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

6/23/2022

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2022 DOE Vehicle Technologies Office Annual Merit Review

Project ID: mat209

Project Overview

Timeline

- Project start: October 2020
- Go/No-go Milestone: September 2021
- Project end: September 2023
- Percent complete: ~50%

Budget

	To Date	Total Project
DOE Funding	$500,000 (FY 22) $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.

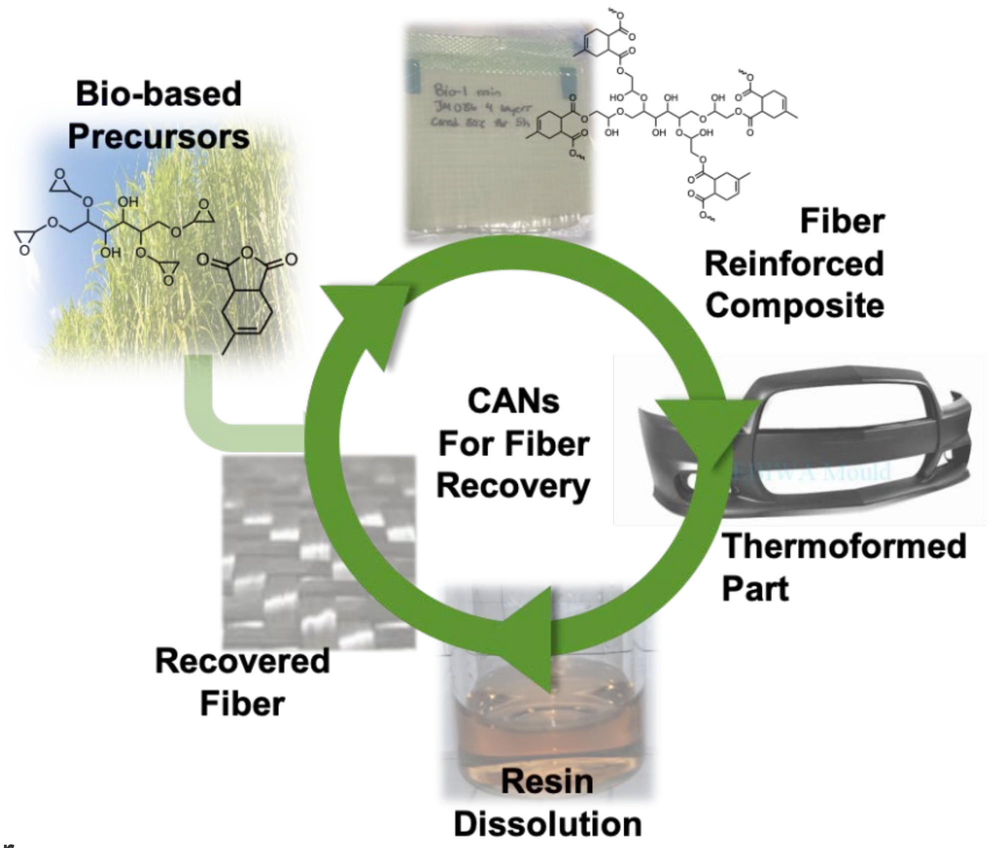
Relevance

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 developing resins that can undergo exchange reactions, CFs can be recycled, and thermomechanical properties can be modulated.
- By leveraging bio-based starting blocks, this work has the potential to decarbonize the processes associated with vehicle part manufacture, especially in the second life of materials and beyond.

Objective

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



Approach

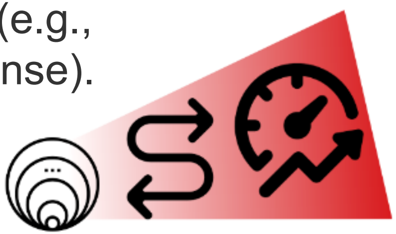
This project is divided into four tasks aimed at taking CFRCs from fiber and resin to a part and back again, across multiple length scales.

Task 1: CAN-CFRC synthesis

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

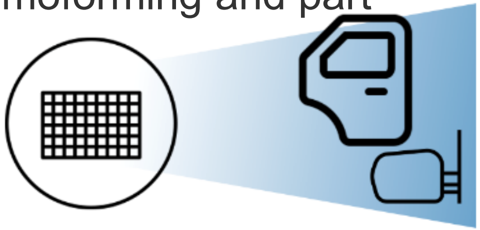
Task 2: Develop sizing of fibers that improve performance

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.



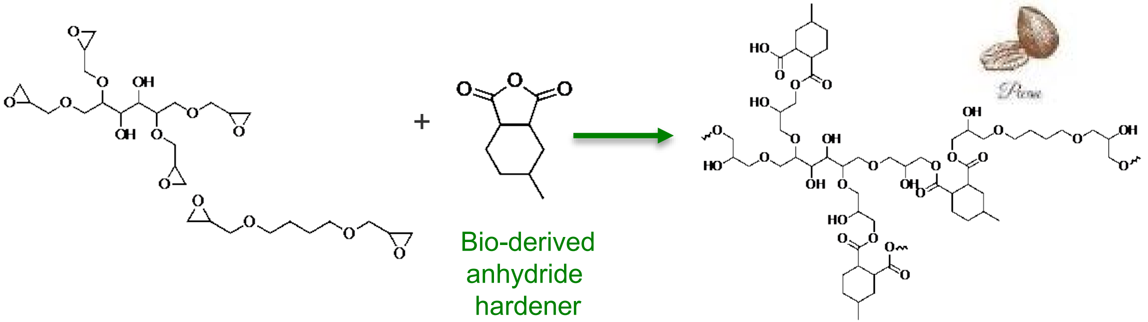
Task 4: Analysis

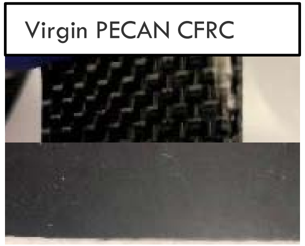
Perform techno-economic analysis (TEA) and supply chain analysis across multiple lives to estimate selling price and greenhouse gas (GHG) emission reductions.

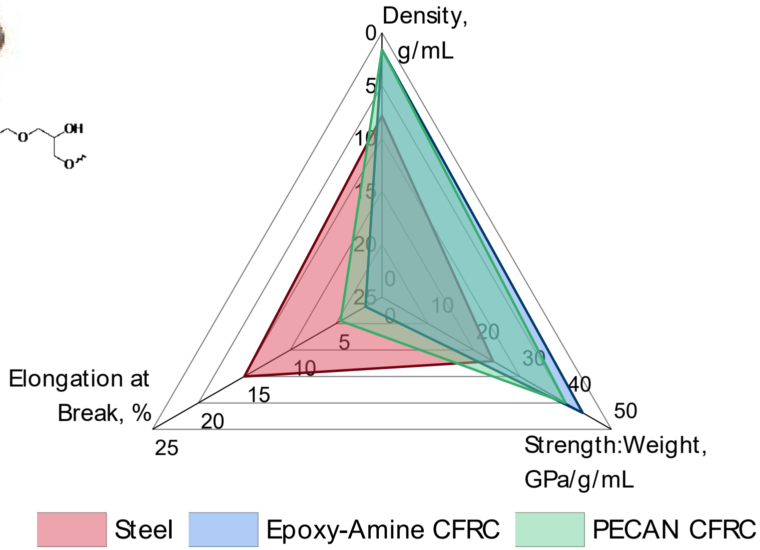
Milestones

Description of Milestones and Go/No-Go Decision	End Date & Status
Report the properties of CAN-CFRC with fibers beyond CF, including glass and basalt fiber at a minimum.	**December 2021** Complete
Explore the use of thermoplastic resin (e.g., polyethylene terephthalate [PET], phenoxy) to modify the CANs to augment material properties. Report the thermomechanical properties of the neat resin and CFRCs, aiming for a more ductile material response over the baseline material.	**March 2022** Complete
Deliver TEA and Materials Flow through Industry (MFI) updates based on new experimental findings, and conduct sensitivity analysis including minimum selling price, energy consumption, and carbon footprint; **Demonstrate and report on the synthesis of at least two different sizing modifications to a minimum of CF and glass fiber that can exchange with the selected polyester CAN chemistry.**	**June 2022** Ongoing
Demonstrate the influence of resizing fibers post PE-CAN recycling to either maintain PE-CAN properties across multiple lifetimes and/or enable exchange between the fiber and CAN. **Commission a thermoforming mold at NREL. Additionally, implement a polyester CAN into a fabricated part (e.g., bumper, panel, or other parts specified by discussions via our industry engagement and outreach activities) via a thermoforming process. Report on part properties and thermoforming conditions. Specific properties to be reported on include tensile testing, impact testing, and material creep.**	**September 2022** On target
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** Planned

Technical Accomplishments – FY21 Recap



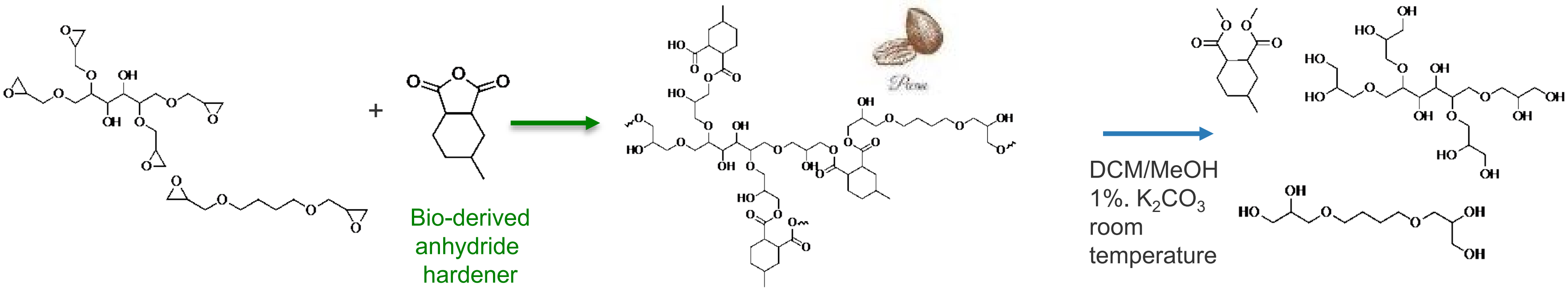




Polyester covalently adaptable networks (PECAN) are recyclable-by-design

- 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



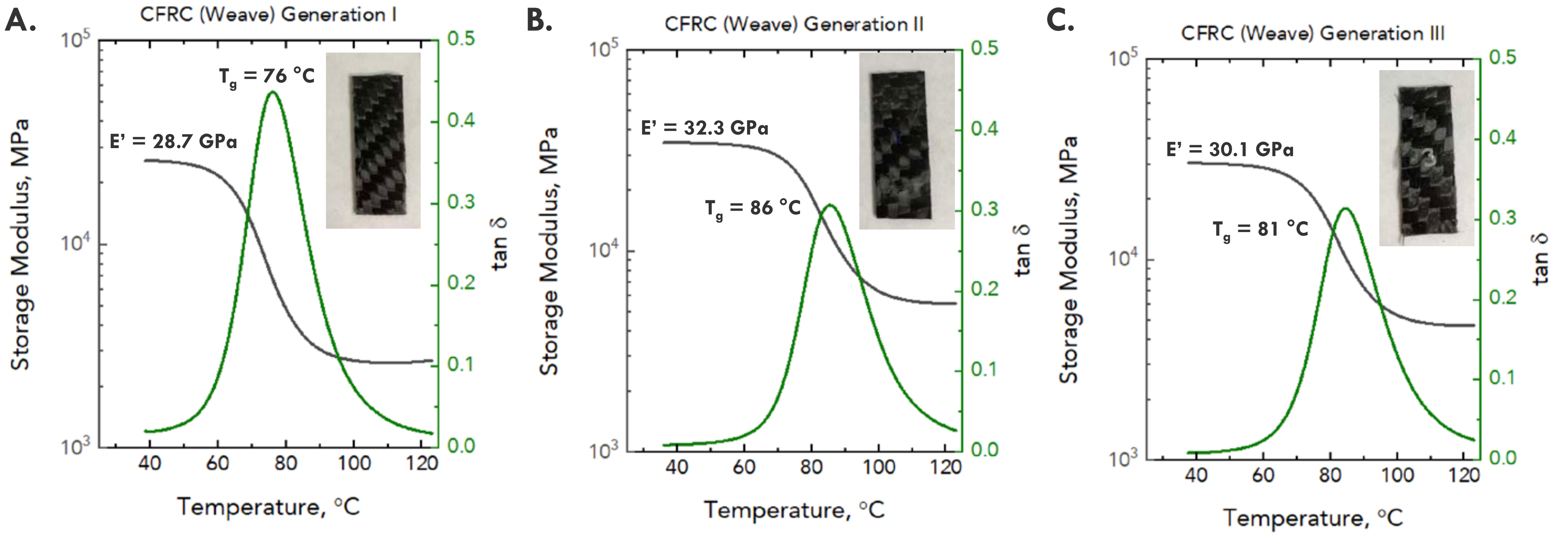
Virgin PECAN CFRC

Depolymerized CFRC

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 dichloromethane (DCM); under reflux, the depolymerization occurs in less than a day.
  - The part thickness and form factors affect time.
  - Alternative solvents, such as acetone, have also been employed.

Technical Achievements – Performance Across Lives



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

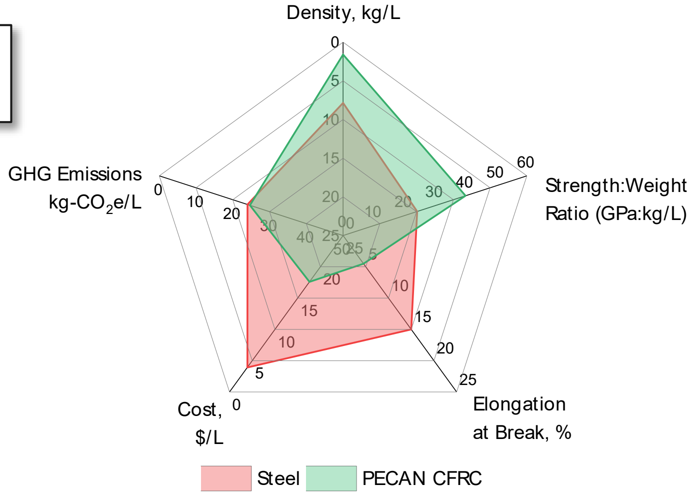
- The PECAN CFRCs exhibit consistent properties within equipment error across multiple lives.
- Supplementary results indicate that the depolymerization bath does not affect fiber sizing negatively.

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

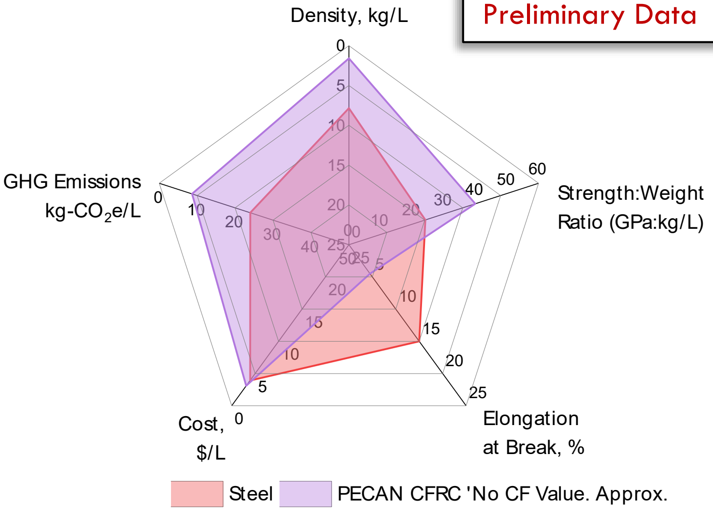
Fiber estimate price:
$21.5/kg (variable)

Hexion estimate price: **≥ $2.03/kg**

Estimate initial selling price: **≥ $2.17/kg**



Preliminary Data

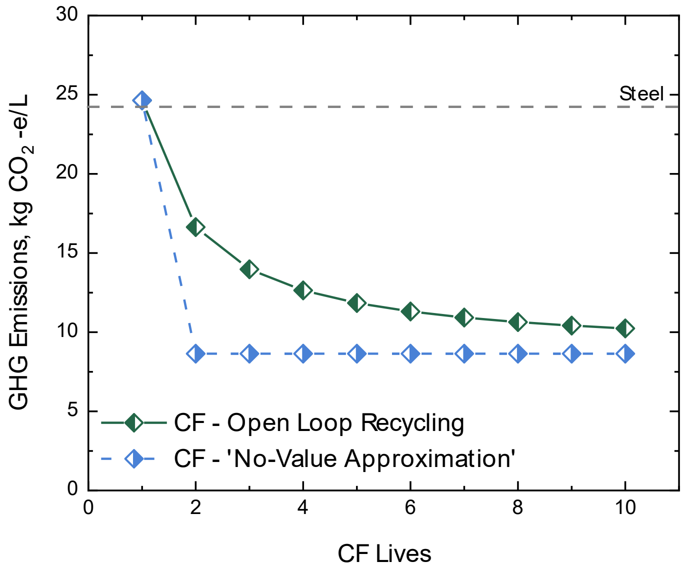


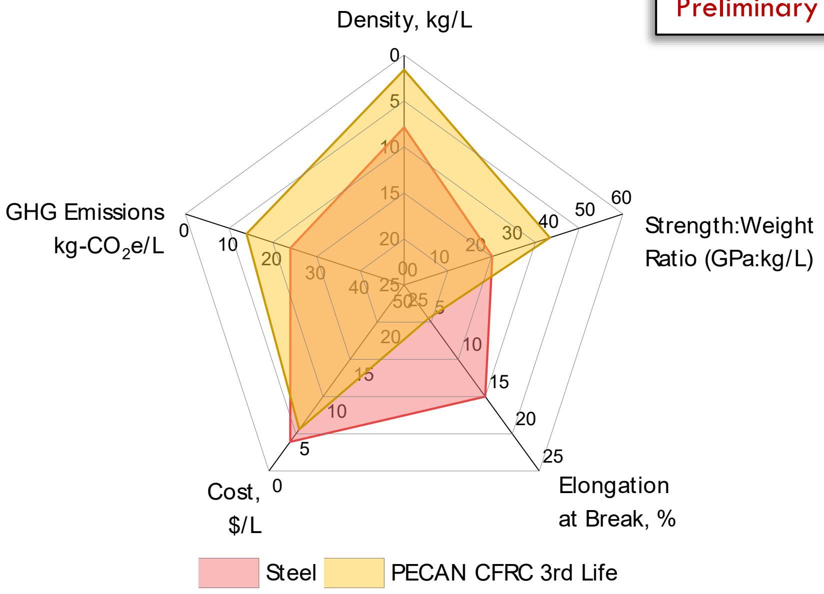
Our <u>active Q3 milestone</u> at the time of AMR preparation: Focusing on the CFRC GHG emissions across multiple lives

- Virgin PECAN CFRC synthesis is comparable to steel GHG emissions on a volume basis.
- When the first life of the CFRC is not accounted for, nor the recovery of monomers, the GHG impacts of all subsequent lives are ~10 kg/L.
  - Resin depolymerization and CF recovery accounts for 4.4 kg CO_2-e/kg_{CFRC} and cost $1.70/$kg_{CF}$
  - TEA for depolymerization is still ongoing. Early economics are favorable and still need to account for the recover of the anhydride, which can be sold ($2–$4/kg) to bolster economics.

Technical Accomplishments – Enhanced TEA/LCA

Preliminary Data

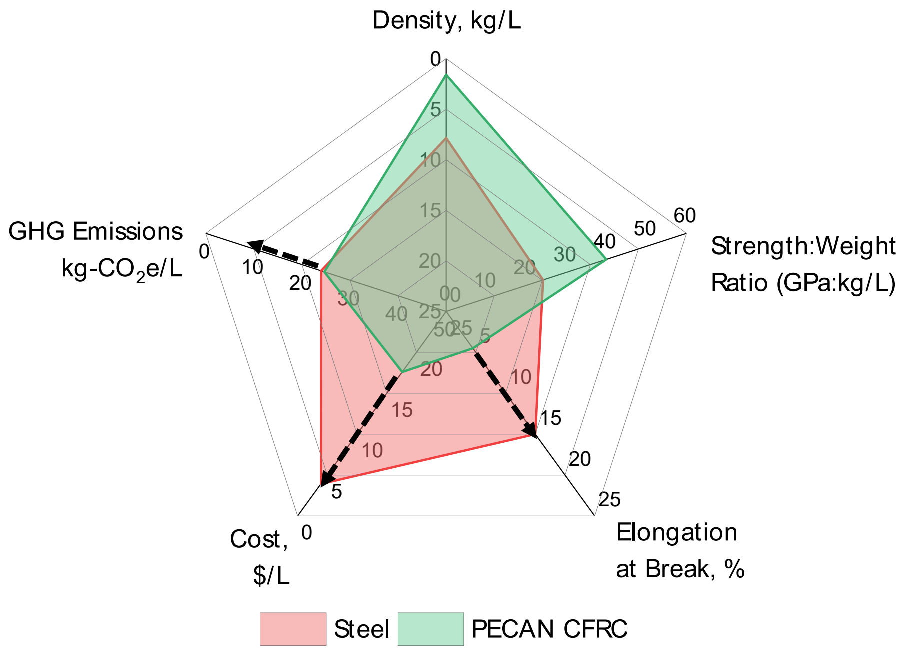




Our <u>active Q3 milestone</u> at the time of AMR preparation: Focusing on the CF GHG emissions across multiple lives

- An open-loop analysis approach can be applied to PECAN-CFRC synthesis to spread its impact across multiple lives.
- GHG and cost benefits are seen with just two material lives.
  - After five material lives, additional benefits are diminished.

Technical Achievements – FY22 Milestones



Addressing FY21 challenge of enhancing material properties

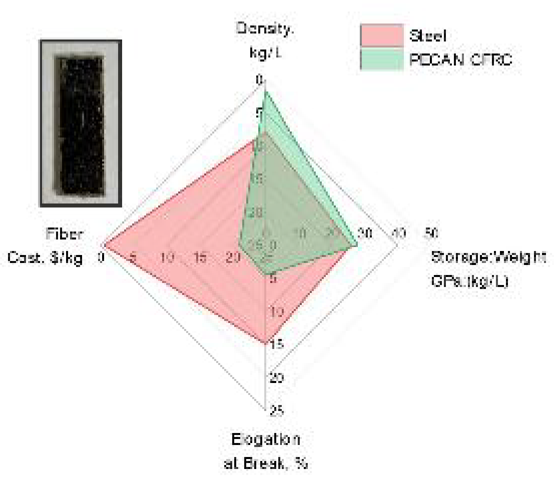
Our milestones this year aim to understand the material, economic, and environmental phase space we can explore with our PECAN-CFRC.

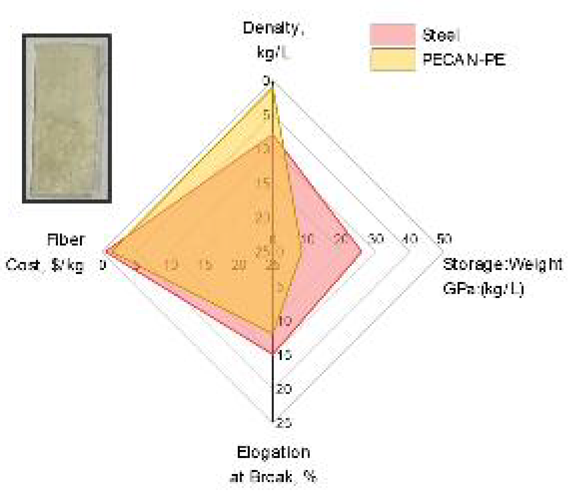
Each component of a vehicle will require a slightly different material profile, so we aim to develop ***a mastery of this phase space*** *to tune resin composition to component requirements.*

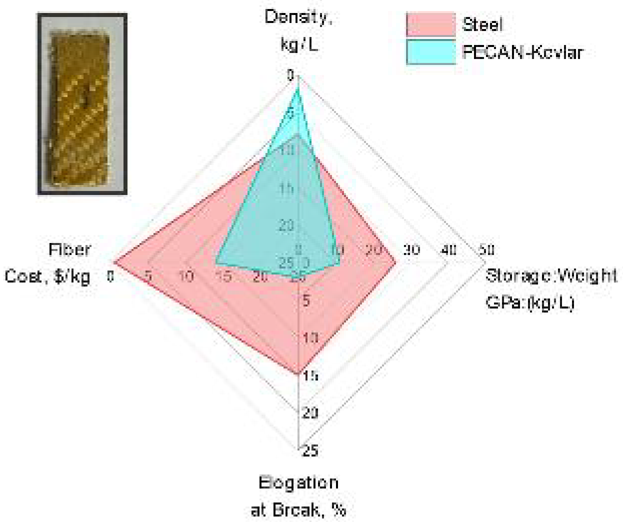
Overall, each milestone focused on improving a different CFRC component:

- Q1 – Alternative fibers
- Q2 – Additives and alternative formulations
- Q3 – Alternative sizings
- Q4 – Sizings post-depolymerization and thermoforming.

Technical Achievements – Alternative Reinforcements



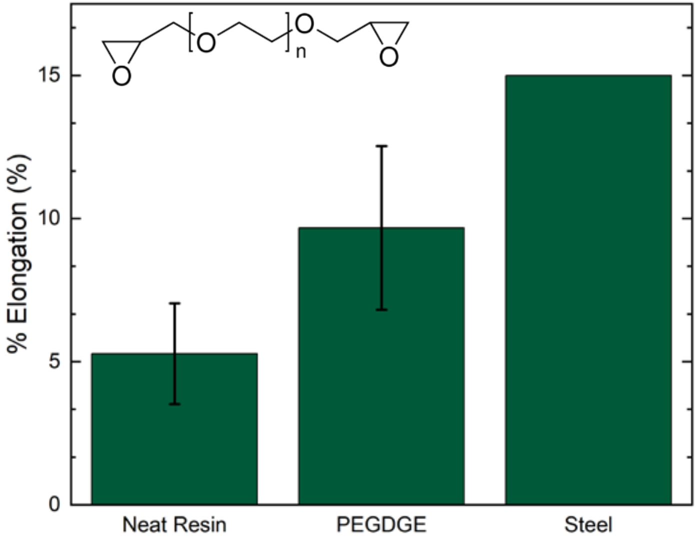


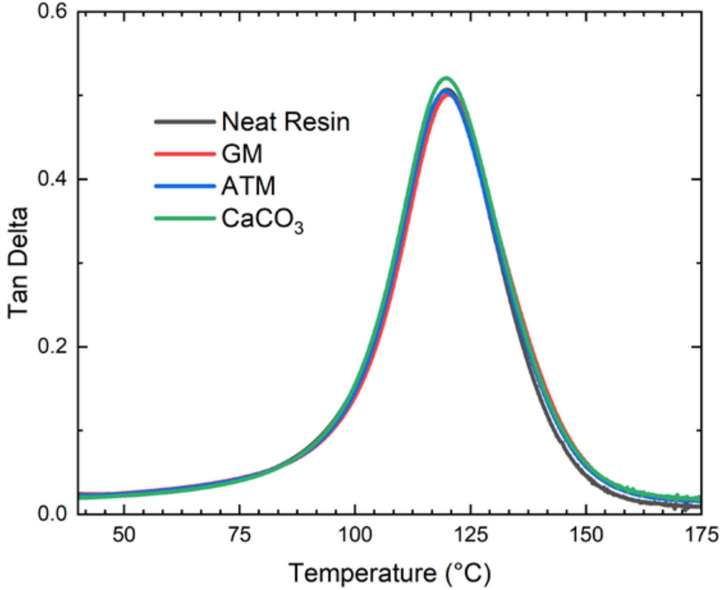


Fiber redesign can tune material and economic performance

- In general, the trend with fibers is consistent to what has been observed with traditional epoxy-amine-based CFRCs. During this milestone, we screened >10 alternative reinforcements.
  - Additionally, all fibers (except PET) can be recovered post-depolymerization.
- Polyethylene (PE) fibers over CF enhance ductility while reducing density and cost.
- Blends of PE and CF are a promising future direction to enable steel replacements.

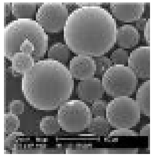
Technical Achievements – Formulating to Target





Calcium carbonate ($CaCO_3$) $0.1/kg ($0.27/L)

Aluminum tri-hydrate (ATH) $0.5/kg ($1.23/L)

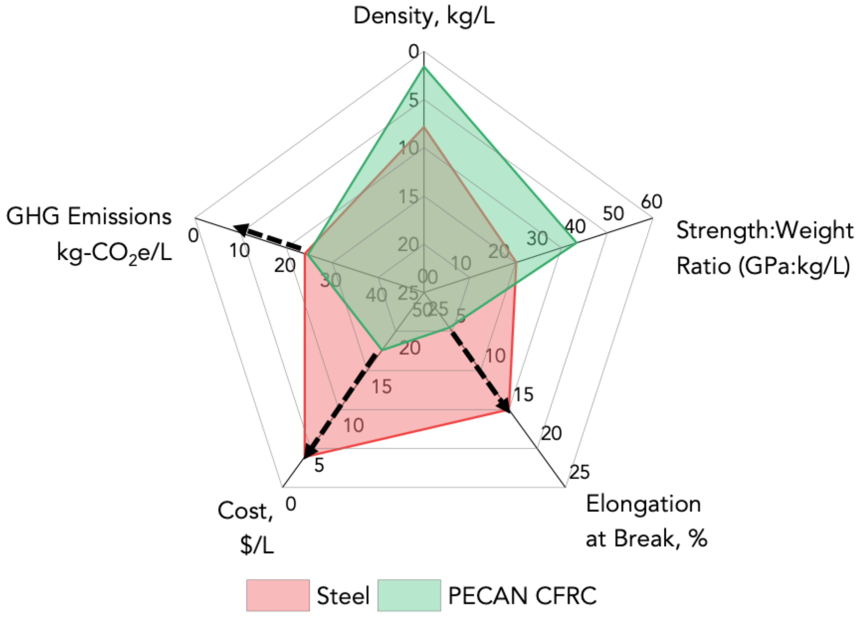


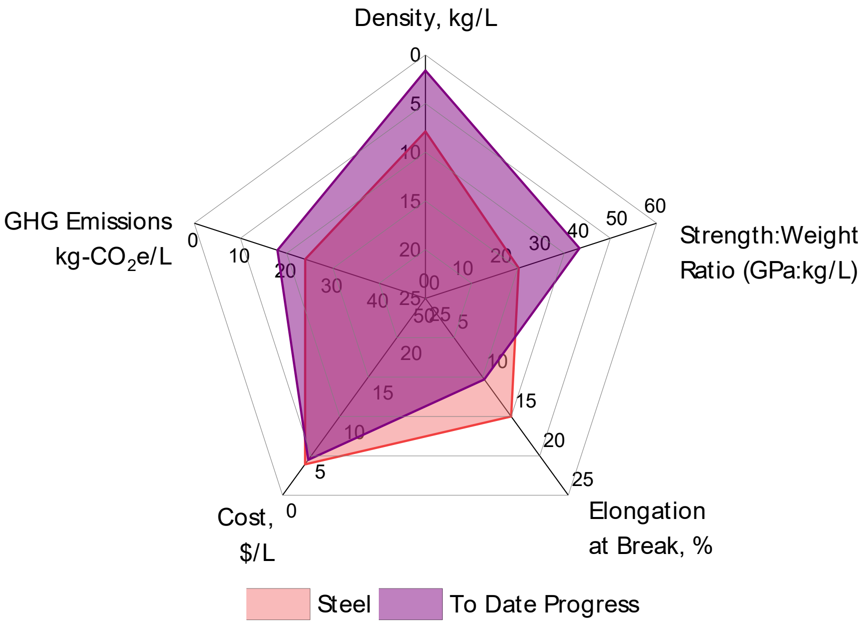
Glass microspheres (GM) $0.66/kg ($0.10/L)

Enhanced ductility, lower cost, and improved performance

- Across the past fiscal year, we have created >30 alternative formulations targeting augmented properties including thermoplastic additives, alternative formulations, cost-reducing fillers, and transesterification catalysts.
- The incorporation of alternative epoxies, notably polymeric epoxies, can lead to enhanced material ductility
- Cost reducers or flame retardants can be used in loadings up to 10 wt % with no detriment to properties.

Technical Achievements – Accessible Phase Space





Formulating for a phase space mastery

- Utilizing CF for multiple lives enables cost prices in line with steel for subsequent lives with reductions in GHG emissions.
  - TEA is ongoing; however, the early results indicate that the second life of the CF will be <$5/kg due to the low energy process and selling of coproducts, aligning with VTO goals.
- Reformulation and the use of additives enable access to a more robust material phase space.

Responses to Previous Year Reviewer's Comments

We thank the reviewers for their time and comments, such as "The reviewer stated that this project clearly leverages other efforts, and the team delivered outstanding results in the first year."

Comment: The presentation states that the depolymerization at room temperature takes less than 2 days but can be faster at elevated temperatures. For future commercialization, the reaction would need to be much faster than a day to be attractive to composite recycling companies.

- Response: Depolymerization can maintain fiber alignment as long as the temperature is below reflux and is also dependent on part thickness, temperature, and form. Depending on the conditions, ***depolymerization can occur in under 1 day or under 1 hour.*** We have reflected this in our remaining challenges and future milestone section and also ***highlight the importance of TEA analysis, which is ongoing, to understand the effect of time fully***

Comment: After the depolymerization, the reviewer was curious about how the project team envisions the resulting fibers will be reused. For example, if a woven fabric is recovered, the reviewer asked if the weave would remain in its current state as a tight weave or whether it would start to fall apart during the solution process. It will be hard to recover continuous tows of fibers for re-use as a continuous tow since fiber weavers and filament winders typically use spools of fiber that are thousands of feet

- Response: There is still a large potential for future work to evaluate what reinforcements need to be used for what vehicle component. As demonstrated in other projects, weave and unidirectional fibers are not always needed. ***There is still a huge potential to address depolymerization at scale, and our milestones in FY23 aim to address this after initial thermoforming***.

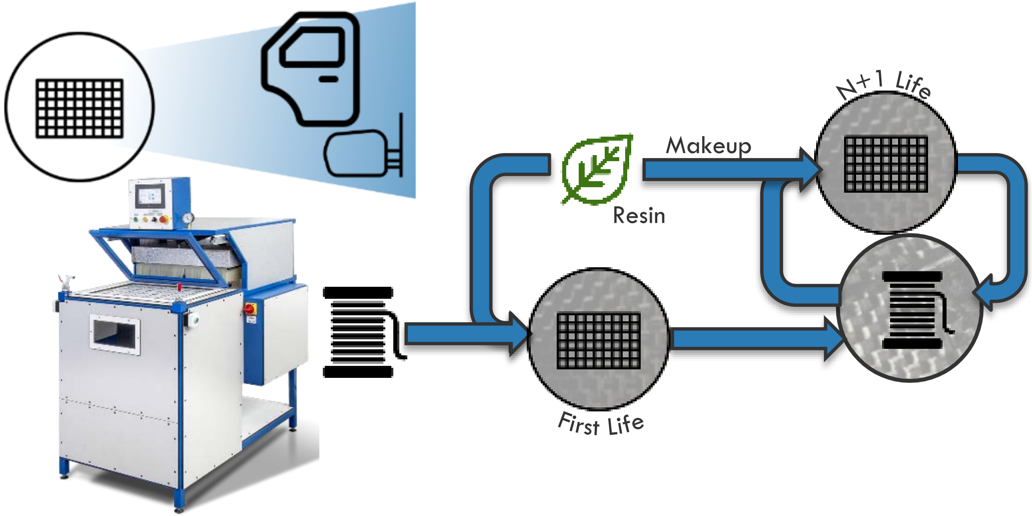
Comment: The reviewer encouraged collaboration with organizations having a strong background in composites manufacturing, and technology transition to the industry should be established.

- Response: We have begun conversations with multiple chemical companies about the use of bio-derived resins. ***This includes the active negotiations of NDAs and licensing with various companies***.

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

Remaining Challenges and Barriers – Scale-Up

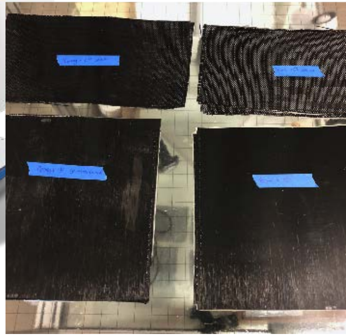


Part manufacture, thermoforming, and depolymerization at scale

- To date, we have demonstrated a large degree of tunability within our phase space for the PECAN-CFRCs.
  - Initial thermoforming trials have demonstrated that we do require enhanced ductility for rapid thermoforming or slower thermoforming times. Thus, there are still challenges to address.
- Depolymerization has been evaluated on panels but will need to be demonstrated on actual parts made with different fiber orientations to understand how changes in orientation will affect part performance across multiple lives.

Proposed Future Research – Key Milestones

Description of Milestones and Go/No-Go Decision	End Date & Status
Commission a thermoforming mold at NREL and implement a polyester CAN into a fabricated part.	**September 2022** On target
Demonstrate the capability of virgin CAN to repair the composites. Repair will be quantified by restoring properties to within 5% of the virgin material.	**December 2022** Planned
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** End-of-project goal Planned

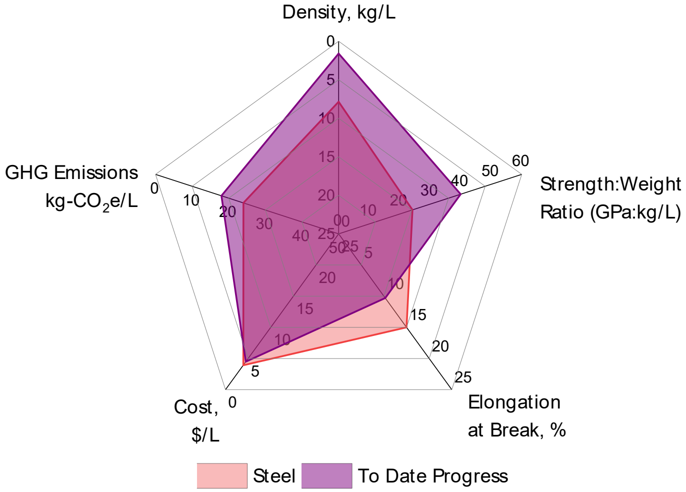


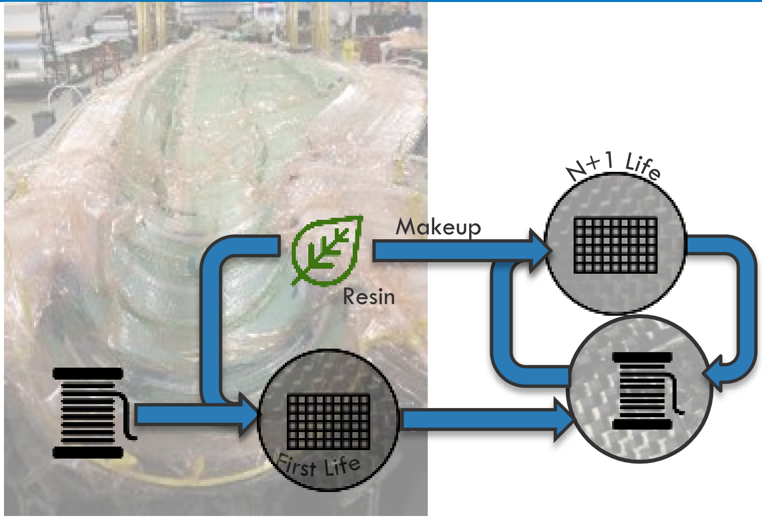
Thermoforming, repair, and post-part reuse

- We are on target to demonstrate thermoforming to a small-scale car hood, possibly ahead of the milestone.
- We are also on track to demonstrate that our materials can be healed post-injury, which will help extend material life.
- Finally, by the end of project, we will reuse or thermoform parts across multiple lives.
  - This component aligns with reviewer comments.

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 relative to automotive manufacture (1 kg).
- 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.

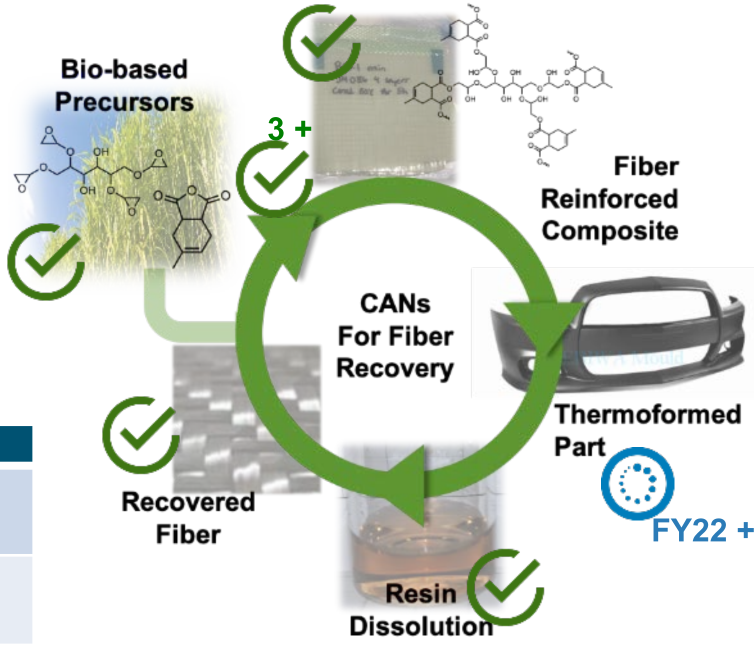
Any proposed future work is subject to change based on funding levels.

Summary

Polyester-CANs are a promising resin to enable the recycling and enhanced performance of CFRCs ideal for vehicle applications

- All targets *have been met or are on track* for completion.
- CF can be reused across at least three material lives with no detriment to performance.
- Resins can be formulated to tune properties, exceeding or matching performance of today's non-recyclable resins, and enable ductility.
- Preliminary TEA/LCA is promising that if performance can be maintained, the cost and GHG impact of second-life CFRCs and beyond can be greatly reduced (<5+/kg and ~10 kg CO_2-e/kg_{CFRC}).

Goal	Progress
Utilize alternative fiber reinforcements with the PECAN resin; understand what advantages to properties they may bestow.	**December 2021** Complete
Implement additives to augment the material properties, aiming for an increase in ductility.	**March 2022** Complete
Explore the effect of fiber sizing on properties. Deliver expanded TEA/LCA on multiple CFRC lives.	**June 2022** On target
Demonstrate initial thermoforming of the material.	**September 2022** On target



Acknowledgments

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Thank You!

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NREL Transforming ENERGY

Reviewer-Only Slides

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. 2022. "Recyclable-by-design resins for fiber-reinforced composites from sugar derived building blocks." Under review.
- Presentation: *Invited ACS talk. August 2022.*

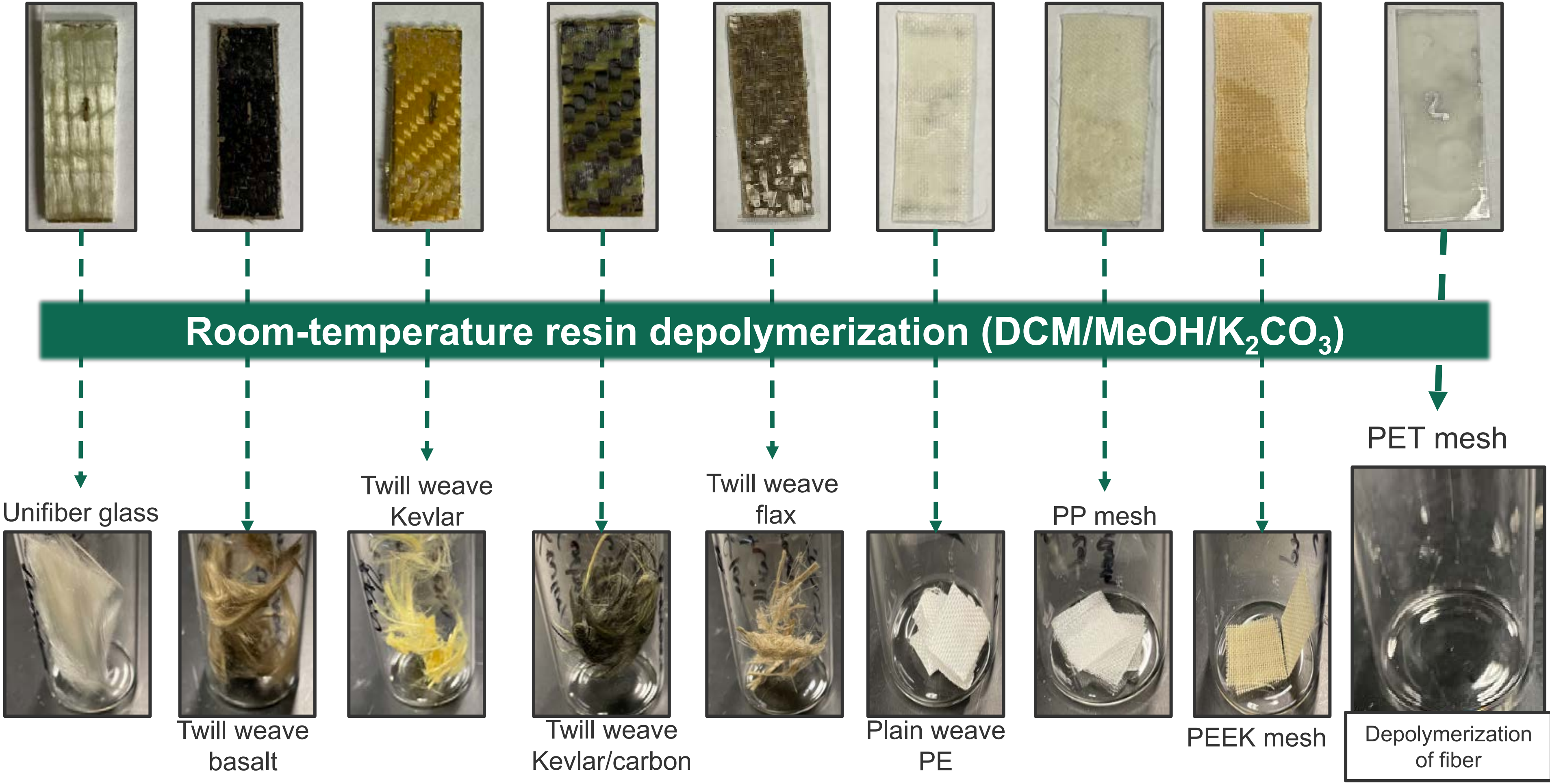
Critical Assumptions and Issues

- We assume that our polyester CAN-CFRCs can be thermoformed.
  - We have demonstrated that the use of zinc can induce relaxation in the CFRCs to enable relaxation through bond exchange, which in turn can aid with the thermoforming process.
  - We will have to balance performance properties with the ability to be thermoformed.
  - We have also showed that changes to reformulation can enhance ductility and thus can be used to aid in thermoforming if necessary.

- 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.

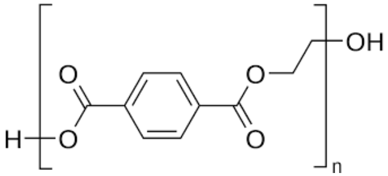
- We assume that fibers can be used in multiple lives.
  - We have demonstrated this is true on moderate scales (100+ g); however, scale-up is an evolving scientific question.
  - We also plan to understand the practical number of lives for a material through supply chain modeling and engagement with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

Technical Backup Slides – Depolymerization Visualization

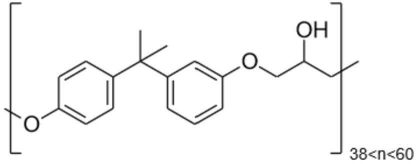


Technical Backup Slides – Formulating for Improved Properties

Ductility Modifies

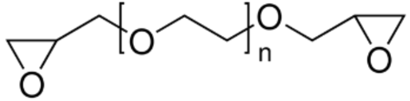


Thermoplastic PET

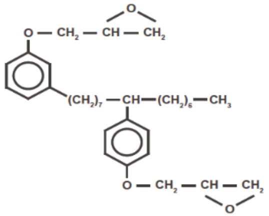


Reactive phenoxies

Formulation Development

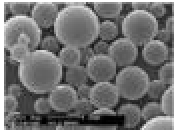


Polyethylene glycol diglycidyl ether



Cardolite NC-54

Cost Reducers



Zn(Stearate), $CaCO_3$, glass bubbles, etc.

Three classes of "new formulations"

- For the Q2 milestone, we explored the addition of thermoplastics or formulation to enhanced ductility while looking at fillers to reduce cost.
- Across the past fiscal year, we have created >30 alternative formulations targeting augmented properties.