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

Presenter : Dr. ITO Hiroshi, Graduate School of Organic Materials Science, Yamagata University
PM : Dr. ITO Kohzo
Graduate School of Frontier Sciences, The University of Tokyo
Implementing organizations : The University of Tokyo, Mitsubishi Chemical Corporation, Bridgestone Corporation, Teijin Limited, Kureha Corporation, Kyushu University, Nagoya University, Yamagata University, Research Institute of Innovative Technology for the Earth (RITE), National Institute of Advanced Industrial Science and Technology (AIST), Ehime University, Tokyo Institute of Technology

Yamagata University
Control of Higher-Order Structure and Toughness of Marine Degradable Polymers through Polymer Processing

MS 伊藤 PJ

Yamagata University has been conducting materials research on various polymer alloys, blends, and composites by means of special polymer processing technologies.

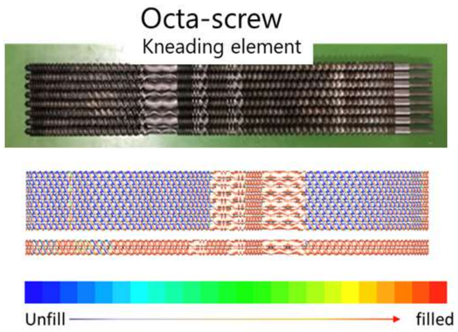
In this project, we will conduct the following two missions to achieve structural control and toughening of marine degradable polymers.

1. Propose optimal processing conditions/new processing methods in polymer processing technology
2. Support the practical application and commercialization of processing methods to realize tougher polymers through collaboration with participating research institutes and companies.

In our research on the polymer alloy and composites using octa-screw melt kneading extruder, we have attempted to modify various polymers and have succeeded in creating high toughness polymer blends by applying additives and functional polymers (e.g. polyrotaxane) through long reactive processes.

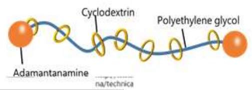
Based on our knowledge, we will evaluate the processability of new marine degradable polymers (film drawing, melt spinning, injection molding, etc.) and control the higher-order structure to create materials that maintain sufficient industrial properties for normal use and on-demand degradation.

Octa-screw kneading machine

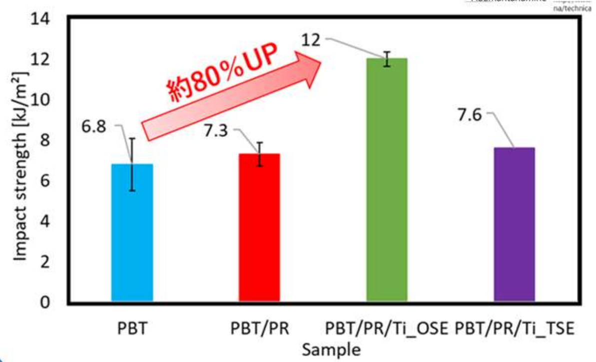


Optimization of octa-screw kneading process and CAE flow analysis

Polyrotaxane (PR) is an elastomer containing Cyclodextrin (CD) as a cyclic molecule.



Effects of kneading time and reaction promoter on impact value



山形大学
Yamagata University

1. Challenges in 2029

2023 **2025** **2027** **2029**

Development of toughening methods | **Toughening marine-degradable polymers with a multi-lock system**

(1) Realizing a plastic product using semicrystalline and marine-degradable polymers

・Toughening with polymer blends and composites

(Special kneading technology)

・Toughening directions for degradable polymers

・Development of processing methods for marine-degradable polymers
(Target of crystal structure)

(Processing of films and fibers)

Completion of development to replace petroleum-based polymers

・Methods controlling higher-order structure

・Cost-competitive polymer processing

・Preparing for industrial mass production

(2) Elucidation of the principle between toughness, marine degradability and polymer structure

・Mechanism of toughness (tear strength)

・Preparation of samples with various crystal structure, and its relation to degradability

(MD simulation)

2.1 Outline (2020-2021 yr)

(1) Project of industry

Mitsubishi Chemical Corp. project

Development of tough bioplastics with multi-lock-decomposition mechanism

Toughening by polymer blend, elucidation of fracture mechanism by EWF method

KUREHA Corp. project

Development of biodegradable and tough biopolymers for fishing nets

Toughening using a special kneading method, and controlling crystal and molecular orientation by processing

TEIJIN Limited project

Development of tough biopolymers based on highly degradable polyester with multi-lock mechanism and its fibers

Nanostructure control by processing, physical property control by melt spinning

(2) Project of academia

Common issue: Controlling crystal structure suitable for marine-degradation

Control of various crystal structures by processing technology

Propose a method of toughening through strength inspection

Yamagata University

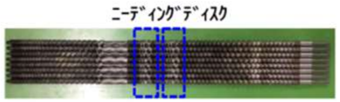
Control of Higher-Order Structure and Toughness of Marine Degradable Polymers through Polymer Processing

MS ITO PJ

2.2 Advantage of Yamagata University

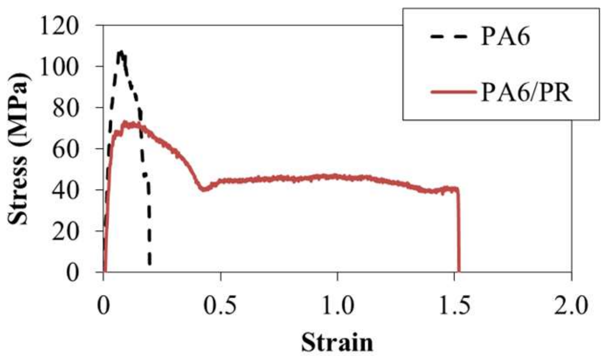
(1) Processing technology

Example of special kneading technology (using 8-screw kneading equipment)

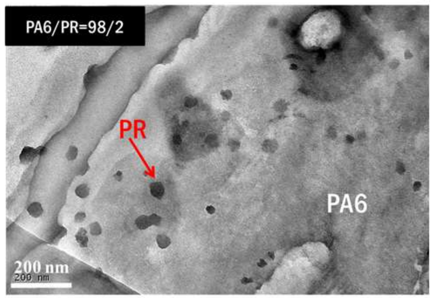


Example for PA6/PR blends

High speed tensile test Test speed : 1 m/s (60,000 mm/min)



TEM micrograph



*High-Mw-PR

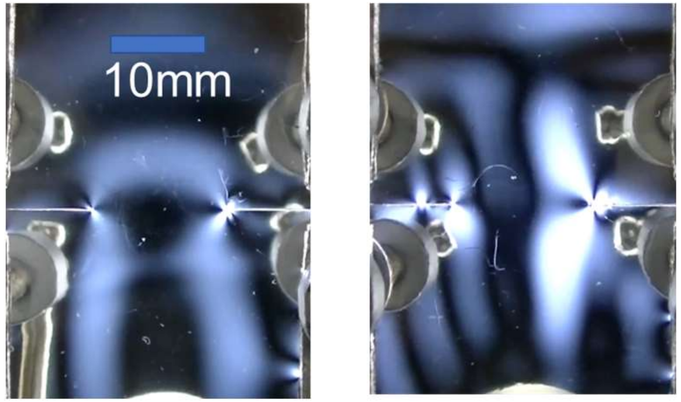
Toughening by polymer blend and composites
- Morphology of hard matrix and soft domain
- Introducing polyrotaxane(PR)
- Roll of micro voids in plastic deformation regions and density fluctuations

(2) Analysis of higher-order structure and properties

Example of EWF (Essential Work of Facture) evaluation

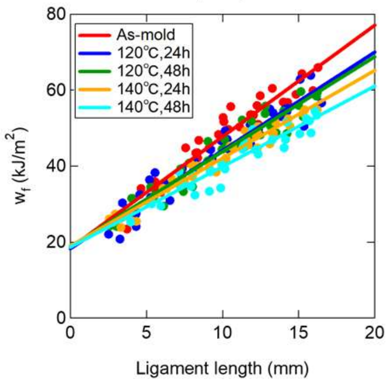
- **Polycarbonate (PC)** as-mold

M_v=19,500 M_v=30,000



The higher the molecular weight PC showed the wider range of plastic deformation. It means large energy dissipation.

M_v=30,000

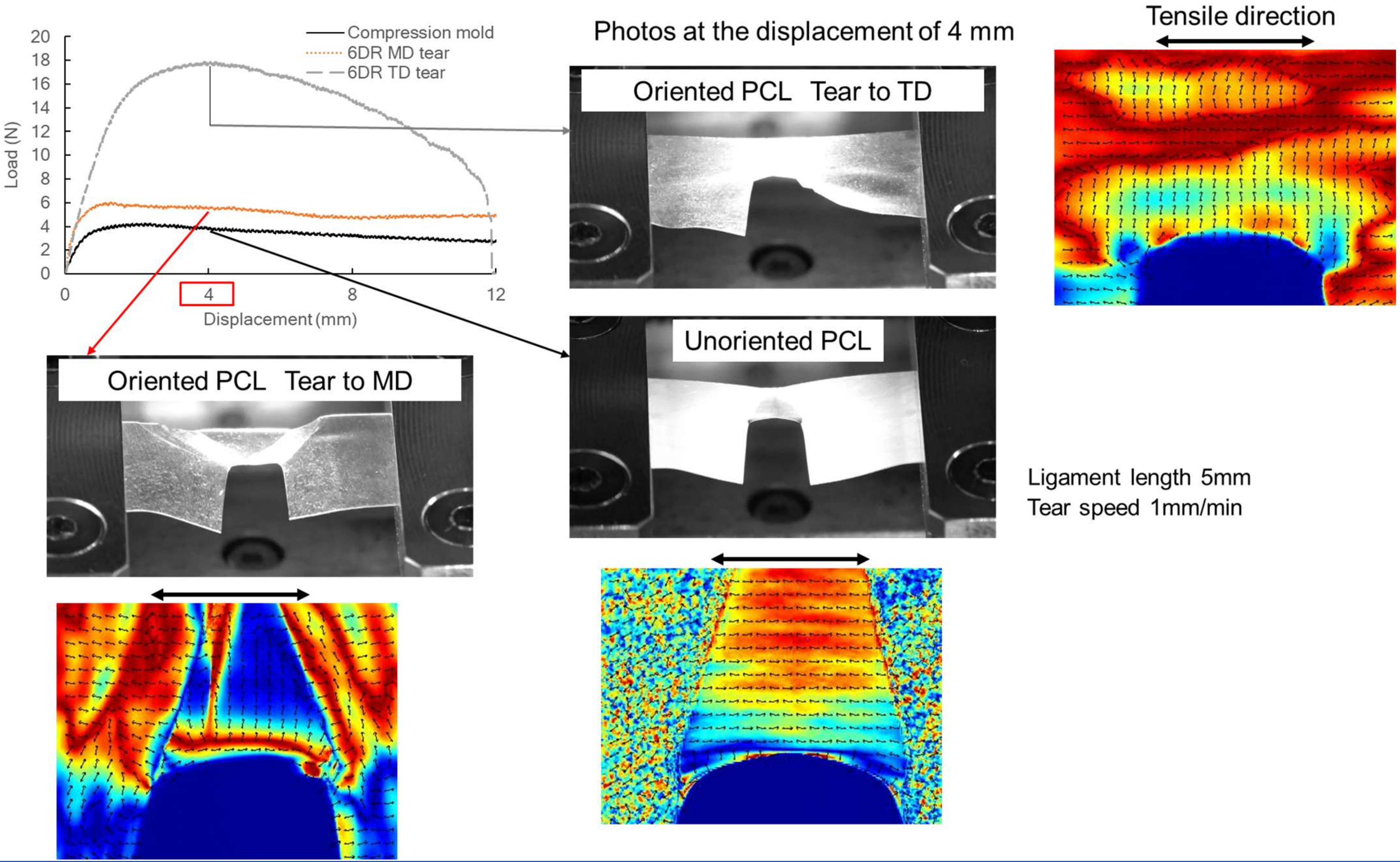


Crack energy did not change with heat treatment.
The energy required for deformation in the plastic region decreased with heat treatment.

Anneal treatments influenced the energy used in the plastic region.
This trend was independent of molecular weight.

3. Achievement at present

3.1 Understanding the relationship between tear strength and crystal morphology using PCL as a model



3. Achievement at present

3.2. Examining the effect of water molecules on crystals using PLA as a model

Initial crystal morphology and hydrolytic degradation

(1) Viewpoints

・We would like to determine the possibility that the hydrolytic property may change depending on the initial crystal morphology.

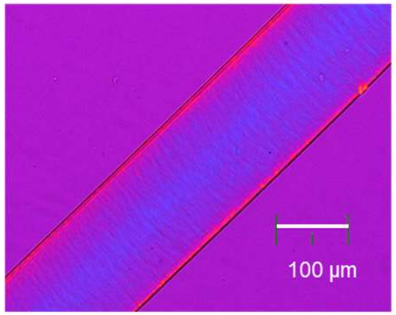
・As a model, the change in crystal morphology of polylactic acid (PLA) due to water absorption is used.

・Experimentally search for a crystal morphology that exhibits hydrolyzability equivalent to amorphous.

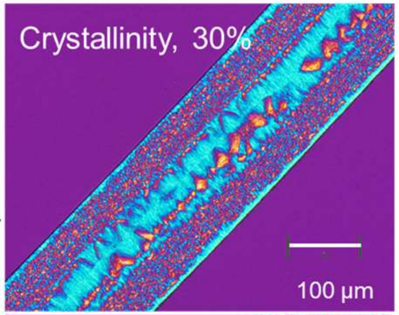
(2) Production of samples with a crystallinity of 30% and different crystal morphologies

Melt → Quenching

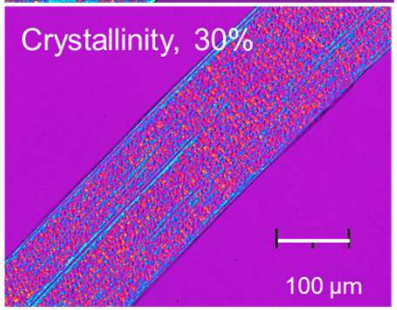
Amorphous PLA



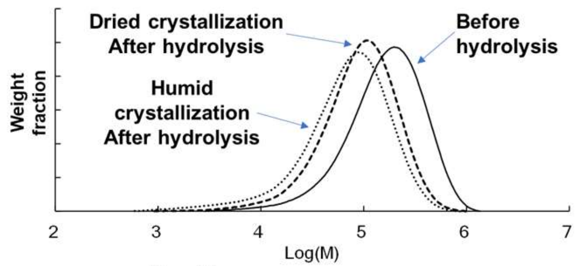
Crystallization at 110℃ for 2 h under reduced pressure

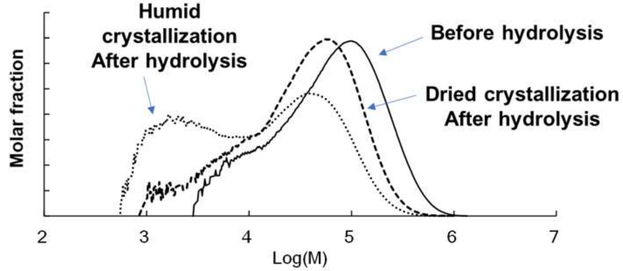


Crystallization at 70℃, 95%RH for 1h



(3) Changes in molecular weight distribution after hydrolysis (25h; 70oC, 95%RH)





	Mw (x1000)	Mn (x1000)	PD
Before hydrolysis	217	99.6	2.2
Humid crystallization After hydrolysis	98.1	31.9	3.1
Dried crystallization After hydrolysis	122	55.3	2.2

4. Summary (2020-2021yr)

Polymer blends of marine degradable polymers for high toughness

(As the industry project) Achieved toughening of marine-degradable polymers such as PGA

Control of crystal structure that can achieve both marine-degradation and physical properties (toughening)

(1) Toughening films by controlling crystal structure

Progress
We have investigated the processing methods to precisely control the crystal orientation of PCL and PLA according to the balance between melting and glass transition temperatures.
In order to clarify the influence of the crystal structure, the temperature dependence of the tearing strength was measured.

(2) Initial crystal structure and hydrolytic degradation

Progress
The hydrolysis behaviour of PLA crystallised under controlled water content was measured. The results suggest that PLA crystallised under dry conditions undergoes random hydrolysis, whereas PLA crystallised under water absorption undergoes further reduction of small molecules.
The mechanism of the development of tear strength of PLA crystallised with controlled moisture content was investigated.