Low-Cost, High-Performance Carbon Fiber for Compressed Natural Gas Storage Tanks

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University of Virginia

DE-EE0009239
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DOE Hydrogen Program
2023 Annual Merit Review and Peer Evaluation Meeting

AMR Project ID: ST236

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Project Goals

- Develop and validate methods for scalable production of low-cost, high-performance carbon fiber
- Design low-cost, lightweight, composite CNG storage tanks that meet ANSI NGV2 standards
- Establish a methodology for manufacturing the prototype Type IV tanks at scale

Target metrics for low-cost, high-performance CFs and CF composites compared to Toray T700S.

Property	**Fiber**			**Composite**		
	Phase 1	Phase 2	*T700S*[1]	**Phase 1**	Phase 2	*T700S*[1]
Tensile Strength (ksi)	**> 600**	> 700	*711*	**> 300**	> 400	*415*
Tensile Modulus (Msi)	**> 28**	> 32	*33.4*	**> 17**	>19	*19*
Tensile Strain (%)	**1-2.1**	1.5-2.1	*2.1*	**0.8**	1-2	*2*
Cost ($/lb)	**< $6.80**	< $5.80	*$13.00*	**< $16.00**	< $14.00	*$21.00*

Overview

Timeline

- Project Start Date: 10/1/2022
- Project End Date: 9/30/2027

Budget

- Total Project Budget: $7,809,744.00
- Total DOE Share: $5,847,627.00
- Total Cost Share: $1,962,117.00
- DOE Funds Spent: $1,329,235.18
- Cost Share Funds Spent: $497,980.35
- * As of ~ 03/31/2023

Barriers and Targets

- Lightweight CNG and H_2 storage tanks needed for vehicle energy efficiency and payload capacity
- Contemporary carbon fiber is prohibitively expensive; accounts for half the cost of the tanks
- Low-cost alternative precursors can reduce carbon fiber cost significantly
- Carbon fiber composite matrix interface enhancement can reduce carbon fiber volume

Partners

Project Lead:

- Xiaodong “Chris” Li (University of Virginia)

Co-PIs:

- Merlin Theodore / Frederic Vautard (ORNL)
- Charles James (SRNL)
- Desmond Cook (Solvay / Cytec Engineered Materials)
- Rick Rashilla (Hexagon Lincoln)

Potential Impact

Reduce CNG and H_2 storage tank cost

- Cost reduction of 35% (< $14/lb) via low-cost, high-performance carbon fiber and enhanced composite interfacial properties

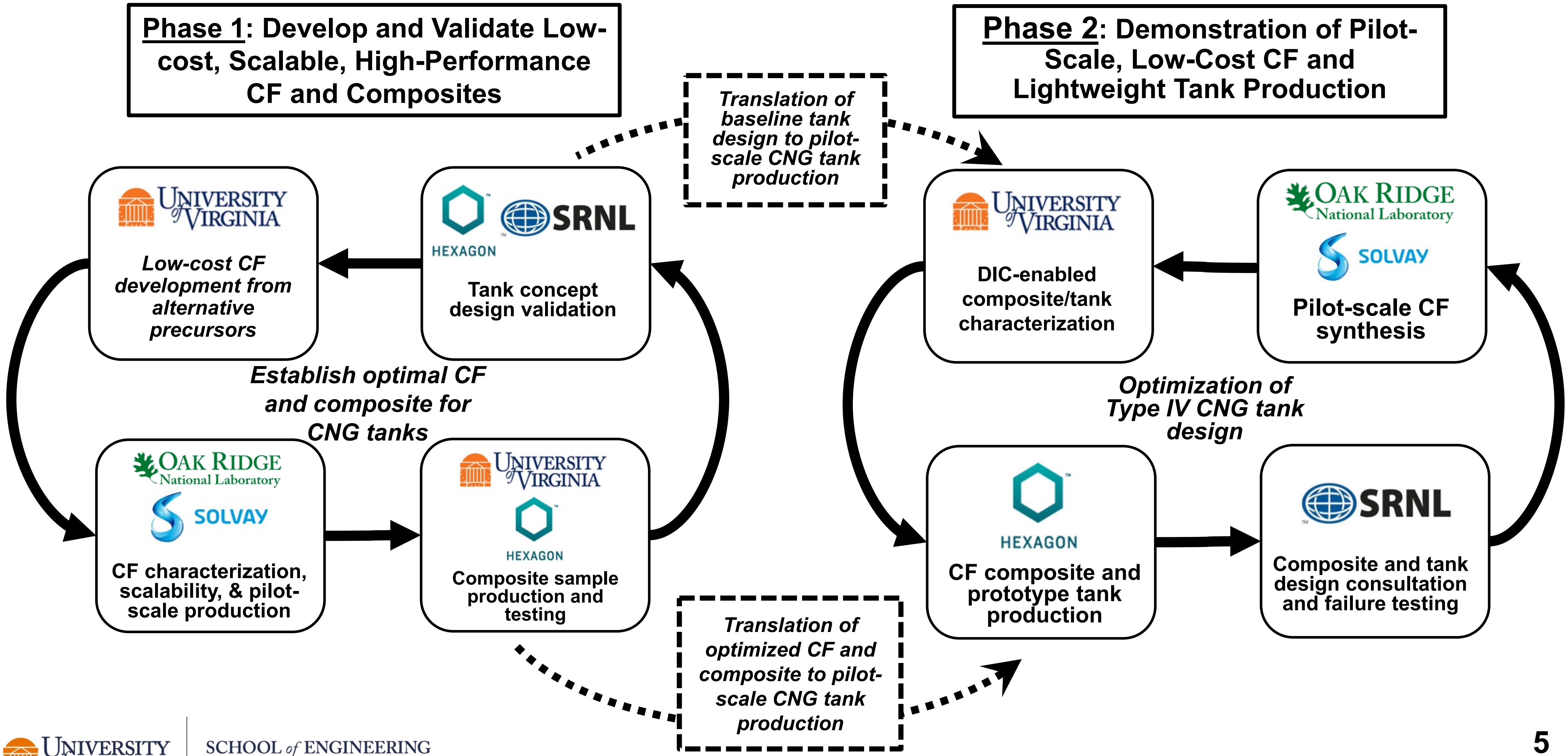
Broaden high-performance CF and composite adoption

- Reduce high-performance CF cost by ~47%
- Reduce CF volume by improving load transfer efficiency from 86% to 90%
- Achieve low-cost, high-performance composites for all sectors
  - *Pipelines, static H_2 fuel cells, wind turbine blades, vehicle components, etc.*

Advance domestic carbon fiber manufacturing industry

- Lower cost = greater demand = bigger market for domestic production
- Creates more and new high paying technical jobs

Approach



Phase 1: Develop and Validate Low-cost, Scalable, High-Performance CF and Composites

Low-cost CF development from alternative precursors

Tank concept design validation

Establish optimal CF and composite for CNG tanks

CF characterization, scalability, & pilot-scale production

Composite sample production and testing

Translation of baseline tank design to pilot-scale CNG tank production

Translation of optimized CF and composite to pilot-scale CNG tank production

Phase 2: Demonstration of Pilot-Scale, Low-Cost CF and Lightweight Tank Production

DIC-enabled composite/tank characterization

Pilot-scale CF synthesis

Optimization of Type IV CNG tank design

CF composite and prototype tank production

Composite and tank design consultation and failure testing

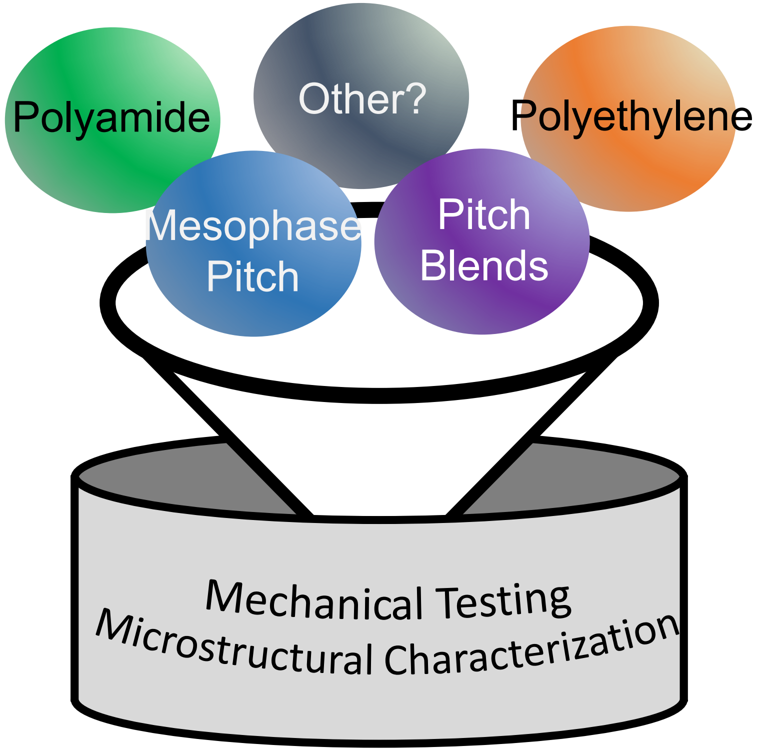
Approach

- Low-cost alternative CF precursors have been identified and examined
  - Mesophase Pitch
  - Polyethylene
  - Nylon
  - Blends
- Nanoadditive coatings explored for fiber-matrix interface enhancement
  - Performed in batch and continuous operations
- Most promising candidates scaled to pilot-scale for performance and cost evaluation

Month / Quarter	Milestone Description / Deliverable	Status (4/10/23)
M3 / Q1	Synthesize and characterize hybrid recipes: PE/nylon, nylon/pitch, PE/pitch	Complete
M6 / Q2	Begin CF composite synthesis and fiber sizing analysis	Complete
M9 / Q3	Rank monocomponent and hybrid precursors based on cost and properties to assist downselection	Complete
M12 / Q4	Demonstrate (i) a CF conversion recipe and (ii) CF composite architecture capable of properties within 20% of the Table 1 Phase 1 target metric	Complete
M15 / Q5	Identify at least one most promising CF recipe and transfer to industry partners for production scale-up study	Complete
M18 / Q6	Evaluate initial scale-up pilot run of continuous multifilament fibers and identify mitigation strategies	Complete
M24 / Q8	Present performance and cost projections based on incorporating candidate CF into existing Type IV tank design	In Progress
M24 / Q8	(i) Produce at least 100 continuous meters of 100-filament tows of the selected CF recipe, (ii) Demonstrate a CF conversion recipe achieving Table 1 Phase 1 targets, (iii) Present mechanical properties of continuous filament carbon fiber impregnated tows evaluated according to ASTM D4018, (iv) Projected tank performance and cost using CF recipe improves upon DOE 2019 status values	In Progress

Technical Accomplishments and Progress

Precursor Downselection



Primary candidate:

Mesophase pitch and pitch-based blends

Mechanical Properties as of 4/14/2023

Precursor	Strength (GPa) [ksi]	Elastic Modulus (GPa) [Msi]	Strain
Target	**4.14 [600]**	**220.6 [32]**	**1%**
Pitch	3.34 [484.4]	**374 [54.2]**	0.92%
Pitch-blend	2.04 [295.9]	199 [28.9]	**~1%**

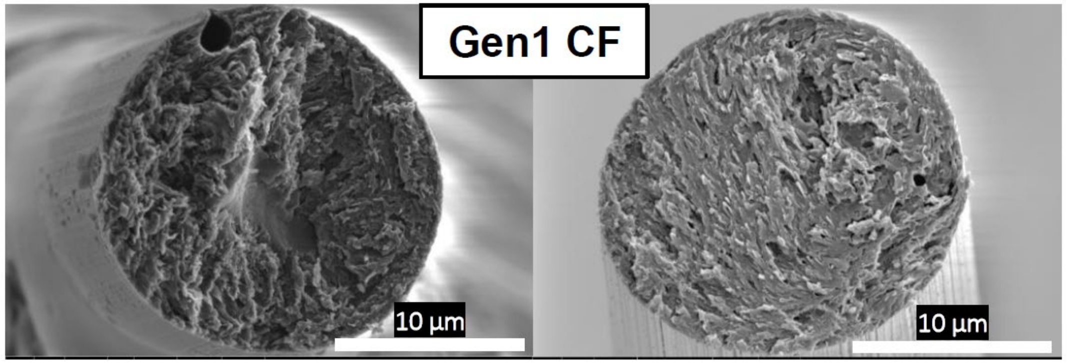
Work on other alternative precursors continues in limited fashion to discover opportunities to further enhance primary candidate

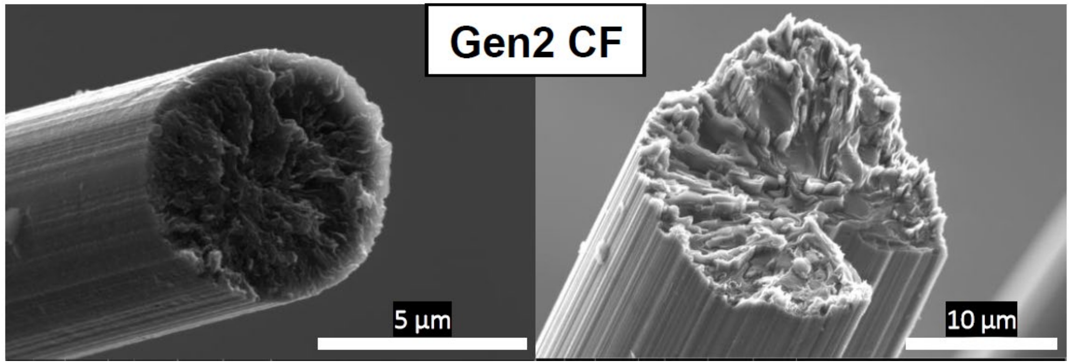
Any proposed future work is subject to change based on funding levels

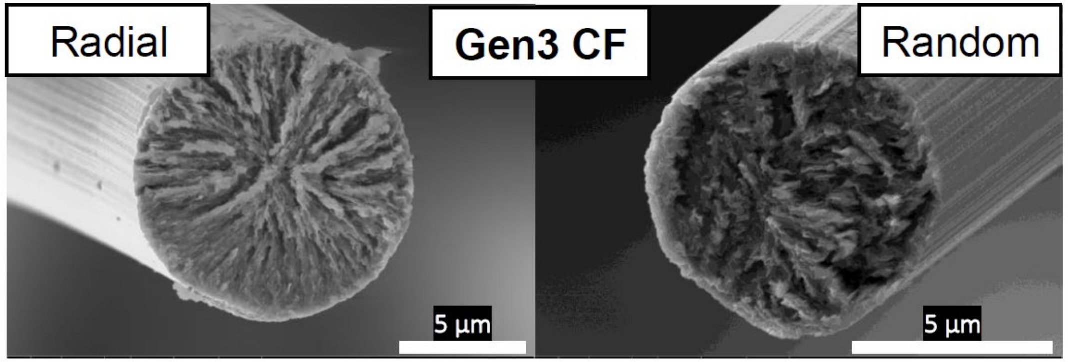
Technical Accomplishments and Progress

Alternative Precursor: Mesophase Pitch

- **Generation 1 carbon fiber**
  - Large pores in structure (> 200 nm), poor directional texture, low tensile strength and modulus
  - Large diameters and a lack of windability
- **Generation 2 carbon fiber**
  - Development of texture along fiber axis
  - Tensile strength and modulus significantly improved over Generation 1 fibers
  - Microstructure is still uncontrollable between fiber spin trials
- **Generation 3 carbon fiber**
  - Microstructure fully controllable through spinneret geometry and spin conditions
  - Defects on nano-scale, difficult to image
  - Tensile strength and modulus significantly improved over Generation 2 fibers
  - Tensile strength is notably higher for random structure over radial structure



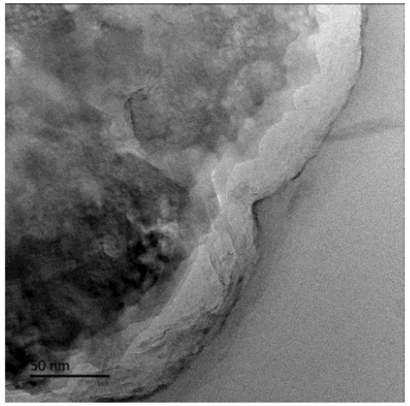




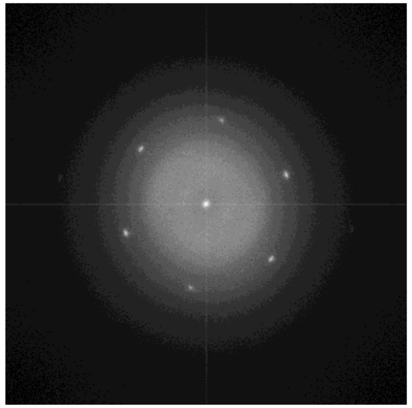
Technical Accomplishments and Progress

Alternative Precursor: Mesophase Pitch

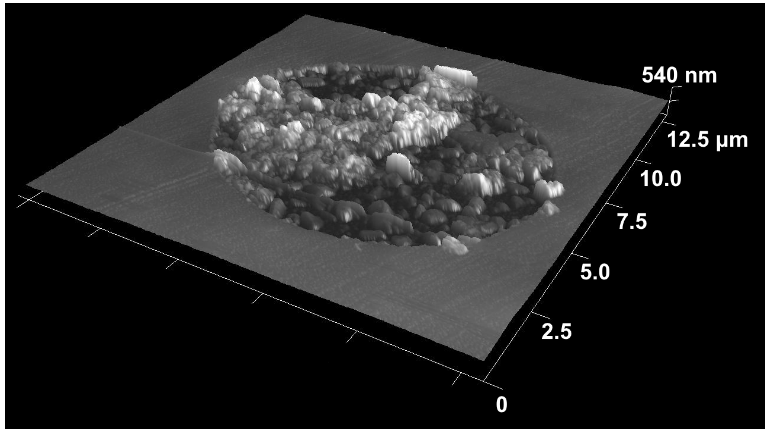
- Ongoing work involves in-depth characterization of the different microstructures produced in CF
- Evaluation of the anisotropic crystallites through WAXS and TEM, analysis of bonding through Raman spectroscopy, mapping of domain structure through atomic force microscopy, pore size distribution from SAXS
- Goal: establish a microstructure – property relationship in CFs, dictated by the initial conditions used to produce the precursor fiber



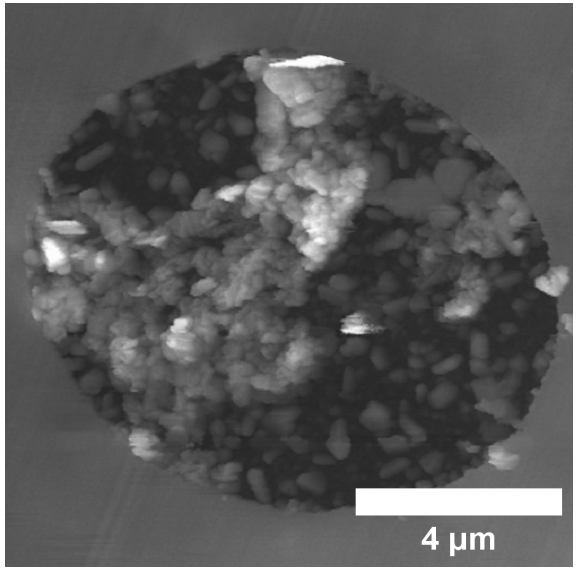
TEM image of random CF

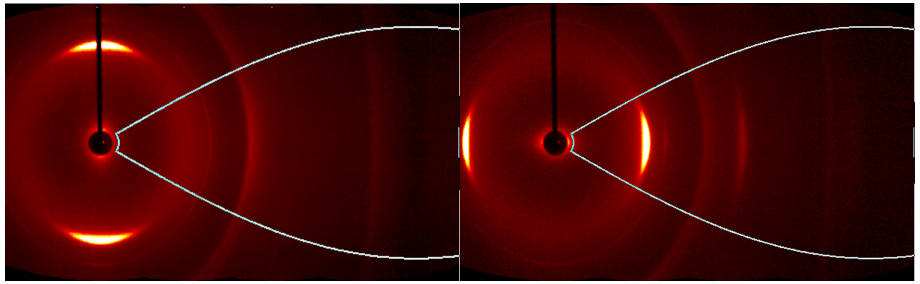


FFT of TEM image



AFM map of microtomed radial CF





2D WAXS patterns of radial CF
(left: pseudo-meridional ($L_{a\perp}$), right: equatorial (L_c))

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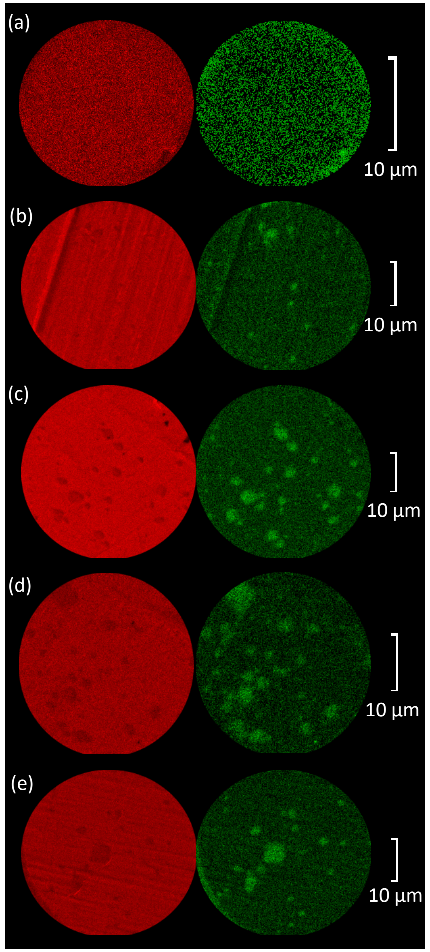
Technical Accomplishments and Progress

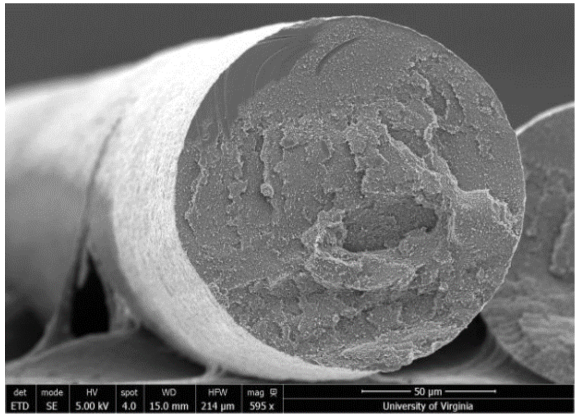
Alternative Precursor: Blended mesophase pitch + Proprietary Polymers

- Blend 1: Mesophase Pitch + Waste Polymers
  - Lack of compatibility leads to porous carbon fibers, lower mechanical properties
- Blend 2: Pitch + Proprietary Polymer
  - Blending trials demonstrated compatibility
  - Precursor fiber spinning ongoing
    - Reduce diameter, scale-up to multifilament tow
  - Conventional conversion process possible
    - Direct insertion to existing lines

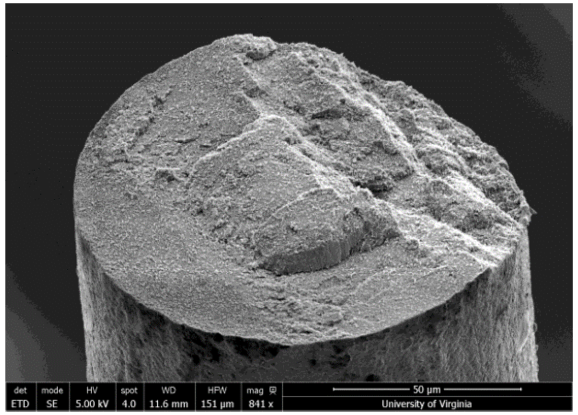
EDS of pitch-PET:
Carbon & Oxygen

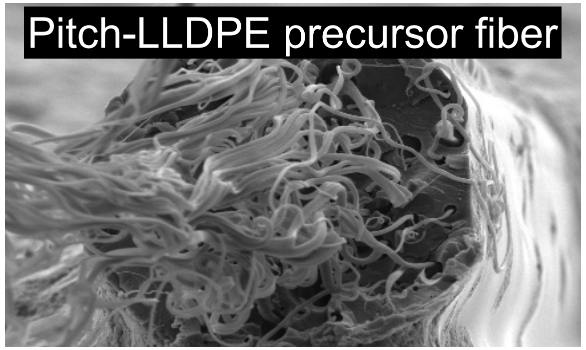


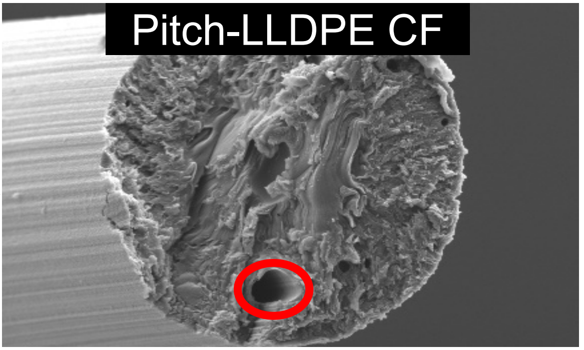
Pitch-Solvay polymer



Pitch-Solvay polymer




Pitch-LLDPE precursor fiber


Pitch-LLDPE CF

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Technical Accomplishments and Progress

Carbon Fiber Production Scale-Up Evaluation

- Lab-scale fiber spinning capability expanded to multi-filament
  - Gas-pressure drive and screw extrusion capabilities
- Pilot-scale spinning trial scheduled for late April
  - Attempt pitch and pitch-blend precursor spinning
  - Generate 100+ m tows of 100+ filaments
- Pilot-scale conversion trials scheduled for May

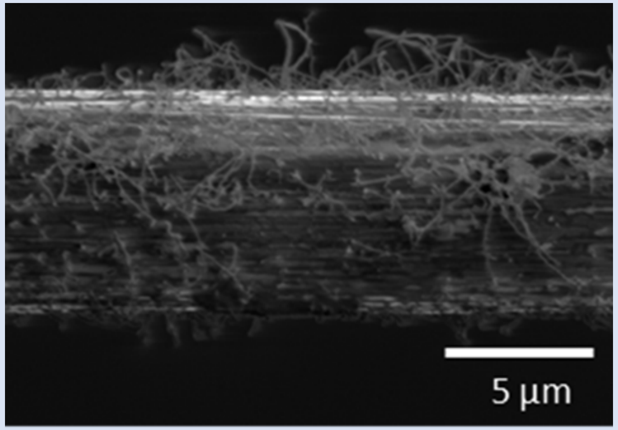
Technical Accomplishments and Progress

Matrix-Fiber Interface Optimization – Lab Scale

Nanoparticles deposited on fiber surface for improved interfacial properties

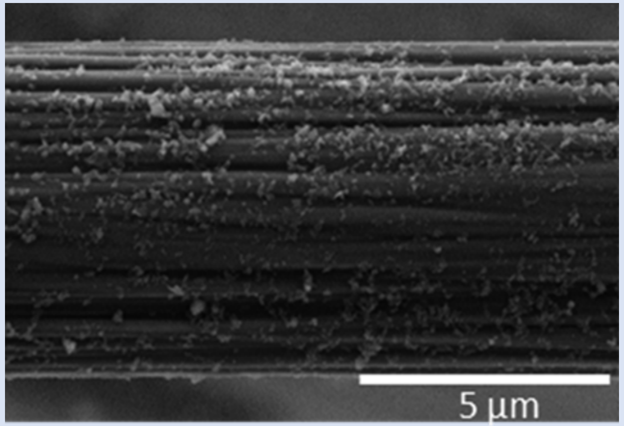
- 2 sizing recipes were evaluated for coating quality and mechanical performance at **lab scale**

Sizing v1
Nanowire morphology with sparse coverage

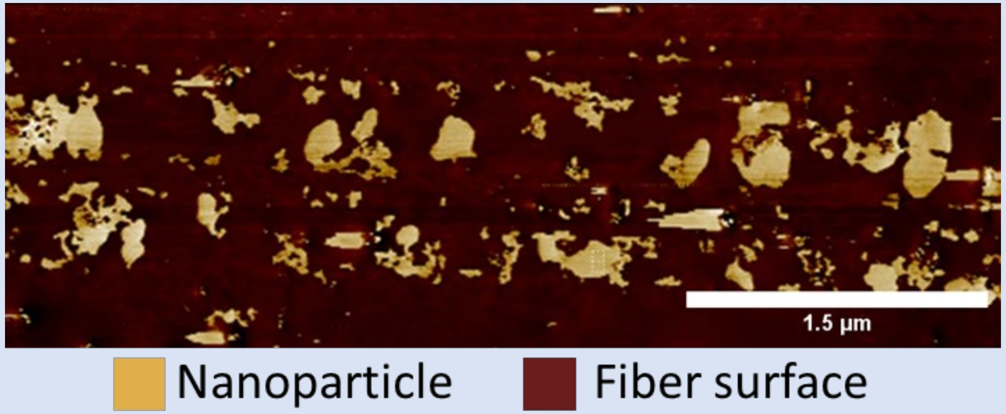


SEM

Sizing v2
Nanoplatelet morphology with higher coverage uniformity
Microstructure hypothesized to yield superior mechanical properties



SEM

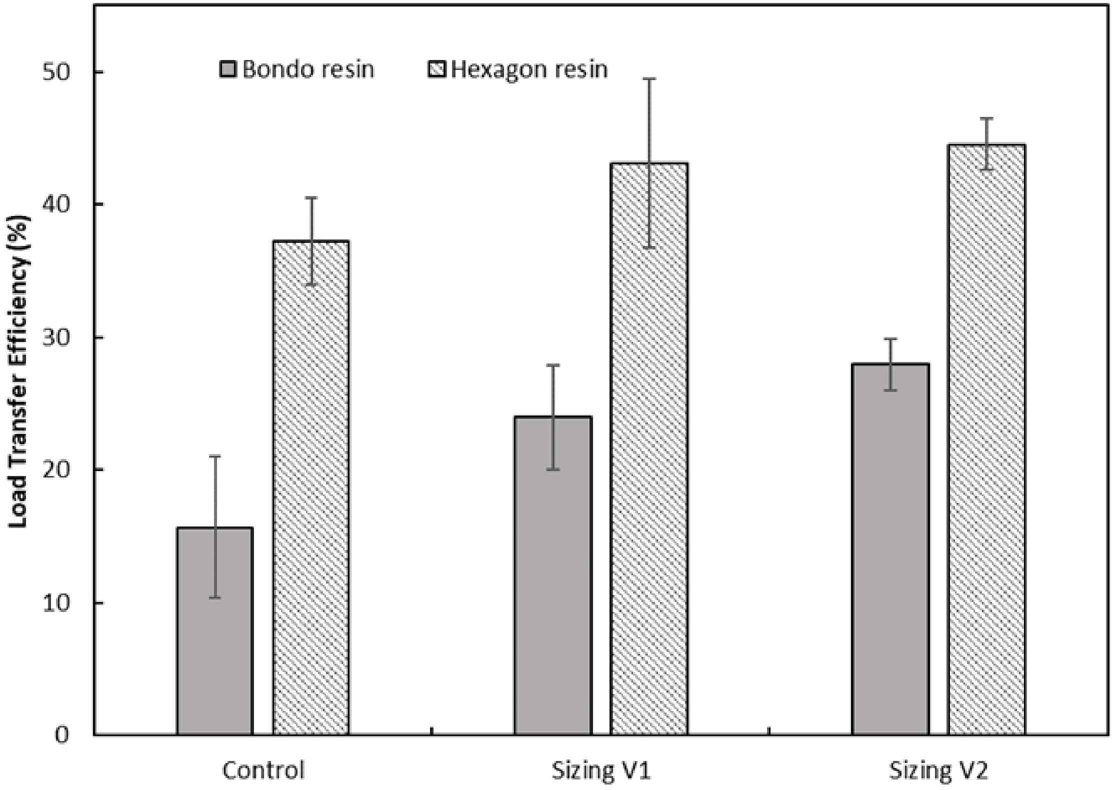


AFM (phase)

Technical Accomplishments and Progress

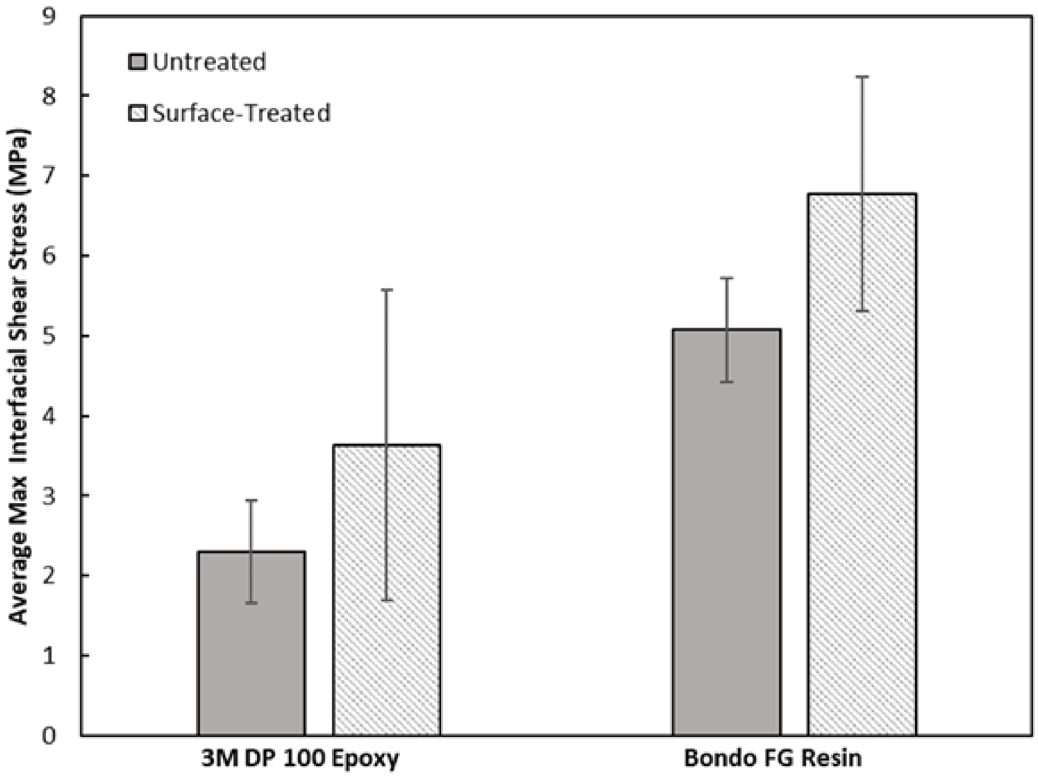
Matrix-Fiber Interface Optimization – Lab Scale

4-Point Bend Testing to Quantify Load Transfer Efficiency



Average Load Transfer Efficiency

Single Filament Adhesion Testing to Quantify Max Interfacial Shear Stress for Coating v2



Average Interfacial Shear Stress

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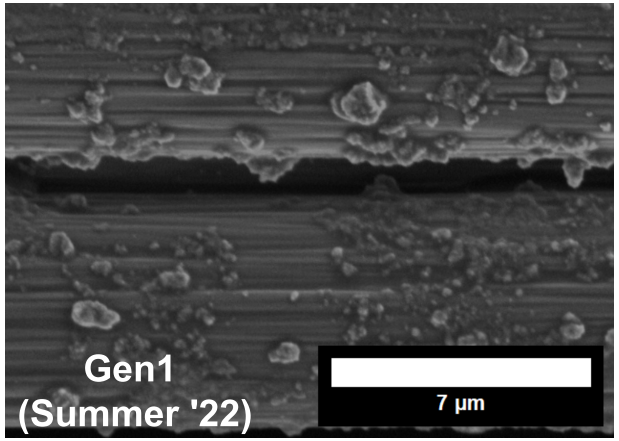
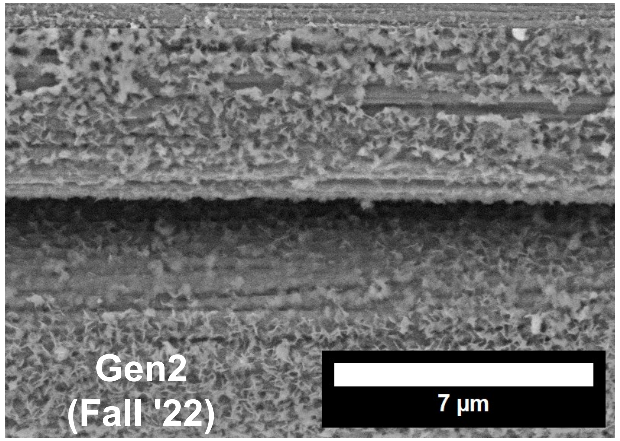
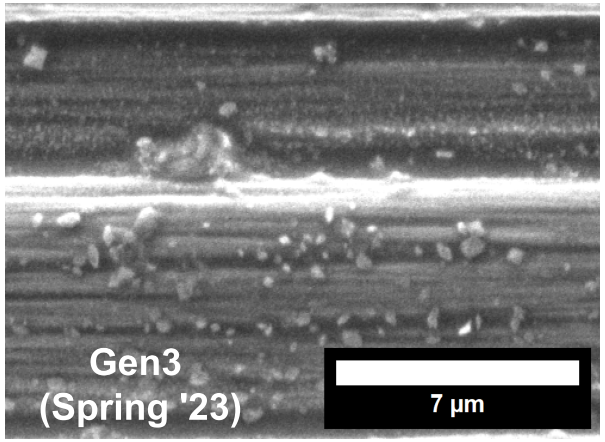
Technical Accomplishments and Progress

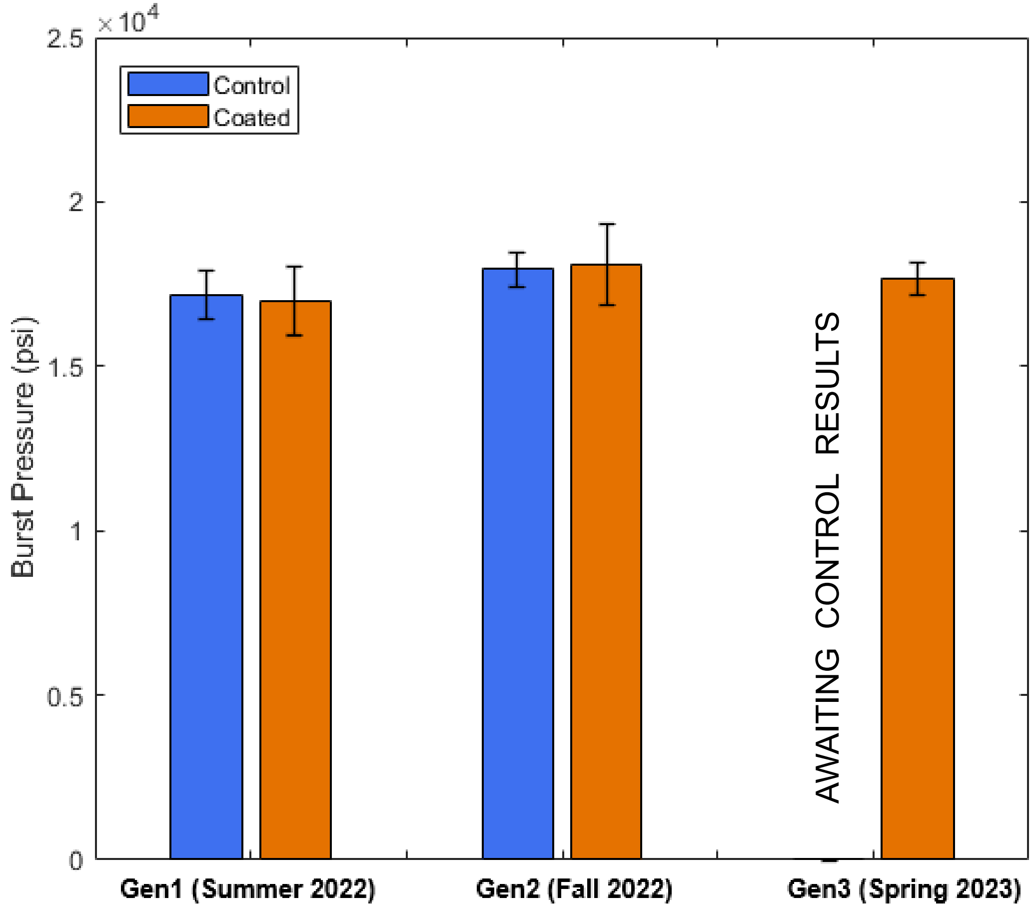
Matrix-Fiber Interface Optimization – Pilot Scale

- Nanoparticle coating continuously applied in pilot-scale bath line
  - Bath line optimizations have yielded *smaller particles*, *uniform coating* and improved *repeatability* in testing results
  - 24m tows prepared for ring burst testing









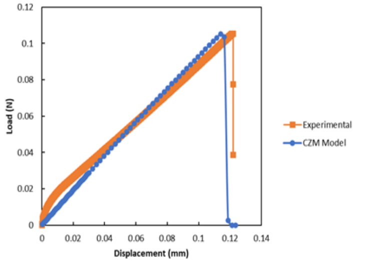
Any proposed future work is subject to change based on funding levels

Technical Accomplishments and Progress

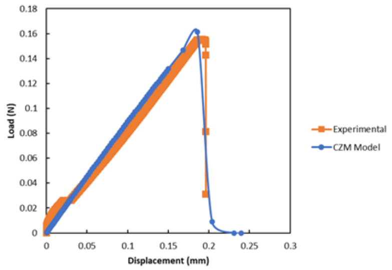
Matrix-Fiber Interface Optimization - Simulation

- 2D Axisymmetric Model of Single Filament Adhesion testing
    - Utilized cohesive zone modeling parameters to evaluate phases of debonding
    - Identified Static-Dynamic friction coefficient transition point
    - Simulation results show small (< 50 µm) region of fiber responsible for onset of deboning point

Sim Results vs Experimental

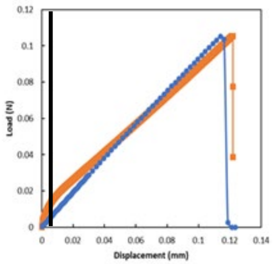


Uncoated:
Sim vs Experimental

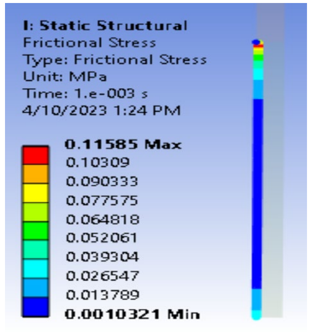


Nanoparticle Coated:
Sim vs Experimental

Initial Load applied to fiber: Static Friction Coefficient Dominated



Position on Load/Disp curve

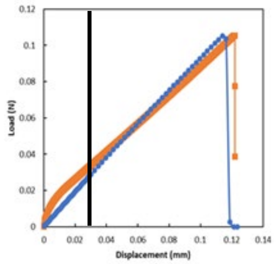


I: Static Structural
Frictional Stress
Type: Frictional Stress
Unit: MPa
Time: 1.e-003 s
4/10/2023 1:24 PM

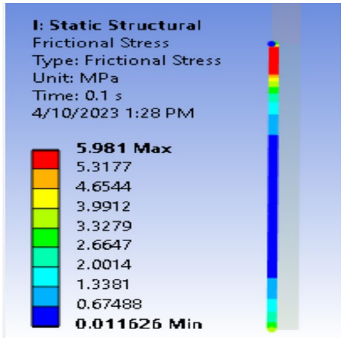
0.11585 Max
0.10309
0.090333
0.077575
0.064818
0.052061
0.039304
0.026547
0.013789
0.0010321 Min

IFSS at Fiber/Matrix Interface

Early Buildup of Stresses Along Fiber/Matrix Interface: Static Friction Coefficient Dominated



Position on Load/Disp curve

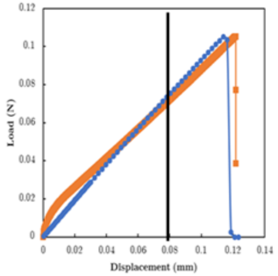


I: Static Structural
Frictional Stress
Type: Frictional Stress
Unit: MPa
Time: 0.1 s
4/10/2023 1:28 PM

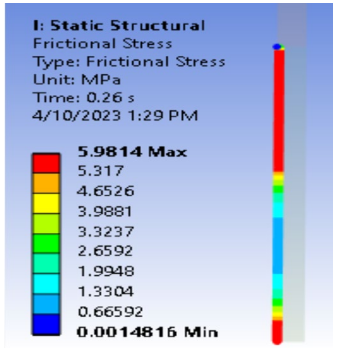
5.981 Max
5.3177
4.6544
3.9912
3.3279
2.6647
2.0014
1.3381
0.67488
0.011626 Min

IFSS at Fiber/Matrix Interface

Onset of Debonding: Static to Dynamic Friction Coefficient Transition Point



Position on Load/Disp curve

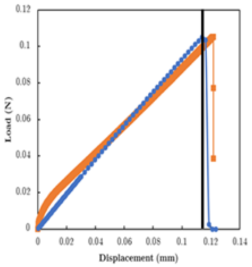


I: Static Structural
Frictional Stress
Type: Frictional Stress
Unit: MPa
Time: 0.26 s
4/10/2023 1:29 PM

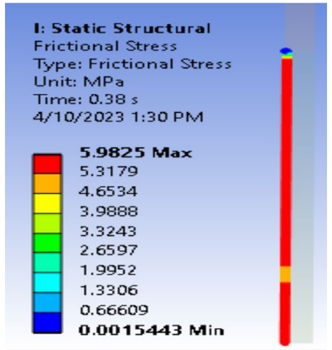
5.9814 Max
5.317
4.6526
3.9881
3.3237
2.6592
1.9948
1.3304
0.66592
0.0014816 Min

IFSS at Fiber/Matrix Interface

Rapid Failure: Dynamic Friction Coefficient Dominated



Position on Load/Disp curve



I: Static Structural
Frictional Stress
Type: Frictional Stress
Unit: MPa
Time: 0.38 s
4/10/2023 1:30 PM

5.9825 Max
5.3179
4.6534
3.9888
3.3243
2.6597
1.9952
1.3306
0.66609
0.0015443 Min

IFSS at Fiber/Matrix Interface

Technical Accomplishments and Progress

Response to Reviewer Comments

Collaboration and Coordination

University of Virginia | **Prime**
- Project lead, synthesis and characterization of alternative-precursor carbon fibers and composite matrix for enhanced interfacial strength

Oak Ridge National Laboratory | **Subcontractor**
- Alternative precursor production scale-up evaluation and testing

Savannah River National Laboratory | **Subcontractor**
- Composite sample and prototype compressed gas tank testing

Solvay / Cytec Engineered Materials | **Subcontractor**
- Characterization of alternative-precursor carbon fibers, industry guidance on fiber conversion process and scale-up suitability

Hexagon Lincoln | **Subcontractor**
- Design and testing of prototype compressed gas tanks, industry guidance on composite matrix materials and composite forming processes

Remaining Challenges and Barriers

Challenge: Increase pitch-CF strength

- Spin finer precursor fibers
- Optimize conversion for higher mechanical properties
- Spin small diameter pitch-proprietary polymer blend fibers to leverage polymer properties for higher strength

Challenge: Improve nanoparticle dispersion in sizing *at pilot-scale*

- Continuous deposition process promising, but need to translate to results at ring burst pressure test

Challenge: Demonstrate cost advantage of selected precursors

- Techno-economic modeling of candidate production at industrial scale to be performed by project partners
- Pilot-scale production required to estimate cost

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

Proposed Future Work

- Achieve target mechanical properties for pitch- and pitch-blend-based CFs
  - Reduce pitch- and pitch-blend precursor fiber diameters
  - Optimize conversion process for pitch-blend precursor fibers
- Optimize continuous nanoparticle dispersion method for improved composite properties
- Demonstrate nanoparticle coating on CF derived from candidate precursor
- Analyze cost of CF production from candidate precursors at industrial scale
- Design Type IV prototype tank based on candidate CF and composite properties to demonstrate feasibility

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

Summary

- Mesophase pitch and pitch-blends have been selected as the leading candidate alternative carbon fiber precursor materials
- Nanoparticle surface coatings applied to a continuous tow have shown significant increase in fiber-matrix interface load transfer efficiency
- Pilot-scale production trials of the leading candidate precursors have commenced
- Ongoing work is focused on:
    - Continuing to increase fiber and composite mechanical properties
    - Analyzing the candidate fiber and composite cost
    - Designing a prototype tank featuring the candidate fibers and composite

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

Technical Backup Slides

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Technology Transfer Activities

- Collaborative efforts are made to ensure the technologies developed in this work have the potential for domestic scale-up and commercialization.
  - In-lab spinning and conversion informs pilot-scale trials
  - Continuous tows of precursors are converted for full process perspective
- Industry partners, Solvay and Hexagon, are closely integrated with the team.
  - Provides real world perspective on lab discoveries
  - Delivers technical expertise for faster and smoother transition

Publications and Presentations

1. C.A. Love-Baker, T.M. Harrell, · Alexander Scherschel, Z. Gao, N. Song, K.R. Brown, F. Vautard, Ilia Ivanov, J. Klett, Xiaodong Li, Unveiling the microstructural evolution of carbon fibers derived from polyamide-6, *J. Polym. Res*. 30 (2023) 72. https://doi.org/10.1007/S10965-023-03455-6.

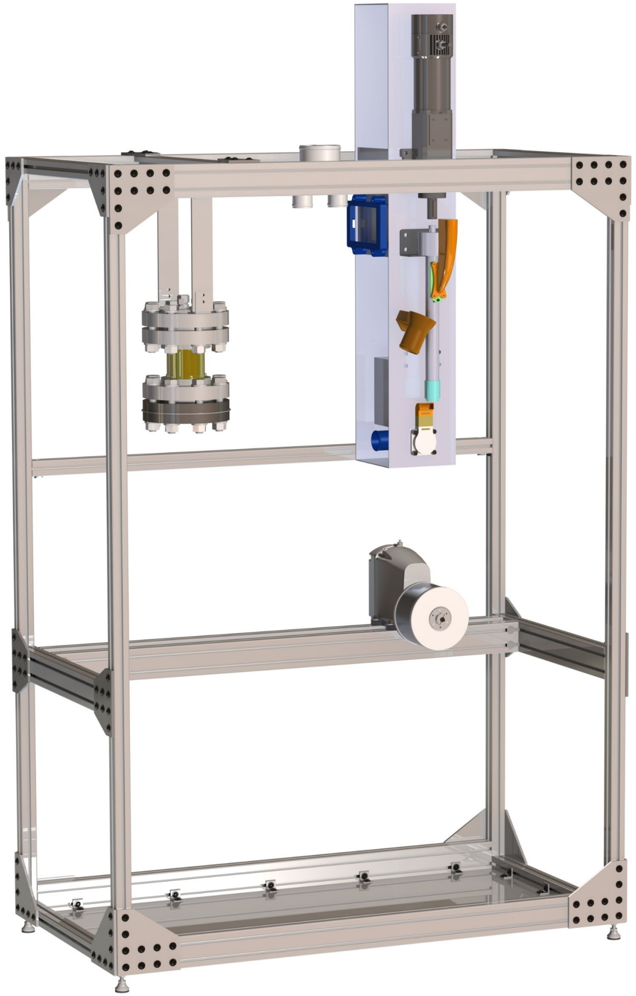
2. A. Scherschel, C. Love-Baker, A. Sushchenko, T.M. Harrell, K.R. Brown, X. Li, Compatibility of mesophase pitch and linear low-density polyethylene for low-cost carbon fiber. *J. Polym. Res.* 30 (2023) 82. https://doi.org/10.1007/s10965-023-03466-3.

3. T.M. Harrell, C. Love-Baker, K.R. Brown, C.H. Bumgardner, X. Li, Extracting single fiber transverse and shear moduli from off-axis misalignment fiber tensile testing, *Compos. Part A Appl. Sci. Manuf.* 163 (2022) 107204. https://doi.org/10.1016/j.compositesa.2022.107204.

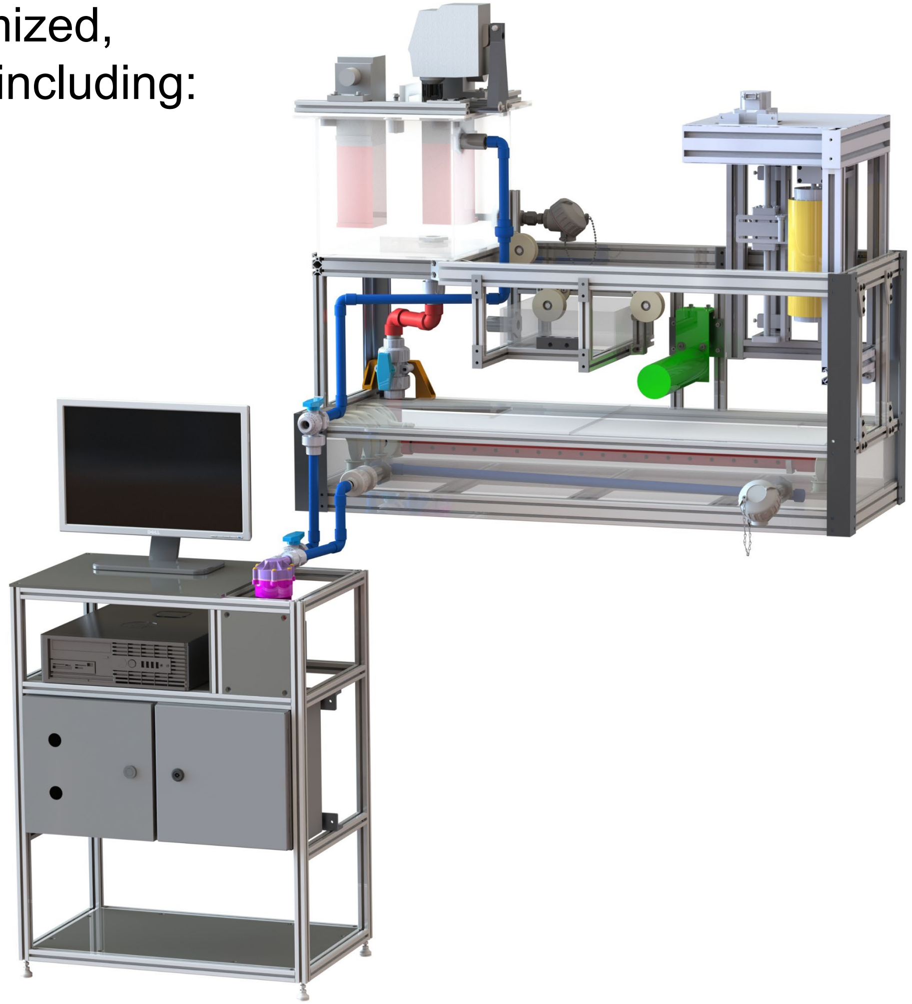
4. K.R. Brown, T.M. Harrell, L. Skrzypczak, A. Scherschel, H.F. Wu, X. Li, Carbon fibers derived from commodity polymers: A review, *Carbon*. 196 (2022) 422–439. https://doi.org/10.1016/J.CARBON.2022.05.005.

5. K.R. Brown, X. Li, Continuous Fiber Bath Treatments at Pilot Scale: A Novel Testbed System [Poster Presentation], *SAMPE* 2022, Charlotte, NC.

Fiber Spinning and Processing Capabilities



UVA has designed and fabricated customized, modular carbon fiber synthesis stations, including:



A fiber melt spinning system featuring:
- Two screw extruders
- One gas-pressure driven extruder
- Up to 1500 m/min fiber takeup rate
- Monofilament and multi-filament spinning

A solution-processing fiber spinning system:
- Gel-spinning line
- Wet-spinning line

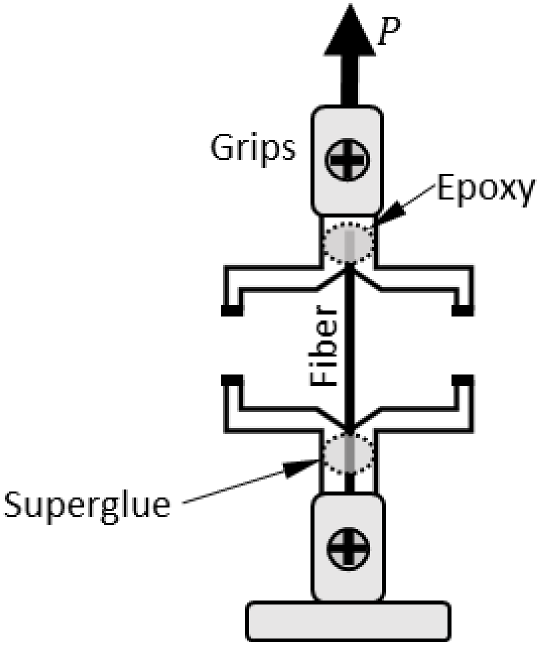
Continuous fiber bath treatment system:
- Corrosive and acidic solution resistant
- Heated, cross-flow bath (up to 80 °C)
- Residence time up to 2 hr
- Adjustable line tension (150 – 500 g)
- Max package fiber layer thickness of 10 mm
- Fiber can be rinsed and dried prior to spooling

Matrix Interface Test Methods

4-Point Bend Testing Setup

$$E_{composite} = \eta \cdot V_{fiber} \cdot E_{fiber} + (1 - V_{fiber}) \cdot E_{epoxy}$$

Single Filament Adhesion Schematic



$$\tau_{max} = \frac{F_{fiber}}{\pi \cdot l_{embedded} \cdot d_{fiber}}$$