U.S. DEPARTMENT OF ENERGY

2023 PROJECT PEER REVIEW

U.S. DEPARTMENT OF ENERGY
BIOENERGY TECHNOLOGIES OFFICE

Trojan Horse Repeat Sequences for Triggered Chemical Recycling of Polyesters for Films and Bottles

April 4, 2023

Plastics Deconstruction and Redesign

Eric W. Cochran
Chemical and Biological Engineering
IOWA STATE UNIVERSITY OF SCIENCE AND TECHNOLOGY

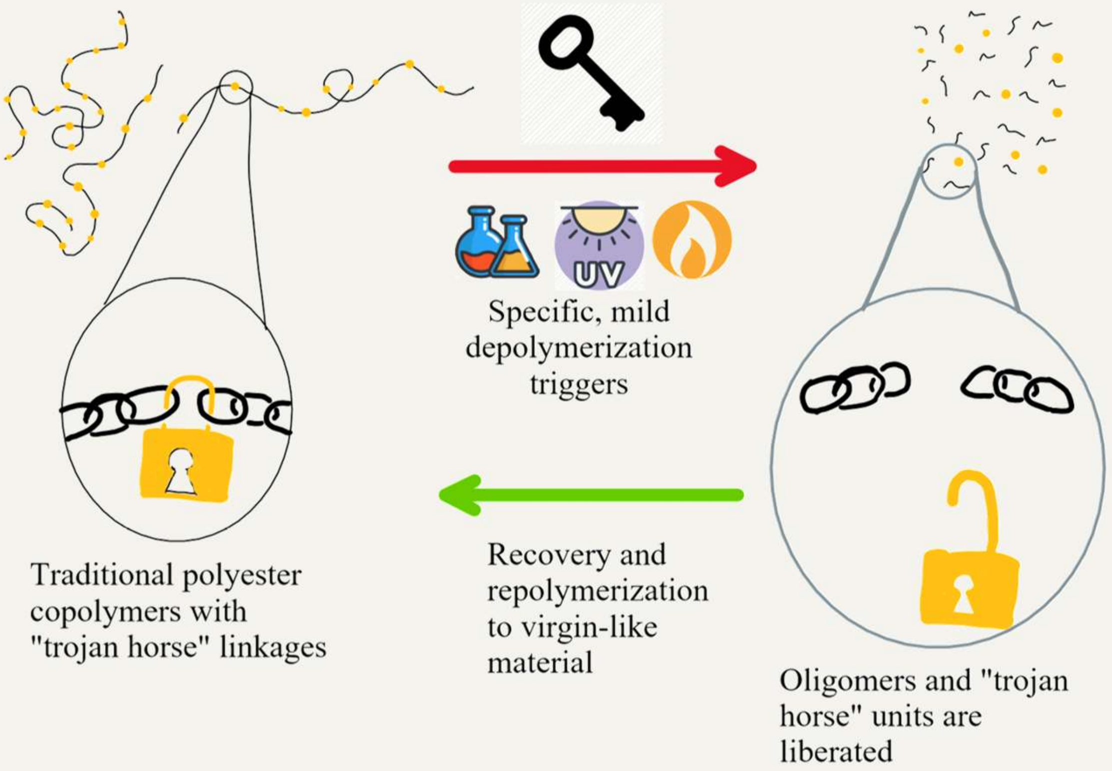
with

3M ADM DIAGEO

Project Overview

Can plastics be designed with end-of-life in mind?

- Mechanical recycling is limited in scope, cumbersome, and yields low quality product
- Biodegradables are only part of the solution to Plastic Solid Waste
    - Nobody wants a biodegradable truck bumper
    - New materials require new infrastructure and design
- Can we modify plastics we already use to fall apart when exposed to specific stumuli?
    - Salt water for marine-safe packaging
    - Dilute metal cations at elevated temperature for durable goods
    - Dilute bases at moderate temperature for general single use packaging



1 - Approach

Project Team – Main Participants

Val Camelo
CBE Senior

Demetrius Finley
Chemistry PhD Student

Ana McCaslin
CBE Junior

Aadhi Subbiah
CBE Freshman

Shiva Karimadekordi
CBE Phd Student

Sharan Raman
CBE Phd Student

Dhananjay Dileep
CBE Phd Student

Michael Forrester
CBE Phd Scientist

Alexsei Ananin
Chemistry PhD Student

Patrick Wang
CBE Postdoc

Nacu Hernandez
CBE Phd Scientist

Madhura Joglekar
CBE Phd Scientist

Eric Cochran
CBE Professor

George Kraus
Chemistry Professor

Mark Mba-Wright
M. Eng. Professor

DIAGEO

Rich Hoch
Senior Manager
Packaging Technology

3M

Kevin Lewandowski
Staff Scientist

ADM

Erik Hagberg
Manager
Industrial Chemicals R&D

ADM

Karl Albrecht
Manager
Catalysis R&D

ADM

Chicheng Ma
Process Chemist

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1 - Approach

Project Team – Roles and Responsibilities

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- Small molecules
- Polymers
- Life Cycle Assessment

3M

Kevin Lewandowski
Staff Scientist

- Manufacturing feasibility
- Polymer Scale-Up
- Polymer Processing
- End-User of Films

ADM

Erik Hagberg
Manager
Industrial Chemicals R&D

Karl Albrecht
Manager
Catalysis R&D

Chicheng Ma
Process Chemist

- Biobased feedstocks
- Manufacturing Feasibility
- Technoeconomic data

DIAGEO

Rich Hoch
Senior Manager
Packaging Technology

- Packaging Design
- Bottle Manufacturing
- PET recycling ecosystem
- End-User of Bottles

1 – Approach

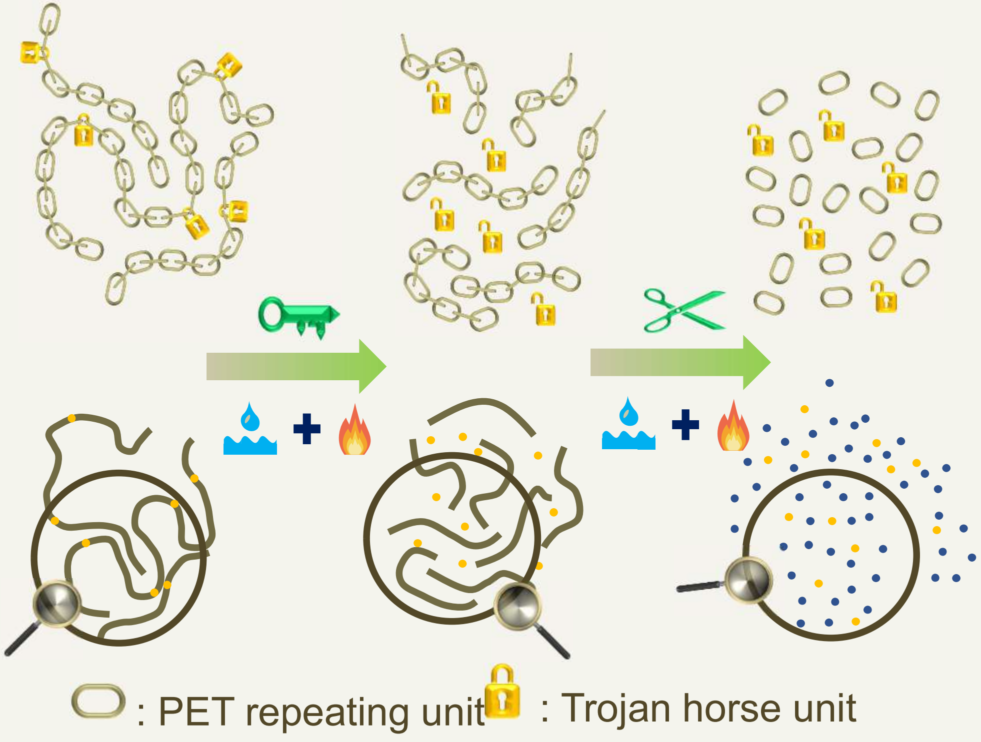
Team Communication

- Research teams communicate regularly in person, via Slack, and email.
- Each site has regular biweekly project meetings.
- All-hands meetings (ISU, ADM, 3M, Diageo) are held via video-conference every 4-6 weeks.

Related Project Interaction

- Ph. D. graduate Dr. Ting-Han Lee now a postdoc at IBM, working on a BOTTLE project in collaboration with NREL

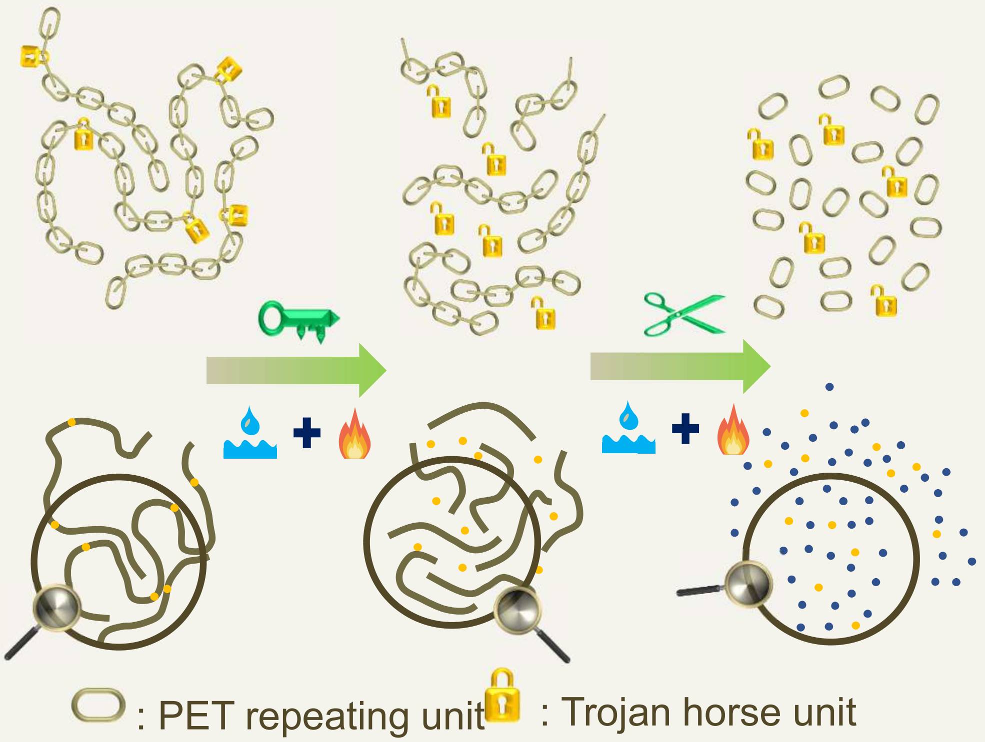
- Ph. D. student Dhananjay Dileep, Cochran, and Nic Rorrer planning application for Office of Science Graduate Student Research Award funded internship at NREL



1 – Approach

Diversity, Equity, and Inclusion

- 2 of 6 Principal Investigators identify with minoritized identities.
- 40% of researchers identify as female
- Successful graduate recruiting from minority serving institutions, e.g. Tuskegee University
- Project interacts with ISU outreach programs such as **Science Bound**: pre-college through college program to increase the number of racially and ethnically minoritized Iowa youth in STEM



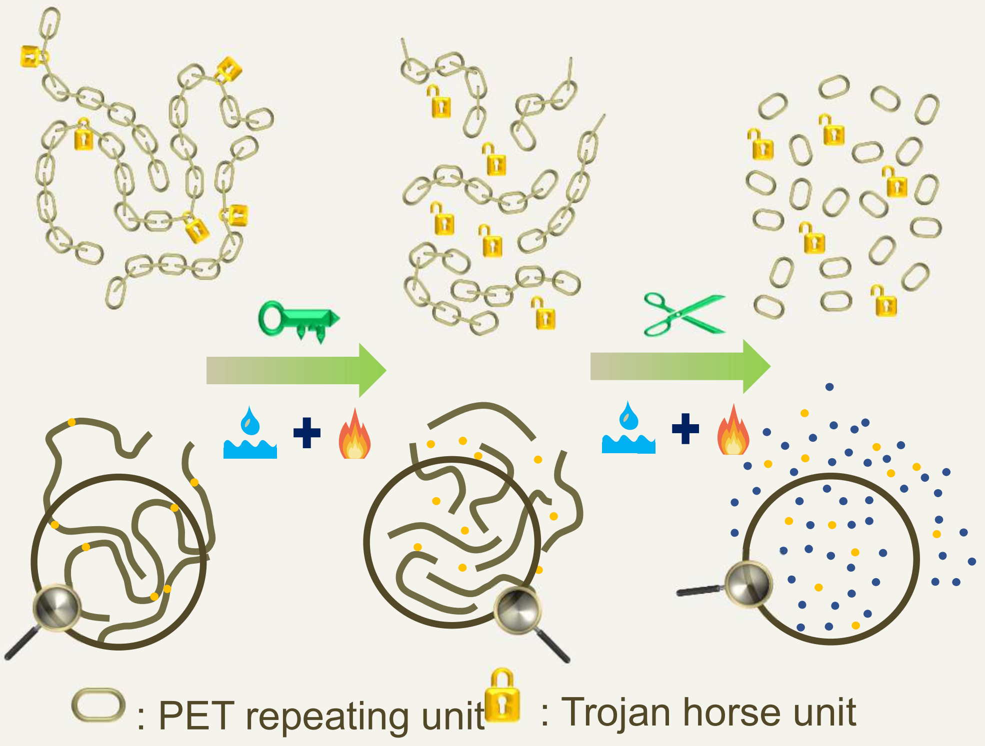
1 - Approach

Budget Period 2 – Prototype Chemically Circular PET

- BP2 Go-No Go Objective (***Attained***)

Synthesis of at least 5 g PET/TH

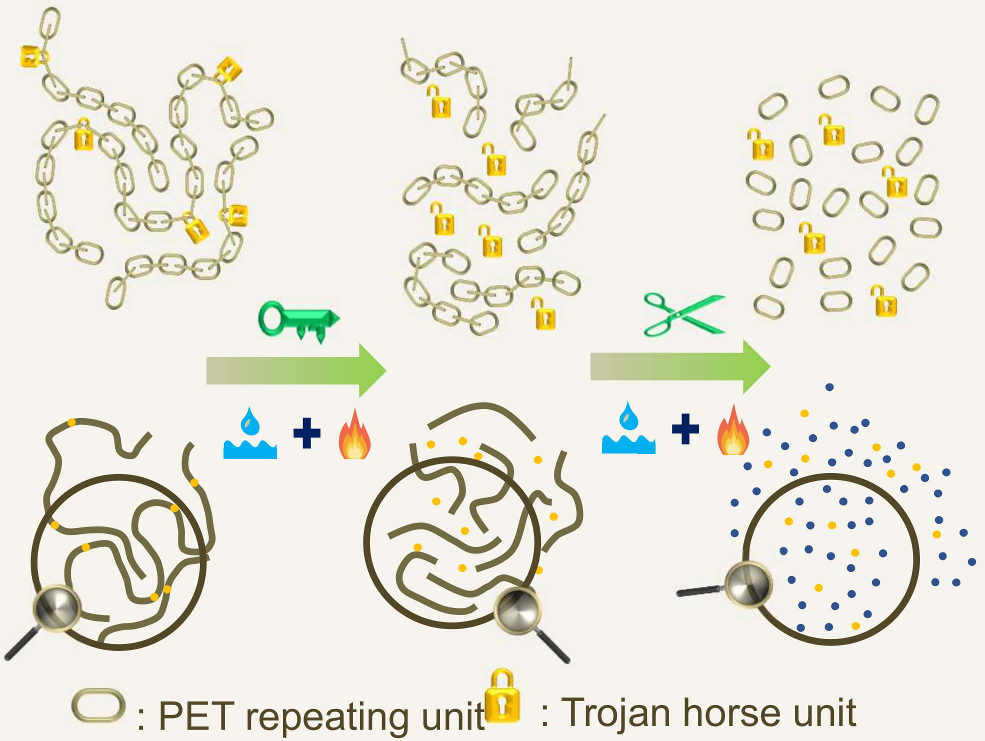
- to at least 15 kDa
- decomposition to at least 25 wt % monomers.
- At least 1 g of recovered monomers/oligomers will be repolymerized to at least 1 kDa (via GPC) and characterized by DSC.



1 – Approach

Budget Period 3 – Scale-up, optimize, and demonstrate

- BP3 Go-No Go Objective (***In-progress***)
- **End of Project Goal:** The project team demonstrates the synthesis of at least 10 kg PET/TH
  - with at least 50 wt % non-food-starch-based content to at least 15 kDa and
  - subsequently shows decomposition to at least 50 wt % monomers or polymerizable oligomers (MPOs).
  - The MPOs can be repolymerized to at least 10 kDa recycled PET/TH at 50% yield or greater.
  - Compared to virgin PET, barrier performance of recycled PET/TH is at least 50% (no greater than 200% permeability) with respect to water, ethanol, CO_2, and $O_{2;}$
  - tensile strength of at least 50% of virgin PET is achieved.

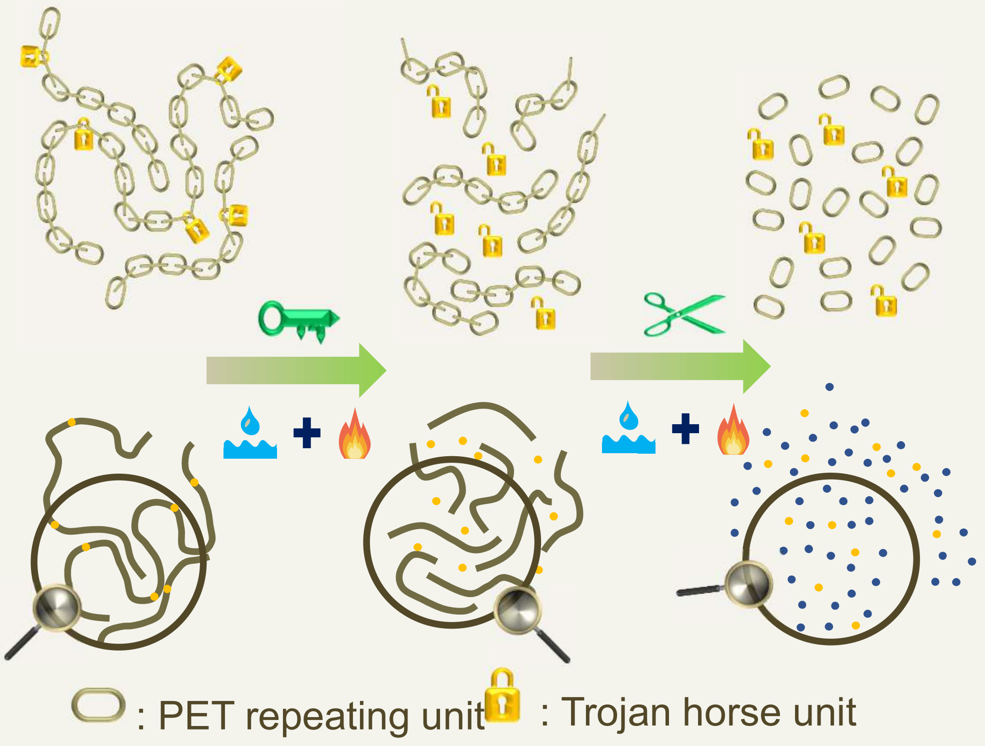


1 – Approach

Risk Mitigation

- Risk

Risk	Mitigation
Inadequate properties	Several Trojan Horse candidates.
Depolymerization too costly	Several depolymerization pathways (hydrolysis, methanolysis, glycolysis) Several Trojan Horse designs change depolymerization condition requirements
Monomer recovery too difficult	Several depolymerization pathways (hydrolysis, methanolysis, glycolysis)

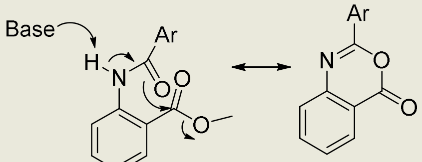


2 – Progress and Outcomes

Budget Period 2 – Prototype Chemically Circular PET

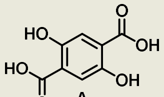
1. Identify Trojan Horse candidates

Neighboring group participation:



Internally catalyzed TPA-like comonomers

Many possibilities!



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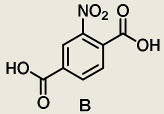

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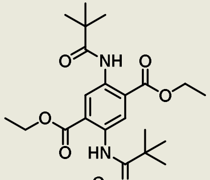
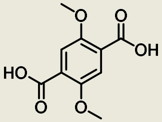


C



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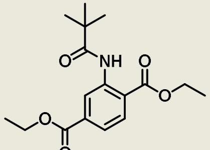

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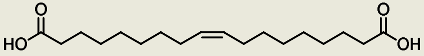

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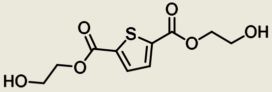

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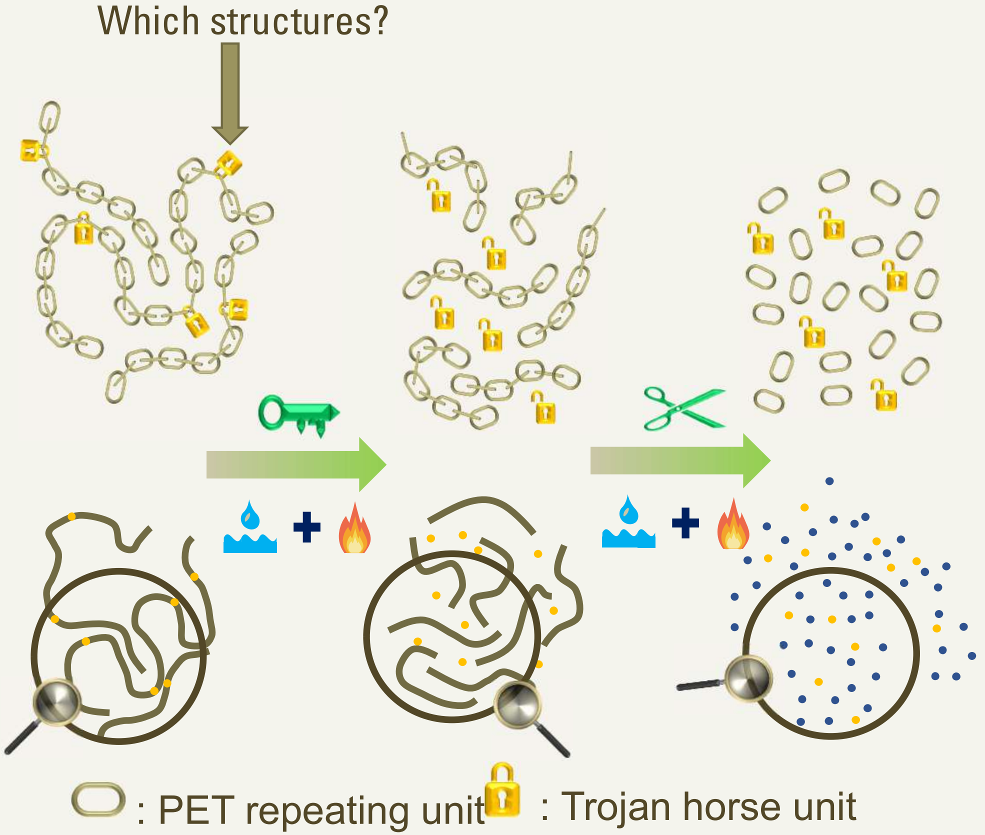
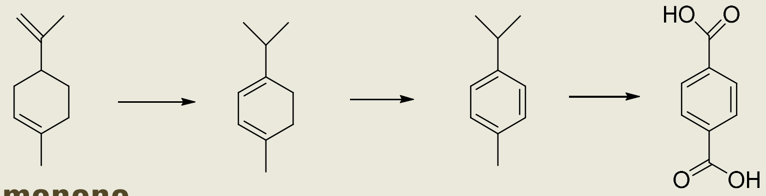


2 – Progress and Outcomes

Budget Period 2 – Prototype Chemically Circular PET

❷ Explore non-food routes to bio-TPA



Limonene
Citrus peel
waste extract

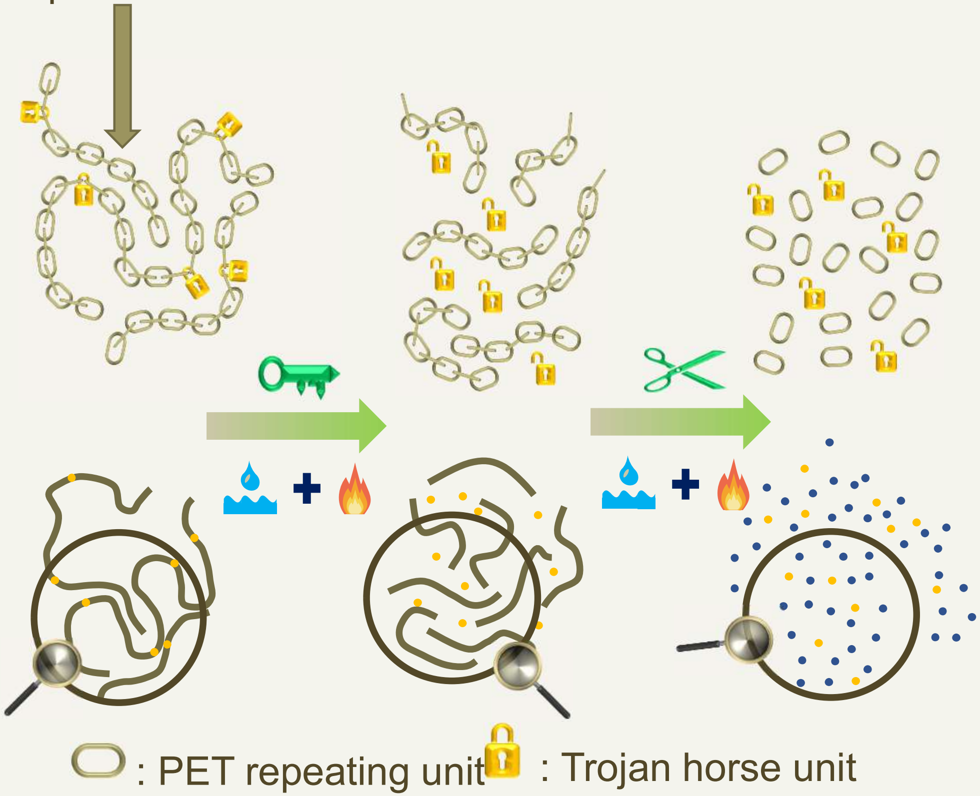
ADM

BioTPA
300,000,000
Pound per
year potential

Dehydrogenation
- 100% Conversion
- 75% isolated yield
- Reaction time 2h

Oxidation
- Mid-Century oxidation
- Explore to improve yield

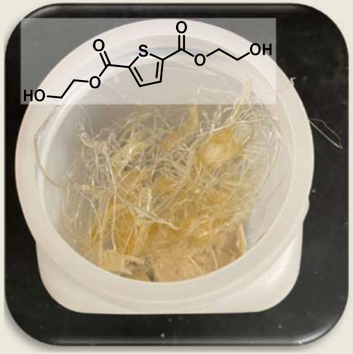
Improve bio-based content

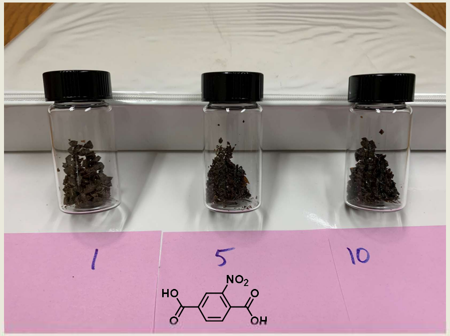


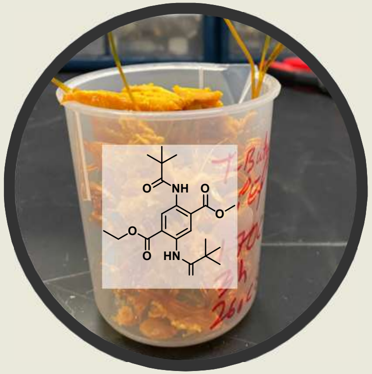
2 – Progress and Outcomes

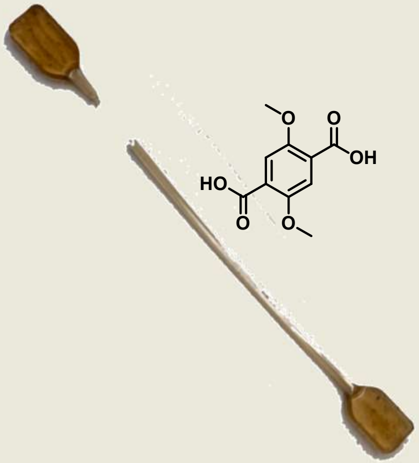
Budget Period 2 – Prototype Chemically Circular PET

❸ Prepare PETTH copolymers

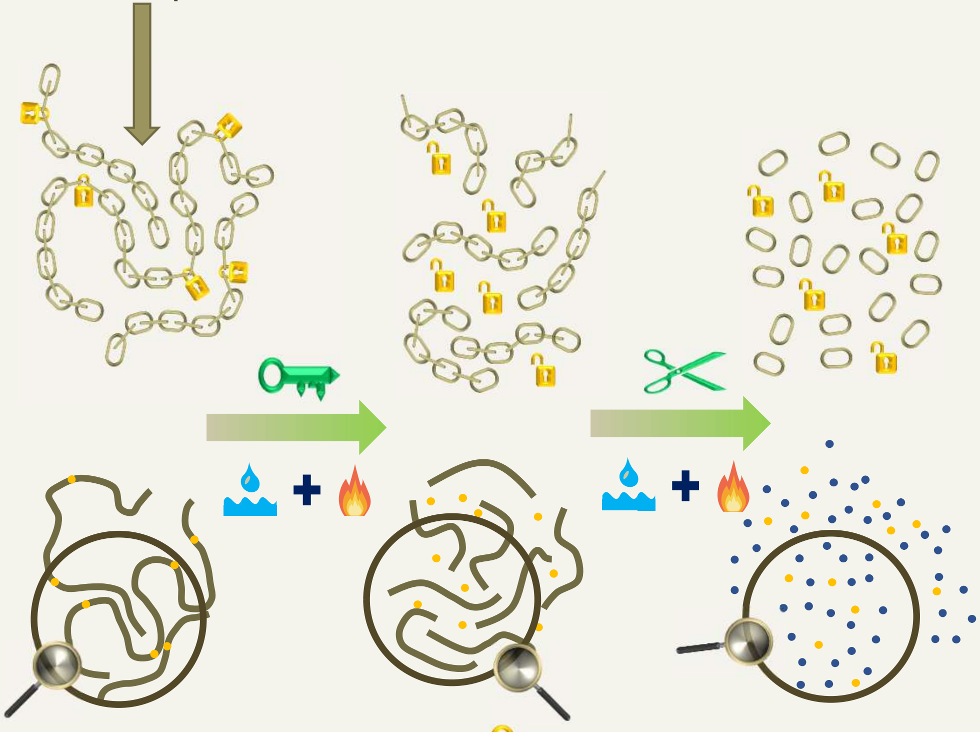








Make examples of these

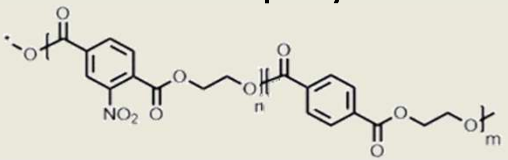


: PET repeating unit : Trojan horse unit

2 – Progress and Outcomes

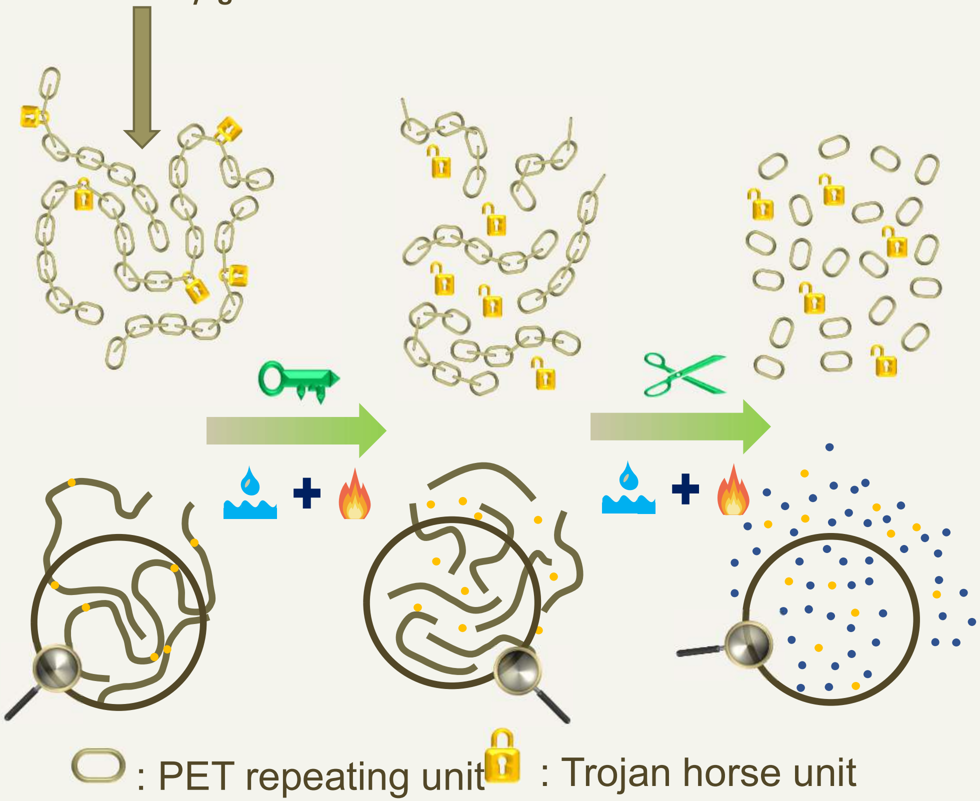
Budget Period 2 – Prototype Chemically Circular PET

❹ Evaluate PETTH copolymers



Sample name	% Inc.	Mn	Mw	Tg (°C)	Tm (°C)
PET (polyscience)	100/0	18.7	38.0	77.3	253.4
Dak-PET	100/0	-	-	77.5	245.32
PETNT-1	95/5	15.4	46.8	70.3	239.40
PETNT-2	97/3	21.4	70.1	73.5	244.4
PETNT-3	96/4	-	-	78.2	236.98
PETNT-4	89.5/11.5	22.1	61.4	74.3	230.7
PETNT-repoly	95/5	9.3	23.9	82.0	224.5
PETNT-1%	99/1	12	29.6	86.8	252.9
PETNT-5%	95/5	11.8	37.7	81.3	244.5
PETNT-10%	90/10	13.3	57.4	71.1	218.3

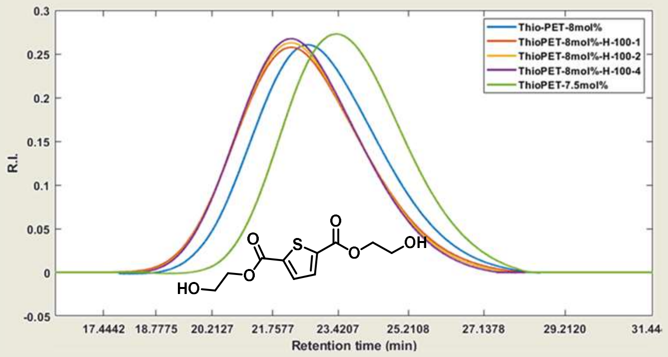
Are these any good?

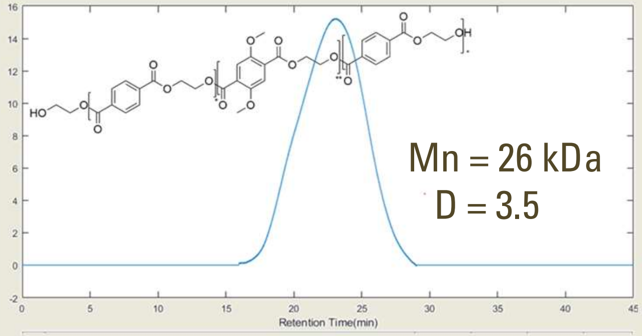


2 – Progress and Outcomes

Budget Period 2 – Prototype Chemically Circular PET

❹ Evaluate PETTH copolymers





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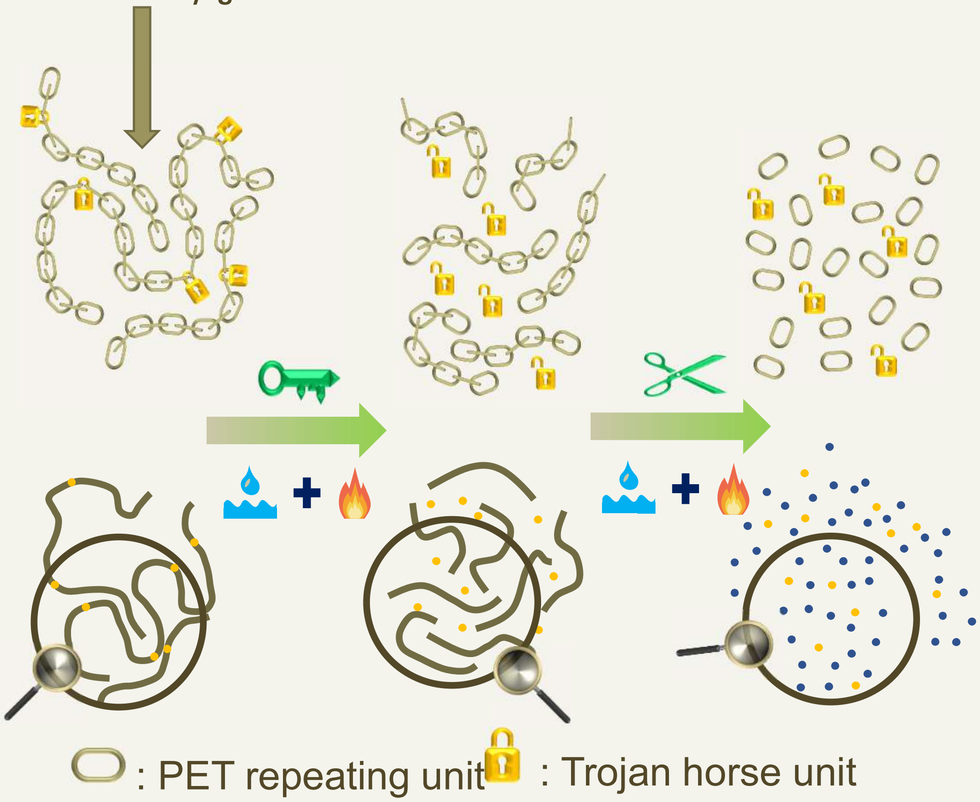
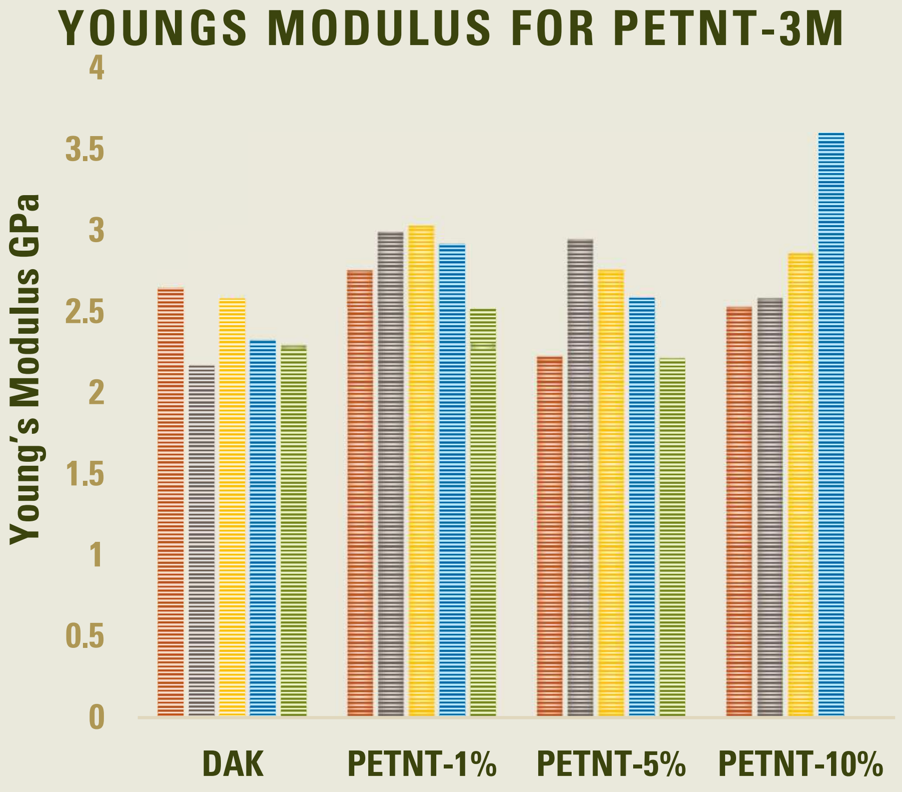
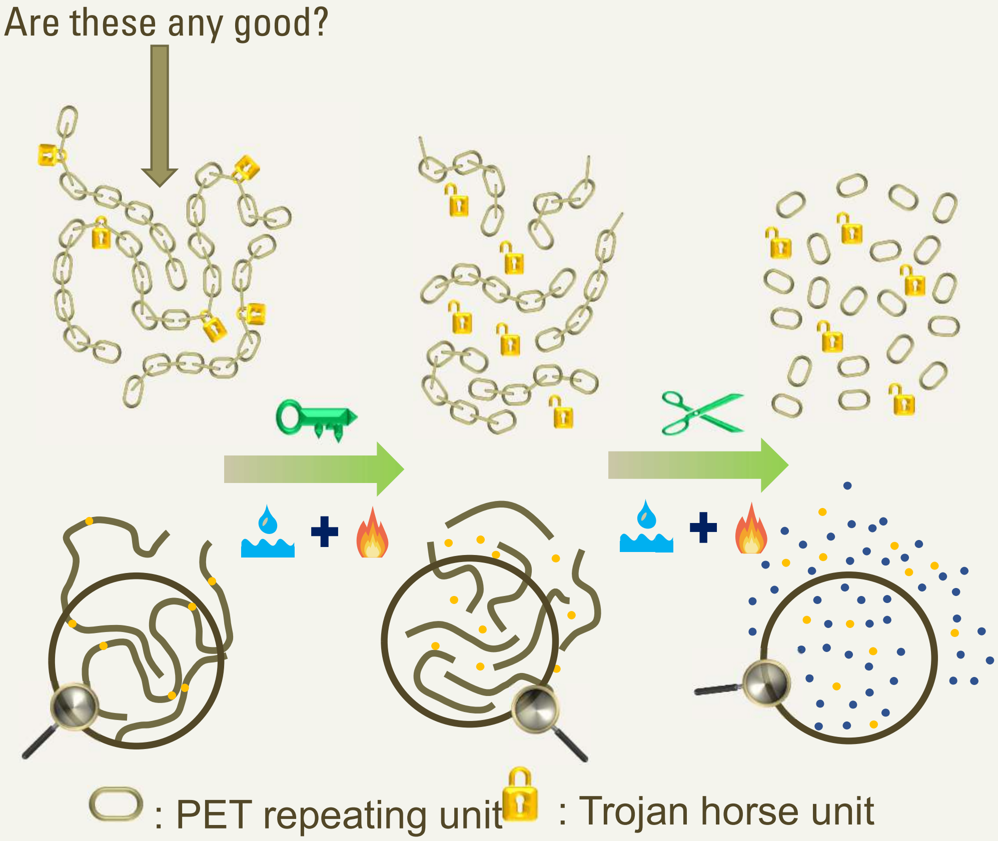


2 – Progress and Outcomes

Budget Period 2 – Prototype Chemically Circular PET

❹ Evaluate PETTH copolymers



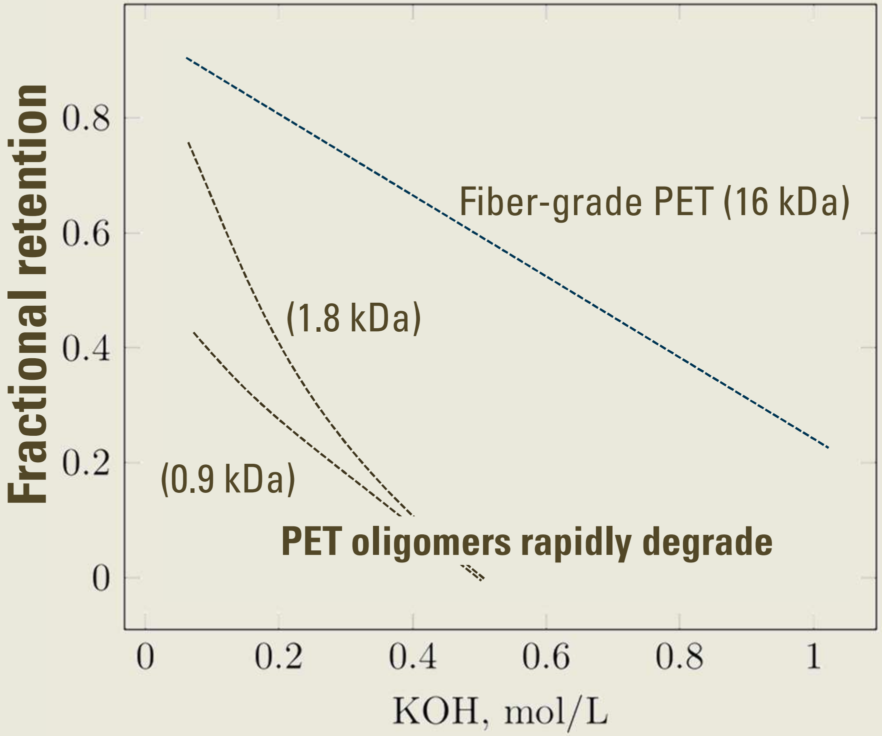


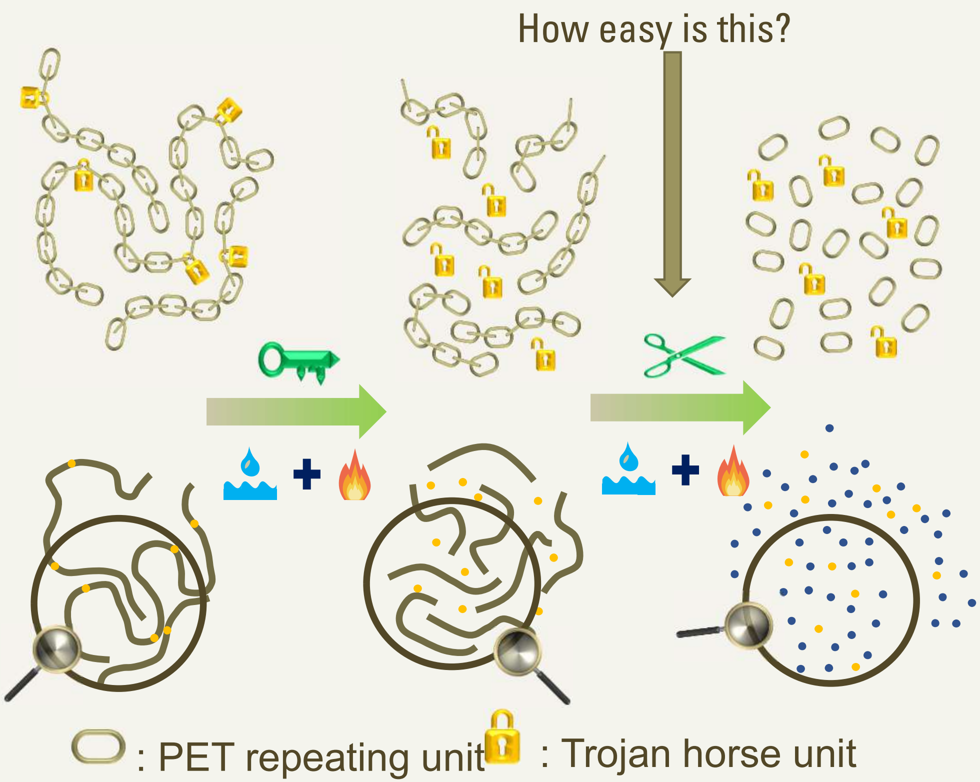
2 – Progress and Outcomes

Budget Period 2 – Prototype Chemically Circular PET

5 Depolymerize PETTH copolymers

24 h hydrolysis, 100 °C, KOH catalyzed

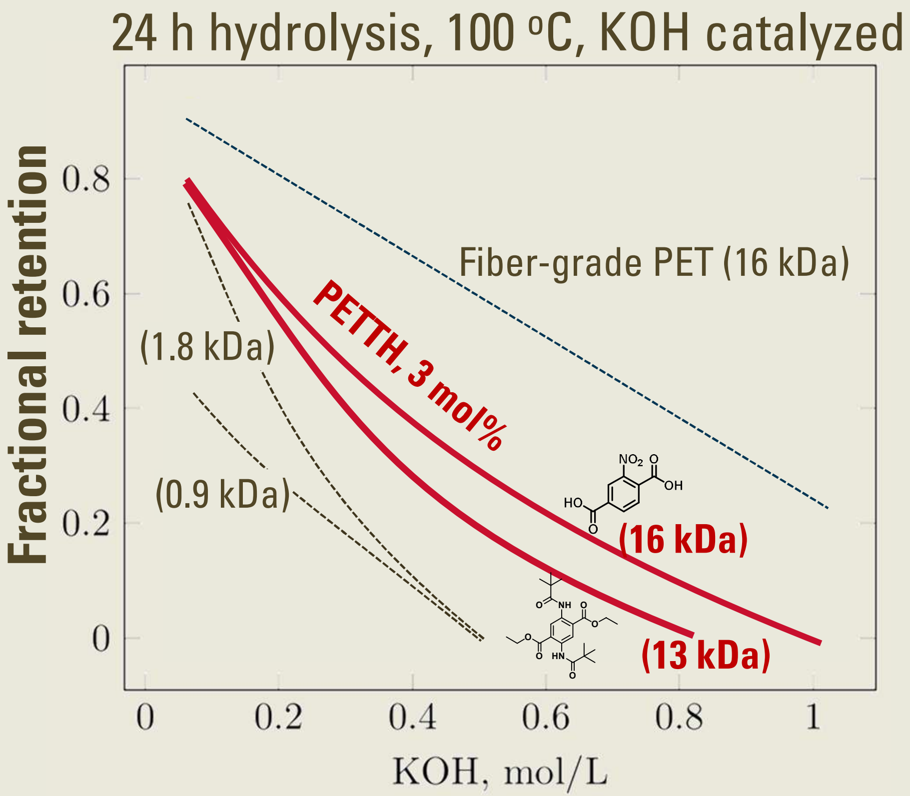


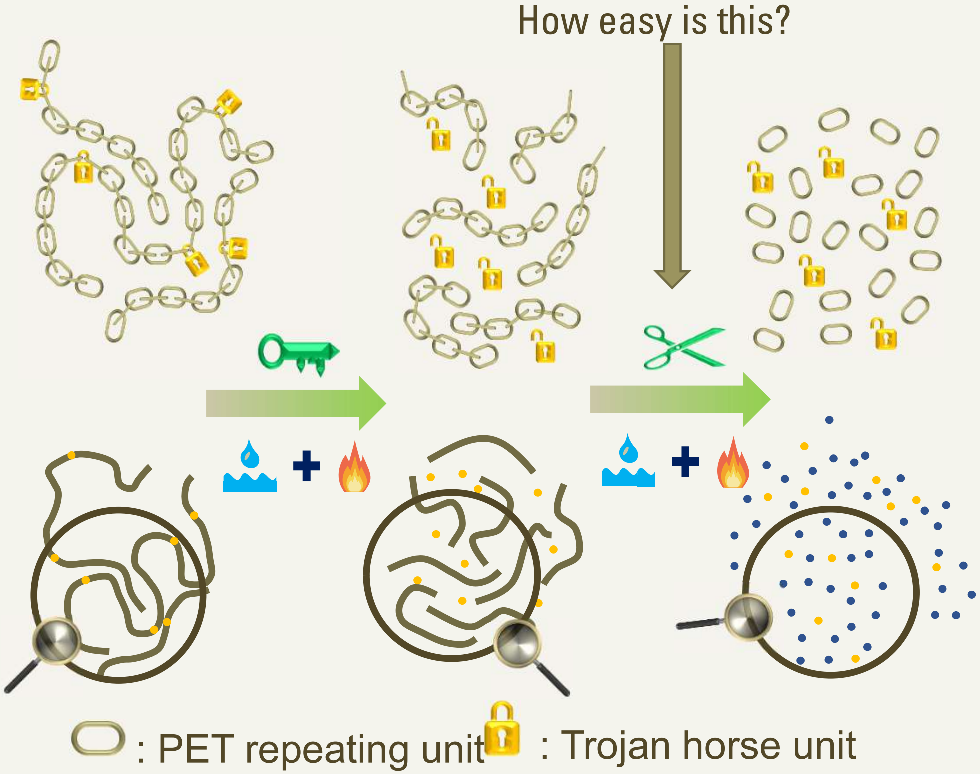


2 – Progress and Outcomes

Budget Period 2 – Prototype Chemically Circular PET

❺ Depolymerize PETTH copolymers

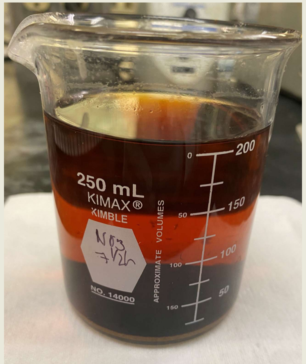




2 – Progress and Outcomes

Budget Period 2 – Prototype Chemically Circular PET

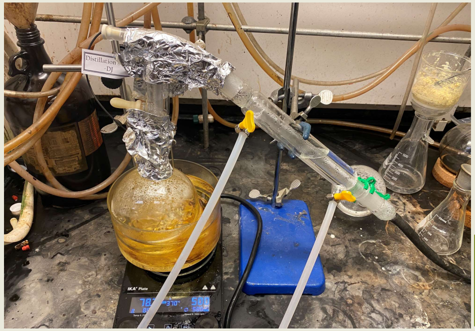
❻ Analyze decomposition products



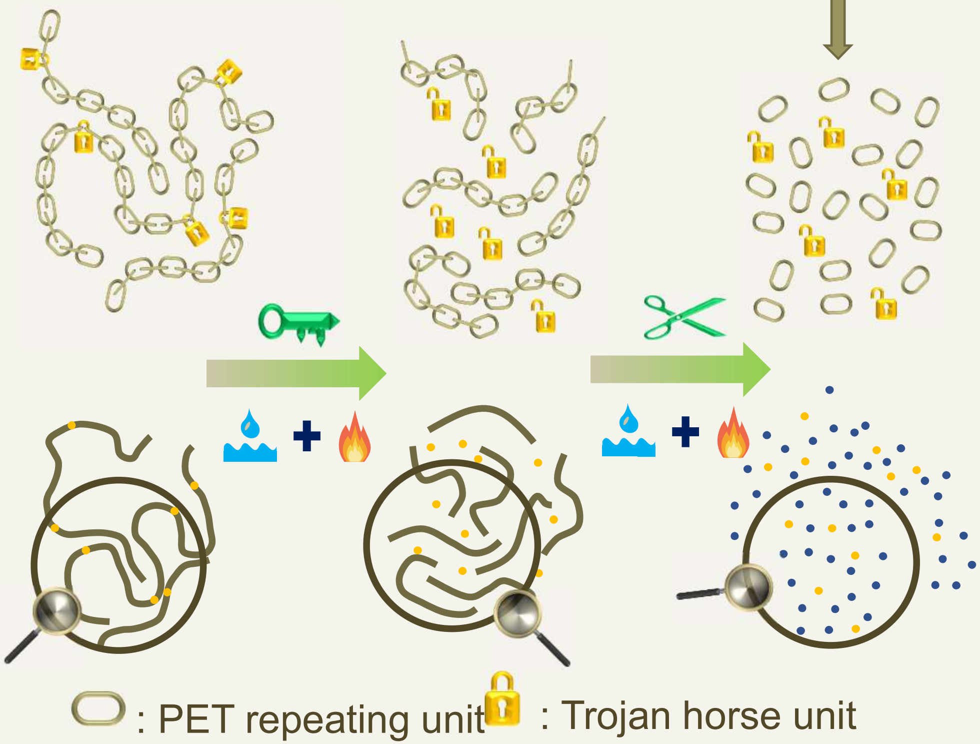
Filtrate post depolymerization

Unreacted polymer vs recovered monomer

82% TPA yield in 24 h



Distillation of Ethylene glycol from water

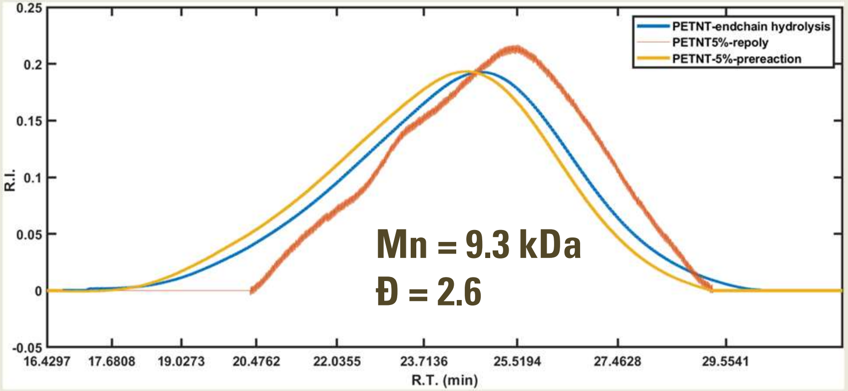


2 – Progress and Outcomes

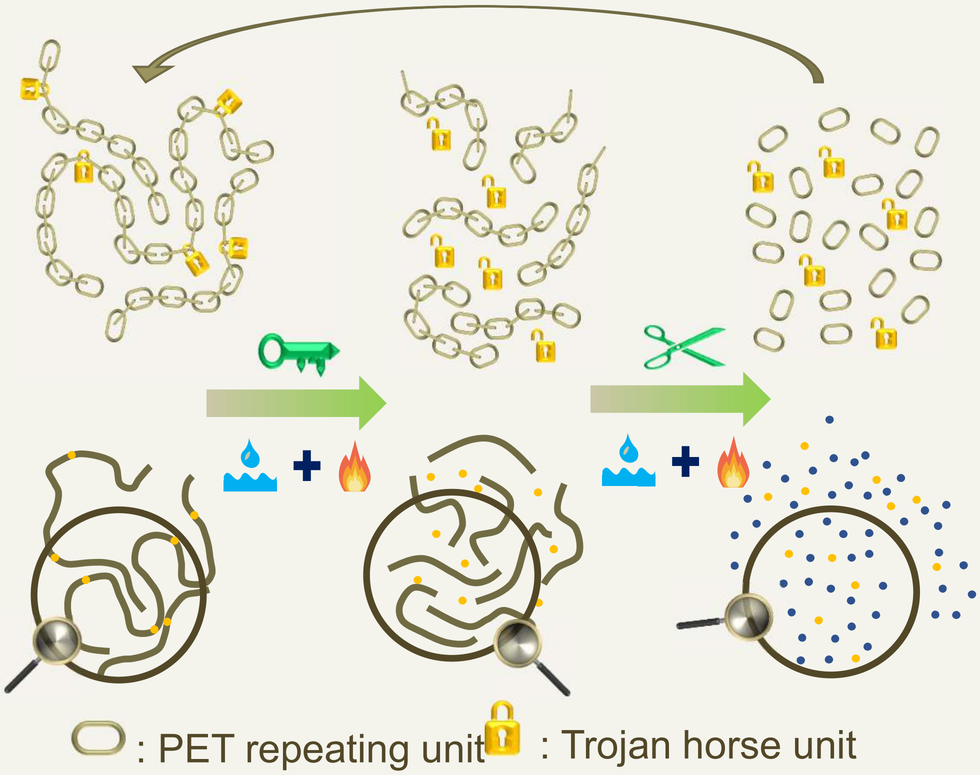
Budget Period 2 – Prototype Chemically Circular PET

8 Recover and repolymerize

Repolymerized in a vial at 240 ℃



Can we go back to the beginning?



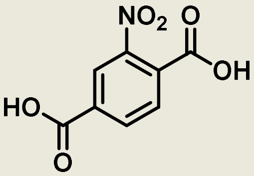
2 – Progress and Outcomes

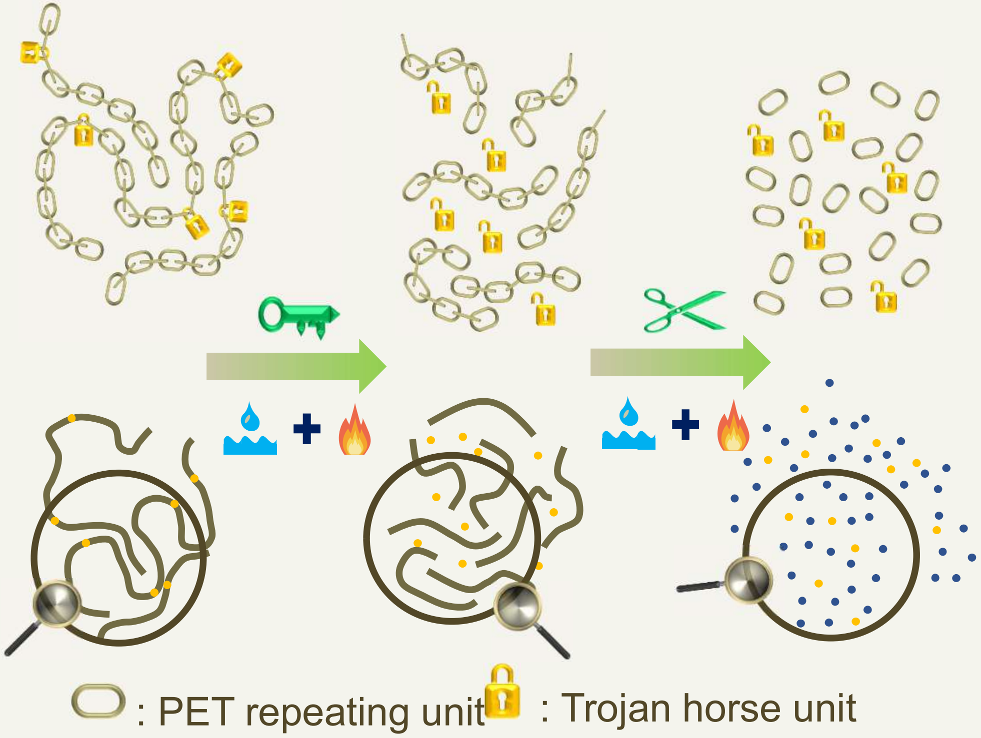
Budget Period 3 – Scale-up, optimize, and demonstrate

9 Scale-up

- **3M made 2 kg ea of 3 PETTH Compositions**
- **Biaxially oriented films are being evaluated**
- **New compositions with minimal discoloration are planned**
- **100 pounds of bottle production with Diageo on track for late 2023 / early 2024.**

3M

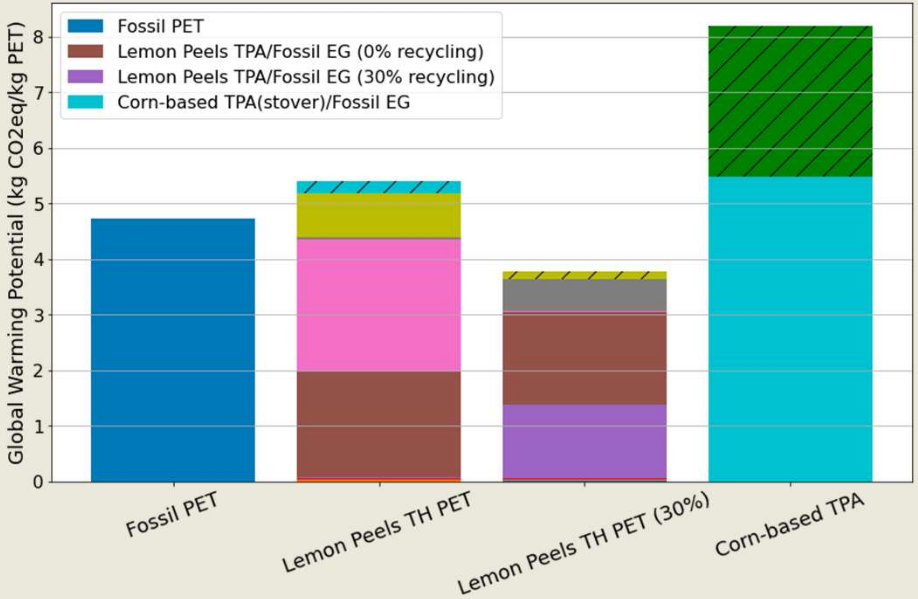


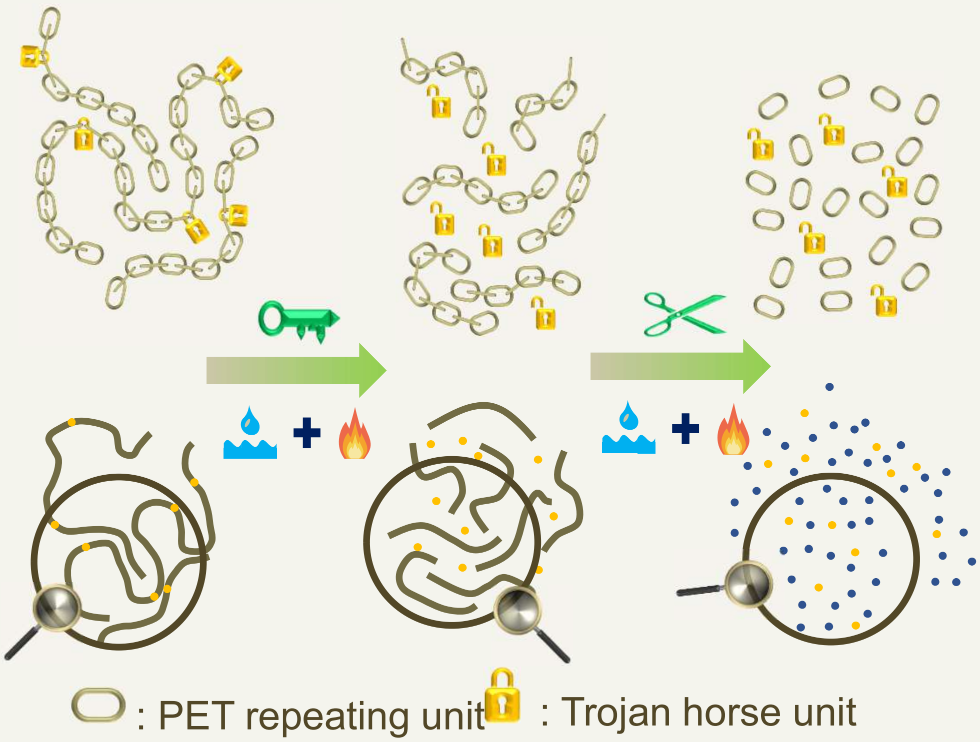


2 – Progress and Outcomes

Budget Period 3 – Scale-up, optimize, and demonstrate

10 Life cycle assessment





3 – Impact

Journal Articles

Recently Accepted:

- Lee, Ting-Han; Yu, Huangchao; Forrester, Michael; Wang, Tung-ping; Shen, Liyang; Liu, Hengzhou; Li, Jingzhe; Li, Wenzhen; Kraus, George; Cochran, Eric W. "**Dihydroxyterephthalate: A Trojan Horse PET Counit for Facile Chemical Recycling**". Advanced Materials, February 2023. https://doi.org/10.1002/adma.202210154. In Press.

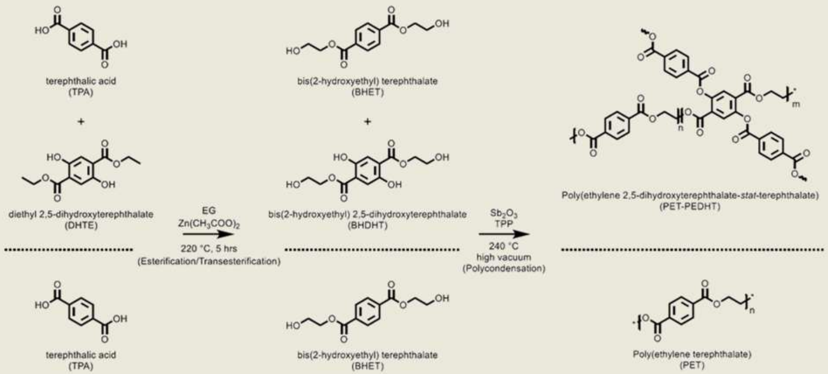


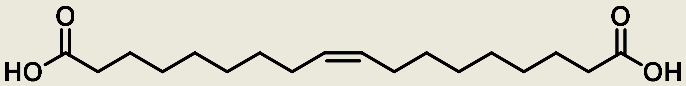
Figure 2: Step-growth polycondensation of pure PET and PET-PEDHT copolymer via a two-step polymerization

Draft of proposed cover art

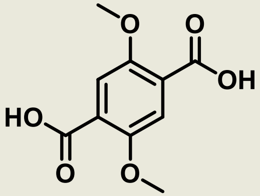
3 – Impact

Journal Articles

- In Progress
  - This Trojan Horse operates through oxidative cleavage



  - This Trojan Horse shows high performance in water with little discoloration



Patent Application

- Filing (ADM)
  - Process innovations related to lemon peel-to-TPA conversion.

Patent Application

- Provisional filing Jan 2023 (ISU)
  - Several polymer compositions covering PET/TH concept

Student education

- Sharan Raman, M. Sc. 2022
- Dhananjay Dileep, M. Eng. 2022 (ongoing Ph. D.)
- Ting-Han Lee, Ph. D. 2022
- Patrick Wang, Ph. D. 2022
- Brianna Burton, B. Sc., admitted to 5 top 10 Ph. D. programs
- Other undergraduates mentored: Jacques Attinger, Emma Fetters, Elijah Erickson, Eagan Kirk, Kyle Tsujimoto, Aadhi Subbiah, Jefferson Roberts-Dobie, Ana Soares, Jacob Gebis

Summary

- Plastics can be re-designed for responsible end-of-life management
- ISU, ADM, 3M, and Diageo are an integrated team
  - ISU – technology development and prototyping
  - ADM – Biobased feedstock development
  - 3M – Polymer manufacturing and end-user
  - Diageo – Bottle manufacturing and recycling
- The PET/TH copolymerization strategy for chemical recycling is effective
- Scale-up and bottle demonstration ongoing over next 12 months
- Life cycle assessment will guide selection of "optimal" PET/TH design.

Iowa State University
of Science and Technology

Quad Chart Overview

Timeline
- *4/1/2021*
- *3/31/2024*

	FY22 Costed	Total Award
DOE Funding	*(10/01/2021 – 9/30/2022)* *$655,968*	*(negotiated total federal share)* *$2,165,000*
Project Cost Share *	$158,509	$ 557,420

TRL at Project Start: 2
TRL at Project End: 5

*Only fill out if applicable.

Project Goal
To demonstrate the technical performance, commercial viability, and life cycle impact of a highly recyclable biobased polyethylene terephthalate/Trojan Horse (PET/TH) copolymer.

End of Project Milestone
The project team demonstrates the synthesis of at least 10 kg PET/TH with at least 50 wt % non-food-starch-based content to at least 15 kDa and subsequently shows decomposition to at least 50 wt % MPOs. The MPOs can be repolymerized to at least 10 kDa recycled PET/TH at 50% yield or greater. Compared to virgin PET, barrier performance of recycled PET/TH is at least 50% (no greater than 200% permeability) with respect to water, ethanol, CO2, and O2; tensile strength of at least 50% of virgin PET is achieved

Funding Mechanism
DE-FOA-002245 Joint FY20 Bioenergy and Advanced Manufacturing FOA BOTTLE: Bio-Optimized_Technologies to keep Thermoplastics out of Landfills and the Environment

Project Partners*
- Iowa State University
- Archer-Daniels Midland
- 3M
- Diageo