

## IV.G.3 High Strength Carbon Fibers

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### 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/Operatability
- (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 T700 at substantially reduced production costs:

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

### Accomplishments

- Successfully synthesized copolymers with sufficiently high molecular weight and target compositions. High molecular weight and specific compositions were established by project team members as targets that will likely produce acceptable downstream processing conditions and yield desirable final carbon fiber properties with continuing development.
- Demonstrated that copolymerization of macromonomers with acrylonitrile (AN) can lead to effective glass transition temperature (T<sub>g</sub>) depression. Modification of the T<sub>g</sub> allows processing at temperatures that do not degrade the polymer.
- Successfully melt-spun a four-filament mini-tow with AN/vinyl acetate (VA) copolymer. This accomplishment demonstrates a formulation that can be melt-spun at least at small-scale.



### 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). Costs for compressed gas storage systems stored at 350 and 700 bar (5,000 and 10,000 psi) can be reduced by lowering the cost of carbon fiber through materials and process improvements and moving to higher volume manufacturing processes through advanced manufacturing research and development (R&D). 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 polyacrylonitrile precursor. Manufacturing R&D is needed to develop lower cost, high quality polyacrylonitrile or alternate precursors and reduced energy or faster carbonization process for carbon fiber, such as microwave or plasma processing. In addition to improved carbonization processes, other steps in the process, such as oxidation and graphitization need to be improved. 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].

Most carbon fiber in use today is based on the technology developed over many years for production of aerospace grade materials where performance requirements clearly justifies higher costs than for other structural materials. The major contributors to the cost of high strength fiber are: 1) presently, all high-strength carbon fibers are manufactured from relatively costly PAN precursor which is wet spun into fiber in an expensive process; 2) precursor fiber is converted into carbon fiber in bundles, or “tows”, which are optimized for performance versus cost; 3) carbon fiber is typically processed at line speeds optimized for “conservative” production of aerospace properties; 4) conventional fiber production utilizes large, massive furnaces in which most energy is lost to the environment; and 5) rigorous qualification, certification, inspection, and documentation requirements can contribute very significantly to the cost of aerospace grade fibers. This project addresses all of these factors, the most critical of which is the raw material and processing costs involved with precursor production.

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, conversion process improvements, process integration, and business analysis. 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 these technological advances are demonstrated independently, work will also be initiated to make all the modules work together as a robust system focusing on the implementation of an optimized system design and operating procedures to satisfy technical targets at minimum cost. As the system integration is completed, the energy efficiency and overall economics of the complete system will be evaluated and forecast for production scale up.

## Results

As described in the approach, our initial focus is on developing and demonstrating melt-spinnable PAN, the necessary processes to spin these material into fibers, and projecting converted carbon fiber properties adequate for down-selecting this or other candidate precursor materials for system integration and technology demonstration. Accordingly, ORNL and its project partners at Virginia Tech have devoted most project resources to this effort as described below.

### Alternative Precursor Synthesis

Earlier research has shown that partially sulfonated PAN copolymers (PAN-AMPS) affords highly miscible blends with poly(ethylene glycol) (PEG) due to an apparent intermolecular interaction between the sulfonated groups and PEG. This enables effective depression of the T<sub>g</sub> of the blends. In addition to this

external plasticization technique, T<sub>g</sub> depression of PAN may be achieved by copolymerizing with appropriate monomers or macromonomers (graft copolymers). During this quarter, PEG-grafted and polycaprolactone (PCL)-grafted PAN copolymers were synthesized and characterized as presented below to explore the possibility of the internal plasticization technique. Both PEG and PCL have T<sub>g</sub> values of -60 to -70°C, which may allow reduction of the PAN copolymer processing temperature to be below the PAN degradation temperature (~200°C). PCL is known to be more thermally and oxidatively stable than PEG.

### Synthesis of PEG-Grafted PAN Copolymer

PEG-grafted PAN copolymers were synthesized via a traditional free radical copolymerization route using the two commercially available monomers, AN and monomethoxypoly(ethyleneglycol) methacrylate (PEGMEMA). The number-average molecular weight of the PEGMEMA used in this study is 475. We named this statistically random PAN copolymer PAN-PEGMEMA(x); here, x means the PEG contents in weight %.

### Synthesis and Characterization of PCL-grafted PAN Copolymer

PCL is also a polymeric material of a T<sub>g</sub> of about -60°C and is often used as a plasticizer for resins polyvinyl chloride and polycarbonate. PCL-grafted PAN copolymers (PAN-HEMA-g-PCL) were also synthesized via the free radical copolymerization route as PAN-AMPS and PAN-PEGMEMA. However, synthesis of PCL-grafted copolymer involves a prerequisite step, which is the synthesis of the PCL-grafted macromonomer by the ring-opening polymerization of  $\epsilon$ -caprolactone (CL), using 2-hydroxyethyl methacrylate (HEMA) and stannous octoate (Sn(Oct)<sub>2</sub>) as initiator and catalyst, respectively. The molecular weight of PCL can be controlled by adjusting the molar ratio of CL to HEMA. In this study PCL-grafted macromonomers with two different molecular weights (1,400 and 1,800 g/mol) were prepared and used.

The characterization results of the grafted copolymers are summarized in Table 1. From the gel permeation chromatography (GPC) and 1H-nuclear magnetic resonance (NMR) results, it has been confirmed that copolymers with sufficiently high molecular weight and target compositions were synthesized. Our differential scanning calorimetry (DSC) results also indicates that copolymerization of the macromonomers with AN can lead to effective T<sub>g</sub> depression. Molecular weight characterization of the graft copolymer is in progress.

The next step is to control the molecular weight which is critical for melt processing. Both initiator concentration and the use of chain transfer agents such as dodecyl mercaptan will be employed.

### Fiber Spinning

A key accomplishment was successful generation of a four-filament mini-tow with AN/VA copolymer. The scanning electron microscope (SEM) micrographs from this work showed that the fibers have void size similar to that of as-spun fibers produced by BASF as reported in their patent. At the conclusion of this period we are working to generate a 10-filament mini-tow using a new 10-hole spinneret to meet the new milestone. The new spinneret works but more work needs to be done to get filaments with the desired size. We also tried using PAN/methyl acrylate (MA) copolymers in fiber spinning and succeeded in generating some fibers from polymers containing 95% AN. To investigate the stability of hydrated PAN/VA melt, the time dependence of melt pressure was measured during the fiber spinning. The result showed that, under the spinning condition (195°C), the hydrated P(AN/VA) melt was stable as long as the residence time was less than 30 minutes (a time that is long enough for melt spinning). In addition, the DSC thermogram of PAN/VA fibers was measured and compared with that of pristine copolymer. The two thermograms observed are quite similar, indicating that no serious degradation took place during the fiber spinning process.

**TABLE 1.** Preliminary Characterization of PAN-PEGMEMA and PAN-HEMA-g-PCL Copolymers

	Mn of macromonomer (g/mol)	IV (dL/g)	Weight fraction of PEG/PCL (%)		T <sub>g</sub> (°C)
			Target	From 1H-NMR	
PAN	-	2.38	-	-	100
PAN-PEGMEMA(5)	475	1.89	5.0	6.2	94
PAN-PEGMEMA(10)	475	2.28	10.0	12.2	83
PAN-HEMA-g-PCL(5)	1,400	TBD	5.0	TBD	92
PAN-HEMA-g-PCL(5)	1,800	TBD	5.0	TBD	TBD

TBD – to be determined

**SEM Micrograph of As-Spun PAN/VA Fibers**

SEM analysis was carried out to study the morphology of melt-spun PAN/VA fibers, including single filament and four-filament fibers produced in the last quarter. The as-spun fibers are substantially void free when examined in cross section at 2,000X or lower magnification (see Figures 1a and 2a). Any voids which are observed in the as-spun fibers when a cross section is examined are generally  $\leq 0.2$  micron (see Figures 1b and 2b). Note that this size of voids is at the same level as that observed in the as-spun acrylic fibers produced by BASF (see U.S. Patent 5,168,004). That is, we were able to use just water to produce precursor fibers with the same void size as that generated by using water and acetonitrile.

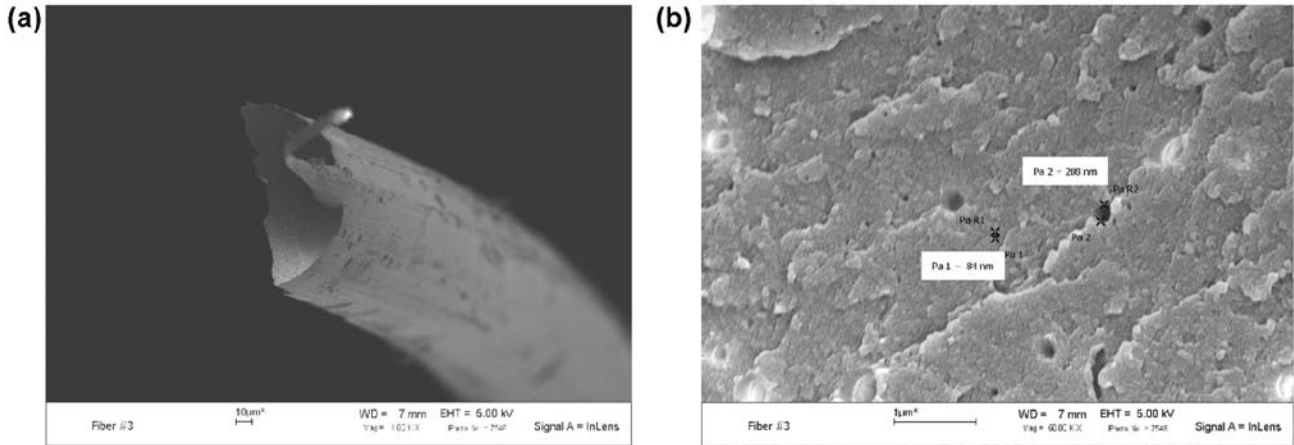
**Spinning of PAN/VA 10-Filament Mini Tow**

In order to meet the milestone on spinning of the 10-filament mini-tow, we designed and fabricated a new

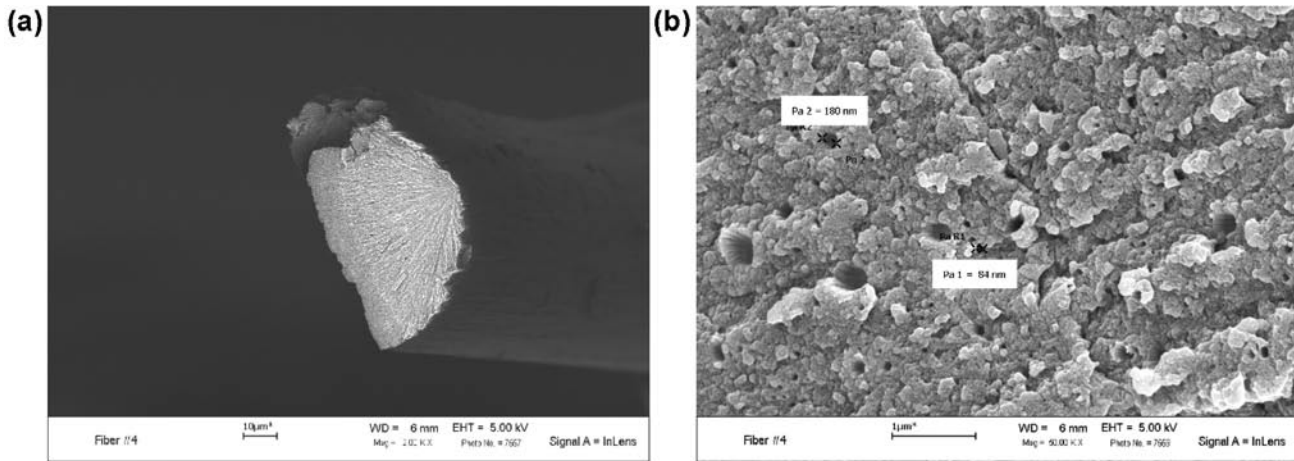
spinneret with 10 holes (0.01” in diameter). We have made trial spinning runs with the new spinneret several times. Some 10-filament mini-tows were generated successfully with PAN/VA mixed with 17 wt% water. However, we still could not produce a 10-filament tow with fibers of diameter  $\leq 50$  microns continuously. Some filaments broke easily as we tried to increase the take-up speed and the draw ratios. We are working to find the solution and generate a 10-filament tow with filaments of desired size and properties. The appropriate conditions seem to be a function of the melt temperature and the subsequent drawing and cooling conditions.

**Spinning of PAN/MA Copolymer Fibers**

We also tried to spin PAN/MA fibers with three copolymer samples (see Table 2) made available to us. Fiber spinning was carried out by using the same conditions as were used for generating PAN/VA copolymer fibers. It turned out that neither sample #1 nor #2 worked. The molecular weight (and viscosity)



**FIGURE 1.** SEM Micrograph of Melt-Spun PAN/VA Fibers (Single Filament with Diameter of about 100  $\mu$ m) at (A) 1,000X Magnification and (B) 50,000X Magnification



**FIGURE 2.** SEM Micrograph of Melt-Spun PAN/VA fibers (Four-Filament with Diameter of about 50  $\mu$ m) at (A) 2,000X Magnification and (B) 50,000X Magnification

**TABLE 2.** Spinnability of Hydrated Melt of PAN/MA Copolymers

Sample No.	Provider	Composition (mol/mol)		IV (dL/g)	Spinnability with hydrated melt
		Nominal	NMR		
1	Aldrich Co.	AN/MA=96/4	90.7/9.3	5.41	Unable to draw fibers
2	Exlan Co.	AN/MA=95/5	92.7/7.3	4.09	Unable to extrude
3	ORNL 6/22/10	AN/MA=95/5	95.0/5.0	1.13	OK

of sample #2 is so high that we could not even extrude the melt out of the capillary. In contrast, the spinning of sample #3 went quite well. Some fibers were generated successfully. Because the PAN/MA sample has higher AN content and is more stable in comparison with the PAN/VA samples, using new PAN/MA samples could improve the properties of PAN fibers as carbon fiber precursors.

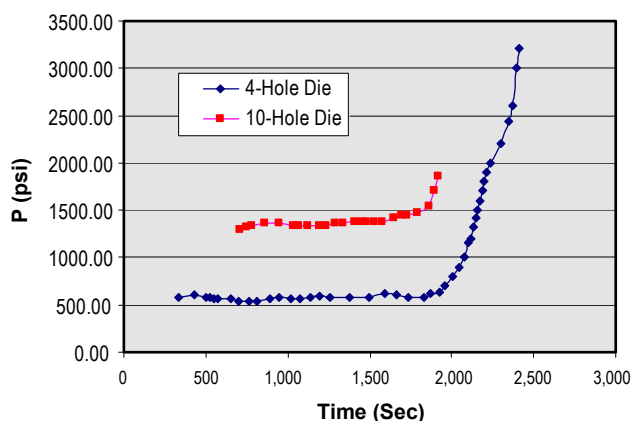
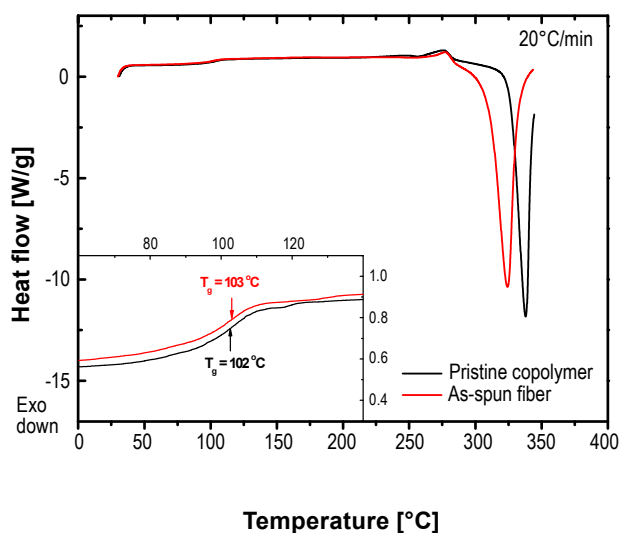
### Stability of Hydrated P(AN/VA) Melt

The viscosity of the polymer melt is sensitive to the polymer structure. Under constant extrusion temperature and speed, the shear viscosity of the polymer is proportional to the pressure drop over the die hole (capillary) and approximately proportional to the melt pressure in the barrel. For this reason, if molten polymer undergoes structural change or becomes unstable, the viscosity of the melt may change and so would the melt pressure. So time dependence of melt pressure could provide information about melt stability or degradation of polymer melt.

Figure 3 presents the time dependence of the hydrated AN/VA copolymer melt pressure during the fiber spinning at an extrusion temperature of 195°C. The extrusion (plunger) speed is 0.06 cm/min. Note that  $t=0$  was set as 6 minutes after the sample was inserted into heated barrel of an Instron Rheometer. It shows that, when  $t$  is less than 30 minutes, the melt pressure was approximately constant, suggesting that the melt was stable during this period of time. In contrast, when  $t$  is greater than 30 minutes, the melt pressure went up quickly, indicating that the polymer might undergo structural change and become unstable. As 30 minutes should be long enough for melt spinning, it can be concluded that the P(AN/VA) – water system is suitable for application in the melt-spinning process.

### DSC Analysis of Melt-Spun AN/VA Copolymer Fibers

The DSC analysis was carried out for both AN/VA copolymer (pristine powder) and melt-spun AN/VA fibers (as-spun fibers with  $t < 30$  min). Both samples were dried in a vacuum oven at 80°C for 20 hours before testing to remove any residual water/moisture in the polymer or fibers. A heating rate of 20°C/min was used in the analysis. The result is shown in Figure 4. It is apparent that the thermograms for the two samples are

**FIGURE 3.** Pressure of Hydrated P(AN/VA) melt at 195°C at Extrusion (Plunger) Speed of 0.06 cm/min as a Function of Time**FIGURE 4.** DSC Scans of P(AN/VA) Copolymer Powders (Pristine Copolymer) and As-Spun Fibers in Nitrogen Atmosphere at Heating Rate of 20°C/min

quite similar, especially in the temperature range less than 280°C. At temperatures higher than 280°C there is a large exotherm produced by the cyclization reaction of adjacent nitrile groups. Both samples exhibited the same glass transition temperature (102~103°C) and the exothermic reaction (cyclization reaction) which starts at

about 280°C. However, the positions (temperatures) of the exothermic peaks are different. For the fiber sample, the peak temperature is 324°C, which is some 14°C lower than that of the pristine polymer sample. It suggests that the cyclization reaction of fiber is faster than that of pristine polymer. From this result and the fact that the fiber sample has much higher molecular orientation than the pristine sample, it is possible that the orientation of polyacrylonitrile molecules may accelerate the cyclization reaction of adjacent nitrile groups.

Based on the above thermal analysis and melt pressure data, we believe that the melt-spun fiber generated with the continuous technology ( $t < 30$  minutes) would have a chemical structure similar to or very close to that of the pristine polymer samples.

## Conclusions and Future Directions

Significant accomplishments were achieved in precursor development during the past year in successfully synthesizing copolymers with sufficiently high molecular weight and target compositions and demonstrating that copolymerization of macromonomers with AN can lead to effective  $T_g$  depression. We were also able to successfully melt-spin a four-filament minitow with AN/VA copolymer. Plans are to build on this work in progressing towards a melt-spinnable 95/5 AN/MA system. The development of a melt processing scheme for the AN/MA copolymer system will require an intensive effort involving synthesis and rheology along with refinements of the processing scheme. The first phase of the project is to develop a correlation between the copolymer ratio and molecular weight. The molecular weight distribution and intrinsic viscosity of various copolymer systems will be determined using GPC and solution viscosity techniques, respectively. Although some of these resins will be provided by ORNL, others will be synthesized by the Virginia Tech group in order to find an acceptable AN/MA copolymer suitable for melt processing. In addition to molecular weight, the melting, and  $T_g$  temperatures will be determined via DSC.

The new resins after plasticization with water will then be evaluated rheologically using a specially designed rheometer capable of measuring viscosity of materials containing plasticizers such as water which require pressurization of the extruded material. These measurements will allow us to determine conditions (processing temperature, thermal stability, viscosity, spinning pressure) suitable for melt spinning a given composition (i.e. AN/MA ratio and molecular weight). Once these conditions are established, then suitable amounts of the composition will be synthesized and then spun into fibers.

In addition to the synthesis of AN/MA, copolymers will be synthesized for evaluation as well. Macromonomers containing methacrylate functionality and a side chain of poly(caprolactone) with molecular weights of 1,000 to 5,000 will be prepared and co- or ter-polymerized with AN and MA to assess whether they can improve melt processibility.

Once the desired composition (i.e. AN/MA ratio and molecular weight) is identified, the processing conditions are established, and sufficient quantities of polymer are synthesized, the resins will be spun using a specially designed spinning system being developed. The spinning system allows the extruded filaments to be spun into a pressurized environmental chamber which cools the filaments and suppresses foaming. The filaments leaving the chamber will then be drawn on heated draw rolls to remove water and impart orientation and increased tensile strength. The mechanical properties of the filaments will be measured to obtain the modulus and tensile strength.

ORNL will characterize the 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 first generation filaments. We are targeting 18 Msi modulus and 200 ksi strength in second generation filaments.

## FY 2010 Publications/Presentations

1. Jianhua Huang and Donald G. Baird, "Rheological Behavior of Polyacrylonitrile Copolymers Plasticized With Water", *Proceedings of the 68<sup>th</sup> Annual Technical Conference*, Orlando, FL, May 16–20, 2010.
2. Felix L. Paulauskas, "High Strength Carbon Fibers", poster presentation at 2010 DOE Hydrogen Program and Vehicle Technologies Annual Merit Review and Peer Evaluation Meeting, June 7–11, 2010.
3. Felix L. Paulauskas, "Potential Cost Reduction of High Strength Carbon Fibers and Status Report", presentation at Hydrogen Storage Tech Team Meeting, May 20, 2010.

## 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.