No. A-15-1E

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

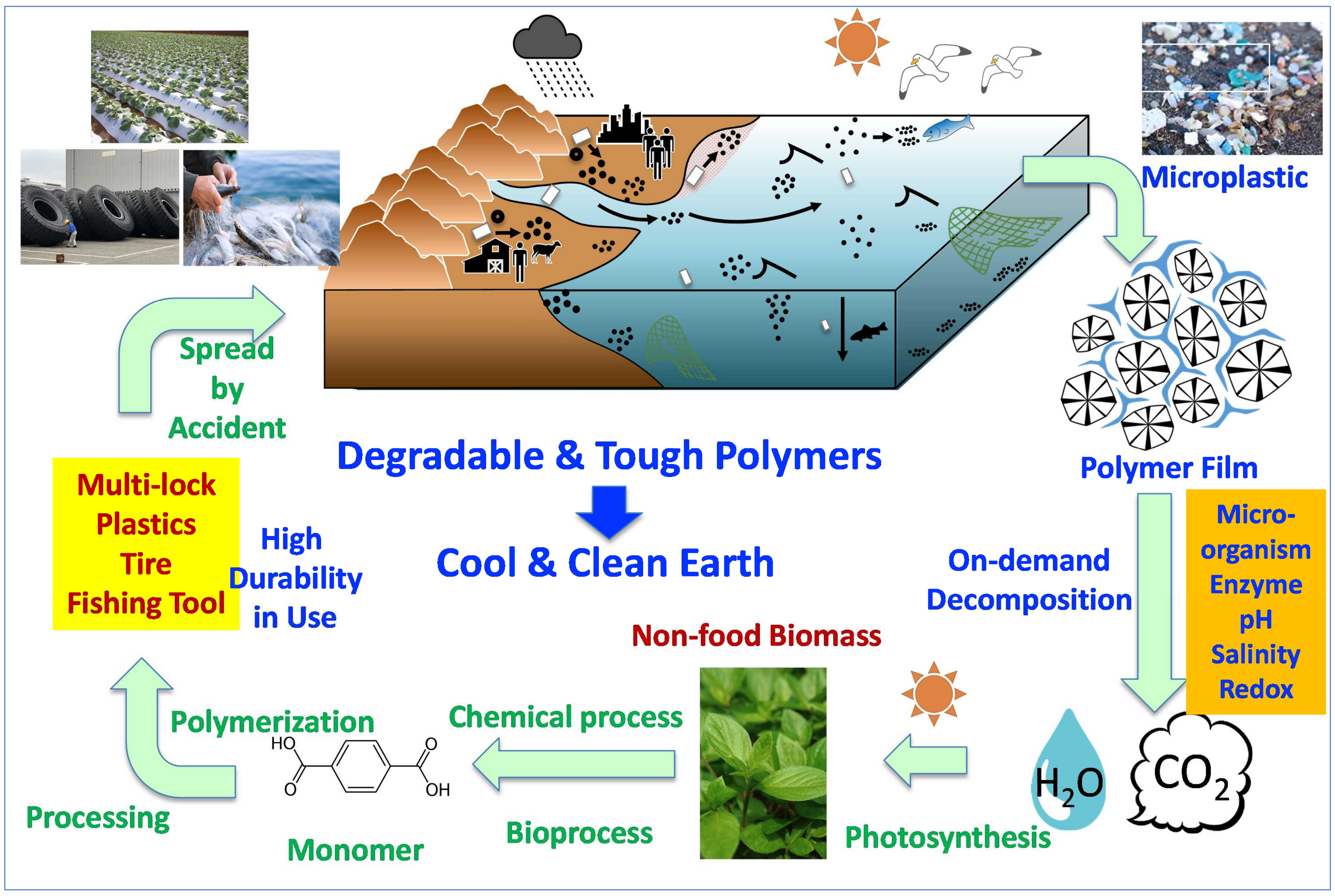
Organization: University of Tokyo
Contact: Kohzo Ito (kohzo@edu.k.u-tokyo.ac), Naoki Kato (naokikato@g.ecc.u-tokyo.ac.jp)

NEDO

MOONSHOT RESEARCH & DEVELOPMENT PROGRAM

For seawater decomposition of difficult-to-collect plastics, tire wear debris, and fishing gear, we have introduced a multi-lock mechanism that achieves both degradability and durability, and realizes on-demand disassembly. In addition, by using non-edible biomass as a raw material, CO2 reduction can be achieved at the same time.

OVERVIEW



Organization

NEDO

Materials Technology and Nanotechnology Department Bioeconomy Promotion Division

ITO PJ
Project Manager
Kohzo Ito

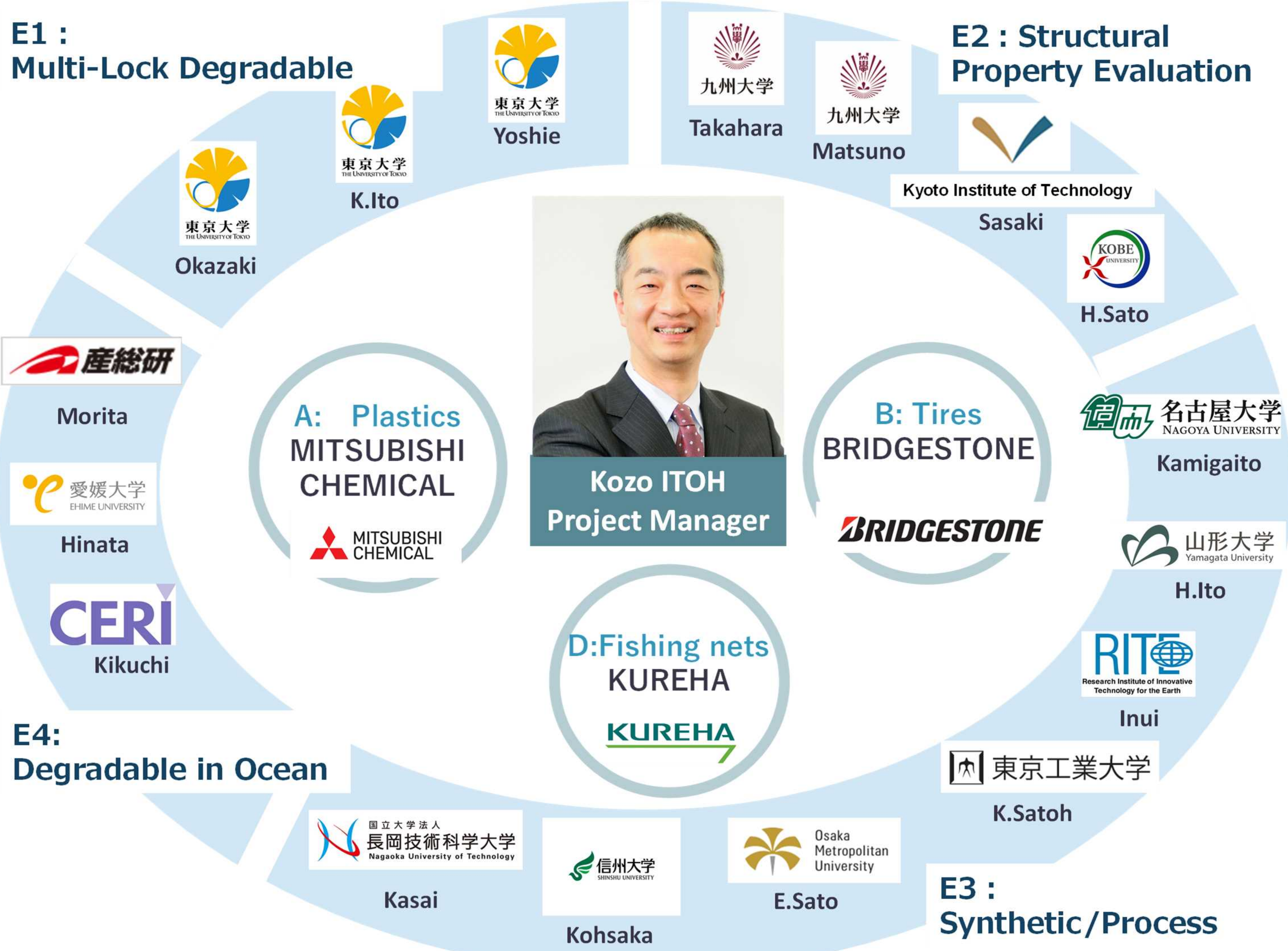
Project Office

Entrusted organization : 11
Reentrusted organization : 6

Company : 3
Academia : 14
(17Gr)

No.	Entrusted organization / Reentrusted organization	Leader
2	Mitsubishi Chemical	Asushi Kusuno
3	Bridgestone	Satoshi Hamatani
5	Kureha	Takashi Masaki
1	The University of Tokyo	Kohzo Ito
		Susumu Okazaki
		Naoko Yoshie
	Kyoto Institute of Technoligy	Sono Sasaki
	Kobe University	Harumi Sato
	Osaka City University	Eriko Sato
	Shinshu University	Ysuhiro Kohsaka
	Nagaoka University of Technology	Disuke Kasai
	CERI	Tkako Kikuchi
6	Kyushu University	Jun Takahara
7	Nagoya University	Masami Kamigaito
8	Ymagata University	Hiroshi Ito
		Hisao Matsuno
9	RITE	Masayuki Inui
10	AIST	Hiroshi Morita
11	Ehime University	Hirofumi Hinata
12	Tokyo Institute of Technology	Kotaro Sato

(敬称略)



	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, Tokyo Tech, AIST, Osaka City Univ, Shinshu 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, Tokyo Tech, Shinshu 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 plastic using seaweed (Macroalgae) with excellent CO2 fixation performance provided by ARPA-E as a raw material, and evaluate its marine biodegradability and mechanical properties (joint research with ARPA-E)	Univ Tokyo, Nagoya Univ, RITE, Tokyo Tech, Osaka City Univ, Shinshu Univ, Ehime Univ, CERI, Yamagata Univ

No. A-15-2E

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

Theme: Research and development of marine degradable multi-lock biopolymers from inedible biomass

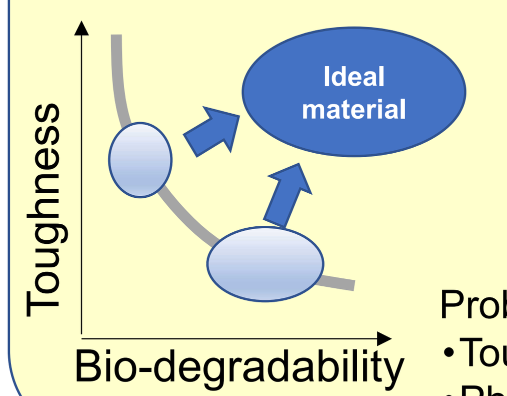
Organization:Mitsubishi Chemical Corporation
Contact: Atsushi Kusuno atsushi.kusuno.mf@mcgc.com

1. Objectives and concept

【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

2.Targets

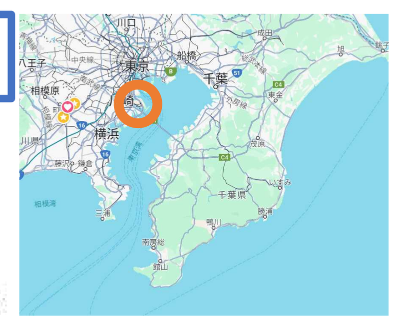
- FY2022 Intermediate Target: Proof of the multi-locking concept
  - Degradation rate is more than 3 times higher for multiple external stimuli than for a single external stimulus.
- FY2024 Intermediate Target : Achieve both high toughness and multi-locking mechanisms
  - Degradation rate is more than 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

3. Academia/Mitsubishi Chemical research content

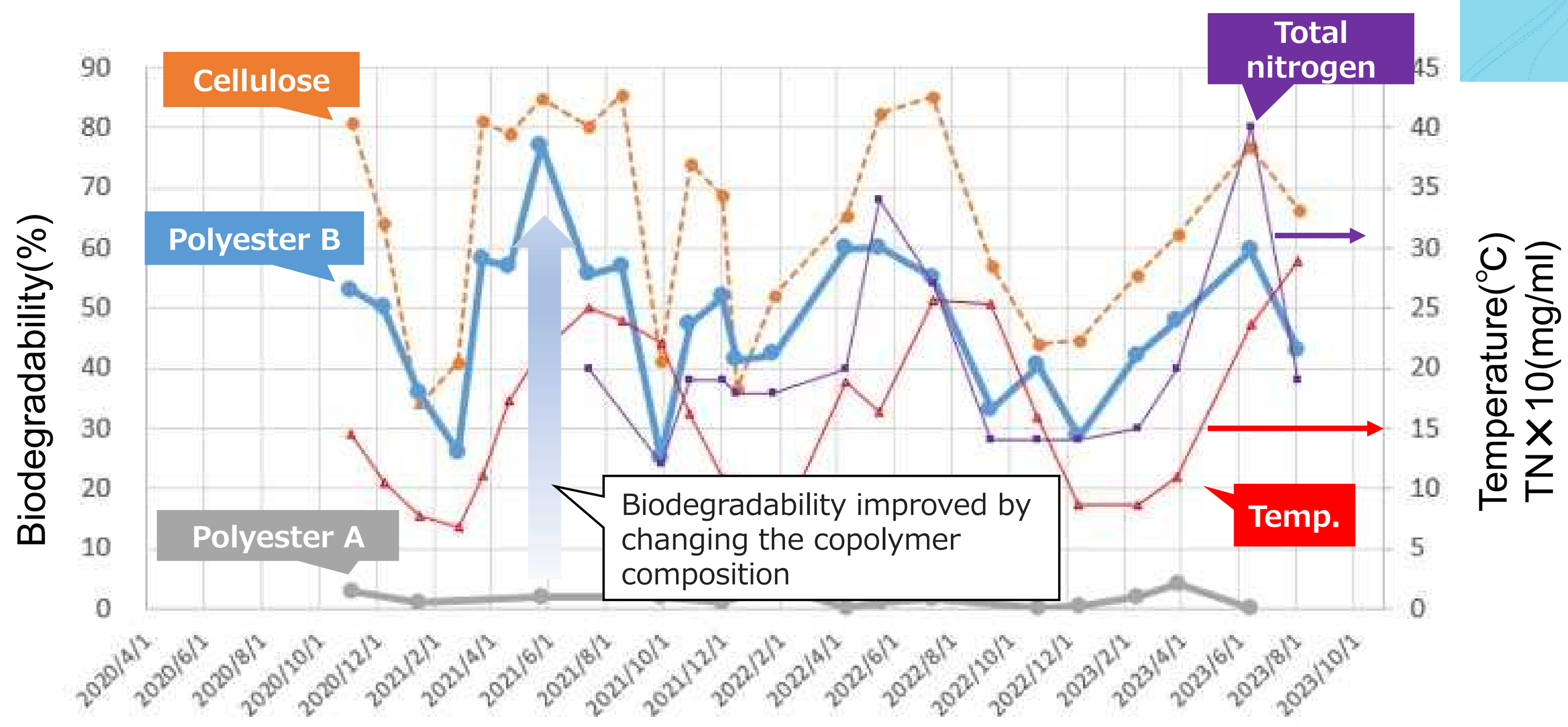
・Schedule for 2023-2024
① Biodegradability control (clarification of biodegradation mechanism, introduction of trigger mechanism)
②Improvement of tear strength (clarification and improvement of tear)

PIC	Study Items
Tokyo Univ. Prof. Ito	Improving toughness and promoting biodegradation (application using PR)
Yamagata Univ. Prof. Ito	Improvement of toughness (clarification of tearing mechanism and kneading technology)
Yamagata Univ. Prof. Matsuno	Analysis of enzymatic degradation behavior in water (AFM)
Kyoto institute of technology Prof. Sasaki	Time-resolved X-ray scattering measurement during tearing process (SPring-8)
Kyushu Univ. Prof. Takahara	Structural changes and degradability due to photooxidative degradation (natural environment model)
Kobe Univ. Prof. Sato	Effect of degradability on higher-order structure and intermolecular interactions (terahertz, low frequency Raman spectroscopy)
Mitsubishi Chemical Corporation	Introduction of multi-lock mechanism (expression of switch function by introducing copolymer monomer, biodegradation accelerator, and degrading enzyme)

4. Seasonal changes in biodegradation



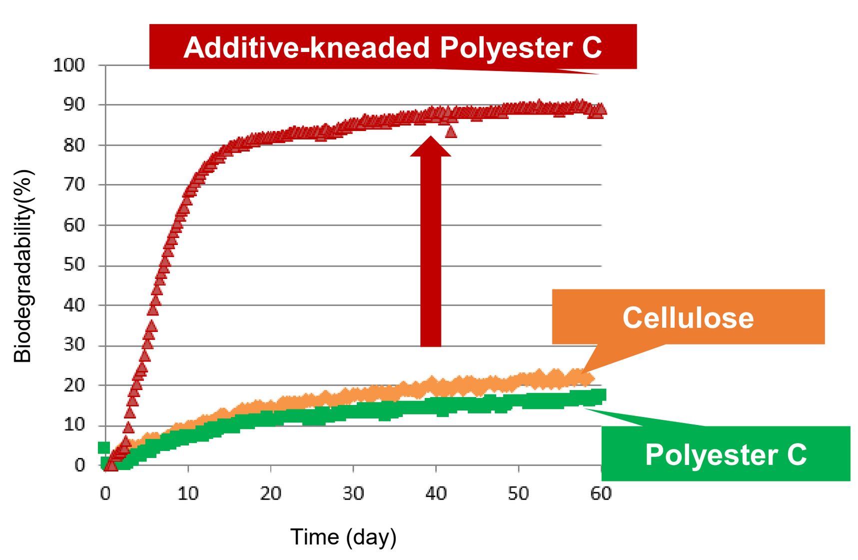
・Evaluation of seasonal changes in biodegradability of cellulose and polyesters A and B using seawater sampled at a fixed point (Tokyo Bay)



- 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.

5. Biodegradation accelerator kneaded polyester

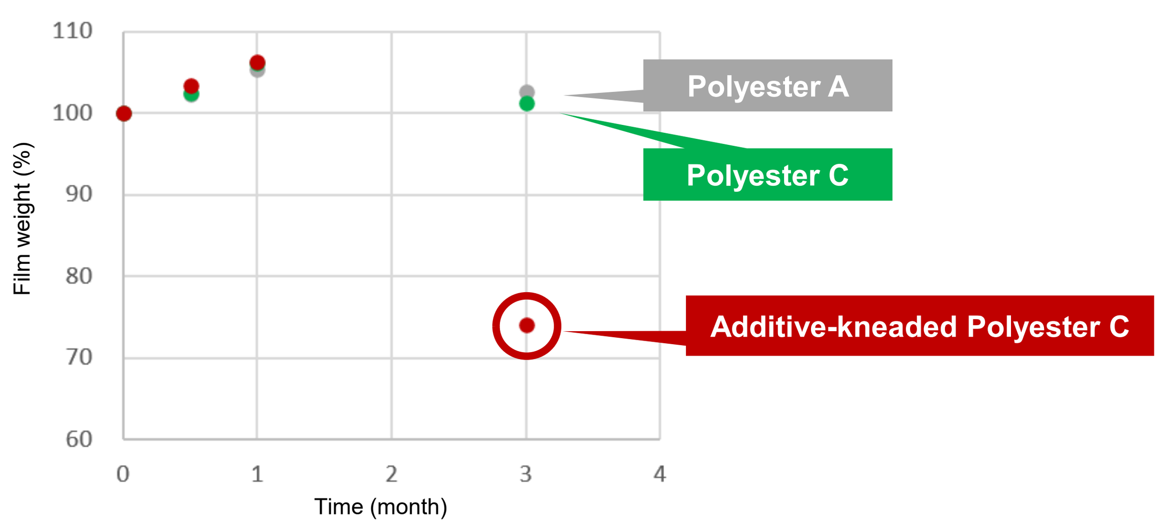
・Various additives were kneaded into Polyester C and biodegradability was evaluated.



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

6. 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

7. Summary and Future plans

●Results in FY2023
- Succeeded in tracking nano structural changes in the torn part during in situ PBS and PBSA film tearing process. (Kyoto Institute of Technology, Professor Sasaki)
- Detection of crystal structure change from α crystal to β crystal during the PBS tearing process. Examined PBS/PR/catalyst blend to improve tearing. (Yamagata University, Professor Ito)
- Confirmed that toughness and biodegradability were improved by adding PR and PPR nanosheets to PBSA. Study of introducing degrading enzymes onto the surface of PPR nanosheets. (Professor Ito, University of Tokyo)
- Confirmed repeated changes in crystal structure and hydrogen bond state of PBS copolymer film in extracted seawater. (Kobe University, Professor Sato)
- Observe α → β crystal transition due to photooxidative decomposition of PBS and PBSA. Photodecomposition proceeds preferentially in the amorphous region. Biodegradability is promoted by UV irradiation. (Kyushu University, Professor Takahara)
- Surface structure changes due to PBSA hydrolase were evaluated by in situ AFM observation. Clear differences in biodegradation rates were confirmed due to differences in crystal orientation. (Yamagata University, Professor Matsuno)
- Confirmed the high seawater biodegradability of PBS copolymer throughout the year. Weight reduction confirmed in field test of additive-kneaded copolymerized polyester. (Mitsubishi Chemical)

●Future plans
① Degradability control (introduction of point control)
② Improvement of tear strength

No. A-15-3E

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

Theme: Development of Non-Food Biomasses Based Biodegrade Rubber Compound in Wear Particle for Tire

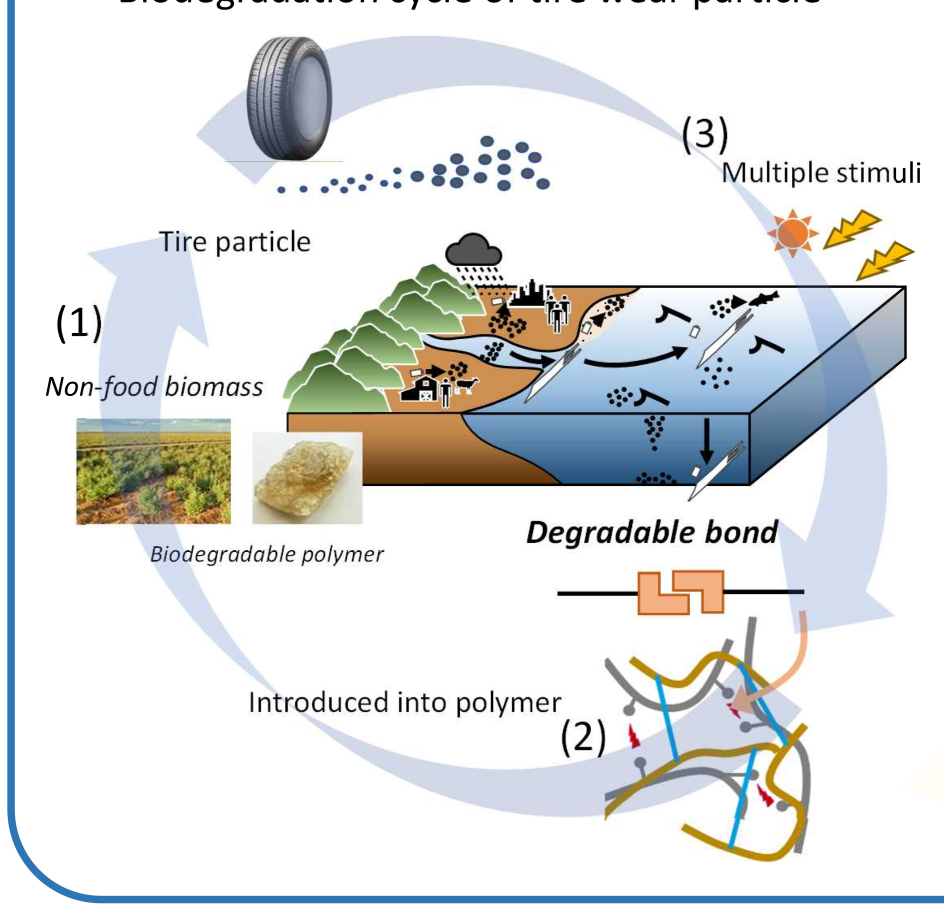
Organization: Bridgestone Corporation

Contact: Innovative Materials Technology Strategy & Research Department, Rubber Chemicals & Filler Research Section.

Research outline of this project

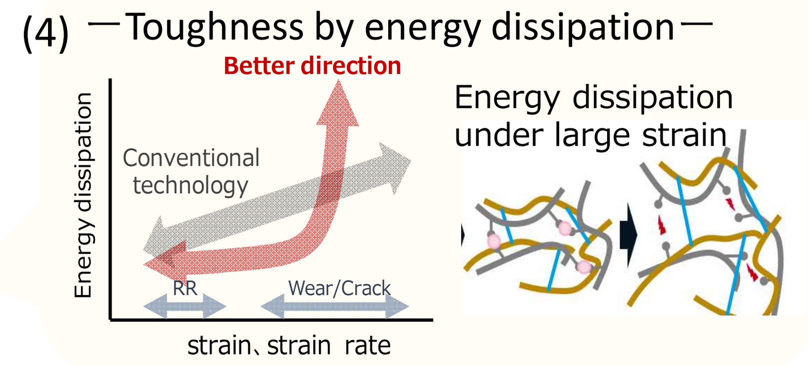
In recent years, there has been growing concern about the influence of tire wear particle on the environment. While its substantial contribution to the environment is still debatable, technological development is desired from a view of environmental pollution/ circulation of resources. In this study, 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, 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

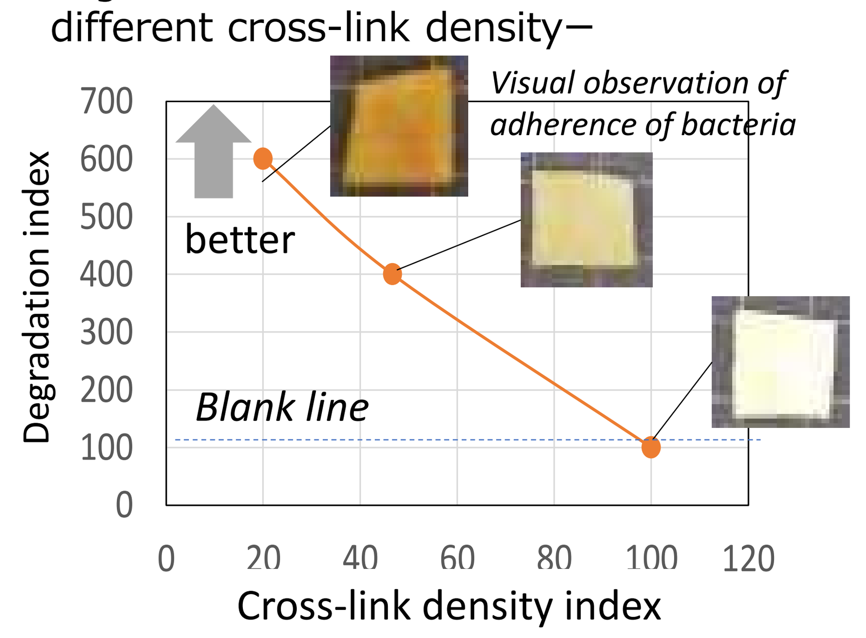
(4) —Toughness by energy dissipation—



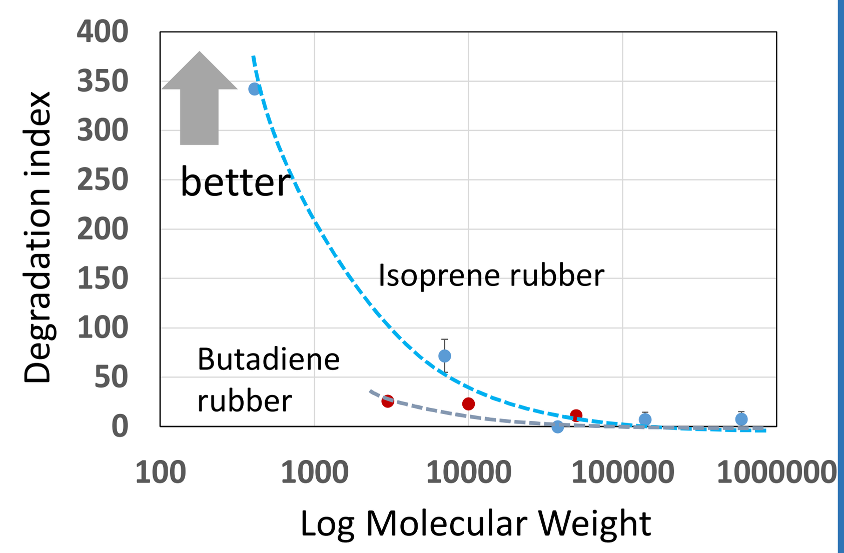
Multi-lock degradable system

★Two locks need to be unlocked for Rubber biodegradation !

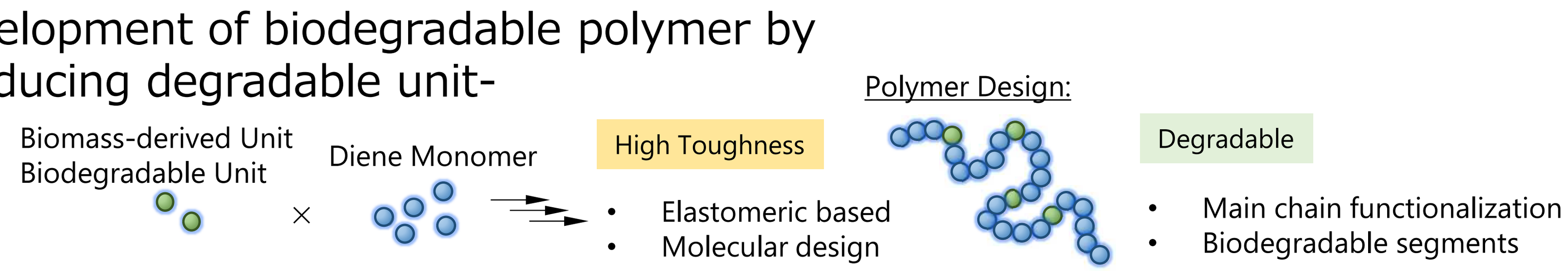
—Degradation test result of rubber with different cross-link density—



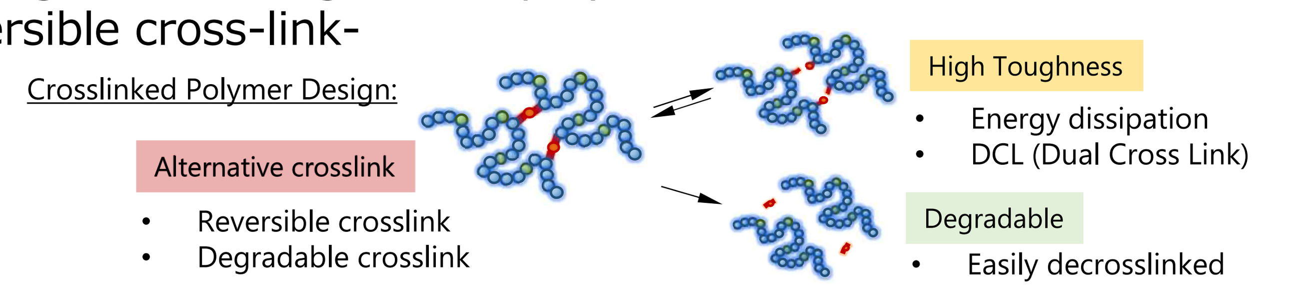
—Marine biodegradation test result of rubber with different molecular weight —



-Development of biodegradable polymer by introducing degradable unit-

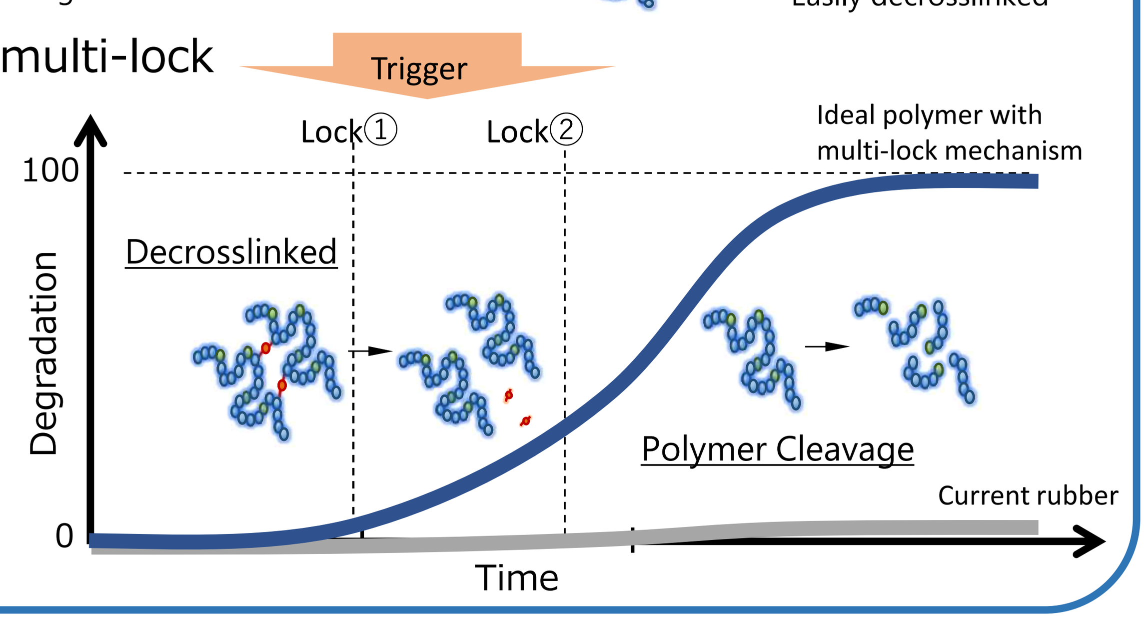


-Development of tough and biodegradable polymer by introducing reversible cross-link-



-Biodegradable scheme by multi-lock mechanism

Location	Possible Trigger
Road	UV exposure, Soil bacteria, High temperature
River	Soil bacteria, High temperature, PH (6~8)
coastline	UV exposure, Soil bacteria, High temperature
Ocean	Marine bacteria, PH (alkali~8), Pressure, Metal ions (Na+, Mg2+), salt concentration, amino acids, proteins, etc.

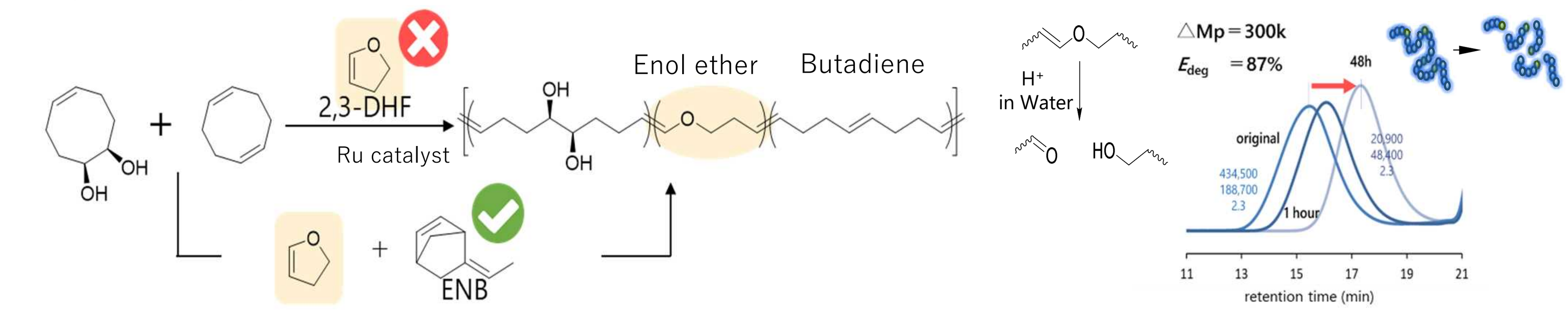


Biodegradation technology by introducing degradable unit

To develop diene rubber copolymer which can be decomposed by multiple stimuli cooperating with academia

-Polymer Design-

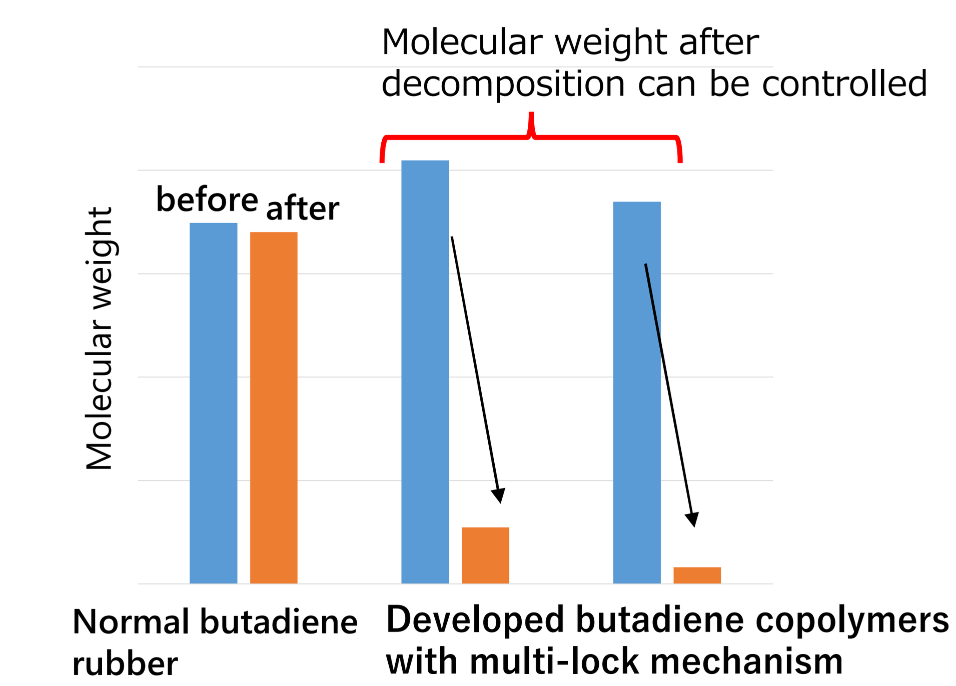
Enol ether decomposition reaction



Discovered synthetic route for introduing decomposition unit

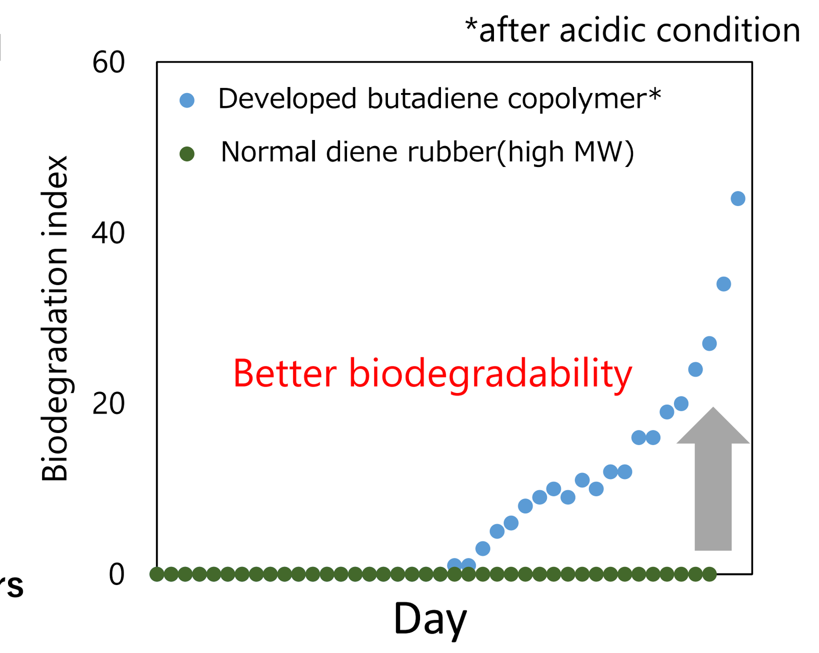
⇒ <u>Butadiene copolymer with multi-lock mechanism was developed</u>

—lab decomposition test result —



Fast decomposition in acidic condition (molecular weight reduced to 1/10)

—Marine biodegradation test result —



Improved biodegradability due to lower molecular weight

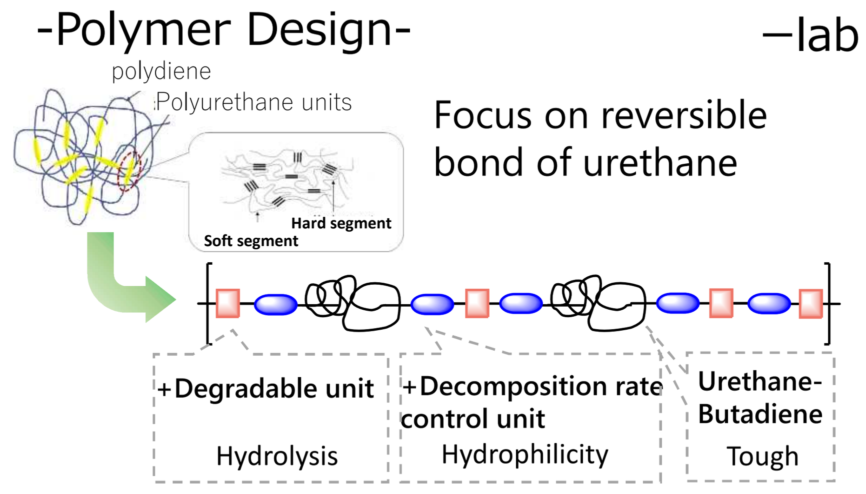
<u>Diene copolymer with multi-lock system was developed. POC, that improves biodegradability by more than 10 times, was achieved.</u>

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

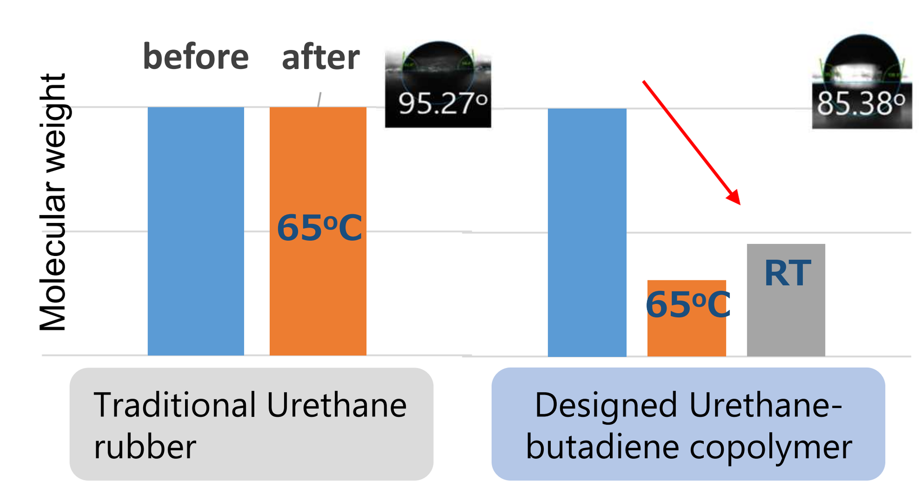
With extending reversible bond technology that strengthen rubber by effective energy dissipation, we newly designed degradable cross link system cooperating with academia.

★Introduced lock unit to diene rubber polymer chain to control tough and decomposition

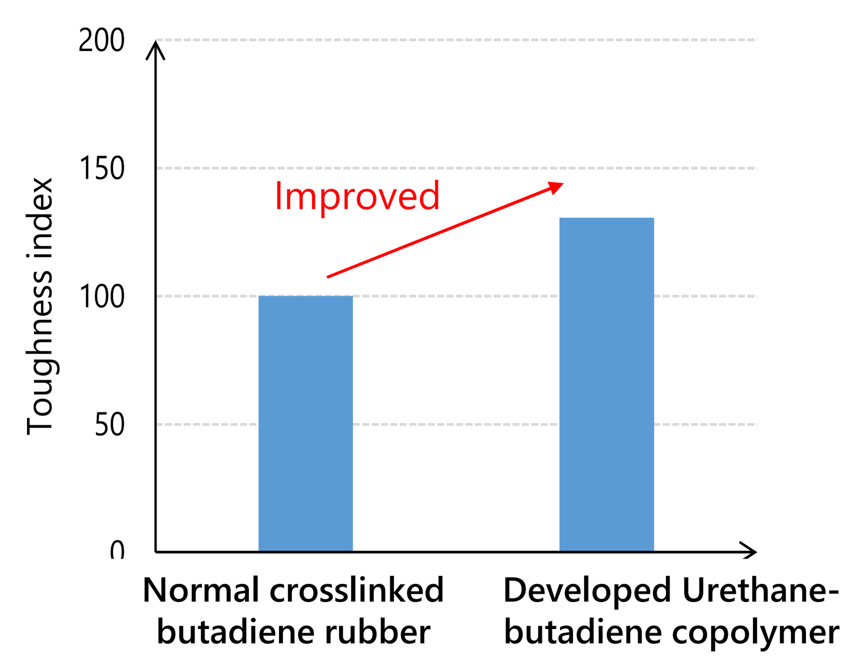
-Polymer Design-



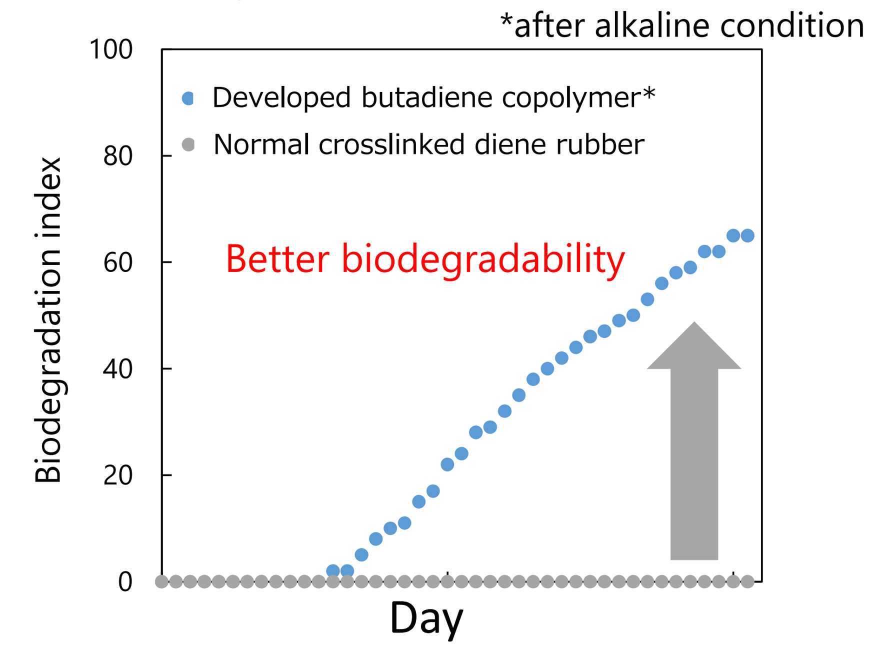
—lab decomposition test result —



—Physical property test result—



—Marine biodegradation test result —

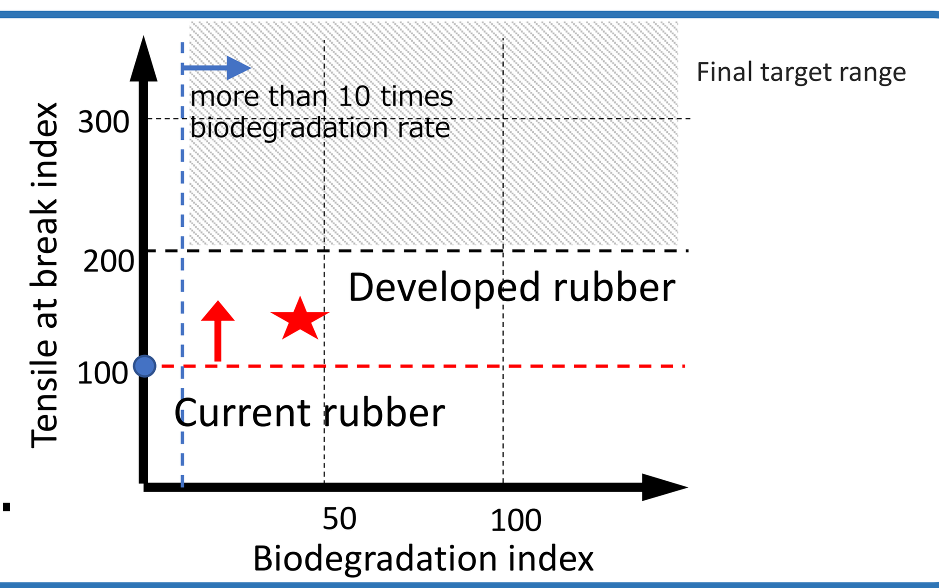


<u>Tough diene copolymer with multi-lock system was developed. More than 10 times higher degradability without sacrificing toughness was achieved.</u>

Summary

- We developed diene copolymer with multi-lock system cooperating with academia.
  ⇒POC, that improves biodegradability by more than 10 times, was achieved.

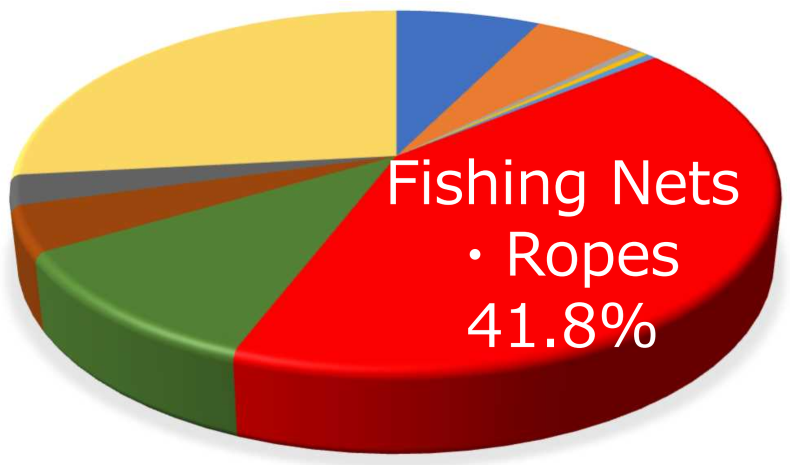
- Tough diene copolymer with multi-lock system was developed by introducing lock unit to diene rubber polymer chain to control tough and decomposition.
  ⇒More than 10 times higher degradability without sacrificing toughness was achieved.



No. A-15-4E
PJ: Development of Multi-lock Biopolymers Degradable in Ocean from Non-food Biomasses
Theme: Development of biodegradable and tough biopolymers for fishing nets
Organization: KUREHA CORPORATION
Contact: Takashi MASAKI / taka-masaki@kureha.co.jp

➢ Introduction

<Classification of Drifted Plastics> <Problem of "Ghost Gear">



Cited from 「Recent trends in sea garbage」 by Ministry of the Environment

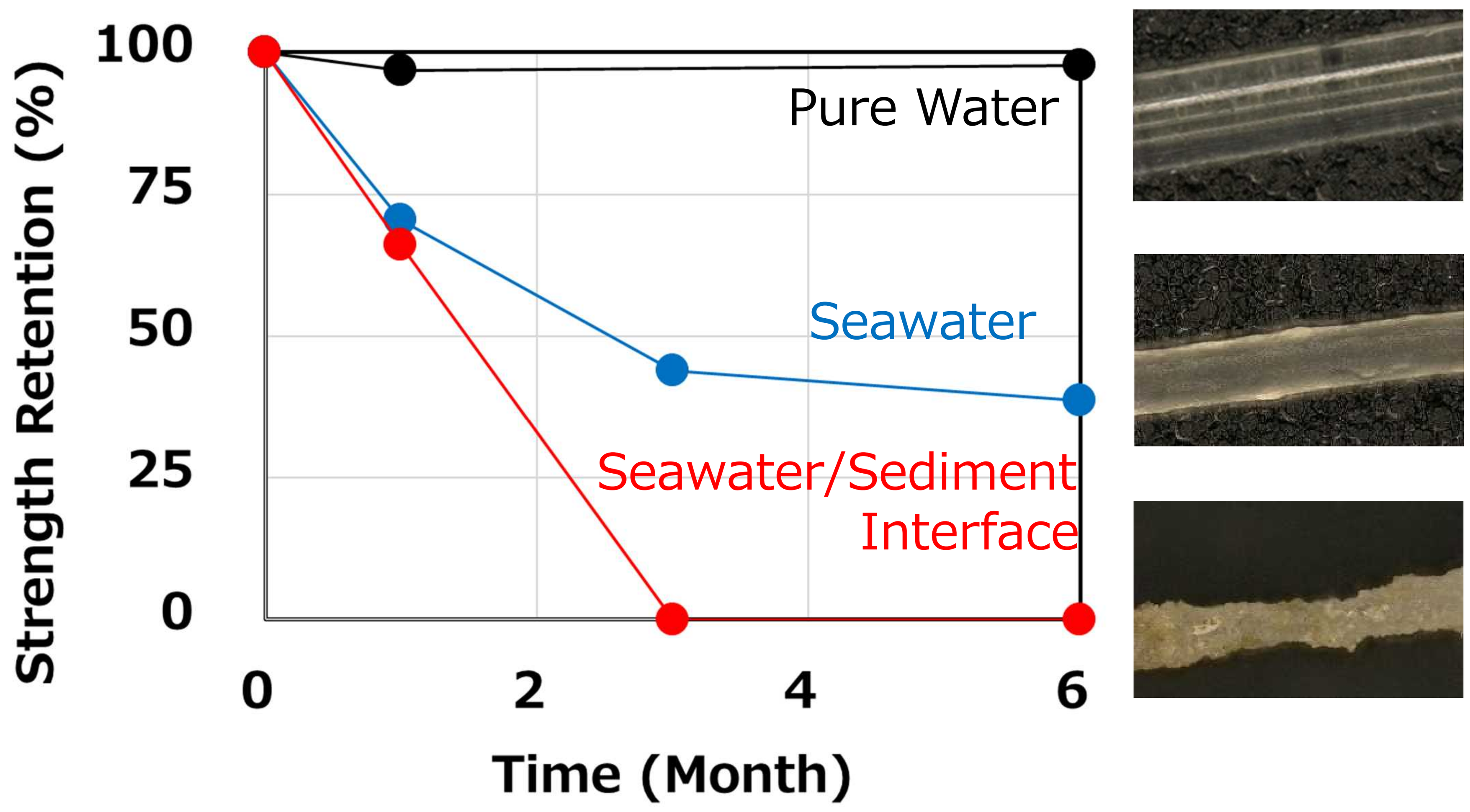
Cited from Wikipedia

- ✓ Fishing nets and ropes make up about 40% of the drifted plastics and they cause a problem called "Ghost Gear".
- ✓ Some biodegradable products are commercialized, however, they generally have inferior mechanical strength and degrade by hydrolysis during use.

➢ Marine Biodegradability (Lab. Test)

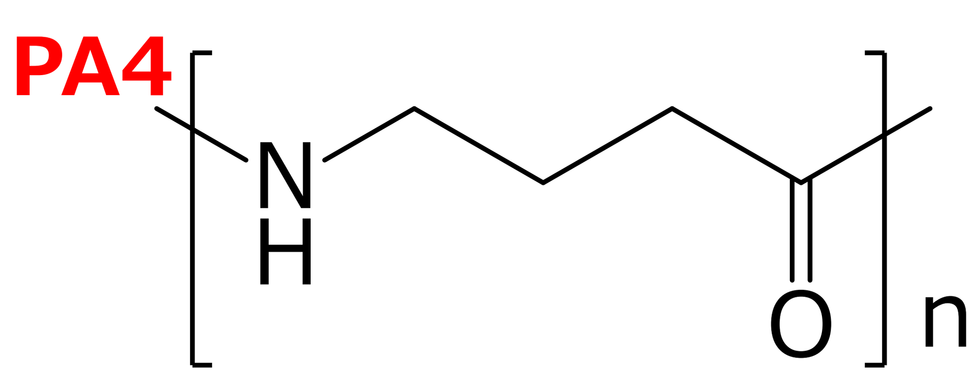
<Degradation Test of the Developed Fiber in Laboratory >

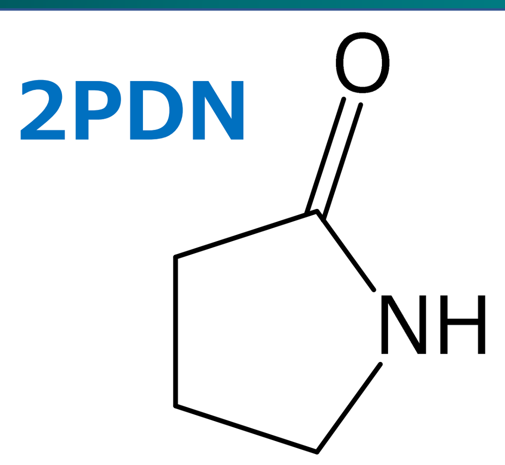
Seawater and sediment were collected from the Pacific Ocean (Fukushima pref.).



- ✓ In pure water, there was almost no reduction in strength.
- ✓ At seawater/sediment interface, degradation was faster than in seawater.

➢ Polyamide 4 (PA4)

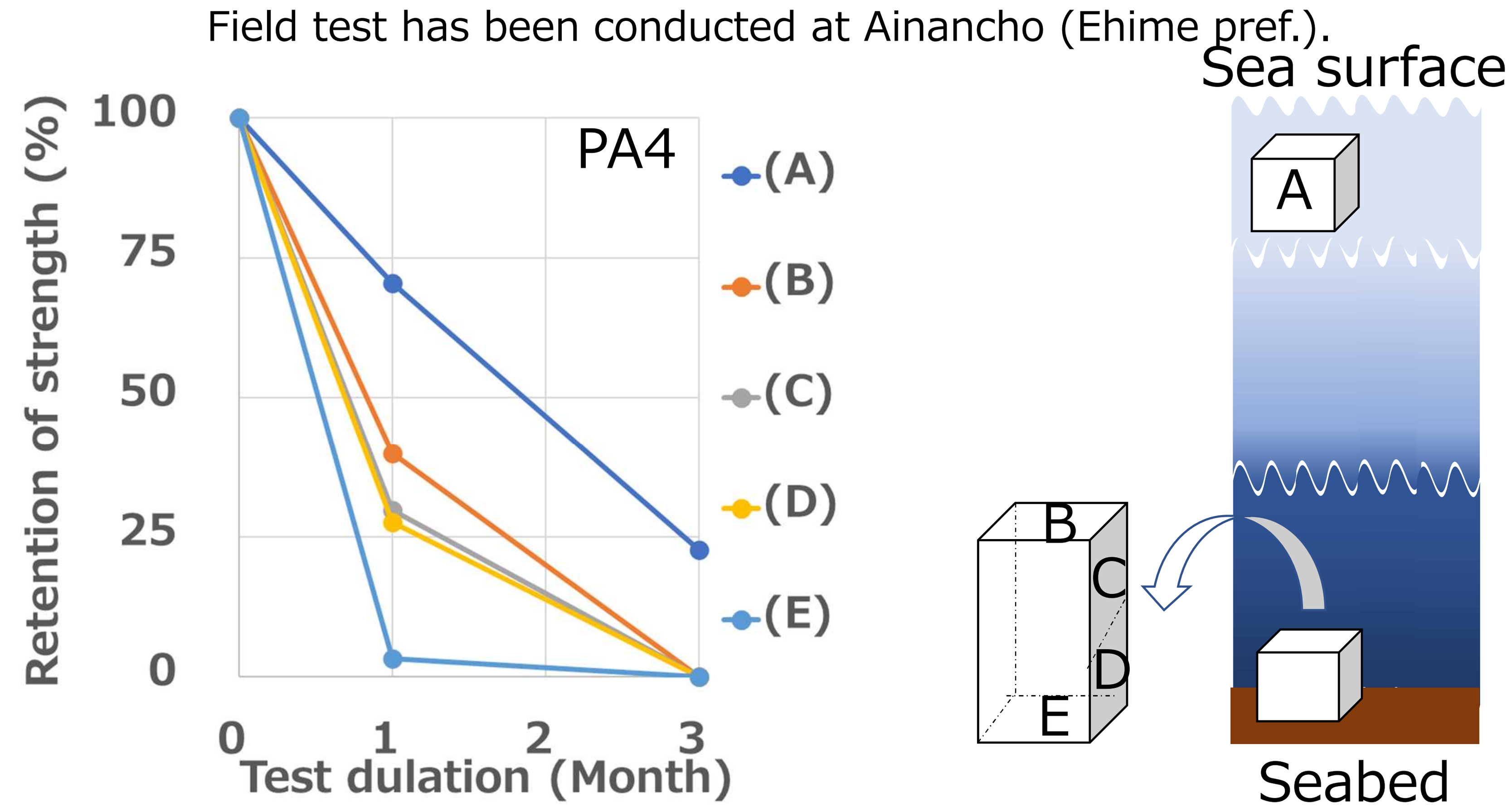




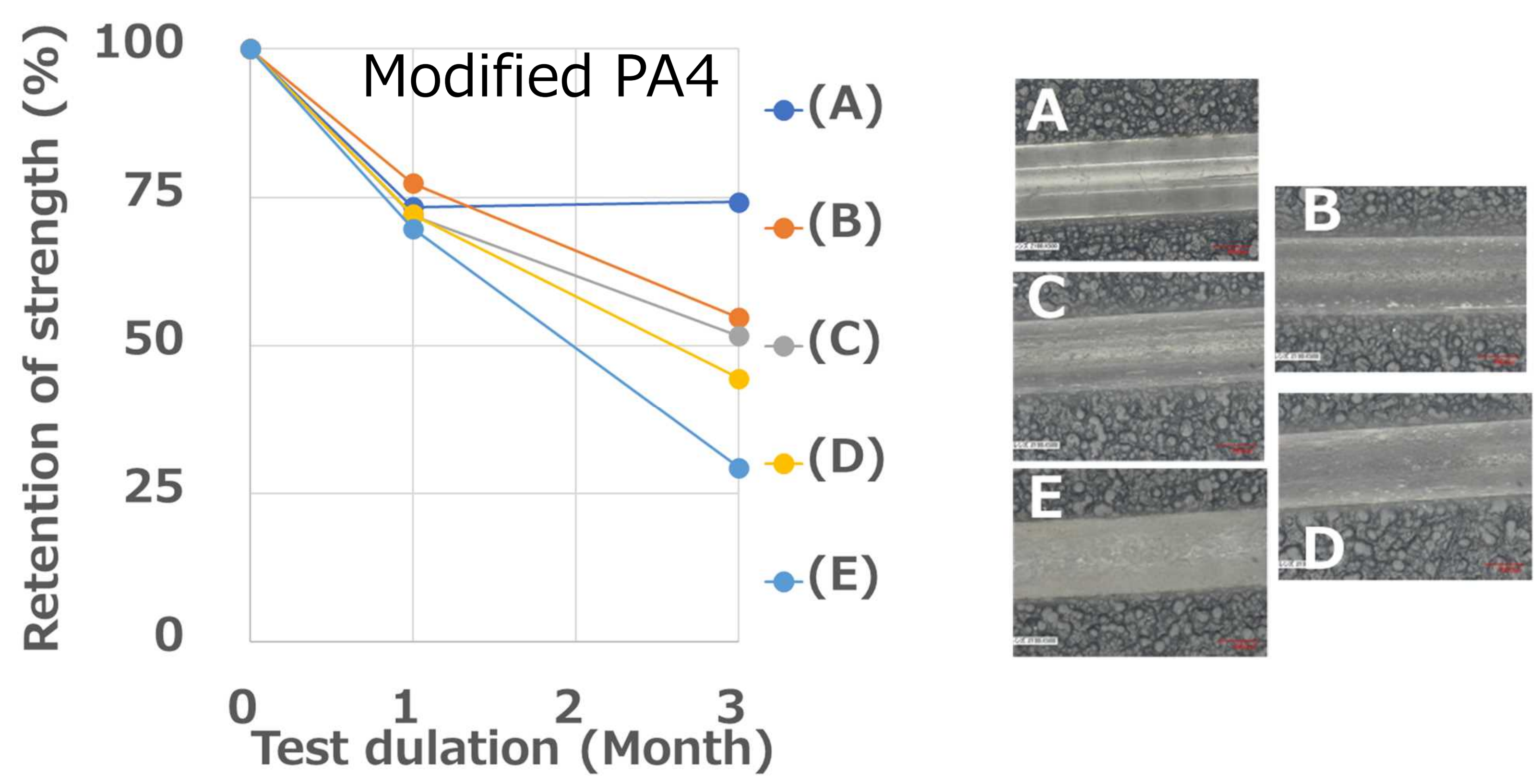
- ✓ PA4 is an aliphatic polyamide (nylon) synthesized from 2-pyrrolidone (2PDN).
- ✓ PA4 degrades in natural environments such as soil, sea, etc.
- ✓ In general conditions, PA4 is stable and not hydrolyzed.
- ✓ The mechanical property of PA4 is superior to Nylon6, on the other hand, PA4 has poor processability because it's thermal decomposition point is close to melting point.

➢ Marine Biodegradability (Field Test)

Field test has been conducted at Ainancho (Ehime pref.).



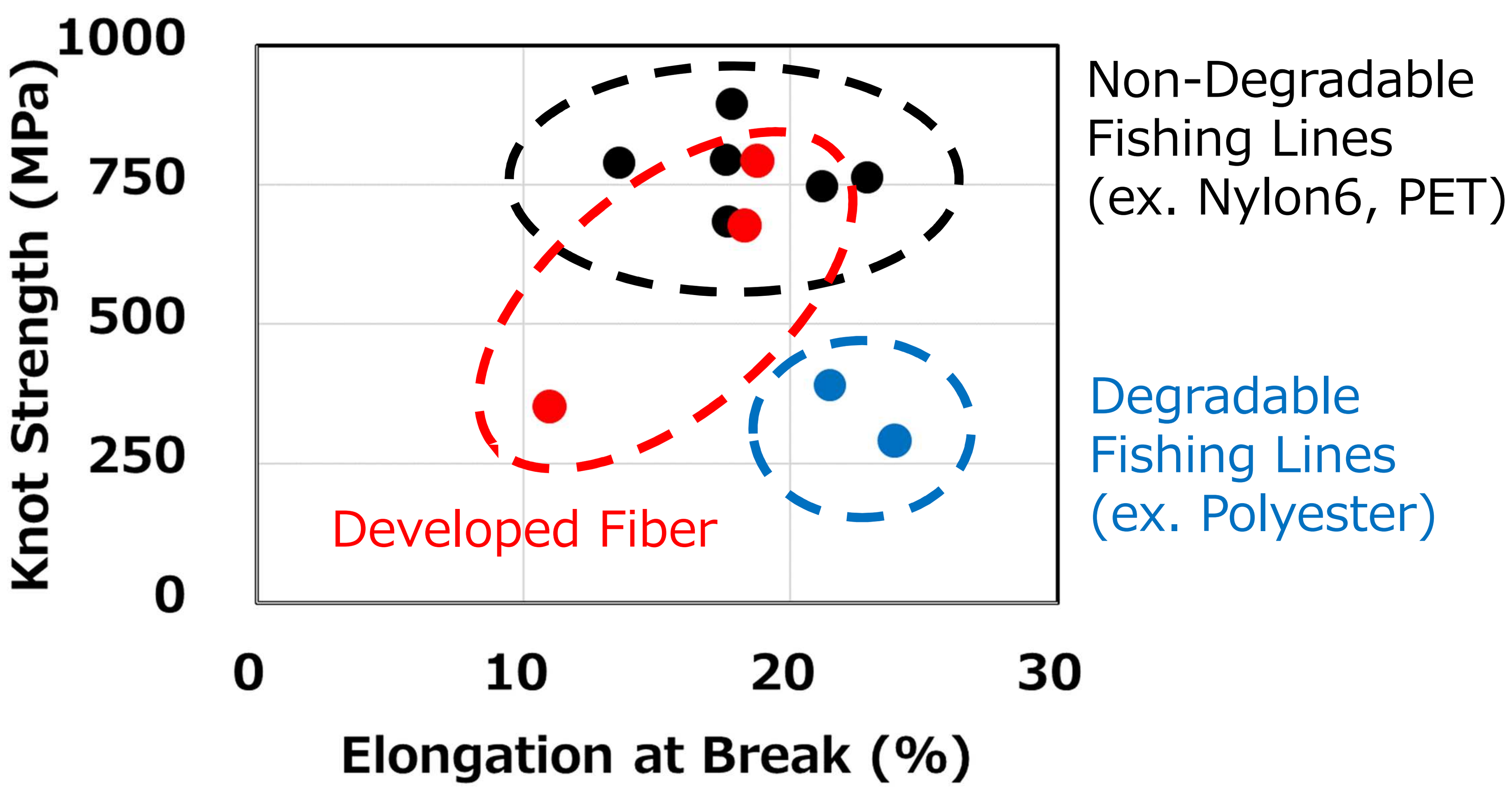
➢ Control of Degradation



➢ Mechanical Strength of the Developed Fiber

<Comparison of Knot Strength and Elongation>

Knot Strength Test



- ✓ **The strength and elongation of developed fiber is equivalent to commercial non-degradable fishing lines.**

➢ Summary

- ✓ We are developing biodegradable and tough biopolymer for fishing gears based on polyamide 4.
- ✓ The knot strength and elongation of developed fiber is equivalent to commercial non-degradable fishing lines.
- ✓ Marine biodegradability of the fiber was confirmed by lab. and field test.
- ✓ The degradation rate of modified fiber was reduced to 1/3.

番号:A-15-5E

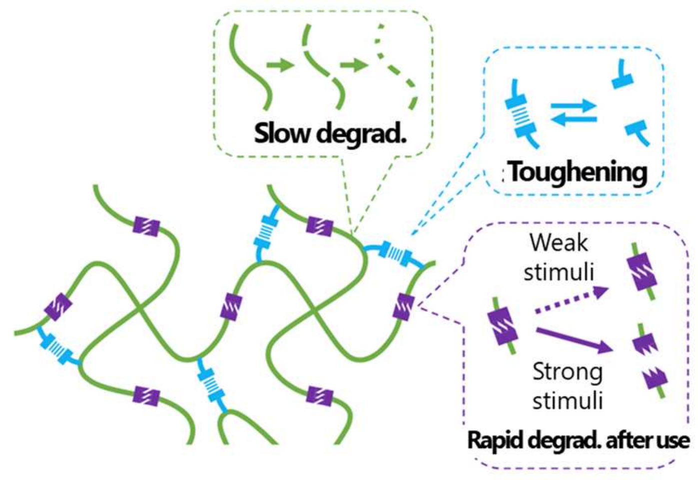
PJ: Development of Multi-lock Biopolymers Degradable in Ocean from Non-food Biomasses

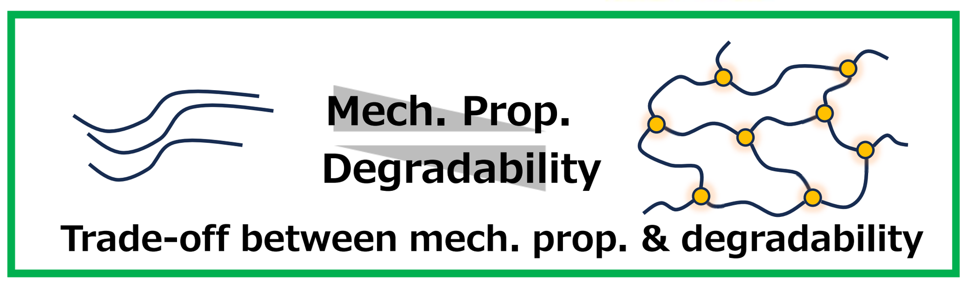
Theme: Development of biodegradable polymers with multi-lock degradability and practical mechanical performance

Organization: Yoshie Lab., The University of Tokyo Contact: Naoko Yoshie | yoshie@iis.u-tokyo.ac.jp

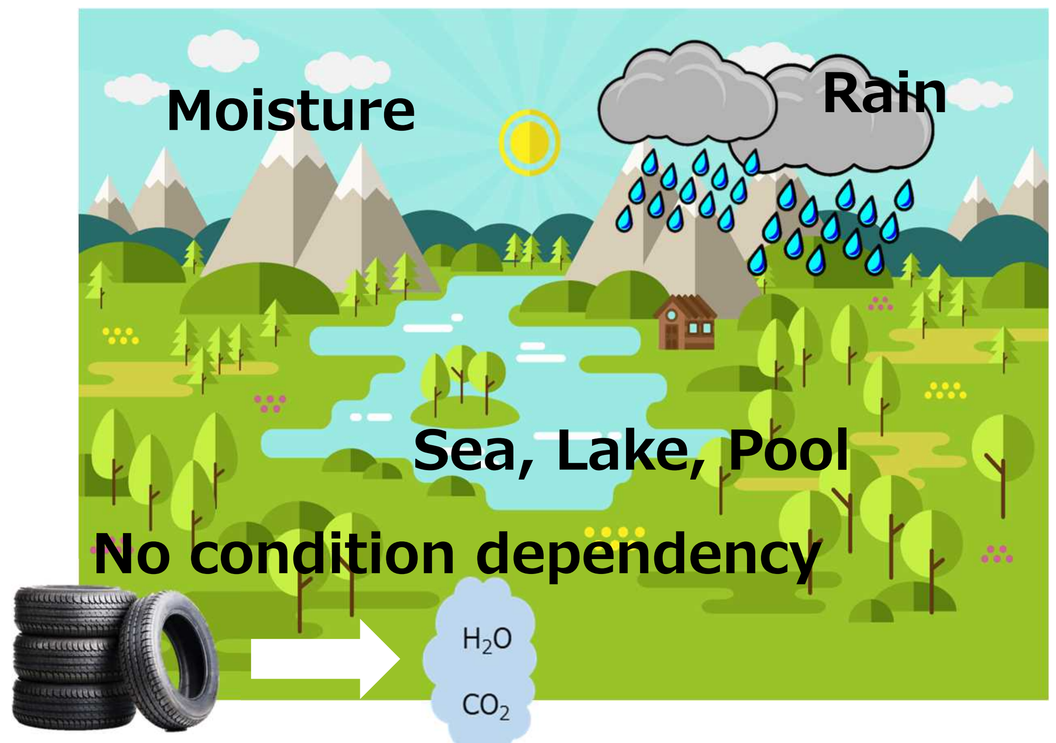
Introduction

Topic 1: Development of multi-lock mechanism



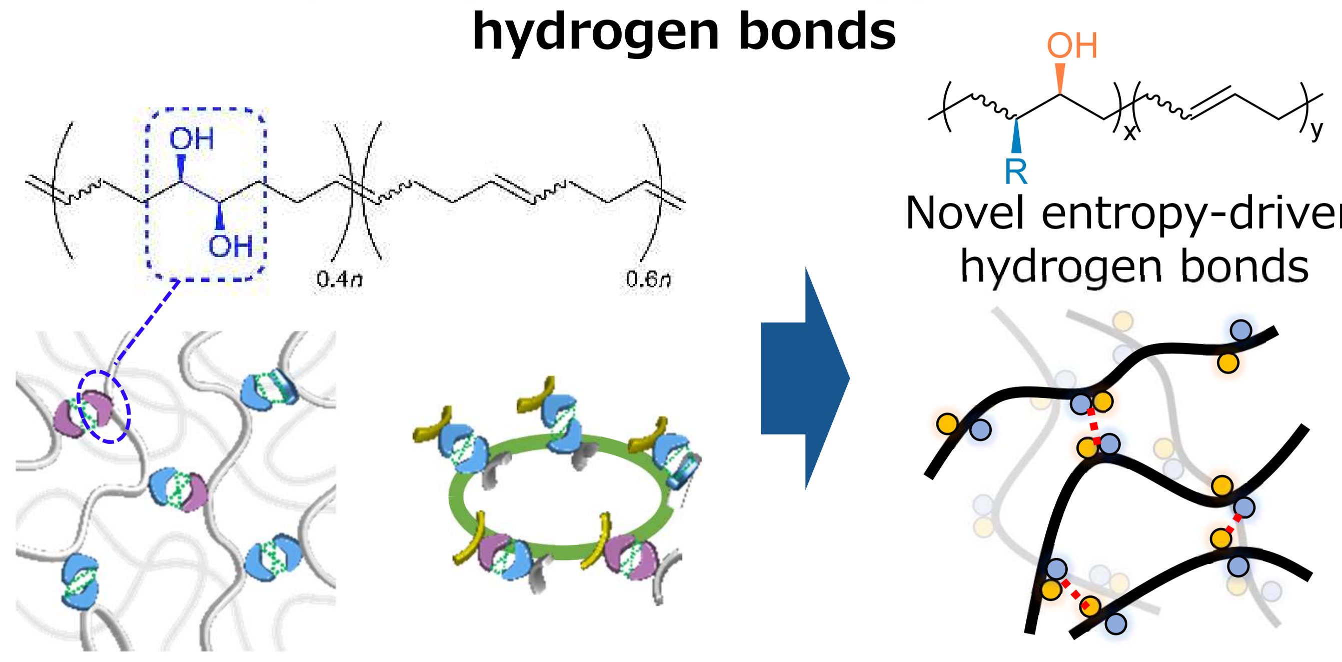


Need for high mechanical strength during use and rapid degradation in environment after use



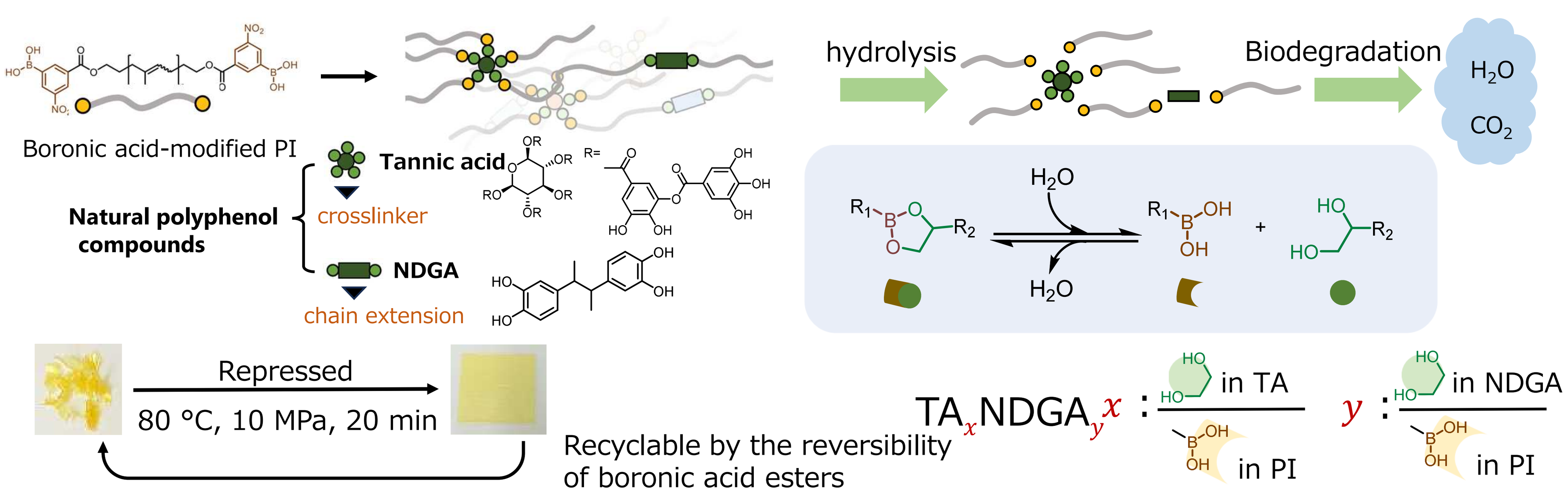
Topic 2: Combine crosslinking and degradability

Exploring of novel entropy-driven hydrogen bonds

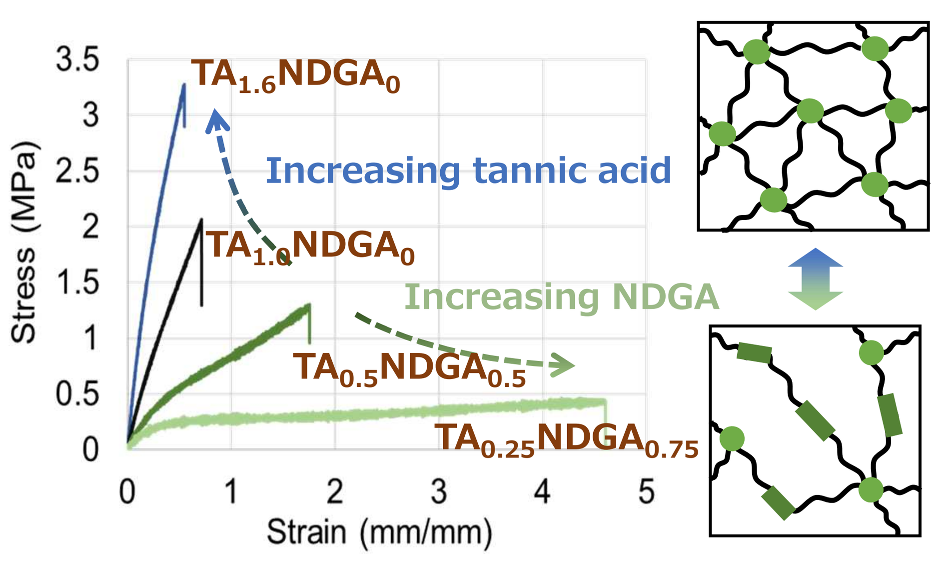


Hydrogen bond optimization

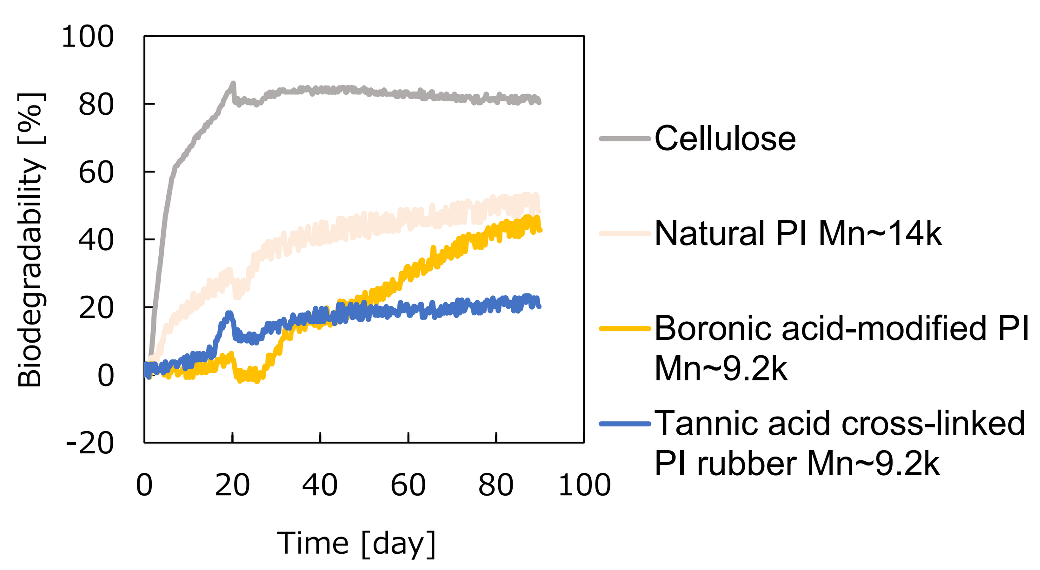
Tuning degradability using water-responsive dynamic bonds by using boronate esters



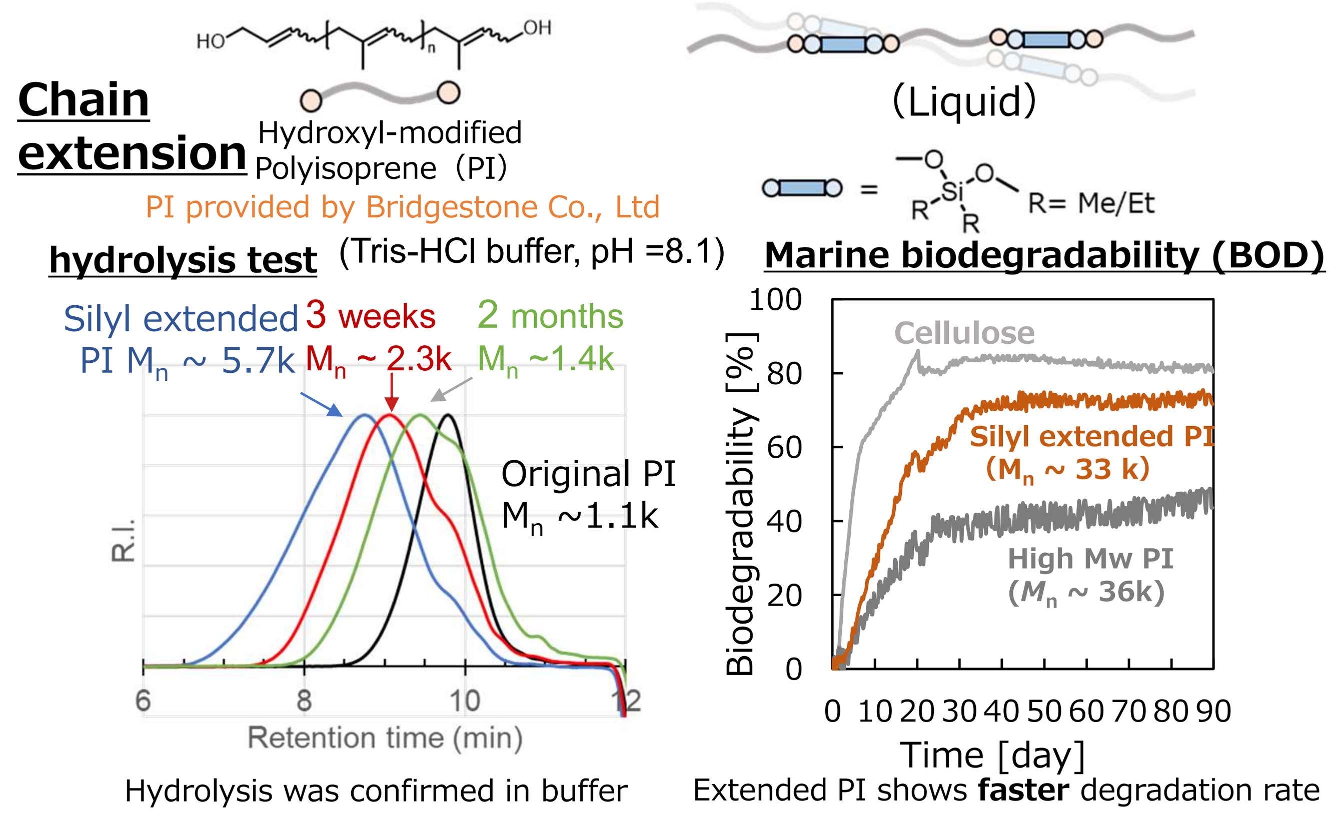
Uniaxial tensile test

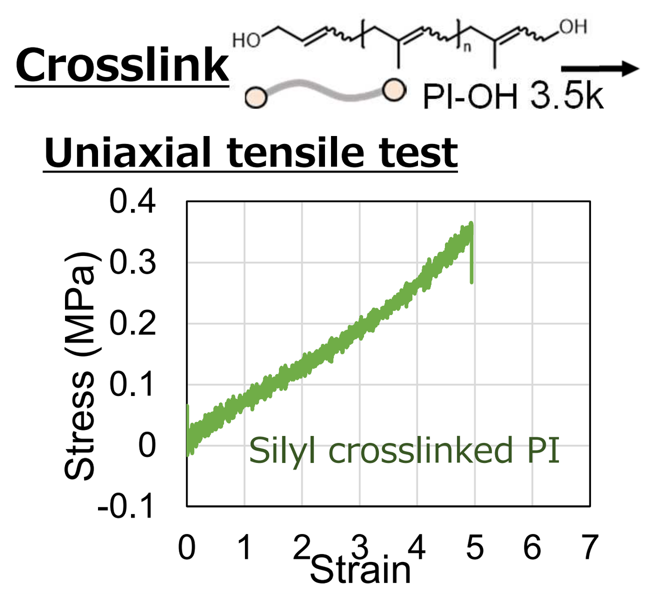


Marine biodegradability (BOD)



Utilization of silyl esters

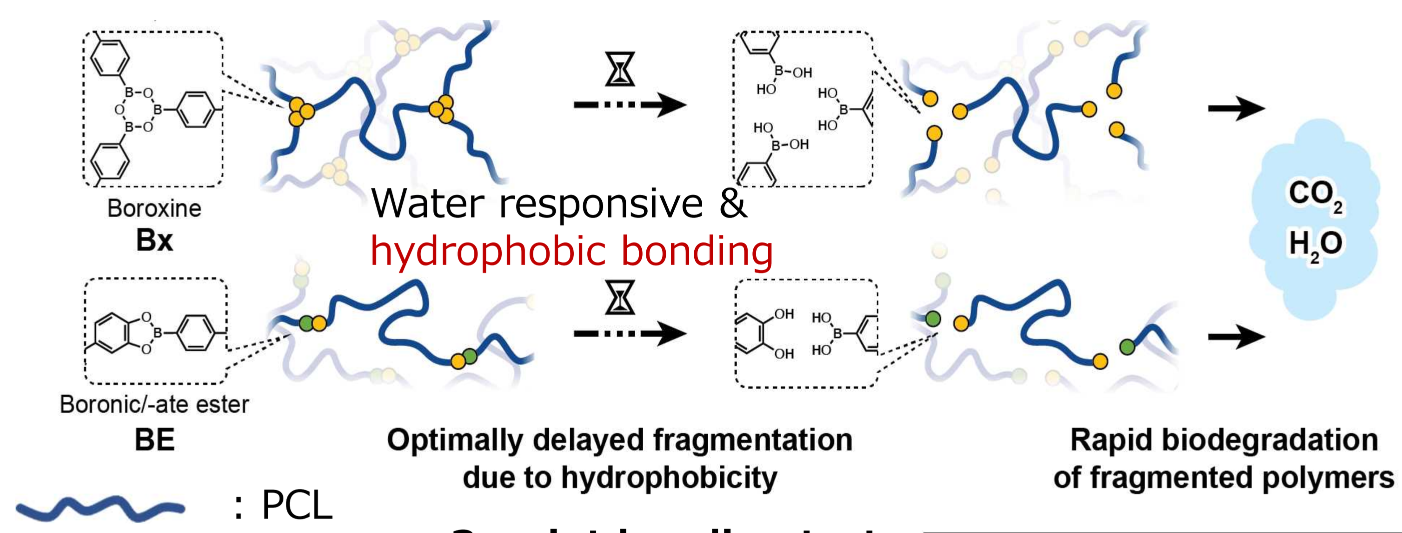


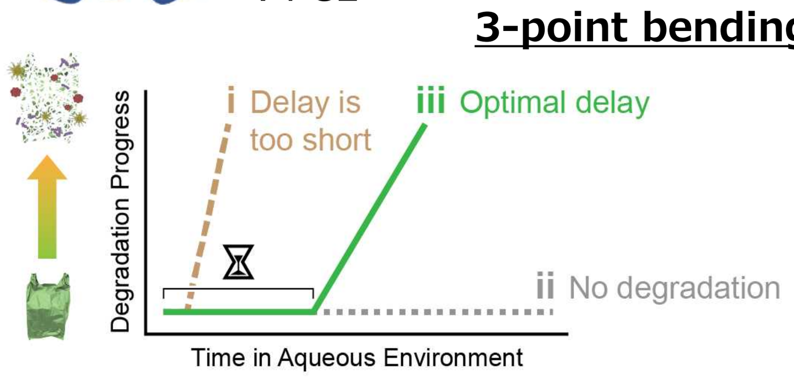


Silyl crosslinked PI

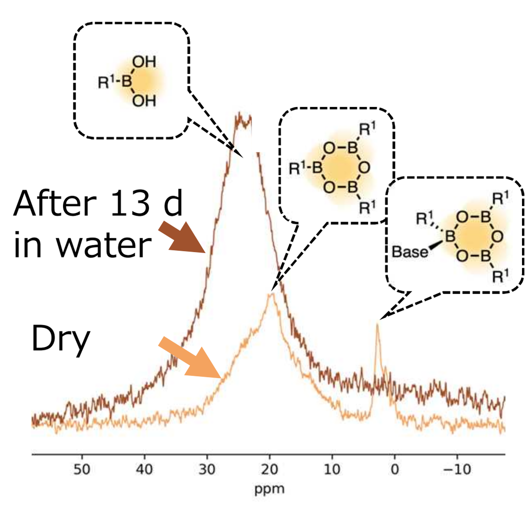
Rubber materials cross-linked by silyl ether were successfully obtained. Degradability under test

Tuning degradability of fast biodegradable PCL



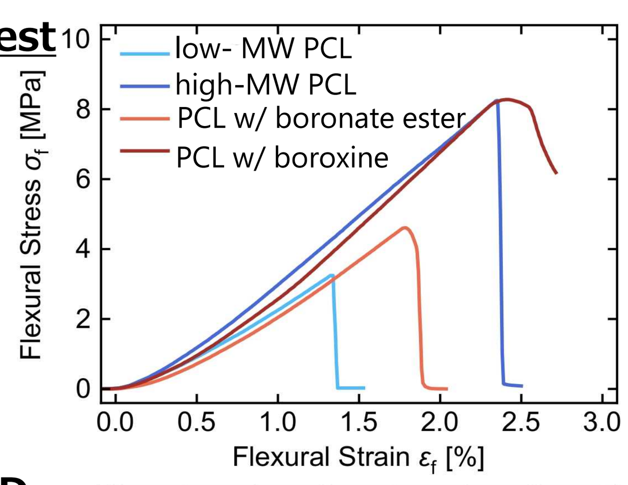


Solid-state 11B NMR

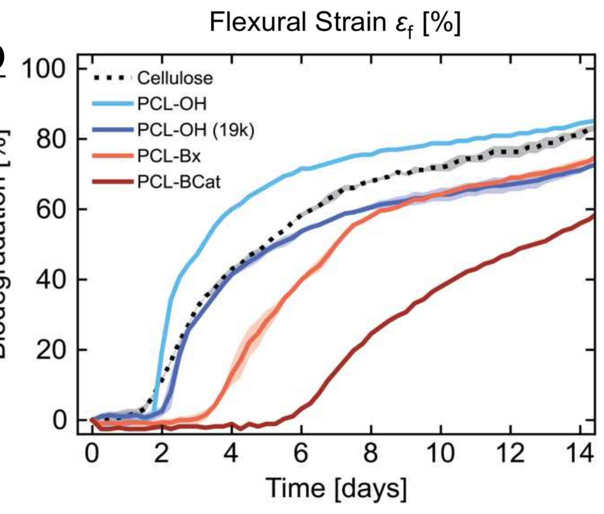


Bond dissociation by water was confirmed.

3-point bending test

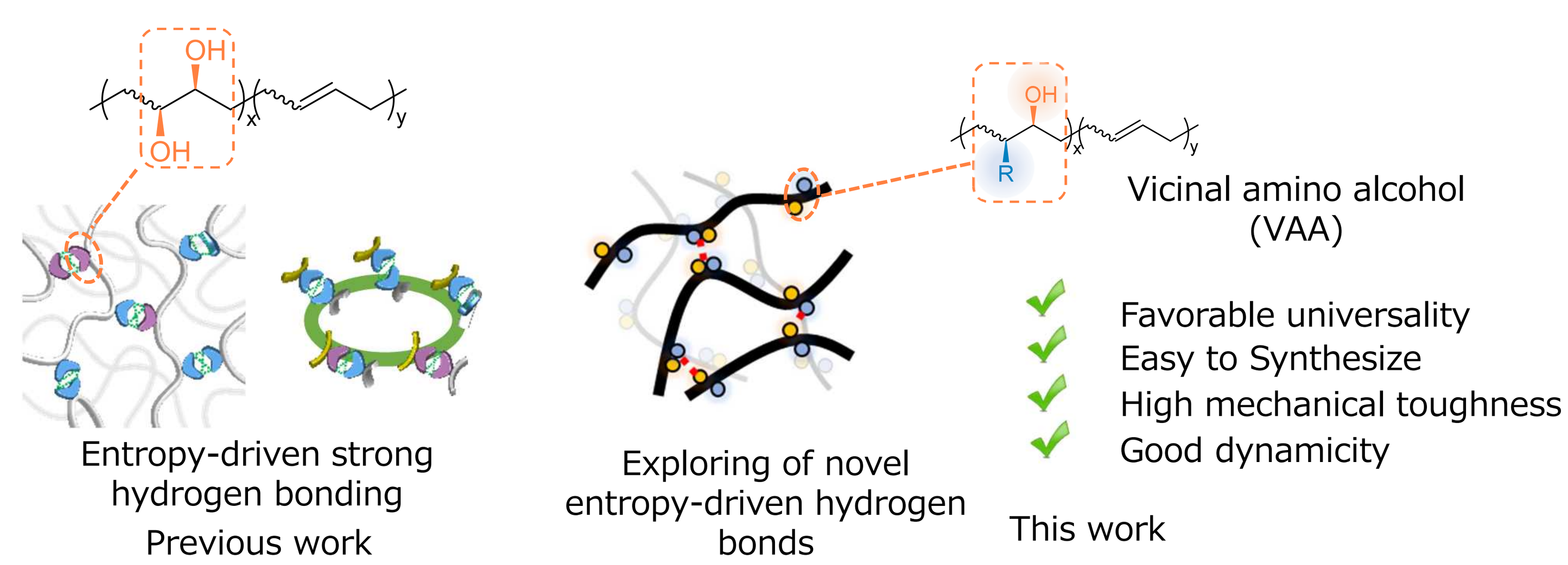


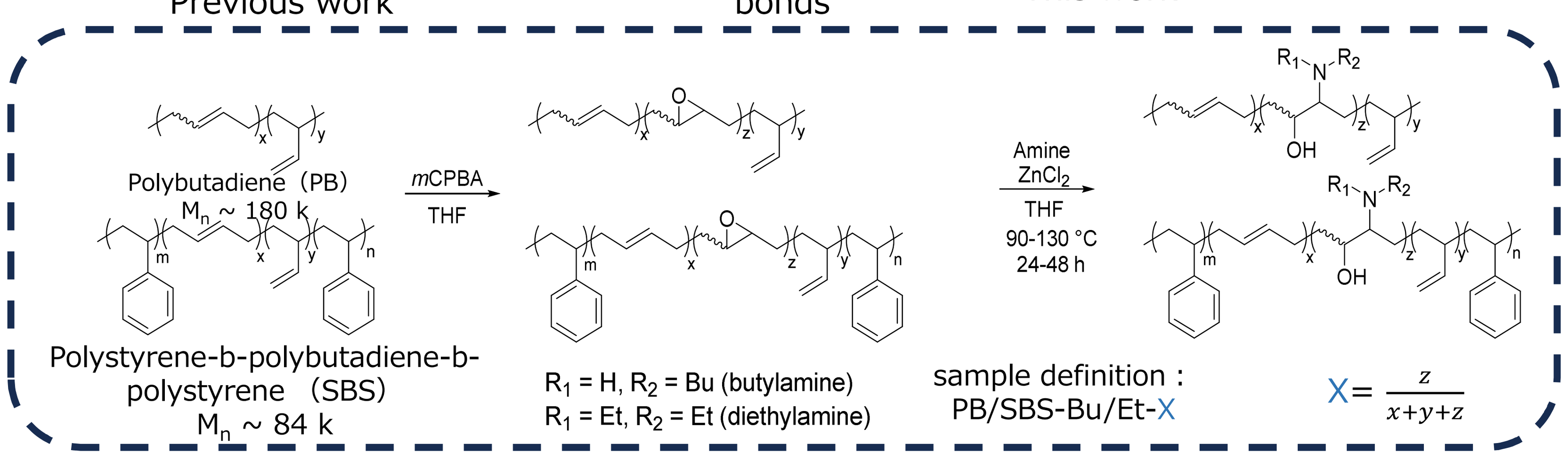
BOD



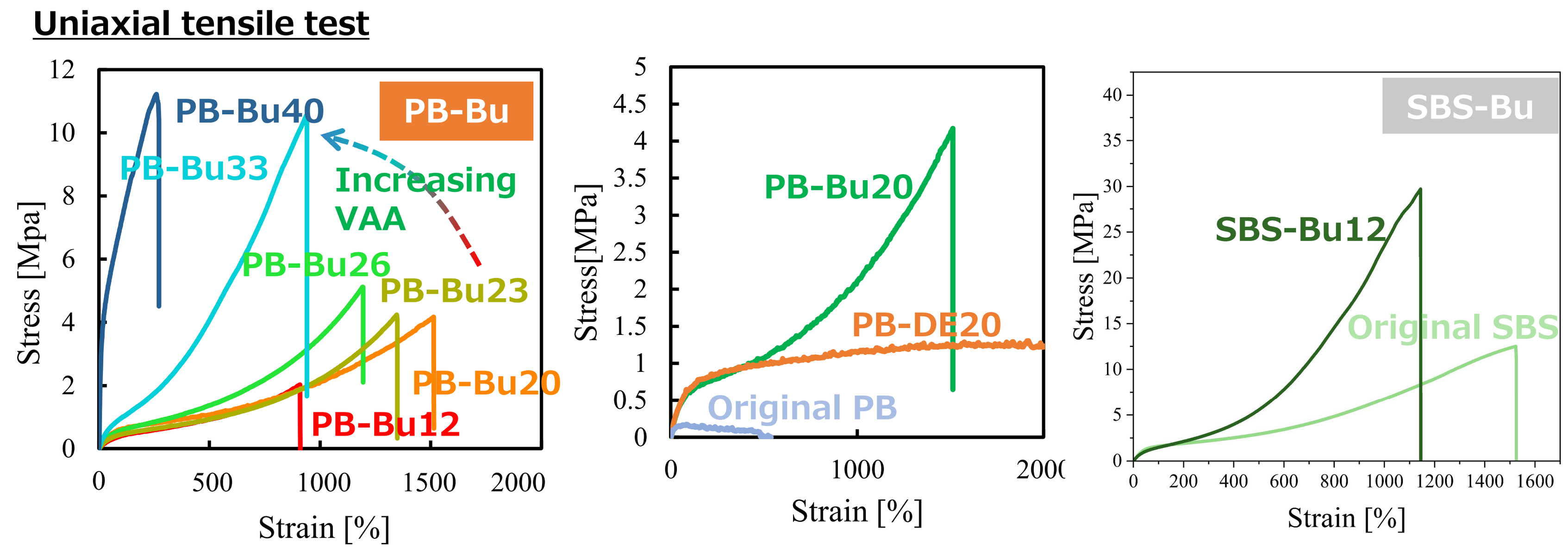
Optimally delayed fragmentation due to hydrophobicity

Exploring of novel entropy-driven hydrogen bonds





Uniaxial tensile test



No. A-15-6E

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

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

Organization: National Institute of Advanced Industrial Science and Technology（AIST）

Contact: Hiroshi Morita

1. Introduction

Our technology

・Multi-scale simulation technology for polymer materials from atomic to mesoscopic scales.

・Material analysis using informatics technology

Issues in development of multi-lock-type polymer materials

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

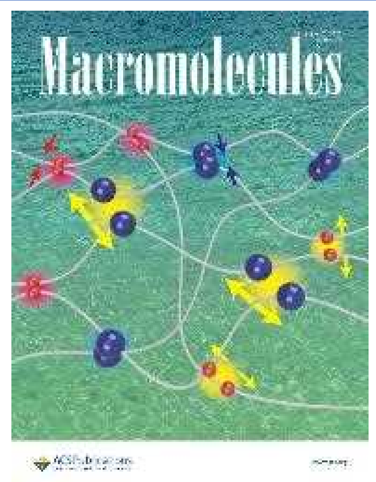
●Material designs for toughened polymer with physical cross-linking

Objective until end of FY2024

・ Model study of degradation of multi-lock polymer ：Yoshie et al developed the dynamic bond elastomer having the functions of toughness in use and degradation in marine. In this study, we made the model of dynamic bond elastomer to clarify the functions of both toughness and degradation. In the near future, we will design its material having those functions in high level.

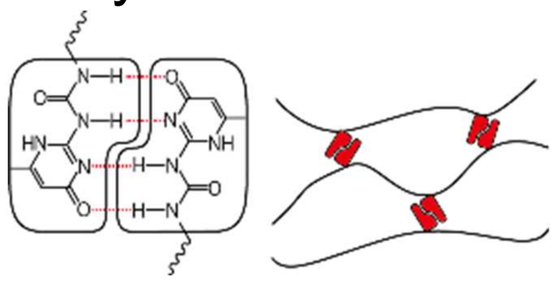
2. Model study of degradation of multi-lock polymer

Y. Yasuda, et al., Macromolecules, 2023, 56(18), 7432

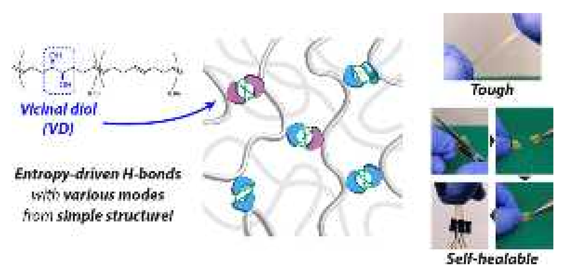


2.1 Modeling of Dynamic bond elastomer

・Dynamic bond elastomer developed by Yoshie et al

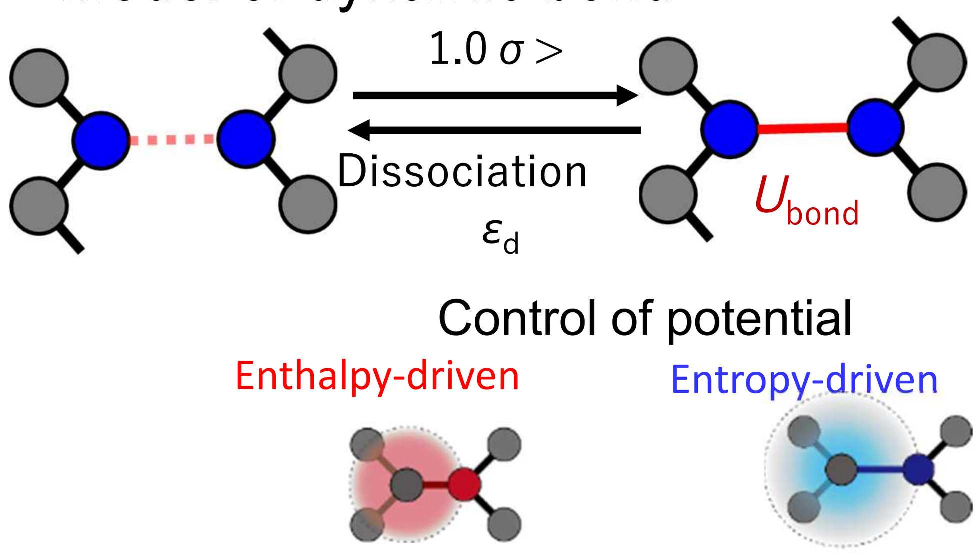


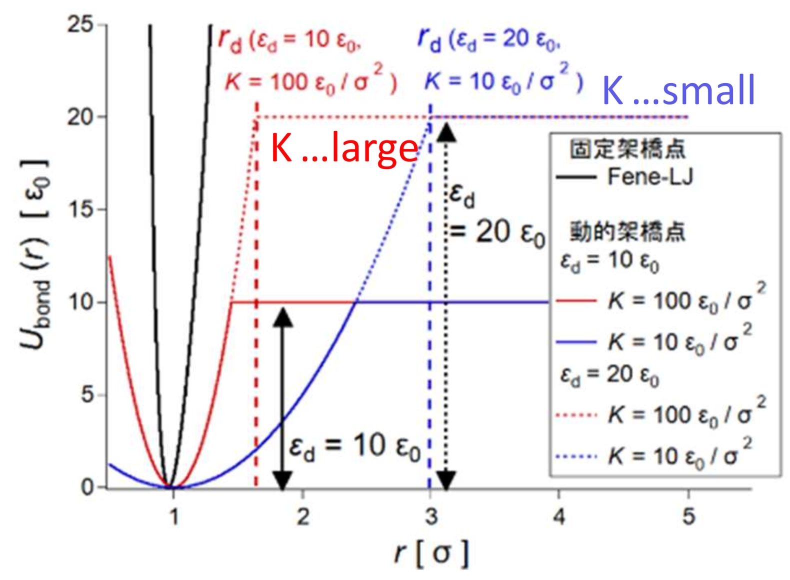
Enthalpy-driven (UPy)



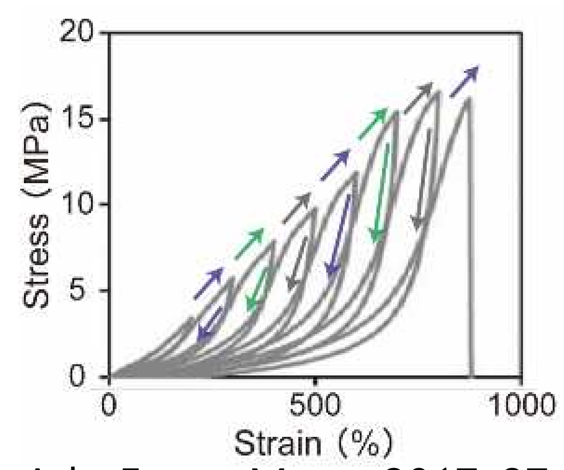
Entropy-driven (vicinal diol)

・ Model of dynamic bond





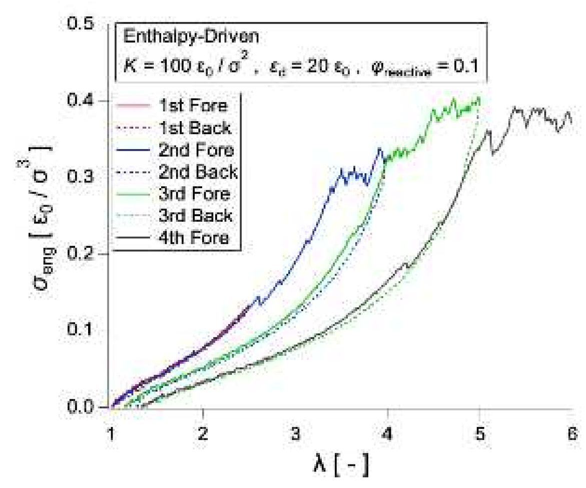
・Reproducing experimental results



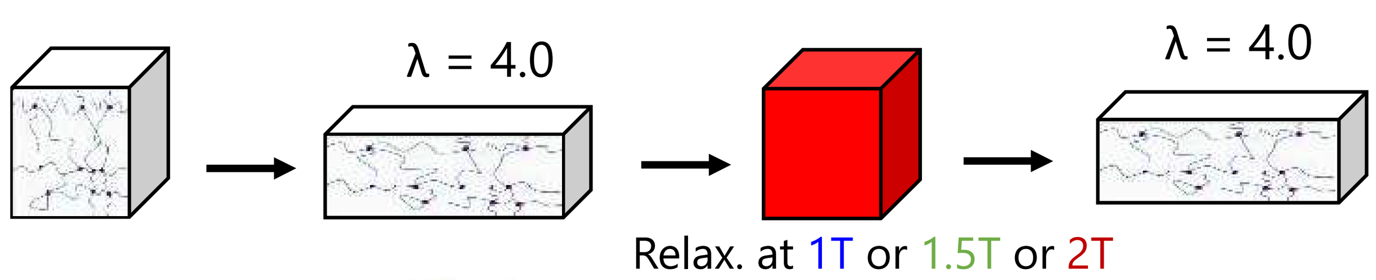
Experimental result

Adv. Funct. Mater. 2017, 27, 1701670

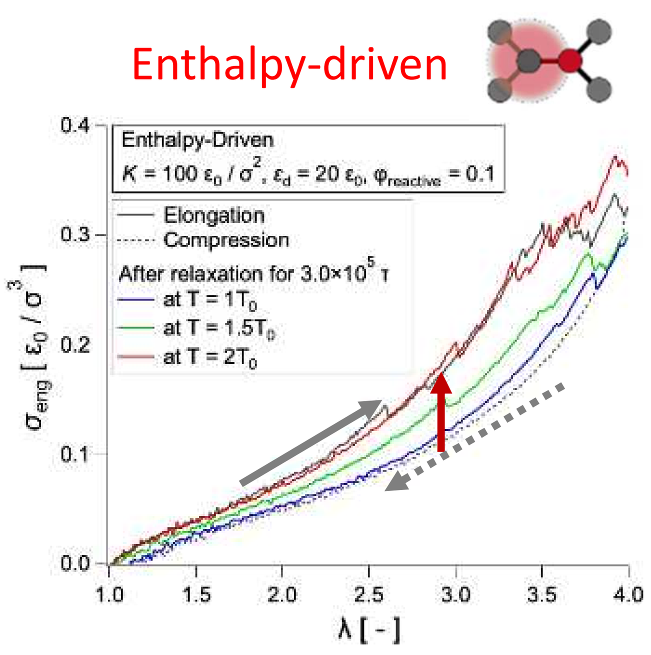
Simulation result



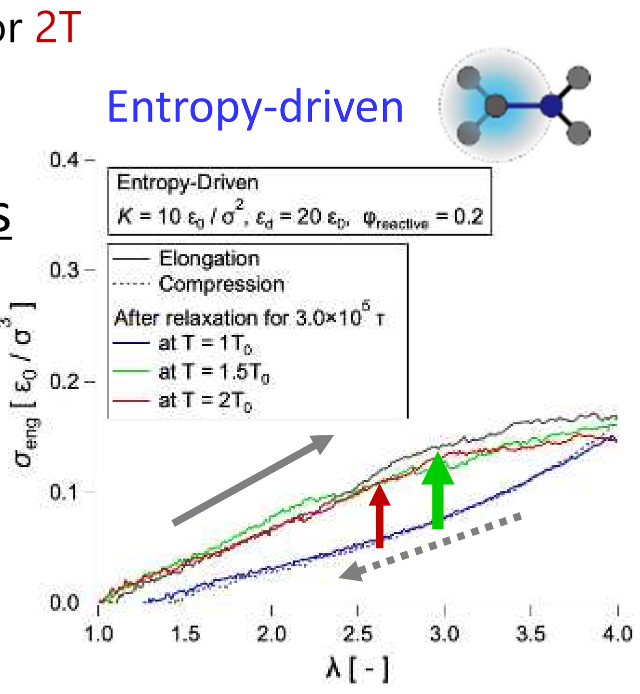
2.2 Stress recovery of dynamic bond elastomer



Enthalpy-driven



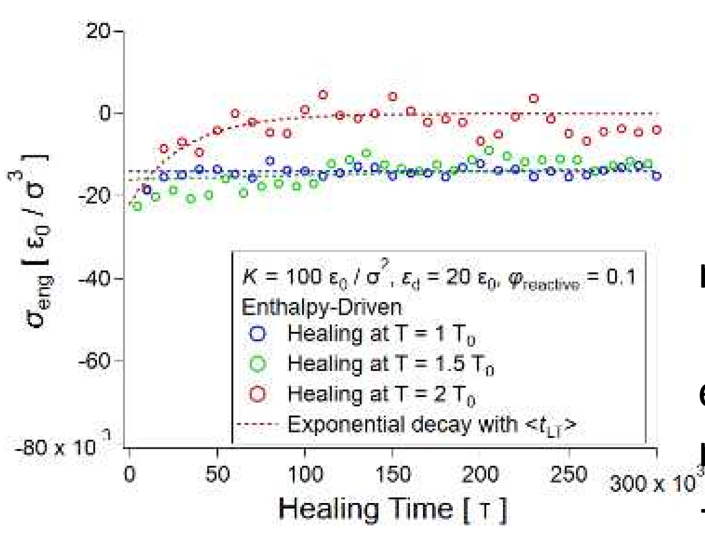
Entropy-driven

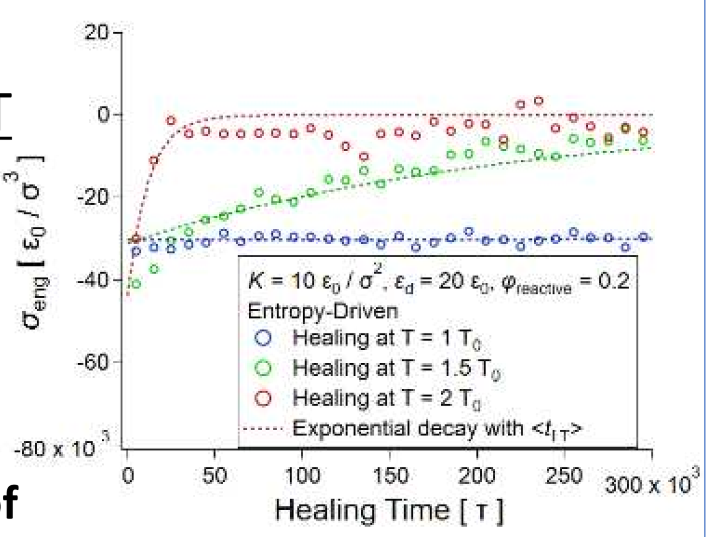


Stress-strain curves

・At high T, all curves recovered.

・At T=1.5T, curve of entropy driven recovered.





Stress-relaxation curves at several T

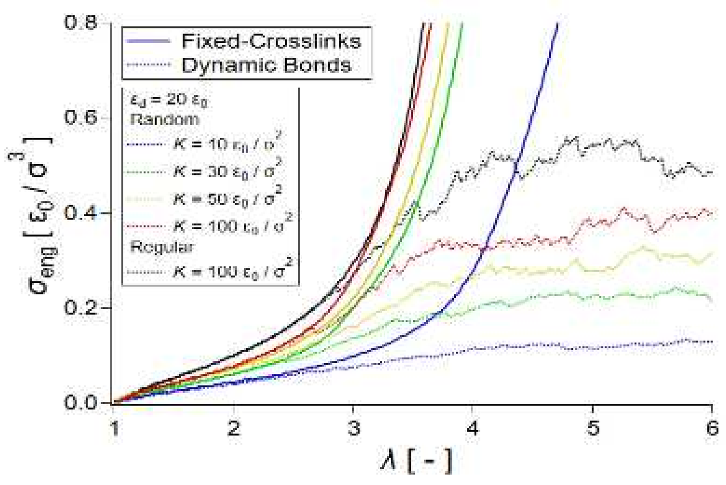
・At high T, stress recovered.

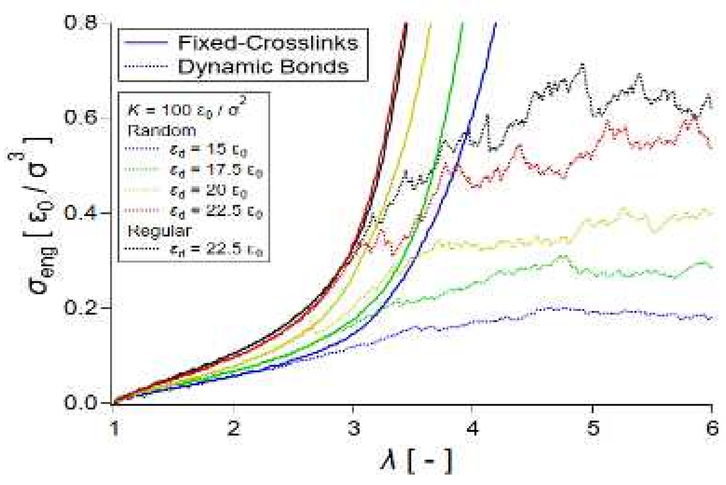
・ At T=1.5T, stress of entropy driven recovered.

→Related to lifetime of dynamic bond

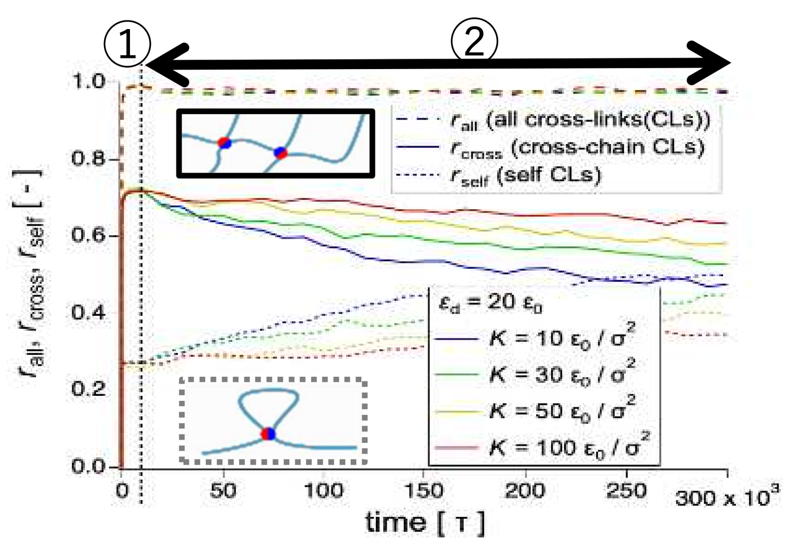
2.3 Change in the cross-linked structures of dynamic bond

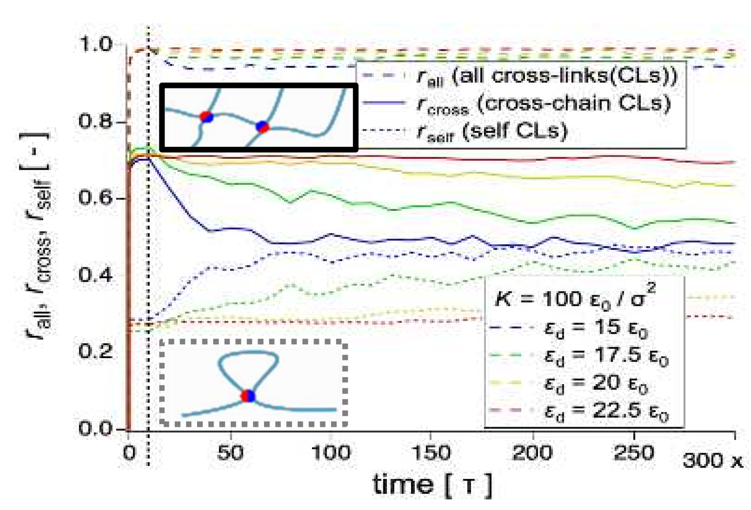
➢ K dependence（$\varepsilon_d = 20\ \varepsilon_0$） ➢ ε_d dependence（$K = 100\ \varepsilon_0 / \sigma^2$）





・in the case of small K (entropy driven) low ε_d (small dissociation energy), initial elastic modulus and maximum stress become smaller.





・At ① term(early term), network formed under kinetic control. At ② (following term), network reconfigured to thermodynamically stable structure.

・ in the case of small K (entropy driven) low ε_d (small dissociation energy), number of self cross-link increased.

4. Future work

Model study of degradation of multi-lock polymer

・Refinement of the model along the corresponding experiment and simulation study using its model. Conducting a detailed analysis of the state of the association, which is not known by experimentation.

・In-depth collaborative research with companies by the simulations contributed to material design.

番号： A-15-7E

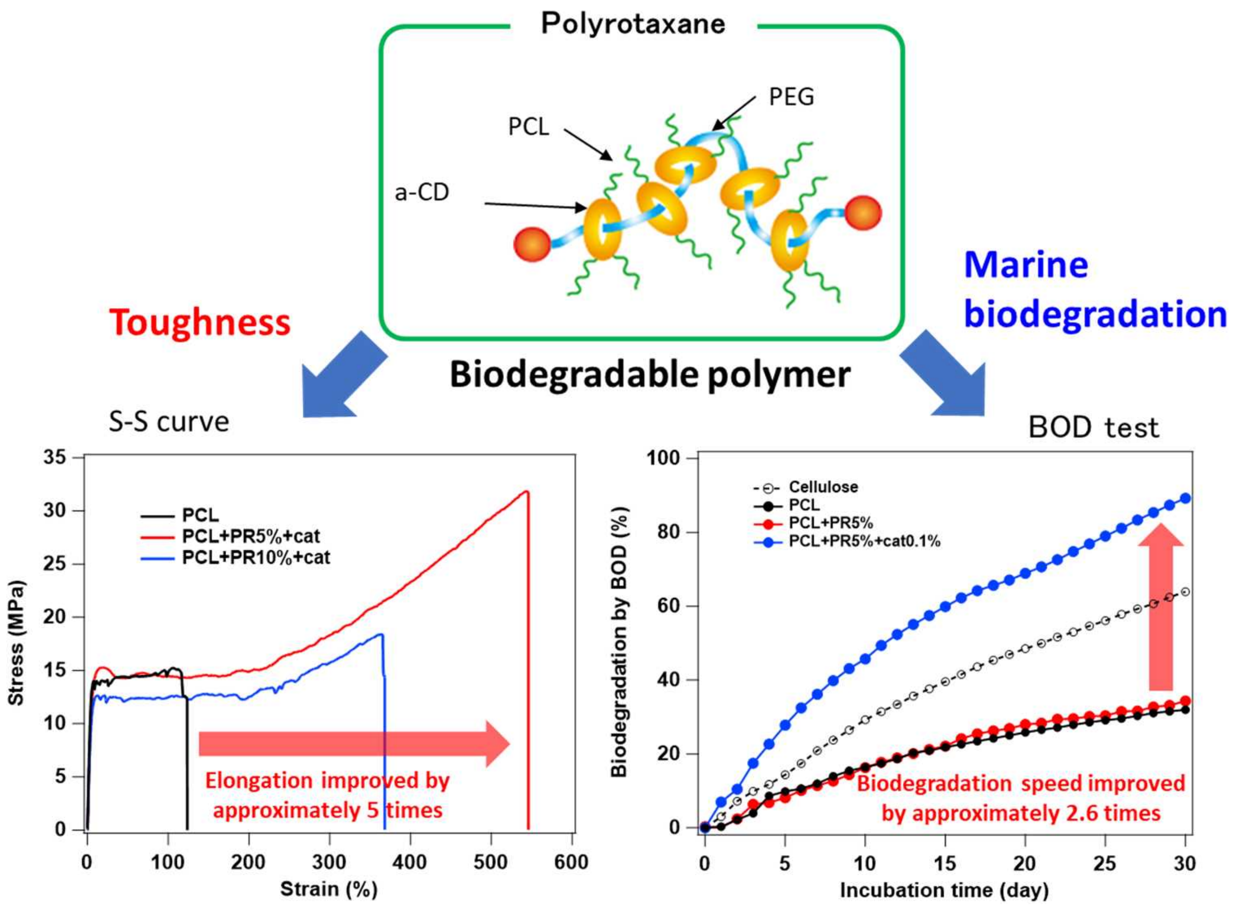
PJ:Development of Multi-lock Biopolymers Degradable in Ocean from Non-food Biomasses

Theme: Research and Development of Degradable Supramolecular Polymers with Combined Multi-locking Mechanism and Toughness

Organization: University of Tokyo

Contact: Kohzo Ito, Shota Ando

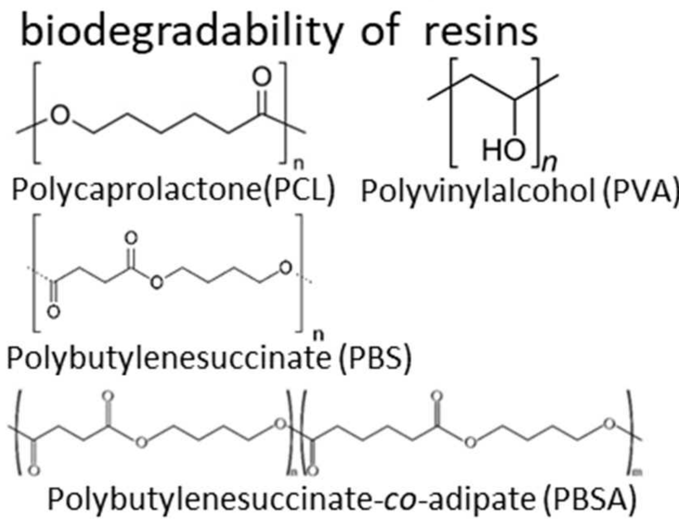
Biodegradable resin with polyrotaxane addition for both toughness and seawater degradability



Achieved both toughness and seawater degradability (speed control). Aiming to elucidate point control and biodegradation mechanism using PR.

Effect of adding PR

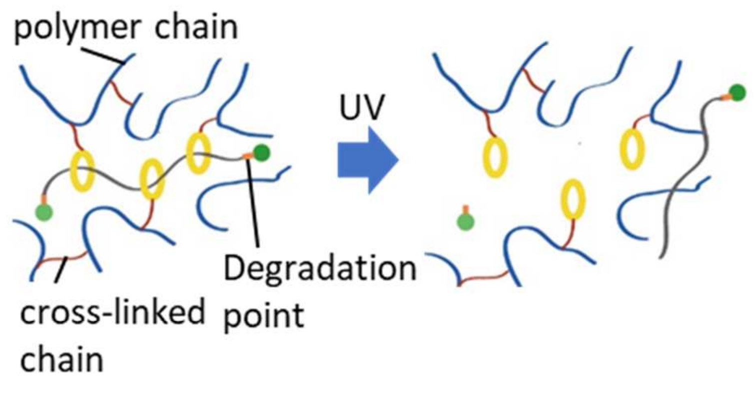
- Combination of toughness and biodegradability of resins



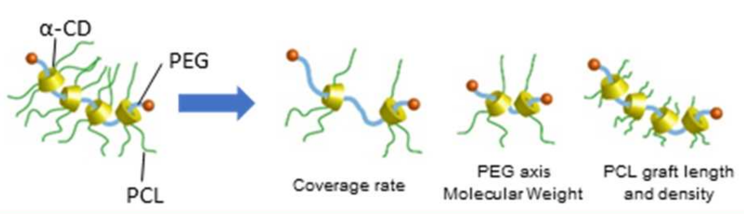
- Combines toughness and biodegradability through ester exchange reaction
- Achieved toughening and biodegradability of ester-exchange vitrimers

Multi-lock function

- Synthesis of end-stimulated degradative PR

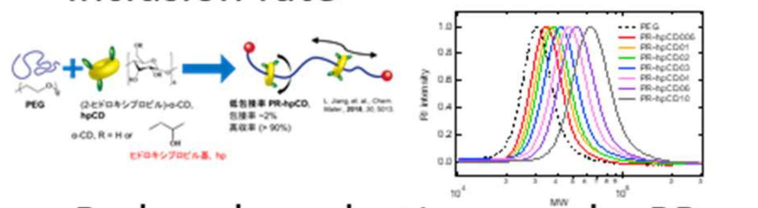


- Controlled structural parameters such as coverage ratio, axial molecular weight, and graft density

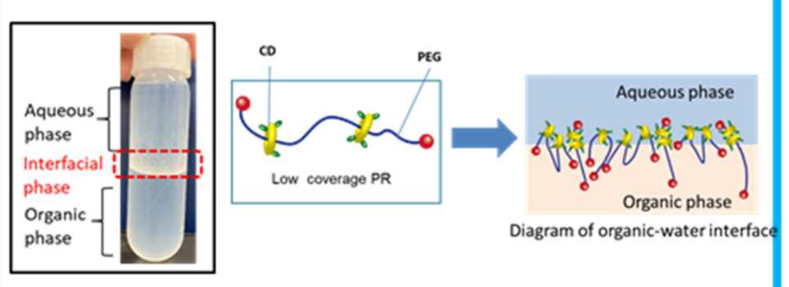


Social integration

- One-pot synthesis of PR to reduce production cost and control inclusion rate

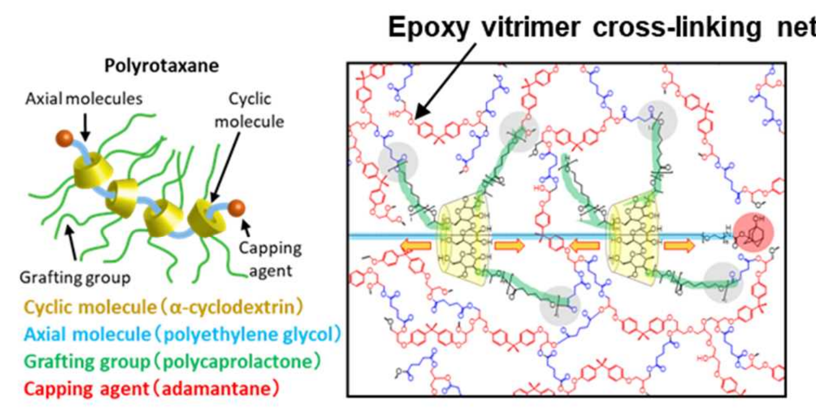


- Reduced production cost by PR extraction and purification method

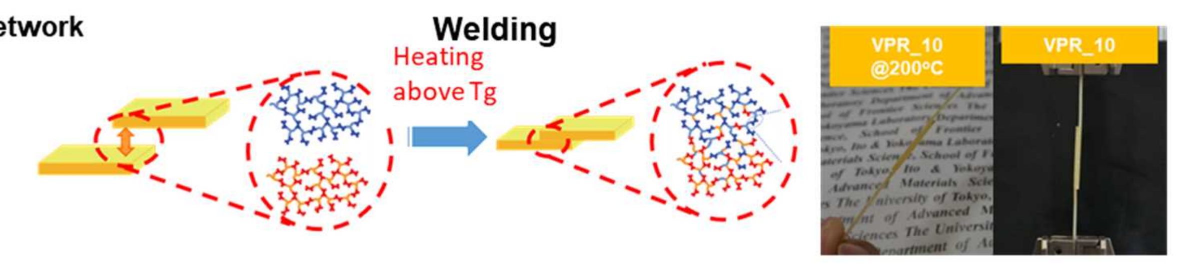


- Raw materials such as components, solvents, etc. Cost reduction

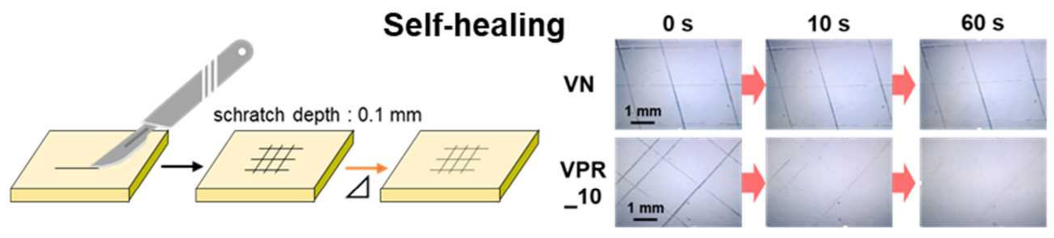
Toughening of epoxy vitrimer resins containing polyrotaxane

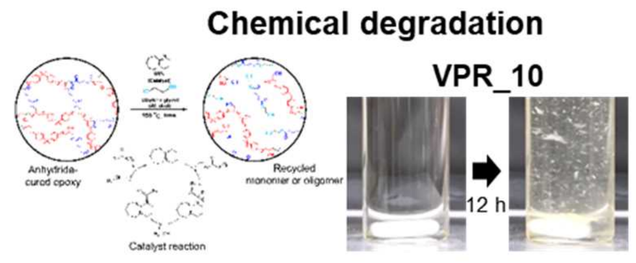


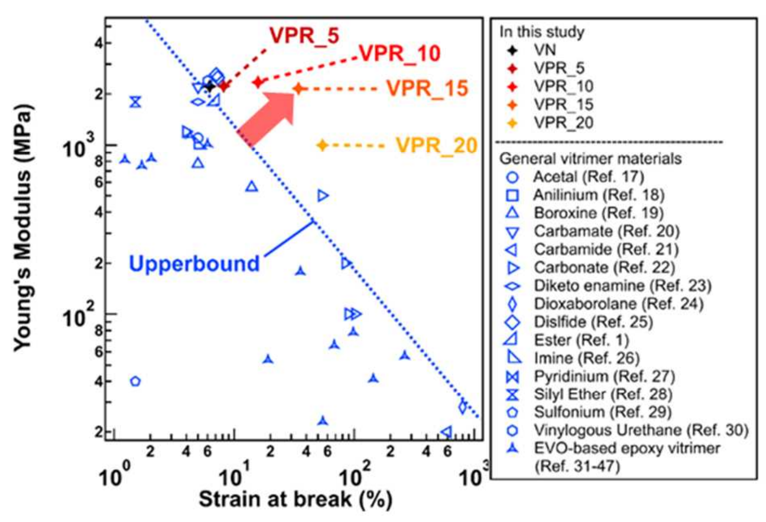
Homogeneously dispersed due to chemical bonding of PR and cross-linking network



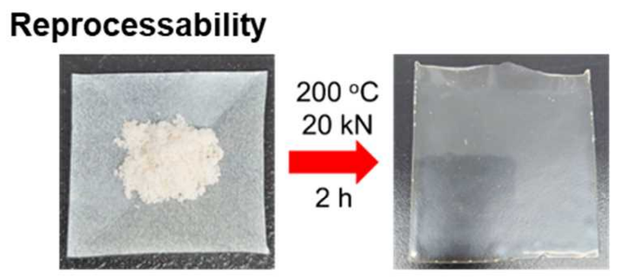
In addition to the toughening due to the addition of PR, the energy potential of the bond exchange reaction due to sliding motion is reduced.

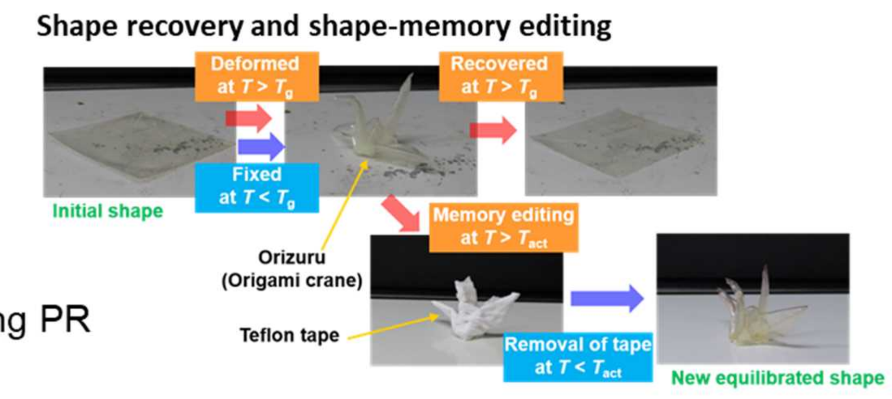


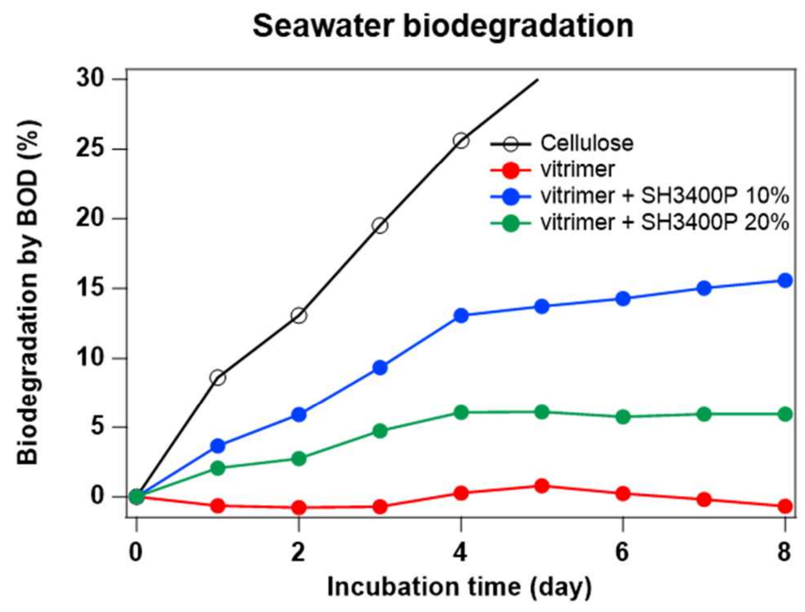


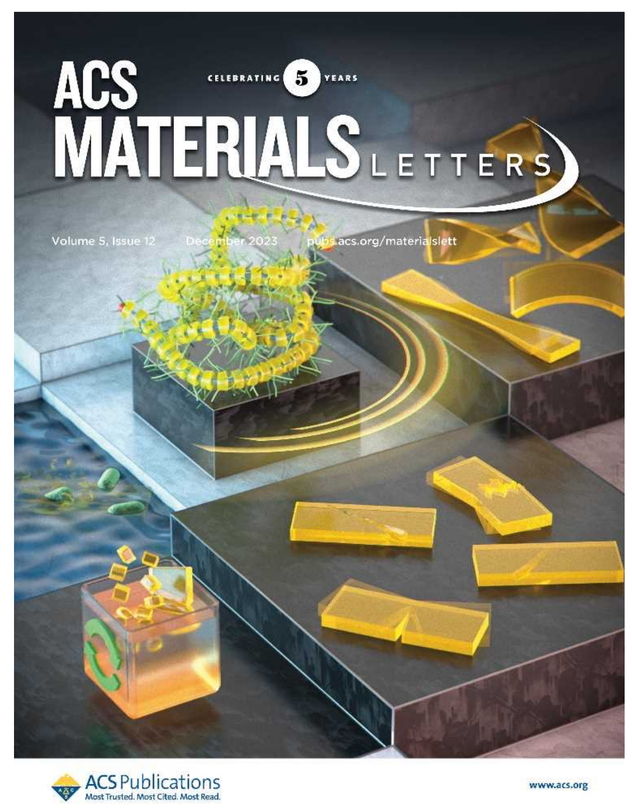


Toughened without changing hardness by adding PR





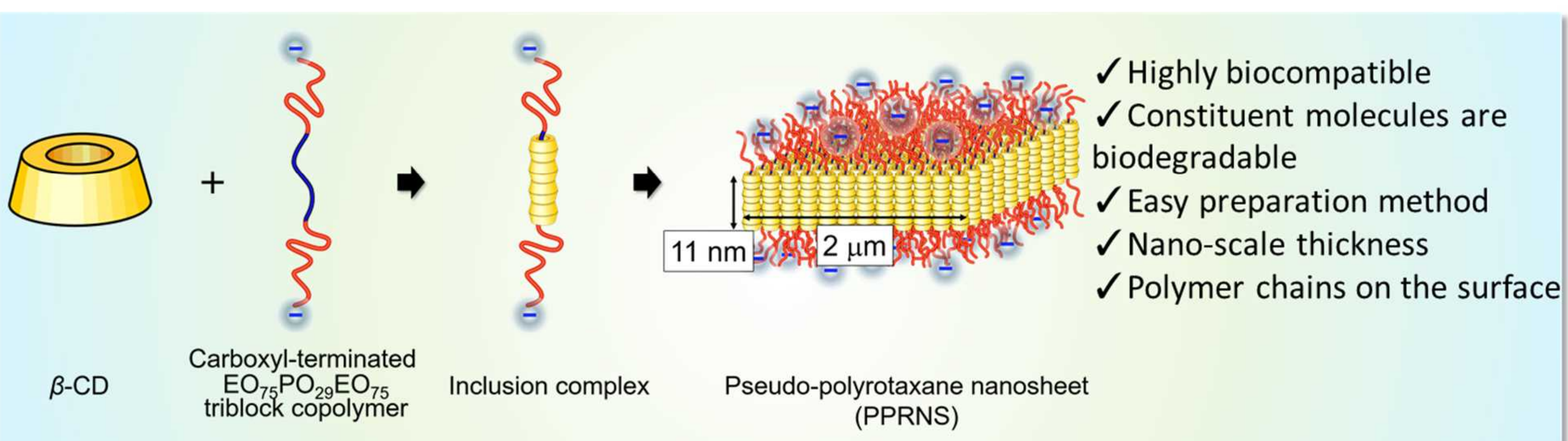




S. Ando, M. Hirano, L. Watakabe, H. Hideaki, K. Ito, "Environmentally Friendly Sustainable Thermoset Vitrimer-Containing Polyrotaxane", ACS Materials Lett., 2023, 5, 3156.

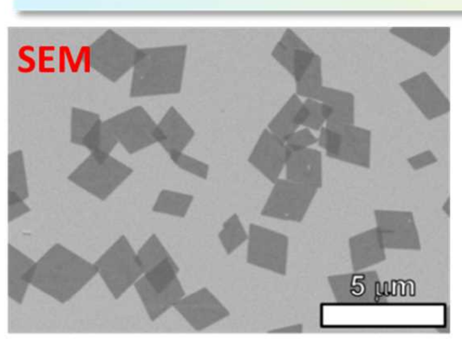
Development of enzymatic switching degradation by utilizing suspected polyrotaxane nanosheets

A completely new type of nanosheet material consisting of the non-covalent assembly of cyclic oligosaccharides (cyclodextrins) and polyethers, discovered in our laboratory in 2019.

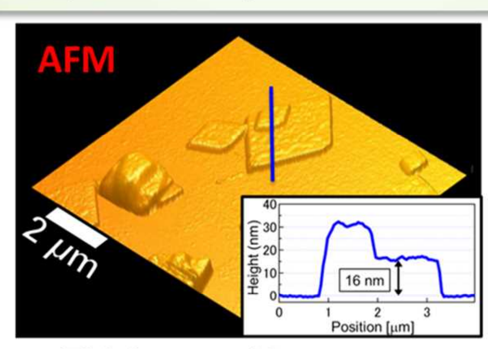


- ✓Highly biocompatible
- ✓Constituent molecules are biodegradable
- ✓Easy preparation method
- ✓Nano-scale thickness
- ✓Polymer chains on the surface

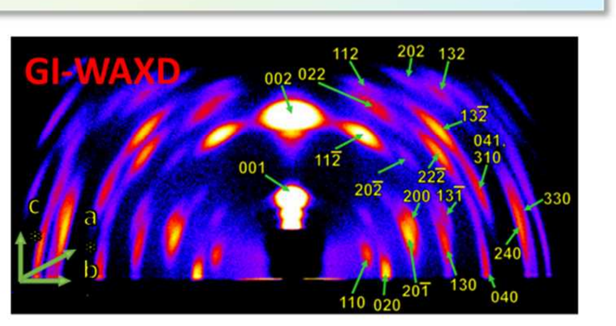
Chem. Commun, 2019. **55**, 4158.



Size: 1-2 μm

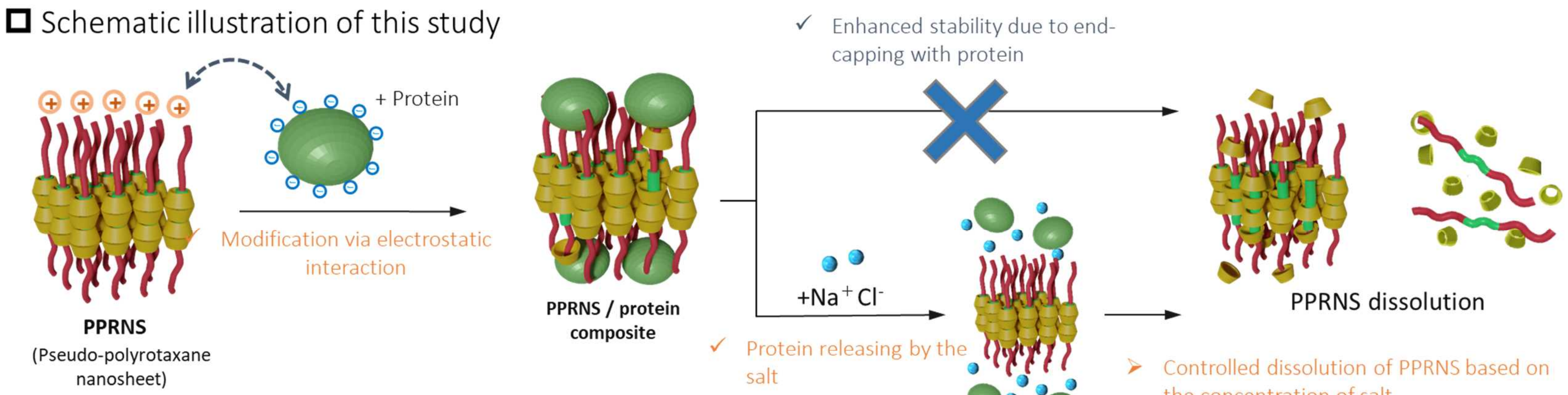


Thickness: 16 nm

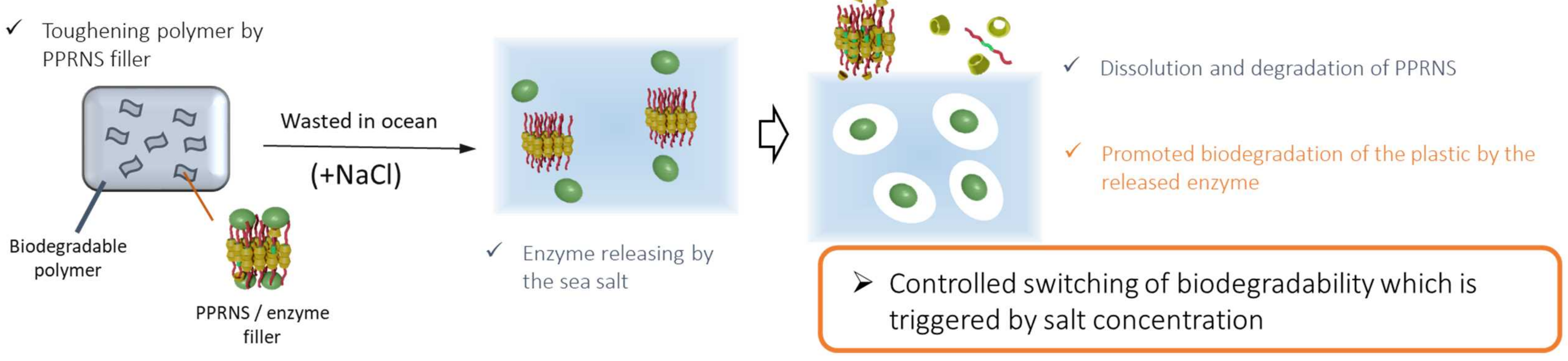


Monoclinic crystal: a =1.91 , b =2.43, c = 1.57(nm) , $\alpha = \gamma = 90°$, β = 111°

☐ Schematic illustration of this study



☐ Application in biodegradable plastics in ocean

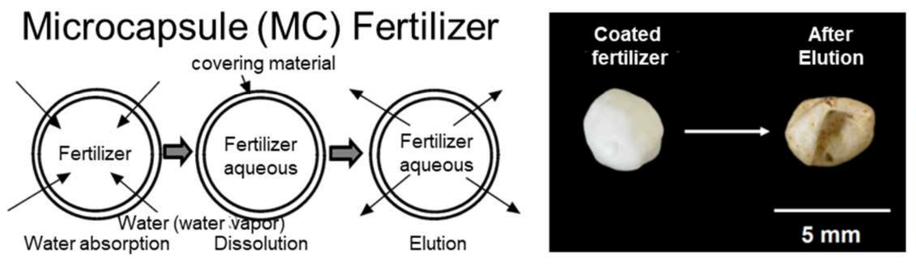


➢ Controlled switching of biodegradability which is triggered by salt concentration

Corporate Collaboration (Mitsubishi Chemical)

〇Application of PBS and PBSA to agricultural coated fertilizer shells

Microcapsule (MC) Fertilizer



Plastic film fertilizer coating can supply a fixed amount of fertilizer to plants for a long period of time. It is used in approximately 60% of rice paddies in Japan.

Plastic shells collected at the beach

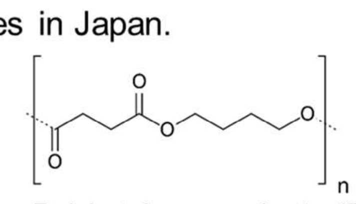
Ref) NHK web news

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™

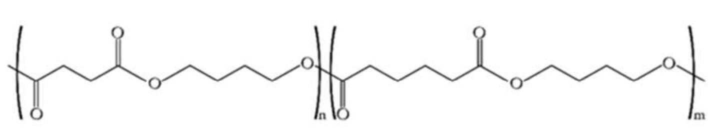
MITSUBISHI CHEMICAL



Polybutylenesuccinate (PBS)

High strength but brittle
Low marine biodegradability

Addition of PR with low inclusion rate improves ductility and biodegradability while maintaining strength

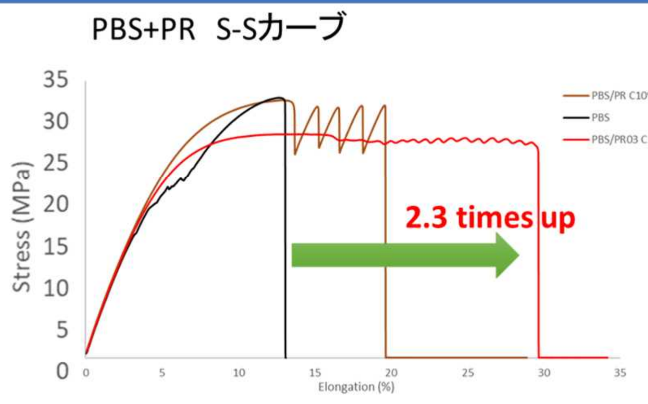


Polybutylenesuccinate-*co*-adipate (PBSA)

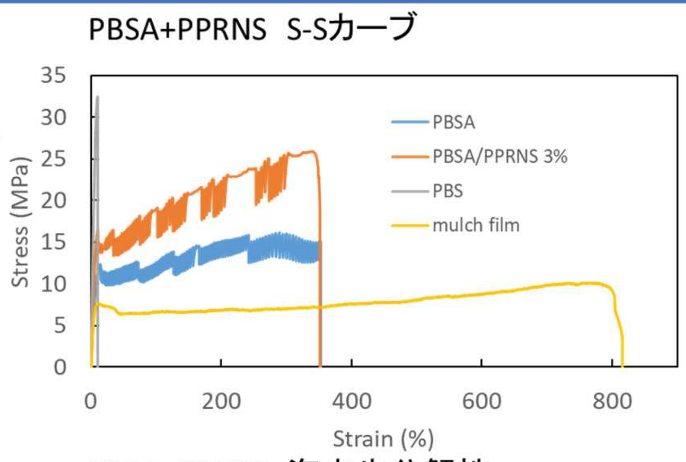
Softer and more ductile than PBS
Highly marine biodegradable

PPRNS addition improves strength while maintaining ductility and biodegradability

PBS+PR S-Sカーブ



PBSA+PPRNS S-Sカーブ

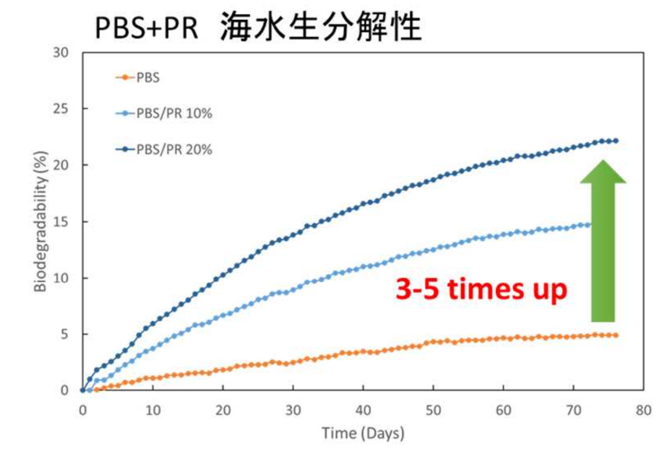


Fracture toughness
PPRNS Effect
1.5 times up

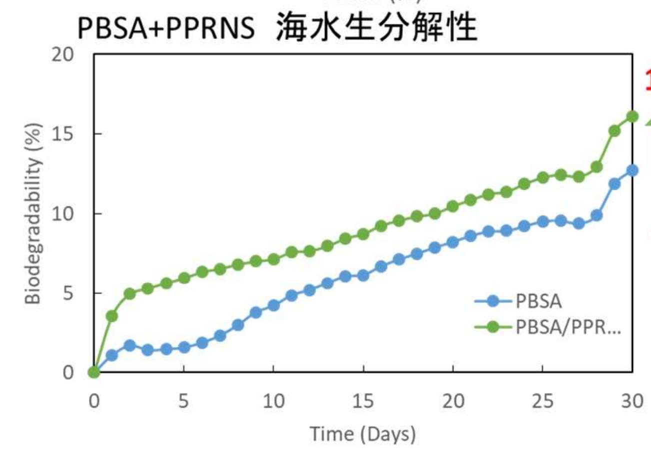
PE vs.
1.7 times up

PE mulch film

PBS+PR 海水生分解性



PBSA+PPRNS 海水生分解性



Toughness and biodegradability improved by addition of PR and PPRNS

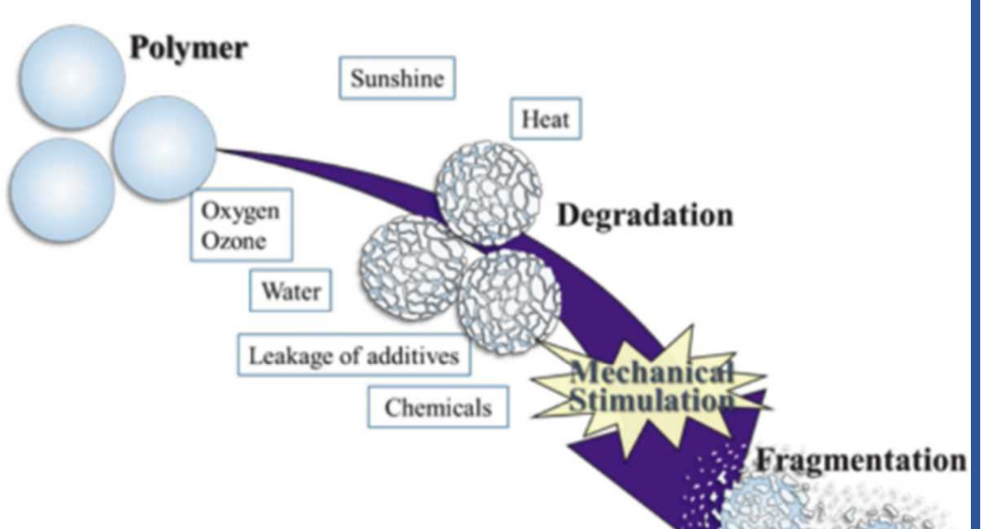
No. A-15-8E

PJ : Development of Multi-lock Biopolymers Degradable in Ocean from Non-food Biomasses
Theme: Structure and Properties of Multi-lock Biopolymer during the Environmental Degradation

Organization: E2: Kyushu University
Contact: takahara.atsushi.150@m.kyushu-u

Photooxidation and Fragmentation Behaviors of *it*PP Films

Microplastic formation Process



MPs collected from Tsushima Strait

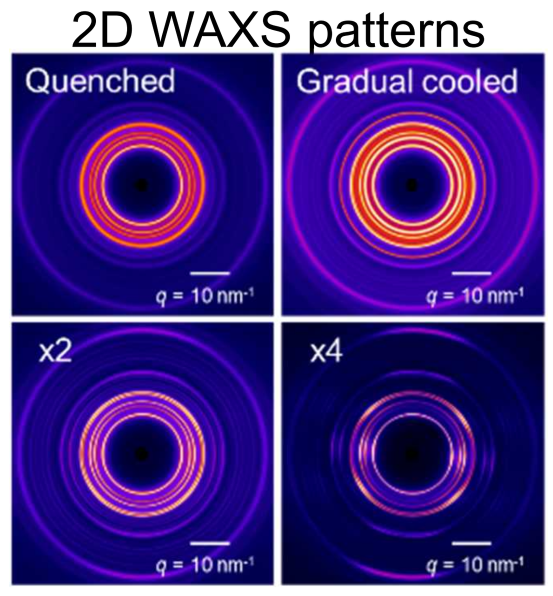
Purpose: Investigate the photooxidation and fragmentation behaviors of *it*PP to simulate the MPs formation in ocean.

Experimental

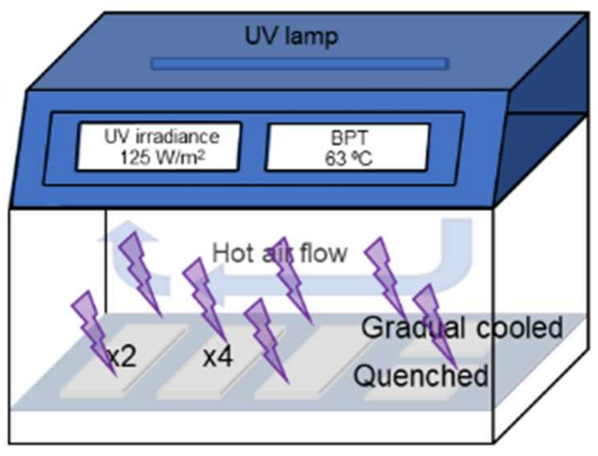
Sample information

*it*PP films	X_c (%)	f_{040}
Quenched	41.8	0
Gradually cooled	55.2	0
x2	56.0	0.379
x4	60.2	0.477

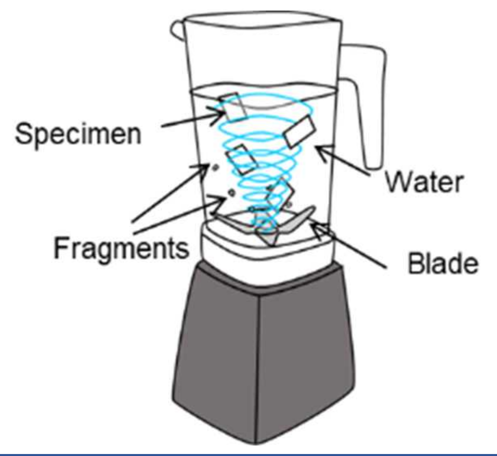
2D WAXS patterns



UV exposure test



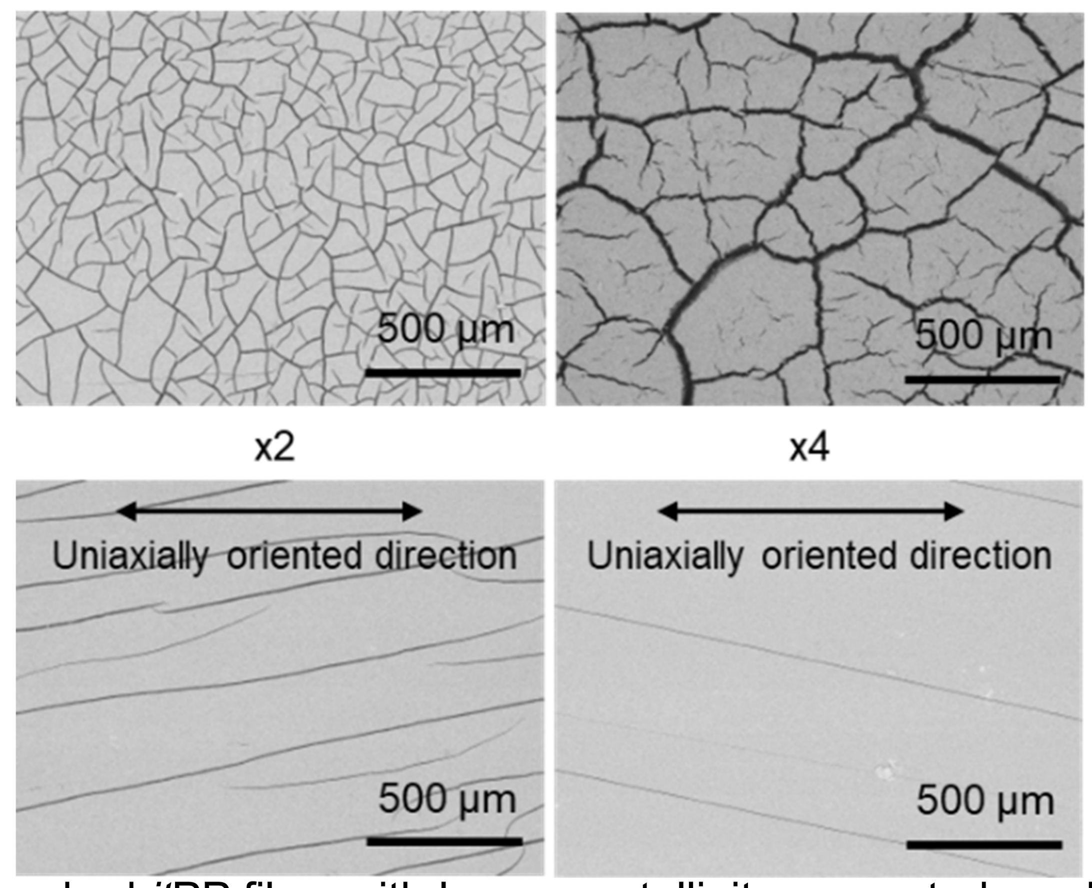
Fragmentation test



UV exposure test

Surface morphology

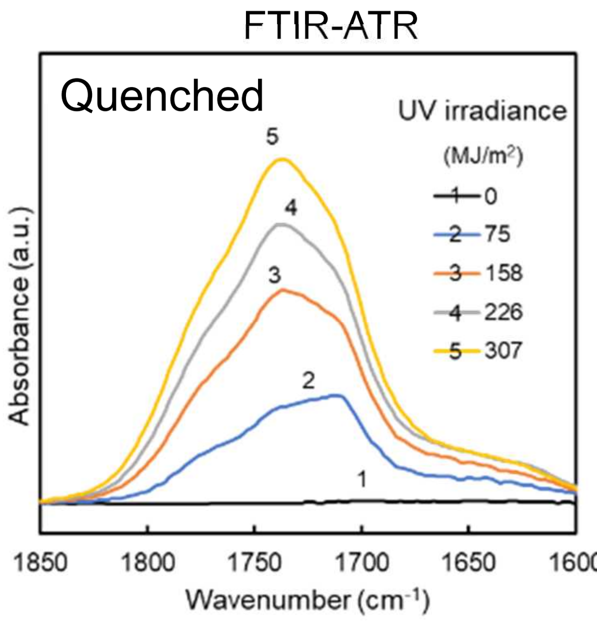
Quenched Gradually cooled



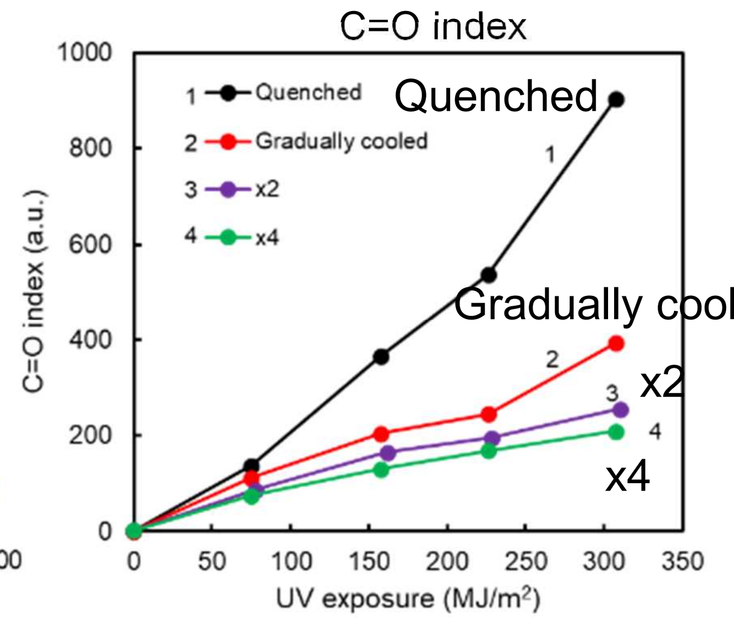
Quenched *it*PP films with lower crystallinity generated much denser cracks. Cracks were parallel to draw direction.

Surface chemical structure

FTIR-ATR

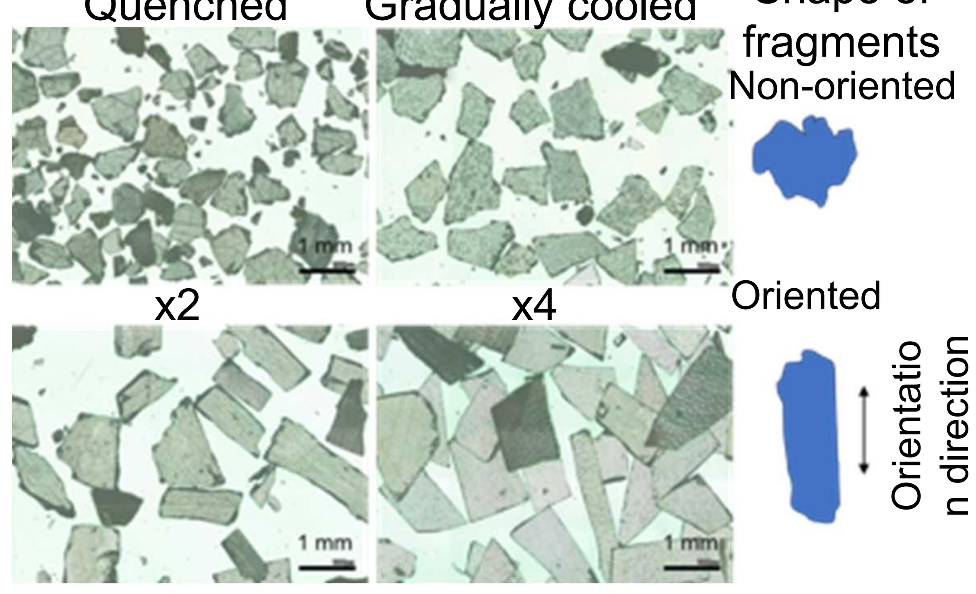


C=O index



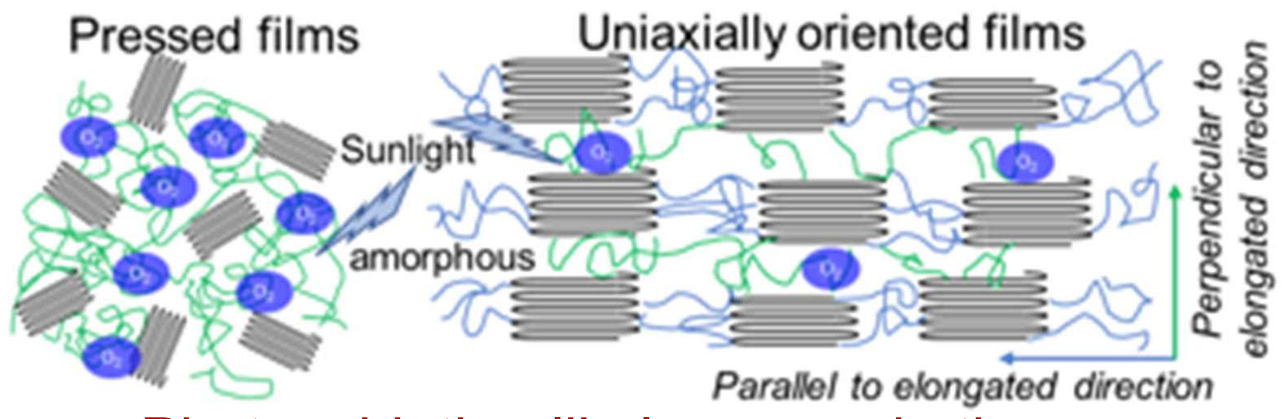
- Photooxidation occurred in UV-exposed *it*PP films.
- Photooxidation was inhibited by the crystalline structure and oriented molecular chains.

Fragmentation test



Uniaxially oriented *it*PP films produced larger fragments than pressed films. The oriented structure was observed in fragments generated from oriented *it*PP films.

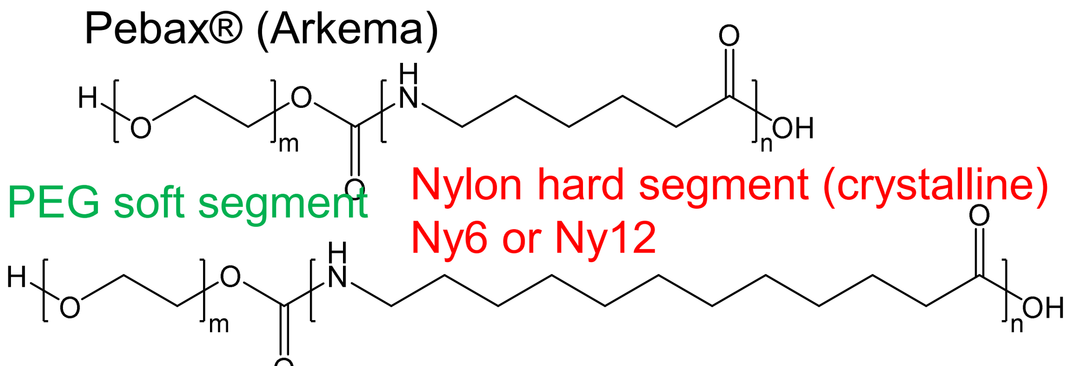
Summary

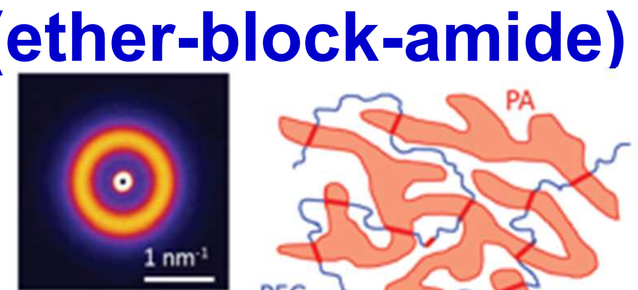


- Photooxidation likely occurs in the amorphous phase of *it*PP.
- Fragments with oriented crystalline structure were generated after fragmentation test.
- Ocean MPs were formed through photooxidation and fragmentation.

Environmental Degradation of Poly(ether-block-amide)

Pebax® (Arkema)





Ny6/PEG56 SAXS 2D image

Microphase separation structure formed between hard and soft segments.

Purpose: Investigate the environmental degradation behaviors of Ny/PEG multi-block copolymers with different hard segments.

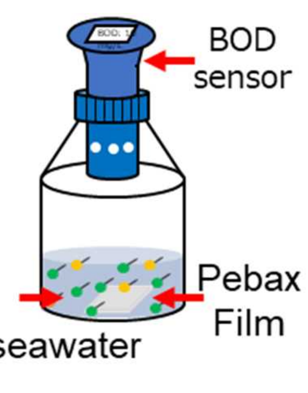
Experimental

Pebax	PEG (wt%)	Hard segment
1657	56	Ny6
1074	48	Ny12
1041	24	Ny12

1) Sample preparation
- Compression molding

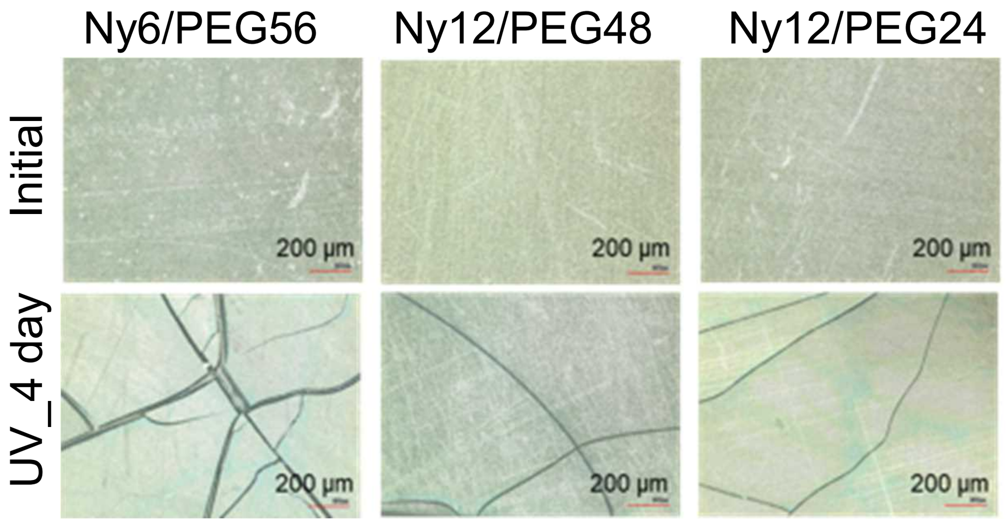
2) Environmental degradation
- UV exposure test (125 W/m², BPT: 63ºC)
- Biodegradation(BOD) test with extracted sea water

Setup of BOD test



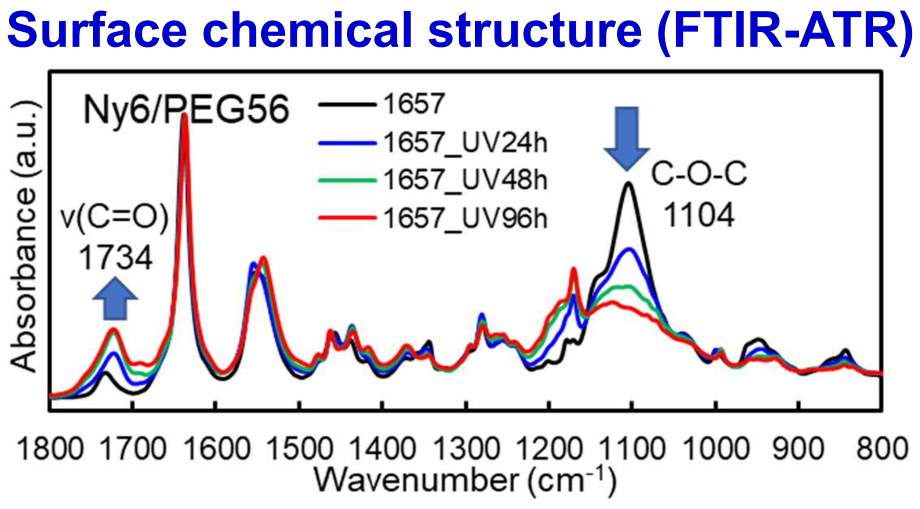
UV exposure test

Surface morphology



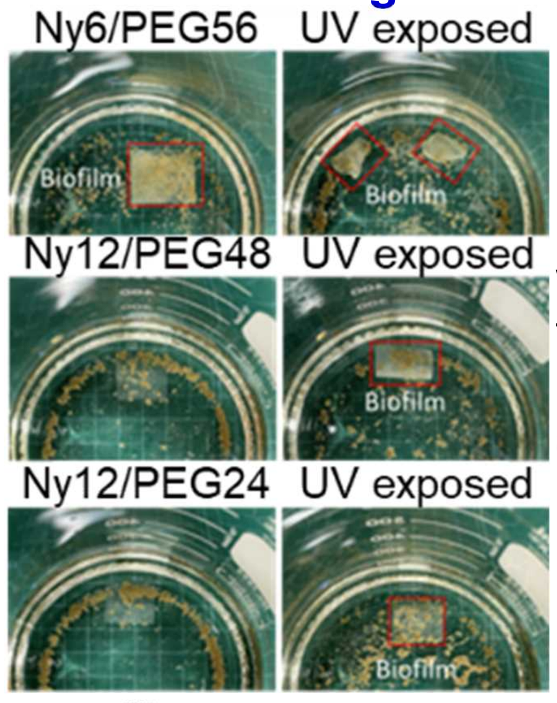
Much denser cracks formed on poly(ether-block-amide) copolymer with higher PEG content.

Surface chemical structure (FTIR-ATR)

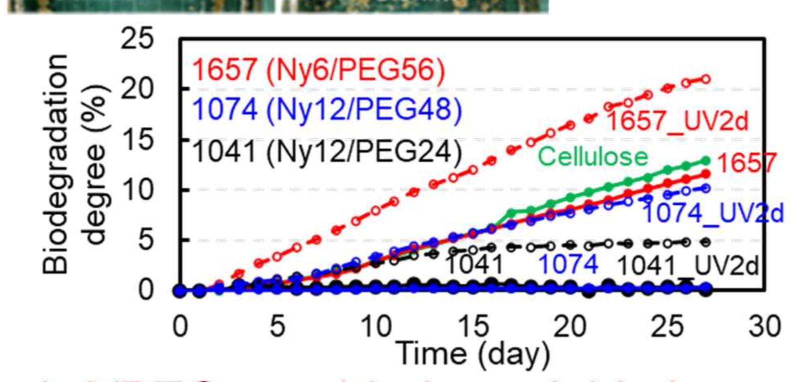


IR indicates degradation of PEG segment in Ny/PEG films by photooxidation.

Biodegradation test



Biodegradation was observed for sample with biofilm attachment

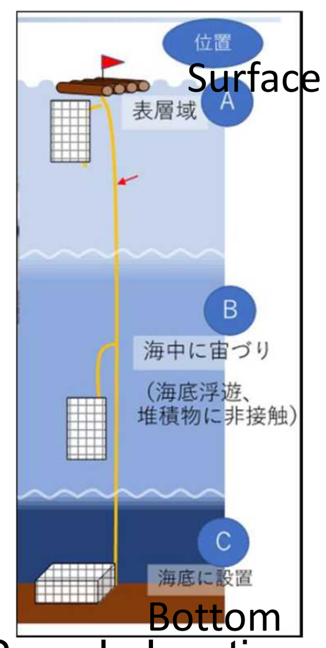


- Ny6/PEG was biodegradable in ocean.
- Biodegradation was promoted by photooxidation.
- Ny6 oligomer is biodegradable.

Field Test of Polypropylene Containing Oxo-biodegradable Additives (P-Life)

Purpose: To establish advanced characterization method for field test samples

Field test (23.06-12)

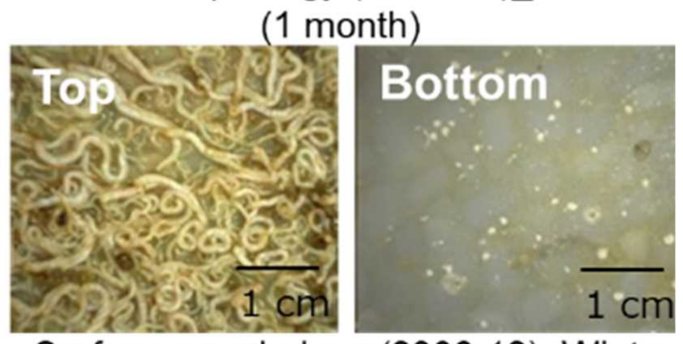


Sample location

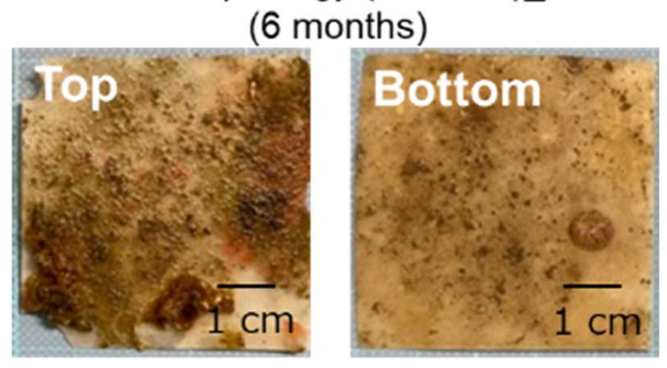
Sample: PP containing oxo-biodegradable additives* (P-Life)
Samples were fixed in frame and immersed in seawater
*Fatty acid Mn salt additives that promote oxidation under sunlight exposure were banned worldwide.

Surface Morphology

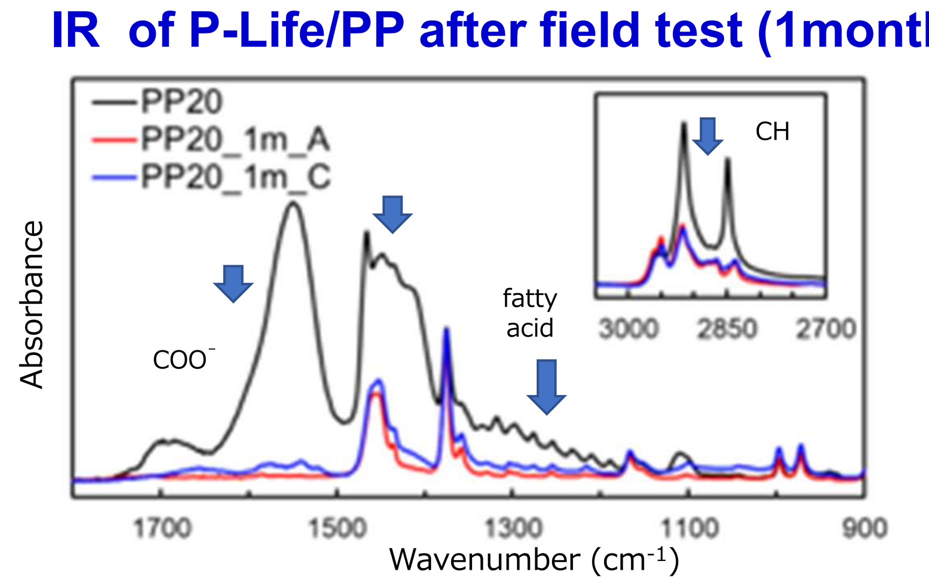
Surface morphology (2306-07)_Summer (1 month)



Surface morphology (2306-12)_Winter (6 months)

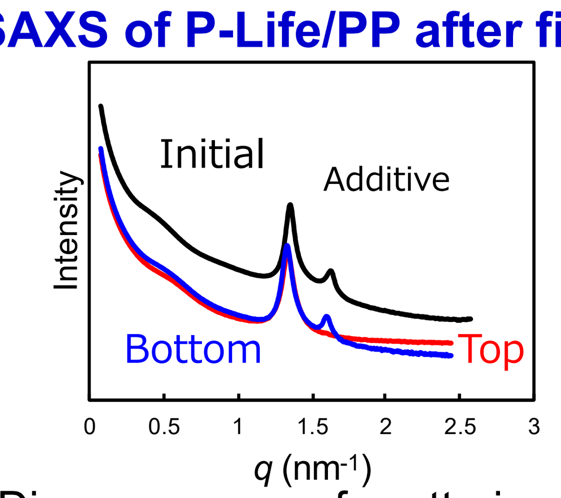


IR of P-Life/PP after field test (1months)



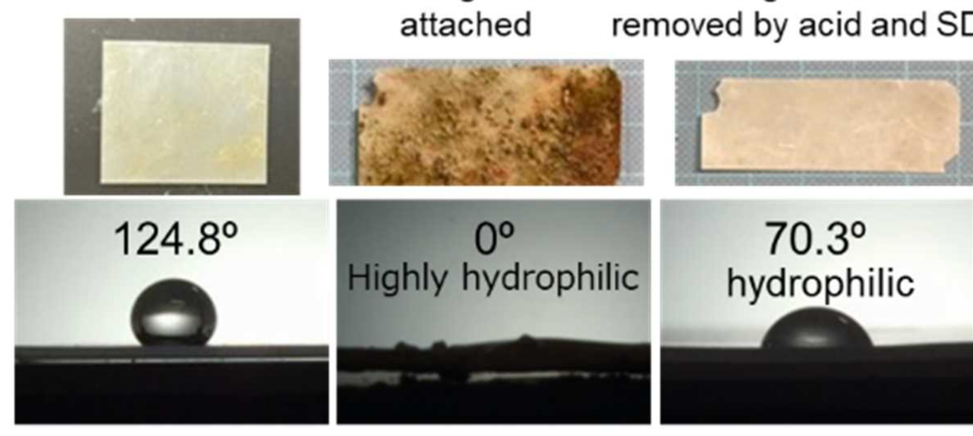
Additive was disappeared after 1 month field test.

SAXS of P-Life/PP after field test



Disappearance of scattering from oxo-biodegradable additives.

Water contact angle after field test(6months)



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.