

IV.F.2 Melt Processable PAN Precursor for High-Strength, Low-Cost Carbon Fibers

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ORNL's Precursor Development System and yielding 20 Msi modulus and 200 ksi strength.

Technical Barriers

High-strength carbon fibers account for approximately 65% of the cost of the high-pressure storage tanks. 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:

- (A) System Weight and Volume
- (B) System Cost
- (D) Durability/Operability
- (G) Materials of Construction

High strength carbon fiber enables the manufacture of durable, lightweight, compressed hydrogen storage vessels for use in high-pressure storage. Unfortunately, current high strength carbon fiber products are far too expensive to meet DOE goals for storage system costs.

Technical Targets

Working targets are approximate equivalence with Toray T-700 at substantially reduced production costs:

- 700 ksi ultimate tensile strength
- 33 Msi tensile modulus
- Production cost reduction of at least 25% versus baseline

FY 2013 Accomplishments

- Improved spinning and drawing equipment and processes have been developed and implemented for producing initial sample quantities of melt-spun polyacrylonitrile (PAN) precursor adequate to meet feasibility demonstration milestones. Appropriate conversion recipes were developed to match the precursor characteristics. The Go/No-Go milestone of 15 Msi modulus and 150 ksi strength was achieved with converted carbon fiber demonstrating basic feasibility of this approach.
- A number of "engineering" obstacles associated with this approach have been resolved and approaches for further scaling up to the next level of development have been identified. Properties projected to be met in FY 2014 of 25 Msi modulus and 250 ksi strength were actually achieved with one sample during this period, but

Overall Objectives

- Demonstrate means to achieve cost reduction of $\geq 25\%$ in manufacture of carbon fiber meeting properties of industry baseline carbon fiber utilized in fabrication of composite vessels for hydrogen storage.
- Develop and demonstrate new chemistry and spinning techniques and assess capability for advanced conversion technologies to meet needs in reducing carbon fiber manufacturing costs for fiber meeting project performance goals.

Fiscal Year (FY) 2013 Objectives

- Demonstrate spinning of a sample tow of ~10-12 micron fibers from high molecular weight ($>200,000$ MW) dope that can be easily spooled and de-spooled for conversion at ORNL's Precursor Development System and yielding 15 Msi modulus and 150 ksi strength.
- Demonstrate spinning of a sample tow of ~10-12 micron fibers from high MW ($>200,000$) dope for conversion at

larger scale precursor processing, enhanced chemistry, and more optimized conversion processes are required to meet ultimate project objectives. Based on success to date, a roadmap to achieve these goals has been outlined for execution in the following reporting periods.



INTRODUCTION

The exceptional strength-to-weight ratio of carbon fiber composite tanks makes them prime candidates for use with materials-based, cryogenic, or high-pressure gas for both vehicular and stationary storage applications. Cost is the primary issue with composite tank technology. A critical challenge lies in the cost of the fiber and the manufacture of composite tanks. Current projections of the manufactured cost per unit for high production volumes are about a factor of nine above storage system targets, and it is estimated that about 40-70% of the unit cost is due to the base cost of the carbon fiber (approximately 40% of the fiber cost is due to the precursor and the remainder due to thermal processing). Research and development (R&D) is needed as composite storage technology is most likely to be employed in the near term for transportation applications and will be needed for most materials-based approaches for hydrogen storage.

Currently, composite tanks require high-strength fiber made from carbon-fiber grade PAN precursor. Manufacturing R&D is needed to develop lower cost, high quality PAN or alternate precursors and reduced energy or faster conversion processes for carbon fiber, such as microwave and/or plasma processing. Developing and implementing advanced fiber processing methods has the potential to reduce cost by 50% as well as provide the technology basis to expand U.S. competitiveness in high-strength fiber manufacturing [1]. This project will leverage previous and ongoing work of the FreedomCAR's program to develop a low-cost, high-strength carbon fiber. Analysis is ongoing in related DOE projects to determine appropriate targets for storage systems as a function of construction materials and fabrication costs. Until targets are definitively established, this project will seek to develop carbon fibers with properties equivalent to Toray's T700/24k fiber (24k tow, 700 ksi ultimate tensile strength, 33 Msi tensile modulus), and reduce production costs of the fiber by at least 25%.

APPROACH

This project is structured into tasks focused on precursor development and conversion process improvements. Development and demonstration of melt-spinnable PAN is the project's primary precursor option. If successful, melt spinning is projected to be significantly less costly than wet spinning with capability to produce high quality, relatively

defect-free precursor. This requires concurrent activities in both development of melt-stable PAN copolymer and blends as well as the processes necessary to successfully spin the formulations into filamentary tows. Melt processing of PAN is a difficult issue, although Virginia Tech and others have made modest progress over the last decade [2-6]. One of the principal problems is that PAN degrades (cross-links) even without main chain scission or weight loss, and this essentially precludes melt processing. Reactions of the side groups have been discussed in many reports [7-10]. These degradative reactions can take place both in an intra-molecular manner, but also via inter-molecular branching and gelation, which quickly alters the capacity for these materials to be melt-fabricated. At 200-220°C, the material can quickly increase in viscosity, thus rendering an intractable material in a very short time. Ideally, one would like to maintain constant viscosity for a required period, and practical considerations suggest that this should be at least 30 minutes or longer. Backup options include other precursor alternatives such as textile PAN, polyolefins, and incorporation of nanomaterials.

Demonstrating and down-selecting a precursor capable of meeting performance targets utilizing conventional conversion processing defines the pathway for the balance of project activities. In conversion, critical processability parameters include: (i) highly controlled temperature and stretching, especially during pre-treatment and stabilization; (ii) residence time in various conversion modules; (iii) optimal graphitization for maximum strength; (iv) uniform treatment of fibers throughout the tow; and (v) strict control of each of these parameter through all of the various stages of conversion operation. Related ORNL work in advanced processing technologies address these issues, with a focus on increasing line speed in a reduced footprint, with reduced energy consumption. Means to adapt these emerging processes will be developed and evaluated for applicability to meeting requirements of this program area. As the alternative approaches are demonstrated, the energy efficiency and overall economics of the complete system will be evaluated and forecast for production scale up.

RESULTS

During this period, the project team with sponsor encouragement decided to put precursor chemistry development work on hold in order to focus limited resources on demonstrating feasibility of the melt-spinning approach. For this demonstration effort, some baseline high MW PAN-based formulations are being utilized that, while representative of the processing requirements ultimately required to meet project goals, probably cannot be converted themselves into carbon fiber meeting those performance goals. Significant "engineering" obstacles have been encountered in utilizing the very simple experimental

equipment available in this project; a number of these hurdles have been overcome during this period and we have identified solutions for resolving others we expect to encounter on the pathway to our goals. Examples already implemented include improved spinneret design and construction, improved filtration, means for maximizing small sample utilization with integration of purging materials for maintaining open holes as the sample is expended, enhanced extrusion barrel heating, larger spinning pressure chamber, indexed take-up winding patterns, etc. Most recently, capability for precursor fiber drawing in a separate process between spinning and conversion has been incorporated. As we continue to resolve these issues, we have gained confidence that the approaches we have proposed do have great potential for meeting program goals given appropriate levels of resources.

A batch fiber drawing system was built to stretch as-spun PAN fibers. The system is good for trying and determining the drawing conditions for a specific fiber sample, but it is not good for generating long and continuous filaments. So a new continuous fiber drawing system was designed and built this year (see Figure 1). The system can use a steam bath, water bath or electric oven to heat the fibers, but the steam bath seems to work the best for PAN fibers.

The as-spun fibers were de-spooled and wound on an aluminum bobbin after passing through a water bath containing an antistatic agent, which made further handling of the fibers easier (Figure 2). The filaments were then put in a convection oven at 150°C for about five minutes for pre-conditioning. This was to remove the residual plasticizers from the fibers and reduce the voids in the fibers. The bobbin of annealed fibers was mounted onto the fiber drawing system and the fibers were drawn under saturated steam where up to a 600% draw ratio was reached so far with the diameter of drawn fiber reaching about 13 microns (see Table 1 and Figure 3). The drawn fibers (both sample #1 and #2) from Virginia Tech (VT) were sent to ORNL for evaluation.

The drawn PAN/VT fibers have been successfully converted to carbon fibers. The tensile strength and modulus



FIGURE 2. Drawn PAN/VT Fibers Generated with Water and Acetonitrile

TABLE 1. Spinning and Drawing Conditions for PAN/VT Fibers

As-spun fibers	Polymer	PAN/VT with 93 mol% PAN
	Plasticizer and content	Water 14 wt%, acetonitrile 14 wt%
	Spinning temperature	165°C
	Fiber formation zone P	170 psi, N ₂
	Number of spinneret holes	18
	Diameter of holes	55 μm
	Diameter of as-spun fibers	~35 μm
Drawn fibers #1	Heating media	Saturated Steam
	Steam pressure	18 psi
	Steam temperature	124°C
	Draw ratio (second stretch)	4
	Filament number	8
	Filament diameter	18 microns (to be confirmed)
Drawn fibers #2	Heating media	Saturated Steam
	Steam pressure	18 psi
	Steam temperature	124°C
	Draw ratio (second stretch)	6
	Filament number	8
	Filament diameter	13 microns (to be confirmed)

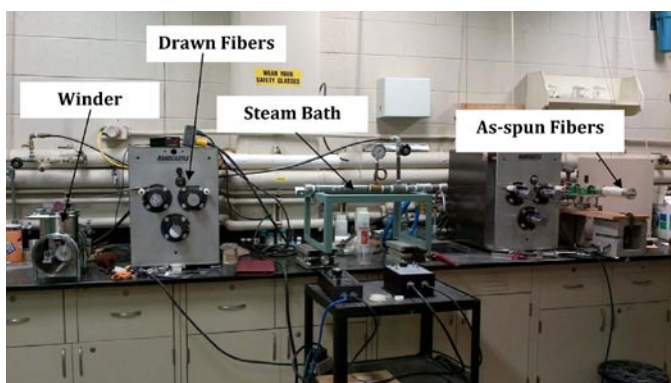


FIGURE 1. New Continuous Fiber Drawing System with Steam Bath

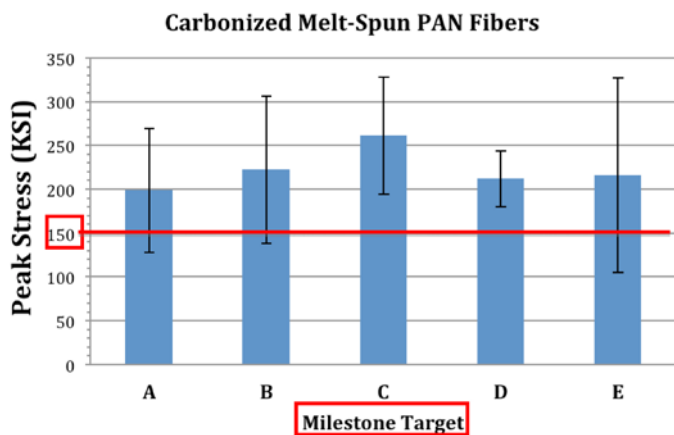


FIGURE 3. Tensile Strength of Carbonized Melt-Spun PAN Fibers—March 2013's Milestone is 150 ksi

of the carbonized fibers is shown in Figures 3 and 4, respectively. The strength over 150 ksi and modulus higher than 15 Msi for the carbonized fibers meets the goal of the critical Go/No-Go milestone for feasibility demonstration. Other samples significantly exceeded this critical milestone target including one sample with properties over 250 ksi and 25 Msi.

CONCLUSIONS AND FUTURE DIRECTIONS

The critical Go/No-Go milestone chosen by the project and program management team of 15 Msi modulus and 150 ksi strength for converted carbon fiber was achieved during this period. This milestone was chosen to establish a baseline indicative of technical feasibility for this project approach. Several samples processed during this period significantly exceeded this baseline property level.

Significant progress has been made in demonstrating melt spinning processes and producing precursor fiber in sufficient quality and quantity to begin carbon fiber conversion investigations. Mechanical properties of the melt spun precursor fiber are approaching those of commercially produced fibers. Initial conversion protocols have been developed and demonstrated indicating that we are indeed taking an effective approach and making progress beyond the stage-gate milestone established for taking this initiative to the next level of development.

Near-term objectives are for Virginia Tech to produce longer and more uniform tows that are then drawn in a secondary step as previously described. ORNL will characterize fiber and conduct more extensive conversion trials on precursor filaments generated using its precursor evaluation system. In this next stage of development, we will resume working the precursor chemistry we believe necessary to enhance baseline properties and move towards the ultimate goals of 33 Msi modulus and 700 ksi strength. We will

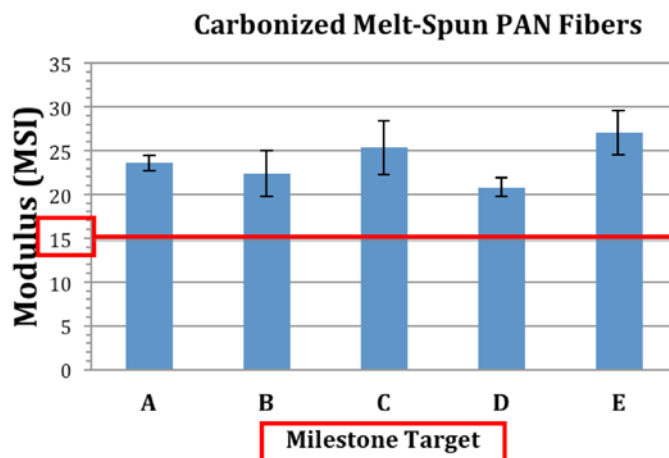


FIGURE 4. Tensile Modulus of Carbonized Melt-Spun PAN Fibers—March 2013's Milestone is 15 Msi

need to scale the spinning processes up so that we can work with larger tow sizes and more continuous tows in further enhancing the conversion processes and providing feedback to the chemistry and fiber forming development. The filaments at various steps of the conversion process will be fully characterized and the data used to commence optimization of precursor chemistry and the filament generation process. In order to fully address application requirements, we will also need to evaluate and implement appropriate post treatment operations including surface treatment and sizing for the fiber. We will also evaluate whether advanced plasma-based conversion processes (oxidative stabilization and carbonization) under development at ORNL are appropriate for these fibers in reducing costs while meeting performance goals. As the technology is being successfully demonstrated at the Carbon Fiber Technology Facility in Oak Ridge, ORNL will concentrate on the commercialization strategy for technology transfer and implementation.

FY 2013 PUBLICATIONS/PRESENTATIONS

1. Felix L. Paulauskas, "High Strength Carbon Fibers", presentation at 2013 DOE Hydrogen Program and Vehicle Technologies Annual Merit Review and Peer Evaluation Meeting, May 13–17, 2013.
2. Felix L. Paulauskas, "High Strength Carbon Fibers and Status Report", presentation at Hydrogen Storage Tech Team Meeting, April 18, 2013.

REFERENCES

1. Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan Planned program activities for 2005-2015, October 2007 update.
2. Wiles, K.B., V.A. Bhanu, A.J. Pasquale, T.E. Long, and J.E. McGrath, *Journal of Polymer Science: Part A: Polymer Chemistry*, Vol. 42, 2994-3001 (2004).

3. Bhanu, V.A., P. Rangarajan, K. Wiles, M. Bortner, S. Sankarapandian, D. Godshall, T.E. Glass, A.K. Banthia, J. Yang, G. Wilkes, D. Baird, and J.E. McGrath, *Polymer*, 43, 4841-4850, (2002).
4. Godshall, D., P. Rangarajan, D.G. Baird, G.L. Wilkes, V.A. Bhanu, and J.E. McGrath, "*Polymer* 44 (2003), 4221-4228.
5. Rangarajan, P., V.A. Bhanu, D. Godshall, G.L. Wilkes, J.E. McGrath, and D.G. Baird, *Polymer* 43, 2699-2709 (2002).
6. Bortner, Michael J., Vinayak Bhanu, James E. McGrath, and Donald G. Baird, *Journal of Applied Polymer Science*, 93(6), 2856-2865 (2004).
7. Peng, Fred M., "Acrylonitrile Polymers," in Mark, Herman F.; Bikales, Norbert M.; Overberger, Charles G.; Menges, Georg; Editors. *Encyclopedia of Polymer Science and Engineering*, Vol. 1: A to Amorphous Polymers. (1986), 843 pp, pages 426-470, and references therein.
8. Back, Hartwig, C, and Knorr, Raymond S. "Acrylic Fibers," in Mark, Herman F.; Bikales, Norbert M.; Overberger, Charles G.; Menges, Georg; Editors. *Encyclopedia of Polymer Science and Engineering*, Vol. 1: A to Amorphous Polymers. (1986), 843 pp, pages 334-388, and references therein.
9. Capone, Gary J.; Masson, James C. Fibers, acrylic. *Kirk-Othmer Encyclopedia of Chemical Technology* (5th Edition) (2005), 11 188-224
10. Frushour, Bruce G.; Knorr, Raymond S. Acrylic fibers. *International Fiber Science and Technology Series* (2007), 16(*Handbook of Fiber Chemistry* (3rd Edition)), 811-973.