Lower Cost Carbon Fiber Precursors

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C. David (Dave) Warren
Field Technical Manager
Transportation Materials Research

Oak Ridge National Laboratory
P.O. Box 2009, M/S 8050
Oak Ridge, Tennessee 37831-8050
Phone: 865-574-9693
Fax: 865-574-0740
Email: WarrenCD@ORNL.GOV

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More Affordable Precursors are Needed

3 Current Precursor Options
1. Textile Grade PAN (MA or VA formulations)
2. Lignin Based Precursor (Hardwood or Softwood)
3. Polyolefins (not shown on chart)

Carbonized Textile Precursor

Current Carbonized Textile Properties:
- Strength: 400 KSI
- Modulus: 35 MSI

PE: (KSI)
- 86% C Content;
- 65-75% Yield
- $0.50-$0.75/lb;
- Melt Spun

Processed Precursor Fibers from a Hardwood/Softwood Lignin Blend.
**Textile Precursors – Purpose, Barrier, Approach**

**Purpose:** Scale-up chemical modification of textile precursors, in conjunction with an industrial partner. Identify and develop textile based precursor. Develop optimal processing parameters. Incorporate both in commercial production facilities at industrial scale.

**Barriers:** New precursors are needed for carbon fiber manufacturing cost reduction. They must be scaled for industry production and conversion parameters must be optimized. Lower cost fiber enable CF composite applications.

**Approach:**
1. Complete previous effort by scaling to the CF production line.
2. Assist CF converters with processing protocol.
3. Optimize processing protocol for improved properties.
4. Incorporate modification in CF demonstration line.

**Budget:** $150K

**Project End:** Sept 2011
Textile Precursors

Early Work Done by Hexcel 2001-2004 under LM Subcontract

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

Chemically treated textile could be undergo oxidative stabilization in less time but a slightly higher temperature.
Began: January 2007  Partner: FISIPE (PT)

FISIPE uses a VA co-monomer

Guided FISIPE choosing a polymer composition and in installing the chemical bath which installed in their pilot line facility and also in optimizing the chemical pretreatment.

FISIPE produces precursor which we evaluate to determine the optimum conversion conditions.

Due to export control restrictions, FISIPE does not know the conversion conditions. We will work directly with the converter to transfer that.
Multiple Spinnerettes Solvent Extraction, Washing and Tensioning Crimping Drying with Tension Spooling or Bailing in Bulk

Slightly Modified versions of polymer selected

Starts with a large “tank farm” which polymerizes PAN and other co-monomers

Chemical Pretreatment
1\textsuperscript{st} Potential textile formulations were evaluated:

Note: for Proprietary Reason, Final formulation not Shown
Textile PAN_VA Co-monomer
Formulation proprietary to FISIPE
26,600 filament tow size
Chemically treated with a proprietary solution treatment at “normal” processing temps
Oxidized and Carbonized using both the Precursor Evaluation Line and the Pilot Line
Test data from both tow tests and single filament tests
Wide Angle XRD Profiles: Comparison Between Commercial Panex 33 and Textile Grade Carbon Fiber

Materials

Virgin Textile PAN Precursor used for Manufacturing Carbon Fiber (Sterling)

Zoltek Panex 33

Carbon Fiber from Chemically Treated Textile PAN Precursor (Sterling)
**Mechanical Properties – Strength**

**Target Properties:**
Strength: 1.72 GPA (250 KSI)

**Current Properties:**
Strength: 3.13 GPA (454 KSI)

**Commercialization Target**

**LM Minimum Target**

<table>
<thead>
<tr>
<th>Strength (KSI)</th>
<th>Goal</th>
<th>8.8</th>
<th>10.29</th>
<th>1.3</th>
<th>1.6</th>
<th>1.25</th>
<th>3.13</th>
<th>3.17</th>
<th>3.27</th>
<th>9.18</th>
<th>10.9</th>
<th>3.19</th>
<th>6.25</th>
<th>7.24</th>
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<tbody>
<tr>
<td><strong>Years</strong></td>
<td>FY07</td>
<td>FY08</td>
<td>FY09</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Managed by UT-Battelle for the U.S. Department of Energy
**Mechanical Properties – Modulus**

**Target Properties:**
- Modulus: 172 GPA (25 MSI)

**Current Properties:**
- Modulus: 220 GPA (~32 MSI)

**Commercialization Target**

**LM Minimum Target**

<table>
<thead>
<tr>
<th>材料</th>
<th>商业化目标</th>
<th>LM最小目标</th>
</tr>
</thead>
<tbody>
<tr>
<td>Goal</td>
<td>172 GPA</td>
<td>220 GPA</td>
</tr>
<tr>
<td>8-8</td>
<td>160 GPA</td>
<td>210 GPA</td>
</tr>
<tr>
<td>10-29</td>
<td>150 GPA</td>
<td>200 GPA</td>
</tr>
<tr>
<td>1-3</td>
<td>140 GPA</td>
<td>190 GPA</td>
</tr>
<tr>
<td>1-6</td>
<td>130 GPA</td>
<td>180 GPA</td>
</tr>
<tr>
<td>1-25</td>
<td>120 GPA</td>
<td>170 GPA</td>
</tr>
<tr>
<td>3-13</td>
<td>110 GPA</td>
<td>160 GPA</td>
</tr>
<tr>
<td>3-17</td>
<td>100 GPA</td>
<td>150 GPA</td>
</tr>
<tr>
<td>3-27</td>
<td>90 GPA</td>
<td>140 GPA</td>
</tr>
<tr>
<td>9-18</td>
<td>80 GPA</td>
<td>130 GPA</td>
</tr>
<tr>
<td>10-9</td>
<td>70 GPA</td>
<td>120 GPA</td>
</tr>
<tr>
<td>3-19</td>
<td>60 GPA</td>
<td>110 GPA</td>
</tr>
<tr>
<td>6-25</td>
<td>50 GPA</td>
<td>100 GPA</td>
</tr>
<tr>
<td>7-24</td>
<td>40 GPA</td>
<td>90 GPA</td>
</tr>
</tbody>
</table>

FY07 | FY08 | FY09
Final Properties Depend upon:

**Time – Temperature - Tension**

Based on broom straw test method measured in our labs (Not from Co. brochure)
This Year the ability to spin circular fibers was achieved.
Textile Precursors – What is Happening and Left Undone

FISIPE has retrofitted production line and ready to sell precursors.

Companies in Germany, Italy, Turkey, Chile and China are trying to duplicate.

To be Done:
1. A major CF manufacturer has asked for help in learning how to process FISIPE fiber.
2. FISIPE has developed spinning capability for “round” fibers. Would eliminate decrease in compression strength.
3. Reduction in Coefficient of Variation.
4. Development of MA based precursor for higher strength applications.
5. Complete validation of transfer from pilot line to production line precursor.

Current work is: 1. Optimization of properties.
2. Validation and Verification of Production Line output.
3. Assistance to CF Converters to use Precursor.

Materials

Current work is: 1. Optimization of properties.
2. Validation and Verification of Production Line output.
3. Assistance to CF Converters to use Precursor.
Papers:


4. “Multi-Task Research Program to Develop Commodity Grade, Lower Cost Carbon Fiber”; proceedings of the 2008 SAMPE Fall Technical Conference; September 8-11, 2008; Memphis, TN.


Purpose: Develop the lowest cost potential carbon fiber precursor while meeting program targets. Current project is in early stage development.

Barriers: New precursors are needed for carbon fiber manufacturing cost reduction. They must be scaled for industry production and conversion parameters must be optimized. Lower cost fiber enable CF composite applications.

Approach:
1. Identify high carbon content melt-processible precursors and modify/functionlize those with suitable chemicals to render it infusible.
2. Design and develop a reactor for functionalization and identify carbonization parameters.
3. Commercialize the technology with precursor manufacturer(s) in USA.

Budget: $ 200K FY09
        $ 400K FY10
        $ 600K FY11
        $ 600K FY12

Project End: Sept 2012
Polyolefin-based carbon fibers offer:

– Significant cost benefit through
  • High carbon yield
  • Low raw material cost
  • Possibility of using recycled raw materials
  • Ease of precursor fiber handling and processibility

– Performance/property benefits
  • Potentially higher properties than those are achievable with other LCCF precursor under investigation

CF derived from polyolefin can provide higher value in terms of performance to cost ratio than any other precursor we are currently working on.
Polyolefins have been investigated by others as carbon fiber precursors. Japanese in the 70’s, Hexcel in early 2000’s

Obtained Properties: 30 MSI; 380 KSI

But

Required a 10 – 24 h elevated temperature sulfonation in Sulfuric Acid
Making it an uneconomical process

Dr. Naskar has developed a 1 hour sulfonation process that is:

1. not 100% liquid phase;
2. uses a chemical/process used in an industry that sells 1000’s of tons of material for less than $0.20 a pound.
3. the process leaves the precursor ready to carbonize and by passes the entire oxidative stabilization process (80 – 120 minutes)
**Polyolefin Precursors**

<table>
<thead>
<tr>
<th>Precursor type</th>
<th>Yield (%)</th>
<th>$/lb (as-spun)</th>
<th>Melt-spinnable</th>
<th>Best achieved properties</th>
<th>Problem</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Theoretical</td>
<td>Practical</td>
<td></td>
<td>Strength (KSI)</td>
<td>Modulus (MSI)</td>
</tr>
<tr>
<td>Conventional PAN</td>
<td>68</td>
<td>45-50</td>
<td>&gt;4</td>
<td>No</td>
<td>500-900</td>
</tr>
<tr>
<td>Textile PAN*</td>
<td>~68</td>
<td>45-50</td>
<td>1-3</td>
<td>No</td>
<td>300-400+</td>
</tr>
<tr>
<td>Lignin*</td>
<td>62-67</td>
<td>40-50</td>
<td>0.40 - 0.70</td>
<td>Yes</td>
<td>160</td>
</tr>
<tr>
<td>Polyolefin**</td>
<td>86</td>
<td>65-80</td>
<td>0.35 - 0.5</td>
<td>Yes</td>
<td>380</td>
</tr>
</tbody>
</table>

* Ongoing work  
** Hexcel work (2004)

Eliminating Oxidative Stabilization Reduced conversion time to 15 – 30 minutes
Flow Diagram of Work

Commencement of project

Obtain polyolefin resin

Chemical/physical modification of resin: melt-spinnable

Produce precursor fiber (melt-spinning)
Variable: two size (100 to 1000), precursor composition & diameter of filaments

Stabilization of fibers
Parameters: time, temperature, tension, & reaction mix

Are the filaments infusible enough?
Yes
No

Carbonization of stabilized fibers
Parameters: time, temperature, & tension

Are the properties satisfactory??
Yes
No

Scale-up (3k) & demonstrate continuous carbon fiber productions from polyolefins

End of development project – commence scale-up project

Characterization of precursor & carbonized filaments: DSC, TGA, DMA, TMA, GC-MS, XRD, Raman Spectroscopy, tensile testing
• During FY2009 (six months of the project) precursor fibers were produced in collaboration with a melt-spinning equipment manufacturer in USA.
  – Fibers from polyblend were successfully obtained without problem with spinnability.

• Precursor fiber properties could be tailored for desired target.
## Tensile properties of the neat and functionalized fibers.

<table>
<thead>
<tr>
<th>Fiber Sample</th>
<th>Tensile Strength (MPa)</th>
<th>Tensile Modulus (GPa)</th>
<th>Ultimate Elongation (%)</th>
<th>Yield Stress (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>98 ± 14</td>
<td>0.16 ± 0.06</td>
<td>187 ± 24</td>
<td>42 ± 8</td>
</tr>
<tr>
<td>R2</td>
<td>138 ± 27</td>
<td>0.41 ± 0.12</td>
<td>117 ± 48</td>
<td>77 ± 14</td>
</tr>
<tr>
<td>R3</td>
<td>169 ± 23</td>
<td>0.63 ± 0.09</td>
<td>115 ± 27</td>
<td>116 ± 13</td>
</tr>
<tr>
<td>R2S1</td>
<td>91 ± 12</td>
<td>0.83 ± 0.41</td>
<td>29 ± 3</td>
<td>-</td>
</tr>
<tr>
<td>R2S2</td>
<td>78 ± 10</td>
<td>1.19 ± 0.46</td>
<td>18 ± 3</td>
<td>-</td>
</tr>
</tbody>
</table>

- Increase in draw ratio increases filament strength and modulus and lowers ultimate elongation.
- Functionalization increases modulus (3 fold) and lowers both strength and elongation.
SEM-Micrographs of LLDPE-Based Fibers

Materials

SEM micrographs of stabilized by new method - < 1hour residence time

SEM micrographs of carbonized (Run-II) fibers

- Optimal temperature range for accelerated process is identified.
Functionalization and Conversion

- Incomplete functionalization leaves hollow carbon fibers. Figures below show that incomplete stabilization caused hollow carbon fiber. However, adequate stabilization (with stabilization time <1 h) eliminated hollow core formation during carbonization.

- Evolved gas analysis during pyrolysis of stabilized fibers was conducted to understand the stabilization and carbonization chemistry. Due to proprietary reasons those results are not reported here.
Milestones

• GATE Milestone FY’09: Spin modified polyolefin-based filaments and demonstrate conversion via accelerated sulfonation route.
  - We have demonstrated a functionalization time (<60 min) that is significantly less than the residence time for prior works produces carbonized fibers.
  - A series of precursor fiber has been spun and characterized.
  - Carbon yield as high as 70% were obtained from the stabilized fibers.

Gate Milestone FY’10: Meet initial minimum properties
  - 150 KSI Strength
  - 15 MSI Modulus
• To date the researchers have demonstrated accelerated stabilization of polyolefin precursor fibers.

• Earlier work required prolonged functionalization (6-10 h) to obtain good carbon fiber (380 KSI and 28 MSI). In this work it has been demonstrated that stabilization can be achieved within 1 h period. However mechanical properties were low (110 KSI & 7 MSI) and that could be either due to nature of the precursor fiber or lack of tension during stabilization and carbonization. A tension controlled stabilization protocol is being developed.

• It is anticipated that at the end of FY’12 researchers will be able to demonstrate target properties (250 KSI and 25 MSI).

• A cooperative research program with USA based precursor producer is under development.
• Polyolefin precursor fibers (modified and unmodified) have been produced for stabilization and conversion studies.

• Tows (288 filaments) with different draw ratios and filament diameters (8-15 mm) were produced.

• Accelerated (t < 60 min) stabilization of polyolefin fiber has been demonstrated.

• Carbon yield as high as 70% were obtained from the stabilized fibers.

• Optimization of precursor processing parameters for production of low-cost carbon fiber is underway.
### Polyolefin Precursors – Cost Potential

**Materials**

#### Diagram from Harper International

<table>
<thead>
<tr>
<th>Spooling &amp; Packaging</th>
<th>Surface Treatment</th>
<th>Carbonization/Graphitization</th>
<th>Stabilization &amp; Oxidation</th>
<th>Precursors</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0.61</td>
<td>$0.37</td>
<td>$2.32</td>
<td>$1.54</td>
<td>Baseline Today - $9.88 $5.04</td>
</tr>
<tr>
<td>$0.41</td>
<td>$0.33</td>
<td>$1.48</td>
<td>$0.99</td>
<td>High Volume - $7.85 $4.64</td>
</tr>
</tbody>
</table>

**High**
- $0.41
- $0.33
- $1.48
- $0.20
- $3.32
- $0.90

**Low**
- $0.41
- $0.33
- $1.25
- $0.10
- $2.74
- $0.65

Less Effluents
Faster throughput
Less Incineration

### Polyolefin Precursors – Cost Potential

<table>
<thead>
<tr>
<th>Large tow CF Precursor</th>
<th>Small tow (&lt;24k) CF Precursor</th>
<th>Textile Precursor</th>
<th>Polyolefin Precursor</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-Spun Fiber ($/lb)</td>
<td>$ 3-5</td>
<td>$ 4-6</td>
<td>$ 2-3</td>
</tr>
<tr>
<td>Carbon Yield</td>
<td>~45%</td>
<td>~50%</td>
<td>~50%</td>
</tr>
<tr>
<td>Precursor Cost ($/lb CF)</td>
<td>$ 6.5-11</td>
<td>$ 8-12</td>
<td>$ 4-6</td>
</tr>
<tr>
<td>Stabilization</td>
<td>85 - 120 min</td>
<td>75 - 100 min</td>
<td>75 - 100 min</td>
</tr>
<tr>
<td>Carbonization</td>
<td>Same</td>
<td>Same</td>
<td>Same</td>
</tr>
</tbody>
</table>
Questions?