Development of Multi-Lock Biopolymers Degradable in Ocean From Non-Food Biomasses

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Structure and Properties of Multi-lock Biopolymer during the Environmental Degradation

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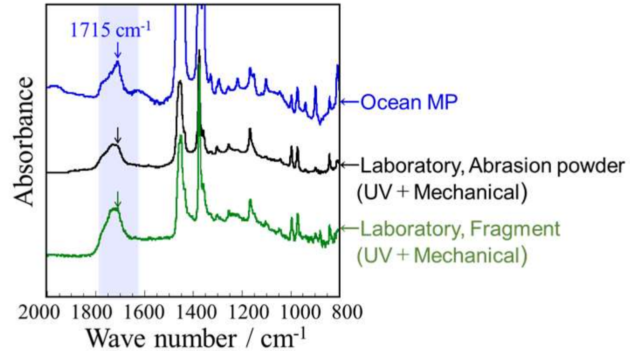
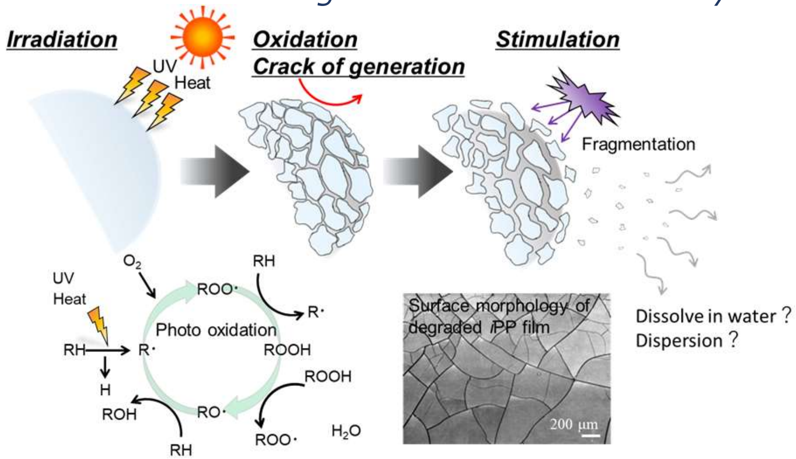
The structure and physical properties of the sample identified as *isotactic* polypropylene (*i*PP) in microplastic (MP) collected from the surface layer of the sea near Japan were characterized. It was revealed that the oxidation proceeded from the surface layer, making the sample brittle. In order to reproduce the MP formation in the environmental decomposition process in the laboratory, the *i*PP film was irradiated with ultraviolet(UV)-rays in the wavelength range of 300-400 nm using a weather meter. In the microscopic image of the *i*PP sample after the weathering test, many cracks were observed on the surface due to photooxidative degradation as the UV irradiation time increased. In addition, as the photooxidation proceeded, carbonyl groups were formed and the sample became embrittled. A mechanical stimulus was applied to this sample, and MP-sized fragment formation was confirmed. Furthermore, infrared absorption spectroscopic experiment revealed that there is a good agreement in oxidation state of ocean MP with MP reproduced in the laboratory.



Infrared spectra of ocean microplastic identified as isotactic PP and MP generated in the laboratory



Mechanism of microplastic formation process

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[Outline of Research] Evaluate physical properties and structure of conventional polymer, biopolymers and multilock biopolymers during marine environmental degradation and reveal the factors influencing degradability and stimuli responsive degradation.

Microplastic Formation Mechanism Revealed by Advanced Characterization

UV light

O_2, water temperature

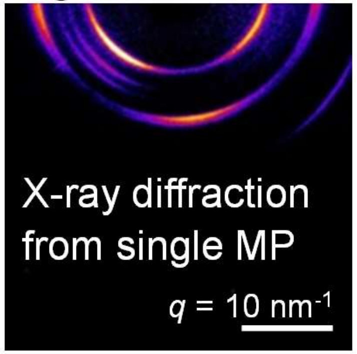
Photo-oxidation

Plastics (Polyolefin etc.)

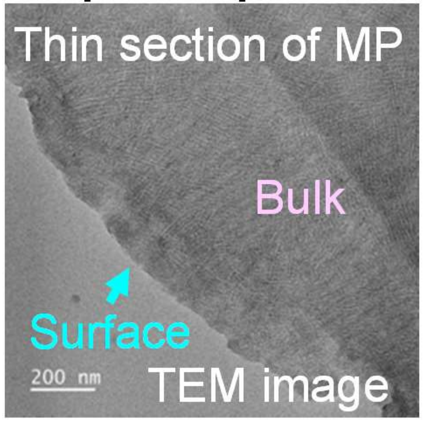
Mechanical Stimulation

Microplastics (MP) collected from sea near Japan, MP are mainly polyolefin. MP density is several pieces/m^3

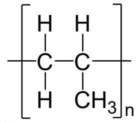
Degradation of amorphous phase in crystalline polymer



Oriented crystalline diffraction of PP

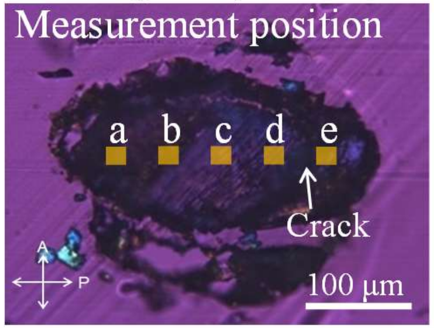


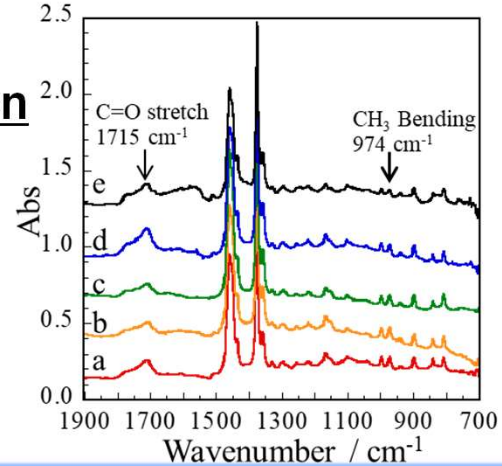
Polypropylene



High resolution transmission electron microscopic image of MP. Crystalline phase of PP is clearly observed.

Photooxidation - C=O group formation





IR spectra from section of MP. Oxidation proceeded near the surface

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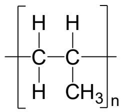
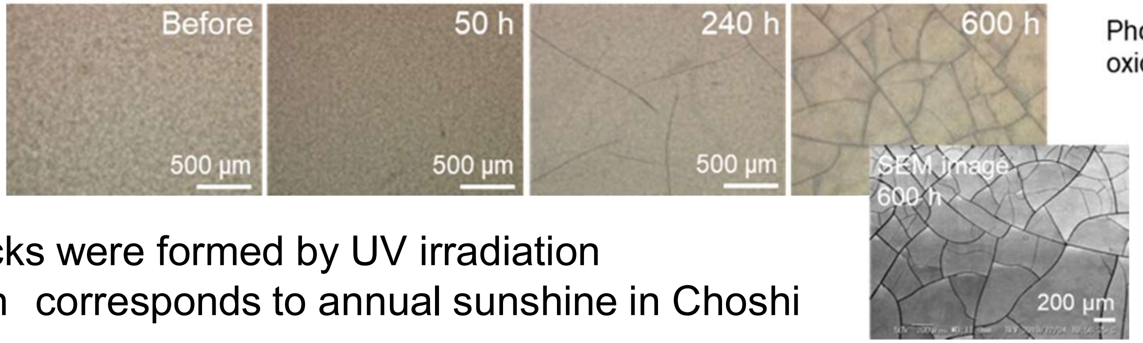
Microplastic Formation in Laboratory
－Prediction of MP formation

Surface morphology change of polypropylene by UV irradiation

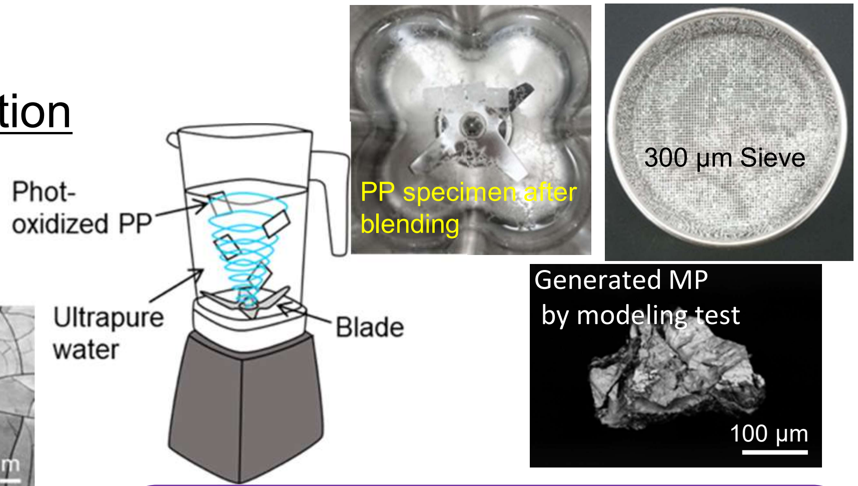
Polypropylene

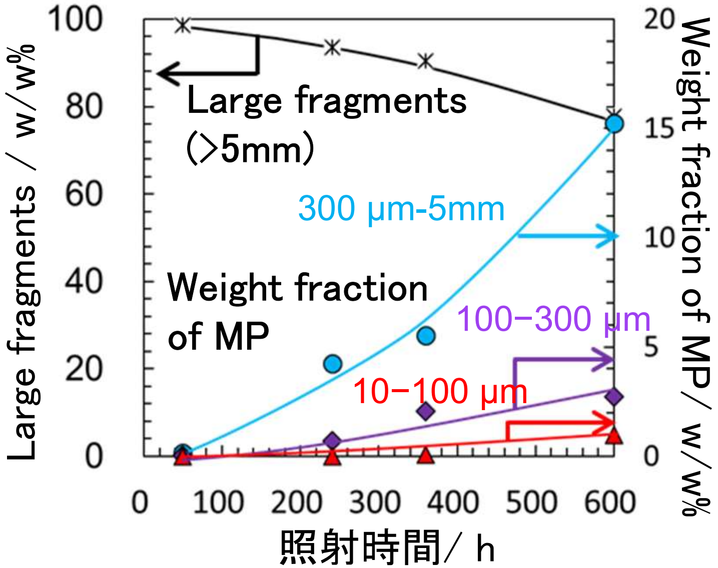




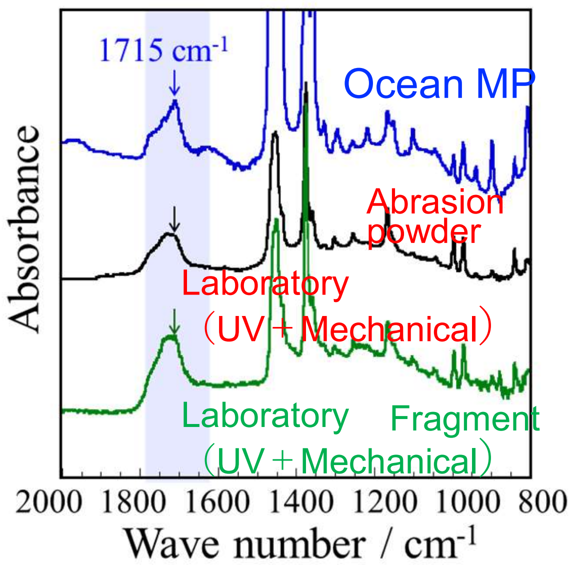
Cracks were formed by UV irradiation
600h corresponds to annual sunshine in Choshi

Fragmentation by Agitation

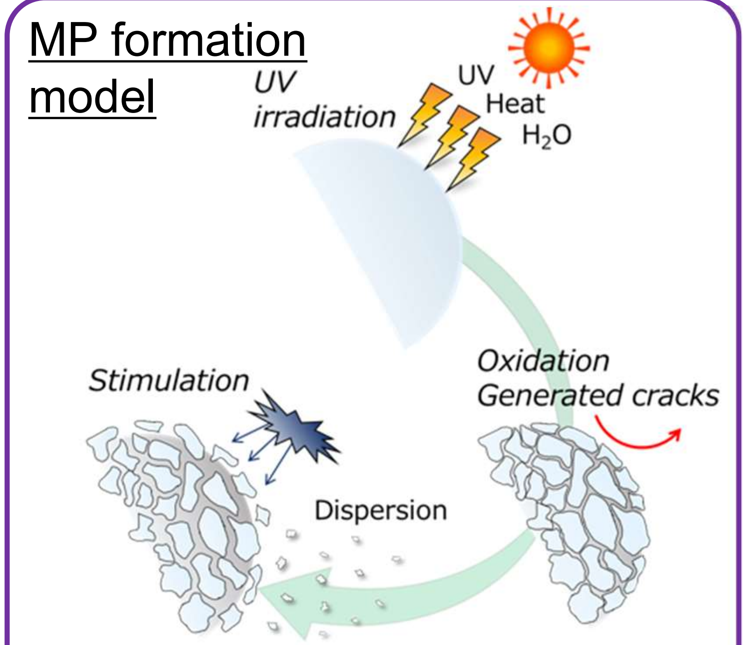




Small fragments were formed after extensive UV irradiation



MP formed in labo. showed oxidation state with ocean MP



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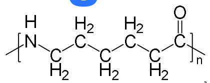
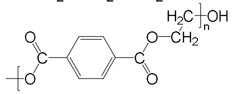
Environmental Degradation of Polymer Fibers (Fishing Line)

Nylon 6 (Ny6)



Poly(ethylene terephthalate)



Poly(vinylidene fluoride) (PVDF)

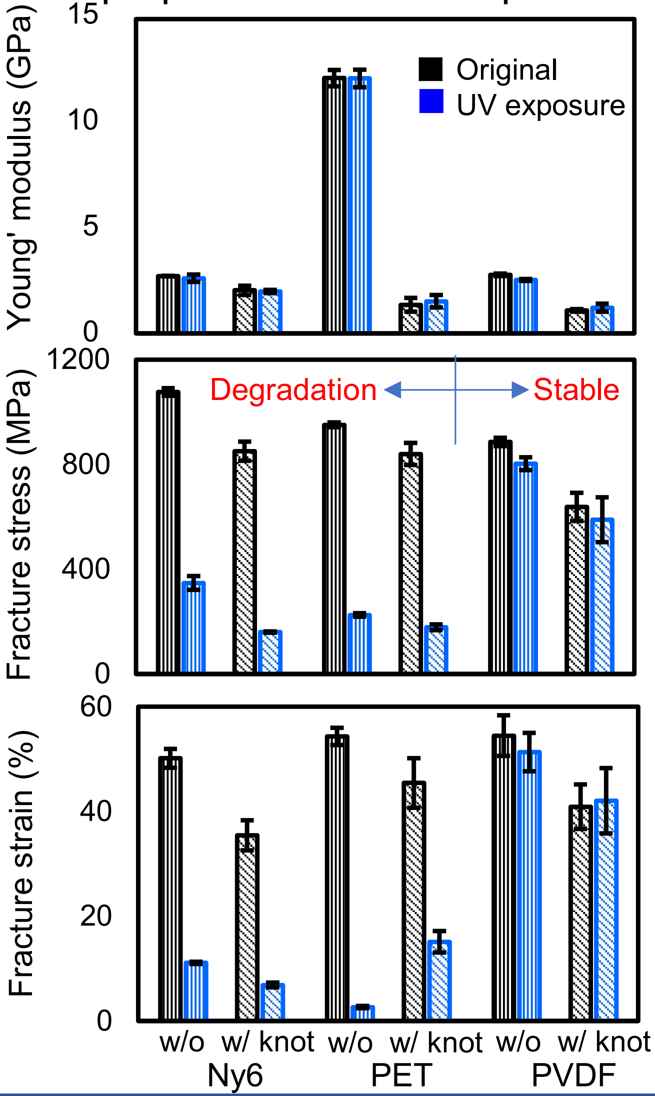
Ghost fishing is what happens when old fishing gear is lost or abandoned at sea. It gets dragged around the ocean by currents and storms, killing fish and damaging marine habitats.

https://www.wwf.or.jp/activities/basicinfo/4452.html

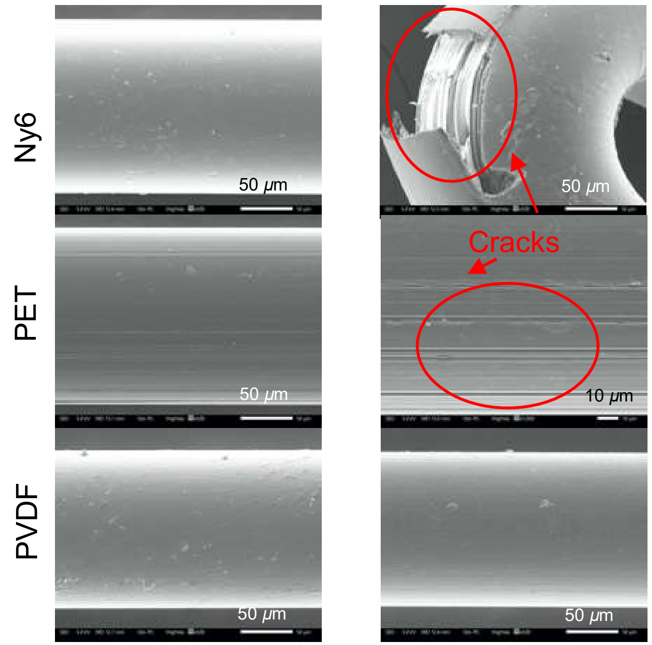
Environmental Degradation

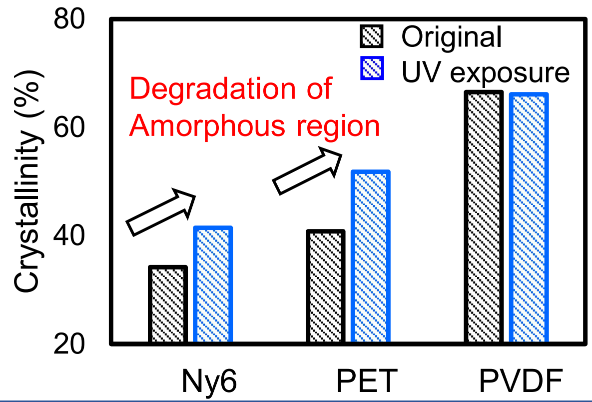
Fishing lines were UV aged by an accelerated weathering machine with total irradiance ca. 300 MJ/m^2 (300-400nm), which is equal to 1 year's irradiation in Choshi. Fibers with knot were employed to simulate the degradation of fishing nets.

Change of mechanical properties after UV exposure



Change of surface morphology





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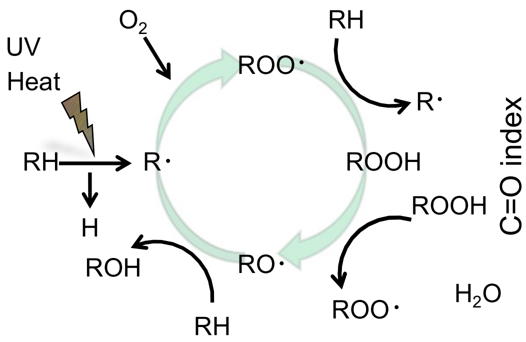
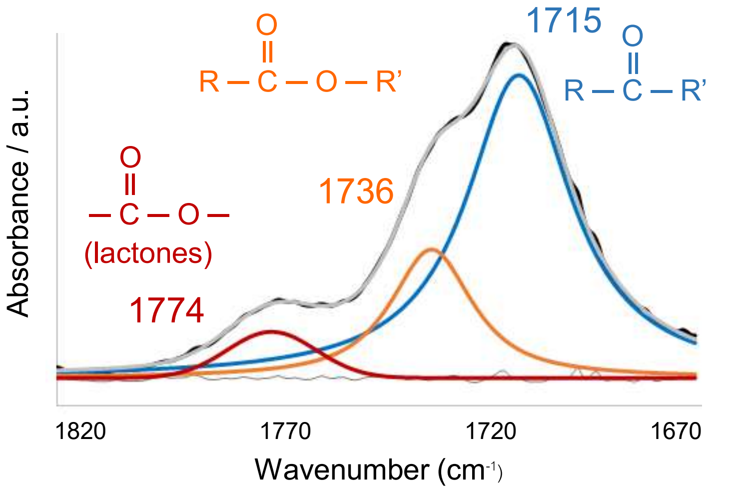
Environmental Degradation Process of Polyolefin with Oxo-degradable Additives

Oxo-degradable additives contain fatty acid salts with transition metal cation. Metal ion promotes oxidation of polyolefin.

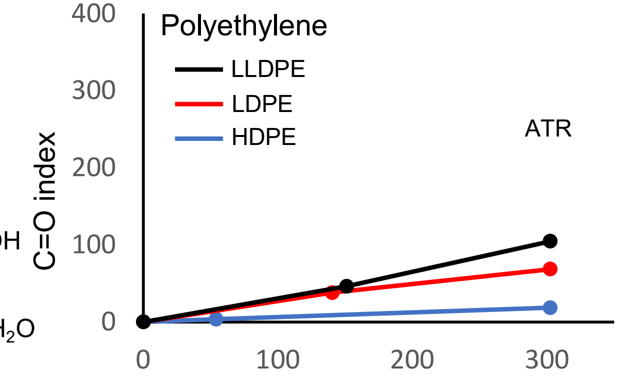


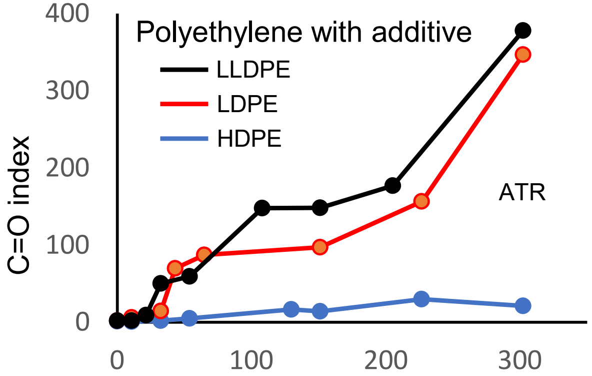
Need to confirm fragmentation and the risk of microplastics

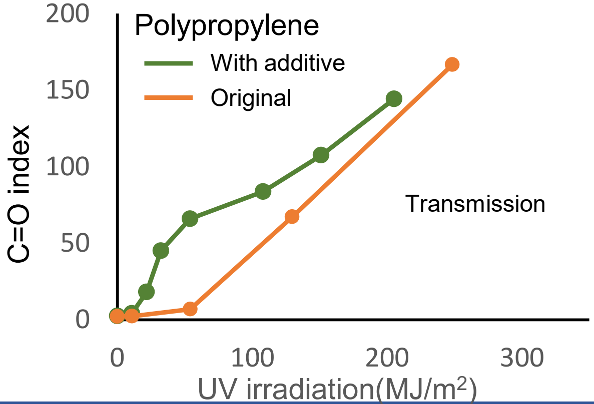
$$\text{C=O index} = \frac{\text{C=O band area (1840-1660 cm}^{-1}\text{)}}{\text{CH band area}}$$

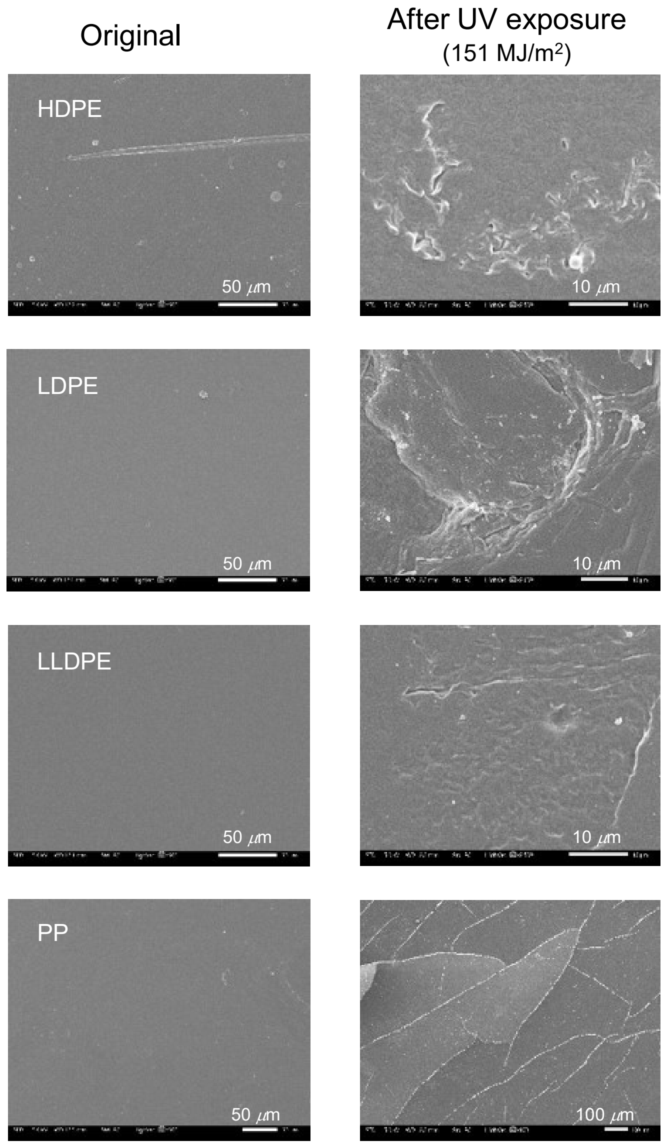


ATR-IR spectral deconvolution in the C=O region of HDPE (with oxo-degradable additive / 2-week weathering)









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Analysis of Degradation Behaviors of Bio-related Polymers in Underwater Environments and Development of Their Control Methods

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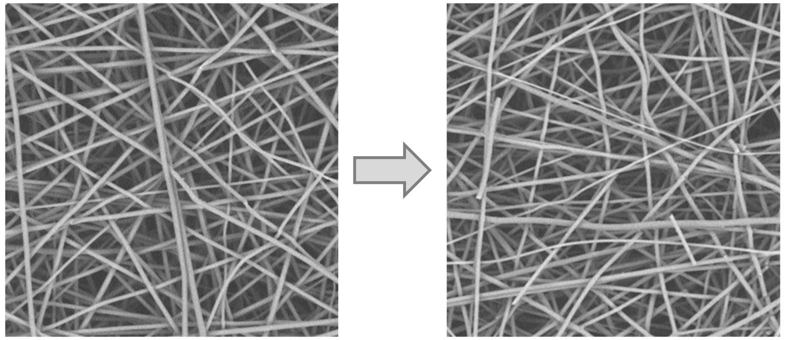
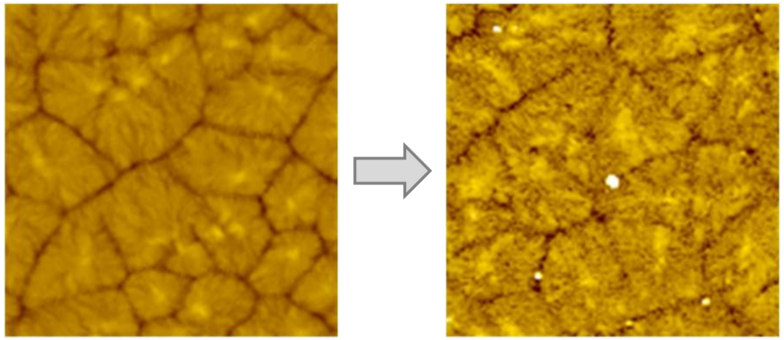
Our objective is to understand structure and physical properties of polymer materials at surface and interfacial regions associated with their degradation in underwater environments. In addition, we will lead to the development of multi rock-type biopolymers based on the establishing of the degradation control methods. Various surface materials such as melt-spun fibers, electro-spun fiber mats, and thin films are used as samples. The surface morphologies are examined by scanning force microscopy. Furthermore, thermal molecular motion and mechanical properties are investigated based on dynamic mechanical analyses and tensile tests, respectively. Local conformation at the water interface is analyzed by sum frequency generation spectroscopy. Polymer samples blended with different polymers such as hyperbranched polymers and enzymes are prepared and various factors are examined. By clarifying the relationships between each factor and degradation behaviors, we aim to create polymer materials that can arbitrarily control their degradation characteristics in underwater environments.

Degradation of Polymer Materials

Fiber mat



Thin film



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Analysis of degradation behaviors of bio-related polymers in underwater environments and development of their control methods

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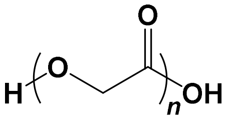
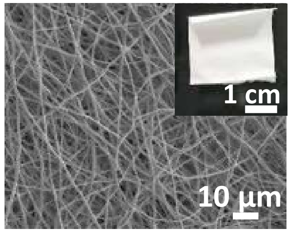
Outline：The objective of this study was to understand the aggregation states and thermal molecular motion of polymers in underwater environments and their effects on the degradation properties. As model samples, polyester-based surface materials such as nanofibers, thin films, and so on were used, and the various structural factors and physical properties affecting the hydrolysis and enzymatic degradation characteristics were revealed.

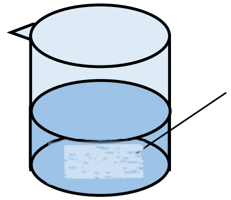
Electrospun polyglycolic acid nanofiber mats (PGA-NF)



Polyglycolic acid (PGA)



Degradation tests for PGA-NFs in phosphate buffered saline (PBS)

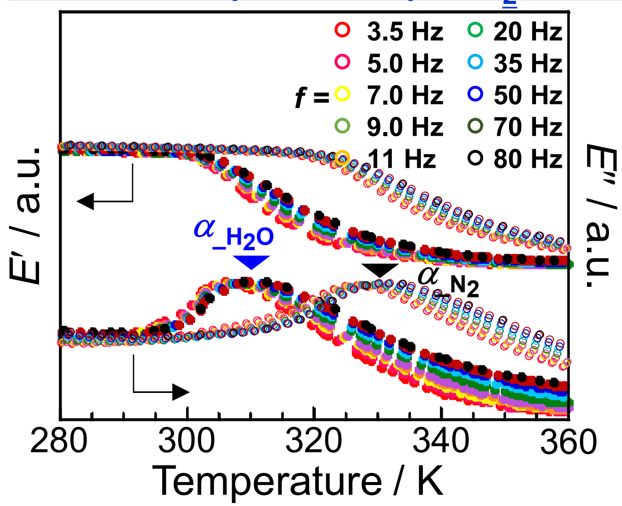


PGA-NF

$T_{g\alpha\_H_2O}$ = 297 K

Test condition：
0.1 M PBS
Temp. (310, 298, 280 K)

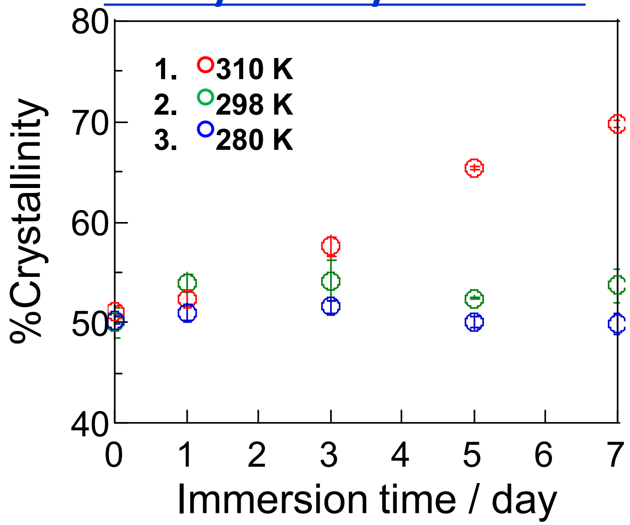
Temperature dependencies of dynamic storage and loss moduli (E' and E'') in N_2 or water



Dynamic glass transition temperature ($T_{g\alpha}$) at relaxation time (τ) = 10^2 sec based on VFT eq.

$T_{g\alpha\_H_2O}$ = 297 K, $T_{g\alpha\_N_2}$ = 317 K

Relationship between the immersion time and the crystallinity of PGA-NF



The degradation of the PGA-NF proceeded well when the test temperature was higher than $T_{g\alpha}$, however, it was suppressed as the test temperature was equal to or lower than $T_{g\alpha}$. In addition, it was found that the degradation proceeded from the amorphous region.

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Analysis of degradation behaviors of bio-related polymers in underwater environments and development of their control methods

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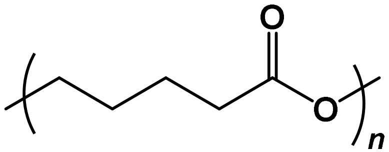
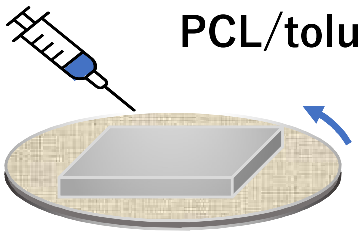
Polycaprolactone (PCL) thin film

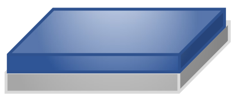


Polycaprolactone (PCL)

PCL/toluene



Spin-coating

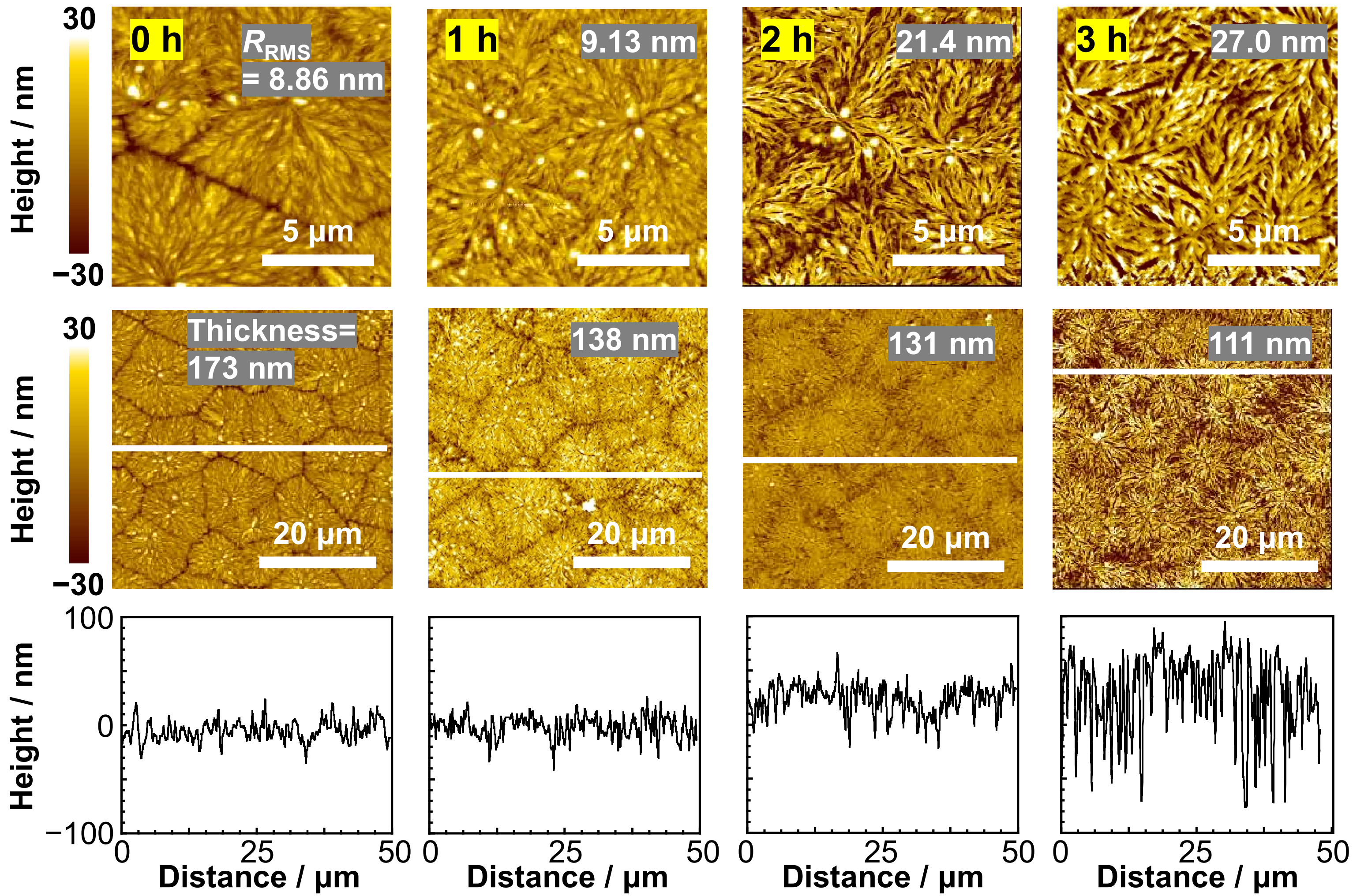


Thermal annealing

Crystalline samples

Atomic force microscopy (AFM) observation

Lipase-based degradation of the PCL films
~ Enzymatic reaction time dependence of AFM height images ~



As increasing the reaction time, the surface of the PCL thin film became rougher and its thickness was decreased. It was also found that the degradation tends to proceed from the vicinity of the grain boundaries of the crystals.

Summary of Kyushu University Group

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E2a:Structure and Properties of Multi-lock Biopolymer during the Environmental Degradation

Achievements

- Reveal the formation mechanism of microplastics.
- Establish modelling experiment of microplastic formation in the laboratory
- Reveal effect of oxo-biodegradable additive on polyolefin degradation
- Reveal effect of crystalline structure on degradation of polymer fibers (fishing lines).

Final target(2029)

- Clarify environmental degradation mechanism of multi-lock biopolymers
- Establish evaluation methods of structure and properties of degradation products.

E2b:Analysis of Degradation Behaviors of Bio-related Polymers in Underwater Environments and Development of Their Control Methods

Achievements

- Reveal effect of thermal molecular motion of polyester nanofiber mats on their degradation behaviors in underwater environments.
- Succeed *in situ* surface observation of enzyme-based polyester degradation

Final target(2029)

- Clarify and control of the degradation of multi-lock biopolymers