Development of Low-Cost, High Strength Commercial Textile Precursor (PAN-MA)

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Project ID: ST099
Project Overview

- **Timeline**
  - Start: Mid FY2011
  - End: FY2013
  - New Project
    - (Planned start: April 1)

- **Budget**
  - FY 2011: $300k
  - FY 2012: $600k
  - FY 2013: $300k
    - This budget is equally split between Vehicle Technologies and Fuel Cell Technologies.

- **Barriers**
  - System Weight and Volume (A)
  - System Cost (B)
  - Materials of Construction (G)
    - High cost of high strength carbon fibers

- **Partners**
  - ORNL (Host site)
    - CF expertise
  - FISIPE
    - Acrylic fiber manufacturer

Project Objectives

• To develop a low-cost, high strength (600-750 KSI) CF based on a textile-grade PAN precursor.

• This work will represent the fast-track (shorter term) approach in the development of a low-cost, high strength CF.

• This project will significantly leverage the previously successful commodity grade textile based CF project.
Conventional PAN Processing

Typical processing sequence for PAN–based commodity grade CF’s

Major Cost Elements

- Precursor: 43%
- Oxidative stabilization: 18%
- Carbonization: 13%
- Graphitization: 15%
- Other: 11%

Automotive cost target is $5 - $7/lb

Tensile property requirements are 250 KSI, 25 MSI, 1% ultimate strain

ORNL is attempting major technological breakthroughs for major cost elements
## Cost Performance Categories

CF’s can be divided into 4 broad performance categories

<table>
<thead>
<tr>
<th>Performance Category</th>
<th>Strength Range</th>
<th>Modulus Range</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Performance</td>
<td>&gt;750 KSI</td>
<td>&gt; 35 MSI</td>
<td>Performance Driven, Cost is not Limiting</td>
</tr>
<tr>
<td>Moderate Grade</td>
<td>500 – 750 KSI</td>
<td>25 – 35 MSI</td>
<td>Cost and Performance Balance</td>
</tr>
<tr>
<td>High Volume Grade</td>
<td>250 – 500 KSI</td>
<td>&lt; 25 MSI</td>
<td>Cost Sensitive, Performance Enabling</td>
</tr>
<tr>
<td>Non Structural</td>
<td>Chemical &amp; Physical Properties of Carbon</td>
<td>Usually Low-Cost and Chosen for Uniqueness</td>
<td></td>
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</tbody>
</table>

Most High Volume Industries would require the last 2 Categories
**Background**

- The CF material represents a significant portion of the overall cost of pressure vessels (> 60%).

- To meet HFC/VT goals, high strength CF is needed for these pressure vessels. Typically aerospace grade CF with a strength requirement of ca. 700 KSI is needed.

- There is a strong need for a reduction in the cost of CF.

- The rapid development of low-cost CF is a commercial/technological necessity.
Technical Approach
For the development of low-cost, high strength CF

• This development will be built on the knowledge and expertise gained from the prior low-cost textile CF project.
• In the prior textile project, a comprehensive approach was implemented to achieve the programmatic goals:
  – Changes and modifications of the chemistry of the precursor
  – Optimization of the spinning parameters
  – Development of pretreatment in the precursor
  – Development of the overall conversion recipe of CF’s
  – Generation of rapid sampling and testing.
• As a result, the technological foundation has been established, and will be modified to the specific requirements of this new project.
Technical Approach

For the development of low-cost, high strength CF

To make the transition from commodity textile based CF to high strength CF, modifications are required. Some of the required modifications are:

- The vinyl acetate (VA) in acrylic fiber will be replaced with methyl acrylate (MA) to improve mechanical properties.
- The acrylonitrile (AN) content must be \( \geq 95\% \) by weight.
- Better quality in the generation of filaments (spinning).
- Incorporation of additional chemical agents may be required.
- Demonstrate program property requirements with lower variability, in processing multiple tows.
What is the difference between making higher performance and industrial grade CF?

<table>
<thead>
<tr>
<th>Attribute</th>
<th>Industrial Grade</th>
<th>Aerospace Grade</th>
<th>Cost Impact</th>
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</thead>
<tbody>
<tr>
<td>Tow Size</td>
<td>12-80K Filaments</td>
<td>1-12K Filaments</td>
<td>Less material throughput</td>
</tr>
<tr>
<td>Precursor Content</td>
<td>≅ 93% AN, MA or VA</td>
<td>≥ 95% AN, MA</td>
<td>Little on raw material; slower oxidation</td>
</tr>
<tr>
<td>Precursor purity</td>
<td>Can tolerate more impurity</td>
<td>Controls UTS</td>
<td>Slower spinning speed</td>
</tr>
<tr>
<td>Oxidation</td>
<td>Quicker due to lower AN</td>
<td>Slower due to higher AN</td>
<td>Time is money, reduced capital &amp; energy cost</td>
</tr>
<tr>
<td>Carbonization</td>
<td>Lower Temp</td>
<td>Sometimes Higher Temp</td>
<td>Small impact</td>
</tr>
<tr>
<td>Surface treatment</td>
<td>Same but utility affected</td>
<td>Same</td>
<td>None but Load Transfer affects amount of fiber needed</td>
</tr>
<tr>
<td>Packaging</td>
<td>Spooled or boxes</td>
<td>Small Spools</td>
<td>More Handling</td>
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<tr>
<td>Certification</td>
<td>None</td>
<td>Significant</td>
<td>Expensive; Prevents incremental Improvements.</td>
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Essentially the same process with slightly different starting materials. Not captured is the fact the CF manufacturers are specialty material makers, not high volume.
Typical PAN Formulations
Various chemistries of commodity precursors. Historical Data

Steepest part of slope determines speed of stabilization.
Location of ramp up start & peak determine oxidative stabilization temp range.

(DSC Analysis)
First Textile Formulations
Different types of textile PAN commodity precursors. Historical Data

Note: For proprietary reason, final formulation not shown

Heat Flow (W/g)

Temperature (°C)

Exo Up

Universal V4.2E TA Instruments

Textile Precursor

Conventional Precursor

Commercial Aerospace 3k

FISIPE textile

Commodity

(DSC Analysis)
Prior Technical Results
FISIPE Commodity Textile PAN Tensile Strength. Historical Data

Target Properties:
Strength: 1.72 GPA (250 KSI)

Current Properties:
Strength: 3.72 GPA (540 KSI)

Program Goal
Commercialization Goal

Strength (KSI)

Goal 8-8 10-29 1-3 1-6 1-25 3-13 3-17 3-27 9-18 10-9 3-19 6-25 7-24 5-18
FY07 FY08 FY09 FY10
Prior Technical Results
FISIPE Commodity Textile PAN Modulus. Historical Data

Target Properties:
Modulus: 172 GPA (25 MSI)

Current Properties:
Modulus: 261 GPA (~38 MSI)

Elastic Modulus (MSI)

Commercialization Goal

Program Goal

<table>
<thead>
<tr>
<th>Goal</th>
<th>8-8</th>
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FISIPE Textile-Based PAN Precursor

For commodity-grade carbon fiber

This product is at the initial stages of commercialization.

Splitable precursor band
(will generate multiple large tows)

Large single tow spools,
Ready for shipment
# Milestones

<table>
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<tr>
<th>Date</th>
<th>Milestone (High Strength CF Project)</th>
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<tr>
<td>July 2011</td>
<td>Down select to most promising precursor formulation based upon test results. Email/Letter report.</td>
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<tr>
<td>August 2011</td>
<td>Conduct first chemical pretreatment trials. Deliver DSC curves and written interpretation.</td>
</tr>
<tr>
<td>September 2011</td>
<td>Achieve carbonized fiber properties of at least 150 KSI strength and 15 MSI modulus to demonstrate feasibility. Deliver Test Data.</td>
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</table>

The dates given are under the assumption that work will commence March 1, 2011.
This high strength CF project will benefit from a decade of prior development in carbon fiber R&D at ORNL:

- Successful development in revolutionary new approaches to precursor and conversion technology.
- Significant intellectual property portfolio in CF has been developed at ORNL.
- Unique physical resources specific to carbon fiber R&D
- Access to ORNL’s extensive materials processing (PES and PL) and characterization capabilities.
- An extensive network consisting of university and industry partners providing unique strengths and intellectual property contributions in the carbon fiber area.
Unique ORNL Capability
Precursor Evaluation System (PES)

• Designed for development of conventional processing recipes with limited quantities of precursor
  – Residence time, temperature, atmospheric composition, and tension are independently controlled in each oven or furnace
  – Can process single filament up to thousands of filaments
  – Precise tension control allows tensioned processing of ~20-filament tows
  – Single stage or multiple stage evaluation during conversion
Unique ORNL Capability
Conventional Pilot Line (PL)

- 1:20 scale of a commercial grade production line
- Capacity for 8 tows
- Upgrades underway for automated operation and production of high strength CF
- Unique capability among FFRDC’s and universities
FISIPE (Project Partner)

- Prominent acrylic fiber manufacturer (in Portugal)
- ORNL and FISIPIE have already conducted extensive work on commodity grade fibers from textile PAN precursor and are currently evaluating large CF tows.
- FISIPE is aggressively pursuing the development of a new textile pan precursor that may be applicable for high strength CF’s.
- Based on past experience, FISIPE has become a reliable and responsive partner with quick turnaround.
- For precursor development, FISIPE has a well-equipped and very flexible pilot line.
- FISIPE participates in this project with significant “in-kind” contribution.
Benefits

• Development of a lower-cost, high strength CF based on existing textile-grade PAN precursor manufacturing technology.
• This project will result in the determination of the optimized processing parameter profiles (i.e., concentration, temperature, exposure time) to render the fiber carbonizable by conventional processes into CF.
• Successful completion of this project will result in processing (conversion) protocols transferable to industry.
• An economic evaluation of its potential at this time is premature. Project has just begun.
Summary

- This work addresses a very important barrier in the application of CF – cost.
- This work will develop a new approach for the generation of a CF PAN precursor for high strength. This method offers a higher short-term potential for achieving a significant cost reduction in the generation of this precursor for CF.
- Significant pre-existing technological background will support this project.
- The higher strength, lower-cost fiber developed in this work will be applicable to other industries (wind, infrastructure, etc.).
Future Work

• **Rest of FY11**
  - Continue efforts for the generation of acceptable textile PAN filaments/precursors, that will produce high strength CF.

• **FY12**
  - Produce higher strength fiber.

• **FY13**
  - Further optimize properties.
  - Modify production facilities at FISIPE.

**Major Program Milestones**

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<th>Date</th>
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<tr>
<td>Sept 2011</td>
<td>Deliver CF’s with properties of 150 KSI strength and 15 MSI modulus.</td>
</tr>
<tr>
<td>Jun 2012</td>
<td>Deliver CF’s with properties of 300 KSI strength and 25 MSI modulus.</td>
</tr>
<tr>
<td>Sept 2012</td>
<td>Deliver CF’s with properties of 500 KSI strength and 33 MSI modulus.</td>
</tr>
<tr>
<td>Sept 2013</td>
<td>Deliver CF’s with properties of 650 KSI strength and 35 MSI modulus.</td>
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