DOE Bioenergy Technologies Office (BETO)
2021 Project Peer Review

Recyclable Thermoset Polymers from Lignin Derived Phenols

March 9, 2021

Performance-Advantaged Bioproducts, Bioprocessing Separations, and Plastics

Ian Klein, PhD

Spero Renewables

Mission & Value proposition

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

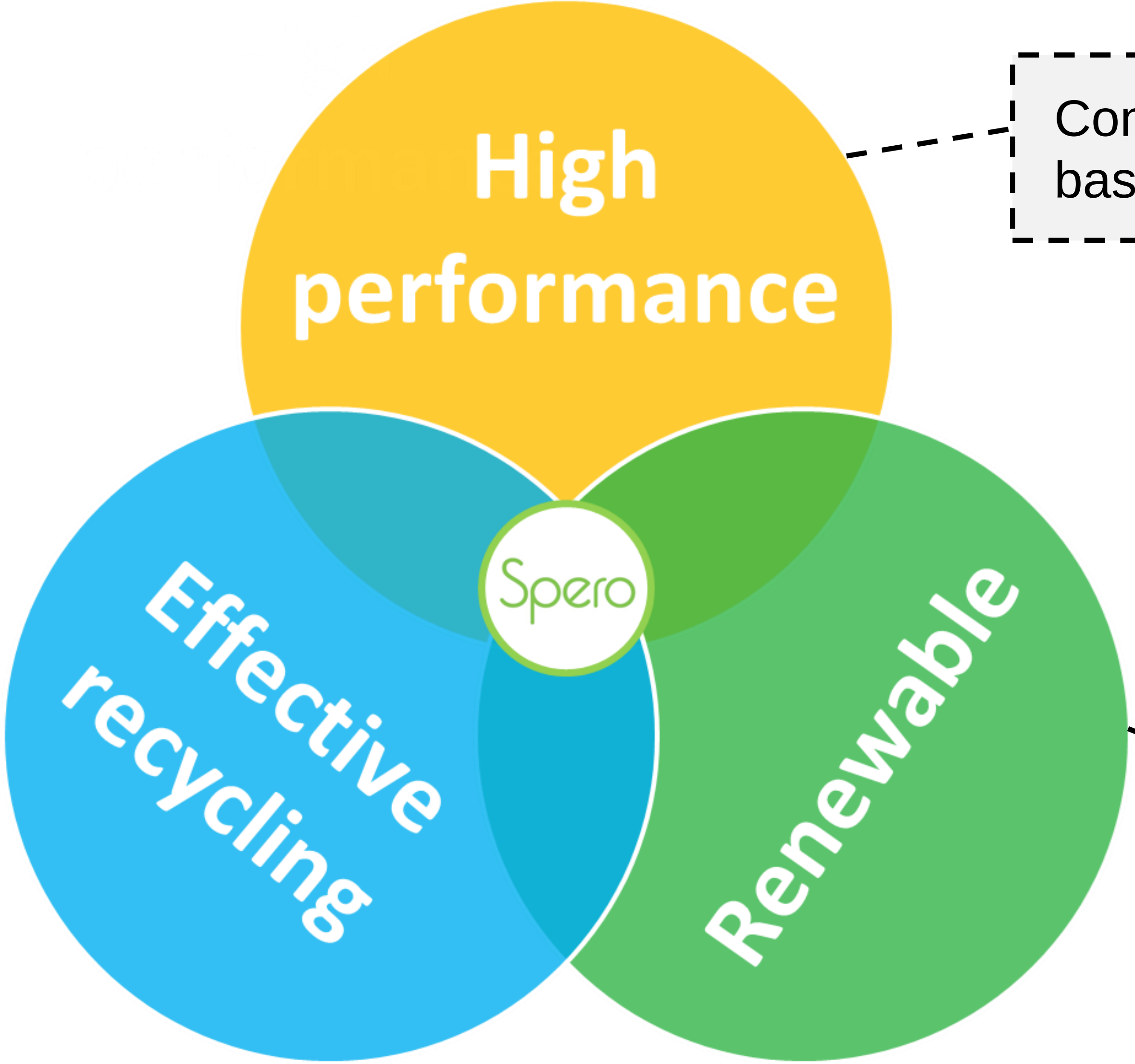
Advanced composites for growing markets

- ✔ Low-weight & high-strength
- ✔ Improved auto efficiency
- ✔ Crash performance
- ✖ High manufacturing waste
- ✖ Non-recyclable
- ✖ Expensive

Project Overview & Goals

Comparable to BPA-based materials

Mild conditions & high efficiency

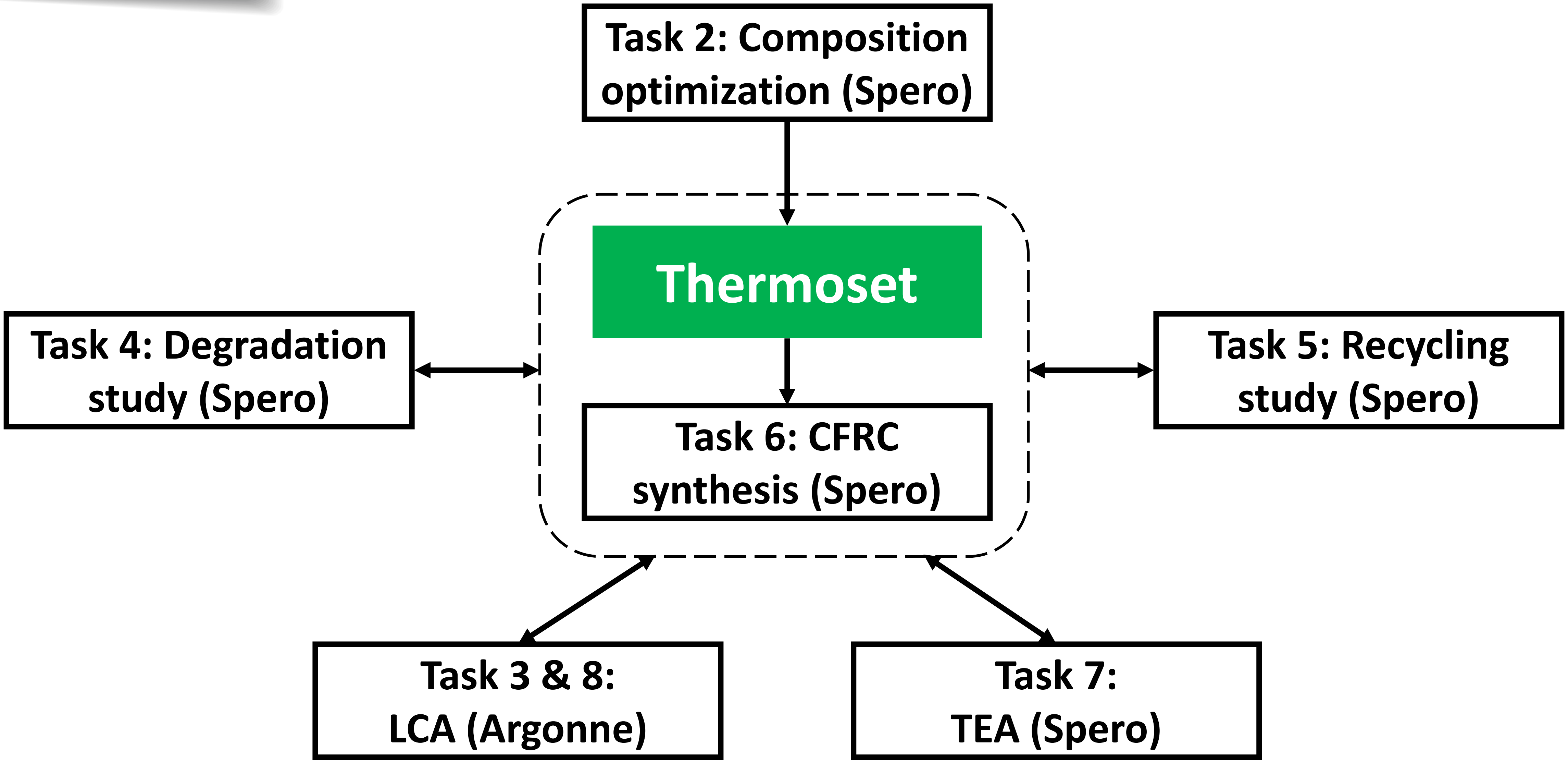


> 50 wt% renewable feedstock

Management – Objectives & Structure

Task 1: Initial Verification
Task 2: Optimize thermoset synthesis
Task 3: Preliminary Life-Cycle Analysis (LCA)
Task 4: Thermoset decomposition
Task 5: Thermoset recycling
Task 6: Carbon fiber reinforced composite (CFRC) synthesis
Task 7: Technoeconomic Analysis (TEA) product synthesis / recycling
Task 8: LCA thermoset & CFRC synthesis / recycling

Management - Structure



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Spero Management team

Mahdi
CEO

Ian
CTO

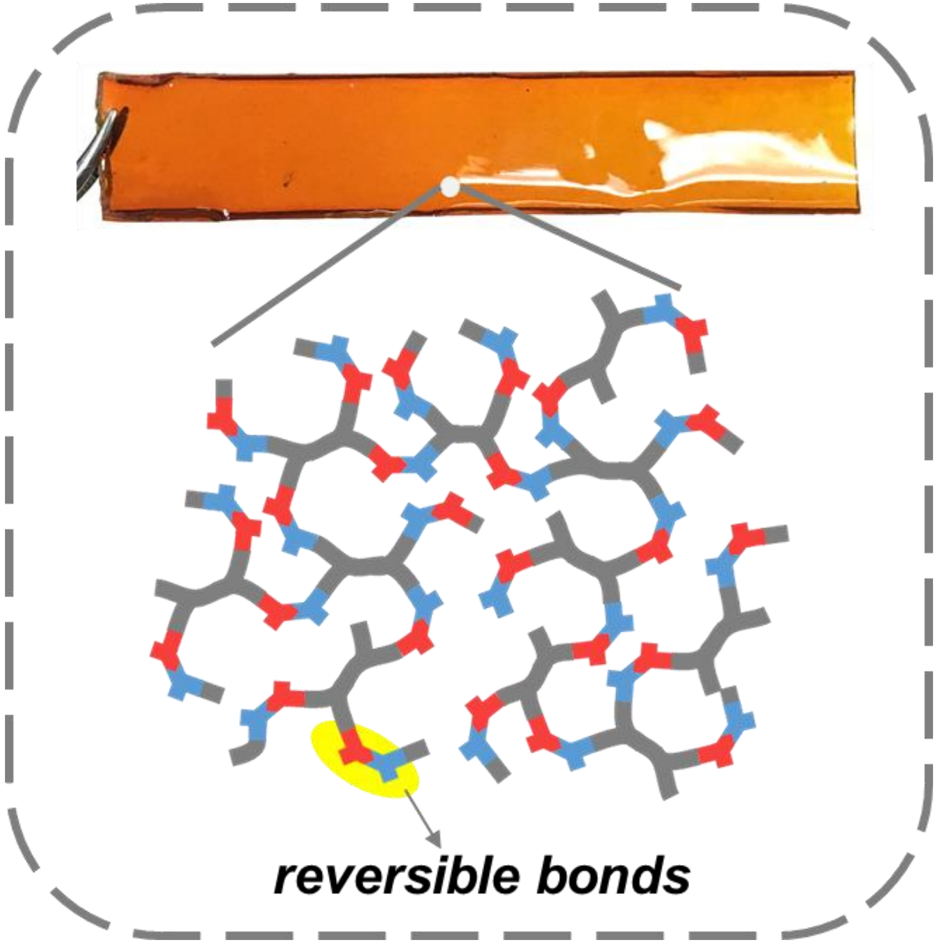
Eric
Eng.

Jasmine
BD

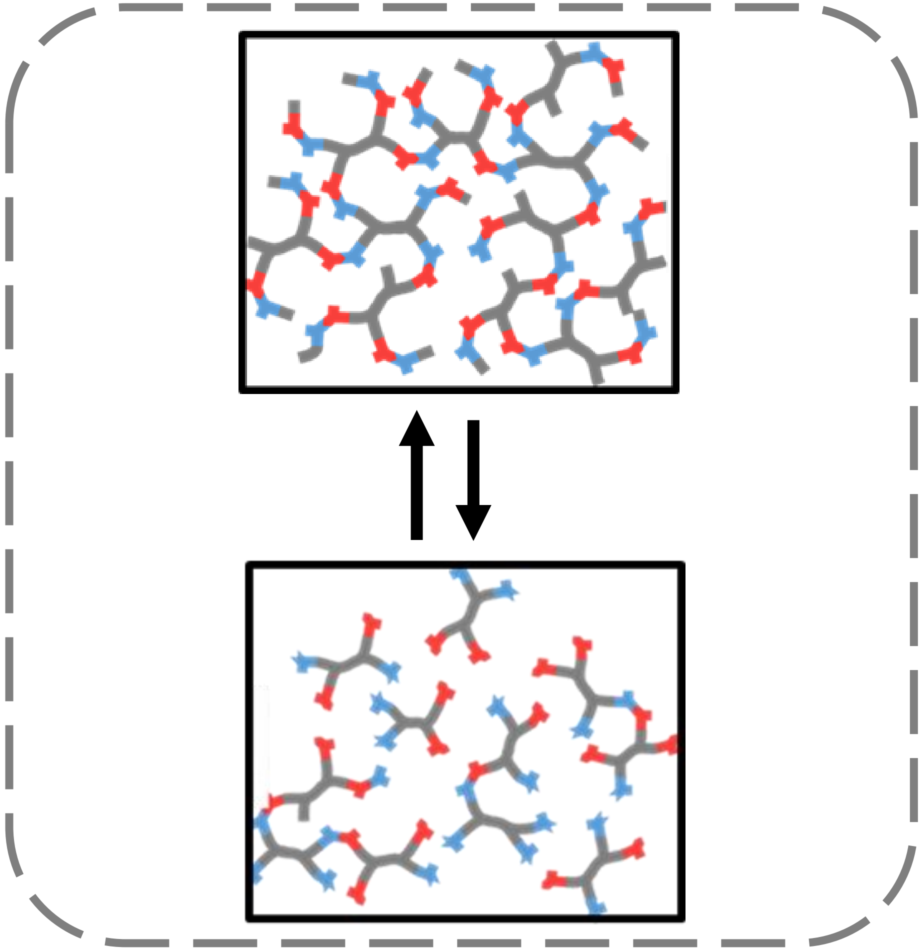
- 20+ year of R&D management experience
- Technology translation & major JDA with multi-nationals
- Forbes 30 under 30
- Board/advisors include co-founder of a major oil exploration company, a former CTO of a major chemical company, and a world expert in polymers.

Approach: Chemically Recyclable Resin

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



(B) ***Bond breakage/reformation***



Approach: Potential challenges

Improved water resistance

- **Improve water resistance through adjusting network *hydrophobicity* and developing *coating* approach**

Degradation & recycling

- **Mild degradation condition with > 95% efficiency;**
- **High recycling efficiency to retain the strength (> 85%) of original resins**

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Technical Approach

Task	Technical Approach
2) Thermoset Synthesis	• Optimize & scale-up prepolymer & thermoset • Water resistance
3,8) Life-cycle analysis (LCA)	• Comparison to BPA thermosets • GREET sub-model, GHG & energy report
4) Thermoset decomposition	• Solvent based decomposition • Solution analysis (GPC & NMR)
5) Thermoset recycling	• Quantify mechanical properties recycled material • Investigate lap-welding & press-remolding
6) CFRC synthesis & recycling	• Synthesize CFRCs, recycle all components • Investigate compression molding & welding
7) Technoeconomic analysis (TEA)	• Process model, cost equipment, CAPEX/OPEX • ASPEN simulations

Impact - Composite waste is a pressing issue

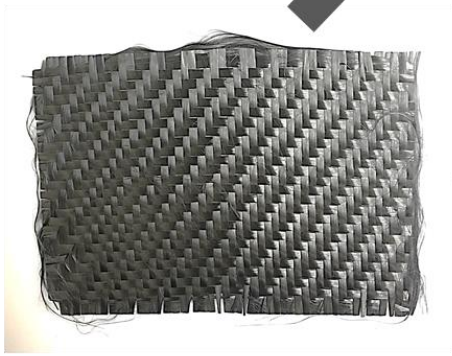
Global wind turbine blade waste: 43 million tons by 2050

Impact - Composite waste is a pressing issue

Spero resin & composites

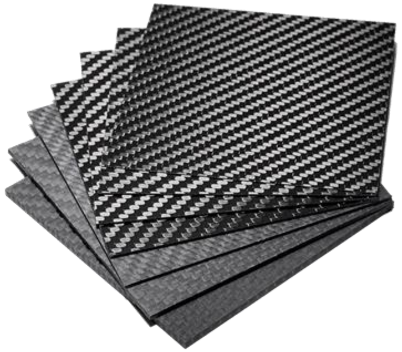
Recyclable carbon fiber composite

CF car with excellent strength & light-weight property



Recycled carbon fiber in woven state

Conventional composites



Chopping + pyrolysis

Chopped carbon fiber product

Carbon fiber pieces with significant strength/value loss

Impact: Success through Industry Engagement

Spero collaborations

- Resin manufacturers
- Chemical companies
- OEM’s
- Automotive & wind turbine companies
- Prototype development

Next: Pilot & commercialize through JDA

Progress and Outcomes

Task 2: Optimize thermoset synthesis

Milestone	Description	Status
2.1	Optimize pre-polymer monomer synthesis. Isolated yield >80%, purity 90%. GC-FID or NMR quantification	✓ (03/2020)
2.2	Scale pre-polymer monomer to 1 kg/day capacity. (GC-FID or NMR quantification)	✓ (06/2020)
2.3	Optimize thermoset synthesis. Match BPA properties while retaining recyclability. Evaluate structure with NMR, FTIR. Physical properties by DSC, DMA, TGA.	✓ (09/2020)
2.4	Thermoset water resistance to maintain ≥90% strength after ASTM water testing.	50% complete Due by 06/30/2021

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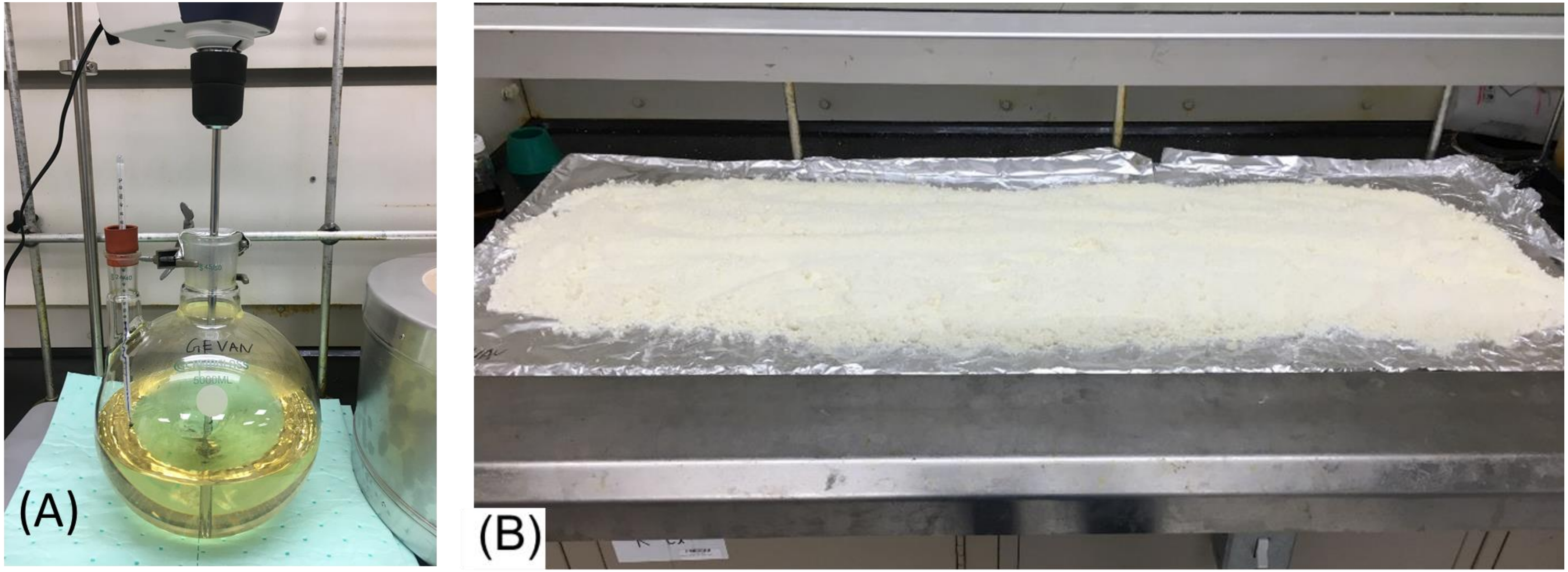
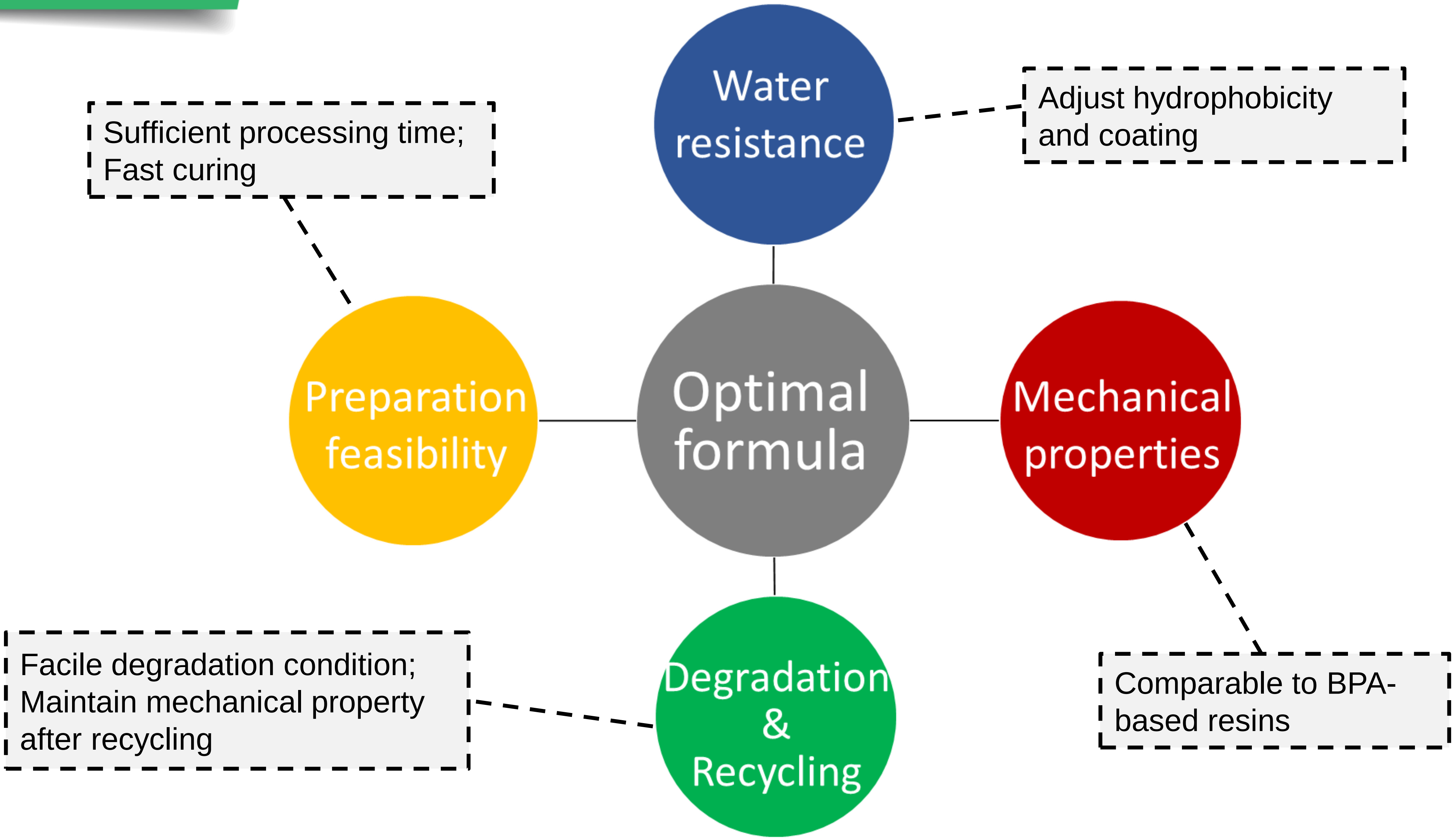
Kg-scale synthesis of the prepolymer

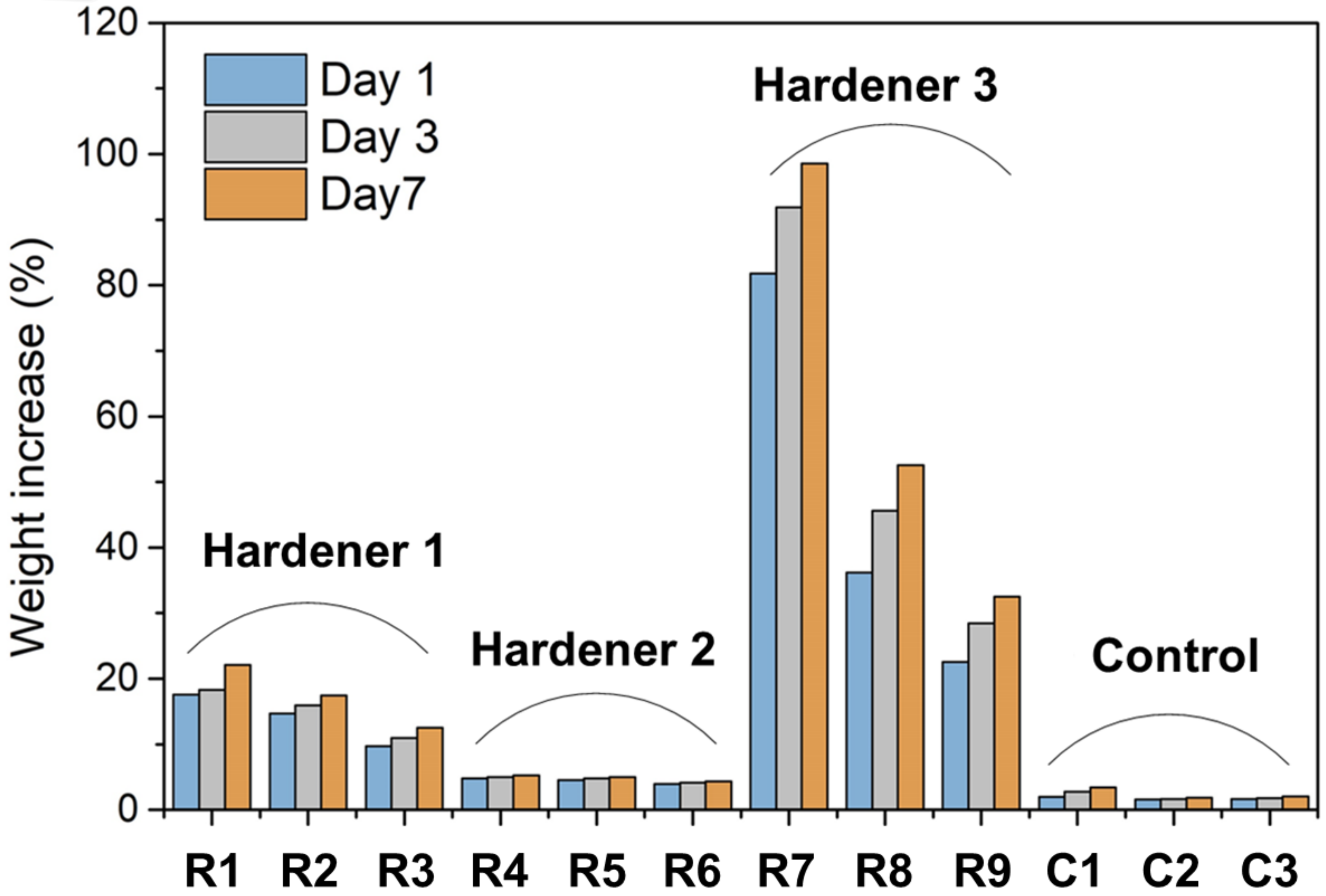


(A) Picture of the experimental setup for the 1 kg-scale synthesis. (B) Air drying of the product in a hood.

Development of the optimal compositions



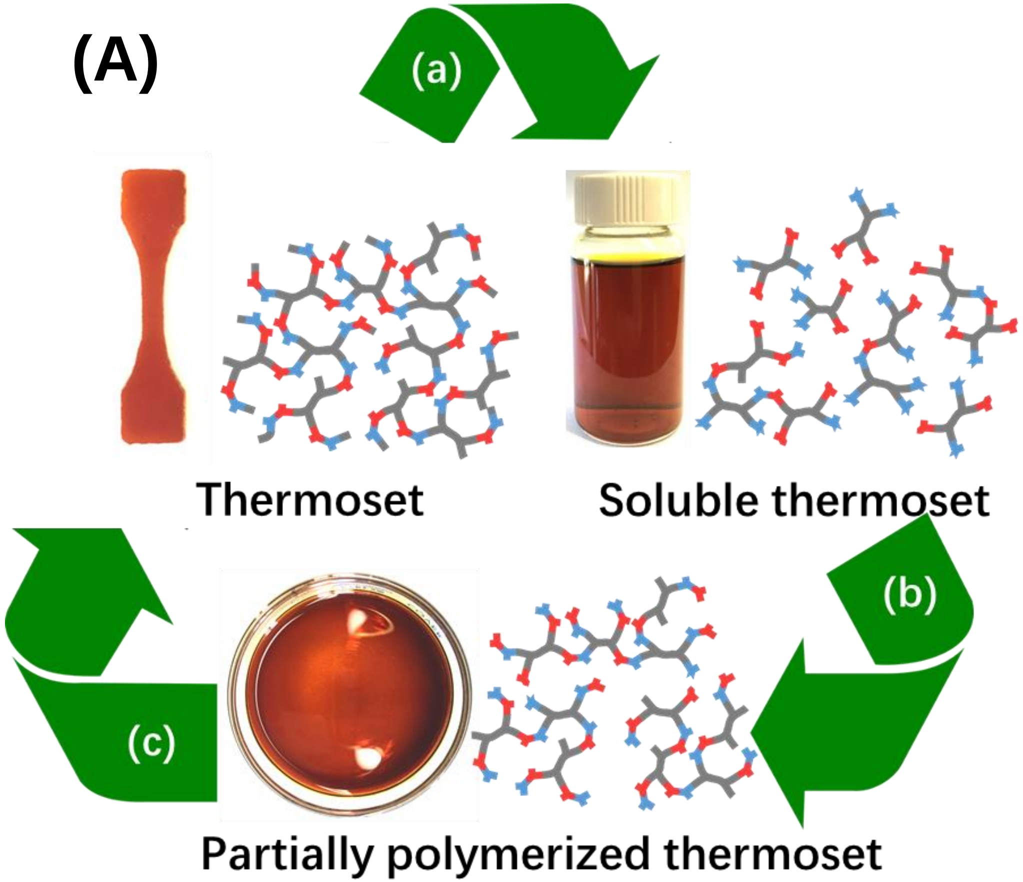
Water resistance tests

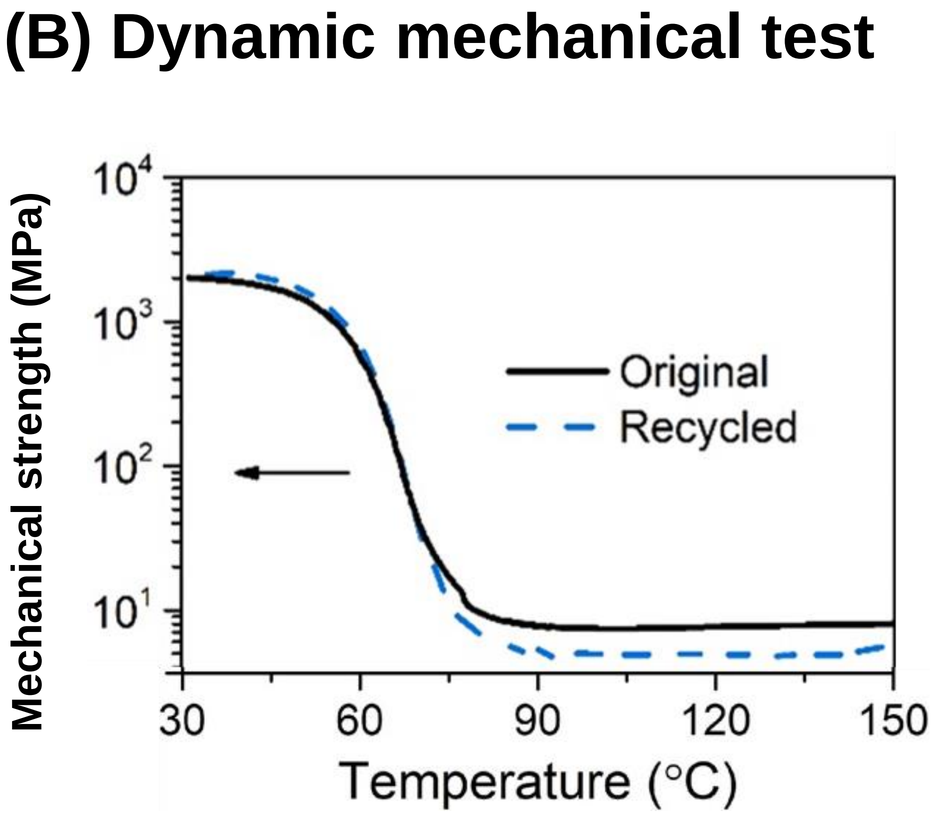


Progress and Outcomes
Task 4: Thermoset decomposition

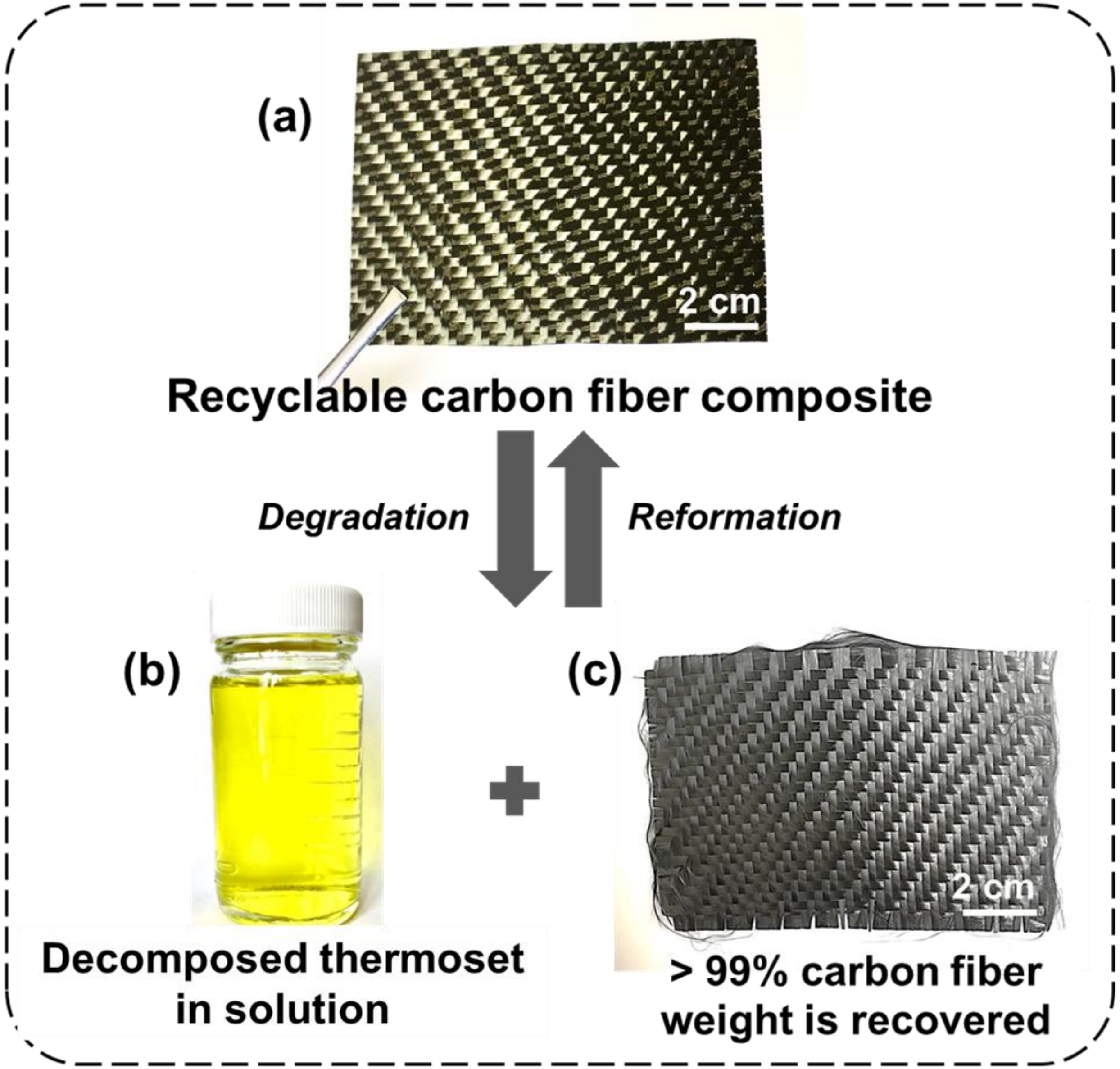
Milestone	Description & Verification	Status
4.1	Decompose ≥ 90% mass of leading thermoset from Task 2. Verify decomposition by GPC and NMR.	50% complete Due by 06/30/2021
GNG 2	Verify thermoset water resistance: Must retain ≥ 90% original strength following ASTM “Standard Practices for Evaluating Resistance of Plastics” water testing. Verify decomposition: Decompose (dissolve) ≥ 90% mass using mild conditions (temperature < 100 °C, atmospheric pressure, low solvent and time inputs	Due by 06/30/2021

Thermoset degradation & recycling





Damage-free method for recycling carbon fiber from carbon fiber reinforced composites (CFRCs)



Many sophisticated CFRC prototypes can be made in house

Skateboard


Plate frame


Shin guard


Surfboard reinforcement

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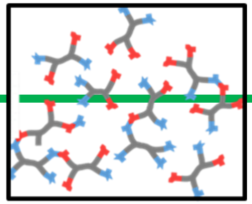
Milestones and conclusions

Composition

Kg-scale synthesis from bio-based chemicals;
Optimal composition has improved water resistance



Degradation

> 90% degradable under mild conditions

Recycling

> 85% of original strength is recovered

CFRC applications

Making demos and JD

Year 1 *Year 2* *Year 3*

Acknowledgements

Shou Zhao
John Stair
Mahdi Abu-Omar
Eric McFarland
Ian Klein

Hannah J. Loizzo
May Wu

Quad Chart Overview

Timeline
- 10/01/2019
- 9/30/2022

	FY20 Costed	Total Award
DOE Funding	$75,213	$1,850,000
Project Cost Share	$30,870	$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

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Publications

ACS Sustainable Chemistry & Engineering

Impact Factor 2019: 7.632

pubs.acs.org/journal/ascecg

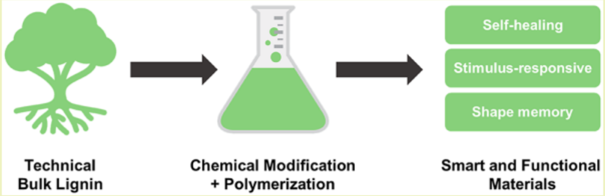
Perspective

Materials Based on Technical Bulk Lignin

Shou Zhao* and Mahdi M. Abu-Omar*

Cite This: https://dx.doi.org/10.1021/acssuschemeng.0c08882

Read Online



ABSTRACT: Lignin is the second most abundant biopolymer and the main source of aromatic structures on earth. Lignin has long been produced as a byproduct of the pulping process and utilized in low value-added applications like heat. However, lignin has received increased attention in recent years to improve its value through various chemical processes. This Review compiles recent progress in synthesis, properties, and applications of lignin-based materials. The lignin for material applications can often be classified into three categories: technical bulk lignin (TBL), lignin-derived oligomers (LDOs), and lignin-derived phenols (LDPs). This Review focuses on the chemical modifications of TBLs and their applications in novel smart materials like self-healing, stimulus responsive, and shape memory polymers. The conversion of TBL to polymers can be briefly divided into two steps: (1) introduction of polymerizable functional groups into the lignin backbone and (2) polymerization that achieves desired materials. Both lignin functionalization and polymerization approaches are discussed in detail. As such, this work attempts to provide a comprehensive overview that highlights the importance of these approaches for the utilization of the abundant but largely ignored biopolymer.

KEYWORDS: *Technical bulk lignin, Chemical modification, Polymerization, Smart material, Self-healing, Stimulus responsive, Shape memory polymer, Review*

ACKNOWLEDGMENTS

Work at Spero Renewables on renewable and recyclable composites is supported in part by a contract from the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy (EERE), award no. DE-EE0008929.