NREL
Transforming ENERGY

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

6/23/2021

Gregg Beckham, NREL

2021 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: ~20%

Budget

	FY21	Total Project
DOE Funding	$500,000	$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 CFRCs

Project Partners

- N/A at this time

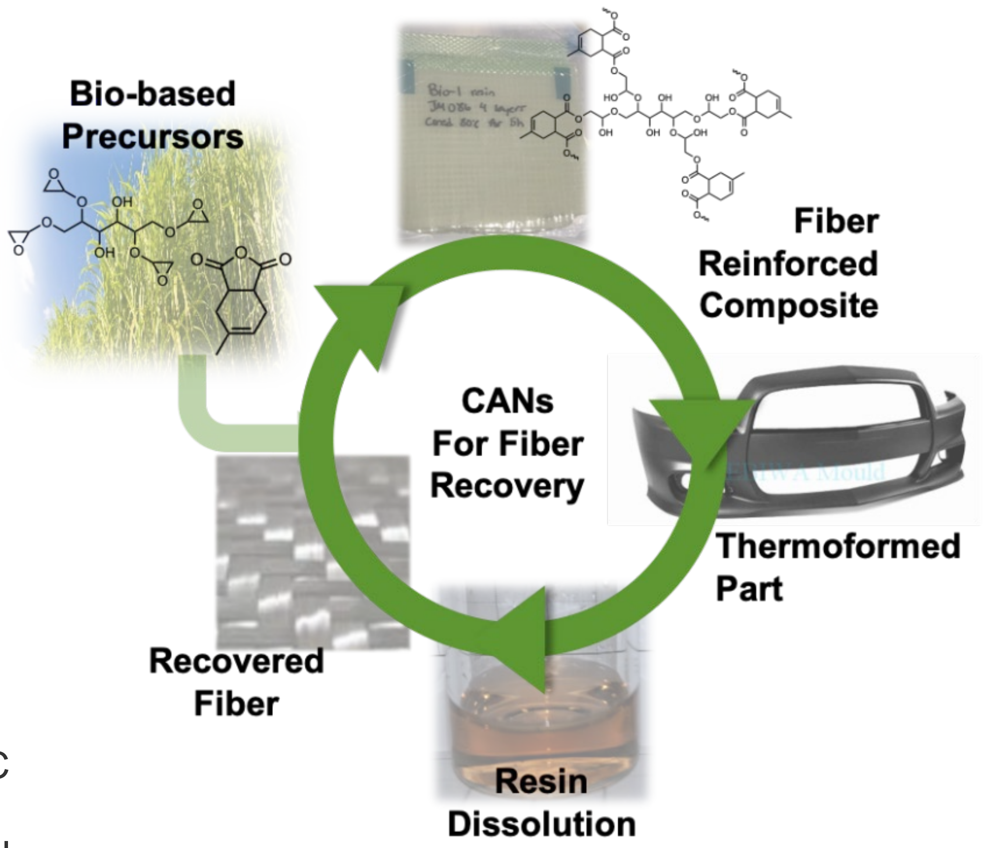
Relevance

Impact

- Carbon fiber reinforced composites (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 biobased starting blocks, this work has the potential to decarbonize the processes associated with vehicle part manufacture, especially in the second+ life of materials

Objective

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



Approach

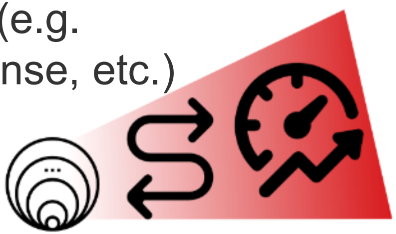
This project is divided divided into four (4) tasks aimed at taking CFRCs from fiber and resin to a part and back again, across multiple length scales.

Task 1: CAN-CFRC Synthesis

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

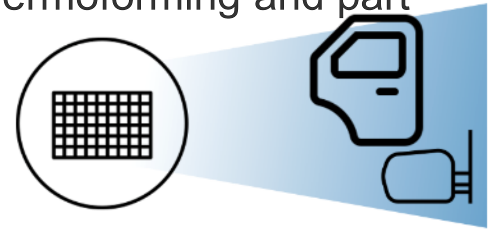
Task 2: Develop sizing of fibers that improve performance

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



Task 3: Validation and Scale-up

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



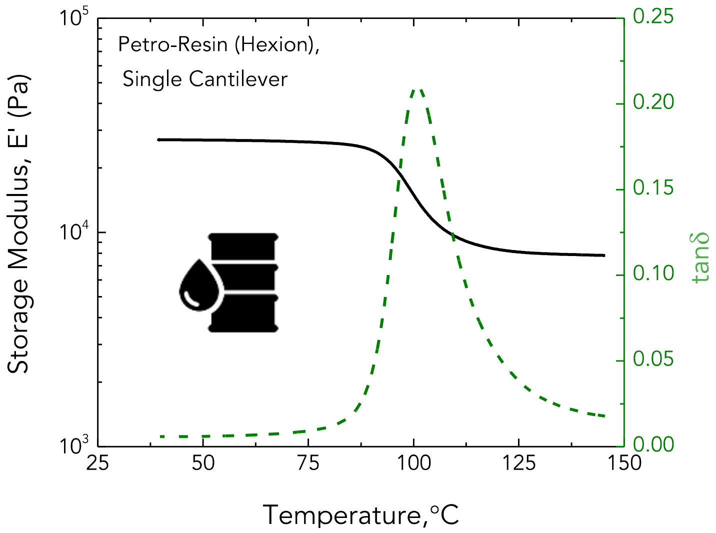
Task 4: Analysis

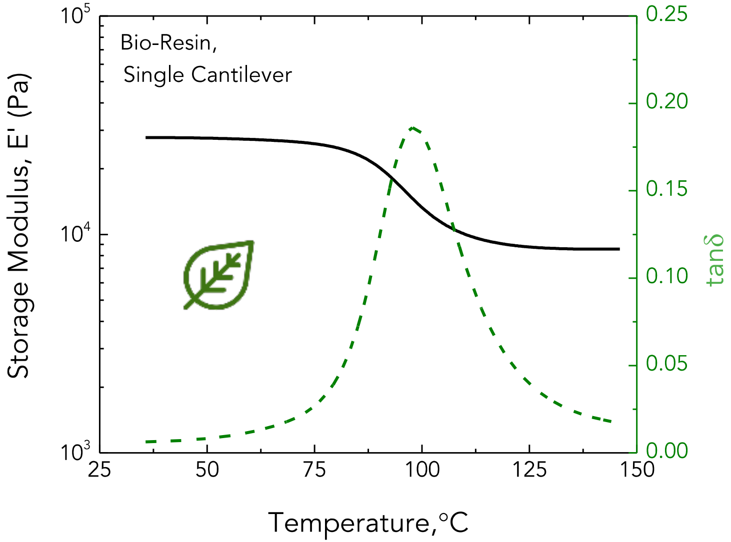
Perform technoeconomic analysis (TEA) and supply chain analysis across multiple lives to estimate selling price and GHG emission reductions

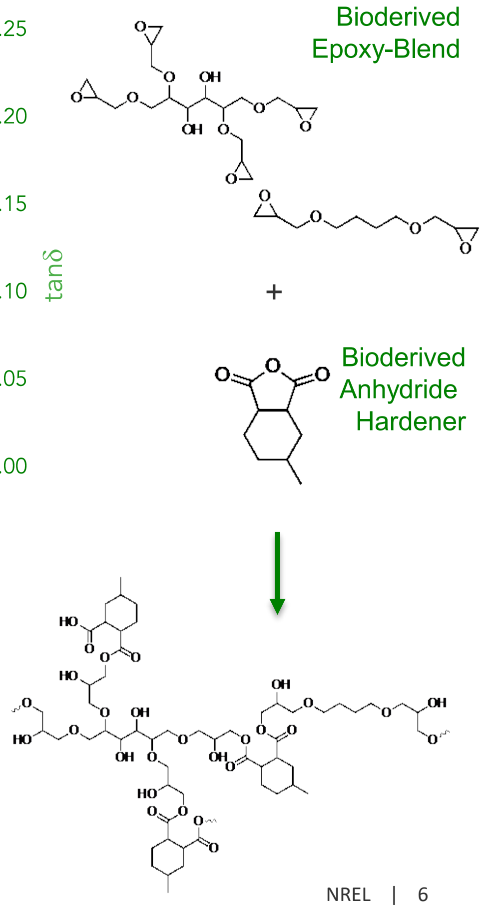
Milestones

Description of Milestones and Go/No-Go Decision	End Date & Status
Report and baseline the CAN-CFRC properties relative to a standard epoxy-based CFRC.	**December 2020** Complete
Determine and optimize the processing conditions for the synthesis and the subsequent depolymerization of the CAN-CFRC, targeting a depolymerization temperature of < 250°C.	**March 2021** Complete
Demonstrate the reuse of the fiber and report on the variation in material properties. **Deliver baseline TEA and MFI (Materials Flow through Industry) models on both epoxy-amine and CAN polymers.**	**June 2021** On Target
Demonstrate the properties of recycled PE-CAN CFRC across three cycles to be within a 20% variance every cycle. Compare the properties with the epoxy-amine resin subject to the same recycling conditions. **Additionally, produce CAN-CFRCs panels (≥1 kg scale)** **Go: Continue with the project as planned. No-Go: Rescope project to target a different CAN (e.g., trans-thioesterification, amine-imine reaction) that undergo faster exchange reactions rate to enhance recycling.**	**September 2021** On Target
Demonstrate the influence of re-sizing 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

Technical Accomplishments – Resin Development



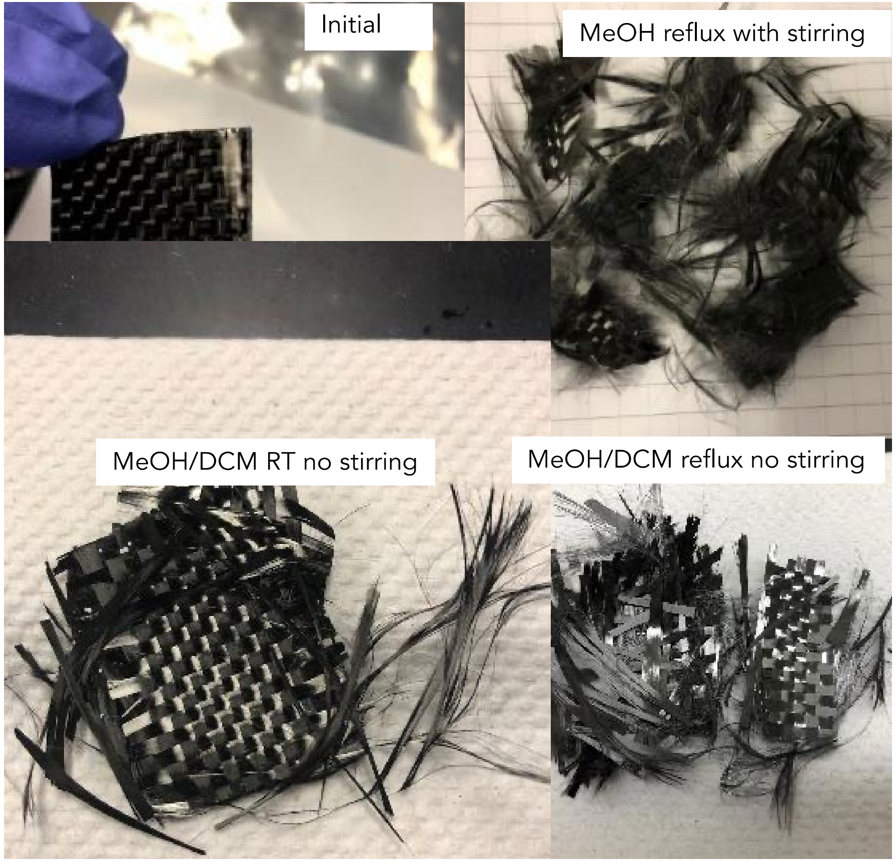


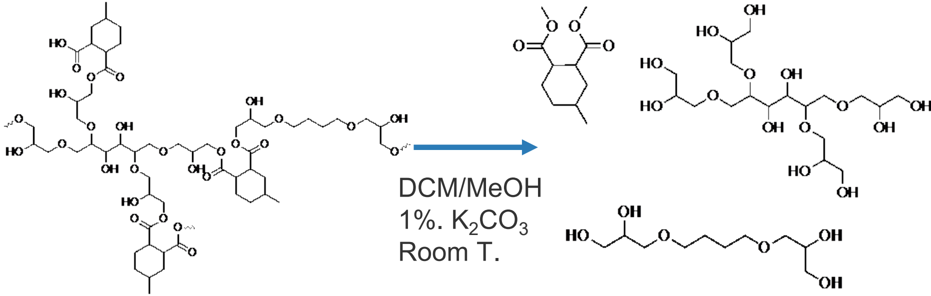


Demonstrated a bio-derived epoxy-anhydride resin that exceeds the thermo-mechanical properties of petroleum derived epoxy-amine resins

Properties consistent across multiple tests: DMA testing indicates that we can formulate resins to match storage and loss moduli and T_g (maximum of tanδ)

Technical Accomplishments – Low T Depolymerization

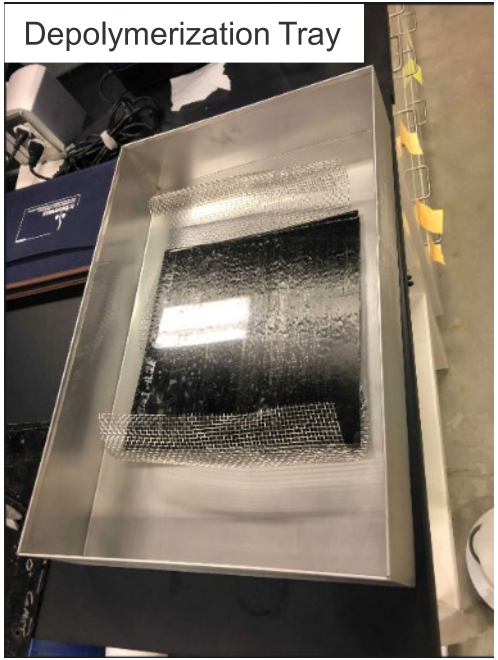


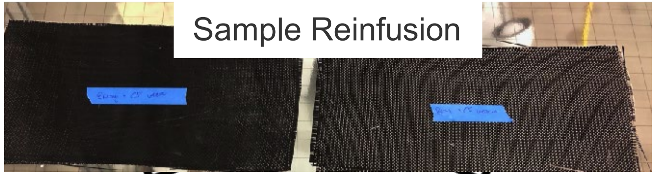


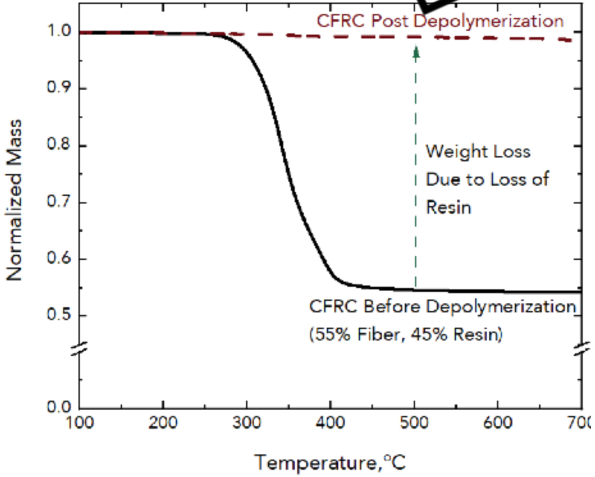
Room temperature depolymerization of CFRCs can be achieved t < 2 days while maintaining fiber integrity

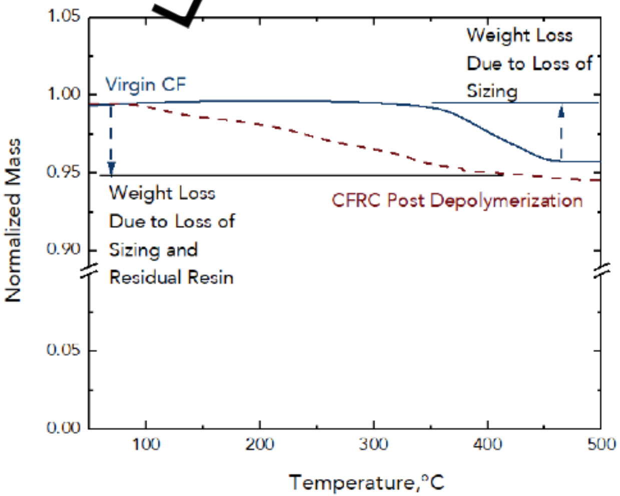
- Reactions triggered with the catalyst and do not occur in neat solvent. At elevated temperature, depolymerization is faster
- Developed chemical methods to recover and recycle the anhydride-hardener from the depolymerization mixture

Technical Accomplishments – Fiber Re-Use





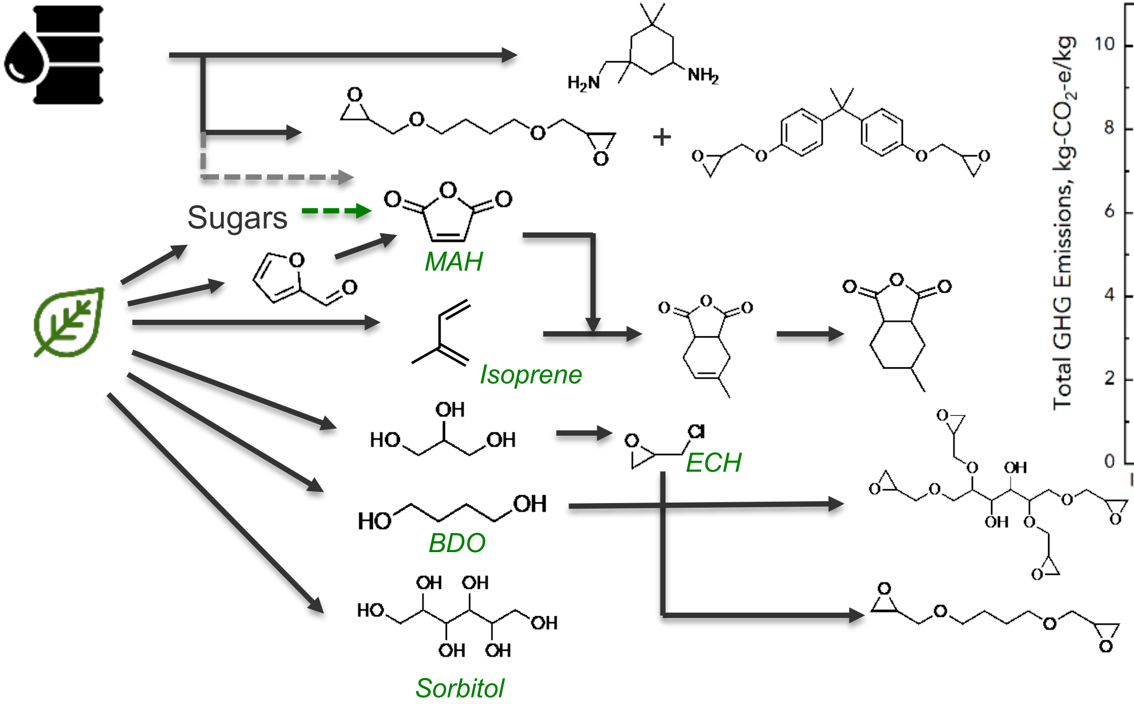


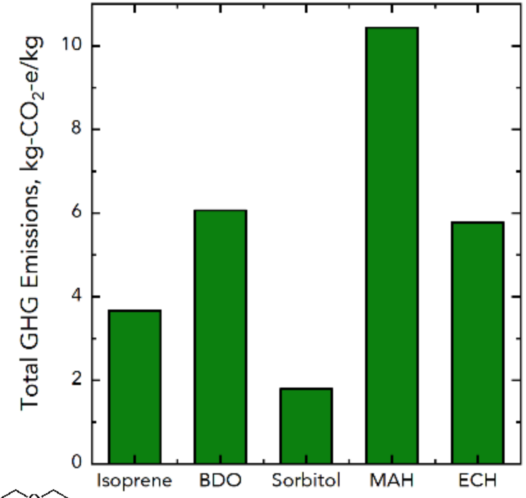


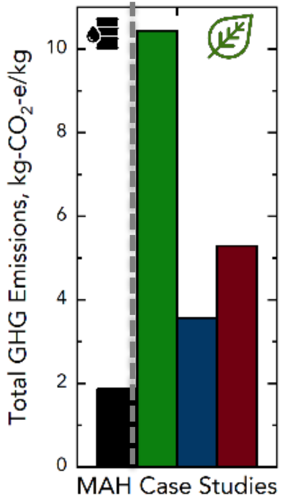
This work aligns with our current Q3 milestone and is ongoing. We are applying the methodology from Q2 at a larger scale and plan to reinfuse the panels via VARTM

TGA results also indicate no detrimental effect to the CF sizing post depolymerization. Residual resin may further aid re-use due to exchange reactions

Technical Accomplishments – Initial TEA/LCA







Hexion Estimate Price: **2.03+ /kg**

Estimate Initial Selling Price: **2.17+ /kg**

Fiber Estimate Price: **21.5/kg (Variable)**

Initial results indicate the bio-resin is comparable with Hexion; however, we are exploring alternative pathways for price and/or GHG emissions reductions

Reductions are mainly focused on maleic anhydride for cost and GHG reduction

Data are preliminary and represents our current milestone

Responses to Previous Year Reviewer's Comments

This is the first year this project has been reviewed, with a start date of October 1st, 2020.

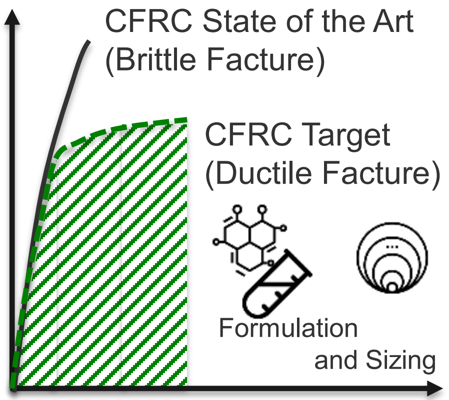
Collaboration and Coordination with Other Institutions

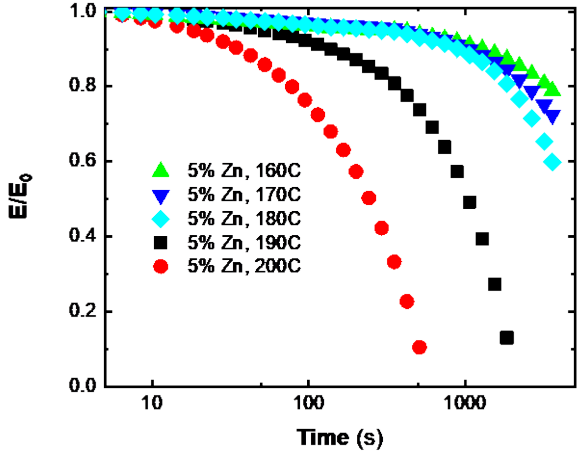
- National Renewable Energy Laboratory – Wind Technology Center
  - Focus on scale-up activities and infusion of panels

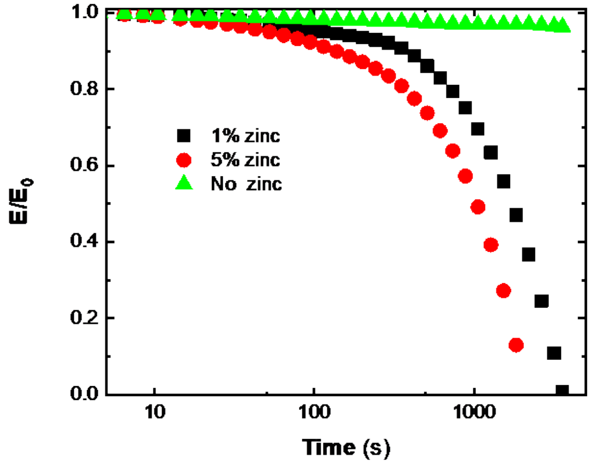
- BOTTLE Consortium
  - Collaboration that provides scientific input on redesign, formulation, and recycling. Includes technical advisory board and a wide range of industry contacts

- Companies engaged through the Renewable Carbon Fiber Consortium
  - Contacts serve as technical advisors to help inform research (e.g. parts and properties to target, etc.)

Remaining Challenges and Barriers - Performance







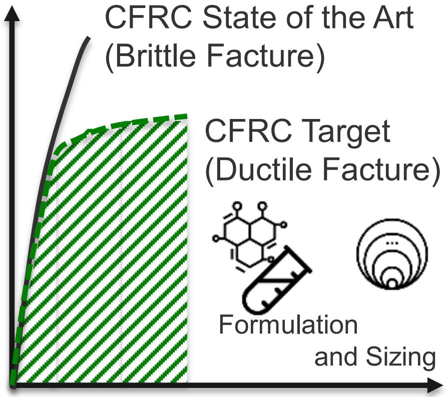
Enhancement of Material Properties

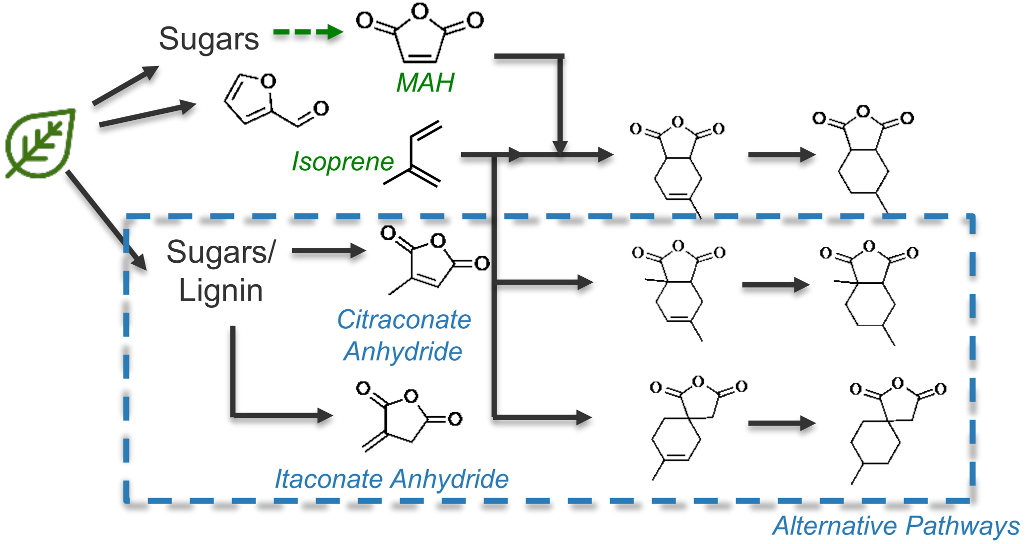
- CFRCs are known for a brittle response. In FY22 we will explore fiber sizing and/or the addition of additives (e.g. zinc, phenoxy resins, etc.) to see if we can prompt a more ductile response, akin to steel

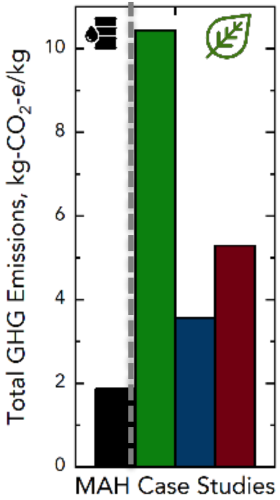
- Showing “weldability” of the CAN-CFRCs when subject to damage or when parts are laid up with each other
  - Balance material performance and additional attributes
  - This can be enabled by the addition of additional resin and trace catalyst, such as zinc

- Thermoforming should be possible above the T_g but may be aided with the addition of catalyst

Remaining Challenges and Barriers - Formulation







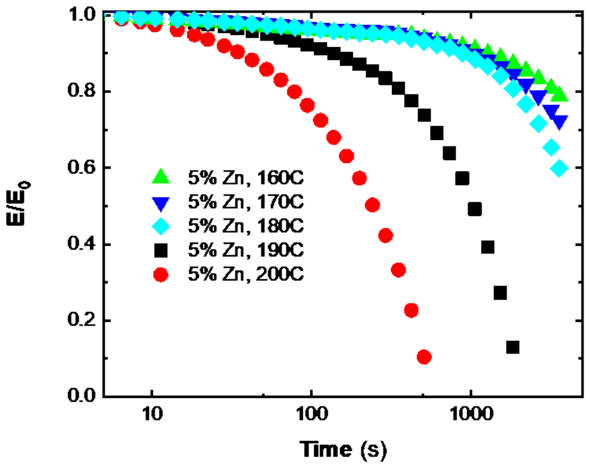
Enhancement of Process

- The potential to adjust our formulation may enable a facile thermoforming or better thermomechanical properties (e.g. a T_g)

- In order to enable greater reductions in GHG emissions compared to petroleum manufacture, we plan to examine the potential to make other anhydrides from bio-catalysis pathways
  - Based on previous analysis from our group, we expect that alternative pathways (e.g. cellulosic sugars, lignin monomers) can offer further reductions (> 1kg CO_2-e/kg$_{monomer}$) in emissions

Proposed Future Research – Key Milestones

Description of Milestones and Go/No-Go Decision	End Date & Status
Demonstrate the reuse of the fiber and report on the variation in material properties. **Deliver baseline TEA and MFI (Materials Flow through Industry) models on both epoxy-amine and CAN polymers.**	**June 2021** On Target
Demonstrate the properties of recycled PE-CAN CFRC across three cycles to be within a 20% variance every cycle. Compare the properties with the epoxy-amine resin subject to the same recycling conditions. **Additionally, produce CAN-CFRCs panels (≥1 kg scale)** **Go: Continue with the project as planned. No-Go: Rescope project to target a different CAN (e.g., trans-thioesterification, amine-imine reaction) that undergo faster exchange reactions rate to enhance recycling.**	**September 2021** Go/No-Go On Target



FY21 – Analysis and fiber re-use

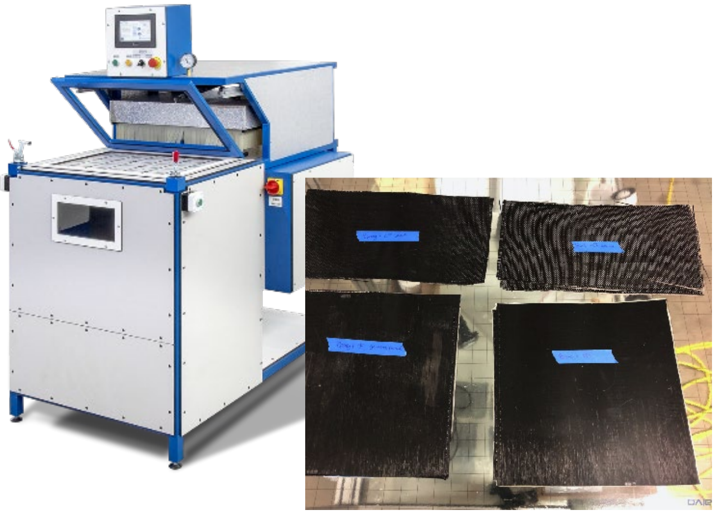
On-target for remaining FY21 milestones: aim to finish analysis and maintain performance across multiple material lives, including our Go/No-Go milestone at the end of this year

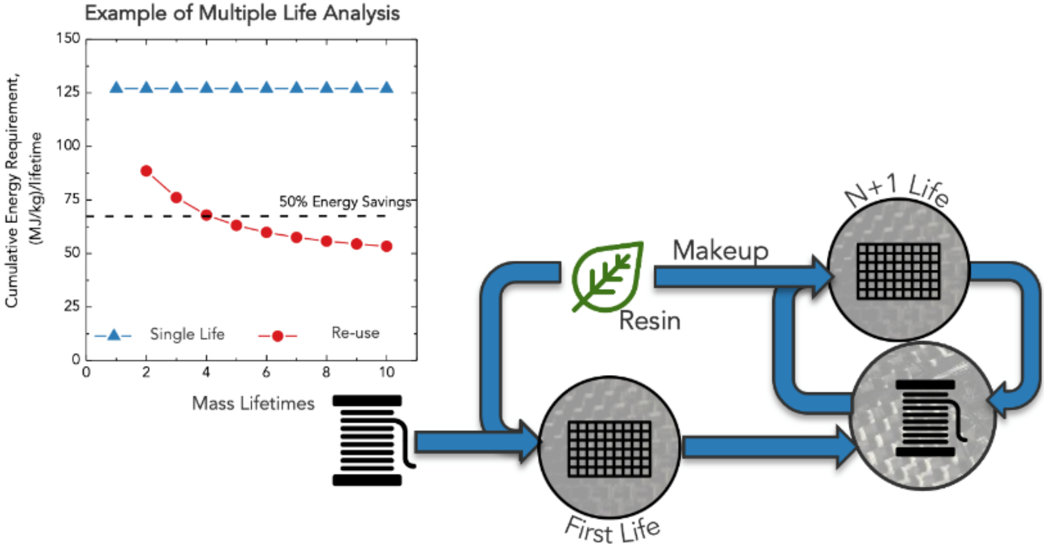
FY22: Sizing and thermo-forming

In FY22 we aim to investigate the effect of different sizing and additives (as outlined on the key challenges slide)

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

Proposed Future Research – Scale-Up and Analysis





We have made panels on a 1.2 kg scale and have access to a thermo-former

- Addresses part of the Q4 milestone and part of the FY22 Q4 milestone
- Infrastructure is in place to enable continued development

Carbon fiber in its first life can cost >$15/kg and consume >500 MJ/kg of energy while emitting >30 kg CO_2-e/kg

- Effects of the fiber outweigh the resin
- We plan to conduct analyses in line with previous work from our group to see what benefits in cost and energy are available from future lives

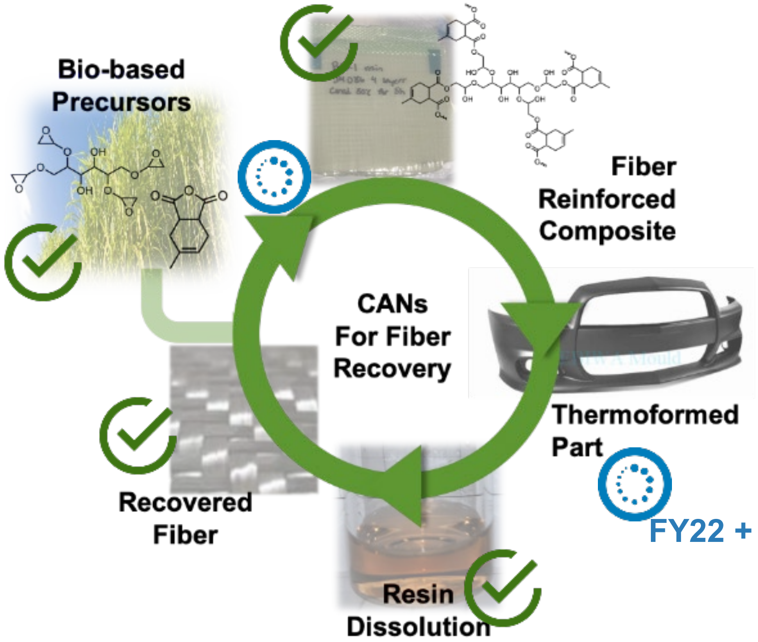
Any proposed future work is subject to change based on funding levels.

Summary Slide

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
- Resins can be formulated to tune properties, exceeding or matching performance of today's non-recyclable resins
- Resin depolymerization can be triggered to depolymerize at 25°C
- Fiber integrity can be maintained post depolymerization

Goal	Progress
Demonstrate the capabilities of tuning the polyester CAN to have properties that match a petroleum derived resin.	**December 2020** Complete
Achieve CFRC depolymerization at a temperature less than 250C	**March 2021** Complete
Demonstrate the reuse of the fiber and report on the variation in material properties.	**June 2021** On Target
Deliver baseline TEA and MFI (Materials Flow through Industry) models	**June 2021** On Target
Produce CFRCs at a scale > 1kg.	**Sept. 2021** Completed - Ahead of Target



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