IV.F.3 Development of Low-Cost, High Strength Commercial Textile Precursor (PAN-MA)

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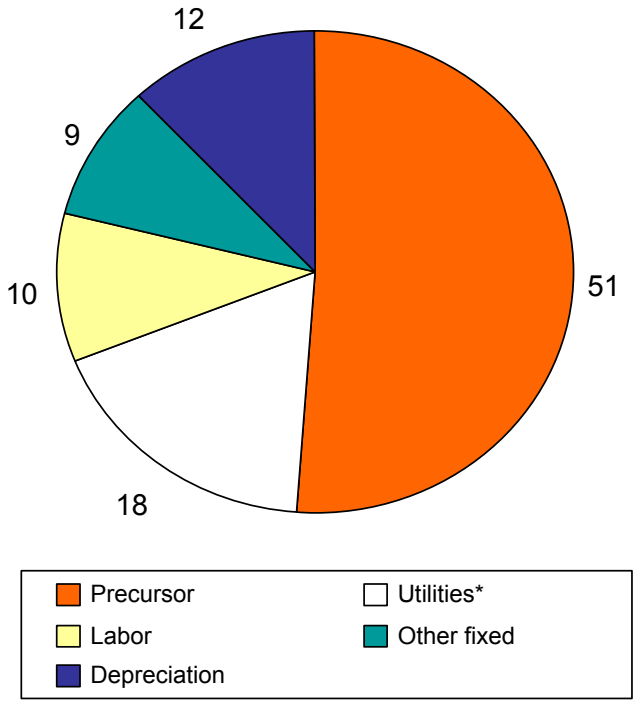

FIGURE 1. Carbon Fiber Production Costs

Fiscal Year (FY) 2012 Objectives

- Down-select from 11 polymer candidate polymer compositions to three for spinning fibers.
- Evaluate three fiber compositions to yield guidance for selecting the best fiber composition.
- Demonstrate at least 300 KSI breaking strength and 30 MSI modulus. (Gate Milestone)
- Down-select to one to two fiber compositions for property optimization.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(B) Storage System Costs

(A) System Gravimetric Capacity

Technical Targets

The hydrogen storage team has been conducting a project to develop lower cost carbon fiber precursors to reduce the cost of carbon fiber for hydrogen storage tanks. Precursors account for a little more than half of the finished carbon fiber cost and the cost of carbon fiber can account for up to 75% of the storage tank cost (Figure 1). This proposed effort is to develop a solution spun textile grade polyacrylonitrile with methyl acrylate (PAN-MA) precursor with strengths in the range of 550-750 KSI. This project is for a shorter-term, lower-risk approach to addressing the same issue as is being addressed by the melt-spun polyacrylonitrile (PAN) project. Ideally, the fiber developed in this proposal could be ready for commercialization within two to three years to meet programmatic needs. The melt-spun PAN when developed could be ready for market introduction a few years later. Both precursors would be suitable for applications in a wide range of other industries.

TABLE 1. Progress towards Meeting Technical Targets for PAN-MA-Based Lower Cost Carbon Fiber for Hydrogen Storage Tanks

	Strength (KSI)	Modulus (MSI)	Estimated Production Costs
Current Market Fibers	750	38	$15-20/lb
Target	650-750	35-38	$10-12/lb
Current Status of Candidate Precursors	350-400	25-35	$10-12/lb

FY 2012 Accomplishments (as of 1 July 2012)

- Down-selected from multiple polymer compositions down to 11 candidate compositions.
- Down-selected from 11 polymer candidate compositions down to three for spinning fibers for carbonization trials.
- Evaluated two of the three fiber compositions to yield guidance for selecting the best fiber composition. The third fiber composition is currently being evaluated.
- Demonstrated at least 300-400 KSI breaking strength and 27-36 MSI modulus from the first fiber composition.
- Demonstrated at least 300-400 KSI breaking strength and 25-36 MSI modulus from the second fiber composition.

Introduction

During the past several years, the Vehicle Technologies Program has been developing technologies for the production of lower cost carbon fiber for use in body and chassis applications in automobiles. Program goals target materials that have tensile strengths in excess of 250 KSI and modulus of at least 25 MSI. Past work included the development of a vinyl acetate co-monomered, lower cost precursor and methods for manufacturing precursors into finished carbon fiber. The basic premise of the project was to be able to use PAN material produced in a high volume textile production process for a carbon fiber precursor rather than the specialty material that is typically used for carbon fiber precursors. A textile line that formerly made knitting yarn has been retrofitted to commercialize that fiber.

The previously developed fiber has strengths slightly below 500 KSI, which is far above strengths suitable for automotive structural applications but insufficient for many higher demanding applications with higher performance requirements such as the manufacture of hydrogen storage tanks. In order to preserve the cost advantages of using a high volume PAN fiber, and simultaneously meet the needs of higher performance applications, it was proposed to develop the capability to use methyl-acrylate based, textile grade, PAN as a carbon fiber precursor and to manufacture that precursor on a textile line.

The purpose of this project is to take one precursor technology, textile-based PAN, while using a higher performance formulation, from the technical feasibility stage and scale up to technology demonstration. This project will result in the determination of the best polymer formulation and conversion protocol (time-temperature-tension profiles) to produce the best carbon fiber while also being readily and inexpensively manufacturable in existing textile PAN plants. Successful completion of this project will result in defining the precursor formulation and preliminary manufacturing methods to produce carbon fiber. A follow-on step may be necessary to optimize the properties, optimize the manufacturability in high volume and transfer the technology to a carbon fiber manufacturer. Deliverables include spools of fully carbonized and sized carbon fiber and composites made from that carbon fiber. This project is on the critical path for the development of lower cost carbon fiber.

Approach

The first step to developing a new precursor is to define and analyze candidate precursor formulations. Those are then down-selected and multiple candidate polymer formulations are produced. In this case, Fibras Acrilicas Portugese (FISIPE) down-selected to 11 candidate formulations. Those polymer formulations were sent to ORNL for evaluation from which three polymer formulations were selected to be spun into precursor fiber for attempted conversion into carbon fiber. FISIPE worked to determine how to spin each of those three formulations into precursor fiber tows and send them to ORNL for conversion trials. Developing uniformly round fibers and maintaining fiber consistency from fiber to fiber and along the length of each fiber were critical parameters.

Upon receipt of the precursor spools, ORNL began the thermal evaluations to pinpoint conversion temperatures of the precursor, particularly the temperatures to be used for oxidative stabilization. The next step was to determine the limits of fiber stretching that can be achieved in each of the oxidative stabilization stages. As a general rule, higher levels of tension (i.e. percentage of stretching) will promote better polymer chain alignment along the axis of the fiber and will result in higher breaking strengths of the fiber. It is therefore necessary to apply the maximum tension to the fiber, especially during the early stages of oxidative stabilization, without breaking the filaments.

The amount of stretching in each stage of conversion, the optimum temperatures for conversion and the time that the precursor is exposed to those conditions must be developed for each of the seven stages (Prestretching, Oxidation 1, Oxidation 2, Oxidation 3, Oxidation 4, Low-Temperature Carbonization and High-Temperature Carbonization) of processing. These must be done sequentially completing each processing step before proceeding to the next. Only after completing all of these steps can the final properties of the fiber be determined. The plan is to evaluate the three formulations, pinpointing processing parameters in approximate ranges and then down-select to one final formulation. For that formulation, all spinning and conversion parameters will then be optimized.

Results

The down-selection of chemical compositions and formulation started in April of 2011. The main issue related

to achieving the proper formulation was the generation of the PAN-polymer with a higher acrylonitrile (AN) content. Dealing with AN co-monomered polymer required some changes to FISIPE's equipment and standard practices which required three months. They were able to generate 11 candidate compositions. Three compositions were down-selected and sent to ORNL for evaluations. Differential scanning calorimetry (DSC) curves and other technical data for those compositions were generated for comparison to each other and to known aerospace and industrial grade precursors.

Upon receipt of the precursor spools, ORNL began the thermal evaluations to pinpoint conversion temperatures of the precursor, particularly the temperatures to be used for oxidative stabilization. Two features are prominent and were expected from the thermal evaluations: (1) The onset of the exotherm occurs at a slightly different temperature from traditional precursors indicating a different starting temperature for oxidative stabilization; (2) The exothermic curve is steeper than the PAN-vinyl acetate (VA) precursors indicating a slower temperature ramp up being necessary during oxidative stabilization.

Figure 2 shows the DSC curves for one of the new precursors at various stages of oxidation. Each "stage" in the legend corresponds to the resulting material property after exposure to a different temperature and gives a strong indication of the temperatures necessary in the oxidative stabilization ovens during conversion of the precursor. From these curves, we derive the first indication of both the times and temperatures necessary in each of the later three stages of oxidative stabilization. The profile is very similar to typical aerospace grade precursors with the only surprise being how far the stabilization process has progressed after stage 3. Similar curves were generated

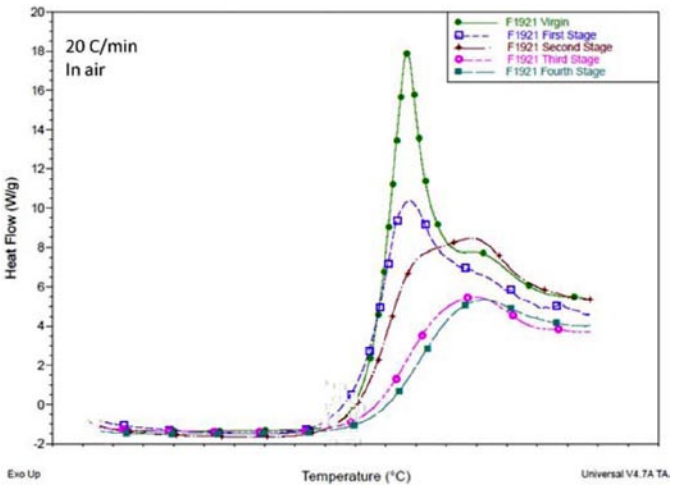

FIGURE 2. DSC curves for F1921 precursor after subsequent Oxidative Stabilization Treatments

comparing this new precursor to a typical 3,000 filament aerospace grade precursor after four each of the four stages of oxidative stabilization. That data indicated that we may need to proceed with a slightly higher temperature during oxidative stabilization in the final stage. The data collected in these types of evaluations gives a strong indication of the temperatures necessary for processing and a beginning understanding of the exposure times. After completion of the thermal analysis, ORNL then began the process of determining the optimum conversion protocol (combination of time, temperature and tension).

The next step was to determine the limits of fiber stretching that can be achieved in each of the stages during oxidative stabilization. As a general rule, higher levels of tension (i.e. percentage of stretching) will promote better polymer chain alignment along the axis of the fiber and will result in high breaking strength of the fiber. It is therefore necessary to apply the maximum tension to the fiber, especially during the early stages of oxidative stabilization, without breaking the filaments. Figure 3 shows the tension and percent stretching for fibers after exposure to the temperatures determined in the previous step. Of particular interest are the points marked with a triangle which indicate the upper tension limit of the processing window for these precursors. Export control restrictions require that all tension loads, stretching percentages, oven temperatures and residence times not be publicly disclosed, therefore axis values are intentionally left off of these charts. Filament diameters for the new precursor were measured at 11.7 microns which is within the desired range for an oxidized precursor. Normal ranges are 11-12 micron to produce a 7-micron diameter carbonized fiber.

The amount of stretching in each stage of conversion, the optimum temperatures for conversion and the time that the precursor is exposed to those conditions must be developed for each of the seven stages (Pre-stretching, Oxidation 1, Oxidation 2, Oxidation 3, Oxidation 4, Low-Temperature Carbonization and High-Temperature Carbonization) of processing. We have completed determination of the baseline conversion protocol for two of the precursors.

One issue that had to be dealt with for these precursors was "fuzzing" of the fiber tow during processing. Figure 4 shows an example of this. Fiber fuzzing is typically due to small, not fully developed "baby" fibers present in the precursor. Upon tensioning, these fibers see a higher than average stress, exceed their strength and break. This issue has been resolved.

The first carbonization trials were held in January with the first precursor. In the initial trials, a strength of 282 KSI and modulus of 27 MSI were achieved. Two weeks later, with further refinement, fibers were produced with strengths of 383 KSI and modulus of 36 MSI. The gate milestone for the end of March was to achieve 300 KSI and 30 MSI. This

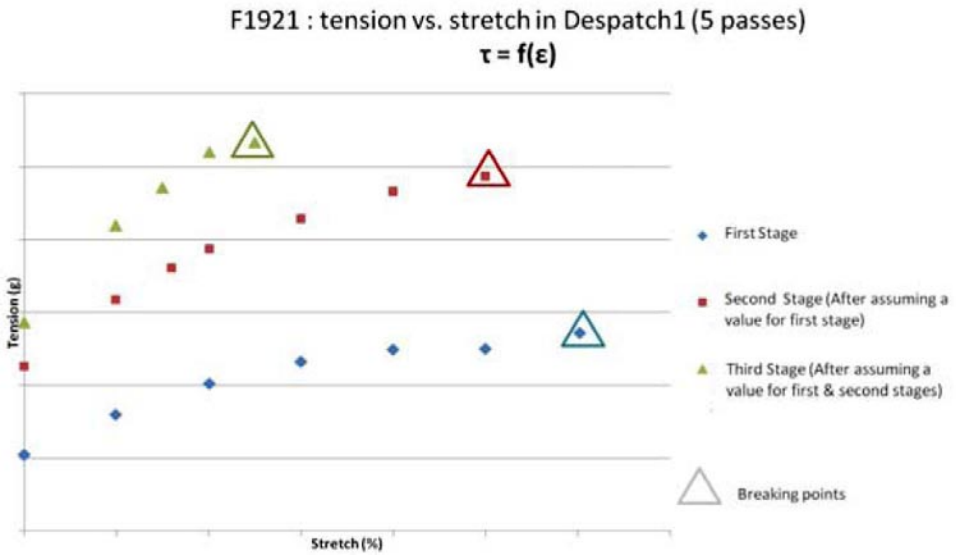

FIGURE 3. Tension vs. Percentage Stretching for the F1921 Precursor after various Oxidative Stabilization Treatments to Determine the Tension Limits during Processing

FIGURE 4. Left: "Fuzzing" of Filament Tow during Oxidative Stabilization; Right: Tow not Exhibiting "Fuzzing"

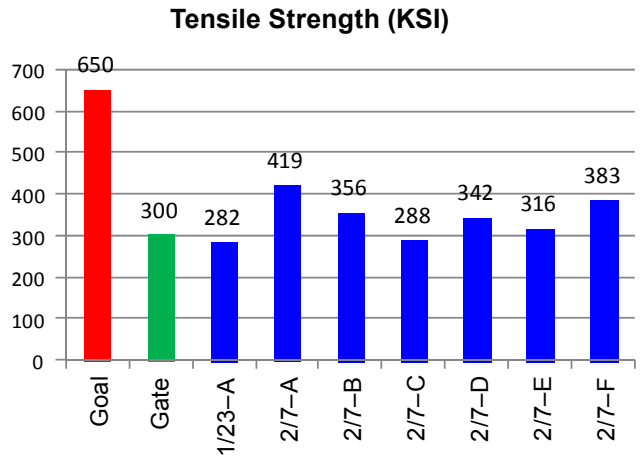

FIGURE 5. Tensile Strength as a Function of Time for the F1921 Precursor

milestone was completed. Figures 5 and 6 are the property as a function of time charts for tracking precursor progress. Each data point is the average of 18 tests.

Next we turned our attention to developing the conversion protocol for the second precursor. Initial values for this precursor were low but with further refinement have been demonstrated at an acceptable level for us to still consider this precursor a viable option. By reviewing some of the oxidation data, we will be revising some conversion parameters which should allow us to reach significantly higher values with this precursor. Figures 7 and 8, are the property as a function of time charts for tracking precursor progress. Each data point is the average of 18 tests.

We have recently received precursor spools from the other selected material F2027. Those are being evaluated and preliminary processing parameters being determined.

Conclusions and Future Directions

Both precursor evaluated meet our minimum screening criteria for properties. The gate milestone for project continuation has been met. We will be completing screening

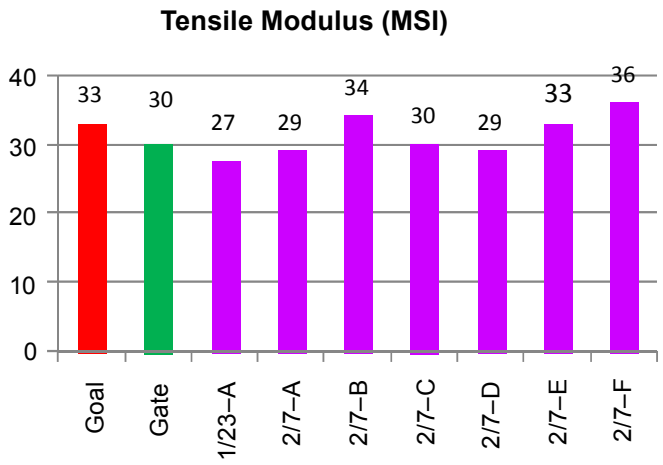

FIGURE 6. Tensile Modulus as a Function of Time for the F1921 Precursor

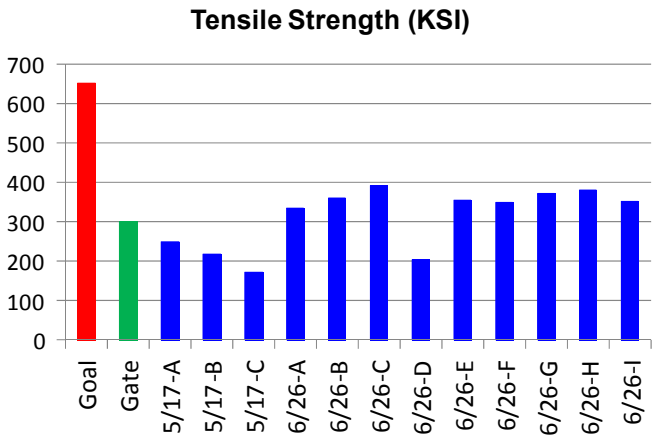

FIGURE 7. Tensile Strength as a Function of Time for the F1999/2000 Precursor

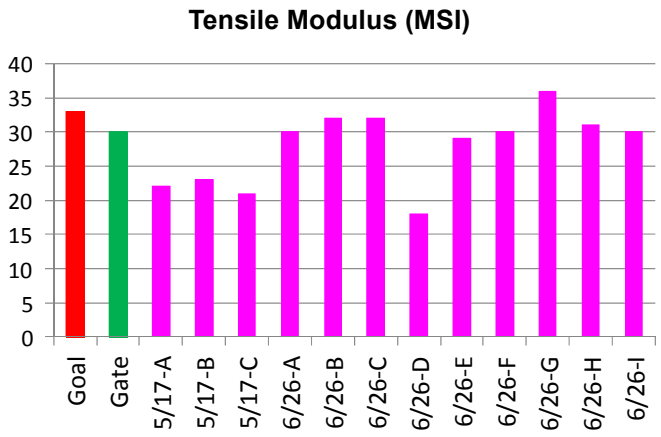

FIGURE 8. Tensile Modulus as a Function of Time for the F1999/2000 Precursor

of the third precursor and then will make a decision as to which formulation to pursue for property optimization. Some work in fiber to fiber consistency during precursor spinning will also be part of the work plan for the next year. The final carbon fiber achieved will be incorporated in a fiber plaque and tested in an epoxy resin system. If minimal fiber properties of 650 KSI strength and 35 MSI modulus are achieved, then closer work with a carbon fiber manufacturer will be warranted to incorporate this precursor into a production facility and optimize surface treatment and sizing protocols.

Special Recognitions

1. Dr. Felix Paulauskas won the 2012 DOE Vehicle Technologies Program R&D Award for carbon fiber research

FY 2012 Publications/Presentations

1. Warren, C.D. "Lower Cost Carbon Fiber in High Volumes for 21st Century Industries", Presented at and published in the proceedings of the SPE Automotive Composites Conference & Exhibition, Detroit, MI, 13–15 September, 2011.