DOE Bioenergy Technologies Office (BETO) 2023 Project Peer Review

Designing Recyclable Biomass-Based Polyesters

April 4, 2023

Plastic Deconstruction and Resdesign

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University of Wisconsin-Madison

Quad Chart Overview

Timeline

- *Project start date: October 1, 2021*
- Project end date: September 30, 2024

	FY22 Costed	Total Award
DOE Funding	*$643,662*	*$2,500,000*
Project Cost Share *	$201,904	$625,000

TRL at Project Start: 2
TRL at Project End: 4

Project Goal

The overall goal of this project is to design new biomass-based polyesters that have improved thermal or mechanical properties compared to polybutylene adipate terephthalate (PBAT) and also are chemically recyclable and biodegradable.

End of Project Milestone

Demonstrate the production of at least one biomass-based polyester having the environmental, economic targets. .

Funding Mechanism
DE-FOA-0002245

Project Partners*

- University of Oklahoma
- National Renewable Energy Laboratory
- Colorado State
- StoraEnso, Amcor, Pyran

*Only fill out if applicable.

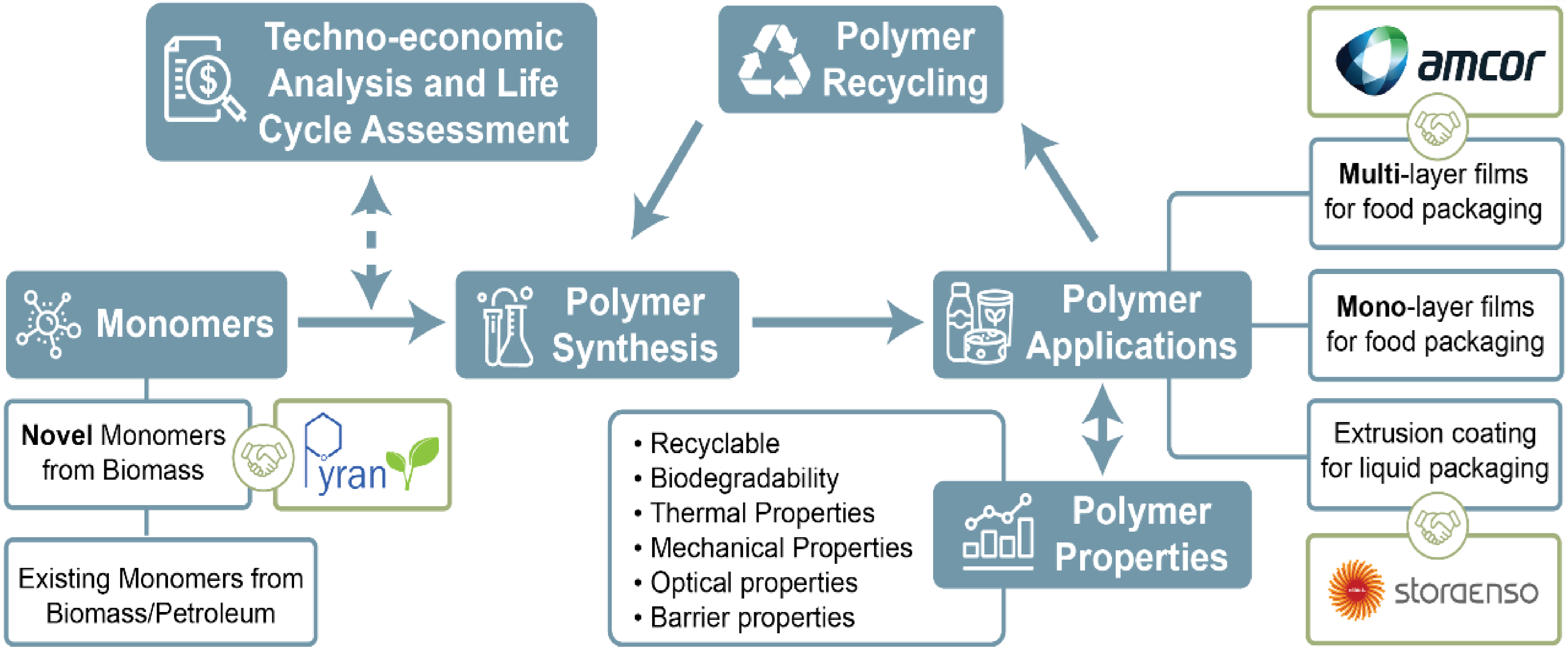
1. Approach: Objectives for BOTTLE Project

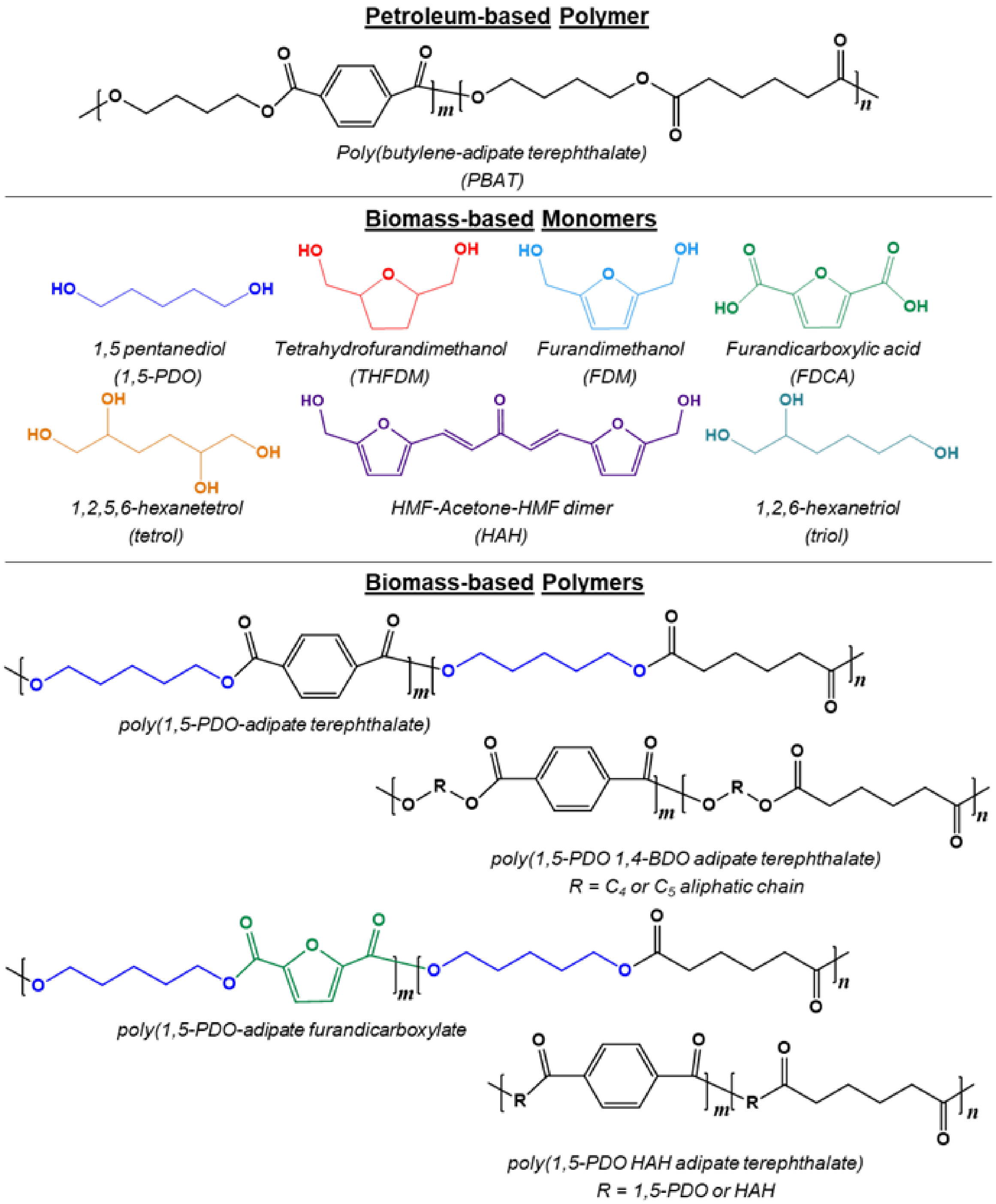
The overall goal of this project is to design **new biomass-based polyesters** that have improved thermal or mechanical properties compared to PBAT and are also chemically recyclable and biodegradable. We will test these polyesters in three different commercial applications.

The goal of this project is to design a new class of polyesters with the following properties:

1. **50 to 70%** lower energy input than conventional petroleum polymers.
2. Biomass based content from **50 to 100 wt%**.
3. Costs **30-50%** lower than PBAT.
4. **60%** biodegradable in 180 days by ASTMD6400.
5. Modulus at least **200 MP**a and elongation at break at least 350% (similar to LDPE and linear-low density poly-ethylene (LLDPE)).
6. Melting temperature **105-115^{o}C** (similar to LDPE and LLDPE).
7. Haze index for a 25 µm film ~10 according to ASTM D1003 (similar to LDPE and LLDPE).
8. O_2 transmission rate equal to or lower than ~8000 $cm^3/(m^2$ day) (LDPE and LLDPE).

1. Approach:
Designing Recyclable Biomass-Based Polyesters





1. Approach

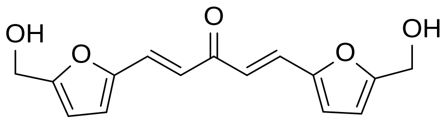
- PBAT is a biodegradable polymer (260 ktons/year) that is sold as a biodegradable polymer (blended with PLA) mainly for agricultural mulching applications.
- PBAT is blended with PLA to improve mechanical properties
- Challenge is that PBAT is expensive and has worse mechanical properties than LDPE requiring more PBAT for the same
- Team has 15+ years in making monomers from biomass.
- Pyran is commercializing the route to produce 15 PDO from biomass.
- StoraEnso is commercializing the route to produce HMF and FDCA from biomass.
- UW has a patent to produce tetrol
- application (up to 50% amount of PBAT)
- Key hypothesis of this proposal is that we will be able to design new types of biodegradable polyaliphatic-polyaromatic polyesters that have improved properties compared to PBAT.

1. Approach: Technical Scope Summary for BOTTLE Project

The project is divided into three budget periods over a **3-year period**.

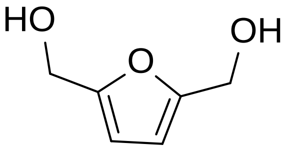
- Budget period 1 (3 months): Verify to the DOE verification team that the information we provided in the proposal is correct. (10/1/2021-1/1/2022)
- Budget period 2 (18 months): Synthesize one new biomass-based polyester that meets the proposed physical and economic targets outlined in this project. (1/1/2022- 8/31/2023)
- Budget period 3 (15 months): Test the biomass-based polyesters in three different commercial applications. (8/31/2023-12/1/2024)

2. Outcomes: Have been able to Synthesize and Purify a Wide Range of Monomers



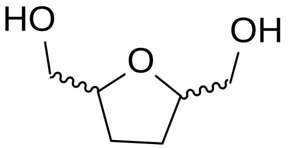
HMF-acetone-HMF dimer (HAH)

➔ 20 g per day in a 1L batch reactor



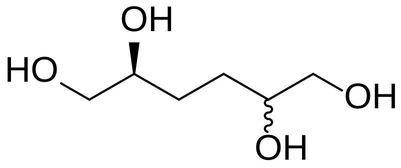
furandimethanol (FDM)

➔ 8 g per day in a 75 ml batch reactor OR 40 g per day in a continuous flow reactor



tetrahydrofuran-dimethanol (THFDM)

➔ 8 g per day in a 75 ml batch reactor OR 40 g per day in a continuous flow reactor



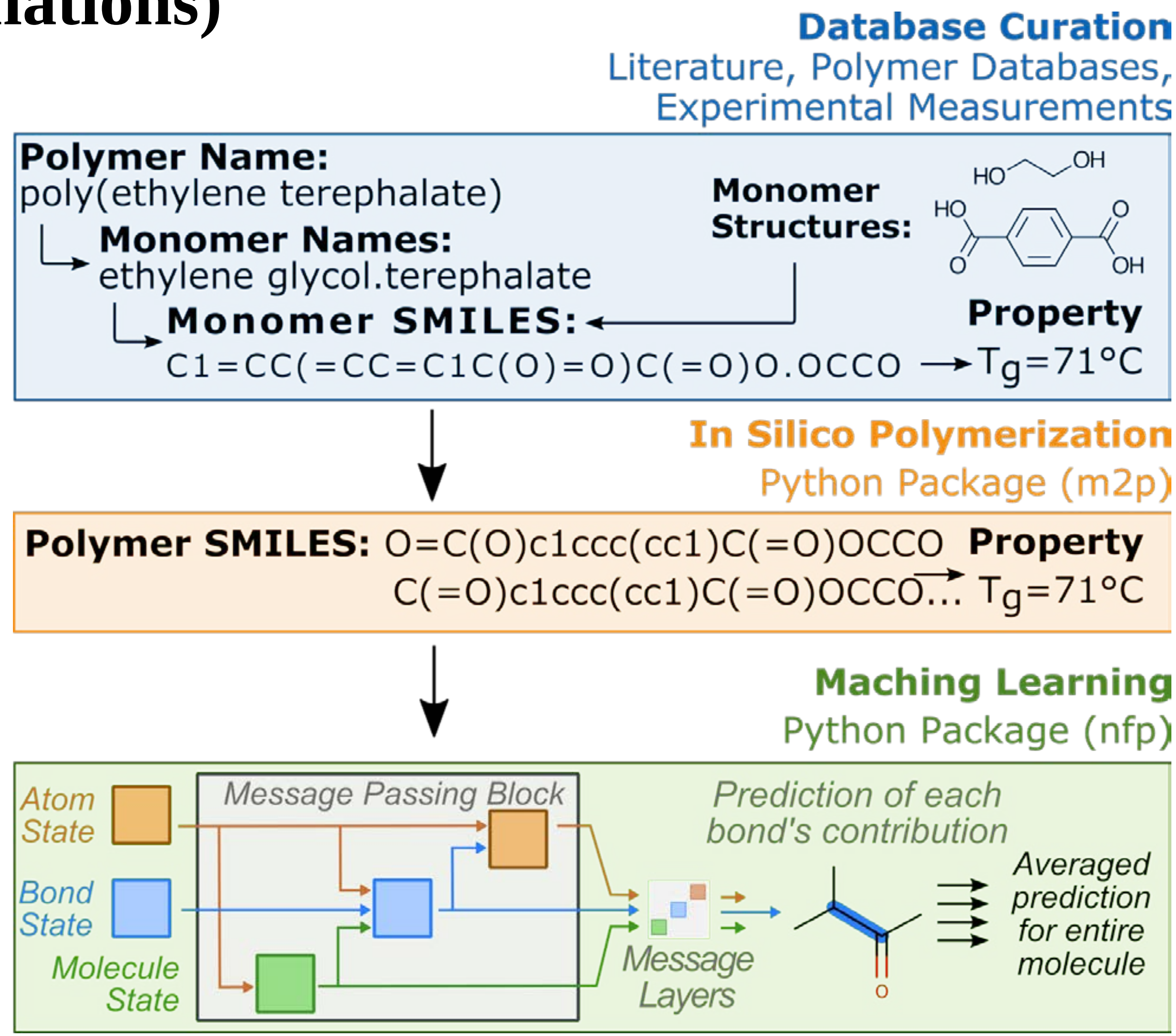
1,2,5,6-hexanetetrol (tetrol)

➔ 300 g of tetrol was synthesized by using a 2L batch reactor

2: Outcomes: We have been using Machine Learning Database (PolyML to screen through Polymer Formulations)

Pipeline Components

- Database - links monomer structure to polymer property (~2,000 unique polymer structures in database)
- Automated, *in silico* structure generation
- Message passing neural network



2: Outcomes: Abbreviations

Monomers = 1,5-pentanediol, adipic acid and furandicarboxylic acid

Polymer = Poly(pentylene adipate-co-furandicarboxylate), **Abberivation = $PPeC_6F_{70}$**

P = Poly

Pe = 1,5-Pentanediol

C_6 = 6 C-atom linear diacid: $HOOC(CH_2)_4COOH$

F_{70} = 70 mole% furandicarboxylic acid (FDCA)

Polymer = Poly(pentylene adipate-co-terephthalic acid), **Abberivation = $PPeC_6T_{60}$**

P = Poly

Pe = 1,5-Pentanediol

C_6 = 6 C-atom linear diacid: $HOOC(CH_2)_4COOH$

T = 60 mole% Terephthalic acid (TPA)

2: Outcomes: FDCA Polymers do not meet the Temperature Specifications

Monomers = 1,5-pentanediol, adipic acid and furandicarboxylic acid

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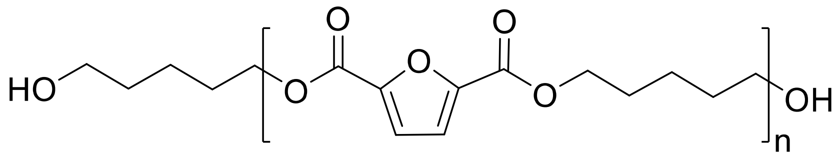
Polymers	**T_g (°C)**	**T_m (°C)**	**T_m-T_g (°C)**
$PPeC_4F_{50}$	-28.4	-	
$PPeC_6F_{50}$	-20.9	46.0	66.9
$PPeC_6F_{70}$	-21.5	44.8	66.3
$PPeC_6F_{90}$	3.7	55.3	59.0
$PPeC_8F_{50}$	-39.3	-	
$PPeC_8F_{70}$	-33.0	44.8	77.8
$PPeC_9F_{50}$	-37.7	-	
$PPeC_{10}F_{50}$	-29.2	-	
$PPeC_{10}F_{70}$	-29.3	46.4	75.7
$PPeC_{12}F_{50}$	-36.0	34.3	70.3
$PPeC_{12}F_{60}$	-32.3	40.5	72.8
$PPeC_{12}F_{70}$	-25.1	38.0	72.8
$PPeC_{12}F_{80}$	-22.07	41.68	60.2
$PPeC_{12}F_{90}$	-4.2	56.0	66.3
PPeF[1]	25	95	70.0
PPeF[2]	24.8/19.6	76.1/66.2	51.3/46.6
PPeF[3]	9.9	66.2	56.7

1) H.Z. Xie, L.B. Wu, B.G. Li, P. Dubois, Biomacromolecules 20 (2019) 353. 2) E. Chen, CSU, data 3) B. Grady OU Data

2: Outcomes: Thermal and Barrier Properties of PPeF by Polycondensation



Poly(pentamethylene furanoate) (PPeF)

PPeF 1

M_n = 20.9 kg/mol
M_w = 35.7 kg/mol
$Đ$ = 1.7

T_d = 341 °C

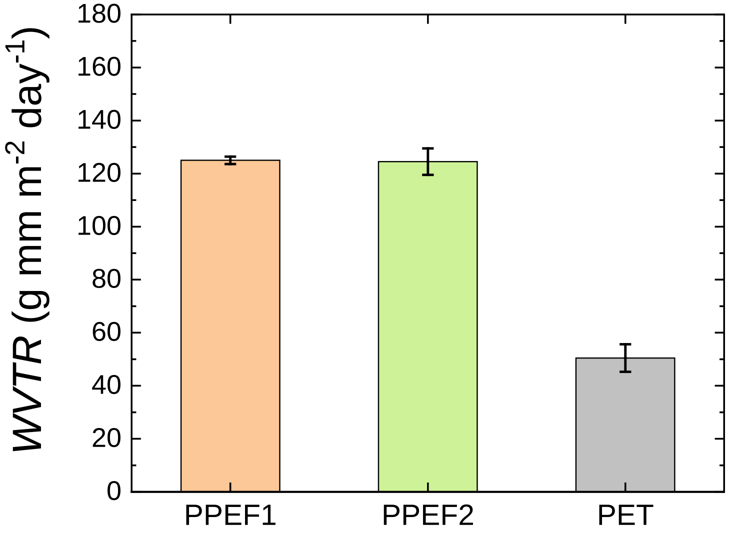
T_g = 24.8 °C
T_m = 76.1 °C
ΔH_m = 28.5 J/g

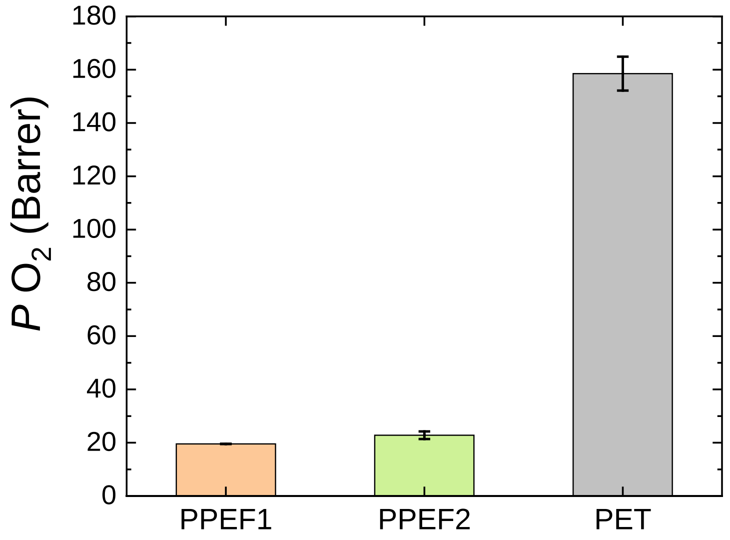
PPeF 2

M_n = 26.9 kg/mol
M_w = 37.8 kg/mol
$Đ$ = 1.4

T_d = 345 °C

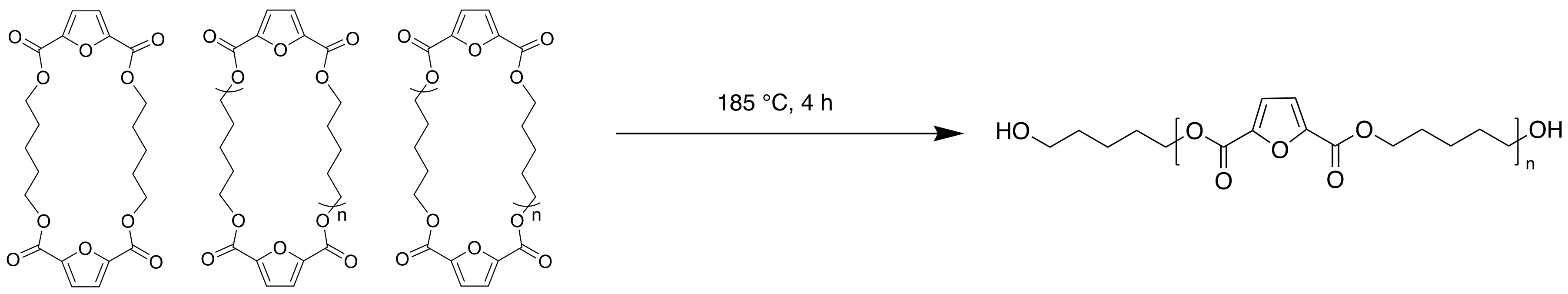
T_g = 19.6 °C
T_m = 66.2 °C
ΔH_m = 31.3 J/g





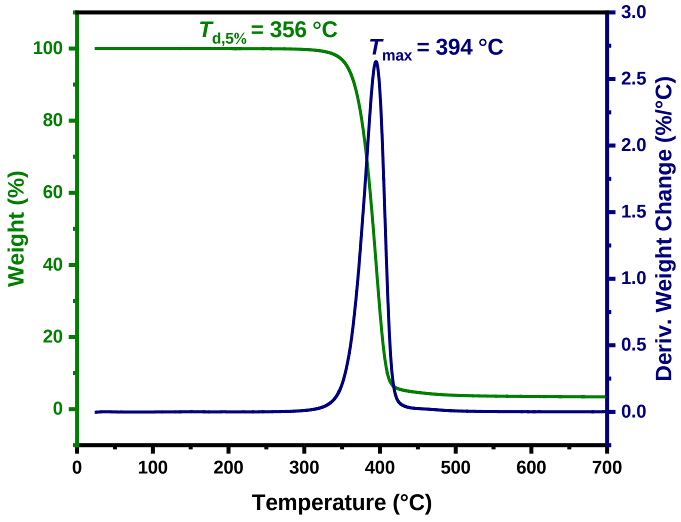
- PPeF showed ~ 8-fold improvement in oxygen barrier over PET
- PPeF, with elongation at break > 1000%, is much more flexible than both PEF and PET

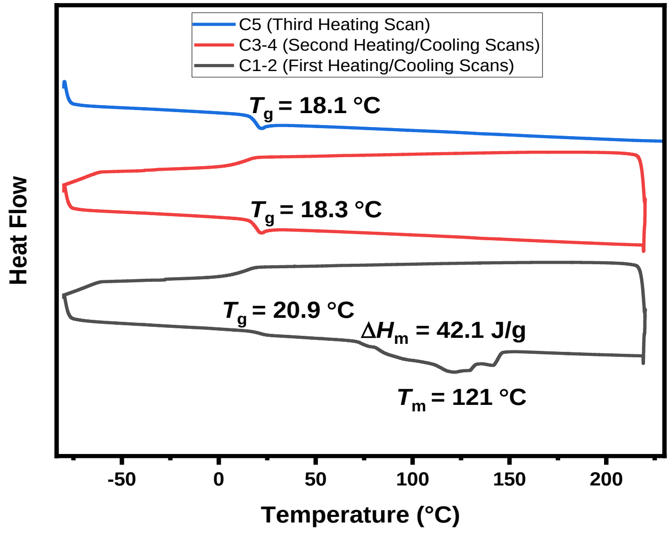
2: Outcomes: Chain-growth ring-opening polymerization route to PPeF



C1 **C2**, n = 2 **C3**, n = 3

Structurally characterized





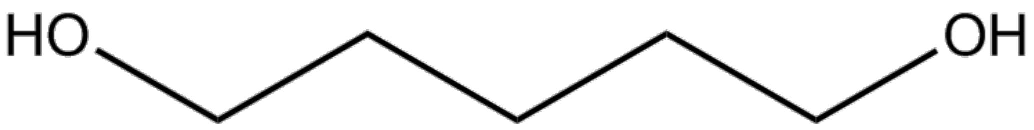
- Solvent free, melt polymerization
- High T_m PPeF was achieved
- Depolymerization reforms cyclic macromers C1, C2, and C3
- Potential pathway for chemical circularity

PYRAN

2:Outcomes

Cost advantaged

- High molar yields (over 85% for entire process)
- Cheap and stable catalysts
- Low separation costs



1,5-Pentanediol (1,5-PDO)

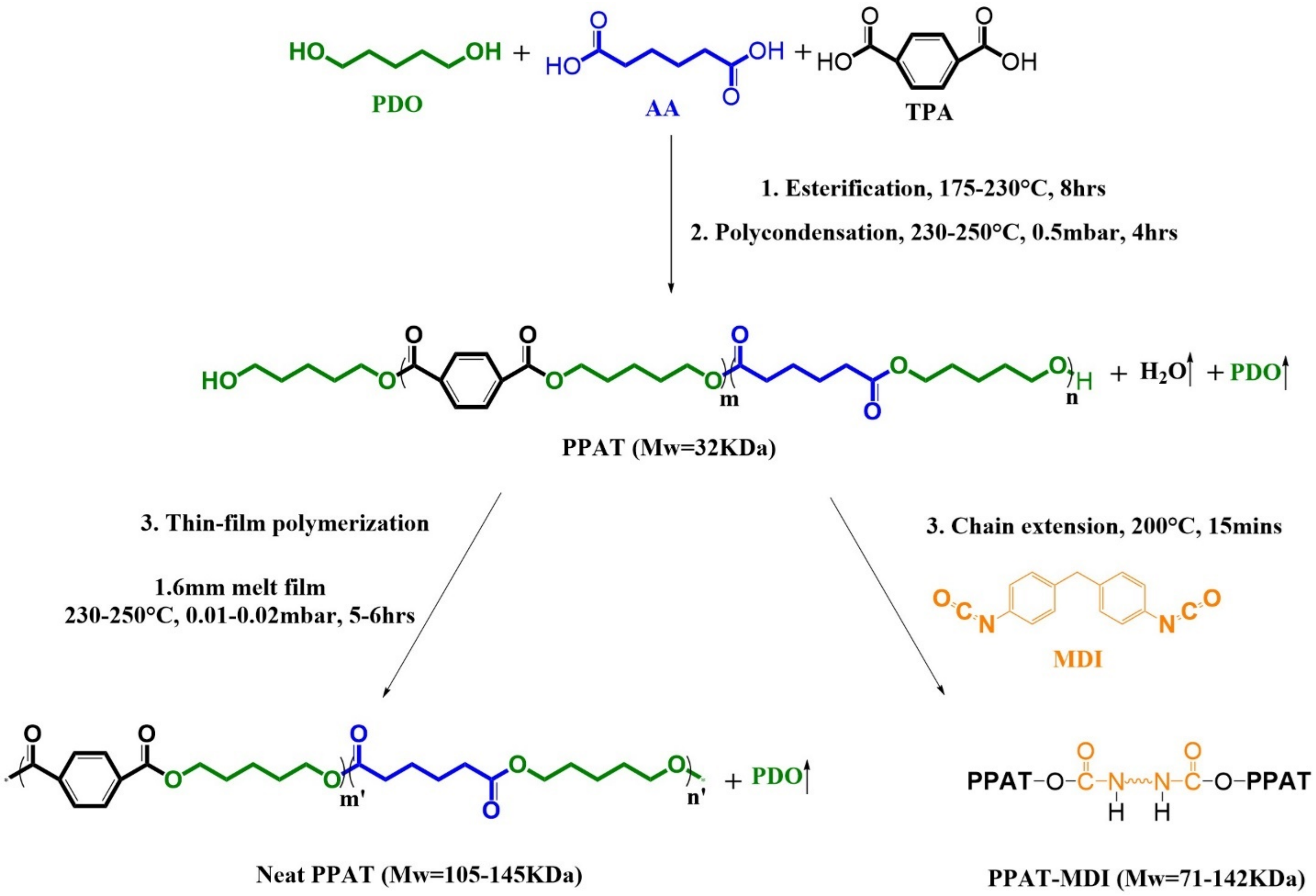
Clean and Renewable

- Clean process – no byproducts, only wastewater treatment
- Renewable biomass-derived feedstock (furfural)
- Over 60% reduction in greenhouse gases (GHGs)

www.pyranco.com

kjbarnett@pyranco.com

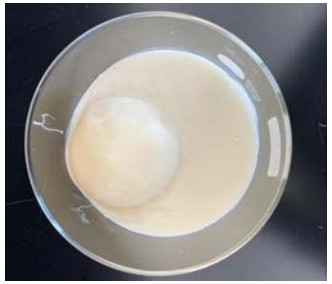
2 Outcomes: Synthesis of $PPeC_6T$ (PPAT)



Biomass content $PPeC_6T$ = 42% if only PDO is from biomass

Lei Zheng, Min Soo Kim, Shu Xu, Meltem Demirtas, George W Huber, John Klier, Biodegradable high molecular weight poly (pentylene adipate-co-terephthalate): synthesis, thermo-mechanical properties, microstructures, and biodegradation (submitted)

2 Outcomes: $PPeC_6T_{60}$ Meets Temperature Specification



$PPeC_6T_{60}$

$PPeC_6T_{60}$
0.3 % Glycerol

$PPeC_6T_{60}$
0.5 % 1,2,5,6-Hexanetetrol

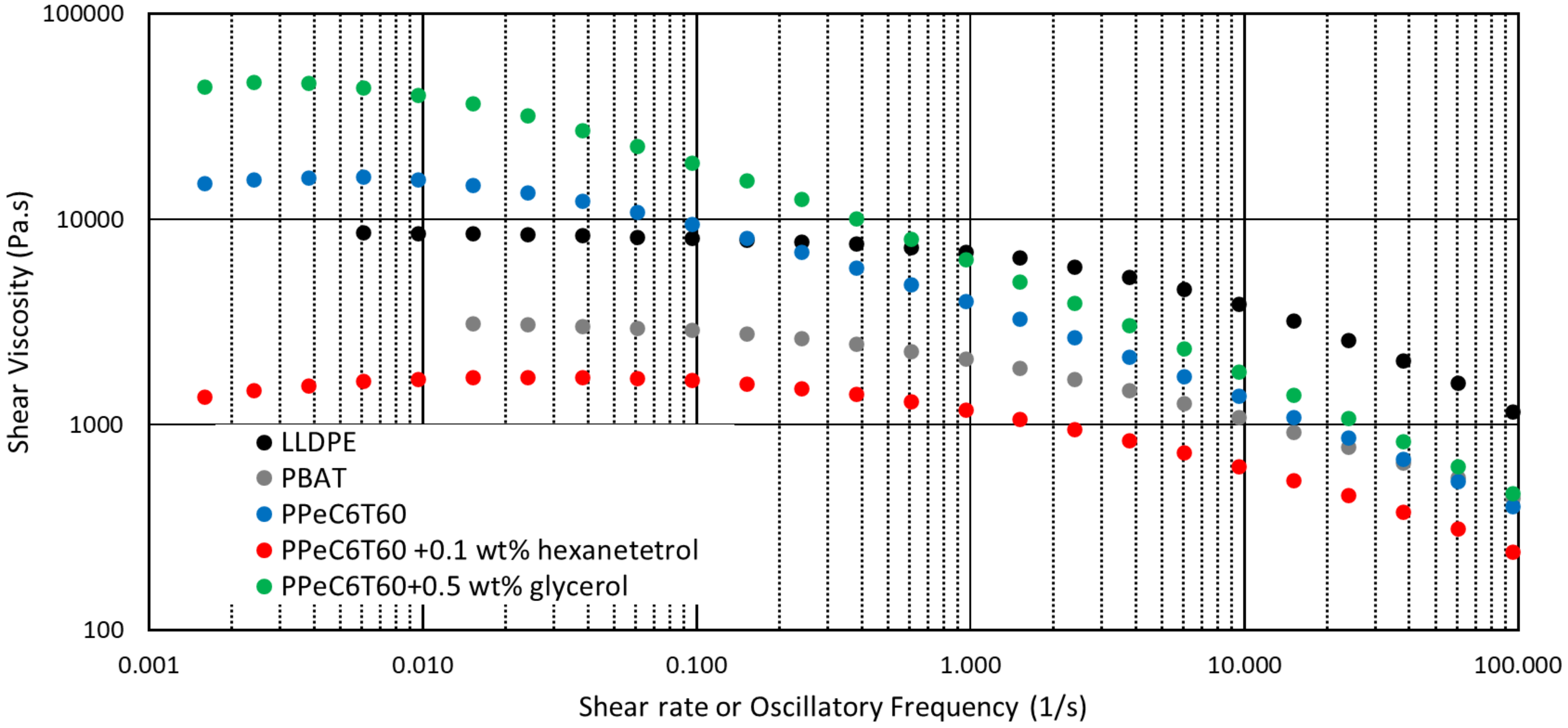
Polymers	T_g (°C)	T_m (°C)	T_m-T_g (°C)	M_n	M_w
$PPeC_6T_{60}$	-29.1	82.1	114.7	19947	24047
$PPeC_6T_{70}$	-17.1	96.1	113.2	20710	25375
$PPeC_6T_{60}$	-9.1	100.8	109.9	106450	188553
$PPeC_6T_{60}$ + 0.5% Glycerol	-13.3	88.4	101.7	99605	156611
$PPeC_6T_{60}$ + 0.1% 1,2,5,6-Hexanetetrol	-11.4	99.1	110.5	88433	141278
PBC_6T_{50} (PBAT)	-30	125	155	97848	148803

May want to reduce slightly T percentage to ~50 to reduce T_g

2 Outcomes: $PPeC_6T_{50}$ has 75% Higher Modulus of Elasticity Than PBAT

Samples	E (MPa)	δ_y (MPa)	ε_y (%)	δ_b (MPa)	ε_b (%)
$PPeC_6T_{60}$	140	11	18	30	801
$PPeC_6T_{60}$+ 0.5% Glycerol	127	10	14	24	782
$PPeC_6T_{60}$+ 0.1% 1,2,5,6-Hexanetetrol	140	10	13	17	615
PBAT=PBC_6T_{50}	79	/	/	26	842
LLDPE	201	11	69	31	694

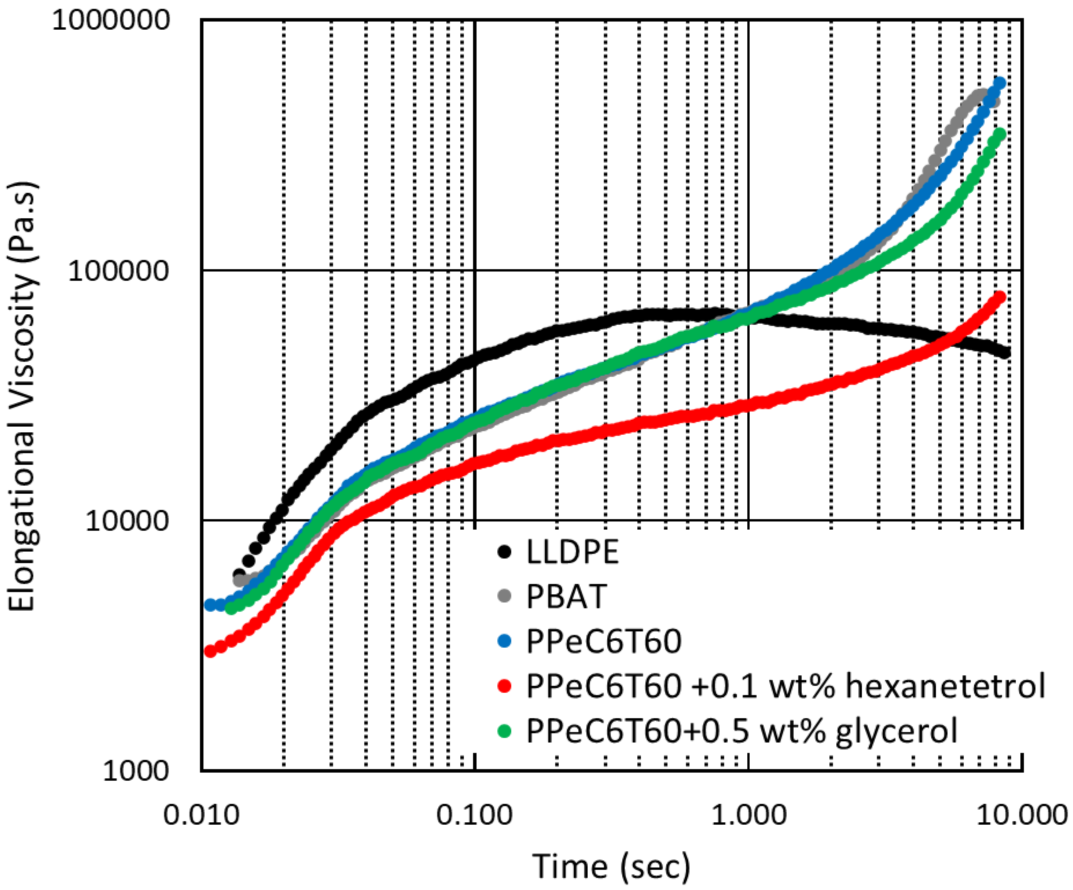
2. Outcomes: Shear Rheology Comparison at 190°C



2 Outcomes: Extensional Viscosity at 130°C and 0.3 s^{-1}

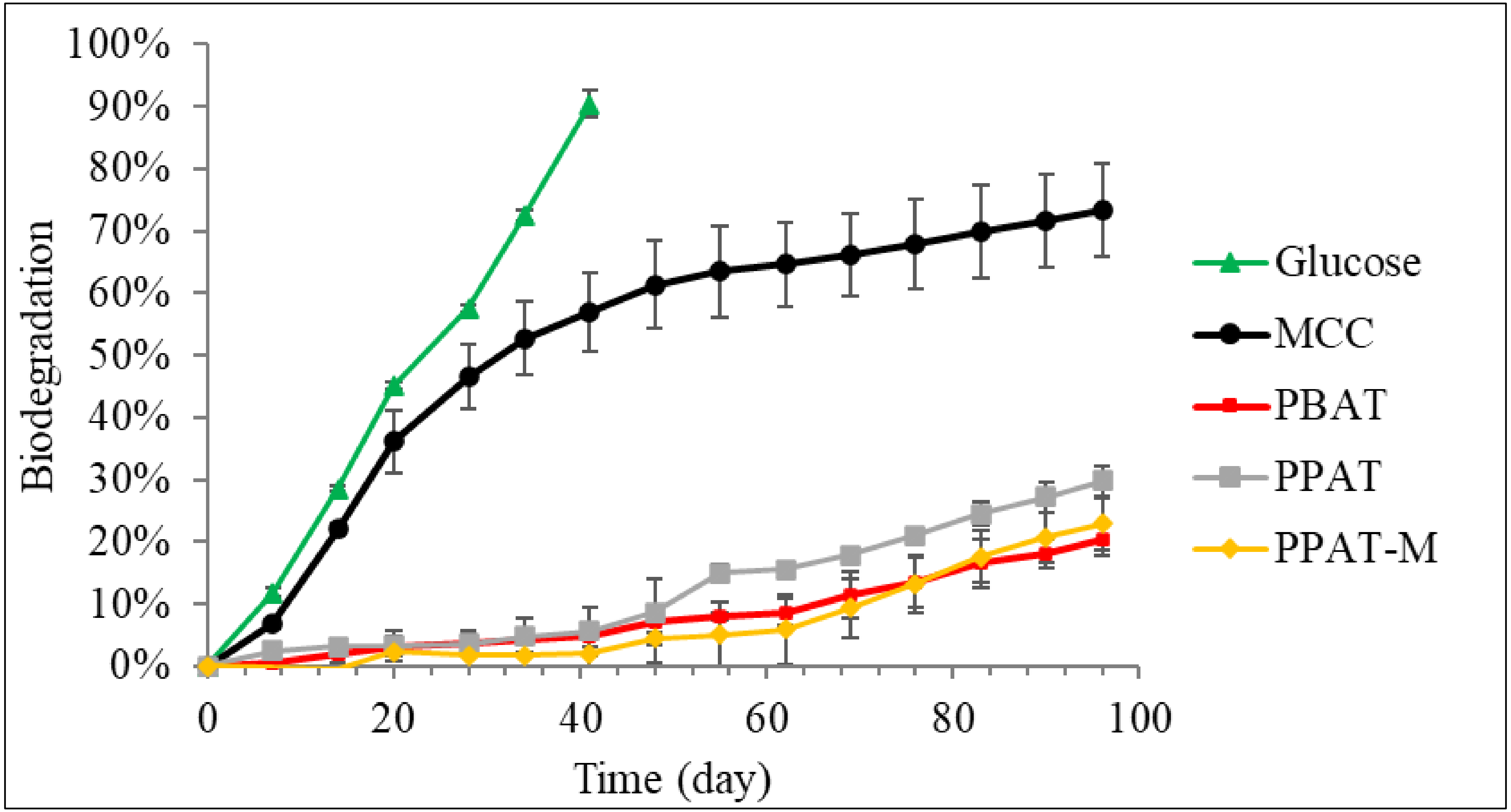
(Value at Hencky strain of 2.5)*

Samples	η_E (Pa*s)
$PPeC_6T_{60}$	562294
$PPeC_6T_{60}$+ 0.5% Glycerol	350234
$PPeC_6T_{60}$+ 0.1% 1,2,5,6-Hexanetetrol	78102
PBAT=PBC_6T_{50}	349278
LLDPE	46833



*A Hencky strain of 2.5 at an elongational rate of 0.3 s^{-1} were found to be representative values for the film blowing (Härth and Dörnhöfer, Polymers 2020, 12, 1605)

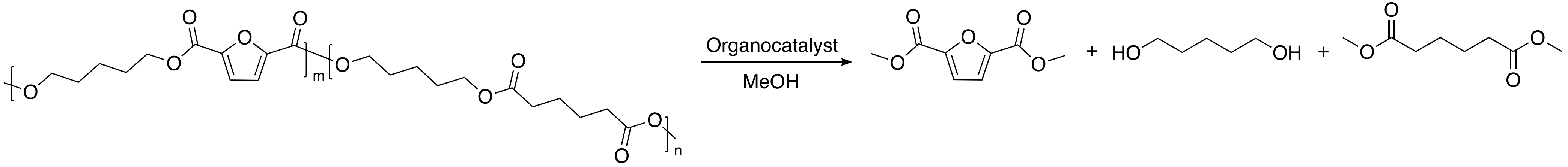
2 Outcomes: $PPeC_6T$ or PPAT has similar soil and aquatic biodegradability as PBAT



Lei Zheng, Min Soo Kim, Shu Xu, Meltem Demirtas, George W Huber, John Klier, Biodegradable high molecular weight poly (pentylene adipate-co-terephthalate): synthesis, thermo-mechanical properties, microstructures, and biodegradation (submitted)

2 Outcomes: Methanolysis as a recycling strategy

Sample depolymerization reaction:

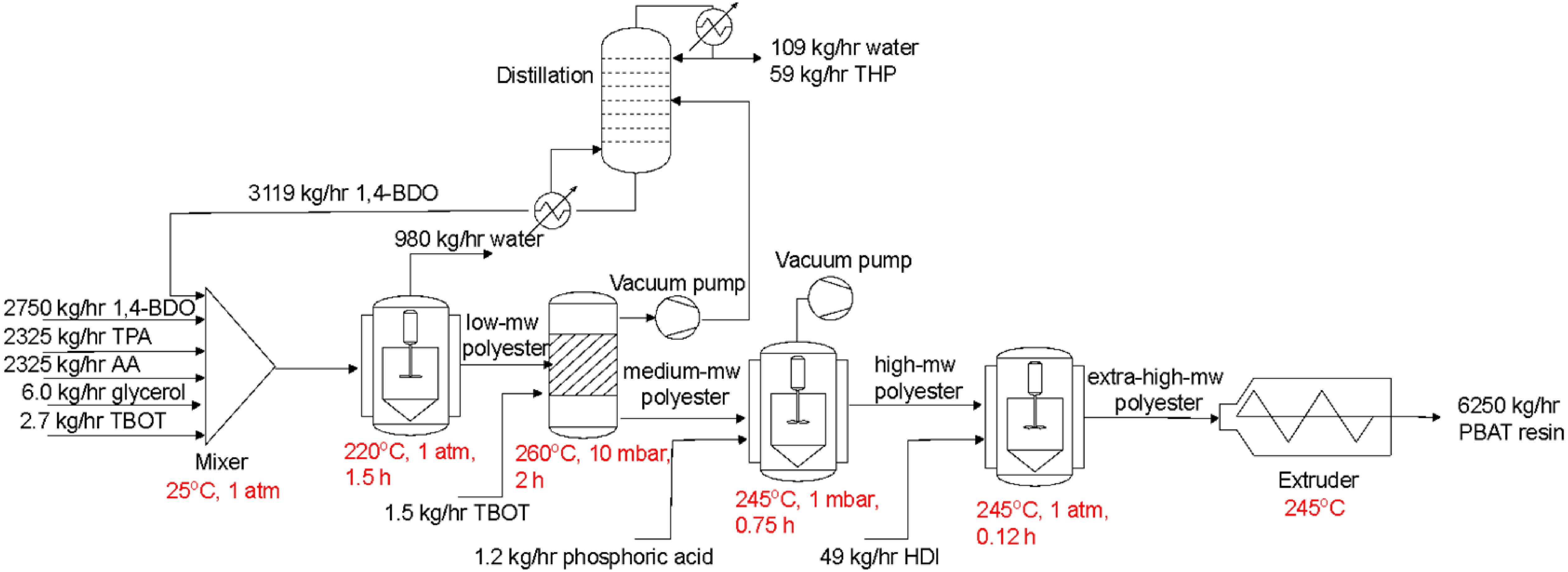


Analytical Strategy: Quantify monomer products by a combination of HPLC-UV and HPLC-MS with instruments that already exist at NREL

Reaction progress can also be assessed by NMR spectroscopy and GPC analysis of reaction samples

2 Outcomes: Process Flow Diagram for PBAT

(Basis: 50,000 tons/year)



Witt, U. ;Yamamoto, M., *Method for the continuous production of biodegradable polyesters (US9040639B2).* **2015**

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The goal of this project is to design a new class of polyesters with the following properties:

1. **50 to 70%** lower energy input than conventional petroleum polymers. (currently >26% lower if PDO from biomass more if TPA and AA come from biomass)
2. Biomass based content from **50 to 100 wt%**. (Currently 22% with PDO from biomass and other monomers from petroleum more if TPA and AA come from biomass)
3. Costs **30-50%** lower than PBAT. (Currently >25% lower depending on scale)
4. **60%** biodegradable in 180 days by ASTMD6400.
5. Modulus at least **200 MP**a and elongation at break at least 350% (similar to LDPE and linear-low density poly-ethylene (LLDPE)). (140% improvement compared to PBAT)
6. Melting temperature **105-115^{o}C** (similar to LDPE and LLDPE). (95-105 C)
7. Haze index for a 25 µm film ~10 according to ASTM D1003 (similar to LDPE and LLDPE). (working on testing)
8. O_2 transmission rate equal to or lower than ~8000 $cm^3/(m^2$ day) (LDPE and LLDPE).

3 – Impact

- Creating new biomass-based biodegradable polymers
- Have improved economics and environmental impacts compared to existing biodegradable PBAT/PLA bledns
- Provide new markets for biomass- monomers
- Finding new applications for bio-based polymers (improved barriers, biodegradability)

Additional Slides

Responses to Previous Reviewers' Comments

- No previous comments

Publications, Patents, Presentations, Awards, and Commercialization

- Lei Zheng, Min Soo Kim, Shu Xu, Meltem Demirtas, George W Huber, John Klier, Biodegradable high molecular weight poly (pentylene adipate-co-terephthalate): synthesis, thermo-mechanical properties, microstructures, and biodegradation (submitted)
- MS Kim, Hochan Chang, Lei Zheng, Qiang Yan, Brian F Pfleger, John Klier, Kevin Nelson, Eric L. –W Majumder, George W. Huber, A Review of Biodegradable Plastics: Chemistry, Applications, Properties and Future Research Needs, (submitted)
- Raka G Dastidar, Min Soo Kim, Panzheng Zhou, Zaneta Luo, Changxia Shi, Kevin J Barnett, Daniel J McClelland, Eugene Y-X Chen, Reid C Van Lehn, George W Huber, Catalytic production of tetrahydropyran (THP): a biomass-derived, economically competitive solvent with demonstrated use in plastic dissolution, Green Chemistry, (2022) 24,23, 9101-9113.

Task	Year 1				Year 2				Year 3			
	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
Task 1: Initial Verification												
M1.1-1.3: Verification of synthesis, biomass-monomers and PolyML												
M1.4: DOE verification of experimental data process models from proposal **(Go/No-Go/SMART)**												
Task 2: Synthesis/characterization of polyesters												
M2.1.1:Properties 1,5-PDO polyesters with PolyML												
M2.1.2, M2.1.3: Synthesis of 1,5-PDO polyesters **(SMART)**												
M2.1.4 - M2.1.8: Properties of 1,5-PDO polyesters												
M2.2.1: Properties of THFDM, HAH, FDM polyesters with PolyML												
M2.2.2, M2.2.3: Synthesis of THFDM/FDM + TPA + AA and THFDM/FDM + FDCA												
M2.2.4-M2.2.8:Properties THFDM/FDM polyesters												
M2.3: Improve accuracy of PolyML.												
M2.4: Identify the least expensive biomass-based polyester compared to PBAT and optimal properties for film applications **(Go/No-Go/SMART)**												
Task 3: Chemical Recycling of Polyesters												
M3.1.1, M3.1.2: Recycling of up to 80% of 1,5-PDO polyesters back into monomer components **(SMART)**												
M3.2.1, M3.2.2: Recycling of up to 80% of THFDM, FDM polyesters back into monomer components												
Task 4: TEA and LCA												
M4.1-4.2: TEA and LCA model for production and recycling of 1,5-PDO derived polyesters												
M4.3- M4.4: TEA and LCA model for THFDM/FDM derived polyesters and recycling												
Task 5: Scaling of Polyester and Application												
M5.1, M5.2: Scaling polyester to 2.5 kg/week												
M5.3-M5.5: Testing of biomass-derived polyester in 3 applications												
M5.6, M5.7: Refined TEA and LCA.												
End of Project Goals: M 5.1-M5.7 Write publication, patents, DOE final report. **(SMART)**												

Go/No-Go Ongoing Work Task Duration