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

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Implementing organizations : The University of Tokyo, Mitsubishi Chemical Corporation, Bridgestone Corporation, Teijin Limited, Kureha Corporation, Kyushu University, Nagoya University, Yamagata University, Research Institute of Innovative Technology for the Earth (RITE), National Institute of Advanced Industrial Science and Technology (AIST), Ehime University, Tokyo Institute of Technology

Moonshot Program

Development of Multi-lock Biopolymers Degradable in Ocean from Non-food Biomasses

PM　Kohzo Ito（The University of Tokyo）
Deputy PM　Naoko Yoshie（The University of Tokyo）

Member
【Academias】 The University of Tokyo (UT), Kyushu University (Kyushu U), Nagoya University (NU), Yamagata University(YU), Research Institute of Innovative Technology for the Earth (RITE), National Institute of Advanced, Industrial Science and Technology (AIST), Ehime University (EU), Tokyo Institute of Technology (TIT), Kyoto Institute of Technology (KIT), Kobe University (Kobe U), Osaka City University (OCU), Shinshu University (SU), Nagaoka University of Technology (NUT), Chemical Evaluation and Research Institute, Japan (CERI)

【Industries】 Mitsubishi Chemical Corporation, Bridgestone Corporation, Teijin Limited, Kureha Corporation

Moonshot
ITO P J

Organization (2022/1)

NEDO

Materials Technology and
Nanotechnology Department
Bioeconomy Promotion Division

ITO PJ
project manager
Kohzo ITO

PROJECT OFFICE

Entrusted organizations : 12 inst.

Re-entrusted organizations: 7inst.

Company : 4 inst.
Academia : 14 inst.
(18Gr)

(honorific title)

	Entrusted organization / Reentrusted organization	Leader
2	Mitsubishi Chemical Corporation	Satoshi KATO
3	Bridgestone	Satoshi HAMATANI
4	TEIJIN	Tomoyoshi YAMAMOTO
	TEIJIN FRONTIER	Kazuhiro MORISHIMA
5	KUREHA	Takashi MASAKI
1	The University of Tokyo	PM Kohzo ITO
		Susumu OKAZAKI
		Naoko YOSHIE
		Kosuke SUZUKI
	Kyoto Institute of Technology	Sono SASAKI
	Kobe University	Harumi SATO
	Osaka City University	Eriko SATO
	SHINSHU UNIVERSITY	Yasuhiro KOHSAKA
	Nagaoka University of Technology	Daisuke KASAI
	CERI	Takako KIKUCHI
6	KYUSHU UNIVERSITY	Atsushi TAKAHARA
		Hisao MATSUNO
7	Nagoya University	Masami KAMIGAITO
8	Yamagata University	Hiroshi ITO
9	RITE	Msayuki INUI
10	AIST	Hiroshi MORITA
11	EHIME UNIVERSITY	Hirofumi HINATA
12	Tokyo Institute of Technology	Kotaro SATOH

Moonshot
伊藤ＰＪ

Common R&D Issues

Common issues		Targets	Member
E1+ E3	Multi-lock decomposion mechanism (switch function)	Develop a multi-lock degradation mechanism for model resins and elastomers that can be degraded on demand by multiple stimuli expected in the marine.	UT, NU, RITE, TIT, AIST, OCU, SU, NUT
E2	Elucidation of degradation mechanisms	Elucidate the degradation mechanisms of model resins and elastomers in natural environments, including the ocean.	Kyushu U,KIT, Kobe U, AIST, CERI
E3−1	Polymer syntheses from non-food Biomass	Monomers made from non-foode biomass will be synthesized using enzymes and organic synthesis.	NU, RITE,TIT, SU
E3−2	Improving the Durability and Toughness	Improve the durability and toughness of environmentally degradable polymers.	YU, Kyushu U, UT, NU, AIST
E4	Evaluation of environmental degradability	The dynamic analysis of plastic wastes in the ocean and the development of a fast decomposition evaluation method.	EU, CERI
E5	Marine safety of oligomers	Synthesize oligomers and evaluate their marine degradability and safety.	Kyushu U, NU, TIT, SU, CERI

Development of switch function (multi-locking)

Multiple conditions for degradation (copolymers, dynamic cross-linking, supramolecules, additives, light, water, oxygen, salt, enzymes, microorganisms...) to achieve switching functions

- **Copolymer + water and/or marine microorganisms and/or others**
  Degradation unit (Companies, NU, TIT, SU, OCU)

- **Enzymes + Marine Environment**
  Enzymes (RITE, NUT)

- **Additives + light and/or salt and/or marine microorganisms**
  Cluster catalyst (UT), Polyrotaxane (UT)

- **Dynamic bridge + water and/or marine microorganisms**
  Hydrogen bonding (UT)

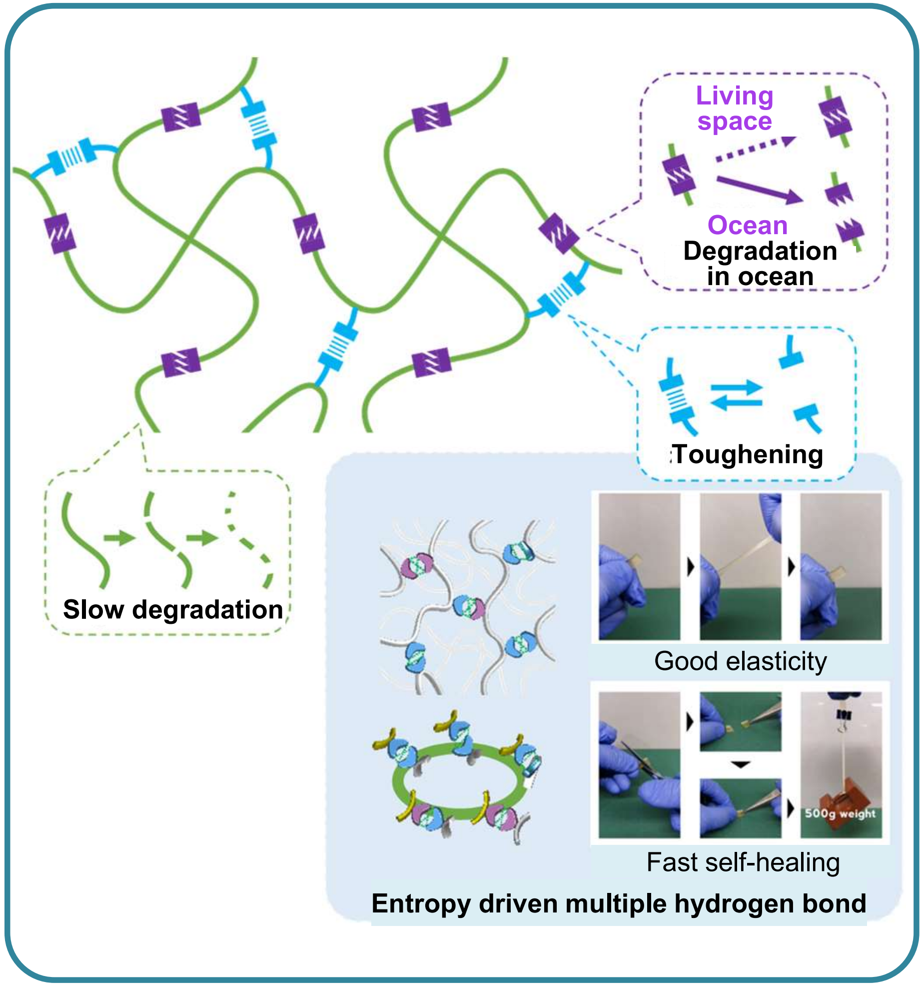
Institute of Industrial Science, The University of Tokyo
Development of multi-lock polymers with complete biodegradability and practical toughness

MS伊藤PJ

We try to realize multi-lock polymers with complete biodegradability and practical toughness by combining the following three strategy:

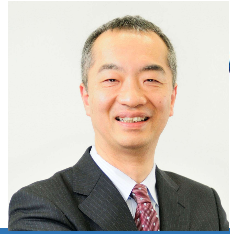
- **"Low speed degradability" for complete degradation:** Developing polymers that are stable during practical use but quickly degraded after oligomerization.
- **"Multi-lock degradation mechanism":** Introducing to polymer main chain degradable bonds that break only when receiving multi-stimuli for unlock at the same time.
- **"Toughenig" for practical use:** Introducing dynamic bonds and/or controlling higher order structure to toughen polymers.

We also develop the concept of **"Entropy driven multiple hydrogen bond"** proposed by our group to realize good elastic properties only with physical crosslinks.



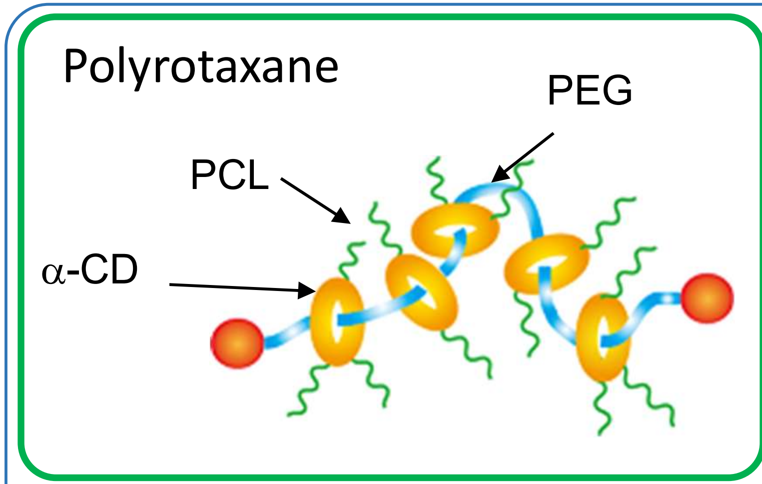
東京大学生産技術研究所
Institute of Industrial Science, The University of Tokyo

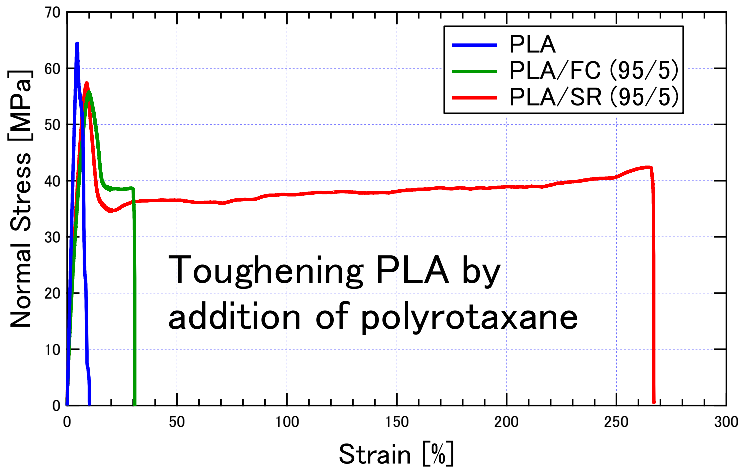
The University of Tokyo
Research and Development of Degradable Supramolecular Polymers with Both Multi-lock Mechanism and Toughness



MS伊藤PJ

In polymeric materials, there is a trade-off between toughness and degradability, and it is generally difficult to achieve both at the same time. We are trying to improve the toughness and marine biodegradability of polymeric materials by using polyrotaxane as an additive for various polymeric materials. Polyrotaxane is a necklace-shaped supramolecule, and it is known to disperse local stress by sliding of cyclic molecules, suppressing crack propagation and improving tear strength of materials. In fact, the addition of 5% polyrotaxane to poly(lactic acid) increased the elongation at break by more than 20 times. In addition, since polyrotaxane is composed of marine biodegradable molecules such as cyclodextrins and polycaprolactones, its use as an additive is expected to promote the biodegradability of polymeric materials.





Logo of the company or academia

The University of Tokyo

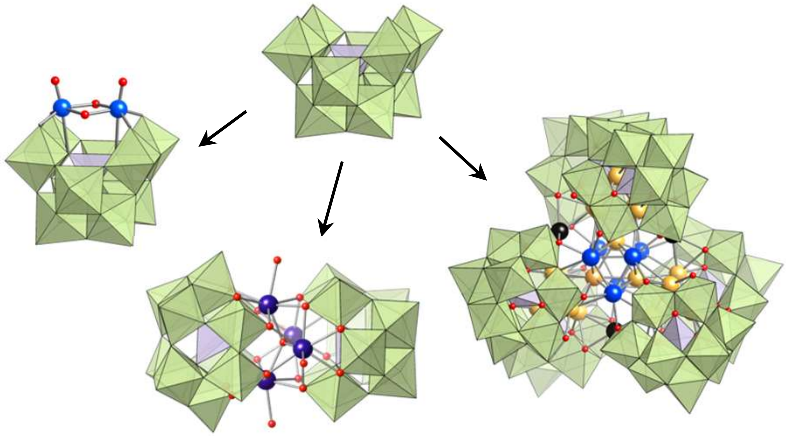
Research and Development of Multi-lock Biopolymers Using Metal Oxide Hybrid Cluster Catalysts

MOONSHOT RESEARCH & DEVELOPMENT PROGRAM NEDO

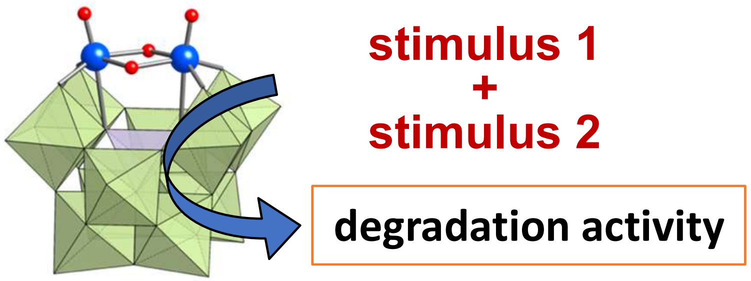
MS伊藤PJ

The purpose of this study is to develop polymers that have both multi-lock degradation mechanism and toughness in ocean. In order to realize the multi-lock degradation, it is important to introduce a new mechanism that can quickly decompose polymers when they flow out into ocean although they are stable under usage environment. By utilizing our synthesis methods of meal oxide clusters, we will develop catalysts that exhibit degradation activity when two or more of the stimuli, such as light, heat, oxygen, water, salts, enzymes, microorganisms, are present at the same time, and use these catalysts to perform on-demand degradation of polymers.

Design of metal oxide cluster catalysts



Development of multi-lock mechanism



東京大学 THE UNIVERSITY OF TOKYO

The University of Tokyo
Molecular Dynamics Simulation Study of Multi-Lock Biopolymers and Development of Data Base of Polymer Dissociation and Fracture

MOONSHOT RESEARCH & DEVELOPMENT PROGRAM NEDO

MS伊藤PJ

1. Fracture Mechanism of Crystalline Polymers

Molecular mechanism of elasticity, yielding, and fracture of biodegradable crystalline polymers is investigated based on all-atom molecular dynamics calculation. In particular, we focus on lamella structures in polycaprolactone (PCL). Change in mechanical properties of amorphous region of crystalline polylactic acid (PLA) caused by water molecules is also investigated.

2. Dissociation Mechanism of Double-Lock Polymers

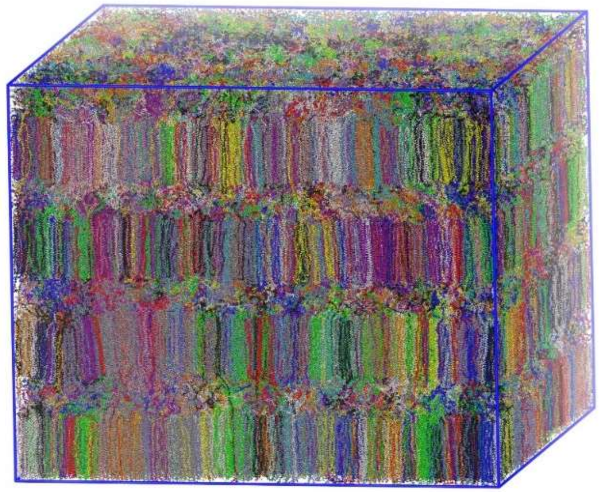
Electronic mechanism of dissociation of double-lock polymers by metal cluster catalysts is investigated based on quantum chemical calculations. Light and sea water opening the double locks on the polymer dissociation are investigated in detail.

3. Data Base

Data base archiving dissociation and fracture properties of polymers is developed. Input tool can produce tagged tree-type meta-data which enables systematic search of the data. The data base will be managed on NIMS PDF and served for machine learning studies.

Number of molecules：9,900,825
Degree of polymerization：2000
Number of chains：275
Periodicity：10 nm
Thickness of the lamella：7 nm
Thickness of amorphous phase：3 nm

富岳



A lamella structure of PCL constructed by 10 million atoms.

東京大学 THE UNIVERSITY OF TOKYO

Osaka City University　Eriko Sato

Design and Evaluation of Molecularly Dismantlable Bio-based Polymers

MS伊藤PJ

Aiming for the development of degradable bio-based polymers under marine environment, we are working on the design and development of a molecularly dismantlable unit that can be selectively cleaved by external stimuli such as heating and ultraviolet light irradiation. In particular, we are focusing on the development of a multi-lock mechanism enabling that can be accomplished by discontinuous control of the activation energy for bond cleavage in order to achieve both stability in use and quick dismantling after disposal (right figure).

In addition to synthesizing polymers having molecularly dismantling units, we are also working on precise reaction tracking in model reaction systems by tracing the reaction behavior of low molecular weight compounds containing molecularly dismantling units.

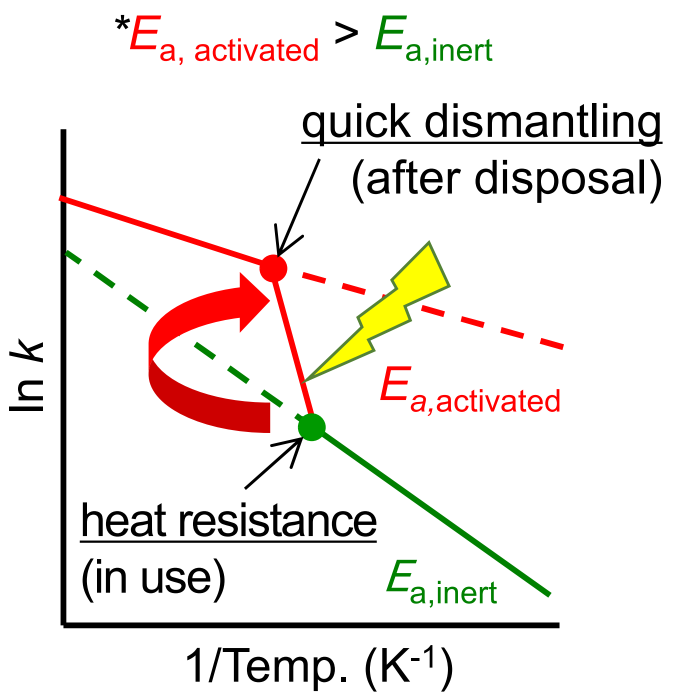


Fig. Discontinuous control of activation energy for bond dissociation by external stimuli.

大阪市立大学 OSAKA CITY UNIVERSITY

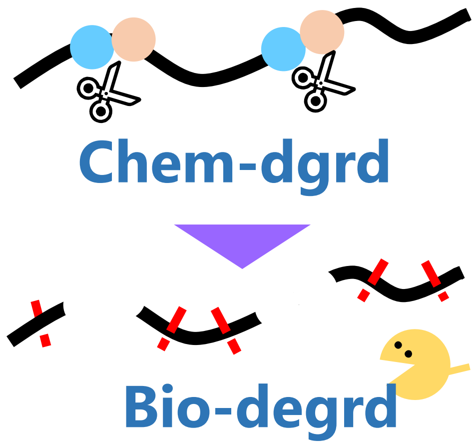
Shinshu University
Development and Practical Use of Chemically Degradable Unit for Multi-Locked Polymers prepared by Inedible Biomass

MOONSHOT RESEARCH & DEVELOPMENT PROGRAM NEDO

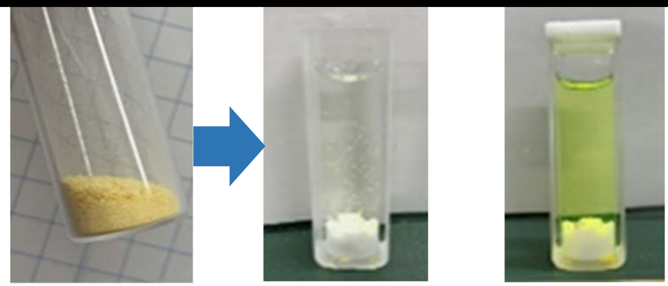
MS伊藤PJ

This research provides a mechanism of polymer degradation using natural chemicals in order to help biodegradation and to control the rate and occasion of degradation. For example, **chemical degradable units decomposed by amino acids and ammonia** have been developed and incorporated to biodegradable polymers. Furthermore, the chemical degradation have a potential to change common non-biodegradable polymers to biodegradable chemicals.

We will design and examine several candidates for chemically degradable units using the hydrolysis of active amides and the retro-aldol reaction of β-keto alcohols. Among them, ***conjugate substitution reaction*** of α-(substituted methyl)acrylates are attractive to realize both stability and degradability. We have already discovered the main chain scission by conjugate substitution reaction in water-suspension and solid-state, whereas the incorporation of the degradable units to biodegradable polyesters have been achieved. We will make more efforts to develop more effective degradable units and their application to multi-locked polymers.



Polymer degradation by aqueous ammonia



信州大学 SHINSHU UNIVERSITY

Nagaoka University of Technology
Development of poly(*cis*-1,4-isoprene)-degrading enzyme for establishment of natural rubber biodegradation technology

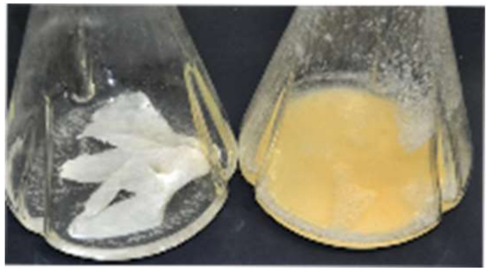
MOONSHOT RESEARCH & DEVELOPMENT PROGRAM NEDO

MS伊藤PJ

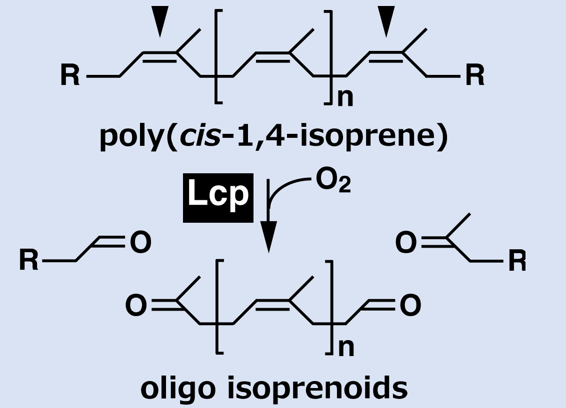
To develop an enzymatic degradation system for rubber wastes including poly(*cis*-1,4-isoprene), an efficient production system for poly(*cis*-1,4-isoprene) degrading enzymes (LCP) will be constructed.

1) Efficient production of LCP: To achieve highly efficient LCP production, the recombinant strain will be constructed by genetic modification of the LCP expression and secretory systems.

2) Activation and stabilization of LCP enzyme: To develop a high-performance LCP, modification of the optimum temperature and improvement of the stability of LCP will be performed by substitution of amino acid residues based on three-dimensional structure information of the protein.



Biodegradation of latex gloves by natural rubber degrading bacteria



Enzymatic degradation of poly(*cis*-1,4-isoprene)

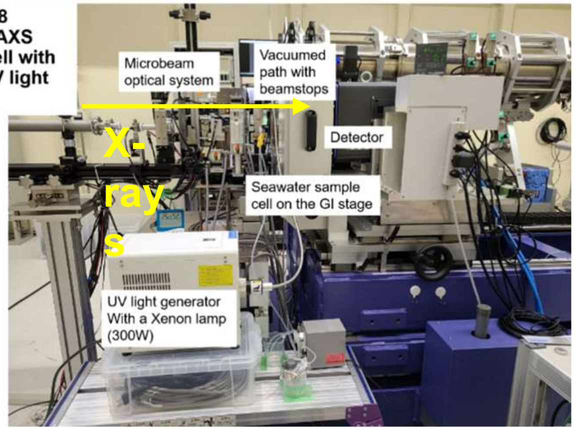
長岡技術科学大学
Nagaoka University of Technology

E2c Kyoto Institute of Technology
Precision Structure Analysis of Polymeric Materials Using Synchrotron Radiation X-rays

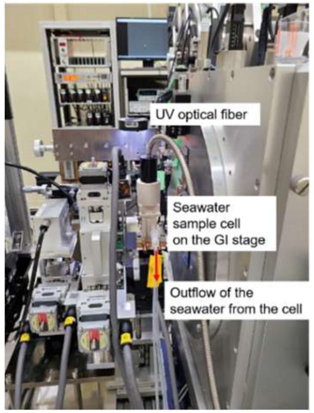
MS伊藤PJ

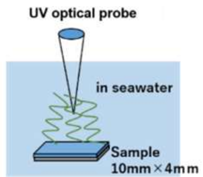
We have developed a grazing-incidence X-ray scattering (GIXS) measurement system using synchrotron microbeam X-rays in SPring-8 (RIKEN, Hyogo, Japan) which is dedicated for investigation of the surface and fine structure of polymer thin films immersed in seawater. This measurement system includes functions of media-circulation, irradiation of ultraviolet light and temperature control of the media. We are planning to conduct in-situ GIXS measurements to trace hierarchical structure change of polymer thin films with that measurement system. On the basis of the experimental results of a pretest with the GIXS measurement system, it was found that polycaprolactone (PCL) thin films were decomposed relatively fast in immersion conditions. PCL might be an appropriate sample to trace surface decomposition behavior in seawater by using the microbeam GIXS measurement system.

BL05XU/SPring-8
Microbeam GIWAXS
with a sample cell with
seawater and UV light
July, 2021



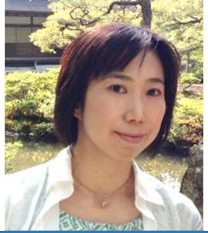
RIKEN
/SPring-8





Kobe University

Visualization of higher-order structure and intermolecular interaction of polymers by terahertz and low-frequency Raman spectroscopy

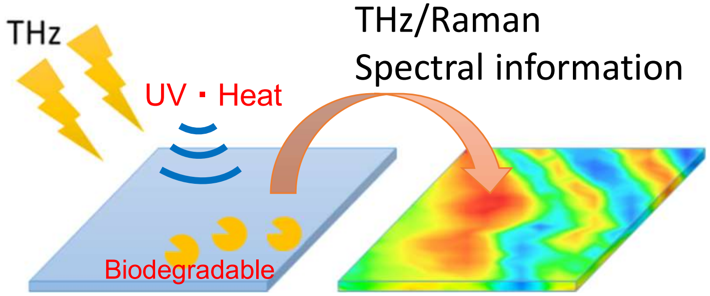


MS伊藤PJ

Terahertz (THz) and low-frequency Raman spectra contain modes of intermolecular vibrations and intermolecular hydrogen bonding in the crystal structure. In particular, Raman spectra can be measured from low to high frequency regions in the same sample at the same time, providing information on intermolecular hydrogen bonding and higher-order structure.

In this study, we will also try to understand the surface and inside information of polymer materials by 2D (THz, Raman) and 3D (Raman) imaging. Non-destructive observation of changes in intermolecular interactions during biodegradation, UV degradation, and thermal degradation of polymers will provide useful insights into the mechanisms of marine degradation of polymers.

THz/Raman
Spectral information



Polymer materials

Non-destructive
Non-contact

Intermolecular hydrogen bonding
Higher-order structure

- Crystallisation process
- Biodegradation
- UV degradation
- Thermal degradation
- etc.

↔

- Crystal structure
- Biodegradability
- Mechanical properties
- Distribution
- Depth Analysis
- etc.

valuable insights
mechanisms of marine degradation of polymers

Chemical Evaluation and Research Institute, Japan
Development of evaluation of Multi-Lock Biopolymers biodegradability

MOONSHOT RESEARCH & DEVELOPMENT PROGRAM NEDO

MS伊藤PJ

The evaluation method of biodegradability in seawater as ISO has some issues such as poor reproducibility, length of test period. The number and activity of microorganisms in seawater vary depending on the season and sea area. We have developed accelerated evaluation method of biodegradability in seawater utilizing extracted microorganisms from marine sediments, furthermore the addition of nutrients accelerated the process.

Experimental condition was followed ISO 23977-1. As the inoculum, raw seawater "Control", seawater including extracted microorganisms "Extracted" and added nutrients(0.1 g/L KH_2PO_4, 0.05 g/L NH_4Cl) to "Extracted" at the start "Extracted+N,P", collected from Isshiki coast, Kanagawa Prefecture at Aug. 2021.

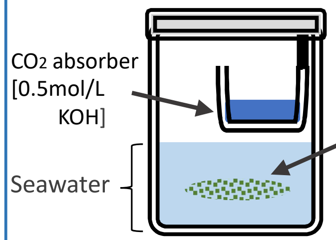


Fig.1 Test apparatus (followed ISO 23977-1)

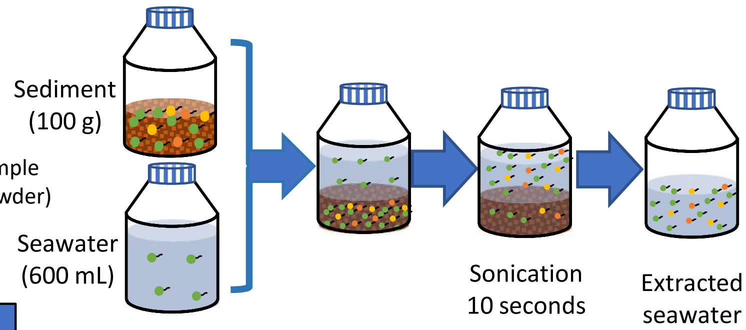


Fig.2 Preparation of extracted seawater

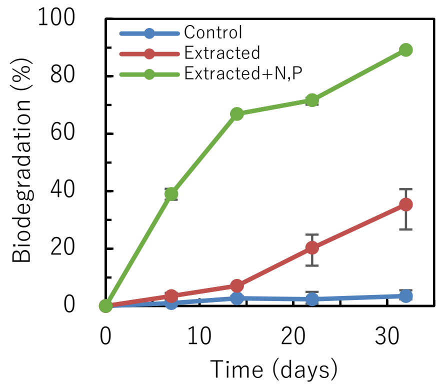


Fig.3 Biodegradation of reference material, Cellulose

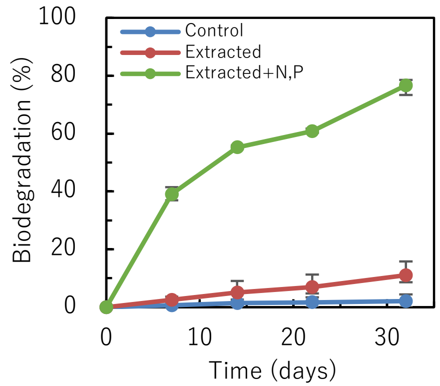


Fig.4 Biodegradation of Polycaprolactone(PCL)

CERI 一般財団法人 化学物質評価研究機構
Chemicals Evaluation and Research Institute, Japan

Results Topics

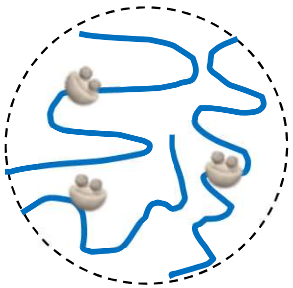
Research and Development of Multi-lock Biopolymers Using Metal Oxide Hybrid Cluster Catalysts

MOONSHOT RESEARCH & DEVELOPMENT PROGRAM NEDO

MS伊藤PJ

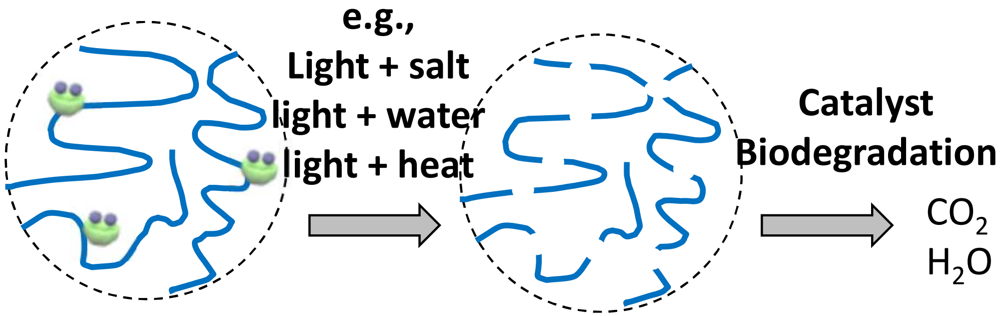
Suzuki (U. Tokyo)

Usage environment

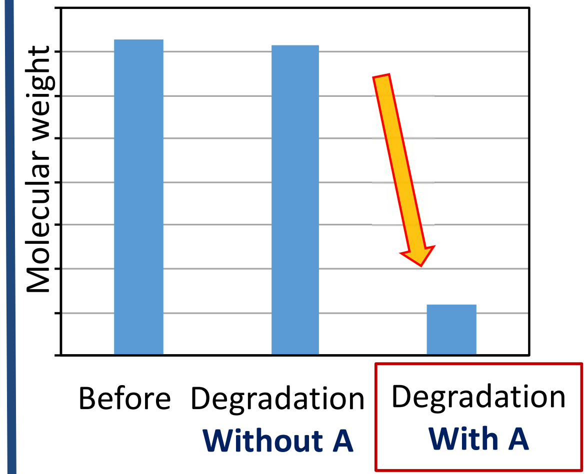


Degradation, **No**

Introduction of multi-lock degradable mechanism:
Decomposition progresses under multiple stimuli assuming ocean

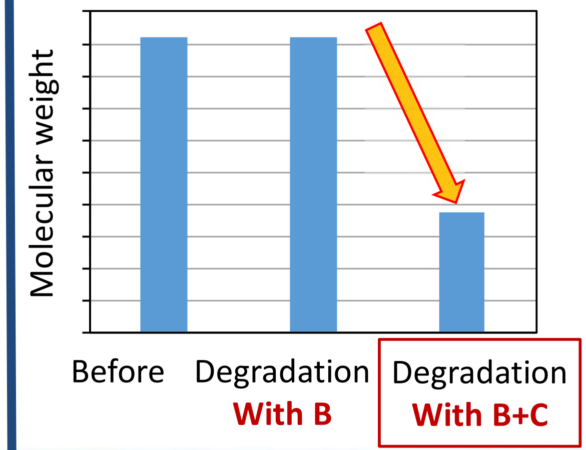


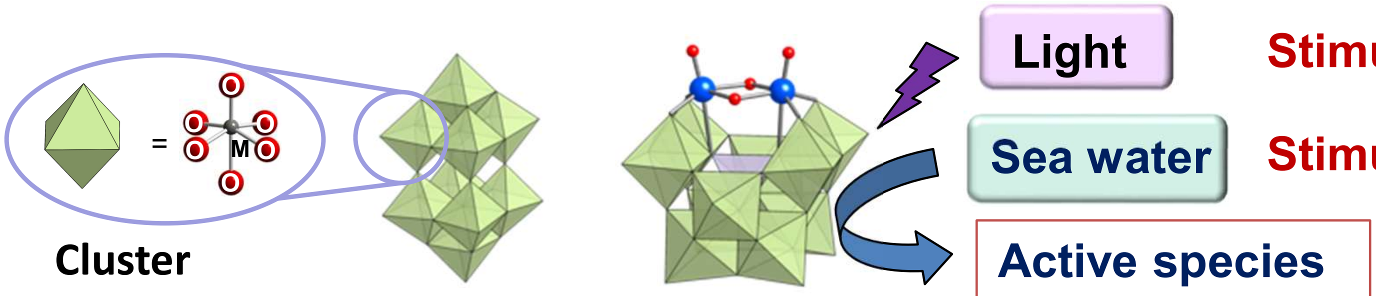
Degradation activity, **Yes**



Decomposition in both catalyst B and additive C for the marine environment. → **Switch function**

Degradation of PTHF





Stimuli 1

Stimuli 2

Cluster Catalyst **Catalyst A** **Catalyst B**

Assumed reaction mechanism

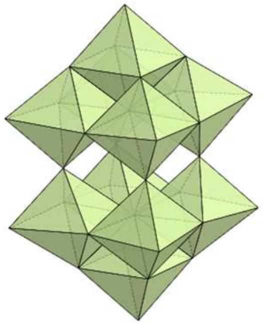
MOONSHOT RESEARCH & DEVELOPMENT PROGRAM NEDO

MS伊藤PJ

Okazaki (U. Tokyo)

Elucidate the degradation mechanism using quantum chemical calculations

Light



TBAW10

1. Stable electronically excited state

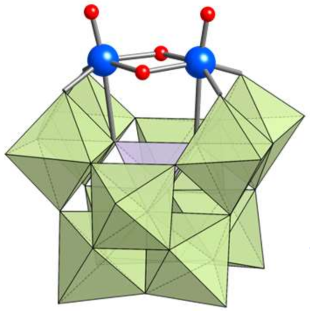
TBAW10 → TBAW10* ⤻ H-TBAW10

light $h\nu$

RH → R•

2. Hydrogen extraction reaction

Light+Sea water



TBAPV2W10

Explain the switch function theoretically

1. Stable electronically excited state

2. No reaction

RH → R• (crossed out)

light $h\nu$

PV2W10 → PV2W10* ⤻ H-PV2W10 (crossed out)

PV2W10* ⤻ $PV2W10^{-}$

Sea water

Cl^{-} → Cl• ⤻ HCl

3. Cl radical

RH → R•

4. Hydrogen extraction reaction

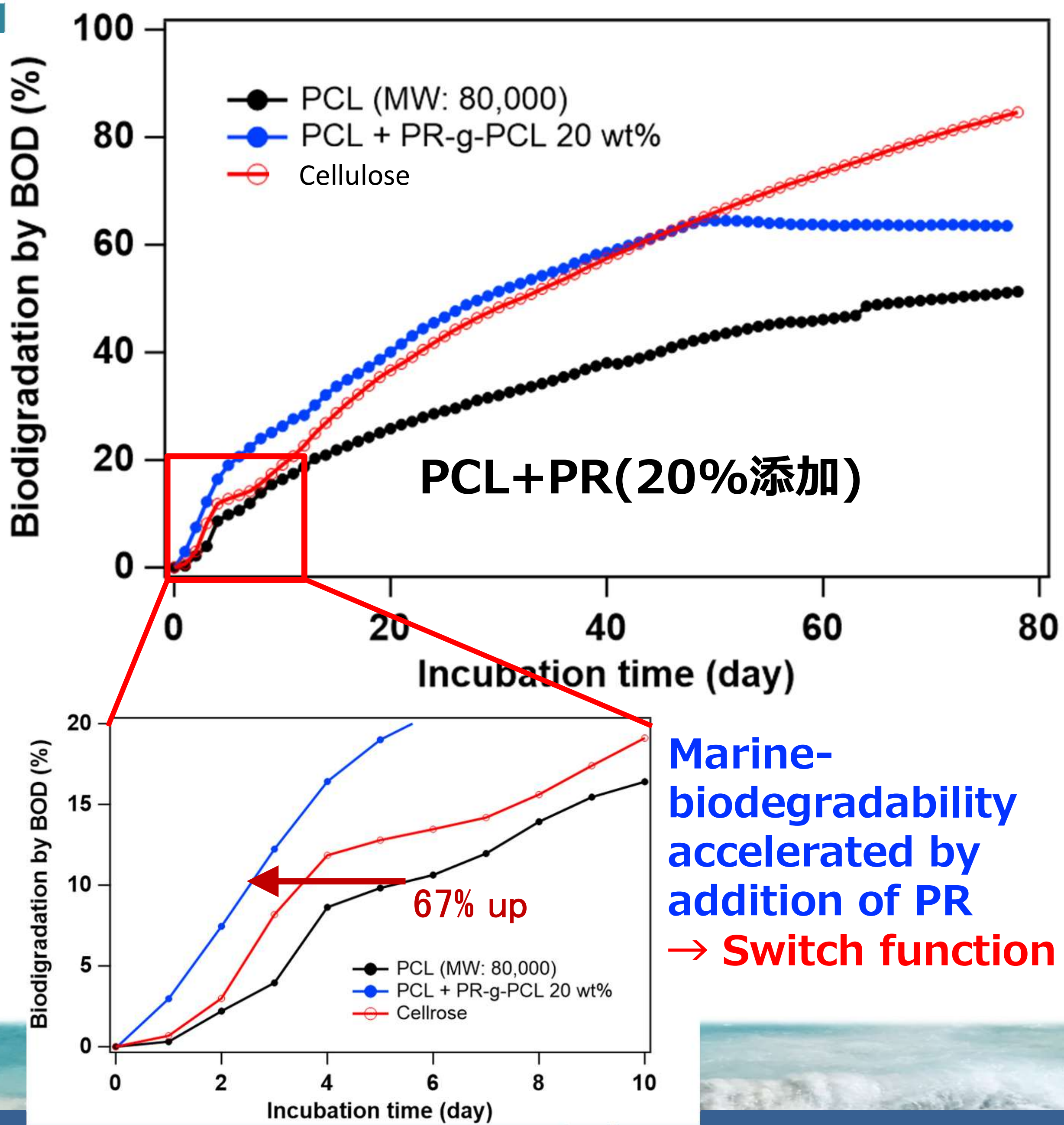
K^{+}, Na^{+}, Mg^{2+}, Ca^{2+}, Sr^{2+}

F^{-}, Cl^{-}, Br^{-}, BO_3^{3-}, SO_4^{2-}

Marine Biodegradability of PCL with Polyrotaxane

Ito (U. Tokyo)

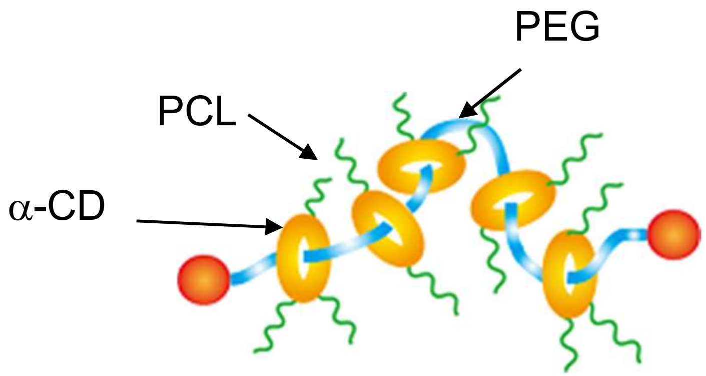
MS伊藤PJ



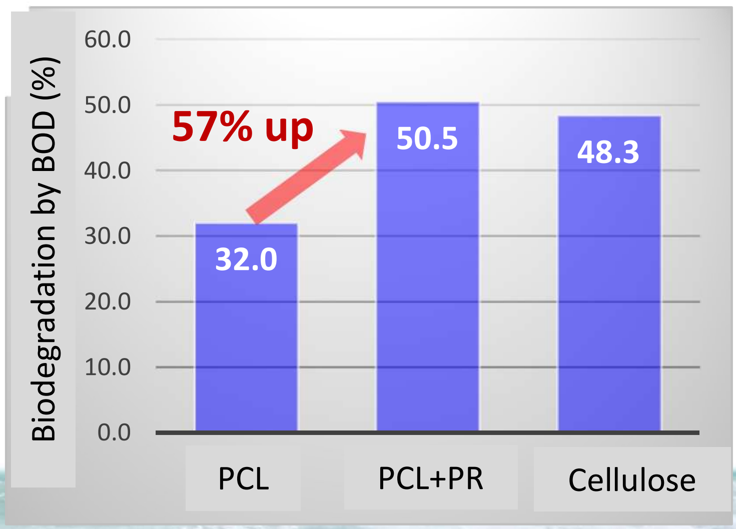
Marine-biodegradability accelerated by addition of PR

→ Switch function

Polyrotaxane consisting of marine biodegradable molecules

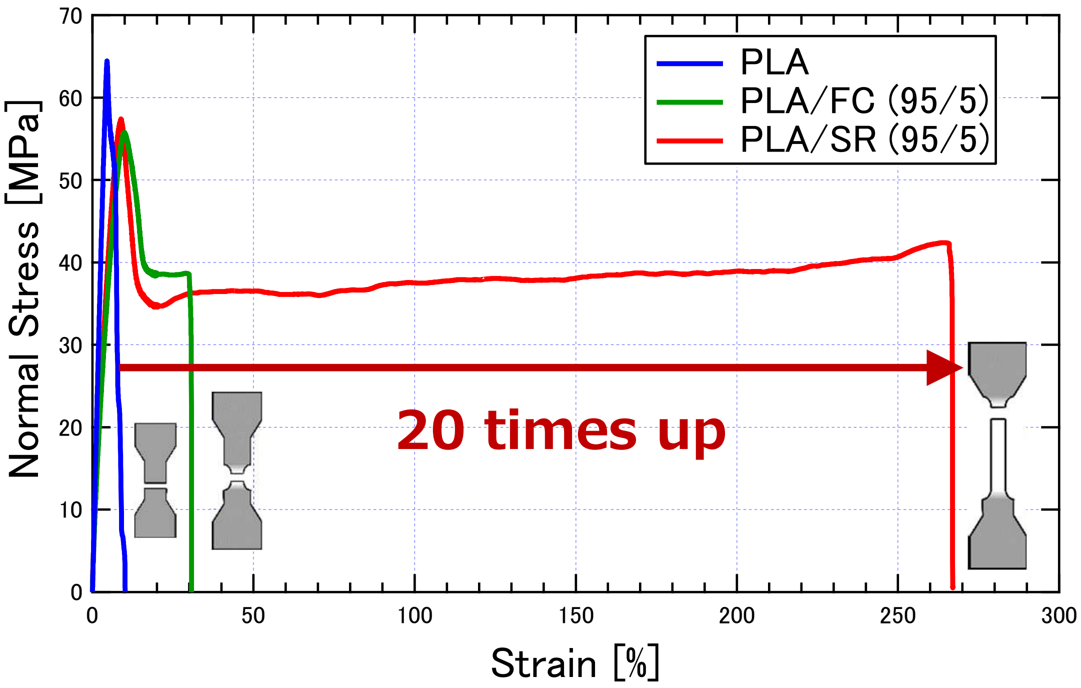


After 30 days



Mechanical Properties of PLA (Uniaxial Elongation Test)

MS伊藤PJ



	Young modulus	Elongation at break	Yield stress
PLA	3.7 GPa	15 %	64 MPa
PLA/FC (95/5)	3.0 GPa	30 %	55 MPa
PLA/SR (95/5)	3.1 GPa	287 %	57 MPa

Ito (U. Tokyo)

PLA

Elongation at break: 15% (Brittle)

PLA/FC (95/5) Graft copolymer 5%

Elongation at break: 30% (A little ductile)

PLA/SR (95/5) Polyrotaxane 5%

Elongation at break: 287% (Ductile)

Addition of a small amount of 5% polyrotaxane increases the elongation at break by ca. 30 times for PLA without significantly reducing Young's modulus.

↓

Aim to realize the toughness and switch function in the marine biodegradability at the same time by addition of PR.

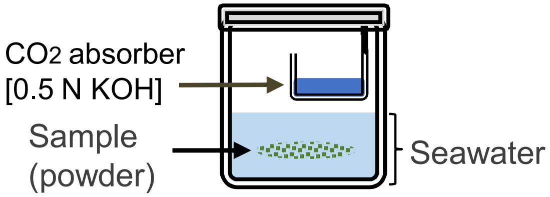
Chemical Evaluation and Research Institute, Japan

Development of evaluation of Multi-Lock Biopolymers biodegradability

MS伊藤PJ

Accelerated evaluation of biodegradability in seawater

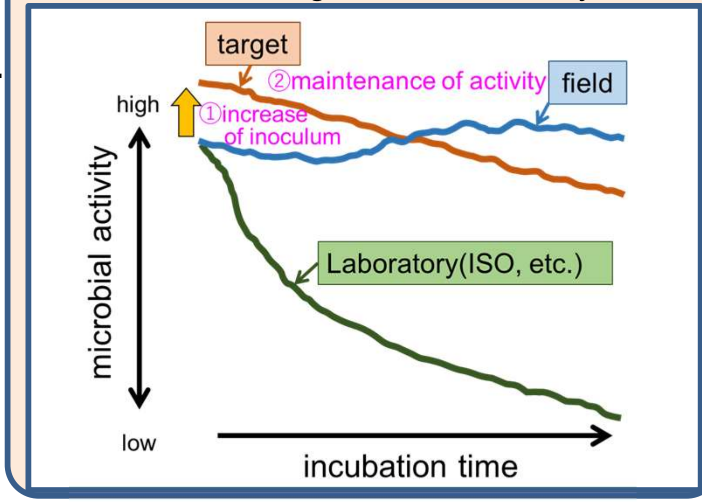
The evaluation of biodegradability in marine has some issues such as reproducibility and variability of the test, and long test period (6-24months).



Test apparatus
[ISO 23977-1]

Accelerated evaluation of biodegradability by activated inoculum

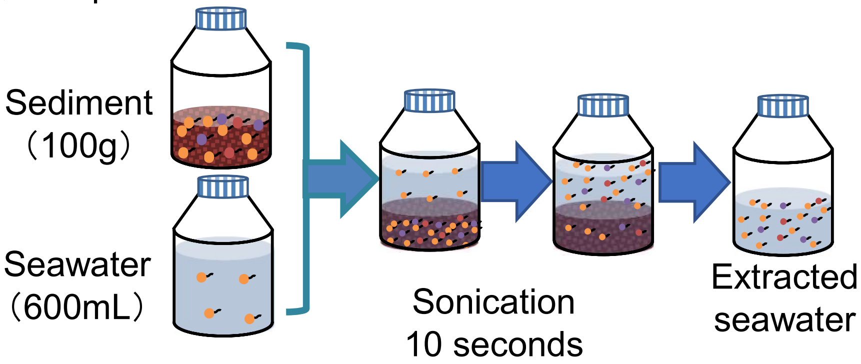
Diagram based on a model of enhancing microbial activity



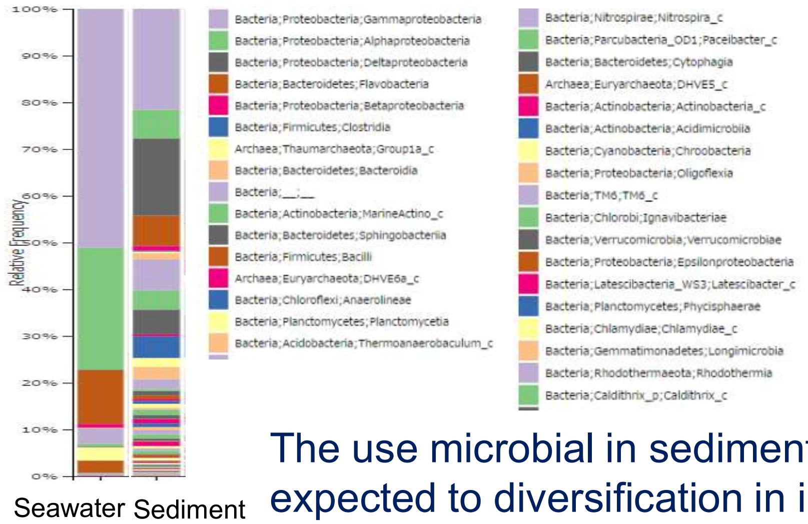
Experiment

(1) Activation of initial inoculum by utilized microbial in sediment

1） Preparation extracted seawater



2） Microbial community composition of seawater and sediment



The use microbial in sediment is expected to diversification in inoculum

(2) Preservation of microbial activity by addition nutrients

・Add KH_2PO_4 [0.1 g/L], NH_4Cl [0.05 g/L] as nutrients

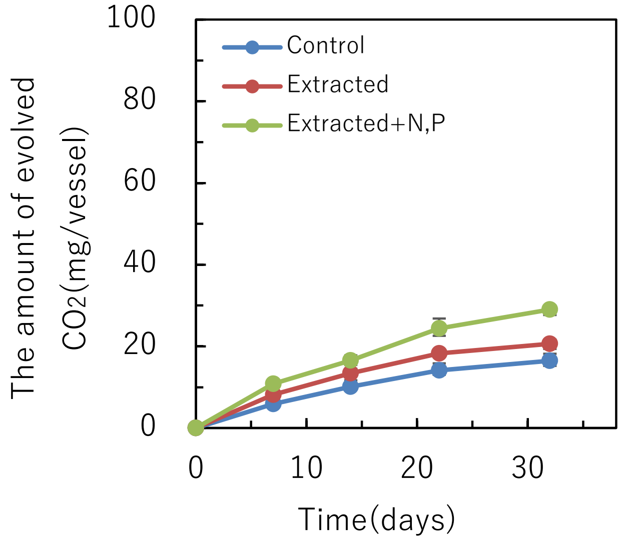
Results and future work

Source of inoculum : Issiki coast, Kanagawa (2021/8)

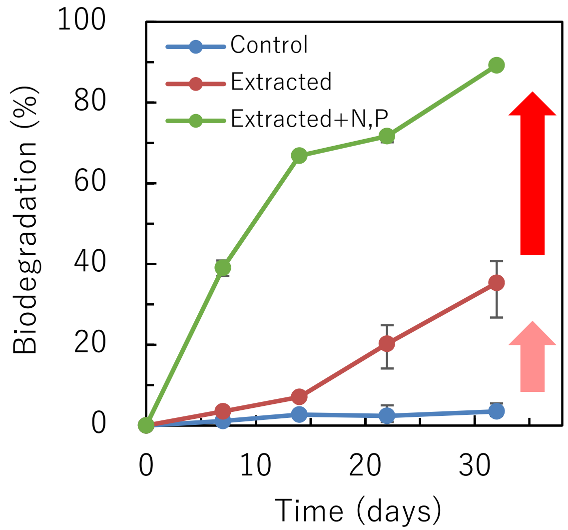
Inoculum : Raw seawater (Control)
Extracted seawater (Extracted)
Extracted seawater add nutrients (KH_2PO_4 [0.1 g/L], NH_4Cl [0.05 g/L], add before incubation)

	Total organic carbon	Total-N	Total-P
Seawater	2.0 mg/L	2.6 mg/L	0.1 mg/L
Sediment	1.3 mg/g	0.4 mg/g	0.2 mg/g

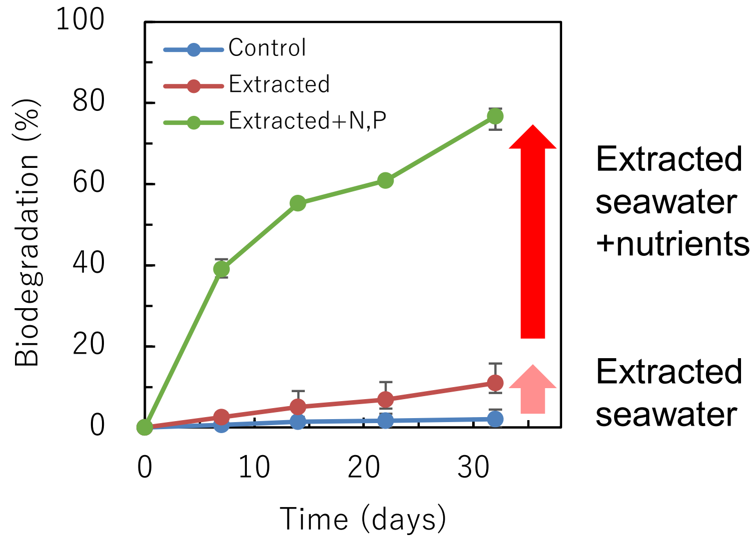
The amount of evolved CO_2 from blank vessels



Reference material, Cellulose



PCL (Polycaprolactone)



✓The biodegradation activity was improved by the seawater with microorganisms extracted from sediment and the addition of nutrients.

Accelerate BOD test and suppress the seawater dependence.

Future works

✓Evaluation of ecotoxicological effects of potential intermediates of biodegradation process.

✓Comparative evaluation of the biodegradation process between accelerated biodegradability tests in the laboratory and field tests.

MOONSHOT
RESEARCH & DEVELOPMENT PROGRAM