

## IV.F.1 High Strength Carbon Fibers

Felix L. Paulauskas (Primary Contact),  
Bob Norris (Project Manager), Amit Naskar,  
Soydan Ozcan, and Ken Yarborough  
Oak Ridge National Laboratory (ORNL)  
MS 6053  
Oak Ridge, TN 37831-6053  
Phone: (865) 576-1179  
E-mail: ffp@ornl.gov

### DOE Manager

HQ: Ned Stetson  
Phone: (202) 586-9995  
E-mail: Ned.Stetson@ee.doe.gov

### Subcontractors:

- Donald G. Baird, James E. McGrath, Jianhua Huang, Myoungbae Lee, Yu Chen, and Ozma Lane; Virginia Polytechnic Institute and State University, Blacksburg, VA
- Fibras Sinteticas de Portugal (FISIPE), SA, Lavradio, Portugal

Project Start Date: November 2006

Project End Date: Project continuation and direction determined annually by DOE

### Fiscal Year (FY) 2011 Objectives

- Reduce the manufacturing cost of high-strength carbon fibers by using melt-spun polyacrylonitrile (PAN) precursor technology which has the potential to reduce the production cost by >30%.
- Develop advanced conversion techniques that will significantly reduce the production cost of high-strength carbon fibers suitable for use in compressed hydrogen storage vessels by an additional 20%.

### 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 Storage section of the Fuel Cell Technologies Program 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 2011 Accomplishments

- Acrylonitrile copolymers were successfully prepared in controlled molecular weight by classical free radical copolymerization. It has been extended to copolymers with methyl acrylate. The materials have been characterized by melt rheology, fiber spinning, mechanical testing, microscopy and size exclusion chromatography (SEC).
- Demonstrated it is possible to use water as the only plasticizer (instead of water plus organic solvents like acetonitrile) to generate melt-spun PAN fibers as carbon fiber precursors.
- Demonstrated it is possible to melt-spin PAN precursor fibers with the desired denier (10 to 20 microns in diameter) with a one-step spinning/drawing process.



### 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. At this time, the cost and property targets needed for compressed hydrogen storage are not well understood. Analysis is underway at DOE to determine appropriate targets. 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 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. 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. Backup options include 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 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) characterization of filaments at 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

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 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.

Random copolymers have been made either by aqueous suspension processes or emulsion systems using polyvinylpyrrolidone for the suspension aid and common organic initiators such as azobisisobutyl nitrile (AIBN) and peroxides. Monomers such as acrylonitrile methyl acrylate, hema, caprolactone and 2-acrylamido-2-methyl-1-propanesulfonic acid were purchased from laboratory supply houses. The suspension reactions were conducted mostly in a Parr reactor, which prevents loss of monomer through typical three-neck type apparatus systems. Conversions can be very high; molecular weights were controlled primarily with temperature, initiator concentration, and especially the use and concentration of dodecyl mercaptan as a chain transfer agent. Characterization of the co- and terpolymers utilized spectroscopic methods various rheological measurements.

In some cases, preliminary experiments were done in dimethyl sulfoxide, again using AIBN to produce effective random copolymers. Macromonomer grafts were prepared by utilizing hydroxy ethyl methacrylate to initiate caprolactone in the presence of catalytic quantities of stannous octanoate. The resulting methacrylic functionality macromonomer of about 1,000 to 2,000 molecular weight was successfully introduced into the terpolymerization scheme with acrylonitrile and methylacrylate. The rheological behavior was investigated for the copolymers and concurrently for the terpolymers. As shown in Figure 1, there was a noticeable effect of composition on the apparent melt viscosities; 90% or less could produce in many cases a melt processible material, which evidenced little if any degradation over a 30-minute processing period.

A laboratory-pressurized spinning system was developed, which enabled viscosity shear rate behaviors to be generated as a function of temperature and water content. A descriptive plot of viscosity vs. shear rate is provided in Figure 2. The resulting materials could be processed into fibrous materials, which are undergoing continued evaluation. All of the materials described were well characterized by SEC, which has been invaluable in establishing which compositions and molecular weights are indeed melt processible. The work is ongoing and an updated presentation will be given at the meeting.

In FY 2010, the project achieved success in generating a ten-filament mini-tow with AN/VA copolymer. The scanning electron microscope micrographs showed that the void size of the fibers is similar to that of as-spun fibers produced by BASF. The tensile strength of melt spun fibers was about 50 to 70% of industrial precursor fibers which were solution

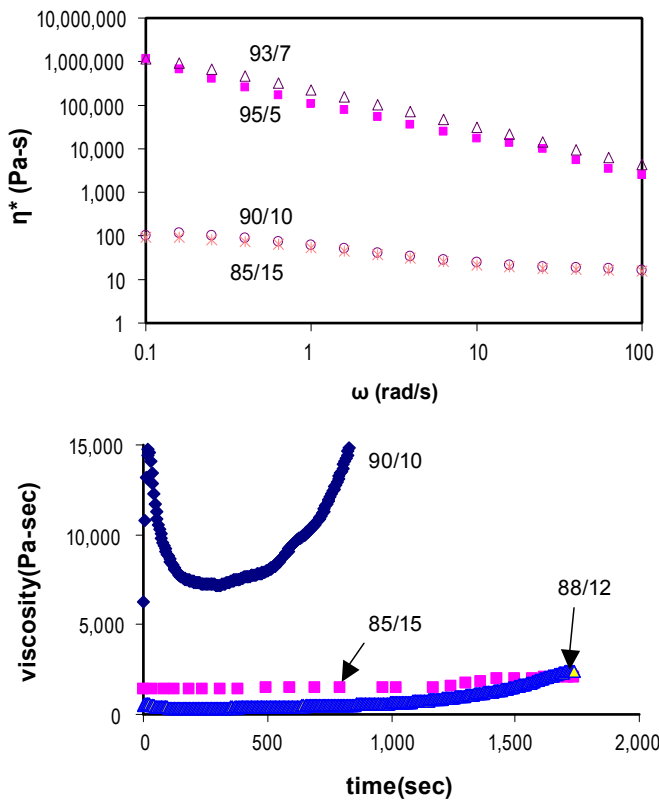
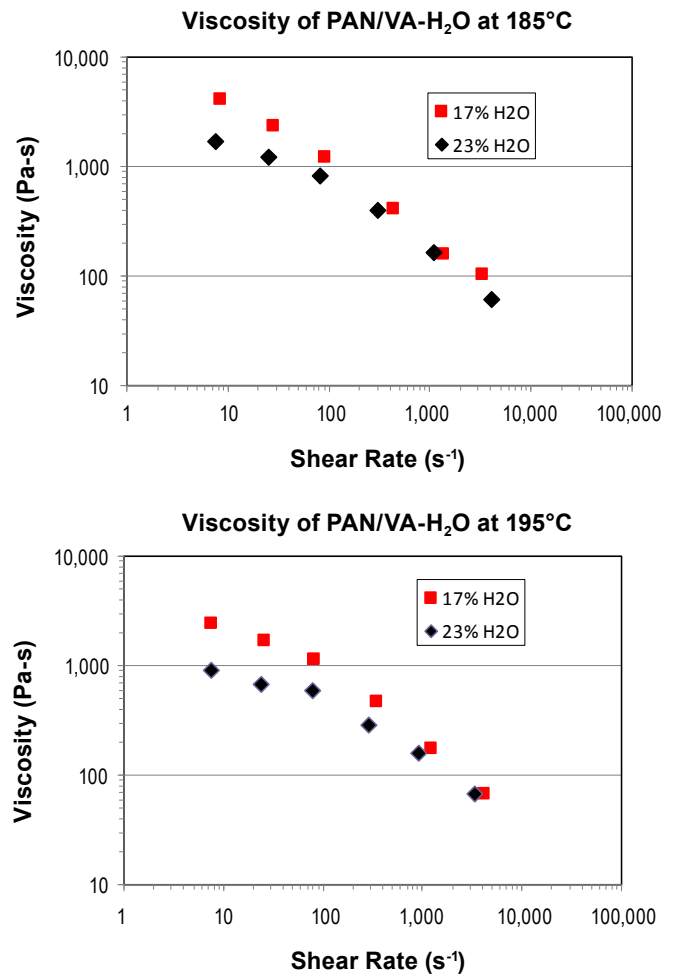


FIGURE 1. Correlation between Melt Viscosity and Copolymer Composition

spun and about four times smaller in diameter. It is expected that with a new spinneret that fibers in the range of 10 μm will be produced with significantly improved strength.

In Table 1, the tensile mechanical properties of VT melt-spun PAN fibers are presented. The properties of industrial precursor fibers are also included in the table/figures for comparison. The strength of VT melt-spun fibers is lower than all industrial precursor fibers, whereas the elongation of VT fibers is similar to that of the industrial fibers, especially Courtaulds and Hexcel fibers. Note that VT fibers are four times larger than all industrial fibers. Because smaller fibers usually have higher strength, the higher strength of melt-spun fibers would be expected when the fiber diameter is reduced to 10 μm or so with the new spinneret.



The viscosity of melt decreases as water content increases.

FIGURE 2. Viscosity of AN Copolymer-H<sub>2</sub>O Melt

In FY 2011 efforts were made to design and fabricate a new spinneret (with diameter of 55 microns) and use it to generate a multi-filament (≥10 filaments) precursor tow with AN/VA copolymer (containing 93% AN), targeted at filaments with diameter of 10 to 20 μm and porosity of no more than 1 vol%. Success was achieved in generating melt-spun PAN precursor fibers with diameter of 10 to 20 microns. Effort is now focused on issues associated with

TABLE 1. Mechanical Properties of VT Melt-Spun and Commercial PAN Precursor Fibers\*

Name/ Manufacturer	Polymer Composition	Spinning Process	Fiber Diameter (μm)	Peak Stress (KSI)	Strain at Break (%)
VT-1	AN/VA	Melt/H <sub>2</sub> O	67.1 (3.1)	37.6 (3.7)	11.89 (1.16)
VT-2	AN/VA	Melt/H <sub>2</sub> O	53.8 (4.8)	35.3 (4.0)	10.76 (1.08)
FISIPE-1	AN/VA	Solution	14.15	54.2 (8.5)	15.7 (0.9)
FISIPE-2	AN/VA	Solution	13.7	64.9 (5.5)	14.99 (0.51)
COURTAULDS	AN/MA	Solution	11.7	73.5 (10.5)	11.21 (1.36)
HEXCEL	AN/MA	Solution	12.9	76.6 (5.6)	10.53 (0.76)

\* All data were provided by ORNL. Data in parenthesis represent the standard deviation.

generating filaments or a mini-tow with uniform diameter and length greater than 10 ft and preferably up to 100 feet.

A new spinneret with 18 capillaries was designed and built for evaluation. The capillary has a diameter of 55 microns and L/D of 5. It turned out that the spinneret was poorly machined with unacceptable deviation in the capillary diameters. The design was modified and a better qualified company was found to machine the spinneret. As can be seen from Figure 3, the latest spinneret has 19 capillaries with diameter of 55 microns and aspect ratio (L/D) of 2. The spinneret was received on April 19 and appears to be well machined.

PAN fibers produced with the new spinneret are shown in Figure 4. The fibers have a diameter of 10 to 20 microns. The evaluation of the fibers including mechanical property and morphology of the fibers is now underway.

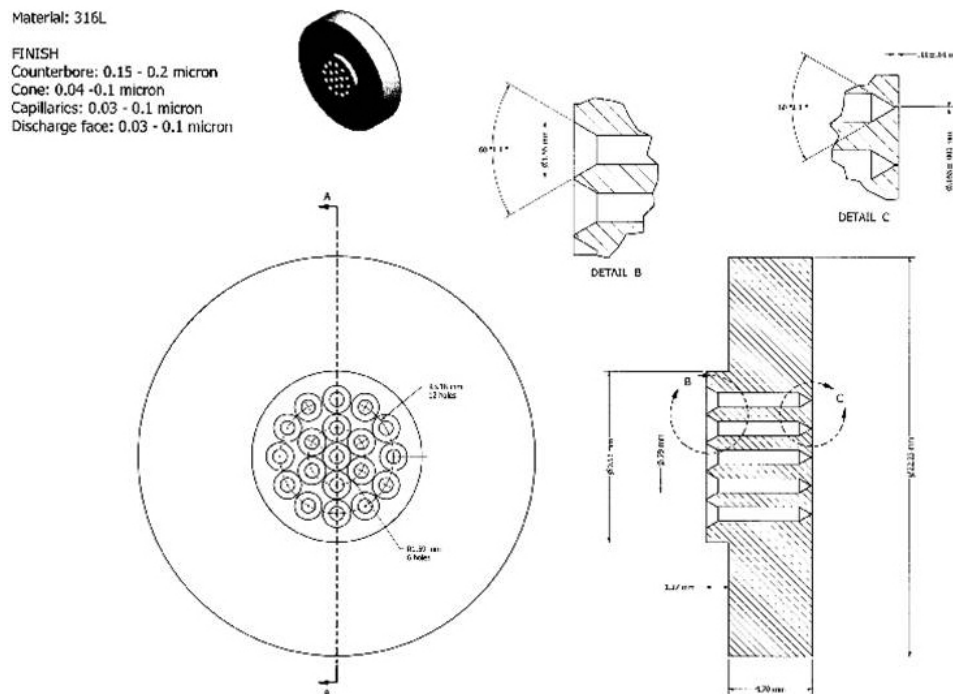
### Conclusions and Future Directions

Acrylonitrile copolymers were successfully prepared in controlled molecular weight by classical free radical copolymerization. It has been extended to copolymers with methyl acrylate. The materials have been characterized by melt rheology, fiber spinning, mechanical testing, microscopy and SEC. Stabilization appears to require 1 or 2 wt% of a novel stabilizer. The stabilization mechanism is unknown, but one speculates a sort of pH control which retards the intra and inter molecular cyclization process. Small amounts of water are observed to be released and a

significant increase in  $T_m$  has been reported. This suggests that the stabilizer may also serve as a nucleating agent, which could be very important. The utilization of water as a plasticizer has been one of the critical observations



**FIGURE 4.** Melt-spun PAN/VA fibers using 19-filament die (0.0022" in diameter). The diameter of fibers is about 10 to 20 microns.



**FIGURE 3.** Drawing of new spinneret for Instron rheometer fiber spinning system. The spinneret has 19 capillary holes with diameter of 55 microns.

developed thus far that generally permits melt spinning via decreasing the dipole interactions. Controlled (living) radical copolymerization is currently also being explored. This is expected to afford narrower molecular weight distributions and possibly lower branching and chain end unsaturation.

The fiber spinning research so far reveals that:

- It is possible to use water as the only plasticizer (instead of water plus organic solvents like acetonitrile) to generate melt-spun PAN fibers as carbon fiber precursors.
- It is possible to melt-spin PAN precursor fibers with the desired denier (10 to 20 microns in diameter) with a one-step spinning/drawing process.
- In order to generate PAN precursor fibers with desired size and quality, one must have a quality spinneret with small capillary size. However, it was found very difficult to remove the residual PAN polymer from capillaries with diameter of 55 microns or so. Effort is ongoing to overcome this difficulty.
- It was found to be very difficult to remove the residual PAN polymer from the capillaries with diameter of 55 microns. Using solvent to dissolve the polymers at elevated temperature, or using high temperature (~400°C) plus oxygen to burn-off the polymers and then clean the capillaries have been attempted. Unfortunately, none of the methods could clean the capillary completely even after days/weeks of treatment. We are still working on this issue so that we can keep running the fiber spinning experiment with the small capillary diameter spinneret.

Near-term objectives are to:

- Generate a multi-filament ( $\geq 10$  filaments) precursor tow with AN/VA copolymer (from ORNL with 93% AN), targeted at filaments with diameter of 10 to 20  $\mu\text{m}$ , porosity of no more than 1 vol%, and length of greater than 10 feet.
- Generate a multi-filament ( $\geq 10$  filaments) precursor tow with AN/MA copolymer (from ORNL, with 95% AN) with desired size and properties.
- Test mechanical property and morphology of PAN/VA and PAN/MA fibers and compare them with that of industrial precursor fibers.
- Consider the design of an extrusion process using an extruder which will allow the generation of a larger quantity of fibers.

ORNL will characterize fiber and conduct conversion trials on precursor filaments generated using its precursor evaluation system. 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. We expect to achieve carbon fiber tensile properties of 15 Msi elastic modulus and 150 ksi tensile strength with 1<sup>st</sup> generation filaments. We are targeting 18 Msi modulus and 200 ksi strength in 2<sup>nd</sup> generation filaments.

## FY 2011 Publications/Presentations

1. Felix L. Paulauskas, "High Strength Carbon Fibers" presentation at 2011 DOE Hydrogen Program and Vehicle Technologies Annual Merit Review and Peer Evaluation Meeting, May 9–12, 2011.
2. Felix L. Paulauskas, "High Strength Carbon Fibers and Status Report", presentation at Hydrogen Storage Tech Team Meeting, June 30, 2011.

## 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.