Upcycling of CFRP Waste: Viable Eco-friendly Chemical Recycling and Manufacturing of Novel Repairable and Recyclable Composites

April 7, 2023

Technology Area Session:
Designing Novel Methods for Deconstructing and Upcycling Existing Plastics

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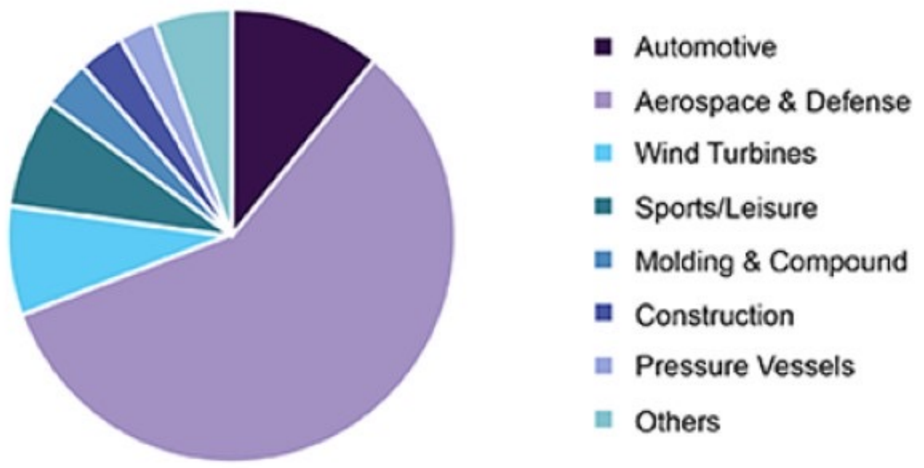
Washington State University

Project Overview - Importance

Global carbon fiber reinforced plastic market share, by application, 2017 (%)



Source: www.grandviewresearch.com

The global Carbon fiber market size is projected to grow from $3.7 billion in 2020 to $8.9 billion by 2031, at a CAGR of 8.6%. (marketsandmarkets.com)

Converting the recovered CF to new products uses less than 10% of the energy required to produce the original CF and leads to nearly an 85% reduction in CO_2 emissions. --- *Composites World, 2/2019*

The fate of CFRP products at the end-of-life?

Recycle
Reuse

Landfill

Project Overview - CFRP recycling methods in literature

- **Mechanical recycling: shredded or ground to particles**
  - Low value (virgin CF \$33 – 66/kg vs. ground CFRP \$5/kg)

- **Thermal degradation (Pyrolysis, Fluidized-bed process, etc.)**
  - Energy intensive
  - Secondary waste from the degraded polymers
  - Strength reduction: ≥ 20% for CF, ≥ 50% for GF
  - Virgin CF \$33-66/kg; recycled CF \$13-19/kg

- **Acid digestion (in strong acid, e.g., sulfuric acid, nitric acid)**
  - Lack of use of the degraded polymer
  - Generate a lot of waste acid
- **Chemical treatment in near-critical or supercritical fluid**
  - Very high temperate and pressure
  - Lack of use of the degraded polymer
  - Time consuming (heating, cooling, and reaction)

Earlier chemical recycling requires hash reaction conditions, results in secondary waste and lack utilization of the decomposed polymers; while mechanical recycling gives low-value fillers and is energy-intensive as well.

Project Overview - Objectives

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Overarching goal

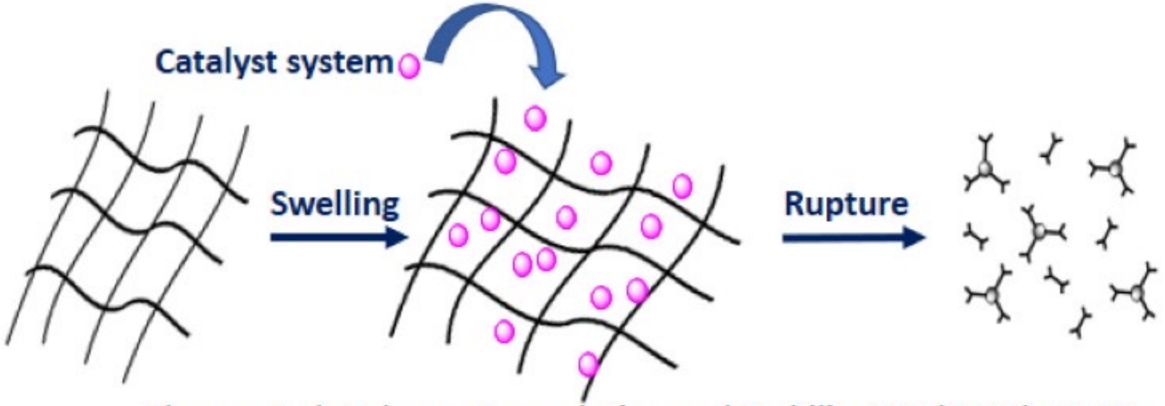
To develop an eco-friendly, energy-efficient and cost-effective chemical recycling technology in breakdown of the matrix polymer network structure and makes use of ***both*** recovered CF and decomposed matrix polymer in new composite manufacturing.

Specific objectives

1) Chemically degrade CFEP under the catalysis of organic zinc salt in aqueous medium at ≤ 250 °C;
2) Develop thermoplastic composites using the recyclate as reinforcement;
3) Develop vitrimer composites using the recyclate as a feedstock.

Approach

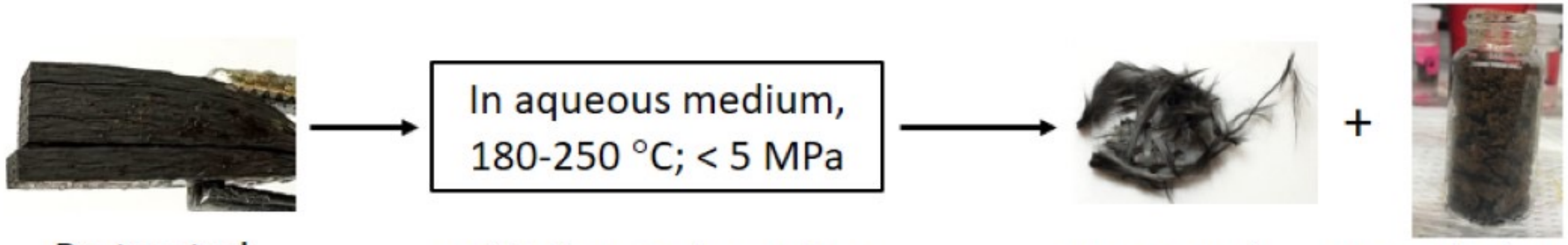
1. Pretreatment



Zhang, et al. *Polymer Degradation and Stability* 139 (2017): 20-27.

a) Pre-swell CFEP at elevated temperature in acetic acid solution.
b) De-crosslink CFEP by short-time thermal treatment.

2. Mild chemical degradation in aqueous medium



Pretreated CFEP waste → Mild chemical recycling → Recovered CF (rCF) + Degraded matrix polymer (DMP)

- Lower temperature & pressure
- Little damage to CF
- Utilization of both rCF & DMP
- Little or no secondary waste

Management

Team Communication Flow
Quarterly Teleconference, email, internal discussions

Industry partners raw materials supply & feedback to project Team (GFS)

Mild Chemical Recycling Technology
J. Zhang (PI/PM); T. Liu (WSU)
K. Simmons (PNNL)

Thermoplastic composite technology
L. Jiang (NDSU);
J. Zhang (WSU)

Technoeconomic analysis
M. Wolcott;
X. Zhang (WSU)

Vitrimer composite technology
J. Zhang;
T. Liu (WSU)

Future Stakeholders
Dissemination Plan

Transportation industry
Aerospace industry
Sporting goods industry
Energy industry

Journal publications
Conference presentations
Industry publications
News release

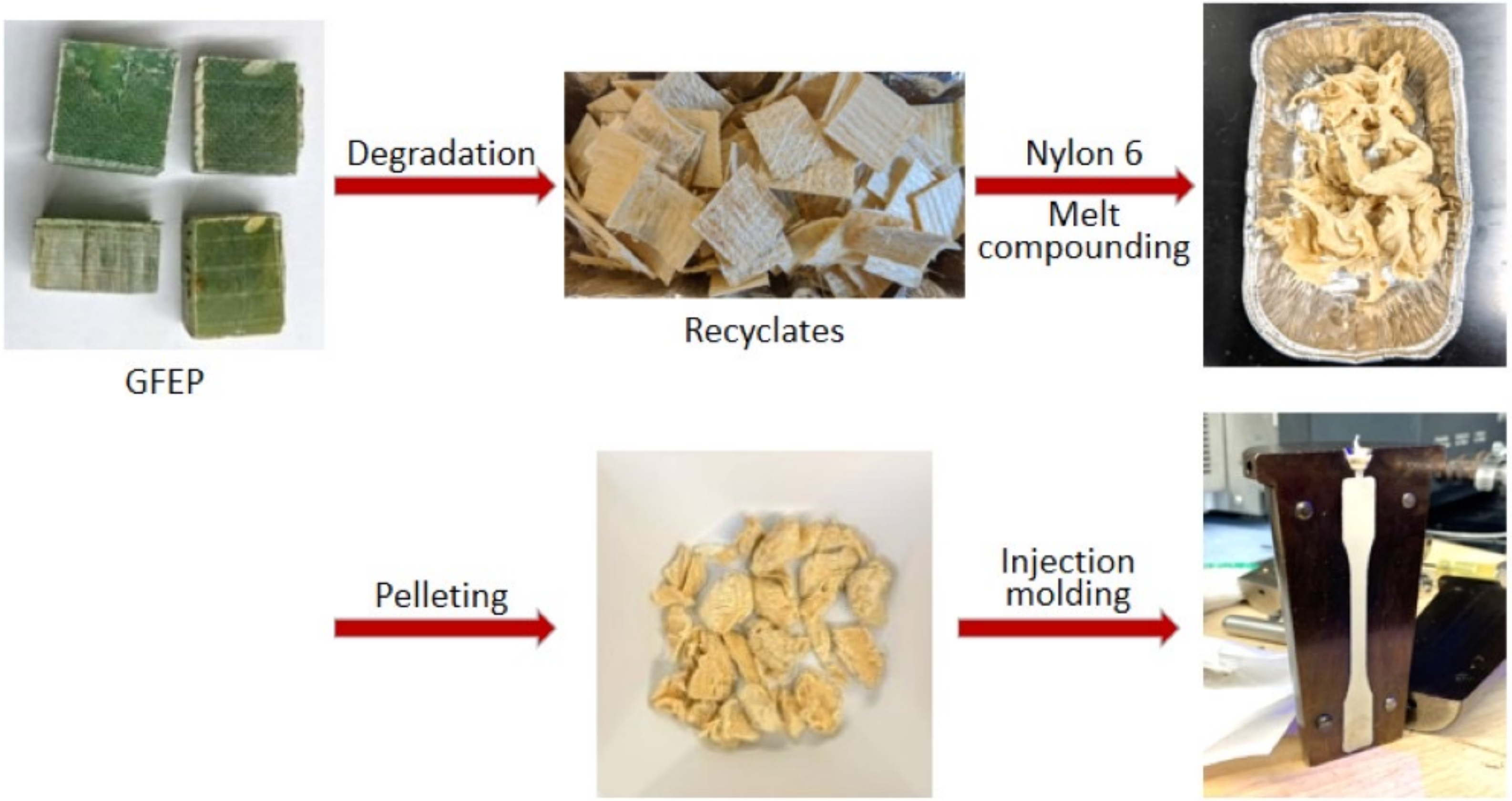
Impact

This project will address the most significant cost/technology barriers for recycling of thermosets and enhance market penetration upon the attainment of following breakthroughs:

- Establish a mild chemical recycling platform for CFEP to reduce waste and save energy;
- Utilize both the recovered CF and decomposed matrix polymer in preparation of new high- value and high-volume polymer composites;
- Contribute to reduction of carbon footprint of CFRP manufacturing by reuse of recovered CF.

Progress and Outcomes

Task 1. Project Verification (Milestone 1 ✓).



Chemical recycling of CFEP and GFEP and the reuse of recyclates for new materials can be achieved.

Task 2. Pretreatment

- Delaminated automobile CFEP at ≤ 120 °C within 3 hours under atmospheric pressure (**Milestone 2.1**✓).
- Delaminated aerospace CFEP at ≤ 200 °C within 3 hours in a pressure reactor (**Milestone 2.1** ✓).
- Decreased the T_g of aerospace CFEP from 199 to 140 °C by thermal treatment at 300 °C for 30 min (**Milestone 2.2** ✓).

Acid Pretreatment

Aerospace CFRP

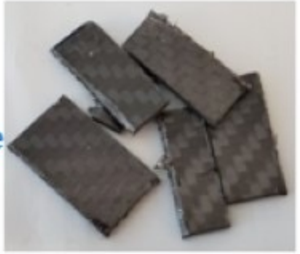
Thickness = 4 mm

180 °C, 3 h

Acetic acid

Thickness = 6 mm

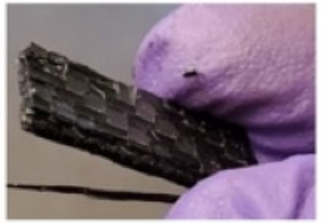
Automobile CFRP



Thickness = 1 mm

80 °C

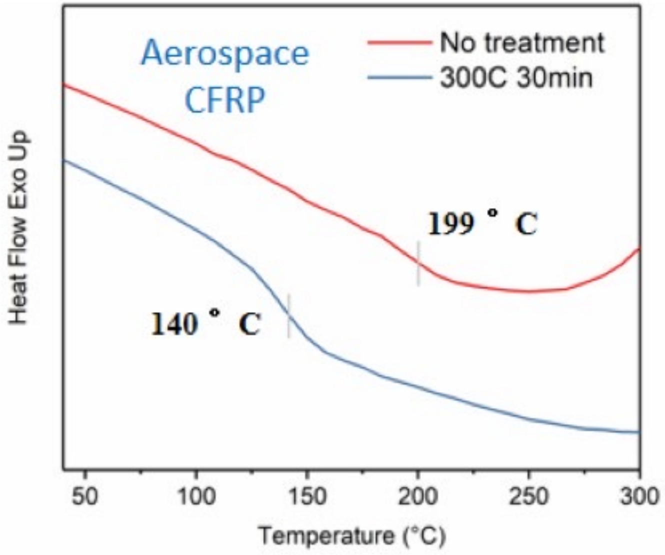
Acetic acid/Water 1/1



1 h

2 h

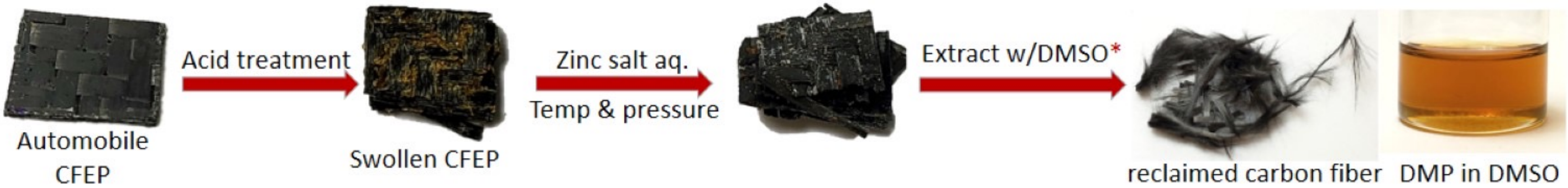
Thermal Pretreatment



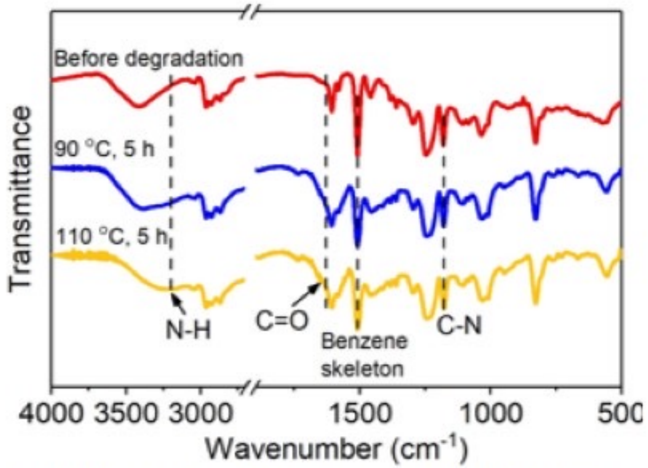
Progress and Outcomes

Task 3. Decomposition of CFEP

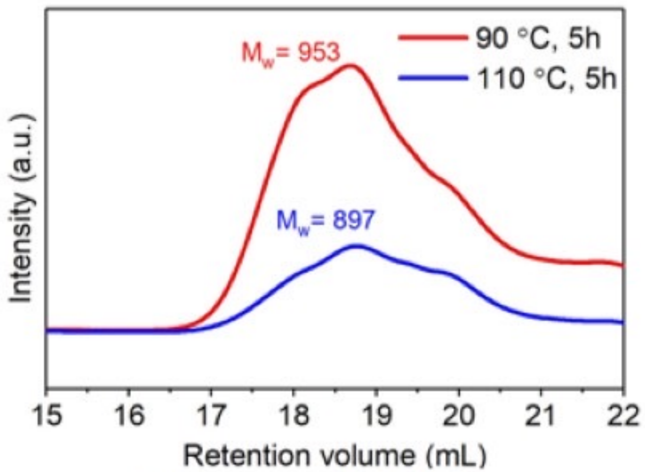
- Achieved degradation of CFEP at ≤ 250 °C using ≤ 20 wt% of zinc salt (**Milestone 3.1** ✓).
- Molecular weight of DMP is ≤ 5000 Da (**Milestone 3.2** ✓).



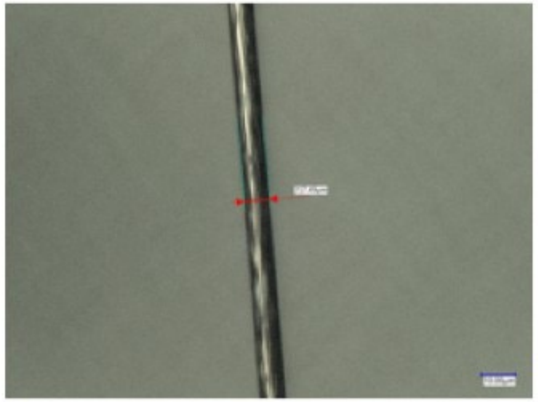
(*Extraction with DMSO is not required for reuse of rCF and DMP, it is only used to calculate the degradation degree.)



FTIR spectra of epoxy matrix before and after decomposition



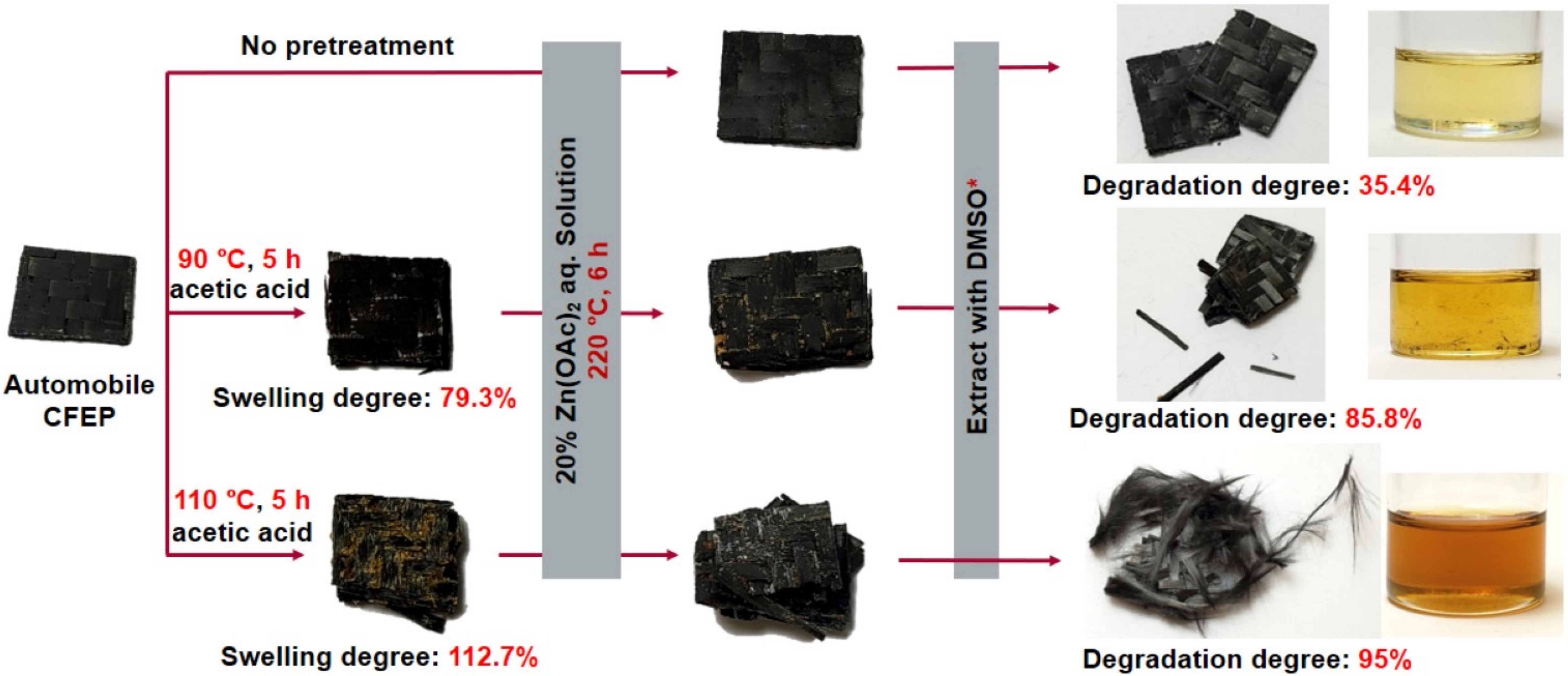
GPC curves of DMP from different acid pretreatments



Digital photo of rCF

Progress and Outcomes

Task 3. Effect of Acid Pretreatment

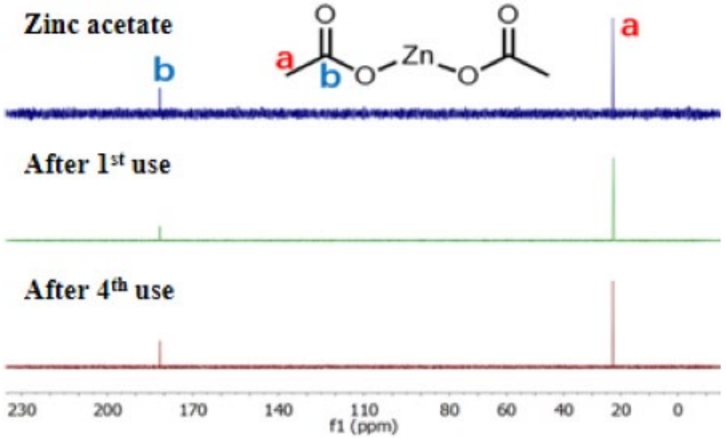


(*Extraction with DMSO is not required for reuse of rCF and DMP, and it is only used to calculate the degradation degree.)

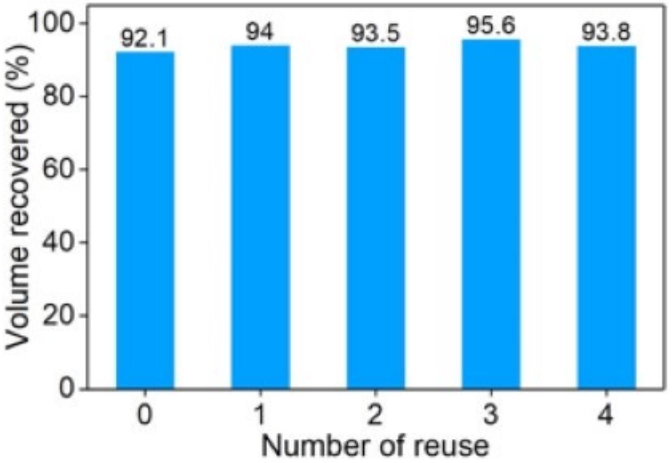
Progress and Outcomes

Task 3. Reuse of catalyst solution (without replenishing, Milestone 3.1 ✓).

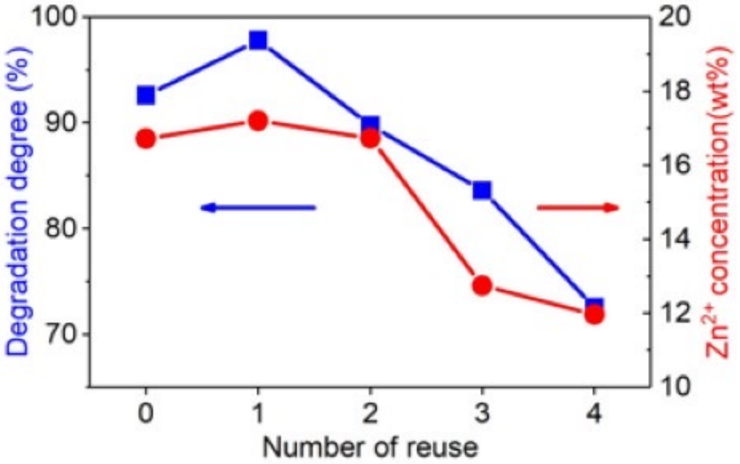
Recovered solid catalyst after each reuse.



^{13}C NMR spectra of the recycled catalyst.



Volume percent of the recovered catalyst solution after each reuse



Catalyst content in the recycled solution and the associated degradation degree.

Progress and Outcomes

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Task 3. One-Step: Combining pretreatment and degradation (beyond SOPO ✓).

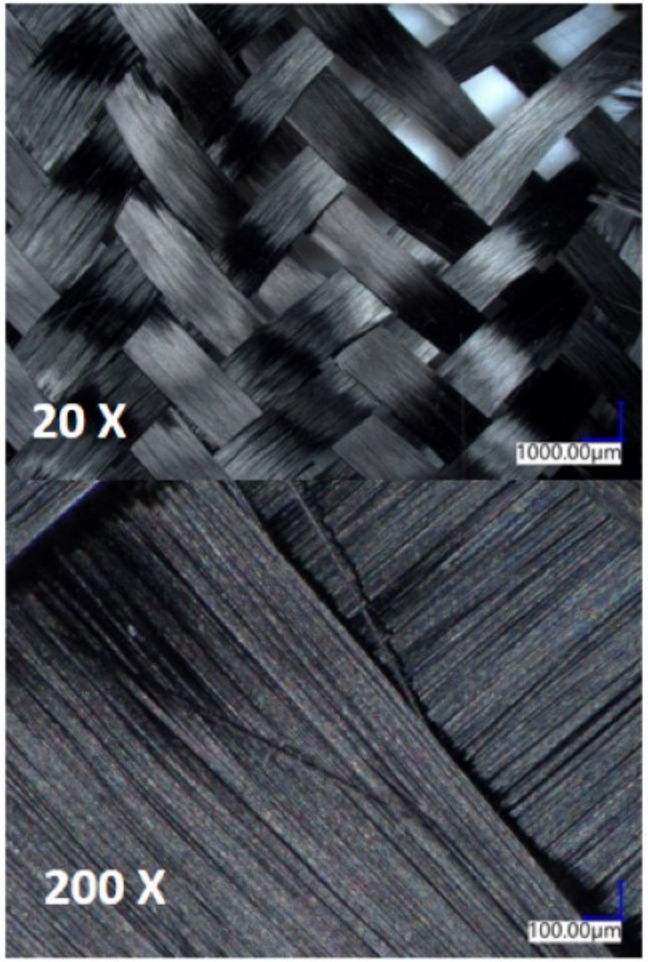
Automobile CFEP

- CFEP sample: DETA cured DER epoxy (T_g ~ 120 °C) with 10 layers of CF mats. Resin content: 45.0%.
- Catalytic solution: 20 wt.% of zinc acetate + 10 wt. % of acetic acid + 70 wt. % of water, pH = 4.8.
- Degradation conditions: **444 g** of CFEP sample was degraded in **475 g** of catalytic solution at 220 °C and 300 psi for 6 h in a 1 L pressure reactor. High feedstock ratio! The reaction time could be shorter (3h), and the catalyst concentration could be lower (10 wt.%).
- The whole process did not require additional conditions such as stirring, condensation or special atmosphere, etc.

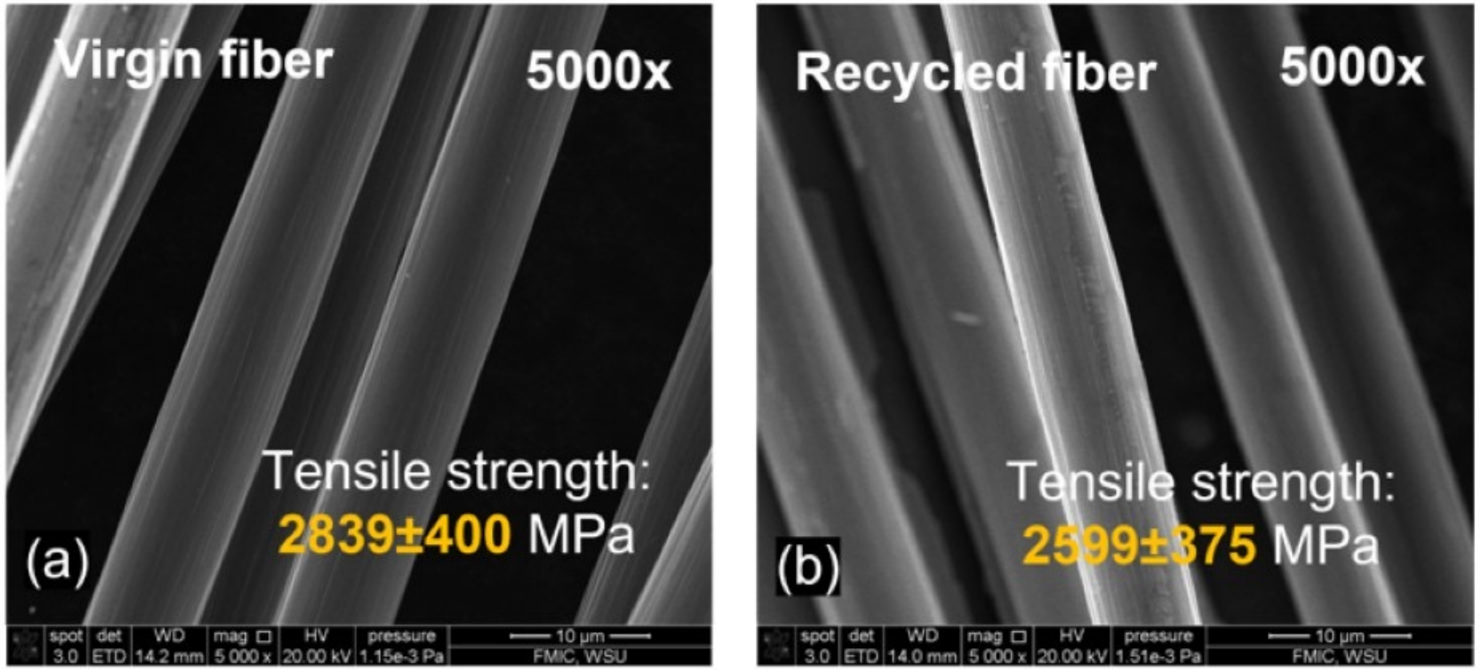
Progress and Outcomes

Task 3. One-Step Decomposition of Automobile CFEP (beyond SOPO ✓).

(To characterize the rCF and DMP, acetone was used to dissolve the DMP and separate it from rCF.)



Digital pictures of reclaimed carbon fiber.



SEM images and tensile properties of single textile virgin carbon fiber (a) and recycled carbon fiber (b).

rCF retains 91.5 % tensile properties of the neat CF.

Progress and Outcomes

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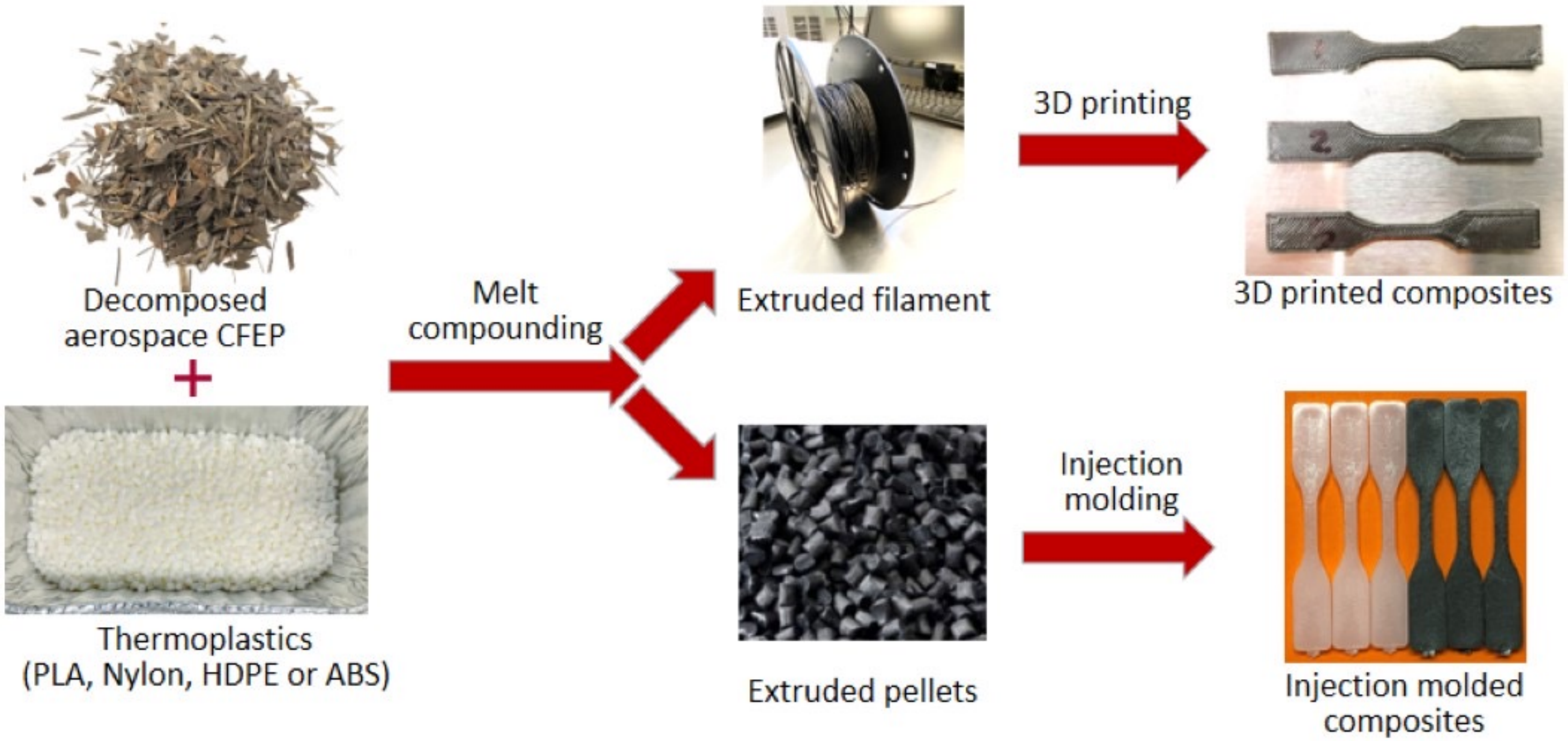
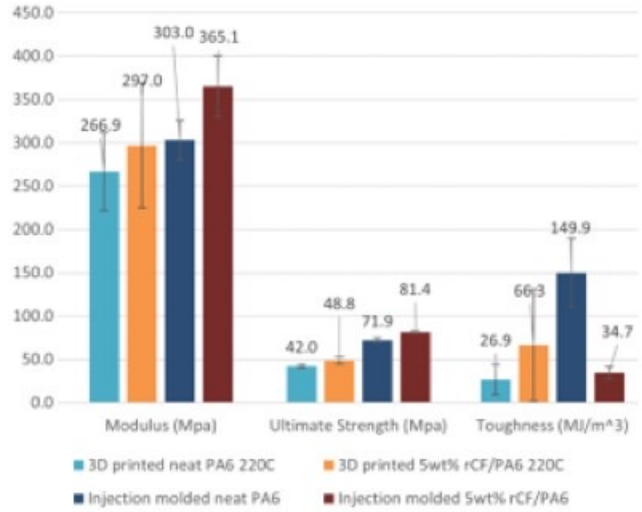
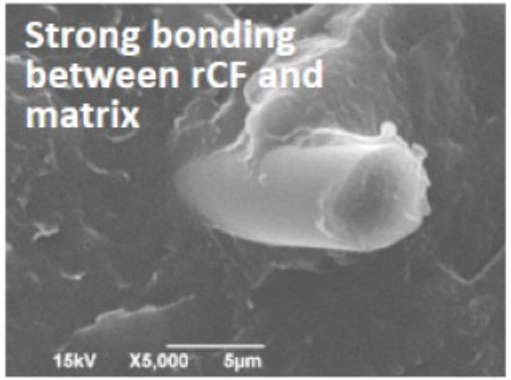
Task 4. Preparation of thermoplastic composites and 3D printing

- Direct use of rCF and DMP in extrusion compounding (**Milestone 4.1**✓).
- Direct use of rCF and DMP in 3D printing (**Milestone 4.2** ✓).



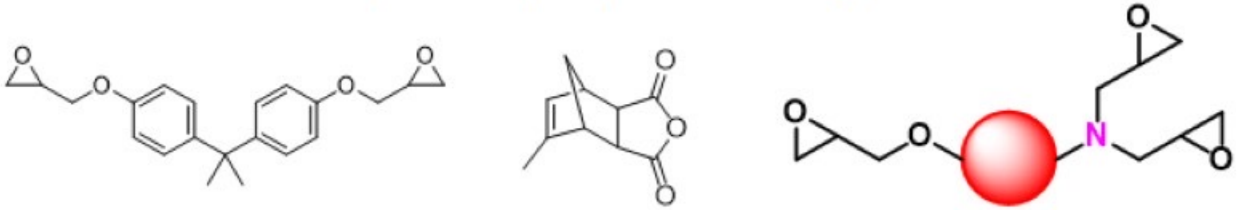




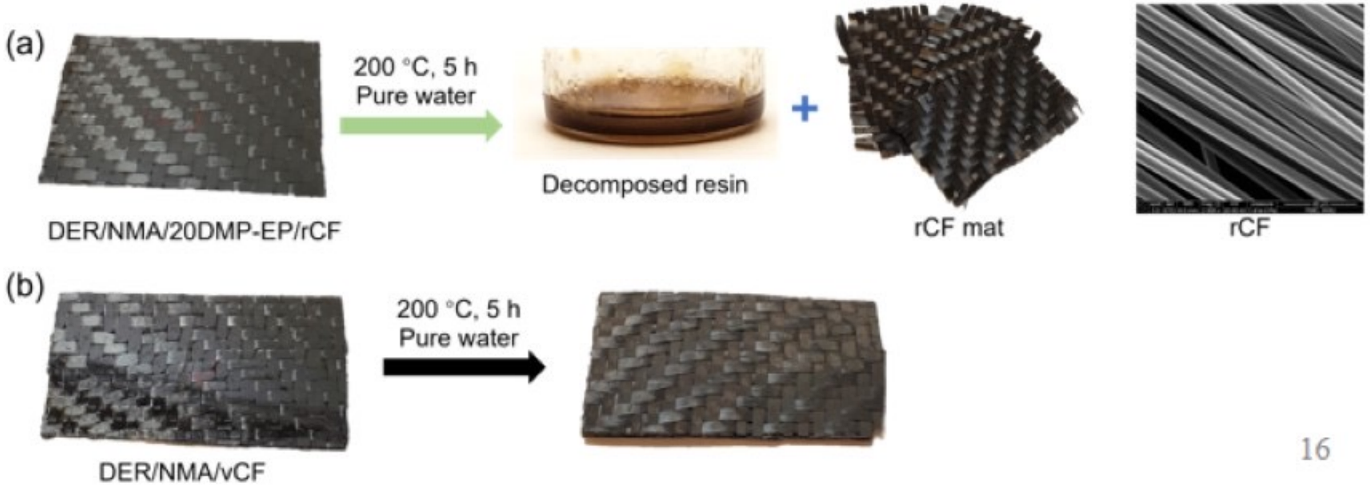
Progress and Outcomes

Task 5. Preparation of vitrimers and vitrimers composites

- Hydrothermally recyclable vitrimer composites prepared using both DMP and rCF (**Milestone 5 ✓**).

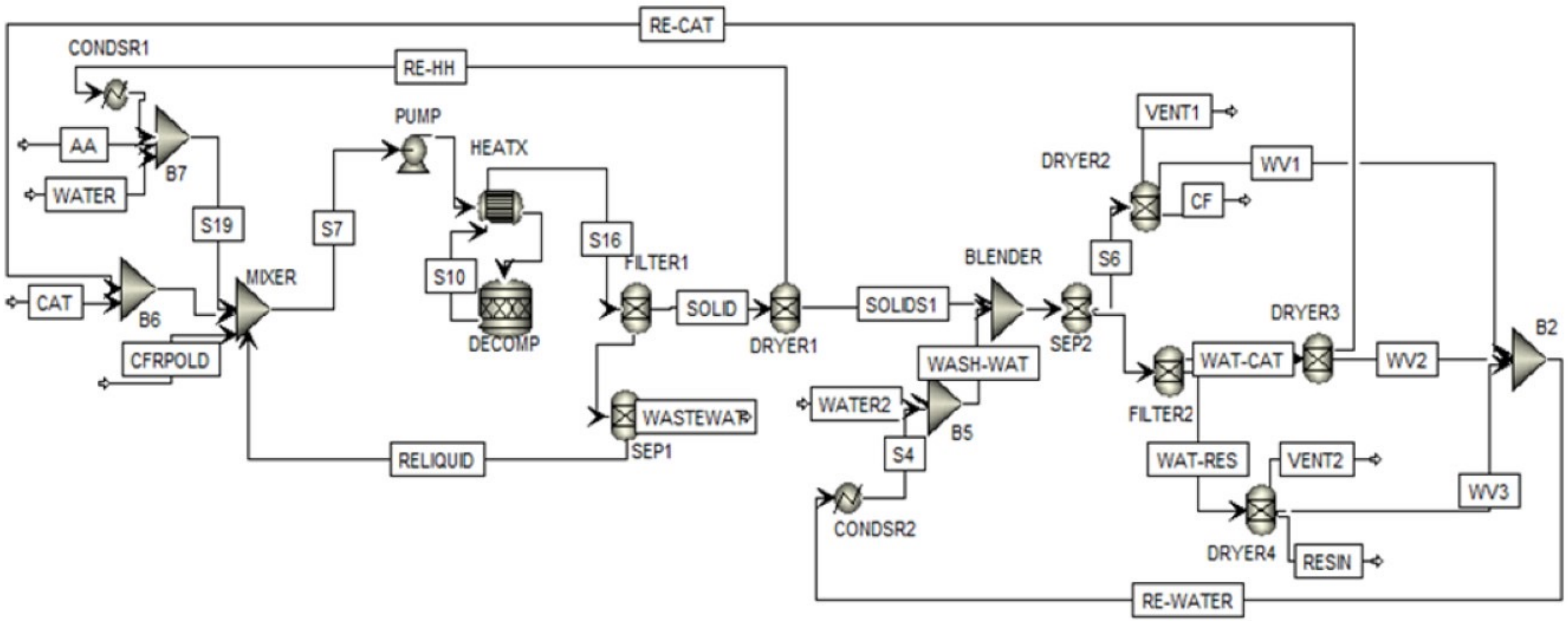


Sample	Tensile strength (MPa)	Tensile modulus (GPa)	Fiber content (wt%)
DER/NMA/vCF	415.7 ± 36.4	25.5 ± 1.3	63.5
DER/NMA/20DMP-EP/rCF	373.1 ± 44.8	21.0 ± 1.5	60.1



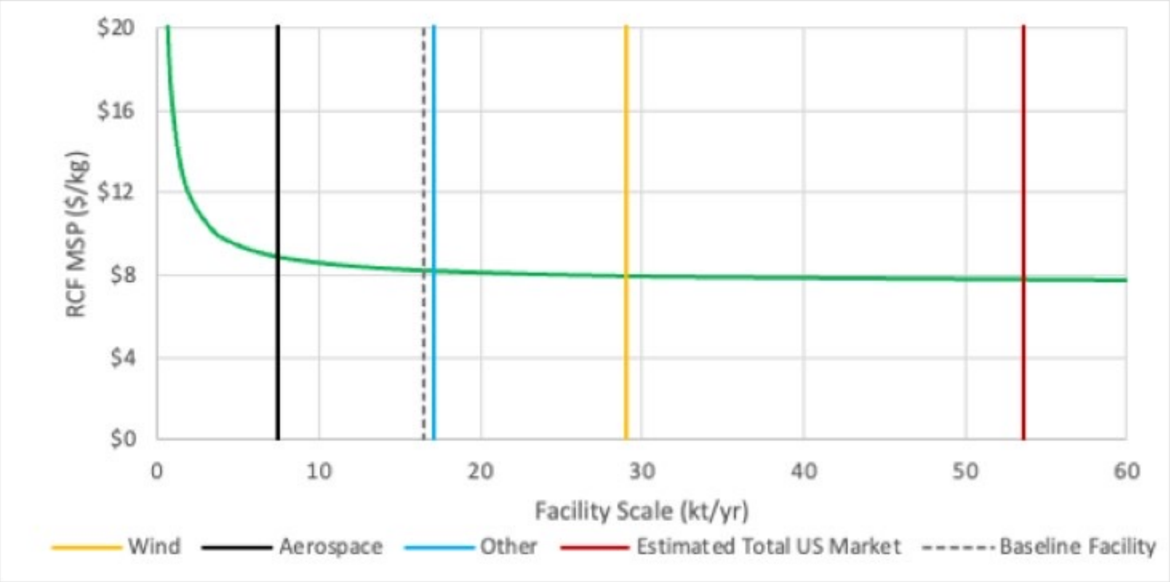
Progress and Outcomes

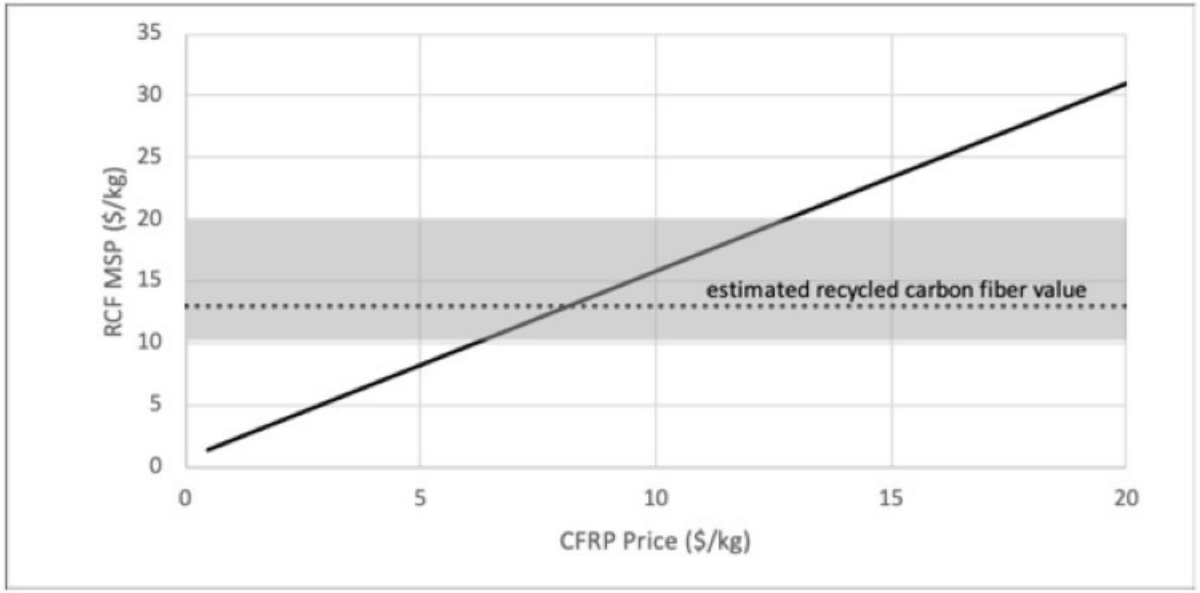
Task 6. Aspen Process Diagram



Progress and Outcomes

Task 6. Techno-economic analysis (Milestone 6 ✓).





Progress and Outcomes

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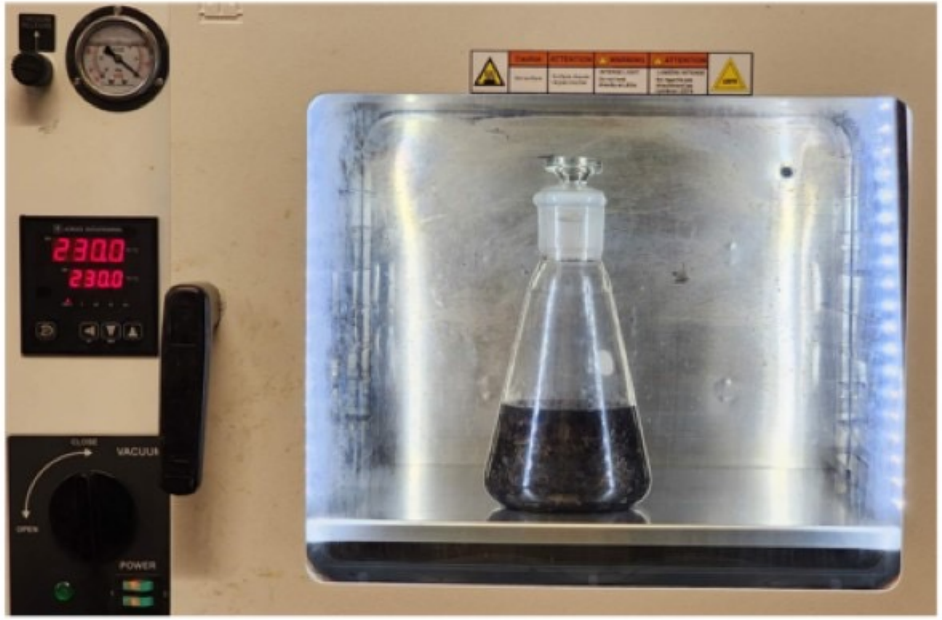
Beyond-SOPO: Degradation of CFEP wastes at atmospheric pressure

a)



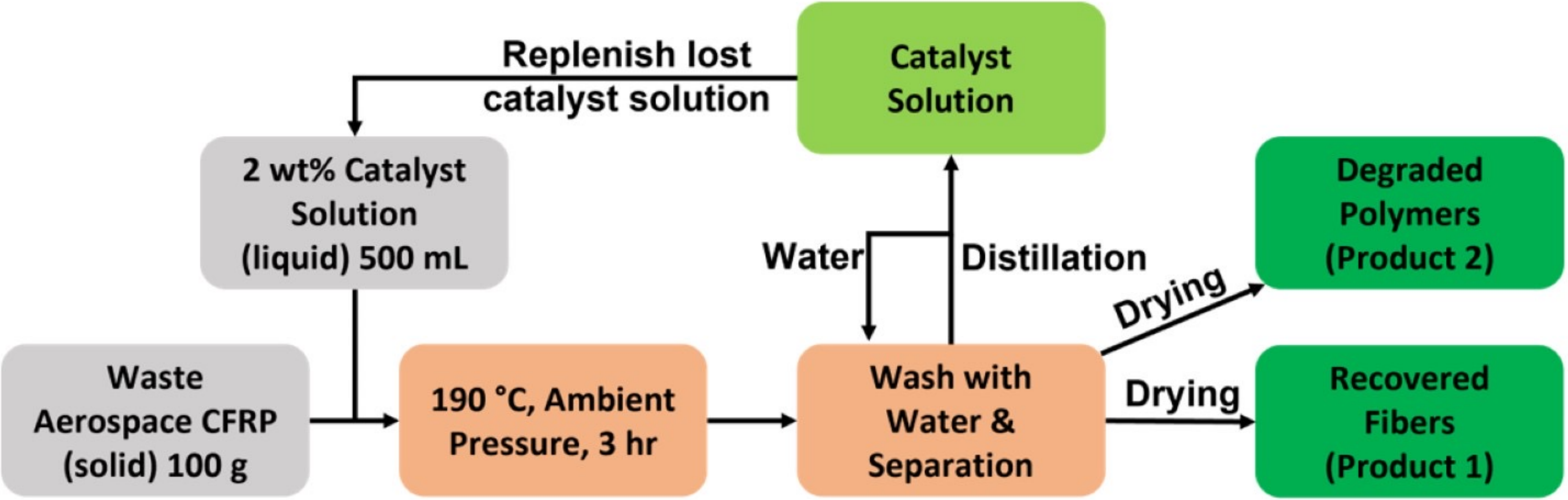
b)

- 100 g of aerospace CFEP waste in 500 mL of catalyst solution in an eco-friendly high boiling point solvent.
- 3 -5 wt.% common Lewis acid, 180 - 200 °C, 3- 4 hours.

No pressure reactor needed!

Progress and Outcomes

Beyond-SOPO: Flow chart of the new recycling process



Summary

- Degradation of automobile/wind turbine CFEP at temperature ≤ 220 °C within 6 h using zinc salt/H_2O solution; mission accomplished✓
- Degradation of aerospace CFEP at temperature ≤ 250 °C within 6 h using zinc salt/H_2O solution; mission accomplished✓
- The recovered catalyst solution can be reused for 3 times in the degradation reaction; mission accomplished✓
- Direct reuse of DMP and rCF in the preparation of thermoplastic composites; mission accomplished✓
- Preparation of intrinsically recyclable vitrimers and vitrimers composites from DMP and rCF; mission accomplished✓
- Techno-Economic Analysis and commercial validation; mission accomplished✓
- Degradation of CFEP wastes at atmospheric pressure. beyond SOPO ✓

Quad Chart Overview (Competitive Project)

Timeline

- **Project start date: 10/01/2019**
- **Project end date: 06/30/2023**

	FY20 Costed	Total Award
DOE Funding	(10/1/19 – 12/31/22) *$ 845,506 (WSU)* *$156,28 (NDSU)*	**(negotiated total federal share)** ***$ 1,249,804***
Cost Share	**$ 423,003.03**	**$ 442,066**

Project Partners

- North Dakota State University
- Pacific Northwest National Laboratory
- Global Fiberglass Solution

Project Goal

Introduce an eco-friendly and economically viable chemical recycling technology for CFEP, and reuse of the recyclate in new composites.

End of Project Milestone

- Identify a simple eco-friendly pretreatment method and an alternative thermal pretreatment method
- Identify optimum reaction and processing parameters for mild chemical decomposition
- Develop thermoplastic composites using recyclate
- Develop vitrimer composites using recyclate
- Techno-economic analysis and porotype development

Funding Mechanism

FY19 Bioenergy Technologies Office Multi-topic FOA – DE-FOA-0002029

Publications, patents and disclosures

- **Journal publication: 4 papers published; 1 manuscript revised, 3 manuscript under preparation**
  - Cheng Hao, Tuan Liu, Wangcheng Liu, Mingen Fei, Lin Shao, Wenbin Kuang, Kevin Simmons, Jinwen Zhang.* Recyclable CFRP with Extremely High Tg: Hydrothermal recyclability in Pure Water and Upcycling of the Recyclates in New Composite Preparation, *Journal of Materials Chemistry A* 2022, **10**,15623 - 15633.
  - Tuan Liu, Cheng Hao, Lin Shao, Wenbin Kuang, Lelia Cosimbescu, Kevin L. Simmons, Jinwen Zhang.* Carbon Fiber Reinforced Epoxy Vitrimer: Robust Mechanical Performance and Facile Hydrothermal Decomposition in Pure Water, *Macromolecular Rapid Communications*, 2021, **42**, 2000458 (DOI: 10.1002/marc.202000458).
  - Baoming Zhao, Cheng Hao, Yu-Chung Chang, Yiding Cao, Tuan Liu, Mingen Fei, Lin Shao, Jinwen Zhang*. Photo-curing 3D Printing of Thermosetting Sacrificial Tooling for Fabricating Fiber-Reinforced Hollow Composites, *Advanced Functional Materials*, 2023, DOI: 10.1002/adfm.202213663.
  - Lin Shao, Yu-Chung Chang, Cheng Hao, Ming-en Fei, Baoming Zhao, Brian J. Bliss, Jinwen Zhang*. A chemical approach for the future of PLA upcycling: from plastic wastes to new 3D printing materials, *Green Chemistry*, 2022, **24**, 8716-8724.
  - Lin Shao, Yu-Chung Chang, Baoming Zhao, Xinyan Yan, Brian J. Bliss, Ming-en Fei, Chenhao Yu, Jinwen Zhang* Bona Fide Upcycling Strategy of Anhydride Cured Epoxy and Reutilization of Decomposed Dual Monomers into Multipurpose Applications, *Chemical Engineering Journal (revised & to be accepted)*
- **Patents and disclosures**
  - Jinwen Zhang, Tuan Liu, Junna Xin. Methods for chemical degradation of epoxies using organic salts as catalysts, US Pat. No. 10,696,815 B2
  - 3 provisional patens pending.
- **3 presentations at technical conferences**

Future Plan

- Further exploration of mild chemical recycling under atmospheric pressure
  - Optimization of degradation condition
  - Initial scaleup of the recycling process
  - Secondary decomposition of the degradation product
- Technology transfer
- Industrial collaboration

GLOBAL FIBERGLASS SOLUTIONS

BOEING

TORAY

Where do old boats go to die?

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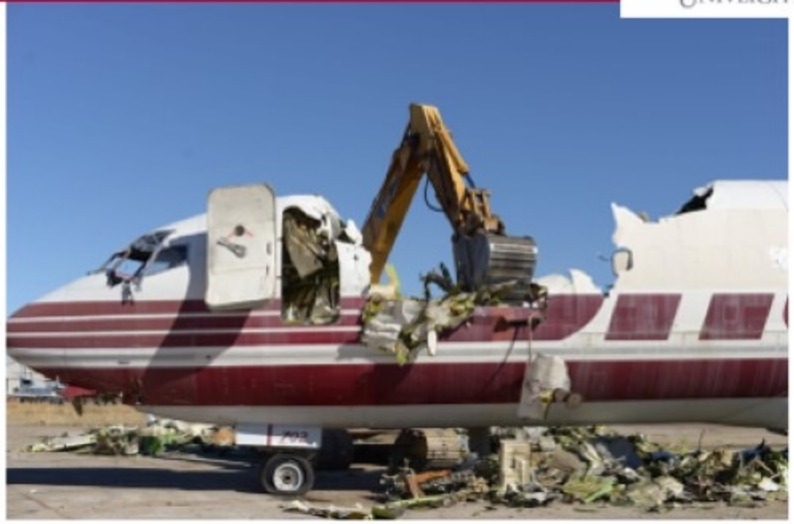
- boats that were built in the fibreglass boom of the 1960s and 1970s are now dying.
- Most boats currently head to landfill.
- The problem of end-of-life boat management and disposal has gone global, and some island nations are even worried about their already overstretched landfill.
- However, many are also disposed of at sea, usually by simply drilling a hole in the hull and leaving it to sink someplace offshore.

(https://theconversation.com/abandoned-fibreglass-boats-are-releasing-toxins-and-microplastics-across-the-world-143857)

Where airplanes go to die—and be reborn

- For the retired airplanes, there are several facilities (boneyards) in the United States to strip down planes and recycle the important and valuable innard parts and metals (~ 85 to 90 percent of an aircraft by weight).
- However, when it comes to plastics and their composites in the planes that are difficult to break down, or worth little money, landfilling is still the fate of these waste materials.



- For now, the insulation, carpeting, seat cushions, floorboards and wall or ceiling panels are usually sent to landfills. "The amount of labor it takes to strip out these things isn't really worth the time".
- One challenge is that airplanes are built from many different types of materials stuck together, which is not ideal for recycling.
- "Some newer planes, like the Boeing 787 Dreamliner, are made with carbon fiber. These mixes of carbon and plastic—are lightweight and enable planes to need less fuel. But it's not yet clear how they will be recycled. "Ironically, the very composites that make an aircraft lighter and improve fuel efficiency are also very difficult to deal with environmentally." (a remark in an analysis from International Air Transport Association)

(https://www.popsci.com/airplane-recycling/)

How about recycling of automobile composites

- 75% by weight of a modern car is composed of ferrous and non-ferrous metals, which are readily recycled back into the metals industries.
- However, the remaining 25% is composed of plastics, rubber and other components, which are currently disposed of in landfill. Compounding this problem is the automotive industry's desire to use new, lighter materials, particularly plastic composites, to reduce weight and so improve fuel efficiency.
- Unfortunately, composite plastic materials are generally regarded as being unrecyclable owing to the reinforcing fibers.
- Typically, 10% of a vehicle's weight (wt%) is made up of plastics and plastic composites, and for some lightweight vehicles this may be up to 20 wt%. Composites are increasingly used since they have the advantages of strength, durability and corrosion resistance together with low weight.

https://www.azom.com/article.aspx?ArticleID=2130

Remarks

- Current methods for recycling CFRP are still focused on recovery of CF, and controlled pyrolysis appears the most scalable one, at this point.
- Reuse of the decomposed matrix polymers from those processes, however, is rarely discussed in the literature, no matter it is in the reports from industry or publications from academia.
- The methods for recycling CFRP (and for GFRP too) are there, and researchers continue to introduce new methods, regardless viable or not viable, but the supply chain just hasn't been vetted.
- It is obviously <u>easier</u> to recycle the CF manufacturing scraps and out-of-date prepregs as they are uniform, and the resin has not been cured yet.
- It is also much <u>easier</u> to recycling manufacturing CFRP offcuts from post-curing as they are not contaminated with other materials.
- "To recycle or not to recycle" is first hinged on the supply chain of such composite waste, similarly as it is for the recycling of single-use plastic waste.
- We believe that our method that depolymerizes matrix polymer in eco-friendly solvent under atmospheric pressure and moderate temperature (180 - 200 °C) is the most promising chemical recycling method reported so far.