OAK RIDGE National Laboratory

New Frontier in Polymer Matrix Composites via Tailored Vitrimer Chemistry

PI: Tomonori Saito

Oak Ridge National Laboratory

June 23, 2021

2021 DOE Vehicle Technologies Office Annual Merit Review

Project ID: mat204

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

- Start Date: Oct 2020
- End Date: Sep 2023
- Percent Complete: 20%

Budget

- Total project funding $1500k
- DOE Share: $1500k
- Funding for FY21: $500k
- Funding for FY22: $500k
- Funding for FY23: $500k

Partners

- Project Lead: ORNL
- As the project progresses, we will identify partners especially for commercialization

Barriers and Technical Targets

- Critical Challenges in Carbon Fiber Reinforced Polymers (CFRPs)*
  - ✓ Low-Cost High-Volume Manufacturing
  - ✓ Joining and Repair
  - ✓ Recycling

- The overarching goal is to develop fast-processable, repairable, recyclable and affordable CFRPs, while exhibiting superior mechanical properties by incorporating vitrimer chemistry into the fibers and resins

*From Light-Duty Vehicles Technical Requirements and Gaps for Lightweight and Propulsion Materials Workshop Report, February 2013

Relevance

Impact

•New frontier of CFRPs based on novel ‘vitrimer’ resins offer:

- Outstanding mechanical and chemical resistance similarly to thermoset epoxy resins
- Malleability, allowing rapid manufacturing, recycling and repair
- Exceptionally strong fiber-resin interfacial adhesion

•The focus is on lightweight materials for vehicles; it also opens other markets:

- Aerospace industry
- Water, oil and natural gas distribution (composite pipelines and pipeline repairs)
- Infrastructure repair (patches to concrete bridge pillars)
- Military (unmanned aerial vehicles with extended flight times)
- Space vehicles (cryogenic fuel tanks)
- Tooling, parts, sports gears

Objectives

1. Develop cost-effective new vitrimer resins for carbon fiber composites
2. Develop the manufacturing process of CFRPs and improve the fiber-matrix interfacial adhesion
3. Validate the manufacturing of fast-processable, recyclable and repairable vitrimer resins and CFRPs while maintaining their superior mechanical properties

Milestones

Milestone/Deliverable Name/Description FY21, FY22	End Date	Status
Design of molecules, functional groups, building blocks	12/31/2020	Complete
Synthesize at least two types of vitrimers with different dynamic chemistry, functional groups, building blocks, exhibiting 25 MPa tensile strength	3/31/2021	Complete
Verification/Quantification of functional groups on carbon fiber surface	6/30/2021	On-track
Identify and summarize the vitrimer processing temperature, and viscosity and curing time	9/30/2021	On-track
Variation of the concentration of functional groups on the fiber	12/31/2021	On-track
Quantification of bonding to vitrimer matrix via short beam shear testing of unidirectional composites	3/30/2022	On-track
Increase in interlaminar shear strength of at least 15% with the addition of functional groups to the fiber surface	6/30/2022	On-track
Demonstration of CFRP manufacturing by both prepregs and stamping	9/30/2022	On-track

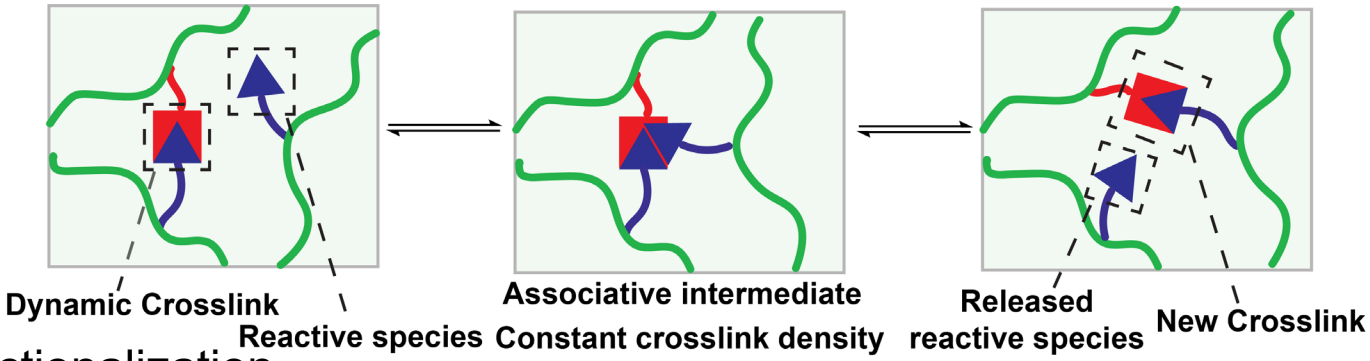
Go/No-Go	Description	Date	Status
Mechanically robust vitrimer and fabrication to CFRPs	Synthesize at least one type of vitrimers, exhibiting 35 MPa tensile strength, and demonstrate the fabrication to CFRPs	9/30/2021	On-track
Mechanically robust CFRPs	Prepare Vitrimer-based CFRPs and achieve 500 MPa composite tensile strength	9/30/2022	On-track

End goal: By the end of year 3, achieve 700 MPa tensile strength with vitrimer-based CFRPs and complete initial techno-economic analysis of down-selected vitrimer-based CFRPs

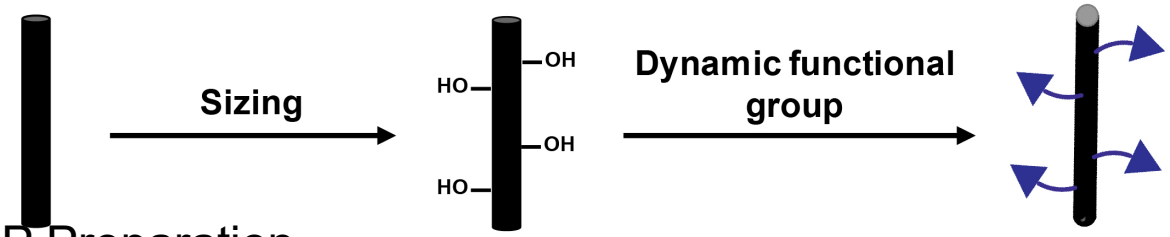
Approach

Develop fast-processable, repairable, recyclable and affordable vitrimer-based CFRPs

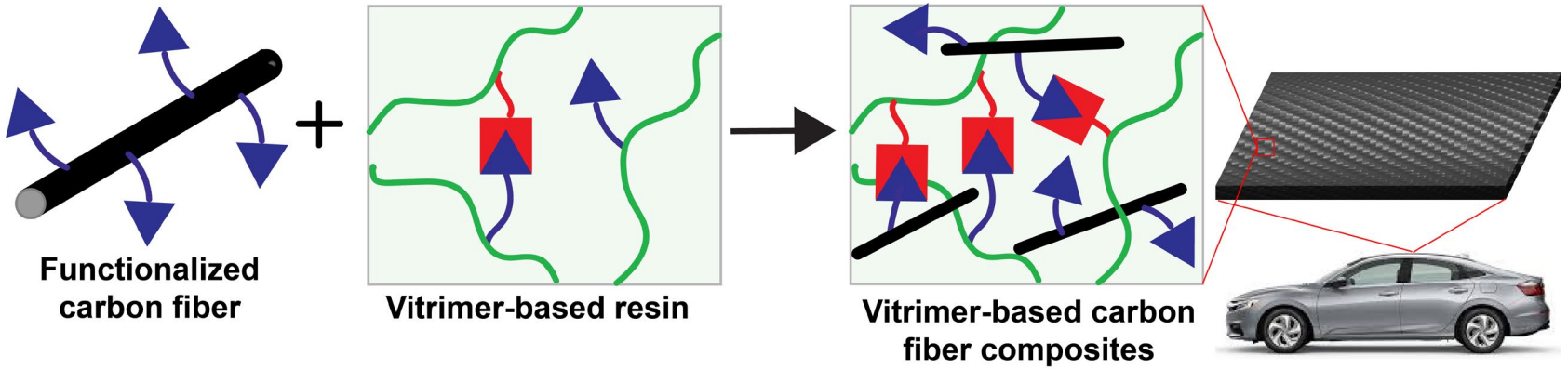
- Cost-effective, Scalable Vitrimer Resins



- Carbon Fiber Functionalization



- Vitrimer-based CFRP Preparation

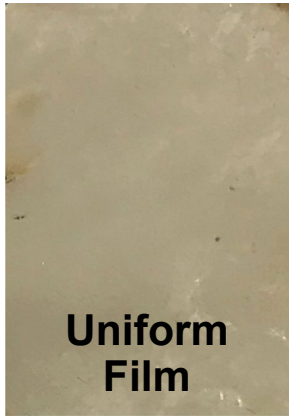


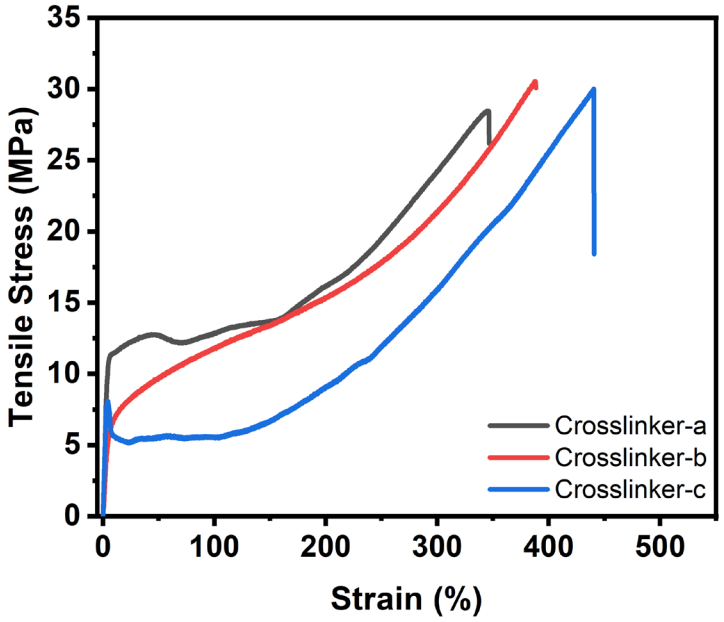
- ✓ Fast-processable
- ✓ Repairable
- ✓ Recyclable
- ✓ Mechanically Robust
- ✓ Solvent-resistant
- ✓ Strong interfacial adhesion

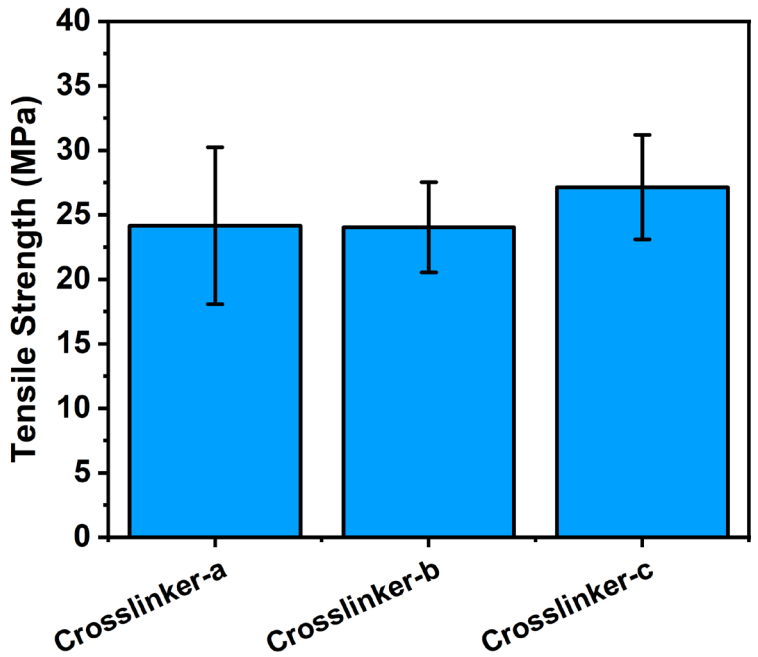
Accomplishments and Progress

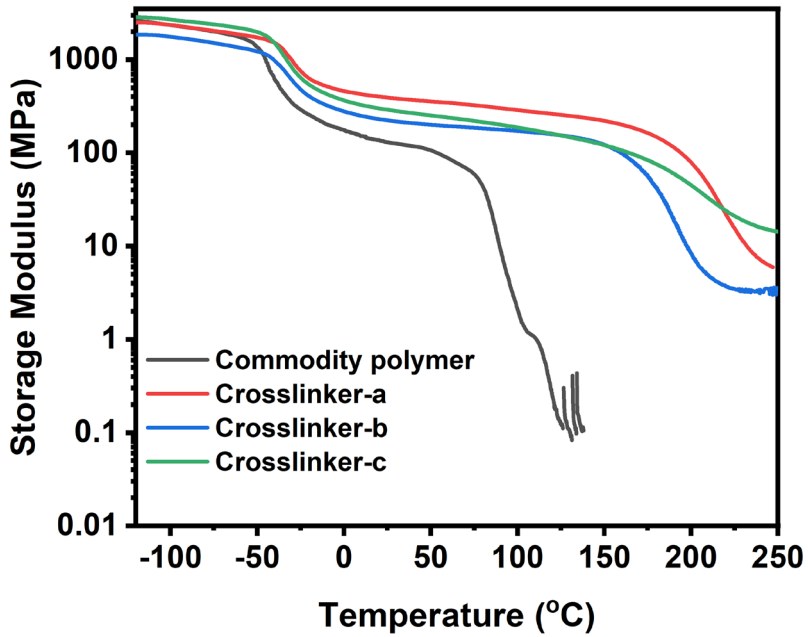
Preparation of Vitrimer Resin 1:

- ✓ Functionalized commodity polymers with dynamic bonds
- ✓ Readily scalable new vitrimers
  - This vitrimer exhibited ~30 MPa tensile strength
  - Three different dynamic crosslinkers were used







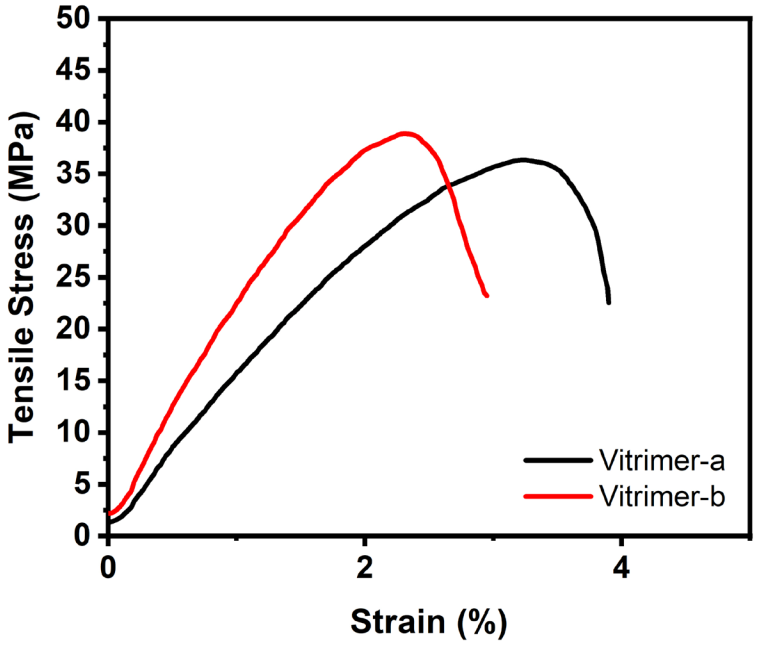


Crosslinked Tough Vitrimers with Processibility

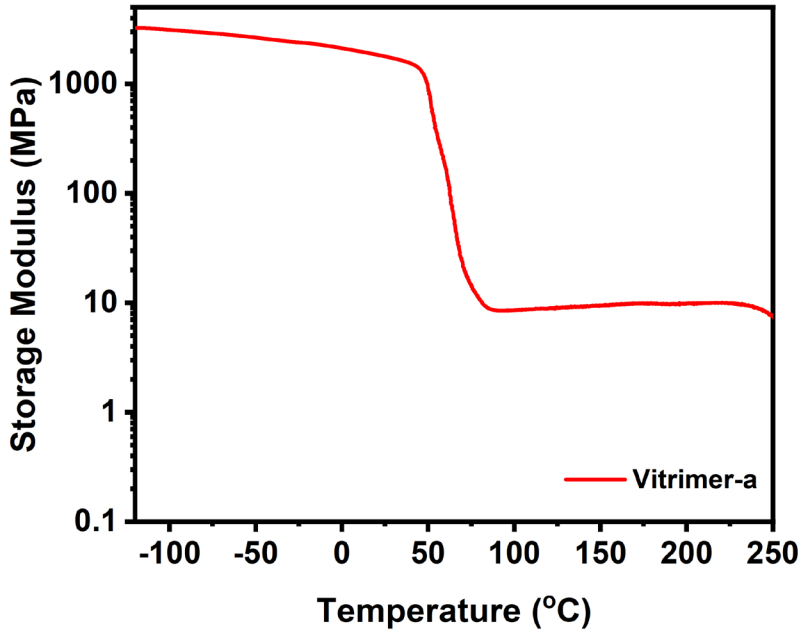
Accomplishments and Progress

Preparation of New Vitrimer Resin 2

- ✓ Novel vitrimer resin building blocks with facile scalability
  - Two-part chemistry similar to epoxy resins, but cured resins are readily processible (e.g., by stamping)
- ✓ These vitrimers exhibited >35 MPa tensile strength



	Tensile Stress (MPa)	Tensile Strain (%)
Vitrimer-a	35.9 ± 0.29	3.25 ± 0.02
Vitrimer-b	37.7 ± 3.45	2.43 ± 0.02

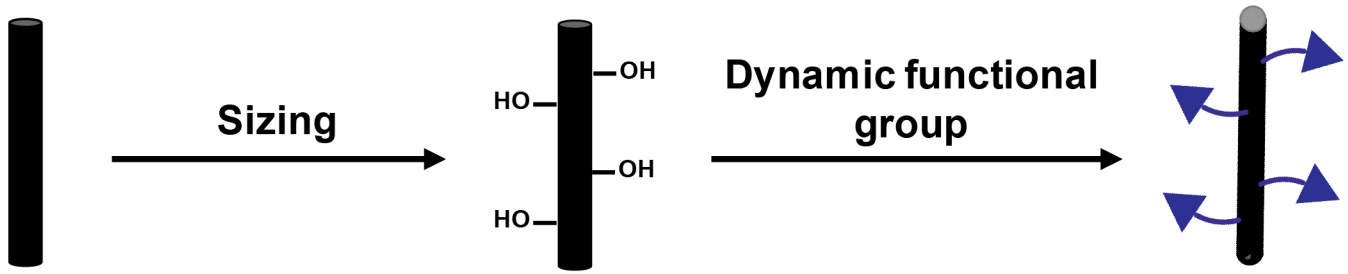


Successfully met FY21Q1 (design of vitrimers) **and FY21Q2** (25 MPa for two different vitrimers) **milestones, and partially met FY21Q4 Go/No-Go milestone** (35 MPa)

Accomplishments and Progress

Carbon Fiber Functionalization

- ✓ Functionalized carbon fibers with dynamic bonds
  - The functional groups on the fibers are complementary only to resins and will not exhibit undesirable fiber-fiber bonding
- ✓ Functionalization of carbon fibers was confirmed by X-ray photoelectron spectroscopy (XPS)

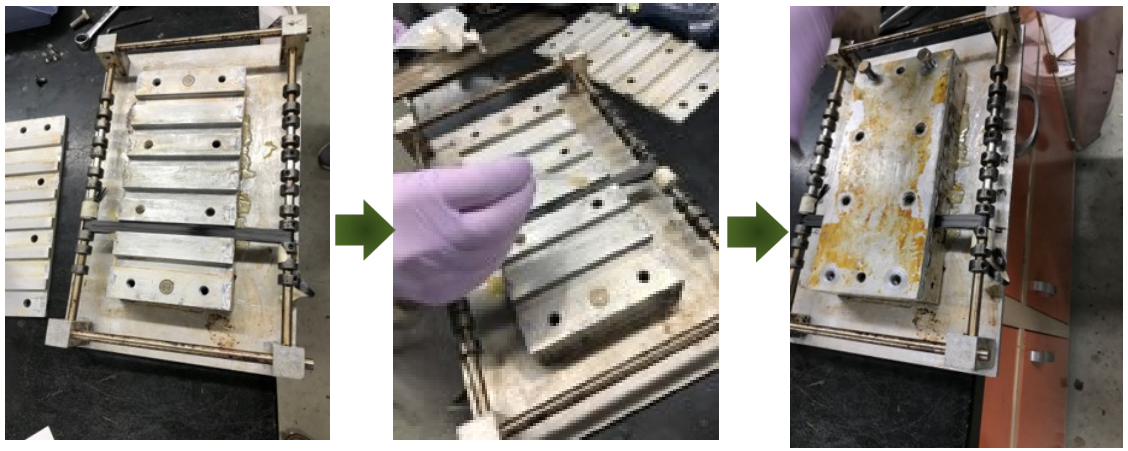


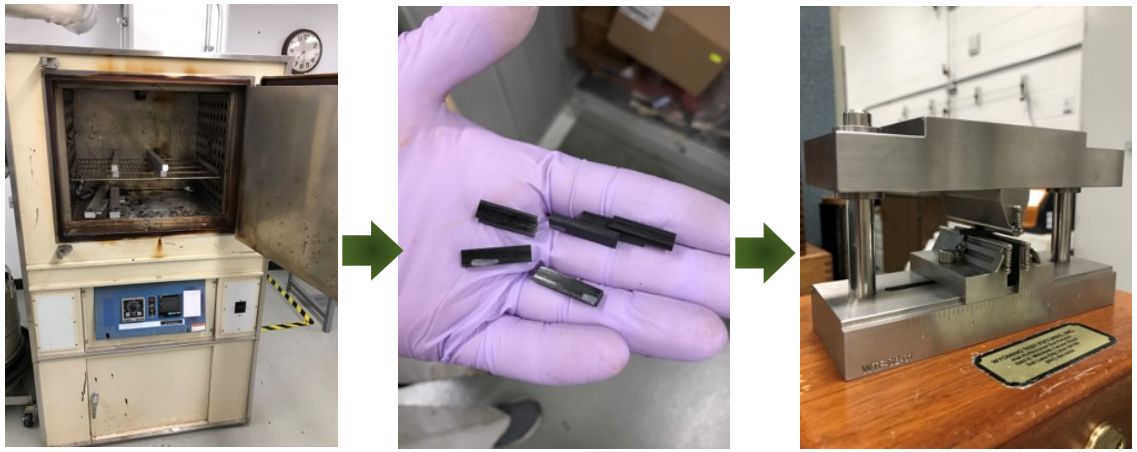
Partially met FY21Q3 milestone (6/30/2021 Verification/Quantification of functional groups on carbon fiber surface)

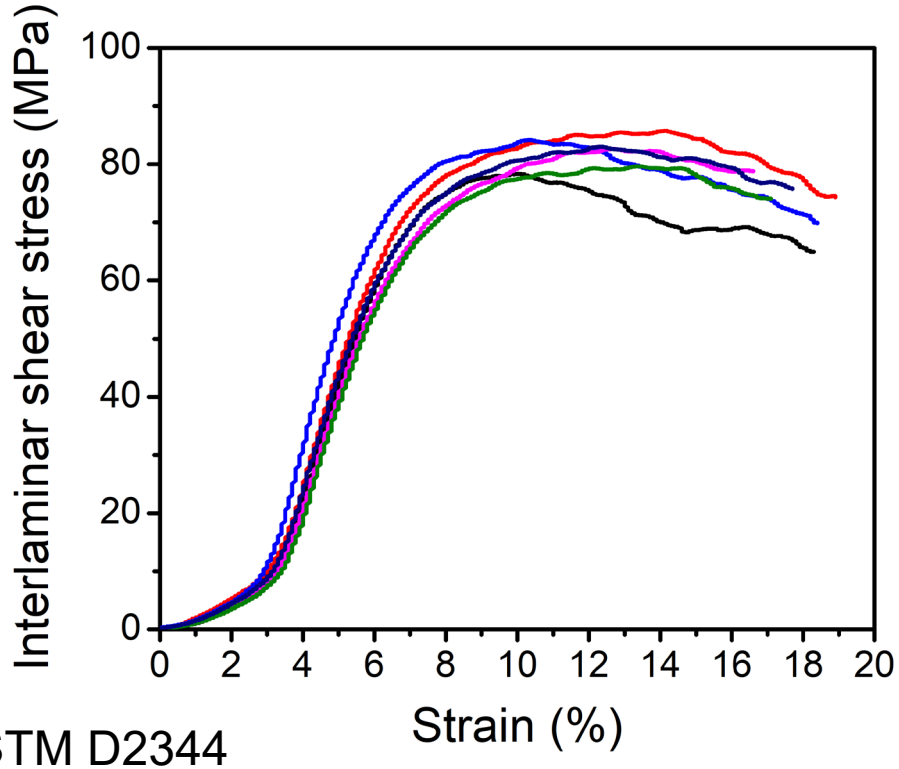
Accomplishments and Progress

CFRP Fabrication

CFRPs with conventional epoxy resins, Hexion EPON Resin 862 + Epikure W, have been fabricated and tested







ASTM D2344

- Short-beam Shear Strength 82.3 ± 2.5 MPa
- Modulus 17.4 ± 1.1 GPa

CFRPs with conventional resins provide a baseline method and performance

Responses to Previous Year Reviewers' Comments

- This is the first year that the project has been reviewed

Collaboration/Partner

- While we have had some communications, we have not had official collaborators or partners at this early stage of the project
- As the project progresses, we will identify partners especially toward commercialization

Potential Partners

1. Carbon Fiber Manufacturers (e.g., Hexcel, Toray etc.)
   - We will also be able to test low-cost carbon fibers produced in-house (e.g., CFTF in ORNL)
2. Resin Companies (e.g., Huntsman, Hexion etc.)
3. Automotive Industry (e.g., Ford, GM etc.)

Remaining Challenges and Barriers

Mechanically robust vitrimers and fabrication to CFRPs

- Optimize vitrimer resin chemistry and their composition, fiber functionalization, and composite fabrication process
- Identify the resin formulation, viscosity, temperature for rapid manufacturing

Demonstration of recyclability/reprocessability, reparability and stability of CFRPs

- Demonstrate at least 3 times recyclability of the vitrimer-based CFRPs
- Validate a long-term stability by monitoring the mechanical strength and functionality change (no change) over time

Cost of Vitrimer-based CFRPs

- Conduct techno-economic analysis

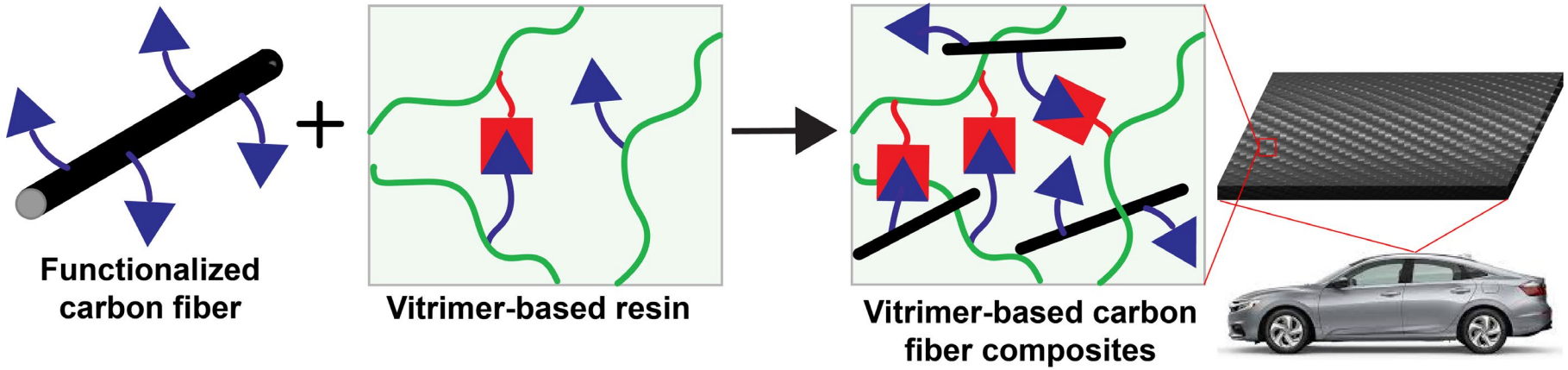
Proposed Future Research

FY21

- Further tailor vitrimer resin chemistry and fiber functionalization
- Identify and summarize the vitrimer processing temperature, viscosity and curing time
- Demonstrate the fabrication of CFRPs using novel vitrimer resin system and functionalized carbon fibers

FY22

- Achieve varied degree of functional groups on the carbon fiber
- Quantify bonding to vitrimer matrix via short beam shear testing of unidirectional composites
- Increase interlaminar shear strength of CFRPs at least 15%
- Demonstrate CFRP manufacturing by both prepregs and stamping
- Prepare Vitrimer-based CFRPs and achieve 500 MPa composite tensile strength



*Any proposed future work is subject to change based on funding levels

Summary

Relevance:

- Developing novel vitrimer-based CFRPs will enable high-volume, high-performance, and affordable CFRPs with reprocessability/recyclability, repairability, and fast-processability, and thus significantly contribute to achieving VTO goals of lightweight vehicles

Approach:

- Scalable vitrimer building blocks are identified and the composition and chemistry will be further tailored
- Tailor the fiber functionalization to enable dynamic exchange reaction with vitrimer resins
- Demonstrate fast-processability, repairability, recyclability of novel vitrimer-based CFRPs

Technical Accomplishments:

- A few different types of new vitrimers with different dynamic functional groups were successfully designed (12/31/2020) and synthesized, exhibiting higher than 35 MPa tensile strength (3/31/2020 milestone "Synthesize at least two types of vitrimers with different dynamic chemistry, functional groups, building blocks, exhibiting 25 MPa tensile strength")
- Initial carbon fiber functionalization and CFRP fabrication were successful

Future work:

- Scalable vitrimer building blocks are identified, and the composition and chemistry will be further tailored
- Tailor the fiber functionalization to enable dynamic exchange reaction with vitrimer resins
- Demonstrate high mechanical strength, fast-processability, repairability, recyclability of novel vitrimer-based CFRPs