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

May 14-18, 2012

Status as of Middle February 2012

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Project ID: ST099

U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY

MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

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

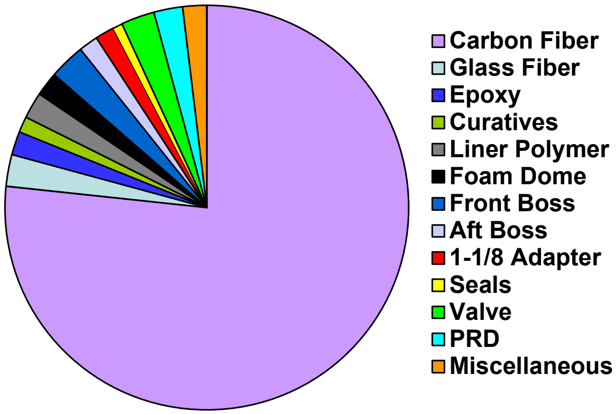
- Barriers addressed
  - High cost of carbon fiber
  - CF accounts for more than 65% of the cost of the high pressure storage tanks.
  - Inadequate supply base for low cost carbon fibers

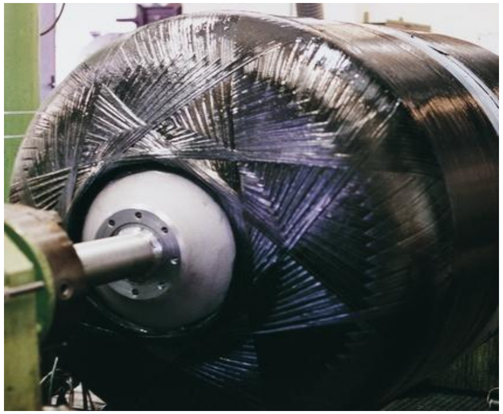
Partners

- 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

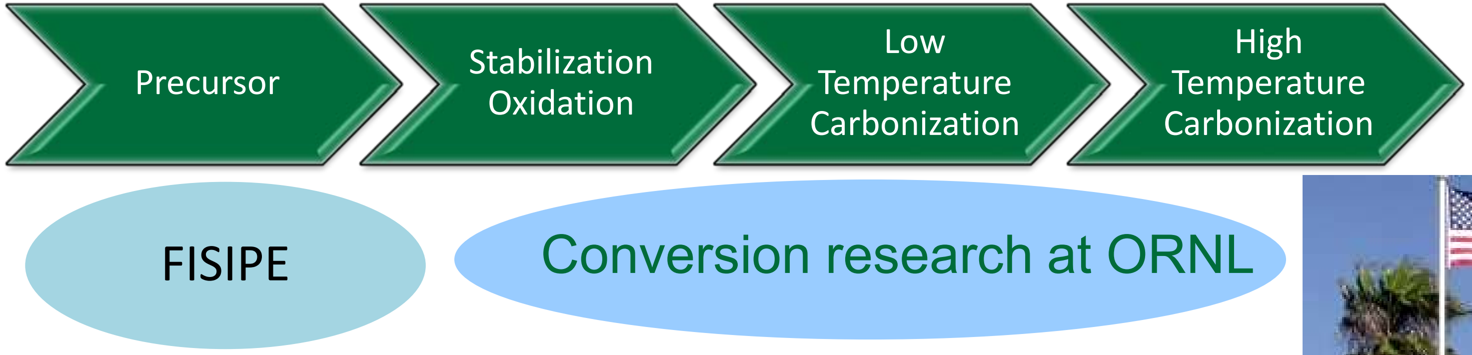
- Project History
- Need and Opportunity
- Industrial Grade vs. Aerospace Grade Differences
- Approach
- Project Status
- Milestones
- Cost Implications
- Potential Markets
- Future Work
- Conclusions

Note:
In this presentation many axis labels and data values are intentionally omitted due to export control regulations.

PAN-MA Precursors – Project History

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.)



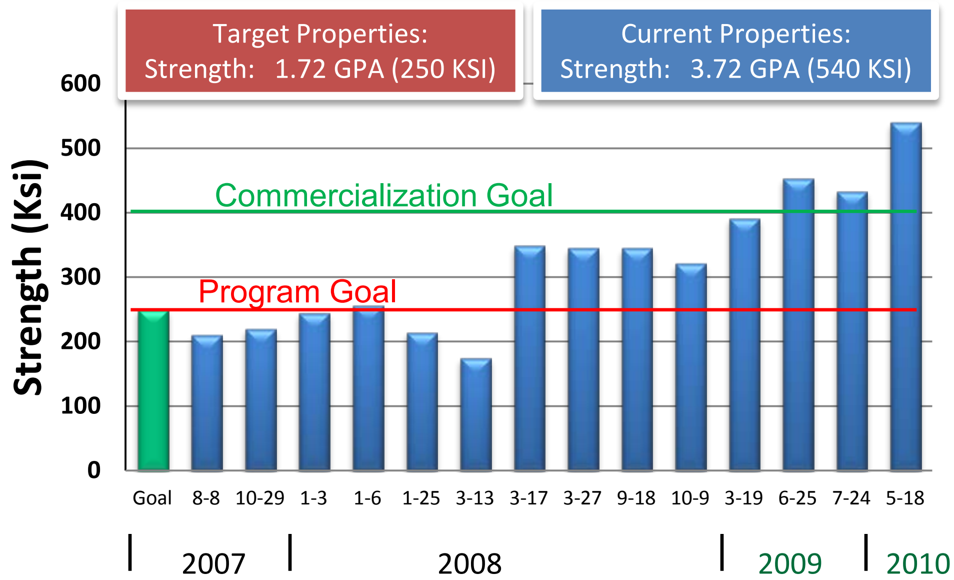
The precursor is now available on the open market and produced on a line that use to supply knitting yarn.

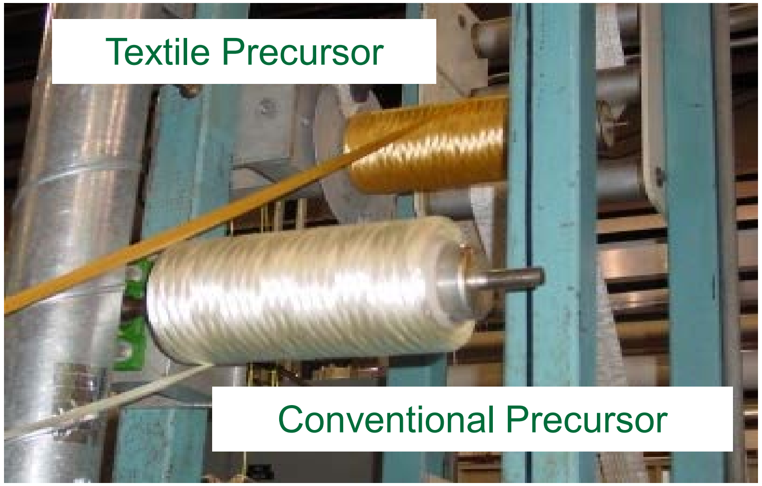
Final properties: 540 KSI and 38 MSI

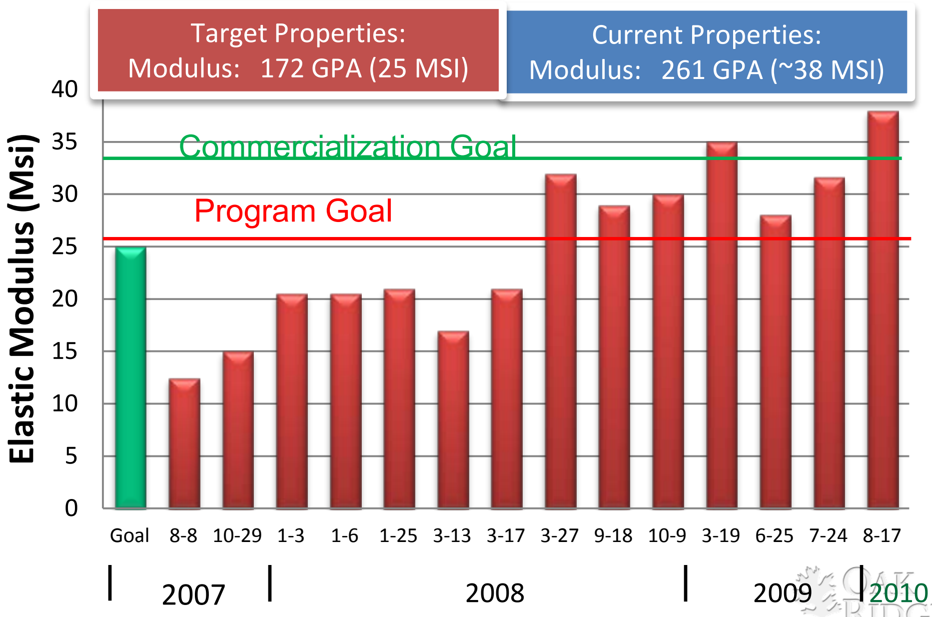
Project Started: June 2007
Project Ended: Sept 2011
Partner: FISIPE (Lisbon, Portugal)

Textile PAN-VA Strength & Modulus

H_2 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?

Attribute	Industrial Grade	Aerospace Grade	Cost Impact
Tow Size	12-80K Filaments	1-12K Filaments	Less material throughput
Precursor Content	< 92% AN, MA or VA	> 92% AN, MA	Little on raw material; slower oxidation
Precursor purity	Can tolerate more impurity	Controls UTS	Slower spinning speed
Oxidation	Quicker due to lower AN	Slower due to higher AN	Time is money
Carbonization	Lower Temp	Sometimes Higher Temp	Small impact
Surface treatment	Same but utility affected	Same	None but Load Transfer affects amount of fiber needed
Packaging	Spooled	Small Spools	More Handling
Certification	None	Significant	Expensive; Prevents incremental Improvements.

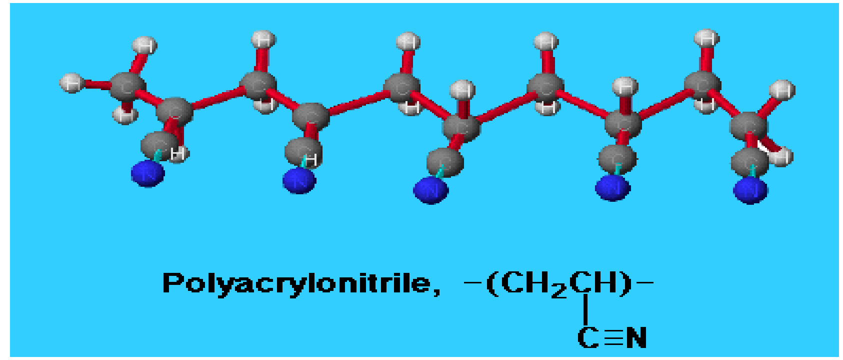
Essentially the same process with slightly different starting materials. Not captured is the fact the CF manufacturers are specialty material makers, not high volume.

Project Approach

ST099

H_2 Storage

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.
5. Work out conversion protocol. Time – Temperature – Tension.

Project Status

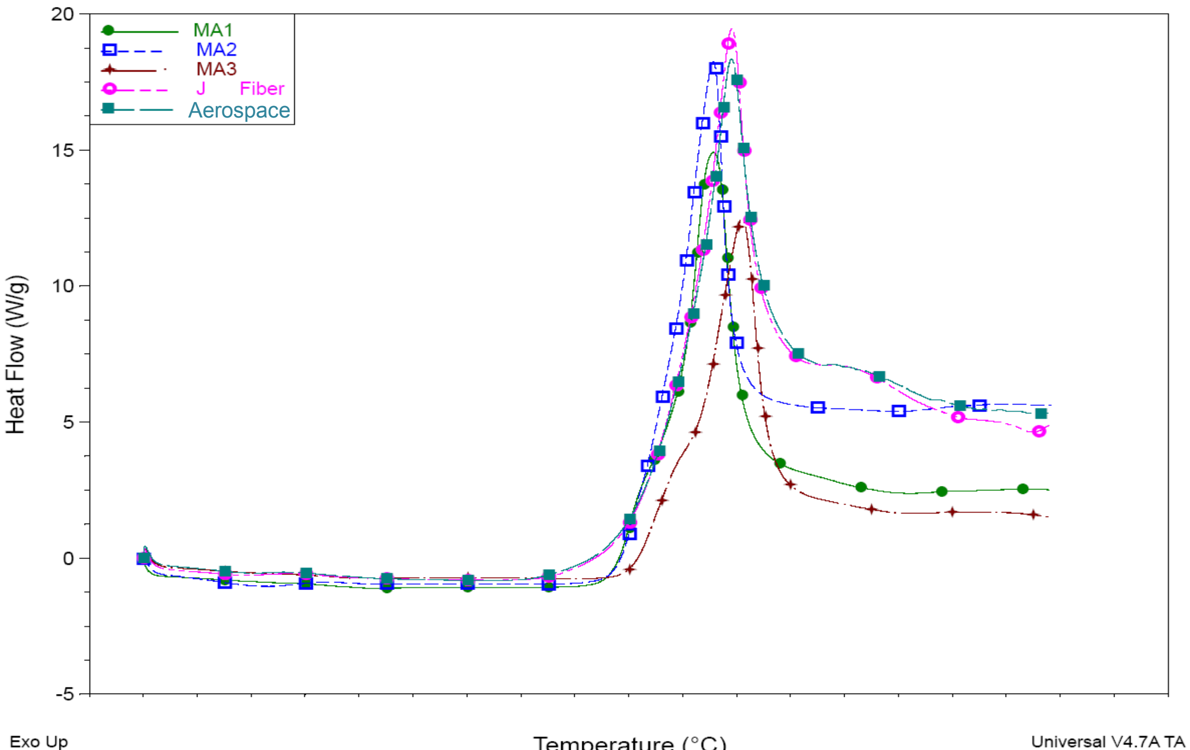
Kick-off Telecon 21 April 2011

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.

DSC of 3 FISIPE materials vs 2 Conventional Precursors



Project Status

As a result of that analysis the F1921 formulation was chosen for the first spinning trials. Two more formulations to follow.

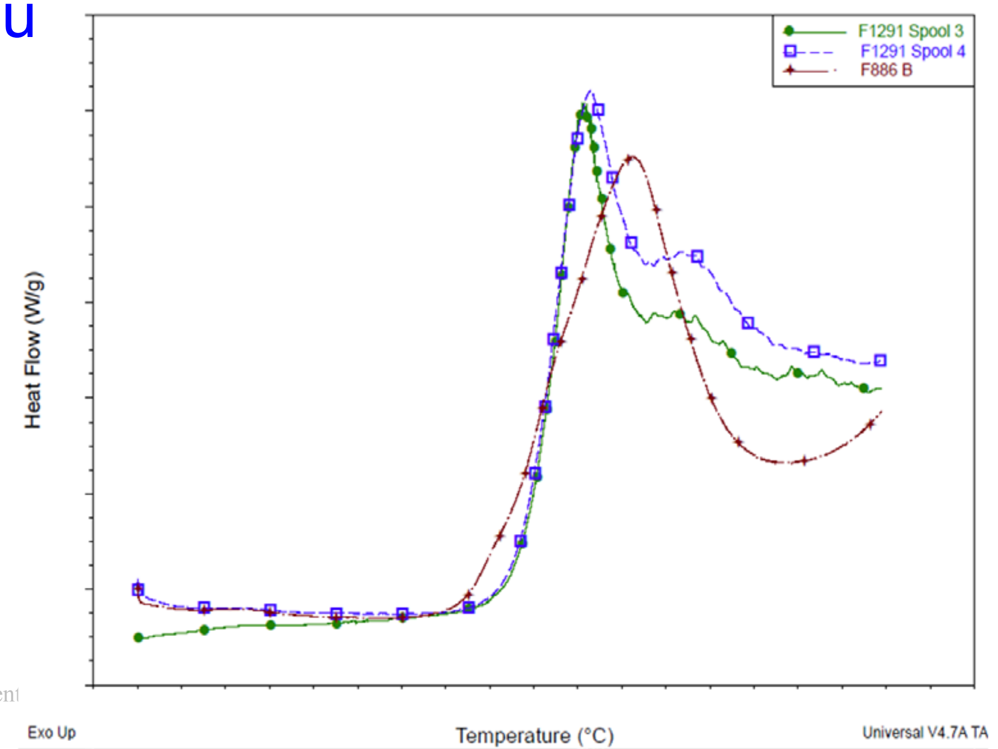
Fiber received Dec 2011 and development of the conversion protocol began. (7 step process: pretreatment, 4 oxidation ovens and 2 carbonization ovens) Each must be done sequentially.

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

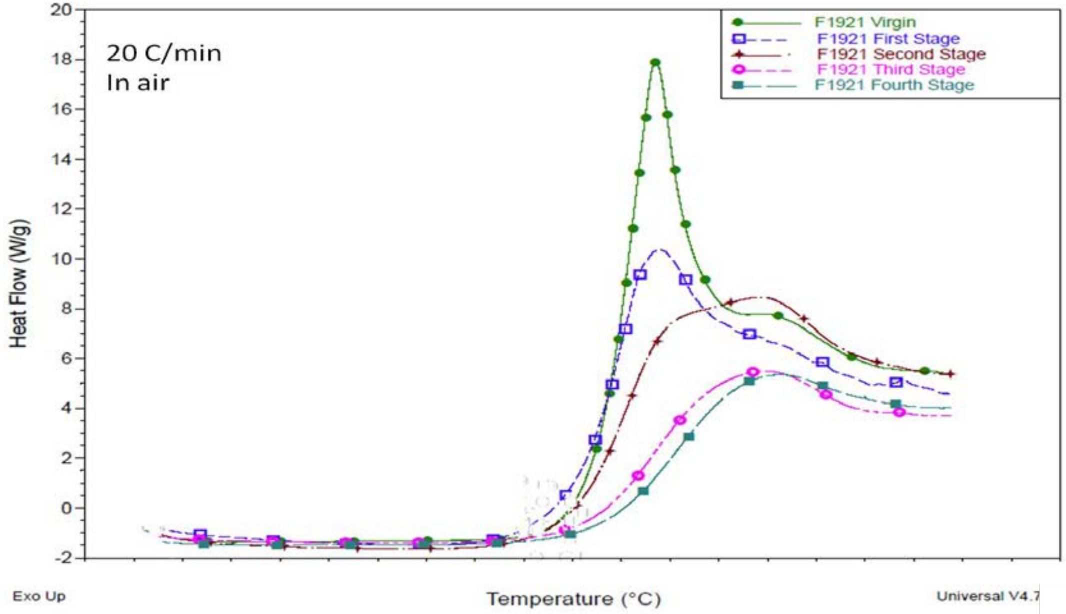
First trial 282 KSI, 28.4 MSI

Oxidation profile compares favorably with the VA precursors.

DSC of F1921 vs F886B

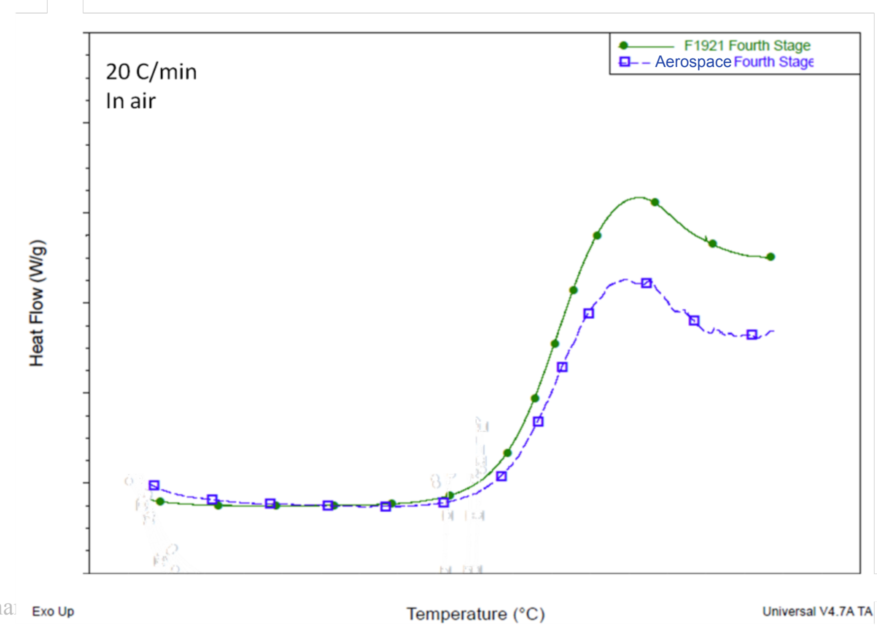


Project Status



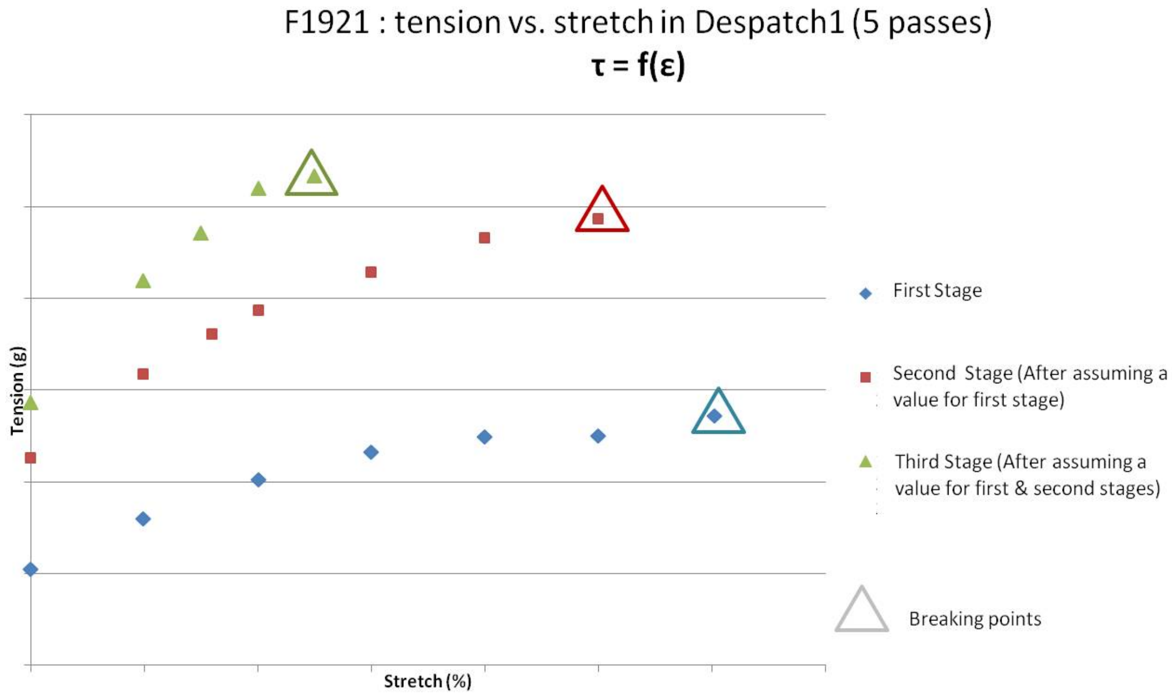
Degree of processing during each stage of oxidative stabilization.

Degree of Stabilization after stage 4 when compared to an aerospace precursor.



Project Status

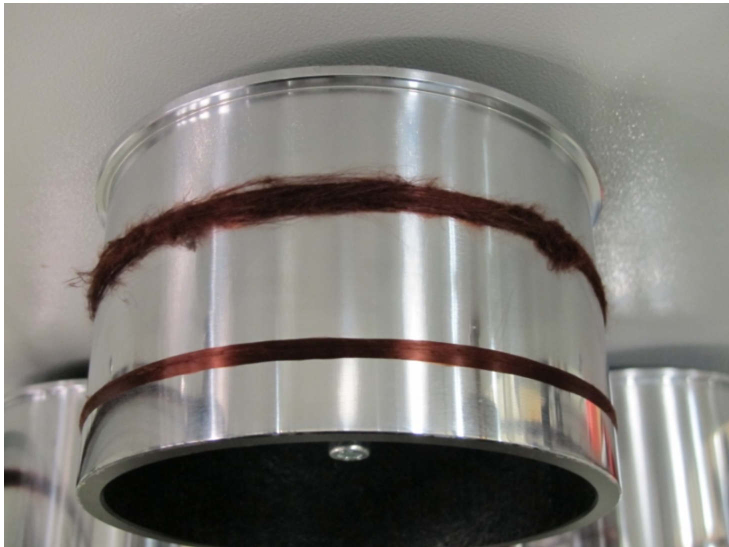
Stretching is critical to obtaining molecular alignment and developing higher strength properties. Therefore a critical step was to define the tension limits that can be applied without breakage.



Tension vs Percentage stretching for the F1921 Precursor after various oxidative Stabilization Treatments to determine the Tension Limits during processing.

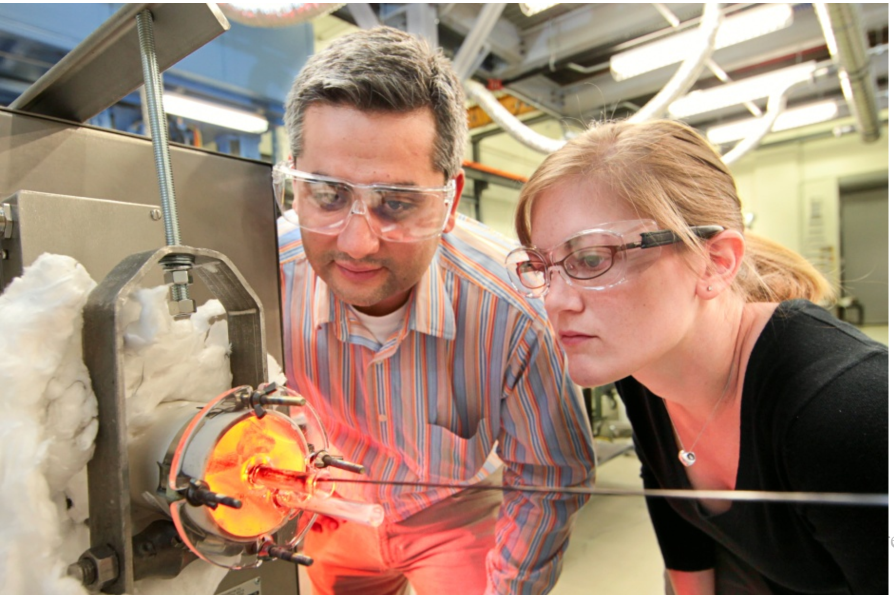
<u>Current Major Issue:</u>

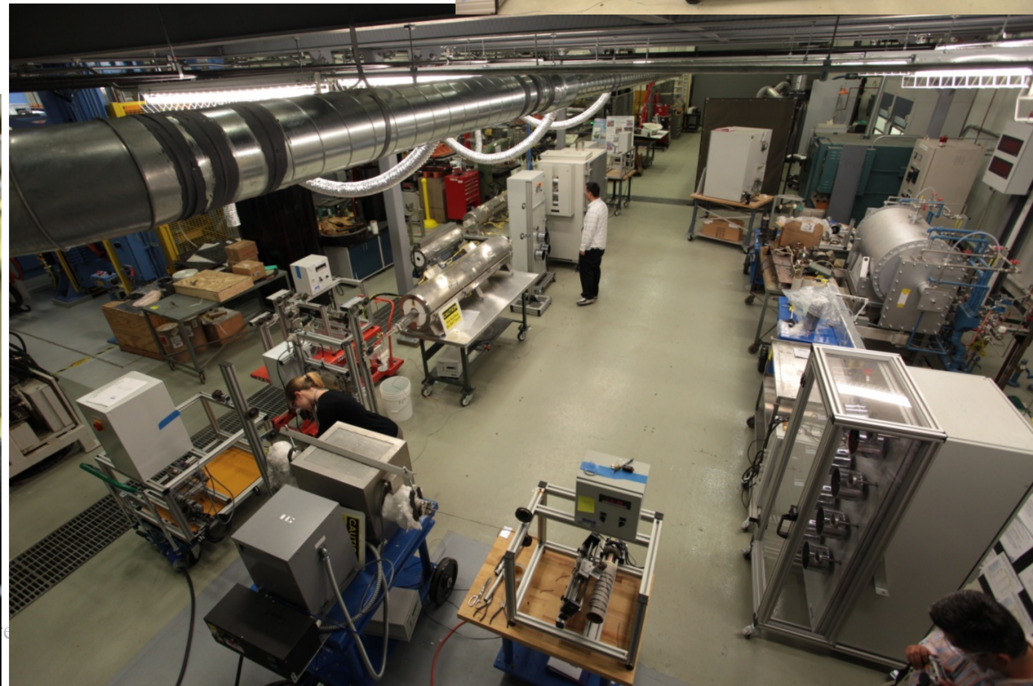
Fiber fuzzing is limiting stretch, which limits molecular alignment which limits strength. This is due to "Baby Fibers"



Facilities Used - Precursor Evaluation System

- 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 $\geq$20 filament tows
  - Temperature capability from room temperature to 1,700ºC; 2,500ºC furnace

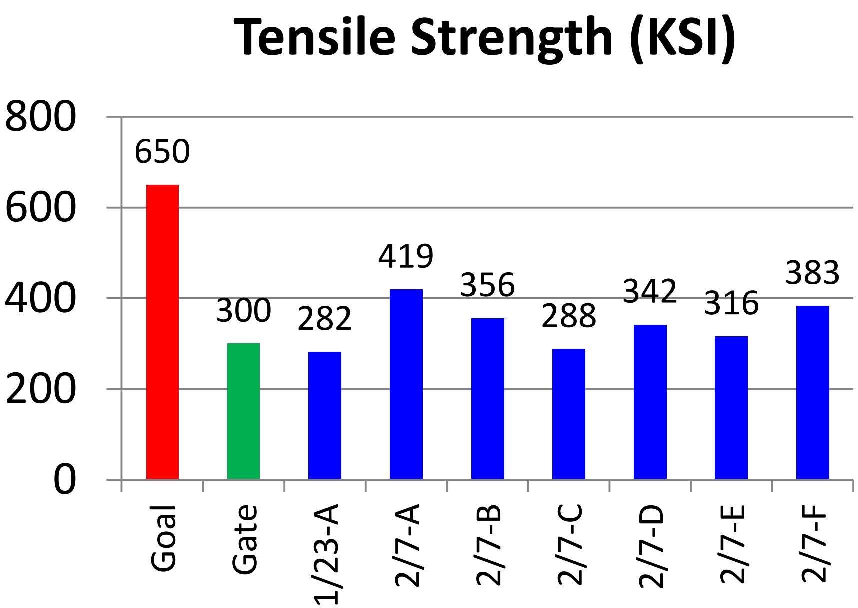


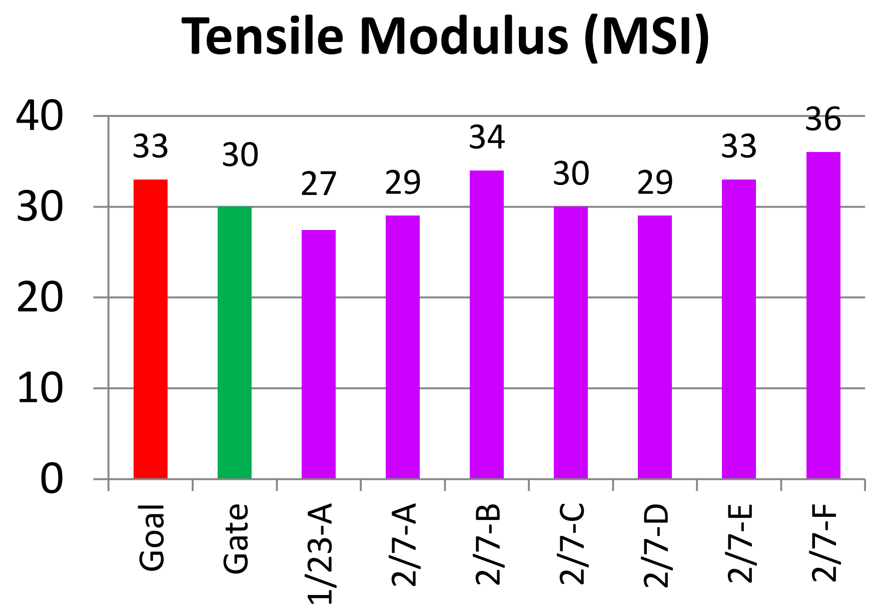


GATE MILESTONE Due 31 March 2012:

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)





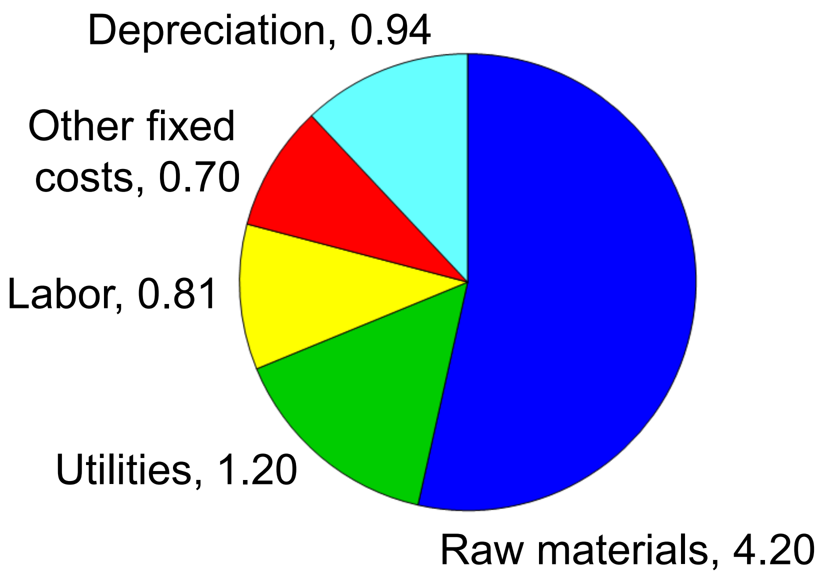
Each data Point Average of 18 tests.

Milestones

Date	Milestone	Status
July 2011	Down select to most promising precursor formulation based upon test results.	Complete
August 2011	Conduct first chemical pretreatment trials. Deliver DSC curves and written interpretation. Determined not necessary.	N/A
September 2012	Achieve carbonized fiber properties of at least 150KSI strength and 15MSI modulus to demonstrate feasibility.	Complete
March 2012 GATE	Achieve carbonized fiber properties of at least 300 KSI strength and 30 MSI modulus.	Complete
April 2013	Carbonize tows of methy-acrylate co-monomered textile fiber and size to confirm that material properties meet program requirements of 550-750 KSI strength.	Future

Cost Implications

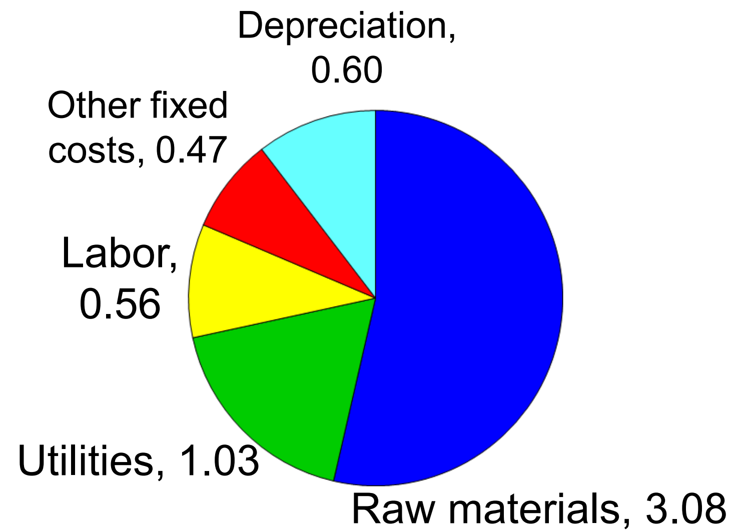
High Volume Baseline
Conventional PAN Precursor



Total: $7.85/lb

Cost Model for PAN-VA Project

High Volume Baseline
Textile Precursor



Total: $5.74/lb

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.

Potential Markets and Needs

Industry	Benefit	Applications	Drivers	Obstacles	Current Market	Potential Market
Automotive	Mass Reduction: 10% Mass Savings translates to 6-7% Fuel Reduction	Throughout Body and Chassis	Tensile Modulus; Tensile Strength	Cost: Need $5-7/lb; Fiber Format; Compatibility with automotive resins, Processing Technologies	< 1M lbs/yr	> 1B lbs/year
Wind Energy	Enables Longer Blade Designs and More Efficient Blade Designs	Blades and Turbine Components that must be mounted on top of the towers	Tensile Modulus; Tensile Strength to reduce blade deflection	Cost and Fiber Availability; Compression Strength; Fiber Format & Manufacturing Methods	1-10 M lbs/yr	100M - 1B lbs/yr
Oil & Gas	Deep Water Production Enabler	Pipes, Drill Shafts, Off-Shore Structures	Low Mass, High Strength, High Stiffness, Corrosion Resistant	Cost and Fiber Availability; Manufacturing Methods	< 1M lbs/yr	10 - 100M lbs/yr
Electrical Storage and Transmission	Reliability & Energy Storage	Low Mass, Zero CTE transmission cables; Flywheels for Energy Storage	Zero Coeficient of Thermal Expansion; Low Mass; High Strength	Cost; Cable Designs; High Volume Manufacturing Processes; Resin Compatibility	< 1M lbs/yr	10-100M lbs/yr
Pressure Vessels	Affordable Storage Vessels	Hydrogen Storage, Natural Gas Storage	High Strength; Light Weight	Cost; Consistent Mechanical Properties	< 1M lbs/yr	1-10B lbs/yr

250+ KSI, 25 MSI Fiber

550 - 750 KSI, 35 - 40 MSI Fiber

Potential Markets and Needs (Continued)

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

250+ KSI, 25 MSI Fiber

550 - 750 KSI, 35 - 40 MSI Fiber

Low Cost Carbon Fiber: Common Issues and Needs

Civil Infrastructure
Rapid Repair and Installation, Time and Cost Savings

Bio-Mass Materials
Alternative Revenue
Waste Minimization

FUELING OUR FUTURE BIOMASS 2008

Non-Traditional Energy
Geothermal, Solar & Ocean Energy

Non-Aerospace Defense
Light Weight, Higher Mobility

Aerospace
Secondary Structures

Electronics
Light Weight, EMI Shielding

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

Energy Storage
Flywheels, Li-Ion Batteries, Supercapacitors

Power Transmission
Less Bulky Structures
Zero CLTE

Oil and Gas
Offshore Structural Components

Vehicle Technologies
Necessary for 50+% Mass Reduction

Wind Energy
Needed for Longer Blade Designs

Pressurized Gas Storage
Only Material With Sufficient Strength/Weight

Status Update

The results presented are for the 1st of 3 precursors.

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

Second Precursor Received
14 March

Future Goals, Publications, Presentations, Patents

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.
4. Major concentration on maximizing properties in the conversion protocol. Time – Temperature – Tension.
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)

"Low Cost Carbon Fiber Overview", Presented at the 2011 Society of Automotive Engineers Conference, Detroit, MI, 13 May, 2011.

"Lower Cost Carbon Fiber in High Volumes for 21st Century Industries", Presented at and published in the proceedings of the SPE Automotive Composites Conference & Exhibition, Detroit, MI, 13-15 September, 2011.

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?