

## IV.D.7 Melt Processable PAN Precursor for High Strength, Low-Cost Carbon Fibers (Phase II)

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determined annually by DOE

will allow spinning precursor that can be fully processed through conversion, while not necessarily meeting ultimate project performance goals. Utilize an integrated effort of formulation and processing by team members. With baselines established, the optimum chemistry will be developed in iterations moving towards these ultimate objectives.

- Implement better and more precise stretching tools to facilitate low temperature drawing immediately after spinning and conversion trials with precursors. This is to minimize the time required in developing and demonstrating appropriate conversion protocol for producing carbon fiber.

### 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 manufacturing of durable, lightweight, compressed hydrogen storage vessels for use in high-pressure storage (i.e., 700 bar). 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

### Accomplishments

- Successfully completed a carbon fiber precursor production milestone: Based on results of continuing trials with polyacrylonitrile co-polymerized with vinyl acetate (PAN-VA) process development materials, the

### Overall Objectives

- Demonstrate means to achieving cost reduction of  $\geq 25\%$  in the manufacturing of carbon fiber, which meets the properties of industry baseline carbon fiber utilized in the fabrication of composite pressure vessels for hydrogen storage.
- Develop and demonstrate new chemistry and spinning techniques, while assessing the capability for advanced conversion technologies to meet the needs of carbon fiber manufacturing costs reduction for meeting program performance goals.

### Fiscal Year (FY) 2016 Objectives

- Completed the required modifications to the extruder necessary to produce and improve melt spun precursor samples that meet progressively greater properties as demonstrated by the testing of converted carbon fiber. Key precursor target is polyacrylonitrile co-polymerized with methyl acrylate (PAN-MA) fibers with greater than 100 filaments and continuous lengths  $>100$  m by June 30 to facilitate production of carbon fiber achieving 22 Msi modulus and 250 ksi strength with 25–50 m tow by September 30.
- Down-select appropriate chemistry, PAN-MA. Constituent levels and molecular weight of this recipe

team down-selected processing conditions and water–plasticizer formulations and demonstrate spinning of >100 filament tows of length >10 m.

- Improvements continue to be implemented in developing simplified processes for pelletizing the carbon fiber precursor material for near-term trials. At the time of this report, fiber has been produced with the modified spinning system, but the quality of this fiber in terms of length (~10 m), fiber count (~140 filaments) and fiber diameter (>40 microns) is not sufficient for proceeding with conversion trials.
- Initiated a series of spinning–extrusion trials utilizing twin screw extrusion equipment and expertise at Leistritz in late March as a parallel effort and backup approach to complement the spinning work with the single screw extruder at Virginia Tech. The team was able to extrude some short sections of polyacrylonitrile (PAN) plasticized with water and/or acetonitrile at up to a foot in length, but success was inconsistent.
- Processes for producing and characterizing specific formulations of PAN and MA have been established, along with the effectiveness of various plasticizer approaches in suppressing the melt temperature to acceptable processing temperatures in the range of 145°C–175°C which is significantly below the cross-linking temperatures. Significant data including melt temperatures and viscosity as a function of temperature as well as other characteristics on a wide variety of formulations has been produced to guide the program in establishing spinning baselines and then providing alternatives for improving properties towards program goals.
- A baseline PAN-MA blend at a specific molecular weight (~150,000) and PAN-MA (93:7) ratio have been selected. This was performed via collaboration among the chemistry, spinning, and conversion teams and procured via contract in quantities adequate to support several months of further formulation development and spinning trials.



## INTRODUCTION

High strength carbon fiber enables the manufacturing 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 [1]. 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. This is 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 United States, 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 in earlier work. Phase II is scaling the process up from very small batch quantities to continuous extrusion and improving properties towards the program targets.

## 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—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. This 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 min or longer.

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

- Melt-spun precursors are being formulated for evaluation, with the goal of developing a pelletized form for later melt spinning.
- Methods for handling, melting, and spinning the polymer are being developed to produce precursor fiber for the oxidative stabilization and carbonization conversion processes.
- Processing of the new polymer into finished carbon fiber will be necessary to demonstrate achievable properties, beginning with conventional processes.
- Processing of the new polymer into finished carbon fiber using the alternative manufacturing processes will be assessed.

## RESULTS

The project team has made accomplishments during this period in advancing techniques required to produce adequate quality and quantities of precursor fiber necessary to establish stable and continuous conversion processes. To facilitate progress in spinning, the team utilized lower cost and somewhat easier to process samples of PAN-VA formulations. Note, making the full transition to PAN-MA formulations projected is necessary to achieve both economic and ultimate performance goals during this period. To establish spinning baselines, the team set molecular weight, molecular weight distribution, and acrylonitrile content ranges to focus on during this project period. All of these parameters, in conjunction with the plasticizer type, plasticizer and content, and spinning parameters will determine the spinnability of a particular composition. The current objectives are to provide trial materials with approximately 93–95 wt% acrylonitrile and 5–7 wt% methyl acrylate. The materials are being screened in the modified capillary rheometer spinning apparatus using plasticizers such as water and acetonitrile to determine the spinnability.

### Formulation Development

The overall objective is to develop a melt spinning process for polyacrylonitrile copolymer fibers that can be converted to high strength carbon fibers. PAN is typically spun from solutions of dipolar aprotic solvents such as dimethylformamide (DMF), which is subsequently extracted in a downstream water bath. The solvent is necessary, because the copolymers have melting points that are far above the onset temperature of cyclization (i.e., accompanied by an increase in melt viscosity), and therefore they cannot be melt-processed without special conditions. Formulations containing plasticizers can reduce both glass transition

temperature ( $T_g$ ) and melting temperature ( $T_m$ ) relative to the base copolymers alone. Thus, the team's approach includes determining thermal and rheological properties of polyacrylonitrile copolymers, and thermal and rheological effects of including "external" plasticizers in the copolymer formulations. The plasticizers tend to disrupt strong polar interactions among nitrile groups along the polymer chain, thus lowering the glass transition and melting temperatures of the polymer [11]. This is critical for melt processing because neat polyacrylonitrile copolymers melt at such high temperatures (~320°C) that decomposition and cyclization occur before the high melting point can be overcome. In addition to their propensity to lower the transition temperatures, the choice of additive is based on ease of removal from the spun fibers, any potential toxicity, boiling point, and flash point, all of which can contribute to the overall cost of fiber production as well as to the quality of the resulting fibers.

A compilation of potential plasticizers is provided in Table 1. All of the additives in Table 1 are synergistic with water in terms of lowering the melting points of the copolymer formulations. One consideration is how difficult it may be to quantitatively remove the additive(s) following spinning, and thus a high boiling point–low vapor pressure additive may cause challenges. N-methylpyrrolidone (NMP) acts similarly to DMF as a plasticizer in terms of reducing the polymer transitions, but NMP has a higher boiling point. It is reasoned that it may be more difficult to extract NMP from the fibers once they are spun. Isopropanol functions similarly to ethanol and likely could be substituted.

**TABLE 1.** Plasticizers and Their Properties Pertinent to Melt Spinnability

Plasticizer	Boiling point	Vapor pressure (20°C)	Flash point	Toxicity
DMF	152–154°C	516 Pa	58°C	Not a carcinogen. May cause birth defects.
Ethanol	78°C	5,950 Pa	~14°C	Non-toxic
Adiponitrile	295°C	0.3 Pa	93°C	Not a carcinogen. Skin exposure may cause skin irritation.
Acetonitrile	81°C	9,710 Pa	2°C	Not classified as a carcinogen. Modestly toxic in small doses.

Melt extrusion will require a temperature window of opportunity that lies above the melting point of the particular formulation and below the temperature–time upper limit, as characterized by the onset of cyclization. Additives that open up this window by depressing the melting points are thus of great interest. Thermograms illustrating depressions of transition temperatures of PAN-MA/water/second plasticizer formulations are depicted in Figures 1–4. These properties

were measured by differential scanning calorimetry (DSC) at a heating rate of 10°C/min in “high volume pans” to avoid any contamination of the instrumentation caused by any evolution of additives. All reported data are from second heating scans. The equilibrium maximum water uptake was measured at 25°C for both the PAN-MA copolymer and the PAN–vinyl acetate–vinyl alcohol copolymer. The PAN-MA copolymer absorbed ~6 wt% of water, whereas the PAN–vinyl acetate–vinyl alcohol copolymer absorbs significantly more water (16 wt%) under these conditions. Figure 4 shows glass transition temperatures of blends of the PAN-MA copolymer with varied amounts of water added. It should be noted that it is difficult to make such blends for DSC analysis with these low water contents and know exactly how much water is added to the DSC pan, since some of the blends are heterogeneous. The peak centered around 0°C corresponds to the melting endotherm of the water and the discontinuity in heat flow at the higher temperatures denote the  $T_g$ s of these blends. One observes a large depression in  $T_g$  from the PAN-MA alone (104°C) to the blends with very little water added (~75°C). However, with further increases in water, no additional depression is observed. This is likely related to the equilibrium water uptake being low. It is reasoned that excess water may be “free” water that does not interact effectively with the copolymer.

Melting endotherms for the PAN-MA–water–DMF and PAN-MA–water–acetonitrile are depicted in Figures 2 and 3, respectively. In all of these cases where melting points are depressed, water is synergistic with the second plasticizer. In Figure 2, the lower thermogram is of a blend of the PAN-MA with 30 wt% of DMF, and no melting point is observed within the needed temperature range for extrusion. The

orange curve (second from bottom) is for a blend of PAN-MA containing 20 wt% of water and no DMF. From Figures 1 and 2, this blend has a  $T_g$  of 75°C and a  $T_m$  of 156°C. As varied amounts of DMF are added to the PAN-MA–20 wt% water blend, the melting point continues to decrease. This suggests a synergism between these two additives regarding melting point depression. Figure 3 shows a similar trend as acetonitrile is added, but the effect is even more substantial.

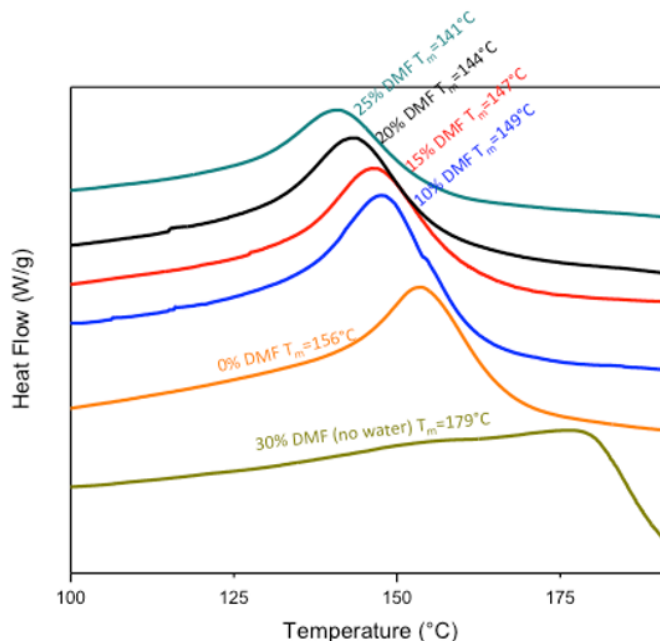


FIGURE 2. Melting endotherms of PAN-MA containing water and DMF

DSC of PAN-MA (1106) at Various Water Percentages

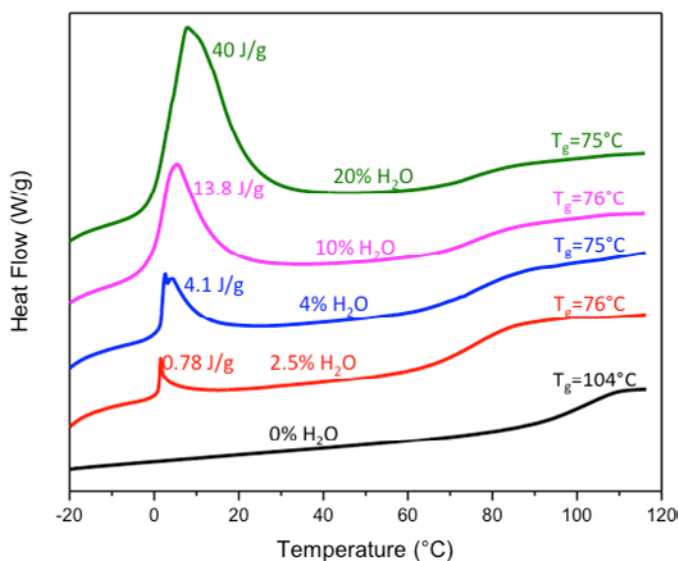


FIGURE 1. Glass transition temperatures of PAN-MA–water blends

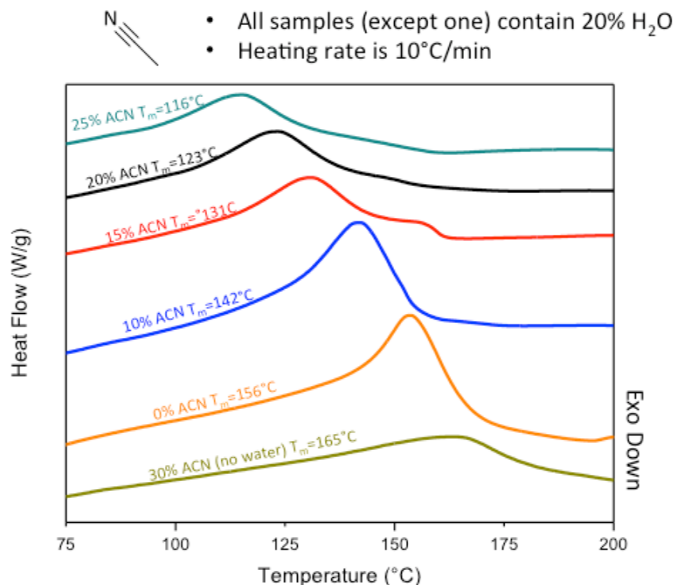


FIGURE 3. DSC thermograms showing melting endotherms of PAN-MA–water–acetonitrile formulations



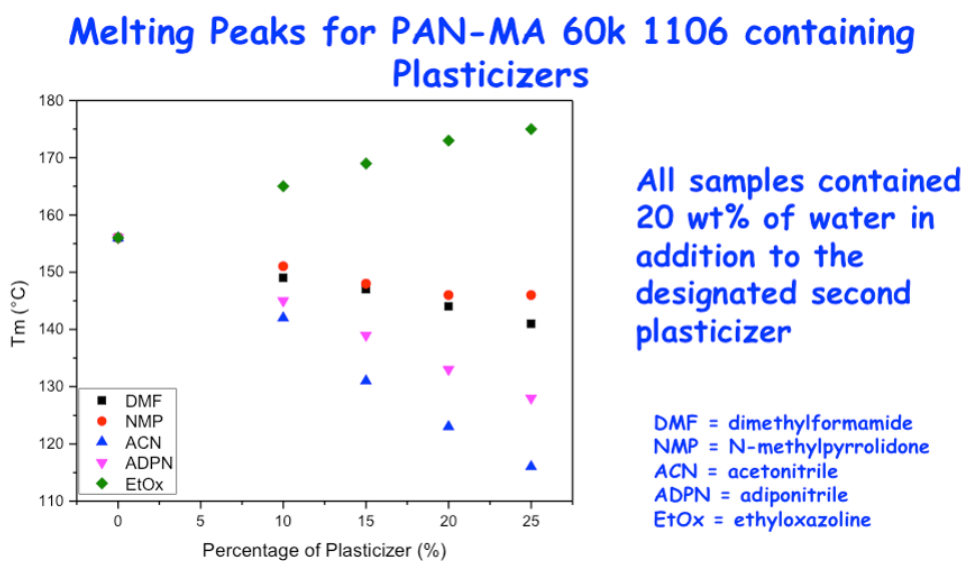
With a formulation of 70% PAN-MA–20% water–10% acetonitrile, the melting point is depressed to 142°C, whereas a similar formulation with DMF shows a melting point at 149°C. Neither water alone nor do any of the other plasticizers alone depress the melting points as effectively as the combinations. A select compilation of melting points with PAN-MA–20 wt% water–second plasticizer is shown in Figure 4 and Table 2. DMF, NMP, and acetonitrile are good solvents for the copolymer, whereas water and ethanol are non-solvents. The mechanism by which the plasticizers depress the thermal transitions of the formulations are not yet understood. Figure 4 shows that the melting points with acetonitrile and adiponitrile (both containing nitriles) are the lowest, and that DMF and NMP (both dipolar aprotic solvents for the copolymer) are in the intermediate range.

### Spinning Process Development

Rheological testing is being performed on formulations of interest to support spinning process development. Generally, both time-dependent viscosity measurements and shear rate-dependent viscosity measurements for polyacrylonitrile copolymers with various plasticizers were conducted. Some of the data is presented and analyzed.

Figures 5 and 6 show the time-dependent rheological data for PAN-VA–EtOH–H<sub>2</sub>O and PAN-VA–H<sub>2</sub>O. Generally, the viscosity increased when temperature was higher than 180°C. This suggests that the PAN-VA copolymer begins to cyclize under these conditions. However, there was no significant viscosity increase within 35 min even at 190°C. That suggests that the team may spin the PAN-VA fiber at such a temperature without significant cyclization with concomitant viscosity increase with a residence time of at least 30–35 min. However, because tails in the residence time distribution in the extruder can exceed 30 min, cyclization of the PAN-VA can occur at temperatures above 180°C.

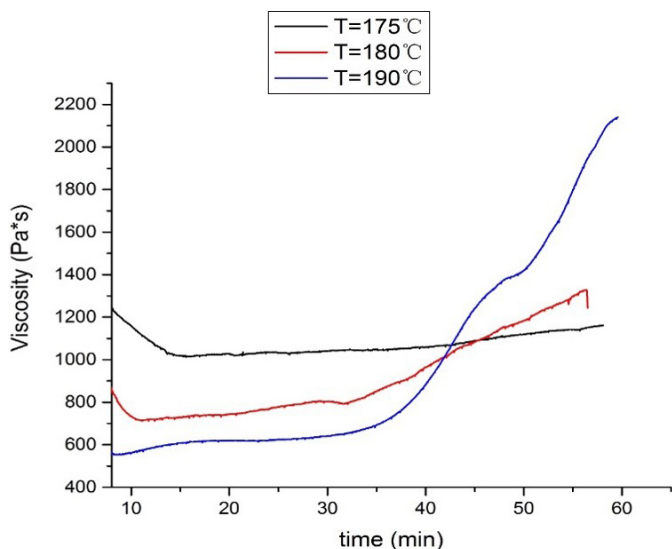
Various purge materials have been evaluated as a means for initial sealing of the extruder to assist in maintaining the volatile plasticizers, while initiating spinning as well as cleaning the extruder when spinning is completed. Evaluated purge materials include those shown in Table 3, as well as other formulations. With the mixture of PAN-VA, ethylene carbonate, and water being used as the purge material, the team could start fiber spinning and obtain PAN-VA filaments wound on a bobbin successfully. However, there was a common problem observed in all spinning trials. That is, the pressure of the PAN melt dropped about 20 min after the fibers first exited from the spinneret. At the same time,



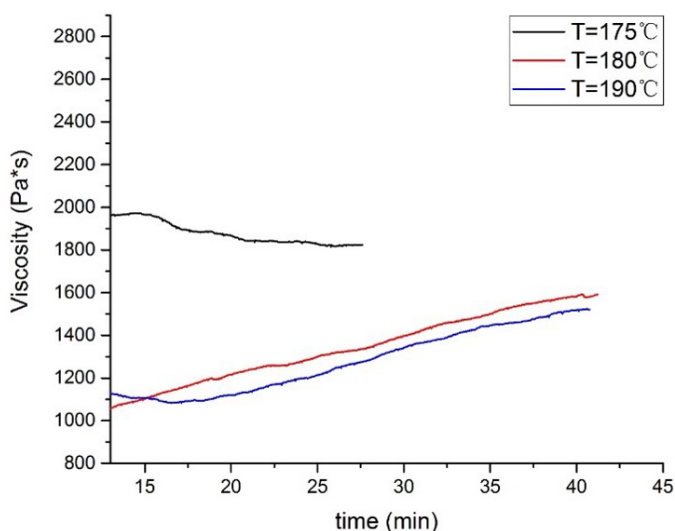
**FIGURE 4.** Melting points of PAN-MA–20 wt% water–second plasticizer formulations

**TABLE 2.** Thermal Properties of PAN-MA Plus Plasticizer Compositions

70 wt% PAN-MA–20 wt% H <sub>2</sub> O	+ 10 wt% DMF	+ 10 wt% Ethanol	+ 10 wt% Adiponitrile	+ 10 wt% Acetonitrile
T <sub>m</sub> 156°C	T <sub>m</sub> 149°C	T <sub>m</sub> 148°C	T <sub>m</sub> 145°C	T <sub>m</sub> 142°C
60 wt% PAN-MA–20 wt% H <sub>2</sub> O	+ 20 wt% DMF	+ 20 wt% Ethanol	+ 20 wt% Adiponitrile	+ 20 wt% Acetonitrile
T <sub>m</sub> ~156°C	T <sub>m</sub> 144°C	T <sub>m</sub> 149°C	T <sub>m</sub> 133°C	T <sub>m</sub> 123°C



**FIGURE 5.** Time dependent apparent viscosity data for the PAN-VA copolymer plasticized with water-ethanol



**FIGURE 6.** Time dependent apparent viscosity data for the PAN-VA plasticized with water only

**TABLE 3.** Summary of PAN-VA Fiber Spinning (Plasticized with 20 wt% of Water) Initiated with Purge Materials

Purge Materials (PM)	Form of PM	Temperature (°C)	PM passes spinneret?	Were PAN fibers obtained?	Observation/Comments
Barex*	Pellet	190	No	No	190°C may be too low for the Barex
Polyethylene	Pellet	190	Yes	No	PAN degraded seriously inside the spin pack
PAN-VA + H <sub>2</sub> O + Ethylene Carbonate	Powder	190	Yes	No	PAN degraded seriously inside the spin pack
PAN-VA + H <sub>2</sub> O + Ethylene Carbonate	Powder	185	Yes	Yes	No serious PAN degradation

\* Commercial name for 65AN/25MA/10Elastomer Copolymer.

the number of filaments decreased and the fiber diameter decreased.

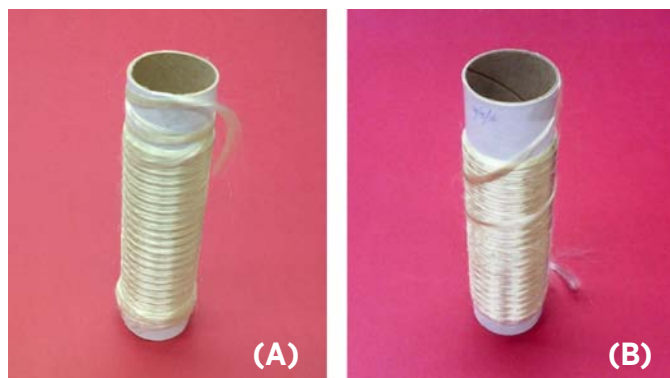
A further study confirmed that the PAN-VA pellets had stopped feeding some 20 min after the spinning began. It is believed the reason for this is that some of the water in the hot zones may have evaporated and then condensed in the cold zone (feed section). It is believed that the pellets in the feed section may have absorbed the condensed water and become too wet to be fed continuously.

Several methods were investigated to solve this problem, including the use of an open hopper, increasing the hopper/extruder pressure, use of a nitrogen purge in the hopper and starved feeding of materials (PAN pellets). The starved feeding method was successful. For the device needed for this method, the team started with a valve to control the feeding speed manually, and then designed and constructed a motor-driven feeder to control the feed speed automatically. The feeder was mounted between the hopper and the feed section and was designed and outfitted to operate under pressure.

Since the feeder was implemented, it was found easier to feed the PAN pellets continuously. The melt pressure was also more stable.

Figure 7 shows the PAN-VA fibers generated in March and April of 2016. The spinning was conducted at 185°C with water (20 wt%) as a plasticizer. The fiber tow generated in March (Figure 7A) had a length of 20 m and a filament number of 280, whereas another generated in April met the DOE milestone of December 31, 2015 which read as: “Down-select processing conditions and water/plasticizer formulations for PAN-VA and demonstrate spinning of >100 filament tows of length >10 m.”

Experiments showed that it was difficult to feed the PAN powders mixed with water (as a plasticizer) through the extruder. Thus, PAN pellets were made first and then used in the fiber spinning process. Several methods have been developed and evaluated at varying levels of success; additional work is continuing in this area.



**FIGURE 7.** PAN-VA fiber tow with a filament number of 280 and length of 20 m generated on March 22, 2016 (A), and another with a filament number of 315 and length of 50 m generated on April 25, 2016 (B)



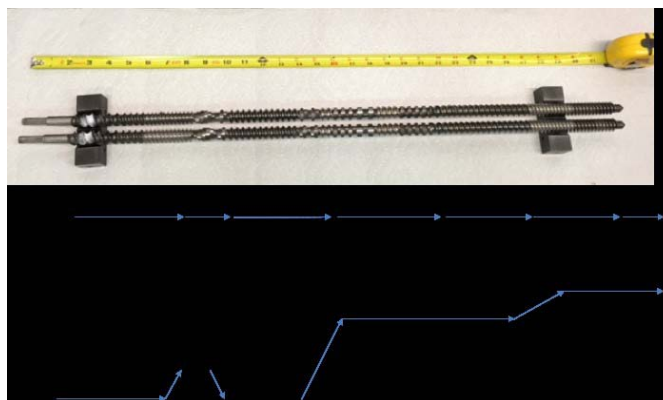
**FIGURE 8.** PAN-MA fibers generated on April 5, 2016

The focus of the team’s spinning work has been moved from PAN-VA to PAN-MA, since a key milestone was achieved in March 2016 when PAN-VA fibers were successfully generated. The team was able obtain some fibers and wind them on a bobbin. One of the fiber tow samples had 140 filaments that were approximately 10 m long (see Figure 8). This is promising, but will require further investigations to improve the feeding process and also adjust the plasticizer and temperature parameters to lower the melt viscosities over the residence time needed for extrusion.

As a parallel effort and backup approach to complement the spinning work with the single screw extruder at Virginia Tech, a series of spinning/extrusion trials utilizing twin screw extrusion equipment and expertise was initiated at Leistritz to investigate potential benefits of a twin-screw approach. Specific capabilities of interest in their laboratories include (1) modular construction allows rapid change-out of screw types overall and sections of the screw along the length as well as adjustment of screw length and barrel as shown in Figure 9, (2) production rates are more tunable in optimizing conditions, and (3) Leistritz extruder modules have ports available for downstream injection of second and third phases – powder can be fed dry and the plasticizers then injected downstream. Early trials demonstrated capability to extrude some short sections of PAN plasticized with water and/or acetonitrile, but success was inconsistent. At the time of this report, potential for the twin screw extrusion approach is still inconclusive.

**CONCLUSIONS AND FUTURE DIRECTIONS**

Continuing progress is being made in improving melt spinning processes towards producing precursor fiber in sufficient quality and minimum quantity to begin carbon fiber conversion investigations. Work on the precursor chemistry necessary to enhance baseline properties and move



**FIGURE 9.** Example screw setup at Leistritz showing modularity and functions of various screw sections

towards the ultimate goals of 33 Msi modulus and 700 ksi strength is making significant progress. Near-term objectives are for Virginia Tech to produce longer and more uniform tows that are then drawn in a secondary step. ORNL will characterize fiber and conduct more extensive 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. 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.

## FY 2016 PUBLICATIONS/PRESENTATIONS

1. Felix L. Paulauskas and Bob Norris, “Melt Processable PAN Precursor for High Strength, Low-Cost Carbon Fibers,” presentation at 2016 DOE Hydrogen and Fuel Cells Program and Vehicle Technologies Office Annual Merit Review and Peer Evaluation Meeting, June 8, 2016.

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