No. A-11-1E

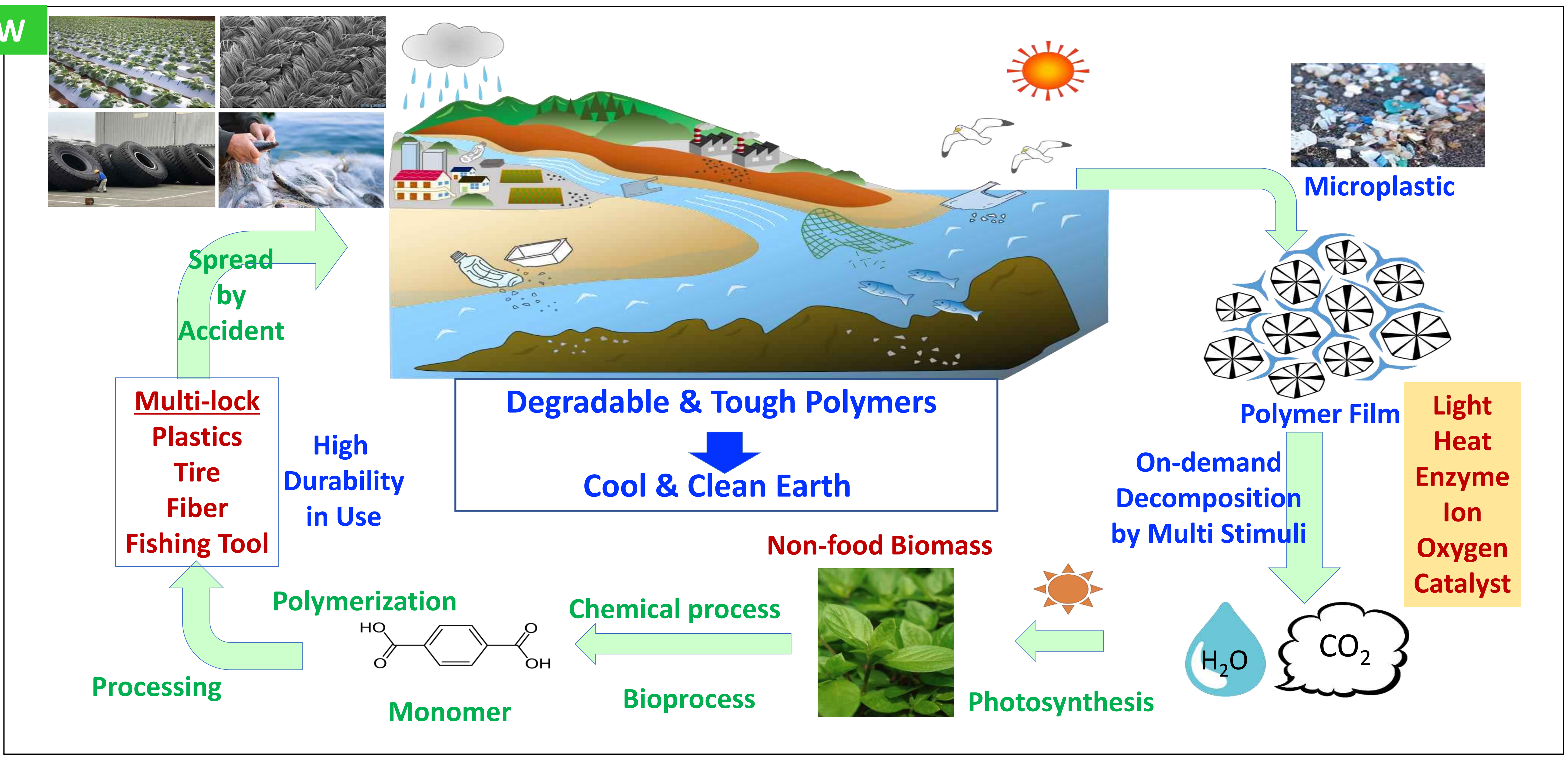
PJ: Development of Multi-lock Biopolymers Degradable in Ocean from Non-food Biomasses

Organization: University of Tokyo

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

For seawater decomposition of difficult-to-collect plastics, tire wear debris, fiber scraps, 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 P J
project manager
Kohzo ITO

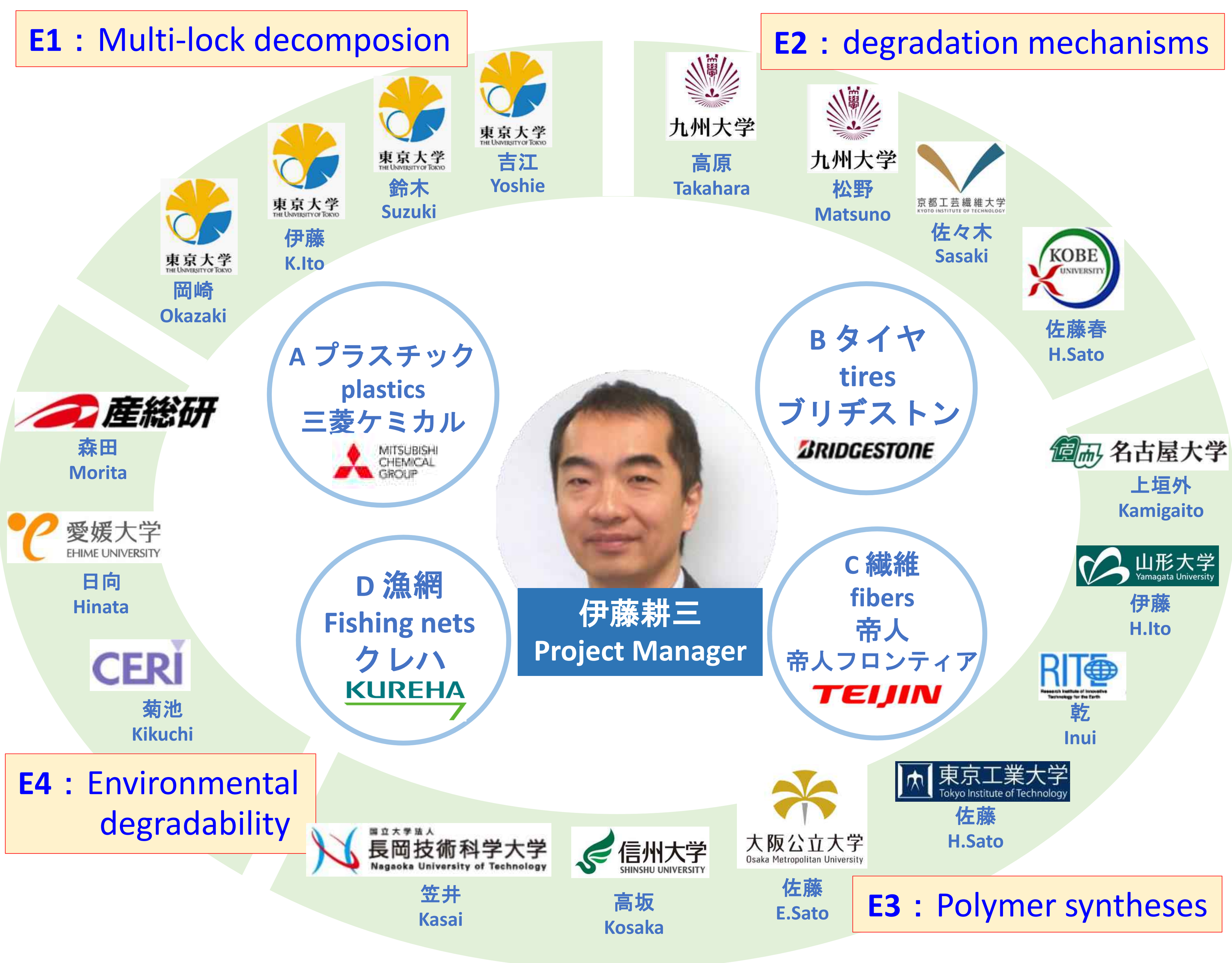
PROJECT OFFICE

Entrusted organizations：12 inst.

Re-entrusted organizations: 7inst.

Company： 5 inst.
Academia：14 inst.
(18Gr)

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



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

No. A-11-2E

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

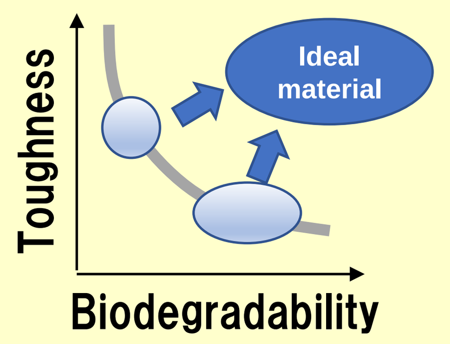
Contact: Kusuno Atsushi kusuno.atsushi.mf@m-chemical.co.jp

1. Concept and objectives

【Objectivs】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 PBS (polybutylene succinate) resin.

【Concept】Moonshot program led by the Cabinet Office

Achieve both high toughness and high biodegradability



・Tough enough to use without problems
・Decomposed into H2O and CO2 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. Plan (FY2020-FY2029)

Fiscal Year	20	21	22	23	24	25	26	27	28	29
Intermediate/Final target			▲ concept proof: Multi-locking		▲ Achieve both multi-locking and high toughness			▲ Bench-scale production		▲ Final target
Multi-locking mechanism		concept proof →				optimization →	Scale-up →			
Toughening (Improving tear strength)		Establishing the methodology →				Optimization, scale-up (Kneading) →				
Production						Scale-up →				
Material properties	Marine biodegradability evaluation →	Evaluation of physical, thermal and practical properties →								

4. Academia study contents

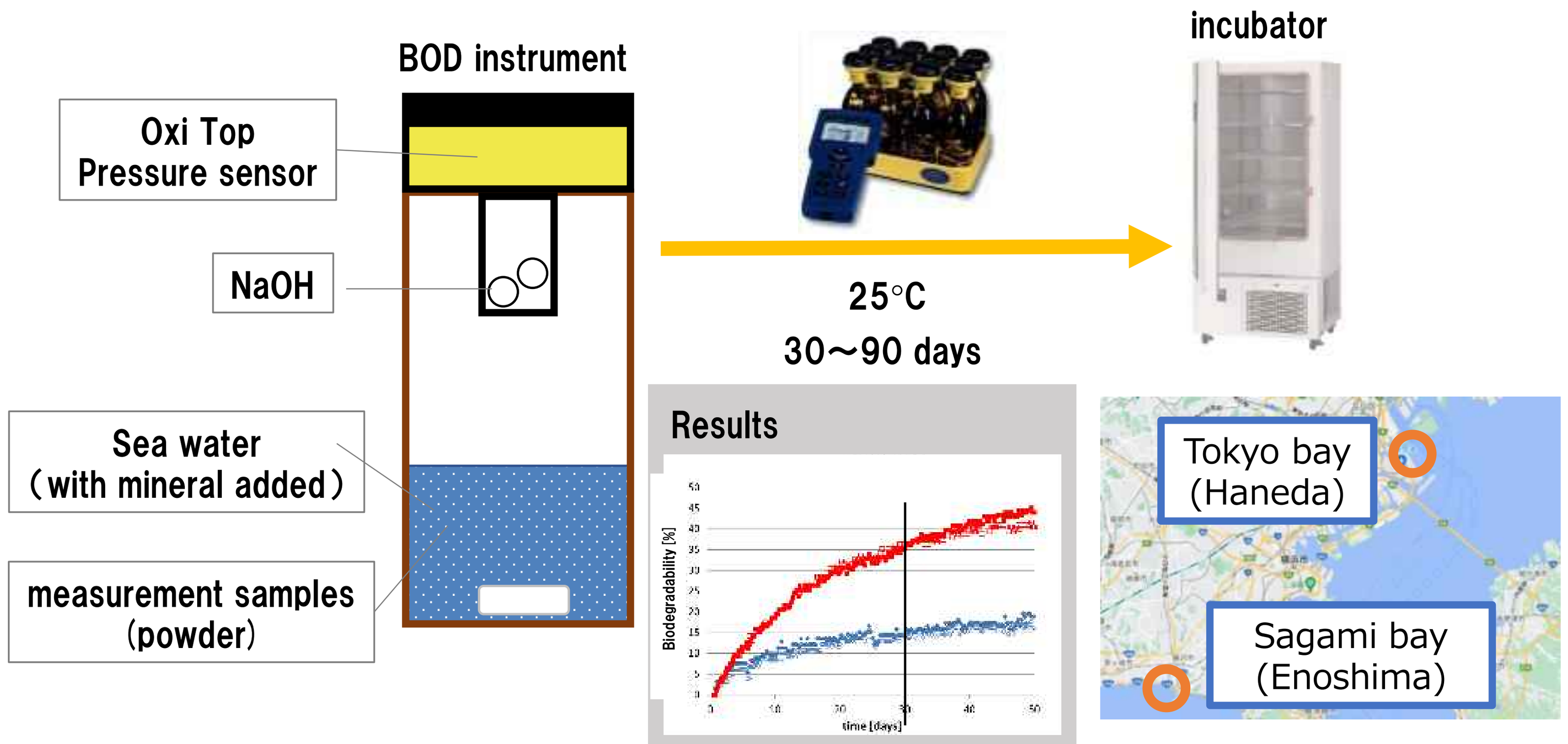
Study items		Targets (in the end of FY2022)	PIC
Primary	secondary		
Biodegradability	Relationship between biodegradability and hydrogen bonding	Proposal for a primary structure with excellent marine biodegradation	Kobe Univ. Prof. Sato
	Effect of higher order (interfacial) structure (Biofilm, bacteria, Interaction with enzyme)	Proposal for a primary structure with excellent marine biodegradation	Kyushu Univ. Prof. Takahara Prof. Matsuno
Biodegradability /Toughness	Improve marine biodegradability and toughness	Proposal formulation with excellent marine biodegradation	Tokyo Univ. Prof. Ito
Toughness	Relationship between crystal structure and tear strength	Compounding with superior toughening and process study	Yamagata Univ. Prof. Ito
	Crystal structure changes before and after tearing (in situ)	Establishing analysis method	Kyoto institute of technology Prof. Sasaki

5. Evaluation of marine biodegradability by BOD test

BOD: Biochemical Oxygen Demand [mg/L]

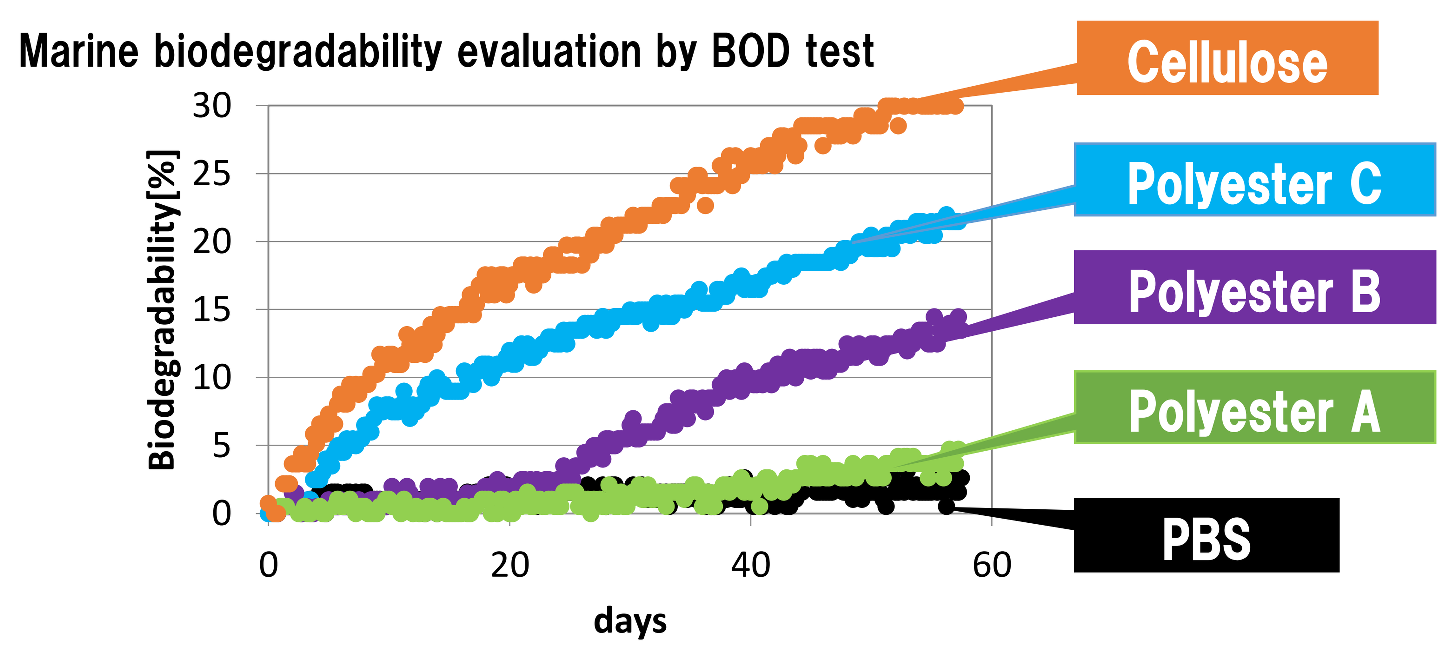
Biodegradation: consume O_2, produce CO_2

BOD test:measuring O_2 consumption (NaOH absorbs CO2)→ calculate degree of biodegradability



6. Results of marine biodegradability improvement study

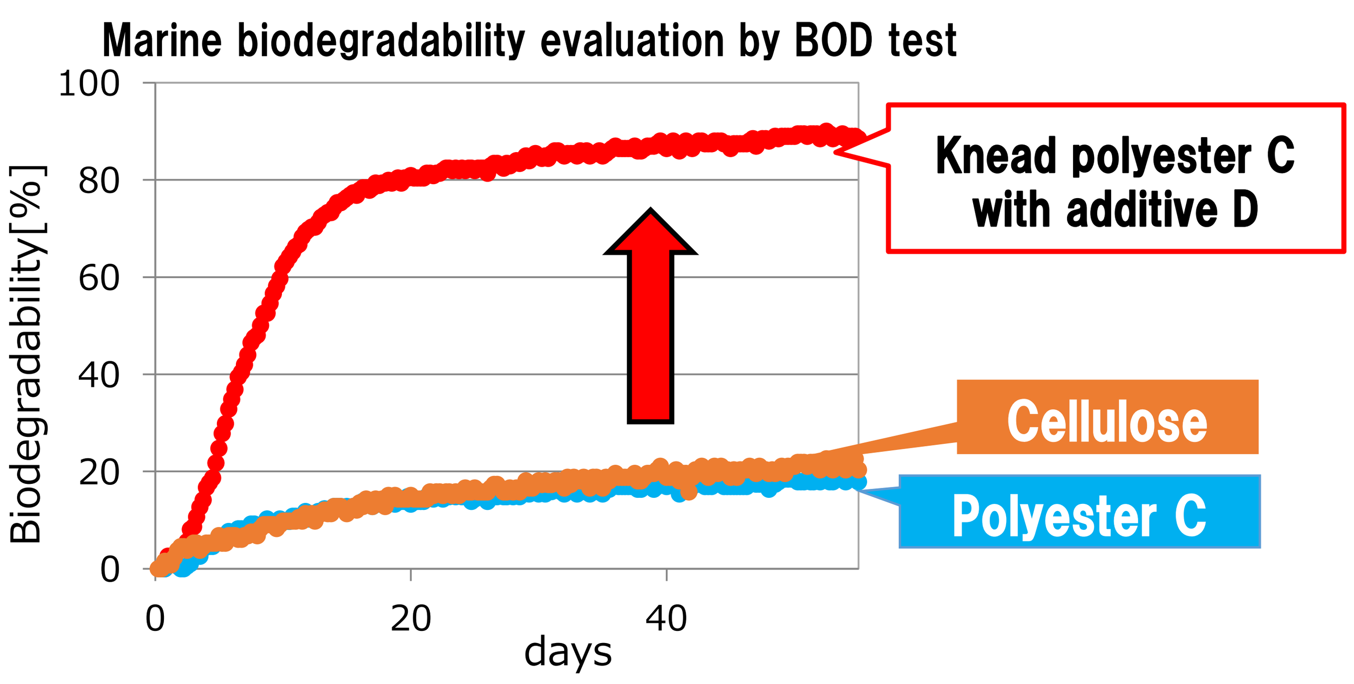
Copolymer composition study to improve marine biodegradability of PBS



- New comonomers are added through copolymerization → Improved marine biodegradability

7. Results of marine biodegradability improvement study

Additives were investigated to improve marine biodegradability of copolymerized polyesters.



Biodegradability was greatly accelerated by kneading additive D

switch function

- Coexistence of "certain additives" with marine biodegradable resins → Improved marine biodegradability

8. Summary and Future Plans

FY2022 Results

- The crystal structure change before and after in situ tearing was clearly observed. (Prof. Sasaki, Kyoto Institute of Technology)
- Retardation analysis of the tearing tip confirmed the difference in behavior between polymers. (Prof. Ito, Yamagata Univ.)
- Improvement of toughness and biodegradability was confirmed by adding PR (polyrotaxane) to PBSA (polybutylene succinate adipate). (Tokyo Univ., Prof. Ito)
- Changes in crystal structure and hydrogen bonding state of copolymerized biodegradable resins were confirmed (Prof. Sato, Kobe Univ.).
- The higher-order structural change by weathering test and the promotion of biofilm formation by weathering test degradation were confirmed. (Prof. Takahara, Kyushu Univ.)
- Surface structure change by hydrolytic enzyme was confirmed. (Prof. Matsuno, Kyushu Univ.)
- Improvement of biodegradability was confirmed by examining the copolymerization composition of PBS and additives. (Mitsubishi Chemical Corporation)

- Achievement level against target: Progress as planned
- Future Plans

(1) Degradability control (elucidation of degradation mechanism and introduction of trigger mechanism)

(2) Improvement of tearing strength (elucidation and improvement of tearing)

No. A-11-3E

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

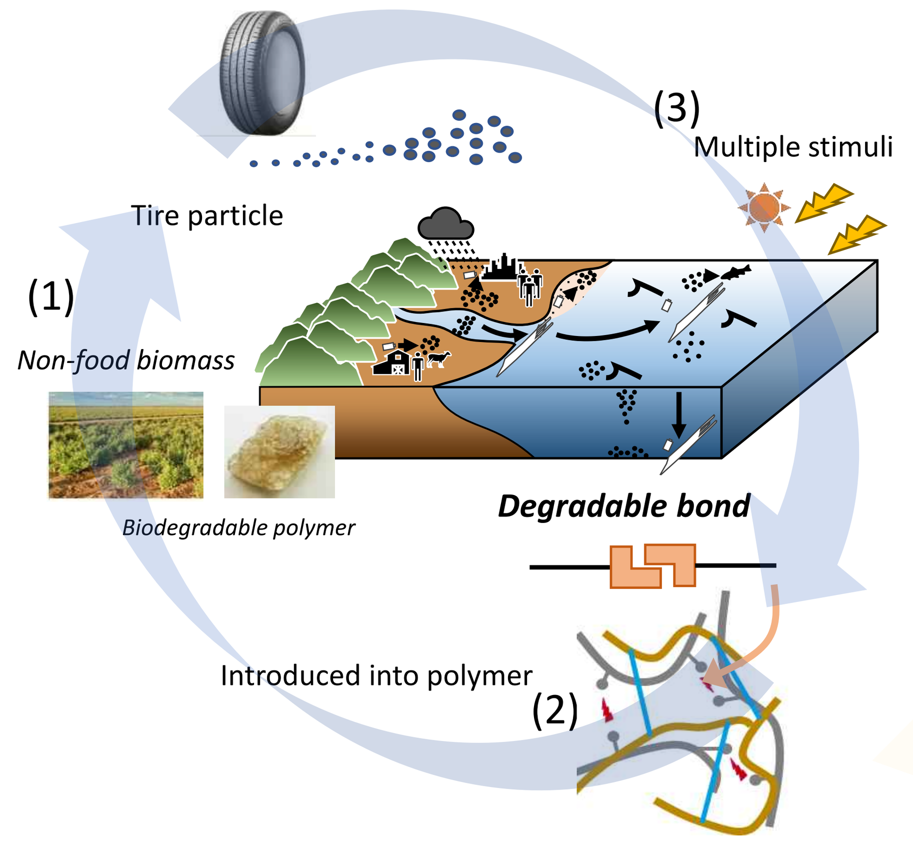
Organization: Bridgestone Corporation

Contact: Advanced Materials Div., Satoshi Hamatani (satoshi.hamatani@bridgestone.com)

Research outline of this project

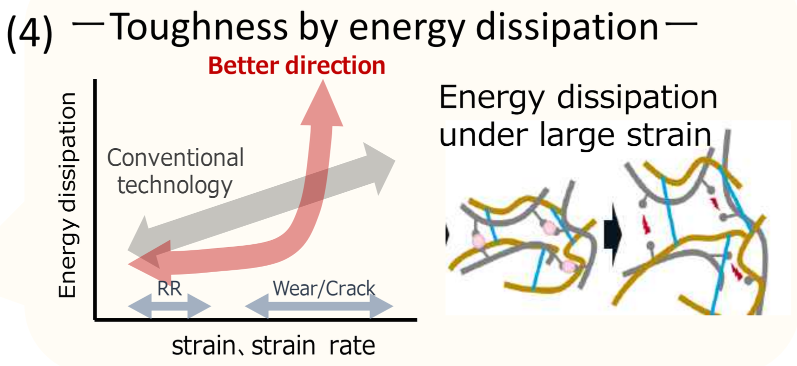
In recent years, there has been growing concern about the influence of tire wear particle on marine as microplastics. While its substantial contribution to the environment is still debatable, technological development is desired from a view of environmental pollution/ circulation of resources. In this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



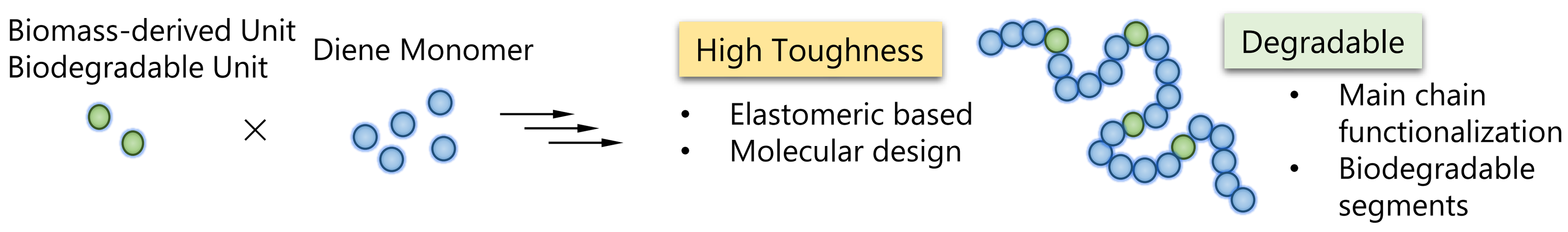
(1) development of non-food biomasses based biopolymer synthesis
(2) development of multi-lock degradability technology
(3) development of degradability evaluation method/degradability
(4) compound design for highly balancing degradability and toughness by energy dissipation

(4) —Toughness by energy dissipation—



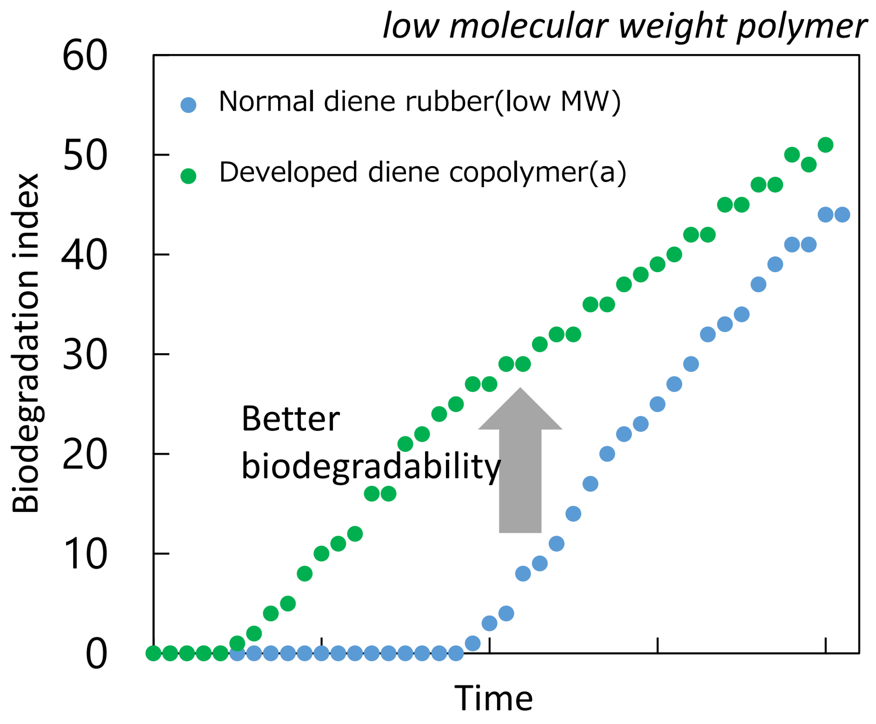
Biodegradation technology by introducing degradable unit

Biomass-derived degradable unit was introduced to diene rubber copolymer cooperating with academia.

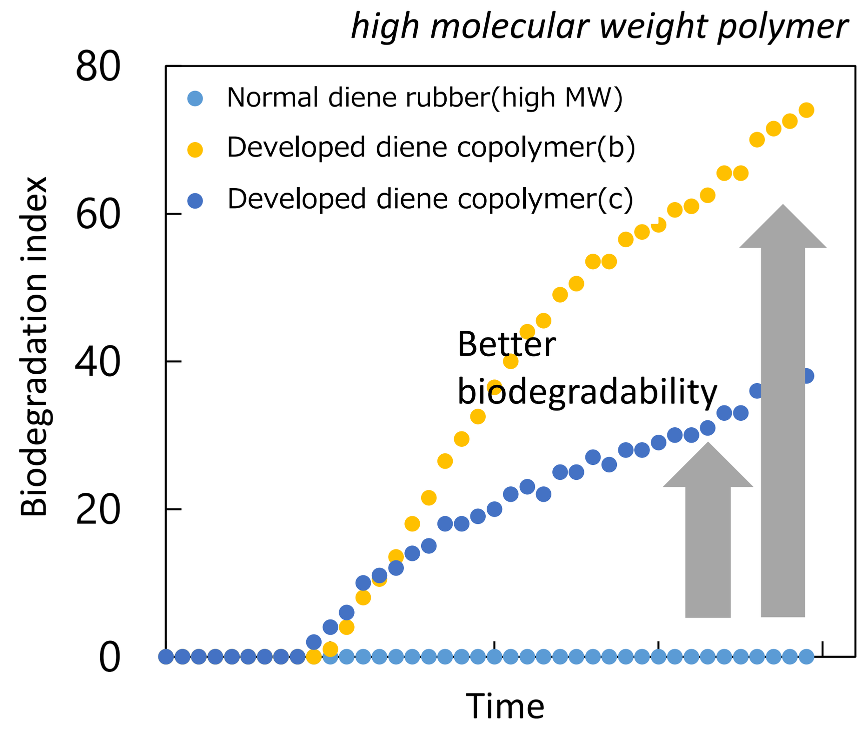


We have succeeded in synthesizing diene rubber copolymers which was introduced several biomass-derived units/degradable units. It was verified that these copolymers can improved the biodegradation rate.

—Marine biodegradation test result —



Improved biodegradability compared with the same molecular weight



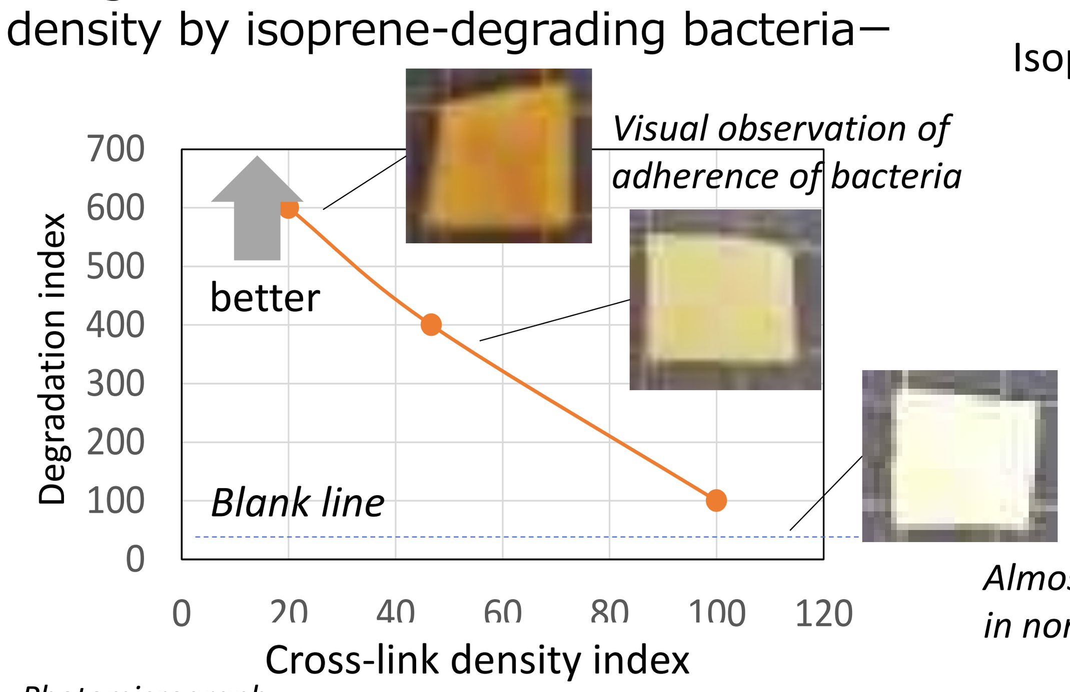
Very effective for high molecular weight polymer

Biodegradability improved by more than 10 times with degradable unit introduction rubber

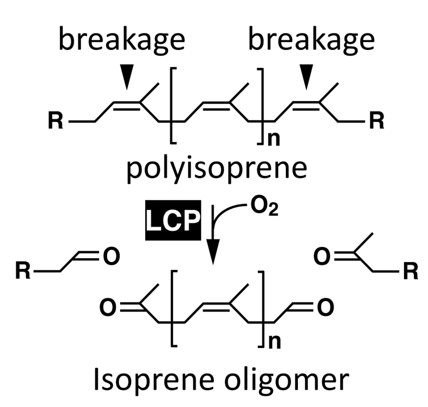
Degradability analysis of rubber

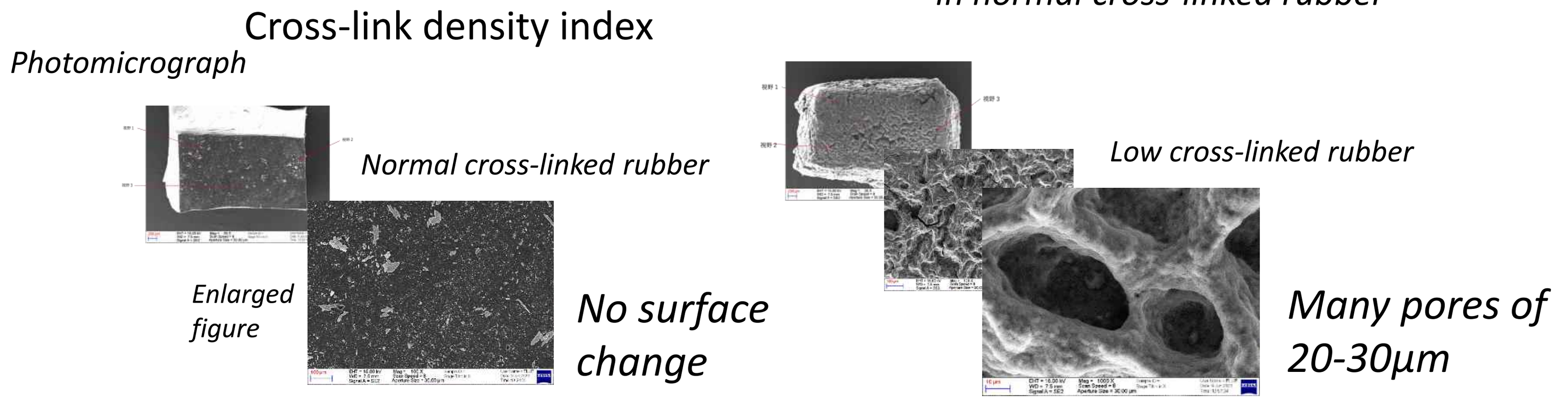
Rubber biodegradation mechanism is carried out cooperating with academia. The effect of cross-link on rubber degradation behavior was analyzed using the bacteria that has ability to decompose cross-linked rubber. Contributions of cross-link density and molecular weight to degradation behavior have been clarified.

—Degradation test result of rubber with different cross-link density by isoprene-degrading bacteria—



Isoprene degradation scheme by LCP*



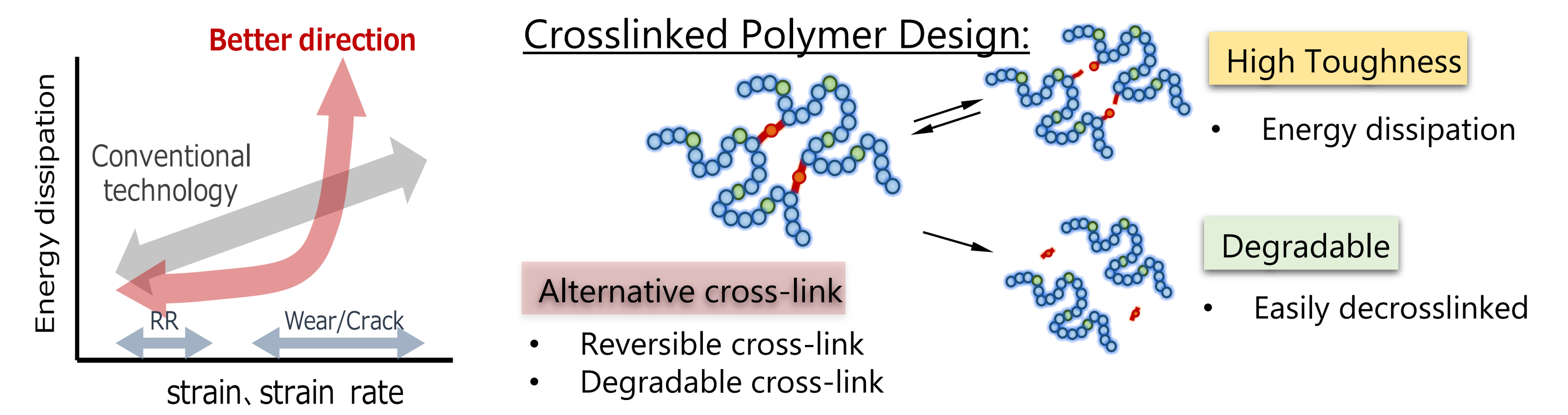


Natural rubber and synthetic isoprene rubber showed same degradation trend in polymer main chain. No degradation was observed in conventional cross-link density. In our studies, we have found that the degradation rate is strongly associated with cross link density and molecular weight. With decreasing cross link density and molecular weight, degradation rate increases.

*D.Kasai: Kagaku to Seibutsu 58(2) 77 (2020)

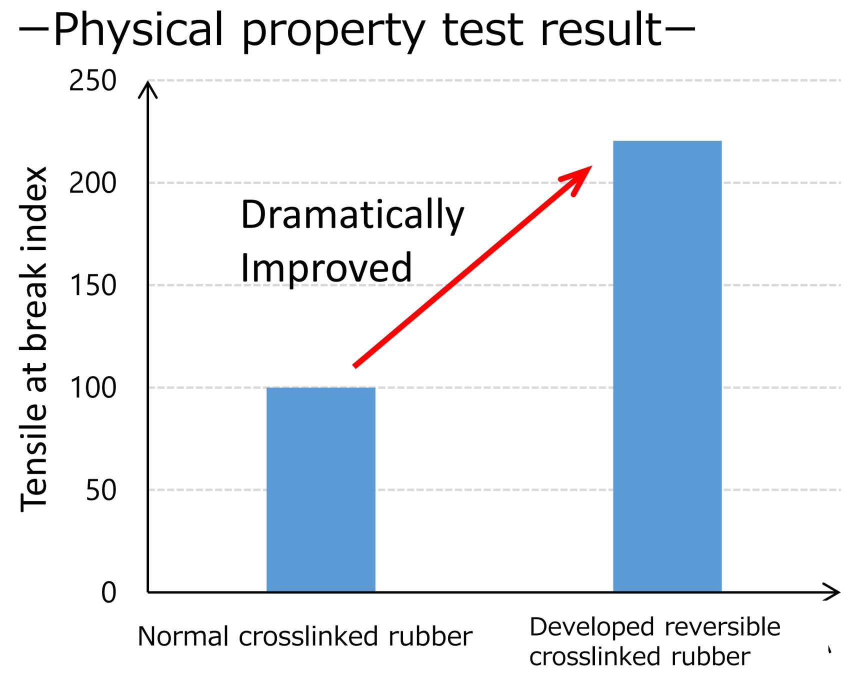
Technology for balancing biodegradation and toughness by reversible cross-link

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

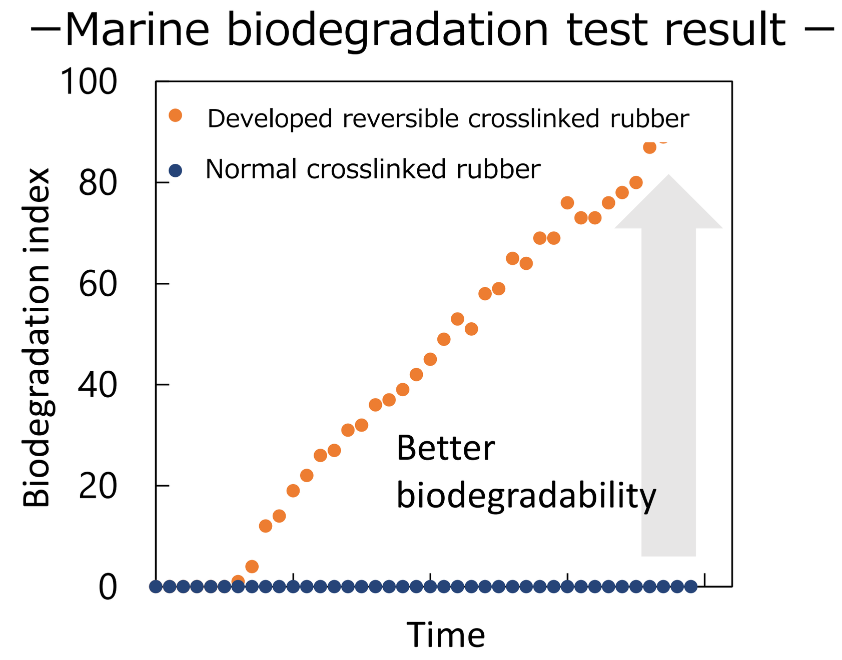


We have succeeded in improving the toughness of rubber by energy dissipation through reversible and degradable cross-links. In addition, we developed diene rubber copolymers with reversible and degradable cross-links and verified whether the toughness and biodegradation rate of these copolymers are both improved.

—Physical property test result—



—Marine biodegradation test result —

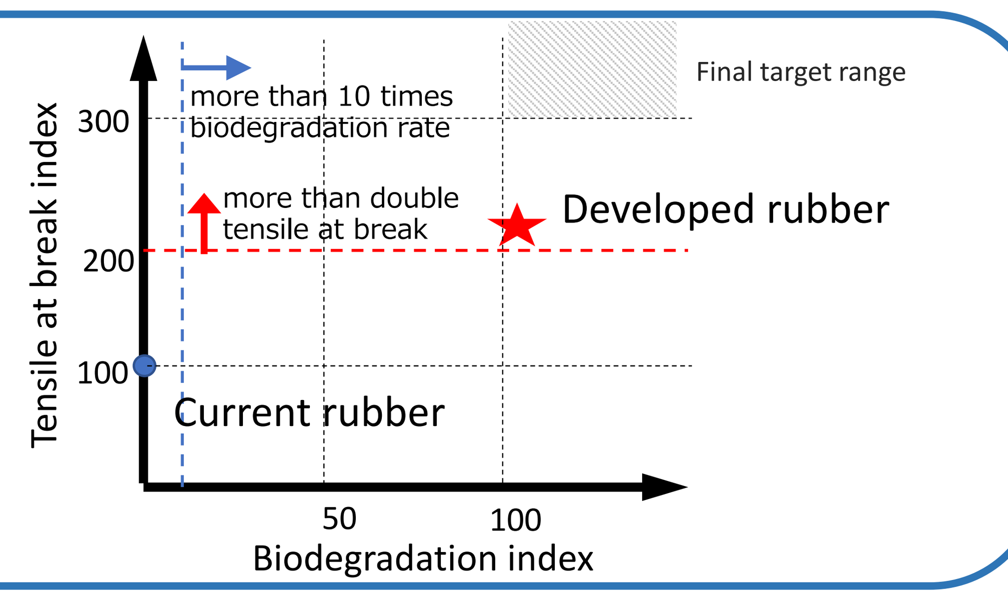


Both toughness and biodegradation are both significantly increased by introducing reversible and degradable cross-links

Summary

●We developed copolymer with biomass-derived degradable unit cooperating with academia, and achieved POC that improved degradation rate by more than 10 times faster compared to current rubber.

●We developed diene rubber copolymers with reversible/degradable cross-links cooperating with academia, and achieved more than 2 times higher strength and 10 times faster biodegradation rate.



Achievement level to target: Fully achieved the mid term target for the year 2022

No. A-11-4E

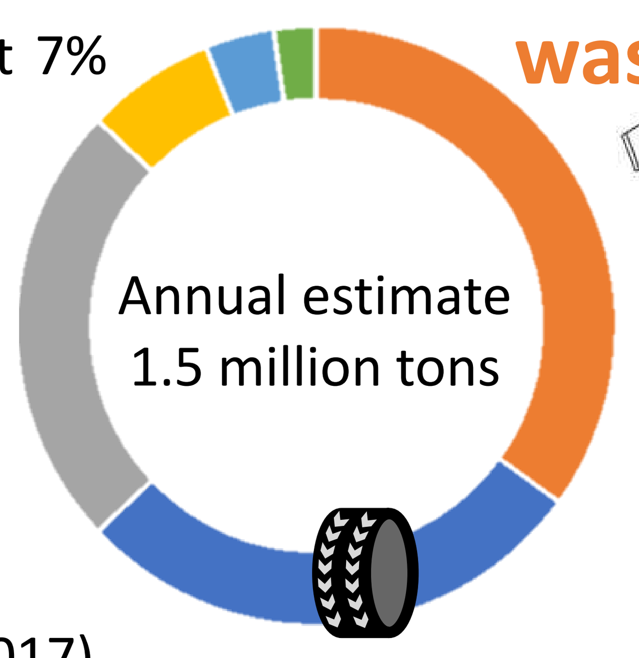
PJ: Development of Multi-lock Biopolymers Degradable in Ocean from Non-food Biomasses

Theme: Development of highly degradable polyester-based multi-lock type bio-tough polymer and its fibers

Organization: TEIJIN LTD., TEIJIN FRONTIER Co., LTD.

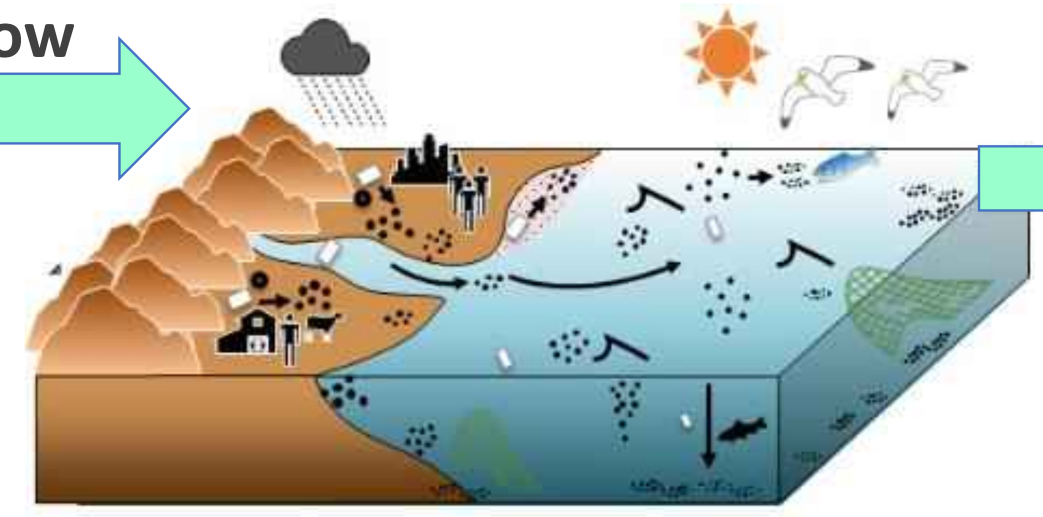
Contact: TEIJIN, Material Technology Center, Tomoyoshi Yamamoto (tom.yamamoto@teijin.co.jp)

Microplastics from fibers waste



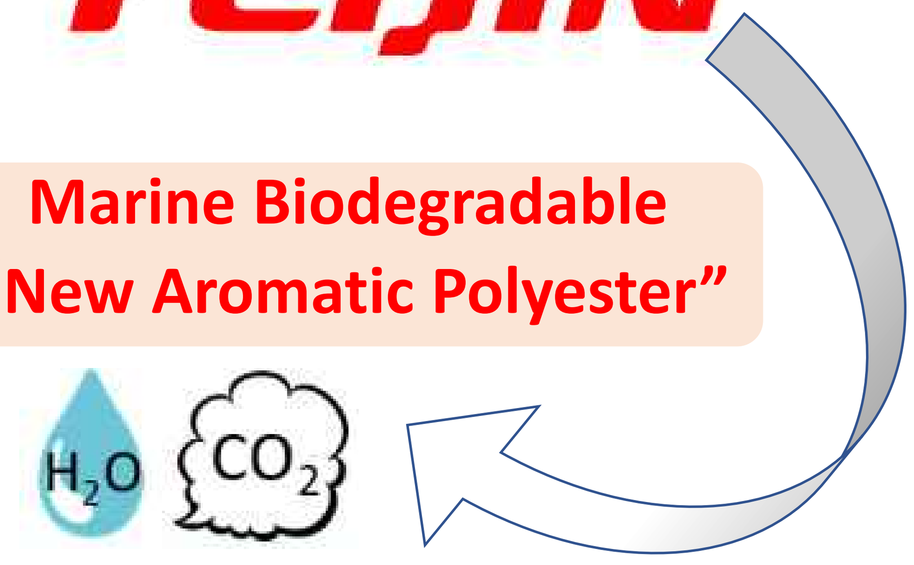
Ref：
Report of IUCN (2017)

Out flow



TEIJIN

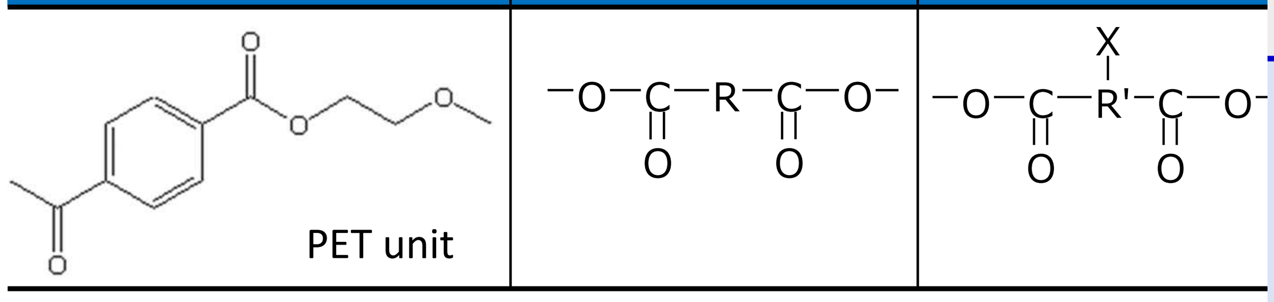
Marine Biodegradable "New Aromatic Polyester"



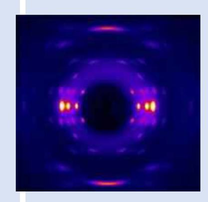
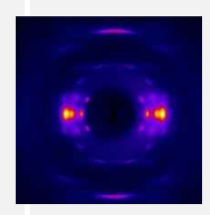
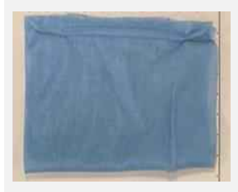
Marine Biodegradable "New Aromatic Polyester" fiber

Copolymer × Decomposition Accelerator

Terephthalic acid unit	Decomposable unit	Hydrophilic unit

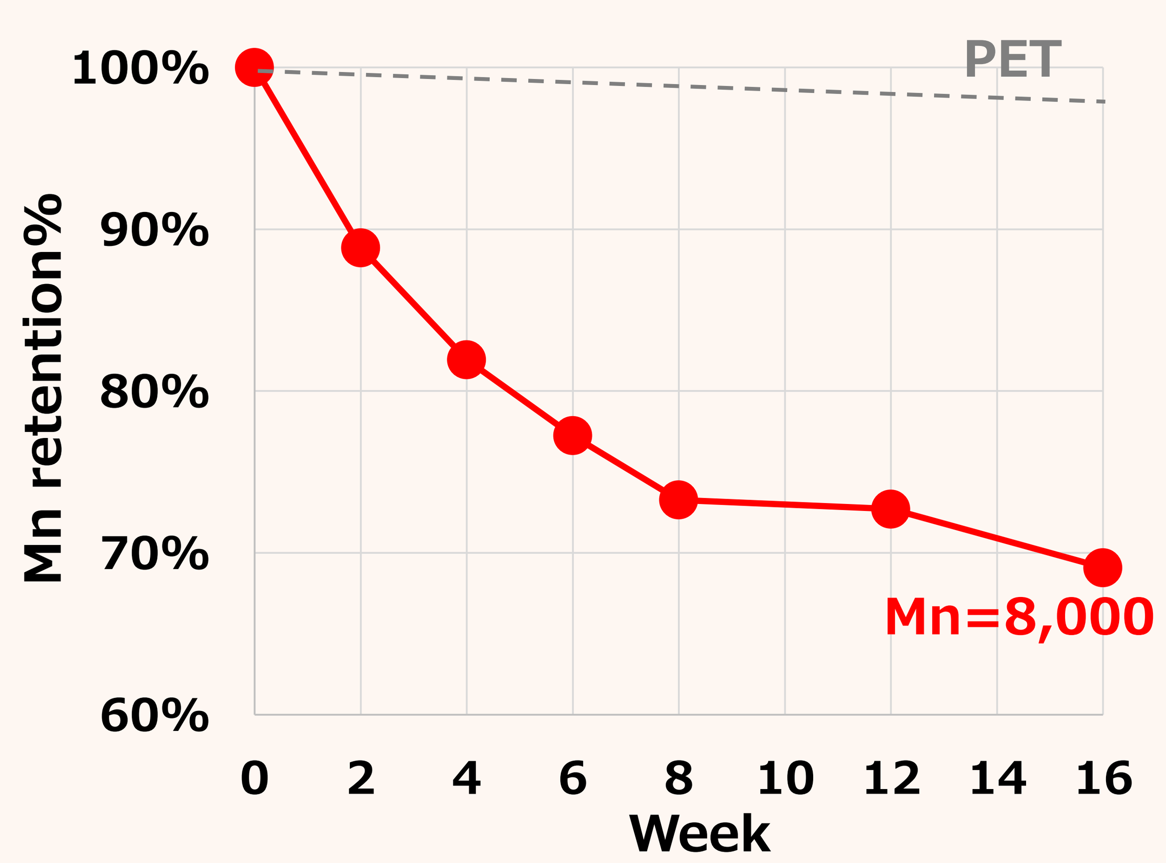


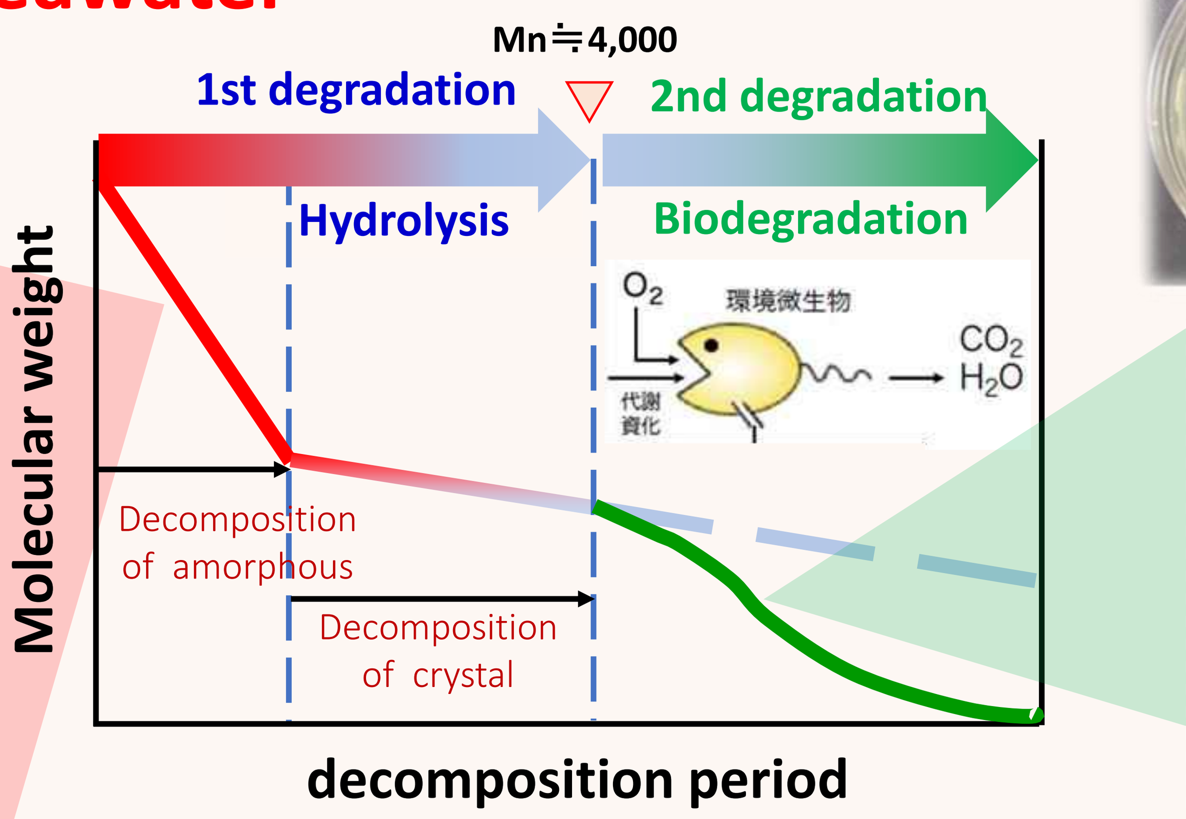
Molecular weight (Mn)	Tg ℃	Tm ℃	ΔH_m J/g
1.2×10⁴	50	211	30

	Fiber properties Target 3cN/dtex				WAXD/SAXD						Dyeability	Washing durability Target >2cN/dtex
	Denir Dtex	Filament number	Strength cN/dtex	Elongation %	Crystal -linity %	Crystal face	Crystal Size Nm	Fiber identity period (-103) nm	Long period nm	WAXD	St. after dyeing cN/dtex	St. after washing cN/dtex
New Fiber MD1	46	24	2.9	19	68.1	010 110 100	5.5 4.3 4.3	1.10	7.56		 2.4	L50：2.7 L100 : 2.2
PET	50	36	4.7	36	43.2	010 110 100	3.4 3.1 2.8	1.15	5.36		 3.9	L50 : 4.5 L100 : 4.5

Hydrolysis & Biodegradation in Seawater

Hydrolysis in Seawater @30˚C

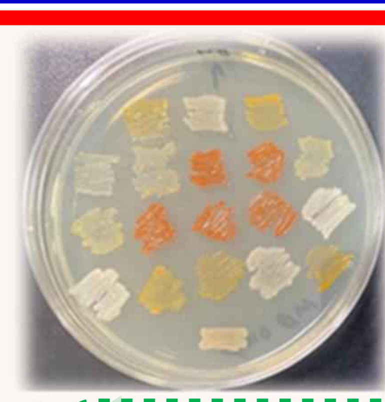




Initial hydrolysis rate equation by Arrhenius analysis

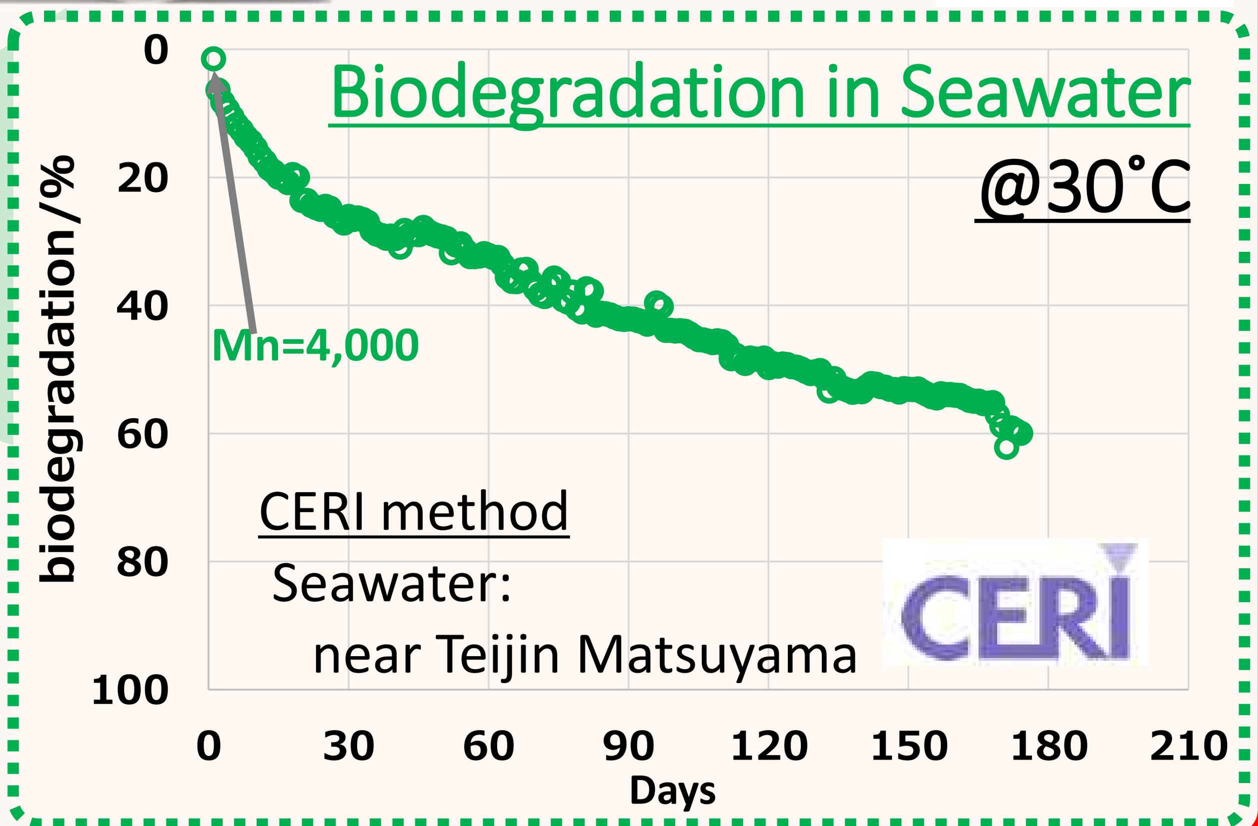
$$\frac{1}{M_t} = 8.19 \times 10^4 \cdot \exp\left(-14.3 \times 10^3 / RT\right) \cdot t + \frac{1}{M_0}$$

M_t, M_0:molecular weight T:temp(K), t: time(week)



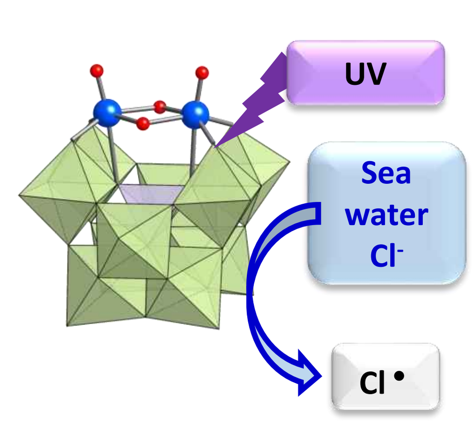
7 species of Bacteria assimilating PET oligomer were identified from natural seawater

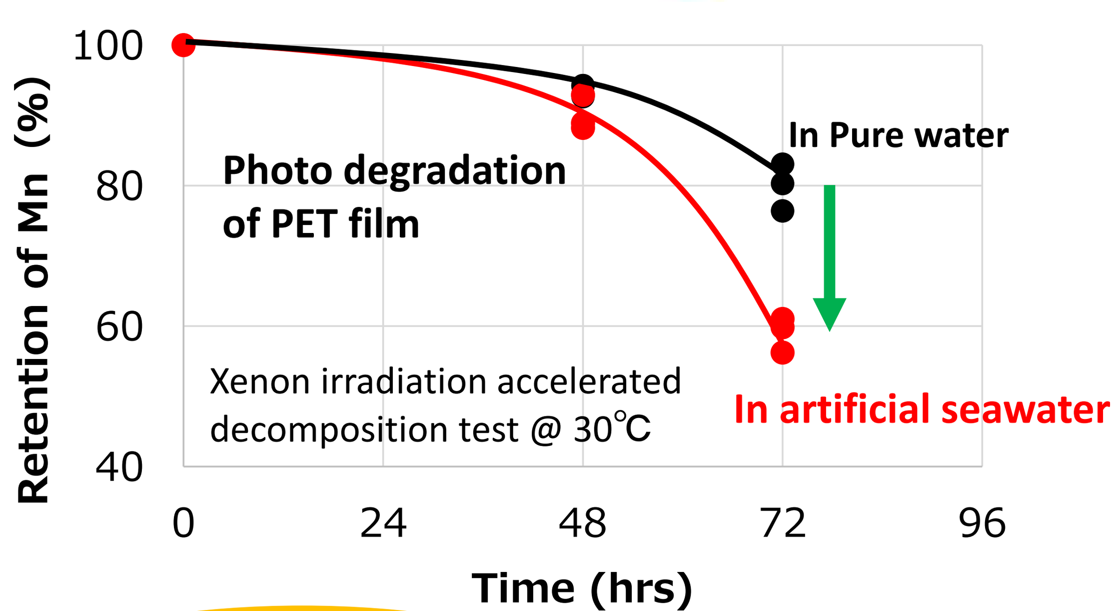
Biodegradation in Seawater @30˚C



New switching function for decomposition

Metal Oxide Hybrid Cluster Catalysts

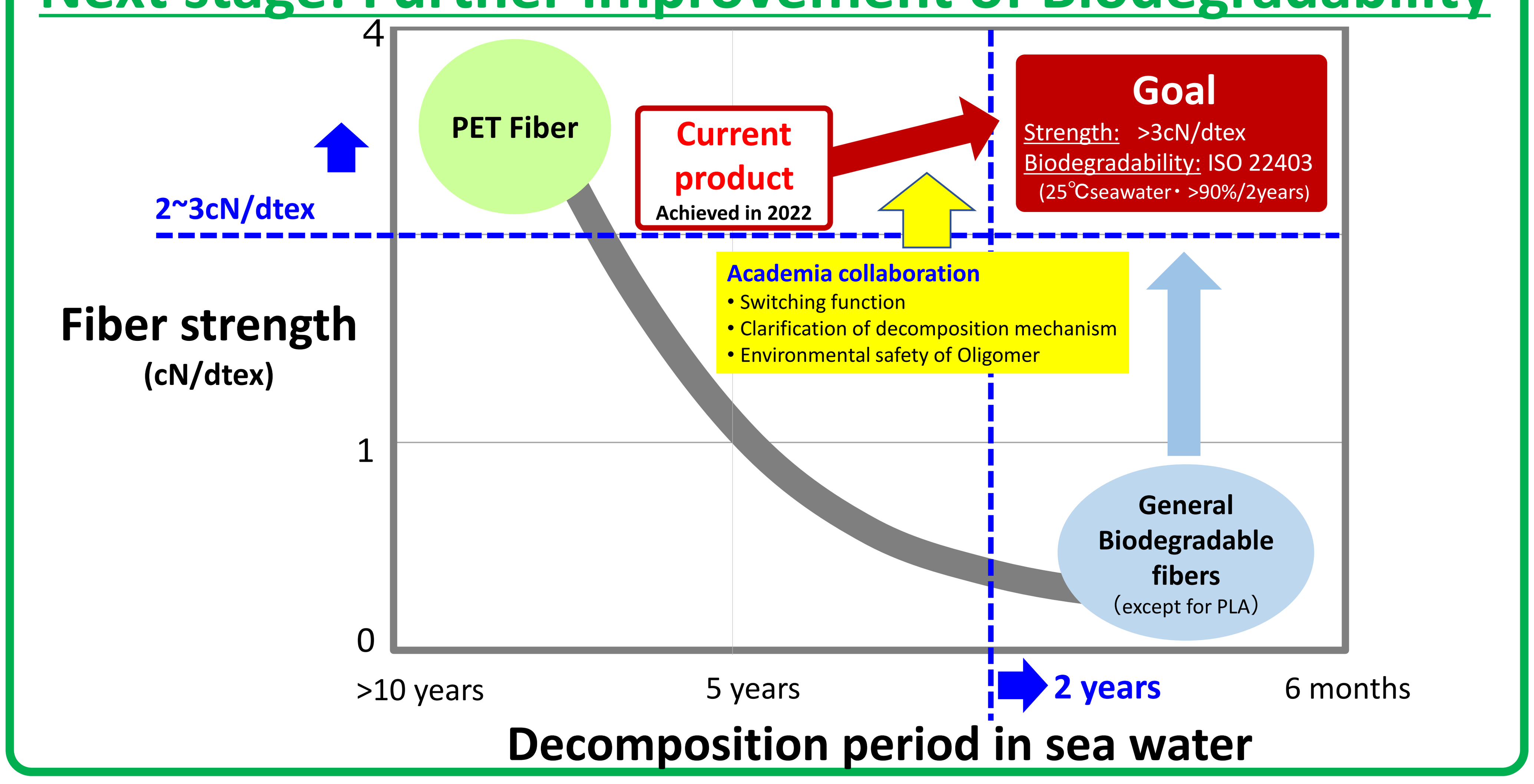




Other technology

- 山形大学 Yamagata University: Compound technology
- 信州大学 SHINSHU UNIVERSITY / 名古屋大学 NAGOYA UNIVERSITY: Development of easily degradable polymer
- 神戸大学 KOBE UNIVERSITY: Analysis of decomposition mechanism

Next stage: Further improvement of Biodegradability



No. A-11-5E

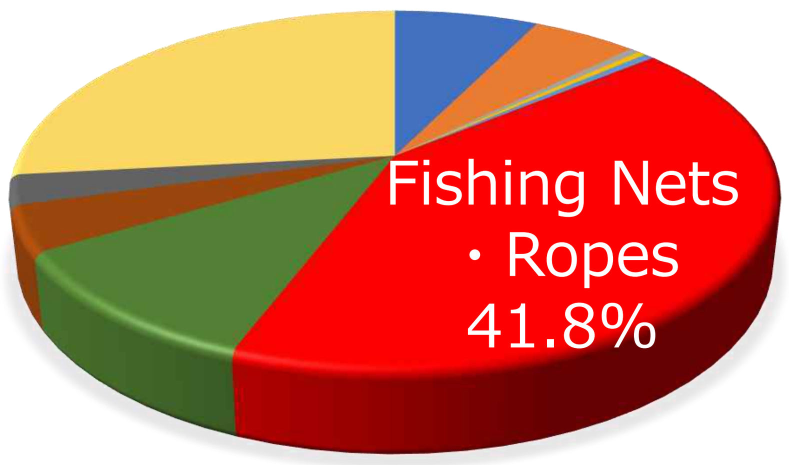
PJ: Development of Multi-lock Biopolymers Degradable in Ocean from Non-food Biomasses

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

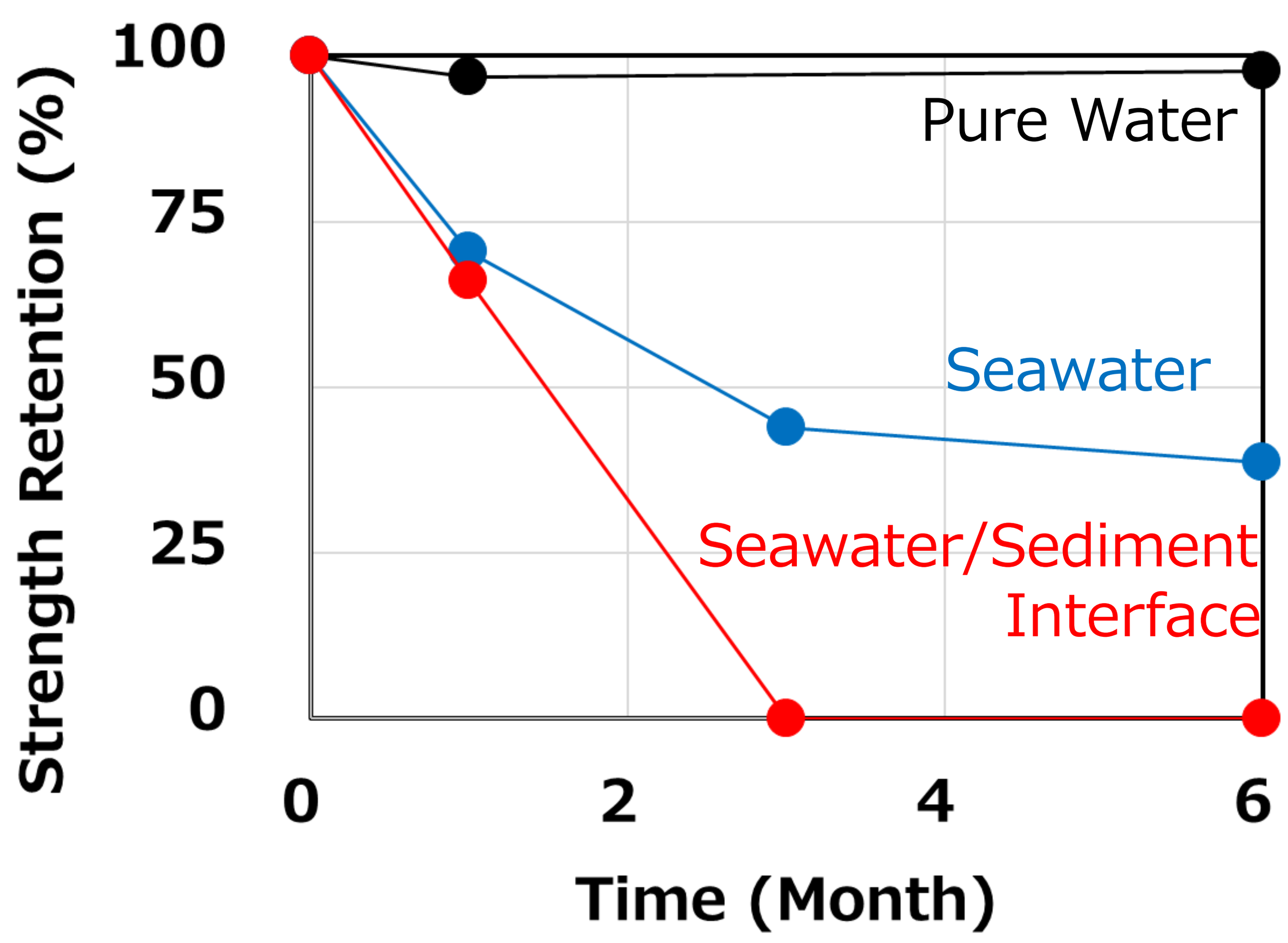
Cited from Wikipedia

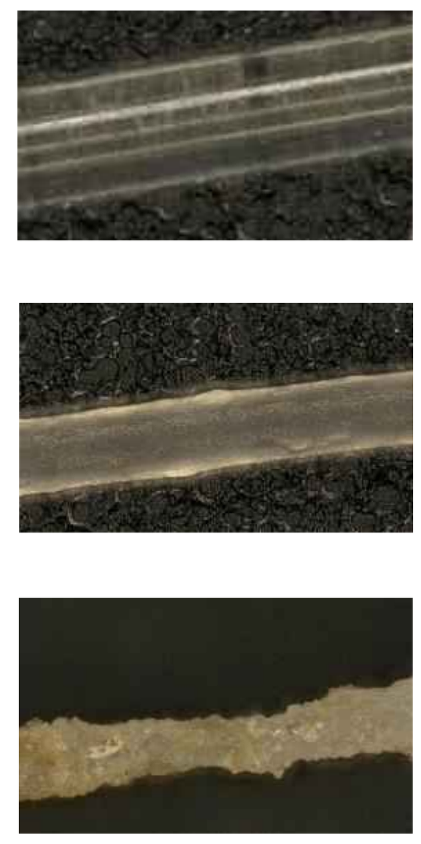
- ✓ Fishing nets and ropes make up about 40% of the drifted plastics and they cause a problem called "Ghost Gear".
- ✓ Some biodegradable products are commercialized, however, they generally have inferior mechanical strength and degrade by hydrolysis during use.

➢ Marine Biodegradability

<Degradation Test of the Developed Fiber in Laboratory >

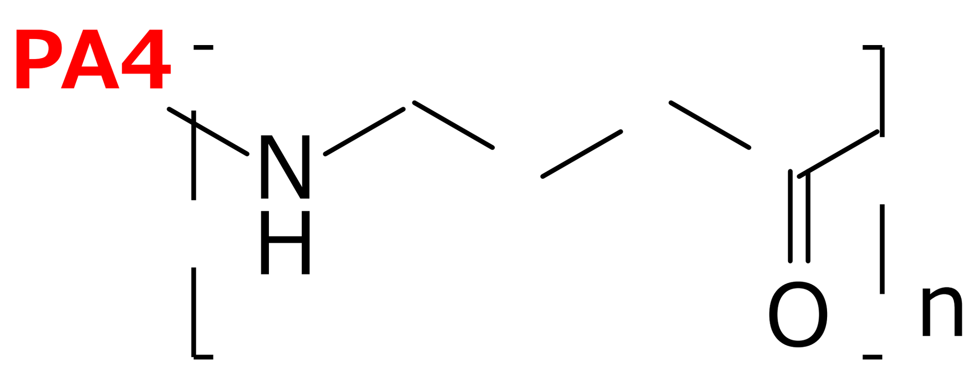
Seawater and sediment were collected from the Pacific Ocean (Fukushima pref.).

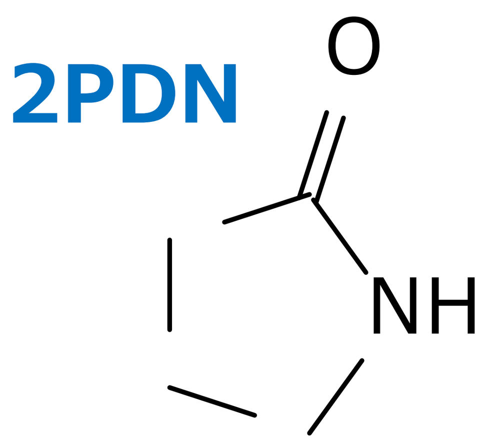




- ✓ In pure water, there was almost no reduction in strength.
- ✓ At seawater/sediment interface, degradation was faster than in seawater.

➢ Polyamide 4 (PA4)



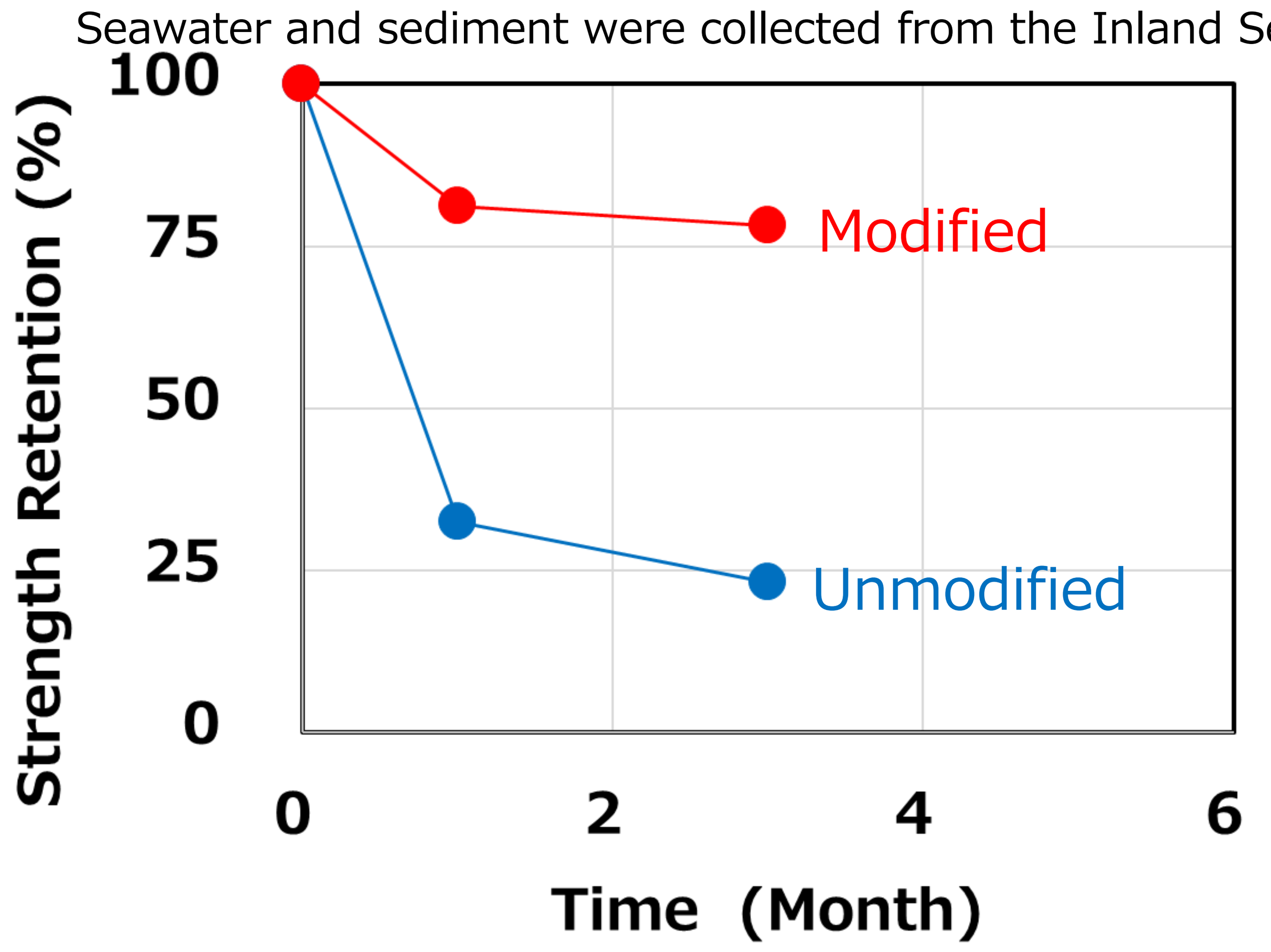


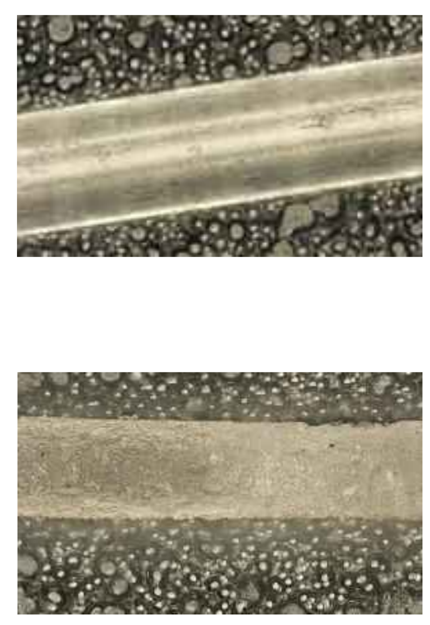
- ✓ PA4 is an aliphatic polyamide (nylon) synthesized from 2-pyrrolidone (2PDN).
- ✓ PA4 degrades in natural environments such as soil, sea, etc.
- ✓ In general conditions, PA4 is stable and not hydrolyzed.
- ✓ The mechanical property of PA4 is superior to Nylon6, on the other hand, PA4 has poor processability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

➢ Control of Degradation

<Comparison of Degradation at Seawater/Sediment Interface>

Seawater and sediment were collected from the Inland Sea (Ehime Pref.).



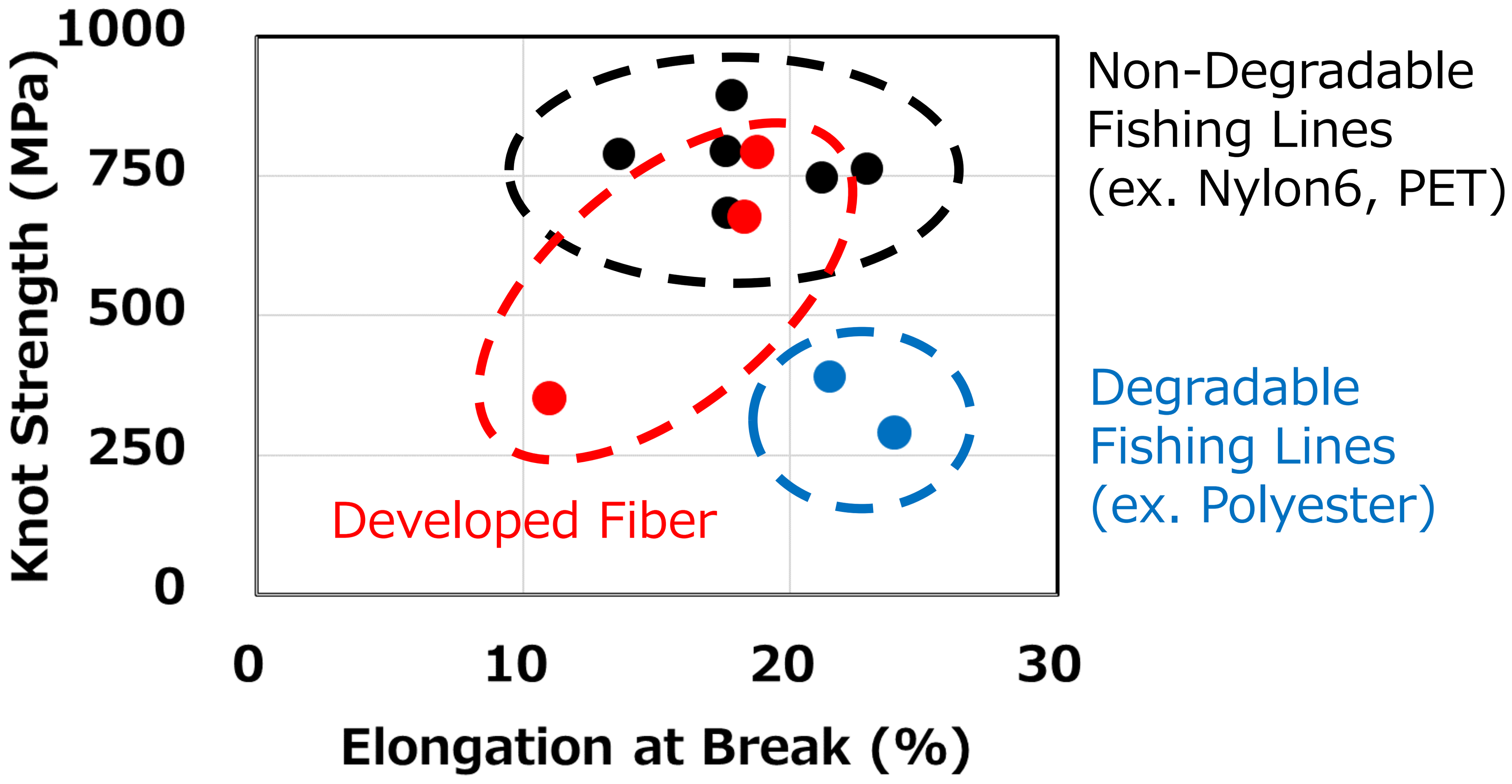


✓ **Degradation rate of modified fiber was reduced to 1/3.**

➢ 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 strength and elongation of developed fiber is equivalent to commercial non-degradable fishing lines.
- ✓ The degradation rate of modified fiber was reduced to 1/3.

➢ Ongoing / Future Plan

- ✓ Collect degradation data under various environments
- ✓ Develop utilization technique of biobased raw materials
- ✓ Combine with other degradation control technologies (ex. Sheath-core conjugate fiber)

No. A-11-6E

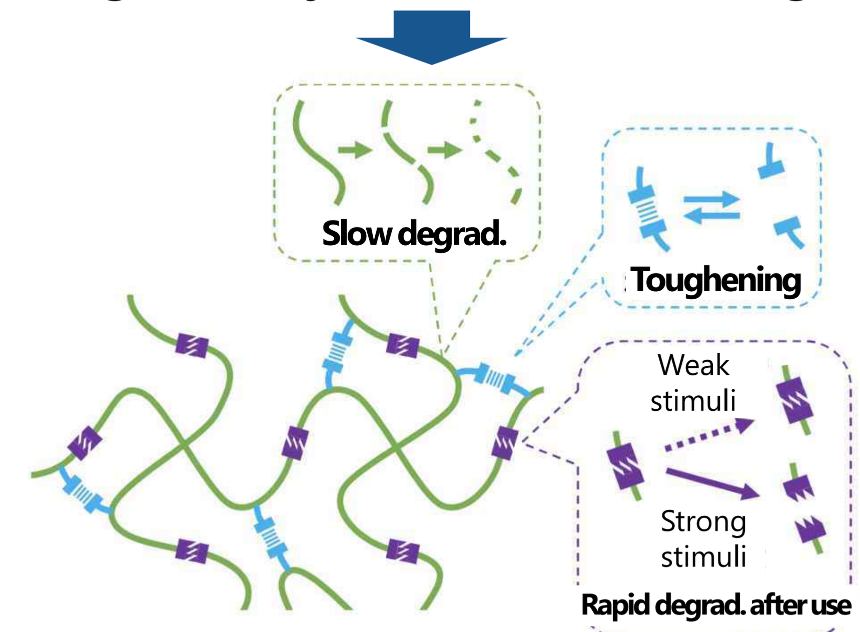
PJ: Development of Multi-lock Biopolymers Degradable in Ocean from Non-food Biomasses

Theme: Development of biodegradable polymers with multi-lock degradability and practical mechanical performance (E1+E3)

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

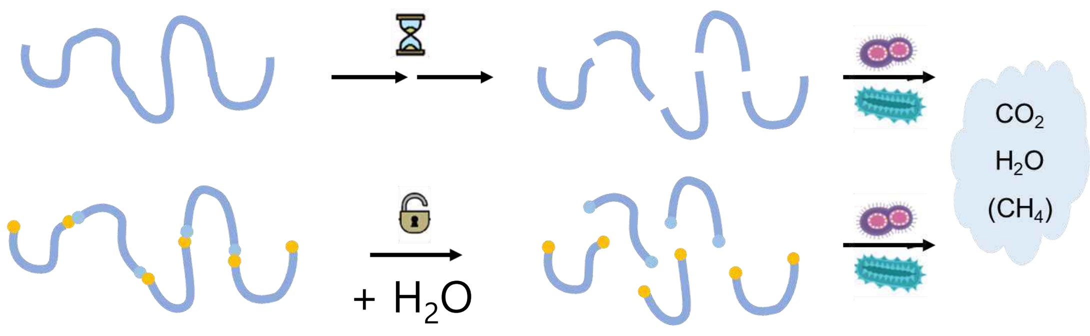
Introduction

There is generally a trade-off between degradability and mechanical strength.



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

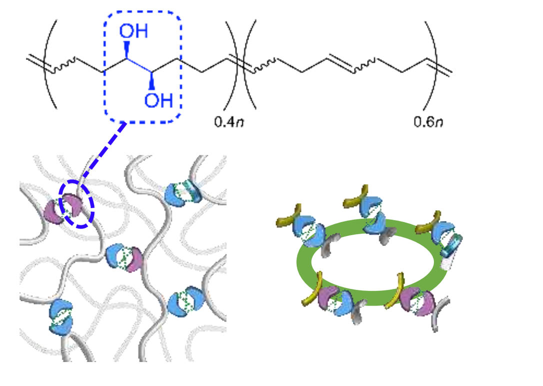
Topic 1: Development of multi-lock mechanism



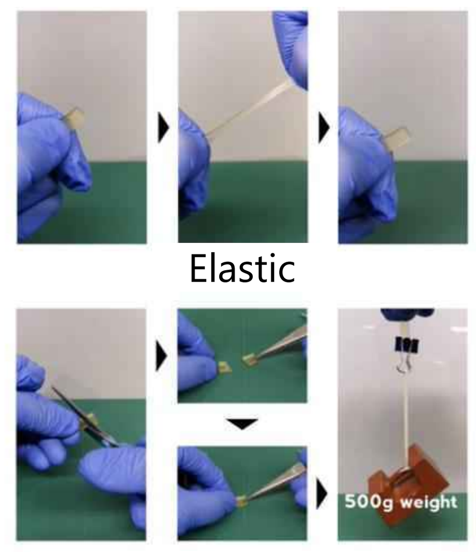
Introduction of dynamic bonds responsive to environmental stimuli

Accelerate degradation by facilitating the time-consuming oligomerization process

Topic 2: Combine crosslikking and degradability

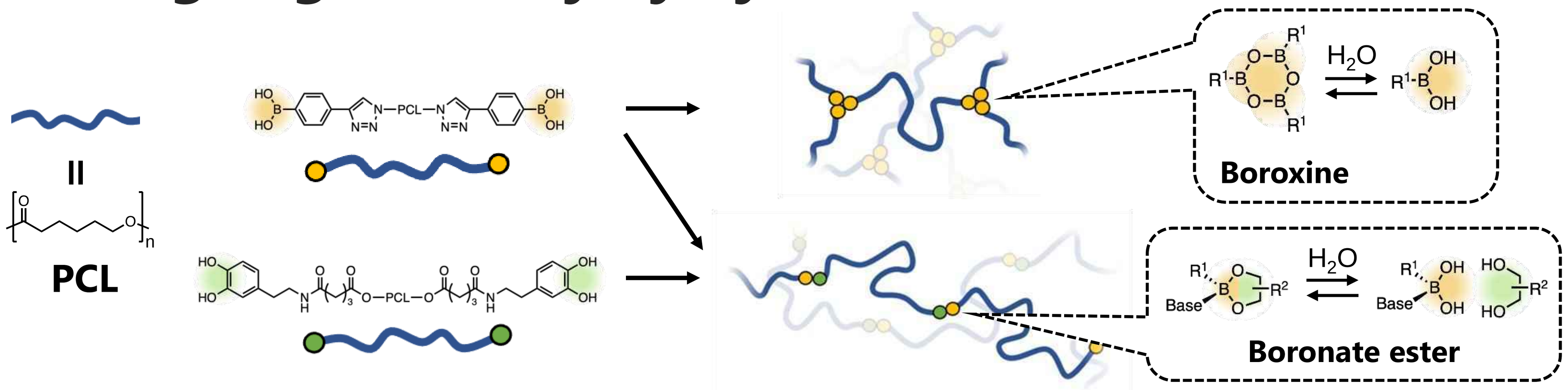


Various bonding modes = "entropy-driven"



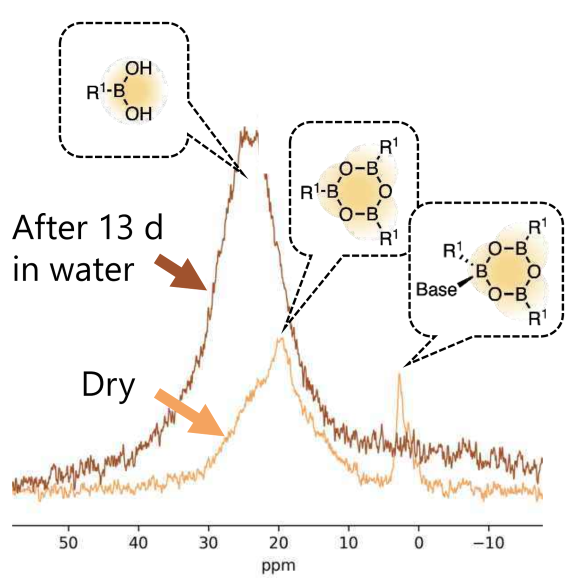
Realize excellent toughness using the "entropy-driven" multidentate hydrogen bonds

Tuning degradability by dynamic B chemistries



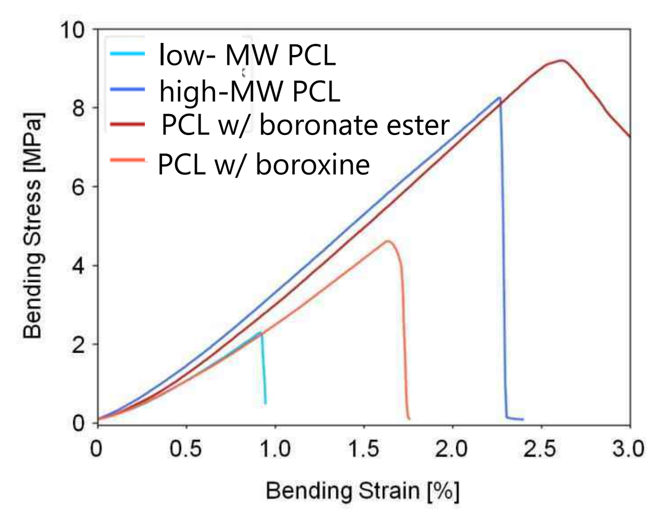
Model polymers crosslinked/chain-extended with boronate ester/boroxine were successfully synthesized.

Solid-state ^{11}B NMR

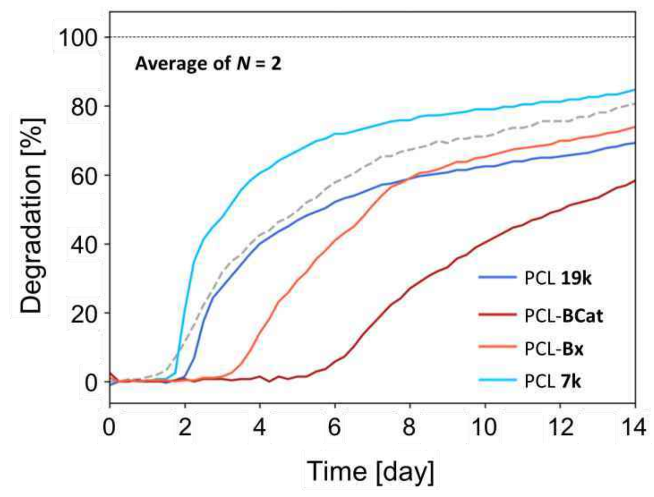


Bond dissociation by water was confirmed.

3-point bending test



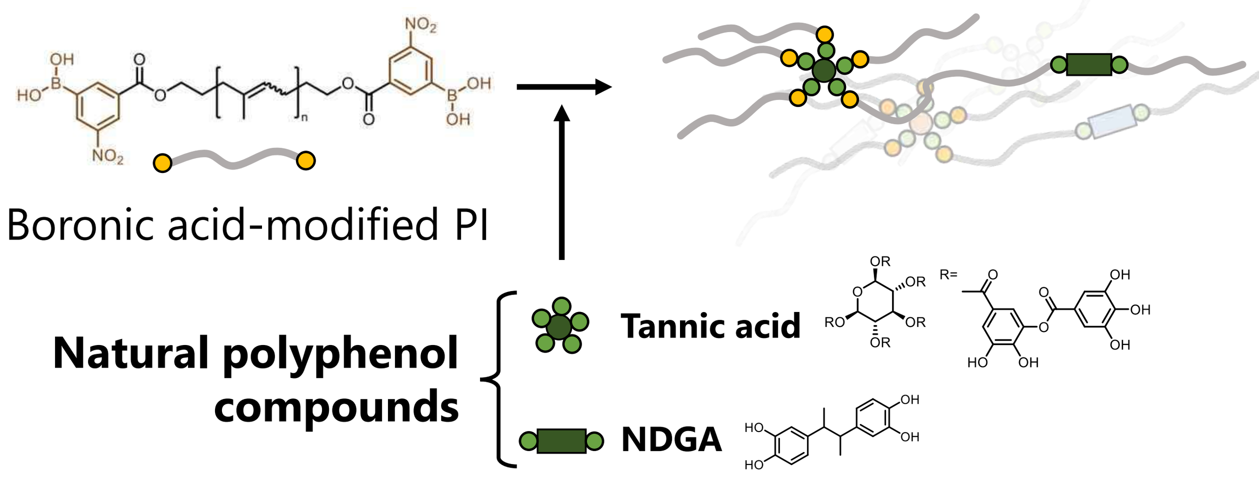
Marine biodegradability (BOD)



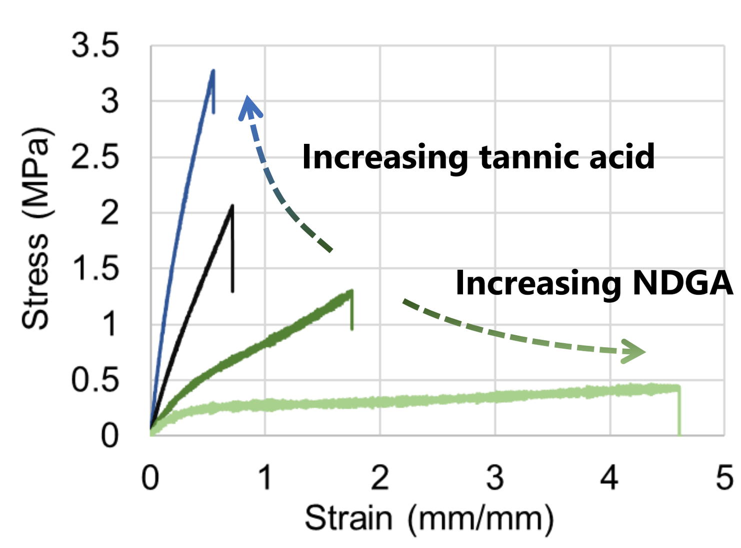
Mechanical performance was enhanced without sacrificing biodegradability.

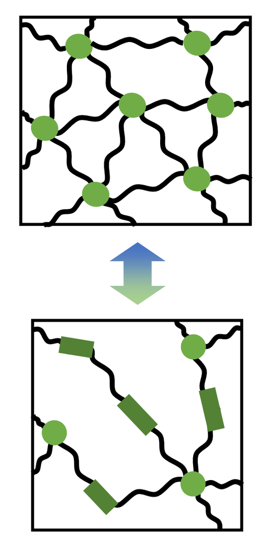
Rubber crosslinked by boronate esters

We developed polyisoprene (PI) rubber crosslinked by boronate ester.



Uniaxial tensile test

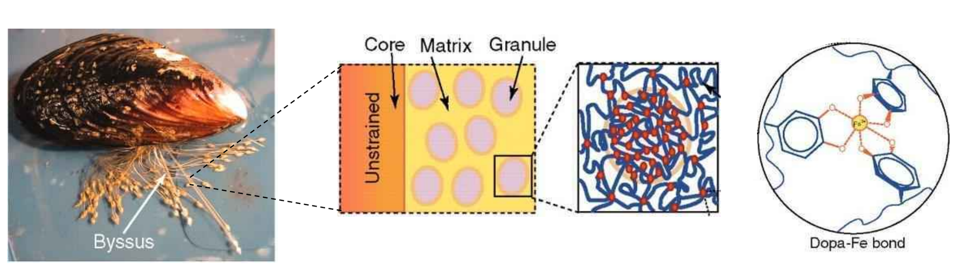




Rubbery materials were obtained solely by boronate ester crosslinking.

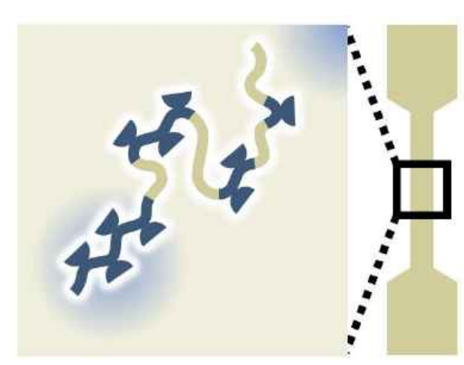
Toughening by controlled placement of dynamic bonds

Publication: Ishizaka et al. *Polymer* **2022**, *246*, 124748.

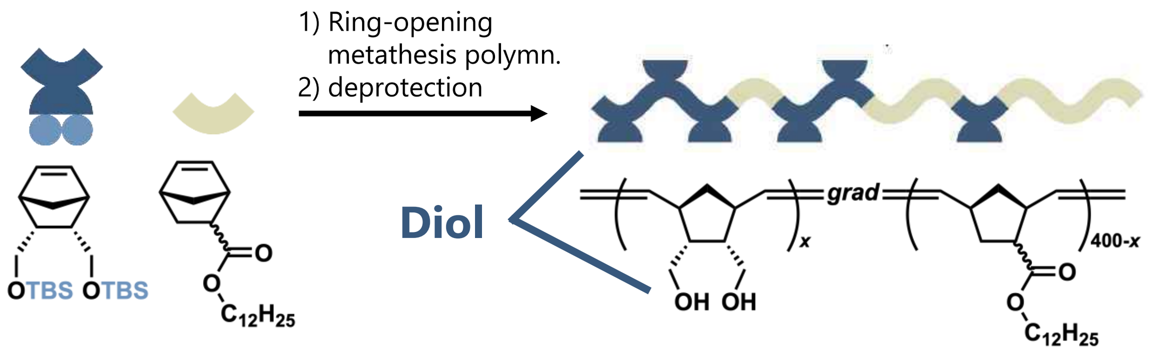


Toughening mechanism in nature by controlling dynamic bond placement

Harrington et al. *Science* **2010**, *328*, 216.

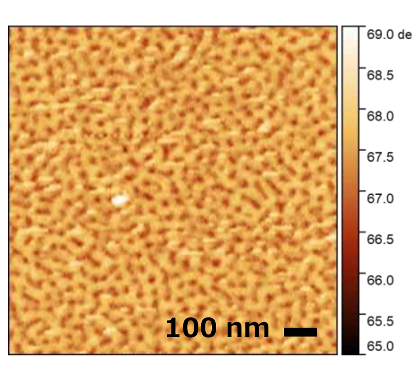


Application to artificial tough polymers



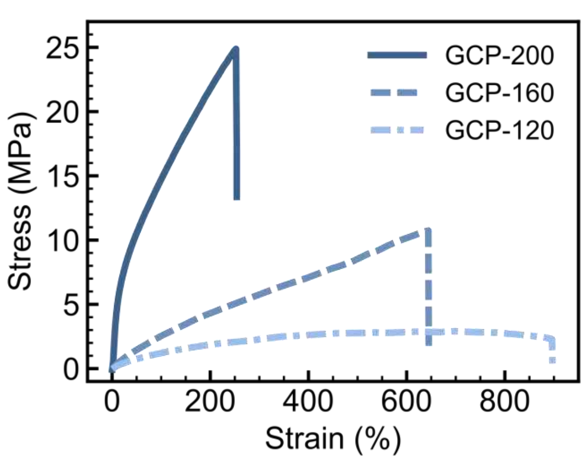
Gradient copolymer

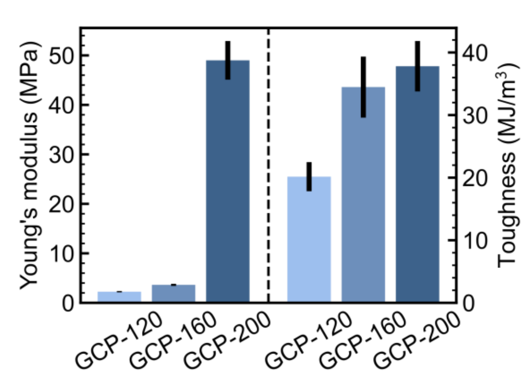
Atomic force microscopy



Nano phase separation

Uniaxial tensile test

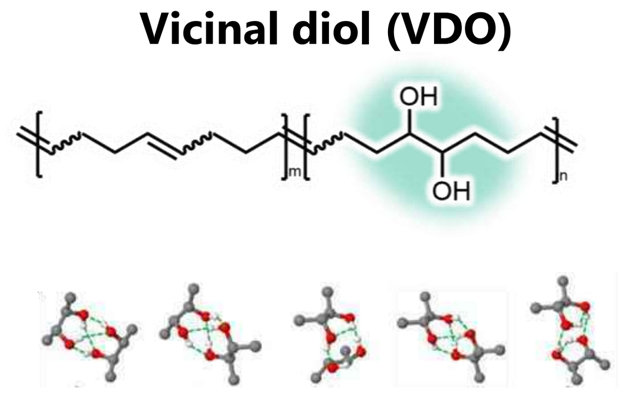




Toughness was realized by inhomogeneous distribution of hydrogen-bonding diols

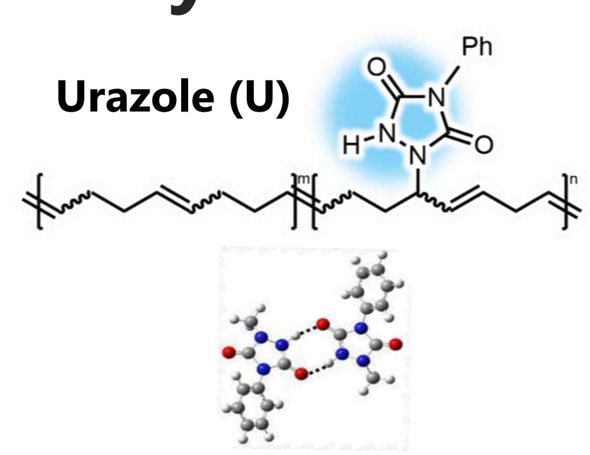
Evaluation of entropy-driven dynamic bonds

Vicinal diol (VDO)



vs.

Urazole (U)

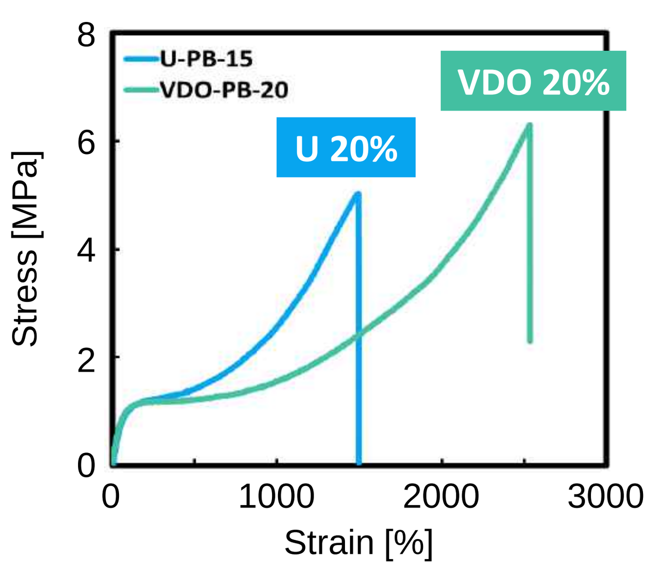


Many stable bonding modes → "soft" entropy-driven type

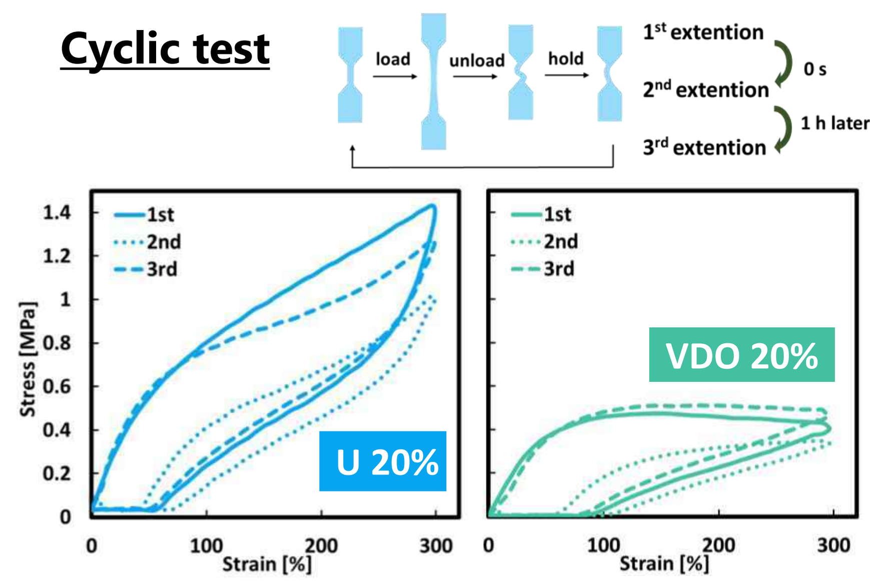
Only one stable bonding mode → "hard" enthalpy-driven type

Evaluate the characteristics of the bonds by examining the mechanical properties of the model polymers

Uniaxial tensile test



Cyclic test



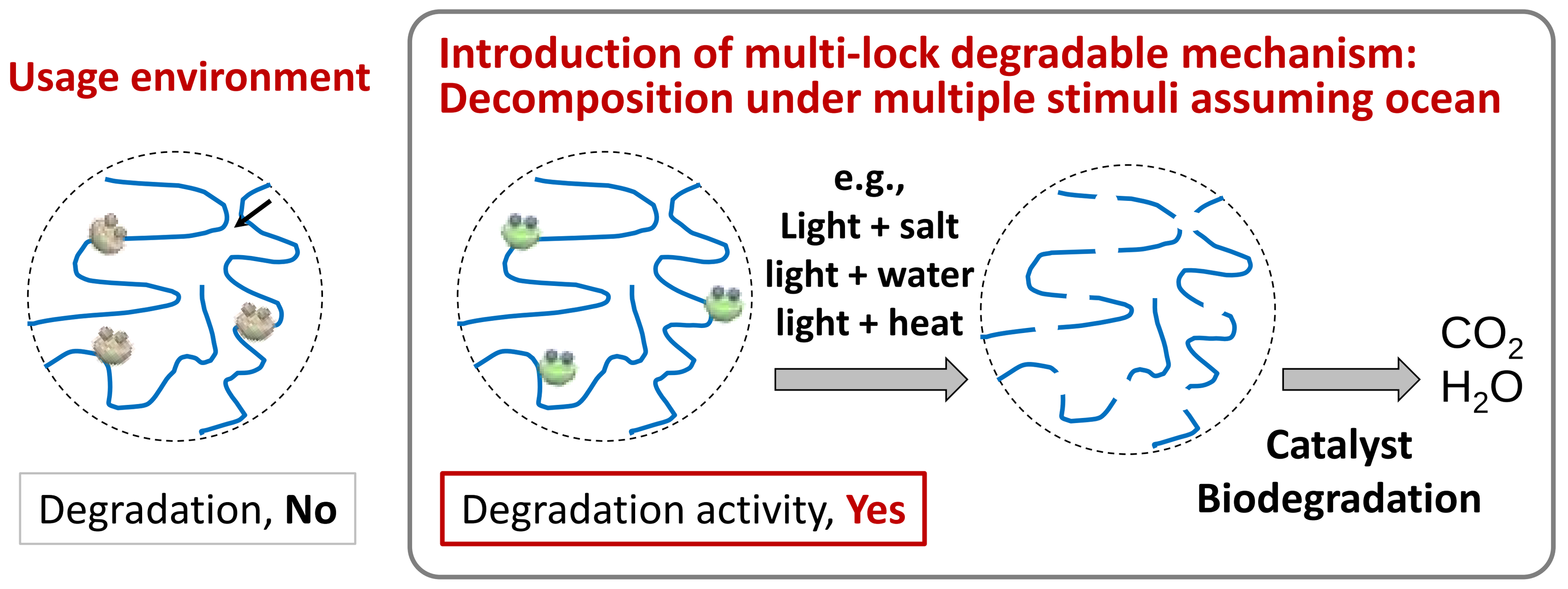
Recovery = 76% 96%

Physical crosslinks between VDOs are weaker but easier to reform → unique feature of soft, entropy-driven multidentate hydrogen bonds

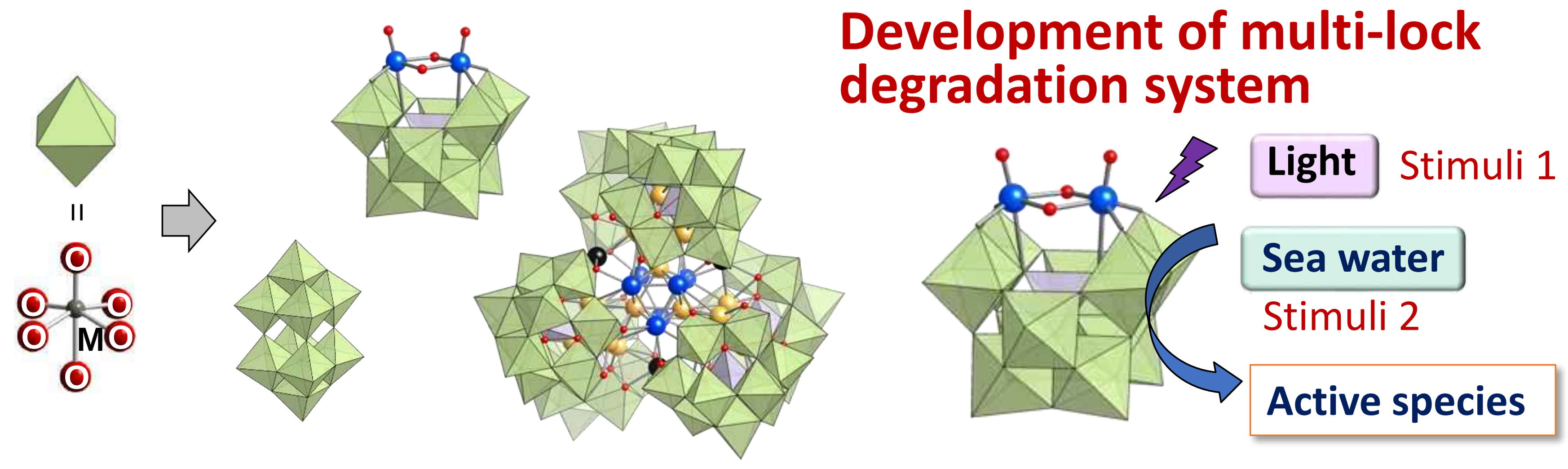
No. A-11-7E
PJ: Development of Multi-lock Biopolymers Degradable in Ocean from Non-food Biomasses
Theme: Development of Multi-lock Polymers Using Metal Oxide Cluster Catalysts
Organization: The University of Tokyo (E1+E3)
Contact: Kosuke Suzuki (ksuzuki@appchem.t.u-tokyo.ac.jp)

1. Research contents in this project

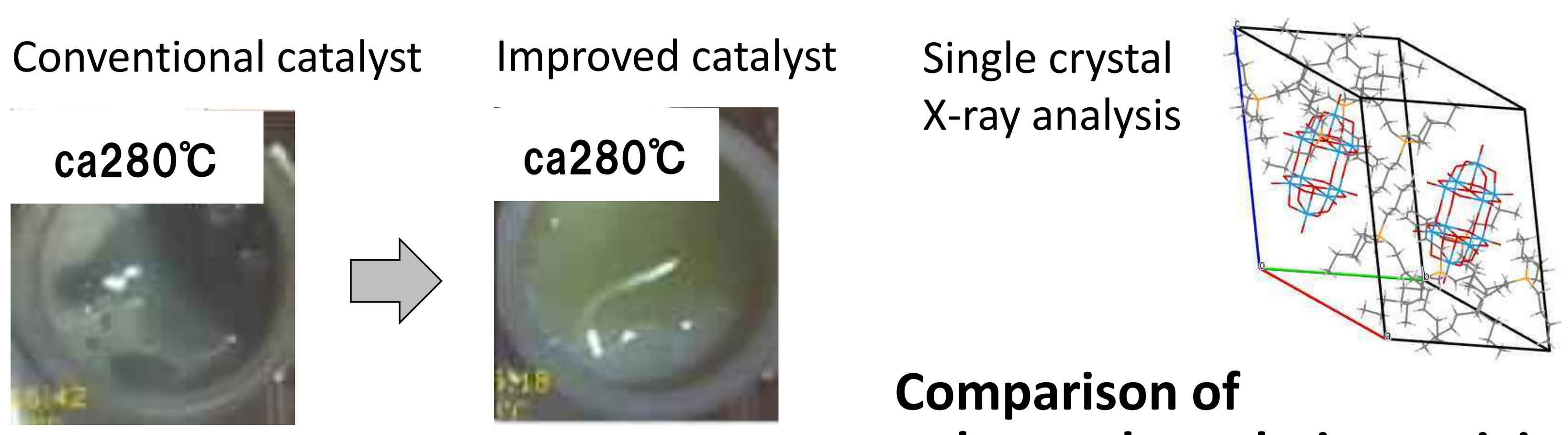
The purpose of this study is to develop polymers that have both multi-lock degradation mechanism and toughness in ocean. By utilizing our synthesis methods of meal oxide clusters, we will develop catalysts that exhibit degradation activity when two or more of the stimuli, such as light, heat, oxygen, water, salts, enzymes, microorganisms, are present at the same time, and use these catalysts to perform on-demand degradation of polymers.



Design of metal oxide cluster catalysts

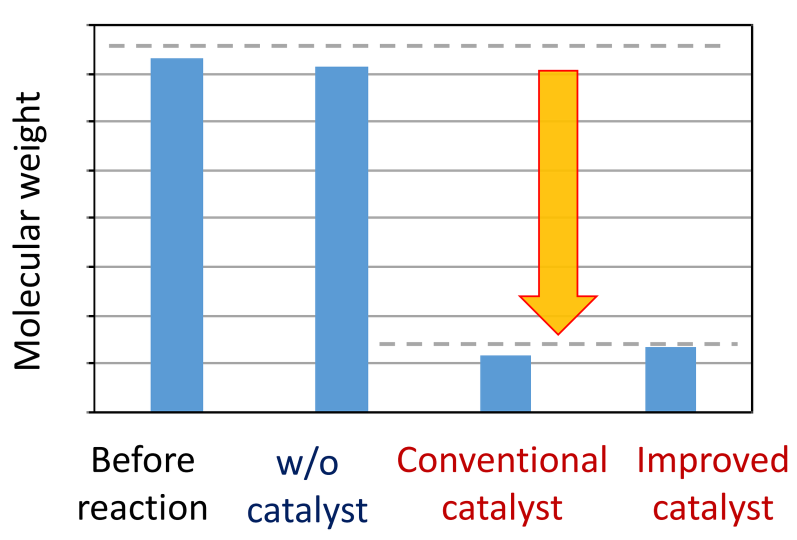


Development of catalyst with heat resistance



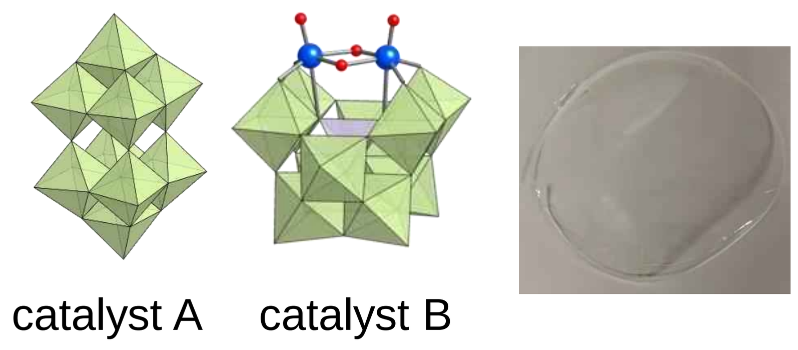
- Low melting point of catalyst
- Improved heat resistance
- High catalytic activity

Comparison of polymer degradation activity



2. Common Issues

Preparation of catalyst-containing polymer films

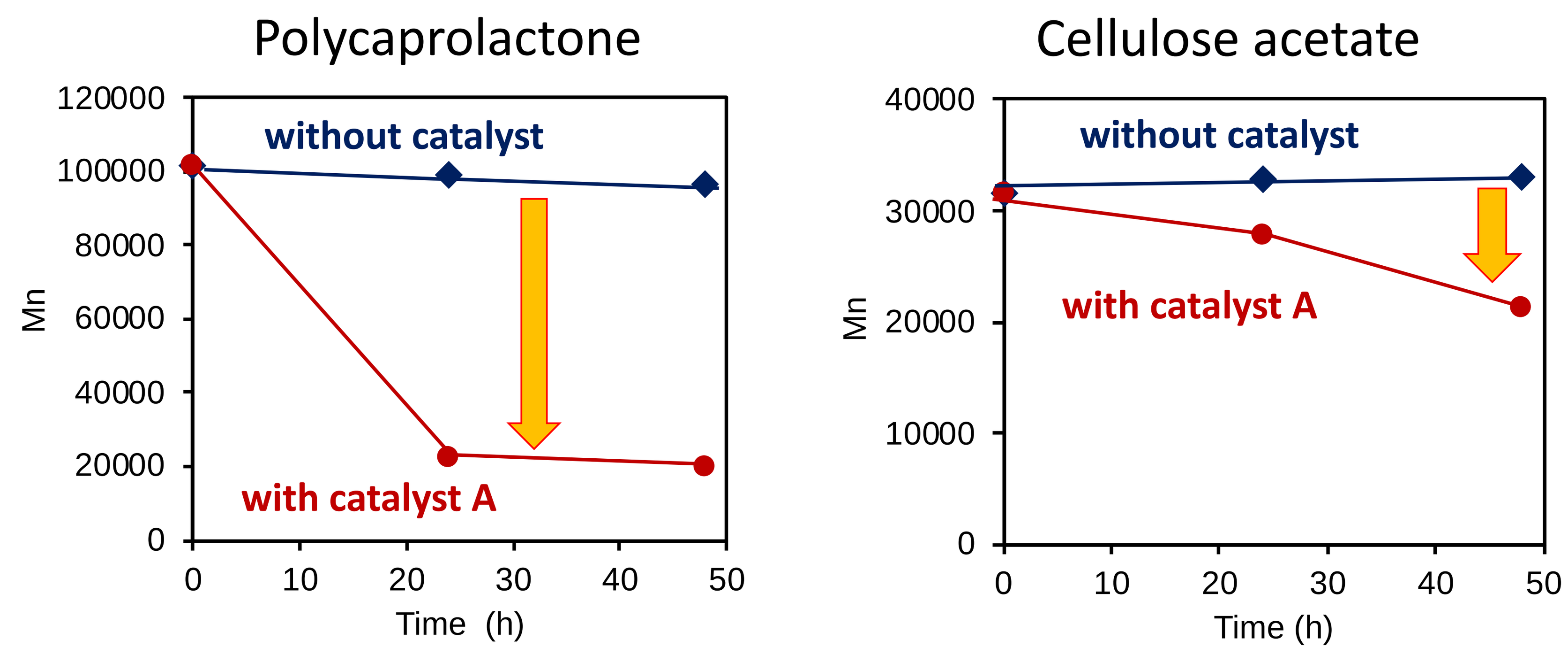


Sample	M_n
Polycaprolactone	112458
Polycaprolactone + cat A	106664
Polycaprolactone + cat B	115858

Catalysts do not affect molecular weight of polymers during film preparation

Photodegradation of catalyst-containing polymer film

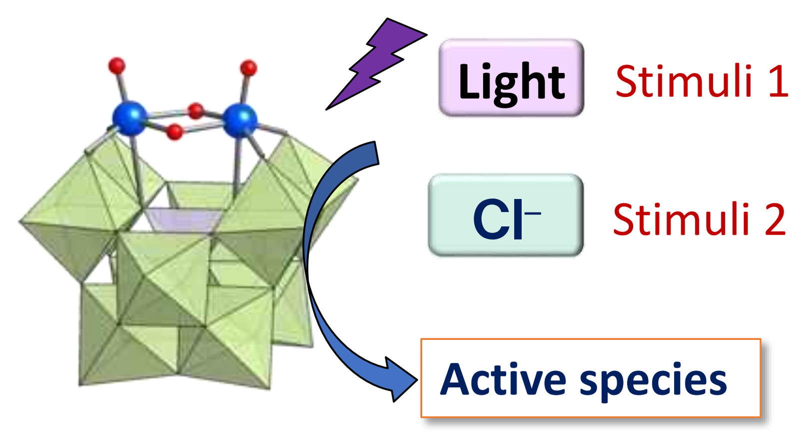
Molecular weight change of polymers under Xe-lamp irradiation



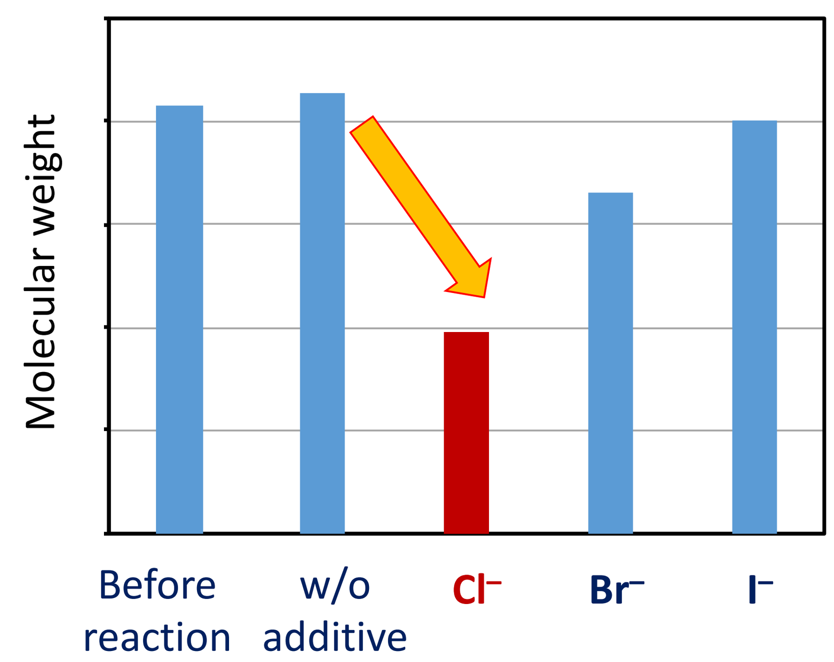
Catalyst-containing polymer films undergo accelerated photodegradation

Multi-lock degradation using chloride ions (Cl^-)

Additive effect on polymer degradation under Xe-lamp Irradiation

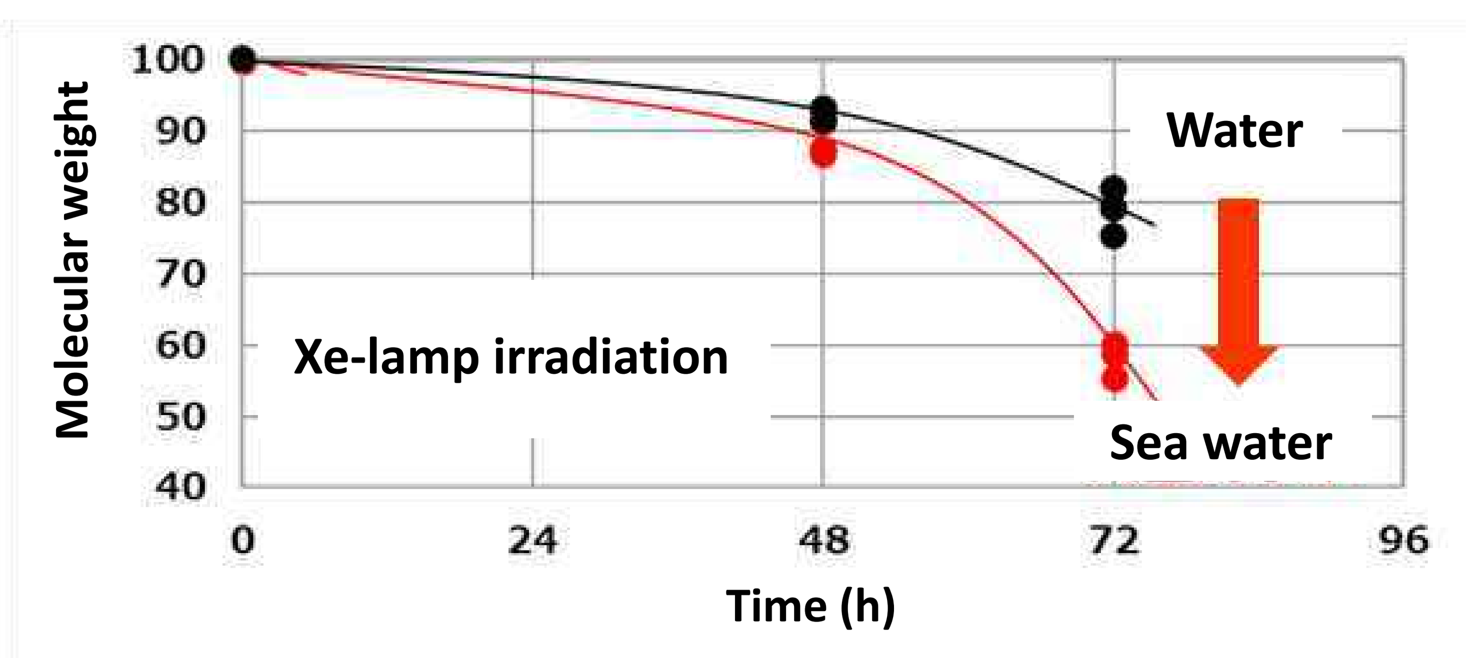


Chloride ion accelerates photodegradation of polymers



3. Collaboration with companies

Degradation of catalyst-containing PET polymer



Catalysts accelerate photodegradation of PET polymer in artificial seawater

4. Collaboration with academia

University of Tokyo

Yamagata University

5. Future Plans

Computational chemistry for elucidation of reaction mechanisms

Consideration for reducing the amount of catalyst and additives

Development of new multi-lock degradation mechanisms

Investigation combining catalytic degradation and biodegradation