Recycling of Composites and Prepregs by Oxidative Catalysis

WP20-1491

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University of Southern California

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14. ABSTRACT
The technical objectives of this project were to: demonstrate catalytic oxidation to disassemble epoxy composites; recover C fibers with retained architecture; demonstrate recovery of small molecules of value; and reduce hazmat waste from composite mfg.

15. SUBJECT TERMS
Recycling of Composites, Prepregs, Oxidative Catalysis

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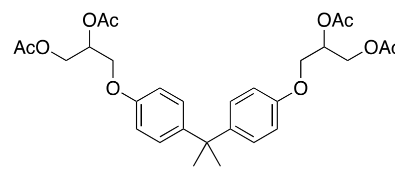
Prescribed by ANSI Std. Z39.18

Technical Objectives

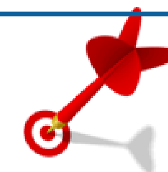
Demonstrate catalytic oxidation to disassemble epoxy composites

Recover C fibers with retained architecture

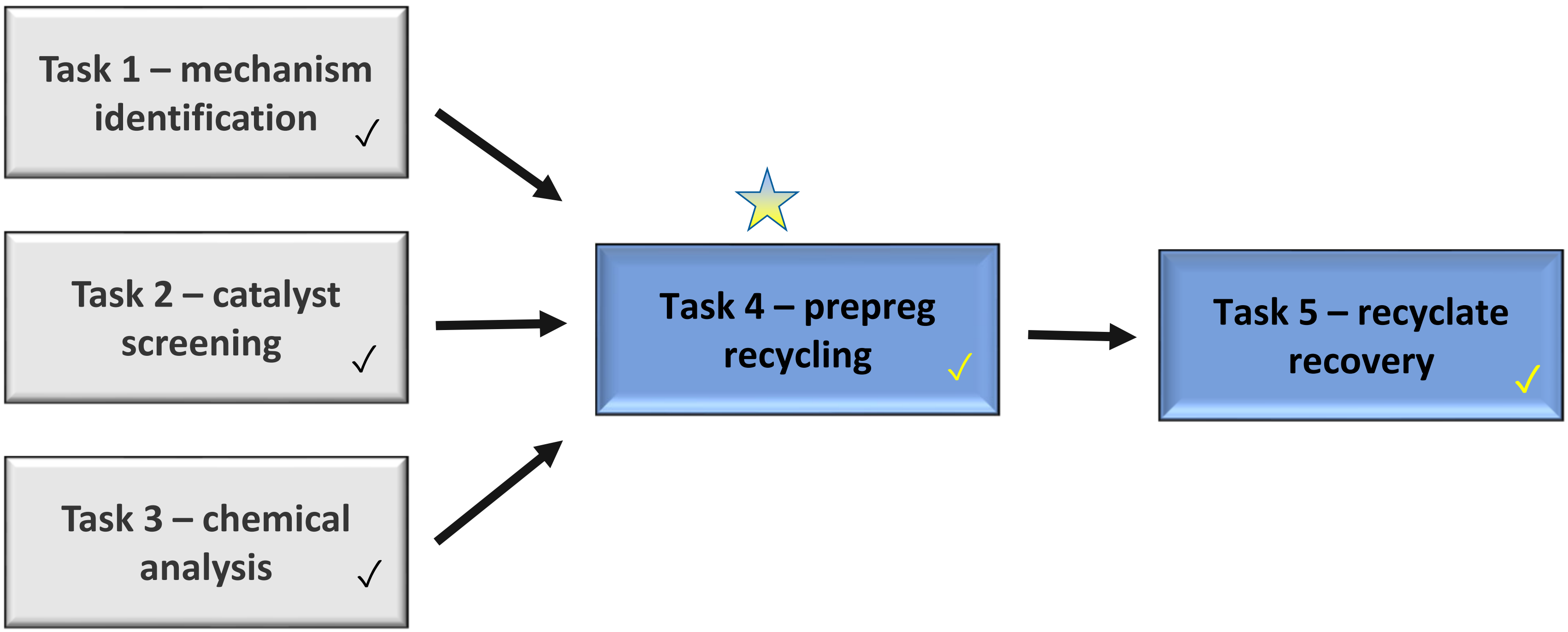
Demonstrate recovery of small molecules of value



Reduce hazmat waste from composite mfg



Technical Approach



Project Team

Dr. Steve Nutt

PI, Advisor

M.C. Gill Composites Center Director

Dr. Travis Williams

Co-PI, Advisor

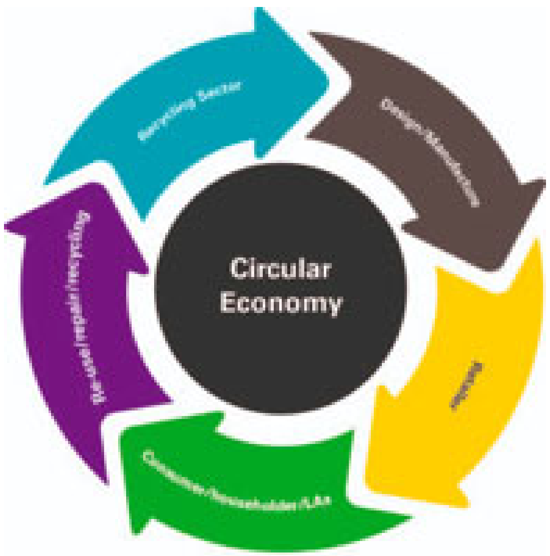
USC Chemistry Professor

Carlos Navarro

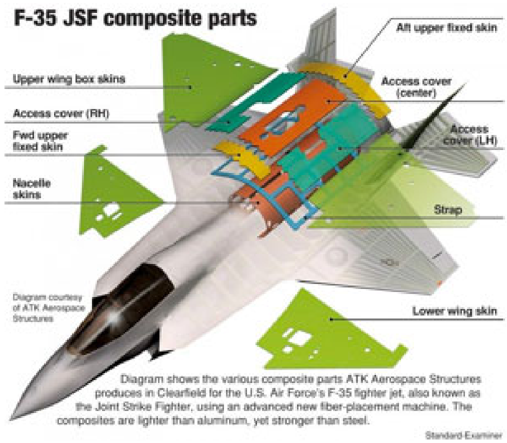
USC Ph.D. Student, Chemistry

Background

- Project initiated 2019
- NEED: Sustainable M&P for recycling/reuse of PMC's to reduce waste, exposure.

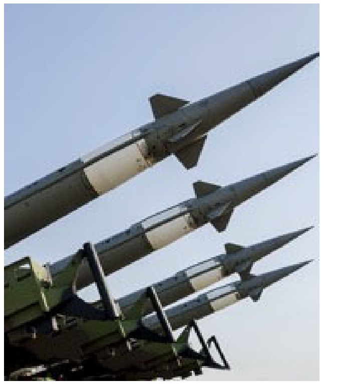


Background



JSF composite parts

composite body armor



Tactical rocket motors

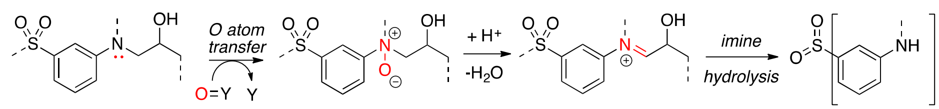
Autonomous Sea Hunter drone warship with CFRP hull

Panels and armor in ground vehicles

Results

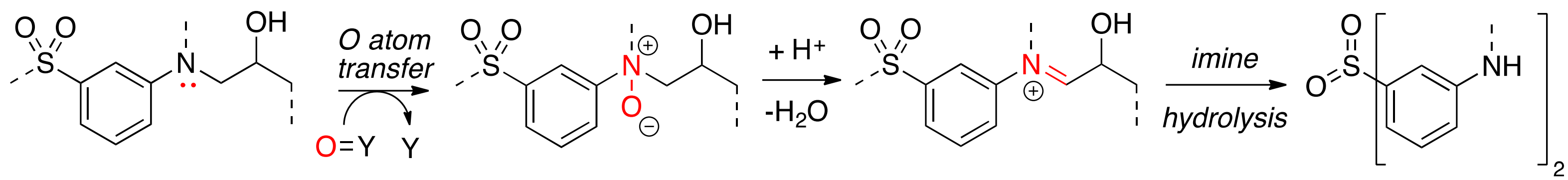
- Describe results as they relate to the key tasks in your technical approach.

- Describe methods and techniques that were used and how they helped to accomplish the objective of the research.



- Reason to continue.

Mechanism identification – Task 1

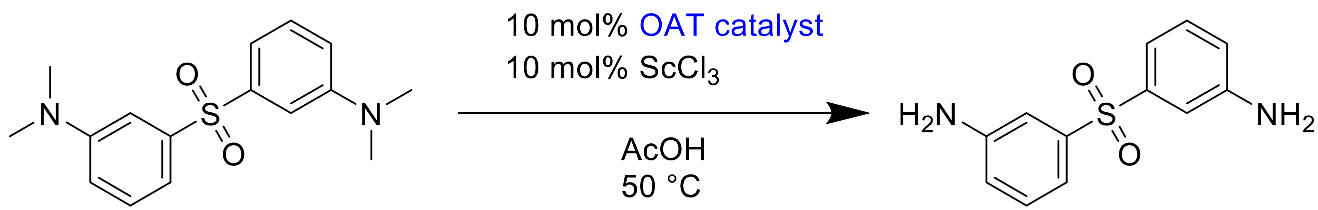


Can we move from H_2O_2 to air with a catalyst?

Elimination

Polymer cleavage

Catalyst screening – Task 2



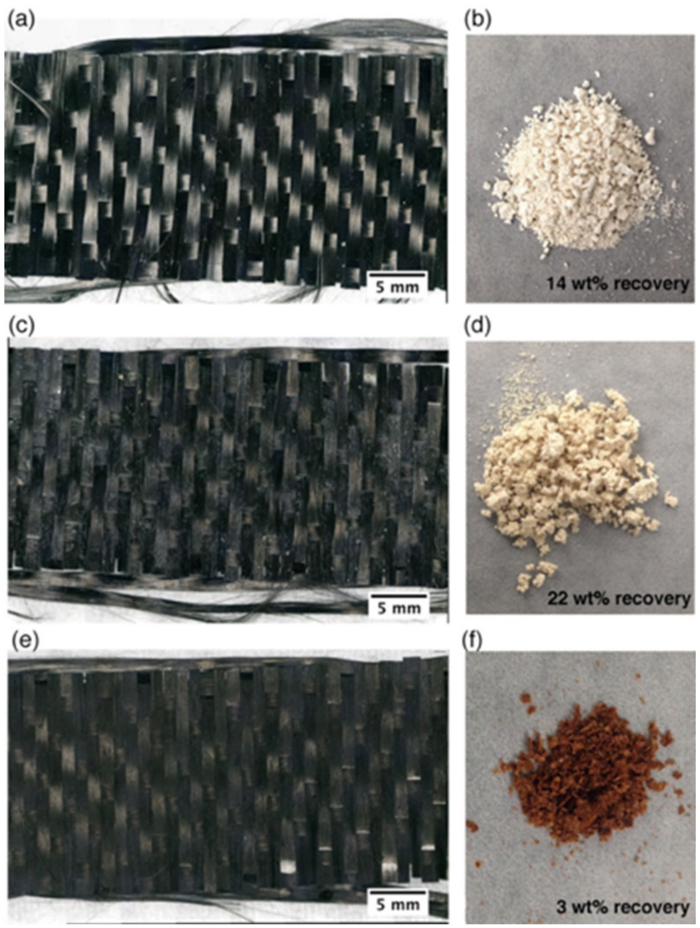
Me_4DDS — Simulated polymer

DDS — Cleavage Product

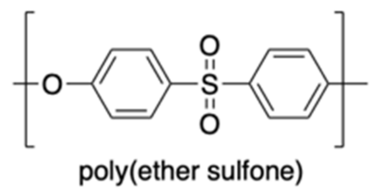
Metal	No ligand	1,10 - Phen	Salen
Fe(II)	Red	Red	White
Mn(II)	Blue	Green	Green
Ru(III)	Red	White	Red
Cu(I)	Blue	Green	Green
Co(II)	Red	Red	White

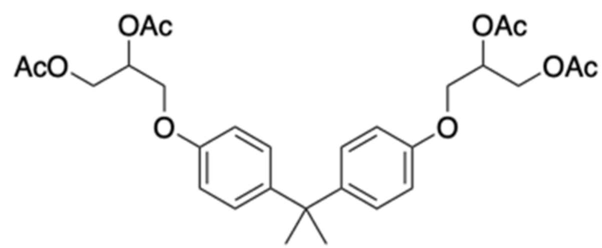
Green = consumed < 1 day
Blue = consumed in 2 days
Red = low / no reactivity
White = untested

Chemical analysis – Task 3

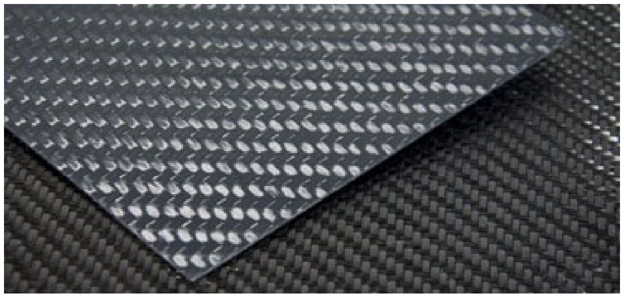


(mix of organic monomers)





Prepreg recycling – Task 4



5320-1/8HS
"100 wt%"

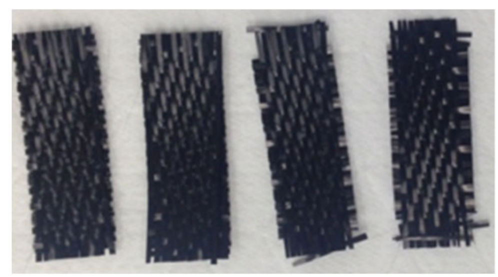
BnOH → Swollen, permeablized product
200 °C, 4 h

125 wt%

O_2 (10 atm)
$MnCl_2$, $AlCl_3$ (5 wt%)
AcOH, 180 °C, 43 h

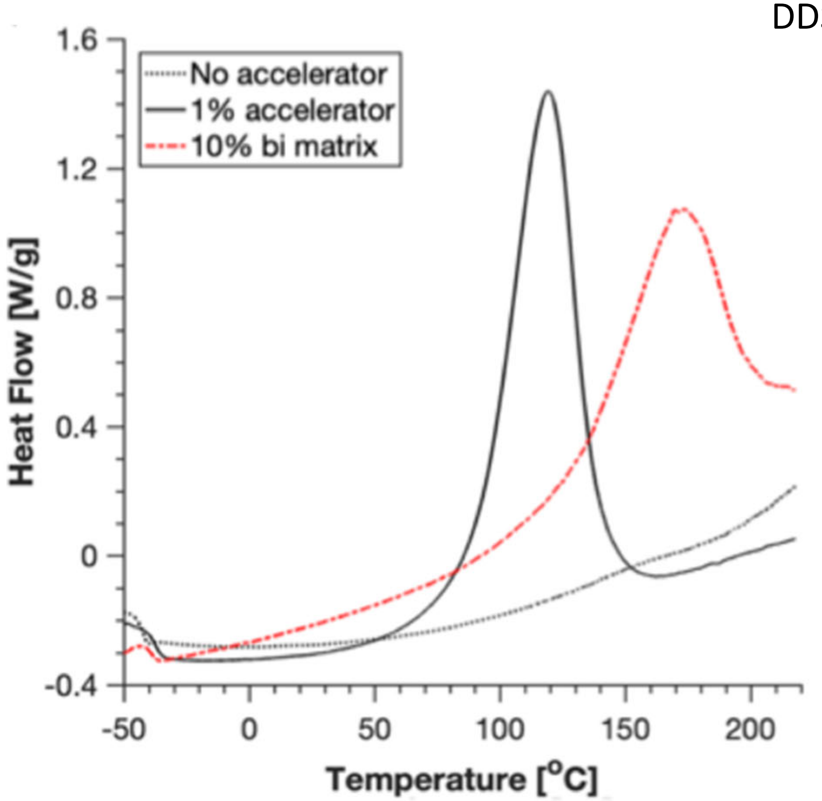
pH 11 → organics
1 wt%

10 wt%

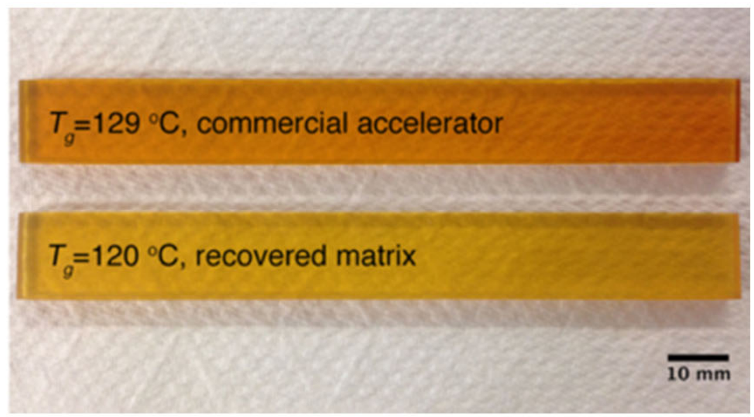


62 wt%

Recyclate recovery – Task 5



DDS by-products are accelerators for resin cure reaction



Next Steps

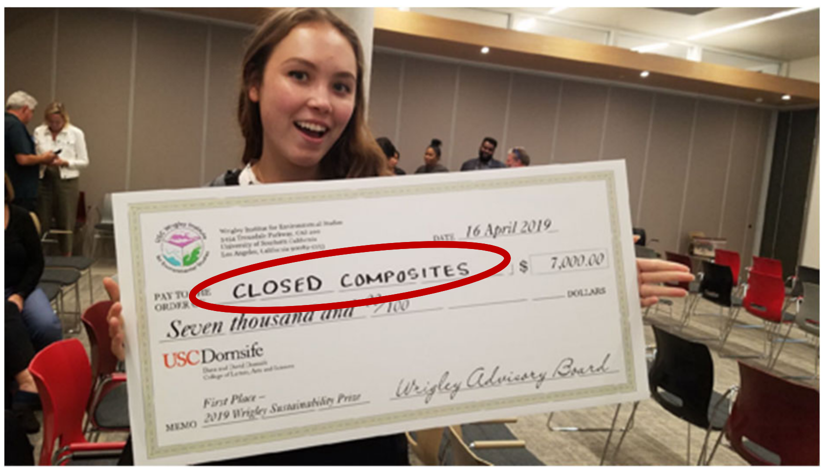
- Demonstrate property retention in recycled PMCs
- Scale up
- Accelerate

Technology Transfer

- Technology transfer is a critical and mandatory part of every SERDP project. The most successful technology transfer will include multiple types of approaches to reach multiple audiences.
- Consider the types of technology transfer that may be best suited to your project and provide a list of potential products/presentations as well as completed items. See examples on next slide.
- Target audiences should include EPA & State regulators, consultants, DoD Remedial Program Managers, and researchers.

Technology Transfer

- Startup formed - Closed Composites, LLC
- Funding awards



Wrigley competition

ASU competition

Startup – Closed Composites, LLC

Carlos Navarro

President

USC Ph.D. Student, Chemistry

Dr. Travis Williams

Board Secretary, Advisor

USC Chemistry Professor

Dr. Steve Nutt

Board Member, Advisor

M.C. Gill Composites Center Director

IP Landscape

- Lo, J.; Nutt, S. R.; Williams, T.J. "Recycling of Fiber Reinforced Polymers via Catalytic Oxidation" United States Provisional Patent 62/479,431, filed March 31, 2017.

  Provisional was abandoned and claims were rolled in to US2018 16/234,062

- Ma, Y.; Navarro, C.; Nutt, S. R.; Williams, T. J. "Aerobic Depolymerization of Fiber-Reinforced Composites" United States Patent Application, US2018 16/234,062, filed December 27, 2018.

  Non-provisional coverage of CFRP digestion

- Williams, T. J.; Nutt, S. R.; Ma, Y.; Navarro, C. A. "Recovery and Reuse of Acid Digested Amine/Epoxy-Based Composite Matrices" US Provisional Patent No. 62/902,158, filed September 18, 2019

  Converting to PCT at VC request. Covers SERDP-sponsored inventions.

Key Points

- Take-aways
  - ♦ CF-epoxy parts are disassembled under moderate conditions
  - ♦ Fiber architecture and properties retained for reuse
  - ♦ Matrix components of value recovered for reuse
  - ♦ Scaling, accelerating, commercializing ahead

Future Research

- Tasks
  - Demonstrate depolymerization of cured CFRP from diverse sources
  - Scale up
  - Accelerate
  - Addressed mixed feedstocks
  - Develop routes for reuse (CFRP processing and properties, fiber surface treatments, tougheners)
- Rough cost estimate for follow-on research: $700K/yr for 3 yrs

BACKUP SLIDES

Publications

Materials Horizons

ROYAL SOCIETY OF CHEMISTRY

FOCUS

View Article Online
View Journal

Check for updates

Cite this: DOI: 10.1039/d0mh01085e

A structural chemistry look at composites recycling

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Composite materials, especially carbon fiber-reinforced polymers (CFRPs), are high-performance class of structural materials now commonly used in aircraft, marine, and other applications, with emerging large-scale use in the automotive and civil engineering applications. The difficulty of recycling these materials is a key obstacle preventing their further application in larger markets. For decades, the engineering community has pursued physical methods to recover value from end-of-life composite waste. This work has generated scalable methods to recover modest value from CFRP waste, but because of their low value recovery, these are applied to a small fraction of CFRP waste. By contrast, relatively few methods to recycle CFRPs have been based on strategic approaches systematically to deconstruct the thermoset polymers that hold them together. In this Focus Article, we will show the emergence of these structure-focused approaches to CFRP recycling and illustrate the path of this research toward the ultimate realization of methods to recover both the reinforcing fibers and the thermoset materials that comprise modern CFRPs.

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rsc.li/materials-horizons

Introduction

Fiber-reinforced polymer (FRP) composites are structural materials that offer superior specific properties (strength and modulus), longer life, and increased efficiency compared to conventional structural metals.[1] FRPs are now commonly used in aerospace, wind turbine, marine, and sporting goods applications, with emerging large-scale use in the automotive industry and some civil engineering applications. Most of the parts by weight. FRPs are also important in the wind energy industry: glass fiber-reinforced polymers are currently the primary structural material in wind turbine blades. The wind industry is motivated to transition to carbon fiber for manufacturing larger turbines. With blade lengths now exceeding 100 m, carbon fiber is used selectively in spar caps to provide the stiffness required to prevent column collisions under gust loads. Composites are also widely seen in high performance sporting goods, ranging from marine vessels to racing bicycles, golf shafts

“A Structural Chemistry Look at Composites Recycling” CA Navarro, CR Giffin, B Zhang, Z Yu, SR Nutt, TJ Williams, *Matls Horizons* Aug (2020) DOI

Polymer Degradation and Stability 175 (2020) 109125

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ELSEVIER

Recovery and reuse of acid digested amine/epoxy-based composite matrices

Check for updates

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ABSTRACT

Chemical recycling of thermoset composites has been focused largely on recovering high-value carbon fibers with property retention, while recovery and reuse of decomposed polymer matrix residues is generally overlooked, despite the fact that matrix recycling constitutes an essential component of a sustainable approach to the overall problem. Our previous study demonstrated that oxidative acid digestion can be deployed effectively to recover near-virgin quality carbon fibers from amine-cured epoxy composites. In the present study, we investigate the viability of recovery and reuse of the decomposed amine/epoxy residue after acid digestion of the matrix, effectively closing the recycling loop. We find that polymer matrix residues recovered from acid digestion solutions via neutralization and precipitation contain molecular components of the epoxies in which aromatic regions are preserved. The recovered matrix residues are blended into virgin resin formulations and two approaches are evaluate for potential reuse. Approach I utilizes the matrix residue as an accelerator for a virgin anhydride/epoxy formulation that contains no accelerator and thus cannot be self-catalyzed. We discover that adding matrix residue produces catalytic effects on the curing reaction. In general, anhydride/epoxy samples blended and cured with recovered matrix residues are homogenous and exhibit thermal and mechanical properties comparable to specimens cured with a commercial accelerator. Approach II deployed the matrix residue as a filler for virgin anhydride-based epoxies with a commercial accelerator to produce blended formulations. In such cases, blended formulations yielded acceptable retention of thermal and mechanical properties, provided the fraction of matrix residue added did not exceed 10 wt%.

“Recovery and reuse of acid-digested amine/epoxy composite matrices” Y Ma, CA Navarro, TJ Williams, SR Nutt, *Polymer Degradation & Stability* **175** (2020) 109125 DOI

Project Funding

	FY20
Funds received to date ($K)	$200K
% Expended	100%
Funds Remaining ($K)	-

Technology Transfer Examples

- Presentations at key conferences
- Web-based tools (see example at link)
  - http://t2.serdp-estcp.org/
- Technology fact sheets
- SAMPE LA chapter open house

Supporting Material

- Provide any appropriate supporting material that could not be included in the brief, if necessary