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# Bio-Based, Inherently Recyclable Epoxy Resins to Enable Facile Carbon-Fiber-Reinforced Composites Recycling

Nicholas A. Rorrer (He/Him), NREL

# Project Overview

## Timeline

- Project start: October 2020
- Go/No-go Milestone: September 2021
- Project end: September 2023
- Percent complete: ~90% (At time of AMR Preparation)

## Budget

| | To Date | Total Project |
|---|---|---|
| **DOE Funding** | $500,000 (FY 23)<br>$500,000 (FY 22)<br>$500,000 (FY 21) | $1,500,000 |

## Barriers addressed

Recycling

- Our resin design is aimed at being recycled under triggered conditions, enabling the recovery of precursors and fibers.

Low-cost fibers

- By maintaining fiber integrity across multiple lives, we can in turn reduce the average cost of the fiber.

Durability

- Through formulation and fiber sizing, we aim to introduce a more ductile response into carbon-fiber-reinforced composites (CFRCs).

*Vehicle Technologies Office. 2013. *Workshop Report: Light-Duty Vehicles Technical Requirements and Gaps for Lightweight and Propulsion Materials*.

## Project Partners

- Under discussions to form NDAs and execute licensing agreements on patents.

# Acknowledgments


**NREL Composites Manufacturing Education and Technology Facility (CoMET) Team**

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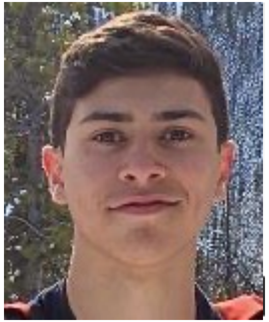


**Jason DesVeaux**
Analysis Lead

**Oliver Greener**
Analysis Intern

**Thanks to VTO for funding and Felix Wu as our Technology Manager!**

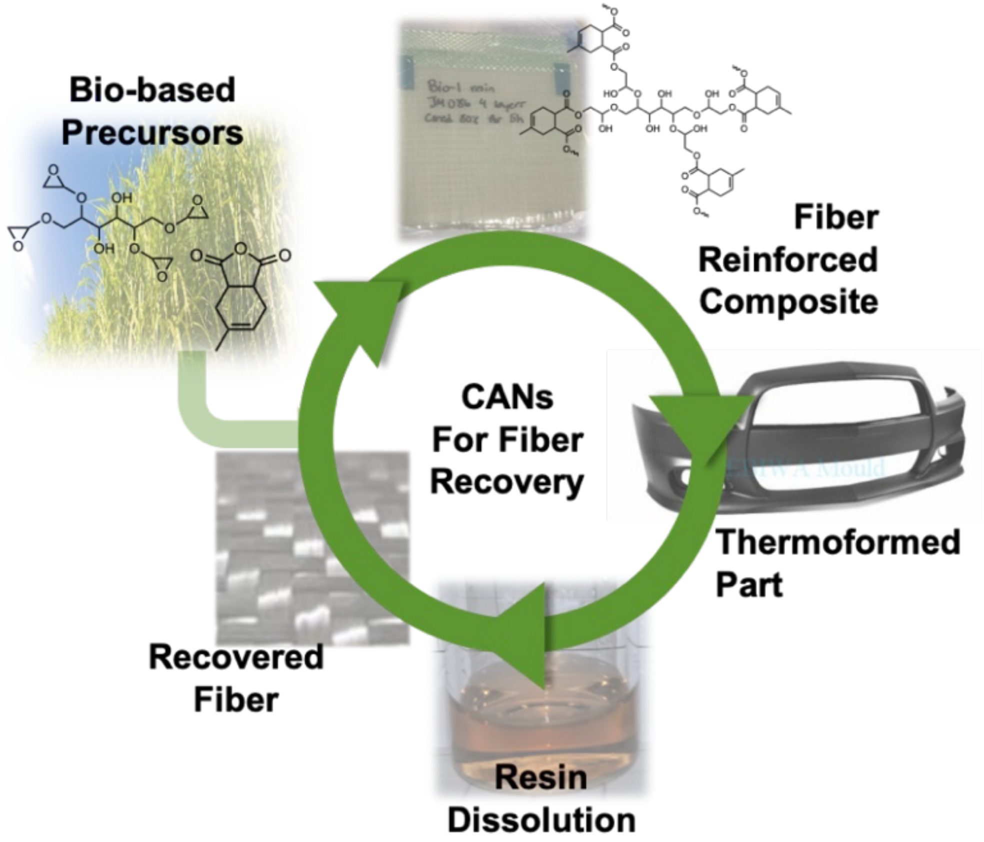
# Relevance

## Impact

- CFRCs can light-weight vehicle parts up to 60%–70%, but the cost of carbon fiber (CF) remains very high and CFRCs can undergo mechanical failure due to brittleness.
- By leveraging bio-based starting blocks to form recyclable polymers, we can decarbonize first life by 10-20% ***while reducing the cost and emissions of the CF in subsequent lives by >90%***

## Objective

- This work aims to produce recyclable-by-design CFRCs that leverage a bio-derivable polyester covalently adaptable network (PECAN) from epoxy-anhydride resins for better material and environmental performance.



# Approach

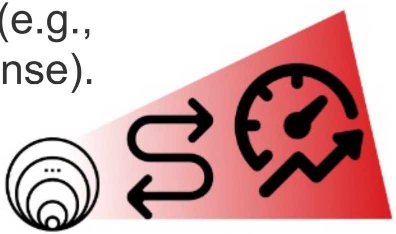
This project is divided into four tasks aimed at taking CFRCs from fiber and resin to a part and back again, across multiple length scales.

### Task 1: CAN-CFRC synthesis

Formulated epoxy-anhydride covalently adaptable networks from bio-derivable precursors.

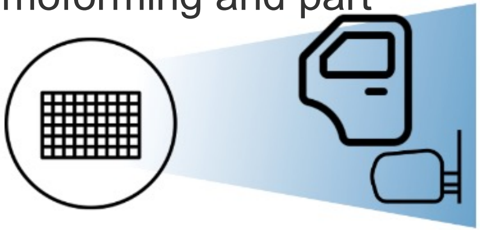
### Task 2: Develop sizing of fibers that improve performance

This work began in FY22, aimed at improving fiber properties (e.g., introducing a ductile response).



### Task 3: Validation and scale-up

Produce CFRC panels on a >1-kg scale acceptable for initial thermoforming and part manufacture.

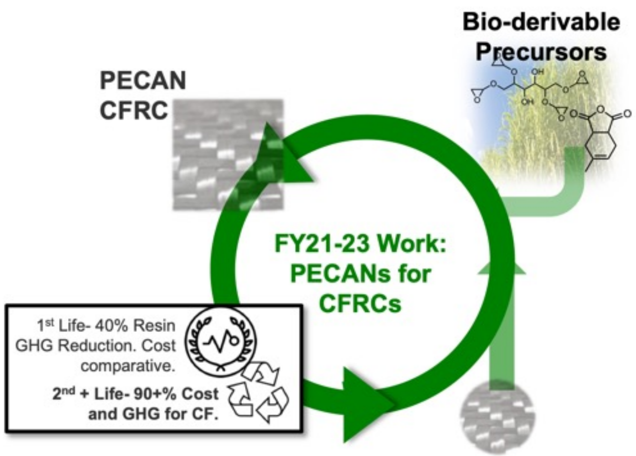


### Task 4: Analysis

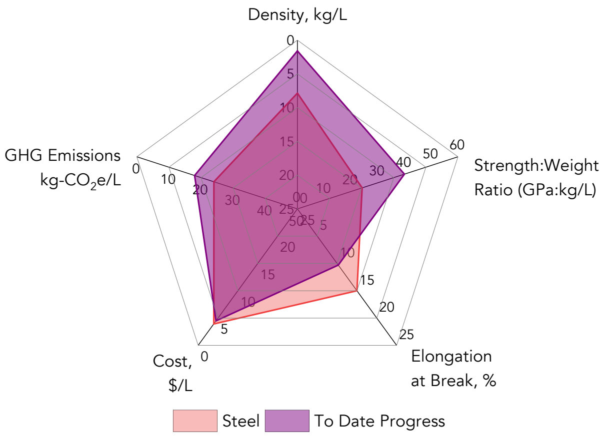
Perform techno-economic analysis (TEA) and supply chain analysis across multiple lives to estimate selling price and greenhouse gas (GHG) emission reductions.

# Technical Accomplishments – Overview

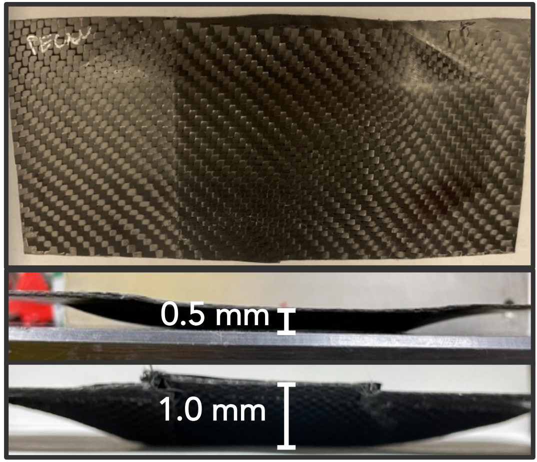
## Bio-derivable and Recyclable (FY21)




## Tunable (FY22 +)

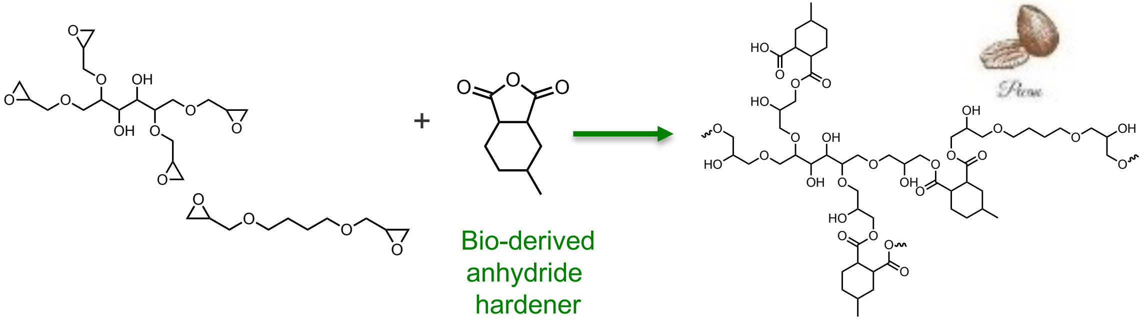



## Thermoformable (FY23)

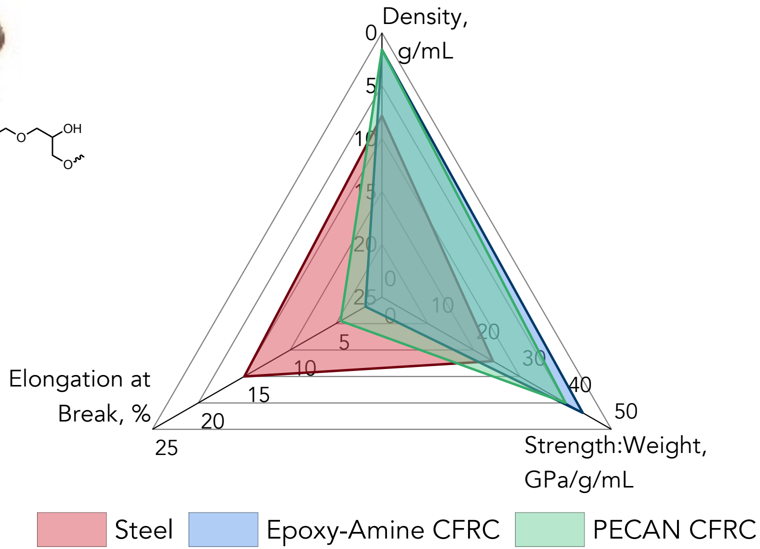



**CFRCs made with <u>p</u>oly<u>e</u>ster <u>c</u>ovalently <u>a</u>daptable <u>n</u>etworks (PECAN) resins offer multiple desirable benefits for vehicle applications**

# Technical Accomplishments – PECAN Overview



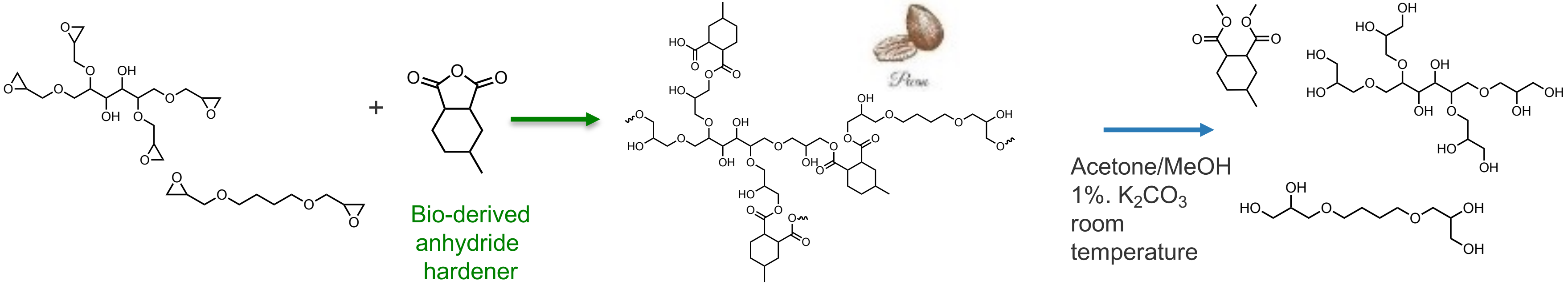

Virgin PECAN CFRC

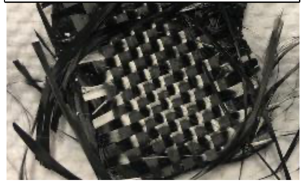



## PECAN CFRCs are recyclable-by-design

- The PECAN resin can be sourced from sugar-derivable monomers, specifically epoxies and anhydrides.
- The PECAN possess the same strength:weight ratio as epoxy-amine resins with a slight enhancement in ductility.
- PECAN CFRCs have been scaled up beyond 1-kg panels.

# Technical Accomplishments – FY21 Recap

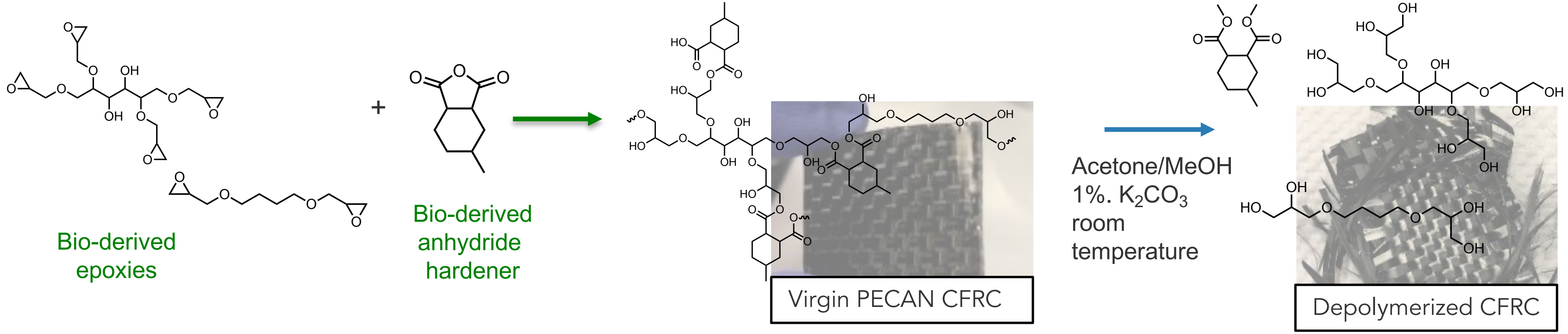


## PECAN CFRCs can be recycled at room temperature

- In order to maintain CF integrity, processes without vigorous agitation must be used.
- At room temperature, the recycling occurs within two days in acetone; under reflux, the depolymerization occurs in less than an hour.

# Technical Accomplishments – FY21 Recap

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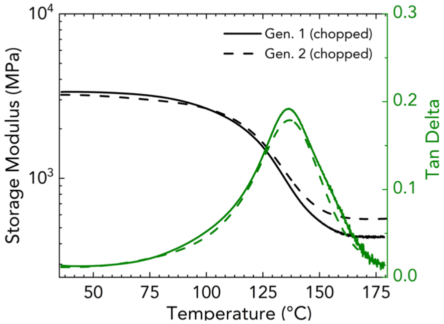
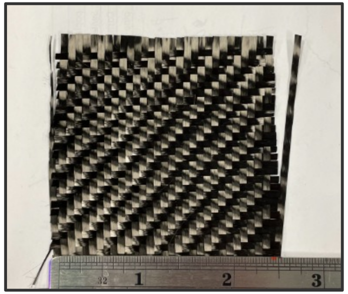
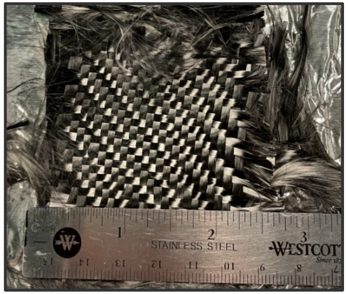
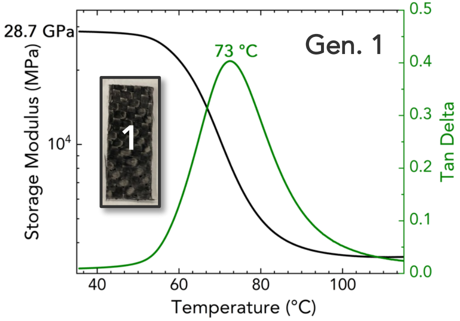
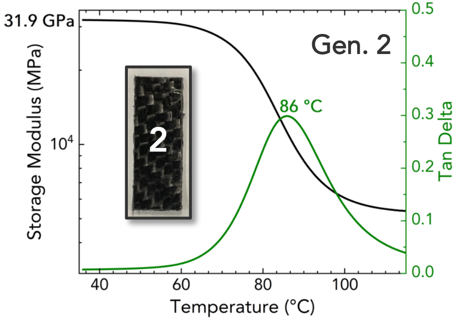
# Technical Accomplishments – Performance Across Lives

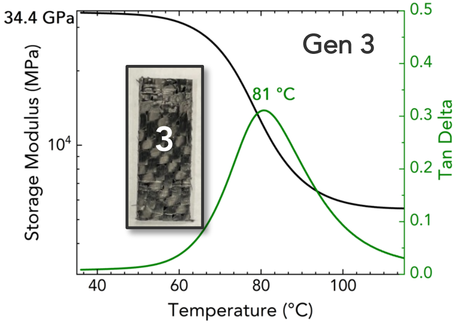




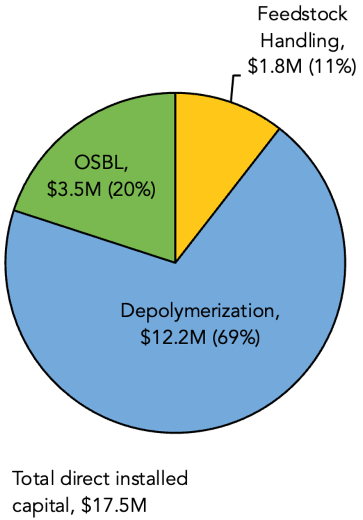



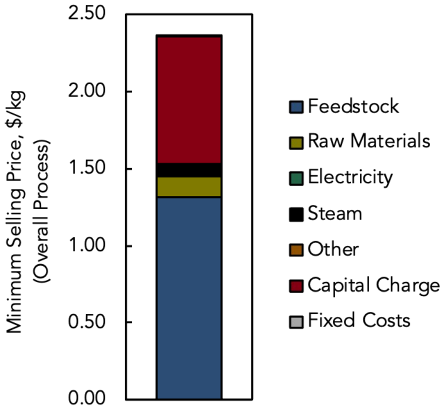



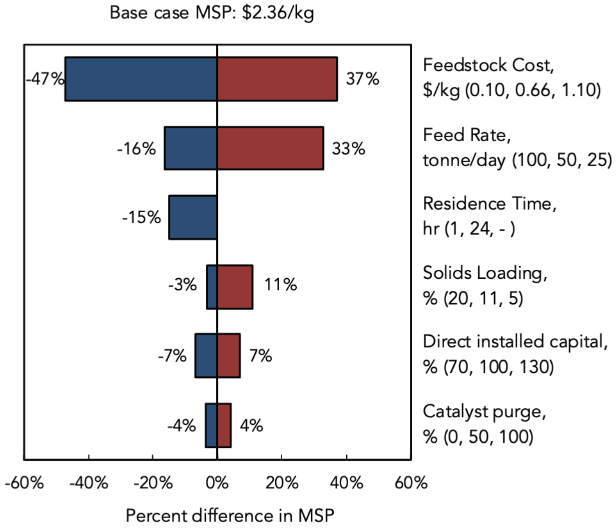

## Our FY21 Go/No-go demonstrated we can maintain CFRC performance across multiple lives

- The PECAN CFRCs exhibit consistent properties within equipment error across multiple lives.

# Technical Accomplishments – Technoeconomic Analysis (TEA)



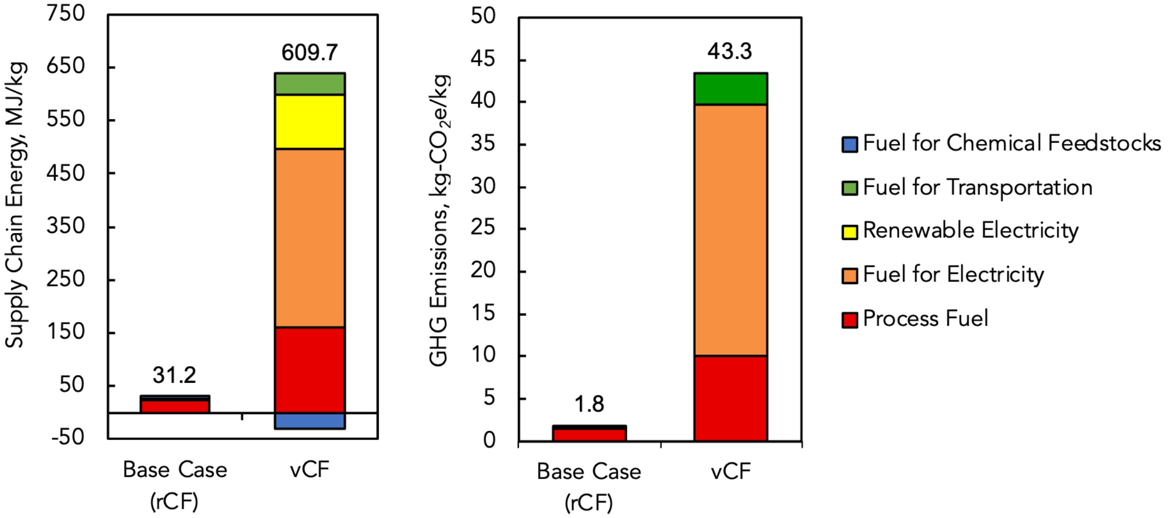



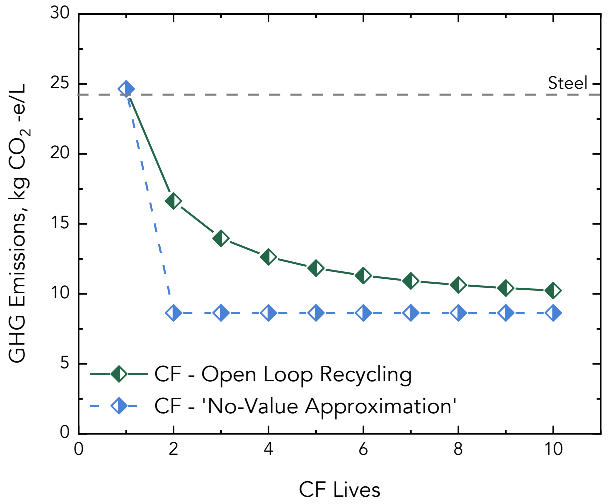

**PECAN CFRC Benefits – Slight first life reductions, dramatic subsequent life reductions**

Initial analysis indicated that the resin can be cost competitive and GHG reduced relative to today's epoxy-amine CFRC standard.

- When the recycling process used here is modeled, subsequent life fibers can be prepared at $2.36/kg$_{CF}$
- The driving cost is reclaiming the fiber, the belt reactors employed (capital charged), and plant size

# Technical Accomplishments – Enhanced TEA/Life Cycle Analysis (LCA)



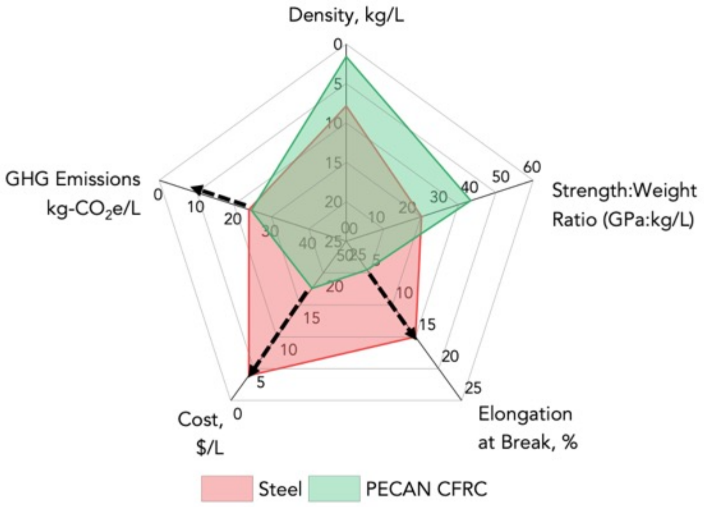



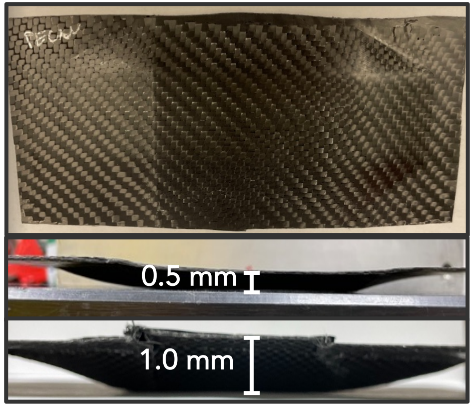

**PECAN CFRC Benefits – Slight first life reductions, dramatic subsequent life reductions**

Supply chain energies and GHG of the process exhibit >94% reductions

- These emissions for the subsequent lives of the CF are less than first life polyolefin manufacture
- This modeling assumes that the resin is sent to waste and not recovered
- Across multiple lives, *this can decarbonize the manufacture of CFRCs to be lower than steel on a volumetric basis*

# Technical Accomplishments – FY23 Milestones



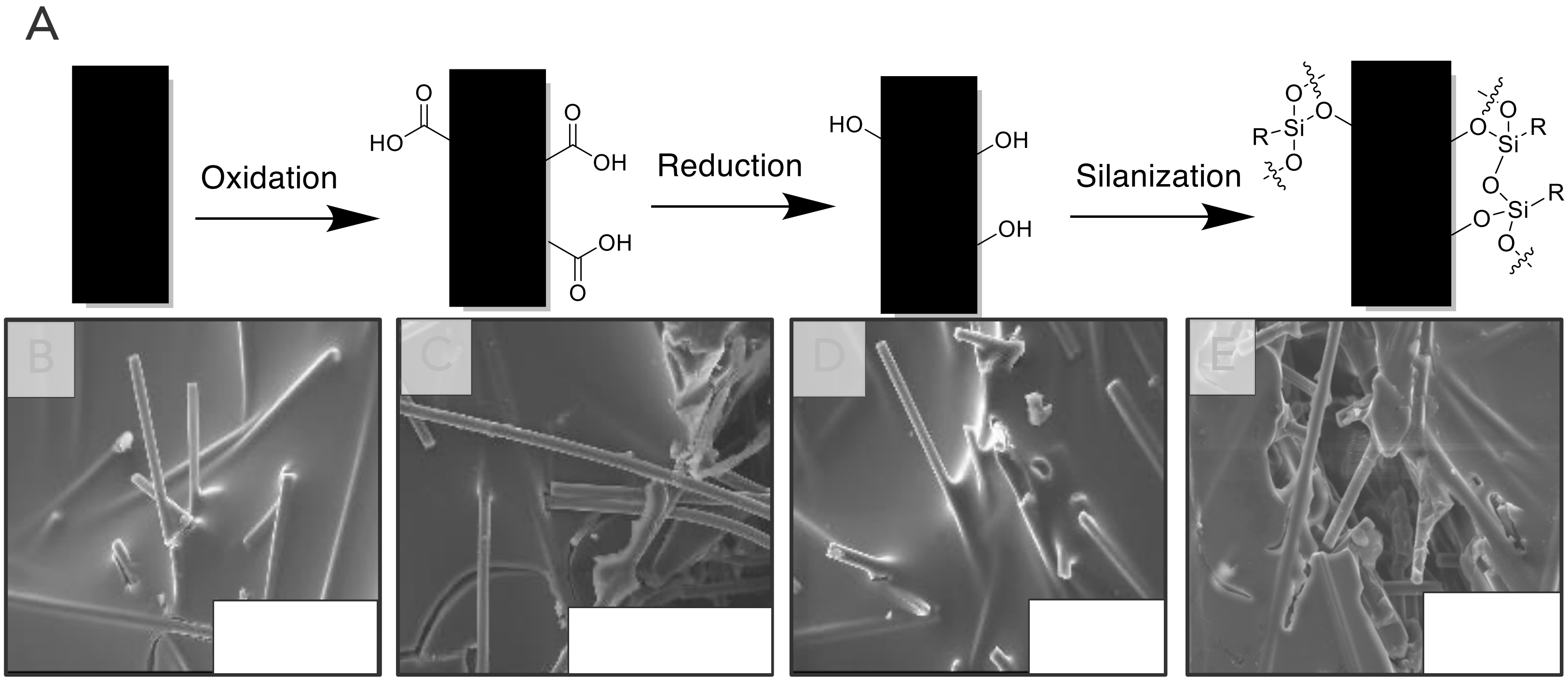

**FY22 and FY23 focused on the use of the CFRCs in multiple parts**

This can be either accomplished through the augmentation of material properties or the shaping of the materials

Overall, each milestone focused on:

- FY22 Q4 – Understand the influence of sizing and demonstrate thermoforming
- FY23 Q1 – Demonstrate repair-ability and weldability
- FY23 Q2 – Prepare a publication and update analysis
- FY23 Q3 – Thermoform at least two (2) parts
- FY23 Q4 – Demonstrate reuse of two **parts**

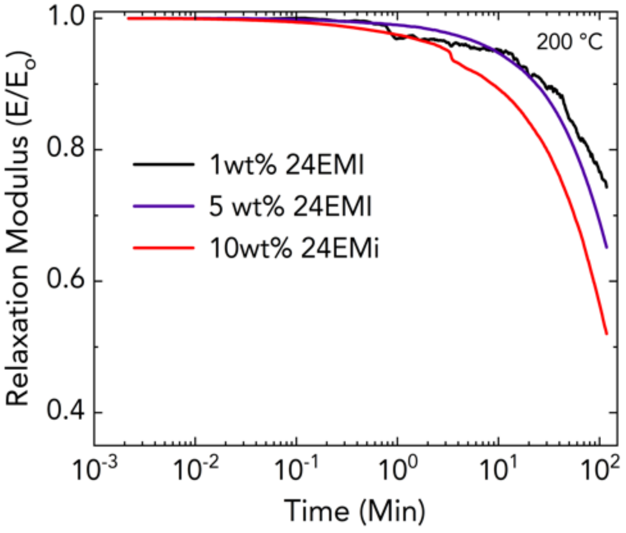
# Technical Accomplishments – Sizing Compatibility

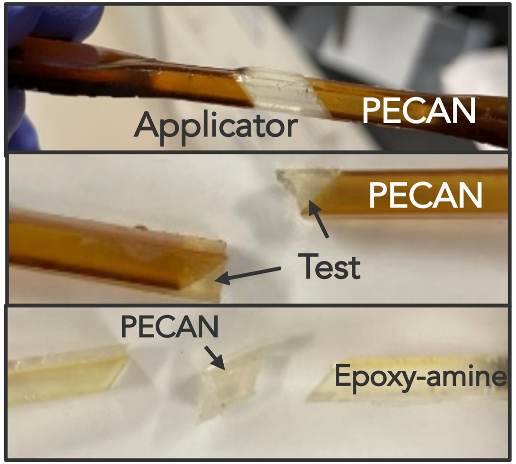


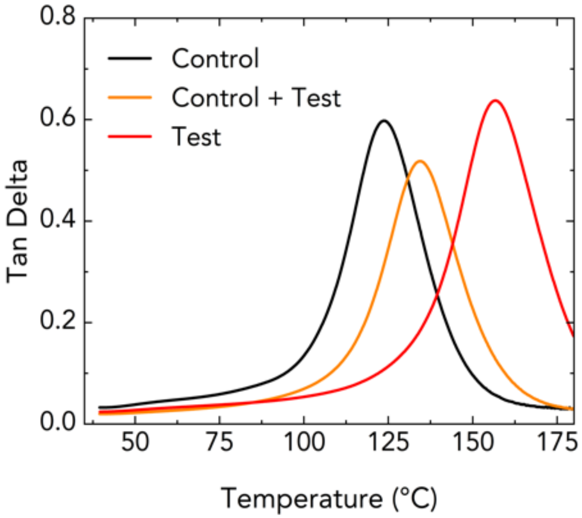

**PECAN resins are shown to be amphilic and compatible with a wide variety of chemistries**

- This work was our FY22 Q4 milestone and represents more value propositions that are available to the PECAN resin

# Technical Accomplishments – Repair-ability



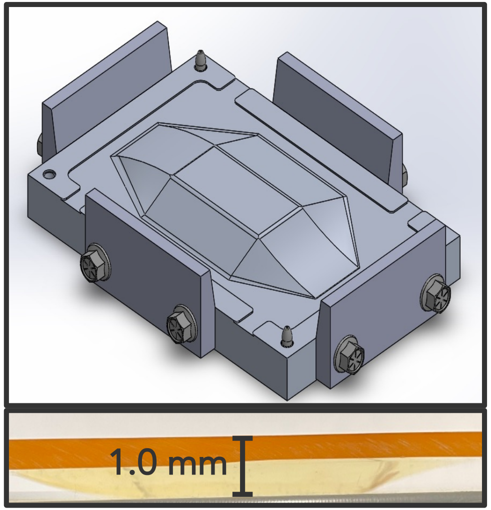



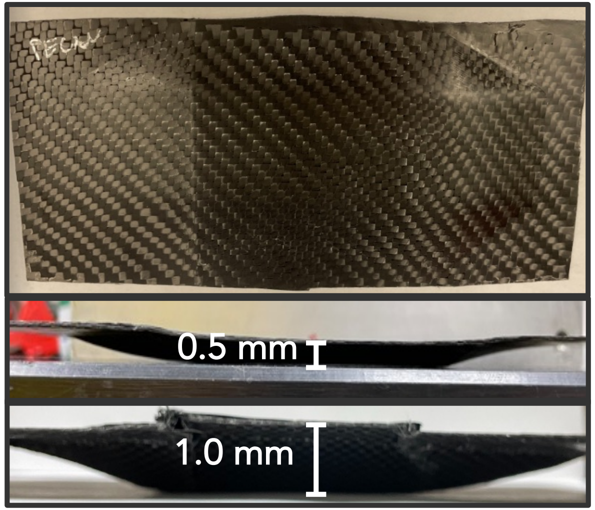



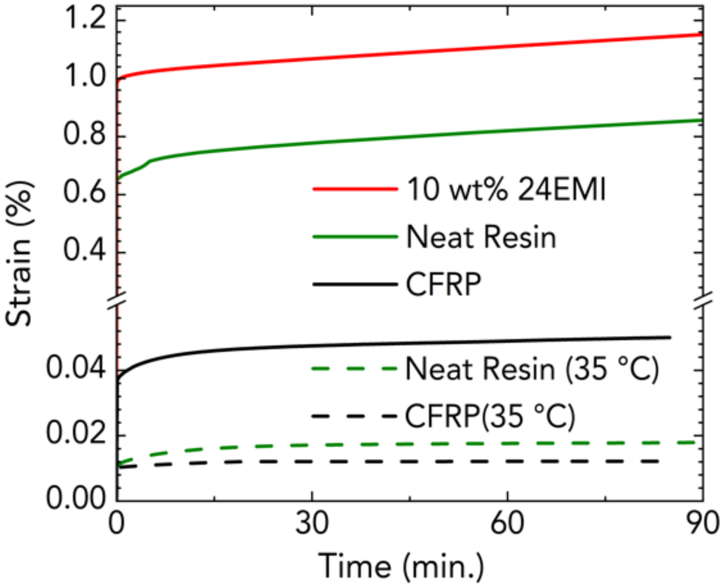

**PECAN CFRCs are able to ‘relax’ and thus the resin can be used to repair broken resins**

- DMA relaxation studies (*left*) demonstrate that the polymerization catalyst can be used to control these relaxation studies
- Artificial damage *(middle*) and repair visually demonstrate repair-ability
- DMA temperature sweeps (*right*) indicate a homogenous material is made after repair

# Technical Accomplishments – Thermoformable



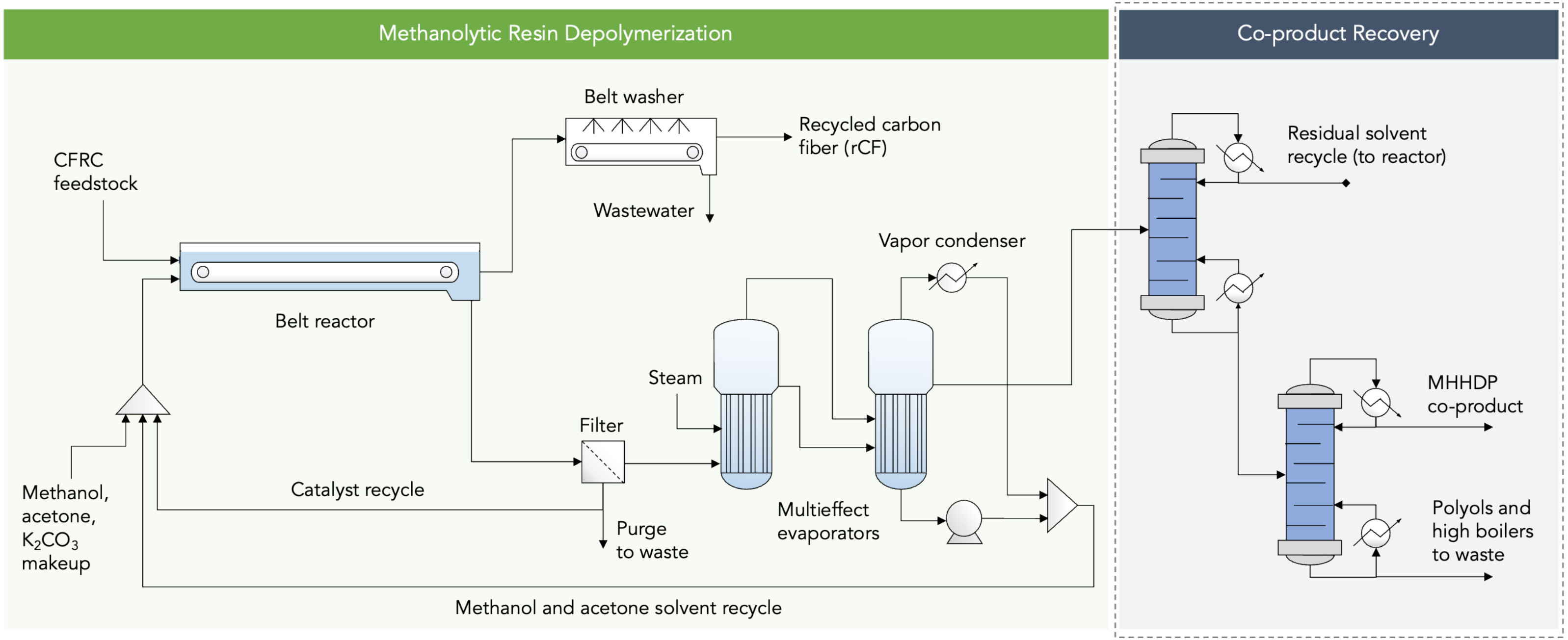




**The repair-ability of the PECANs translates into the thermoformability of the CFRCs**

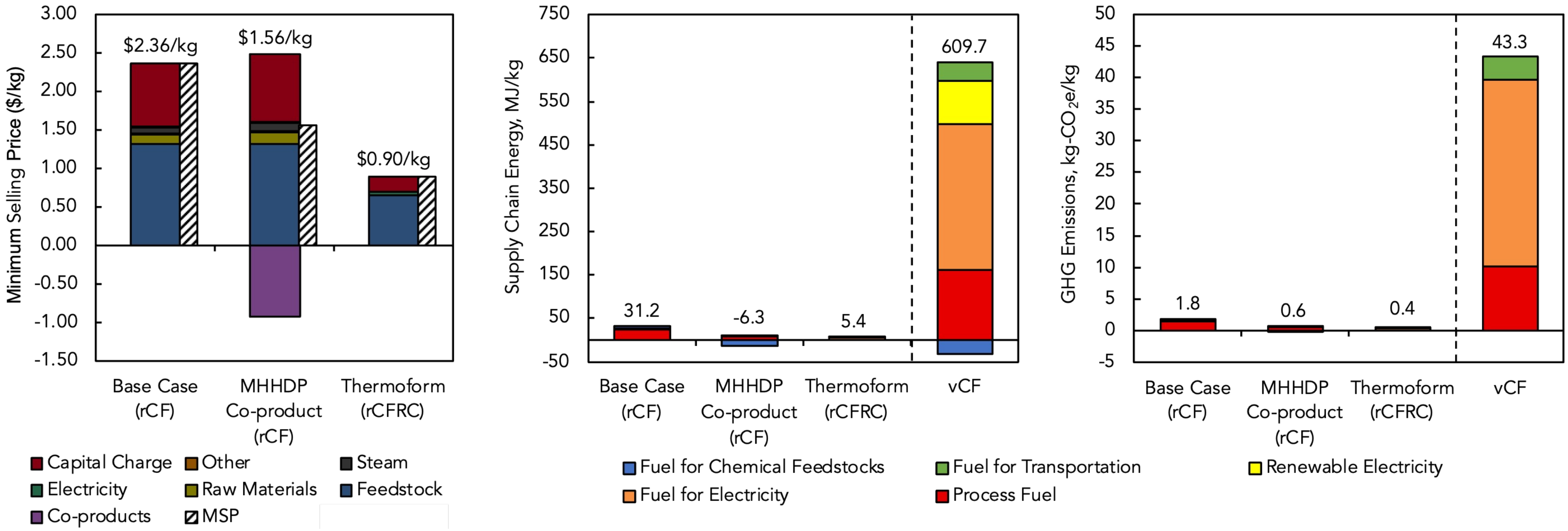
- DMA iso-stress relaxation studies (*right*) can be used to assess the thermoform potential of a formulation.
- At ambient temperature, the CFRCs do not relax/creep but can be formed at elevated temperatures

# Technical Accomplishments – Expanded Analysis




**Initial analysis only included the recovery of the CF. Expanded analysis included the recovery of the anhydride alongside thermoforming.**

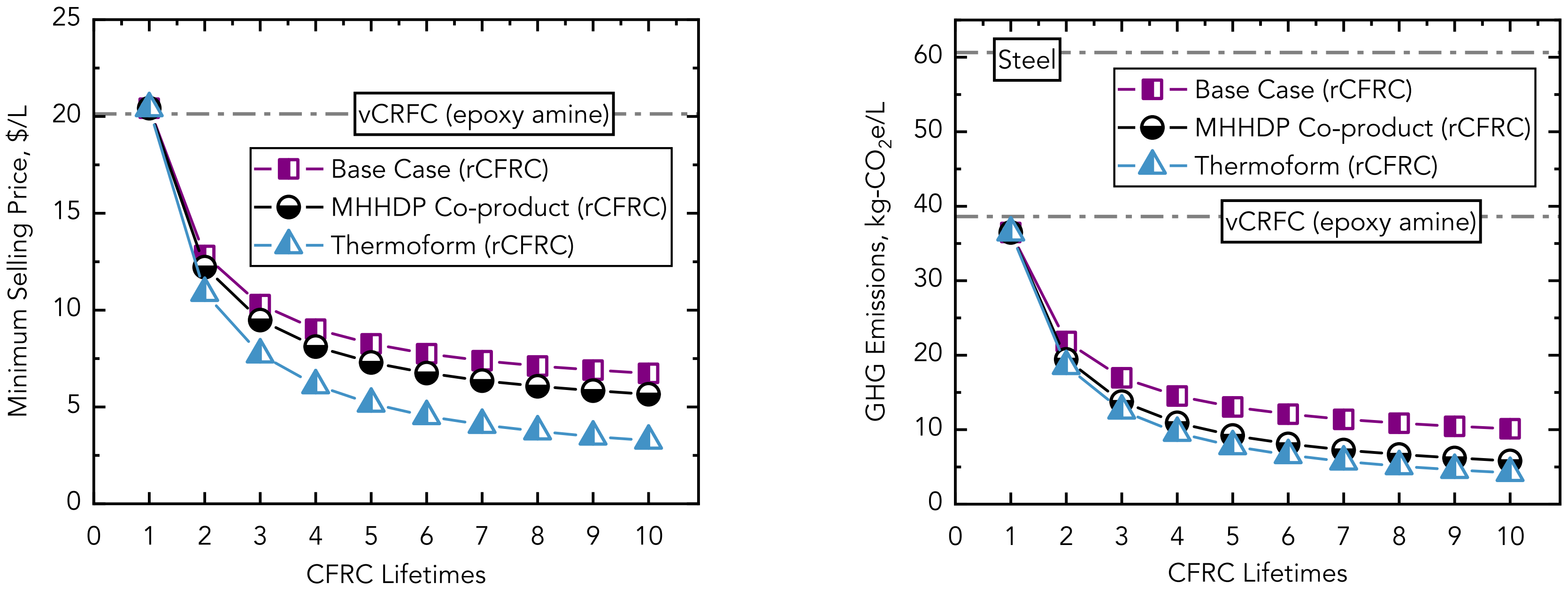
# Technical Accomplishments – Expanded Analysis




**Expanded analysis studies demonstrate that selling a resin co-product or thermoforming instead of chemical recycling can yield great benefits**

- When we can re-use part of our resin, subsequent life CF manufacture is further reduced by 35% (or from a 90% to 95+% reductions compared to first life CF)
- Supply chain energy and GHG benefits are also enhanced by 50% reductions (or from 95% to 99+% reduction compared to first life CF)

# Technical Accomplishments – Expanded Analysis




**Expanded analysis studies demonstrate that selling a resin co-product or thermoforming instead of chemical recycling can yield great benefits**

- When we translate results to CFRCs, instead of just the fiber, we can see broad benefits.
- Thermoforming, as it does not need to use fresh resin, is the best-case scenario

# Responses to Previous Year Reviewer’s Comments

**We thank the reviewers for their time and comments, such as stating the that project is “Well Designed, well planned, […] and has a logical approach” and that the “TEA and LCA analysis are excellent”**

Comment: One of the matrix components was linear poly(ethylene glycol)-based epoxied which are known to absorb water and can have detrimental effects on vehicle applications.

- Response: We agree with the reviewer and have explored other methods, such as alternative fibers, for enhanced ductility. PEG was only in one example in the FY22 presentation. Also, alternative anhydride elicit the desired response. (More on that shortly).

Comment: The collaborators listed in the presentation seemed more aligned with larger consortium instead of collaborators specific to this project.

- Response: This project began as a low TRL project (TRL <3) and has been elevated to TRL 4+. We have spent a portion of FY23 actively engaging with composite companies and are planning to include this with our approach in any new projects now that we have promising results and IP.

Comment: A complete and clear explanation of the selection of thermoforming manufacturing process thereby should be presented.

- Response: We thank the reviewer for the comment and thus have designed a mold to show a wide variety of vehicle relevant geometries. The final two prototypes are based off vehicle components (roof and a hood) for the vehicles alignment

Comment: The project supports the overall DOE objectives. It was shown in the TEA that in the second life of the CF **would be less than $5 per kg**, which is a sought-after goal within VTO to achieve more economical vehicle lightweighting.

- Response: We agree with the reviewer and want to highlight this comment as it highlights our approach

# Collaboration and Coordination

- National Renewable Energy Laboratory, Wind Technology Center
  - Focus on scale-up activities and infusion of panels.

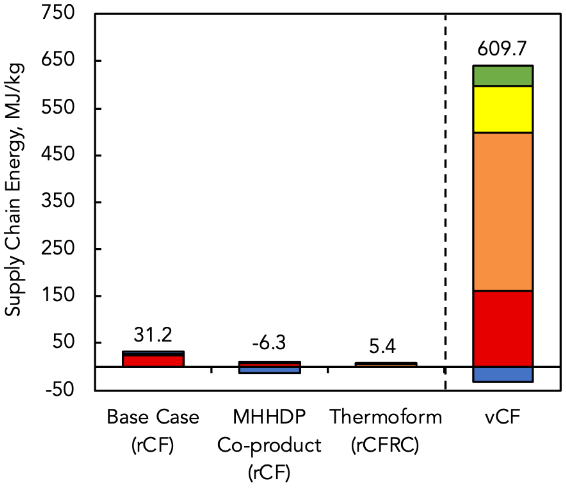
- Bio-Optimized Technologies to keep Thermoplastics out of Landfills and the Environment (BOTTLE™) consortium
  - Collaboration that provides scientific input on redesign, formulation, and recycling. Includes technical advisory board and a wide range of industry contacts.

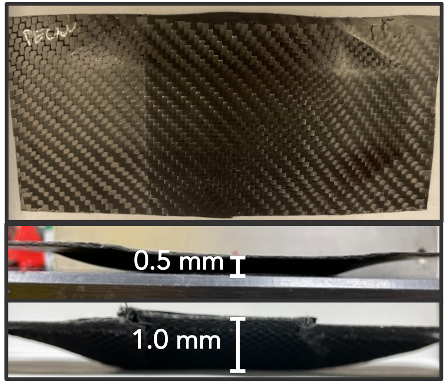
Companies engaged through the Renewable Carbon Fiber Consortium and **continued industrial engagement (150+ hours in FY23)**. Logos not shown due to copyright restriction.

Contacts serve as technical advisors to help inform research (e.g., parts and properties to target).

# Proposed Future Research – Key Milestones

| Description of Milestones and Go/No Go Decision | End Date & Status |
|---|---|
| **Thermoform the CFRC into at least 2 prototypical parts of different shapes with multiple replicates for testing and will conduct thermomechanical property analysis post thermoforming.** | **June 2023**<br>In Progress |
| **Demonstrate that the fiber parts from the FY23 Q3 milestone can have their fiber recovered after an initial life for reuse in a subsequent material application.** | **September 2023**<br>End-of-project goal<br>Planned |



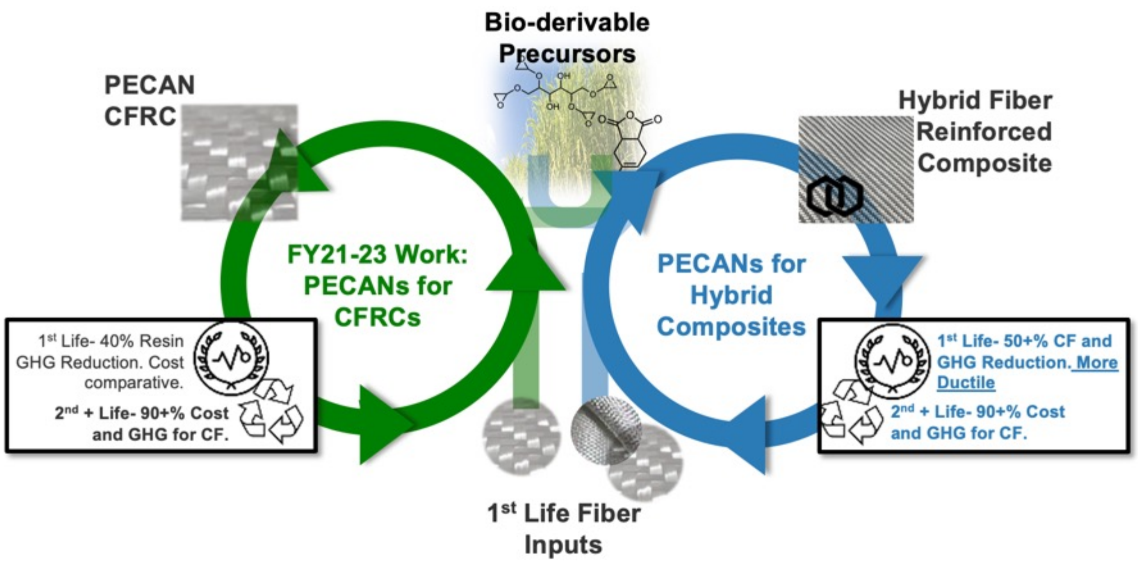



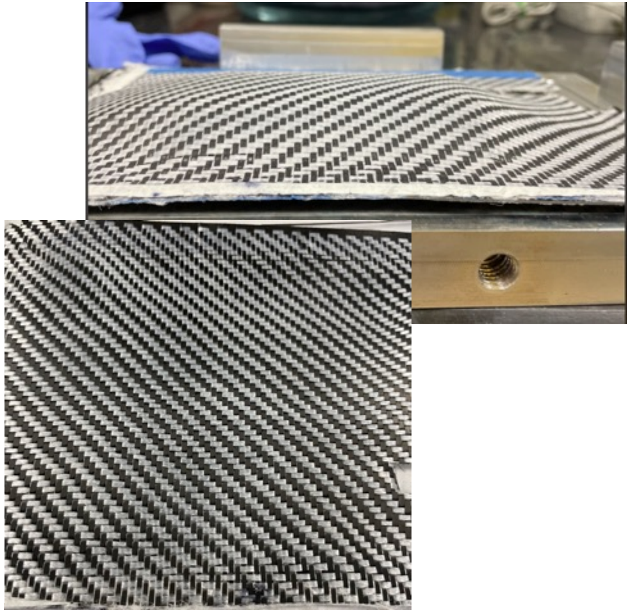

**Final validation of concepts is what is left in this initial seed AOP project**

- We are on target to complete all project milestones by the end of the project

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

# Proposed Future Research – Hybrid Composites



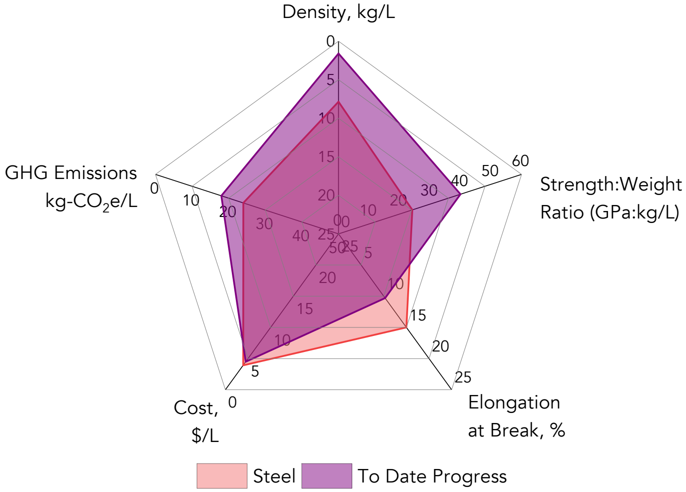



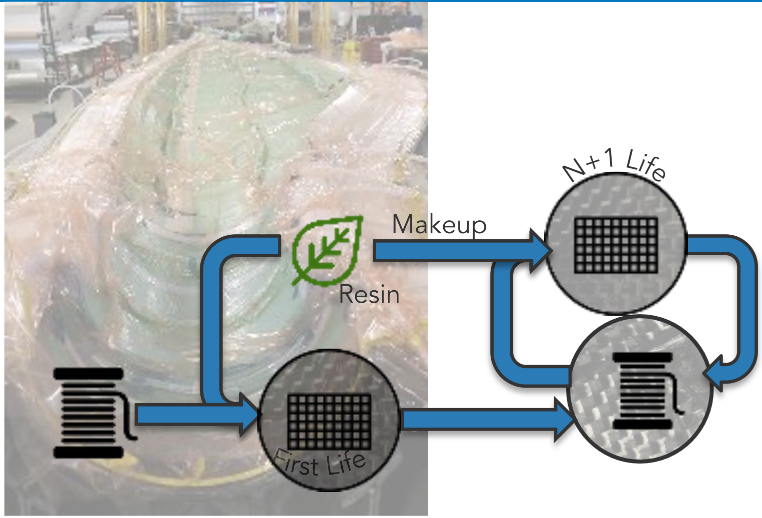
**Although this project is at its end, there is great promise for this platform for continued research, especially with hybrid composites**

- Results of composites made with PE and CF show maintained strength with enhanced ductility alongside reduced first life cost and emissions

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

# Proposed Future Research – Tunability and Scale-Up




## Tunability to part performance

- By the end of project, we will have shown only select production of vehicle parts.
  - Each part will need a different phase space.
- Thicker components (e.g., support beams) will need investigation into their tunability and material cure, as well as depolymerization.

## Scale-up for depolymerization

- Depolymerization has been demonstrated at a small scale (1kg) relative to automotive manufacture.
- Future milestones will aim at reusing parts post-thermoforming.
- There is still a large and transformative potential to develop depolymerization at scale, such as through vacuum-assisted methods.

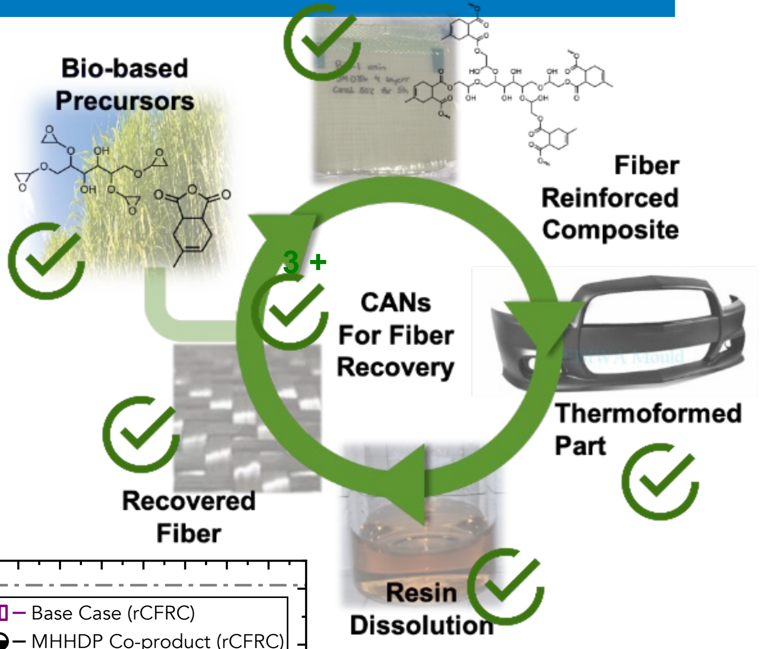
Any proposed future work is subject to change based on funding levels.

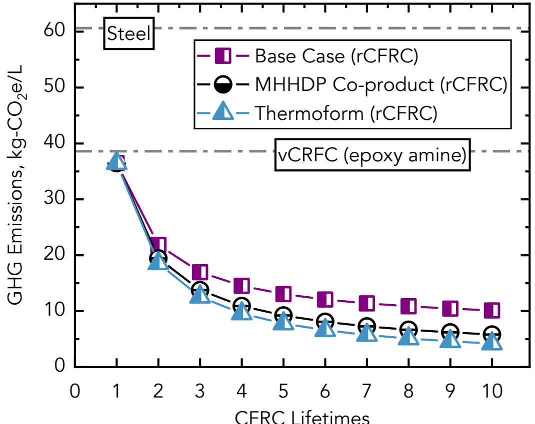
# Summary

**PECANs are a promising resin to enable the recycling and enhanced performance of CFRCs, ideal for vehicle applications.**

- CF can be reused across at least three material lives with no detriment to performance *through either chemical recycling or thermoforming.*
- Resins can be formulated to tune properties, exceeding or matching performance of today's non-recyclable resins, and enable ductility.

**Importantly, process analysis indicates that this approach has major benefits aligned with VTO goals (<$5/kg) – namely dramatic reductions in cost and GHG emissions.**



# Thank You!

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# Back-up Slides

# FY23 Milestones

| Description of Milestones and Go/No-Go Decision | End Date & Status |
|---|---|
| Demonstrate the capability of virgin CAN to repair the composites by introducing artificial injuries and applying virgin CAN to the injury. Repair will be quantified by restoring properties to within 5% of the virgin material. | **December 2022**<br>Complete |
| Prepare a publication for submission detailing the technoeconomic and life cycle benefits of re-using carbon fiber over multiple lives alongside material data demonstrating the re-use of the polyester CAN over multiple lives. | **March 2023**<br>Complete |
| Thermoform the CFRC into at least 2 prototypical parts of different shapes with multiple replicates for testing and will conduct thermomechanical property analysis post thermoforming. | **June 2023**<br>In Progress |
| Report on the thermomechanical properties of the part after repair via reapplication of the virgin CAN post-injury. Demonstrate that the fiber parts (e.g., bumper, panel, or other parts specified by our industry engagement) from the FY23 Q3 milestone can have their fiber recovered after an initial life for reuse in a subsequent material application. | **September 2023**<br>In Progress |

# Publications, Patents, Presentations, Awards, and Commercialization

- U.S. Patent Application. 2022. “Bioderived Recyclable Epoxy-Anhydride Thermosetting Polymers and Resins.” U.S. Patent Application 2022/016442 A1, April 7, 2022.

- Chen Wang, Robynne Murray, Avantika Singh, Erik G. Rognerud, Grant Musgrave, Morgan Skala, Paul Murdy, Scott R. Nicholson, Alison Shapiro, Joel Miscall, Ryan Beach, Robert D. Allen, Gregg T. Beckham, and Nicholas A. Rorrer. 2023. “Recyclable-by-design resins for fiber-reinforced composites from sugar derived building blocks.” Under review.
- Erik G. Rognerud, Jason Desveuax, Gregg T. Beckham, and Nicholas A. Rorrer. 202. “Towards a Better Steel Replacement: Carbon fiber reinforced composites enabled by bio-derivable polyester covalently adaptable networks .” Under review.

- Presentation: *Invited ACS talk. August 2022.*
- Presentation: *University Invited Talks at Virginia Tech, Rowan University, Stanford University, and the University of Delaware.* September 2022 – March 2023.
- Presentation: *Invited ACS talk. August 2023.*

# Critical Assumptions and Issues

- We assume that the thermomechanical properties of the bio-based CAN-CFRCs are suitable, or even advantaged, for vehicle applications.
  - We are continuously testing our formulations and panels for their properties, and as demonstrated in our Q1 milestone, their properties can match epoxy-amine formulations.
  - There may be an "upper limit" on material properties with this system, which is applicable to this recyclable-by-design system, but we can always pursue alternate systems.

- We assume that fibers can be used in multiple lives.
  - We have demonstrated this is true on moderate scales (100+ g); however, scale-up is an evolving scientific question.
  - We also plan to understand the practical number of lives for a material through supply chain modeling and engagement with industrial collaborators.