Advanced Oxidation & Stabilization of PAN-Based Carbon Precursor Fibers

May 15, 2011

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Project ID: LM006
Project Overview

Timeline
Phase I
• Start 2004
• End 2010
Phase I completed*
*anticipated shortly once strength is achieved

Phase II
• Start 2011
• End 2015

Budget
• FY 2011: $1,900K

Barriers
• Barriers addressed
  ▶ High cost of carbon fiber
  ▶ Inadequate supply base for low cost carbon fibers
  ▶ High volume manufacturing of carbon fiber

Partners
• ORNL (Host site), carbon fiber expertise, characterization
• SRA, Int. (Experimental site), atmospheric plasma and hardware development
Project Objectives

• Phase I: Produce multiple tows of carbon fiber meeting minimum program specifications using oxidation residence time of 40 minutes or less.
  - Oxidative stabilization is the bottleneck in the production process often requiring 90 to 120 minutes. By developing a 2-3X faster oxidation process, higher throughput and significant cost reduction can be achieved. **Completed**

• Phase II: Demonstrate Phase I capability at pilot scale.
  - This will involve more tows and larger tows at less than 40 min residence time (increased throughput).
Conventional PAN Processing

Typical processing sequence for PAN–based carbon fibers

Major Cost Elements

<table>
<thead>
<tr>
<th>Component</th>
<th>Cost %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precursor</td>
<td>43%</td>
</tr>
<tr>
<td>Oxidative stabilization</td>
<td>18%</td>
</tr>
<tr>
<td>Carbonization</td>
<td>13%</td>
</tr>
<tr>
<td>Graphitization</td>
<td>15%</td>
</tr>
<tr>
<td>Other</td>
<td>11%</td>
</tr>
</tbody>
</table>

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
Approach: Reduce PAN-Oxidation Two Zones Morphology

Single Filament Cross-Section

- Diffusion of oxygen to reactive sites is restricted, sequent reactions follow more slowly
- The limiting factor in the oxidative processing is the diffusion-controlled phase

\[
d_c/d_f : \text{varies}
\]

- 1 when \( t \approx 0 \)
- 0 when \( t >> 0 \)

Where \( t \) is the processing time

- Diffusion of oxygen to reactive sites is restricted, sequent reactions follow more slowly
- The limiting factor in the oxidative processing is the diffusion-controlled phase
Approach: Advanced Oxidation

- Addresses diffusion-controlled stages of conventional oxidation
- Based on non-thermal, atmospheric pressure plasma processing
- Good physical and morphological properties; carbonization and mechanical property validation underway
- Residence time reduced by 2 - 3X (single tow)
- Fiber core better oxidized (digestion profiles)
- System design improvements and scale-up underway

Plasma Discharge Device
# Milestones

<table>
<thead>
<tr>
<th>Date</th>
<th>Milestone</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>June 2010</td>
<td>Report experimental data indicating that plasma oxidized, conventionally carbonized PAN tow (≥ 3k) satisfy program mechanical property requirements.</td>
<td>Incomplete</td>
</tr>
<tr>
<td>September 2010</td>
<td>Report updated evaluation of residence time and unit energy demand.</td>
<td>Complete</td>
</tr>
<tr>
<td>September 2010</td>
<td>Document map of stoichiometry in MTR1 with ≥ 2 tows with ≥ 3k filaments per tow.</td>
<td>Complete</td>
</tr>
<tr>
<td>March 2011</td>
<td>Demonstrate plasma oxidation of large tows (≥ 24K) achieving densities larger than 1.35 gr/cm³.</td>
<td>Upcoming</td>
</tr>
<tr>
<td>September 2011</td>
<td>Report experimental data in large tow of plasma oxidized and conventionally carbonized, achieving programmatic mechanical properties (250 KSI &amp; 25 MSI, 1%).</td>
<td>Upcoming</td>
</tr>
</tbody>
</table>
JOULE Milestone Status

- **JOULE Milestone**: The core focus recently for this project has been the achievement of the minimum program mechanical requirements:
  - Tensile Strength: 250 KSI
  - Modulus: 25 MSI
  - Strain: 1%

- The current status is that the Modulus requirement has been met, but the tensile strength and strain requirements have not.

- Significant work over many months isolated the cause and re-established baseline conditions for optimal fiber.

- The research team has been singularly focused on meeting the remaining requirements, and believes it will accomplish this shortly.
Technical Accomplishments

Project Timeline: Subtask 1
MECHANICAL PROPERTY EVALUATION PROCESS FY 2010- FY 2011

Subtask 1
Evaluation of Impact on mechanical properties from advanced process and hardware

Precursor Problem?

Subtask 2
Conventional Conversion
- Initial results yielded low mechanical values
- Optimized conventional conditions determined experimentally

R&D Line
With new conditions, Advanced processing restored

Initial testing with Textile Precursor

Initial mechanical results LOW

Joule Milestone

FY 2010

FY 2011 Begins

FY 2011

Good mechanical properties σ > 500 ksi tensile strength

*The supplier of the precursor will not provide the optimal conversion conditions. This is considered a trade secret.
Technical Accomplishments
Subtask 1: Advanced Method/Apparatus Evaluation
Apparatus Overview

- Processes up to 6 tows, 3000 filaments per tow.
- Core advanced technology demonstrator
- Vertical design
- Six heating zones
- Pre and Post treatment temperature control
- Fully automated via LabVIEW

Multiple Tow Reactor 1 (MTR1)

- Dual-use for surface treatment and oxidation
- Two temperature zones
- Large cross-sectional area for internal modifications
- Demonstrator for new surface discharge method
- LabVIEW automated

Surface Modification Reactor 2 (SMR2)
Technical Accomplishments

Introduction

Investigation Areas and Issues

• The type of damage being done to the fiber had never been seen before (based on observations from industry consultants).

• The mechanical properties of the plasma oxidized fiber yielded very good properties in density as well as mechanical and morphological properties. Once carbonized, the mechanical properties were inadequate; modulus was achieved, tensile strength not.

• An enhanced plasma application technique utilizing surface discharges significantly improved the fiber quality vs. density, but was not a solution to the damage problem.

Two side issues (reactor/process troubleshooting and precursor conversion recipes) needed to be resolved in order to continue with the main thrust of the R&D work.
Technical Accomplishments

Subtask 1: Advanced Method/Apparatus Evaluation

Investigation Areas

- **Reactive species concentration:** Extensive work was done, looking at the relationship between damage and reactive species concentration and flow from the plasma generator. Parametric tests were performed.

- **Gas contamination, Water/humidity contamination, Inadequate temperature regulation, Flow control/configuration**

- **Overall process rate:** Residence time and line speeds were varied to examine the effect this has on damage.

- **Plasma geometry/position:** Explored multiple internal flow configurations and reactive species enhancements.

This investigation did not turn up conclusive cause of the damage responsible for poor mechanical properties of carbonized fiber. Due to this fact, attention turned to the precursor itself as a possible cause of the damage.
## Technical Accomplishments

### Subtask 1: Advanced Method/Apparatus Evaluation

#### Technical Results

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sample No.</th>
<th>Delivered</th>
<th>Oxidized</th>
<th>Carbonized</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Peak Stress (ksi)</td>
<td>Strain @ Break (%)</td>
</tr>
<tr>
<td>Aerospace</td>
<td>REF 1</td>
<td>ORNL</td>
<td>43.7</td>
<td>25.9</td>
</tr>
<tr>
<td>Commodity</td>
<td>REF 2</td>
<td>ORNL</td>
<td>37.8</td>
<td>20.4</td>
</tr>
<tr>
<td>Textile</td>
<td>REF 3</td>
<td>ORNL</td>
<td>38.8</td>
<td>20.6</td>
</tr>
</tbody>
</table>

**Conventionally Oxidized**

**Plasma Oxidized**

| Mutiple Tow Reactor 1 (MTR1) | SR349  | 6/18/2010 | 27.5 | 0.8 | 3.2 | 174.1 | 27.8 | 0.61 |
| SR370  | 7/8/2010 |         | N/M  | N/M | N/M | 181.6 | 22.6 | 0.74 |
| SR400  | 8/17/2010 |        | 47.4 | 0.8 | 21.5 | N/M  | N/M  | N/M  |
| SR401  | 8/17/2010 |        | 46.2 | 0.7 | 19.7 | N/M  | N/M  | N/M  |
| SR408-5.5 | 8/17/2010 |      | 35.7 | 0.8 | 12.4 | 186  | 23.2 | 0.75 |
| SR409  | 8/17/2010 |        | 50.3 | 0.8 | 17.0 | N/M  | N/M  | N/M  |
| SR415  | 8/23/2010 |        | 27.9 | 0.6 | 8.3  | 142.5 | 24.5 | 0.59 |

**Surface Modification Reactor 2 (SMR2)**

| SR415 SMR2 | 10/25/2010 | 35.4 | 0.6 | 13.9 | 176.8 | 23.9 | 0.74 |
| SR419 SMR2 | 10/25/2010 | 37.7 | 1.0 | 13.9 | 177.8 | 20.9 | 0.83 |

**Program Minimum:** Peak Stress, 250 ksi; Modulus, 25 Msi; Strain, 1%

Selected results from Step 1 work. Results are close to program minimums, but still needs improvement.
Technical Accomplishments

Project Timeline: Subtask 2
MECHANICAL PROPERTY EVALUATION PROCESS FY 2010- FY 2011

Initial mechanical results LOW

Subtask 1
Evaluation of Impact on mechanical properties from advanced process and hardware

Joule Milestone

Precursor Problem?

Subtask 2
Conventional Conversion

Initial results yielded low mechanical values
Optimized * conventional conditions determined experimentally

Good mechanical properties $\sigma > 500$ ksi tensile strength

*The supplier of the precursor will not provide the optimal conversion conditions. This is considered a trade secret.

R&D Line
With new conditions, Advanced processing restored

Initial Testing with Textile Precursor

M A J J A S O N D J F
FY 2010 FY 2011 Begins FY 2011
Technical Accomplishments
Subtask 2: Conventional Conversion/Analysis of Precursor Investigation Areas

• The ORNL precursor evaluation line was utilized for conventional conversion.

• Initial conventional testing showed poor mechanical properties.

• Contamination of the precursor stock was considered, but ruled out.

• The optimal process parameters were not available from the manufacturer.

• The optimal process parameters were determined experimentally.

   New baseline conditions were established that produced mechanical properties greatly exceeding the minimum program requirements.
Technical Accomplishments

Subtask 2: Conventional Conversion/Analysis of Precursor

Technical Results

Initial Conventional Conversion

Aerospace 3k processed at ORNL. Four Methods of conversion.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Oxidized</th>
<th></th>
<th></th>
<th>Carbonized</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Density</td>
<td>Peak Stress</td>
<td>Modulus</td>
<td>Strain @</td>
<td>Density</td>
<td>Dates</td>
</tr>
<tr>
<td></td>
<td>(g/cc)</td>
<td>(ksi)</td>
<td>(Msi)</td>
<td>Break (%)</td>
<td>(g/cc)</td>
<td></td>
</tr>
<tr>
<td>Baseline PL</td>
<td>1.4089</td>
<td>42.7</td>
<td>1.0</td>
<td>14.69</td>
<td>9/2010</td>
<td>217.9</td>
</tr>
<tr>
<td></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Despatch</td>
<td>1.3796</td>
<td>45.0</td>
<td>1.0</td>
<td>17.6</td>
<td>9/2010</td>
<td>168.2</td>
</tr>
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<td></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PES 1 pass</td>
<td>1.4014</td>
<td>44.1</td>
<td>0.9</td>
<td>16.6</td>
<td>9/2010</td>
<td>140.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PES 4 pass</td>
<td>1.4133</td>
<td>46.5</td>
<td>1.0</td>
<td>15.7</td>
<td>10/2010</td>
<td>153.0</td>
</tr>
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Program Minimum: Peak Stress, 250 KSI; Modulus, 25 MSI, Strain, 1 %

In spite of the usage of aerospace grade precursor, the obtained mechanical values of the CF are unacceptable.
Technical Accomplishments
Subtask 2: Conventional Conversion/Analysis of Precursor
Technical Results
Final Evaluations of Conventional Conversion after optimization
Aerospace 3k processed at ORNL.

Mechanical values show a dramatic improvement over the previous table.
Technical Accomplishments

Project Timeline: Back to R&D Line
MECHANICAL PROPERTY EVALUATION PROCESS FY 2010- FY 2011

Subtask 1
Evaluation of Impact on mechanical properties from advanced process and hardware

Joule Milestone

Precursor Problem?

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R&D Line
With new conditions, Advanced processing restored

Initial mechanical results LOW

Good mechanical properties $\sigma > 500$ ksi tensile strength

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Technical Accomplishments
Resumption of Main Advanced Method - Baseline Conditions

• The initial phase in reestablishing baseline parameters in the advanced method was the replication of ORNL conventional testing in the MTR1, without plasma assistance, to generate a set of control results to ensure accurate comparisons. This phase has been completed.

• The next phase is the activation of the advanced method with the new baseline parameters established from above. This phase is currently being implemented.

It is anticipated that the minimum program mechanical requirements will be reached utilizing the plasma-based method will be achieved shortly.
Future Work

**Rest of FY11**
- Refine oxidation process to satisfy program requirements for carbonized tow properties
- Begin scale-up work and transition to Phase II (anticipated mid-year)
- Design, Construct, and Operate MTR2 (pre-pilot-line oxidation oven)
- Demonstrate rapid plasma oxidation of large tow, multiple tows (24K to 80K/3)

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<td></td>
<td>carbonized, achieving programmatic mechanical properties (250 KSI &amp; 25 MSI, 1%].</td>
</tr>
</tbody>
</table>

**FY12**
- Complete stoichiometric analysis of MTR2 process.
- Complete scaling effects impact on process
- Obtain scaled energy consumption data
- Begin design and construction of MTR3 (pilot-line full scale oxidation oven)

<table>
<thead>
<tr>
<th>Date</th>
<th>Milestone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sep 2012</td>
<td>First runs of pre-industrial advance oxidation unit. This will be more advanced unit that the actual lab-multiple tow reactor.</td>
</tr>
</tbody>
</table>
Long Term Milestones/Deliverables

- Demonstrate program property requirements satisfied, with low variability, in processing multiple large tows.
- Demonstrate plasma oxidation of multiple tows of alternative precursor
- Demonstrate program property requirements satisfied, with low variability, in processing multiple large tows in plasma oxidation reactor module
- Optimize oxidation reactor module hardware and controls as required
- Deliver, install, and checkout first plasma oxidation reactor module.
- Review and update key technical and economic drivers for this technology specifically including residence time, projected equipment costs, and energy consumption per unit mass (go/no-go decision gate)
- Deliver equipment specification for a plasma oxidation module for an advanced technology/demonstration pilot line (principal project deliverable).
- Deliver, install, and commence operations of plasma oxidation module in the advanced technology pilot line (likely as part of an integrated technology demonstration follow-on project).
Summary and Conclusions

- Residence time reduced by 2 - 3X to date with one 3k tow (in the Single Tow Reactor 1 – Tube Reactor)
- New surface-plasma processing method refined and improved.
- Materials compatibility testing to determine optimal construction materials of future furnaces is ongoing (not presented here).
- Stoichiometry analysis completed on current chemistry mechanisms.
- Unit energy analysis estimate completed (not presented here).
- Conventional baseline testing resulted in new basic optimal processing parameters. This parameters are currently being incorporated into the advanced method.
- This work directly supports petroleum displacement via improved fuel economy from vehicle weight reduction
- This work addresses the barrier of carbon fiber cost
- The approach is to develop a revolutionary new method for converting carbon fiber, which offers much higher potential for achieving significant cost reduction than evolutionary improvements to existing conversion technology
- Process and equipment scaling will constitute the majority of future work
Thank you for your attention.

Questions?

IONOSPHERE

90 KM

TROPOSPHERE

A SPRITE (NATURAL OCCURRENCE OF PLASMA)
Backup Materials
Oxidation Interfaces

Virgin PAN

White precursor

Processing temperature (°C)

Bulk Density, g/cc

1.20 (thermoplastic virgin precursor)

TBD

Stabilization

Stabilization-Oxidation interface

Oxidation-Carbonization interface TBD

TBD

TBD

Oxidation

Diffusion Controlled Phase

Typ. 1.39/1.40 thermoset (commercial, commodity)

TBD *

Oxidized PAN Fibers (black)

FOP “Fully” Oxidized PAN Fibers

Yellowish to reddish-black
Technical Accomplishments
Subtask 2: Conventional Conversion/Analysis of Precursor Investigation Areas

As a reference, it took over two years to find the proper conversion conditions for the textile precursor. For the aerospace fiber, this time was reduced significantly (~3 months).

Target Properties:
Strength: 1.72 GPA (250 KSI)

Current Properties:
Strength: 3.13 GPA (454 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
Strength (Ksi)
Commercialization Target
LM Minimum Target

Target Properties:
Strength: 1.72 GPA (250 KSI)

Current Properties:
Strength: 3.13 GPA (454 KSI)
Future Work
Projected Project Timeline

Phase I
Technical Analysis and Evaluation

Phase II
Scale-Up

MTR1
Testing at Sentech

MTR2
Testing at Sentech

MTR2, or modular section of,
transferred to ORNL Pilot Lines

Performance Dependent Decision

PATH B
(least likely)

MTR2 Modules Testing at Sentech & ORNL

Technical Specification for Demonstration Scale Device

PATH A
(most likely)

MTR3 Testing at ORNL

Design, Construction of MTR2

Design, Construction of MTR3

End of FY 2010
End of FY 2011
End of FY 2012
End of FY 2013
End of FY 2014
End of FY 2015

Denote Milestones (see next slide)