhibited intermediate ΔH values, indicating comparable H-bonding strength in the amorphous phase. However, they showed markedly different water uptake and biodegradation characteristics. Specifically, Ny6 exhibited moderate hydration and became biodegradable as its crystallinity decreased following cryo-milling. Conversely, Ny6/66 (10/90) showed lower water uptake and did not undergo biodegradation under comparable conditions. These findings indicated that while dry state ΔH serves as a useful indicator of intermolecular interactions, it alone does not fully account for hydration and biodegradability, suggesting the involvement of additional structural factors as well as the effect of differences in hydrophilicity.

To further examine the role of intermolecular interactions, Ny66 samples were treated with inorganic salts (Supplementary Fig. 5) that are known to disrupt H bonding between polymer chains. Thus, otherwise resistant Ny66 showed biodegradation (Fig. 3c). Therefore, the environmental persistence of engineering nylons is governed not only by polymer chemistry, but also by structure-dependent accessibility mediated by hydration.

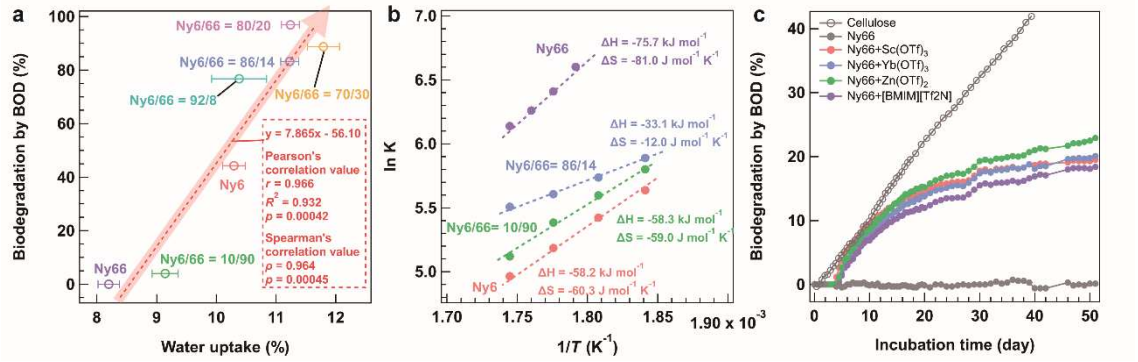


Fig. 3: Hydration-mediated accessibility, a key modulator of structure-dependent biodegradation in engineering nylons. a, Correlation between water uptake and biodegradability across different compositions and structural states. **b,** H-bonding strength enthalpies (ΔH) of amorphous Ny6, Ny66, and Ny6/66 random copolymer. A lower ΔH is indicative of weaker intermolecular interactions. **c,** Effect of salt addition on Ny66 biodegradation.

Microbial depolymerisation of nylons

To determine whether the observed degradation of nylon filaments reflects genuine microbial depolymerisation rather than abiotic deterioration, marine environment-exposed nylon samples were subjected to molecular and microbiological analyses.

Specifically, liquid chromatography–mass spectrometry (LC/MS) analysis of the biofilms associated with the collected samples revealed the presence and accumulation of

soluble nylon oligomers, indicating ongoing depolymerisation under natural seawater conditions (Fig. 4a). Notably, the detected oligomers predominantly comprised Ny6-derived species, whereas Ny66-derived oligomers were not detected, suggesting preferential cleavage of Ny6-type amide bonds during depolymerisation. Moreover, because these oligomers were not detected in artificial seawater, their presence was attributed to microbial activity occurring under natural marine conditions.

Additionally, to investigate the microorganisms potentially involved in the degradation, microbial community dynamics during seawater incubation were analysed via 16S rRNA gene sequencing (Extended Data Fig. 1). This analysis revealed changes in microbial community composition upon polyamide addition relative to the control seawater, indicating selective enrichment of polymer-associated microorganisms. This enrichment followed a two-tiered, successional pattern. First, broadly responsive colonizers (e.g., Rhodobacteraceae, Pseudohongiellaceae) appeared during initial biofilm formation, whereas species belonging to the family Spongiibacteraceae showed transient enrichment, suggesting possible involvement in the nylon depolymerisation process.

Based on these observations, enrichment cultures were established using Ny6/66 copolymer as the sole polymeric substrate. After enrichment, several colonies formed clear zones on marine agar plates containing emulsified Ny6/66 (as described in Methods),

indicating extracellular depolymerisation activity (Fig. 4b). Furthermore, microbial community analysis based on 16S rRNA gene sequencing identified an isolate belonging to the genus *Dasania* within the family Spongiibacteraceae, which was designated *Dasania* sp. strain IWD1.

BOD assays under sterilized extracted seawater further confirmed that *Dasania* sp. IWD1 enhanced oxygen consumption in the presence of Ny6/66 random copolymer (Fig. 4c). Gel permeation chromatography of polymer samples recovered after incubation with this strain also showed a marked decline in the high-molecular-weight fraction of the polymer (Fig. 4d), highlighting microbial chain scission of nylon polymers as a degradation pathway.

A conceptual framework summarizing these observations is provided in Fig. 4e. In brief, biofilm establishment under marine conditions promotes hydration-mediated accessibility and microbial access to polymer chains, resulting in depolymerisation, oligomer production, and subsequent mineralisation of engineering nylon filaments.

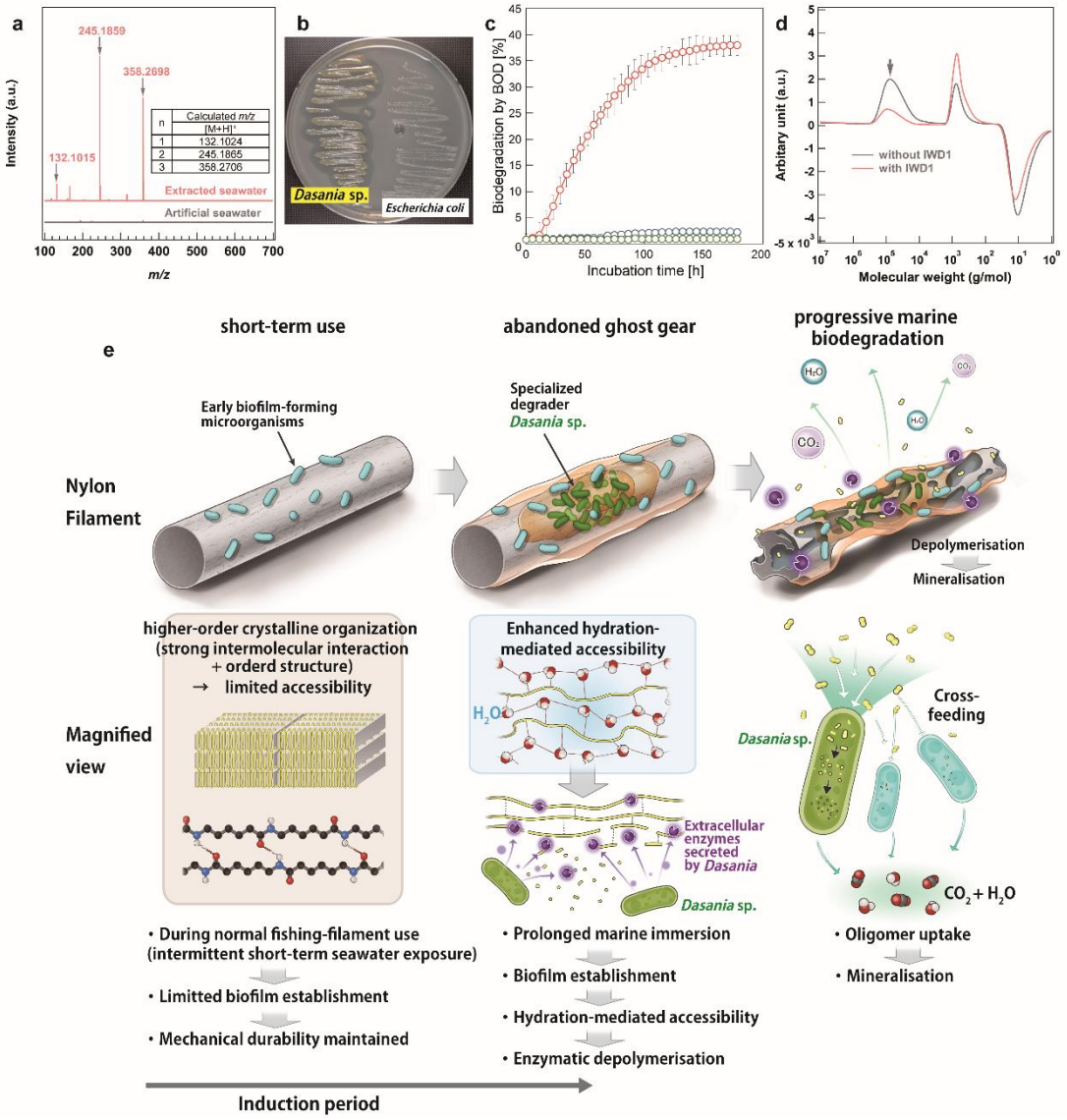


Fig. 4: Microbial depolymerisation of engineering nylons under marine conditions.

a, High-resolution LC/MS analysis results of Ny6/66 samples after immersion in natural seawater (red) or artificial seawater (black). The red trace represents biofilm-associated Ny6/66 recovered from natural seawater, whereas the black trace represents the artificial seawater control. **b,** Representative digital image of clear-zone formation on a marine

agar plate supplemented with 20% (v/v) emulsified Ny6/66 after 3 days of incubation at 25 °C. The left spot indicates inoculated *Dasania* sp. strain IWD1 cells, and the right spot represents *Escherichia coli* as a negative control. **c,** BOD assays of the metabolic assimilation of Ny6/66 by *Dasania* sp. strain IWD1. The assay was performed in sterilized extracted seawater at 25 °C for over 200 h. The red circles represent strain IWD1 incubated with Ny6/66, while the blue and green symbols represent the control conditions of strain IWD1 alone and Ny6/66 alone, respectively. The BOD for each condition was calculated by subtracting the value of the blank control (sterilized extracted seawater only) from the measured oxygen consumption. **d,** Gel permeation chromatography (GPC)-based molecular weight distribution for Ny6/66 recovered from the culture medium following BOD tests. The red lines represent samples incubated with strain IWD1, while the black lines indicate non-inoculated controls. High-molecular-weight peaks corresponding to a weight-average molecular weight (M_w) of approximately 7.6×10^4 are highlighted. **e,** Conceptual framework of accessibility-mediated marine biodegradation of engineering nylons.

Discussion

The unexpected observation of substantial biodegradation in some commercially available nylon fishing lines in natural seawater challenges the long-standing assumption that engineering nylons are intrinsically persistent under marine conditions[13]. The present study demonstrated that even highly crystalline, oriented engineering nylon filaments can undergo substantial biodegradation depending on copolymer composition and structural organization.

Importantly, the copolymer systems examined in this study are not niche biodegradable model materials, but materials that are already used in commercially available engineering nylon fishing lines. Their biodegradability was not an intended design feature, but appears to be driven by an industrially optimized composition and a higher-order structure, suggesting that latent environmental responsiveness may already exist within current engineering nylon designs, but has remained unrecognized owing to the long-standing assumption that nylon persists in marine environments.

Notably, experiments using additive-free filaments prepared using industrially relevant melt-spinning processes showed similar results, indicating that the observed degradation behaviour does not arise solely from additives or surface treatments used in commercial products. The structural disruption of otherwise resistant Ny6 also

demonstrated that nylon biodegradability is not governed solely by polymer chemistry but also by higher-order structural organization and accessibility to microbial processes.

Across all nylon systems examined in this study, biodegradability showed strong correlation with water uptake, suggesting that hydration-mediated accessibility is a key link between polymer structure and environmental degradation. This correlation further highlighted water uptake as an experimentally accessible predictor of biodegradation behaviour under marine conditions. Although intermolecular interactions, particularly H-bonding strength, played a role in this regard, it did not completely account for the observed biodegradation, indicating that accessibility is the result of multiple structural factors acting collectively under marine conditions

The present study further demonstrated that degradation proceeds under environmentally relevant marine conditions. Long-term in situ seafloor exposure experiments, conducted under negligible ultraviolet irradiation revealed progressive whitening, surface erosion, and mechanical deterioration of nylon filaments. These observations indicated that the observed biodegradation could not be attributable to photodegradation and represents a genuine degradation process occurring under natural marine conditions.

Molecular and microbiological analyses further support microbial depolymerisation of the engineering nylons under marine conditions. Previous studies have reported laboratory enrichment-based degradation of Ny6 and Ny66 homopolymers by marine microorganisms, as well as enzymatic depolymerisation of Ny6 under controlled reaction systems. Notably, a recent long-term marine exposure study reported that Ny66 homopolymer remained largely stable and resisted microbial colonisation even after extended seafloor incubation[28], reinforcing the prevailing view of engineering nylons as persistent. The present study extends these observations by demonstrating structure-dependent biodegradation of commercially relevant engineering nylon filaments under natural marine conditions, together with hydration-mediated accessibility, biofilm-associated microbial depolymerisation, and progressive degradation during long-term seafloor exposure. Additionally, soluble nylon oligomers and microbial community profiling revealed a staged "division-of-labour" structure, consistent with successional colonization reported for marine plastics[29–31]. Specifically, initial biofilm formation driven by responsive colonizers was followed by the enrichment of specialized Spongiibacteraceae, particularly, *Dasania* sp. IWD1, which drove oxygen consumption and molecular-weight reduction, demonstrating microbial chain scission of high-molecular-weight engineering nylons. Unlike prior studies, which demonstrated nylon

biodegradation based on mixed consortia or extreme conditions[18,32,33], our findings demonstrate that this single marine bacterium mediates both chain scission and assimilation under ambient conditions, although complete mineralisation in natural seawater may involve broader biofilm-associated microbial processes[34]. Taken together, these findings revealed latent biodegradability in engineering-grade nylons.

An additional feature of the unexpected biodegradation in Ny6/66 copolymer is the presence of a clear induction period preceding biodegradation. Unlike cellulose, which undergoes immediate microbial degradation upon seawater exposure, nylon copolymers initially retained mechanical integrity before degradation accelerates after prolonged exposure. This delayed onset may explain why the marine biodegradability of some nylon fishing lines has remained largely unrecognized despite their widespread use. One possible explanation is that biofilm establishment and localized microbial activity are required before depolymerisation can proceed efficiently at the polymer surface[24, 35], as shown in the conceptual framework summarizing this accessibility-controlled biodegradation behaviour in Fig. 4e. This induction period is consistent with the timescales reported for early biofilm formation and successional maturation on marine plastics, during which specialized degraders such as *Dasania* are progressively enriched.

From an environmental perspective, such induction-time behaviour may have important implications for ghost fishing and marine debris mitigation[36]. Biodegradation may remain dormant during relatively short-term marine use and only becomes active after prolonged environmental exposure. Therefore, if abandoned in marine environments for extended periods, continued biofilm establishment may facilitate progressive biodegradation. Conversely, intermittent retrieval from seawater in practical fishing applications may repeatedly disrupt biofilm formation and thus, delay biodegradation onset and retain the mechanical robustness of the filaments required for normal operation. Generally, these observations suggest a possible strategy for addressing one of the central challenges in marine biodegradable polymers: balancing the trade-off between mechanical durability and environmental degradability. Rather than relying solely on intrinsically unstable polymer chemistries, environmentally responsive degradation controlled by accessibility and induction-time behaviour may offer a pathway to marine plastics that remain functional during use but become degradable after prolonged environmental release.

Detailed enzymatic pathways and catalytic mechanisms governing nylon depolymerisation under marine conditions remain important topics for future investigation. Homologs of Nyl-type hydrolases have been identified in the draft genome

sequence of *Dasania marina* DSM 21967, a type strain of the genus *Dasania*, available in the NCBI Genome database under RefSeq accession number GCF_000373485.1 [37]. This finding suggests that members of this genus may possess the genetic potential for nylon catabolism; however, the enzyme(s) responsible for initiating high-molecular-weight chain scission in strain IWD1 remain unidentified.

Conclusion

This study challenges the widespread assumption that engineering nylons are intrinsically persistent under marine conditions. Specifically, we demonstrated that highly crystalline engineering nylons, including commercially relevant nylon filaments, can undergo substantial biodegradation under natural marine conditions, with long-term seafloor exposure experiments supporting progressive degradation under environmentally relevant marine environments. We also showed that the biodegradability of nylon filaments is not solely governed by polymer chemistry, but also by hydration-mediated accessibility to microbial processes, with degradation proceeding under environmentally relevant marine conditions. Additionally, molecular and microbiological analyses revealed microbial chain scission and the assimilation of high-molecular-weight nylon by marine bacteria, including by *Dasania* sp. IWD1, a newly isolated marine bacterium, and

to our knowledge, this study is the first to demonstrate that *Dasania* sp. IWD1 mediates this process in pure culture. The existence of an induction period prior to biodegradation suggested that engineering plastics retain durability during normal use and become progressively degradable after prolonged environmental exposure. Overall, this study provides a novel perspective for understanding the environmental fate of ghost fishing gear, marine debris, and secondary microplastics and suggests that environmentally responsive degradability may already be achievable within industrially used engineering nylon platforms by controlling nylon composition, higher-order structure, and microbial accessibility.

Online content

Any methods, additional references, Nature Portfolio reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at XXX.

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Methods

Materials

The commercially available fishing filaments used in this study were Extra V-500 No. 1 (Ny6/66 = 86/14; Sanyo-Nylon Co., Ltd.), Queenstar No. 1 (Ny6/66 = 86/14; Sunline Co., Ltd.), and Ginrin No. 1 (Ny6/66 = 95/5), with No. 1 implying a filament diameter of 0.165 mm.

The commercially available nylon pellets used in this study included: 1022B and 1030B (Ny6 homopolymer; UBE Co., Ltd.), 5032B (Ny6/66 = 92/8; UBE Co., Ltd.), 5033B (Ny6/66 = 86/14; UBE Co., Ltd.), 5034B (Ny6/66 = 80/20; UBE Co., Ltd.), 5036B (Ny6/66 = 70/30; UBE Co., Ltd.), 9400S (Ny6/66 = 10/90; Asahi Kasei Co., Ltd.), 1700S (Ny66 homopolymer; Asahi Kasei Co., Ltd.), Novamide 2330J (Ny6/66 = 95/5; Envalior Japan Co., Ltd.), Novamide 2020A8 (Ny6/66 = 86/14; Envalior Japan Co., Ltd.), and Novamide 2420A (Ny6/66 = 80/20; Envalior Japan Co., Ltd.).

To disrupt H-bonding in the nylon samples, the following inorganic salts were used as additives: Scandium(III) trifluoromethanesulfonate (purity: > 98.0%, Tokyo Chemical Industry Co., Ltd.), Ytterbium(III) trifluoromethanesulfonate (purity: > 98.0%, Tokyo Chemical Industry Co., Ltd.), 1,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide (purity: > 98.0%, Tokyo Chemical Industry Co., Ltd.),

and Zinc(II) trifluoromethanesulfonate (purity: > 98.0%, FUJIFILM Wako Pure Chemical Co., Ltd.).

Sample preparation

Highly oriented nylon filaments were prepared via uniaxial drawing processing. In brief, each nylon resin was melt-processed using a twin-screw extruder and extruded through a nozzle as a continuous strand. Thereafter, the extruded strands were passed through a cooling bath containing silicone oil to obtain rapidly-quenched amorphous undrawn filaments, which were then drawn via passage through wet-heat and dry-heat drawing baths to obtain oriented filaments. The wet-heat drawing process was performed in steam generated from a heated water bath, and the draw ratio was defined as the amount of the drawn sample relative to the undrawn sample, expressed as 1×.

For Ny6, the resin was extruded at 271 °C and quenched at −20 °C, followed by first-stage drawing at 3.4× under wet heat at 100 °C and second-stage drawing at 5.8× under dry heat at 200 °C.

For Ny66, the resin was extruded at 291 °C and quenched at −10 °C, followed by first-stage drawing at 3.7× under wet heat at 100 °C and second-stage drawing at 5.5× under dry heat at 240 °C.

For the Ny6/66 (86/14) random copolymer, the resin was extruded at 263 °C and quenched at −20 °C. The filaments were subsequently subjected to first-stage drawing at 3× under dry heat at 60 °C, second-stage drawing at 4× under wet heat at 100 °C, third-stage drawing at 5.5× under dry heat at 160 °C, and fourth-stage drawing at 4.95× under dry heat at 140 °C. Given that direct wet-heat drawing from the undrawn state was challenging for this random copolymer, an initial dry-heat drawing step was introduced prior to wet-heat drawing to develop a preliminary filament structure. Subsequently, additional dry-heat drawing steps were performed to further increase orientation and relax molecular orientation for subsequent optimization.

For the Ny6/66 (10/90) random copolymer, the resin was extruded at 278 °C and quenched at −10 °C, followed by first-stage drawing at 3.7× under wet heat at 100 °C and second-stage drawing at 5.5× under dry heat at 220 °C.

Low-orientation γ-crystal-rich filaments were prepared as undrawn monofilaments using a Capilograph 583 melt spinning apparatus equipped with a melt tension unit (Toyo Seiki Seisaku-sho, Ltd.), with cylinder and die hole diameters of 9.55 and 1.5 mm, respectively, and L/D = 5. Additionally, for the Ny6 polymers, the melt-spinning conditions were as follows: cylinder temperature, 240 °C; extrusion speed, 5

mm s^{-1}; and take-up speed, 5000 mm s^{-1}, and for Ny66 polymers, the cylinder temperature was set to 280 °C.

γ-crystal-rich films were prepared using a vacuum hot press (IMC-11FD, Imoto Machinery Co., Ltd.). In brief, the samples were melted in a 0.4-mm-thick mould at 280 °C under reduced pressure for 30 min and subsequently compression-moulded at 10 kN for 5 min. After this step, the samples were rapidly quenched in liquid nitrogen to induce the formation of γ-crystal-rich structures.

Similarly, to prepare α-crystal-rich films, a vacuum hot press (IMC-11FD, Imoto Machinery Co., Ltd.) was used. First, the samples were melted in a 0.4-mm-thick mould at 280 °C under reduced pressure for 30 min and subsequently compression-moulded at 10 kN for 5 min. Thereafter, the samples were slowly quenched in air at 25 °C to induce the formation of α-crystal-rich structures.

Cryogenically milled powder samples were prepared using a CryoMill system from Retsch GmbH. In brief, a mixture comprising 2–3 g of nylon samples and a 15-mm diameter milling ball were placed in a 50-mL jar and cooled in liquid nitrogen at 5 Hz for 8 min. Subsequently, milling was performed at 30 Hz for 10 min, and the resulting powders were collected and subjected to scanning electron microscopy (SEM) to confirm uniform pulverization, yielding particles with sizes of approximately 10–50 μm.

Ny66 containing inorganic salt additives was prepared using a micro-compounding extruder (IMC-A300, Imoto Machinery Co., Ltd.). Specifically, Ny66 pellets and inorganic salts (1 phr) were melt-mixed under Ar gas flow at 270 °C for 5 min.

Field tests

Field degradation tests were conducted in the coastal waters of Ainan Town (Ehime, Japan) using the experimental aquaculture facilities of the South Ehime Fisheries Research Center, Ehime University (Supplementary Fig. 6a). To evaluate degradation behaviour under environments with distinct external factors, the nylon samples were moored at depths of approximately 1 m (surface layer) and 25 m (seafloor). While the surface environment is strongly influenced by sunlight, ocean currents, and marine biofouling organisms, ultraviolet light scarcely reaches the seafloor environment, which was more susceptible to the influence of sediments. The mooring cages were constructed using poly(vinyl chloride) pipes and polyethylene trical nets. Further, the samples were placed in triangular pyramid-shaped polyethylene mesh bags with an aperture size of 1.571 mm, allowing continuous seawater flow around the samples (Supplementary Fig. 6b). The cages were moored in migratory fish aquaculture pens operated by Ehime University, and the samples were exposed to seawater for 1, 2, 3, and 6 months

(Supplementary Fig. 6c, d), and after retrieval at each time point, they were transported to the laboratory and stored at approximately 5 °C until washing. First, they were immersed in HCl solution (pH = 4, 0.1 mmol/L) and shaken for 48 h using a rotary shaker (RS). Thereafter, the samples were immersed in an aqueous solution of sodium dodecyl sulphate (SDS, 0.2 wt%) to remove biofilms from their surfaces and subsequently shaken overnight using the RS. The next day, the SDS solution was replaced with deionized water, followed by further shaking for 4 h, washing five times with deionized water, and drying under vacuum at 40 °C for 48 h.

The degradation behaviour of the washed samples was evaluated based on changes in surface erosion morphology observed via optical microscopy and SEM, as well as changes in weight, filament diameter, and knot strength. Optical micrographs (OM) were obtained using a BX60 optical microscope (Olympus Corporation) under bright-field conditions. Further, SEM images were acquired using the JSM-7800F field-emission scanning electron microscope (JEOL Ltd.).

The degradation degrees of the samples were evaluated based on changes in sample weight and filament diameter, which were measured using a precision electronic balance and a digital micrometre, respectively. All changes were expressed in relation to the corresponding values recorded before marine exposure.

The extent of degradation-induced mechanical deterioration was further evaluated via knot strength measurements based on uniaxial tensile testing using a universal testing machine (AG-10kNXPlus; Shimadzu Corporation) equipped with a 1-kN load cell. All the experiments were performed at 25 °C. Additionally, filaments with a single knot were tested using a pneumatic capstan yarn grip (Shimadzu Corporation) at a crosshead speed of 100 mm min^{-1}, and changes in knot strength were calculated relative to the initial knot strength (i.e., before marine exposure). All experiments were performed using at least three independent specimens unless otherwise stated.

Marine accelerated biological oxygen demand (BOD) tests

Accelerated marine biodegradation tests based on BOD measurements were performed using the WTW OxiTop- IDS A12 system (Xylem Analytics). In brief, natural seawater collected from Miyagawa Coast (Miura City, Kanagawa) was used as the seed source (Supplementary Fig. 7a). Extracted seawater was also prepared from sediments according to Taguchi et al. (Supplementary Fig. 7b)[1,2]. Thereafter, a 600-mL aliquot of the natural seawater and 100 g of sediment were mixed, and the biodegrading bacteria in the sediment were extracted into the natural seawater via ultrasonication for 10 s using an ultrasonic cleaner (NSD, US-30KS). The sediment used was obtained via filtration from

extracted seawater using a filter bag (As-One; filtration accuracy: 10 μm) with a 2-mm gap. Further, a 150-mL aliquot of extracted seawater and 60 mg of the sediment sample were mixed in a 250-mL OxiTop container and continuously agitated using the stirrer attached to the OxiTop system at 25 °C in a Heratherm IMP400 incubator (Thermo Fisher Scientific). To accurately determine the partial pressure of oxygen consumed by the biodegrading bacteria during biodegradation, NaOH pellets were used to adsorb the carbon dioxide generated during biodegradative metabolism (one granule per 30 d). Thereafter, BOD was calculated from the measured oxygen consumption according to Eq. (1) as follows:

$$BOD(\%) = \frac{BODs - BODb}{ThOD} \times 100 \quad (1)$$

where *BODs* represents to the BOD of the sample, *BODb* represents the BOD of the blank (seawater only), and ThOD represents the theoretical oxygen demand. Extracted seawater was autoclaved at 121 °C for 15 min and stored at 4 °C until use. BOD tests were performed using at least three independent specimens for each sample. The BOD degradation curves shown in the figures represent representative datasets corresponding to the average biodegradation behaviour observed among the replicates.

Gel permeation chromatography (GPC)

Nylon samples were dissolved in 1,1,1,3,3,3-Hexafluoropropan-2-ol (HFIP), filtered using a 0.2-μm PTFE filter, and examined via GPC using Shodex GPC columns (HK-405, 4.6×150 mm; HK-404L, 4.6×150 mm) and a refractive index detector. Further, molecular weight (M_w) was calculated based on calibration using polymethyl methacrylate standards.

Wide-angle X-ray scattering (WAXS) experiments

WAXS experiments were performed on the BL-05XU or BL-03XU beamline at the SPring-8 facility (Hyogo, Japan), with the sample–detector distance set to approximately 0.3 m and the wavelength and beam dimensions at 1.0000 Å and 0.1 mm × 0.2 mm, respectively. Then, to record two-dimensional patterns, we used the PILATUS 1M system (Dectris), with the irradiation time set to 1 s and with a 10-μm-thick Pt layer as the shielding material.

Water uptake measurements

Water uptake measurements were performed to evaluate the hydration behaviour of the nylon samples. Prior to immersion, the samples were dried under vacuum at 30 °C for 5 days, and their initial dry weights were recorded as W_{dry}. The dried samples were

then immersed in deionized water at 25 °C for a predetermined period after which they were removed and the excess water on their surfaces was carefully wiped off using a filter paper. Thereafter, the wet weights of the samples (W_{wet}) were immediately recorded, and water uptake was calculated according to Eq. (2).

$$Water\ uptake\ (\%) = \frac{W_{wet} - W_{dry}}{W_{wet}} \times 100 \qquad (2)$$

where W_{dry} represents initial dry weight before immersion and W_{wet} represents wet weight after immersion. At least three specimens were measured for each sample, and the collected data were expressed as the mean ± SD. Correlations between water uptake and biodegradability were evaluated using Pearson's correlation analysis and Spearman's rank correlation analysis. The corresponding correlation coefficients (R and ρ) and p-values were calculated to assess the strength and significance of the relationships. Statistical significance was defined as $p < 0.05$.

Fourier transform infrared (FT-IR) analysis

FTIR spectroscopy measurements were performed using the Vertex V-80 spectrometer (Bruker) equipped with an MCT detector. Spectra were obtained in the 4000–650 cm^{-1} scan range at a resolution of 1 cm^{-1}, with 64 scans accumulated per sample. Further, temperature-dependent measurements were performed from 190 to 300 °C using

a Golden Gate heated diamond ATR accessory (Specac), and for each measurement, the sample was placed on a diamond prism and fixed by pressing a sapphire anvil onto the sample surface.

For H-bonding analysis, the equilibrium state of H bonds (HBs) was evaluated by calculating the equilibrium constant, *K*, which was defined as the intensity ratio of N–H stretching vibrations originating from the ordered (~3340 cm^{-1}) and disordered structures (~3450 cm^{-1}) in the completely molten amorphous phase. Subsequently, H-bonding strength (ΔH) and orientational ordering (ΔS) were evaluated from the temperature-dependent FTIR spectra via Van't Hoff analysis using the equilibrium constant between H-bonded and free N–H groups[3]. Detailed derivations are provided in the Supplementary Note 1.

Liquid chromatography–mass spectrometry (LC–MS) analysis

Samples recovered after biodegradation and water-immersion tests were collected and immersed in 2 mL of methanol for methanol extraction. The resulting methanol suspensions were sonicated using an ultrasonic generator (US-10KS, SND) at 38 kHz for 60 s and the extracts obtained were filtered through a 0.2-μm membrane filter and analysed via LC-Orbitrap MS using the UltiMate 3000/LTQ Orbitrap XL system

(Thermo Fisher Scientific). For LC, an L-column2 ODS column (100 mm × 2.1 mm, 3 μm particle size; Chemicals Evaluation and Research Institute), with the column temperature, flow rate, and injection volume set to 40 °C, 0.25 mL min^{-1}, and 5 μL, respectively, was used. Mobile phase A was water containing 0.1% (v/v) formic acid and 5 mM ammonium acetate, whereas mobile phases B and C were acetonitrile and 2-propanol, respectively. Gradient elution was performed as follows: initial composition (90% A, 5% B, and 5% C) maintained for 1 min, followed by a linear gradient to 10% A, 45% B, and 45% C for 9 min followed by holding for 10 min.

16S rRNA gene amplicon sequencing

Microbial analysis, based on 16S rRNA amplicon sequencing, was outsourced to Novogene (Beijing, China). DNA libraries were constructed from extracted DNA samples by amplifying the V3–V4 region of the 16S rRNA gene. Thereafter, sequencing was performed using the NovaSeq 6000 system with SP flow cell with over 500 cycles. The paired-end fast data obtained from the sequencing were processed and subjected to quality assessment using QIIME2 (version 2023.7), and noise was removed using DADA2. Subsequently, amplicon sequence variants (ASVs) were extracted and taxonomic annotation was performed using the SILVA 138 reference database and

relative abundances were calculated using the taxa barplot tool in QIIME2, which offers the possibility to visualise the relative distribution patterns of microbial communities.

Preparation of emulsified Ny6/66 for agar screening

To prepare emulsified Ny6/66 for agar screening, 50 mg of nylon random copolymer Ny6/66 (commercial fishing-line material; QueenStar) was dissolved in 10 mL of 2,2,2-trifluoroethanol (TFE) and the mixture was stirred at 250 rpm for 15 min to obtain a homogeneous polymer solution (Solution A). Separately, an aqueous solution of 0.02 vol% Plysurf AL (Dai-ichi Kogyo Seiyaku Co., Ltd.) was preheated to 70 °C and stirred at 550 rpm, and while maintaining stirring, Solution A was slowly added to this preheated Plysurf AL solution. The resulting mixture was then heated at 90 °C for 15 min to evaporate TFE followed by autoclaving at 121 °C for 15 min to remove any residual TFE. After cooling to 30 °C, the pH of the resulting emulsion was adjusted to 7.0 and optical microscopy was performed, which confirmed that the emulsion particles were approximately 1 μm in size and appeared uniform. The resulting Ny6/66 emulsion was then used to prepare the Ny6/66 emulsion agar media.

Enrichment culture and screening of Ny6/66-degrading bacteria

Marine microbial communities involved in Ny6/66 degradation were enriched via incubation in liquid media containing Ny6/66 powder for 14 days. Aliquots of the enrichment culture were spread onto Marine Agar 2216 (Difco BD) supplemented with 20 % (v/v) emulsified Ny6/66 solution and incubated at 25 °C. The formation of clear zones within 3 days served as an indicator of Ny6/66 biodegradation. Therefore, in our analysis, colonies that formed clear zones within 3 days were isolated and taxonomic identification was performed via 16S rRNA gene sequencing.

BOD assays for Ny6/66 utilization by strain IWD1

BOD assays were conducted using sterilized extracted seawater prepared from coastal seawater. Incubations were performed at 25 °C under three conditions: strain IWD1 alone, Ny6/66 alone, and strain IWD1 with Ny6/66. For each condition, BOD was determined by subtracting the oxygen consumption of the blank control (sterilized extracted seawater without strain or substrate) from the measured value. During this experiment, the oxygen consumption associated with microbial respiration, an indicator of Ny6/66 biodegradation activity, was monitored over a period of approximately 200 h. BOD assays were performed in triplicate biological replicates. Data are presented as the mean ± standard deviation.

Methods references

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Data availability statement

The datasets generated or analysed during this study are provided as Source data and included in Supplementary Information. The data are available from the corresponding author on request. More details on the methods are available in the Supplementary Information.

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Author contributions

S.A., D.K. and K.I. conceived the study. K.I. supervised the project. S.A. and D.K. supervised the experiments. T.M., E.U., T.I., Y.K. and H.I, fabricated nylon filaments and film samples, E.U. performed the cryogenic milling experiments, BOD biodegradation tests, and water uptake measurements. M.A. performed GPC and FTIR measurements. M.Y. and D.K. prepared nylon oligomers and analysed the catabolic characteristics of the isolated bacterial strains. Y.A. and A.T., contributed to the

crystalline analysis and cross-validation of the biodegradation experiments. H.T. and T.K. established the extracted seawater preparation protocol and performed LC–MS measurements. H.T., T.K., N.S. and H.H. established and collected samples during the field exposure experiments. H.M. contributed to data analysis. K.T., M.H., Y.S. and M.Y. established a screening method for Ny6/66-degrading microorganisms based on clear-zone formation on an agar medium containing Ny6/66 emulsion. S.A., D.K. and K.I. wrote the manuscript, and all the authors reviewed and approved the final version.

Competing interests The authors declare no competing interests.

Additional information

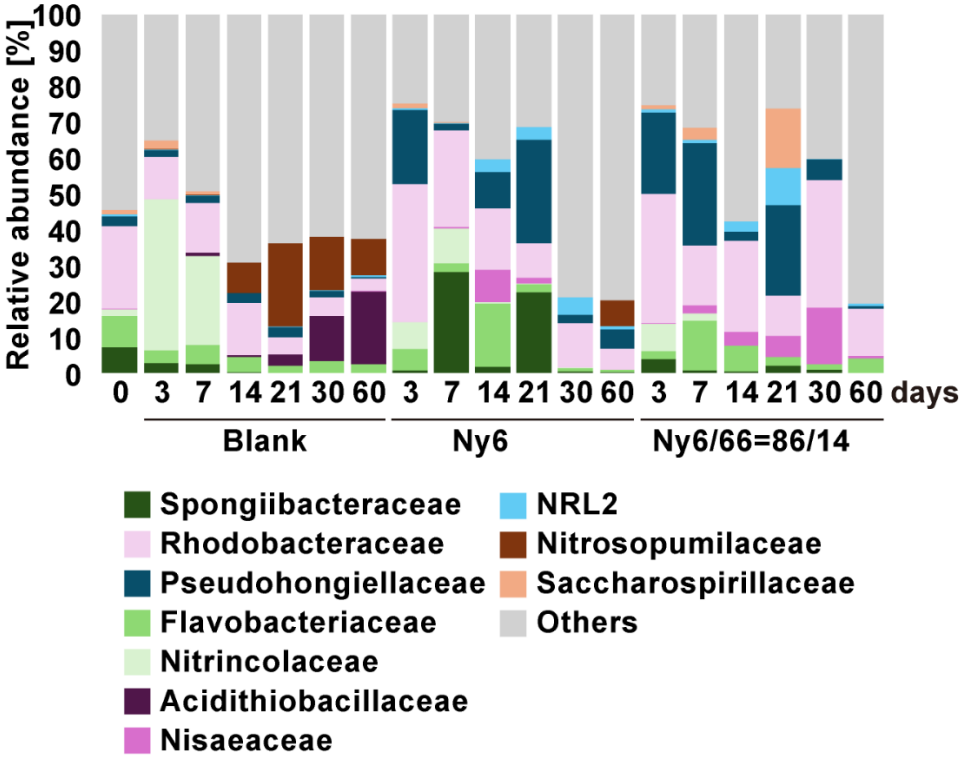
Supplementary information The online version contains supplementary material available at XX.

Correspondence and requests for materials should be addressed to Kohzo Ito, Shota Ando, and Daisuke Kasai.

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Extended Data



Extended Data Fig. 1 Temporal changes in microbial community composition during seawater microcosm incubation. Stacked barplots show the relative abundance (%) of the major bacterial families in blank (Blank), Ny6, and Ny6/66=86/14 seawater microcosms at 0, 3, 7, 14, 21, 30, and 60 days of incubation. Family-level classifications were determined by 16S rRNA gene amplicon sequencing. Biological replicates of n = 3 were used at each time point, except for some specific time points with n = 2; the displayed values represent the mean relative abundance across replicates. Bacterial families with low overall abundance are grouped as "Others".

Supplementary Files

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