D. Advanced Oxidation of PAN Fiber Precursor

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Contract No.: DE-AC05-00OR22725

Objectives

- Develop an improved technique for oxidizing carbon-fiber precursor with increased line speed, reduced carbon-fiber cost, and reduced equipment footprint.
- Verify that finished fiber properties satisfy automotive requirements.
- Conduct a preliminary evaluation of the cost impact of the new oxidation technique.
- Integrate the oxidation module into a prototypical conversion line.

Approach

- Develop a plasma process for oxidation using atmospheric-pressure plasma.
- Develop fiber-handling protocols for continuous processing.
- Conduct parametric studies and perform diagnostics to correlate processing parameters and fiber properties.
- Characterize fibers to confirm that they satisfy program requirements.

Accomplishments

- Developed stable protocol for oxidation of conventionally “pre-stabilized” 3k polyacrylonitrile (PAN) precursor tow with atmospheric-pressure plasma using a continuous process at 0.05 m/min line speed at mid-year, increased to 0.15 m/min by year end.

- Fully oxidized "pre-stabilized" fiber in atmospheric-pressure plasma with approximately 3X reduction in residence time of conventional oxidation.
- Demonstrated plasma oxidation of electron-beam-stabilized and thermochemically-stabilized PAN precursor.
- Carbonized fibers after plasma oxidation and measured mechanical properties.
- Designed, constructed, and commissioned a six-zone reactor that permits parametric control in each zone independently of process parameters in the other processing zones.
- Submitted two patent applications.

Future Direction

- Continue refining the reactor design and processing protocols to achieve high-speed, multiple-large-tow, continuous, plasma oxidation process.
- Refine oxidation recipe and equipment design to interface with stabilization techniques under development.
- Acquire and implement new diagnostic tools. Conduct parametric studies and fiber characterization to better understand process effects and the processing window and to quantify fiber properties.
- Conduct rate-effect studies and update cost analysis.
- Investigate oxidation of alternative precursors.

Introduction

The purpose of this project is to investigate and develop a plasma processing technique to rapidly and inexpensively oxidize PAN precursor fibers. Oxidation is a slow thermal process that typically consumes over two-thirds of the processing time in a conventional carbon-fiber conversion line. A rapid oxidation process could dramatically increase the conversion line throughput and appreciably lower the fiber cost. A related project (see 3.E) has already demonstrated the potential for greatly increasing line speed in the carbonization and graphitization stages, and rapid stabilization techniques are being developed (see 3.C), but the oxidation time must be greatly reduced to effect fast conversion. This project intends to develop plasma oxidation technology that integrates with other advanced fiber-conversion processes to produce inexpensive carbon fiber with properties suitable for use by the automotive industry. Critical technical criteria include (1) ≥ 25 Msi tensile modulus and ≥ 1.0% ultimate strain in the finished fiber; (2) uniform properties over the length of the fiber tow; (3) repeatable and controllable processing; (4) and significant unit cost reduction compared with conventional processing.

Project Deliverable

At the end of this project, the researchers will have developed an advanced oxidation process with residence time much less than that typical of conventional carbon-fiber conversion lines. The advanced oxidation process will be sufficiently well understood and documented that the team can commence scaling it to develop a multiple-large-tow oxidation module for an advanced-technology pilot line.

Technical Approach

The researchers are investigating PAN precursor fiber oxidation using nonequilibrium, nonthermal plasma at atmospheric pressure. Plasma processing is believed to enhance oxygen diffusion and chemistry in the PAN oxidation process. Atmospheric-pressure plasma provides better control over the thermal environment and reaction rates than does evacuated plasma, in addition to eliminating the sealing problems accompanying evacuated-plasma processing. Various fiber characterization tools and instruments are used to conduct parametric studies and physical, mechanical, and morphological evaluations of the fibers to optimize the process.

Atmospheric-Pressure Plasma Processing Results

Exposure to plasma products at or near atmospheric pressure provides superior thermal control because the gas flow should convectively heat or cool the fibers. This is deemed particularly important to avoid fiber melting from exothermic reactions. However, the short mean-free-path and life-span of the chemically reactive species at atmospheric pressure presents another set of challenges principally associated with finding a process recipe that delivers high process stability and short residence times.

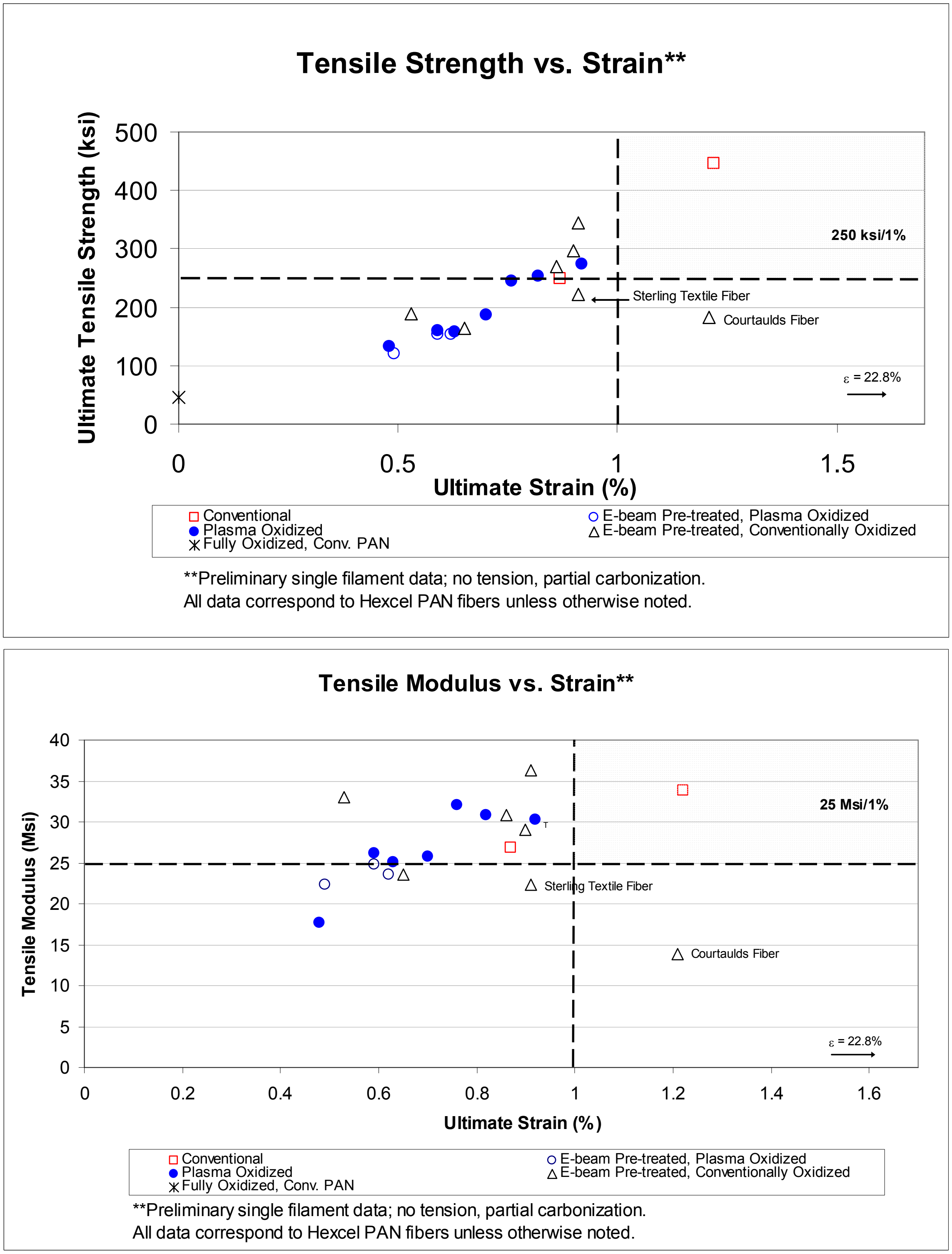
In ORNL's conventional pilot line, which represents the baseline process, PAN stabilization and oxidation occur in four successive furnaces in air, at temperatures increasing from about 200 to 250°C. Although there is not a precise transition from stabilization to oxidation, in general, one can consider stabilization to occur in the first furnace and (chemical) oxidation in the last three, so in this project the researchers are working to reproduce the conversion advancement from the last three furnaces. The advancement from the first furnace is being addressed in the parallel advanced stabilization project (see 3.C).

At the end of fiscal year (FY) 2005, the researchers demonstrated complete oxidation, starting with a "pre-stabilized" precursor, at a continuous processing line speed of 0.05 m/min. In the first half of FY 2006, the researchers continued to refine the reactor design, instrumentation, control, and processing protocols to further reduce residence time and increase the process stability. At the end of this period ~3X reduction in oxidation residence time was achieved in a single-zone reactor (one input point and one exit point for reactive species) designed for ~ 0.05 m/min line speed. By the end of FY 2006, a six-zone reactor was constructed and commissioned, enabling independent control of the chemical inputs in each zone. This reactor is designed for a line speed up to ~ 0.3 m/min in a single pass, but the transport system also readily allows repeated passes to enable higher line speeds. By the end of FY 2006, the researchers had conducted experiments at ~ 0.15 m/min line speed for a single, 3k tow.

During FY 2006, single fibers were carbonized after plasma oxidation, and their mechanical properties measured. The results are shown in Figure 1. Despite the lack of fiber tension, tow spreading, or controlled stretching during conversion, and the low-temperature carbonization, plasma-oxidized fibers were generally about 25 Msi tensile modulus (25 Msi requirement) and ≥ 0.5% ultimate tensile strain (1.0% requirement). These values exceed expectations at this stage of the investigation and inspire confidence that the required properties will be exceeded.

Interfacing the oxidation module to other modules received significant attention during this reporting period. As illustrated in Figure 2, the module interfaces may not occur at the same degree of advancement (marked by increasing density in the conventional process) for conventional and advanced-technology production lines. It was previously reported that plasma oxidation produces a lower radial oxidation gradient in the fiber. Plasma-oxidized fibers generally do not exhibit the "hollow core" structure that is common in conventionally-oxidized fibers. Because plasma-oxidized fibers have a partially oxidized core, earlier onset of carbonization may be possible (i.e., at lower fiber density), as illustrated by the uncertain location of the oxidation-carbonization interface in Figure 2. This would likely reduce the overall conversion residence time. Furthermore, the processing protocols in every module are sensitive to the prior processing history. For example, the researchers found that the oxidation protocols developed for conventionally-stabilized fibers did not work for electron-beam-stabilized fibers, and it was necessary to modify the oxidation process parameters significantly when oxidizing electron-beam-stabilized fibers. Acceptable oxidation process recipes were developed for all stabilization routes run through plasma oxidation thus far.

Plasma oxidation shows great promise. A number of principal metrics has been developed to measure forward progress, and will no doubt be refined as the researchers continue to grow their understanding of technology development and deployment. The researchers' best estimate of current status vs. target metrics is shown in "spider chart" format in Figure 3, and tabulated in Table 1.



**Preliminary single filament data; no tension, partial carbonization.
All data correspond to Hexcel PAN fibers unless otherwise noted.

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Figure 1. Mechanical properties of carbon fibers stabilized and oxidized by various routes, then conventionally carbonized at low temperature. There was no tensioning, controlled stretching, or tow spreading during conversion. Conventional data points are for thermally-shocked and thermally-ramped heating protocols.

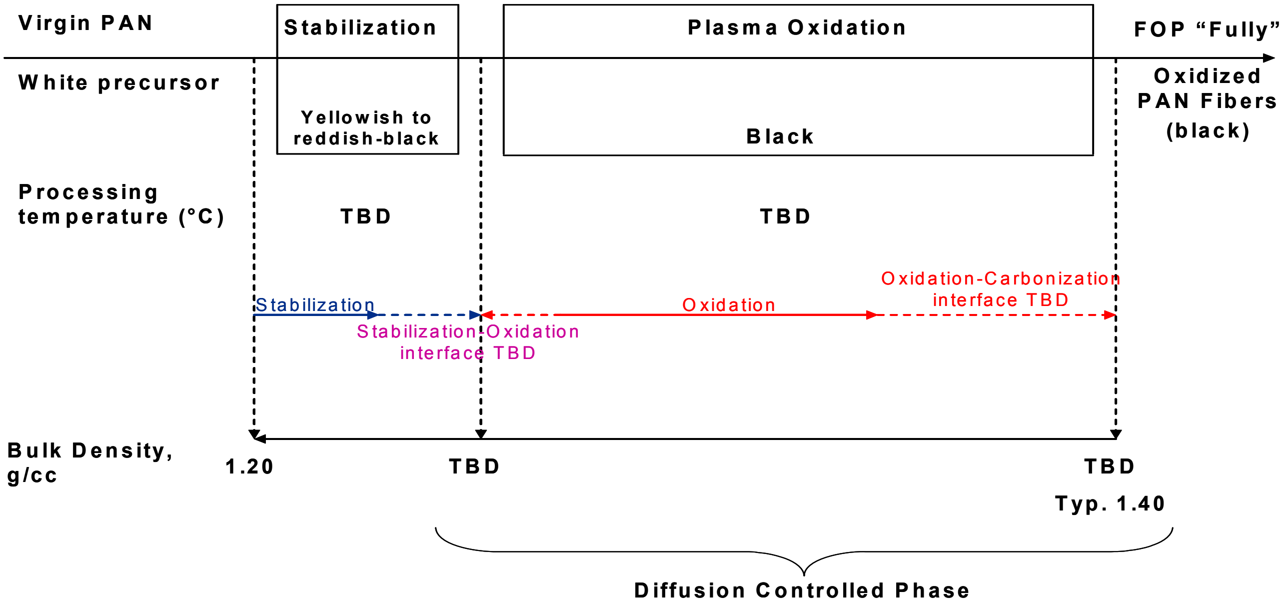

Figure 2. Schematic representation of stabilization and oxidation modules. Conventional module interfaces are represented by the vertical dotted lines. As shown by the horizontal arrows, the interface locations may change with advanced technology.

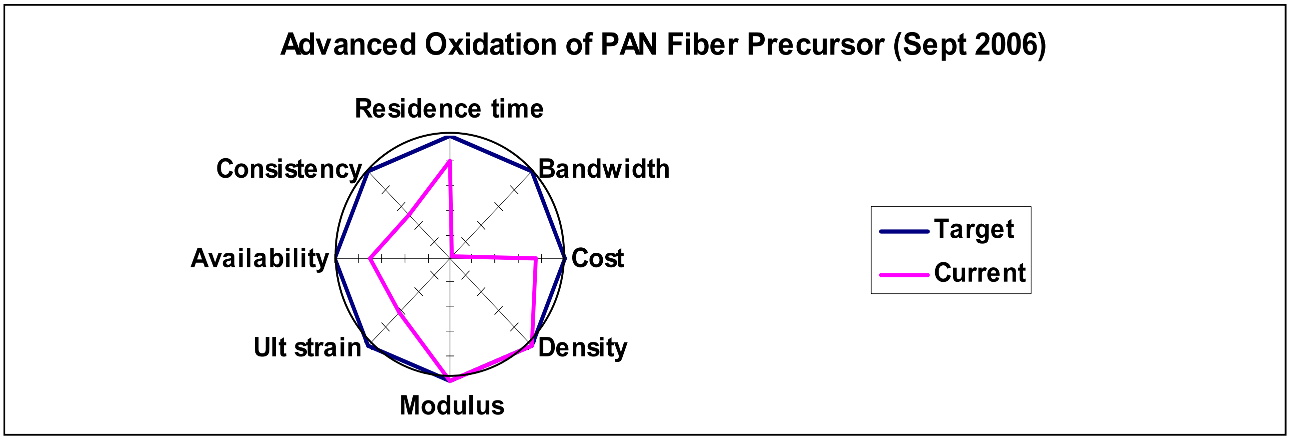

Figure 3. "Spider chart" showing current estimates of plasma oxidation metrics.

Table 1. Current estimates of plasma oxidation metrics.

Parameter	Target	Current	Conventional
Residence time	15 minutes	30 minutes	~ 90 minutes
Bandwidth	350k filaments*	3k filaments	Order 10M filaments
Cost	\$0.40 (\$3/lb)	~ \$0.60†	~ \$1.20†
Density	1.38 - 1.40	1.38	1.38 - 1.40
Modulus	25 Msi	25 Msi	30 – 35 Msi
Ultimate strain	≥1.0%	0.63%	~ 1.5%
Up time	~ 95%	~ 70%‡	~ 85%
Consistency (1 - 3*COV)*100	≥ 90%	~ 50%**	~ 90%

* Based on seven-tow pilot line
† Estimated from cost modeling reports
‡ "Rough order of magnitude" estimate

For patent protection and export control reasons, equipment and process parameters are not published, but they are periodically disclosed to the relevant program managers in oral briefings.

Future Direction

During FY 2007, the project focus will be on parametric studies with improved diagnostics and interfacing the oxidation module to the evolving stabilization module. The researchers will also carbonize plasma-oxidized fiber under more rigorous conditions (tension and temperature) to validate its mechanical properties. Oxidation-carbonization interface investigations will commence if progress on other tasks and budget permit. In future years, the project team will fully address the oxidation-carbonization interface and commence scaling studies to increase line speed, tow size, and bandwidth.

Patents and Publications

Two patents were filed, as follows: F.L. Paulauskas, T.L. White, and D.M. Sherman, "Apparatus and method for oxidation and stabilization of polymeric materials," application # 11/344,573, filed January 2006; and

F.L. Paulauskas and D.M. Sherman, "Apparatus and method for stabilization or oxidation of polymeric materials," application # 11/391,615, filed March 2006.

A paper by S.M. White, J.E. Spruiell, and F.L. Paulauskas, entitled "Fundamental Studies of Stabilization of Polyacrylonitrile Precursor, Part 1: Effects of Thermal and Environmental Treatment," was presented at the spring SAMPE conference in Long Beach, CA.

Education

The materials characterization has been conducted in partnership with the University of Tennessee's (UT's) materials science department. UT graduate students were engaged to provide characterization support to the project.

Partners

ORNL gratefully acknowledges contributions to this project by Hexcel and TohoTenax America. Both have generously provided raw materials and offered technical consultation. Additionally, technical and programmatic consultation has been provided by the Automotive Composites Consortium.

Conclusions

Plasma oxidation of PAN fibers continues to progress toward the goal of reducing the cost of carbon-fiber manufacture. To date, the researchers have reduced oxidation residence time by ~ 3X compared to conventional oxidation. Plasma-oxidized fibers were carbonized and the mechanical properties checked, with good results considering the level of rigor applied and the current stage of process development. A six-zone reactor was commissioned with higher line speed and control of chemistry inputs to each zone independent of chemical conditions in other zones. Continuous oxidation was conducted at 0.15 m/min line speed. The plasma oxidation process was modified to enable interfacing with advanced stabilization technologies; module interfacing is expected to be a significant task for the remainder of the program. Major metrics were developed and good progress was made toward satisfying those metrics.