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

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Status as of Middle February 2012

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Project ID: ST099

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**Project Overview**

**Timeline**
- **Start**: April 2011
- **End**: June 2013

**Budget**
- **FY 2011**: $300K
- **FY 2012**: $500K
- **FY 2013**: $300K
- **FISIPE Cost Share**: $1,277K

**Barriers**
- **Barriers addressed**
  - High cost of carbon fiber
  - CF accounts for more than 65% of the cost of the high pressure storage tanks.
  - Inadequate supply base for low cost carbon fibers

**Partners**
- **ORNL**: carbon fiber conversion, precursor characterization, carbon fiber characterization
- **FISIPE**: precursor formulation, precursor spinning
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, standard modulus grade CF with a strength of ~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.
Presentation Outline

• Project History
• Need and Opportunity
• Industrial Grade vs. Aerospace Grade Differences
• Approach
• Project Status
• Milestones
• Cost Implications
• Potential Markets
• Future Work
• Conclusions

Note:
In this presentation many axis labels and data values are intentionally omitted due to export control regulations.
This work is built off developments in 2 previous projects funded by Vehicle Technologies. The first was conducted by Hexcel, the second:

**Purpose:** Develop a textile based precursor that uses Polyacrylonitrile produced in high volume textile mills. (Carpet, knitting yarn, etc.)

The precursor is now available on the open market and produced on a line that use to supply knitting yarn.

**Final properties:** 540 KSI and 38 MSI

**Project Started:** June 2007  
**Project Ended:** Sept 2011  
**Partner:** FISIPE (Lisbon, Portugal)
**Textile PAN-VA Strength & Modulus**

![Graph](image1.png)

- **Target Properties:**
  - Strength: 1.72 GPA (250 KSI)
- **Current Properties:**
  - Strength: 3.72 GPA (540 KSI)

**Program Goal**

**Commercialization Goal**

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**Textile Precursor**

![Textile Precursor Image](image2.png)

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**Conventional Precursor**

![Conventional Precursor Image](image3.png)

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- **Target Properties:**
  - Modulus: 172 GPA (25 MSI)
- **Current Properties:**
  - Modulus: 261 GPA (~38 MSI)

**Program Goal**

**Commercialization Goal**

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**H₂ Storage**
Need and Opportunity

• The Opportunity:
  – High strength carbon fiber enables the manufacture of durable, lightweight, compressed hydrogen storage vessels

• The Problem:
  – The current 700 ksi carbon fiber is much too expensive
  – Vehicle Technologies’ Low Cost Carbon Fiber Program’s strength targets do not satisfy the strength requirements for compressed hydrogen storage
  – There is a need for a low-cost higher strength (>650 ksi) fiber

• The Proposed Solution:
  – ORNL will employ the expertise, physical resources, and lessons learned from the Low Cost Carbon Fiber Program to develop a reduced cost high strength carbon fiber based on textile spinning processes
BUT there is a difference between the cost of making aerospace and industrial grade carbon fiber?

<table>
<thead>
<tr>
<th>Attribute</th>
<th>Industrial Grade</th>
<th>Aerospace Grade</th>
<th>Cost Impact</th>
</tr>
</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>&lt; 92% AN, MA or VA</td>
<td>&gt; 92% 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</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</td>
<td>Small Spools</td>
<td>More Handling</td>
</tr>
<tr>
<td>Certification</td>
<td>None</td>
<td>Significant</td>
<td>Expensive; Prevents incremental Improvements.</td>
</tr>
</tbody>
</table>

Essentially the same process with slightly different starting materials. Not captured is the fact the CF manufacturers are specialty material makers, not high volume.
Project Approach

Build off the FISIPE project to develop a low cost, high volume, PAN-MA precursor that preserves high volume production economics but yields a higher performing fiber and preserves high volume textile manufacturing cost advantages. (600-700 KSI)

Approach:
1. Identify candidate PAN-MA resins.
2. Determine fiber spinning parameters.
3. Determine the conversion protocol.

Main Challenges:
1. Adapting high speed processes for higher AN concentration.
2. Adapting high speed processes to increase precursor purity (minimize defects).
3. Spinning of round fibers (air gap spinning).
4. Improving consistency, fiber to fiber and along fibers without sacrificing speed.
FISIPE required several months to retrofit their development line to be able to produce a PAN-MA precursor. FISIPE downselected from numerous potential formulations.

11 polymer compositions sent to ORNL for screening.

3 were selected for further development using various analytical techniques.
As a result of that analysis the F1921 formulation was chosen for the first spinning trials. Two more formulations to follow.

Fiber received Dec 2011 and development of the conversion protocol began. (7 step process: pretreatment, 4 oxidation ovens and 2 carbonization ovens) Each must be done sequentially.

You do not know how good you are until you finish all 7.

First trial 282 KSI, 28.4 MSI

Oxidation profile compares favorably with the VA precursors.
Degree of processing during each stage of oxidative stabilization.

Degree of Stabilization after stage 4 when compared to an aerospace precursor.
Stretching is critical to obtaining molecular alignment and developing higher strength properties. Therefore a critical step was to define the tension limits that can be applied without breakage.

**Current Major Issue:**
Fiber fuzzing is limiting stretch, which limits molecular alignment which limits strength. This is due to “Baby Fibers”

**Tension vs Percentage stretching for the F1921 Precursor after various oxidative Stabilization Treatments to determine the Tension Limits during processing.**
• Designed for development of conventional processing recipes with limited quantities of precursor

– Residence time, temperature, atmospheric composition, and tension are independently controlled in each furnace

– Precise tension control and stretching capability allows stretched/tensioned processing of ≥20 filament tows

– Temperature capability from room temperature to 1,700°C; 2,500°C furnace
GATE MILESTONE Due 31 March 2012:
Achieve carbonized fiber properties of at least 300 KSI strength and 30 MSI modulus.

First trial: 282 KSI, 27.4 MSI (Processed 1/23/2012)
Second Trial (6 Conditions): Varied as Below (Processed 2/07/2012)

Tensile Strength (KSI)

<table>
<thead>
<tr>
<th>Goal</th>
<th>Gate</th>
<th>1/23-A</th>
<th>2/7-A</th>
<th>2/7-B</th>
<th>2/7-C</th>
<th>2/7-D</th>
<th>2/7-E</th>
<th>2/7-F</th>
</tr>
</thead>
<tbody>
<tr>
<td>650</td>
<td>300</td>
<td>282</td>
<td>419</td>
<td>356</td>
<td>288</td>
<td>342</td>
<td>316</td>
<td>383</td>
</tr>
</tbody>
</table>

Tensile Modulus (MSI)

<table>
<thead>
<tr>
<th>Goal</th>
<th>Gate</th>
<th>1/23-A</th>
<th>2/7-A</th>
<th>2/7-B</th>
<th>2/7-C</th>
<th>2/7-D</th>
<th>2/7-E</th>
<th>2/7-F</th>
</tr>
</thead>
<tbody>
<tr>
<td>33</td>
<td>30</td>
<td>27</td>
<td>29</td>
<td>34</td>
<td>30</td>
<td>29</td>
<td>33</td>
<td>36</td>
</tr>
</tbody>
</table>

Each data point average of 18 tests.
<table>
<thead>
<tr>
<th>Date</th>
<th>Milestone</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>July 2011</td>
<td>Down select to most promising precursor formulation based upon test results.</td>
<td>Complete</td>
</tr>
<tr>
<td>August 2011</td>
<td>Conduct first chemical pretreatment trials. Deliver DSC curves and written interpretation. Determined not necessary.</td>
<td>N/A</td>
</tr>
<tr>
<td>September 2012</td>
<td>Achieve carbonized fiber properties of at least 150KSI strength and 15MSI modulus to demonstrate feasibility.</td>
<td>Complete</td>
</tr>
<tr>
<td>March 2012</td>
<td>Achieve carbonized fiber properties of at least 300 KSI strength and 30 MSI modulus.</td>
<td>Complete</td>
</tr>
<tr>
<td>GATE</td>
<td>Achieve carbonized fiber properties of at least 300 KSI strength and 30 MSI modulus.</td>
<td>Complete</td>
</tr>
<tr>
<td>April 2013</td>
<td>Carbonize tows of methy-acrylate co-monomered textile fiber and size to confirm that material properties meet program requirements of 550-750 KSI strength.</td>
<td>Future</td>
</tr>
</tbody>
</table>
Cost model for All carbon fiber options is being updated. It does include the two options for High Strength fiber and a baseline for higher strength fiber.
<table>
<thead>
<tr>
<th>Industry</th>
<th>Benefit</th>
<th>Applications</th>
<th>Drivers</th>
<th>Obstacles</th>
<th>Current Market</th>
<th>Potential Market</th>
</tr>
</thead>
<tbody>
<tr>
<td>Automotive</td>
<td>Mass Reduction: 10% Mass Savings translates to 6-7% Fuel Reduction</td>
<td>Throughout Body and Chassis</td>
<td>Tensile Modulus; Tensile Strength</td>
<td>Cost: Need $5-7/lb; Fiber Format; Compatibility with automotive resins, Processing Technologies</td>
<td>&lt; 1M lbs/yr</td>
<td>&gt; 1B lbs/year</td>
</tr>
<tr>
<td>Wind Energy</td>
<td>Enables Longer Blade Designs and More Efficient Blade Designs</td>
<td>Blades and Turbine Components that must be mounted on top of the towers</td>
<td>Tensile Modulus; Tensile Strength to reduce blade deflection</td>
<td>Cost and Fiber Availability; Compression Strength; Fiber Format &amp; Manufacturing Methods</td>
<td>1-10 M lbs/yr</td>
<td>100M - 1B lbs/yr</td>
</tr>
<tr>
<td>Oil &amp; Gas</td>
<td>Deep Water Production Enabler</td>
<td>Pipes, Drill Shafts, Off-Shore Structures</td>
<td>Low Mass, High Strength, High Stiffness, Corrosion Resistant</td>
<td>Cost and Fiber Availability; Manufacturing Methods</td>
<td>&lt; 1M lbs/yr</td>
<td>10 - 100M lbs/yr</td>
</tr>
<tr>
<td>Electrical Storage</td>
<td>Reliability &amp; Energy Storage</td>
<td>Low Mass, Zero CTE transmission cables; Flywheels for Energy Storage</td>
<td>Zero Coefficient of Thermal Expansion; Low Mass; High Strength</td>
<td>Cost; Cable Designs; High Volume Manufacturing Processes; Resin Compatibility</td>
<td>&lt; 1M lbs/yr</td>
<td>10-100M lbs/yr</td>
</tr>
<tr>
<td>Pressure Vessels</td>
<td>Affordable Storage Vessels</td>
<td>Hydrogen Storage, Natural Gas Storage</td>
<td>High Strength; Light Weight</td>
<td>Cost; Consistent Mechanical Properties</td>
<td>&lt; 1M lbs/yr</td>
<td>1-10B lbs/yr</td>
</tr>
</tbody>
</table>

- 250+ KSI, 25 MSI Fiber
- 550 - 750 KSI, 35 - 40 MSI Fiber
<table>
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<th>Industry</th>
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<th>Obstacles</th>
<th>Current Market</th>
<th>Potential Market</th>
</tr>
</thead>
<tbody>
<tr>
<td>Infrastructure</td>
<td>Bridge Design, Bridge Retrofit, Seismic Retrofit, Rapid Build, Hardening against Terrorist Threats</td>
<td>Retrofit and Repair of Aging Bridges and Columns; Pretensioning Cables; Pre-Manufactured Sections; Non-Corrosive Rebar</td>
<td>Tensile Strength &amp; Stiffness; Non-Corrosive; Lightweight; Can be &quot;Pre-Manufactured&quot;</td>
<td>Cost; Fiber Availability; Design Methods; Design Standards; Product Form; Non-Epoxy Resin Compatibility</td>
<td>1-10M lbs/yr</td>
<td>1-100B lbs/yr</td>
</tr>
<tr>
<td>Non-Aerospace Defense</td>
<td>Lightweight Ground and Sea Systems; Improved Mobility and Deployability</td>
<td>Ship Structures; Support Equipment; Tanks; Helicopters</td>
<td>Low Mass; High Strength; High Stiffness</td>
<td>Cost; Fiber Availability; Fire Resistance; Design into Armor</td>
<td>1-10M lbs/yr</td>
<td>10-100M lbs/yr</td>
</tr>
<tr>
<td>Electronics</td>
<td>EMI Shielding</td>
<td>Consumer Electronics</td>
<td>Low Mass; Electrical Conductivity</td>
<td>Cost; Availability</td>
<td>1-10M lbs/yr</td>
<td>10-100M lbs/yr</td>
</tr>
<tr>
<td>Aerospace</td>
<td>Secondary Structures</td>
<td>Fairings; seat structures; luggage racks; galley equipment</td>
<td>High Modulus; Low Mass</td>
<td>Cost of lower performance grades; Non-Epoxy Resin Compatibility</td>
<td>1-10M lbs/yr</td>
<td>10-100M lbs/yr</td>
</tr>
<tr>
<td>Non-Traditional Energy Applications</td>
<td>Enabler for Geothermal and Ocean Thermal Energy Conversion</td>
<td>Structural Design Members; Thermal Management, Energy Storage</td>
<td>Tensile Strength &amp; Stiffness; Non-Corrosive; Lightweight</td>
<td>Design Concepts; Manufacturing Methods; Fiber Cost; Fiber Availability</td>
<td>1-10M lbs/yr</td>
<td>10M-1B lbs/yr</td>
</tr>
<tr>
<td>Electrical Energy Storage</td>
<td>Key Storage Media</td>
<td>Li-Ion Batteries; Super-capacitors</td>
<td>Electrical and Chemical Properties</td>
<td>Design Concepts; Fiber Cost and Availability</td>
<td>1-5M lbs/yr</td>
<td>10-50M lbs/yr</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>11-70M lbs/yr</td>
<td>3-114B lbs/yr</td>
</tr>
</tbody>
</table>

**250+ KSI, 25 MSI Fiber**

**550 - 750 KSI, 35 - 40 MSI Fiber**
Low Cost Carbon Fiber: Common Issues and Needs

Common Issues:
- Fiber Cost
- Fiber Availability
- Design Methods
- Manufacturing Methods
- Product Forms

Bio-Mass Materials
- Alternative Revenue
- Waste Minimization

Non-Traditional Energy
- Geothermal, Solar & Ocean Energy

Non-Aerospace
- Defense
- Light Weight, Higher Mobility

Aerospace
- Secondary Structures

Electronics
- Light Weight, EMI Shielding

Power Transmission
- Less Bulky Structures
- Zero CLTE

Oil and Gas
- Offshore Structural Components

Vehicle Technologies
- Needed for Longer Blade Designs
- Necessary for 50+% Mass Reduction

Wind Energy
- Only Material
- With Sufficient Strength/Weight

H₂ Storage

Civil Infrastructure
- Rapid Repair and Installation, Time and Cost Savings

Energy Storage
- Flywheels, Li-Ion Batteries, Supercapacitors

Power Transmission
- Offshore Structural Components

Chemical Infrastructure
- Rapid Repair and Installation, Time and Cost Savings

Bio-Mass Materials
- Alternative Revenue
- Waste Minimization

Non-Traditional Energy
- Geothermal, Solar & Ocean Energy

Non-Aerospace
- Defense
- Light Weight, Higher Mobility

Aerospace
- Secondary Structures

Electronics
- Light Weight, EMI Shielding

Power Transmission
- Less Bulky Structures
- Zero CLTE

Oil and Gas
- Offshore Structural Components

Vehicle Technologies
- Needed for Longer Blade Designs
- Necessary for 50+% Mass Reduction

Wind Energy
- Only Material
- With Sufficient Strength/Weight

H₂ Storage
The results presented are for the 1\textsuperscript{st} of 3 precursors.

We actually believe the other 2 precursors may be more suitable materials.
Future Plans

1. Improve precursor purity (minimize defects).
2. Improve spinning of rounder fibers (air gap spinning).
3. Improve consistency, fiber to fiber and along fibers without sacrificing speed.
5. Convert & Downselect from this and 2 other formulations.
6. Eliminate “Baby” filaments to increase stretch.
7. Scale-up ability to make precursor to an industrial scale (not part of the current program).

Presentations (Part or the following Program Overview Presentations)


Publications and Patents
None
Summary

- Project Started April 2011

- Long delay was encountered in setting up the polymerization and fiber spinning equipment due to us underestimating the difficulties of that task

- Polymer samples were evaluated and downselected in late 2011 through multiple iterations and interaction between the partners.

- Multiple formulations were downselected to 11 which were downselected to 3 for conversion trials.

- Fiber samples spun and delivered for conversion for the first of 3 formulations.

- While the conversion protocol development is still very young, the GATE milestone was met ahead of time and lost schedule time recovered.
Thank you for your attention.

Questions?