DOE Bioenergy Technologies Office (BETO) 2023 Project Peer Review

BOTTLE: Hybrid Chemical-Mechanical Separation and Upcycling of Mixed Plastic Waste

4/4/2023
Technology Area Session: Plastics Deconstruction and Redesign

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Organization: Case Western Reserve University

Project Overview

Context:

- Packaging is the largest polymer end-use market, accounting for nearly 40% of annual plastic consumption worldwide, or more than 150 MTons in total.

- Approximately 40 MTons (30%+ of the total) of plastics packaging is made up of blended, multilayered or laminated polymers (in e.g., films, bottles, etc.), which are not recyclable.

- The two main classes of polymers used in multi-material packaging are polyolefins (~20 MTon/year) and polyesters (>1 MTon/year).

Project Overview

Context:

- PROBLEM: The two main plastics recycling methods and Mechanical Recycling and Chemical Recycling: None are adequate for upcycling in large quantities!

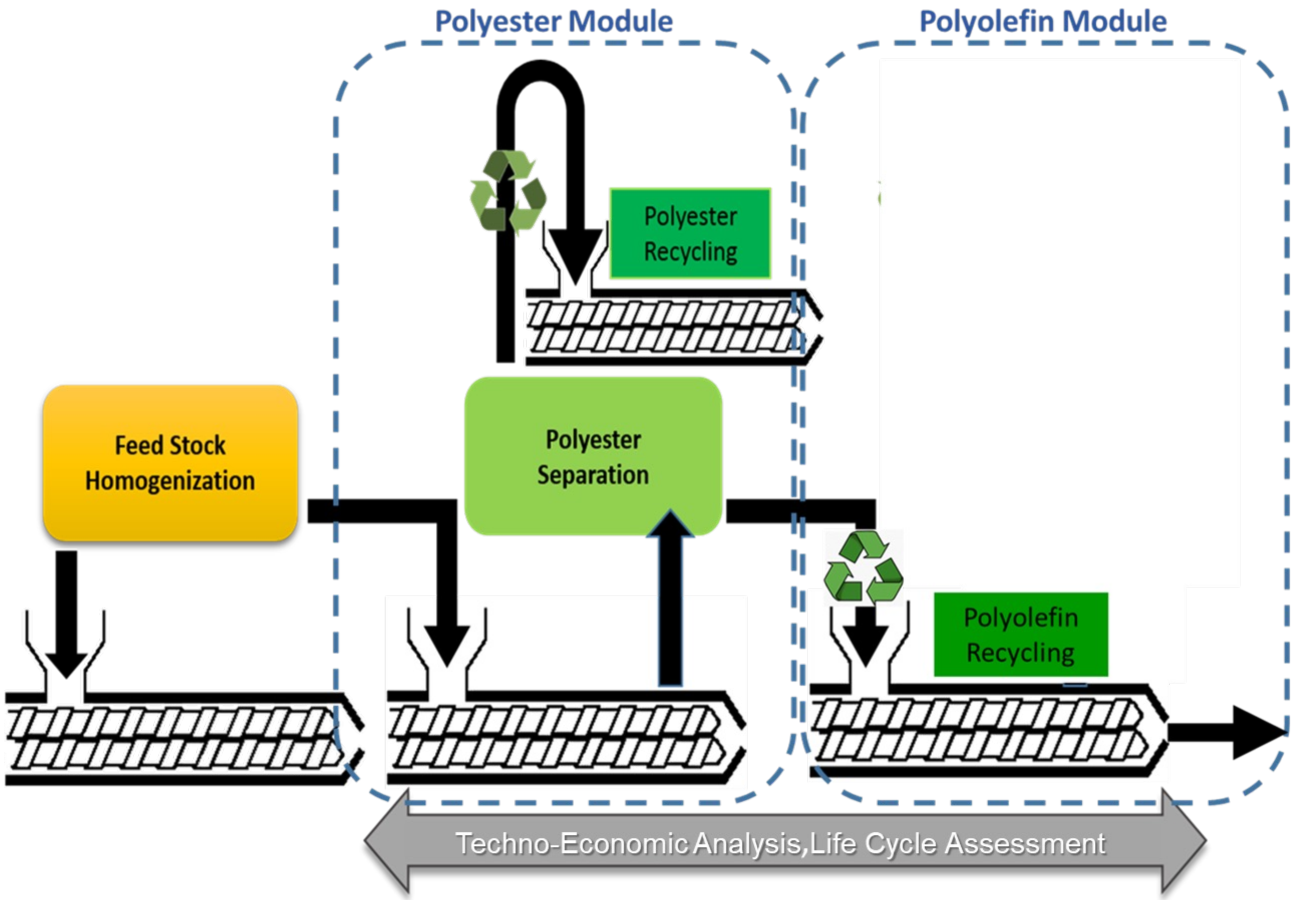
- Mechanical Recycling:
  - ++ High throughputs possible (10^6 Tons/year); Low cost (~\$$10^0$-$10^1$ Million); Significant lifetime savings in the CO_2 footprint compared to virgin polymer.
  - --- Very susceptible to contamination and feedstock variability, so it yields products with poor mechanical properties, i.e., it is a downcycling technique.

- Mechanical Recycling:
  - ++ High added-value recycled products possible.
  - --- Low capacity (~10^5 Tons/year); High cost (~\$$10^2$ Million); High environmental impact from chemicals used; Contamination between phases yields low recycling efficiency.

Project Overview

Objective:

- Integrate and couple chemical and mechanical recycling methodologies to enable *continuous recycling of mixed waste streams* of polyesters and polyolefins, *i.e.*, develop a *Hybrid Mechanical-Chemical Upcycling* capability.



Team:

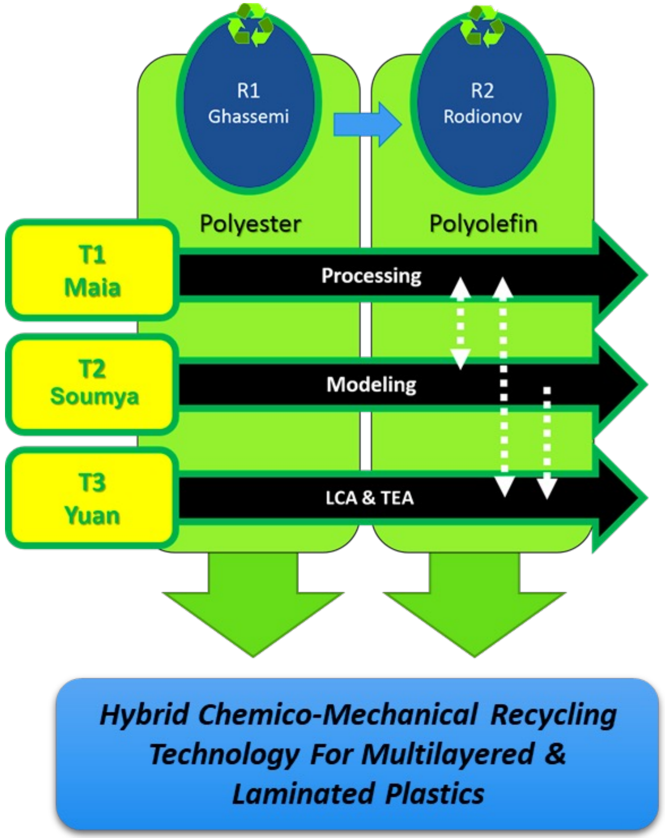
- Case Western Reserve University (Lead).
- Sandia National Laboratories.
- Lawrence Livermore National Laboratory.
- Braskem USA.
- P&G
- Resource Material Handling & Recycling

1 – Approach

TASK R1 - Polyester Separation and Recycling/Upcycling:

To develop and implement the TSE-based technology for separation and recycling/upcycling of PET. The following two pathways for PET separation from PET/PE blends will be explored:

1) *Partial chain extension of PET*, followed by thermo-electro-rheological manipulation of the blend and filtration of the PET phase;
2) *Partial depolymerization of PET*, followed by solubilization in SC CO_2 and removal via degasification.



RISKS/CHALLENGES EXPECTED:

Route 1: Low yield of chain extension by PMDA, which can be resolved by trying the more reactive chain extenders.

Route 2: Low yield of separating depolymerized PET from the blend.

Go/No-Go:

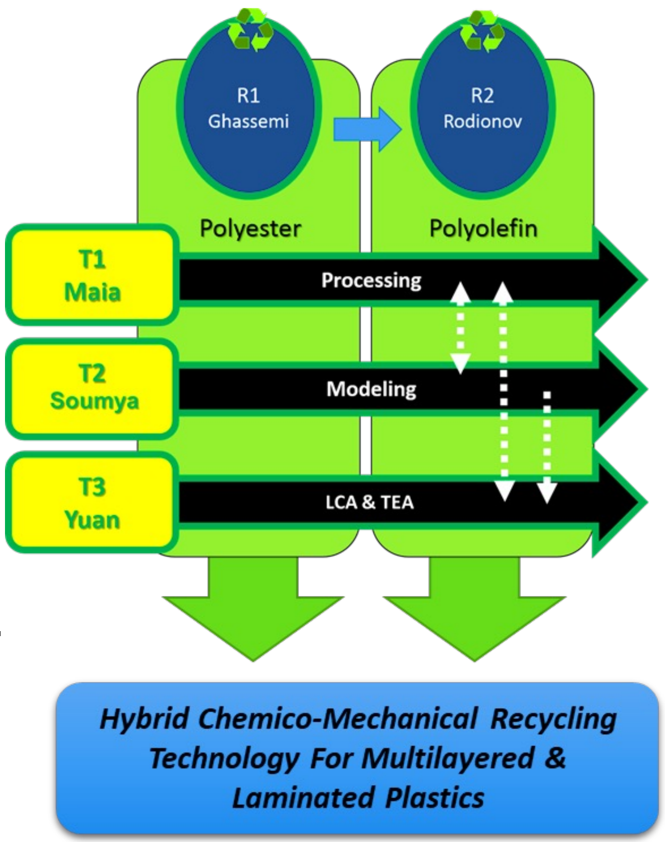
- *Route 1*: At least 80% PET separation from blend.
- *Route 2*: Decrease PET MW by depolymerization >80%.

1 – Approach

TASK R2 - Polyolefin Separation and Recycling/Upcycling:

To implement the continuous TSE-based high-throughput recycling and upcycling of PE post-separation of PET. The specific target is to obtain lower hydrocarbons ($n < 12$), for which a novel low-temperature (<400 ^{O}C) catalytic cracking procedure will be developed:

1. Synthesis of a family of mesoporous superacidic zeolites
2. Batch screening of catalytic activity
3. Screening of catalytic activity under reactive extrusion conditions



RISKS/CHALLENGES EXPECTED:

- Inefficient separation of heterogeneous catalyst from polymer/hydrocarbon melt.
- Carbon fouling of the catalyst due to incomplete PET separation.

Go/No-Go:

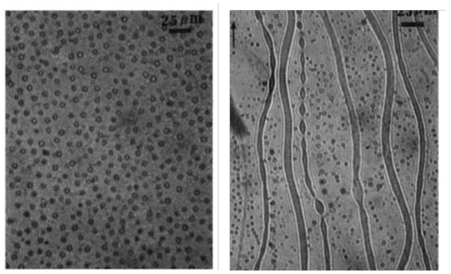
- No/reduced catalytic activity detected; this will require reassessment and possibly, transition to a different catalyst family.

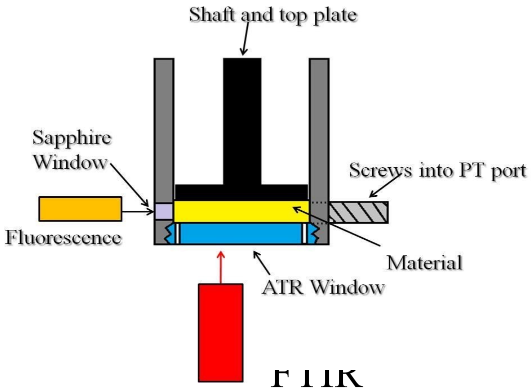
1 – Approach

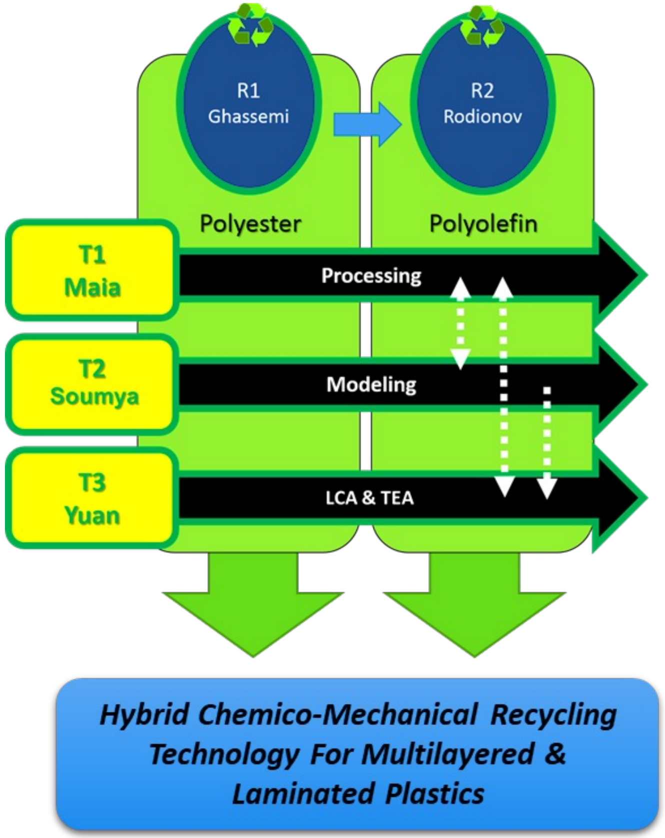
TASK T1 - Processing:

Development of advanced processing and monitoring technologies in support of Tasks R1 and R2. Equipment to be developed include:

1. On-Line Multipurpose (Rheology+NIR) Analyzer (MOLA).
2. Supercritical (SC)CO_2-injection system for Twin-Screw Extruder (TSE).
3. Extruder screen with electrical insulation at low-current for TSE.







RISKS/CHALLENGES EXPECTED:

No major risks or challenges are expected in building the equipment. The main risk is related with possible delays in supply/acquisition of the relative components, e.g., portable rotational rheometer head, CO_2 pump, etc.

Go/No-Go:

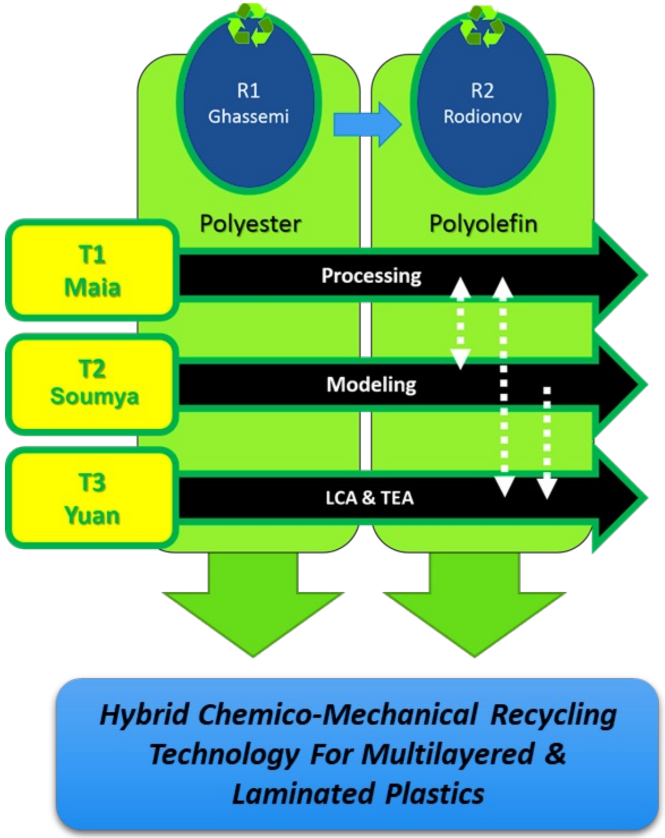
This Task does not contain Go/Go-Go decision points.

1 – Approach

TASK T2.1 - Multiscale Integration (Molecular to Mesoscale):

To study the flow behavior (Rheology) and micro-structural evolution of PET/PE blends as the constituents decompose under the processing conditions: Coupling Molecular Dynamics (MD) simulations with Machine-Learning (ML) algorithms and feeding the corresponding chemical interaction potentials to Dissipative Particle Dynamics (DPD) models at the mesoscale for the prediction of:

1) Reactions and separation efficiency PE/PET systems in Task R1.
2) Potential synthesis routes in the catalytic cracking in Task R2.



RISKS/CHALLENGES EXPECTED:

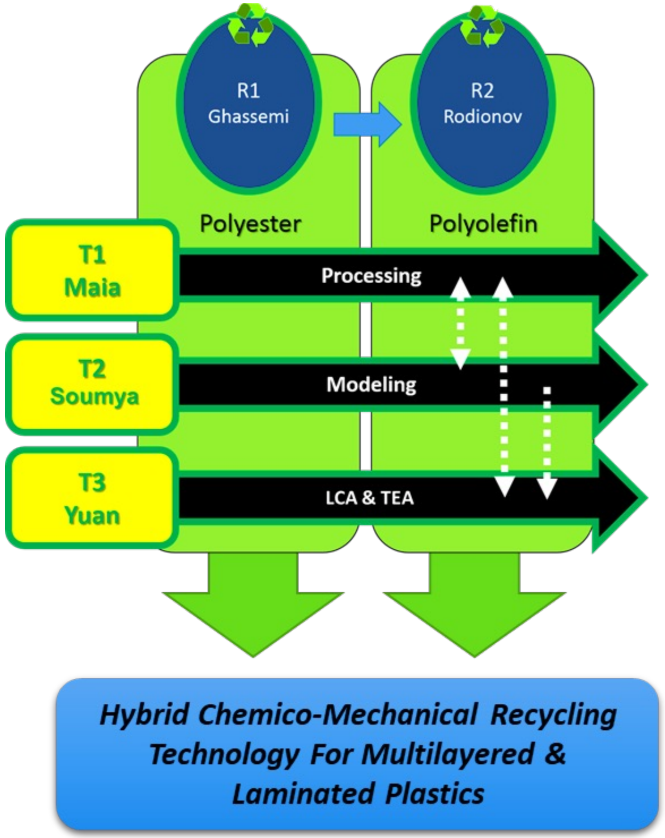
No major risks or challenges are expected. The main challenge is related with selection of the optimal ML algorithm to apply.

Go/No-Go:

This Task does not contain Go/Go-Go decision points.

1 – Approach

TASK T2.2 - Multiscale Integration (Mesoscale to Macroscale):
To achieve the capability to accurately extend mesoscale simulations of structure and properties to the macroscale, in support of the processing operations, both in the laboratory and at pilot and pre-industrial scales. In order to do so we will couple Goma 6.0, an open source multiphysics Finite Element (FE) code, with a mesoscale particulate modeling code (DPD) and Polymer Field Theory (PFT).



RISKS/CHALLENGES EXPECTED:
No major risks are expected. The main challenges are related with physically realistic mapping from the discrete mesoscale (DPD simulations) to the continuum (PFT and FE).

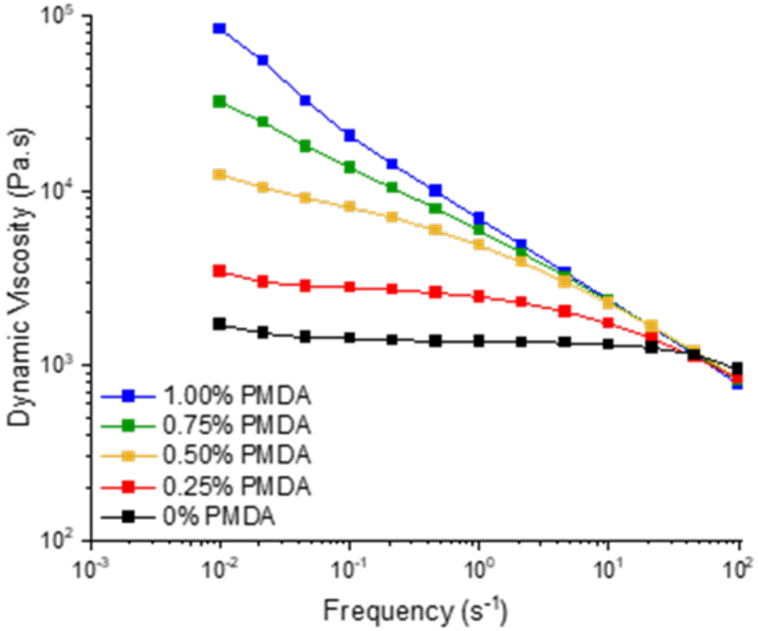
Go/No-Go:
This Task does not contain Go/Go-Go decision points.

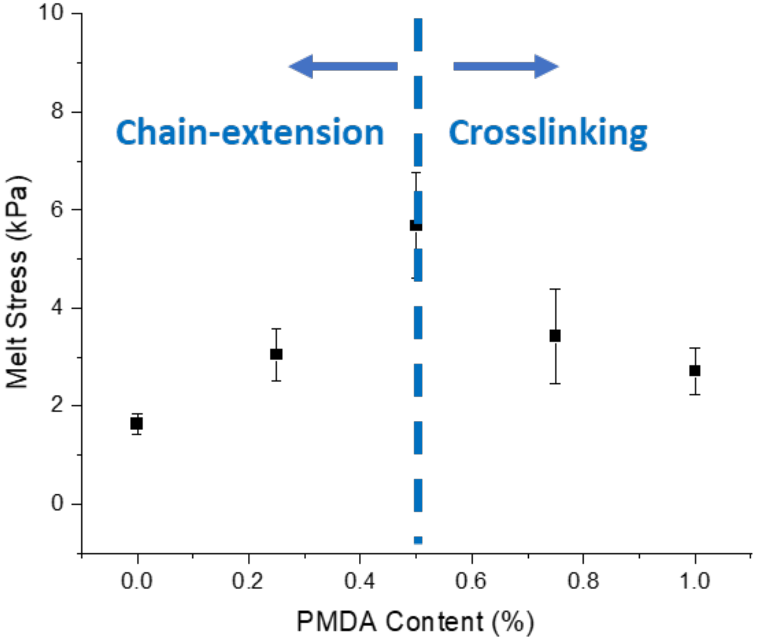
2 – Progress and Outcomes

TASK R1 - Polyester Separation and Recycling/Upcycling

ROUTE 1: Separation *via* PET chain-extension

- Experiments showed that by adding up to 1.5% w/w of pyromellitic dianhydride (PMDA) to PET significant degrees of chain extension can be achieved, but branching became a problem above 0.5% w/w of PMDA.
- Rheological data, namely the value of η' in the Newtonian plateau, shows that chain extension of 80% occurs at 0.5% w/w PMDA. Above this value, branching starts occurring.
- MILESTONE 2.2.1.1. - Processing conditions and PMDA and BADGE content defined for maximum PET chain extension w/o crosslinking concluded.





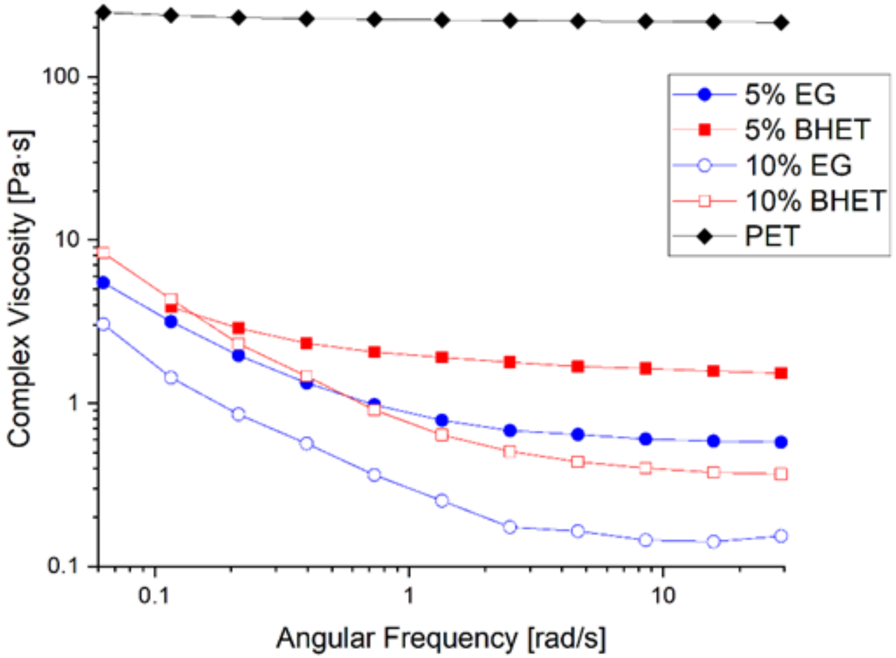
2 – Progress and Outcomes

TASK R1 - Polyester Separation and Recycling/Upcycling

ROUTE 2: Separation *via* PET depolymerization

- Ethylene glycol (EG) and Bis(2-hydroxyethyl) terephthalate (BHET) were added to PET and degrees of depolymerization of up to 99% were achieved.
- EG is a more efficient depolymerizing agent than BHET.
- Work progressing on schedule.

Material	Final Mw (g/mol)	Mw decrease (%)
PET	~11,000	-
PET+5% EG	~480	96
PET+10% EG	~120	99
PET+5% BHET	~1,310	88
PET+10% BHET	~320	91



2 – Progress and Outcomes

TASK R2 - Polyolefin Separation and Recycling/Upcycling

- Synthesis of large-pore zeolites is currently underway. An improved method for washing zeolite products was developed and preliminary BET surface area measurements estimate 780 m^2/g after solvent washing-only, which is a very good number for a first attempt.
- Variation of the synthesis conditions for our catalysts does change the catalyst performance and we have already identified more than one formulation that is better than the commercial ZSM-5.
- Work progressing on schedule.

TASK T1 - Processing

- MOLA: Base rheometer head delivered late 09/22. Final design underway. Manufacturing to be completed by 04/23, and instrument operational by 05/23.
- MuCell SC CO_2 injection system: Delivery delayed until 03/23. Loan of SC CO_2 injection system from Braskem has allowed work to progress unhindered. System operational.
- Electrically insulated extruder screen: System design underway; will be operational by 08/23.
- PET drier: System operational since 10/22.

- Work progressing behind schedule due to delays in equipment delivery, but on track to be completed by 08/23.

2 – Progress and Outcomes

TASK T2.1. – Multiscale Integration (Molecular to Mesoscale)

- Simulation roadmap defined and ML techniques for MD-to-DPD upscaling defined; Random Forest (RF) and Support Vector Machine (SVM) will be utilized.
- Initial ML-informed DPD simulations of polyethylene diffusion and cracking in catalyst underway.
- Work progressing on schedule.

TASK T2.2. – Multiscale Integration (Mesoscale to Macroscale)

- ML-based mapping from the discrete mesoscale (DPD) to the continuum (PFT) developed.
- Integration between PFT and FE underway.
- Work progressing on schedule.

TASK T3 – LCA/TEA

- Baseline process cost calculation based on data collected by Braskem USA complete. A total cost of $134.90/tPCR was calculated, based on the cost of main sub-processes such as pre-recycling treatment, *i.e.*, washing, extrusion I, extrusion II, side extrusion, and SC CO_2 pump etc.
- Work progressing on schedule.

3 – Impact

- The concept of feeding mixed and complex plastic waste to an economic extrusion line that can separate the plastics is a paradigm shifter, a high risk/high reward project.
- The proposed technology is feedstock agnostic, i.e., it does not require upstream separation of the PIR and PCR, an is easily scalable, which means custom-sized facilities can be installed in existing or new compounders and recyclers to serve local or regional markets. Both these factors will provide marked monetary and environmental savings in transportation and will simplify supply chain logistics significantly.
- By comparison with the most advanced pyrolysis-based chemical recycling plants, the proposed technology is projected to achieve similar levels of recycling with 25-30% of the CAPEX or, for the same CAPEX, achieve up to a four-fold increase in capacity.
- A significant number of patents and technologies, as well as numerous scientific publications, and commercialization/exploration agreements are expected to result from this project. All three industrial partners are highly committed to taking this technology to market.

Summary

- We aim to develop the capability to recycle continuously more than 80% of polyolefins and polyesters, which would be competitive with chemical recycling in terms of yield, while maintaining the low cost and high-volume advantage of mechanical recycling.

- The proposed technology is:
  - Feedstock agnostic.
  - Easily scalable on local and regional levels.
  - Significantly more efficient, i.e., lower CAPEX and higher capacity, than pyrolysis-based chemical recycling.

- All three industrial partners are highly committed to taking this technology to market.

Quad Chart Overview

Timeline
- *Start date: 06/01/2021*
- *End date: 05/31/2025*

	FY22 Costed	Total Award
DOE Funding	*(10/01/2021 – 9/30/2022)*	*$2,498,539*
Project Cost Share		*$651,145*

TRL at Project Start: 2-3
TRL at Project End: 6

Project Goal
To develop the capability to recycle continuously more than 80% of polyolefins and polyesters in multi-material flexible packaging.

End of Project Milestone
Separated PET and PE upcycling achieved in industrial setting at pre-industrial scale with industrial and domestic waste, at the same levels as the laboratory scale with model systems (TRL 6 achieved).

Funding Mechanism
FOA: DE-FOA-0002245

Topic Area 2: Novel Methods for Deconstructing and Upcycling Existing Plastics.

Project Partners
- Case Western Reserve University (Lead).
- Sandia National Laboratories.
- Lawrence Livermore National Laboratory.
- Braskem USA.
- P&G.
- Resource Material Handling & Recycling.