# Carbon Composite Optimization Reducing Tank Cost

Duane Byerly (PI), Chris Wilson, Hexagon R&D LLC

DOE Project Award # DE-EE0009240

9 May 2024

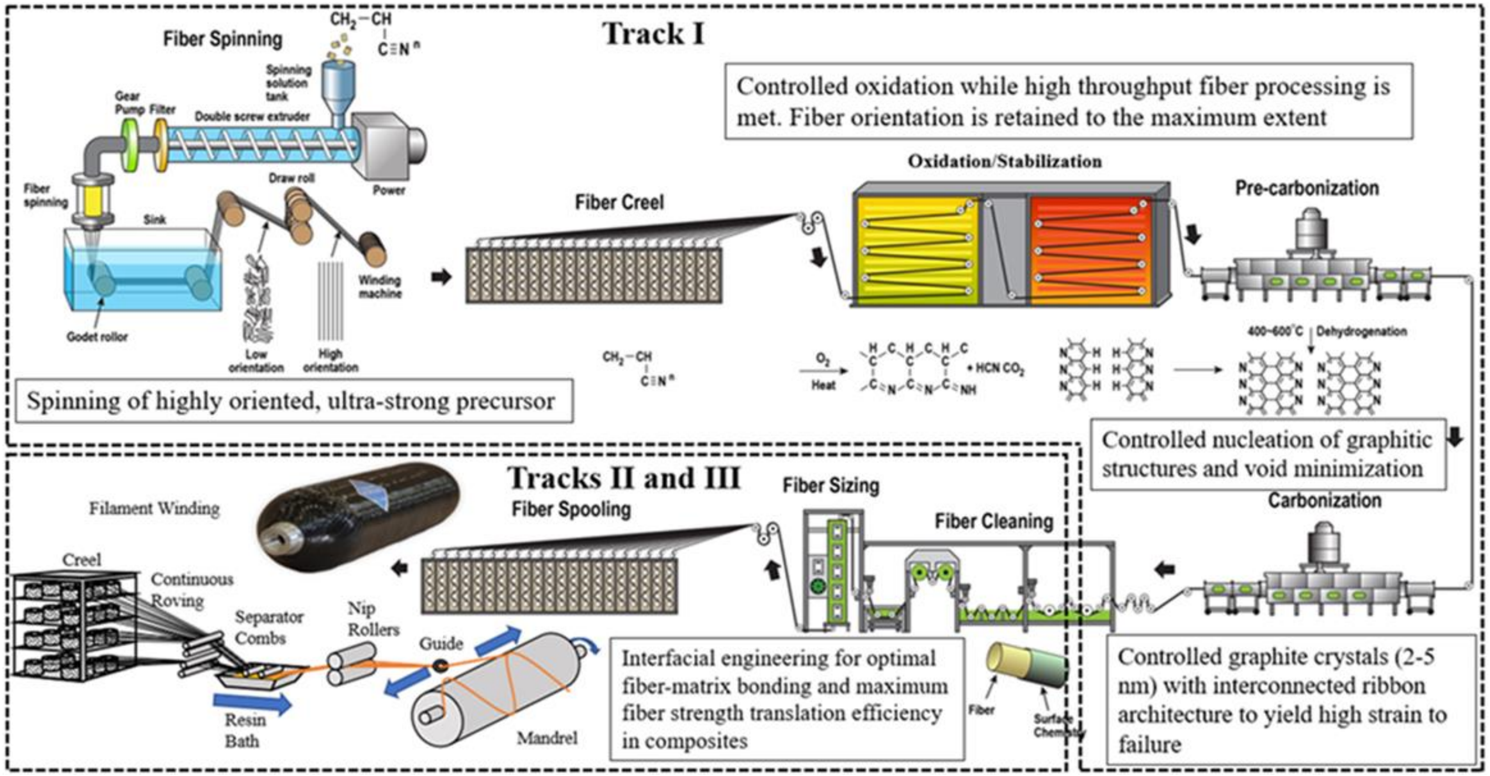
DOE Hydrogen Program

2024 Annual Merit Review and Peer Evaluation Meeting

Project ID: ST237

# Project Goal

- The overall project objective is to reduce compressed hydrogen and compressed natural gas (CNG) storage costs by developing new and optimized technologies to produce low-cost, high strength carbon fiber (CF) with a demonstrated cost of less than $15/kg, tensile strength of 700 ksi, and tensile modulus of 35 Msi.



# Overview

## Timeline and Budget

- Project Start Date: 1/Oct/2021
- Project End Date: 30/Sept/2026
- Phase 2 Start Date: 1/Oct/2023
- Total Project Budget: $10.255M
  - DOE Share: $8.12M
  - Cost Share: $2.13M
  - DOE Funds Spent: $2.99M (*as of Dec 31, 2023*)
  - Cost Share Funds Spent: $779K (*as of Dec 31, 2023*)

## Barriers and Targets

- Barrier: Fiber diameter variability and damage during production, impacting tensile strength and modulus
- Barrier: Current line speeds in oxidation and carbonization impacting fiber cost
- Barrier: Non-optimal fiber kg/H2 kg with current cost model configuration
- Target: Driving carbon cost fiber below $15/kg

## Partners

- Hexagon Agility, Project Lead
- Cytec Engineered Materials (CEM)
- Oak Ridge National Laboratory (ORNL)
- Pacific Northwest National Laboratory (PNNL)
- Newhouse Technology
- Kenworth R&D

# Potential Impact

- Currently, the cost of gas storage tanks is a significant barrier to the mass deployment of cleaner vehicle fuel sources such as hydrogen and CNG.
- CF accounts for approximately 50% of the total hydrogen storage system cost.
- The overall project objective is to reduce hydrogen and CNG storage system costs with newly developed technologies to produce low-cost, high strength CF to accelerate mass deployment of hydrogen and/or CNG fueled vehicles.
  - CF cost target < $15/kg, capable of 700 ksi tensile strength (TS) and 35 Msi tensile modulus (TM)
  - Additional project goals
    - Demonstrate >25% tank system cost reduction
    - Long-term stretch goal of further CF cost reduction
- Project and overall DOE targets

| | Baseline | Project Target | Ultimate Target |
|---|---|---|---|
| Benchmark CF cost | $26-30/kg | $13-15/kg | |
| 250 bar pressure vessel | | 10% cost reduction | |
| Total system cost | $16/kWh | | $8/kWh |



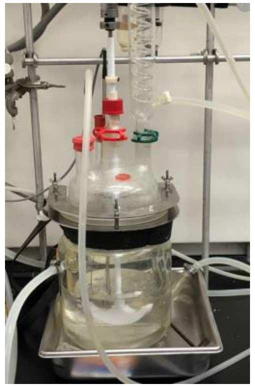
HEXAGON AGILITY

# Collaboration and Coordination

| | Key Roles | Supporting Responsibilities |
|---|---|---|
| **Hexagon Agility (Prime)** | • Program manager and team lead<br>• Lead pressure vessel modeling and testing | • Provide modeling support for pressure vessel material properties and CF reduction in all tasks<br>• Mechanical testing support for all tasks |
| **Cytec Engineered Materials (CEM)** | • Lead development of new low-cost fiber<br>• Lead CF surface modification task | • Coordinate on advanced fibers and resins |
| **Oak Ridge National Laboratory (ORNL)** | • Lead development of new low-cost fiber<br>• Lead CF surface modification task | • Low-cost resin alternatives<br>• Alternative fiber placement and materials<br>• Resin/fiber interface activities |
| **Pacific Northwest National Laboratory (PNNL)** | • Composite material testing and characterization<br>• Lead material modeling<br>• Coordinate the cost model structure | • Coordinate on advanced resins<br>• Coordinate on tank design and fabrication |
| **Newhouse Technology** | | • Composite tank design and modeling support |
| **Kenworth** | | • Consulting on tank geometries and packaging<br>• Support of tank/end use cost modeling |

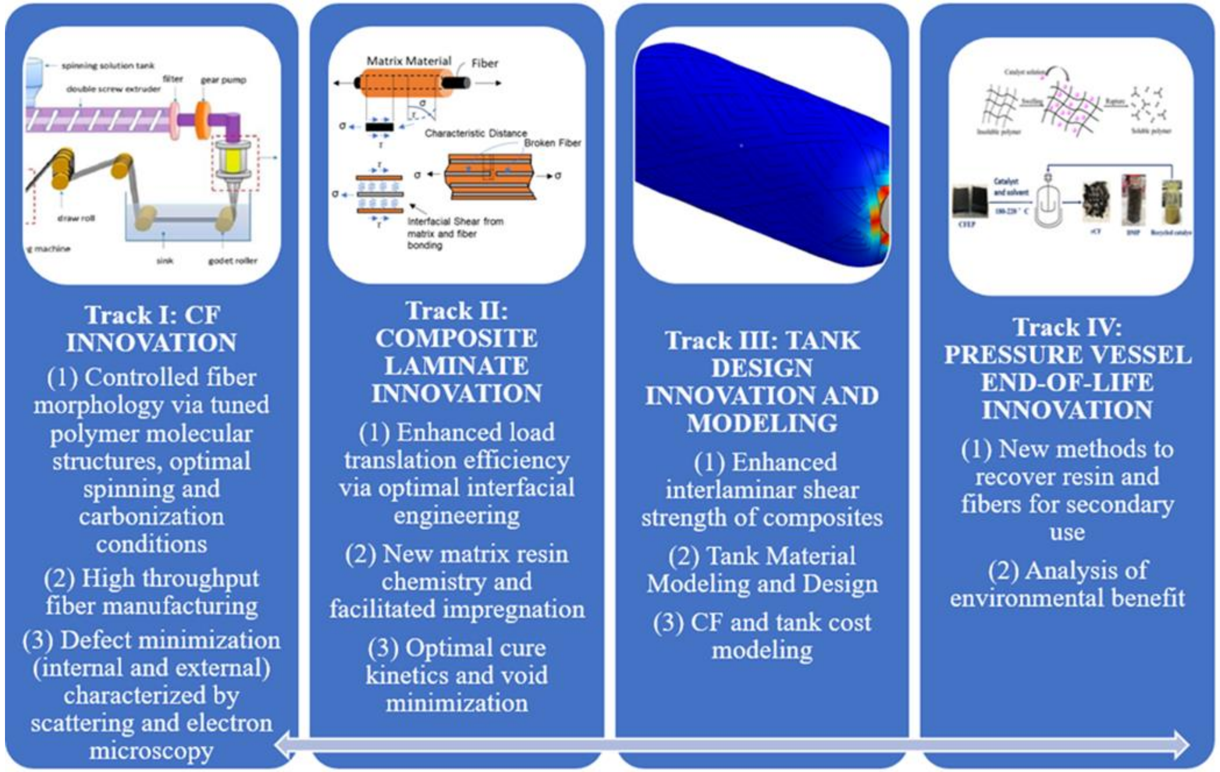
# Collaboration and Coordination

- All encompassing team covers full supply chain, raw material → end user
  - Foundational material research
  - CF research and commercial manufacturing
  - Gas storage tank/system manufacturing, research, and innovation
  - End user
  - End of life recycling



# Approach – Four Tracks of Innovation

- Commercial CF and compressed gas storage cost reductions will be achieved through four tracks of innovation:
  1. Optimizations in CF technology resulting in higher production capacities and higher throughput
  2. Increased composite performance efficiency
  3. Enhanced pressure vessel design and modeling
  4. End of life pressure vessel material recycling




| Task # | Task | Innovation Track |
|---|---|---|
| 1.0 | Development of CF precursor technology | 1 |
| 2.0 | CF precursor fiber spinning | 1 |
| 3.0 | CF conversion | 1 |
| 4.0 | CF sizing | 1, 2 |
| 5.0 | CF cost modeling of new fiber | 1 |
| 6.0 | High performance resin and composite evaluation | 2 |
| 7.0 | Pressure vessel modeling | 3 |
| 8.0 | Filament winding test | 2 |
| 9.0 | End of life recycling | 4 |
| Final | CF strength and cost modeling | All |



HEXAGON AGILITY

# Track I – Carbon Fiber Innovation (Tasks 1, 2, and 3)

- Commercial cost reductions will be realized by achieving higher production capacities and higher throughput via optimizations in all facets of CF manufacturing.
- Focus will be polyacrylonitrile (PAN) based CF

| Precursor spinning and synthesis | Oxidation | Carbonization | Surface treatment and sizing application | Cost modeling |
|---|---|---|---|---|
| • Increased polymer molecular weight (MW)<br>• Reduced polydispersity | • Oxidation stretch<br>• Zone temperature optimization | • Pre-carbonization stretch<br>• Zone temperature optimization | • Optimized surface for improved strength translation | • Cost reduction achieved through increased yield |

# Track II –Composite Laminate Innovation (Tasks 4, 6, and 8)

- Overall target is enhanced load transfer efficiency
- Benefits of enhanced load transfer efficiency include:
  - Reduced pressure vessel cost through reduction in material usage
  - Reduced pressure vessel cost through increased throughput
  - Lighter weight tanks
  - Reduced cylinder envelope

# Track III – Tank Design Innovation and Modeling (Tasks 5 and 7)

PNNL has developed a multiscale modeling approach to model $H_2$ storage pressure vessels incorporating inputs from project partners.

**PNNL, Hexagon**
New resin and composite laminate innovation

**CEM, ORNL**
Low-cost, high-strength CF development, interfacial modification

**Modeling Objectives**
- Burst pressure prediction
- Guide material selection
- Tailor layups
- Meet burst pressure target
- Perform weight and cost analyses

# Track IV – Pressure Vessel End of Life Innovation (Task 9)

- Mild chemical methods to reclaim and/or recycle CF from pressure vessels
  - Depolymerization of the carbon fiber-epoxy composite
  - Determination of recovered carbon fiber and depolymerized resin mechanical properties
  - Testing of composite samples using recycled CF and depolymerized resin

Pressure Vessel Composite Material

Composite Recycling Process

Fiber Recovery

Resin Recovery

# Approach – Safety Planning and Culture/DEIA/Community Benefits Plan

- Project operating under Hexagon Environmental, Health, and Safety policy 0113
- Safety is reviewed during each monthly meeting with partners
- No DEIA plan required for this project
- The project operates under Hexagon Group's diversity and inclusion plan 0105, which can be found here: https://hexagongroup.com/sustainability/ethics-compliance
  - Develop diversity and inclusion training programs
  - Define and develop data to measure, track and promote continuous diversity and inclusion improvements
  - Encourage all employees to support all Hexagon diversity and inclusion initiatives and goals

HEXAGON AGILITY

# 2023 AMR Accomplishments (May 2022-April 2023)

- Precursor spinning and conversion
  - Scaled-up precursor polymer runs have been completed at CEM, resulting in fiber oxidized density of 1.35 g/cc on both the 1K bench-scale and 24K pilot lines
  - Synthesis of PAN at ORNL has been successfully scaled up to 20L with a molecular weight between 150-180 kDa with polydispersity less than 1.5
- Surface treatment
  - Fiber surface treatment/sizing studies at CEM and ORNL demonstrate IFSS compared to baseline, with improvements in line speed at ORNL
- Vessel and cost modeling
  - Vessel resin sensitivity tool can be used to screen resins
  - Cost modeling developed for the carbon fiber process with elements including precursor polymerization and spinning, stabilization/oxidation, carbonization, and post-treatment/packaging
- Comment from the 2023 AMR
  - The project should clarify other anticipated risks or barriers regarding commercialization, assuming tensile properties are maintained and expected fiber cost is reduced.
    - Adjusting from 3k tow to 24k fiber for commercial scale winding
    - Carbon fiber demand from markets other than pressure vessels are not anticipated
    - Uncertainty of the Hydrogen market requiring carbon fiber, especially the scale will dictate the cost of manufacturing
    - Cost of hydrogen and its availability universally

# Phase 1 Accomplishments and Progress – Fiber Spinning

Phase 1 targets:
- Scale up of precursor production volume with molecular weight > 150 kDa, polydispersity < 2.0
- Precursor fiber tensile strength > 100 ksi and elongation of 10%
  - Targets were established to positively impact final CF properties and decreases material losses during spinning and conversion
- Converted fiber achieved a tensile strength > 650 ksi and a modulus ≥ 35 Msi
  - Tensile strength target chosen as 650 ksi was anticipated to favorably translate to pilot-scale development
- Projected CF cost < $15/kg

## CEM Accomplishments

- Precursor synthesis
  - Polymers from CEM's European Carbon Fiber (ECF) 24K pilot line studied producing precursors with a polydispersity index (PDI) < 2.0.
- White fiber production
  - White fiber from ECF facility stretched, yielding elongation < 10% and white fiber tensile strength > 100 ksi
- Carbon fiber conversion
  - Oxidation densities met at 2x normal oxidation line speeds
  - Converted ECF white fiber yielded a 24k carbon fiber tow strength > 725 ksi and tensile modulus > 35 Msi at 1.5x conversion line speeds
  - Carbon fiber cost, reported directly to DOE, between $15/kg and $20/kg
- Carbon fiber tested on two subscale vessels was on par with baseline carbon fiber

## ORNL Accomplishments

- Precursor synthesis
  - Airgap spinning process developed for terpolymer PAN to address inconsistent fiber roundness and fiber surface finish with wet spinning
  - Precursor average molecular weight > 185 kDa and a polydispersity of ~1.7
- White fiber production
  - Trials in airgap spinning yielded elongation of 1.3% and white fiber strength of 120 ksi
- Carbon fiber conversion
  - Conversion optimization using commercially available PAN white fiber yielded a carbon fiber tensile strength of 686 ksi and a modulus of 42 Msi, with single filament testing
  - Tow level testing is believed to increase tensile strength results by ~10%
  - Conversion optimization process will be applied to ORNL air-spun terpolymer

# Phase 1 Accomplishments and Progress – Cost Modeling

Phase 1 targets:
- Demonstrate a projected tank cost efficiency of < $12/kWh and gravimetric capacity of ≥ 1.5 kg/kWh

- Cost model assumptions
  - CSA HGV2 Standard
  - 100,000 units/year factory
  - Vessel manufactured from carbon fiber and general-purpose epoxy resin
  - PA Liner, aluminum bosses, and foam domes derived from Program Record
  - 10% ROI on composite tank processing
  - DOE supplied values:
    - BOP, valve, and regulator data
    - Labor rate of $59,000/year
    - Hydro testing and Helium leak testing
- **Projected tank cost: $12.79/kWh**
- **Gravimetric capacity: 1.71 kg/kWh**

| Cost Model Parameters (100,000 Units) | Units | Program Record | | CORTC | |
|---|---|---|---|---|---|
| | | Cost | Mass (kg) | Cost | Mass (kg) |
| Composite Tank Total Cost and Mass | $ | 1926 | 99 | 1382 | 81.6 |
| Balance of Plant (BOP)<br>$486 (15.4 kg) + $219 (3 kg) + $288 (3.6 kg) | $ | 993 | 22 | 993 | 22 |
| Assembly | $ | 11 | | 11 | |
| Total Tank Cost = | $ | 2930 | 121 | 2386 | 103.6 |
| Tank Cost = | $/kWh | 15.71 | | **12.79** | |
| Tank Mass = | kg/kWh | | 0.65 | | 0.58 |
| Gravimetric Effic. = kWhr/kg (5.6kgH2, 33.31kWh/kg) | kWh/kg | | 1.47 | | **1.71** |
| Gravimetric Effic. = kgH2/kg system | kgH2/kg Syst | | 0.046 | | 0.054 |
| Composite Contribution to System Cost | $ Comp/kWh | 9.99 | | 7.08 | |



HEXAGON AGILITY

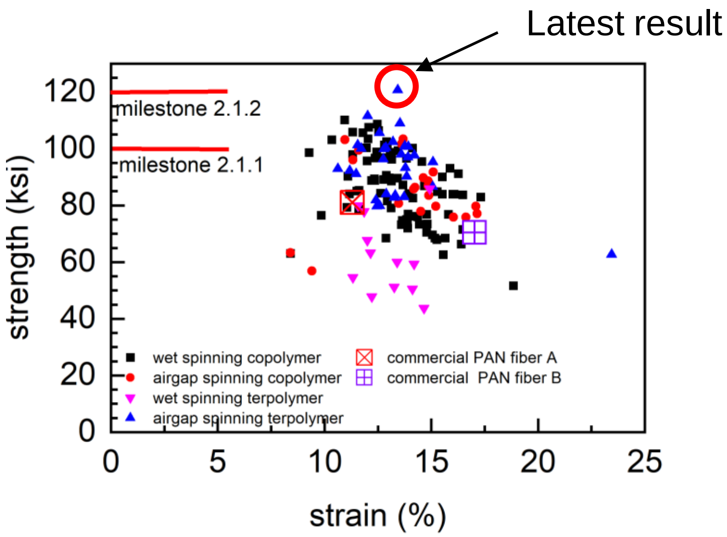
# Phase 1 Accomplishments and Progress – Down-select

• Down-select scoring

| Requirement | Achievement | Downselect Scoring |
|---|---|---|
| Produced 100m continuous CF | Multiple ASTM ring sets wound from CEM and ORNL fiber (245 m continuous fiber required for 1 ring set) | **Go** |
| | 2 Subscale cylinders wound from CEM fiber (100 m continuous fiber required for 1 cylinder) | |
| CF Score ≥ 3 | CEM carbon fiber tensile strength > 725 ksi | 3 |
| | CEM carbon fiber tensile modulus > 35 Msi | 0 |
| | CEM projected fiber cost between \$15/kg and \$20/kg, provided to DOE | 2 |
| | **Total** | **5 (Go)** |
| Tank performance score ≥ 3 | Tank and system projected cost of \$12.79/kWh | 1 |
| | Gravimetric capacity of 1.71 kWh/kg | 2 |
| | **Total** | **3 (Go)** |
| **Final Score (CF score + Tank score x 2)** | | **11 (5 + 3 x 2)** |

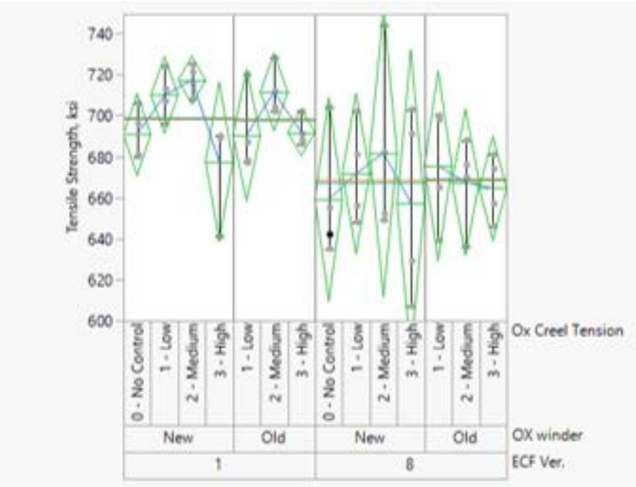
# Phase 2 Accomplishments and Progress – Fiber Spinning and Conversion

- Fiber Spinning
  - Milestone 3.2.2 Progress: CEM characterization of stretched PAN has shown indications of optimal level of fiber stretch and corresponding crystal size
  - Milestone 2.1.2 Progress: ORNL produced 1000+ m PAN fibers with 120 ksi tensile strength and 13% elongation, 50%+ increased spinning line with ORNL synthesized high MW low PDI PAN precursor




Strength vs. Strain of ORNL PAN fiber showing results exceeding Milestones 2.1.1 and 2.1.2

- Fiber Conversion
  - Milestone 3.2.2 Progress: ORNL stabilization and carbonization processes for ORNL PAN fibers produced CF above 650 ksi tensile strength and 42 msi tensile modulus measured by single filament tensile test
  - Milestone 3.2.2 Progress: CEM further refining oxidation process with increases in fiber stretch/line speeds and implementation of tension control, producing equivalent converted fiber exceeding 700 ksi TS
  - 2 subscale Hexagon vessels wound with CEM fiber burst results match or exceed vessels with baseline fiber



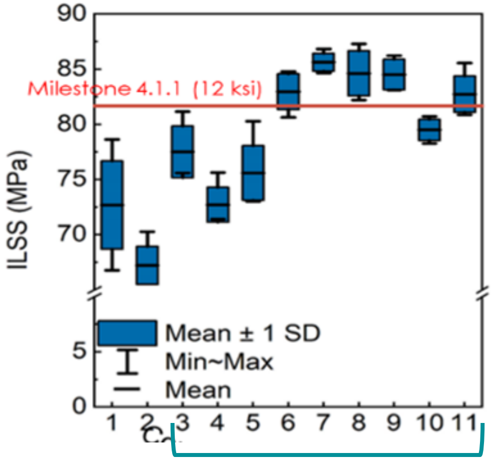

Tensile Strength (TS) of converted CEM fiber processed with various Oxidation creel tension settings

CEM fiber burst results

| Fiber | Burst Difference From baseline |
|---|---|
| Baseline | - |
| CEM | +0.7% |
| CEM | -6% |

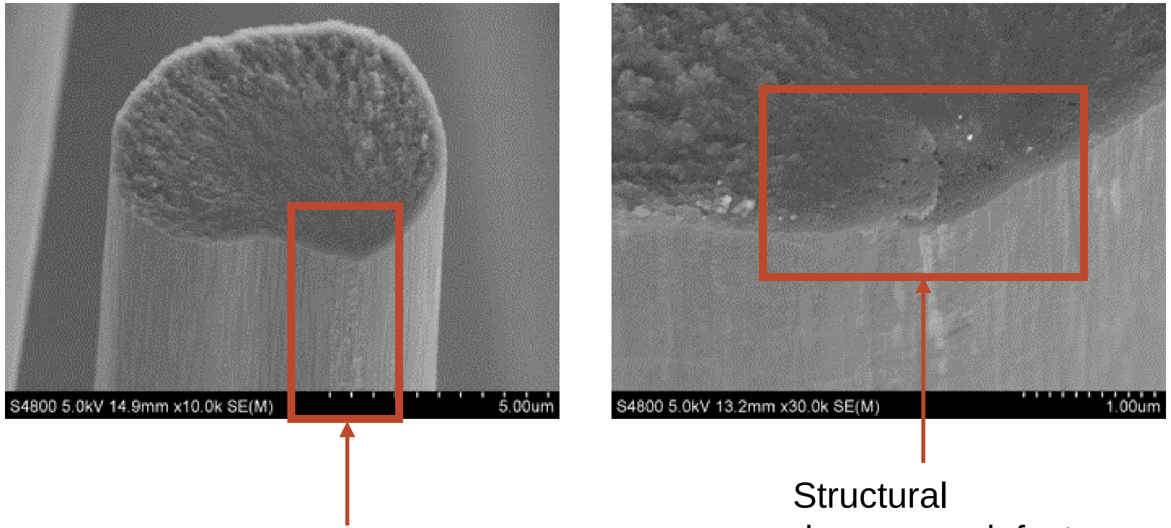
# Phase 2 Accomplishments and Progress – Surface Treatment and Fiber Characterization

- Fiber Surface Treatment
  - Milestone 4.1.2 Progress: CEM sizing epoxy formulation trials show reduced fiber width and variability compared to standard epoxy and phenoxy chemistries, lower fiber tension during processing
  - Milestone 4.1.2 Progress: CEM Optimized surface treatment was able to deliver ILSS > 12 ksi
  - CEM fiber surface treatment process capable of matching baseline fiber surface functionality
  - Milestone 4.4.1 Progress: ORNL single step electrochemical process replaces two individual surface treatment and sizing processes, achieved an ILSS value greater than 12 ksi with converted commercial PAN




ILSS results from ORNL single step electrochemical process performed on commercial fiber, exceeding Milestone 4.1.1 target (Indices 3-11)

- Fiber Characterization
  - ORNL Process shows more uniform distribution of sizing on fiber
  - CEM has implemented a new large tow strander to test 24K tow fiber
  - CEM fiber defect analysis showed fiber defects stemming from sticking, and unsticking, of fiber prior to carbonization impacts CF strength



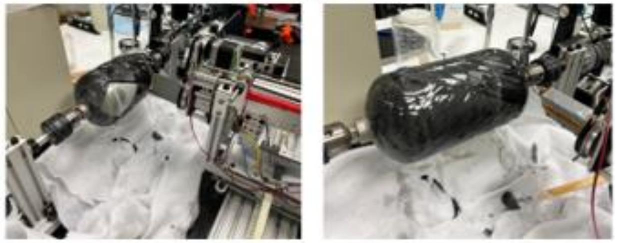

SEM image of CEM showing two different types of fiber damage, sticking and structural damage

HEXAGON AGILITY

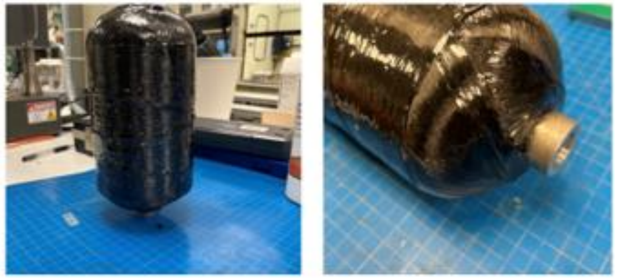
# Phase 2 Accomplishments and Progress – End-of-Life Recycling

## Tank winding using X-winder

Winding Process



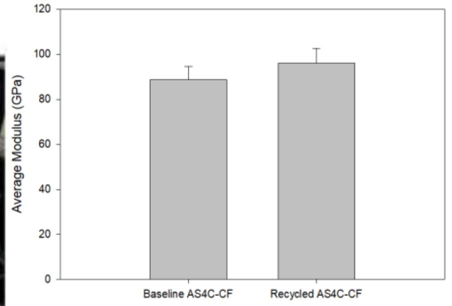
Post Cure

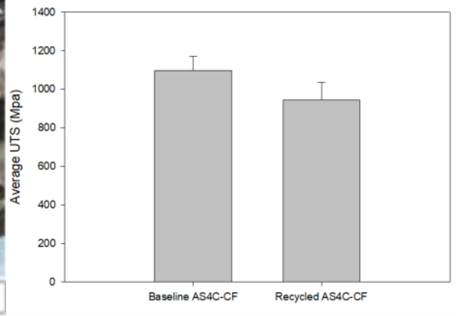


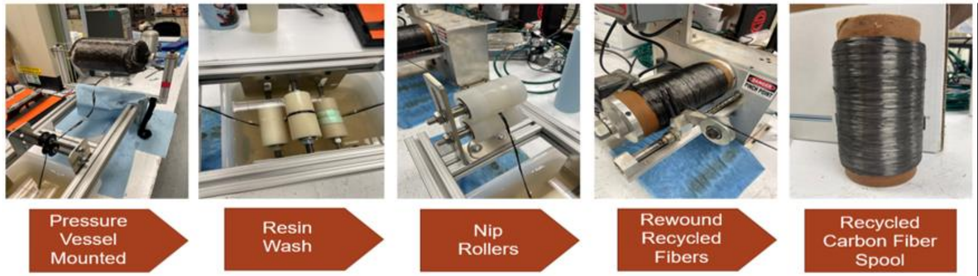
## Solvolysis process to depolymerize resin


## Unwind and reclaim CF

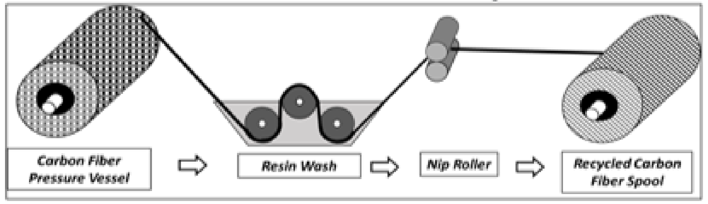
Overview of Functional Unwinding Process




Carbon Fiber Pressure Vessel Unwinding Process




***<u>Phase II progress successfully demonstrated reclaiming long, continuous CF and polymer matrix from overwrapped pressure vessels!</u>***

***Milestones:***

- 9.1.1 – Demonstrate degradation of crosslinked polymer within 90% of initial baseline matrix material, i.e., 90% of matrix polymer is turned into oligomers soluble in organic solvents. **[Q11] – 80% complete**
    - 6.71 g resin recovered from 7.40 g initial weight (~91%);
    - Chemical analysis underway (e.g., NMR)

HEXAGON AGILITY

# Remaining Challenges and Barriers

| | |
|---|---|
| Spinning | • Reduce airgap spun, terpolymer PAN fiber diameter variation at ORNL<br>• Reduce variability between spinning trials at CEM |
| Conversion | • Lower costs through line speed increase at oxidation and carbonization at CEM<br>• Develop advanced stabilization and carbonization processes from ORNL PAN fiber to CF with 700-750 ksi tensile strength and 35 msi tensile modulus, reduce cost in stabilization and sizing processes |
| Scale-Up | • Simulate scenarios for CEM commercial plants |
| Composite Innovation | • Span gap between High Performance (HP) resin and carbon fiber development<br>• Potential benefits of HP resin could offset cost savings of the fiber |
| Testing | • Scale-up testing from single filament fiber to carbon fiber tow |
| Modeling | • Refine cost modeling through analysis of cylinder packaging on vehicle and decreased fiber costs |



HEXAGON AGILITY

# Planned Future Work – Phase 2

- ORNL Planned Future Work
  - Task 2: to improve control of the spinning process with the new spinneret for more uniform PAN fibers;
  - Task 3: to continue developing advanced stabilization and carbonization processes from ORNL PAN fiber to CF with 700-750 ksi tensile strength and 35 msi tensile modulus with reduced cost in stabilization and sizing processes.

- CEM Planned Future Work
  - Reduction of Variability
  - Carbon Fiber Precursor Fiber: Development of OX/Carb. for new Variants
  - Further reduction of Carbon fiber cost : Evaluation of Higher Speeds
  - Tensile Translation : Work on new sizing and new surface treatment techniques
  - Fiber tow spreadability analysis
  - Carbon Fiber Production for bigger size vessels than used in Phase 1

- PNNL Planned Future Work
  - Further develop gas vapor recycling process
  - Continue testing high performance resin to pair with carbon fiber produced by ORNL and CEM
  - Development of recycled resin for pressure vessel use

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

# Planned Future Work – Phase 2

**Milestone Q9**
Demonstrate CFs with high crystalline orientation parameter (f>0.7) (ORNL)

**Milestone Q10**
Demonstrate CFs with 2 to 5 nm crystalline domain (ORNL)

**Milestone Q11**
Demonstrate degradation of crosslinked polymer within 90% of initial baseline matrix (PNNL)

**Milestone Q12**
**4.1.2**
Demonstrate ≥14 ksi ILSS (CEM)
Measure Shear Strength by 0° Short Beam Shear Test

**Milestone Q13**
**3.1.3**
Produce Gen. 2 carbon fiber (24K) for sub-scale Vessel Evaluation (CEM)

**Milestone Q16**
**4.1.3**
Sizing chemistry and process optimized for a 50% reduction in width variability on large scale processing (CEM)

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

HEXAGON AGILITY

# Summary

- Phase 1 Accomplishments
  - Both CEM and ORNL have produced >100m continuous fiber exceeding target TS of 650 ksi and tensile modulus of 32 Msi that have been tested with Hexagon wound test samples
  - CEM project fiber cost from PAN development and process improvements yielded a cost between $15/kg to $20/kg
  - The cost model developed projected a system cost of $12.79/kWh with a gravimetric capacity of 1.71 kWh/kg
- <u>Phase 1 accomplishments led to project selection through down-select process</u>
- Phase 2 Progress
  - Further refinement of equipment at both CEM and ORNL to reduce variation in fiber diameters, increase processing speeds, and add to testing capabilities
  - Fiber surface treatment trials match baseline carbon fiber surface functionality
  - End-of-life recycling demonstrates the ability to wind and unwind a pressure vessel with 91% resin recovery

The project team successfully met the requirements for the down-select review and has transitioned into Phase 2 of the project with progress made to the upcoming milestones.



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