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

**Presenter：Kohzo Ito（The University of Tokyo）**

**PM：Kohzo Ito**

**Professor, Graduate chool of Frontier Sciences, The University of Tokyo**

**PJ Teams：The University of Tokyo、Mitsubishi Chemical Co.、Bridgestone Co.
Kureha Co.、Kyushu University, Nagoya University,
Yamagata University,
Research Institute of Innovative Technology for the Earth,
Agency for Industrial Science and Technology, Ehime University,
Tokyo Institute for Technology**

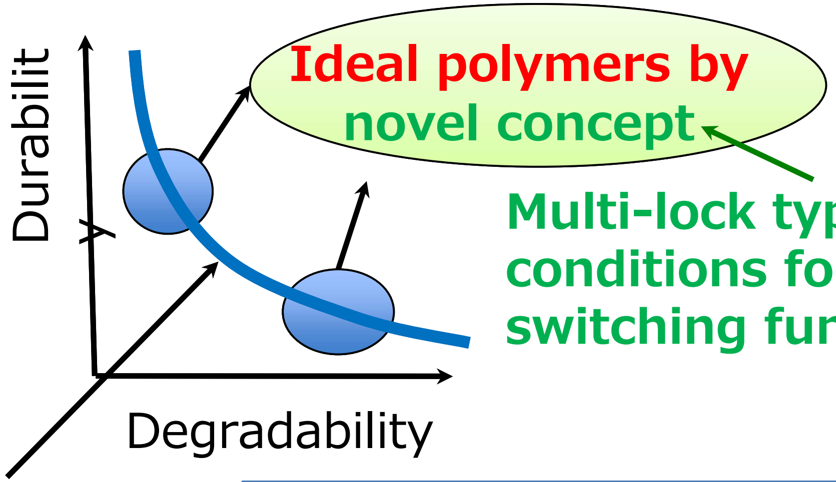
# Compatibility between degradability and durability

**Uncollected plastics, tire wear powder, textile waste, and fishing gear are serious problems for global environment.**

**Problems**

**Difficult of compatibility between degradability and durability**

**The mechanism of environmental degradation has not yet been fully understood.**




**Multi-lock type : Requiring multiple conditions for degradation achieves switching function.**

**Clean & Cool Earth**

**Multi-lock biopolymers realizing compatibility between degradability and toughness are durable when used, and when thrown away, finally break to water and $CO_2$.**

**Non-food biomass-based polymers!**

We need academic experts of biosynthesis and polymerization, biodegradation and polymer process, structural analysis and mechanical properties, simulation, marine engineering and biodegradability evaluation. And companies challenging to create innovative polymers should be involved to achieve the target.

# R&D Organization（Matrix Management）

| | A: Plastic<br>Mitsubishi Chemical<br>TL: Atsushi Kusuno | B: Tire<br>Bridgestone<br>TL: Satoshi Hamatani | C: Textile<br>Teijin<br>TL: Tomoyoshi Yamamoto | D: Fishing Gear<br>Kureha<br>TL: Takashi Masaki | E: Common Issues<br>TL: Kohzo Ito |
|---|---|---|---|---|---|
| **E1: Multi-lock Degradation**<br>Univ Tokyo | ● | ● | ● | ● | ● |
| **E2: Structure and property Analysis**<br>Kyushu Univ., Kyoto Inst Tech, Kobe Univ | ● | ● | ● | ● | ● |
| **E3: Synthesis and Process**<br>Nagoya Univ, Yamagata Univ, RITE、Tokyo Tech, Osaka City Univ, Shinshu Univ, Nagaoka Univ Tech | ● | ● | ● | ● | ● |
| **E4: Marine Degradation**<br>AIST, Ehime Univ, CERI | ● | ● | ● | ● | ● |

Spinout

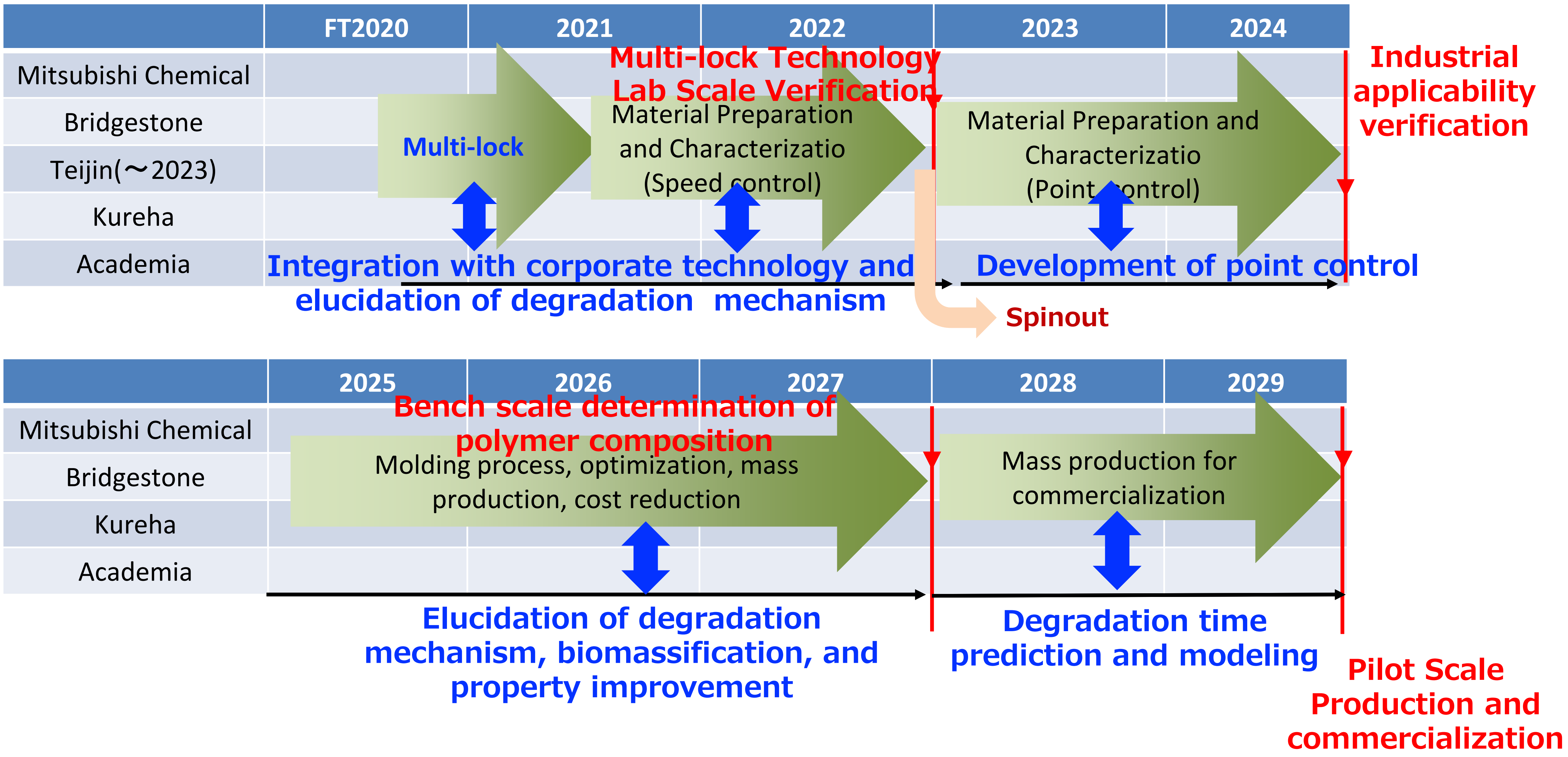
- **A～D are competitive while E is corporation one.**
- **One company conducts joint research with many academia at the same time (synergistic effects)**
- **Flexible combination of companies and academia depending on the development stage.**

# Progress of Each Team

| Organization<br>Subject | Mitsubishi Chemical<br>Plastic | Bridgestone<br>Tire Wear Powder | kureha<br>Fishing Gear | Academia<br>Multi-lock |
|---|---|---|---|---|
| Technology Issues | R&D of marine degradable multi-loc biopolymers from inedible biomass | Development of a tire that combines toughness and degradability from inedible biomass | Development of fishing gear using biopolymers based on polyamide 4 and polyglycolic acid, which are biodegradable resins | Development of a multi-locking mechanism that is both durable and degradable |
| Target 2029 | Demonstrate at the bench or larger scale prototype level that an aliphatic polyester produced from inedible resources has a 40% degree of degradation at 30 days in a BOD test (25℃) and 10 times greater toughness than existing biopolymers. | Develop a multi-loc bio-tough polymer with polymers made from inedible biomass and produce tires with tread application at the pilot level. Confirm that the wear resistance and degradation rate balance in the lab degradation test are improved by more than 10 times. | Achieve both of physical properties and marine biodegradation by introducing a multi-lock degradation mechanism. And we will confirm the cost level of commercial production on a pilot scale, including biomass conversion technology and the various properties required for practical use. | More than 10-fold difference in degradation speed before and after unlocking multilock, more than 10-fold durability of the current product, more than 10-fold improvement in activity of degradation enzymes, and more than 10-fold faster degradation speed in actual sea conditions |
| Outcome TOPICS | In the PBS system, we confirmed that the kneading of the additive greatly accelerated the degradability and succeeded in achieving speed control. Field tests were conducted to evaluate biodegradability in actual seas. The addition of polyrotaxane improved the elongation at break by 2.3 times and marine biodegradability by 3 to 5 times at the same time. | Achieved more than 10-fold improvement in biodegradability through copolymerization of butadiene and introduction of degradation units. Developed a reversible bonding-introduced rubber that degrades in the marine environment. Succeeded in achieving both a 2-fold increase in fracture strength and a 10-fold increase in degradation speed. | Succeeded in developing a fishing line that has the same degree of nodal elongation as non-marine biodegradable fishing line and exhibits marine biodegradability. Degradation of fishing line accelerates when it sinks to the seafloor after abandonment. The degradability of the fishing line was actually confirmed in a field test in an actual oceanic area. | Large-scale field tests were conducted in actual sea areas. We succeeded in improving both toughness and degradability by using polyrotaxane and pseudo-polyrotaxane nanosheets. We discovered thermostable esterases capable of degrading various polyesters. |

Moonshot
伊藤ＰＪ

# Roadmap（Average Image）



# PM Management System

Management Support Team

Advisors
IP Steering Committee

PM

R&D Management Officer: 1
Assistant: 1

■ **Plenary Meeting (PM, Teams, AD)** once a year
Information sharing about the project

■ **Group Meeting (Academia)** twice a year
Discussing common issues
Companies participate as observers

■ **Advisor Meeting (PM, AD)** once a yea
Evaluation of all teams (reflected in budget)

■ **IP Steering Committee**
**(Related teams, experts)** at any time
Discuss IP strategies and operations

■ **Invention Briefing** at any time
Make use of Academia Inventions

■ **Public Symposium**

■ **Team progress meeting**
**(PM, TL, Team member)** Every 2 to 3 months
(including site-visit)

■ **Team Meeting (Related teams)** at any time
Discuss specific and common issues for corporate teams

■ **Young Researcher's Meeting** at any time

■ **Monthly report for companies, Quarterly report for academia**

■ **PM Monthly report**

# Cundamenatal Common Isues

| Common Issues | | Goals | Members |
|---|---|---|---|
| E1+ E3 | Multi-lock degradation mechanism (switch function) | Develop a multi-locked degradation mechanism for model resins and elastomers, utilizing copolymers, dynamic cross-linking, catalysts, and enzymes, which can be degraded on demand by multiple stimuli expected in the marine environment. | Univ Tokyo, Nagoya Univ, RITE, TIT, AIST, OMU, Shunshu Univ, Nagaoka Univ Tech |
| E2 | Elucidation of environmental degradation mechanisms, including marine | Elucidate the degradation mechanisms of model resins and elastomers in natural environments, including the ocean. | Kyushu Univ, Kyoto Inst Tech, Kobe Univ, AIST, CERI |
| E3–1 | Development of polymers from inedible biomass | Monomers from inedible biomass will be synthesized using enzymes and organic synthesis, as well as polymerization methods. | Nagoya Univ, RITE, TIT, Shiunshu Univ |
| E3–2 | Improved durability and toughness of environmentally degradable polymers | The use of molding and processing techniques, dynamic cross-linking, copolymers, and supramolecules will be investigated to improve the durability and toughness of environmentally degradable polymers, including marine, as well as to study self-healing properties. | Yamagata Univ, Kyushu Univ, Univ Tokyo, Nagoya Univ, AIST |
| E4 | Assessment of environmental degradability, including marine | Analyze the dynamics of plastic trash, fiber waste, fishing nets, and tire wear powder in the ocean, evaluate their degradation in the ocean, and study the development of a fast degradation evaluation method. | Ehime Univ, CERI |
| E5 | Marine biodegradability and safety of oligomers | Synthesize oligomers equivalent to polymers developed by each company and evaluate marine degradability and safety | Kyushu Univ, Nagoya Univ, Tokyo Tech, Shinshu Univ, CERI |
| E6 | Development of polymers made from seaweed for CO2 fixation | Synthesize marine biodegradable plastics from seaweed (Macroalgae) with excellent CO2 fixation performance provided by ARPA-E, and evaluate their marine biodegradability and mechanical properties (joint research with ARPA-E). | Univ Tokyo, RITE, Nagoya Univ, TIT, OMU, Shinshu Univ, Ehime Univ, Yamagata UnivCERI |

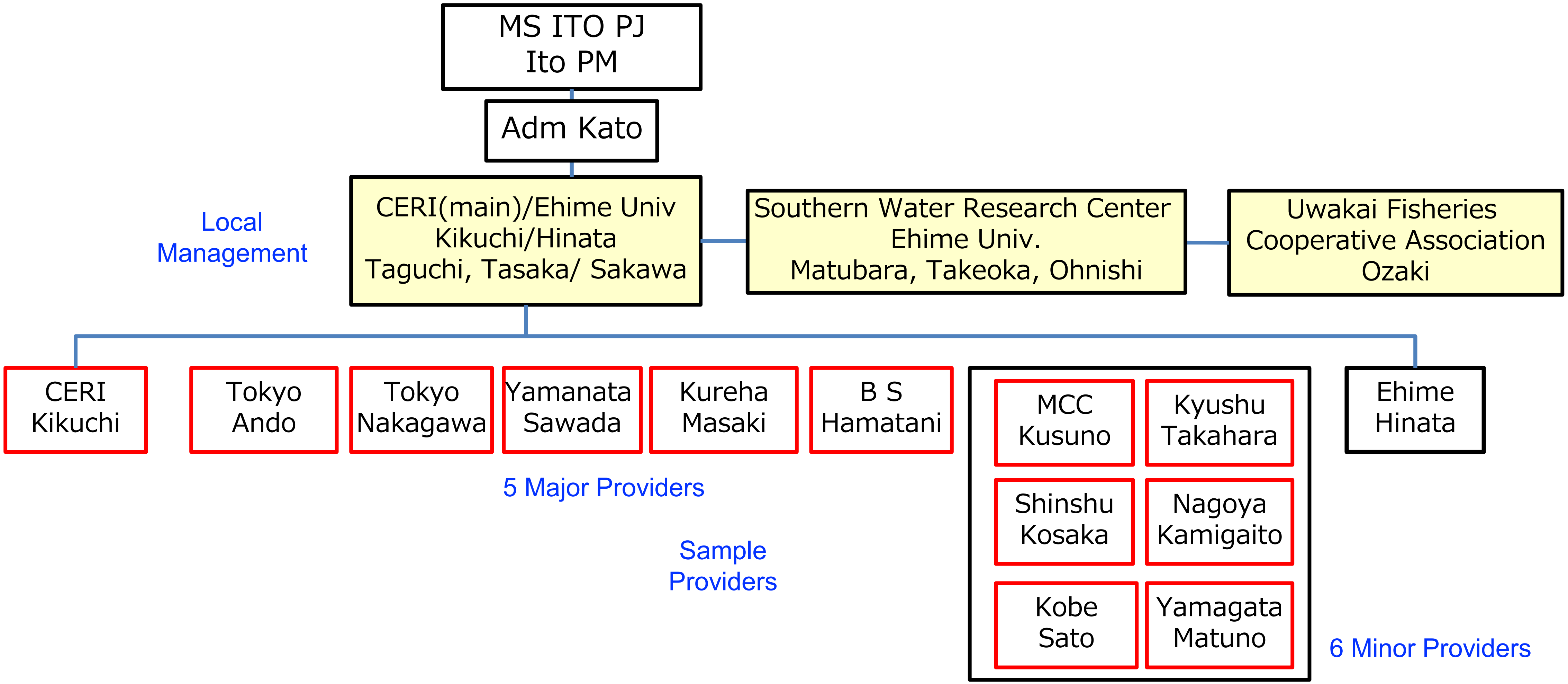
# Contents

- **Field Test**
- スイッチ機能
- 強靭性の向上
- 研究進捗状況（アカデミア、企業）
- 国際連携

# Marine Biodegradation: 2023-Field Tests

■Objective: To obtain data on marine biodegradability evaluation in actual marine environments, in addition to accelerated laboratory testing.

■Test site: Ainan Town, Ehime Prefecture



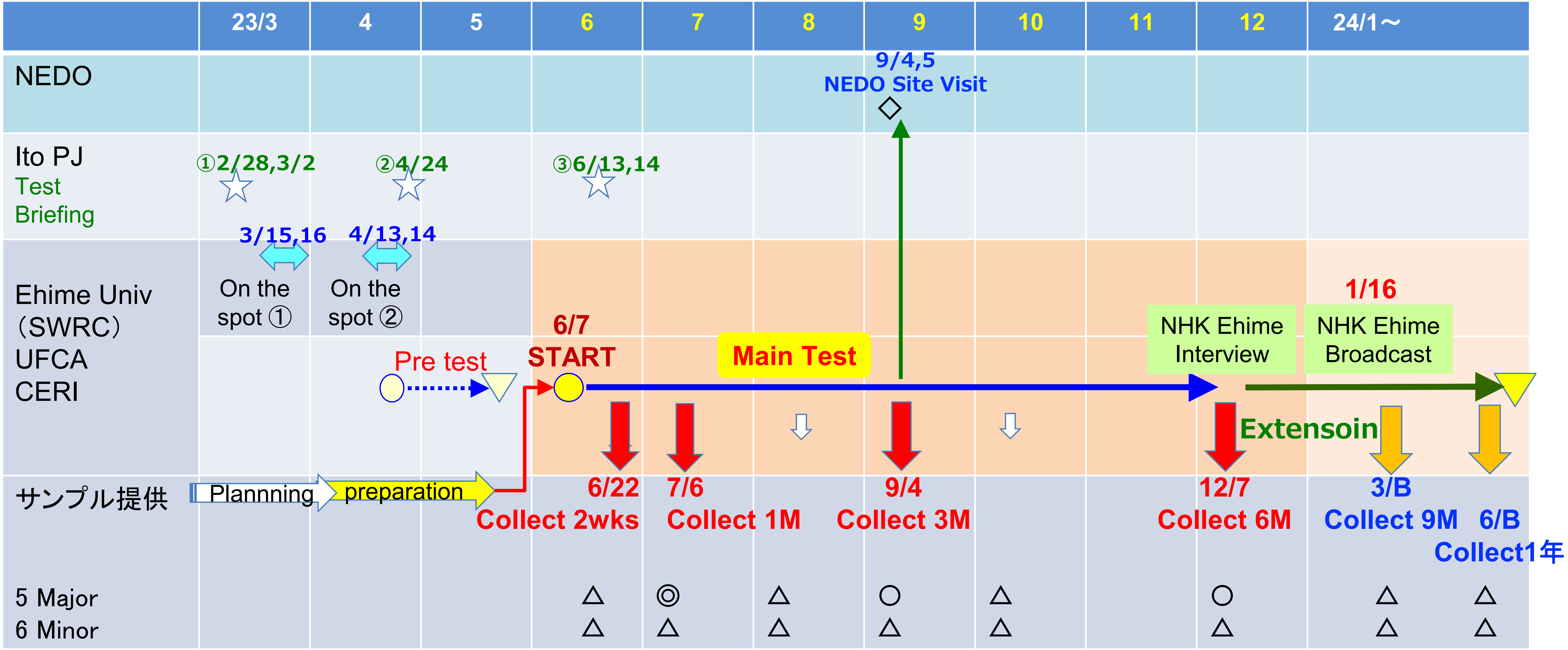
# Exposure Point


| | Ⅰ In the bay (6/8- Test) | Ⅱ Open sea (CERI only) |
|---|---|---|
| Depth | 15-20m | 30-50m |
| Wave | Calm<br>Low risk | 8m (max)<br>High risk |
| Test depth | A Surface<br>C Seabed | A Surface<br>B middle<br>C Searbed |
| Other factors | Possible<br>Riverrine impact | Fast currents |




# Marine Biodegradation: 2023-Field Test Schedule

**Change of plan: Extension from the original plan of 6 months of immersion to 12 months.**




Total samples 1,078 → Database ← Environmental data

# Development of Standard Circular Economy Polymer Database

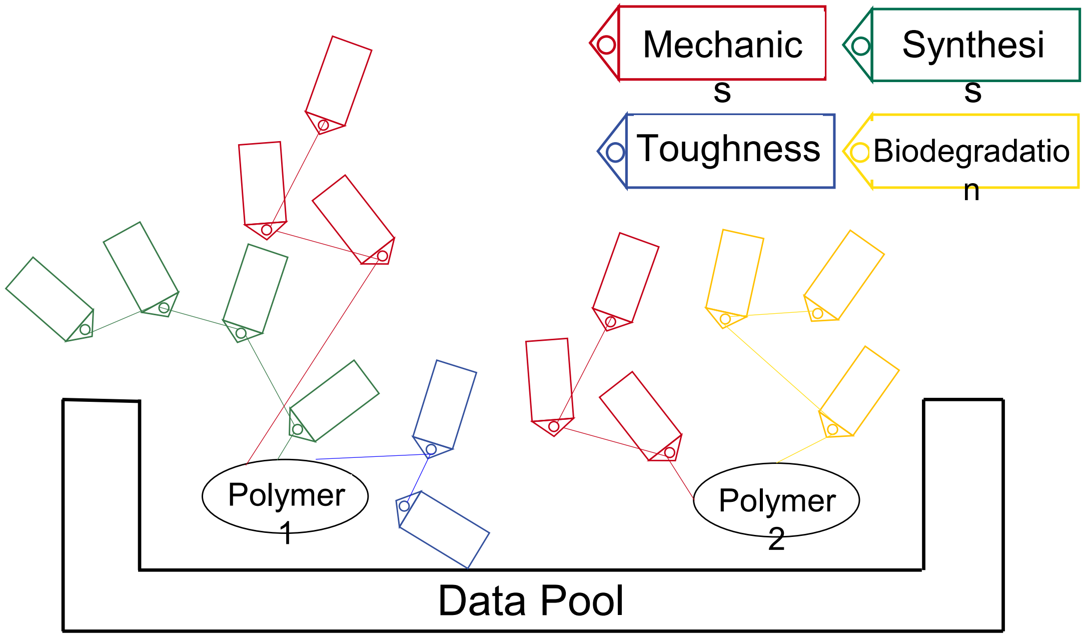
University of Tokyo
OKAZAKI, Susumu

MS Ito PJ

## Input software working on a cloud

### Data management by advanced tag-tree format

Interdisciplinary data collection




## Multi-dimensional data of oceanic degradation test

An example of the biodegradations (CERI)

試験条件に関する情報

| | 項目名称 | 数値・文字列 | 単位 |
|---|---|---|---|
| 植種源 採取場所情報 | 名称 | 徳之島 | |
| | 北緯 | 27° 44'40.1"N | |
| | 東経 | 129° 01'46.2"E | |
| | 水温 | 25 | °C |
| | 気温 | 25 | °C |
| 試験系条件 | 植種 | 海水 | |
| | 海水量 | 150 | mL |
| | 堆積物量 | 1 | g |
| | 塩化ｱﾝﾓﾆｳﾑ | 0.1 | g/L |
| | ﾘﾝ酸二水素ｶﾘｳﾑ | 0.1 | g/L |
| | 試験温度 | 25 | °C |
| | 攪拌 | 200 | rpm |

試験結果のデータ　※時間に対する数値のデータです。

項目名称： CO2発生量

| 試験時間（単位：day） | BKn1 | BKn2 | セルロースn1 | セルロースn2 | PCLn1 | PCLn2 ← サンプル名称 |
|---|---|---|---|---|---|---|
| 0 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 3 | 5.67 | 5.57 | 6.16 | 5.97 | 5.55 | 7.12 |
| 8 | 8.63 | 8.90 | 10.93 | 10.26 | 9.93 | 11.74 |
| 15 | 11.13 | 11.15 | 18.63 | 22.53 | 20.76 | 23.30 |
| 22 | 13.34 | 13.00 | 25.19 | 35.65 | 33.29 | 33.72 |
| 30 | 15.07 | 14.78 | 34.24 | 43.26 | 41.51 | 42.13 |

単位：mg

項目名称： 生分解度

| | | | セルロースn1 | セルロースn2 | PCLn1 | PCLn2 ← サンプル名称 |
|---|---|---|---|---|---|---|
| 0 | | | 0.0 | 0.0 | 0.0 | 0.0 |
| 3 | | | 1.0 | 0.7 | -0.1 | 1.8 |
| 8 | | | 4.1 | 2.8 | 1.4 | 3.7 |
| 15 | | | 14.1 | 21.4 | 11.9 | 15.0 |
| 22 | | | 22.6 | 42.3 | 24.8 | 25.3 |
| 30 | | | 36.4 | 53.3 | 32.8 | 33.5 |

単位：%

## Database of oceanic degradation test for more than 1000 samples

# Contents

- フィールド試験
- **Switch Function**
- 強靭性の向上
- 研究進捗状況（アカデミア、企業）
- 国際連携

# Switch Functions

■NEDO Policy

・Cool Earth's research agenda

Should functions that are currently unrealized (functions to control the timing of biodegradation, function to decompose appropriately in diverse marine environments, safety for living organisms including intermediate products from degradation, etc.)

・Examples of switch functions (still in the research stage, no examples of social implementation)

**Multi-lock type： Requiring multiple conditions for degradation achieves switching function.**

**（Does not decompose under actual conditions of use, but decomposes quickly in the sea or on the seafloor)**

表８．スイッチ機能を有する生分解性プラスチックの開発一例 [24] [25] [26] [27]

| 対象 | 現状 | 技術例 |
|---|---|---|
| スイッチ機能を有する生分解性プラスチック | ラボ | ✓ 分解開始のポイントを制御する技術<br>• pHや塩濃度などの変化によって化学構造が変化することで分解開始<br>• 流出に伴う物理的刺激によって材料内の酵素が活性化することで分解開始<br>✓ 分解のスピードを制御する技術<br>• 結晶化度や結晶厚を変えることで分解速度を制御するもの<br>• バイオフィルムなど微生物による分解速度を制御するもの |

**Timing Control**

**Speed Control**

- **Copolymer + additives, water, marine microorganisms, others**
  **Introduction of degradation unit (Companies, Nagoya Univ, Tokyo Tech Univ, Shinshu Univ, Osaka City Univ)**
- **Enzyme + marine environment**
  **Enzyme (Companies, RITE, Nagaoka Univ Tech)**

- **Additives + light, salt, marine microorganisms**
  **Cluster catalyst (Univ Tokyo), Polyrotaxane (Univ Tokyo)**
- **Dynamic cross-linking + water, marine microorganisms**
  **Hydrogen bonding (Companies, Univ Tokyo)**

Moonshot
伊藤ＰＪ

# Progress on switch function

## Challenging the control of switch functions (point control) using proprietary technology not found anywhere else in Japan or abroad!

1） Entropy-driven dynamic cross-linking (Yoshie (Univ. Tokyo) + Morita (AIST))
→ Switch-on by metal ions in the ocean (also succeeded in improving toughness)
→ Transfer to companies (scale-up)

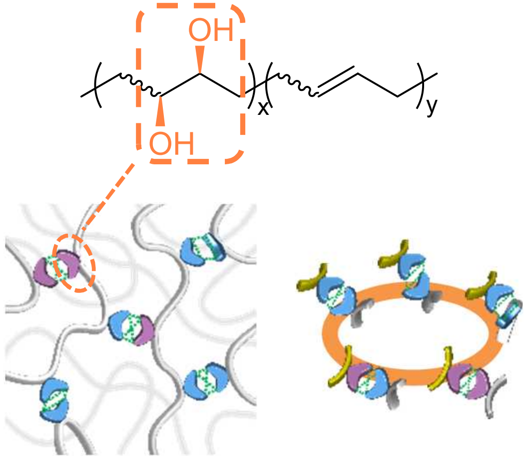
2) Heat-resistant LCC using quasi-polyrotaxane nanosheets as a carrier (Ito (Univ. Tokyo) + Inui (RITE))
→ Switch-on by salt ions in the sea (also succeeded in improving toughness) → Transfer to companies

3) Comprehensive search for new switch bonds and realization of sharp switch function by precision polymerization (construction of switch bond data set)
(Kamigaito (Nagoya Univ) + Sato (TIT) + Sato (OMU) + Kosaka (Shinshu Univ) + Ito (Univ Tokyo)
→ Switch-on by salt ion, redox potential, metal ion, etc. in the sea → Accumulate in database

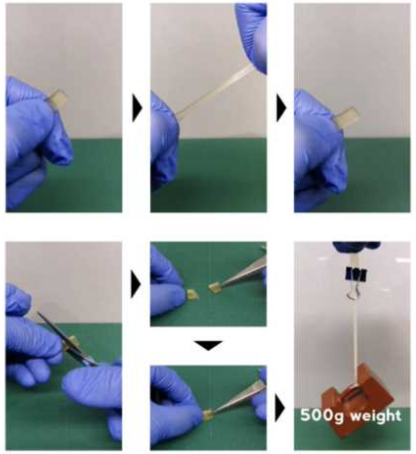
# Realizing muti-lock degradability and toughness using dynamic bonds

Naoko Yoshie (Univ Tokyo)

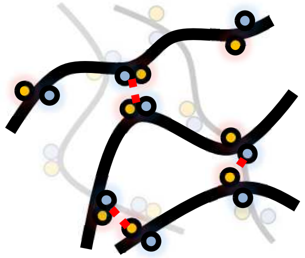
MS伊藤PJ



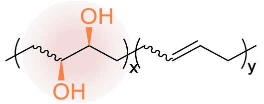

Entropy-driven strong hydrogen bonding




Excellent rubber elasticity and rapid self-healing



Exploring of novel entropy-driven hydrogen bonds

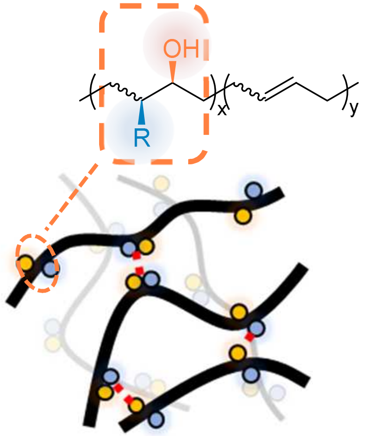



Vicinal diol (VDO)

- ✓ Incredible dynamicity
- ✓ Excellent mechanical toughness
- ✗ Poor universality
- ✗ Synthesis is complex

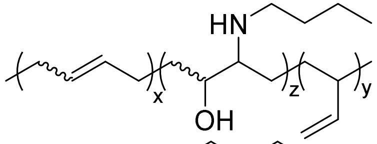
Previous work

## Search for new entropy-driven hydrogen-bonding groups



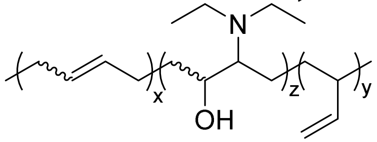

Search for novel entropy-driven hydrogen bonds

PB-Bu-X

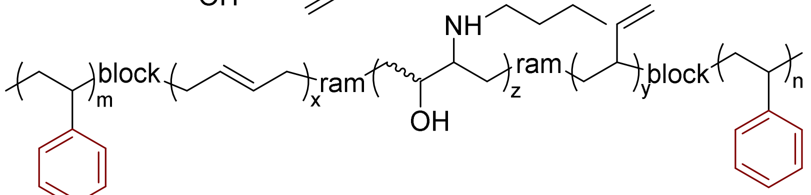


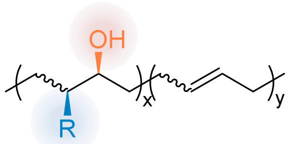

$$X = \frac{z}{x+y+z}$$

PB-DE-X




SBS-Bu-X




Vicinal amino alcohol (VAA)

- ✓ Favorable universality
- ✓ Easy to Synthesize
- ✓ High mechanical toughness
- ✓ Good dynamicity

This work

# Research and development of multi-scale analysis methods for marine degradable polymers from a hierarchical point of view

AIST
Hiroshi MORITA, Yusuke Yasuda

MOONSHOT RESEARCH & DEVELOPMENT PROGRAM NEDO

MS伊藤PJ

AIST

**Issues and Objectives:** Material design and analysis of polymers having the characters of toughness and marine degradability through the multi−locking functions

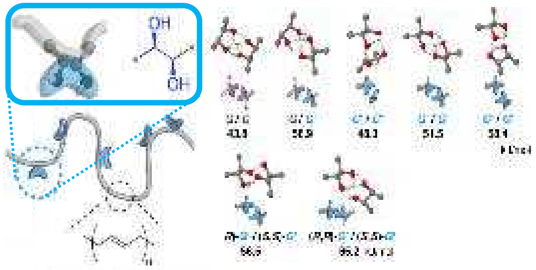
Technology of our group
Simulation for soft materials
& Informatics

**Material designs for toughened polymer** with physical cross-linking

**Elucidation of degradation mechanisms** for the development of multi-lock functions for polymers

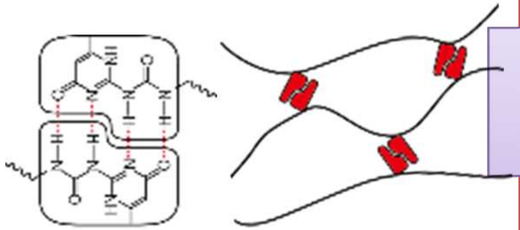
## Development of dynamic bond elastomers by Yoshie's group

### Entropy driven



Kim et al. Macromolecules, 2020, 53, 4121.

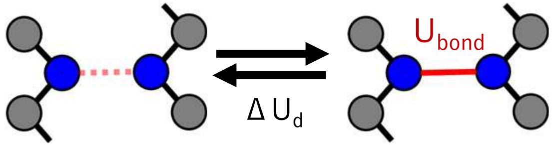
### Enthalpy driven



Yoshida et al. Adv. Funct. Mater. 2017, 27, 1701670.

## Modeling and Simulation of dynamic bond elastomers

### 1st model

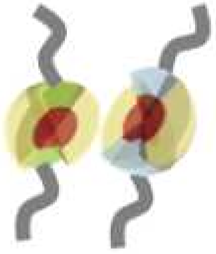



$$U_{\mathrm{bond}}(r) = \frac{1}{2}\boldsymbol{K}(r - 1.0)^2$$

### Updated model

Entropy driven

Enthalpy driven

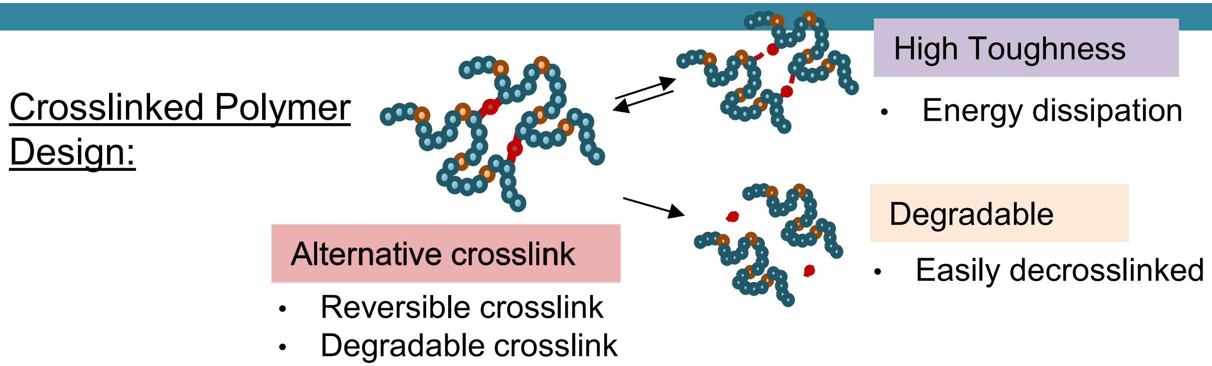


# Technology for both degradation and toughness using dynamic cross-linking

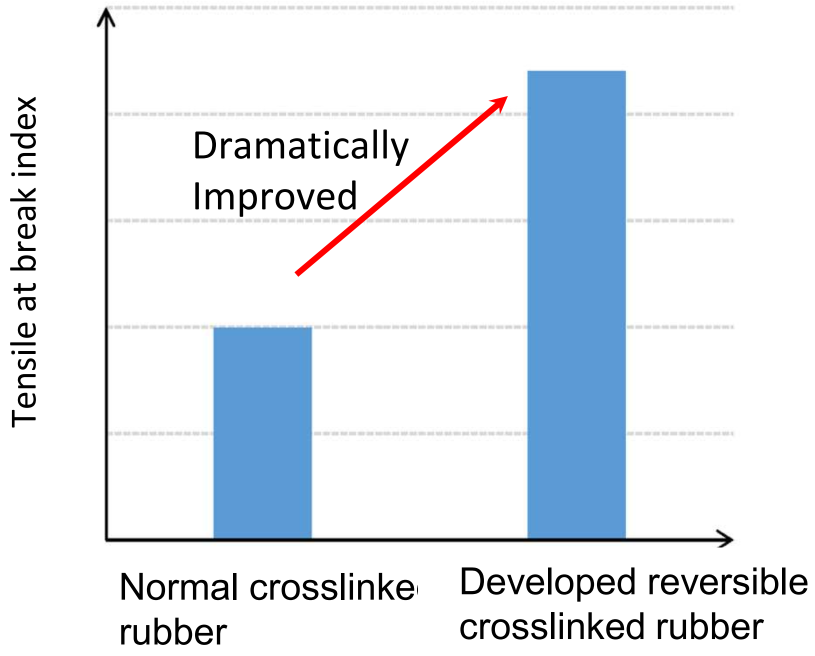
BRIDGESTONE

MS伊藤PJ

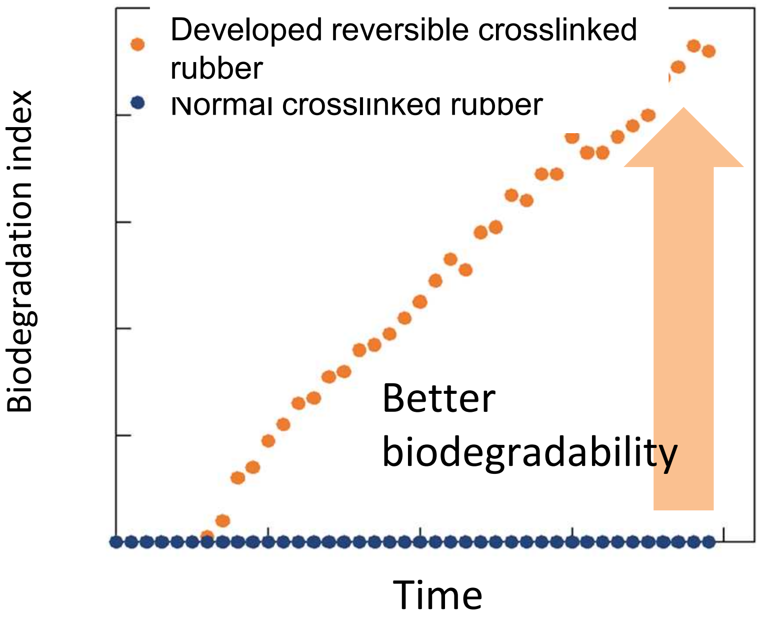
With extending reversible bond technology that strengthen rubber by effective energy dissipation, we newly designed degradable cross link system cooperating with academia.




—Physical property test result—




—Marine biodegradation test result —

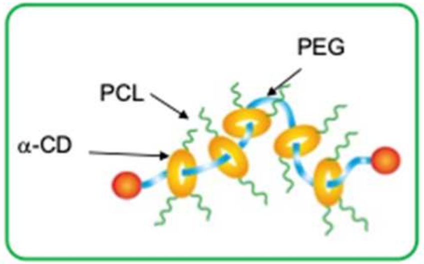



**Both toughness and biodegradation are both significantly increased by introducing reversible and degradable cross-links**

# Simultaneous enhancement of toughness and marine biodegradability using polyrotaxane (PR) and pseudo-polyrotaxane nanosheets (PPRNS)

MS伊藤PJ

## Addition of Polyrotaxane (PR) Simultaneous improvement of biodegradable resin toughness and marine biodegradability

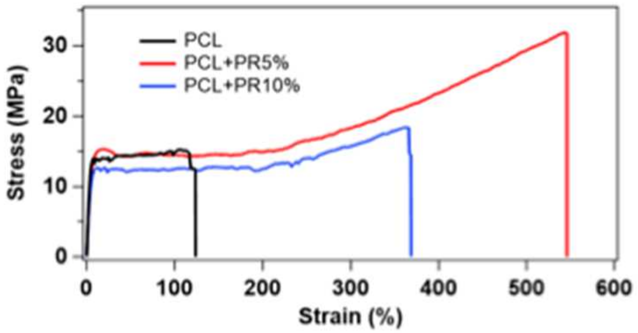


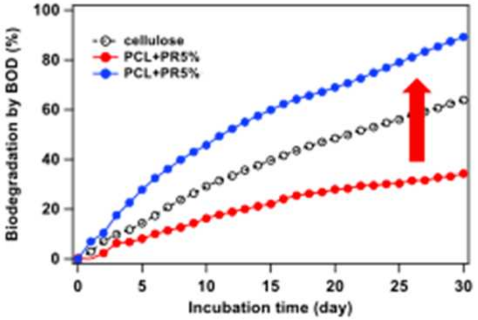

Toughen various polymers

Durability and Degradability

Degradable in ocean

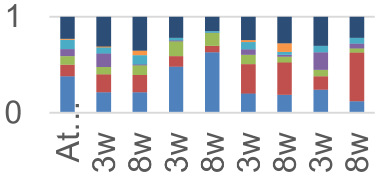
Accelerate bio-degradability of various polymers in ocean



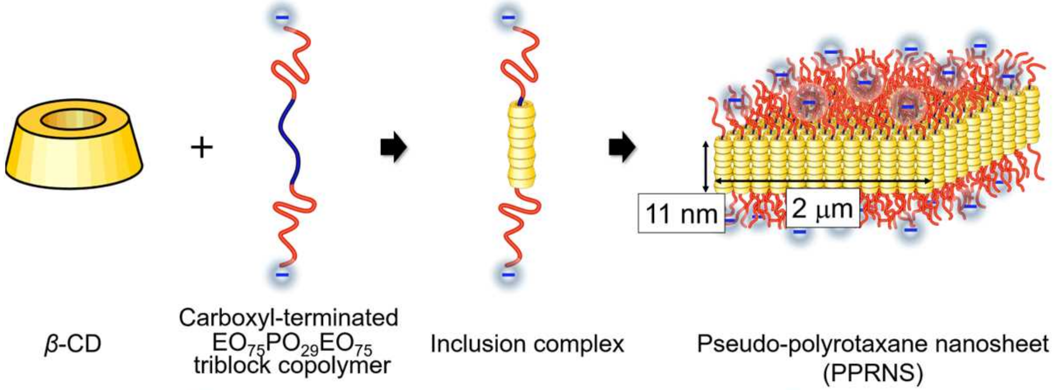




**Achieved both toughness and seawater degradability.**

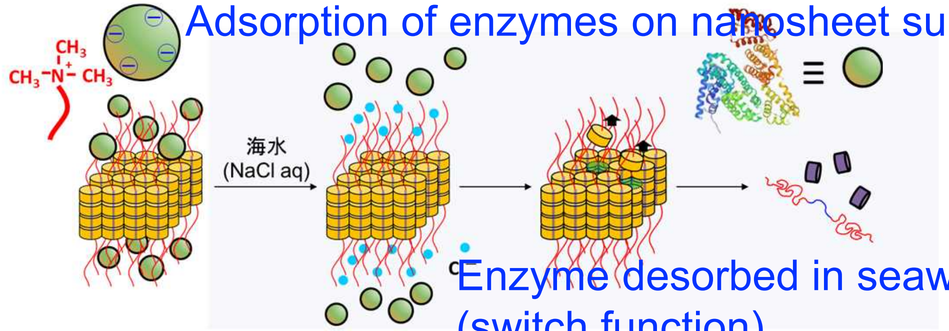
Elucidation of PR degradation mechanism (bacterial flora analysis) collaborated with Dr. Kasai (Nagaoka Tech Univ)




## Pseudopolyrotaxane Nanosheets (PPRNS) as a novel enzyme carrier material

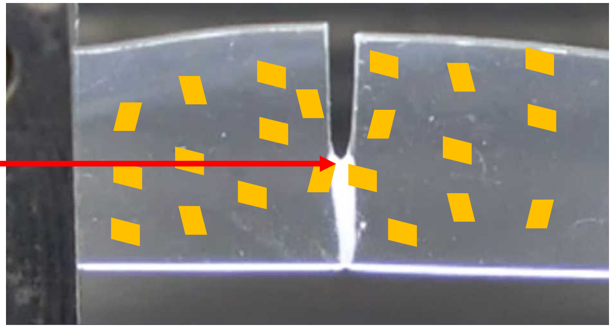



Adsorption of enzymes on nanosheet surface




Enzyme desorbed in seawater (switch function)

Crack Tip



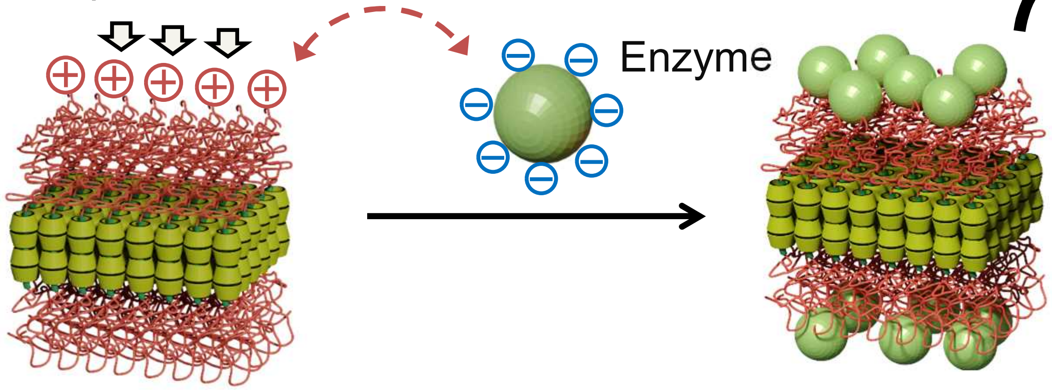
Sheet fillers suppress crack propagation

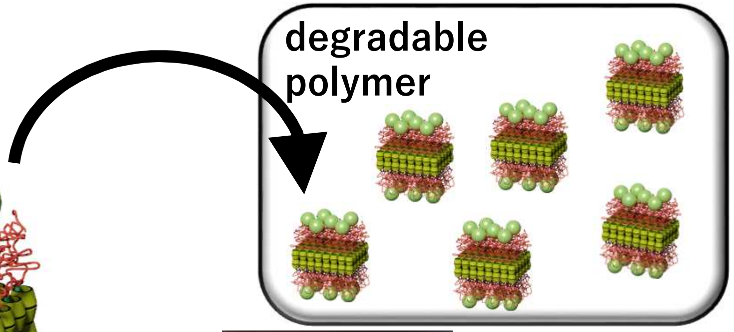
Improve toughness

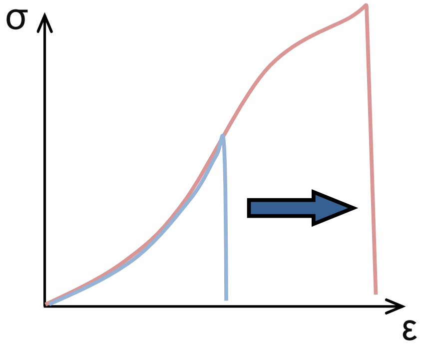
# Enzymatic modification and degradative switching to PPRNS

## ◆ Enzyme loading on PPRNS surface

Ionizing groups at the ends of axial polymers are exposed on the surface



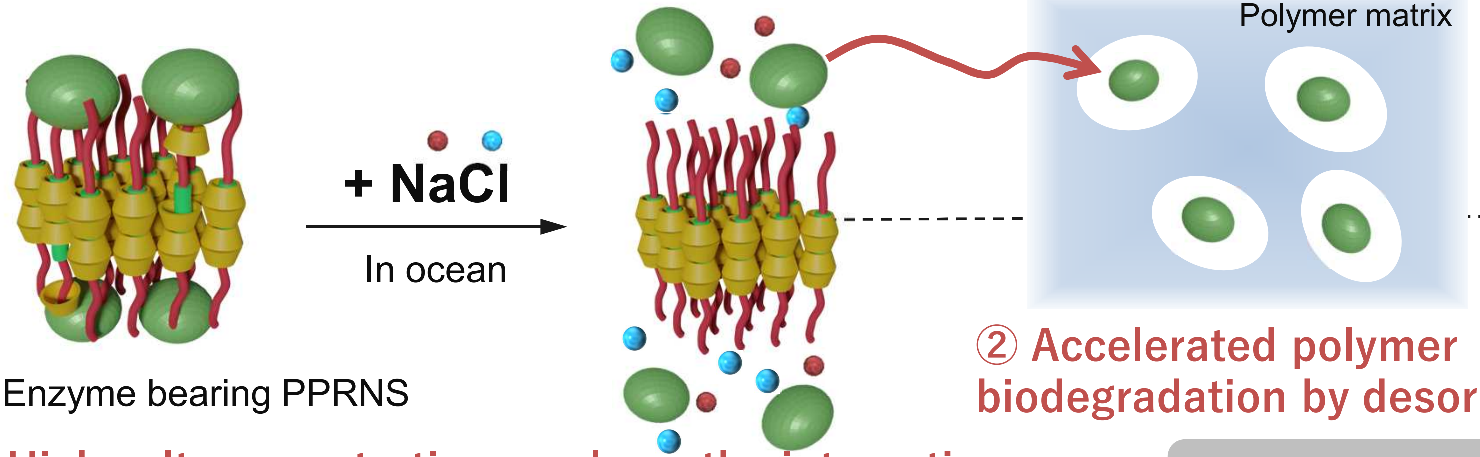



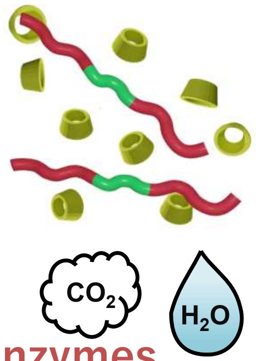



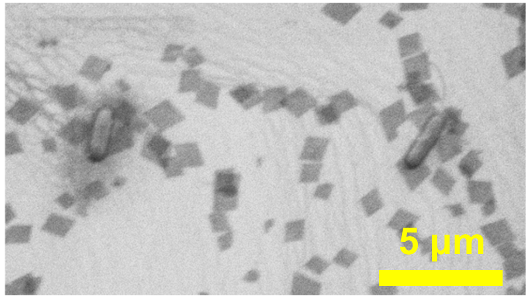

➢ **Degradable polymer toughening by enzyme-loaded PPRNS filler**

## ◆ Degradable switching due to salinity in the ocean

③ PPRNS also gradually decompose and biodegrade




▲ Bacteria found around PPRNS
Bacteria found in the vicinity of PPRNS

② Accelerated polymer biodegradation by desorbing enzymes

① High salt concentration weakens the interaction with PPRNS and the enzyme is desorbed.

➢ **Combination of toughness and biodegradability by switching salt concentration**

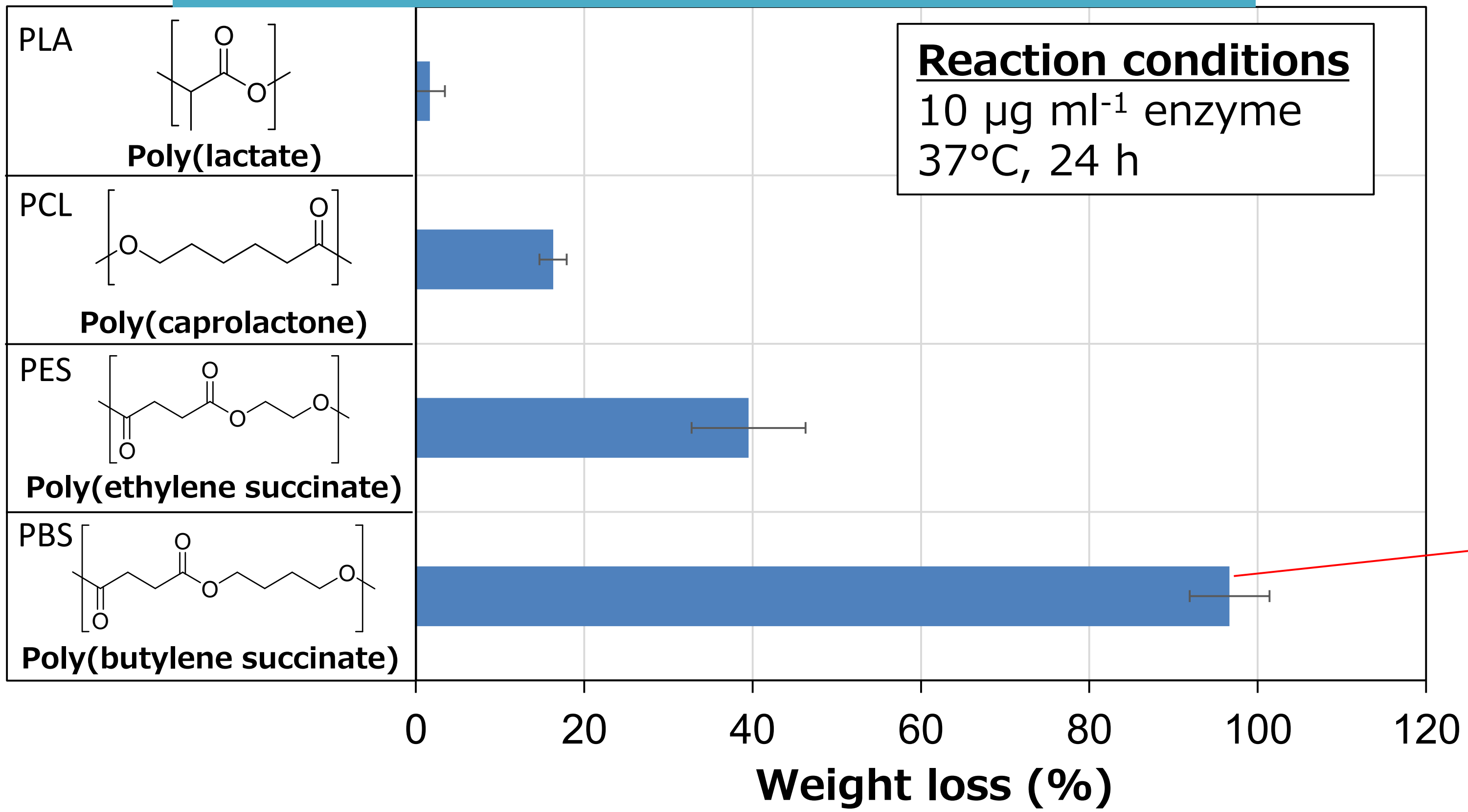
# A thermostable esterase degrading aliphatic polyesters

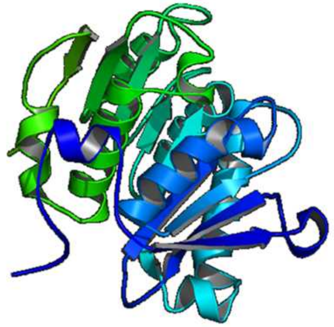
## High-functionalization of polymer-degrading enzymes

Masayuki Inui

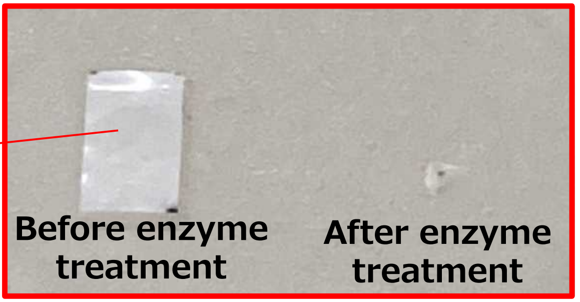
MS Ito PJ

### Weight loss after enzyme treatment



**Thermostable esterase**




**PBS was completely degraded after 24 h**

**We discovered a thermostable esterase that degrades various aliphatic polyesters**

# Salt switching of enzymatic polymer degradation by immobilization to carrier matrix

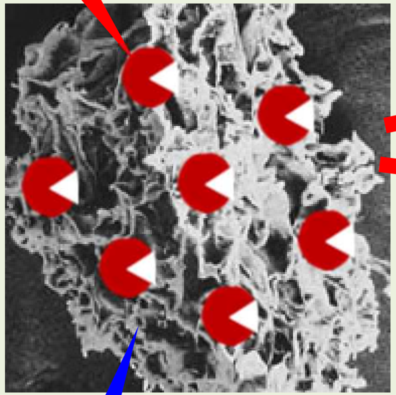
MOONSHOT NEDO

MS Ito PJ

High-functionalization of polymer-degrading enzymes

**Immobilized enzyme**

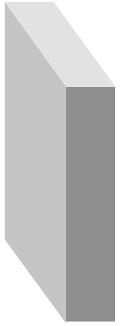
**Polymer degrading enzyme**



**Carrier matrix**

## Without salt

Enzyme is captured by carrier matrix to prevent degradation activity



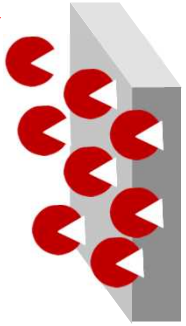
**Polymer**

Degradation (✕)

## With salt (seawater)

enzyme is released from carrier matrix and degrades polymer

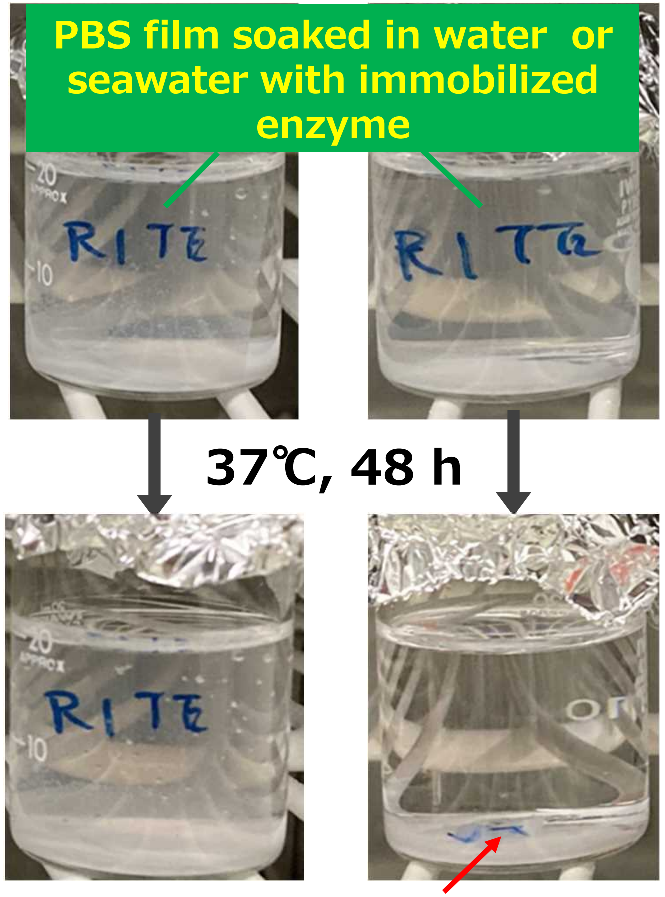
＝switching by salt



**Polymer**

**Degradation**

**Water (without salt)** | **Seawater (with salt)**




**Degraded PBS film**

**Switching of enzyme activity was confirmed in seawater**

# Improved thermostability by powderization and enzyme embedded PBS film

MOONSHOT NEDO

MS Ito PJ

## High-functionalization of polymer-degrading enzymes

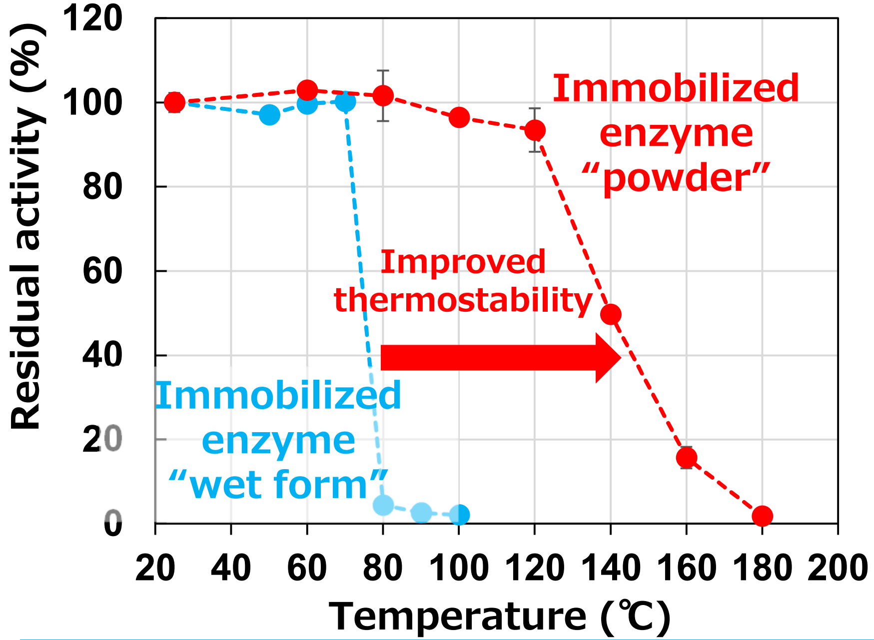
Purified enzyme solution

Immobilization

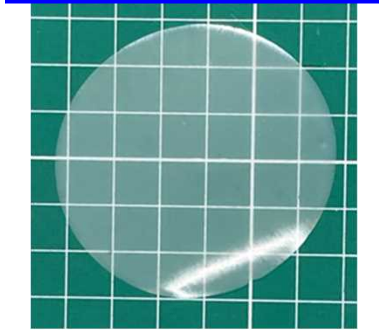
Immobilized enzyme "wet form"

Freeze dry

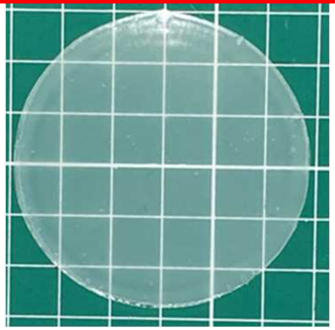
Immobilized enzyme "powder"



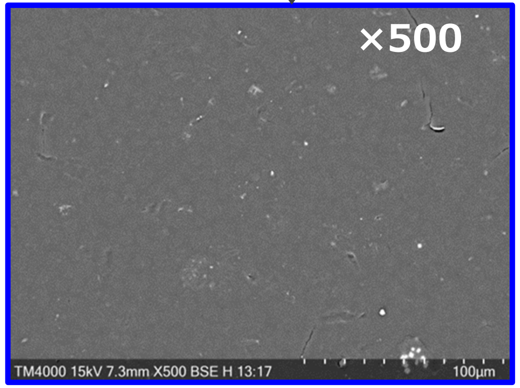

PBS film without enzyme

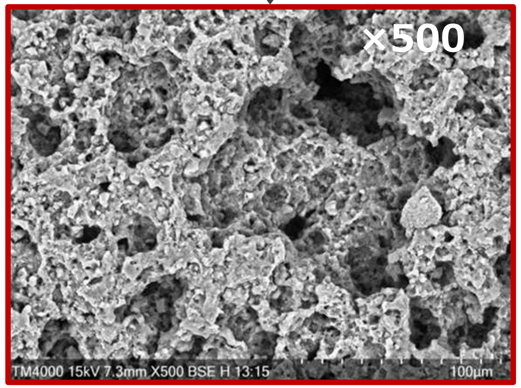


Enzyme embedded PBS film



Seawater, 37℃, 5 days




**Powderization improved thermostability of the immobilized enzyme, which showed enzyme activity even after kneading with PBS**

# Summary of synthesis and decomposition technology development by E3-1 group

MOONSHOT RESEARCH & DEVELOPMENT PROGRAM
NEDO
MS伊藤PJ

1. Introduction of various bonds as switches is possible
→ hydrolysis, pH, redox, metal ions, crystalline amorphous switches, etc.
Acetal, hemiacetal ester, siloxy, thioether, thioacetal, conjugated ester, peroxy bond, etc.
2. introduction into various polymers
→ applicable to a wide range of polymers from polyester to vinyl polymers
PBS, PVL, PCL, polyacrylate, polyacrylamide, polystyrene, polyvinyl acetate, polyvinyl ether, etc.
3. possible to control the length of degradation products
→ important from an environmental standpoint in defining degradation products
Oligomer synthesis of polyesters with uniform degree of polymerization, oligomeric degradation products of vinyl polymers with narrow molecular weight distribution
4. Inedible biomass and renewable resources can be used
→ Important for sustainable technology development
Polyesters such as PBS can be bio-based, bio-production technology for switch parts available, polymerization using oxygen as monomer
5. biodegradability (BOD) and field testing through collaboration
→ important to ensure marine biodegradability
Proof of high biodegradability of PBS with clear structure, BOD and field tests of polymers with various switch functions underway
6. development of new monomers and new polymerization systems
→ important academically and industrially, "challenge with basic science (NEDO)
Oligomer/polymer synthesis technology with controlled degree of polymerization, new controlled degradation technology, synthesis and degradation technology with new monomers

# E3-1: Recent Developments of Synthesis and Degradation Technology

MS伊藤PJ

1．**Various Chemical Bonds for On-Demand Switching → Hydrolysis, pH, Redox, Metal Ion, Crystalline-Amorphous, etc.**

Acetal, Hemiacetal Ester, Silyloxy, Thioether, Thioacetal, Conjugated Ester, Peroxy, etc.

2．**Various Polymers → A Wide Range of Polymers from Polyesters to Vinyl Polymers**

PBS, PVL, PCL, Polyacrylate, Polyacrylamide, Polystyrene, Poly(vinyl Acetate), Poly(vinyl Ether), etc.

3．**Degradation Products with Controllable Chain Lenghts → Well-Defined Degradation Products**

Synthesis of Monodisperse Oligoesters, Degraded Vinyl Polymer Products with Controlled Molecular Weights

4．**Non-Food Biomass and Renewable Resources → Sustainable Developments**

Bio-Production Technology for Switch Part and Polyesters such as PBS, Oxygen ($O_2$) as Monomer

5．**Biodegradability (BOD) and Field Testing through Collaboration → Degradation in Ocean**

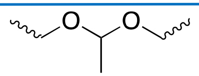
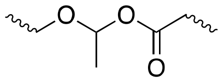
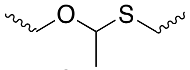
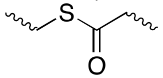
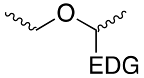
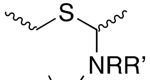
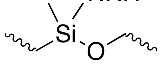
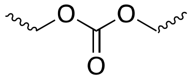
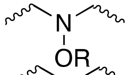
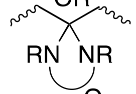
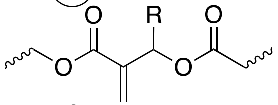
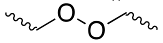
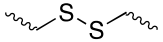
Biodegradable Monodisperse Oligo(butylene Succinate), On-Going BOD and Field Test of Various Polymers with Switch Part

6．**New Monomers and Polymerizations → New Science and Technology, "Challenge with Basics of Science" by NEDO**

New Oligomer/Polymer Synthesis and Degradation Technology Based on New Monomer Design and Polymerization

# E3-1: Recent Developments of Synthesis and Degradation Technology

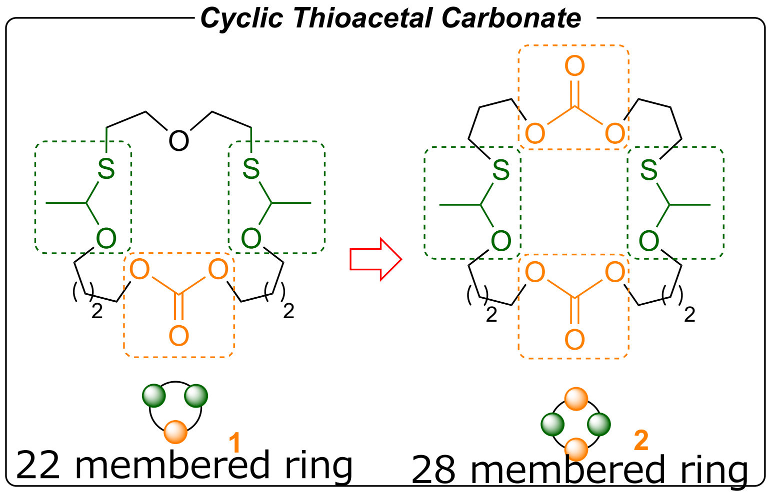
MS伊藤PJ

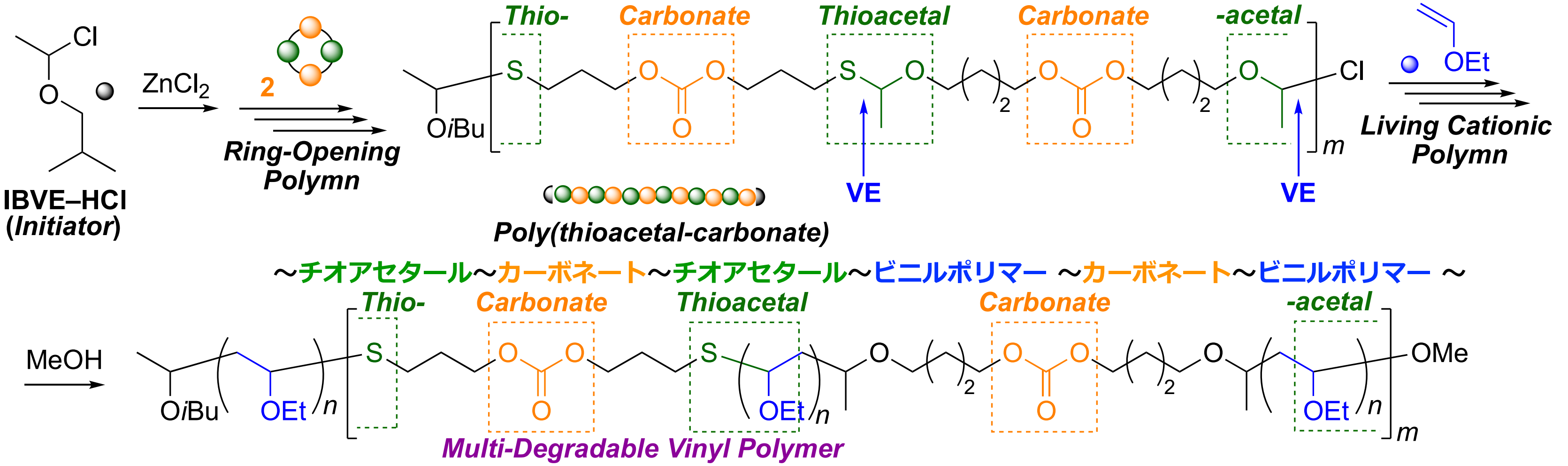
| Chemical Bonds | Structures | Switch | | | Polymers |
|---|---|---|---|---|---|
| | | pH | Redox | Metal Ion | |
| Acetal |  | Y | — | (Y) | Polyester |
| Hemiacetal Ester |  | Y | — | (Y) | Polyester, Poly(vinyl Acetate), Polymethacrylate |
| Thioacetal |  | Y | Y | (Y) | Poly(vinyl ether), Polyacrylate, Polyisoprene |
| Thioester |  | Y | Y | (Y) | Polyacrylate, Polyisoprene |
| Ether |  | Y | — | (Y) | Poly(vinyl Acetate) |
| Thioether |  | Y | Y | (Y) | Polyacrylate, Poly(vinyl Acetate), Polystyrene |
| Silyloxy |  | Y | — | (Y) | Polyester |
| Carbonate |  | Y | — | — | Poly(vinyl ether) |
| Alkoxyamine |  | Y | (Y) | (Y) | Polystyrene, Polyisoprene |
| Aminal |  | Y | — | (Y) | Polyacrylate |
| Conjugated Ester |  | Y | — | — | Polyester |
| Peroxy |  | — | Y | Y | Polydiene |
| Disulfide |  | — | Y | (Y) | Polymethacrylate |

# Living cationic copolymerization of cyclic thioacetal carbonate and vinylether
## Introduction of different degradation switches (C-S and carbonate bonds) and length control of degradation products

上垣外 正己

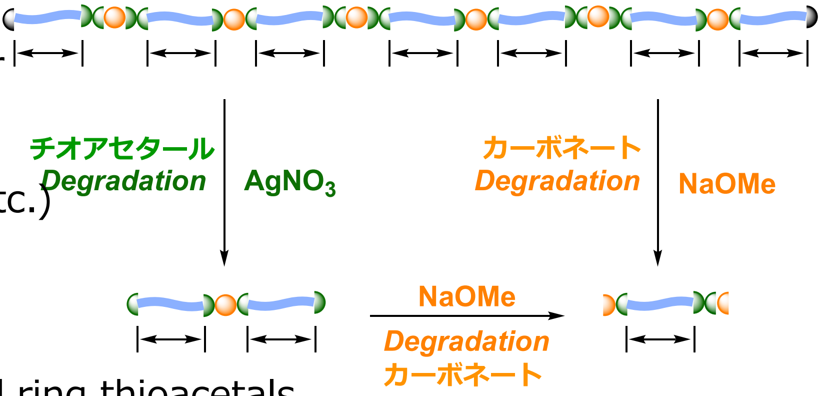
伊藤PJ

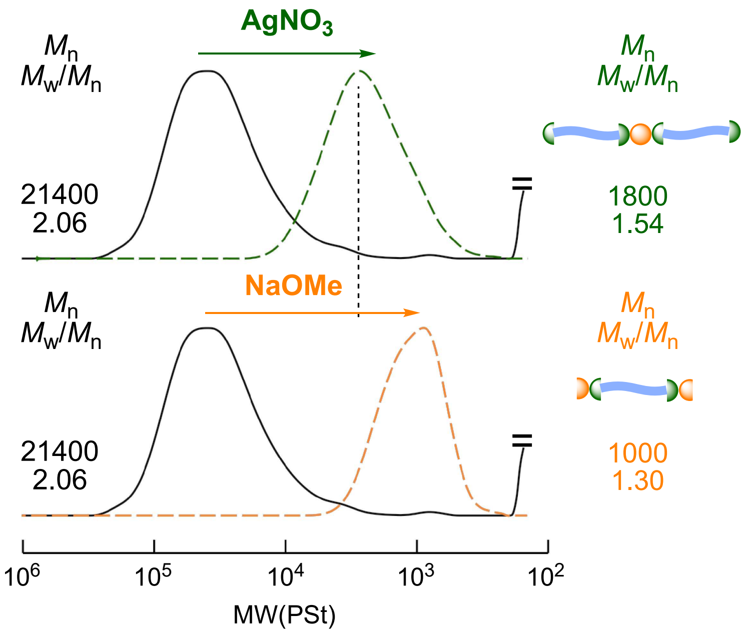


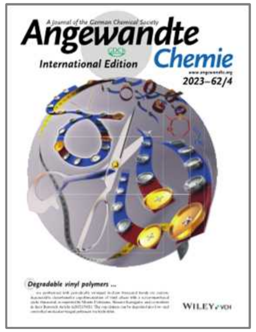



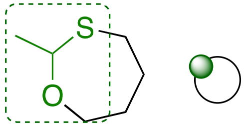

- Synthesis of New Cyclic Thioacetal Carbonates
- Living cationic copolymerization with vinyl ether
- Degradable by both acid and alkali
- Possible to control the length of polymer

→ marine environmental switches (pH, redox, etc.)



- Published papers on 7-membered ring thioacetals
- Living cationic copolymerization with vinyl ether is possible.
- Possible to control the length of polymer before and after decomposition.

Uchiyama, M.; Murakami, Y.; Satoh, K.; Kamigaito, M. *Angew. Chem. Int. Ed.*, **2023**, *53*, e202215021.

（Hot Article, Inside Cover, Nikkei、Nikkan、Kagaku-Kogyo、Nikkei online）

# Design and Evaluation of Molecularly Dismantlable Biopolymers

Osaka Metropolitan University

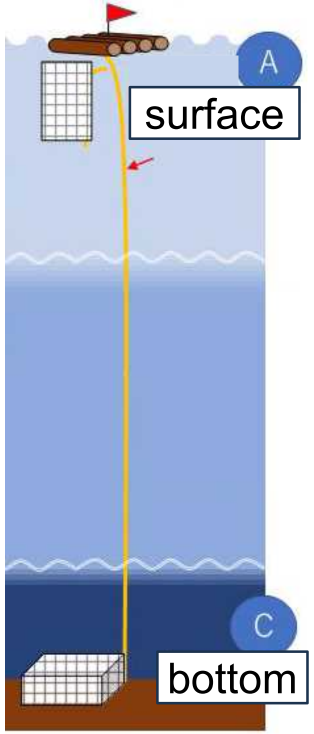
MOONSHOT RESEARCH & DEVELOPMENT PROGRAM NEDO

MS伊藤PJ

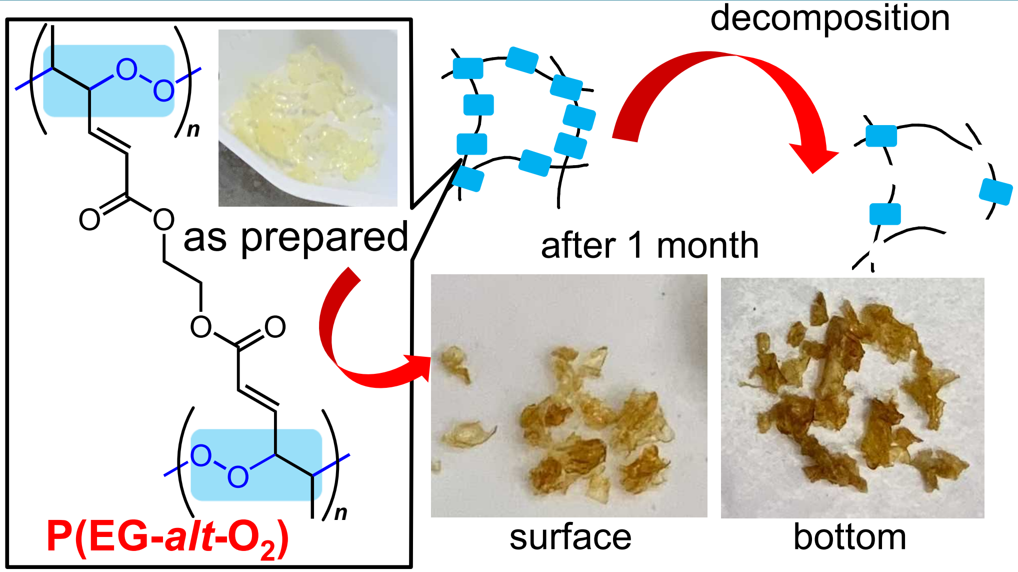
大阪公立大学 Osaka Metropolitan University

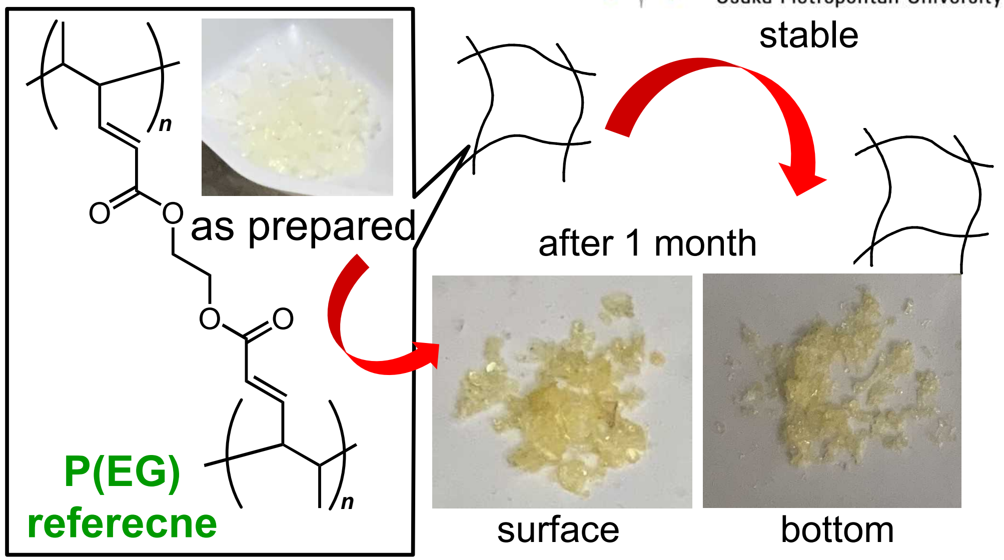
with CERI, Ehime U.

Test area:
Bay, Minamiuwa
Ainan-cho, Ehime
**Aug. 2023-, 1 month**




Depth: 15-20 m




| Polymer / degradable linkage | position | residual polymer (wt%) |
|---|---|---|
| P(EG-*alt*-$O_2$) / peroxide, ester | A, surface | 44 ± 2 |
| | C, bottom | 58 ± 1 |
| P(EG) , reference/ ester | A, surface | 94 ± 6 |
| | C, bottom | 90 ± 18 |

Cross-linked polymer containing peroxy bond and ester bond (P(EG-*alt*-$O_2$)) resulted in ca. 50%-weight loss in real marine environment for 1 month. In contrast, no weight loss was observed for the reference cross-linked polymer containing only ester bond (P(EG)), and it was revealed that peroxy bond was selectively decomposed under the experimental conditions.

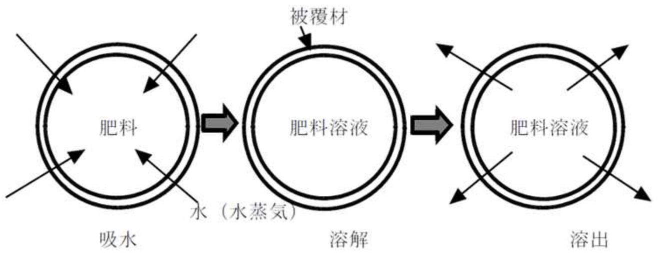
# Contents

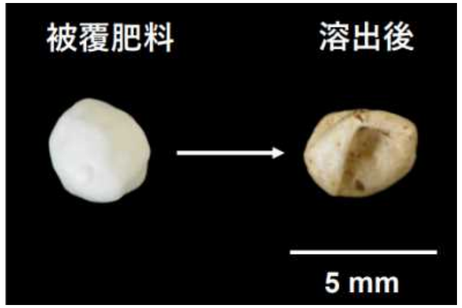
- フィールド試験
- スイッチ機能
- **Improvement of Toughness**
- 研究進捗状況（アカデミア、企業）
- 国際連携

# Application of marine biodegradable polymers to agricultural coated fertilizer shells

## ○ Application of PBS and PBSA to agricultural coated fertilizer shells

Microcapsule (MC) Fertilizer




By covering the fertilizer with plastic film, the plastic film covers the fertilizer and supplies a constant amount to the plants over a long period of time.
Used in approximately 60% of rice paddies in Japan.

Plastic shells collected at the beach

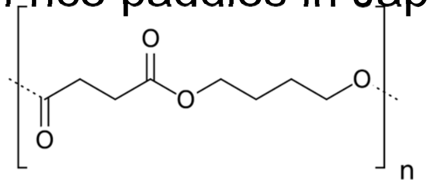

Excerpt from NHK web news

Requires material toughness to release fertilizer in constant amounts; PE is often used.

Expected to be replaced by biodegradable resin with the same level of toughness as PE

BioPBS™

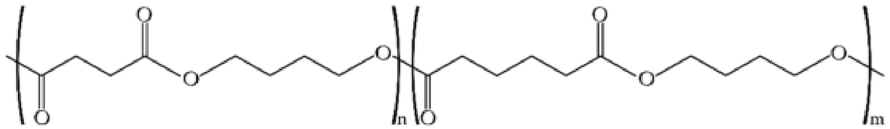
MITSUBISHI CHEMICAL



Polybutylenesuccinate (PBS)

High strength but brittle
Low marine biodegradability

Maintains strength by adding low inclusion ratio PR. Improved ductility and biodegradability while maintaining strength



Polybutylenesuccinate-*co*-adipate (PBSA)

Softer and more ductile than PBS
Highly marine biodegradable

PPRNS addition improves strength while maintaining ductility and biodegradability while maintaining ductility and biodegradability.

# Control of Higher-Order Structure and Toughness of Marine Bio-degradable Polymers through Polymer Processing

Yamagata University
Prof. Hiroshi Ito

MS伊藤PJ

山形大学
Yamagata University

**Outline**

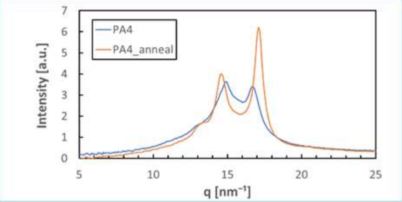
(1) Mission: Giving marine biodegradable polymers the same toughness as petroleum-based polymers based on processing and evaluation technologies

(2) Research items

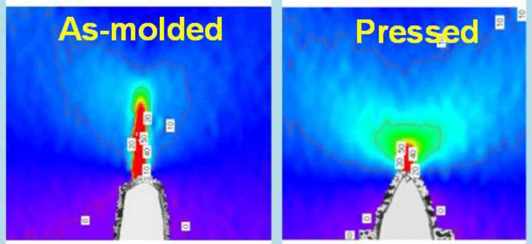
## Academic target

## Industry relations

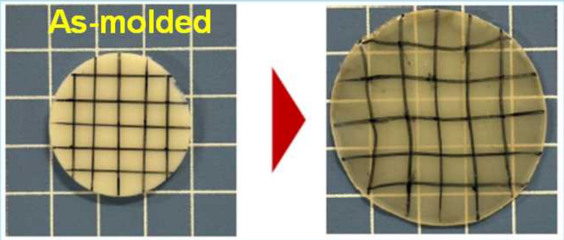
### Controlling high-order structure




**Toughness at tear tip**

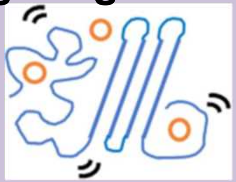



**Controlling crystal and decomposition**



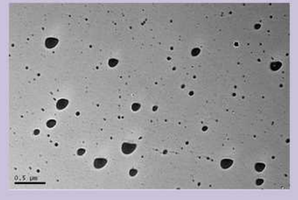

**Good tear properties for marine biodegradable films**

### Molecular design for improving toughness

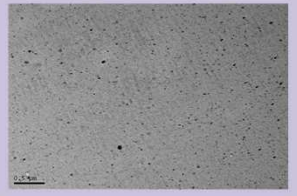


**New processing technology and modifiers for toughening**

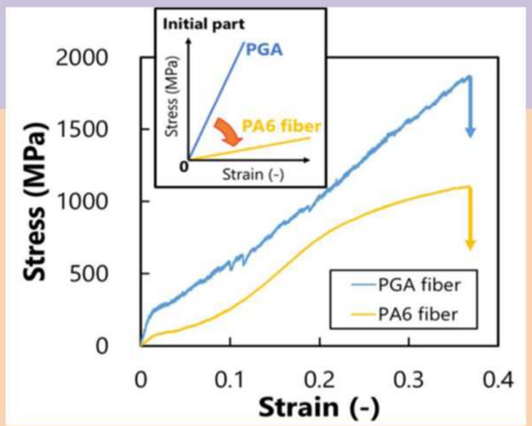
Mechanical mixing



Reactive extrusion



**Marine biodegradable fishing lines**




### Polymer blend and composites

Proteins as filler

Field test in Ehime

**Mixing method to prevent enzyme deactivation**

Bio-degradation in seawater

# Control of Higher-Order Structure and Toughness of Marine Bio-degradable Polymers through Polymer Processing

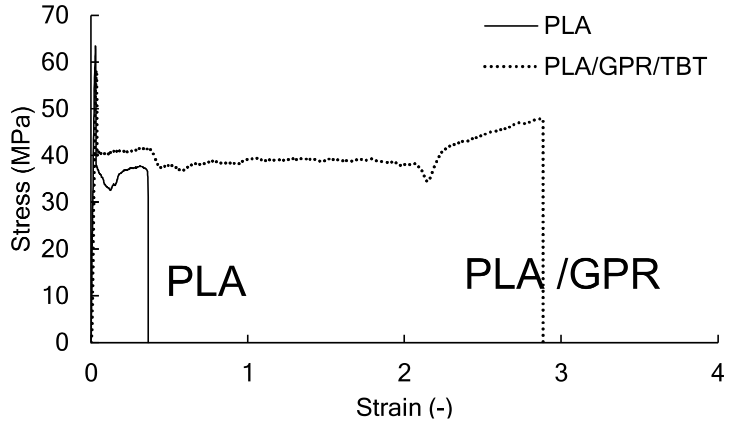
MS伊藤PJ

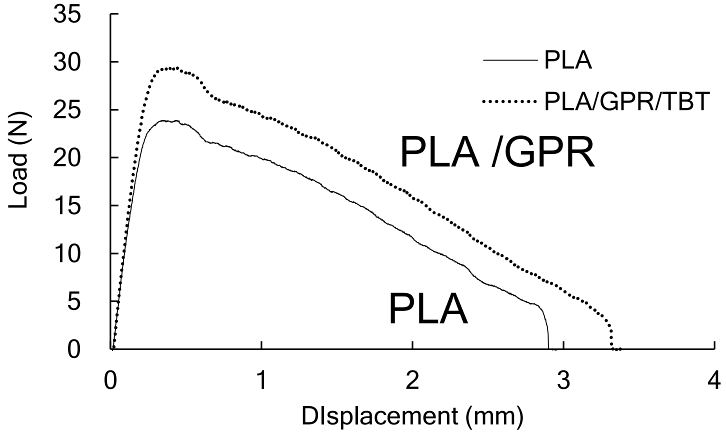
山形大学
Yamagata University

## Study on the relaxation of stress concentration at the tear tip

### (1) Previous achievement and remaining issue

**In the tensile test, toughness was successfully improved, however, tear properties were scarcely changed.**



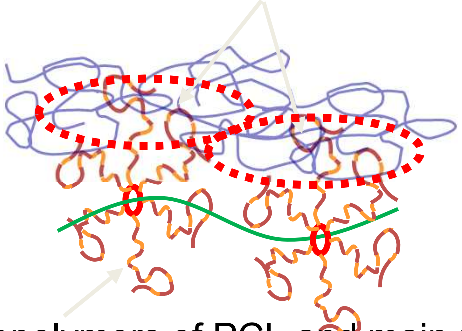

### (2) Situation in this year and next plan

**a) Confirm the graft reaction between matrix and domain polymers**

**Changes in relaxation time**

| | TBT added | Non-TBT |
|---|---|---|
| PBS/GPR | 25.7 s | 24.6 s |
| PLA/GPR | 0.45 s | 0.30 s |
| PGA/GPR | 6.6 s | 4.0 s |

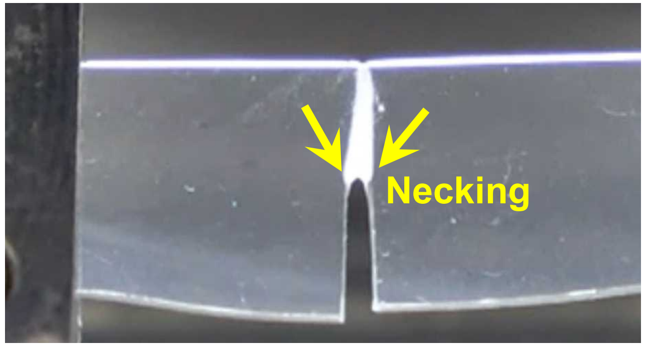
Entanglement of main polymers and branch chains



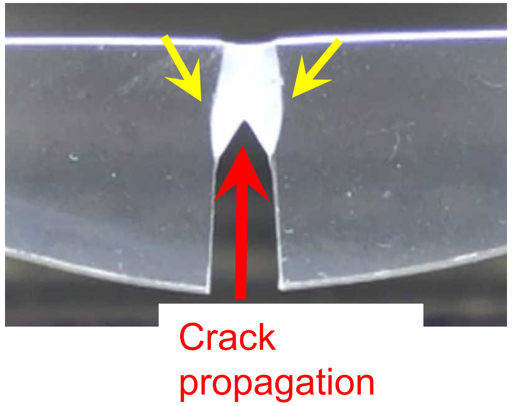
Graft copolymers of PCL and main polymer

**b) Proposal of two steps mechanism on relaxation in the film**

**First relaxation with nano-void formation at the necking point**




**Second relaxation at the tear tip**

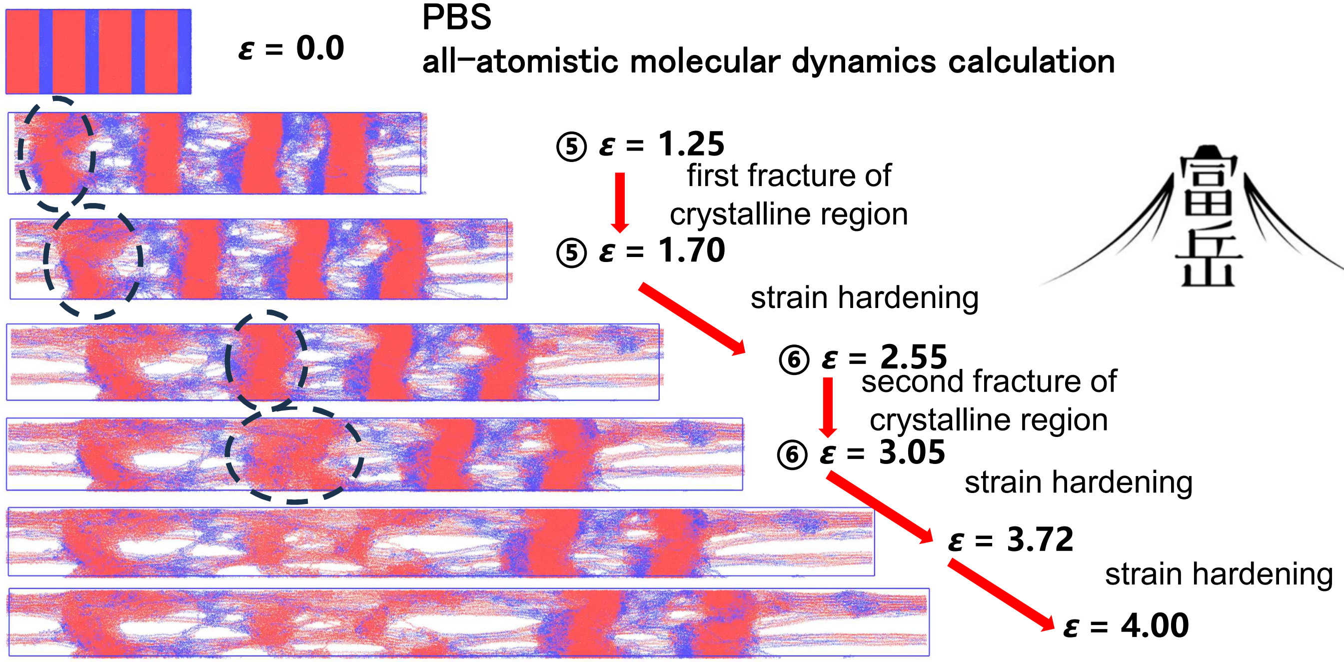


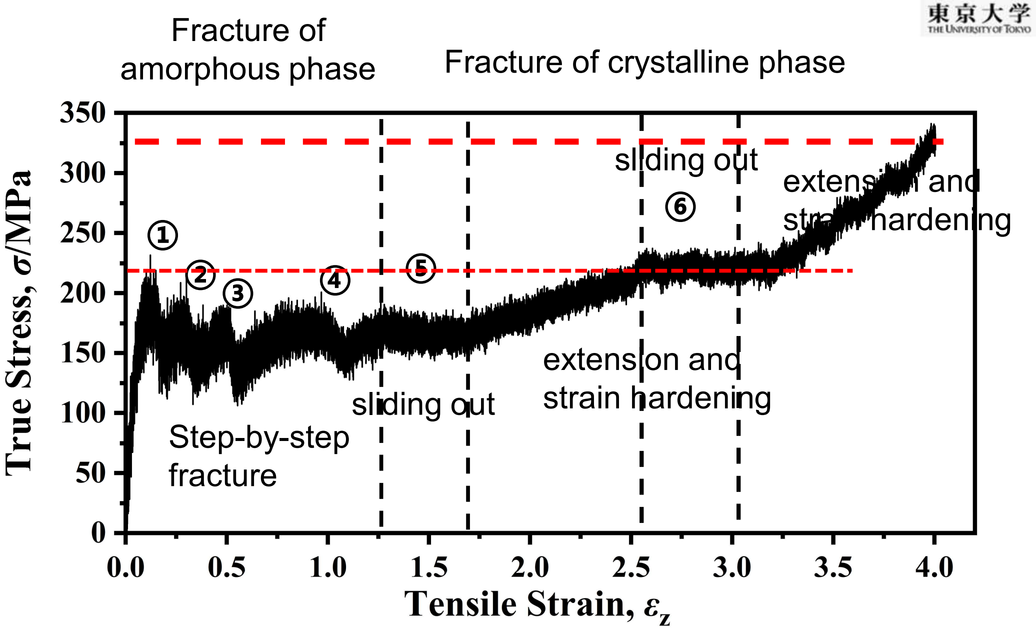
# Toughening of oceanic degradative polymers

University of Tokyo OKAZAKI, Susumu

MS伊藤PJ

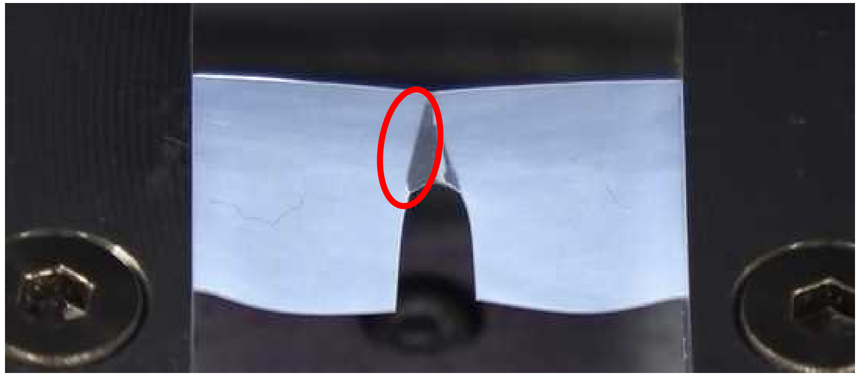
PBS
all−atomistic molecular dynamics calculation




**Molecular mechanism of fracture of lamella structures and necking**

1. first fracture of amorphous phase
2. fracture of crystalline phase before the dissociation of the main chain
3. extension of the unfolded chains and generation of the strain hardening
4. production of greater stress than the yielding stress of amorphous phase
5. new fracture of the amorphous phase at the terminal of the lamella region



Experiment by Ito group at Yamagata Univ.

# Contents

- フィールド試験
- スイッチ機能
- 強靭性の向上
- Research Progress (Academia)、企業）
- 国際連携

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

Kyushu University
Takahara, Atsushi

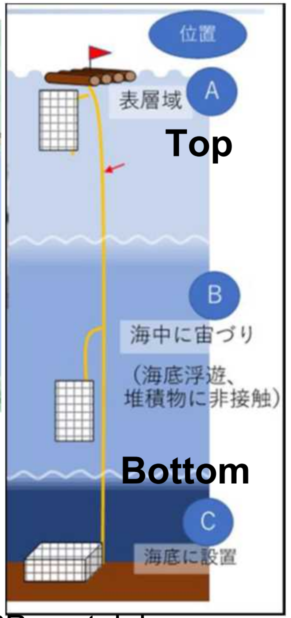
MOONSHOT RESEARCH & DEVELOPMENT PROGRAM NEDO

MS伊藤PJ

## Field test of polypropylene containing oxo-biodegradable additives (P-Life)

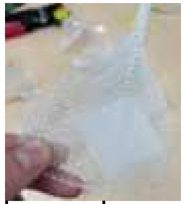
Field test (23.06-12)

Sample location


Samples were fixed in frame and immersed in seawater

Sample: PP containing oxo-biodegradable additive* (Mn salt of fatty acid, P-Life)

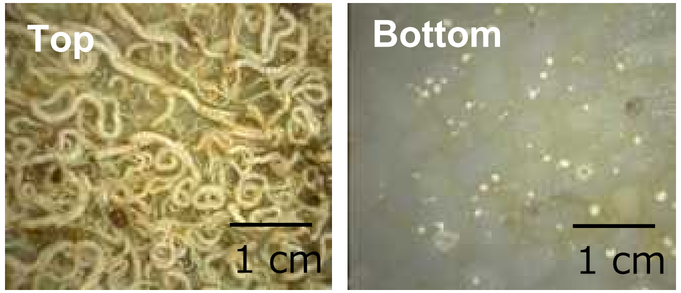


Purpose : To establish characterization method for field test samples

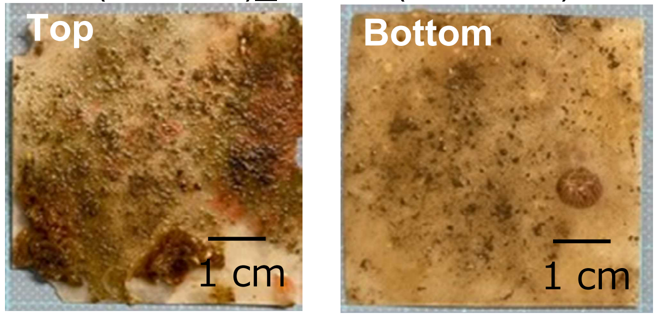
*Additives that induce oxidation under sunlight exposure was banned worldwide.

## Surface morphology

(2306-07)_Summer (1 month)

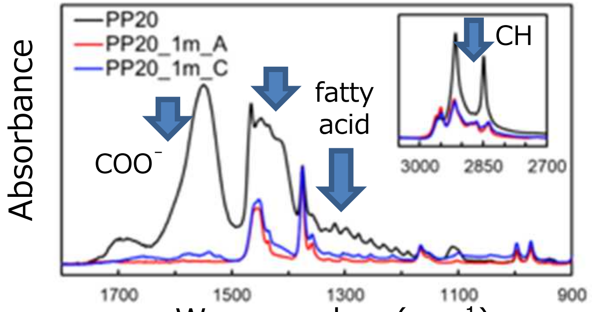



(2306-12)_Winter (6 months)



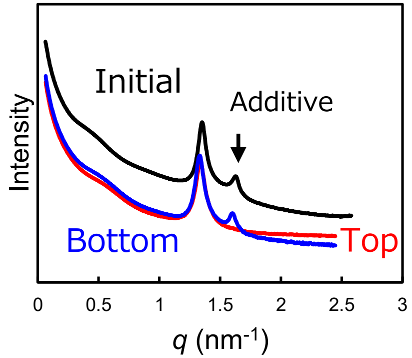

## Characterization of P-Life/PP

FTIR-ATR (1 month)




Additive was disappeared after 1 m field test

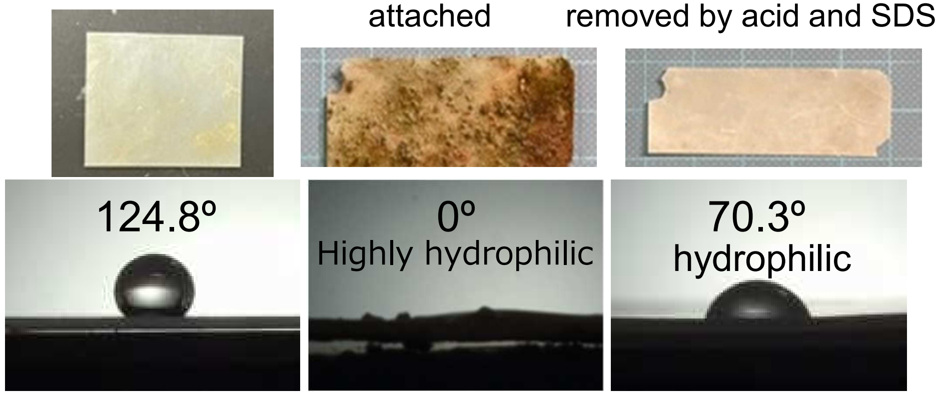
## Small angle X-ray scattering( 1 month)




Disappearance of scattering from oxo-biodegradable additives. Additives were photo-oxidized and dissolved in seawater.

## Water contact angle (6months)

Initial | Microorganisms attached | Microorganisms were removed by acid and SDS




Surface became hydrophilic because of the attachment of microorganisms and photooxidation of polymer.

Contact angle, FT-IR, and X-ray scattering are useful techniques for characterizing the surface properties of field test samples.

# Modeling for fragmentation and sinking process

Ehime University, Hirofumi Hinata

MS伊藤PJ

## ■ Modeling for fragmentation process

Temporal changes in the size distribution of foamed polystyrene (FPS) generated from the milling test

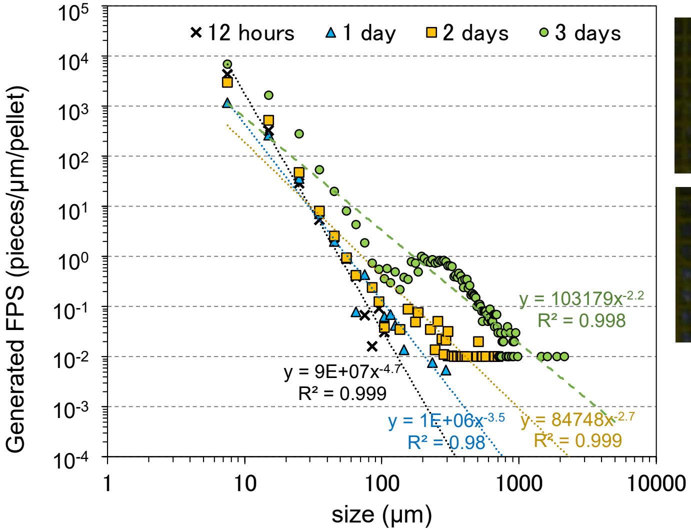
Pot mill (PM-002, AS ONE)

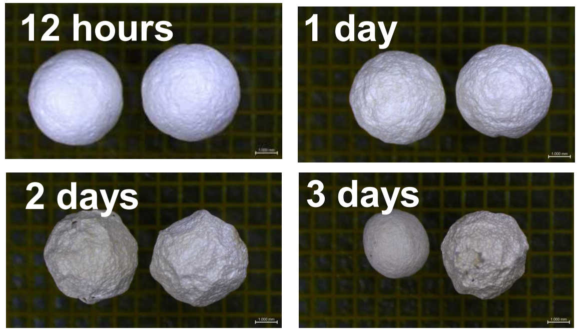
Number of generated FPS particles = Milling test − Blank test

- Milling test: Sand, Ultrapure water, Virgin spherical FPS pellet
- Blank test: Sand, Ultrapure water

Four cases in which the milling time was changed were conducted.

Generated FPS (>5 μm)

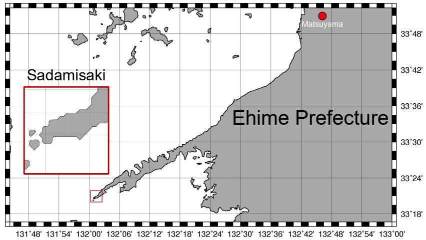


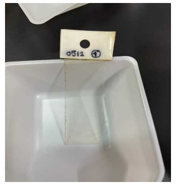
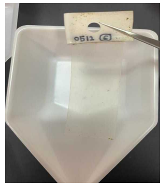



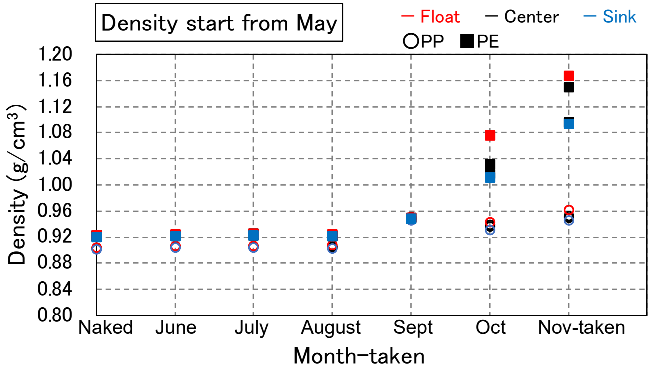

FPS particles larger than 100 μm were generated over 1 day.

## ■ MP sinking process model

Plastic incubation at Sadamisaki for analyzing biofilm growth




| Started from May | June-taken | July-taken | August-taken | September-taken | October-taken | November-taken |
|---|---|---|---|---|---|---|
| **Polypropylene (PP) sample**<br>Size 8 × 2 cm<br>Thick 0.2 mm |  |  |  |  |  |  |
| **Polyethylene (PE) sample**<br>Size 5 × 7 cm<br>Thick 0.04 mm |  |  |  |  |  |  |




We measured the density of plastic samples and the environmental data.

# Development of evaluation of Multi-Lock Biopolymers

CERI, Takako Kikuchi

MOONSHOT RESEARCH & DEVELOPMENT PROGRAM NEDO

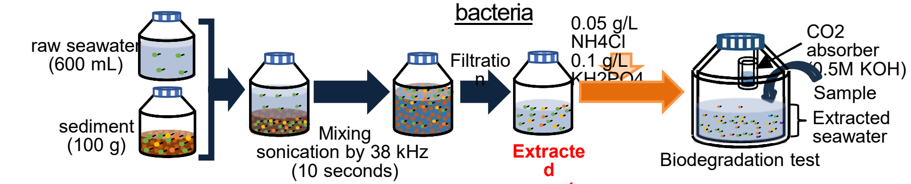
CERI MS伊藤PJ

## (1) Development of the accelerated test method for marine biodegradability

### Outline of development method

Simple operation and quick preparation

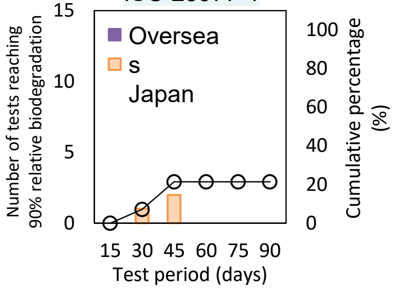
(1) Increasing number and diversity of bacteria (2) Increasing number and diversity of bacteria

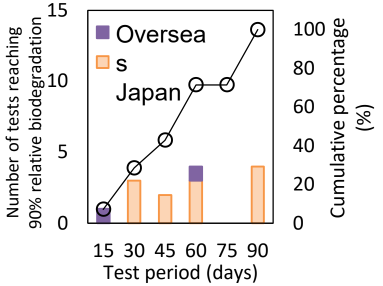



### Validation of the accelerated testing method

（1）15 marine areas in Japan（2）English Channel and Gulf of Thailand

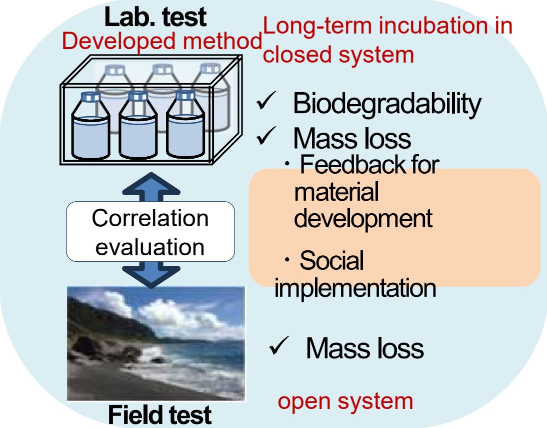
Percentage of testing and duration of testing to reach 90% relative biodegradability of PCL



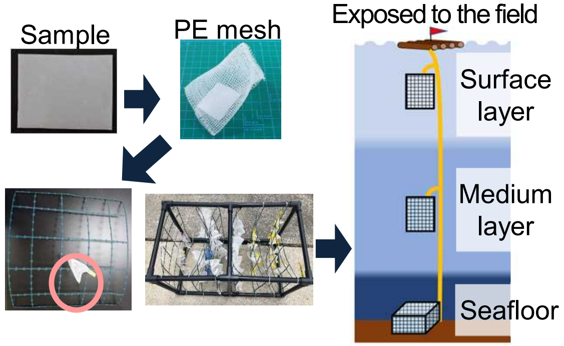



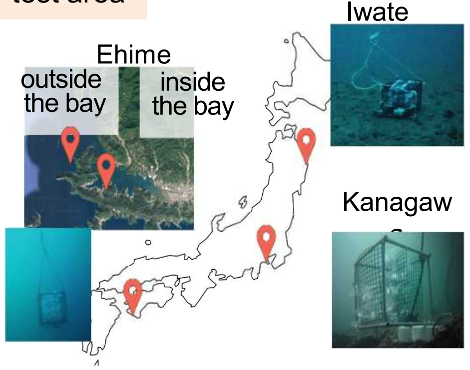

In all areas tested, the accelerated test method was found to be effective in assessing the marine biodegradability potential of the materials.

## (2) Comparative verification of biodegradation rates in the field and in the laboratory

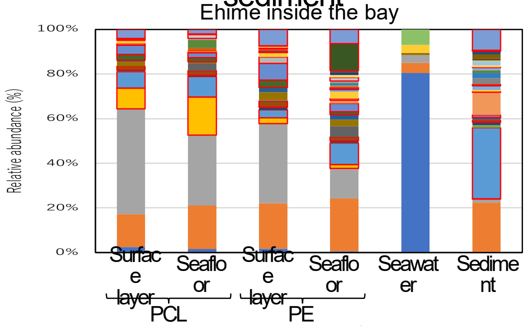



### Overview of field tests



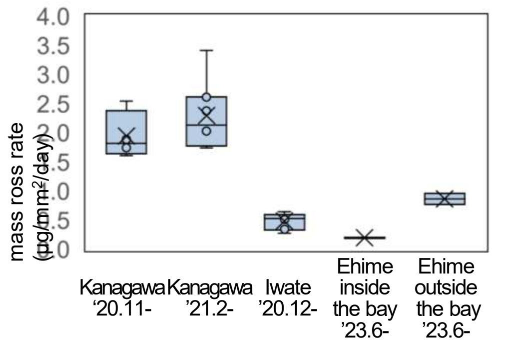




### Phylum level microbial communities of biofilm on plastics, seawater, and sediment



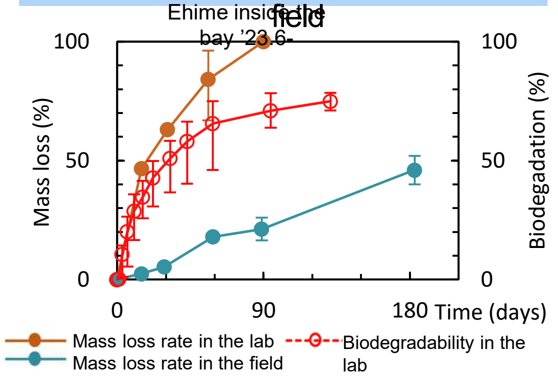

Microorganisms derived from sediment were present in the biofilm of samples exposed on the surface layer.

### PCL initial degradation rate in 5 sea areas




The degradation rates depend on marine area of each

### Comparison of degradability in lab and field




The degradation rates in the lab test diffr from that in the field test

In the future, enzyme activity and genetic analysis of the biodegradation process will be carried out.

We want to find a correlation between the laboratory and the field.

# Contents

- Research Progress (Companies)

# Mitsubishi Chemical Corporation
# Research and development of marine degradable multi-lock biopolymers from inedible biomass

MS Ito PJ

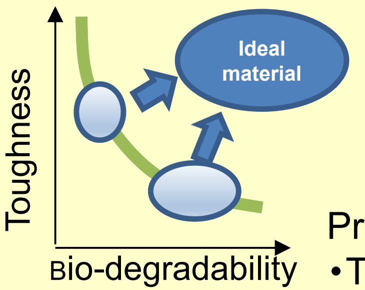
## Concept and objectives

【Objectives】The purpose is to develop a bioplastic that incorporates a multi-locking mechanism in aliphatic polyesters produced from inedible resources and that quickly biodegrades in seawater after being unlocked by multiple external stimuli. We also aim to toughen biodegradable plastics while maintaining good biodegradability by introducing dynamic cross-linking or supramolecules and optimizing of higher-order structures.

In this work, we will investigate the introduction of multi-locking mechanism and toughening of polybutylene succinate(PBS).

【Concept】Moonshot program led by the Cabinet Office

Achieve both high toughness and high biodegradability




- Tough enough to use without problems
- Decomposed into $H_2O$ and $CO_2$ in natural environments

**Overwhelming material development capabilities by the industry-academia-government collaboration**

Problems

- Tough polymers are hard to decompose ⇒ environmental issues
- Physical properties of biodegradable polymers are insufficient

## Targets

- FY2022 Intermediate Target: Proof of the multi-locking concept
  - Degradation rate is more than 3 times higher for multiple external stimuli than for a single external stimulus.

- FY2024 Intermediate Target : Achieve both high toughness and multi-locking mechanisms
  - Degradation rate is more than 10 times higher for multiple external stimuli than for a single external stimulus.
  - 5 times higher tear strength than existing aliphatic polyesters

- FY2027 Intermediate Target : Demonstration of the Bench-scale production
  - Can be manufactured in scales of 20 kg or more

- FY2029 Final Target: Achieve the followings with scaled-up products
  - Marine biodegradation after unlocked :40% biodegradability in sea water (25℃) in 30 days.
  - Tear strength: More than 10 times that of existing biopolymers
  - Polymer production on a scale larger than bench scale

# Mitsubishi Chemical Corporation
# Research and development of marine degradable multi-lock biopolymers from inedible biomass

MITSUBISHI CHEMICAL GROUP

MOONSHOT RESEARCH & DEVELOPMENT PROGRAM NEDO

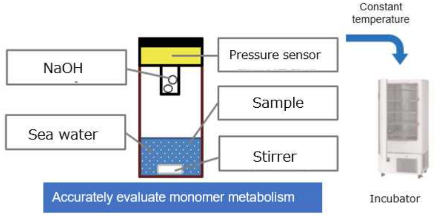
MS Ito PJ

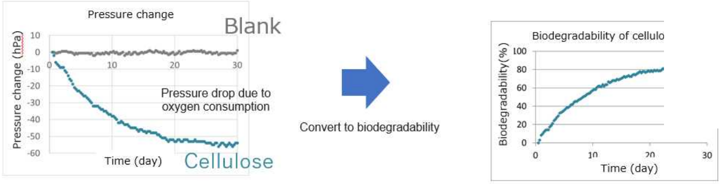
## Biodegradability of copolymerized polyesters

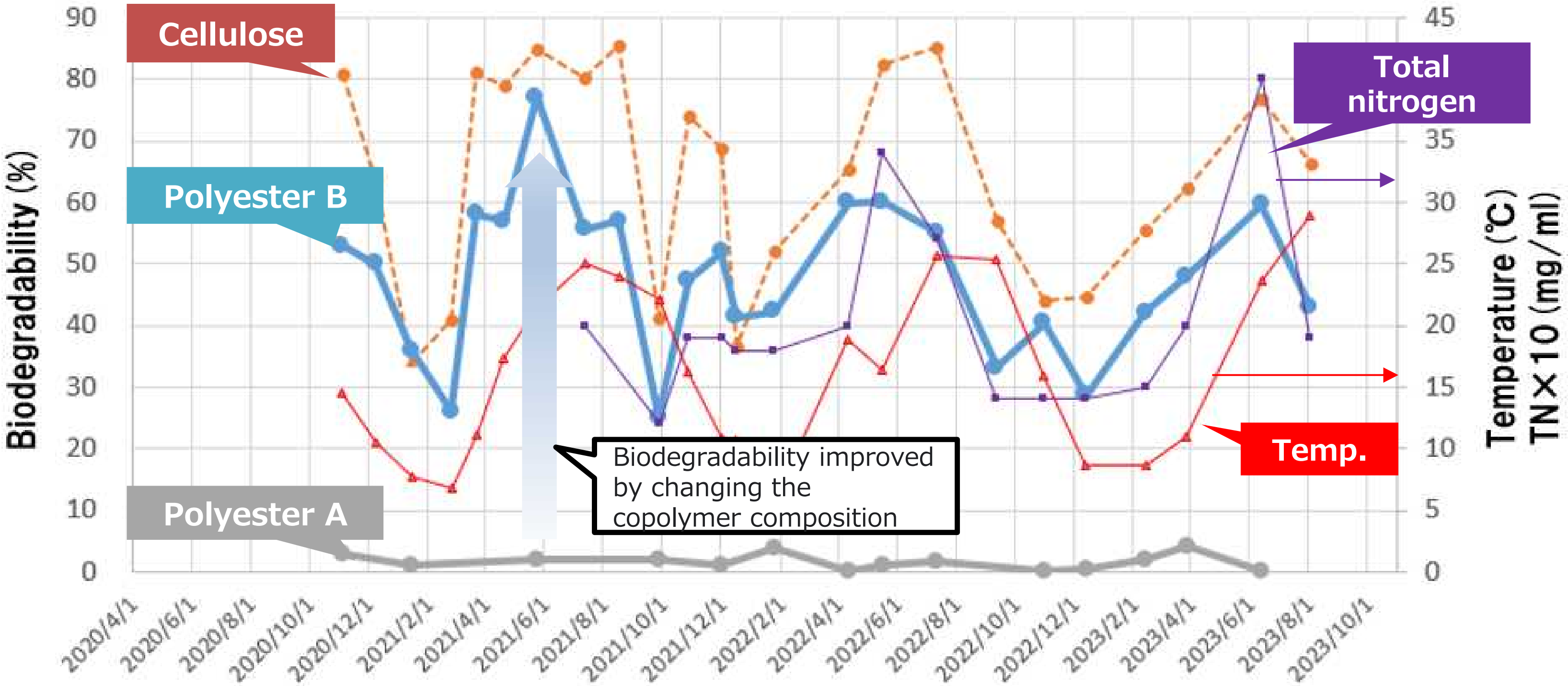
・Evaluation of seasonal changes in biodegradability of cellulose and polyesters A and B using seawater sampled at a fixed point (Tokyo Bay)


BOD: Biochemical Oxygen Demand

Biodegradability is calculated from the amount of oxygen consumed during the metabolic process of biodegradation.




- Seawater biodegradability has been significantly improved by changing the copolymer composition (polyester A → B)
- Polyester B, like cellulose, maintained relatively high biodegradability throughout the year.
- The biodegradability of polyester B and cellulose is correlated with the total nitrogen content in seawater.

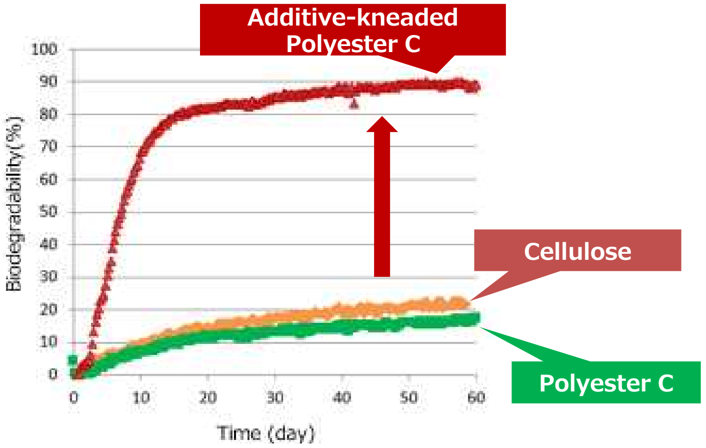
# Mitsubishi Chemical Corporation
# Research and development of marine degradable multi-lock biopolymers from inedible biomass

MITSUBISHI CHEMICAL GROUP | MOONSHOT | NEDO

MS Ito PJ

## BOD of biodegradation promoter-kneaded polyester

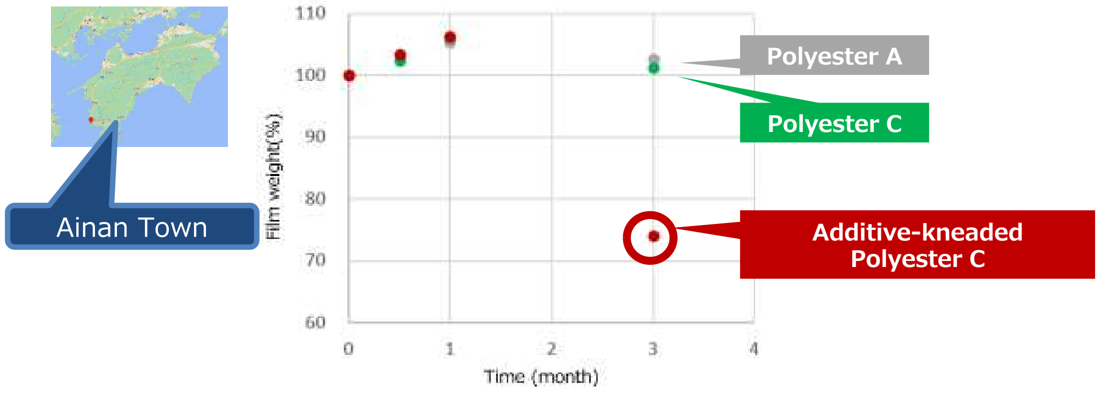
・Various additives were kneaded into Polyester C and biodegradability was evaluated.




・Significantly improved biodegradability by kneading-additives
・Biodegradation promoted by the action of microorganisms in seawater and additives
・Achieved speed-control

## Field test

・Participated in a field test conducted by Ito Project in Ainan Town, Ehime Prefecture
・Evaluation of weight change of various polyester films of 3cm x 3cm x 200μm



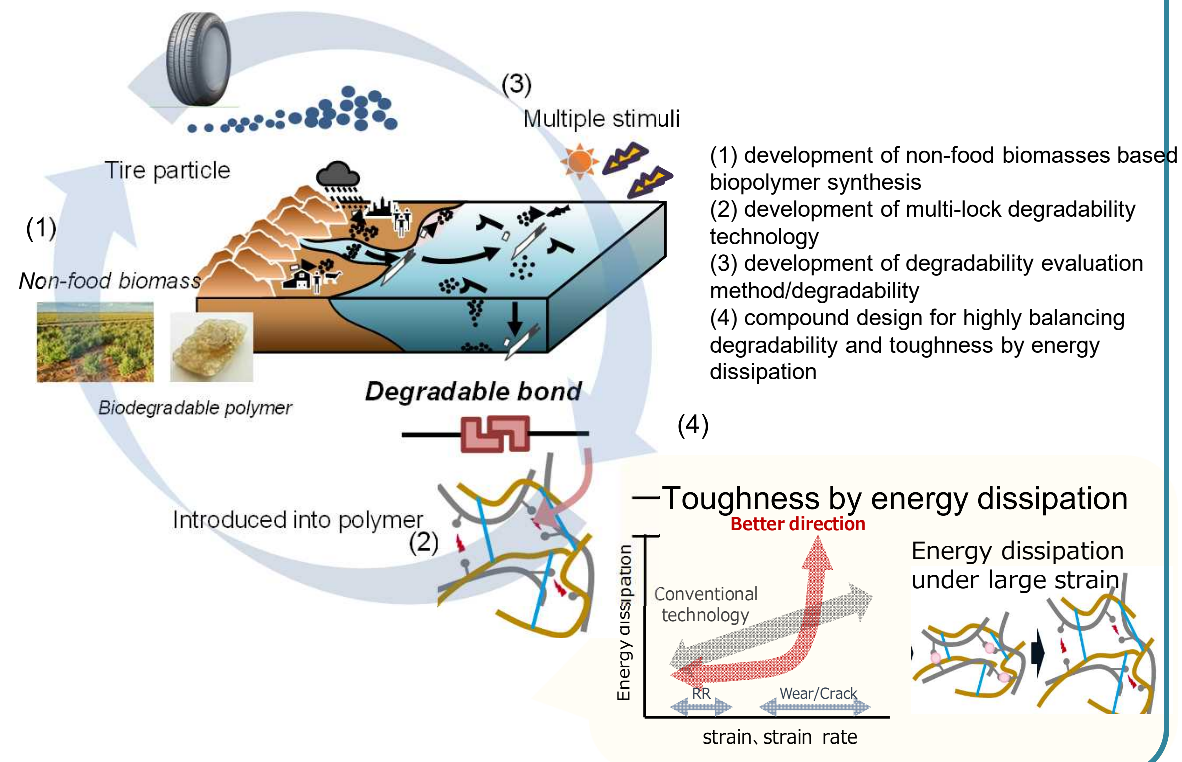

・Significant weight loss after 3 months of additive-mixed polyester C installed on the surface of seawater
・Showed point-controlled decomposition behavior

# Bridgestone Corporation
# Development of Non-Food Biomasses Based Biodegrade Rubber Compound in Wear Particle for Tire

MS伊藤PJ

In recent years, there has been growing concern about the influence of tire wear particle on the environment. While its substantial contribution to the environment is still debatable, technological development is desired from a view of environmental pollution/circulation of resources. In this study, we aim to solve these issues by developing non-food biomasses based multi-lock tough polymer which can be decomposed by multiple stimuli. Combined with the toughness technology by energy dissipation proposed in ImPACT project (2014-2019), the developed tough polymer is applied to tire tread, and it demonstrates toughness by effective energy dissipation in use and quickly decomposes by multiple stimuli (microorganism and combination of light, heat, oxygen, etc.) after use in the state of wear particle.

―Biodegradation cycle of tire wear particle―




(1) development of non-food biomasses based biopolymer synthesis
(2) development of multi-lock degradability technology
(3) development of degradability evaluation method/degradability
(4) compound design for highly balancing degradability and toughness by energy dissipation

BRIDGESTONE

# Multi-lock disassembly mechanism development approach

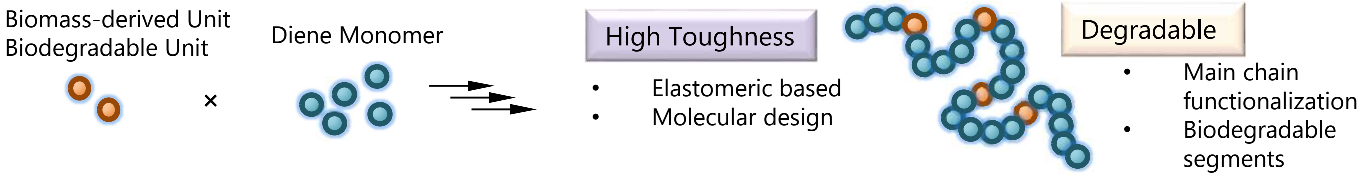
MS Ito PJ

★ Two locks must be unlocked for the rubber to biodegrade!

【 Development of biodegradable polymers for low molecular weight 】

Polymer Design in Academia Collaboration
Plant-derived monomer × diene rubber copolymer
Biodegradable polymer × diene rubber copolymer
Introduction of biodegradable unit into diene rubber

Polymer Design:

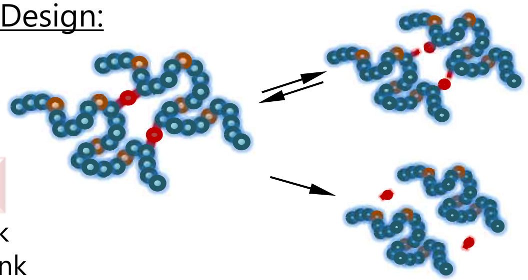



【 Reversible/degradable bond development for low cross-link density 】

Academia Collaboration in achieving both toughness and biodegradation
Bonding Design / DCL Design

Crosslinked Polymer Design:

Alternative crosslink
• Reversible crosslink
• Degradable crosslink

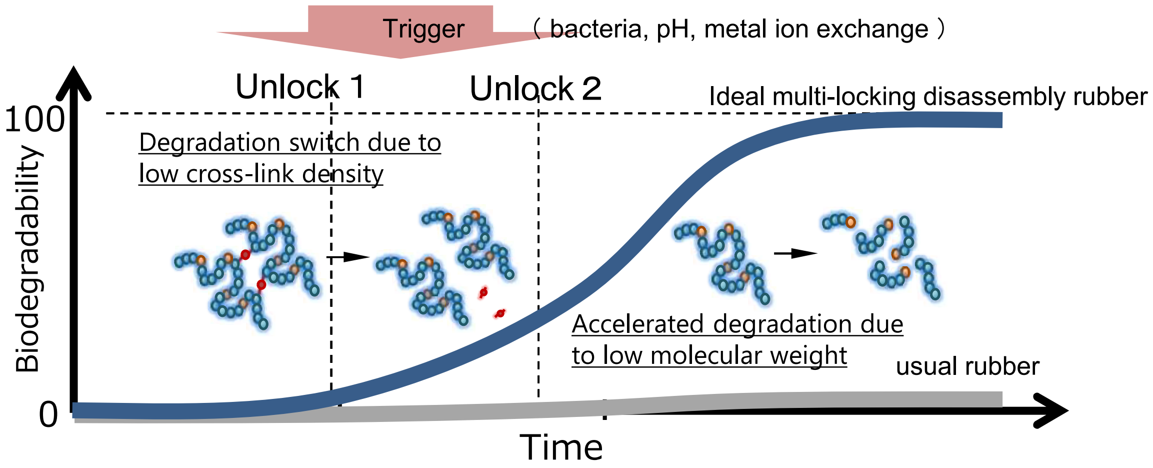



【 Targeted multi-locking disassembly scheme 】

Triggering environmental conditions in tire wear powder condition


IUCN report 2019, Review of plastic footprint methodologies

| Place | Difference from tire use conditions |
|---|---|
| Road | Prolonged UV, soil bacteria, high temperatures |
| River | Soil bacteria, high temperature, pH (about 6-8, weak acid to weak alkaline) |
| Coast | Prolonged UV, soil bacteria, high temperatures |
| Ocean | Marine bacteria, pH (about 8, weak alkaline), pressure, metal ions (Na+, Mg2+), salinity, amino acids, proteins etc. |

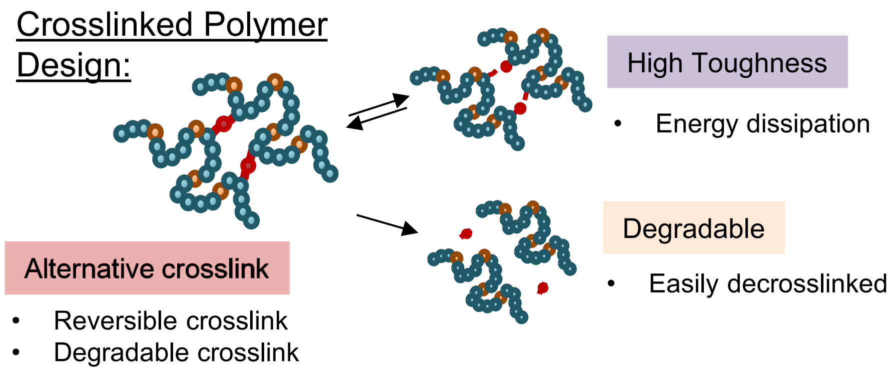



Aiming to improve biodegradability by controlling low molecular weight and low cross-link density

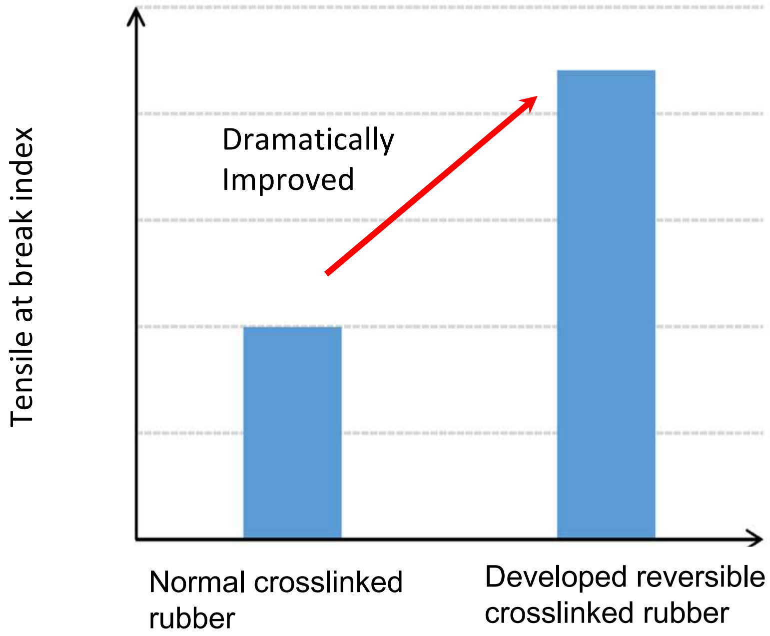
# Technology for balancing biodegradation and toughness by reversible cross-link

MS Ito PJ

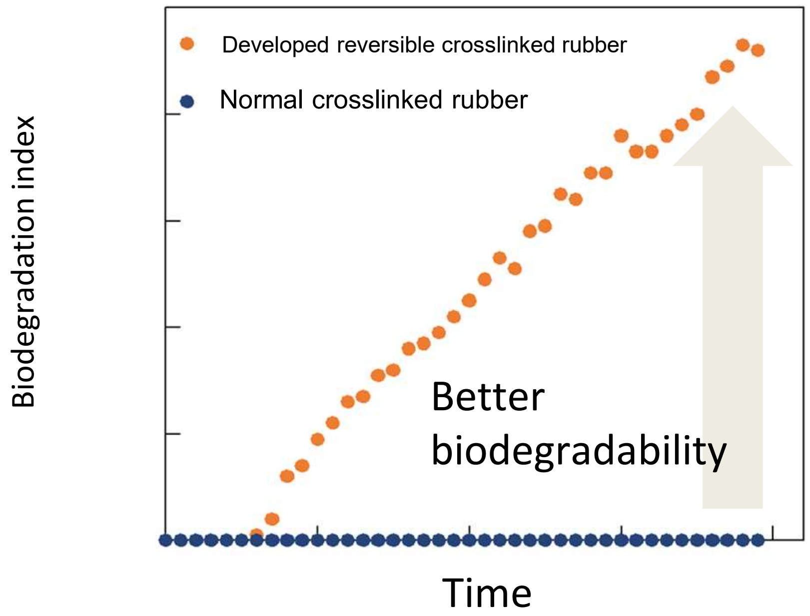
With extending reversible bond technology that strengthen rubber by effective energy dissipation, we newly designed degradable cross link system cooperating with academia.




—Physical property test result—



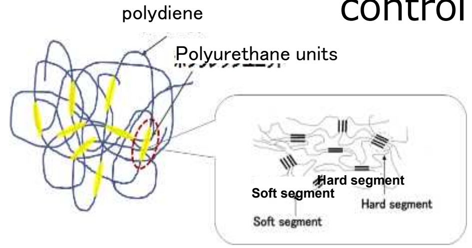

—Marine biodegradation test result —

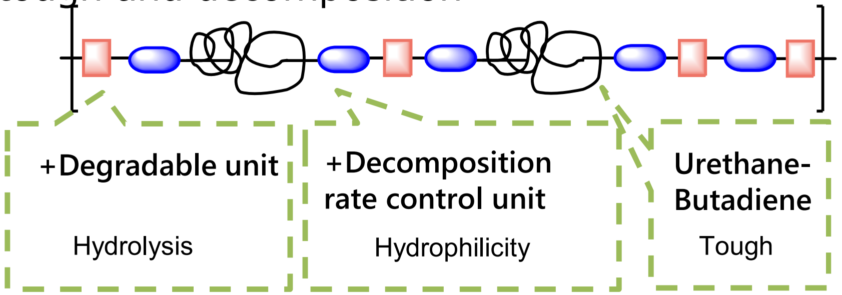



**Both toughness and biodegradation are both significantly increased by introducing reversible and degradable cross-links**

# Technology for highly balancing biodegradation and toughness by introducing multi-lock system

-Polymer Design- Introduced lock unit to diene rubber polymer chain to control tough and decomposition



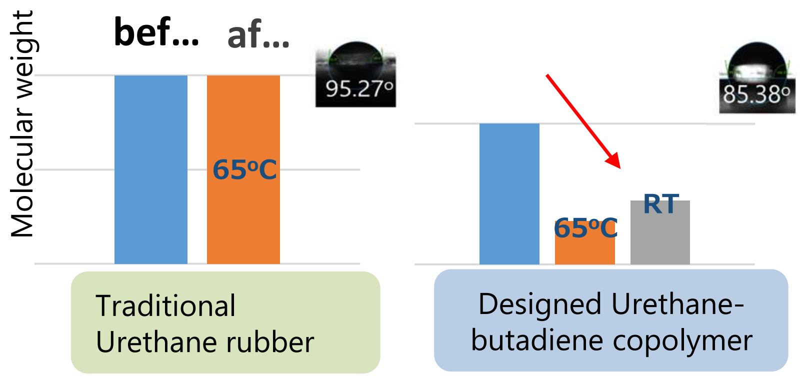




Focus on reversible bond of urethane

⇒ Tough diene copolymer with multi-lock mechanism was developed

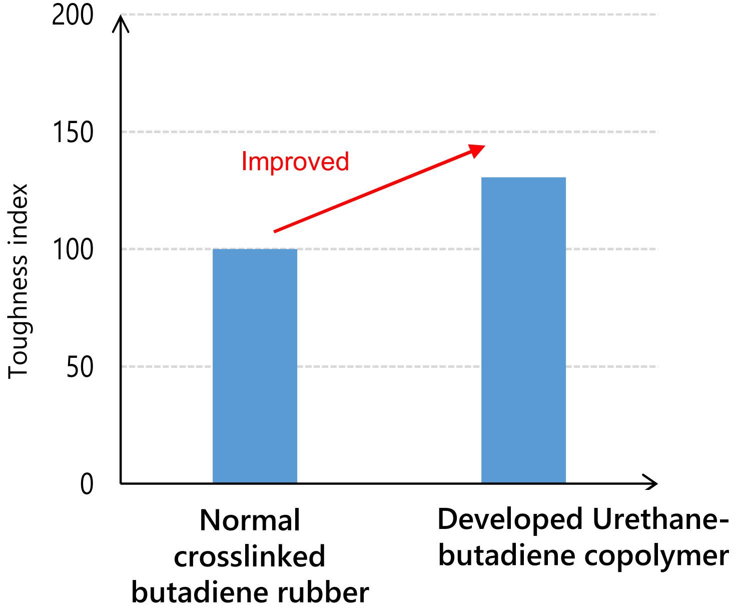
−lab decomposition test result −

in alkaline condition



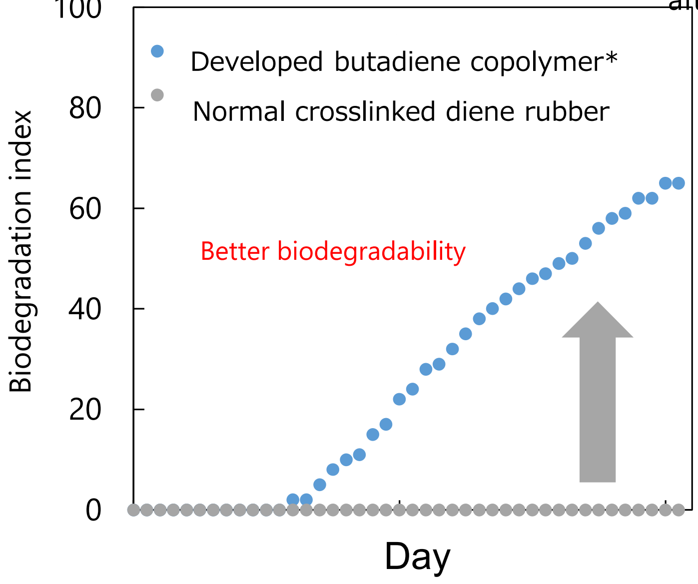

Fast decomposition by multi-stimuli

−Physical property test result−




−Marine biodegradation test result −

*after alkaline condition




Tough diene copolymer with multi-lock mechanism was developed. More than 10 times higher degradability without sacrificing toughness was achieved.

# Development of strong and degradable biopolymers for fishing nets

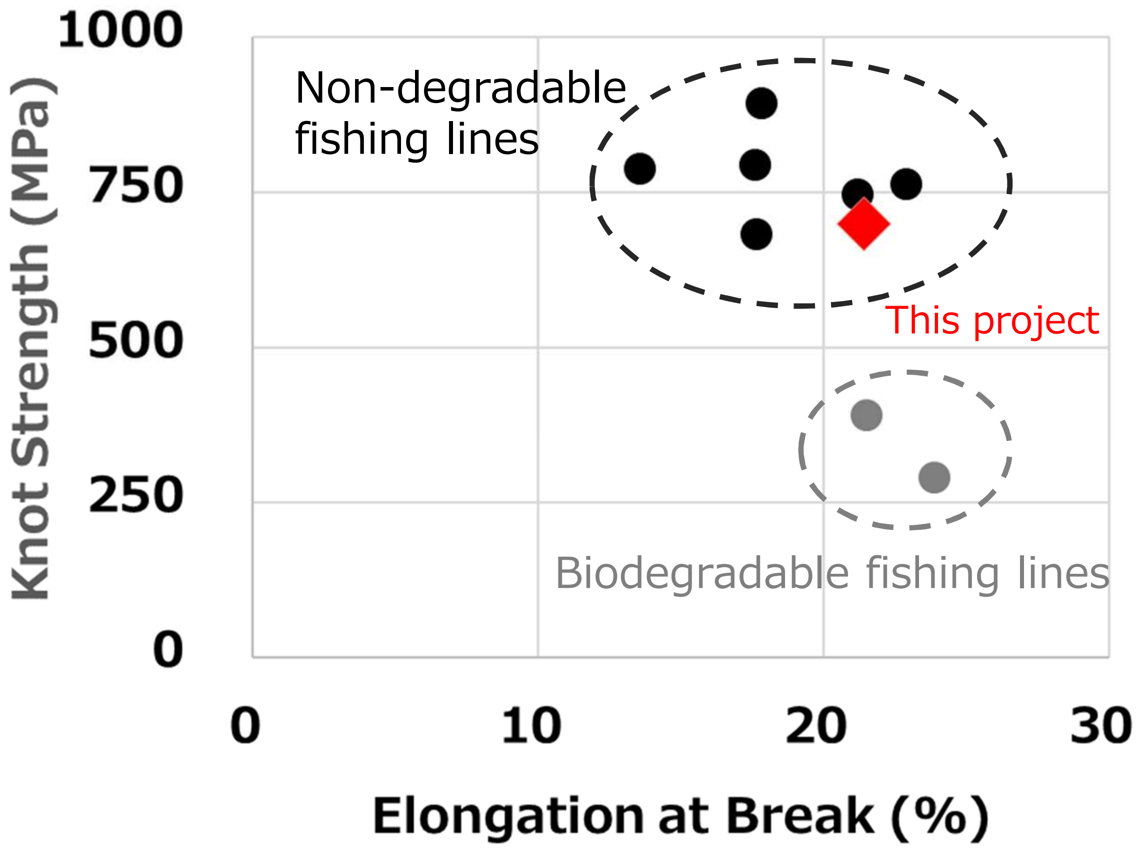
KUREHA CORPORATION

Application of biodegradable polymers towards marine plastic pollution have been investigated. However, there are still remain many problems, for example, the degradation of one of the polymers are quite low in the ocean.

Biodegradable polyamide (PA) and polyglycolic acid (PGA) degrade in sea water and they have extensive high mechanical strength associated with high concentration of amide group or ester group.

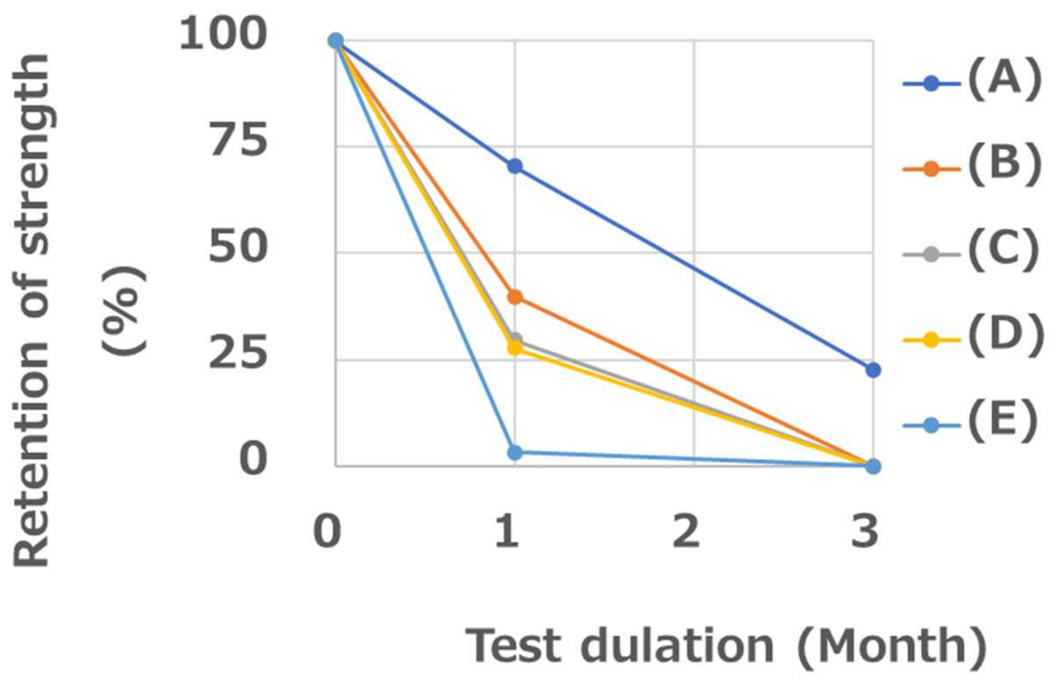
Degradation product of biodegradable PA is amino acid (AA) and that of PGA is glycolic acid (GA). AA and GA exist in natural environments so the impact of them to marine environment is assumed very small. In this project, we develop strong and degradable biopolymers based on PA and PGA for fishing gears.

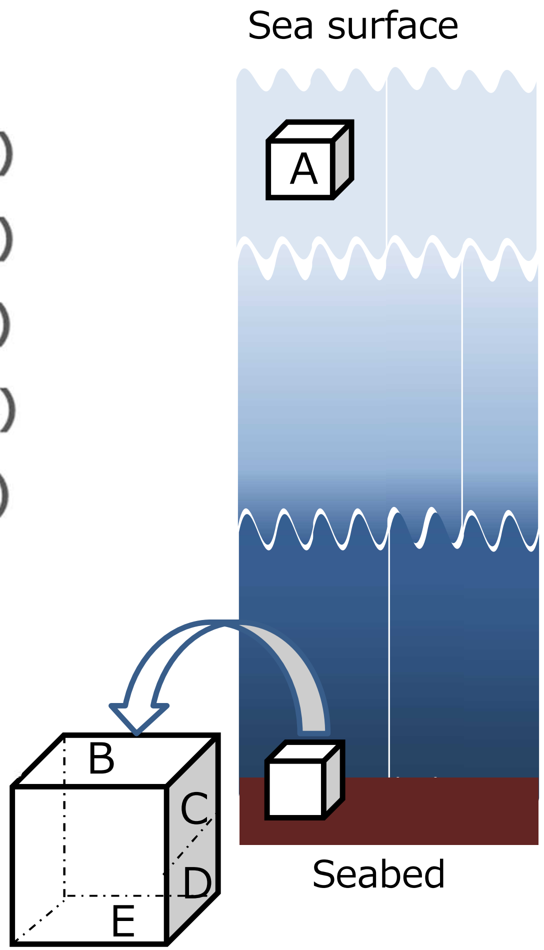
- Knot strength vs. elongation of fishing lines

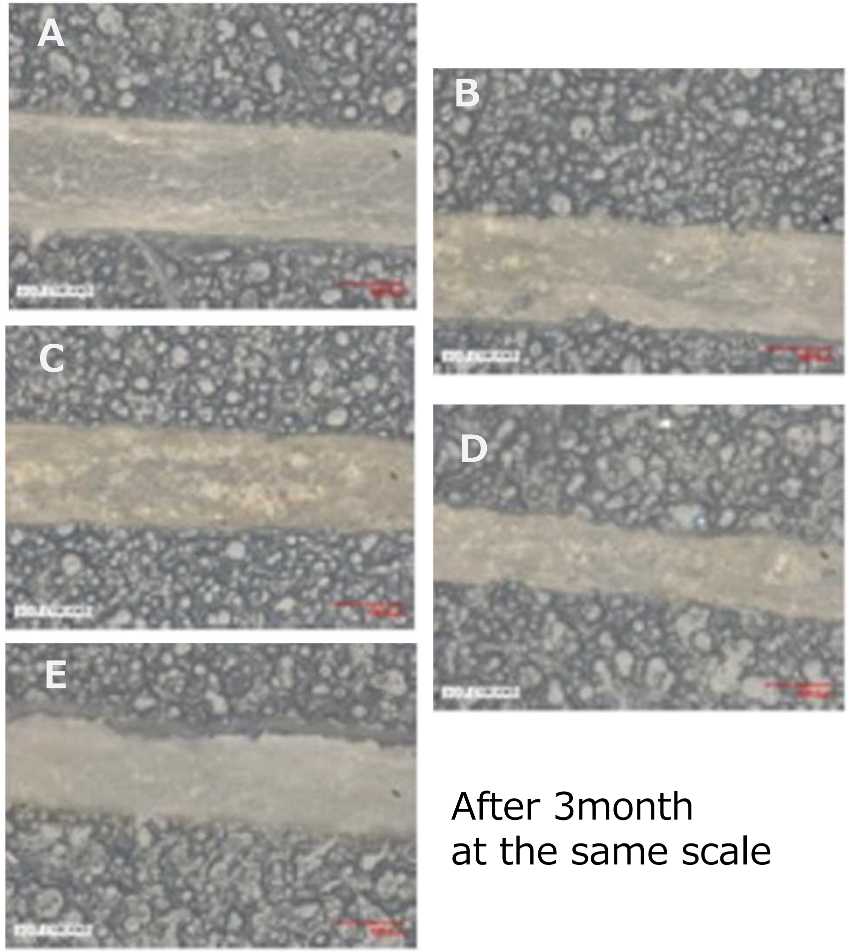


# Biodegradation of developed fiber (Field Test)

- Change of strength (Biodegradable polyamide)



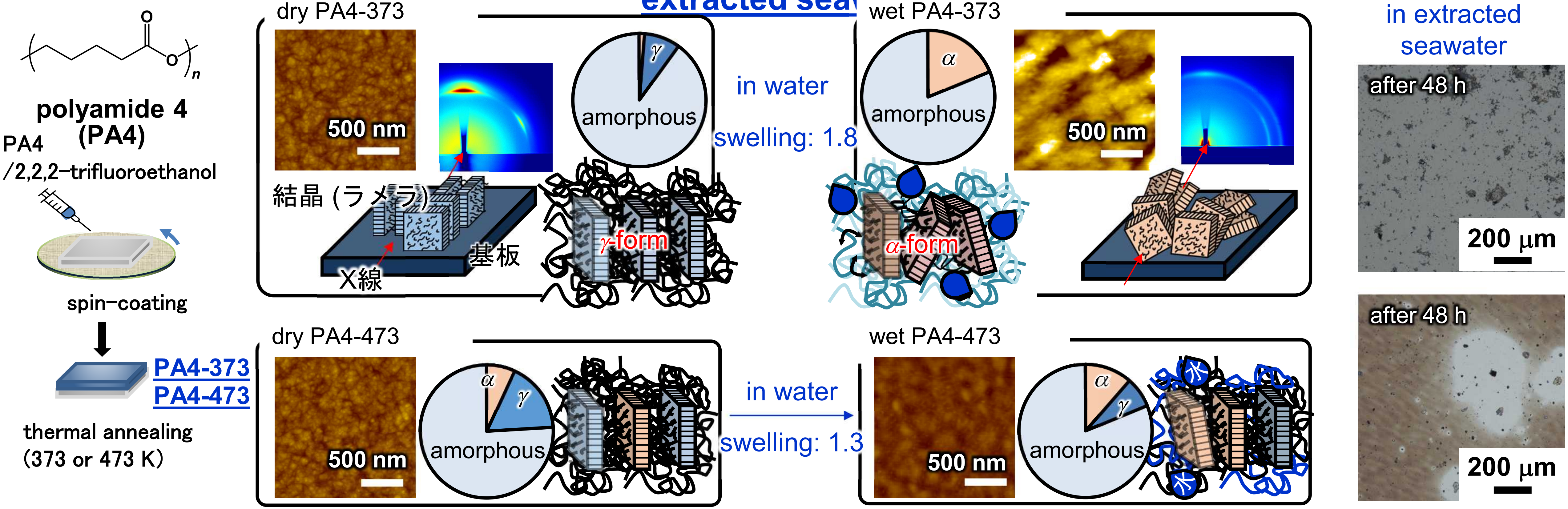

After 3month
at the same scale

MS伊藤PJ

# Analysis and Regulation of Degradation Behaviors of Biopolymers in Underwater Environments

Yamagata University; MATSUNO, Hisao

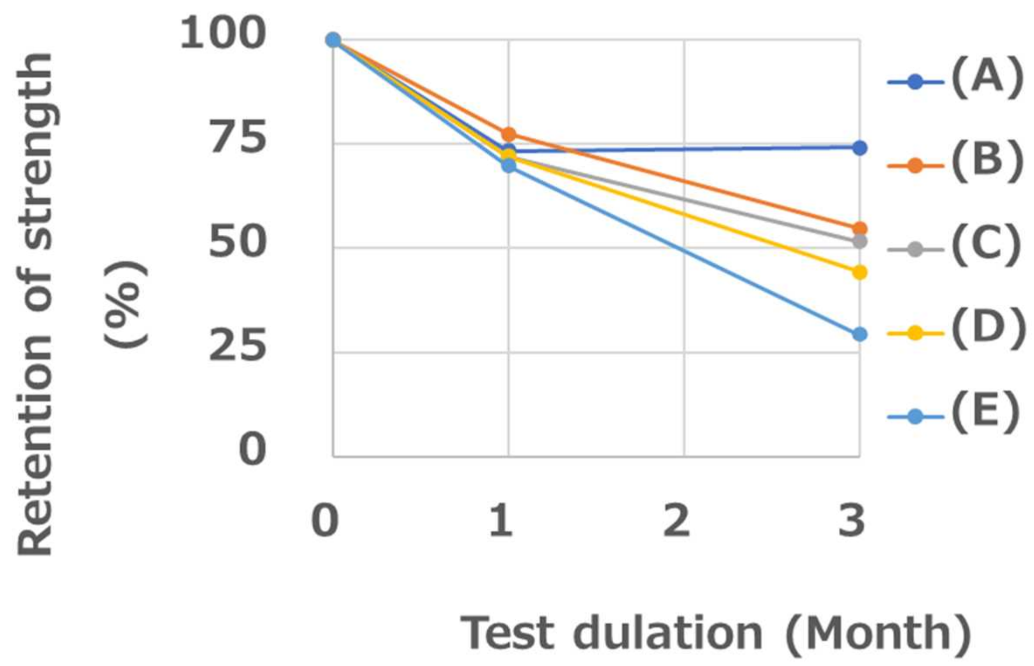
## Crystal polymorph-dependent degradation behaviors of polyamide 4 thin films by extracted sea



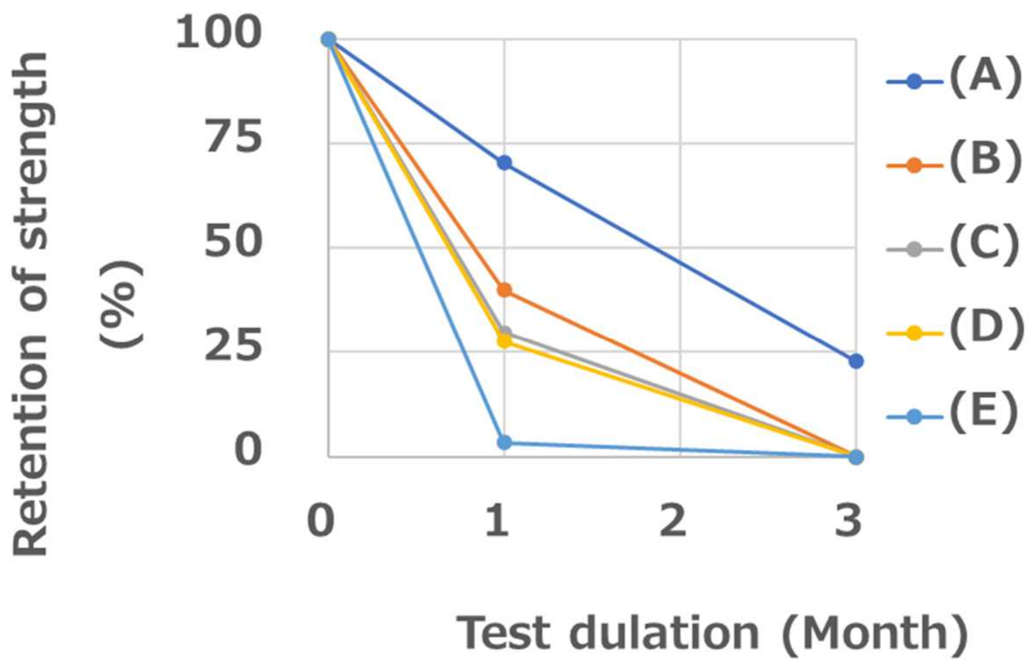

The PA4 thin film contained a mixture of α- and γ-form crystals, and the abundance ratio depended on the annealing temperatures. The PA4-373 thin film with few α-form and lower crystallinity adsorbed more water molecules. In both thin films, γ → α crystal transition occurred with water adsorption. It was found that the PA4-373 thin film, which adsorbs more water molecules, was degraded faster by extracted seawater, and the initial crystal structure affected the degradation behaviors.

# Control of biodegradability

- After modification




- Before modification (same data in previous slide)



# Total Publications

## Papers 69（published）

*Polym. Chem.* *12*, 1186-1198 (2021). (Front Cover, Hot Paper)
*Macromolecules* *54*, 6440-6448 (2021)
*Environmental Pollution* 310 (2022)119811
*Angew. Chem. Int. Ed.* 2023, *53*, e20215021　など

## Review, Books 21

## Patents　25 (Including 14 for companies)
⇒**PCT 11** (Including Country migration 2)

## Invited Lectures　190（Domestic : 123、Oversea : 67）
## Presentations 314（Domestic : 257、Oversea : 57）

## Awards　51

## Press Release　63（Including oversea 26）

2022/10/13 Nikkei Electronic Edition "Discovery of New Adsorption Mechanism of Polymer
2022/10/30 NHK News, "Long-Term Changes in MP Deposition" (Japanese only)
2022/11/21 Nagoya University/Tokyo Institute of Technology Press Release "Development of Degradable Polymers
2022/12/1 Nikkei Electronic Edition, etc. "Development of Degradable Vinyl Polymers
2022/12/9 Nikkei Shimbun "Development of Marine Biodegradable Fishing Line
2023/6/11 NHK Special: The Human Age / The Anthropocene - Desire to engulf the Earth - Achievement University
2023/9/3 The Yomiuri Shimbun "Development of plastic that does not remain in the ocean
2023/10/31 University of Tokyo Press Release "Success in Fabrication of Highly Functional Resin Containi Polyrotaxane that Stretches, Heals, and Degrades


クレハなど漁具用開発
海洋生分解性プラスチック
Tech ワード
海ごみ対策、国際規格目指す
クレハは強度を保ったまま海洋でも分解しやすい漁具用高分子を開発した＝同社提供


化学工業日報
2020年(令和2年) 12月22日 火曜日
海洋プラ問題解決へ
ムーンショット始動
東大・伊藤教授ら
複数の刺激で生分解
プラ・タイヤなど 耐久性と両立
三菱ケミ・BS・帝人・クレハが参画


「人新世」地質時代に加わるか
始まりの痕跡地 別府湾も候補


日本経済新聞
高分子、分解前後の長さ自在　名古屋大学が合成法


海のマイクロプラスチック20年周期で増加か 別府湾の海底調査
2022年10月30日 4時09分
海の生態系への影響が懸念されている「マイクロプラスチック」について、愛媛大学などの研究チームが大分県の別府湾の海底を調べた結果、1960年ごろから20年周期で増えていることが分かり、海洋汚染の実態解明に向けた手がかりになるとしています。

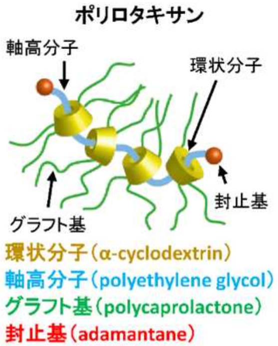


2023年(令和5年)9月3日(日曜日)
海に残らない「プラ」開発
マイクロプラスチックの現状や対策
海で完全に分解する「海洋生分解性プラスチック」
釣り糸 短期間で完全分解
微生物パワーでMP解消
サイエンス Report

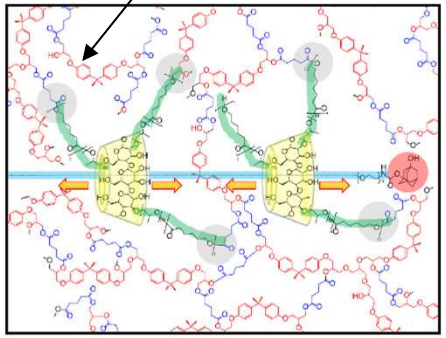
# PR-added epoxy-based vitrimer with marine biodegradability

Shota Ando
Kohzo Ito

## Toughening Study of Polyrotaxane–Doped Epoxy Vitrimer Resin

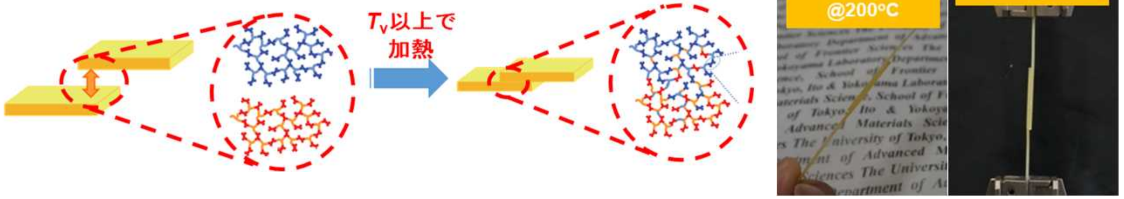



Epoxy–based vitrimer cross–linking network



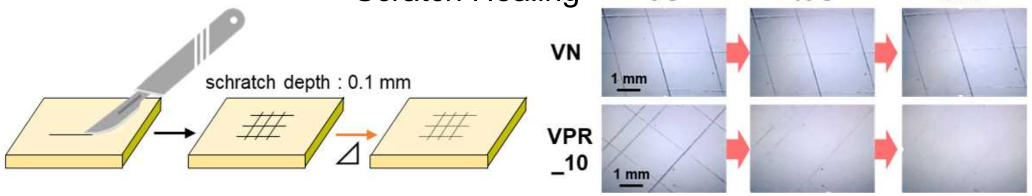
Chemically bonds and homogenously disperses PR and cross-link networks through bond exchange reactions

Weldability

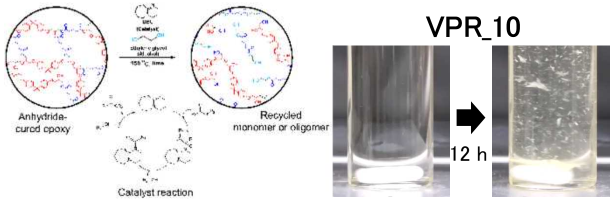



In addition to the toughening due to the addition of PR, the energy potential of the bond exchange reaction due to sliding motion is reduced.

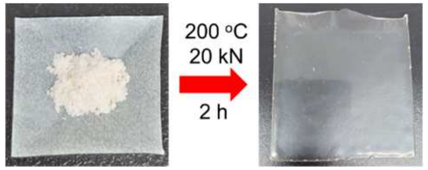
Scratch Healing

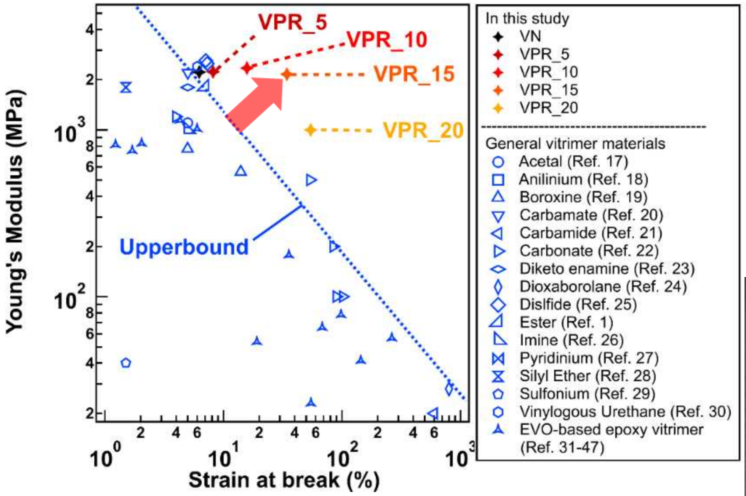



Chemical Recyclability




Reproessability



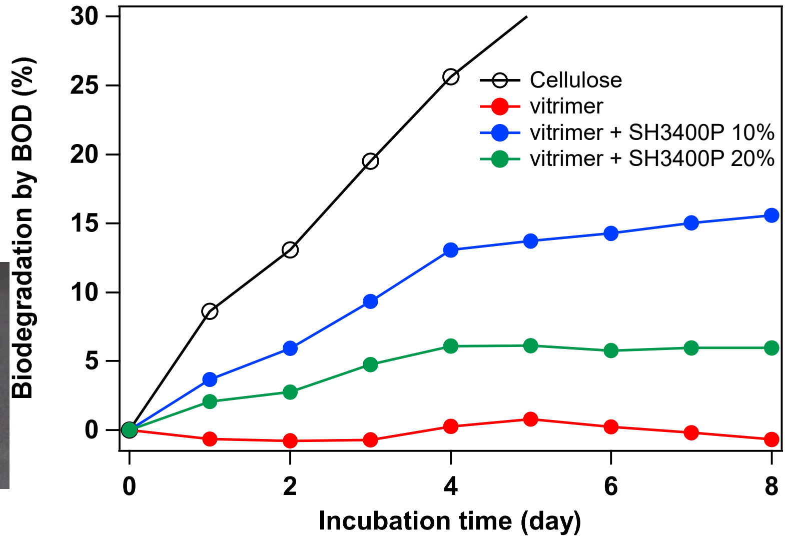




Toughened without changing hardness by adding PR

Shape Memory and Memory Editing

Airplane　Plane　Crane

Marine Biodegradability



# Polyrotaxane-containing vitrimer papers of interest

RETURN TO ISSUE | < PREV | LETTER | NEXT >

## Environmentally Friendly Sustainable Thermoset Vitrimer-Containing Polyrotaxane

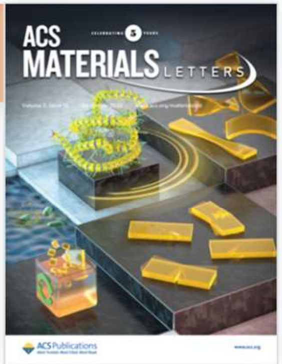
Shota Ando*, Masaki Hirano, Lisa Watakabe, Hideaki Yokoyama, and Kohzo Ito*

**Cite this:** *ACS Materials Lett.* 2023, 5, 12, 3156–3160
Publication Date: October 30, 2023
https://doi.org/10.1021/acsmaterialslett.3c00895


| Article Views | Altmetric | Citations |
|---|---|---|
| 4770 | 200 | - |

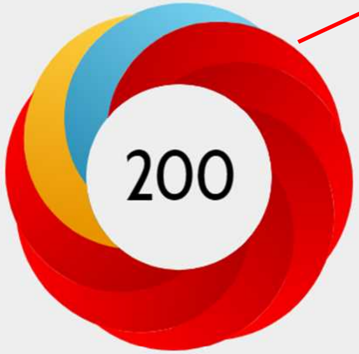
LEARN ABOUT THESE METRICS

Share | Add to | Export
RIS




ACS Materials Letters

Publication date: October 30, 2023
Views and Attention score as of January 4, 2024




About this Attention Score

In the top 5% of all research outputs scored by Altmetric

MORE...

Mentioned by

- 24 news outlets
- 3 blogs
- 7 X users

SUMMARY | News | Blogs | X

| | |
|---|---|
| Title | Environmentally Friendly Sustainable Thermoset Vitrimer-Containing Polyrotaxane |
| Published in | ACS Materials Letters, October 2023 |
| DOI | 10.1021/acsmaterialslett.3c00895 |
| Authors | Shota Ando, Masaki Hirano, Lisa Watakabe, Hideaki Yokoyama, Kohzo Ito |

X Demographics | Mendeley readers | Attention Score in Context

This research output has an **Altmetric Attention Score** of **200**. This is our high-le Attention Score, as well as the ranking and number of research outputs shown be 2023.

| ALL RESEARCH OUTPUTS | OUTPUTS FROM ACS MATERIALS LETTERS |
|---|---|
| #191,379 | #3 |
| of 24,946,857 outputs | of 506 outputs |


Covered by 26 international news outlets,
Top 0.8% of all papers

Youtube 900,000 views, 18,000 likes

Shota Ando

# Contents

- フィールド試験
- スイッチ機能
- 強靭性の向上
- 研究進捗状況（アカデミア、企業）
- **International Relation**

# international collaboration with ARPA-E


| | |
|---|---|
| ARPA-E/NEDO Bioplastics Joint Research Phase 1 (June 2024 - April 2025: 9 months) | |
| ～2024/12 | Most promising seaweed precursor molecules identified and selected U.S. institutions to conduct research |
| 2025/4 | NEDO Hosts Workshop<br>Presentation of research results and setting of development goals for Phase 2 |
| ARPA-E/NEDO Bioplastics Joint Research Phase 2 (April 2025 - December 2026: 21 months) | |
| ～2025/12 | Evaluate target seaweed precursor molecules and confirm their potential as feedstock |
| ～2026/6 | Scale up processing capacity to kg level for extraction and purification of precursor molecules |
| | Evaluate financial costs, industrial competitiveness, carbon emission impact, etc. for commercialization |
| ～2026/12 | Establish various characteristics in light of international standards |
| 2026/12 | ARPA-E Hosts Workshop |

■October 3, 2023 MOU signed between NEDO and ARPA-E, no technology overlap between the two countries (No duplication of technology between the two countries, MOU not limited to moonshots)

# Develop Test Implementation and Public Relations Activities in Southeast Asia Region (Collaborated with Kasuya Project)

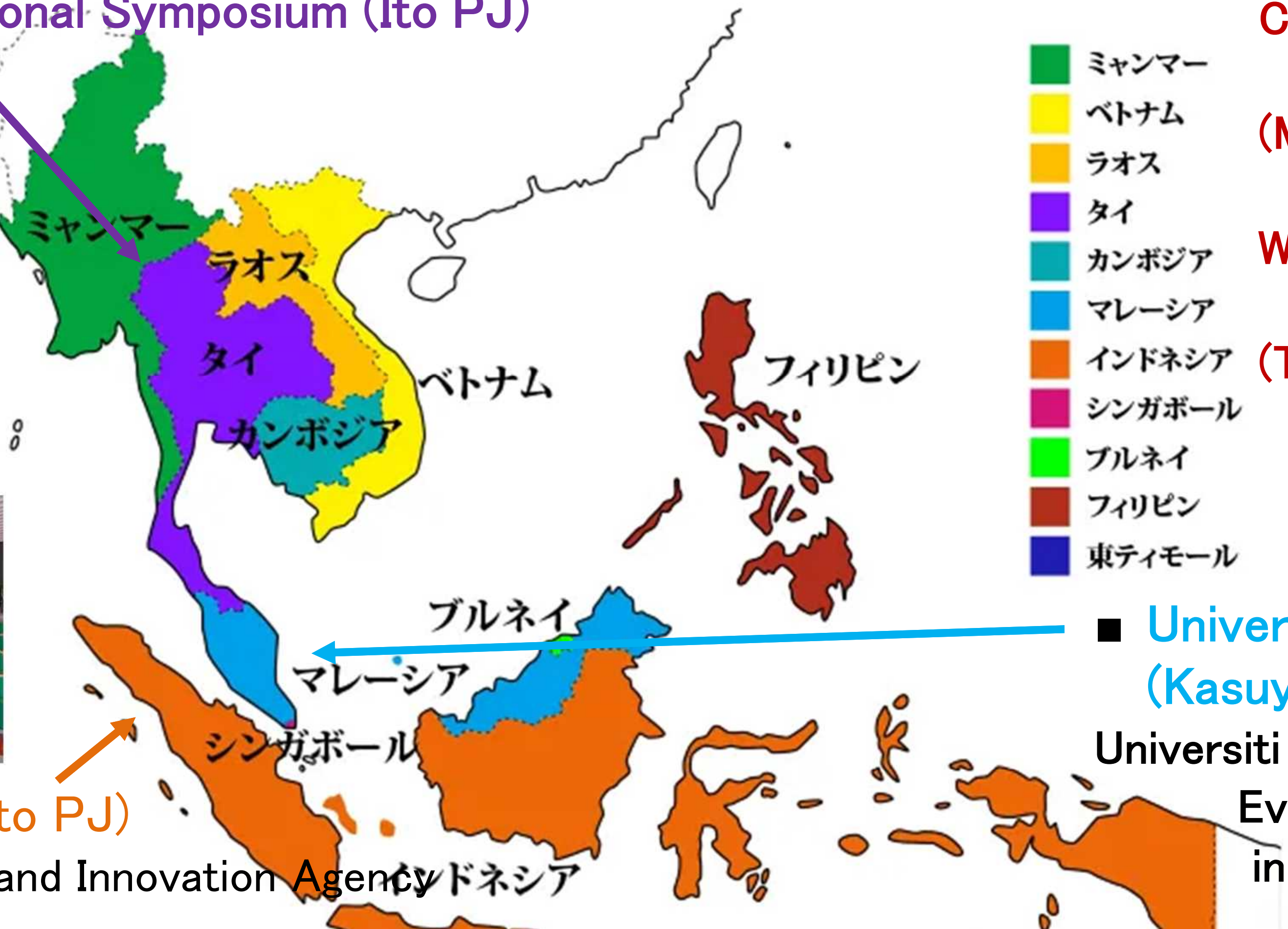
■ Japan–Thailand International Symposium (Ito PJ)

Chulalongkorn Univ.,VISTEC

(10/5–10/10, 2023)

Participants: 160 people

Thailand, Singapore, Taiwan, China. Japan.


Conducted degradation tests of marine biodegradable plastics (Malaysia, Thailand, Indonesia)

Workshops in Thailand and Malaysia (Thailand and Malaysia (2024 fall))

■ Universiti Sains Malaysia (USM) (Kasuya PJ)

Universiti Sains Malaysia (USM)

Evaluation of plastic degradation in mangroves


■ Indonesia Partnership (Ito PJ)

Indonesia National Research and Innovation Agency (BRIN) Jakarta (10/31/2023)


# Legally binding international instruments (conventions) on plastic pollution

**November 13–19, 2023 Japanese Delegation (Ministry of Foreign Affairs, Ministry of Economy, Trade and Industry, Fisheries Agency, Ministry of the Environment)**

Summary of Results of the Third round of Intergovernmental Negotiations

・Restriction of production of primary plastic polymers

・Regulation of chemicals, polymers and problematic plastic products of concern

· Zero additional pollution by 2040 (Japan's claim)

・ Introduction of Japan's related efforts (international harmonization of monitoring methods and database development for plastics in the environment, cooperation with local governments, promotion of marine debris collection through cooperation with fishermen and formulation of various manuals, support for development of alternative materials, etc.) under Theme 2 "Ocean and Marine Environment".


**olymers that spill into the environment and are difficult to recover pollut the ocean**

**Agricultural materials (fertilizer coating materials, etc.), tire wear powder,**

**Fishing materials (fishing lines, nets, buoys, styrofoam, etc.)**

**marine biodegradable polymers.**

# Summary

As a result of progress in joint research between companies and academia, and the utilization of results from academia by companies, R&D is progressing steadily toward social implementation, and the FY2024 target is expected to be fully achieved. Teijin was spun out at the end of FY2023, as it had progressed to a stage close to practical application.

A large-scale (over 1,000 samples) field test in actual sea areas was conducted in Ehime Prefecture. The huge amount of data obtained will be accumulated in a database.

We have developed innovative switch functions triggered by salinity, pH, redox potential, etc. using proprietary technologies that are unparalleled in Japan and overseas, such as entropy-driven dynamic cross-linking, polyrotaxane (PR), pseudo-polyrotaxane nanosheets (PPRNS), thermostable esterases, etc.

Mitsubishi Chemical has confirmed that in the PBS system, the additive kneading greatly accelerates the degradability of the additive. Field tests were conducted to evaluate biodegradability in actual seas, and the addition of PR improved elongation at break by 2.3 times and marine biodegradability by 3 to 5 times at the same time.

Bridgestone achieved a 10-fold or more improvement in biodegradability by copolymerizing butadiene and introducing a degradation unit. Developed a reversible bonding-introduced rubber that degrades in the marine environment. Kureha succeeded in achieving both a 2-fold increase in fracture strength and a 10-fold increase in degradation speed.

Kureha succeeded in developing a fishing line that has the same level of nodal elongation as non-biodegradable fishing line and is biodegradable in the marine environment. The degradation of fishing line is accelerated when it sinks to the seafloor after abandonment. We actually confirmed the degradability of the fishing line in a field test in an actual oceanic area.

The results include 69 papers, 25 patents, 154 invited lectures, and 63 press reports (more than 26 from oversea).

MOONSHOT

RESEARCH & DEVELOPMENT PROGRAM