Oak Ridge National Laboratory

Adopting Heavy-Tow Carbon Fiber for Repairable, Stamp-Formed Composites

Project ID: MAT205

Amit Naskar
Oak Ridge National Laboratory

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2021 DOE Vehicle Technologies Office Annual Merit Review

Overview

Timeline

- Start date: October 2020
- End date: September 2023
- Percent Complete: 16%

Budget

- Total project funding: $1500k/3years
- Funding for FY21: $500k
- Funding for FY22: $500k
- Funding for FY23: $500k

Partners

- Project lead: ORNL
- University of Tennessee- Bredesen Center
  - Graduate research program

Barriers*

- The ability to bond carbon fiber (CF) to certain resins is inadequate to take full advantage of inherent properties of the fiber due to issues in interfacial bonding
- Few fiber/resin systems are very expensive and does not provide rapid cycle time to be compatible with high-volume demands and performance needs
- Models are needed to understand the relationship between material physical properties, mechanical properties, processing, and ultimately to predict behavior
  - Cost-effective analysis tools and databases to support them are not available
  - There is a lack of validated databases on properties of materials to populate models

*Light-Duty Vehicles Technical Requirements and Gaps for Lightweight and Propulsion Materials Workshop Report, February 2013.

Relevance

- High-throughput processing methods for thermally recyclable/repairable CF composites of thermoplastic matrices will enable cost-competitive lightweight materials for automotive fuel efficiency while exhibiting superior mechanical performance and crashworthiness
- Achieving strong interfacial interaction between fiber and commodity polymer has been a challenging task; makes it difficult to take full advantage of fiber properties
- Existing surface treatments or coupling chemistries are not optimized for most thermoplastic resin systems that are used to incorporate CFs

Objectives

- Develop and commercialize high-throughput manufacturing technologies with new interfacial engineering methods to efficiently reinforce thermoplastic matrices by CFs. Translate the developed method towards composites with large-tow CFs
- Deliver repairable low-cost thermoplastic composites with multi-layered structure with outstanding mechanical performance (0.8-1.4 GPa tensile strength, 50-100 GPa Young's modulus, and >5% failure strain)
- Develop processing technologies that enable a 30-50% cost reduction in composite parts

Milestones:

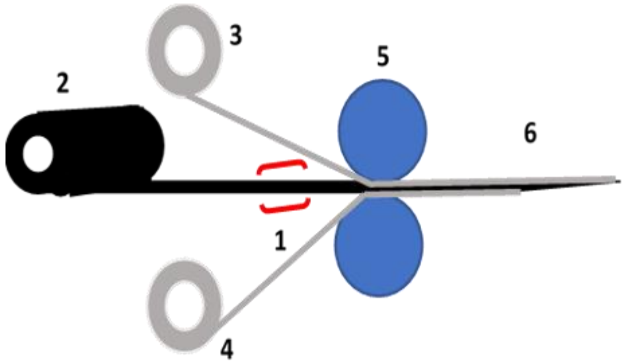
Milestone/Deliverable Name/Description	End Date	Type	Criteria	Status
Develop composite performance data for CF/Epoxy commercial materials and compare with CF/PP performance	12/31/2020	Quarterly (Regular)	Base-line materials preparation and mechanical property data collection	Complete
Exhibit PP matrix discontinuous CFRPs with 100 MPa tensile strength	3/30/2021	Quarterly (Regular)	Mechanical testing of the composite specimens will be conducted on molded specimens	Complete
Establish intermediates' morphology at 100-500 nm and 5-100 mm length scales	6/30/2021	Quarterly (Regular)	Microscopy and SAXS data will deliver structures at multiple length scales	On-schedule
Demonstrate of CFRP stamping process for multi-layered structures	9/30/2021	Annual (Stretch)	Methodology of sample preparation will be documented	On-schedule
Demonstrate 10% immobilized PP on the CF by analytical methods	12/31/2021	Quarterly (Stretch)	Analytical methods confirm that at least 10% matrix is bound to the fibers.	On-schedule
Quantify monomeric, segmental and chain dynamics, at 100-200 nanosecond timescale, and rheological response in a non-equilibrium state	3/31/2022	Quarterly (Regular)	MD simulation data confirms polymer chain dynamics and rheological data	On-schedule
Quantify activation energies for forming chemisorbed matrices and identify stabilized structures of polymer matrix attached to the CF surface by C-C bond	6/30/2022	Quarterly (Stretch)	Thermal analysis data confirms the relaxation behavior of the bound matrix on the fibers	On-schedule
Demonstrate 500 MPa tensile strength in mesoscopic unidirectional intermediate	9/30/2022	Annual (Stretch)	Mechanical testing of intermediates delivers the expected properties	On-schedule
Exhibit aromatic nylon matrix CFRPs with 1 GPa composites tensile strength	12/31/2022	Quarterly (Regular)	Mechanical testing of intermediates delivers the expected properties	On-schedule

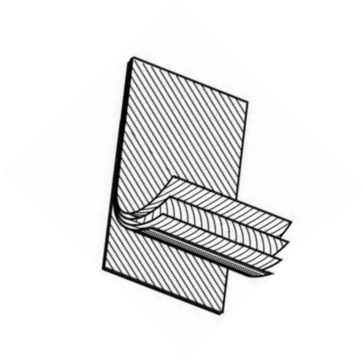
Go/No-Go Decision

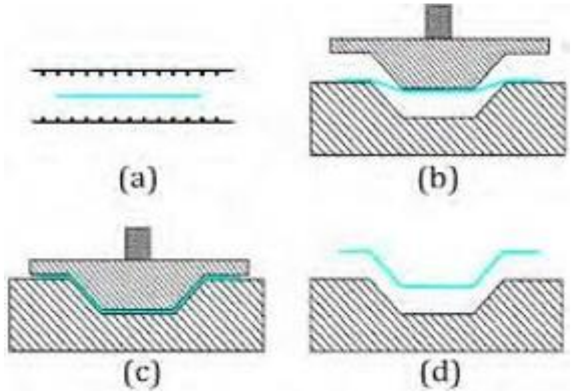
Name	Description	Criteria	Date
Surface functionalization of CF with PP matrix is demonstrated	Demonstrate 10% immobilized PP on the CF by analytical method	Thermal analysis data reveals that 10% of the matrix is immobilized on the CF surface.	12/31/2021

Technical Approach

The proposed research focuses on interface-engineering and high-throughput manufacturing methods for heavy-tow carbon fibers—having >100k filaments in a single bundle—and tailoring its bonding and interactions with thermoplastic matrices to develop new moldable layered structures







(A) **(B)** **(C)** **(D)**

(A) Heavy-tow CF spool; (B) Schematic showing formation of mesoscopic intermediate: legends (1) thermo-chemical surface activation device, (2) heavy-tow of CF, (3-4) spool of thermoplastic film, (5) heated calender roll, and (6) fused laminate; (C) Multi-layer laminate; (D) Rapid stamp forming operation: legend (a) heating, (b) forming, (c) consolidation, and (d) demolding of the part prior to trimming

Research Tasks:

Task 1: Develop new interfacial chemistries for carbon fiber-thermoplastic interaction

Task 2: Discover the interplay of interfacial interactions with processability and laminate intermediate's response to load

Task 3: Establish a relationship between fiber-volume fraction, matrix morphology and performance of the molded multi-layered structures

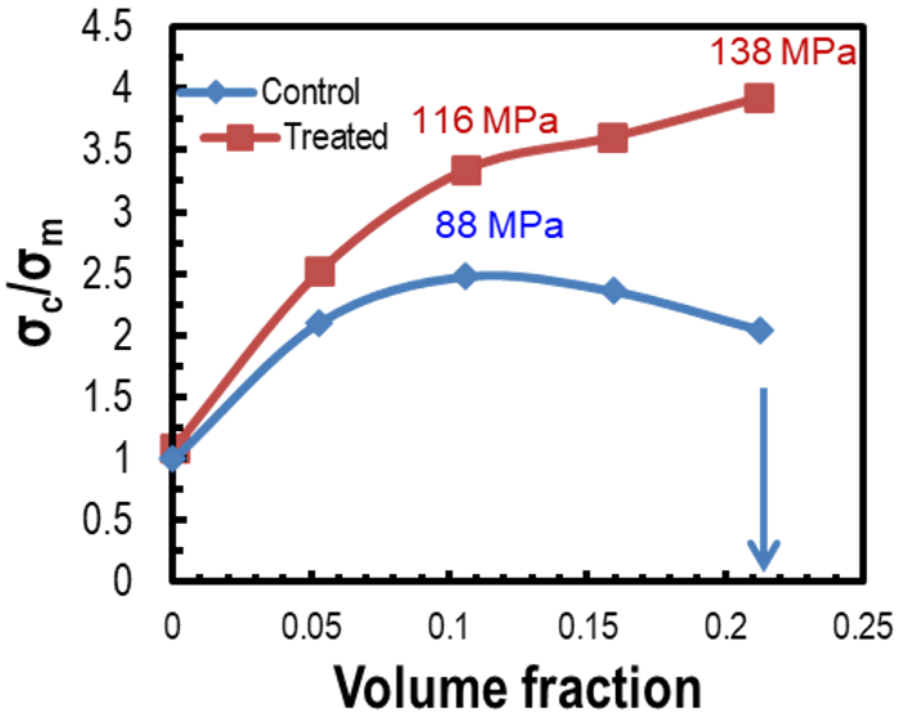
Task 4: Techno-economic analysis of the compositions and process

Technical Accomplishments and Progress

Use of micrometer scale CF offers significant reinforcing effects compared to nanoparticles

Nanocomposites offer improved stiffness in matrix material but not necessarily an improvement in their failure strengths. Therefore, we target achieving rational design and control of the mechanical properties of the polymer matrices by use of commodity carbon fibers.

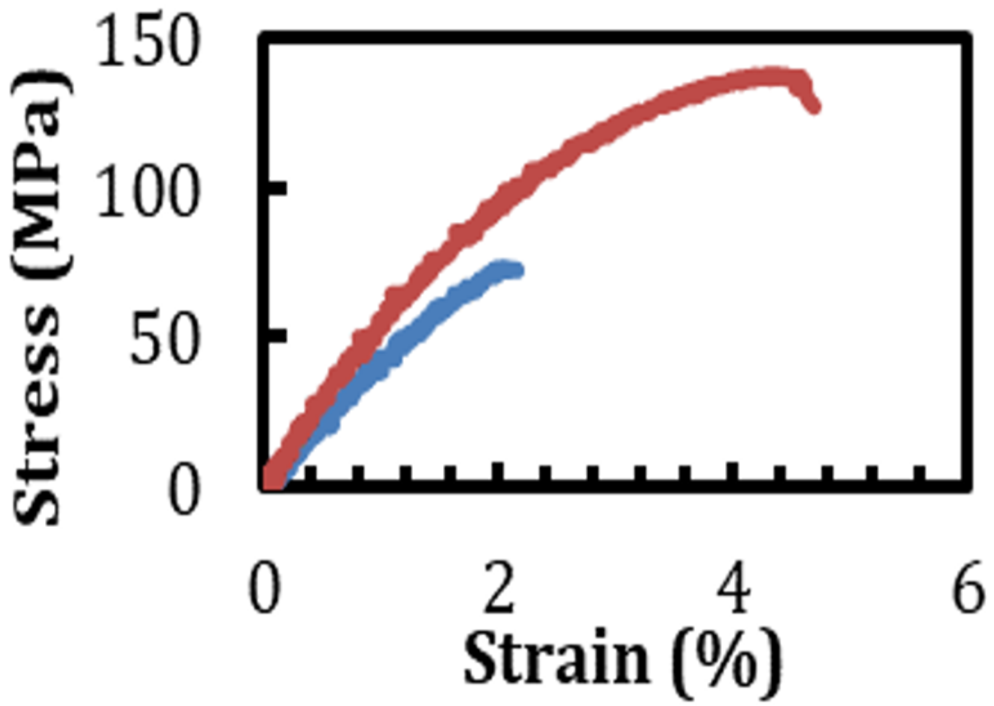
- Very high melt-viscosities of composites hinder rapid manufacturing. Easy-to-flow thermoplastic matrices are of interest for this study.
- How do multi-scale interfacial structures affect the rheological properties? Will this understanding help to design and process composites?



Relative tensile strength of polypropylene (PP) matrix composites with use of untreated CF vs. treated CF

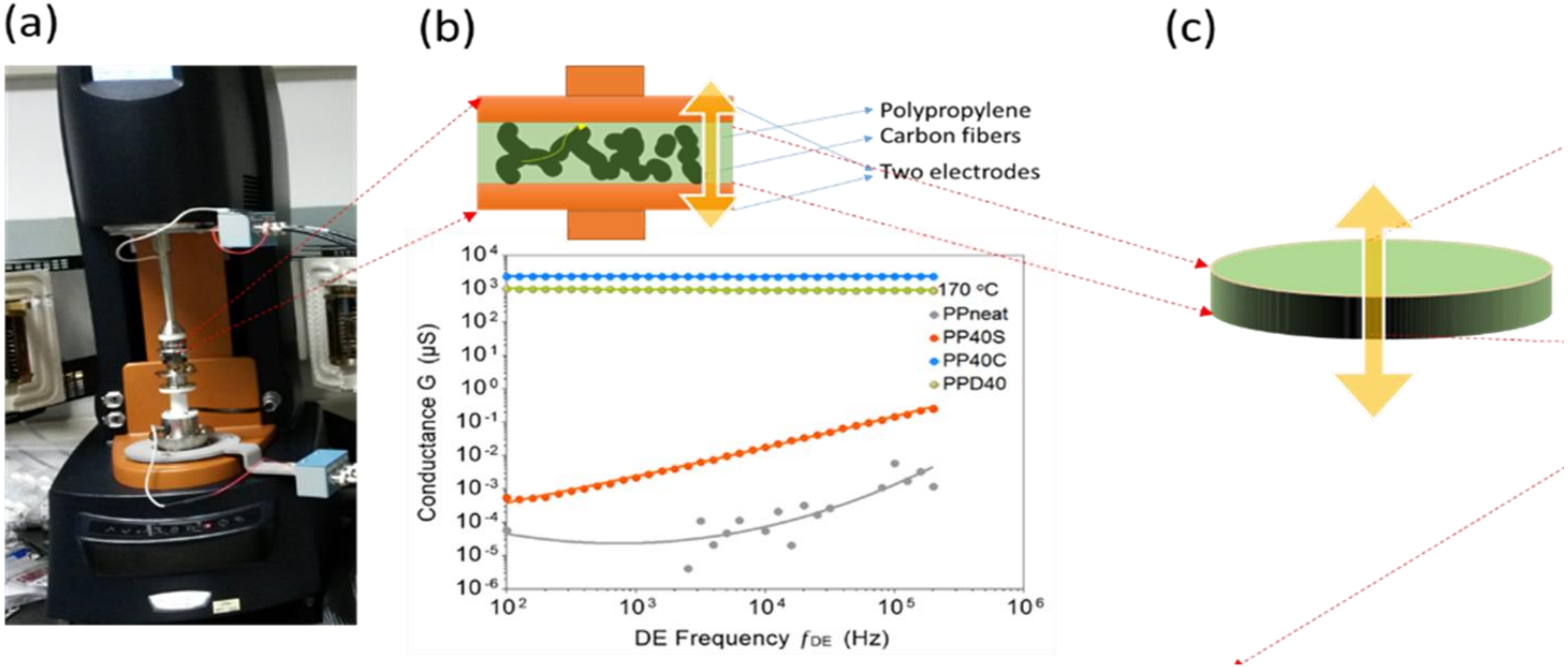
Technical Accomplishments and Progress

- Our goal will be to maximize the interphase volume fraction for efficient load sharing between fiber and matrix
- **Our approach is new and has not been commercially practiced elsewhere**



Tensile properties of composites from unsized heavy tow CF: **surface activated CF-PP** specimens are stronger and tougher than the **control CF-PP** specimens

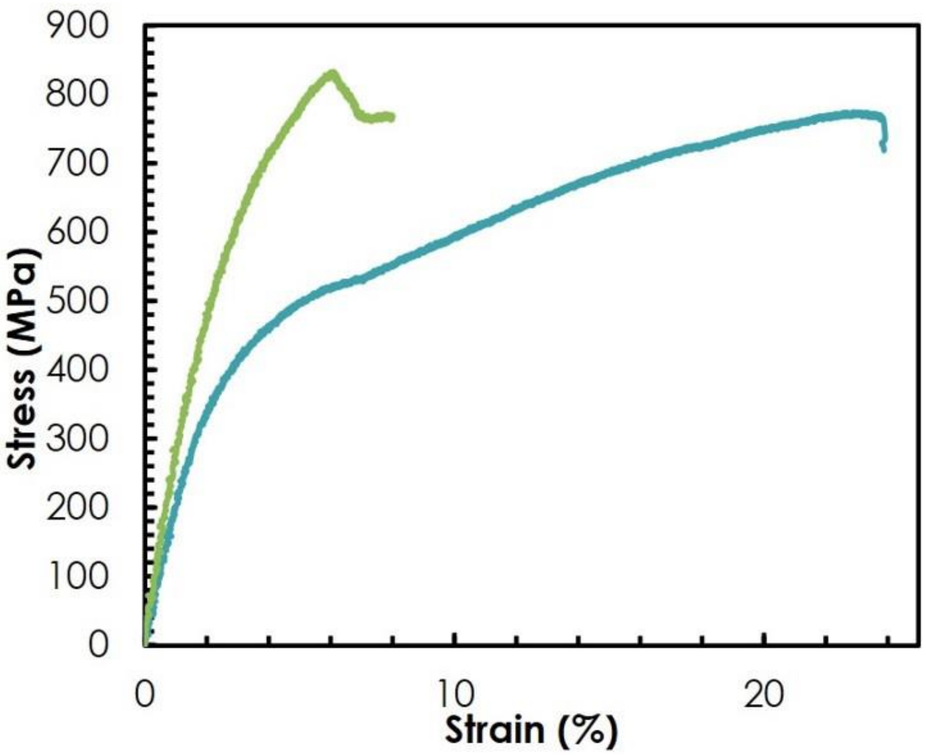
Morphology of the composites could be explained by rheo-dielectric response

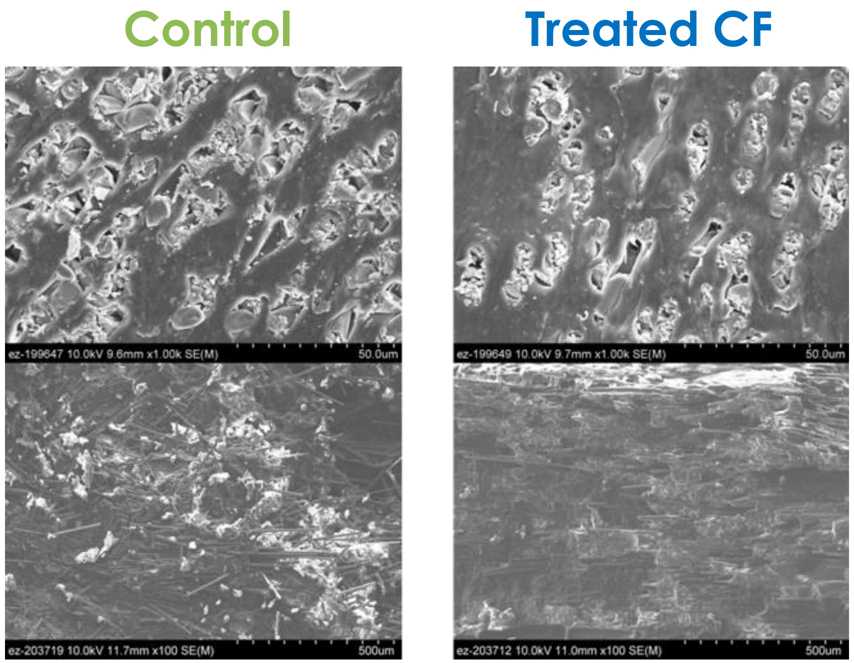


Surface activation and anchoring of PP matrix lower the conductivity of composite through its thickness

Unidirectional PP composite mechanical test results show toughening action by tailored interfacial interaction

C_{fiber} –$C_{polymer}$ interaction enhances ductility (3x) in the composite.



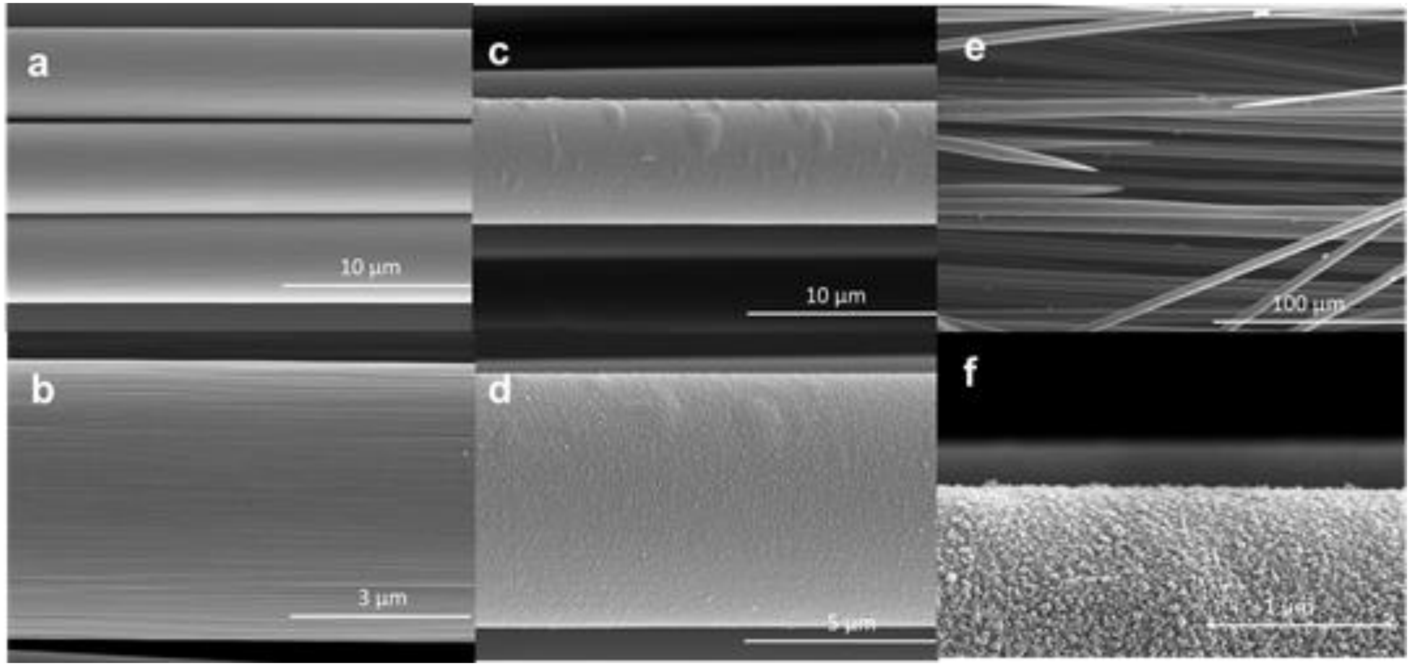


Matrix anchoring on CF offers better wetting of matrix and hence dispersion of fiber in the matrix

Technical Accomplishments and Progress - Continued

Surface activation methods explored

- Photo-processing reduces or eliminates the need for chemicals
- This processing technique can be employed in a continuous process and can be readily tuned to target specific functional group formation on the fiber surface

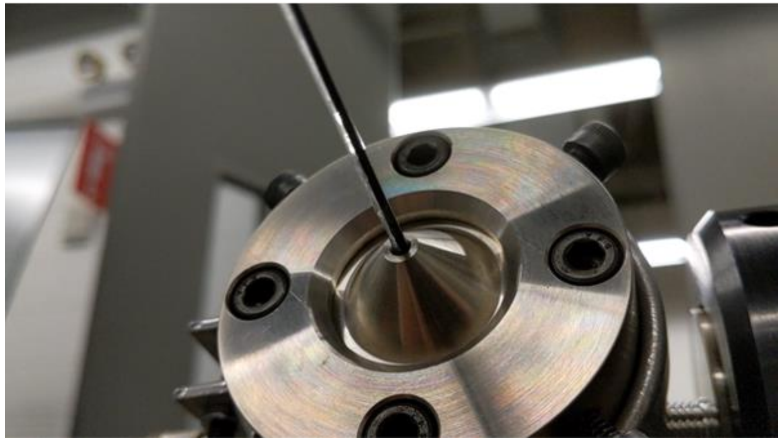


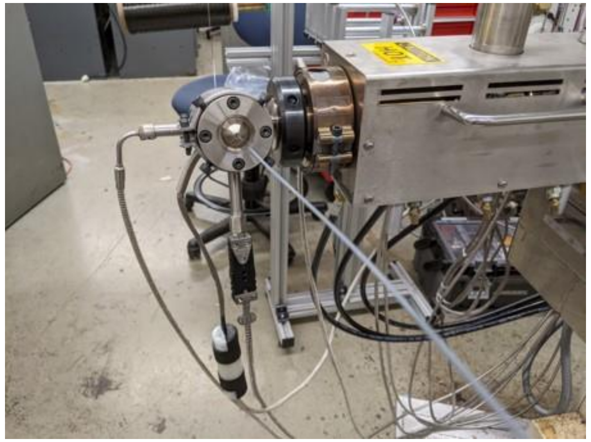
Electron micrograph of pristine (a,b), mildly treated (c,d) and over-treated (e,f) carbon fiber surfaces. These CFs with tailored surfaces will be used for nucleation of semi-crystalline polyolefin matrix for interfacial anchoring of the matrix molecules.

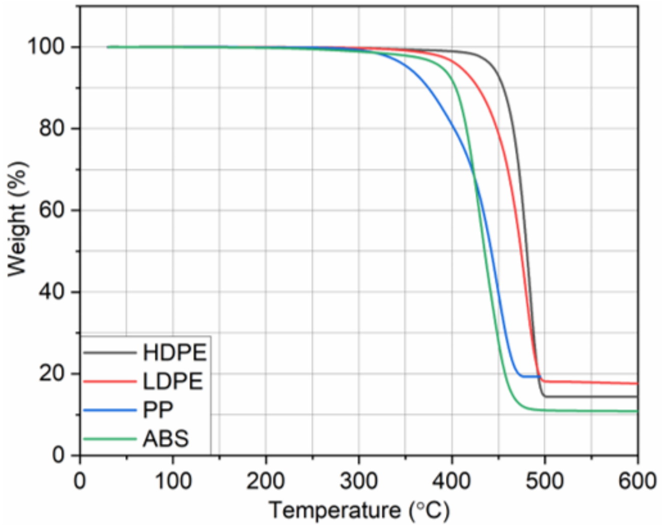
Technical Accomplishments and Progress - Continued

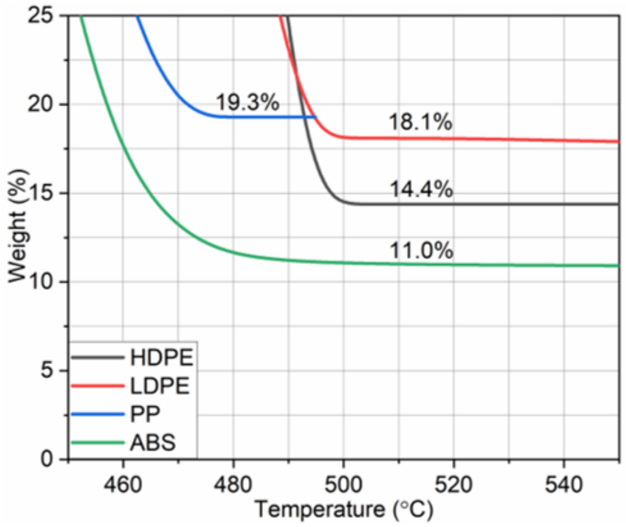
Baseline continuous pristine CF system we have used:

- IM7 CF 12k tow (unsized) with different semi-crystalline and amorphous polymer systems: PP, HDPE, LDPE, ABS, N66
- Baseline composites will be compared with 50 vol% CF Epoxy composites (>1 GPa tensile strength, >100 GPa tensile modulus)









Thermogravimetric Analysis (TGA) of CF composites at different wt.% of CF

Technical Accomplishments and Progress - Continued

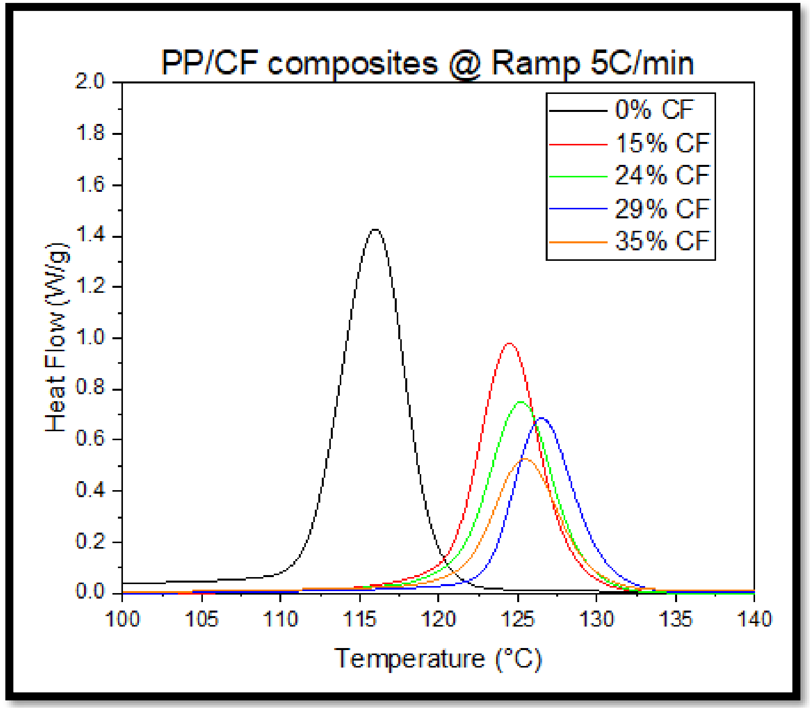
Crystallization behavior with pristine CF

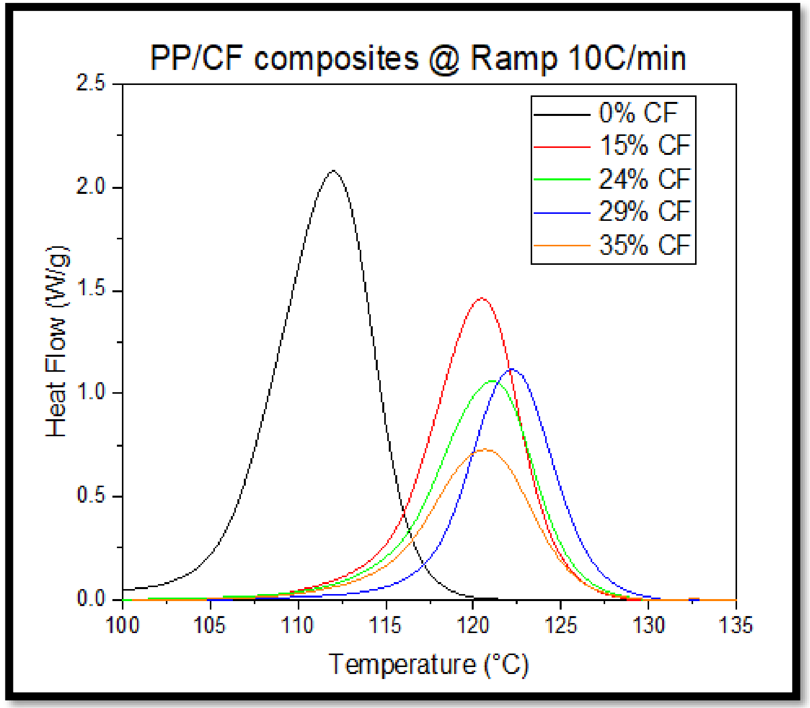
Observations:

- Onset temperature scale with fiber loading- fibers act as micron scale nucleating surfaces
- Crystallization occurs over a wider temperature range

Note: Polymer matrix dewetting at 35% fiber loading

Volume Percent (Density)	Mass Fraction (TGA)
10	15
20	24
30	29
40	35





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Technical Accomplishments and Progress - Continued

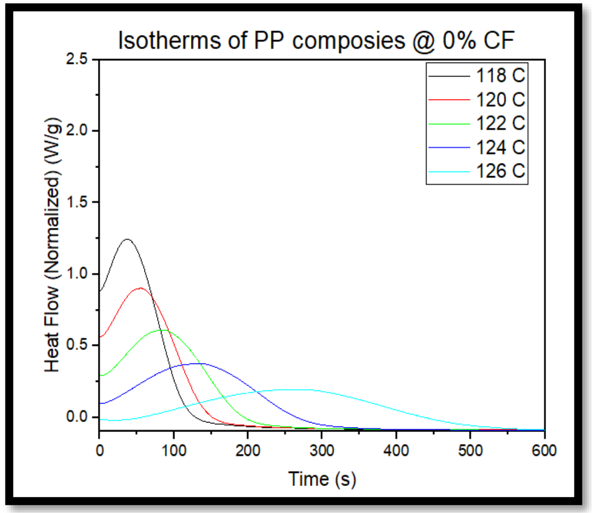
Crystallization behavior with pristine CF

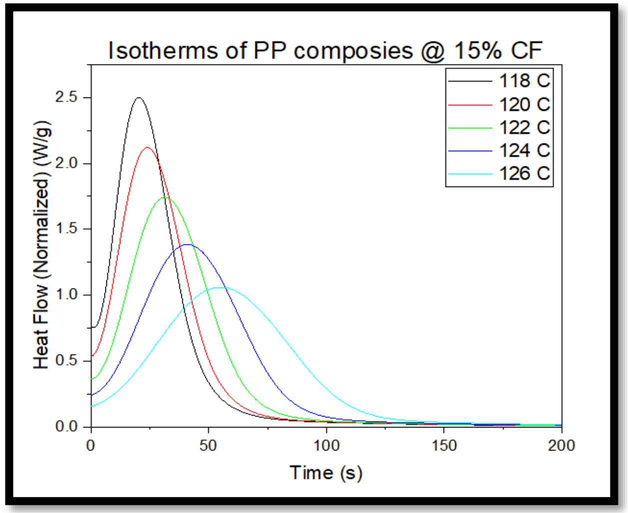
Observations: Onset temperature scale with fiber loading. % crystallinity decreases with increasing fiber loading. At higher fiber loadings, ramp rate is not a factor.

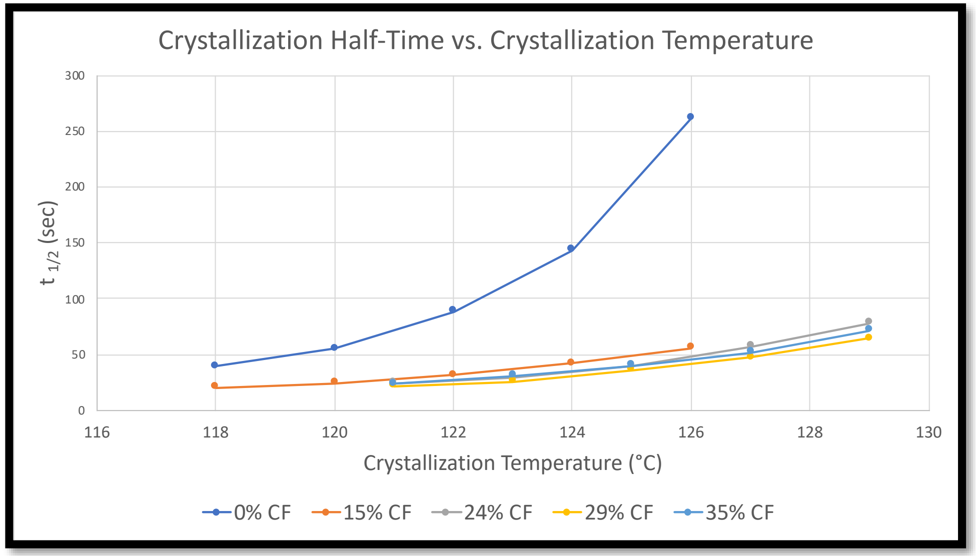
	Ramp @ 1 C/min	Ramp @5 C/min	Ramp @10 C/min
Onset temperature	$T_{Onset, 0\%}$= 131.5 °C $T_{Onset, 15\%}$= 135.6 °C $T_{Onset, 24\%}$= 136.8 °C $T_{Onset, 29\%}$= 138.3 °C $T_{Onset, 35\%}$= 134.1 °C	$T_{Onset, 0\%}$= 119.7 °C $T_{Onset, 15\%}$= 128.2 °C $T_{Onset, 24\%}$= 129.2 °C $T_{Onset, 29\%}$= 130.6 °C $T_{Onset, 35\%}$= 129.7 °C	$T_{Onset, 0\%}$= 116.5 °C $T_{Onset, 15\%}$= 124.8 °C $T_{Onset, 24\%}$= 125.7 °C $T_{Onset, 29\%}$= 126.9 °C $T_{Onset, 35\%}$= 125.9 °C
Enthalpy	$\Delta H_{0\%}$= ~ 181.1 J/g $\Delta H_{15\%}$= ~ 63.3 J/g $\Delta H_{24\%}$ =~ 54.3 J/g $\Delta H_{29\%}$= ~ 43.8 J/g $\Delta H_{35\%}$= ~ 37.0 J/g	$\Delta H_{0\%}$= ~92.8 J/g $\Delta H_{15\%}$= ~ 63.3 J/g $\Delta H_{24\%}$ =~ 52.3 J/g $\Delta H_{29\%}$= ~ 43.6 J/g $\Delta H_{35\%}$= ~ 26.8 J/g	$\Delta H_{0\%}$= ~116.5 J/g $\Delta H_{15\%}$= ~ 61.6 J/g $\Delta H_{24\%}$ =~ 53.0 J/g $\Delta H_{29\%}$= ~ 43.9 J/g $\Delta H_{35\%}$= ~ 35.5 J/g
% Crystallinity, ΔH_{∞}= 207 J/g	$\%C_{0\%}$= ~ 81% $\%C_{15\%}$= ~ 31% $\%C_{24\%}$= ~ 26% $\%C_{29\%}$= ~ 21% $\%C_{35\%}$ = ~ 18%	$\%C_{0\%}$= ~ 45% $\%C_{15\%}$= ~ 31% $\%C_{24\%}$= ~ 25% $\%C_{29\%}$= ~ 21% $\%C_{35\%}$ = ~ 18%	$\%C_{0\%}$= ~ 56% $\%C_{15\%}$=~ 30% $\%C_{24\%}$= ~ 26% $\%C_{29\%}$= ~ 21% $\%C_{35\%}$ = ~ 17%

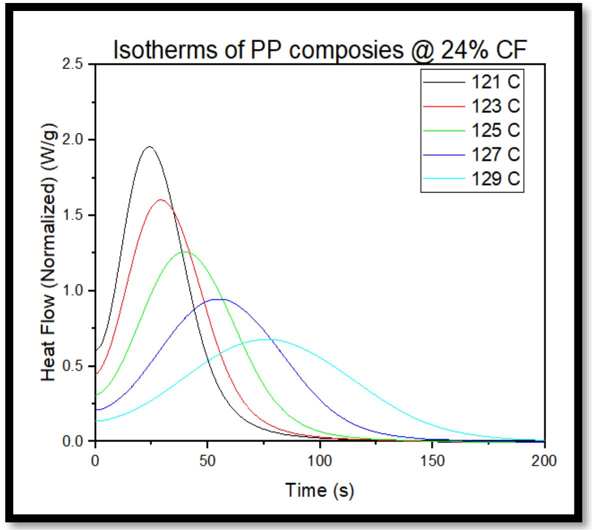
Technical Accomplishments and Progress - Continued

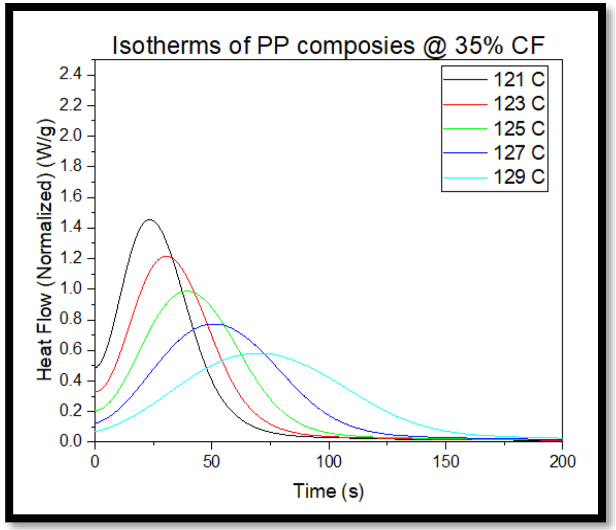
Isothermal Crystallization Time







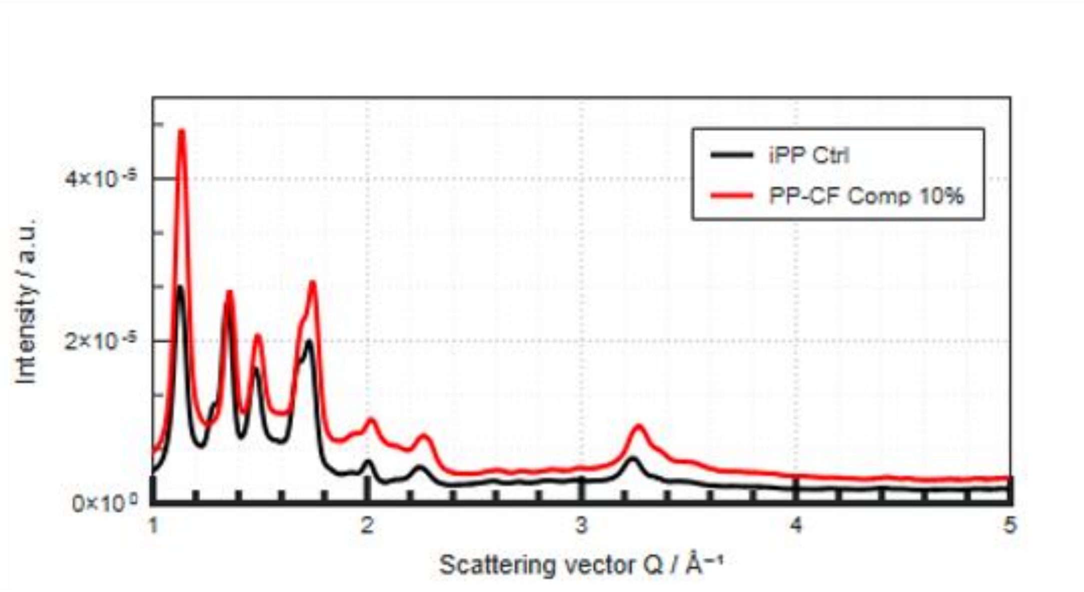


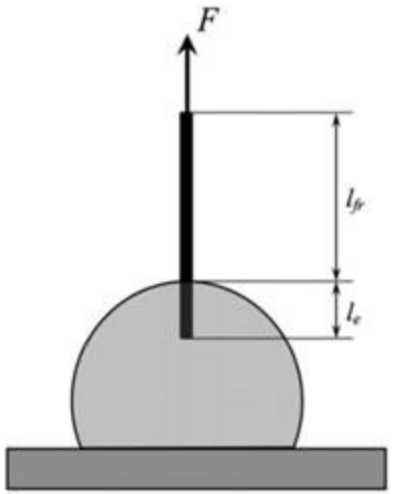


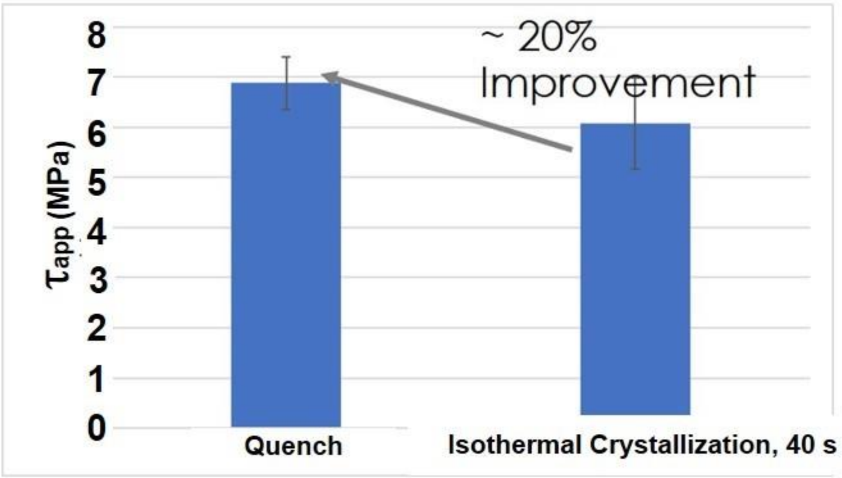
- **As fiber loadings increase, crystallization rates become faster**
- **Eventually results in a lower degree of crystallization due to high fiber content**
- **%crystallinity and faster crystallization rates imply fiber loadings initiate nucleation but inhibit growth**

Technical Accomplishments and Progress - Continued

Crystalline morphologies of PP matrix is retained in presence of CF







- **Analyzing attributes such as % crystallinity and crystal geometry of PP crystal system in the composite parts**

- **Single fiber pullout for PP-CF composite utilizing varying crystallization profiles to improve interfacial bonding**
- **Quenched specimen shows 20% increase in apparent interfacial shear strength compared to Isothermal crystallization at 120 ⁰C**

Responses to Previous Year Reviewers' Comments

This is the first year of the project; hence this project is yet to receive comments from Reviewers

Collaboration and Coordination with Other Institutions

- **University of Tennessee – The Bredesen Center for Interdisciplinary Research and Graduate Education**
  - **This project supports graduate research by Kendra Allen**

- **The project collaborates with various scientists and leverages Basic Energy Sciences user facilities—Center for Nanophase Materials Science (microscopy and x-ray scattering) and Oak Ridge Leadership Computational Facility (molecular dynamics simulation)—for composite characterization via approved user proposals**

Remaining Challenges and Barriers

- Processing of the materials using this methodology for large tow (~50k tow size) CF
- Uniform wetting of the matrix on such large number of filaments remains a grand challenge. We are developing a method to address this challenge.
- Current fiber surface treatment methods are developed for epoxy matrices and are not applicable for thermoplastics with less polarity than the epoxies
  - Suitable surface activation method will be established as part of this project
- Understanding of the correlation of interphase properties, interphase crystallinity and chemical composition with mechanical performance of composites is limited
  - Detailed investigations on different interfacial interactions are required to establish optimal processing parameters that lead to superior mechanical performance of composites
- Developing low-cost and high-throughput manufacturing methods for thermoplastic composites with suitable interfacial chemistry is a challenging task
  - This project focuses on developing cost-effective processing methods for obtaining the most suitable polymer-fiber interfaces as well as high-throughput composite fabrication
  - Techno-economic analysis of the developed method

Future Work

- Develop CF thermoplastic polymer composites with superior mechanical performance using novel interfacial chemistries and high-throughput, low-cost processing
- Establish intermediates' morphology at 100-500 nm and 5-100 mm length scales
  - Microscopy will be performed to characterize fiber-matrix interphase for different interface types – capture property transition trends into bulk matrix
  - Small Angle X-ray Scattering characterization will be performed to study the polymer structure at the nanoscale in the interphase and bulk matrix
- Demonstration of CFRP forming/molding process for multi-layered structures
- Demonstrate 10% immobilized PP on the CF surface by analytical methods – correlate with interphase properties and macroscale composite performance
- Quantify monomeric, segmental and chain dynamics, at 100-200 nanosecond timescale, and rheological response in the non-equilibrium state using MD and coarse-grained simulations
- Quantify activation energies for forming chemisorbed matrices and identify stabilized structures of polymer matrix attached to the CF surface by C-C bond using thermal analysis
- Demonstrate 500 MPa tensile strength in mesoscopic unidirectional intermediate
- Exhibit aromatic nylon matrix CFRPs with 1 GPa composites tensile strength

Any proposed future work is subject to change based on funding levels

Summary

- The project will deliver repairable low-cost thermoplastic composites with a multi-layered stamp-formed structure
- Initial results show promise with CF/PP composites having PP matrix anchored on CF surface
- ½ inch long AS4 CF randomly dispersed PP matrix composite (at 25 vol%) show 130+ MPa tensile strength while the continuous tow composite exhibit 700+ MPa strength
- Composites containing 40-60 vol.% fiber will be fabricated
- Interfacial interactions will be tuned to achieve outstanding mechanical performance of the thermoplastic matrix composites
    - 0.8-1.4 GPa tensile strength; 50-100 GPa Young’s modulus; ~10% failure strain
- Techno-economic analysis will be conducted on the new processing methods (FY22-23)