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

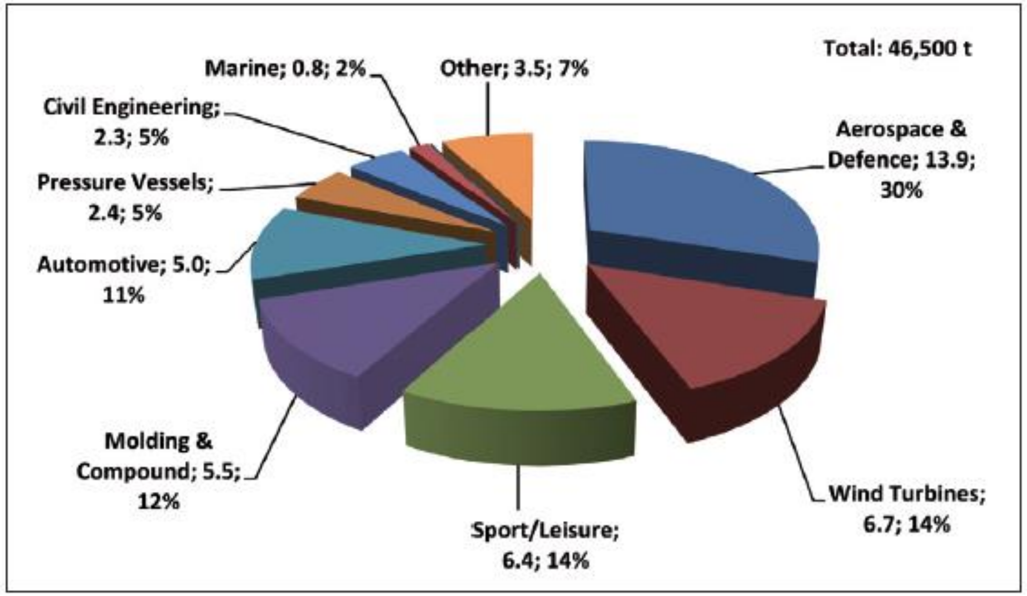
March 8, 2021

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

Jinwen Zhang
Washington State University

Project Overview - Importance

2013 Global carbon fiber (CF) demand by application in thousand tons (Reinforced Plastics, 9/2014)



92.9K tons in 2015, expected to reach 269.5k tons ($27.98B) by 2024, growing at a CAGR of 12.5% from 2016 to 2024 (researchandmarkets.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*

Recycle
Reuse

The fate of CFRP products at the end of life

Landfill

Project Overview - CFRP recycling methods in literature

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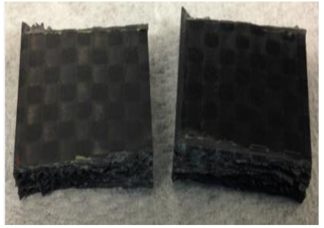
- **Mechanical recycling: shredded or ground to particles**
  - Low value (virgin CF $33 – 66/kg vs. ground CFRF $5/kg)
- **Thermal degradation (Pyrolysis, Fluidized-bed process, etc.)**
  - Energy intensive
  - secondary waste from the degraded polymers
  - Strength reduction: ≥ 20% for CF, ≥ 50% for 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 methods in the literature generally require severe conditions, results in secondary waste and/or lack effective utilization of the decomposed matrix polymers; while mechanical recycling gives low value fillers and energy consuming as well.

Project Overview - Proposed method

Mild Chemical Degration in aqueous medium



CFRP

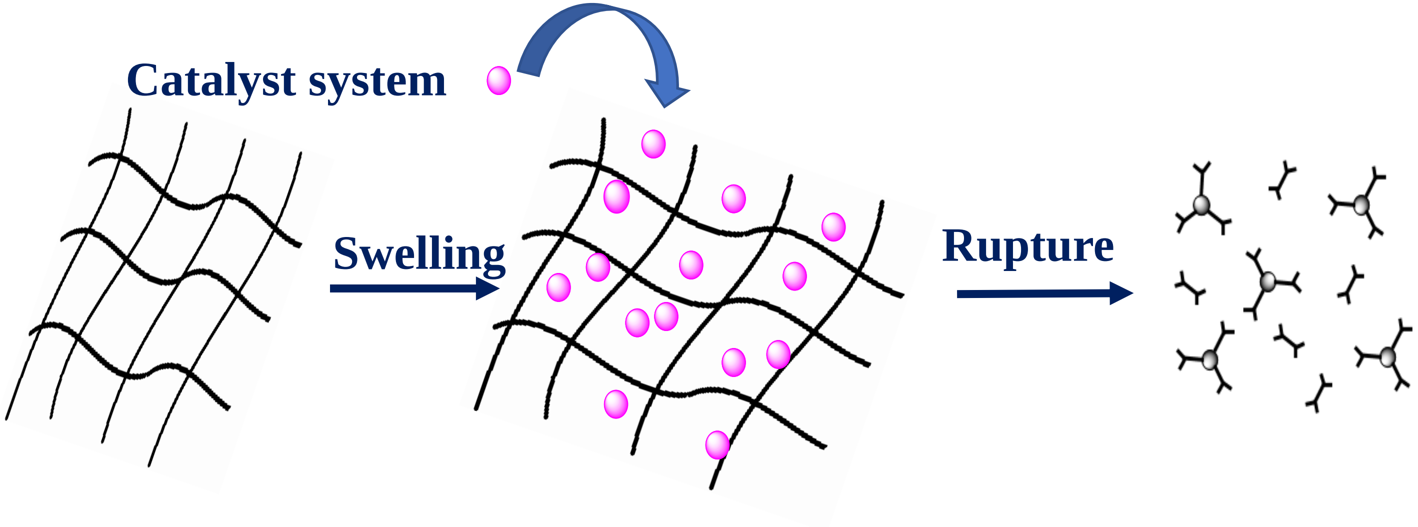
Pressure or atmosphere reactor
In aqueous medium,
180-250 °C; < 5 MPa

Conditions of 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

Illustration of mild chemical recycling process

Project Overview - Objectives

Overall 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

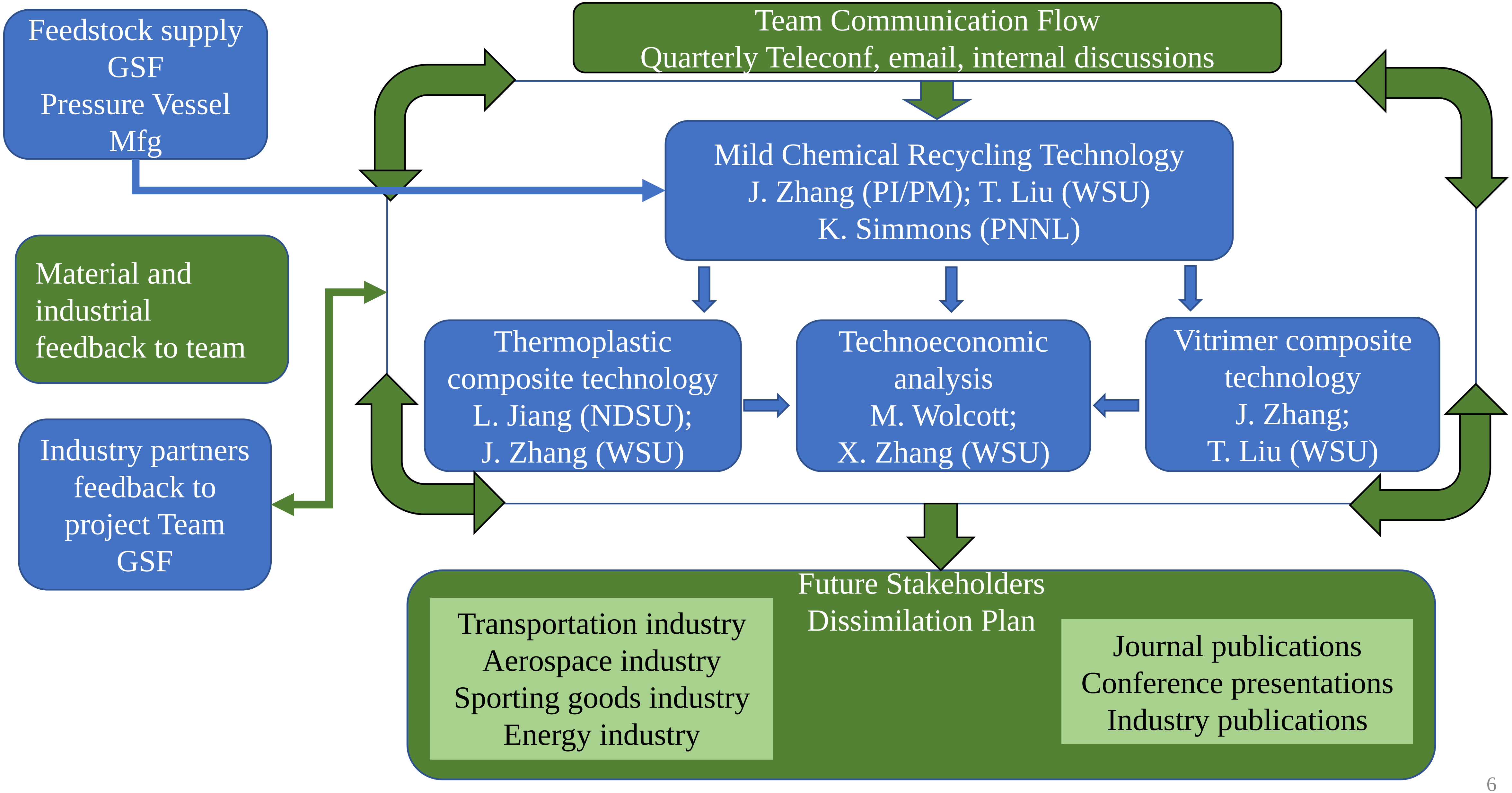
1) Develop pretreatment methods that pre-swell the CFEP waste or decrease its glass transition temperature so that catalyst solution can efficiently penetrate the substrate during the subsequent chemical degradation;

2) Chemically degrade the pretreated CFEP under the catalysis of organic zinc salt in aqueous medium and at temperature ≤ 250 °C;

4) Develop new thermoplastic composites using the recyclate as reinforcement;

5) Develop vitrimer composites using the recyclate as a major feedstock.

Management



Feedstock supply
GSF
Pressure Vessel
Mfg
Team Communication Flow
Quarterly Teleconf, email, internal discussions
Mild Chemical Recycling Technology
J. Zhang (PI/PM); T. Liu (WSU)
K. Simmons (PNNL)
Material and industrial feedback to team
Industry partners feedback to project Team
GSF
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
Dissimilation Plan
Transportation industry
Aerospace industry
Sporting goods industry
Energy industry
Journal publications
Conference presentations
Industry publications

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.

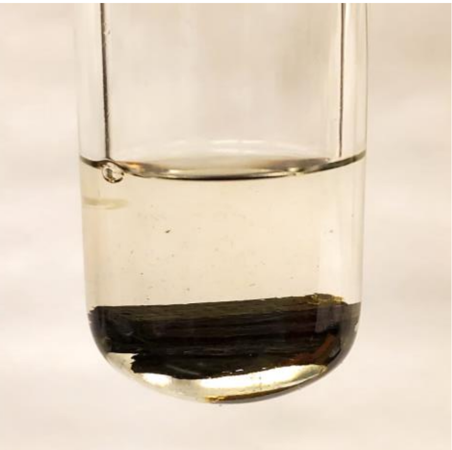
Approach

Development of Pretreatment

- Pre-swell automobile CFEP at elevated temperature and ambient pressure in acetic acid solution.
- Pre-swell aerospace CFEP at elevated temperature and pressure in acetic acid solution.
- Delaminate aerospace CFEP and decrease its glass transition temperature by thermal energy.

Objectives:

- Achieve the delamination of automobile CFEP at elevated temperature under atmospheric pressure.
- Achieve the delamination of aerospace CFEP at elevated temperature in batch pressure reactor.
- Decrease the T_g of aerospace CFEP for at least 15 °C using thermal energy.



Acid pretreatment at ambient pressure

Acid pretreatment at high pressure

Thermal treatment under inert atmosphere

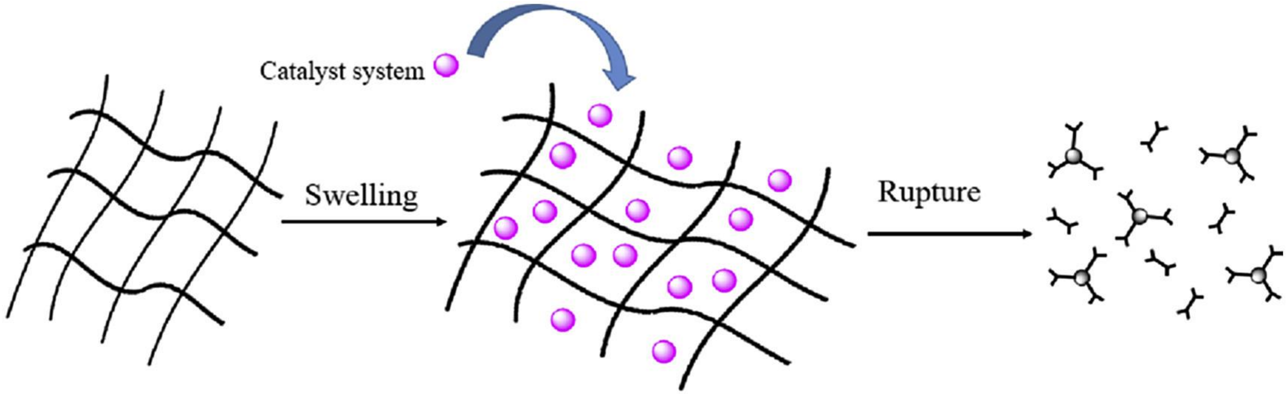
Approach

Decomposition

- Decompose swollen automobile CFEP with zinc acetate aqueous solution in pressure reactor.
- Decompose swollen or thermally pretreated aerospace CFEP with zinc acetate aqueous solution in pressure reactor.
- Recover decomposed polymer and analyze the decomposition process.

Objectives:

- Achieve the degradation of automobile CFEP at temperature ≤ 220 °C using ≤ 10 wt% of zinc salt.
- Achieve the degradation of aerospace CFEP at temperature ≤ 250 °C using ≤ 20 wt% of zinc salt.
- Reuse the recovered catalyst solution for at least 3 times.

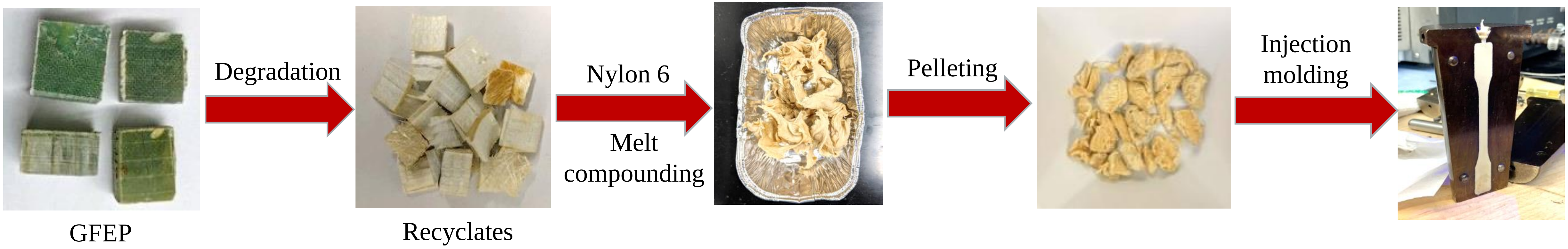


Zhang, et al. *Polymer Degradation and Stability* 139 (2017): 20-27.

Progress and Outcomes

Project Verification – in period 1, the preliminary results listed in the proposal were reexamined and reconfirmed including:

- Degradation of wind turbine GFEP in zinc salt catalyst aqueous solution (**Milestone 1.1 completed**).
- Pre-swelling of wind turbine GFEP in acetic acid (**Milestone 1.2 completed**).
- Preparation of Nylon 6 composites with the recyclates (**Milestone 1.3 completed**).
- Preparation of new epoxy using decomposed polymer as reactive ingredient (**Milestone 1.4 completed**).



Conclusion:

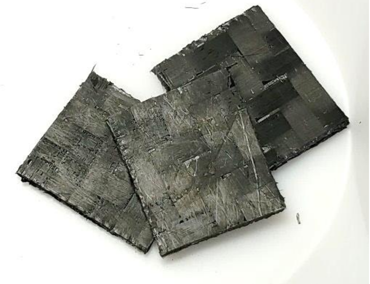
Chemical recycling of CFEP and GFEP and the reuse of recyclates for new materials can be achieved, and Target 1 of the project is completed.

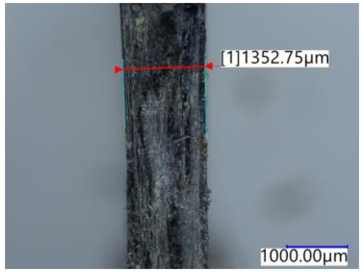
Progress and Outcomes

Acid pretreatment (Milestone 2.1 completed)

- Investigated the effects of acetic acid concentration, treatment temperature and time on the swelling of CFEP.
- Examined the delamination of CFEP with peel tests.
- Achieved the delamination of automobile CFEP at temperature ≤ 120 °C within 3 hours under atmospheric pressure.
- Achieved the delamination of aerospace CFEP at temperature ≤ 200 °C within 3 hours in a pressure reactor

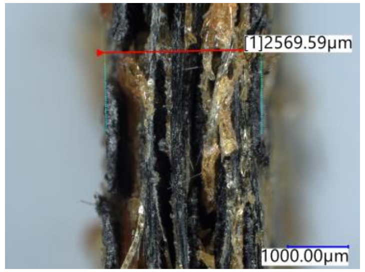
Automobile CFEP



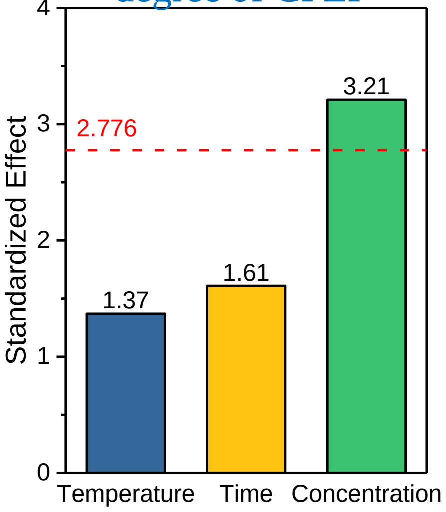


Zinc salt

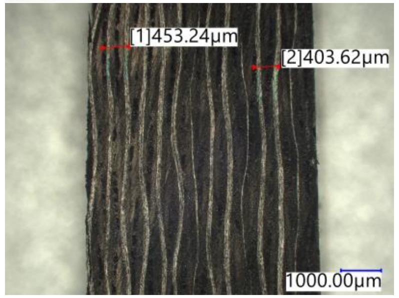
Elevated temp & ambient pressure



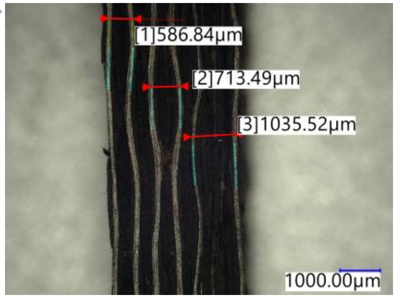
Effects of pretreatment parameters on swelling degree of CFEP



Aerospace CFEP



Temp & Pressure



Progress and Outcomes

Thermal pretreatment (Milestone 2.2 completed)

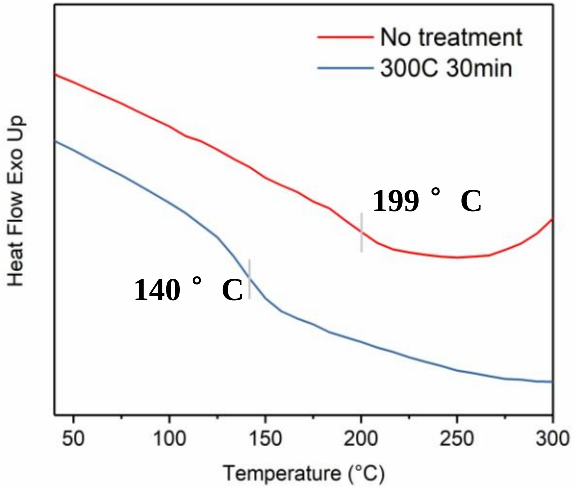
- Investigated the effects of thermal pretreatment time and temperature on the weight loss and T_g change of aerospace CFEP.
- Decreased the T_g of aerospace CFEP from 199 °C to 140 °C by thermal treatment at 300 °C for 30 min

Aerospace CFEP thickness: 5.80 mm

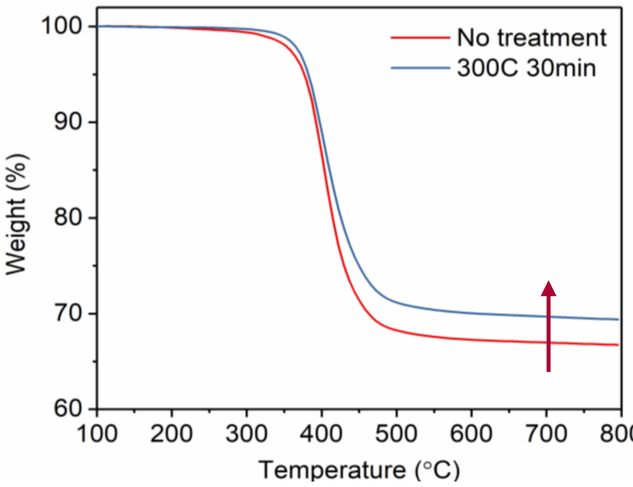
Thermal treatment in tube furnace

300 °C 60 min, thickness: 6.00 mm

330 °C 30 min, delaminated



T_g values determined by DSC



TGA curves of aerospace CFEP before and after thermal pretreatment

Progress and Outcomes

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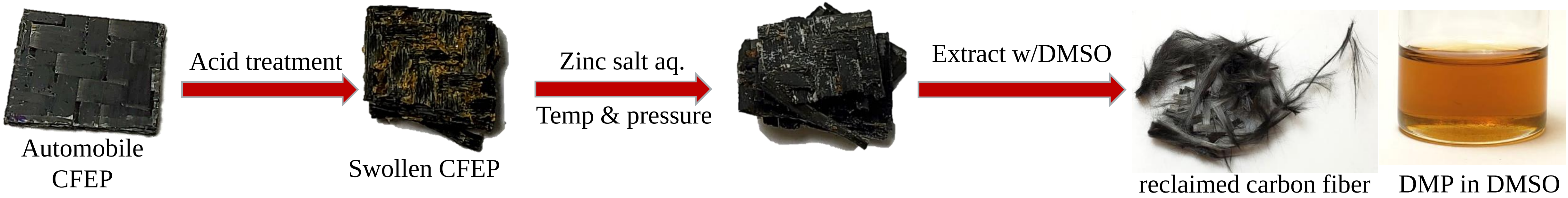
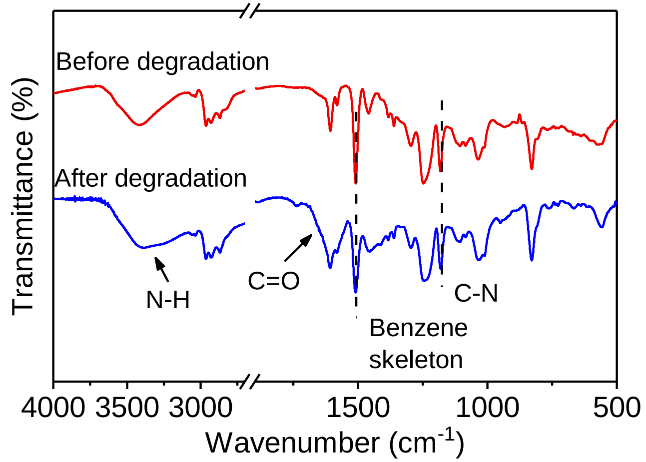
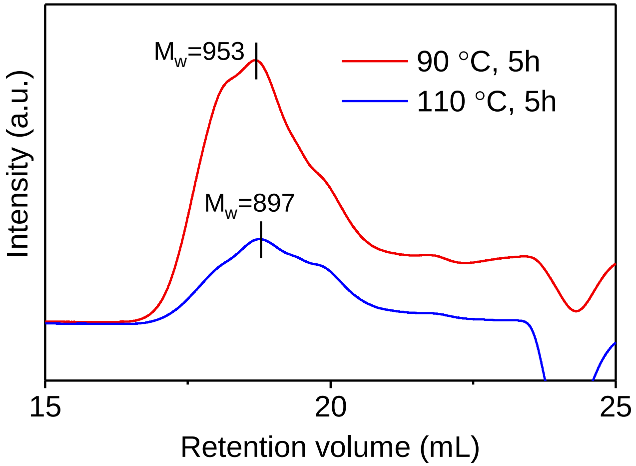
Decomposition of automobile CFEP

- Achieved degradation of automobile CFEP at temperature ≤ 220 °C using ≤ 10 wt% of zinc salt (**Milestone 3.1 partially completed**).
- Characterized decomposed matrix polymer (DMP) with FTIR and GPC. DMP possesses multiple functional chemical groups and the molecular weight of DMP is ≤ 5000 Da (**Milestone 3.2 partially completed).**

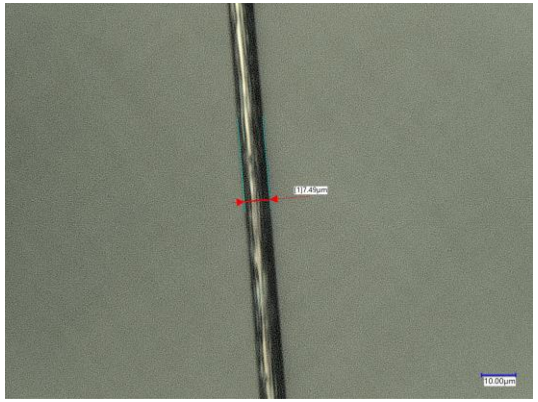




FTIR spectra of epoxy matrix before and after decomposition



GPC curves of DMP from different acid pretreatment



Digital photo of reclaimed carbon fiber

Progress and Outcomes

Decomposition of aerospace CFEP

- Achieved degradation of aerospace CFEP at temperature ≤ 250 °C using ≤ 20 wt% of zinc salt (**Milestone 3.1 partially completed**).
- Characterized decomposed matrix polymer (DMP) with FTIR. DMP possesses multiple functional chemical groups (**Milestone 3.2 partially completed**).

Aerospace CFEP

Thermal pretreatment

Acid pretreatment

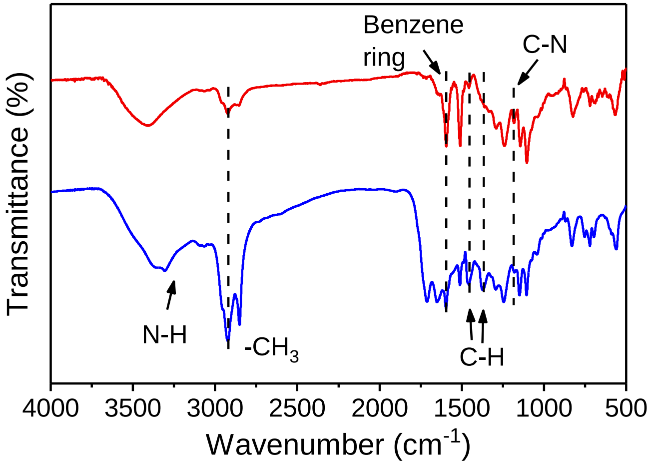
Zinc salt aq.

Temp & pressure

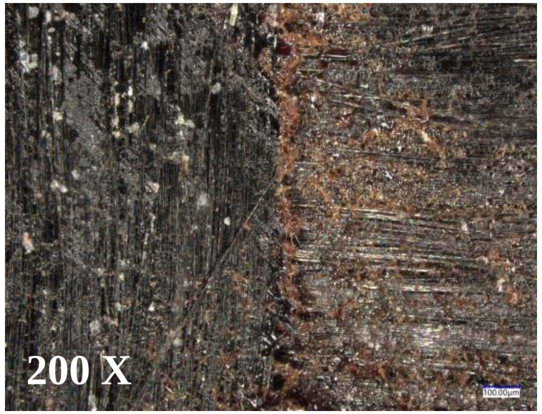
Extract w/DMSO

reclaimed carbon fiber

DMP in DMSO

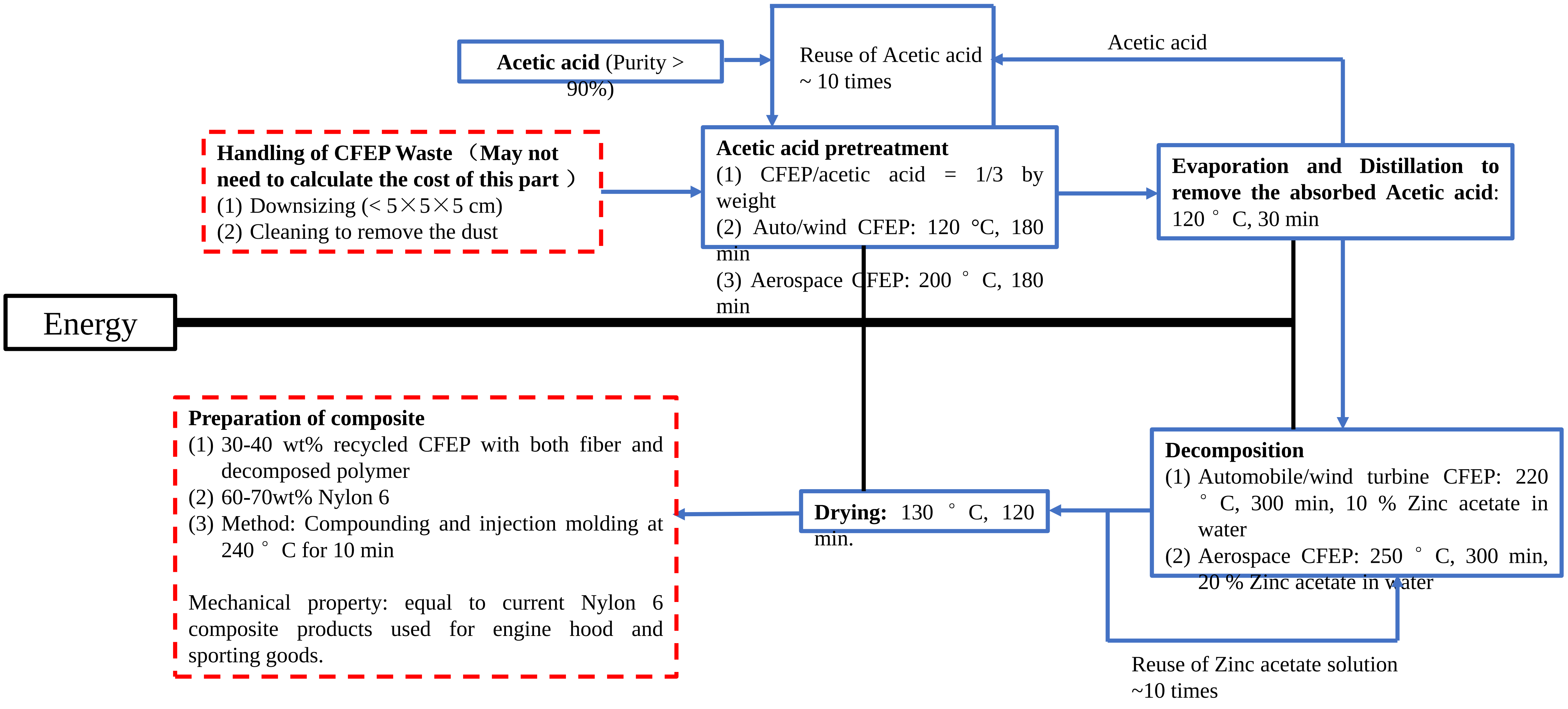


FTIR spectra of epoxy matrix before and after decomposition

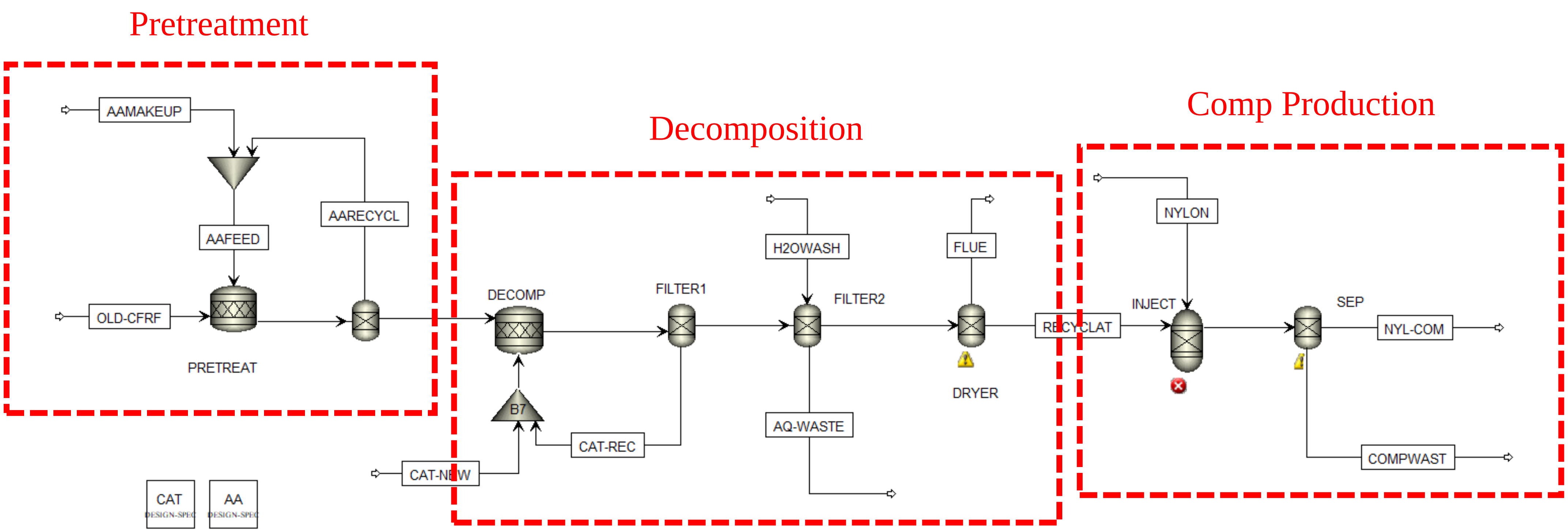


Digital photo of recyclates

Process Diagram



Aspen Process Diagram



Publications and pending patents

- 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 (2020)* , DOI: 10.1002/marc.202000458
- Jinwen Zhang, Tuan Liu, Junna Xin. Methods for chemical degradation of epoxies using organic salts as catalysts, US Pat. No. 10,696,815 B2

COMMUNICATION

Macromolecular Rapid Communications
www.mrc-journal.de

Carbon Fiber Reinforced Epoxy Vitrimer: Robust Mechanical Performance and Facile Hydrothermal Decomposition in Pure Water

*Tuan Liu, Cheng Hao, Lin Shao, Wenbin Kuang, Lelia Cosimbescu, Kevin L. Simmons, and Jinwen Zhang**

US010696815B2

(12) **United States Patent**
Zhang et al.

(10) **Patent No.:** **US 10,696,815 B2**
(45) **Date of Patent:** **Jun. 30, 2020**

(54) **METHODS FOR CHEMICAL DEGRADATION OF EPOXIES USING ORGANIC SALTS AS CATALYSTS**

(71) Applicant: **WASHINGTON STATE UNIVERSITY**, Pullman, WA (US)

(72) Inventors: **Jinwen Zhang**, Pullman, WA (US); **Tuan Liu**, Pullman, WA (US); **Junna Xin**, Pullman, WA (US)

(73) Assignee: **WASHINGTON STATE UNIVERSITY**, Pullman, WA (US)

(52) **U.S. Cl.**
CPC ***C08J 11/26*** (2013.01); ***C08J 11/16*** (2013.01); ***C08J 11/28*** (2013.01); *C08J 2363/00* (2013.01)

(58) **Field of Classification Search**
USPC 523/220
See application file for complete search history.

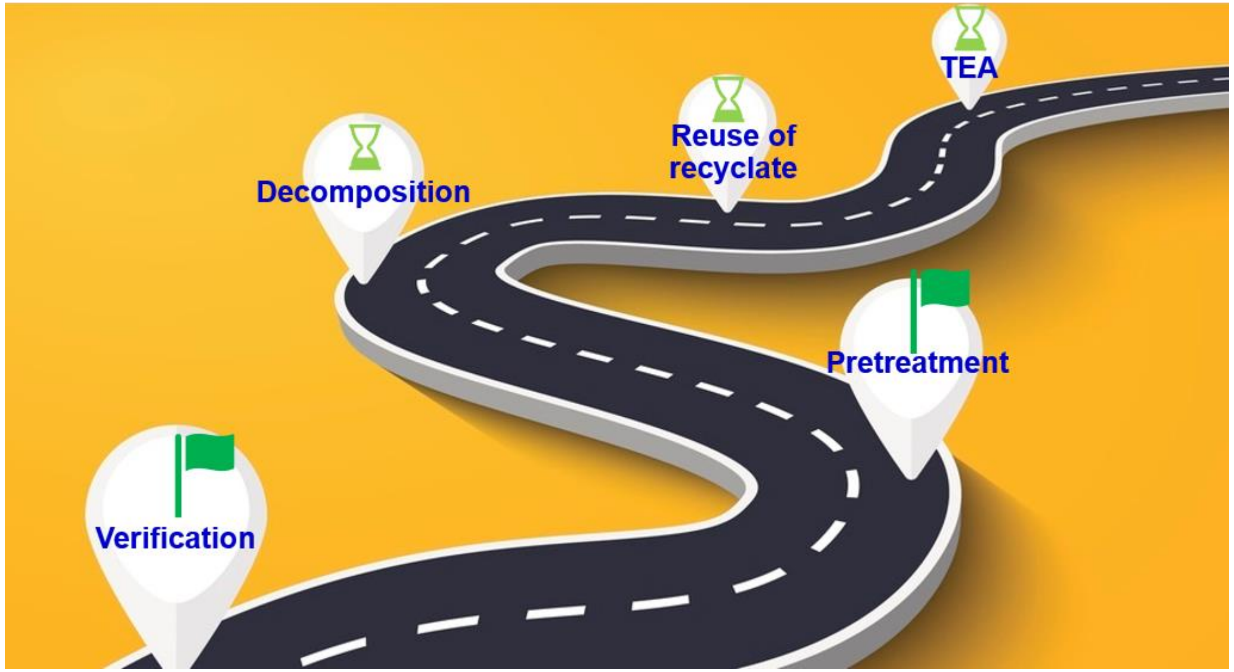
(56) **References Cited**

U.S. PATENT DOCUMENTS

2003/0098649 A1 * 5/2003 Murai C08G 59/1405 313/512

Summary

- Pretreatment of CFEP is an effective and novel approach to facilitate degradation of matric polymer of CFEP under mild condition;
- Pretreatment of CFEP in acetic acid s(solution) or under high temperature leads to initial delamination;
- Depolymerization of the matrix polymer is achieved in relatively low concentration of organic zinc salt solution.



Quad Chart Overview (Competitive Project)

Timeline

- **Project start date: 10/01/2019**
- **Project end date: 12/31/2022**

	FY20 Costed	Total Award
DOE Funding	(10/01/19 – 9/30/20) *$ 99,803.98 (WSU)* *$26,663.96 (NDSU)* *$63,938 (PNNL)*	**(negotiated total federal share)** ***$ 1,249,804***
Cost Share	**$ 33,912.72**	**$ 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