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

Presenter：Kohzo Ito（The University of Tokyo）
PM：Kohzo Ito
Professor, Graduate School of Frontier Sciences, The University of Tokyo
PJ Teams：The University of Tokyo、Mitsubishi Chemical Co.、Bridgestone Co.
Teijin Limited、Kureha Co.、Kyushu University, Nagoya University,
Yamagata University,
Research Institute of Innovative Technology for the Earth,
National Institute of Advanced Industrial Science and Technology,
Ehime University, Tokyo Institute for Technology

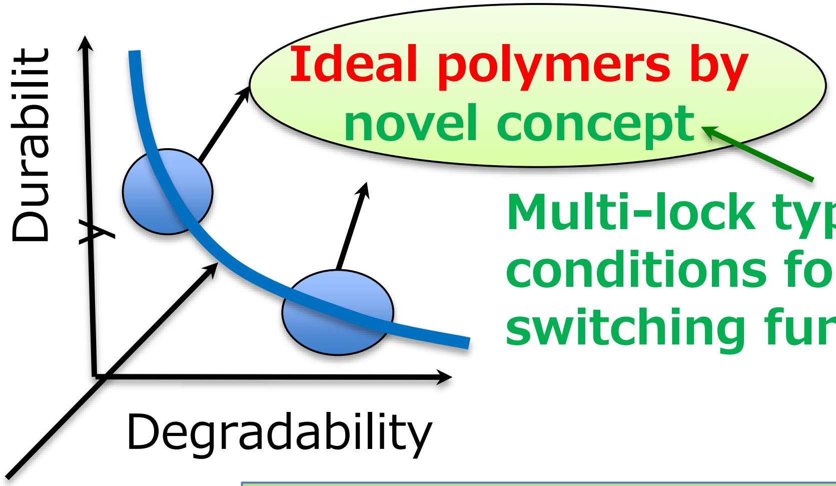
Compatibility between degradability and durability

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.

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

Clean & Cool Earth

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

- **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.**

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 • 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 • 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 ✓ 分解のスピードを制御する技術 • 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 • 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)

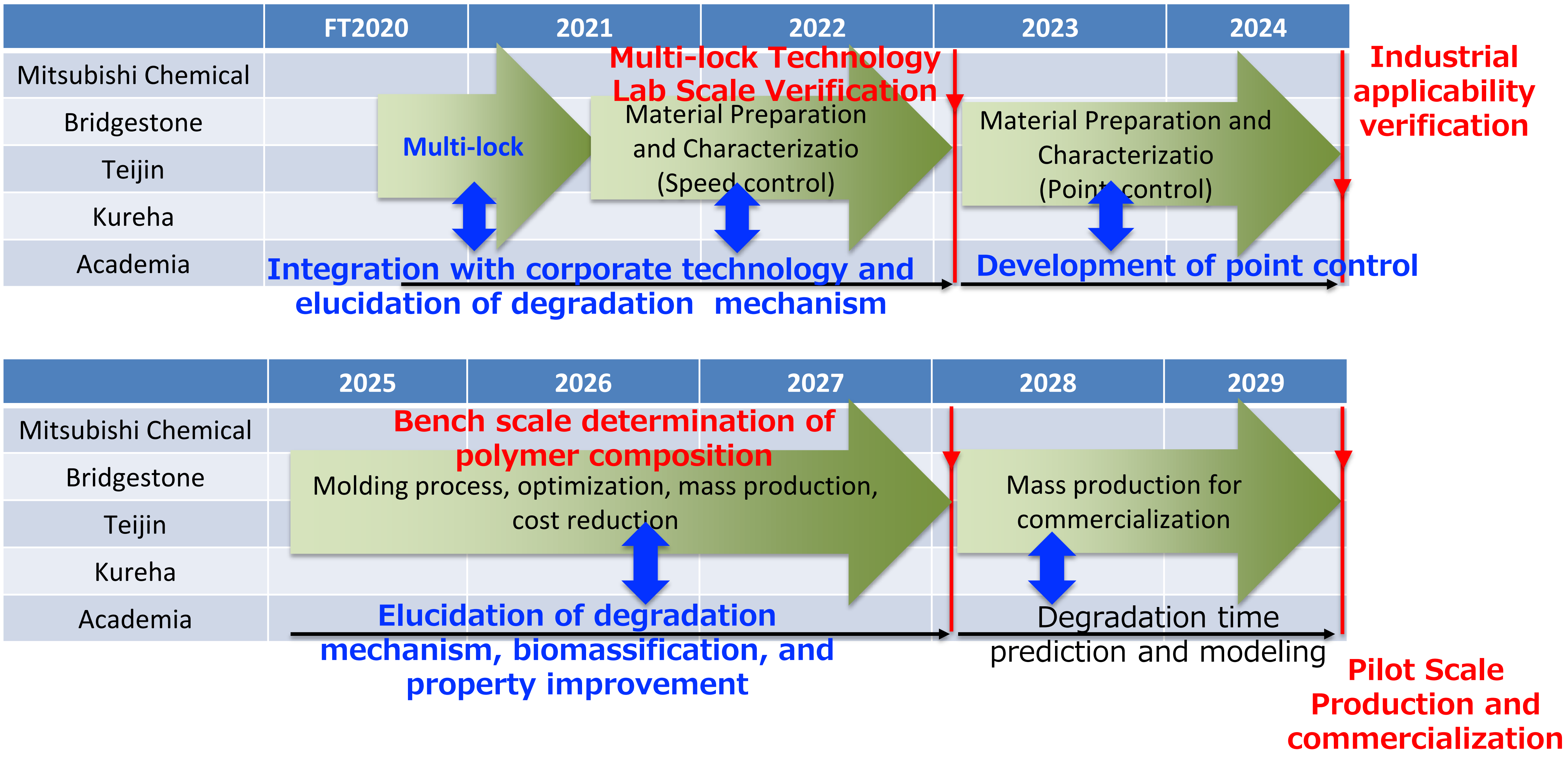
・ **Additives + light, salt, marine microorganisms**
Cluster catalyst (Univ Tokyo), Polyrotaxane (Univ Tokyo)

・ **Dynamic cross-linking + water, marine microorganisms**
Hydrogen bonding (Companies, Univ Tokyo)

Progress of Each Team

Organization Subject	Mitsubishi Chemical Plastic	Bridgestone Tire Wear Powder	Teijin Fiber Scraps	kureha Fishing Gear	Academia 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	Biodegradable, toughened, and bio-engineered non-degradable polymers (PET)	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.	The production technology for polyester-based multi-loc bio-tough polymers and their fibers, which are highly degradable under certain stimuli, will be developed. And a monomer synthesis facility derived from inedible biomass will be comducted. The current marine degradability index is the target.	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 additives greatly accelerates degradability. Speed control was successfully achieved. The addition of polyrotaxane increased tearing strength by a factor of 2.	Succeeded in synthesizing a rubber that introduces a degradable unit. Achieved more than 10-fold improvement in biodegradability. Succeeded in achieving both a 2-fold increase in fracture strength and a 10-fold increase in degradation speed.	PET-based fibers with marine biodegradability and practically usable strength were successfully developed. Seven species of PET oligomer-degrading bacteria were identified.	We have succeeded in developing a fishing line that has the same degree of nodal elongation as non-marine biodegradable fishing line and exhibits marine biodegradability. The degradation of fishing line is accelerated when it sinks to the seafloor after abandonment.	Successfully achieved both toughness and improved degradability using polyrotaxane. Achieved a multi-lock mechanism using metal oxide cluster catalysts, which significantly improved the activity and production of PET degradative enzymes.

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**

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

MS Ito PJ

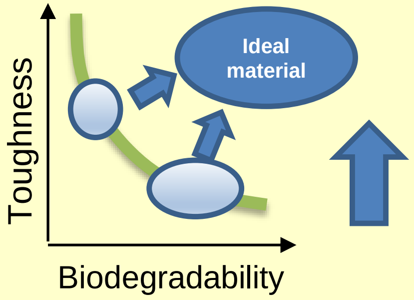
1． Concept and objectives

【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 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

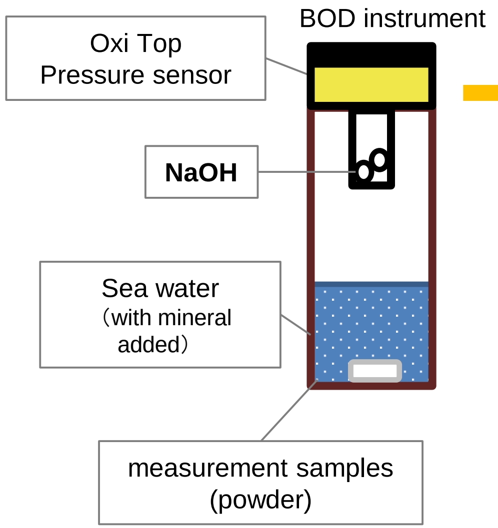
・FY2029 Final Target: Achieve the followings with scaled-up products
- Marine biodegradation after unlocked :40% biodegradability in sea water (25℃) in 30 days.
- Tear strength: More than 10 times that of existing biopolymers
- Polymer production on a scale larger than bench scale

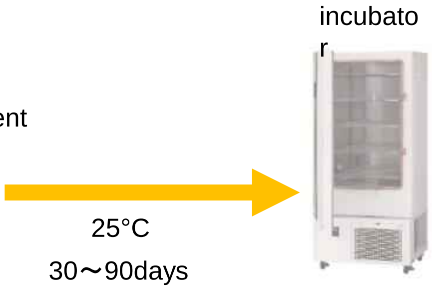
Mitsubishi Chemical Corporation
Topics

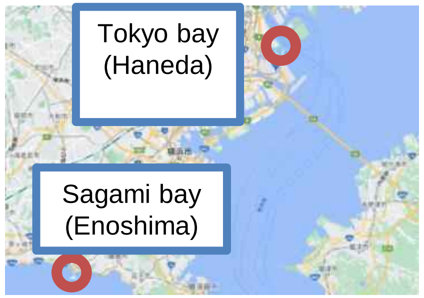
MS Ito PJ

○Evaluation method of marine degradability

BOD: Biochemical Oxygen Demand[mg/L]
Biodegradation： consume O_2, produce CO_2
BOD test：measuring O_2 consumption (NaOH absorbs CO_2)
→ calculate degree of biodegradability



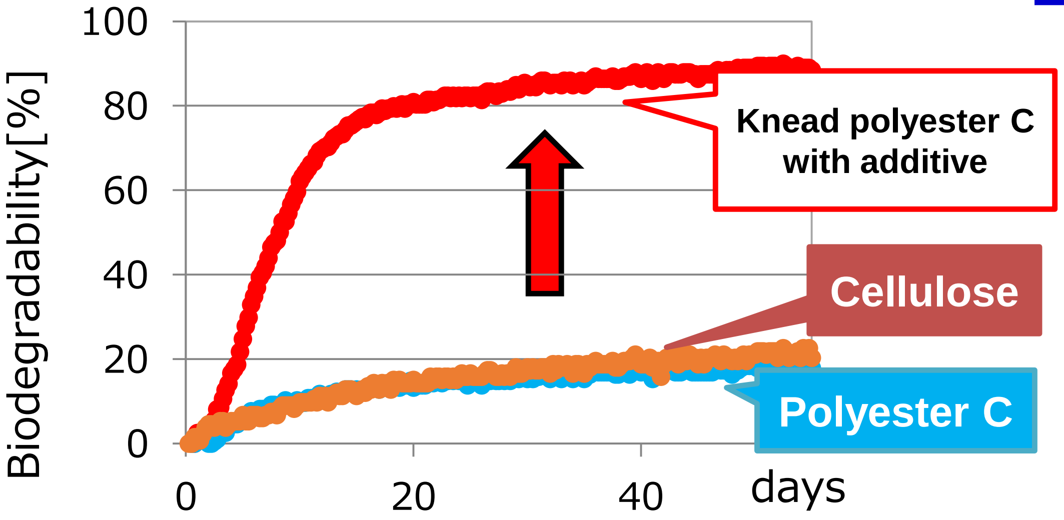




○Additives were investigated to improve marine biodegradability of copolymerized polyesters.

Biodegradability was greatly accelerated by kneading additive D

Marine biodegradability evaluation by BOD test



Speed Control

Point Control + Toughening

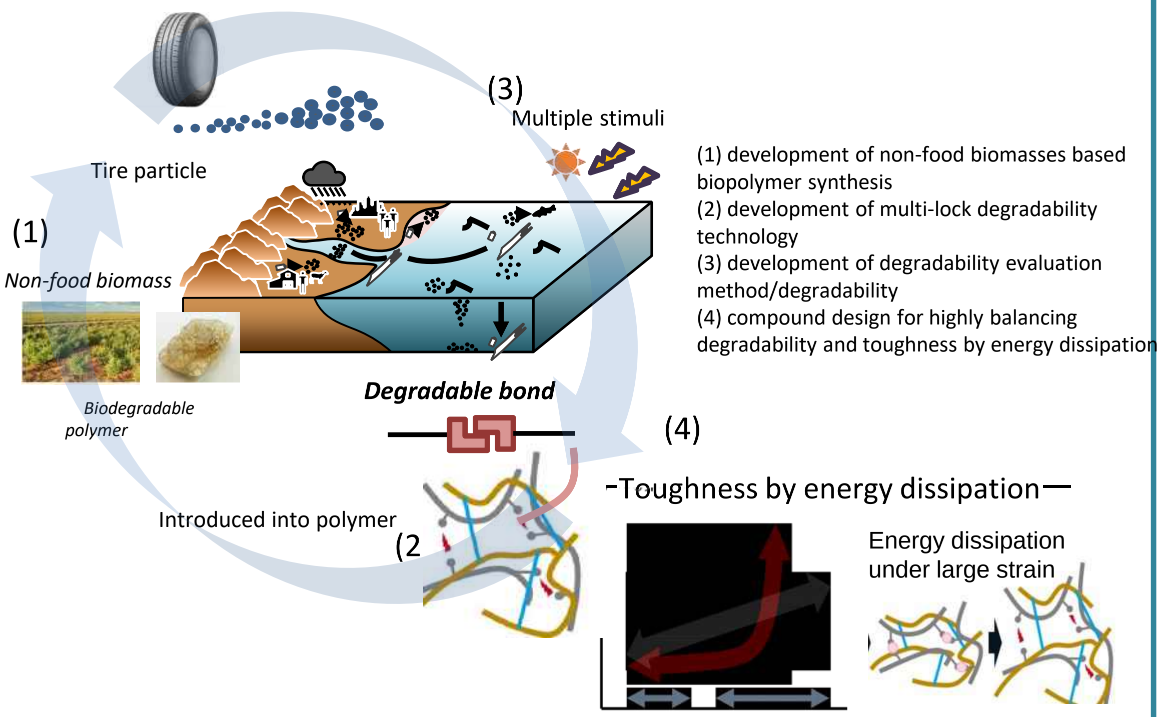
・ Coexistence of "certain additives" with marine biodegradable resins
→ Improved marine biodegradability

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

MS Ito PJ

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—



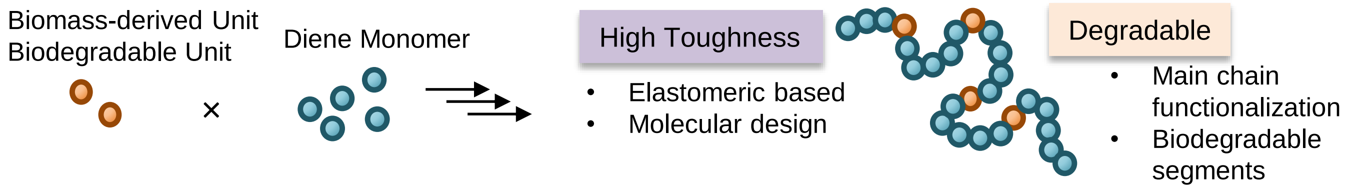
BRIDGESTONE

Biodegradation technology by introducing degradable unit

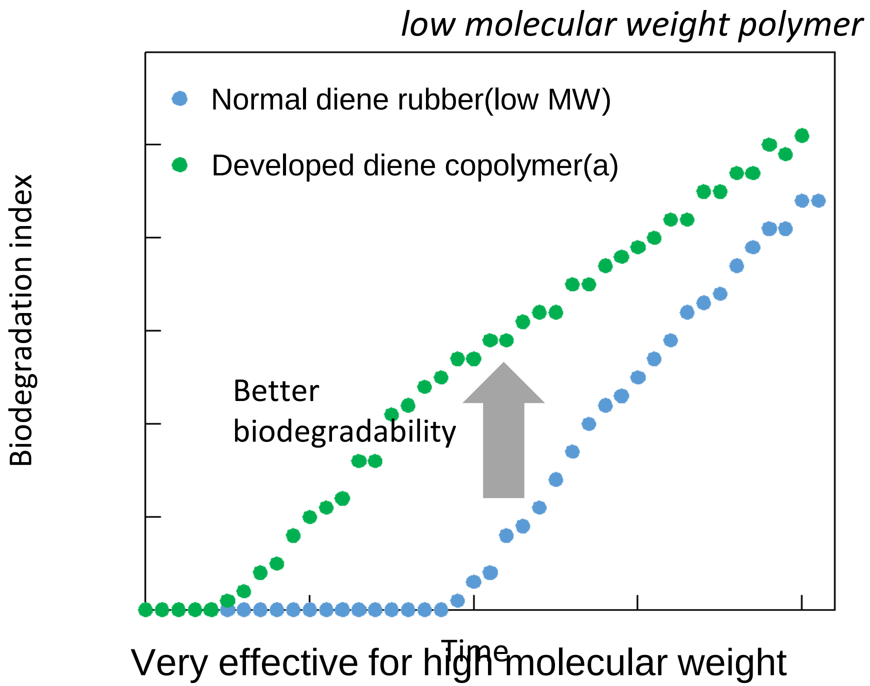
MS Ito PJ

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

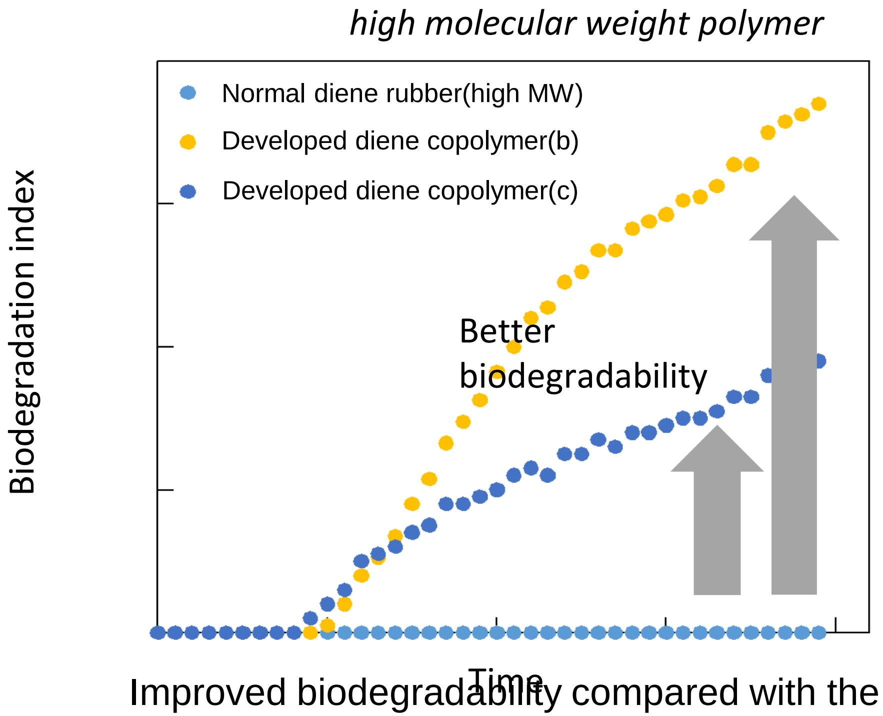
Polymer Design:



―Marine biodegradation test result ―



Very effective for high molecular weight polymer



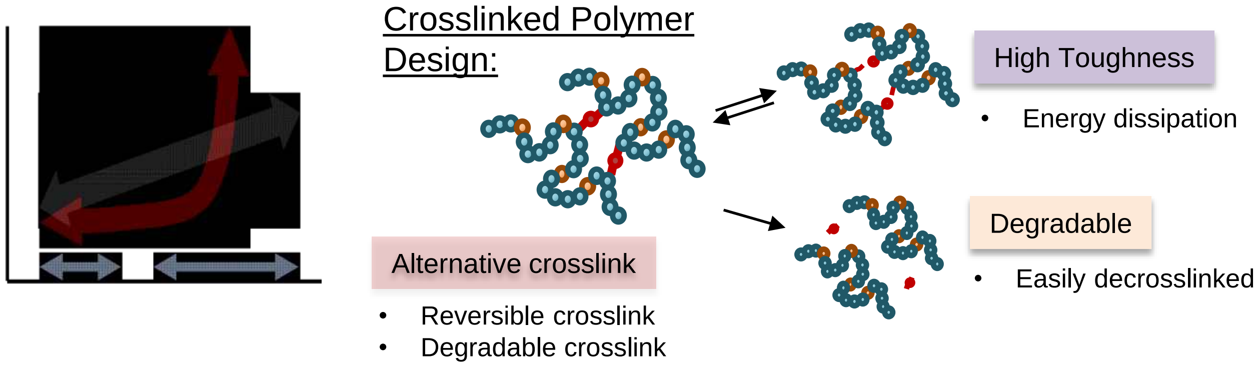
Improved biodegradability compared with the same molecular weight

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

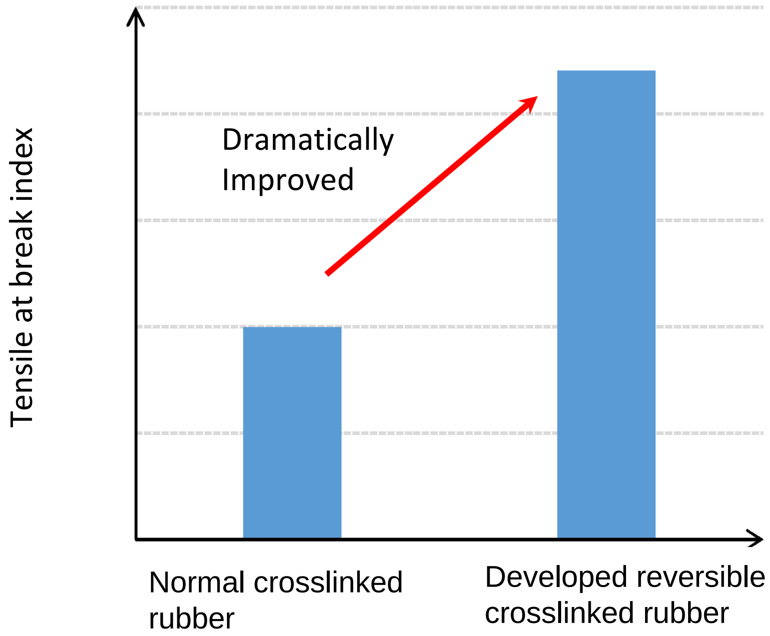
Technology for balancing biodegradation and toughness by reversible cross-link

MS Ito PJ

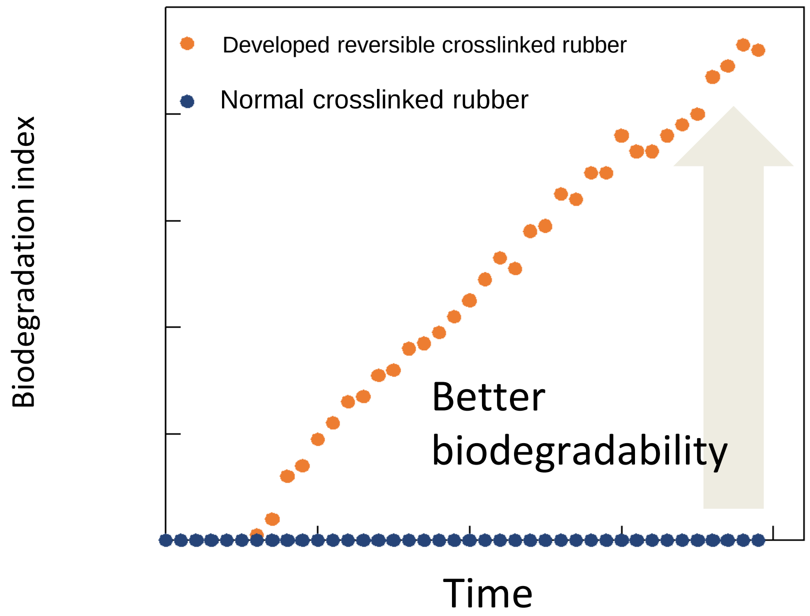
With extending reversible bond technology that strengthen rubber by effective energy dissipation, we newly designed degradable cross link system cooperating with academia.



—Physical property test result—



—Marine biodegradation test result —



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

Teijin Limited / Teijin Frontier Co.,Ltd.

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

MS Ito PJ

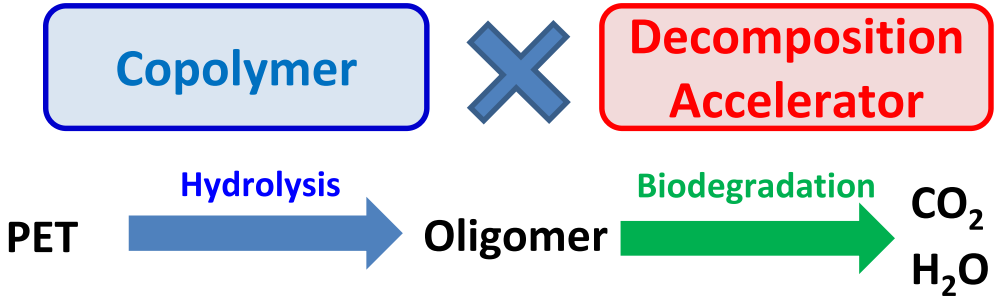
We are developing new aromatic polyester resin & fibers that hydrolyze/biodegrade in seawater with specific stimuli while having practical stability during ordinary use as follows,

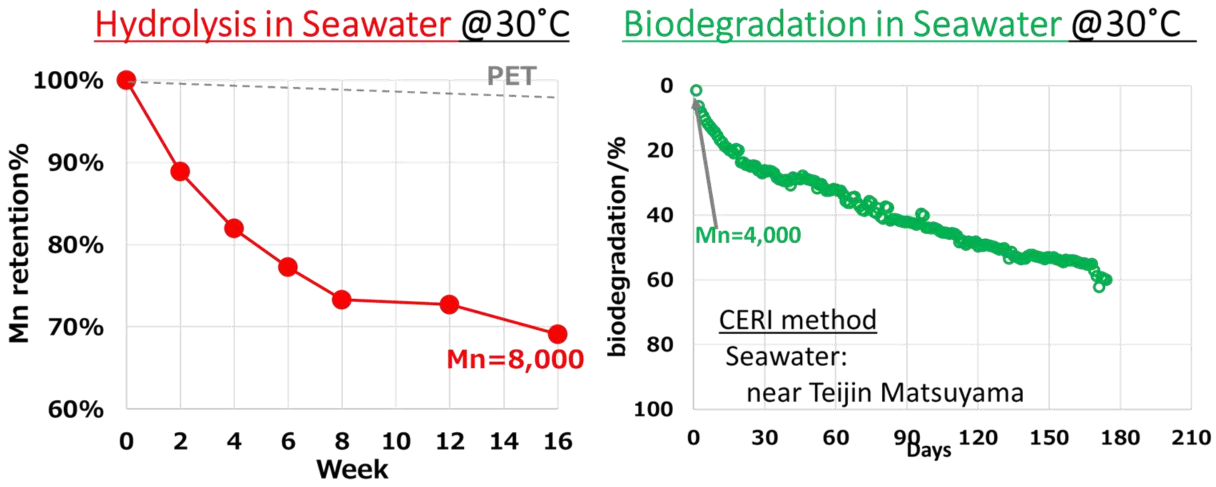
i. Easily degrading components into polymer chain and addition of decomposition accelerators
ii. Processing technology that promote decomposition
   Clarifying of decomposition mechanism
   Safety confirmation of oligomers

The main achievements up to FY2022 are as follows.

- New crystalline co-PET fiber that is hydrolyzed in seawater.
  This fiber has practical mechanical properties and durability
  This fiber has biodegradability at low molecular weight.
  The time required for complete decomposition in ocean at 30˚C is estimated to be 5~6 years.

We will proceed with detailed structural analysis of co-PET fibers, as well as the development of fibers with point control (switch) functions that improve marine biodegradability. At the same time, biobased monomers will be considered.



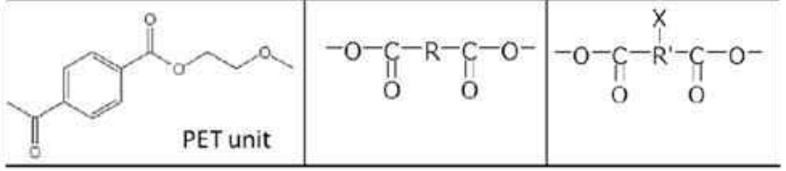


New co-PET fiber with Marine Biodegradability

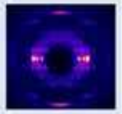
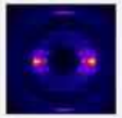
Marine Biodegradable "New Aromatic Polyester" fiber

Copolymer × Decomposition Accelerator

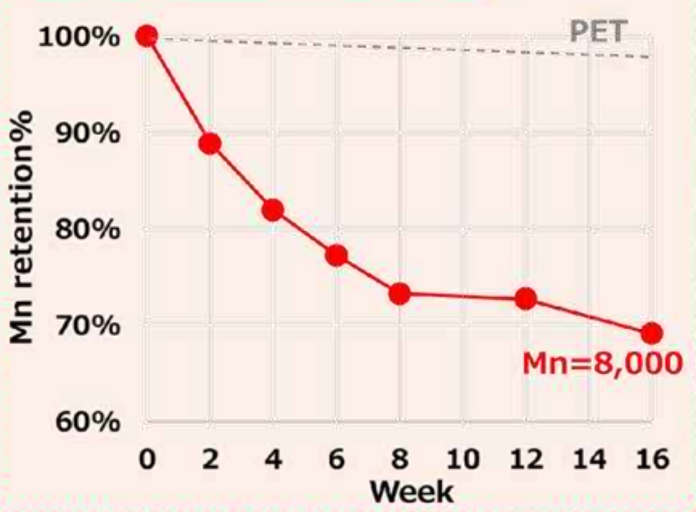
Terephthalic acid unit	Decomposable unit	Hydrophilic unit

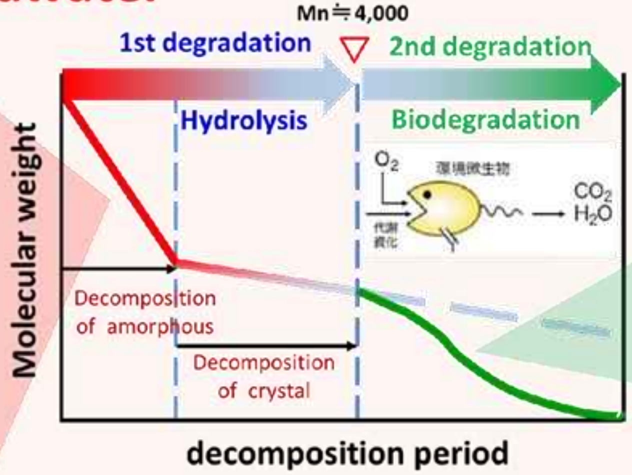


Molecular weight (Mn)	Tg ℃	Tm ℃	ΔH_m J/g
1.2×10⁴	50	211	30

	Fiber properties Target 3cN/dtex				WAXD/SAXD						Dyeability Target >2cN/dtex	Washing durability
	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

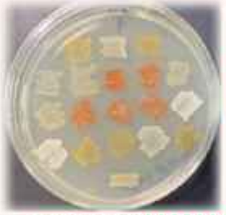




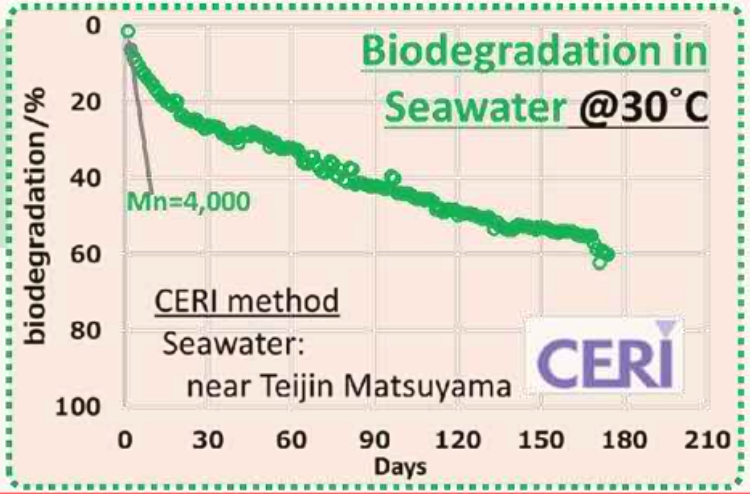
Initial hydrolysis rate equation by Arrhenius analysis

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

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



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

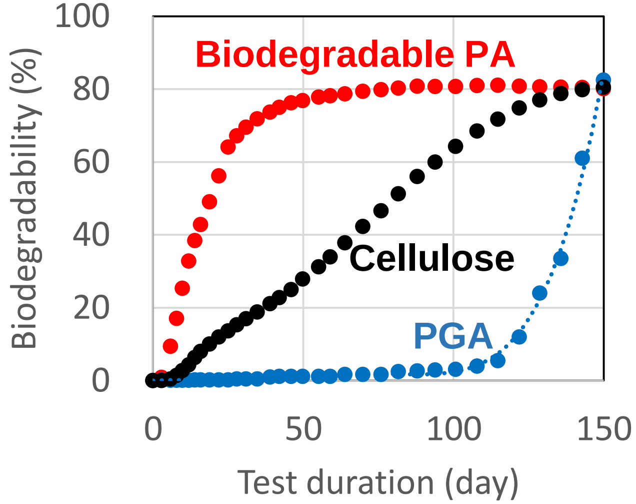


KUREHA CORPORATION
Development of strong and degradable biopolymers for fishing nets

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.

Biodegradation in sea water (ISO19679)



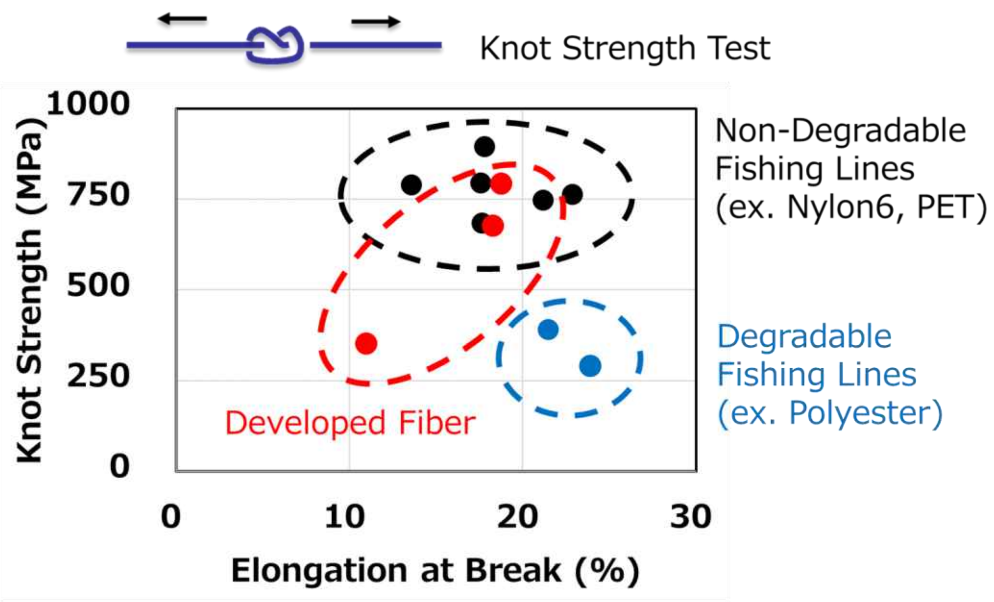
Degradation of PGA ball

KUREHA

Development of strong and degradable biopolymers for fishing nets

MS Ito PJ

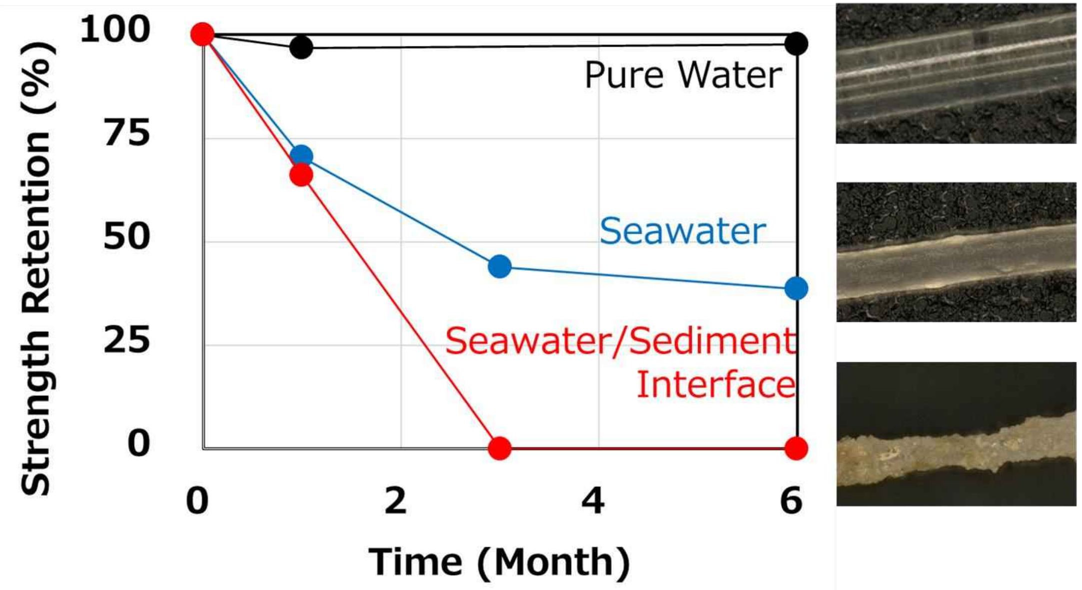
<Comparison of Knot Strength and Elongation>



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

<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.

Nikkei newspaper Dec. 19th, 2022

KUREHA

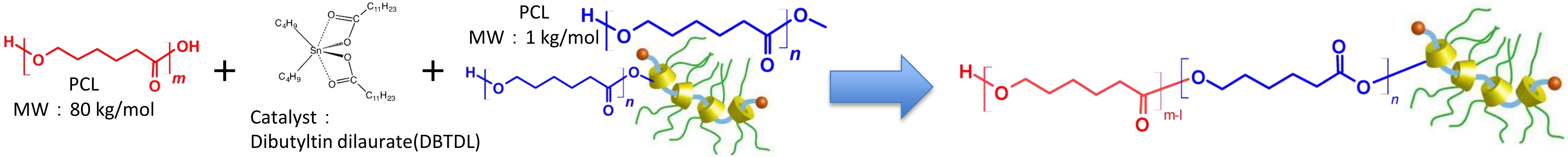
Cundamenatal Common Isues

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, 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

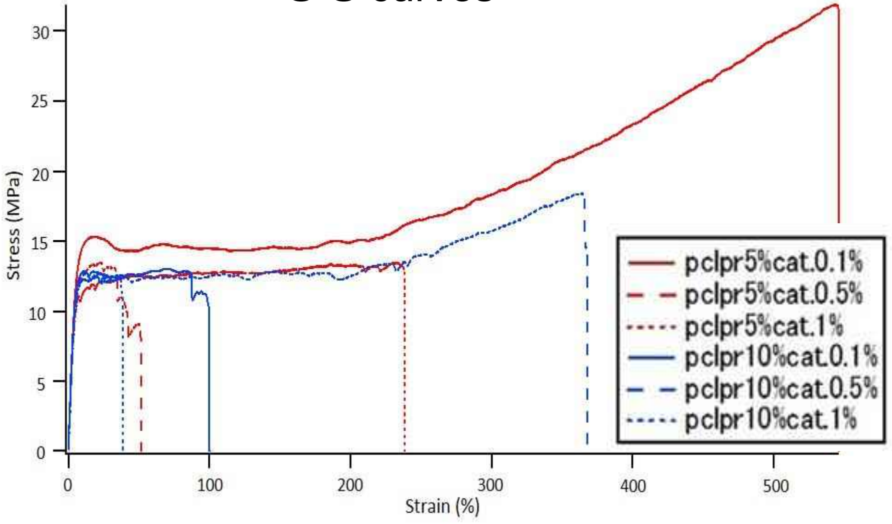
Research and Development of Degradable Supramolecular Polymers with Both Multi-lock Mechanism and Toughness

University of Tokyo
ITO, Kohzo

MS Ito PJ



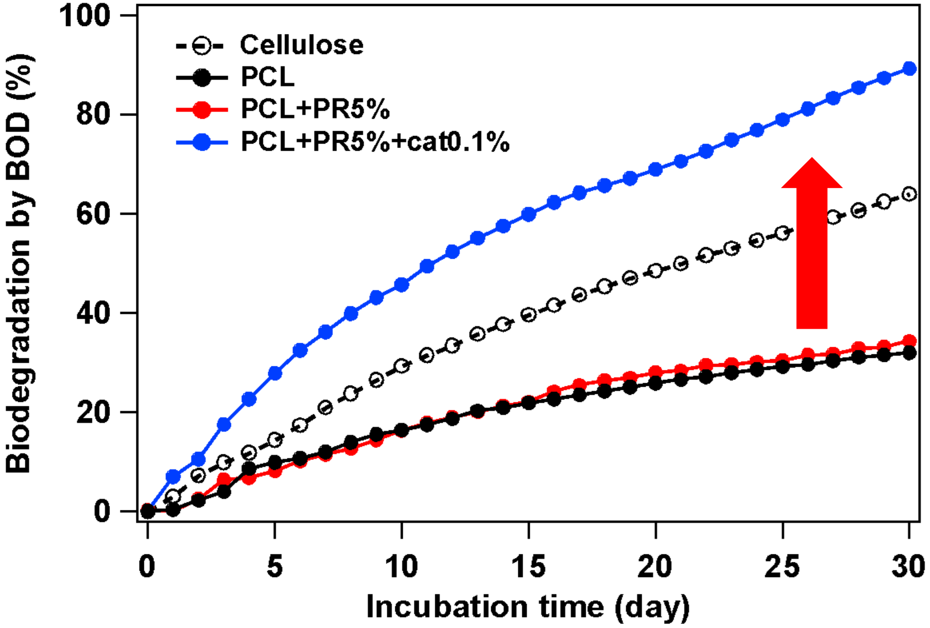
S-S curves



The transesterification between PR and PCL increased the elongation at break by more than 5 times.

The transesterification between PR and polyester has greatly improved seawater biodegradability.

BOD test



Realizing muti-lock degradability and toughness using dynamic bonds

University of Tokyo
YOSHIE, Naoko

MS Ito PJ

Theme 1：Development of multi-lock meechanism

1 ： “Slow degradability” for complete degradation

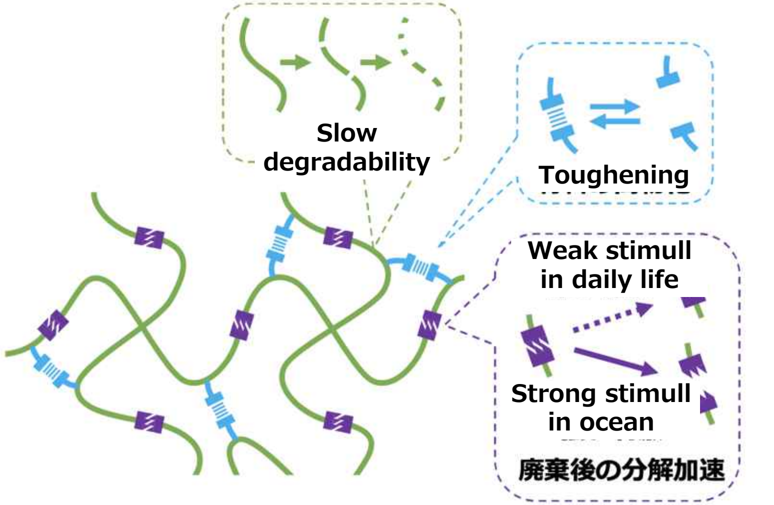
We aim to develop polymers that are stable during use but can quickly degrade after oligomerization by unlocking.

2 ： “Muti-lock” degradation mechanism

We aim to introduce degradable bonds that are activated by more than one external stimuli to accelerate degradability of polymer in marine environment.

3 ： ”Toughening” for practical use

We aim to introduce dynamic bonds and/or to control higher order structure to toughen polymers.



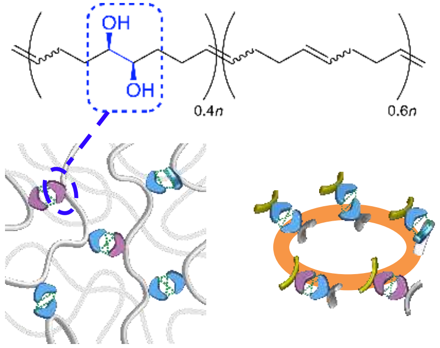
Theme 2： Toughning by physical crosslinks → Crosslinks for biodegradability

1 ： ”Physical crosslinks” to combine good elastic properties, recyclability, and degradability

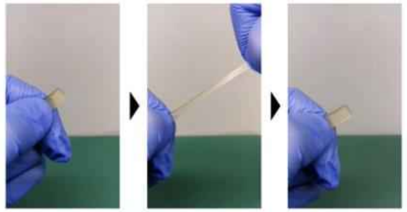
We aim to expand the concept of entropy driven multidentate hydrogen bonds proposed by our group to realize good elastic properties without chemical crosslinks.

2 ： Multi-lock degradability

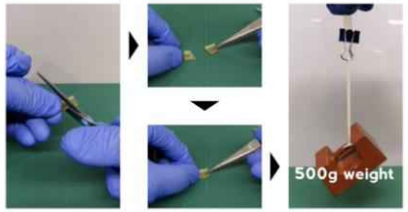
We aim to develop the multi-lock mechanism suitable for elastic materials.



Strong entropy-driven H-bonds



Good elasticity

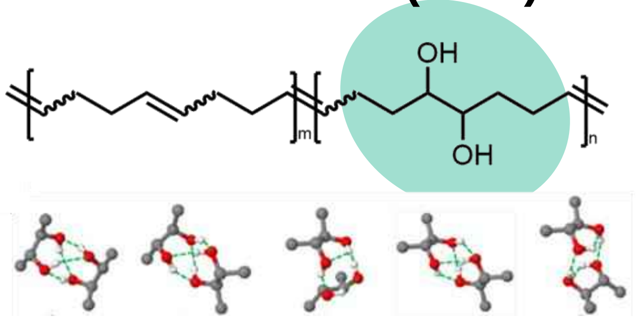


Rapid self-healing

Theme 2 :
Topic 2 : Evaluation of entropy-driven dynamic bonds

MS Ito PJ

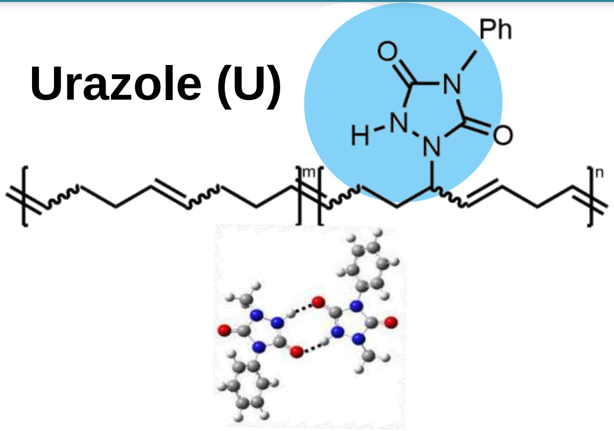
Vicinal diol (VDO)



"Soft" entropy-driven H-bonds

VS.

Urazole (U)

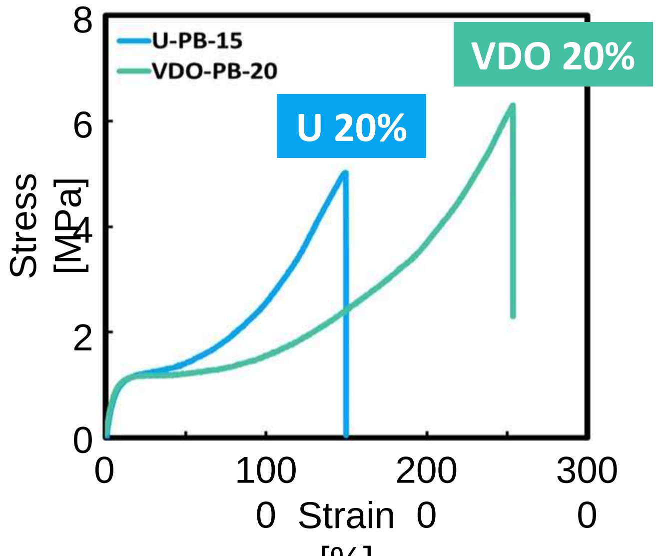


"Rigid" enthalpy-driven H-bonds

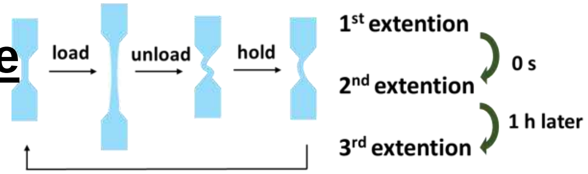
Comparison of the mechanical properties of the two polymers

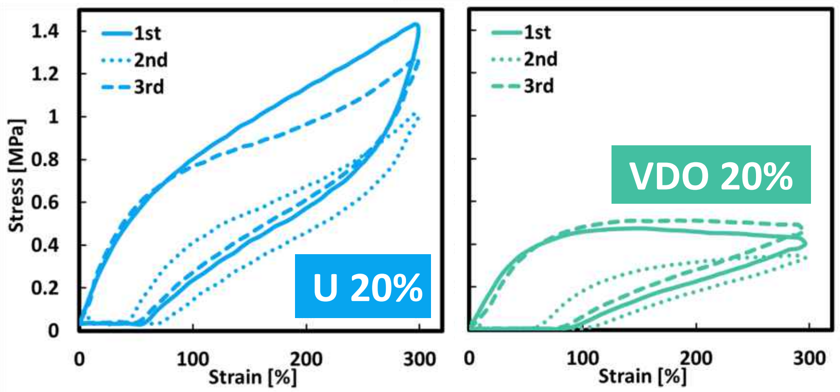
Evaluate the characteristics of the bonds

Uniaxial tensile test



Cyclic tensile test





Recovery = 76% 96%

Physical crosslinks between VDOs are weak but easy to reform

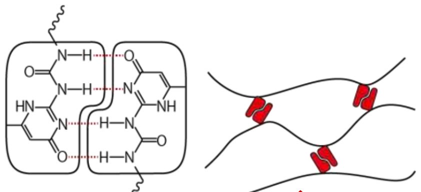
Characteristics of "soft" entropy-driven H-bonds are identified.

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

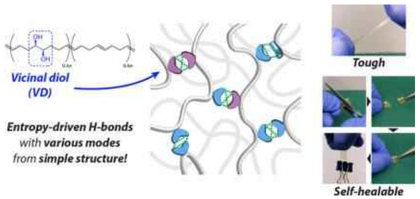
AIST
MORITA, Hiroshi

MS Ito PJ

1. Modeling of two types of dynamic bond elastomers

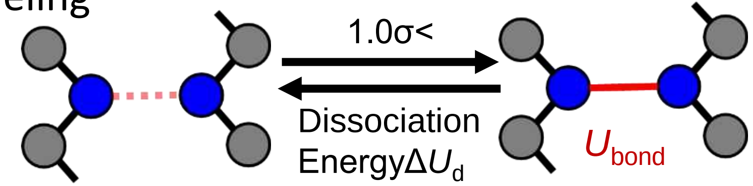


Enthalpy driven type（UPy）



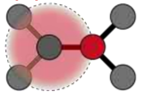
Entropy driven type（vicinal diol）

・Modeling

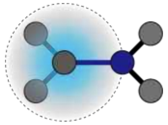


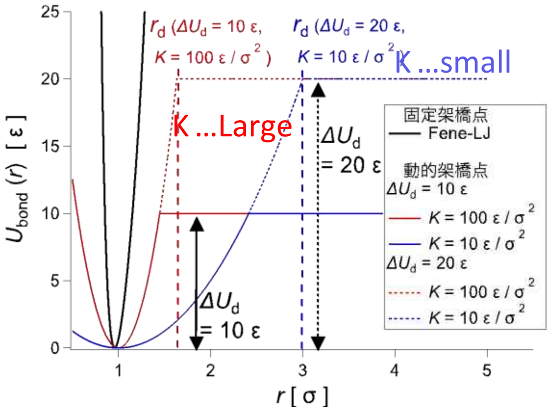
Control of potential

Enthalpy driven



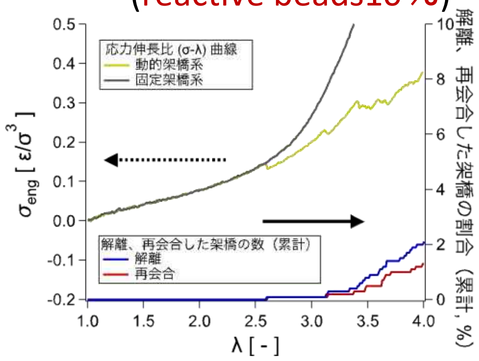
Entropy driven



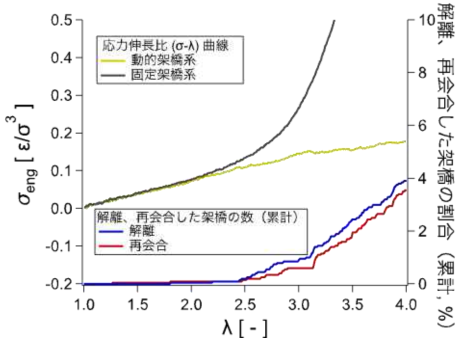


2. Association-dissociation process of two types of dynamic bond elastomers

・Enthalpy driven (reactive beads10%)

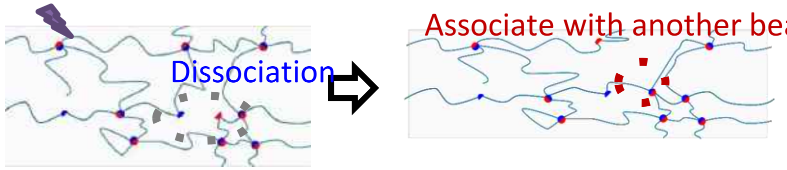


・Entropy driven (reactive beads 20%)



・About 2% diss.
About 1% associ.

・about 4% diss.
about 3.5% associ.



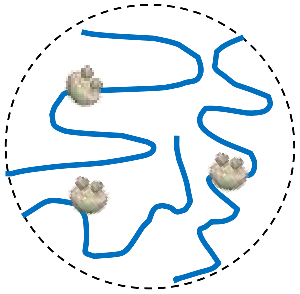
・By the bond dissociation, stress by elongated bond is released, and bond length is limited.
・Network remains by the bond association.
➢In the type of enthalpy driven type, many associations-dissociations occurs.

Development of Multi-lock Polymers Using Metal Oxide Cluster Catalysts

University of Tokyo
SUZUKI, Kosuke

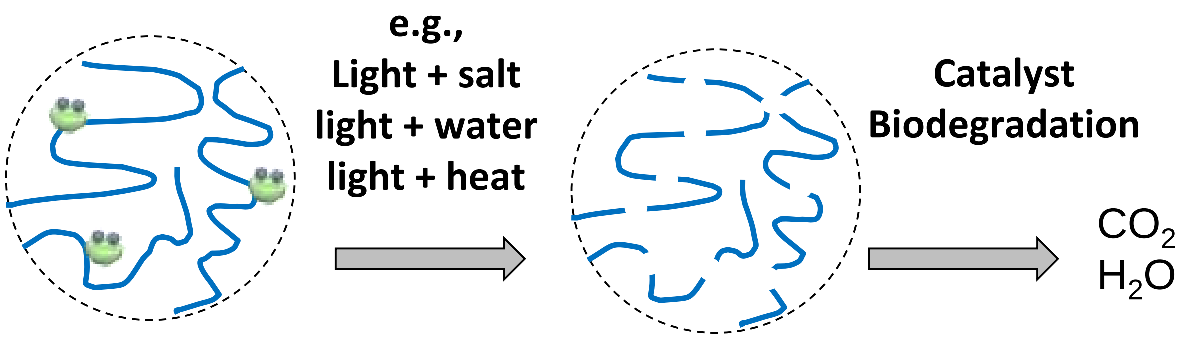
MS Ito PJ

Usage environment

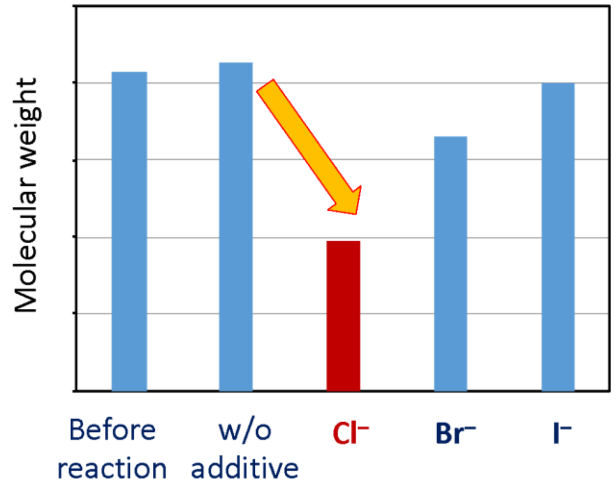


Degradation, **No**

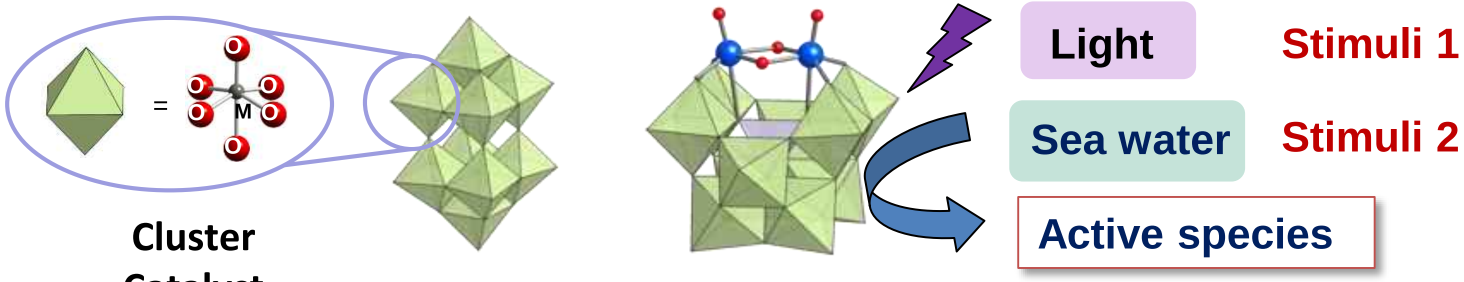
Introduction of multi-lock degradable mechanism: Decomposition under multiple stimuli assuming ocean

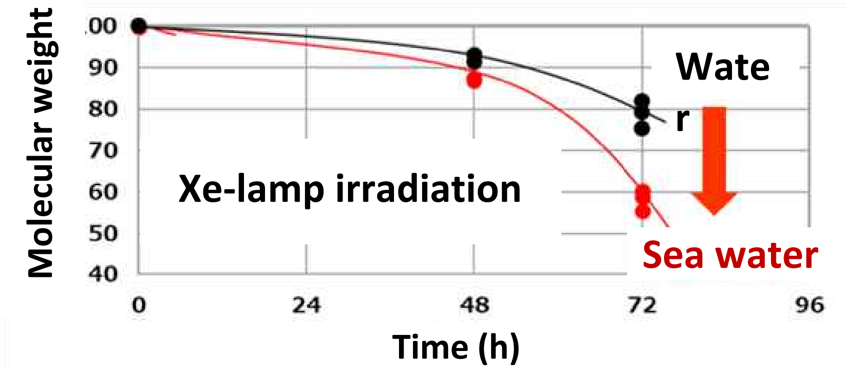


Degradation activity, Yes



Switch function





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

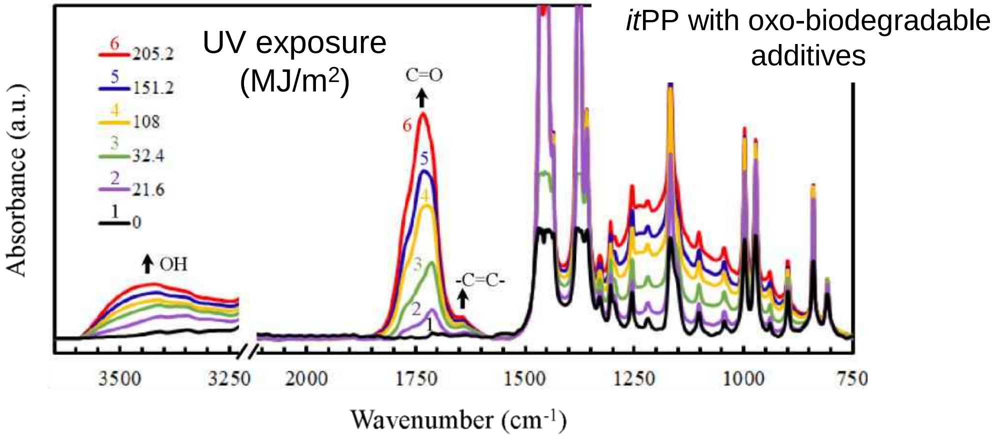
Kyushu University
TAKAHARA, Atsushi

MS Ito PJ

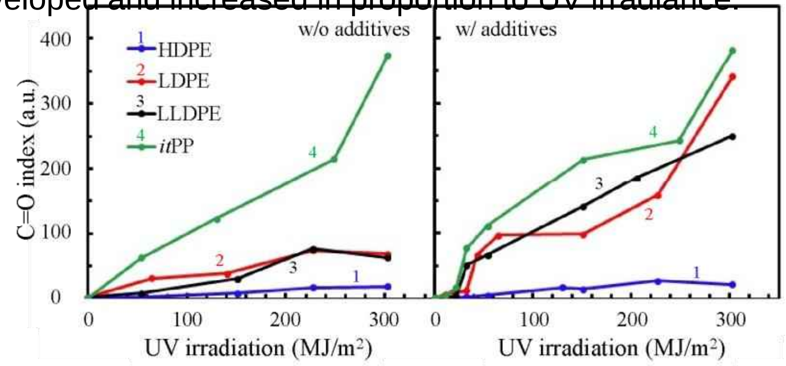
Photo-oxidation and biodegradation behaviors of polyolefins containing oxo-biodegradable additives

The effects of the commercially available pro-oxidants of the oxo-biodegradable type (P-Life Japan Inc.) on the photo-oxidation and biodegradation of polyolefin (HDPE, LDPE, LLDPE, and *it*PP) films were investigated.

FT-IR spectra of *it*PP with the oxo-biodegradable additives



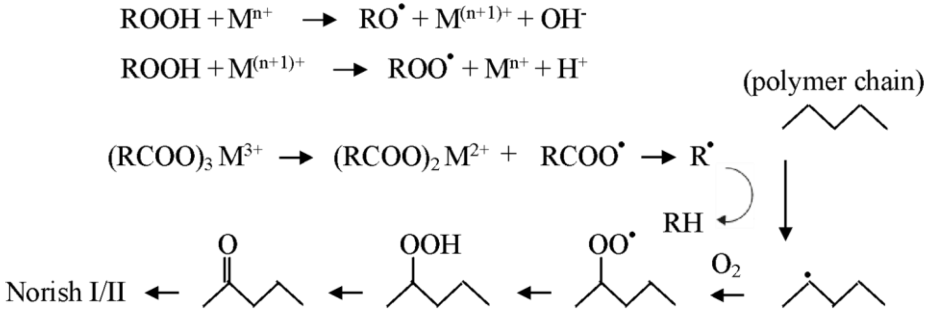
As the photo-aging proceeded, new IR absorption band (C=O) developed and increased in proportion to UV irradiance.



Total UV irradiance was up to ca. 300 MJ/m^2, equal to 1 year UV exposure in Choshi, Japan

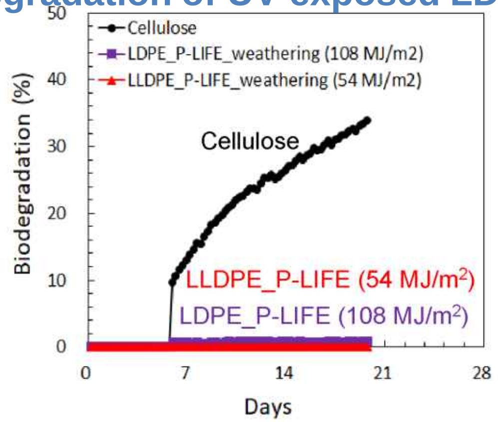
C=O index increased with UV exposure, photooxidation was promoted by additive.

The overall degradation rate of the additive-containing polymers was in the order of *it*PP > LDPE = LLDPE >> HDPE.



Mechanism of oxo-biodegradable additive catalyzed abiotic oxidation of polyolefins

Biodegradation of UV exposed LDPE & LLDPE with additive



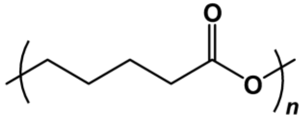
Biodegradability of UV exposed LDPE LLDPE with additive is poor due to UV degradation of the oxo-biodegradable additive.

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

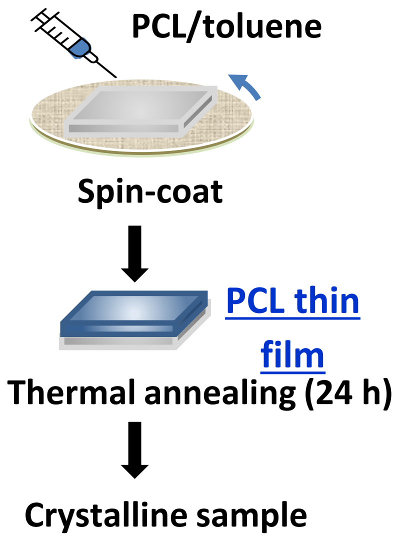
Kyushu University
MATSUNO, Sumio

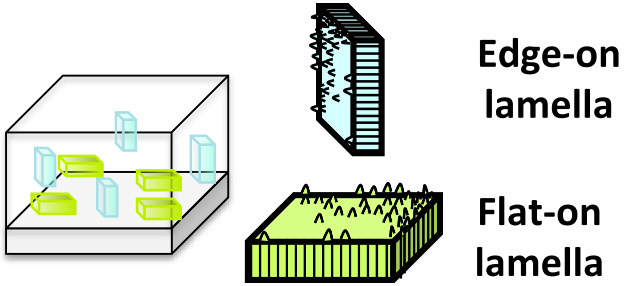
MS Ito PJ

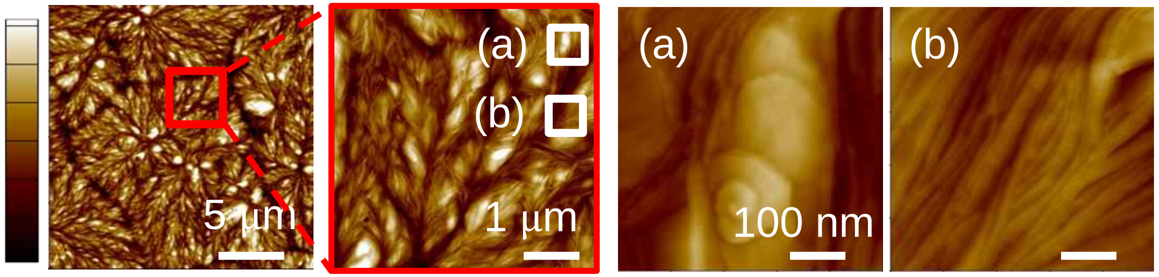
Effect of crystalline lamellae structures of polymer thin films on biodegradability

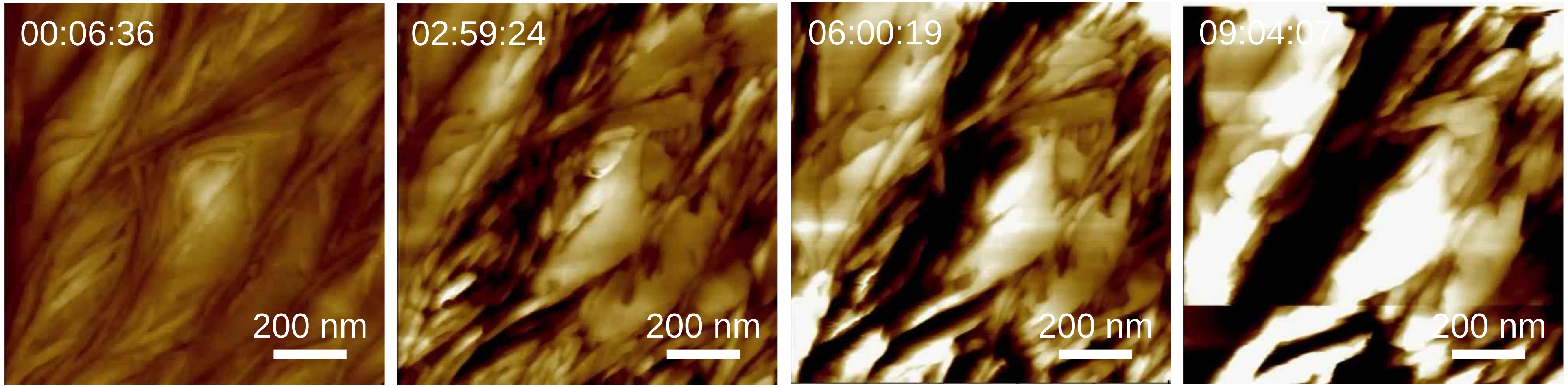


Poly(ε-caprolactone)









In the edge-on lamella-rich region of the PCL thin film, degradation progressed quickly along the film thickness direction, whereas in the flat-on lamella-rich region, degradation progressed slowly and in the plane direction of the thin film.

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

Yamagata University
ITOH, Hiroshi

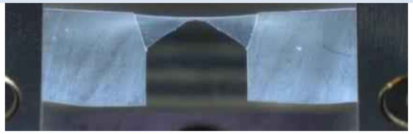
MS Ito PJ

1． Achievement in the PJ

(1) Academic target

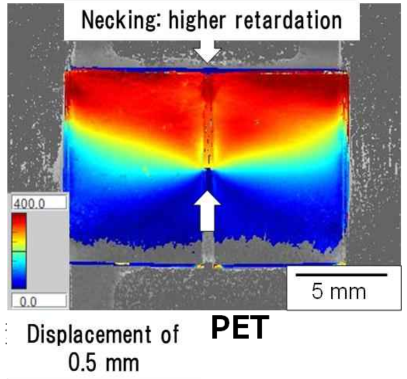
Improving durability and toughness of marine-degradable polymers (Control crystal morphology for the marine degradation)

Propose toughening method through mechanical tests

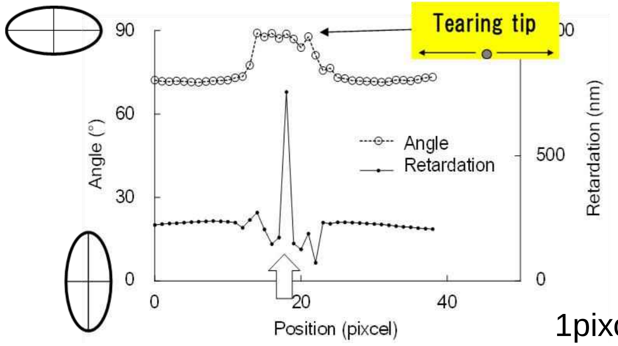


Photograph of tearing PET film just before break

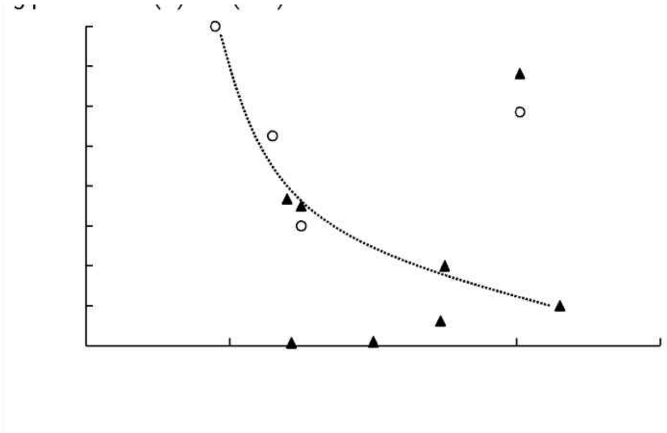
	PLA	PGA	PMMA	PA6	PS	PC	PET	PBS	PCL	HDPE	PP
Tg (°C)	60	40	100	50	90	145	70	-35	-65	-110	0
Max. load (N)	33	25	20.3	14	14.3	24.7	15	15	8	9	13
Max. displacement (mm)	2	4	0.2	7.35	0.14	1.24	7	6	> 16	16	10.5
Apparent modulus (MPa)	3510	4040	3370	890	3000	2660	2170	745	452	1030	1460



PET



1pixcel = 0.05 mm



Optical observation shows that polymers with low tearability have a locally reduced film thickness and tear from these areas.

Differences in the shape of the tearing tip.

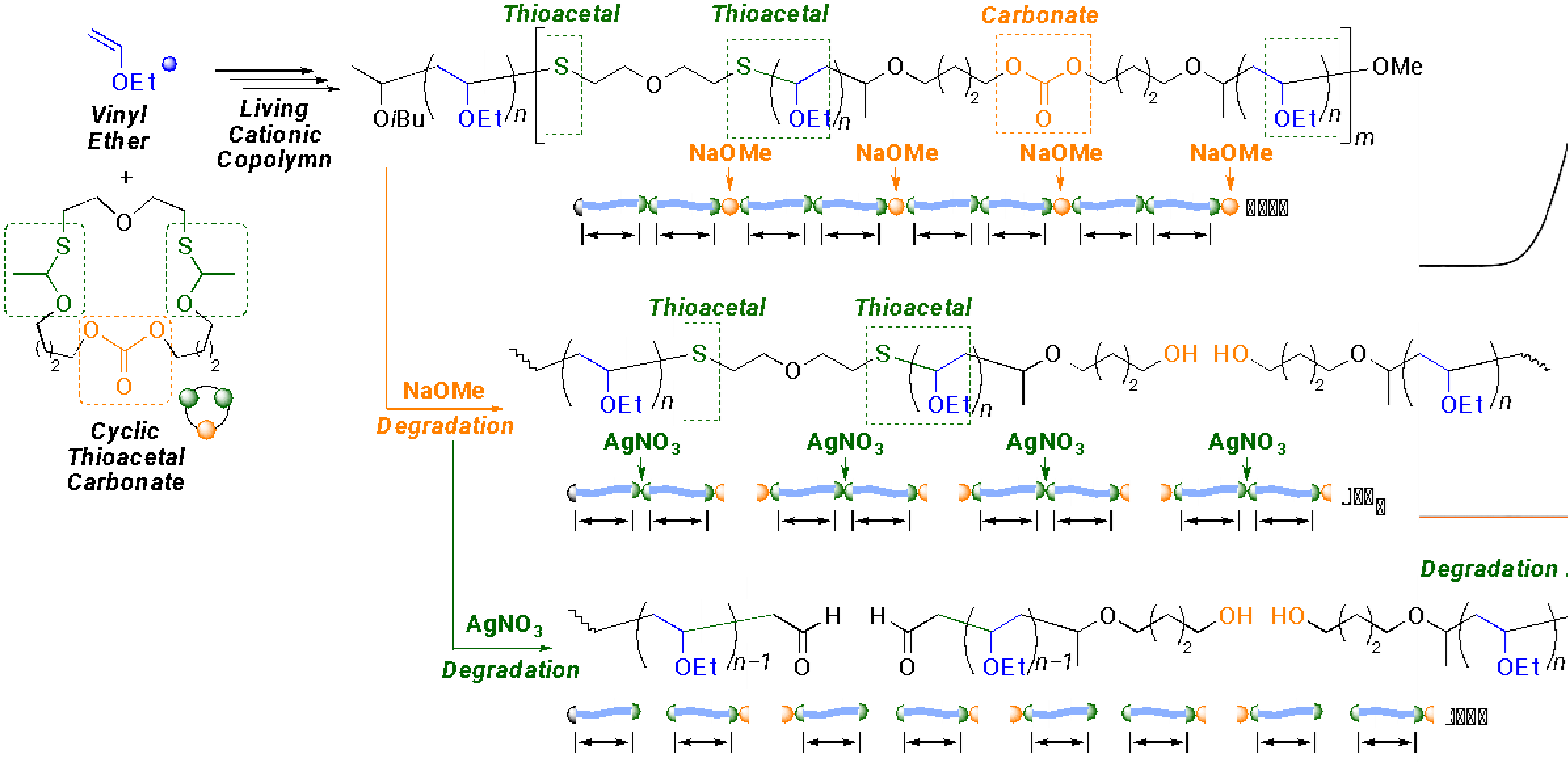
Film cross-sectional image

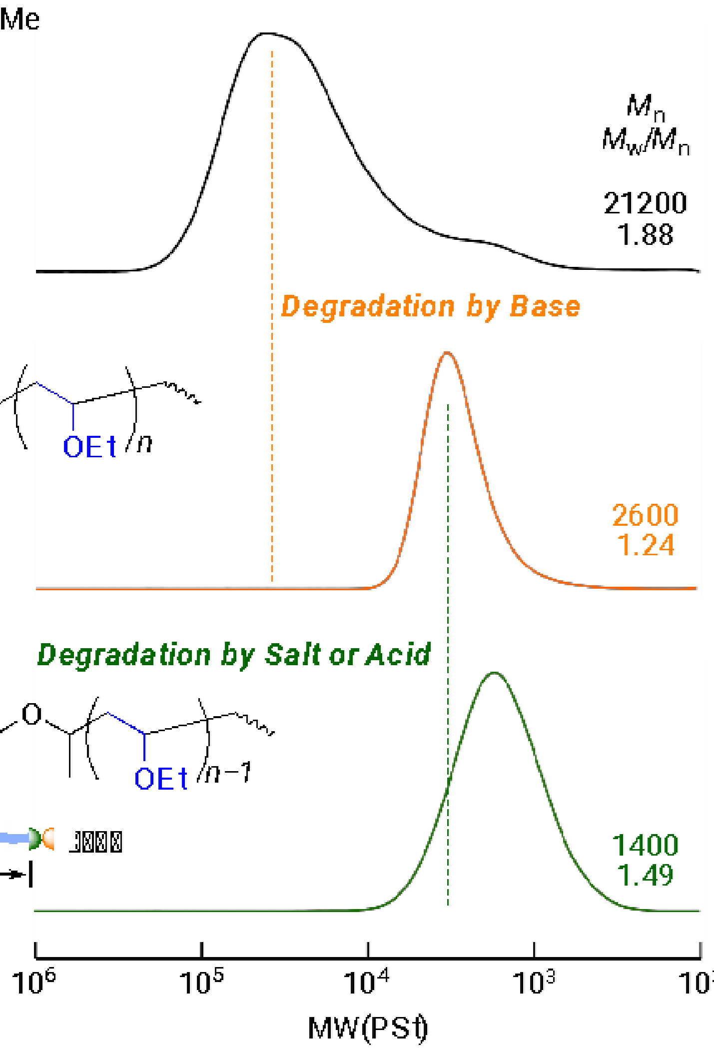
Slow tearing (e.g. PCL) **Fast tearing (e.g. PBS)**

Development of Degradable Polymers Based on Plant-Derived Renewable Resources

Nagoya University
KAMIGAITO, Masami

MS Ito PJ





$[\text{Carbonate}]_0/[\text{NaOMe}]_0$ = 5.0/50 mM in MeOH at 60 °C
$[\text{Thioacetal}]_0/[AgNO_3]_0$ = 5.0/50 mM in THF/H_2O (19/1) at r.t.

名古屋大学 NAGOYA UNIVERSITY

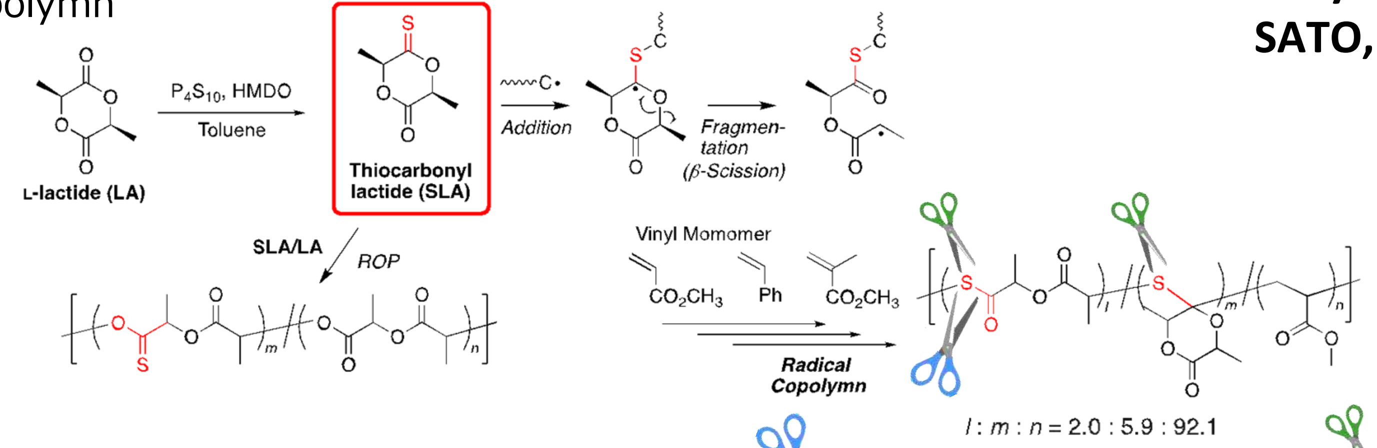
Precision Polymerization of Plant-Derived Monomers for Multi-Locked Degradable Biopolymers

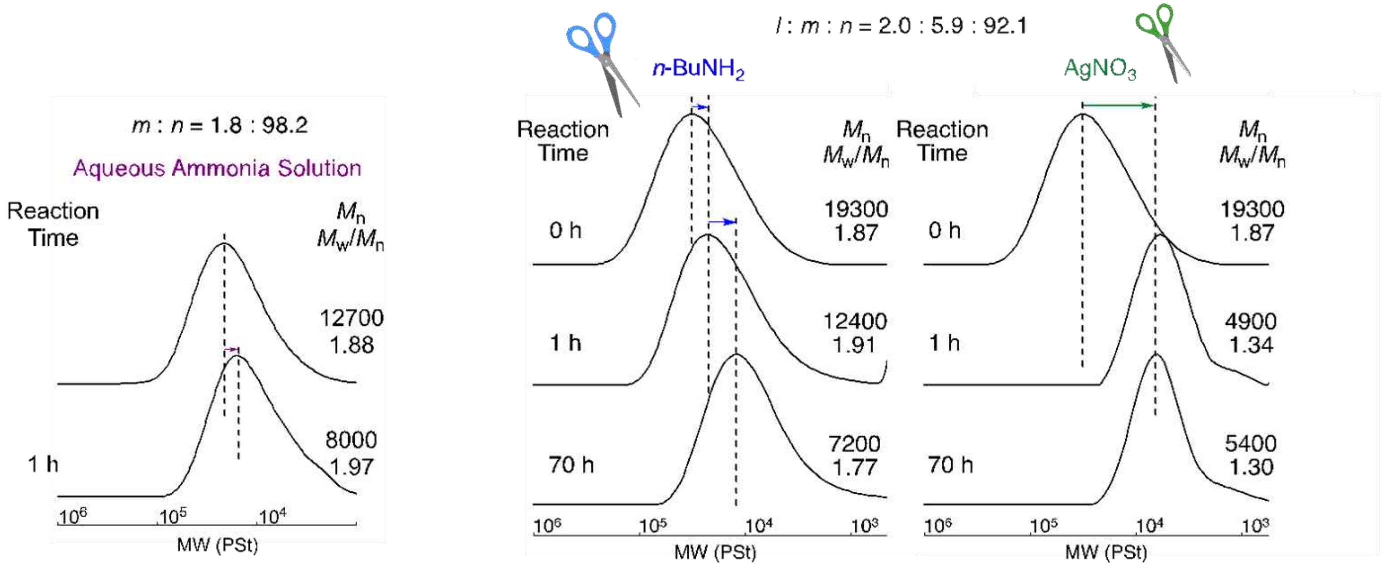
MS Ito PJ

Tokyo Institute of Technology
SATO, Kotaro

・Introducing Degradable Units Using the Fundamental of Precision Polymerization

Thiocarbonyl lactide Copolymn





Dual Degradable Vinyl Copolymers

Publication： Kamiki, Kubo, Satoh* Macromol. Rapid Commun. **2022**, 202200537, *in press*

Student awards： Andrea Mialdea Molina (M2) Symposium on Macromolecules, Best Poster Award（2022 Oct 12）

R&D of polymer from inedible biomass feedstock and polymer-degrading enzymes

INUI, Masayuki

RITE Research Institute of Innovative Technology for the Earth

MOONSHOT RESEARCH & DEVELOPMENT PROGRAM NEDO

MS Ito PJ

【R&D items of RITE】

① High production of biomonomer

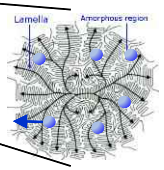
② High-functionalization of polymer-degrading enzymes

Uncollectable ocean plastic litters (high possibility of spilling into the ocean ecosystem)

Fishing tools litter

Fiber litter

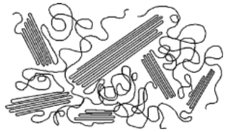
Plastic litter



Spread by accident

Multiple environmental stimuli to unlock

Light
Ion
etc.



On demand decomposition

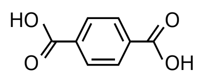
Environmental, chemical and enzymatical

Enzyme

RITE

② High-functionalization of polymer-degrading enzyme

High durability in use



Bioprocess

Monomer

RITE

Non-edible biomass

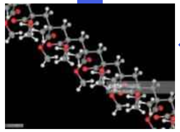
① High production of biomonomer

CO_2

H_2O

Photosynthesis

E1+E3 Development of multi-lock type degrading mechanism



Polymerization, Processing

Multi-lock biopolymer

E3 Development of polymers from non-food biomass

Topic ① Bioproduction of *cis,cis*-muconic acid

Topic ② High-functionalization of PET-degrading enzymes

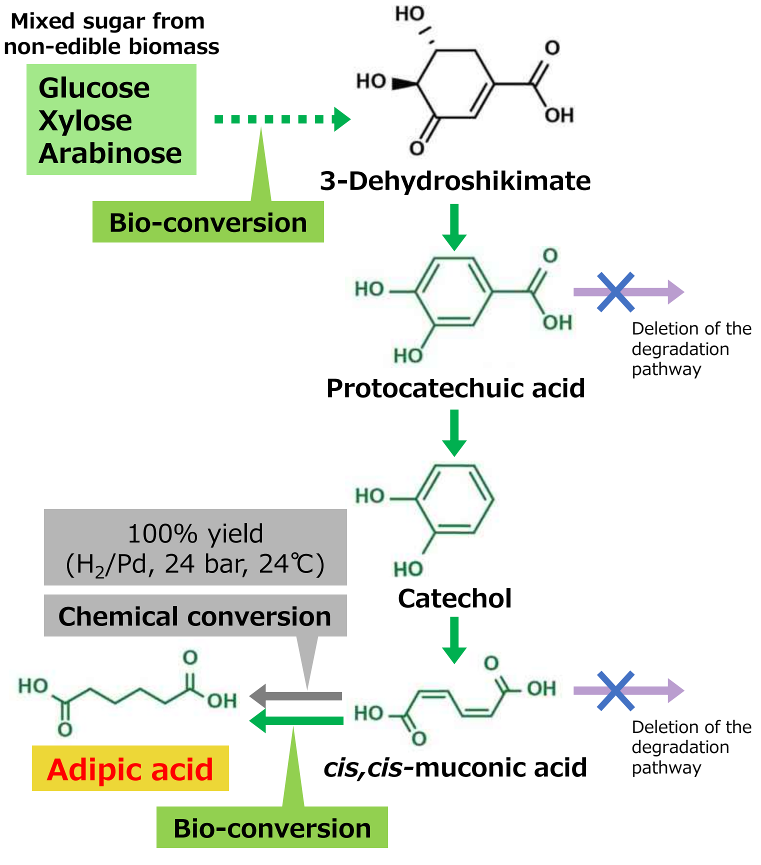
Bioproduction of *cis,cis*-muconic acid, a precursor of adipic acid, from inedible biomass feedstock

High production of biomonomer

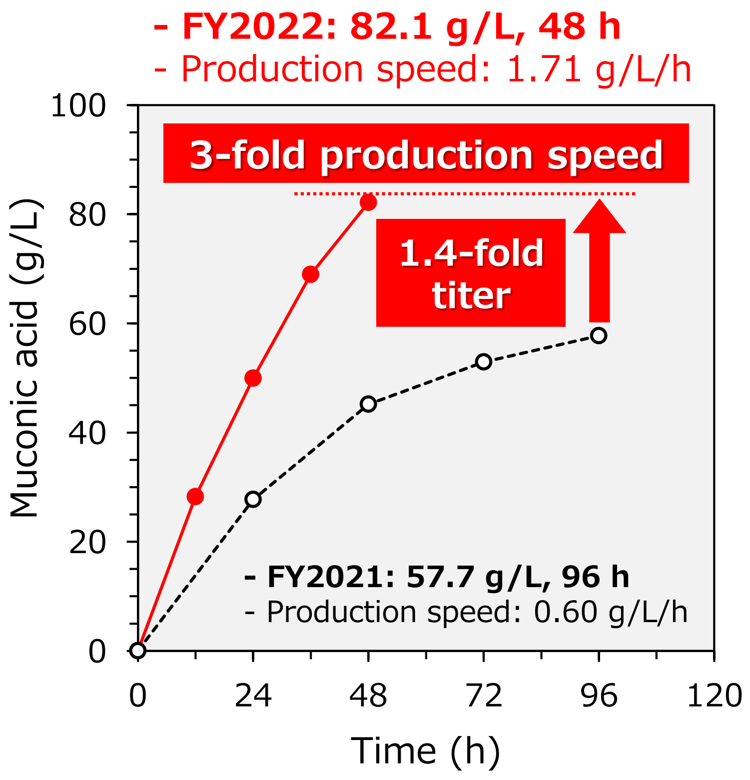
MS Ito PJ

- Successful bioproduction of *cis,cis*-muconic acid, precursors of adipic acid, a raw material monomer for polyamides and polyesters (fishing tools, fibers, bottles, etc.).
- Screening of various genes for adipic acid-producing enzymes is in progress.

Artificial pathway for *cis,cis*-muconate production



Time course of *cis,cis*-muconic acid production



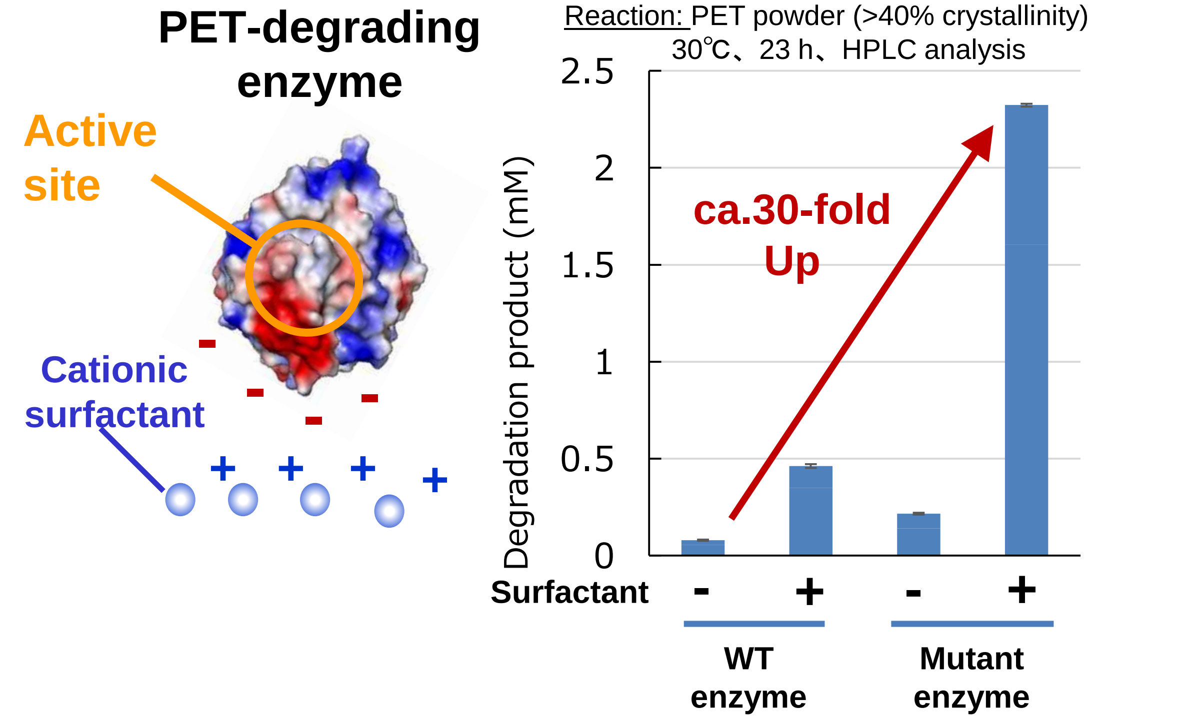
250 mL Jar (fed-batch)
Existed as a sodium munocate in broth

Enhancement of PET-degrading activity and overexpression of the enzyme

High-functionalization of polymer-degrading enzymes

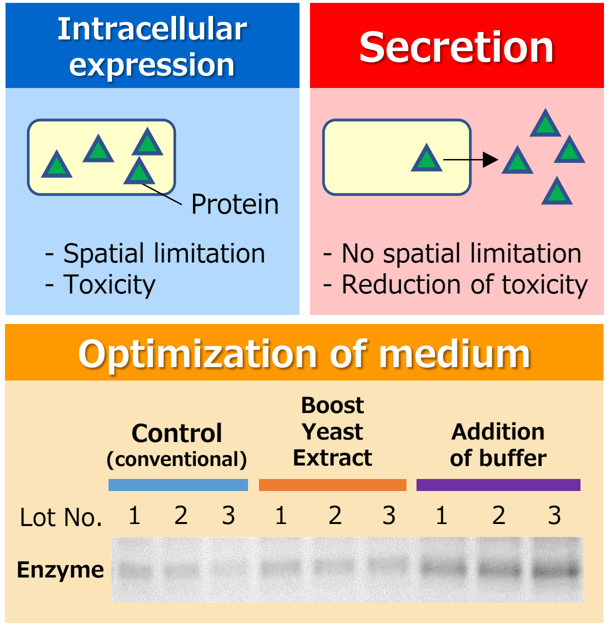
MS Ito PJ

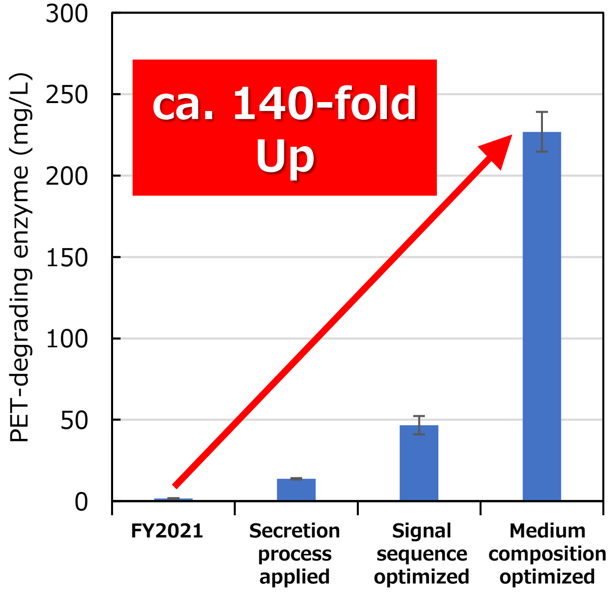
Enhancement of PET-degrading activity



Addition of a very low concentration of cationic surfactant remarkably enhanced the enzyme activity about 30-foldcomparing to the WT enzyme

Overexpression of PET-degrading enzyme





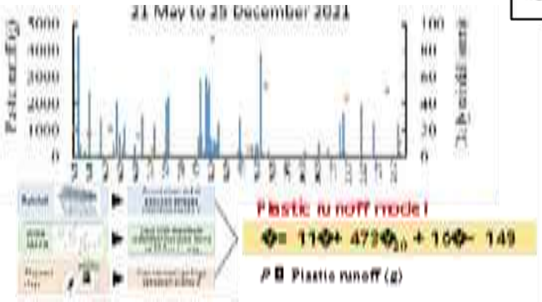
PET-degrading enzyme was overexpresed about 140-fold

Development of a prediction model for long-term impacts of multi-locked new polymers on the marine environment

Ehime University
HINATA, Hirofumi

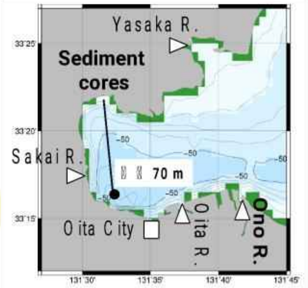
MS Ito PJ

・Estimate of plastic unit runoff by weighing at pump station
・Plastic runoff model using rainfall, wind speed, and elapsed days

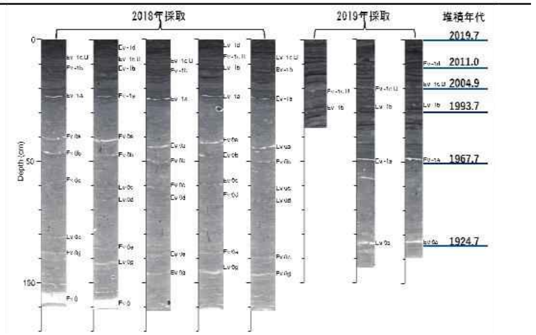


-Long-term variation of MP accumulation rate in Beppu Bay-

Coring site (h=70 m)



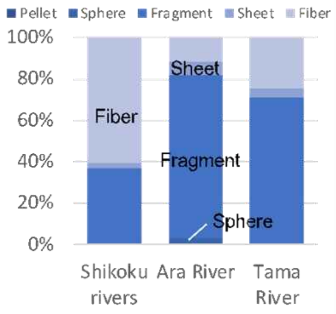
Collected sediment cores and sediment core dating



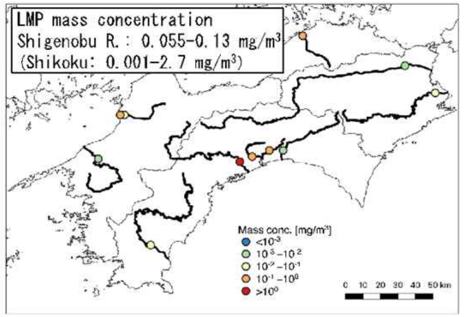
Characteristics and concentration of riverine microplastics in Shikoku region

・Fiber- and fragment-type LMP[*1] particles were predominantly distributed in rivers in Shikoku and Kanto regions, respectively.
・In Shigenobu River, SMP [*2] concentration/LMP concentration was between 10 to 100 times.

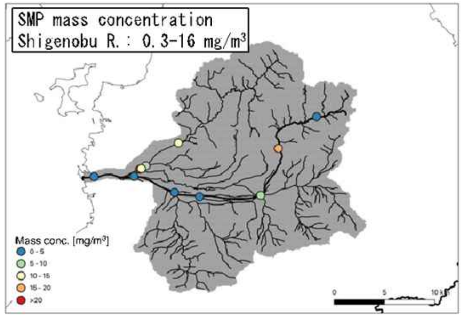
[*1]LMP:Large microplastics(≥0.3mm), [*2]SMP:Small microplastics(<0.3mm)



Composition of LMP in Shikoku and Kanto regions

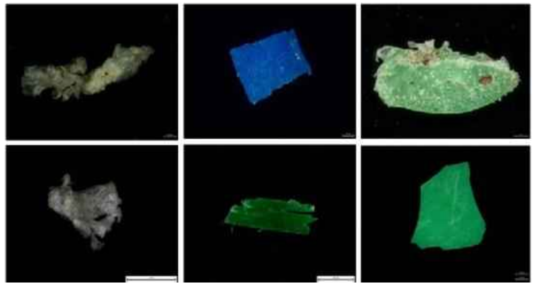


LMP mass concentration in Shikoku rivers

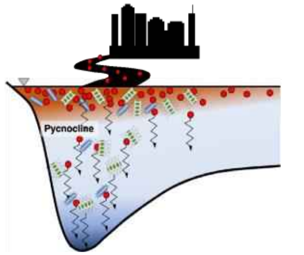


SMP mass concentration in Shigenobu river basin

MP samples from Beppu Bay sediments



Acceleration of sinking flux due to biofilm formation



Development of evaluation of Multi-Lock Biopolymers biodegradability

CERI
KIKUCHI, Takako

MS Ito PJ

In order to carry out a proper marine degradable plastic product design, it is important to know whether a plastic material is inherently biodegradable, degradation mechanism and safety etc. when exposed to marine inoculum.

Accelerated evaluation of biodegradability in seawater

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

The purpose of this study :

- **Development of accelerated evaluation of biodegradability in marine**
- **Comparison of development method and field testing**

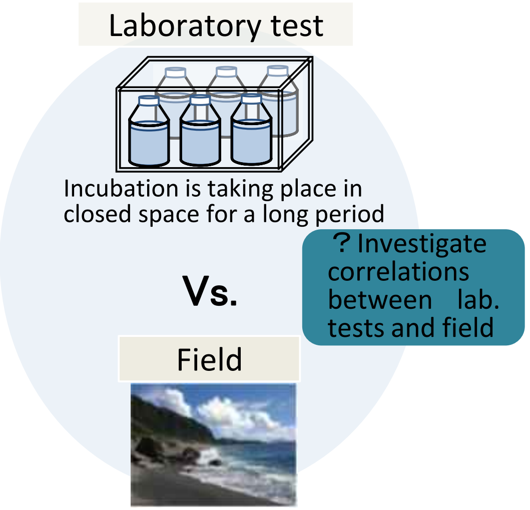
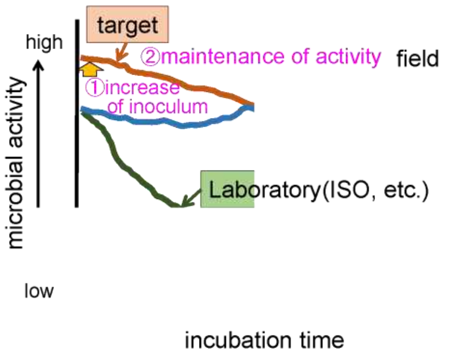


Diagram based on a model of enhancing microbial activity



Outline of development method

(1) Extracting of rich microbial in sediments to seawater

・The microbial density in sediment is generally higher compared to the density determined in seawater.

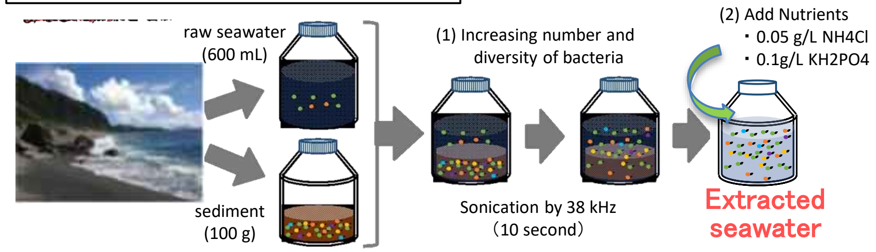
・The use of microbial in sediment is expected to diversification in inoculum.

(2) Preservation of microbial activity by addition nutrients

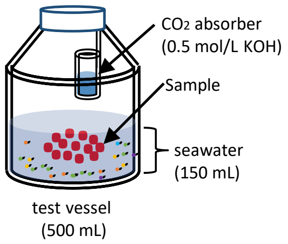
・suppress microbial activity loss

Simple operation and quick preparation

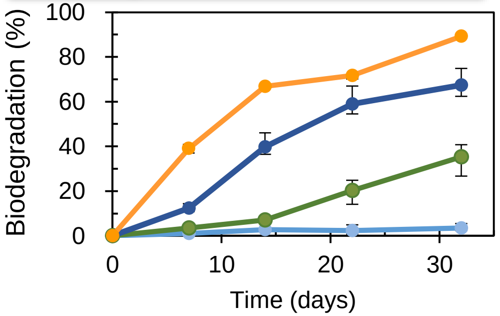
Preparation extracted seawater



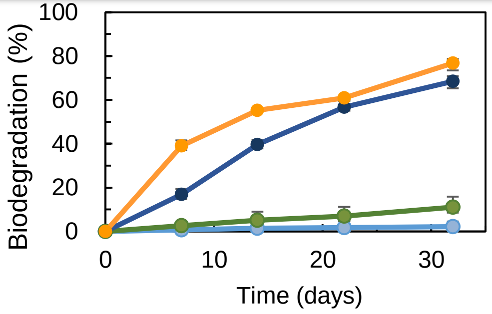
Biodegradation test



Biodegradation of cellulose



Biodegradation of Polycaprolactone (PCL)



raw seawater (ISO 223977-1) — extracted seawater
raw seawater+nutrients — extracted seawater+nutrients (development method)

Total Publications

Papers　42（published）

Polym. Chem. 12, 1186-1198 (2021). (Front Cover, Hot Paper)
Macromolecules 54, 6440-6448 (2021)
Environmental Pollution 310 (2022)119811

Review, Books　13

Patents　　１４
(including ５ patents for companies)
(including 6 PCTs)

Invited lectures　90（Domestic: 62、Oversea: 28 ）

Presentations　179（Domestic : 148、Oversea : 31）

Awards　27

Press　　17

2020/12/22　Chemical Daily, "Biodegradation by Multiple Stimuli"
2021/6/1　　Asahi Shimbun, "Plastic trash in the seabed layer."
2022/10/31　NHK News, "Long-term changes in MP deposition"
2022/12/9　　Nikkei Newspaper, "Development of Marine Biodegradable Fishing Line"


THE CHEMICAL DAILY
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
複数の刺激で生分解
プラ・タイヤなど耐久性と両立
東大・伊藤教授ら
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
海底層に放射性物質やプラごみ


海洋生分解性プラスチック
クレハなど漁具用開発
海ごみ対策、国際規格目指す
Tech ワード
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

Summary

MS Ito PJ

- As a result of progress in joint research between companies and academia and the utilization of academia's results by companies, R&D is progressing steadily toward social implementation, and the FY2022 target has been fully achieved. In particular, significant progress has been made in speed control, one of the switching functions, through various technologies developed in collaboration between companies and academia, and control has reached a stage close to practical application.

- Mitsubishi Chemical has confirmed that in the case of PBS-based products, the kneading of additives greatly accelerates degradability. The addition of polyrotaxane also improved tearing strength by about a factor of two.

- Bridgestone has succeeded in synthesizing a rubber with a degradable unit. The biodegradability was improved by more than 10 times. In addition, they developed a reversible bonding rubber that decomposes in the marine environment, and succeeded in achieving both a 2-fold increase in breaking strength and a 10-fold increase in degradation speed.

- Teijin succeeded in developing PET-based fibers that are marine biodegradable and strong enough to be used in actual applications.

- Kureha succeeded in developing a fishing line that has the same level of nodal elongation as non-marine biodegradable fishing line and is marine biodegradable. The degradation of fishing line is accelerated when it sinks to the seabed after disposal.

- In the common project, we succeeded in improving both toughness and degradability by using polyrotaxane. We also achieved a multi-lock mechanism using a metal oxide cluster catalyst. Furthermore, the activity and production of PET-degrading enzymes were significantly improved.

MOONSHOT
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