DOE Bioenergy Technologies Office (BETO) 2023 Project Peer Review

Highly Recyclable Thermosets for Lightweight Composites

April 4, 2023
Technology Area Session

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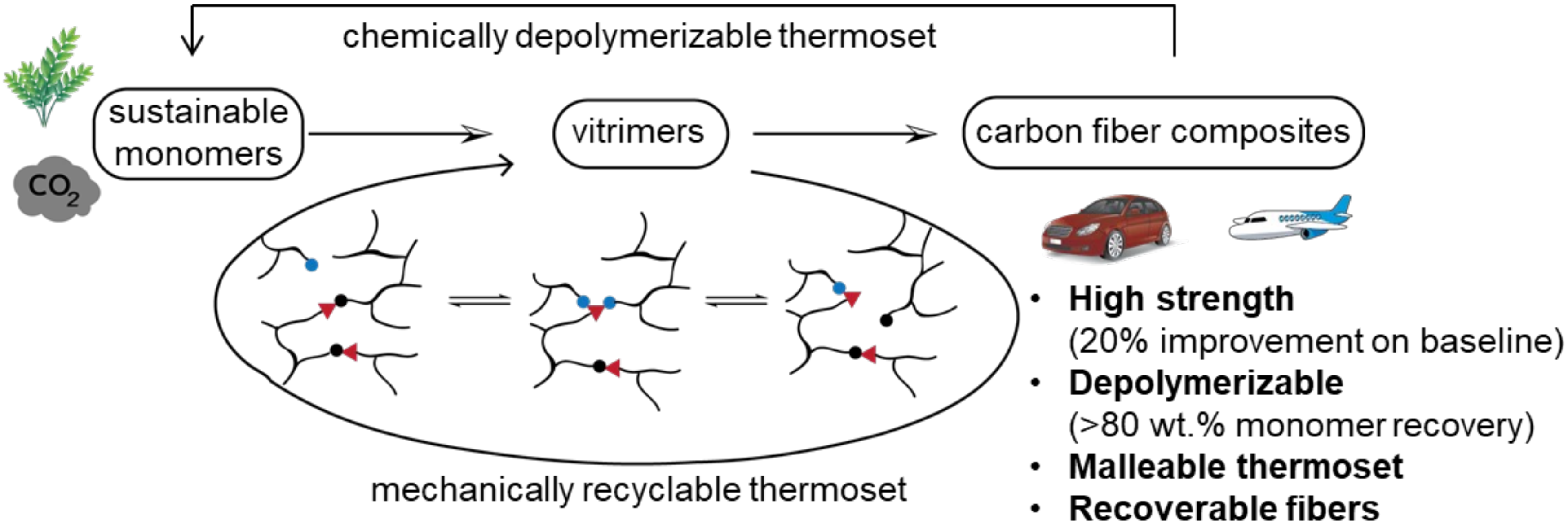
University of Akron

Project Overview



Project goals:

- Preparing thermosets from CO_2-based materials
- Demonstrating the mechanical recycling of thermoset
- Demonstrating the chemical depolymerization of thermosets and carbon fiber recovery
- Modeling the cost and carbon footprints of circular composites

The University of Akron 1870 · Pacific Northwest National Laboratory · Raytheon Technologies

Project Overview

Highly recyclable CFRP

Initial verification (months 0-3)

collaborate on verification report with DOE

Highly recyclable CFRP (months 4-21)

Show >90% of tensile strength retained after recycling

Optimized CFRP (months 22-36)

1. Initial verification

2. Vitrimer testing

3. Prepare recyclable composite materials

4. Composite testing

5. Sustainability analysis

6. Optimize light weight fiber composite

7. Optimize material recycling

8. Comparative analysis

9. Establish market transformation and manufacturing plan

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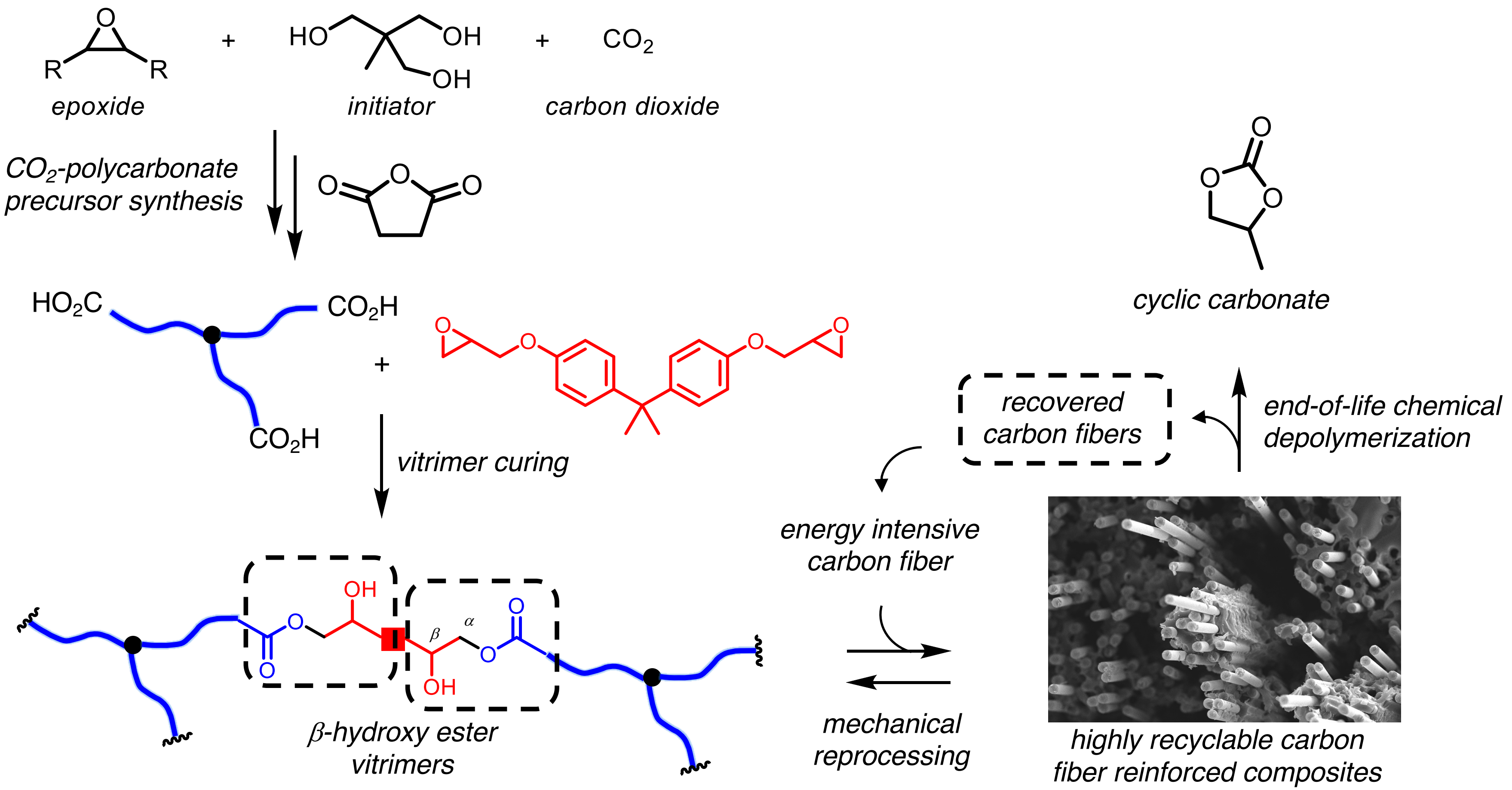
1 – Approach

Technical approach



highly recyclable carbon
fiber reinforced composites

1 – Approach

Potential challenges

- *Long cure time of vitrimer matrix may not be practical for commercialization*
- *High viscosity of the precursor inhibits efficient impregnation of carbon fiber mat*

Go/No-Go decision points

- *Establishing baseline glass transition temperatures and mechanical properties of polyether β-hydroxy vitrimers*
- *Show >90% of tensile strength retained after catalyst-free re-molding*
- *Within 20% of tensile strength and offering 50% cost savings compared with epoxy material*

1 – Approach

Risk analysis and mitigation strategies

- *Risk: Depolymerization under cure or process conditions is a possible risk.*
- *Mitigation: Optimized formulation and processing window to improve thermal stability.*
- *Risk: Cost of the synthesis and material preparation might exceed the target.*
- *Mitigation: Feedback loop strategy has used technoeconomic analysis to identify cost-intensive processes.*

1 – Approach

UA
Matrix synthesis and characterization

PNNL
Composite preparation and testing

RTX
Sustainability analysis

Communication and collaboration

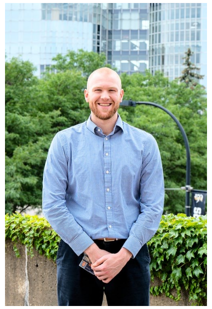
- *Biweekly teamwide research update meeting*
- *Monthly report meeting with the DOE project manager*
- *Regular project meetings on specific tasks, e.g., vitrimer testing, composite preparation, sustainability analysis.*
- *Shared data and documents among the team*

Student participants

Satej Joshi

Seiyoung Yoon

Sophia Aracri



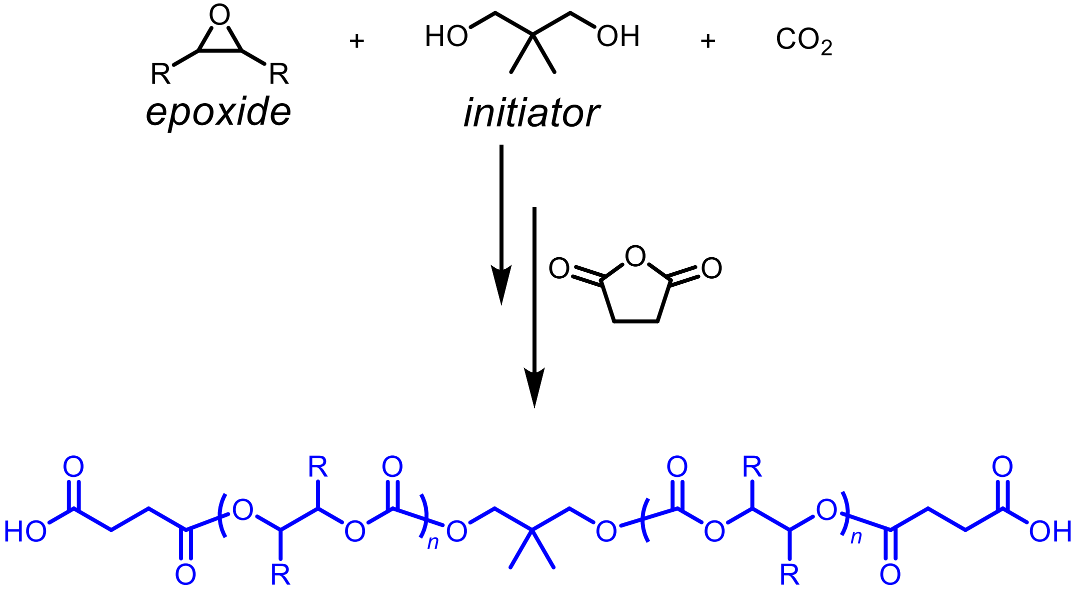
Derek Schwarz

Yuliana Ospina Yepes

Kamrul Hasan

2 – Progress and Outcomes

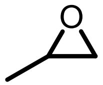
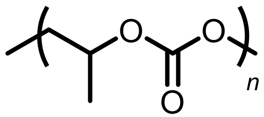
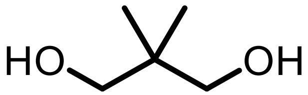
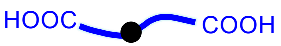
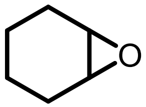
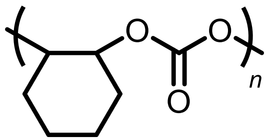
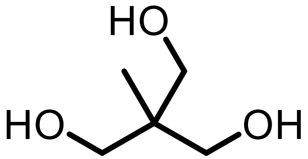
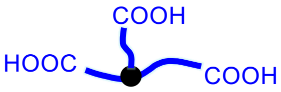
Synthesis of polycarbonate precursor



The polycarbonate glass transition temperature and functionality can be controlled through monomer and initiator choice, respectively.

Variable thermal properties:

Multifunctional architectures:

<u>*epoxide*</u>	<u>*polycarbonate*</u>	<u>*initiator*</u>	<u>*functionality*</u>
	 **T_g = 16 °C**		 *bifunctional*
	 **T_g = 80 °C**		 *trifunctional*

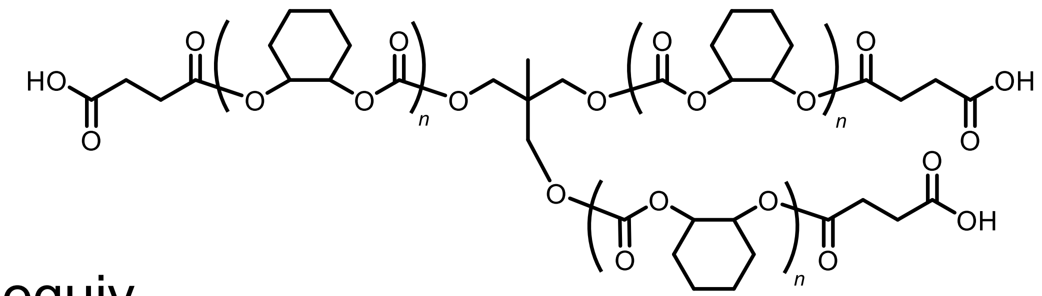

PPC


PCHC

2 – Progress and Outcomes

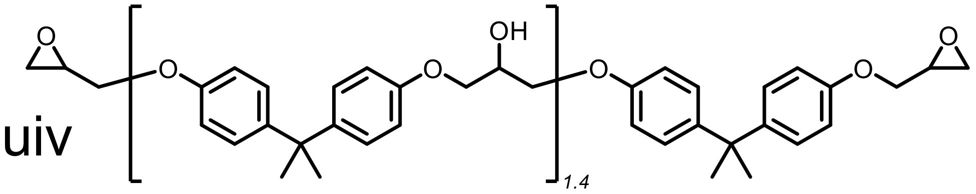
Vitrimer preparation

curing at 150 °C for 4 h



1 equiv

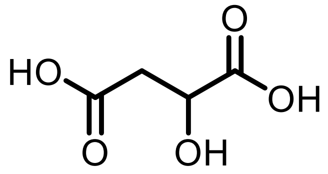
acid functionalized polycarbonate



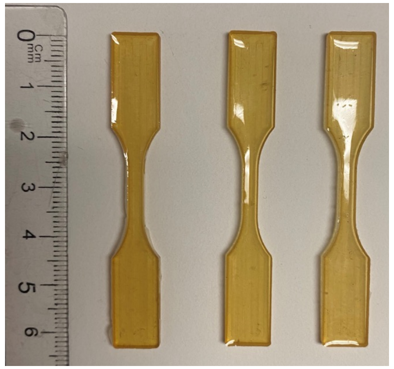
3 equiv

epoxide linker

1 equiv



bio-based acid



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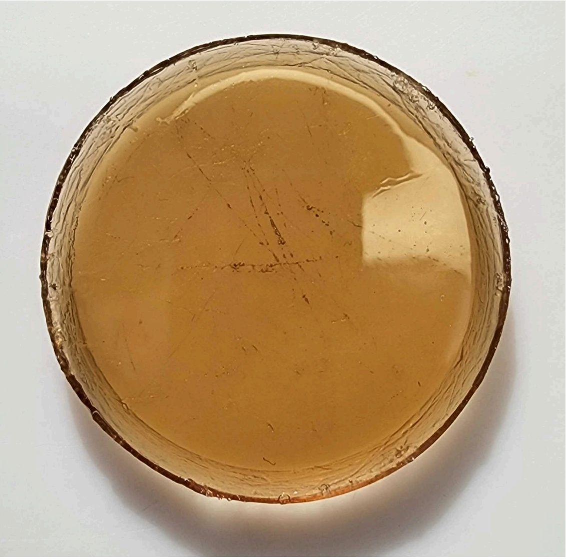
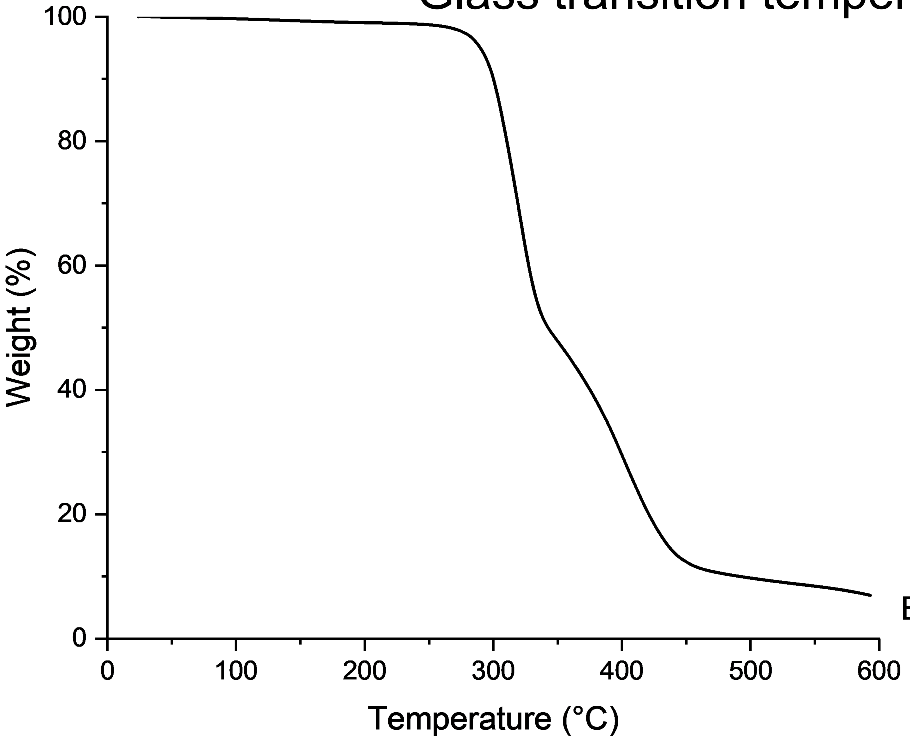
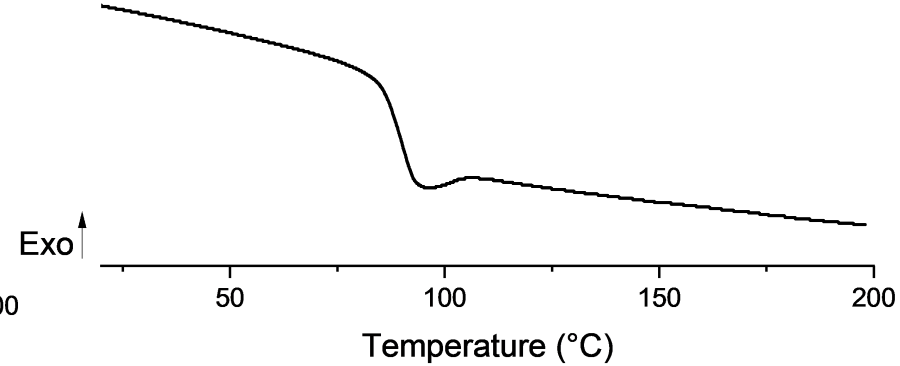
2 – Progress and Outcomes

Thermal properties of vitrimer

- 5% Thermal decomposition temperature from TGA is 290 °C
- Glass transition temperature is 89 °C

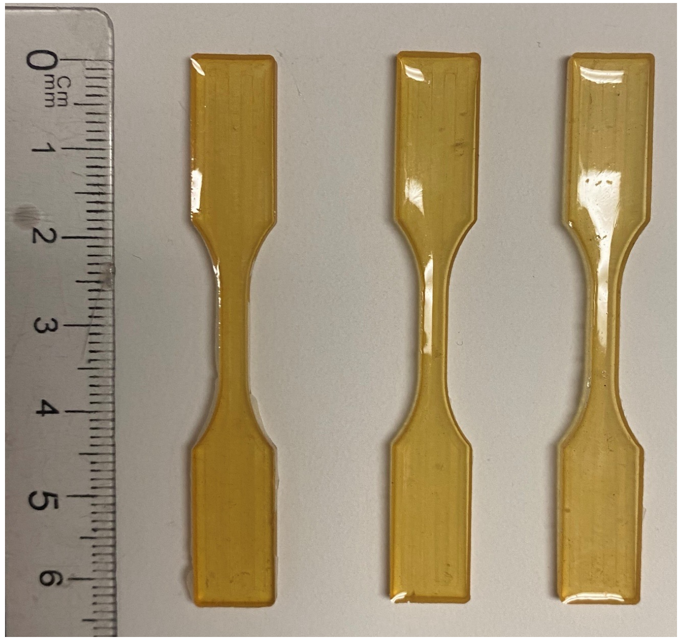


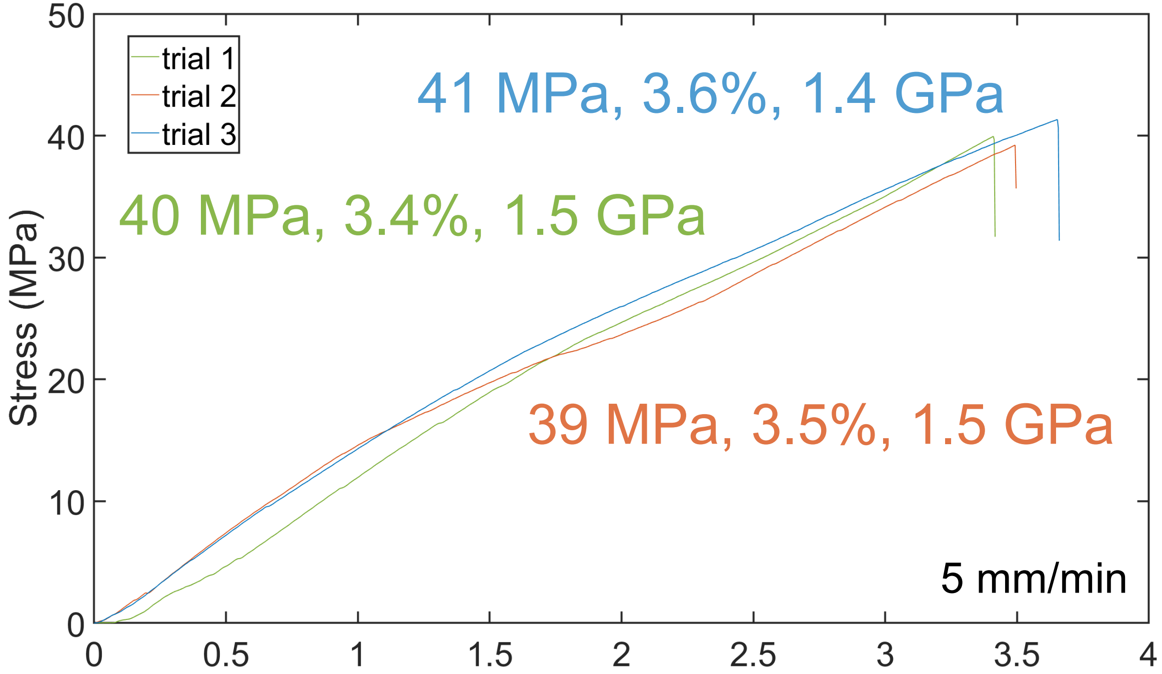




2 – Progress and Outcomes

Tensile properties of vitrimer

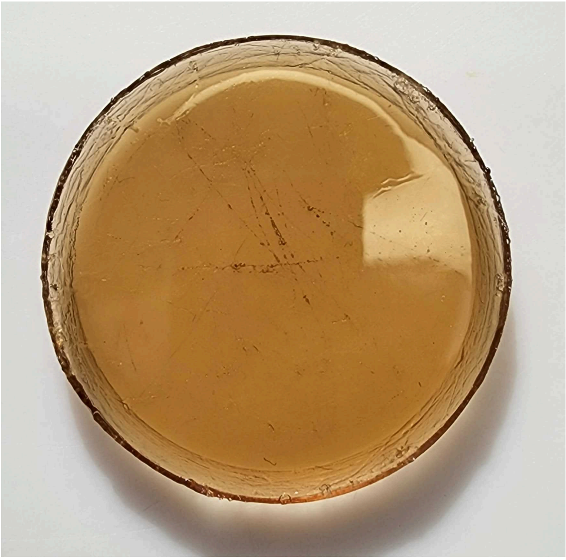


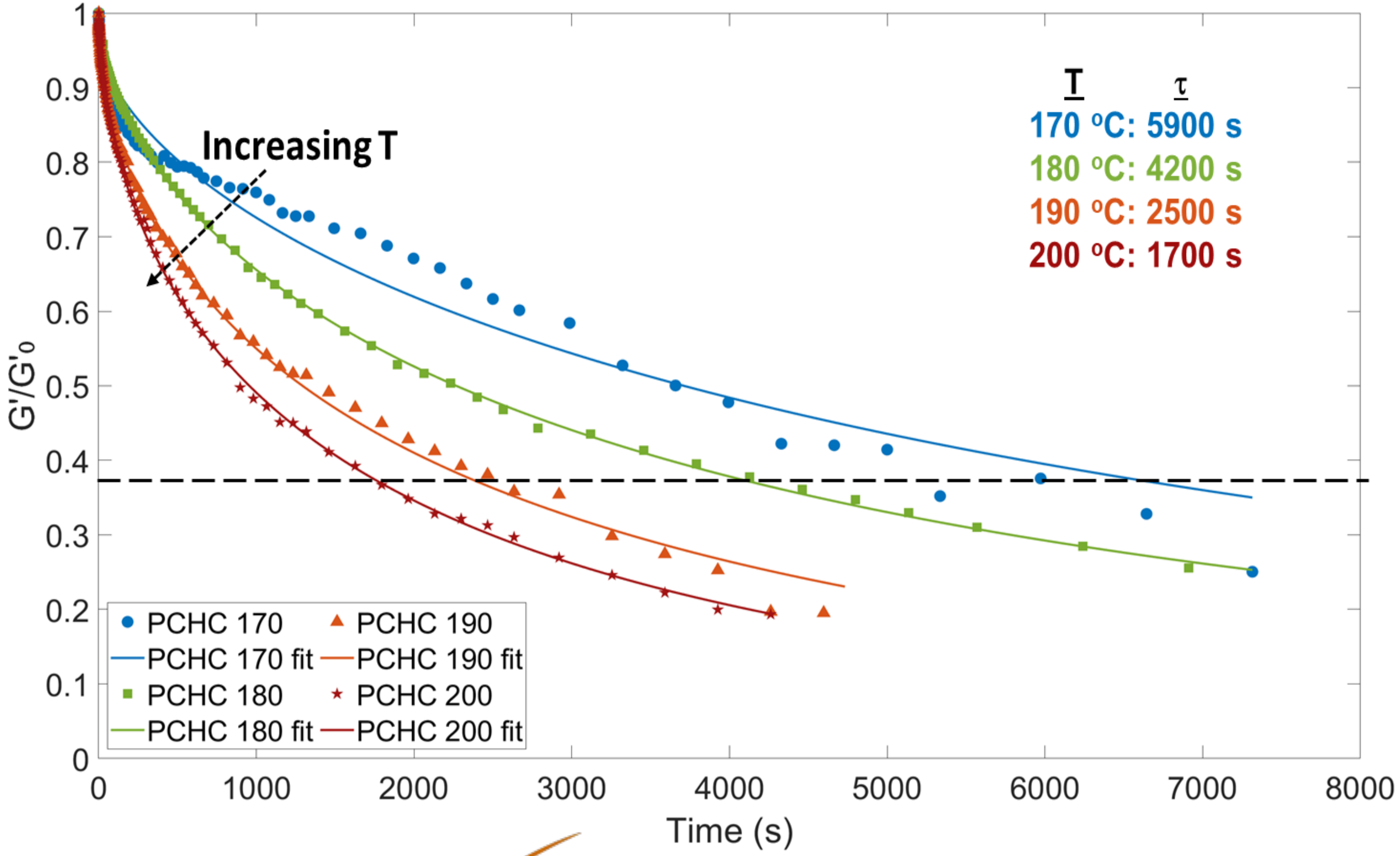


	Young's modulus (GPa)	tensile strength (MPa)
polypropylene	1-1.4	25-38
polycarbonate vitrimer	**1.5 ± 0.07**	**40 ± 1**

2 – Progress and Outcomes

Characteristic time for stress relaxation determined





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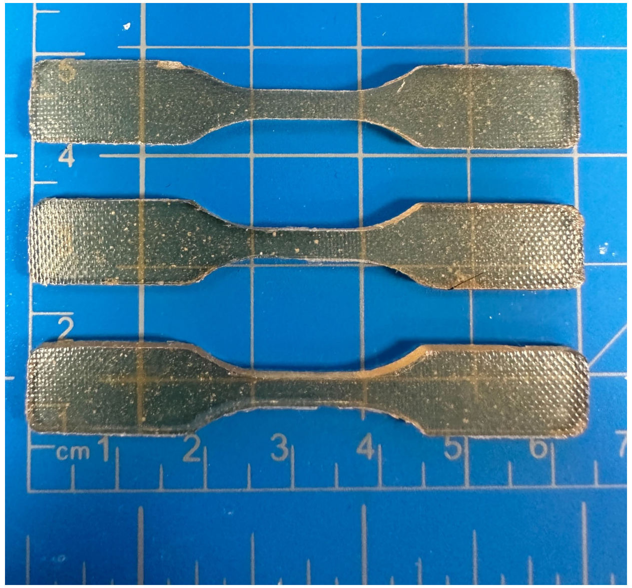
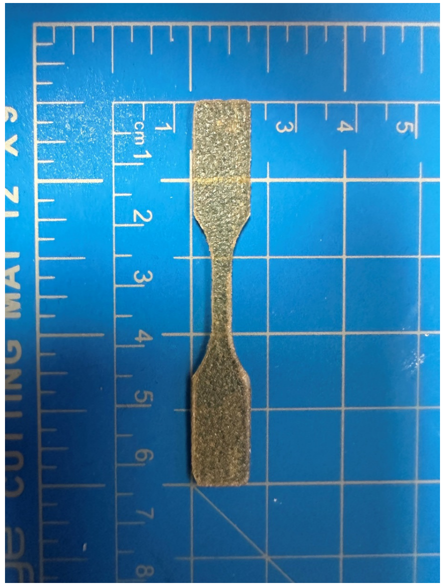
2 – Progress and Outcomes

Reprocessing



2 mm thick sample was prepared after curing at 150 °C for 8 h.
Gel fraction = 96%

Sample was ground into coarse particles via ball mill grinding for 1.5 min



Sample was reprocessed to 1.5 mm thick sample after compression molding at 160 °C for 4 h.

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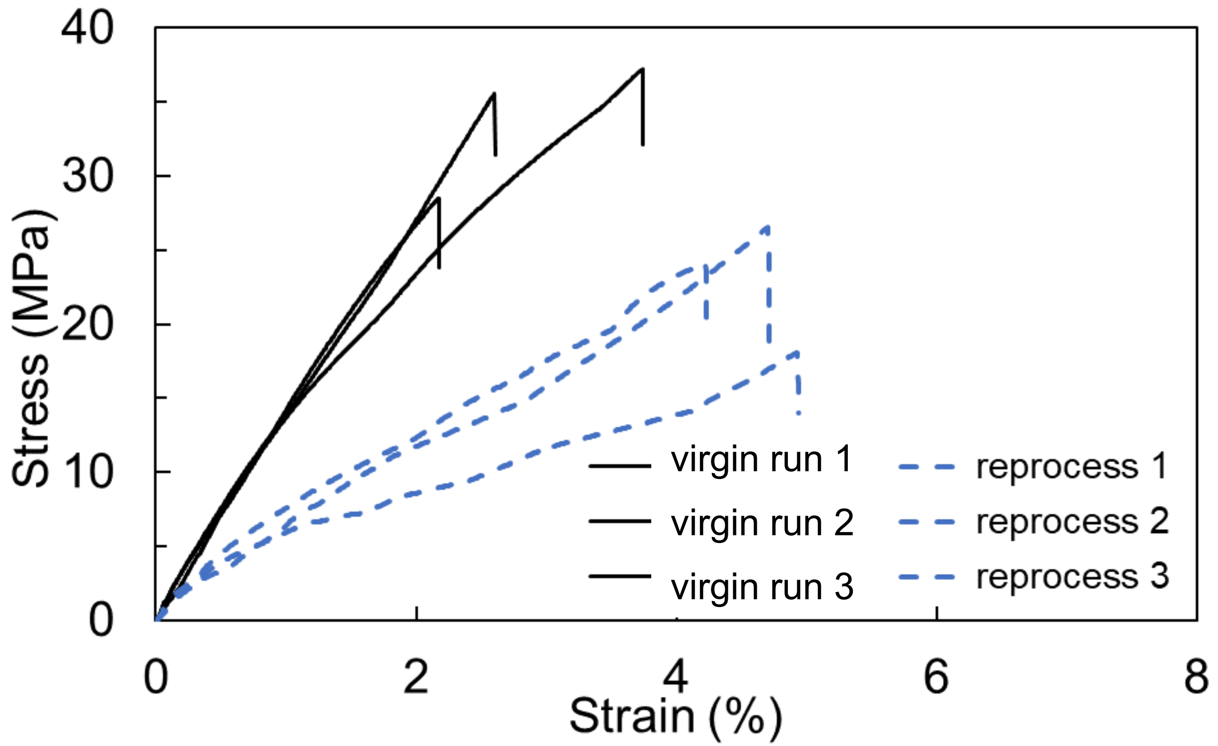
2 – Progress and Outcomes

Reprocessing

60% recovery in tensile properties for reprocessed vitrimer achieved so far



Virgin Samples
33 MPa ± 4.6 MPa, 2.8% ± 0.8%,
1.5 GPa ± 0.17 GPa

Reprocessed Samples
23 MPa ± 4.4 MPa, 4.6% ± 0.36%,
1.0 GPa ± 0.16 GPa

- To achieve >90% recovery, reprocessing conditions will be optimized.

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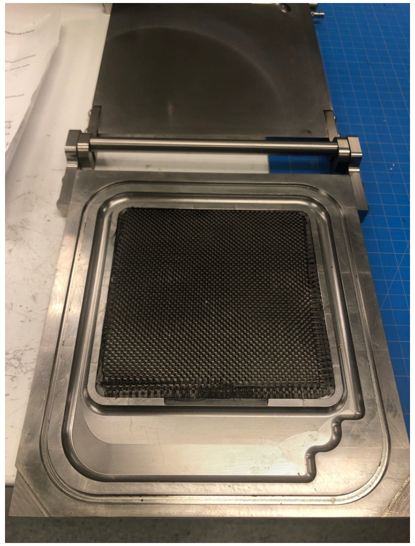
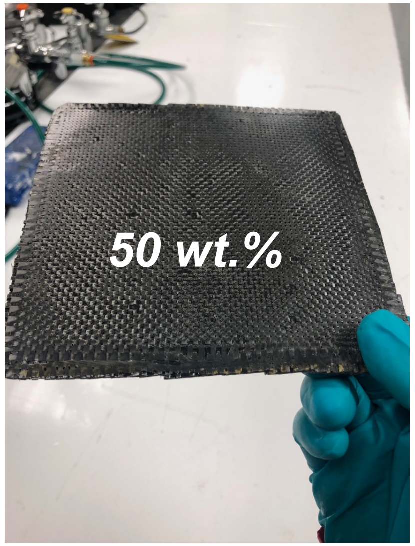
2 – Progress and Outcomes

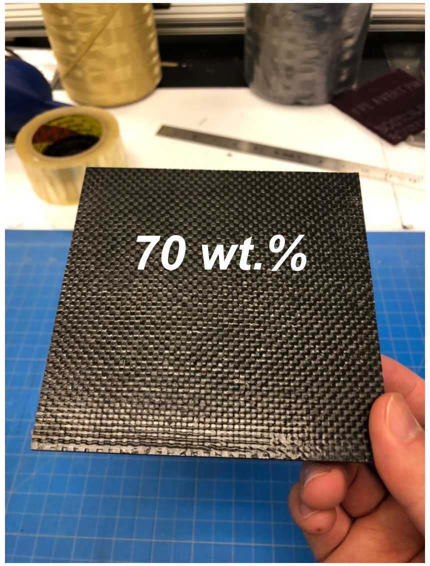
Composite fabrication

- Composites with varying carbon fiber loadings fabricated on 10 g scale using vitrimers. (Complete)



Fabrics stacking in the mold





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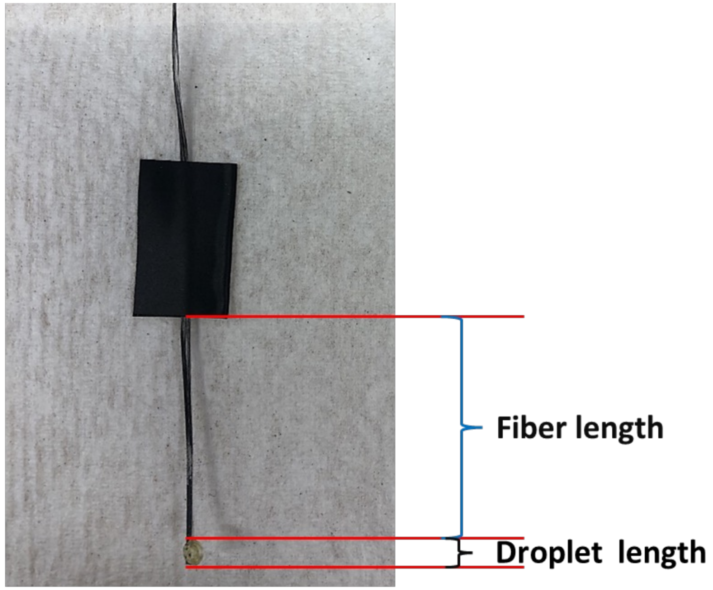
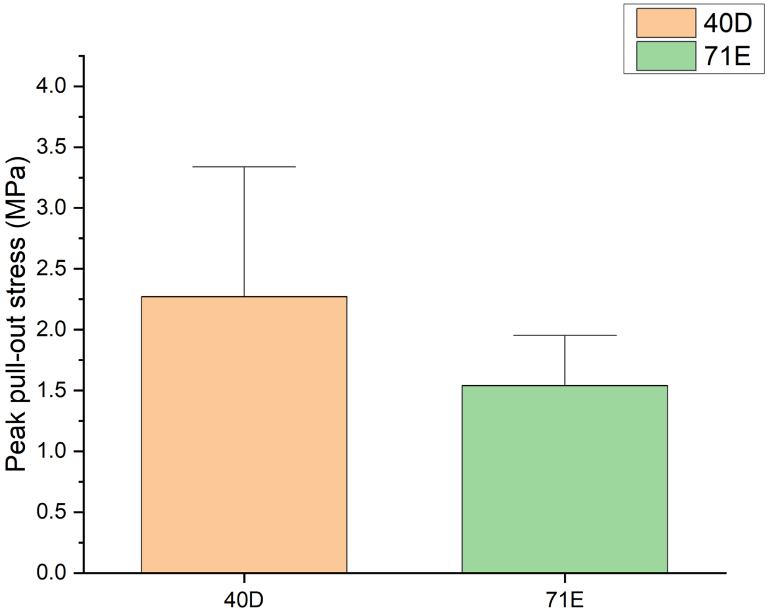
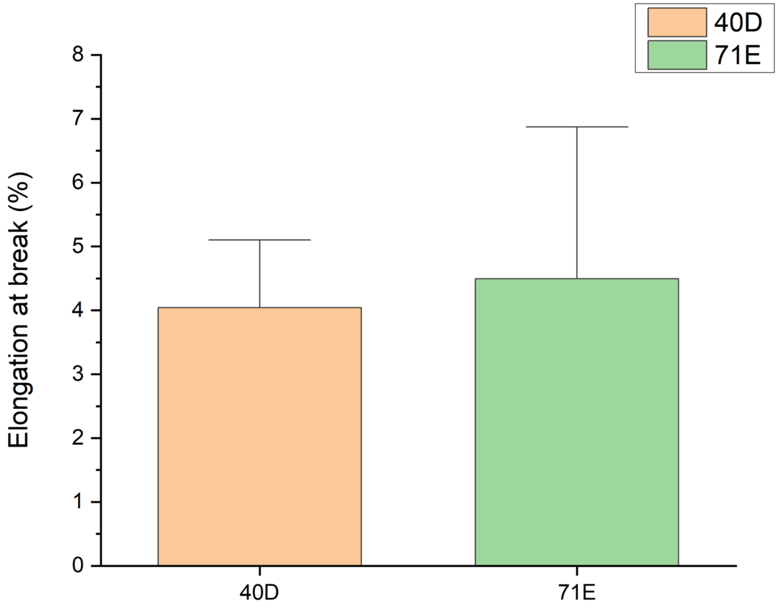
2 – Progress and Outcomes

Fiber pull out

- 40D fiber (~2.25 MPa) is about 50% higher in interfacial shear strength than the 71E fiber (~1.5 MPa) with the developed resin





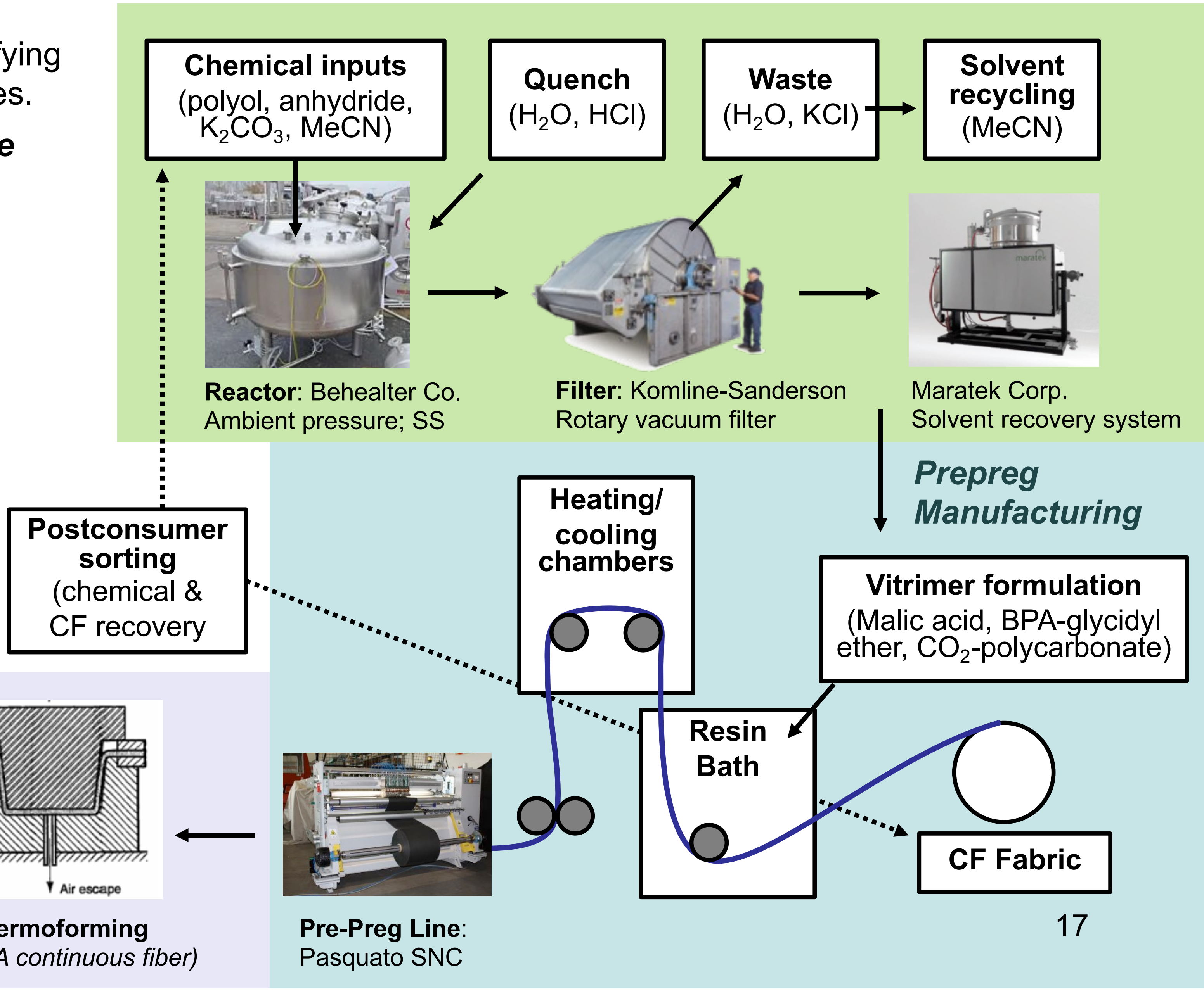


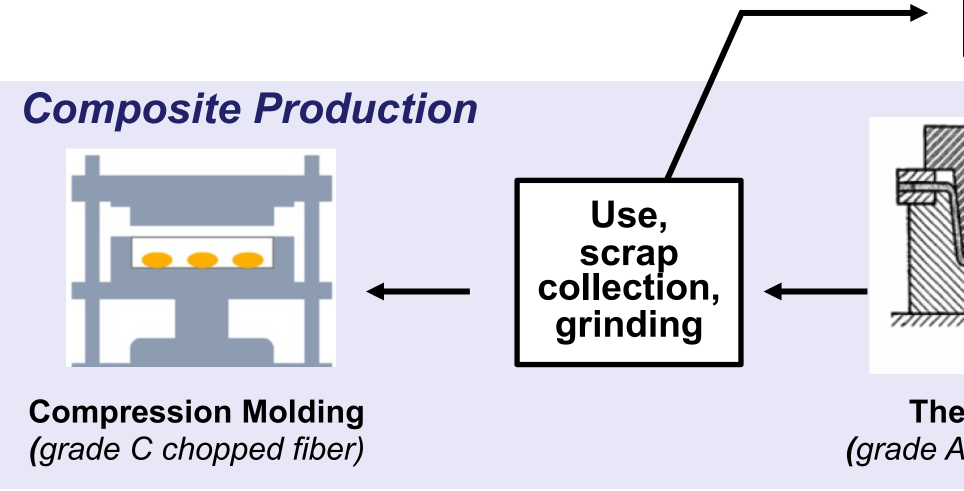
2 – Progress and Outcomes

Technoeconomic and Life Cycle Models for quantifying the cost and carbon footprints of circular composites.

- ***Three stages of production supply chain are being modelled for capital costs and CO_2 / other LCA impacts***
  - Vitrimer precursor synthesis
  - Prepreg manufacturing
  - Composite production

- ***End-of-use circularity is considered for:***
  - Continuous fiber recovery
  - Downcycled chopped fiber recovery
  - Composite reforming
  - Chemical recycling





2 – Progress and Outcomes

Summary of status of key milestones

- Vitrimer stress relaxation and tensile properties as function of cure conditions quantified. (Complete)
- Properties of cured vitrimer resin surpass those of polypropylene. (Complete)
- Stress relaxation and tensile properties of networks quantified. (Complete)
- Reprocess vitrimers without catalyst. (60% complete)
- Composites with up to 70 wt.% carbon fibers fabricated on 10g scale using vitrimers. (Complete)
- Appropriate coupling agents for enhancing fiber-resin interface identified using interface characterization. (Complete)
- Cradle-to-gate LCA for proposed vitrimer fiber composite provides first pass identification of key life cycle stages to reduce carbon footprint. (80% Complete)

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2 – Progress and Outcomes

Tasks leading to technical accomplishments

- Optimized curing conditions of vitrimer system using gel fraction tests
- Investigated mechanical properties of multiple vitrimer compositions
- Identified conditions for which depolymerization occurred for each system (thermogravimetric analysis)

3 – Impact

- *Engagement with national laboratory and industry partner (Raytheon) has been very beneficial.*
- *Technoeconomic analysis and life cycle assessment from Raytheon have guided experimental optimization (e.g., solvent selection and cure-time optimization).*
- *Disseminating results through paper publications and conference presentations.*
- *This project will impact the carbon footprint, material reuse, and carbon fiber recyclability of the composites industry.*
- *Discussions with Raytheon industry partner have identified that the commercial potential will be in automotive industry and aerospace interiors.*

Summary

- *Tensile strength of the vitrimer matrix exceeds polypropylene benchmark*
- *Vitrimer can be reprocessed without catalyst*
- *Composites with up to 70 wt.% carbon fibers fabricated*
- *Cradle-to-gate life cycle assessment has been used to identify processes to reduce carbon footprint*

Quad Chart Overview

Timeline

- *Project start date 04/01/2021*
- *Project end date 03/31/2024*

	FY22 Costed	Total Award
DOE Funding	*(10/01/2021 – 9/30/2022)* *$440,944*	*$1,960,250*
Project Cost Share *	$219,287	$620,724

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

Project Goal

Combine the 1) mechanical recyclability of vitrimers, 2) the chemical recyclability of polycarbonates, and 3) the sustainable feedstocks of CO2 copolymers for recyclable lightweight carbon fiber composites.

End of Project Milestone

End of Project Goal #1: Tensile strength of recyclable composite is 20% higher than baseline polypropylene technology.

End of Project Goal #2: Recover >80 wt.% of carbonate monomer through depolymerization and recover >95% carbon fibers of reusable quality

Funding Mechanism

DE-FOA-0002245 / 000001, Topic Area 1 Highly Recyclable or Biodegradable Plastic, 2020.

Project Partners*

- Pacific Northwest National Laboratory
- Raytheon Technologies

*Only fill out if applicable.

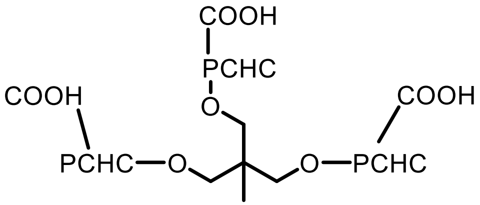
Additional Slides

2 – Progress and Outcomes

Beta-hydroxy ester networks without catalyst exhibit slow stress relaxation consistent with semi-permanent networks.

Acid Crosslinker

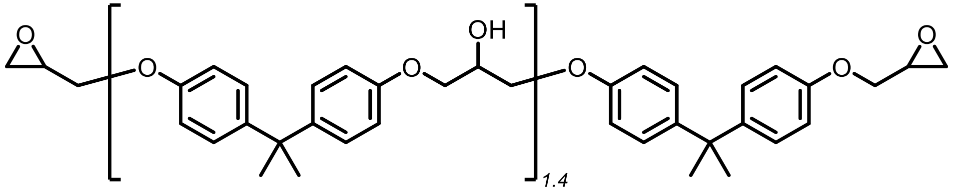
2



Tri-PCHC-COOH

Epoxide Linker

3



EPON 828 (Hexion)

Stress relaxation without any bioacid