Precursor Processing Development for Low-Cost, High-Strength Carbon Fiber for Composite Overwrapped Pressure Vessel Applications

Matthew C. Weisenberger (Primary Contact), E. Ashley Morris
University of Kentucky Center for Applied Energy Research
2540 Research Park Drive
Lexington, KY 40511
Phone: (859) 257-0322
Email: Matt.Weisenberger@uky.edu

DOE Manager: Bahman Habibzadeh
Phone: (202) 287-1657
Email: Bahman.Habibzadeh@ee.doe.gov

Contract No: DE-EE0008095

Project Start Date: September 1, 2017
Project End Date: Project continuation and direction determined annually by DOE

Overall Objectives

- Demonstrate ≥100-filament, air-gap spinning of the small-diameter TechPAN precursor polymer, followed by oxidization, carbonization, and characterization of the resultant carbon fiber.
- Demonstrate single-filament carbon fiber properties approaching 4.9 GPa strength and 230 GPa modulus (similar to T700S).
- Achieve <1 wt% residual solvent in fiber with minimal residence time for the water-minimization strategy.
- Demonstrate ≥10-filament, air-gap, *hollow-fiber* spinning of TechPAN precursor polymer with outer diameter <100 µm and inner diameter <50 µm with specific strength and modulus approaching 635 MPa/g/cc and 8.5 GPa/g/cc.
- Demonstrate lower-energy solvent recovery through sorption in activated carbon modules with capability to capture >50% of the solvent effluent and their thermal regeneration with <15% loss in specific surface area.
- Demonstrate hollow carbon fiber tensile properties approaching 4.9 GPa strength and 230 GPa modulus (similar to T700S), with an analysis of specific strength pertaining to part-weight consideration.
- Deliver a cost analysis of the precursor and carbon fibers with a targeted cost potential of $12.60/kg.

Fiscal Year (FY) 2018 Objectives

- Demonstrate ≥100-filament, air-gap spinning of the small-diameter TechPAN precursor polymer, followed by oxidization, carbonization, and characterization of the resultant carbon fiber.
- Demonstrate single-filament carbon fiber properties approaching 4.9 GPa strength and 230 GPa modulus (similar to T700S).
- Achieve <1 wt% residual solvent in fiber with minimal residence time for the water-minimization strategy.
- Deliver cost analysis showing that a reduction of ≥10%, from $29.40/kg to $26.46/kg, is possible via the low-cost TechPAN polymer.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan[1]:

- System Weight and Volume
- System Cost
- Materials of Construction.

Technical Targets

This project is focused on developing novel precursors for low-cost, high-strength carbon fiber (CF). Insights gained from these studies will be applied to composite overwrapped pressure

[1] https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22

vessels. The carbon fibers developed here seek to fulfill the following DOE 2020 hydrogen storage targets:

- CF cost [1]: $12.60/kg CF
    - Project status (given starting CF cost of $29.40/kg): $25.35/kg CF
- Tensile strength: 4.9 GPa (711 ksi)
- Tensile modulus: 230 GPa (33.4 Msi)

FY 2018 Accomplishments

- Demonstrated ≥100-filament, air-gap spinning of the small-diameter TechPAN precursor polymer, followed by oxidization, carbonization, and characterization of the resultant carbon fiber using the custom-built, strain-controlled thermal conversion device.
    - TechPAN is a low-cost, non-exclusive, special acrylic fiber-grade terpolymer that can be supplied to the fiber industry at the tens of kilotonne scale at an anticipated cost of $3/kg (typical exclusive, aerospace-grade polyacrylonitrile [PAN] polymer costs $7.05/kg [2]).
    - Here, we have proven the capability of this low-cost PAN polymer to be spun and to produce high-quality carbon fibers. This represents a path to lower the polymer-precursor cost by 57%, which lowers the final carbon fiber cost by **13.8%**.
- Demonstrated single-filament carbon fiber properties approaching 4.9 GPa strength and 230 GPa modulus (similar to T700S) using TechPAN precursor.
    - During Phase 1 of the project, it is shown that TechPAN precursor can result in T700-quality properties, well exceeding the modulus metric and clearly showing 700 ksi strength at 10-mm gauge length. This demonstration proves that low-cost TechPAN-derived CF can offer a lower-cost and brand-independent path to T700 properties in CF.
- Achieved a <1 wt% residual solvent in fiber with minimal residence time for the water-minimization strategy.
    - Minimization of water is critical to reducing the cost of solvent recovery, which costs $1.39 per 1 kg of precursor fiber.
- Delivered a cost analysis showing that a reduction of ≥10%, from $29.40/kg to $25.35/kg, is possible via low-cost TechPAN polymer.
- Demonstrated a coagulated fiber with hollow core, coalesced shell, and circular cross section from the 2C-shaped spinneret.

INTRODUCTION

Carbon fiber (CF) is central to produce lightweight, high-pressure, composite overwrapped pressure vessels (COPVs), which are used for onboard storage of hydrogen for fuel cell vehicles. In 2015, CF cost accounted for 62% of the cost of a hydrogen storage system, as COPVs were manufactured with T700S CF at $29.40/kg CF [3]. The high cost of hydrogen storage, largely attributed to the carbon fiber cost, limits the application of fuel cells in vehicles. Therefore, we proposed to develop fiber processing to demonstrate carbon fiber tensile properties similar to T700S with a production cost potential of $12.60/kg or less.

We are investigating solutions to **critical issues stemming from the precursor** that significantly contribute to the cost of CF—namely, high polymer cost, inefficient water use and solvent recovery, low fiber throughput, energy-intensive conversion, and high coefficient of variation between fibers. We anticipate hollow precursor fibers to significantly increase the throughput rate of thermal processing and to offer very high specific tensile properties.

APPROACH

We proposed a three-front approach, leveraging our unique precursor fiber processing capabilities and skillsets. To address the issues described above, we proposed the following three approaches:

1. Use and prove out a *new, low-cost, high-volume, high-quality* PAN-based precursor terpolymer, exclusively under investigation at the University of Kentucky Center for Applied Energy Research (UK CAER), known as TechPAN.
2. Develop *air-gap* solution spinning of small-diameter and *hollow* precursor filaments in multifilament continuous tows.
3. Drastically increase water and energy-use *efficiency* incurred in wash-water/solvent separations using a specially designed wash bath and activated-carbon recovery system.

RESULTS

The first milestone for the project required the demonstration of air-gap stability of nascent TechPAN polymer jets during air-gap spinning. Indeed, using our unique fiber-processing capabilities and skills sets, TechPAN precursor filaments were successfully air-gap spun in multifilament continuous tows, typically collecting 1 km in length on each spool. A typical spool of TechPAN precursor fiber is shown in Figure 1. Further work was successful in producing round cross-section filaments (as opposed to undesirable non-round or bean-shaped cross sections), shown in the inset of Figure 1, with targeted diameters of about 10 μm. These high-quality precursors from low-cost TechPAN are vital to producing high-quality carbon fibers for the replacement of costly T700 CF in COPVs.

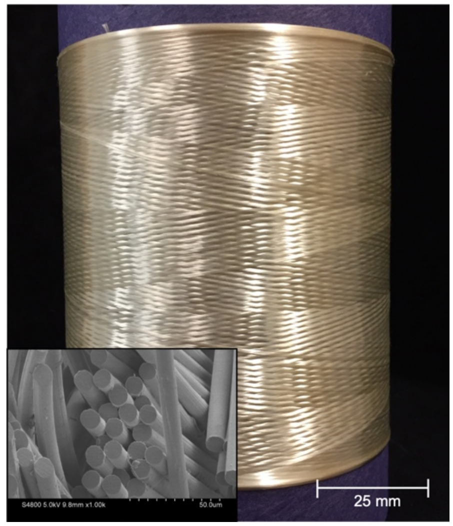

Figure 1. Typical spool of multifilament continuous TechPAN precursor fibers with round, 10-µm fiber cross sections shown in the inset. A typical spool contained 1 km of multifilament tow length.

An efficient strain-controlled thermal conversion apparatus was designed and fabricated to enable batch conversion of TechPAN precursor fibers to CF without the need for large amounts of fiber, as is required for typical continuous thermal conversion ovens. The creation of this apparatus allowed for small-scale, batch conversion of precursor fiber with minimal fiber, while still providing strain control necessary during stabilization and carbonization to produce high-quality CF. Using this system, UK CAER successfully produced CF with tensile properties very close to those of T700 CF. This accomplishment successfully proved that low-cost TechPAN was capable of producing CF with properties amenable for COPV production.

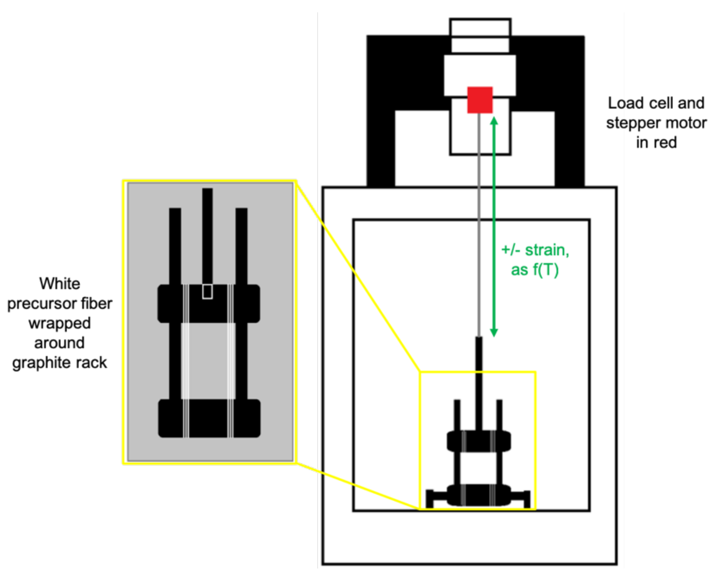

Figure 2. Efficient strain-controlled thermal conversion apparatus capable of applying programmed strain as a function of time (oven temperature) for the small-scale conversion of TechPAN precursors to CF

To reduce the high costs associated with solvent recovery (typically performed with energy-intensive distillation), UK CAER is in the process of minimizing water use during spinning, as well as performing active solvent recovery via an activated-carbon recovery system, as shown in Figure 3. Analyses of commercially available activated carbons (ACs) were made to determine adsorption efficiency for the spinning solvent (dimethylsulfoxide, or DMSO). Breakthrough curves were generated as a function of activated-carbon mass, and studies were completed on DMSO concentration at the beginning and end of the wash bath to determine the increase in DMSO content over time. It was determined that the selected commercially available activated carbon is capable of adsorbing 1 g of DMSO for every 3 g of AC. This performance is indeed much better than expected. Additionally, using the data thus far, it is estimated that the use of AC will reduce freshwater usage by up to 86%. Our goal is to achieve at least a 50% reduction in freshwater use. Work is continuing in this area.

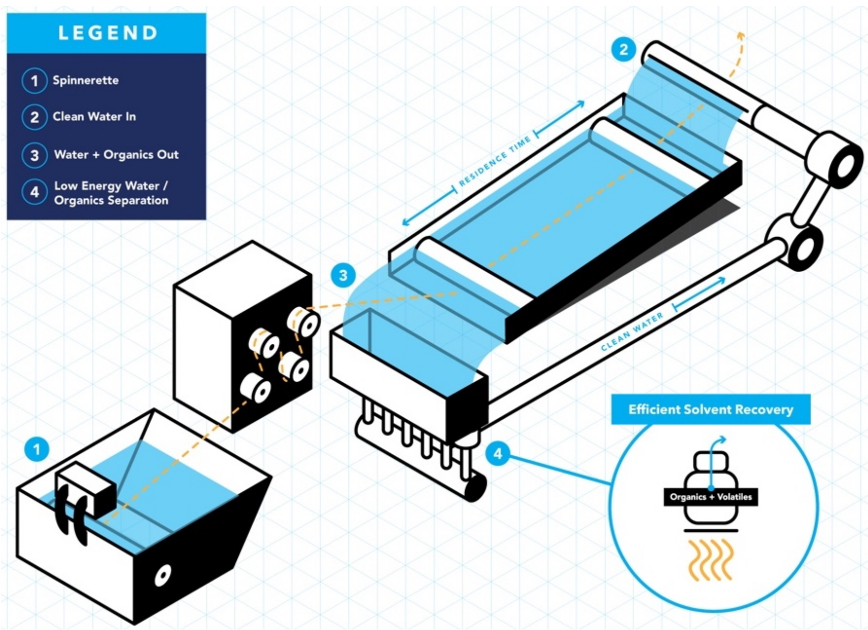

Figure 3. Efficient wash-water–solvent recovery processing concept, where low-energy separation is envisioned using activated-carbon module technology

Finally, the team is ahead of schedule with regard to producing hollow filaments from TechPAN and has already demonstrated coagulated fiber with hollow-core, coalesced-shell, and circular cross section using a 2C-shaped capillary spinneret (a non-bore-fluid approach), shown in Figure 4. The further development of these hollow filaments is the major focus of Budget Period 2.

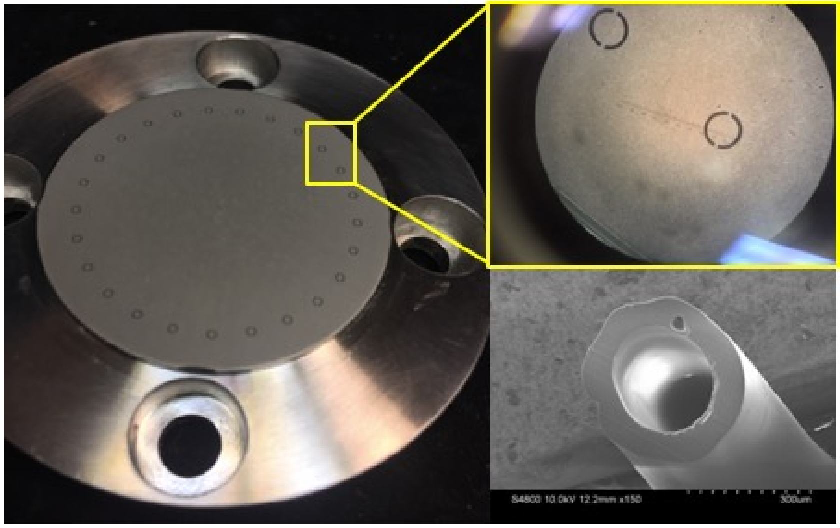

Figure 4. (Left) The 25-hole shaped spinneret "2C" is shown, with a close-up of the capillary design on the top right. The outer radius is 500 microns and the inner radius is 400 microns, with an annulus of 100 microns. Finally, on the bottom right is an image of a TechPAN hollow, circular fiber spun using this spinneret.

CONCLUSIONS AND UPCOMING ACTIVITIES

The work completed in Year 1 (Budget Period 1) has successfully proven the viability of the low-cost TechPAN as a viable precursor to achieve T700 CF properties. Additionally, the work on water minimization and solvent adsorption via activated carbon is proving very promising. Finally, we are ahead of schedule with regard to hollow-fiber spinning, having already produced a hollow-core, coalesced-shell, and circular cross-section fiber.

Future work and accomplishments by UK CAER include:

- Demonstrating ≥10-filament, air-gap, hollow-fiber spinning of TechPAN precursor polymer with outer diameter <100 µm and inner diameter <50 µm with specific strength and modulus approaching 635 MPa/g/cc and 8.5 GPa/g/cc.
- Demonstrating lower-energy solvent recovery through sorption in activated-carbon modules with the capability to capture >50% of the solvent effluent and demonstrating their thermal regeneration with <15% loss in specific surface area.
- Demonstrating hollow carbon fiber tensile properties approaching 4.9 GPa strength and 230 GPa modulus (similar to T700S), with an analysis of specific strength pertaining to part-weight consideration.
- Delivering a cost analysis of the precursor and carbon fibers with a cost potential of $12.60/kg.

FY 2018 PUBLICATIONS/PRESENTATIONS

1. R. Sarabia-Riquelme, N. Hochstrasser, A. Morris, and M. Weisenberger. "Insights into The Relation between Yield Point, Plastic Modulus and Degree of Crystallinity of PAN Precursor Fiber," presented at CARBON 2018, the International Carbon Conference in Madrid, July 1–6, 2018.
2. DOE Fuel Cell Tech Team meeting, Detroit/WebEx, May 16–17, 2018.
3. DOE Annual Merit Review and Peer Evaluation Meeting, Washington, DC, June 13–15, 2018.

REFERENCES

1. DOE Fuel Cell Technologies Office Annual FOA: DE-FOA-0001647, Office of Energy Efficiency and Renewable Energy (2016), https://eere-exchange.energy.gov/.
2. David C. Warren, "Development of Low Cost, High Strength Commercial Textile Precursor (PAN-MA)," DOE Hydrogen and Fuel Cells Program 2014 Annual Merit Review and Peer Evaluation Meeting Proceedings (2014), https://www.hydrogen.energy.gov/pdfs/review14/st099_warren_2014_o.pdf.
3. G. Ordaz, C. Houchins, and T. Hua, "Onboard Type IV Compressed Hydrogen Storage System – Cost and Performance Status 2015," DOE Hydrogen and Fuel Cells Program Record (2015), https://www.hydrogen.energy.gov/pdfs/15013_onboard_storage_performance_cost.pdf.