IV.F.1 Melt Processable PAN Precursor for High-Strength, Low-Cost Carbon Fibers (Phase II)

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Project Start Date: October 2013
Project End Date: September 2016

Overall Objectives

- Demonstrate means to achieve cost reduction of ≥25% in the manufacture of carbon fiber meeting properties of industry baseline carbon fiber utilized in fabrication of composite vessels for 700-bar 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 program performance goals.

Fiscal Year (FY) 2014 Objectives

- Procure, install, and initiate operations with a spinning system capable of melt spinning continuous precursor polyacrylonitrile (PAN) fiber tows of several hundred appropriately sized filaments with a length >100 m that can be easily spooled and later de-spooled for conversion at ORNL's Precursor Development System.

- Restart chemical formulation work focused on advancing polyacrylonitrile co-polymerized with methyl acrylate (PAN-MA) formulations with appropriate plasticizers and monomers to facilitate spinning precursors with characteristics such as molecular weight, molecular weight distribution, orientation, fiber size, fiber mechanicals, etc. consistent with conversion to high-performance carbon fiber with economic advantages

over conventional approaches. (Formulation development had been deferred in late Phase I in order to demonstrate feasibility of melt spinning and converting compounds based on polyacrylonitrile with vinyl acetate [PAN-VA] formulations that were easier to process but not likely capable of meeting longer-term program performance goals.)

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 [1]:

(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 in 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 2014 Accomplishments

- The extruder system needed to produce precursor fiber quantities for continuous conversion processing has been procured and is being set up for operation. Related design and procurements for a metering pump, spin packs, spinnerets, drawing system, etc., are underway based on recent experimental data from ongoing spinning demonstrations utilizing a much smaller scale rheometer. An additional rheometer is being refurbished to facilitate transitioning formulation alternatives to fiber spinning. Most of this equipment is expected to be delivered by the end of FY 2014 while critical supporting activities are ongoing with existing equipment.

- The project has effectively transitioned from demonstrating spinning PAN-VA formulations for feasibility demonstration purposes to advancing PAN-MA formulations projected to be pathway to ultimate cost and performance targets for project. At the conclusion of this time period, precursor fiber properties with melt spun PAN-MA have essentially matched those achieved with PAN-VA formulations in late Phase I.

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INTRODUCTION

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 too expensive to meet DOE goals for storage system costs. Developing and demonstrating a melt-spun PAN approach to producing precursor for carbon fiber will provide a more cost-effective route to achieving performance necessary for high-pressure gas storage. Melt spinning removes significant costs in handling and recovering solvents involved in solution spinning as well as eliminating a significant bottleneck in production rates required by the time, space, and energy utilized in the solvent recovery steps. Although somewhat similar processes have been demonstrated in the past, no PAN-based carbon fiber is produced currently utilizing this approach due to specific materials employed in the previously demonstrated process and lack of investment from industry to revisit and revamp that process. It is anticipated that the melt-spinning approach could save 25% of cost involved in producing carbon fiber for high-pressure gas storage systems and that additional savings may be possible in combination with ORNL advanced conversion approaches. It is also projected that the melt spinning process would be more attractive for PAN fiber production in the U.S., possibly helping to revitalize some of the acrylic fiber business lost due to environmental concerns.

A major milestone was achieved during latter portions of Phase I with demonstration of carbon fiber properties exceeding the Go/No-Go point established at 15 Msi modulus and 150 ksi strength. Properties meeting follow-on milestone levels up to 25 Msi modulus and 250 ksi strength were also achieved. These properties were achieved with melt spun PAN produced at Virginia Tech and utilizing conversion protocol developed by ORNL. The conversion protocol consists of a number of steps in simulating oxidation with differential scanning calorimetry testing and then preliminary tensioning experiments in batch mode utilizing the customized ORNL precursor evaluation system. Small tows as spun at Virginia Tech were combined at ORNL to obtain a tow with ample number of filaments (~100) to enable progressive tensioning during multiple oxidative stabilization steps and specific shrinkage management in low and high

temperature carbonization. During the last year, Phase I has been completed and activities in Phase II are now underway with resumption of the broader approach evaluating new chemical formulations, advanced spinning techniques, and novel conversion processes.

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 polyacrylonitrile 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.

The following have been identified as key elements of the project approach:

- Melt-spun precursors are being formulated for evaluation. The optimum formulation of polyacrylonitrile, methyl acrylate, and a ter-monomer will be determined based upon small scale spinning trials.

- Methods for handling, melting, and spinning the polymer developed in Task 1 above are being developed to produce precursor fiber for the oxidative stabilization and carbonization conversion processes. Critical will be development of the spinning process, including temperature, speed, pressure, and draw profiles.

- Processing of the new polymer into finished carbon fiber will be necessary beginning with conventional processes. By applying conventional processes, a good estimate of the cost benefit of the change in precursor alone will be obtainable and the technology will be developed to allow for introduction of the precursor into current commercial processing lines.

•   Processing of the new polymer into finished carbon fiber using the alternative manufacturing processes will be assessed. By applying the alternative processes, the synergistic cost savings of a less expensive precursor along with less expensive processing technologies will be obtainable.

RESULTS

During this period, the project team has focused on upgrading the capabilities necessary to produce adequate quality and quantities of precursor fiber necessary to establish stable, continuous conversion processes, restarting the chemical formulation development work, and transitioning from the PAN-VA formulations utilized to demonstrate feasibility to PAN-MA formulations projected to be necessary to achieve both economic and performance goals. A Randcastle 5/8" extruder as shown in Figure 1 has been procured specifically to support spinning work at Virginia Tech. Related design and procurements for a metering pump, spin packs, spinnerets, drawing system, etc., are underway based on recent experimental data from ongoing spinning demonstrations utilizing a much smaller scale rheometer. An additional rheometer is being refurbished to facilitate transitioning formulation alternatives to fiber spinning. Most of this equipment is expected to be delivered by the end of FY 2014 while critical supporting activities are ongoing with existing equipment.

FIGURE 1. Randcastle 5/8" Screw Extruder in the Processing Lab at Virginia Tech

The synthesis efforts at Virginia Tech have focused on the preparation of high acrylonitrile (AN) content poly(AN-*co*-methyl acrylate) materials for small scale spinning trials. The parameters to be controlled in the synthesis are the molecular weight and molecular weight distribution and the AN content. All of these parameters, in conjunction with the plasticizer type and content and spinning parameters will determine the spinnability of a particular composition. The current objectives are to provide trial materials with approximately 95 wt% AN and 5 wt% methyl acrylate. The materials will be screened in the standard rheometer and/or the modified capillary rheometer spinning apparatus using plasticizers such as water and acetonitrile to determine the spinnability. The feedback on spinnability will be used to define a target molecular weight for scaling up a batch to be used for extruder trials.

One current objective is to identify an optimum molecular weight for a high AN copolymer for melt spinning. A second objective is to develop a scalable process for such materials so that this composition can be scaled to sufficient quantities for spinning and carbonization studies. A series of copolymers with approximately 95/5 wt/wt AN/MA were synthesized by emulsion free radical polymerization (Table 1) and this work remains in progress. Entry 1 in the table was prepared at a lower temperature and lower percent solids relative to the other samples. For Entry 1, ammonium persulfate was combined with sodium metabisulfite as an activator. All of the remaining samples were prepared by conventional free radical emulsion polymerization using ammonium persulfate as the initiator. Based on our results to date, it appears that an optimum molecular weight range (M_w) lies somewhere between 70 and 140 kg/mole. Thus, the team is working to develop a scalable process for polymers in this molecular weight range and to determine the sensitivity of molecular weight on various reaction parameters, particularly temperature, concentration of initiator, and concentration of the chain transfer agent. Please notice that entry MJ-114 in Table 1 has a M_w in the targeted range, but that this copolymer precipitated during synthesis, and this would make this "non-scalable." There are numerous reports of precipitation polymerization for high AN copolymers in the literature so this is not entirely unexpected, but we need to move away from these reaction parameters to develop a robust and scalable process. Nevertheless, MJ-114 may provide insight into "spinnability" of copolymers with this composition in this molecular weight range. Once spinnable polymers with known molecular weight and high AN composition have been developed, the impact of molecular weight on the mechanical characteristics of the melt spun precursor and carbon fibers can be determined.

Table 2 demonstrates parameters from recent spinning trails utilized to effectively transition from the use of PAN-VA formulations for demonstration purposes to the PAN-MA formulations as focus for the Phase II portion of this work.

TABLE 1. Synthetic Parameters for Scaling Trials

Sample ID	Temp.	[Initiator][a] Mol%	[CTA][b] Mol %	% solids	[Surfac Tant][c]	Time	AN/MA ^{1}H NMR (wt%)	SEC Mw (kg/mol)[d]	Comments
PPP-135*	45	0.12 + 0.02 activator	0.20	20	1.6 wt%	3 h	95/5	70	Filaments failed during spinning
PPP-131	70	0.05	0	25	1 wt%	16 h	95/5	573	Viscosity too high – not spinnable
PPP-133	70	0.05	0.15	25	1 wt%	3 h	95/5	140	Viscosity too high – not spinnable
PPP-129	70	0.1	0.5	25	1 wt%	16 h	94/6	60	filaments failed during spinning;
MJ-114	70	0.1	0.4	25	1 wt%	40 min	96/4	118	Precipitated during synthesis
MJ-131	70	0.1	0.4	25	1 wt%	40 min	96/4	45	Precipitated during synthesis
MJ-121	70	0.1	0.4	28	1 wt%	40 min	96/4	56	

*Synthesized at low temperature using ammonium persulfate activated by sodium metabisulfite

TABLE 2. List of VT PAN Precursor Fibers Generated in this Quarter

Sample ID	VT 04-13	VT 04-14A	VT 04-14B
Polymer mol/mol	PAN-VA 93/7	PAN-MA 95/5	PAN-MA 95/5
Water wt%	12	14	14
AN wt%	12	14	14
Spinning Temp	165°C	165°C	165°C
Draw Ratio	1.7	1.8	1.8
Pressure of FFZ	150 psi	100 psi	50 psi
2nd Draw ratio	4.4	3.8	3.8
Steam condition	19 psi/125C	19 psi/125°C	19 psi/125°C
Fiber diameter	17.8 μm	18.8 μm	18.5 μm
Filament number	14	14	13
Filament length	580 ft (177 m)	542 ft (165 m)	440 ft (134 m)

FFZ - fiber formation zone

FIGURE 2. Tensile Strength of PAN Precursor Fibers

Tensile mechanical properties of the new precursor fibers as well as the commercial wet-spun products are presented in Figures 2-4 for comparison. It can be seen that the strength of the new precursor fibers is close to those of FISIPE-1 and 2 (textile-based PAN fibers produced several years ago as an introduction to a precursor alternative for another project) but a little bit lower than those of the commodity or aerospace products. In contrast, the modulus of our precursor is the same or even higher than that of the wet-spun products including the commodity and aerospace products. The elongation-at-break of our precursor is lower than that of the wet-spun products.

The new Virginia Tech precursor fibers have all been converted to carbon fibers at ORNL. The tensile strength, modulus, elongation (strain at break), and diameter of the carbon fibers are shown in Figures 5-8. Compared to the
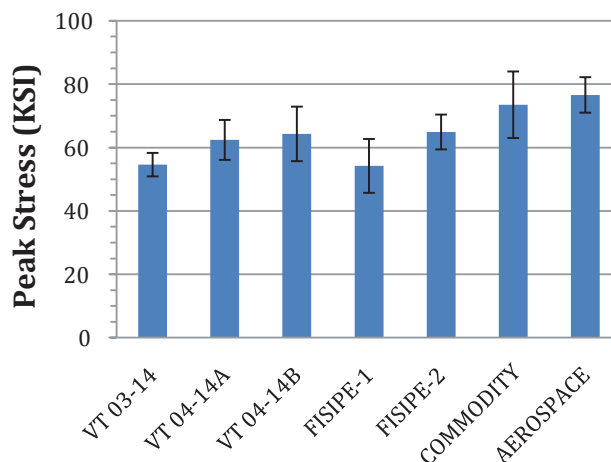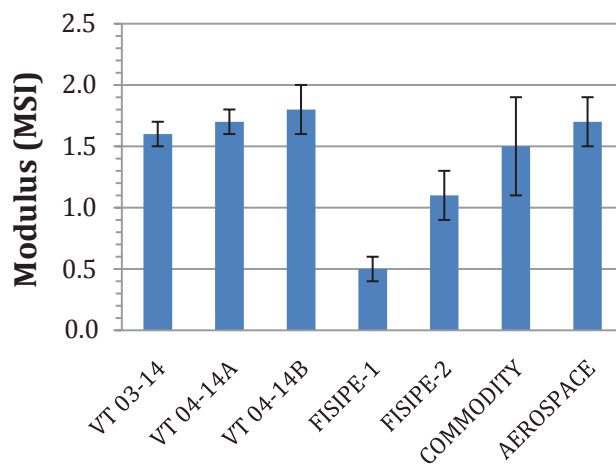

FIGURE 3. Tensile Modulus of PAN Precursor Fibers
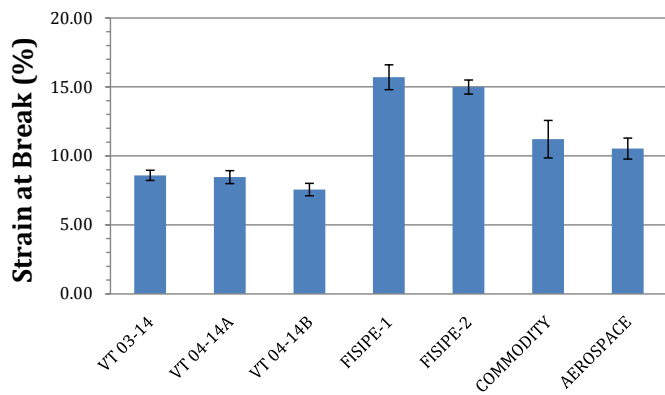
FIGURE 4. Elongation of PAN Precursor Fibers

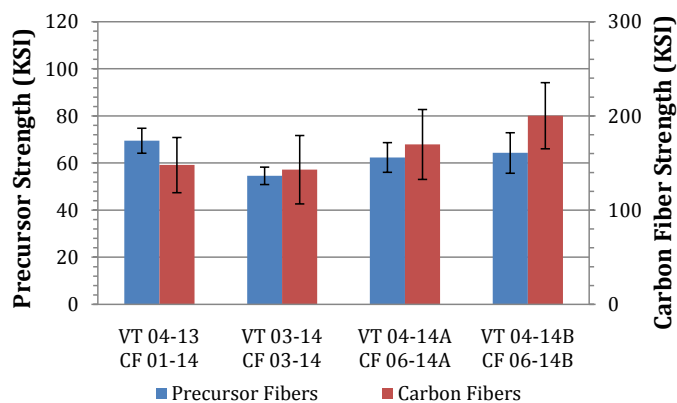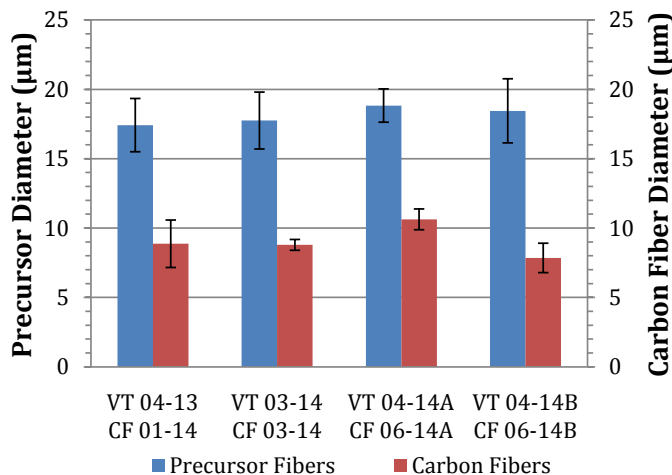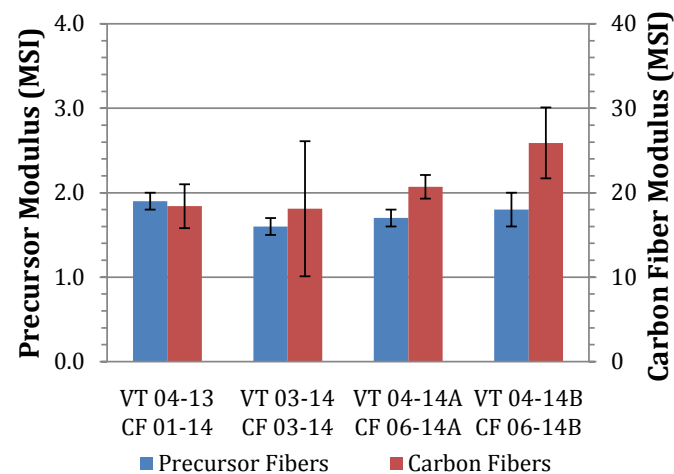**FIGURE 5.** Tensile Strength Of Carbonized Virginia Tech PAN Fibers

FIGURE 6. Tensile Modulus of Carbonized Virginia Tech PAN Fibers

carbon fibers converted from PAN-VA precursor fibers, the carbon fibers converted from PAN-MA precursor fibers have higher tensile strength and modulus. This may be attributed to the fact that PAN-MA we were using has higher AN content, higher molecular weight and more favorable co-

FIGURE 7. Elongation of Carbonized Virginia Tech PAN Fibers

FIGURE 8. Diameter of Carbonized Virginia Tech PAN Fibers

monomer compared to PAN-VA copolymer. The modulus of carbon fibers converted from Virginia Tech 04-14B precursor has a modulus of over 25 Msi which meets our target at the present time. The strength of the carbon fibers is still lower than our target (300 Ksi). The elongation of all carbon fibers is very similar.

CONCLUSIONS AND FUTURE DIRECTIONS

Significant progress has been made in demonstrating and improving melt spinning processes and producing precursor fiber in sufficient quality and minimum quantity to begin carbon fiber conversion investigations. Mechanical properties of the melt spun precursor fiber are comparable to commercially produced fibers. Initial conversion protocols have been developed and demonstrated indicating that we are indeed taking an effective approach and making progress towards project goals.

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. Working on the precursor chemistry necessary to enhance baseline properties and move towards the ultimate goals of 33 Msi modulus and 700 Ksi strength has been resumed and is making progress. Equipment necessary to scale the spinning processes up so that the team 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 has either been obtained or is on order. 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, the team will also need to evaluate and implement appropriate post treatment operations including surface treatment and sizing for the fiber. Plans are also in place to 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 2014 PUBLICATIONS/PRESENTATIONS

1. Bob Norris, Soydan Ozcan, and Felix Paulauskas, "Carbon Fiber and Nanostructured Material Systems for Manufacturing for High Pressure Hydrogen and Natural Gas Storage", Nanomaterials for Industry Conference, April 6–9, 2014.

2. Felix L. Paulauskas and Bob Norris, "Melt Processable PAN Precursor for High Strength, Low-Cost Carbon Fibers", presentation at Hydrogen Storage Tech Team Meeting, April 17, 2014.

3. Jianhua Huang, Donald G. Baird and Felix L. Paulauskas, "Thermal and rheological behavior of plasticized polyacrylonitrile and melt spinning of precursor fibers" ANTEC® 2014 - Proceedings of the Technical Conference & Exhibition, April 28–30, 2014.

4. Felix L. Paulauskas and Bob Norris, "Melt Processable PAN Precursor for High Strength, Low-Cost Carbon Fibers", presentation at 2014 DOE Hydrogen Program and Vehicle Technologies Annual Merit Review and Peer Evaluation Meeting, June 17, 2014.

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