DOE Bioenergy Technologies Office (BETO)
2023 Project Peer Review

Recyclable Thermoset Polymers from Lignin Derived Phenols

April 6, 2023

Biochemical Conversion and Lignin Valorization

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Spero Renewables, LLC

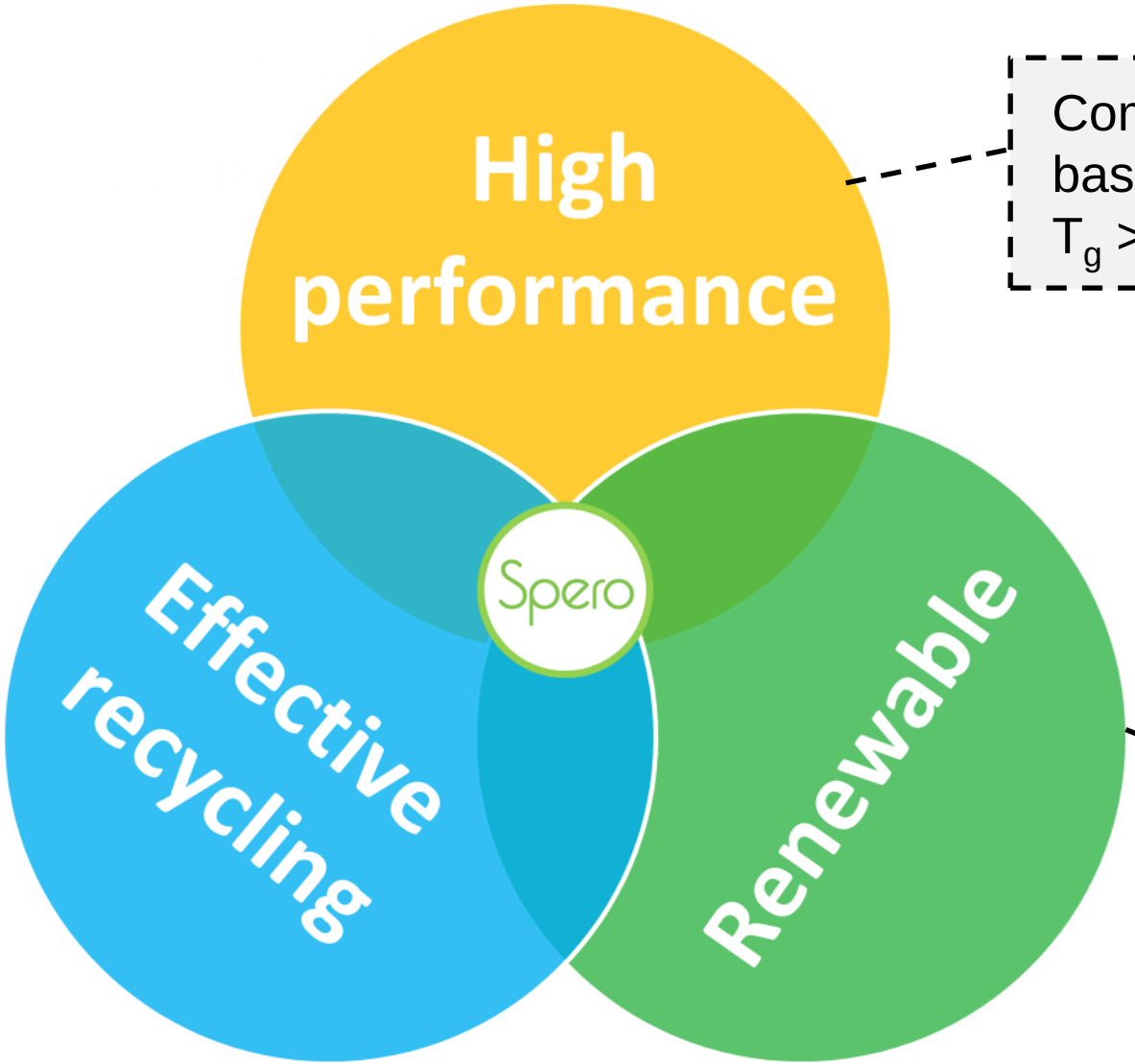
Mission & Value proposition

To provide renewable and cost-effective substitutes to petrochemicals – enhancing the quality of life and the environment

Advanced composites for growing markets

- ✓ Low-weight & high-strength
- ✓ Improved auto efficiency
- ✓ Improved crash performance
- ✗ High manufacturing waste
- ✗ Non-recyclable
- ✗ Expensive

Project Overview & Goals

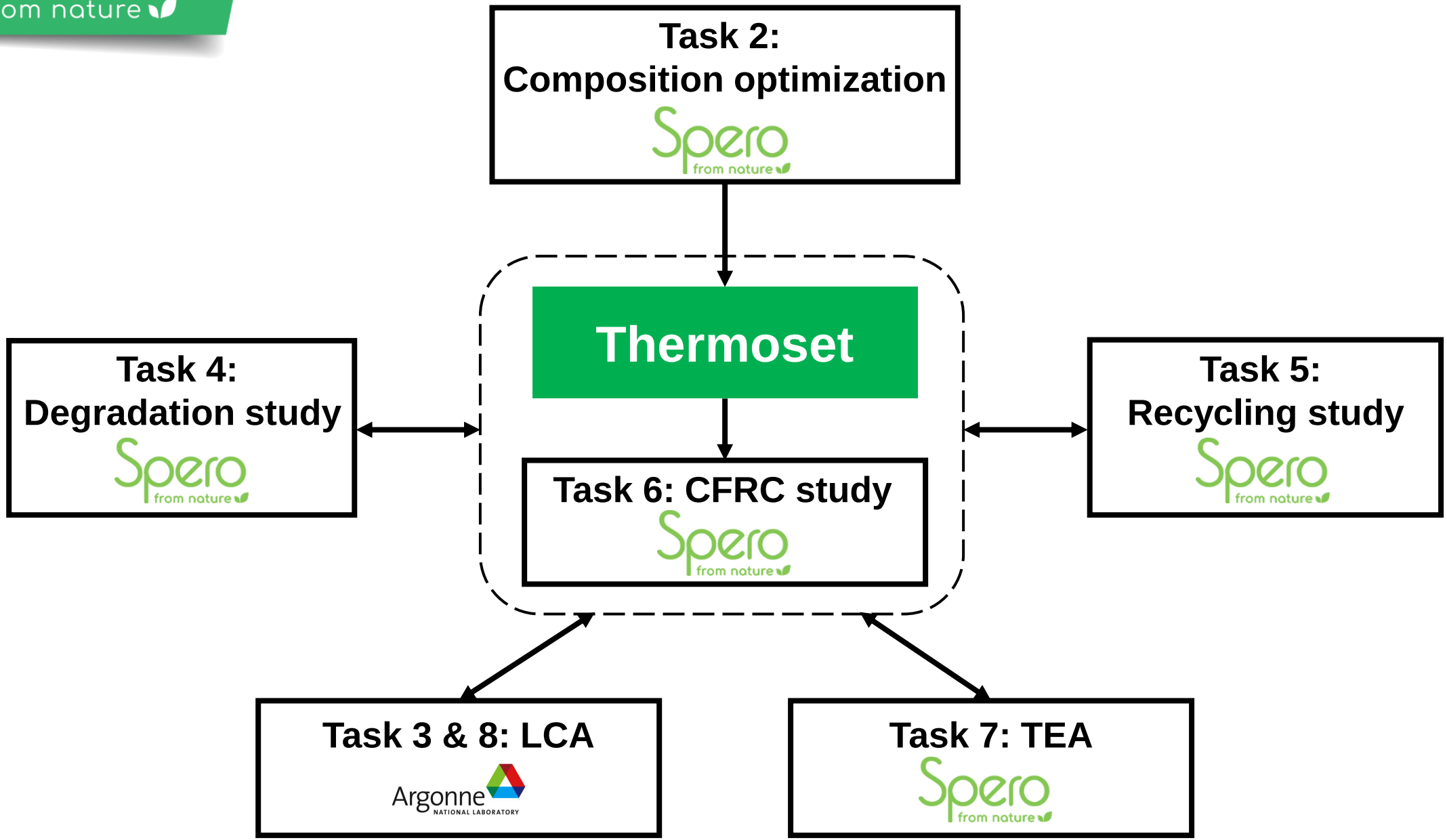


Comparable to BPA-based materials (e.g., T_g > 90 °C)

Mild conditions (e.g., < 100°C) & high efficiency (e.g., > 90%)

> 50 wt% renewable feedstocks

Project Overview & Goals



Impact: Composite waste is a pressing issue

Global wind turbine blade waste: 43 million tons by 2050

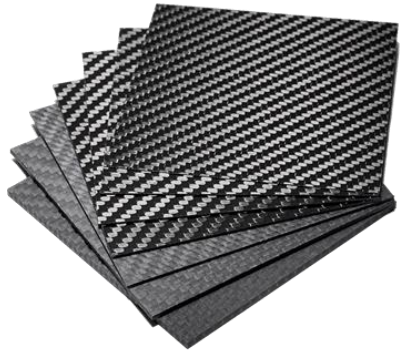
Impact: Communication and collaboration

We are sharing materials for testing with major chemical companies, such as:

- A major Japanese chemical and material company;
- One of the largest paper manufactures and exporters in Brazil;
- A Belgium company that is a global leader in materials and chemicals;
- A Swiss multinational manufacturer of flavors, fragrances and active cosmetic ingredients.

Composite waste is a pressing issue

Conventional composites

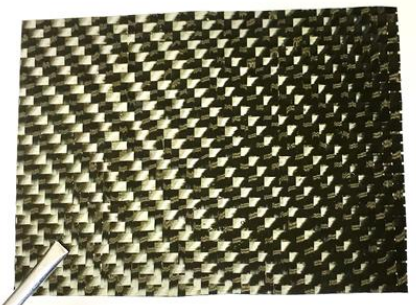


Chopping + pyrolysis

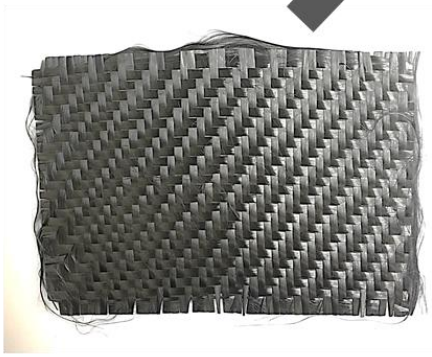
Chopped carbon fiber product

Carbon fiber pieces with significant strength/value loss

Spero resin & composites



Recyclable carbon fiber composite

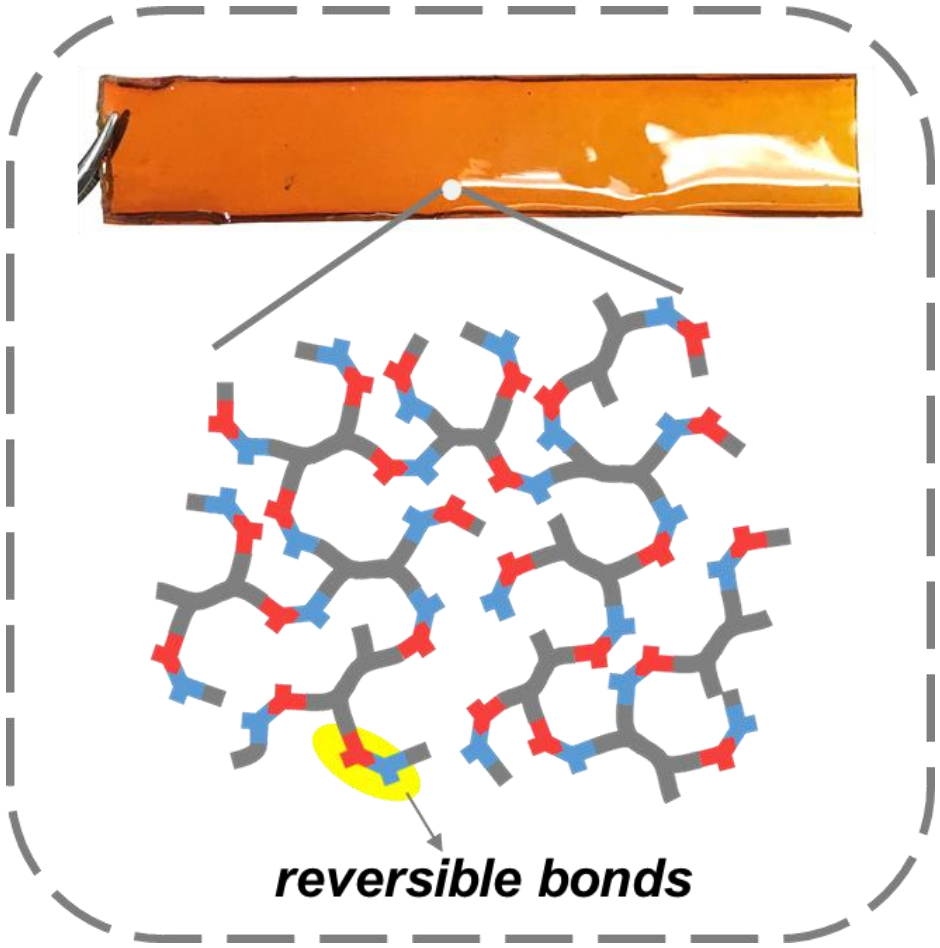


Recycled carbon fiber in woven state

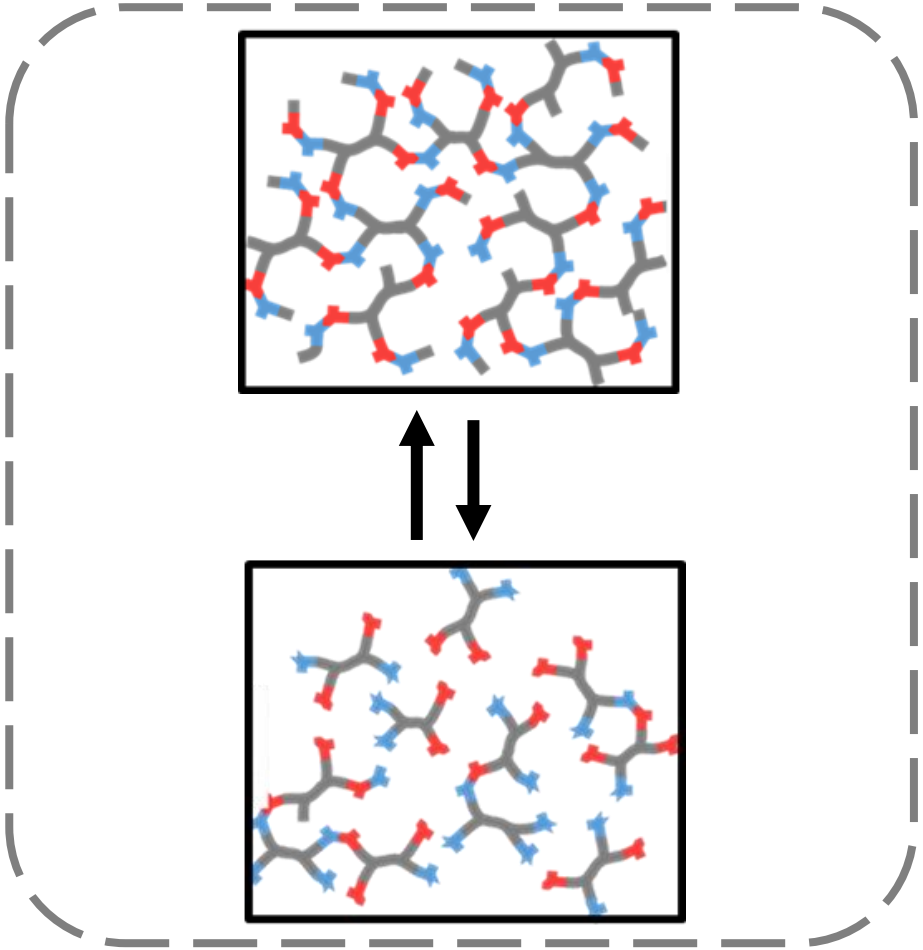
CF car with excellent strength & light-weight property

Approach: Chemically Recyclable Resin

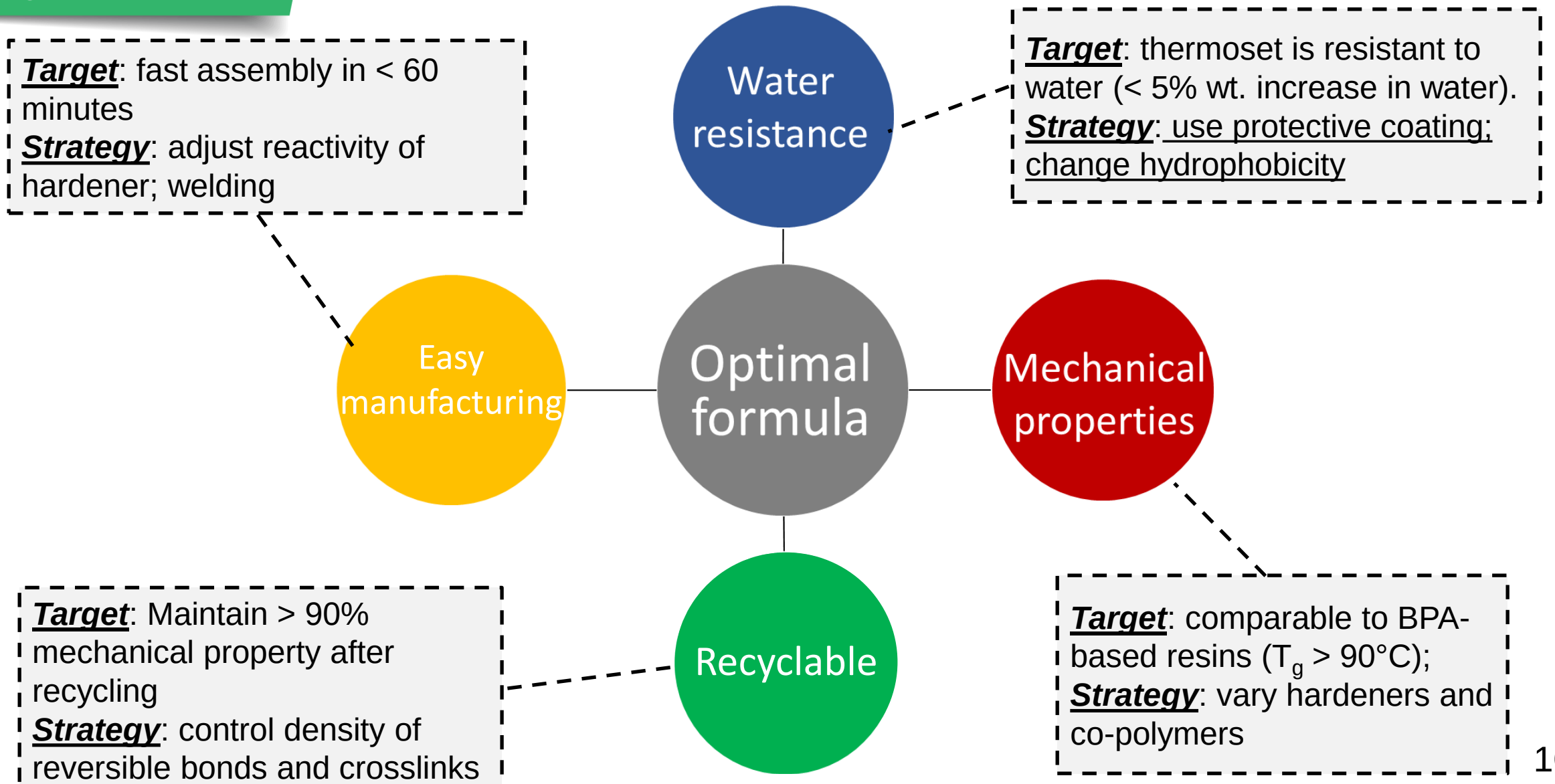
(A) *Network structure of Spero lignin-based resin*



(B) *Bond breakage/reformation*



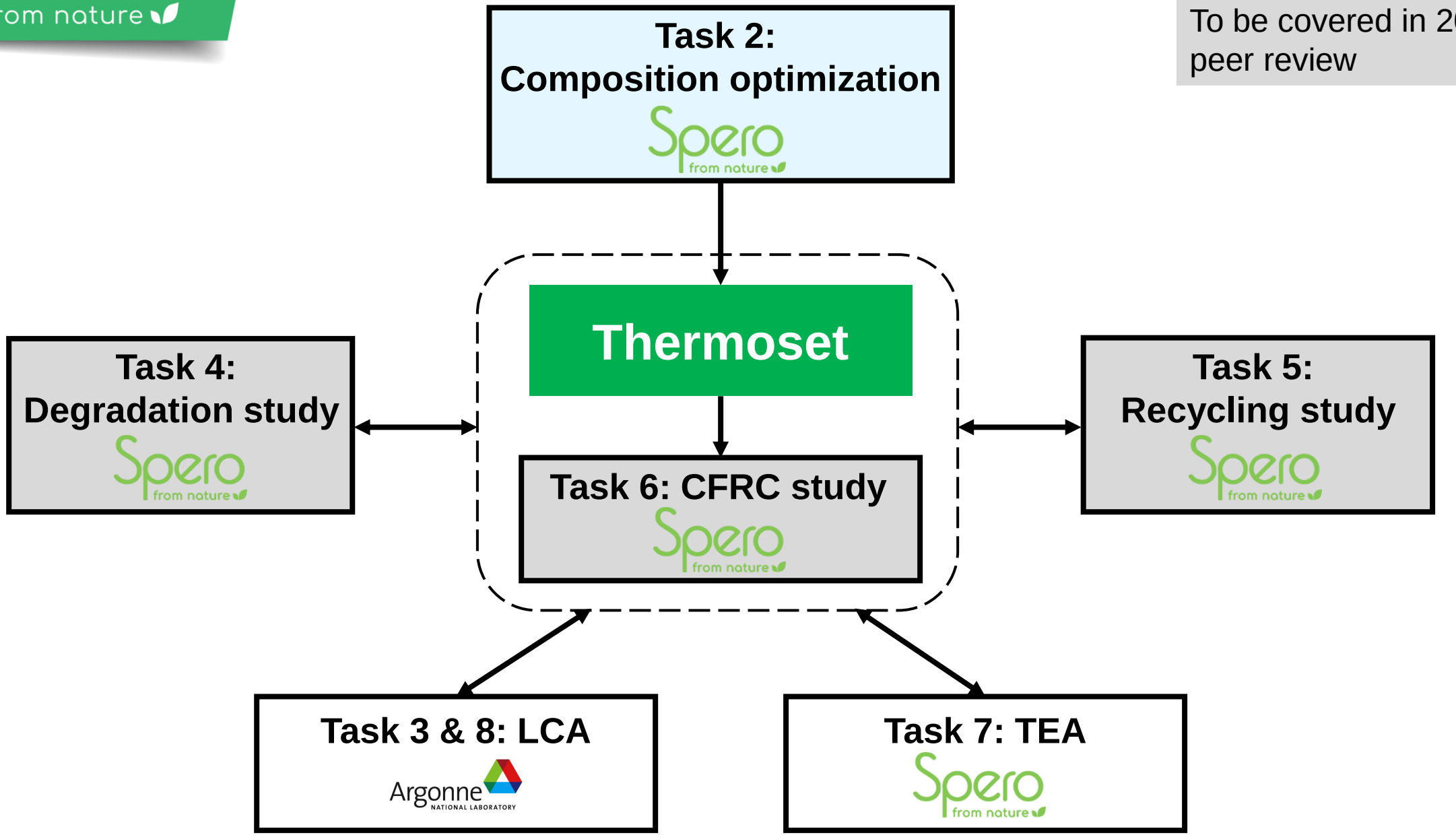
Implementation strategy and risk mitigation strategies



Project Overview & Goals

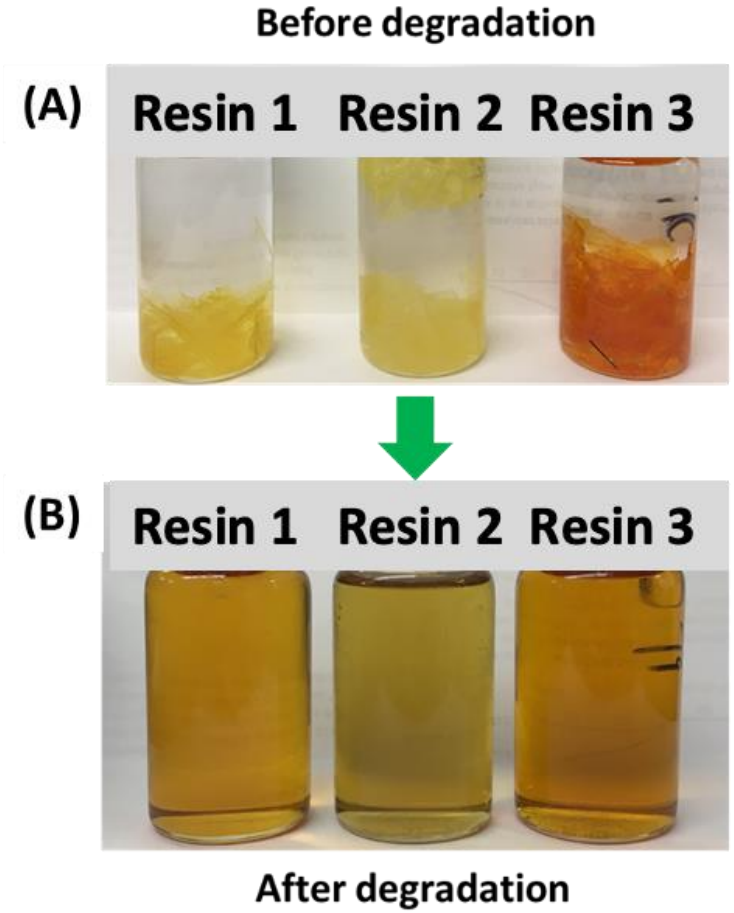
Finished and covered in 2021 peer review

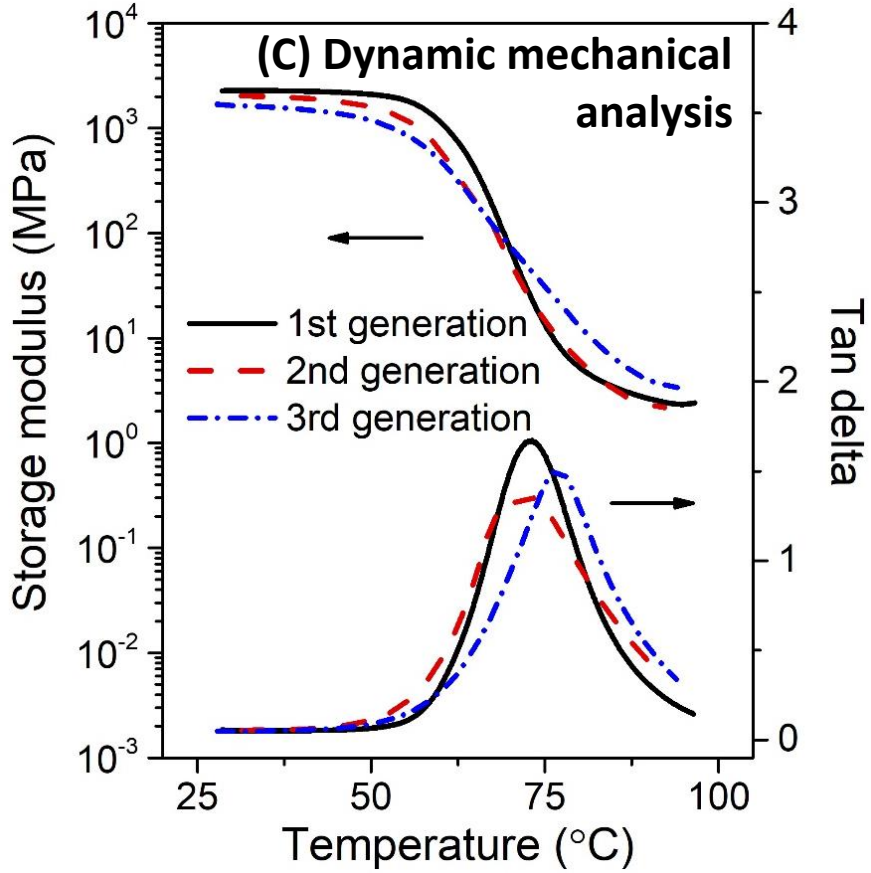
To be covered in 2023 peer review

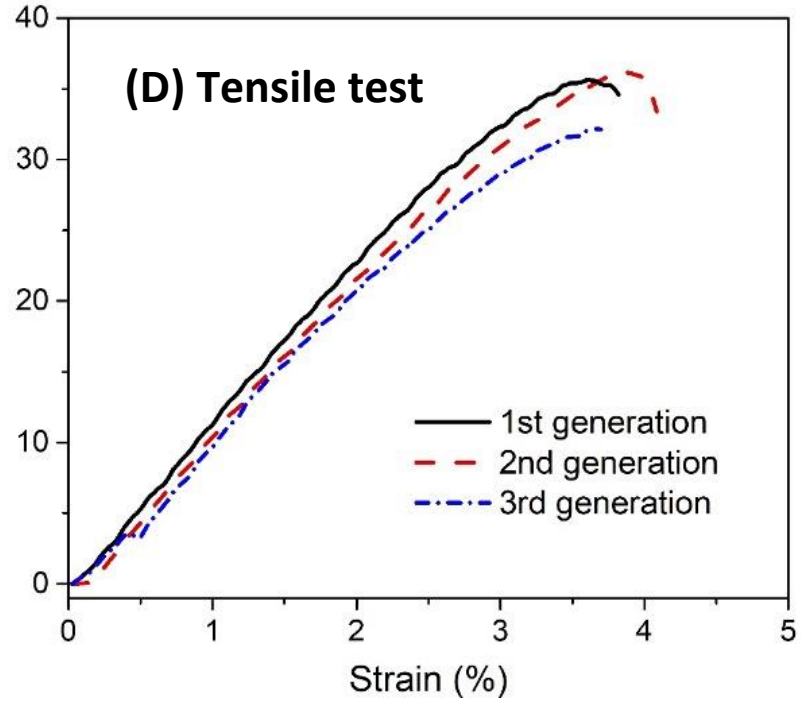


Progress and Outcomes (Task 4)

Resins can be dissolved and reformed through multiple cycles without significant property loss

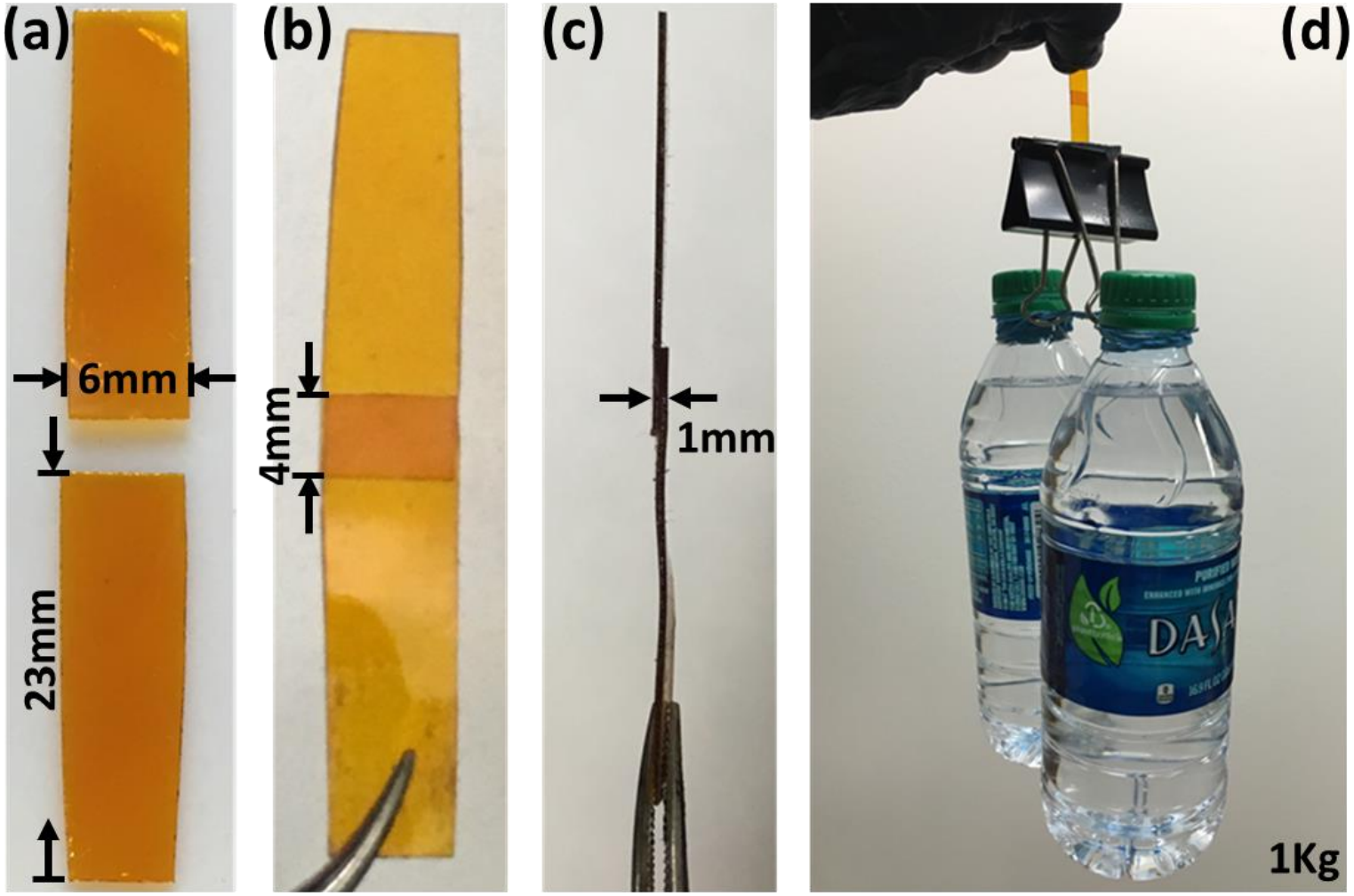






Recycling method: dissolve resin in reagents at 65°C for 3 hours. Then, the solution can be used to crosslink a new batch of epoxy to reform resin

Progress and Outcomes (Task 5)
Thermosets can be repaired through welding



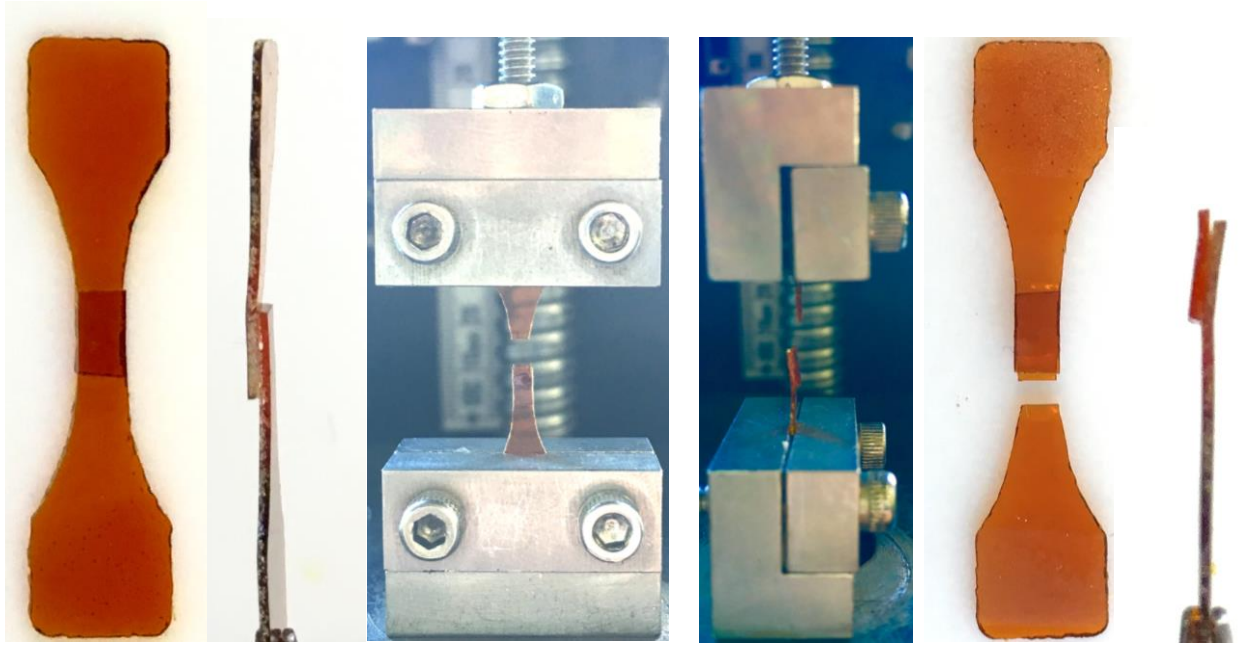
- Apply specific heat & pressure to weld thermoset samples

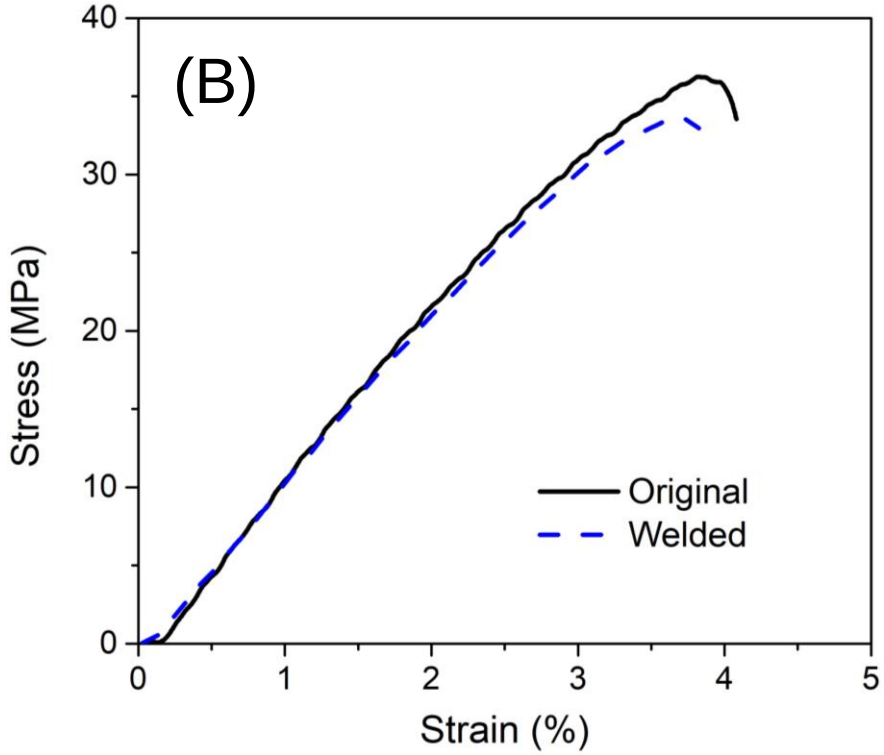
Progress and Outcomes (Task 5)

Welded resin has similar strength to the original.

Welded area is no longer the weakest part.

(A)





GNG 2 was passed on June 7, 2021

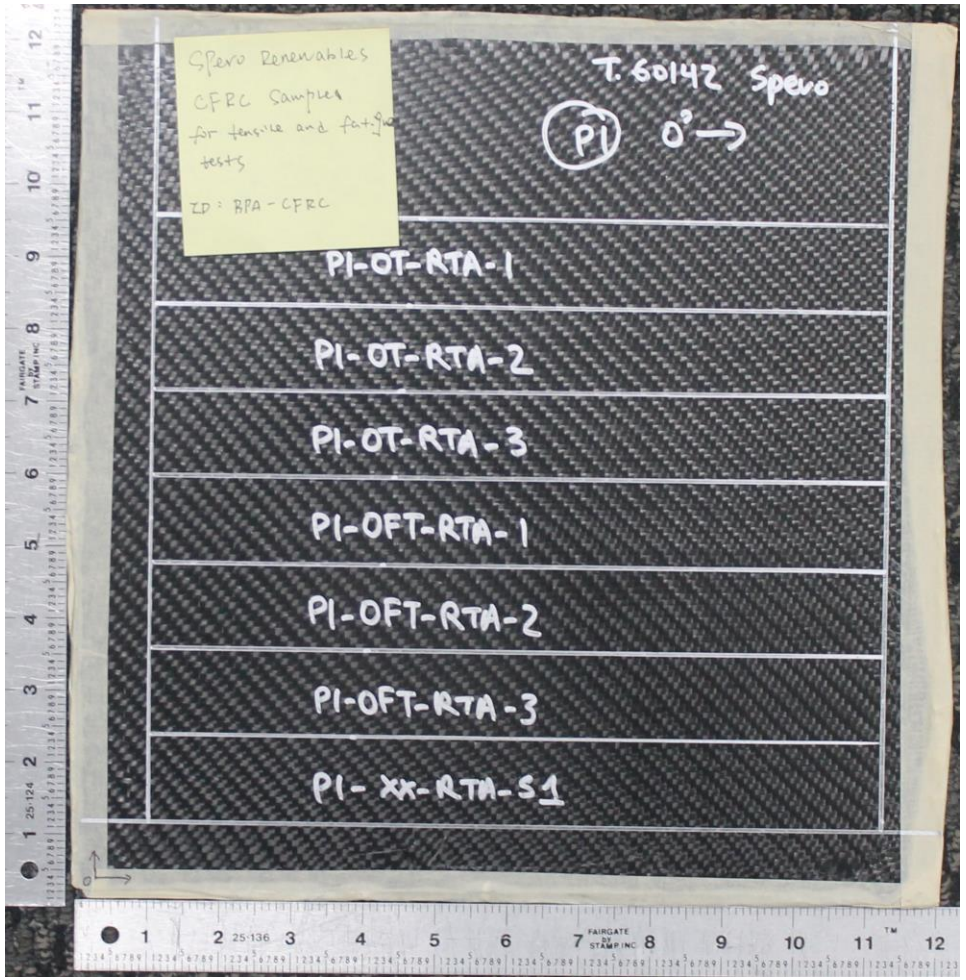
- Thermoset is resistant to water where ≥ 90% of original strength is retained after using ASTM method.

- ≥ 90% of thermoset mass is dissolved in common organic solvents and water under mild conditions (temperature < 100 °C, reagent concentration < 1 M, low solvent, < 4 hours and atmospheric pressure).

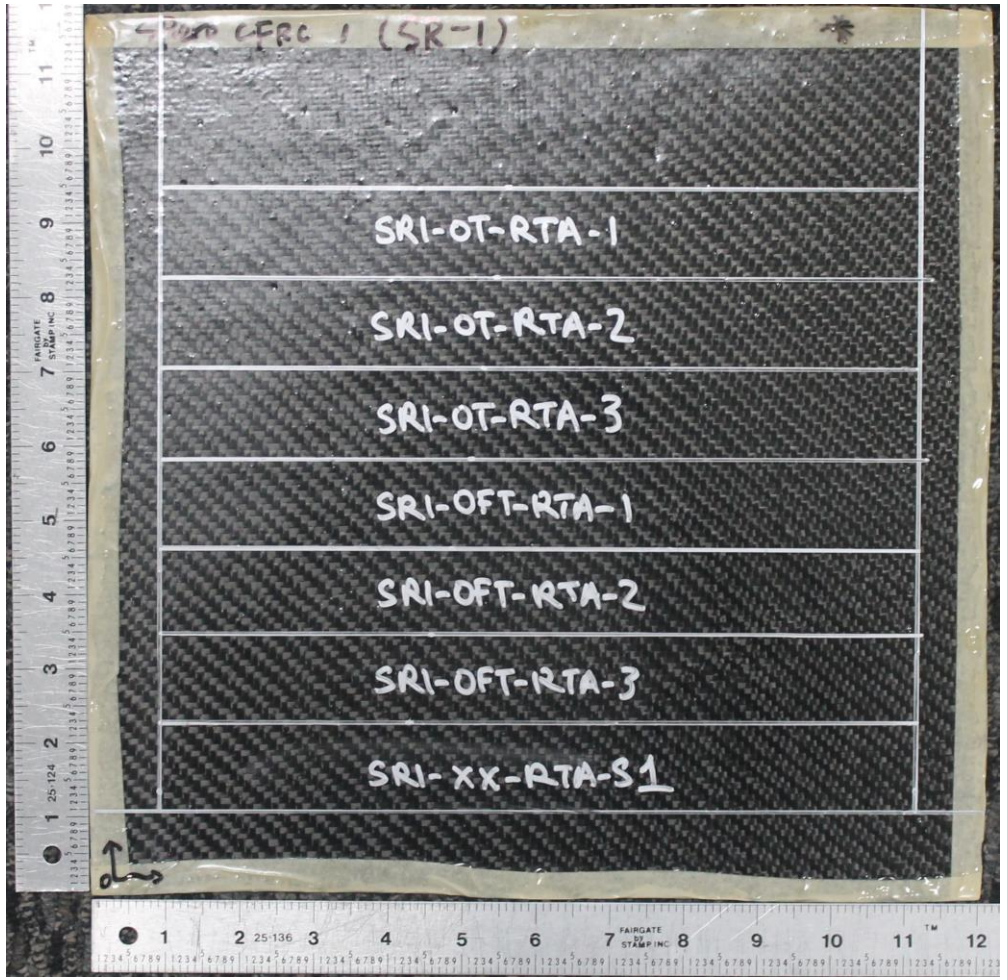
- Decomposition is confirmed by NMR of the dissolved thermoset to verify breaking of reversible bonds.

- Suggestion from verification team: fatigue test on Spero materials.

Fatigue tests setup of CFRCs ASTM D3039-17, conducted by element

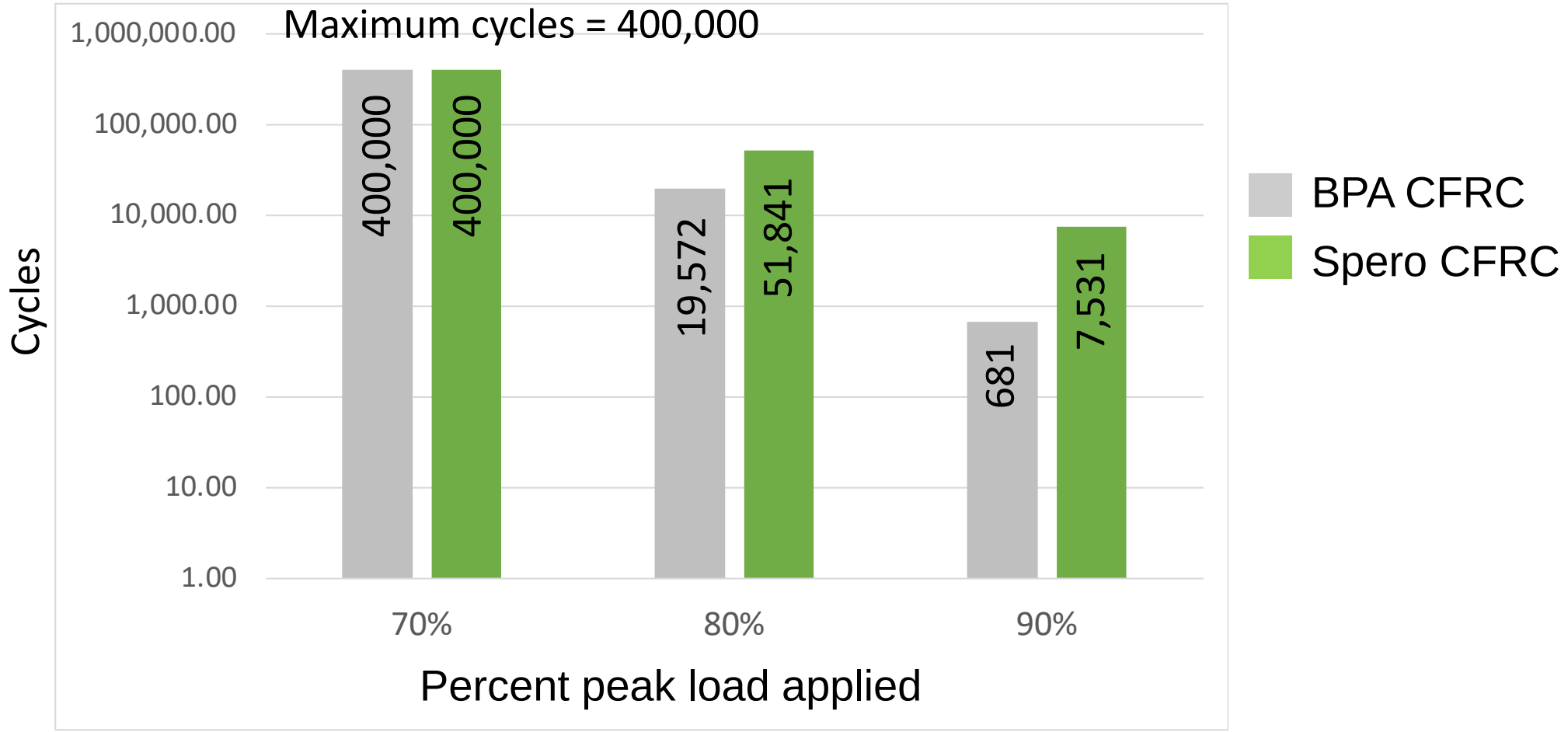


(A) BPA-based CFRC



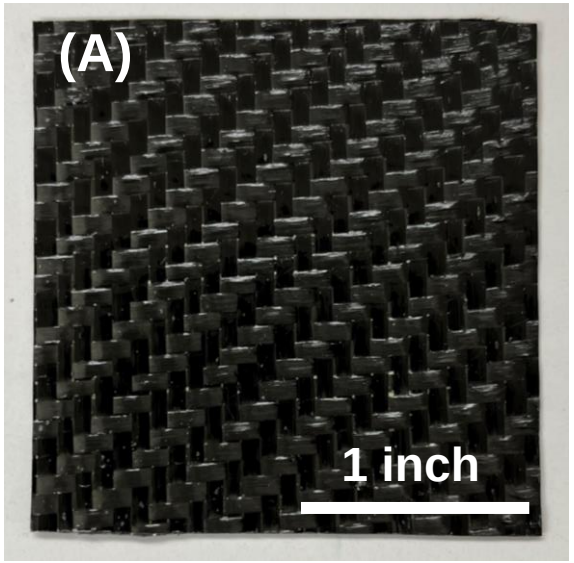
(B) Spero CFRC

Spero CFRC has higher fatigue resistance than BPA based equivalent (Fatigue test: ASTM D3039-17)

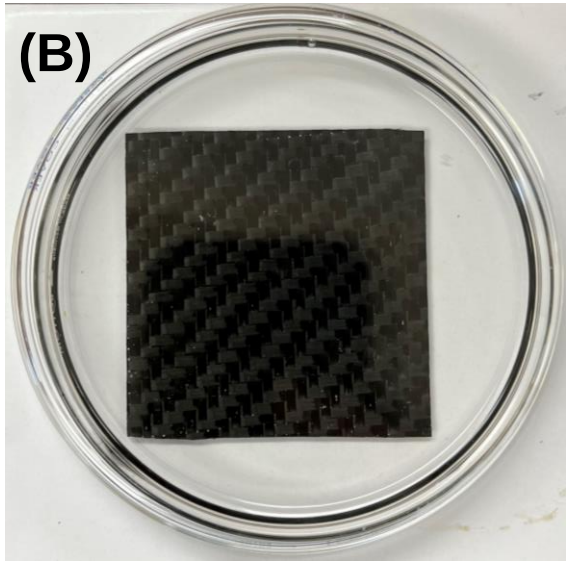


Peak load: Spero CFRC = 69.5 ± 2.81 ksi; BPA CFRC = 59.4 ± 4.07 ksi

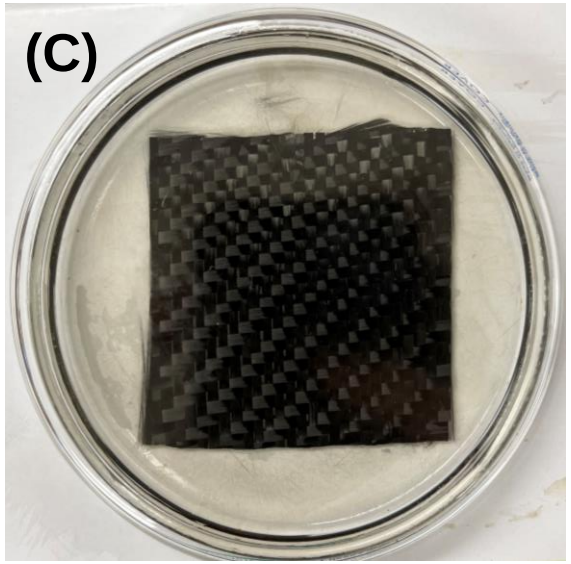
Progress and Outcomes (Task 6)
CF can be easily separated from CFRC while maintaining a woven structure



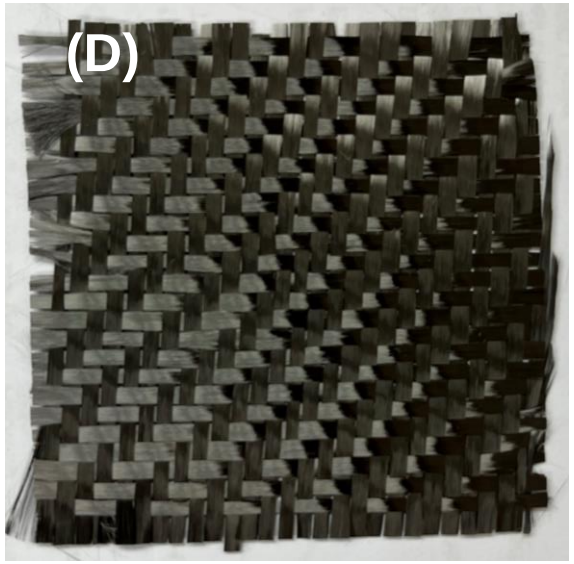
CFRC from lignin-based thermoset



Put (A) in solvent for degradation with reagent

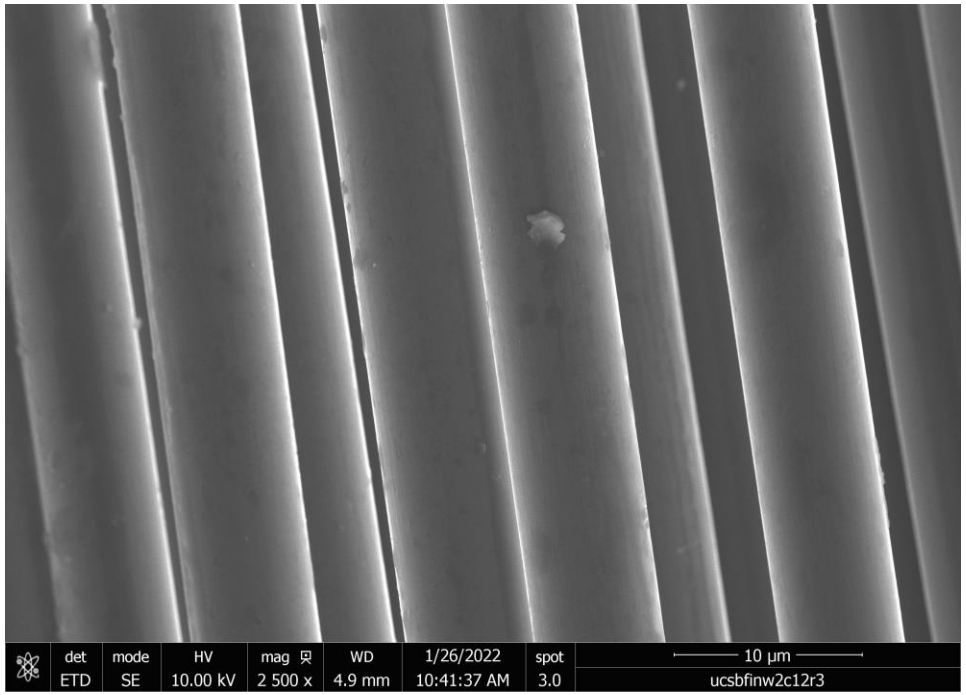


(B) is warmed at 65°C for 2 h

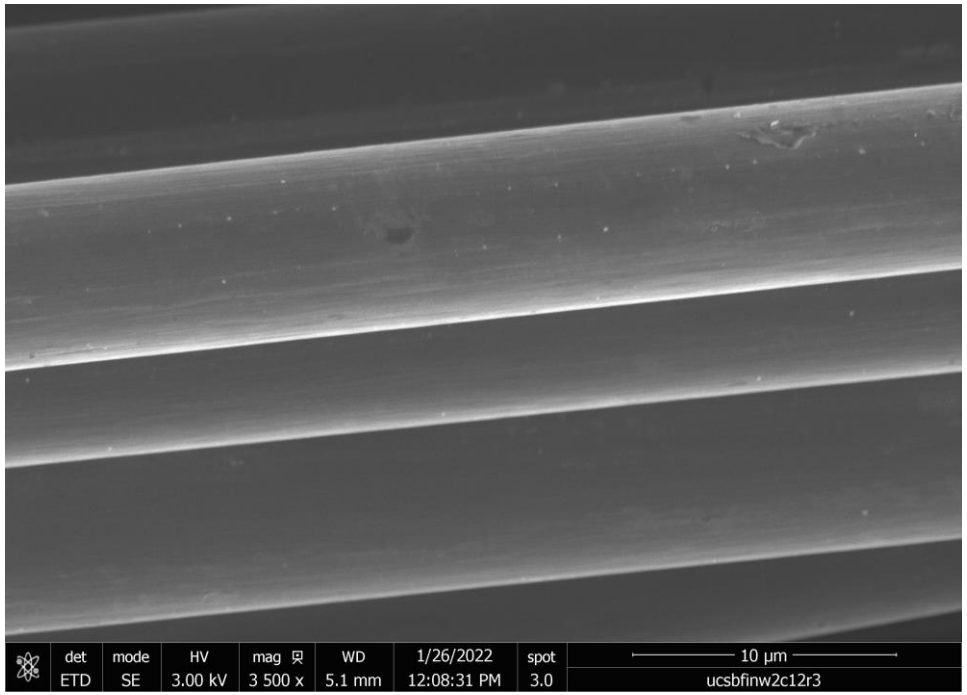


Fiber is collected, washed and dried. > 99% mass recovered.

Progress and Outcomes (Task 6)
Recycled CF is intact as observed by SEM



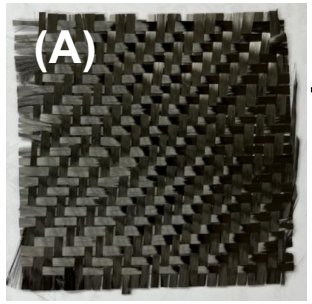
Original carbon fiber



Recycled carbon fiber

- ❑ Image was randomly taken and is representative.
- ❑ No fiber damage or resin residue is observed.

Progress and Outcomes (Task 6)
CFRC can be recycled with no decrease in property

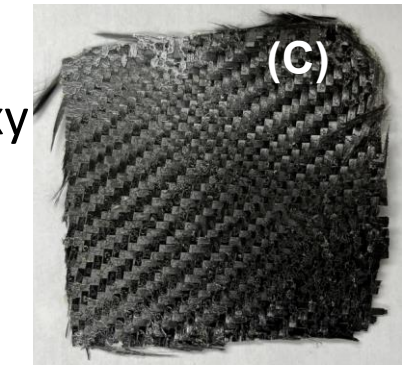


Recovered CF

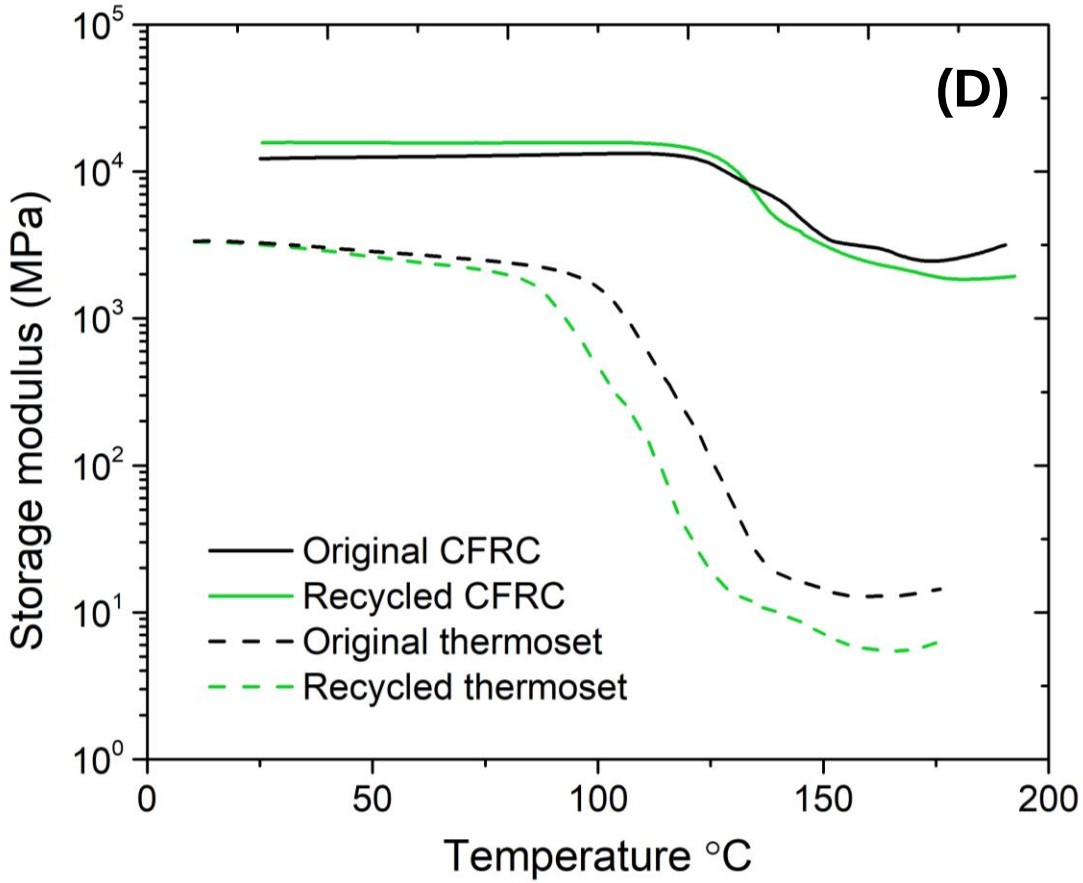
+

Recovered thermoset in solution

Epoxy



2nd generation CFRC



Progress and Outcomes
Task 3 & 8: Life cycle analysis (ANL)

Preliminary LCA completed:

- Defined system boundary for cradle-to-grave (CTG) CFRP system
- Assess recycling scenarios & coordinate with TEA

LCA plans:

- Finalize material & energy flows (when TEA complete)
- Create GREET sub-model & finalize CTG assessment of Spero CFRPs
- Report Greenhouse Gas (GHG) emissions & energy use

Progress and Outcomes
Task 7: TEA CFRC synthesis & recycling

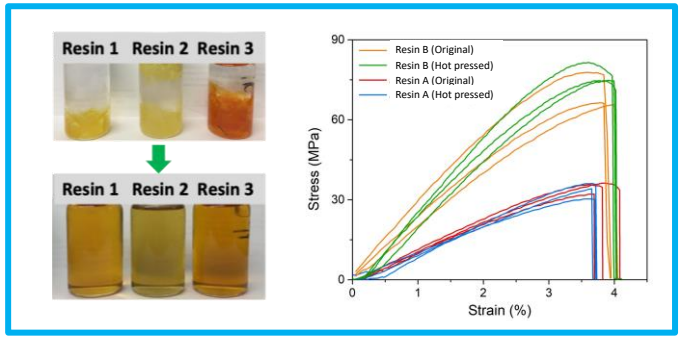
NPV	**$39,373,354**
NPV %	**12%**
ROI	**147%**

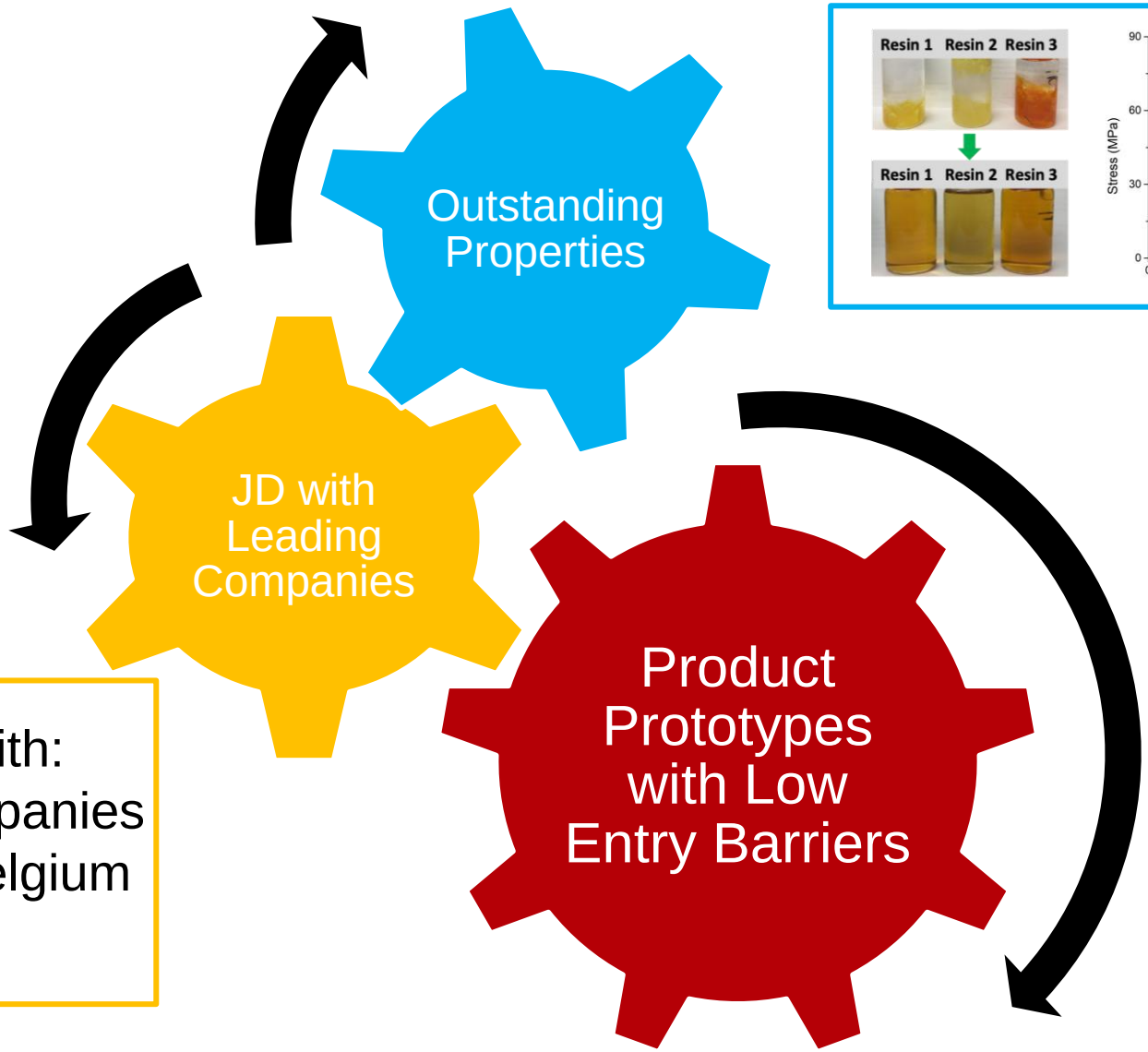
- Profitable at 1 kta CFRC
- 10-year plant lifespan
- Produces biobased epoxies and incorporates in CFRC production. Includes an internal recycler.
- Recycler breaks down CFRC trimmings into carbon fiber scrap and used recycling reagent

	Mass Flows		Prices	
	Name	Mass Flow Rate [kta]	Price [$/MT]	Annual [$MM/yr]
Feedstock	Reagents & Solvent	-	-	-17.4
	Carbon Fiber	0.62	8,000	-4.9
			Feedstock Total	**-$22.3 MM/yr**
OPEX (waste + utilities)	Waste	-	-	-0.35
	Electricity, steam, cooling water	-	-	-0.05
			OPEX Total	**-$0.4 MM/yr**
Product	CFRC	-	-	21.5
Byproducts	Recycling reagent	-	-	11.6
	CF Scrap	0.18	2,500	0.45
			Total Revenue	**$33.6 MM/yr**
			Total Costs	**-$22.7 MM/yr**
			Balance:	**$10.9 MM/yr**

Significant commercialization potential

Recyclable materials retain properties





Spero prototype:
CFRC mirror cover

Spero collaborating with:
Leading material companies from Japan, Brazil, Belgium and Switzerland etc.

Significant impacts for improved sustainability, manufacturing and waste reduction

Energy saving

(CF production: 100–900 MJ per kg; up to 50%* of energy can be saved with Spero's technology)

Improved sustainability

(> 50% wt. bio-based, fully degradable, minimum wastes)

Reduced cost

(CF is a major cost driver. Composite cost will be largely reduced if CF is recycled)

Manufacturing benefits

(Fast, VOC-free, long shelf life)

*To be confirmed by upcoming TEA/LCA work

Acknowledgements

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Mahdi Abu-Omar
Eric McFarland
Ian Klein

May Wu

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Quad Chart Overview

Timeline

- 10/2019 – 07/2024

	FY22 Costed	Total Award
DOE Funding	$721,145	$2,000,000
Project Cost Share	$181,202	$500,000

Project Partners

- ANL

Project Goal

Develop novel thermoset and CFRP prototypes with >50% bio-based content using molecules derived from lignin. Prototypes will match key properties of conventional BPA-based counterparts but can be chemically recycled to new CFRC samples without damage/loss of thermoset or carbon fiber components.

End of Project Milestone

Deliver thermoset/CFRC prototypes with properties comparable to conventional BPA-based counterparts. Thermoset and carbon fiber components recycled into 2nd generation CFRCs with comparable thermomechanical properties to original CFRC. Create compelling economic forecast for commercialization by incorporating TEA and LCA recommendations.

Funding Mechanism

DE-FOA-0002029

Designing Highly Recyclable Plastics

2019

Products

Patents:
Zhao, S.; Klein, I. Recyclable and decomposable epoxy resins: compositions, preparation methods and applications in carbon fiber reinforced composites. PCT/US2022/021932, **2022**

Publications:
Zhao, S.; Abu-Omar, M. M. Materials based on technical bulk lignin. ACS Sustainable Chemistry and Engineering. **2021** 9 (4), 1477-1493

Presentations:
Klein, I. Lignin Conversion and Upgrading to Materials. Presented at Advanced Biofuels Leadership Conference, Washington D.C., March 18, **2021**

Klein, I. Innovations in Selective Lignin Upgrading to Create Profitable and Sustainable Chemical Businesses. Presented at meeting of the American Chemical Society, Chicago, IL, August 23, **2022**

Response to 2021 Peer Review Comments

- Regarding risk management strategy: Specific identified project risks and mitigation techniques are described on slide 10. Furthermore, impact of process changes are assessed using ASPEN modeling to reduce risks. Frequent (monthly) project meetings between Spero team and Argonne National Lab team (LCA task) ensure correct inputs for LCA are used.

- Regarding lignin source: Spero uses a lignin-based starting material for thermoset synthesis. The lignin-based material is commercially available at a much larger scale than the scale at which Spero has modeled production.

- Regarding project partners/customers: Spero agrees it is essential to test our products in the marketplace and work in collaboration with industrial partners. Several key collaborators are listed in general terms on slide 7, however Spero is restricted from sharing names/details of the collaborations by non-disclosure agreements.