
April 7, 2023

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

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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 CO₂ emissions. --- Composites World, 2/2019
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.
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 $\leq 250 \, ^\circ\text{C}$;

2) Develop thermoplastic composites using the recyclate as reinforcement;

3) Develop vitrimer composites using the recyclate as a feedstock.
Approach

1. Pretreatment

   ![Catalyst system diagram](Diagram showing catalyst system leading to swelling and rupture.)
   

   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

   ![Images of pretreated CFEP waste, mild chemical recycling, recovered CF (rCF), and degraded matrix polymer (DMP).](Images showing pretreated CFEP waste, mild chemical recycling, recovered CF (rCF), and degraded matrix polymer (DMP).)

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

Heat Flow vs. Temperature

Aerospace CFRP

- No treatment
- 300°C 30min

$T_g$: 199 °C

$T_g$: 140 °C
Progress and Outcomes

Task 3. Decomposition of CFEP

- Achieved degradation of CFEP at $\leq 250 \, ^\circ\text{C}$ using $\leq 20 \, \text{wt}\%$ of zinc salt (Milestone 3.1 ✓).
- Molecular weight of DMP is $\leq 5000 \, \text{Da}$ (Milestone 3.2 ✓).

(*Extraction with DMSO is not required for reuse of rCF and DMP, it is only used to calculate the degradation degree.*)
**Task 3. Effect of Acid Pretreatment**

- **No pretreatment**
- **90 °C, 5 h acetic acid**
  - Swelling degree: 79.3%
- **110 °C, 5 h acetic acid**
  - Swelling degree: 112.7%
- **20% Zn(OAc)₂ aq. Solution 220 °C, 6 h**
  - Extract with DMSO*
  - Degradation degree: 35.4%
  - Degradation degree: 85.8%
  - Degradation degree: 95%

(*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.

\[ \text{Zinc acetate} \]

\[ \text{After 1}^{\text{st}} \text{ use} \]

\[ \text{After 4}^{\text{th}} \text{ use} \]

\[ \text{13C NMR spectra of the recycled catalyst.} \]

Volume percent of the recovered catalyst solution after each reuse

Catalyst content in the recycled solution and the associated degradation degree.
Task 3. One-Step: Combining pretreatment and degradation (beyond SOPO ✔).

- **CFEP sample**: DETA cured DER epoxy ($T_g \sim 120 \, ^\circ\mathrm{C}$) 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.
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

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 ✓).
Task 5. Preparation of vitrimers and vitrimers composites

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile strength (MPa)</th>
<th>Tensile modulus (GPa)</th>
<th>Fiber content (wt%)</th>
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<tbody>
<tr>
<td>DER/NMA/vCF</td>
<td>415.7 ± 36.4</td>
<td>25.5 ± 1.3</td>
<td>63.5</td>
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<tr>
<td>DER/NMA/20DMP-EP/rCF</td>
<td>373.1 ± 44.8</td>
<td>21.0 ± 1.5</td>
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</table>

(a) DER/NMA/20DMP-EP/rCF

(b) DER/NMA/vCF

200 °C, 5 h Pure water

Decomposed resin + rCF mat = rCF
Progress and Outcomes

Task 6. Aspen Process Diagram
Task 6. Techno-economic analysis (Milestone 6 ✔).
**Beyond-SOPO:** Degradation of CFEP wastes at atmospheric pressure

- 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!
Beyond-SOPO: Flow chart of the new recycling process

- Waste Aerospace CFRP (solid) 100 g
- 2 wt% Catalyst Solution (liquid) 500 mL
- 190 °C, Ambient Pressure, 3 hr
- Wash with Water & Separation
- Drying
- Recovered Fibers (Product 1)
- Degraded Polymers (Product 2)

Steps:
1. Replenish lost catalyst solution
2. Catalyst Solution
3. Water
4. Distillation
5. Drying
Summary

- Degradation of automobile/wind turbine CFEP at temperature ≤ 220 °C within 6 h using zinc salt/H₂O solution; mission accomplished ✓

- Degradation of aerospace CFEP at temperature ≤ 250 °C within 6 h using zinc salt/H₂O 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

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<th>FY20 Costed</th>
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<td><strong>DOE Funding</strong></td>
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<td>(10/1/19 – 12/31/22)</td>
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### 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 prototype development

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

### 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
  - 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**
  - 3 provisional patents 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
Where do old boats go to die?

- 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 somewhere offshore.

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.

• 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 easier 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 easier 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.