

IV.D.5 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: Project continuation and direction
determined annually by DOE

Overall Objectives

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

Fiscal Year (FY) 2015 Objectives

- Complete extruder installation and checkout and any required modifications necessary to begin melt spinning precursor samples meeting progressively greater properties as evidenced by testing of converted carbon fiber. As scale-up from bench scale experiments utilizing a capillary rheometer does not entail just making larger quantities of precursor dope, it was anticipated that this would be completed in early FY 2015, but acknowledged it could take longer.
- Utilizing integrated effort of formulation and processing team members, down-select appropriate chemistry including polyacrylonitrile co-polymerized with methyl

acrylate (PAN-MA) constituent levels and molecular weight of this recipe to allow spinning precursor that can be fully processed through conversion while not necessarily meeting ultimate project performance goals. With baselines established, optimum chemistry will be developed in iterations moving towards these ultimate objectives.

- Establish better and more precise stretching tools to facilitate low temperature drawing immediately after spinning and conversion trials with precursors to minimize 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 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 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

- Extruder installation and checkout were completed and a number of modifications were implemented in order to enable melt spinning of PAN precursor. Related spinning equipment such as spinnerets with larger hole

numbers, spin packs, and larger pressure chamber have been completed and installed. Initial attempts to directly feed PAN powder were met with significant difficulties; these difficulties were overcome by developing a simplified process for pelletizing the 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 is not sufficient for proceeding with conversion trials.

- Chemistry, spinning, and conversion teams collaborated to establish a baseline PAN dope recipe and a contract put in place to procure adequate quantities of a specific PAN-MA blend at a specific molecular weight for initial studies.
- Processes for producing and characterizing specific formulations of PAN and MA along with the effectiveness of various plasticizer approaches in suppressing the melt temperature to acceptable processing temperatures below the cross-linking temperatures have been established.
- Better and more precise stretching tools to (1) facilitate low temperature drawing immediately after spinning, and (2) enhance molecular orientation in conversion trials have been designed, built, and delivered. These tools will serve to more systematically minimize time required in developing and demonstrating appropriate conversion protocol for producing carbon fiber.



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 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. The conversion protocol consists of a number of steps in simulating oxidation with DSC 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 intramolecular manner, but also via intermolecular 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 with the goal of developing a palletized form for later melt-spinning. 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 accomplishments in completing appropriate upgrades and implementing/demonstrating the capabilities required to produce adequate quality and quantities of precursor fiber necessary to establish stable, continuous conversion processes. Although the team continues to utilize lower cost and no longer critical quantities of polyacrylonitrile co-polymerized with vinyl acetate (PAN-VA) formulations employed to demonstrate basic feasibility in Phase I for equipment checkout and technique development, the developmental focus has been fully transitioned to PAN-MA formulations projected to be necessary to achieve both economic and performance goals. The synthesis efforts at Virginia Tech have focused on the preparation of ranges of AN content poly(acrylonitrile-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 acrylonitrile 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% acrylonitrile and 5 wt% methyl acrylate although the team has selected somewhat lower levels for establishing project baselines. 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

Recent formulation work has been focused on characterization of copolymer compositions, thermal properties of the copolymers in the presence of water and ethylene carbonate, and melt viscosities conducted under pressure to accommodate low-boiling plasticizers in the potential spinning compositions. PAN is typically spun from solutions of dipolar aprotic solvents because it has a melting point that is above the onset of cyclization (cross-linking), and therefore cannot be melt-processed without special conditions as sought after in this research. Comonomers, particularly vinyl acetate or methyl acrylate, can be introduced that disrupt intermolecular interactions among the polar nitrile groups and the polymer backbone. Randomly spaced comonomers can increase the distance between pendent nitriles and interrupt the sequences of nitriles. Plasticizers such as water, acetonitrile, and ethylene or propylene carbonate can likely reduce both t_g and t_m relative to the dry copolymers. Thus, the short-term objectives in this phase of the research include determination of thermal and rheological properties of polyacrylonitrile copolymers, and thermal and rheological effects of adding plasticizers to the formulations.

A sample of PAN-MA copolymer from a commercial producer that has a composition of 96 mol% of acrylonitrile and 4 mol% of methyl acrylate has been utilized for sensitivity studies. This corresponds to 93 wt% acrylonitrile and 7 wt% methyl acrylate. It has a weight average molecular weight of approximately 220,000 g/mol. It is anticipated that these copolymer properties may lead to the high strength carbon fibers that will be optimum for reinforcing the composites to be used for hydrogen storage. For comparisons, the project team has synthesized a series of copolymers with PAN-MA compositions. It is anticipated that copolymers with higher acrylonitrile compositions may lead to improved properties in the converted carbon fibers, but that melt-spinning will be more challenging as the acrylonitrile content is increased.

A PAN-MA copolymer that contained 94 mol% of acrylonitrile and 6 mol% of methyl acrylate (i.e., 91 wt% acrylonitrile and 9 wt% of methyl acrylate) was blended with an excess of water, dried down to approximately 20 or 50 wt% of water in the blend, then cold-pressed into pellets. The weight average molecular weight of this copolymer is approximately 130,000 g/mol. The thermogravimetric analysis (TGA) weight loss profiles of that copolymer and a blend of the copolymer with nominally 20 and 50 wt% of water are depicted in Figure 1. One can observe evaporation of the water at ~100°C in approximately the expected amounts, then a weight loss at about 300°C, likely corresponding to loss of some of the comonomer

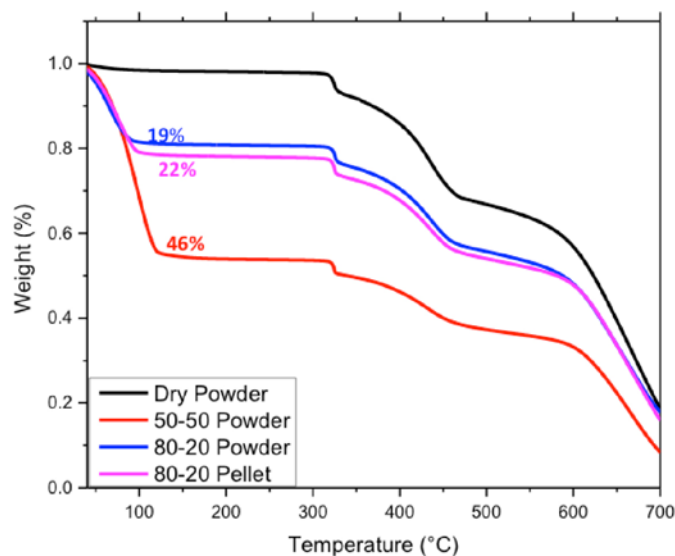


FIGURE 1. Weight loss profiles for PAN-MA with 94 mol% acrylonitrile and 6 mol% methyl acrylate

residues. The amount of weight loss at 300°C is lower in this copolymer relative to the PAN-VA copolymer depicted in Figure 2, and this is likely due to the smaller amount of comonomer in this copolymer relative to that in the PAN-VA. Isothermal TGA scans of these two materials at 325°C show that the time required for the weight loss around 300°C is about 36 minutes for the PAN-MA and 49 minutes for the PAN-VA.

Differential scanning calorimetry (DSC) thermograms of these blends are shown in Figure 2. The dry copolymer has a t_g of 84°C that is depressed to about 66°C in both blends. All of the blends have a broad t_m region that peaks at approximately 155°C but that extends to approximately 175°C. The similarity of the transitions suggests that all of the blends have the maximum amount of water absorbed into the copolymer. It may be noteworthy, however, that the blends with 20 wt% of water show a second small melting endotherm at about 190–200°C that is absent in the blend with 50 wt% of water. It is encouraging that the melting endotherms of these blends are very similar to those observed for the PAN-VA blend. Viscosity profiles as a function of time will be important as a future comparison.

Work with a PAN-VA copolymer blend that contained 20 wt% of water has a maximum temperature in the melting endotherm range of about 180°C. This blend has a melt viscosity of 1,400–1,500 Pa·s at a shear rate of 72 s⁻¹ and the viscosity at this temperature is stable over at least 40 minutes. This suggests that the blend may be spinnable from the melt under pressure. A polymer spinning aid formulation for the PAN-VA that contains the copolymer, a small amount of water, and ethylene carbonate as a plasticizer has a lower melting point by about 20°C than blends of this copolymer with water. This, or a similar composition, may serve as a

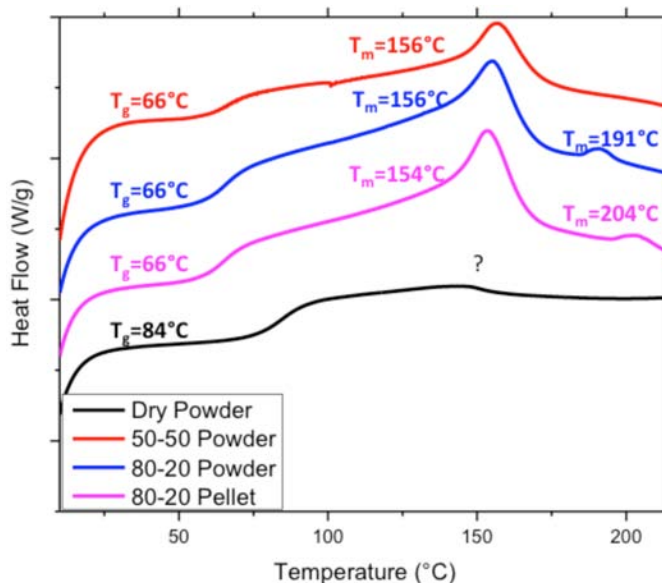


FIGURE 2. Thermal properties of PAN-MA with 94 mol% acrylonitrile and 6 mol% methyl acrylate and blends of that copolymer with water

valuable processing aid for both start-up and clean-up of a melt-spinning operation for PAN-VA. Blends of PAN-MA copolymers will require more investigation to evaluate and identify properties relative to the PAN-VA copolymers.

Spinning Process Development

Significant upgrades have been integrated to the extrusion system during the current reporting period. In addition to modifications to the extruder itself as described below, other key changes include (1) a much larger spin pack was designed, fabricated, sealed, and installed; (2) a larger spinneret was designed and procured; and (3) a larger pressure chamber and winder system was integrated. Even though the project focus has moved from PAN-VA to PAN-MA chemistry, the team decided to utilize older PAN-VA materials to work through feeding and initial spinning problems in order to conserve the more valuable PAN-MA materials for critical work in meeting targeted spun and converted fiber properties. Most spinning extruders are fed via pellets typically compounded by a preparatory melt extrusion process. Since thermal history of PAN dope is critical to not cross-linking the material, it had been hoped that this preparatory pelletization process might be avoided entirely which would both minimize cross-linking and provide additional cost-savings by eliminating a production step. Problems were encountered in getting powder to feed as the tackiness of the moist powder (moisture is required for plasticization) has resulted in nonuniform feed rates. The relatively open feed and extrusion process has also evolved significant portions of the moisture incorporated for plasticization resulting in materials also sticking once they are actually in the extruder.

Although it has not been concluded that the powder feed approach will not work (in fact there is some indication that BASF had some success in their work), the team concluded that it was more important to switch to a pelletizing approach in the near-term. It was thought that a commercial pasta extruder with an electronic cutting knife that could be used with the extruder to cut the strands into pellets at the desired length might be used for this purpose, but testing was not successful. Further more detailed discussion with persons having experience in this area led to consideration of a commercial meat grinder. The grinder as shown in Figure 3 was obtained and after a number of trials, success in making pellets at low temperature with hole diameters of 1/8 in was achieved as shown in Figure 4.

Utilizing the pellets as shown above, trial extrusion was run successfully using PAN-VA pellets plasticized with 20% water. For the first time, steady melt pressure and continuous PAN extrusion were achieved as shown in Figure 5. The efforts to purge PAN-VA out of the extruder/die with polypropylene failed. The screw had to be removed from the extruder for cleaning. Degraded PAN (dark brown in color) was still found on the screw.

Unfortunately most of the spinning trials have been unsuccessful in getting the PAN completely through and ejected from the extruder system. When the system is disassembled, degradation of PAN has been observed in essentially all extrusion experiments as evidenced by significant portions of darkened polymer representative of degradation through excessive cross-linking deposited in the screw chamber as well as frequently in other locations. The degradation is assumed to be a function of time and temperature exposure of the polymer. A contributing factor is believed due to the loss of water (plasticizer) at various places in the extrusion system. An early culprit was

moisture leakage through the open hopper. After the hopper was sealed and pressurized, it was apparent that sealing the hopper only was not enough to prevent the PAN from degrading. The plasticization moisture appeared to now be leaking through the gap between the screw and the barrel resulting in significant degraded deposits on the screw as shown in Figure 6. After evaluation of several approaches to mitigate leaking, the spinning team chose to cut a small groove and install an O-ring on the root part of the screw to seal the gap (see Figure 7). The extruder has been tested under static and dynamic conditions and is now airtight.

Near the end of this reporting period, the team did generate PAN fibers using the 397-hole spinneret for the first time and wound them on a bobbin (see Figures 8 and 9). The polymer pellets used were PAN-VA copolymer containing



FIGURE 3. The LEM Products 12# meat grinder in the spinning laboratory

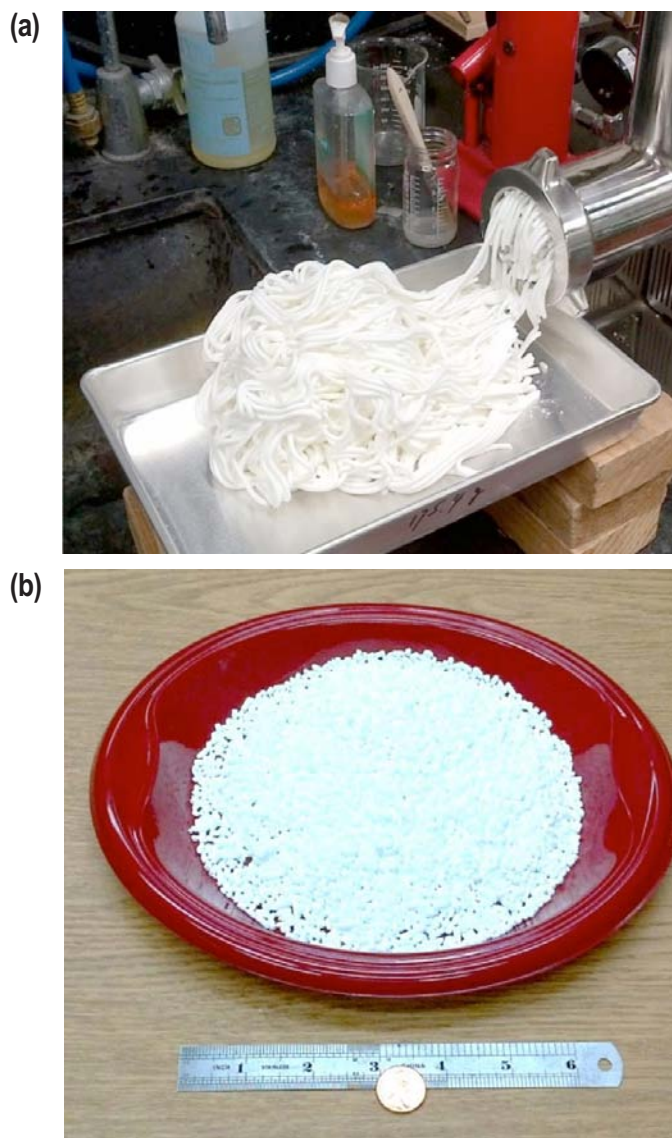


FIGURE 4. Wet PAN strands made with a meat grinder (a) and dried PAN pellets (b)



FIGURE 5. Fiber spinning using PAN pellets without the pressure chamber

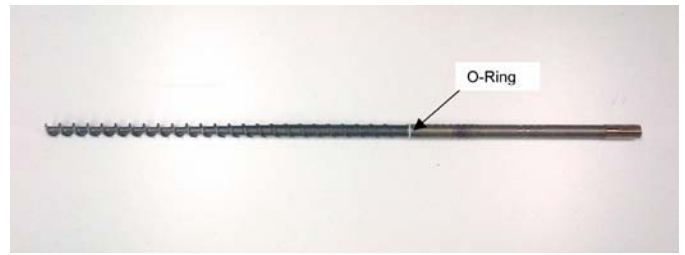


FIGURE 7. Modification of the screw by cutting a groove and installing an O-ring to provide an airtight dynamic seal between the screw and the barrel

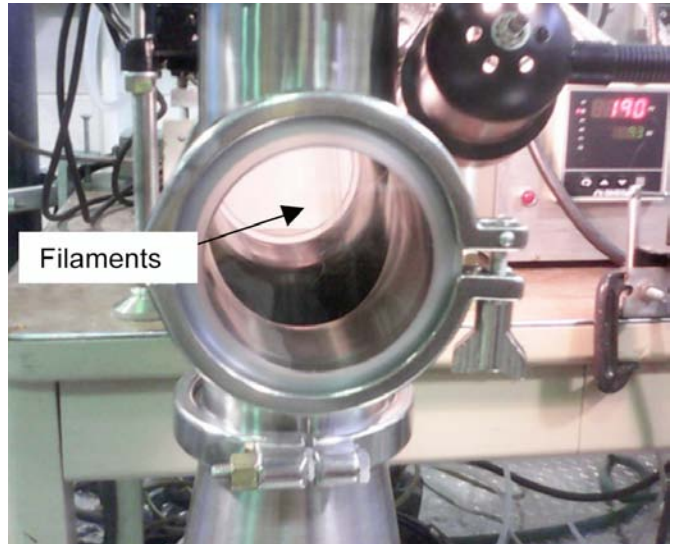


FIGURE 8. Melt-spinning of PAN fibers is in progress; the filaments could be seen through the sight window of the pressure chamber

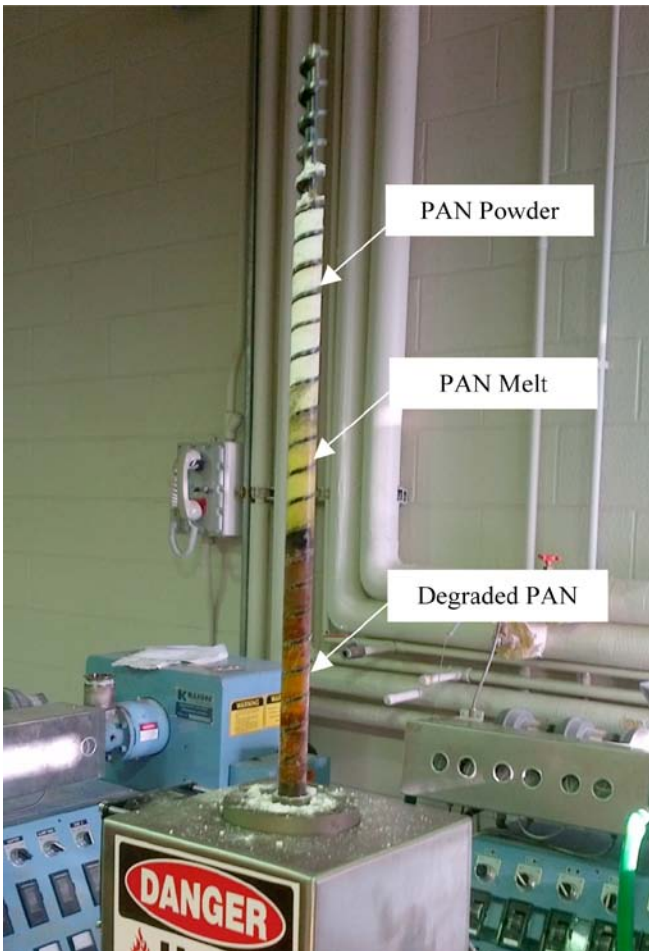


FIGURE 6. Polymer residual on the screw after trial extrusion



FIGURE 9. PAN filaments generated from 397-hole spinneret; the diameter of each filament is about 35 microns

20 wt% of water. The spinning temperature was about 190°C. The fiber tow is estimated to contain hundreds of filaments at about 30 meters in length. The diameter of each filament is about 35 microns. While the fibers did not look good and were difficult to despool (could not find the fiber end), it is an important achievement in the research efforts.

It was noted that this spinning trial lasted about 20 minutes or so before it had to be stopped due to high torque on the screw/motor. This was again apparently caused by degradation of PAN based on the observation on the residual polymers inside the spin pack. Although the quality of this precursor material was not sufficient to conduct conversion trials, the team does feel it is close to that key milestone.

Carbon Fiber Conversion Development

The conversion team technically supported other efforts as described above as well as bringing additional technical resources to the team having past experience in hands-on spinning of similar materials and contracted with an outside support to custom formulate and manufacture PAN dope to project team specifications. The team also designed and procured a steam draw system as shown in Figure 10 and a linear stretcher as shown in Figure 11. These equipment capabilities will facilitate development and demonstration of



FIGURE 10. Steam draw unit for precursor fiber



FIGURE 11. Linear stretcher for conversion processes

optimized conversion recipes for producing carbon fiber from the melt spun precursor.

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 earlier 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 2015 PUBLICATIONS/PRESENTATIONS

1. Bob Norris and Felix Paulauskas, "Melt Processable PAN Precursor for High Strength, Low-Cost Carbon Fibers," presentation at Hydrogen Storage Tech Team Meeting, March 19, 2015.
2. Felix L. Paulauskas and Bob Norris, "Melt Processable PAN Precursor for High Strength, Low-Cost Carbon Fibers," presentation at 2015 DOE Hydrogen Program and Vehicle Technologies Annual Merit Review and Peer Evaluation Meeting, June 10, 2015.

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