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

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Project ID: ST099

Project Overview

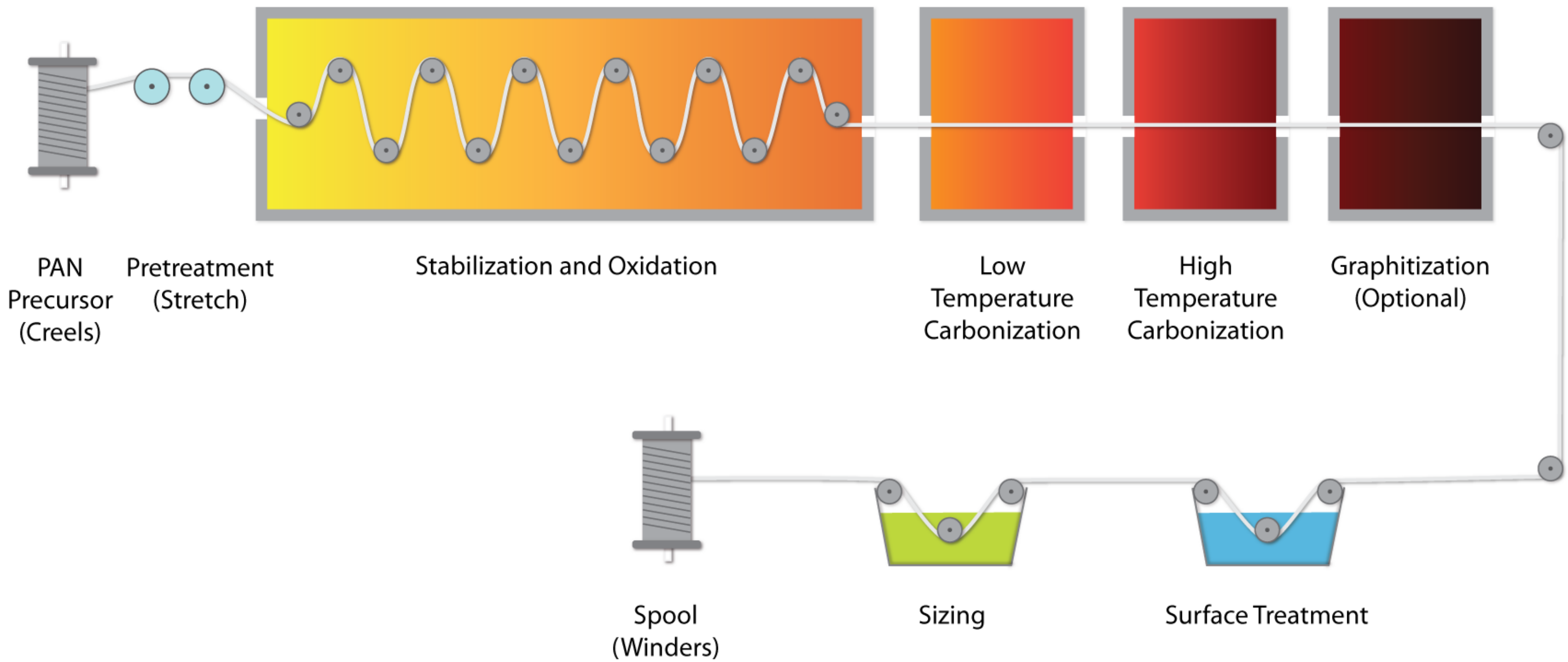
- **Timeline**
  - Start: Mid FY2011
  - End: FY2013
  - New Project
    - (Planned start: April 1)
- **Budget**
  - FY 2011: $300k
  - FY 2012: $600k
  - FY 2013: $300k
    - This budget is equally split between Vehicle Technologies and Fuel Cell Technologies.
- **Barriers***
  - System Weight and Volume (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

*References "On-board hydrogen storage technical barriers" in the Hydrogen Storage Technical Plan

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

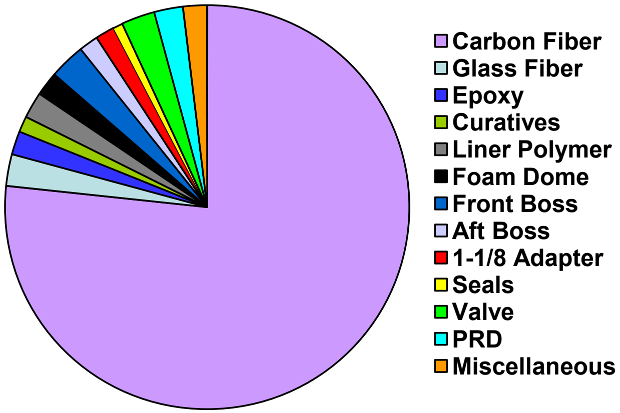
CF’s can be divided into 4 broad performance categories

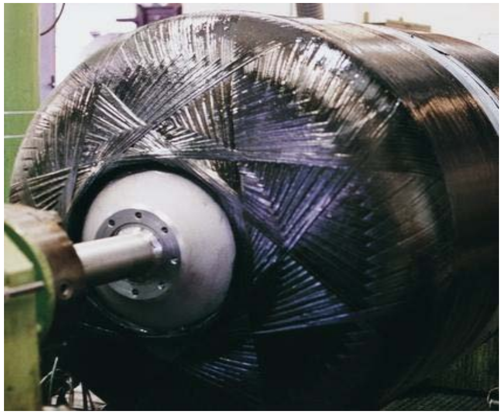
High Performance	**>750 KSI** **> 35 MSI**	**Performance Driven** **Cost is not Limiting**
Moderate Grade	**500 – 750 KSI** **25 – 35 MSI**	**Cost and Performance Balance**
High Volume Grade	**250 – 500 KSI** **< 25 MSI**	**Cost Sensitive** **Performance Enabling**
Non Structural	**Chemical & Physical Properties of Carbon**	**Usually Low-Cost and Chosen for Uniqueness**

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

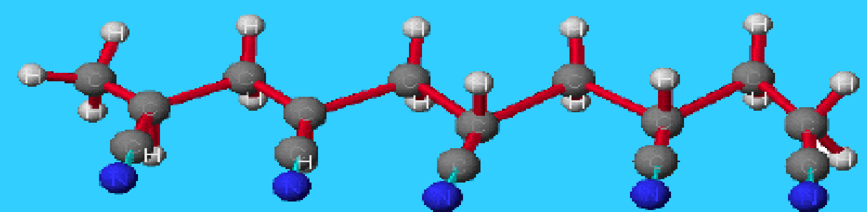
For the development of low-cost, high strength CF

- **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 ≥ 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.



Polyacrylonitrile, $-(CH_2CH)-$ with $C\equiv N$ attached to the CH

What is the difference between making higher performance and industrial grade CF?

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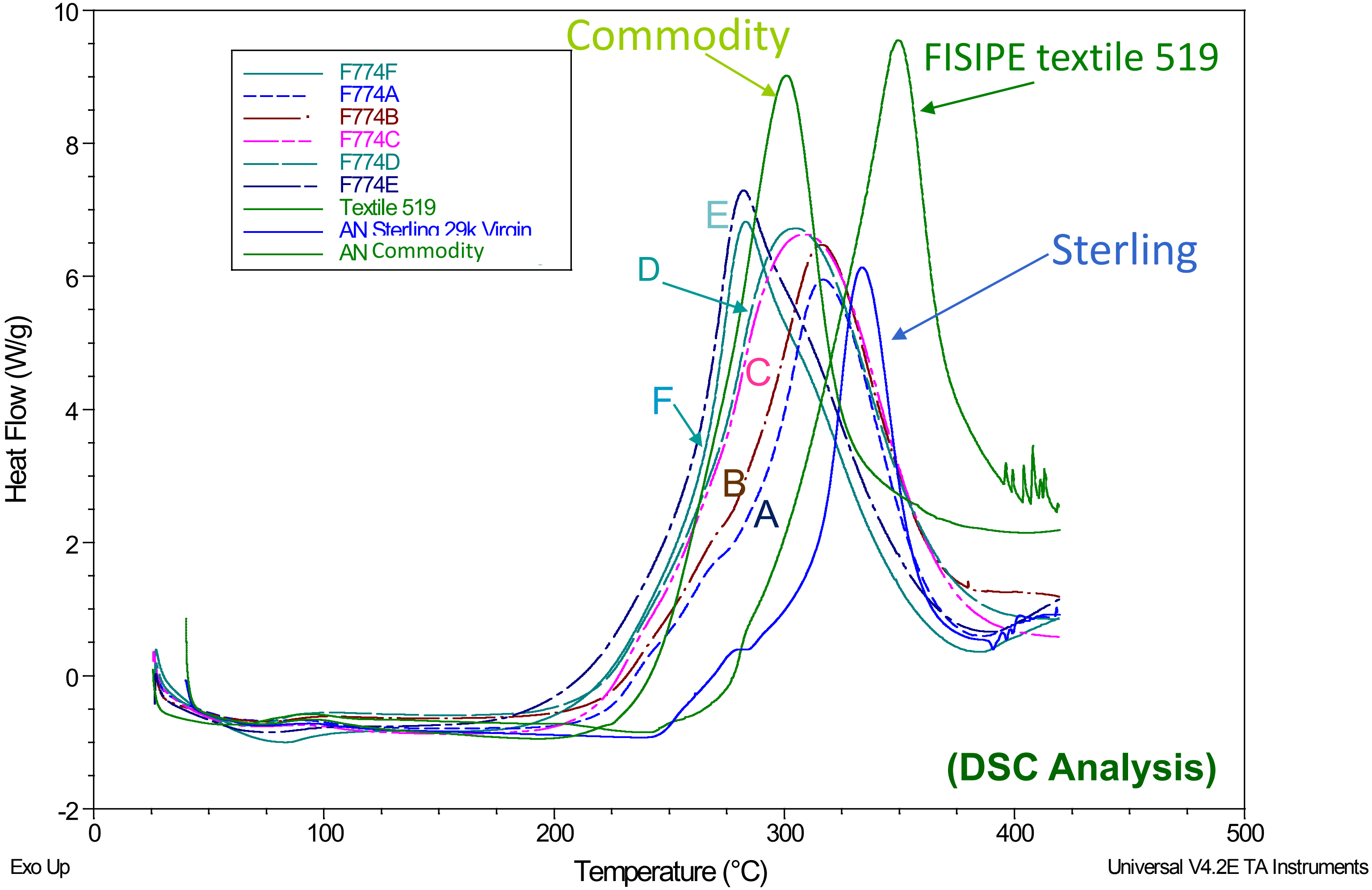
Attribute	Industrial Grade	Aerospace Grade	Cost Impact
Tow Size	12-80K Filaments	1-12K Filaments	Less material throughput
Precursor Content	≅ 93% AN, MA or VA	≥ 95% AN, MA	Little on raw material; slower oxidation
Precursor purity	Can tolerate more impurity	Controls UTS	Slower spinning speed
Oxidation	Quicker due to lower AN	Slower due to higher AN	Time is money, reduced capital & energy cost
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 or boxes	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.

Typical PAN Formulations

Various chemistries of commodity precursors. Historical Data

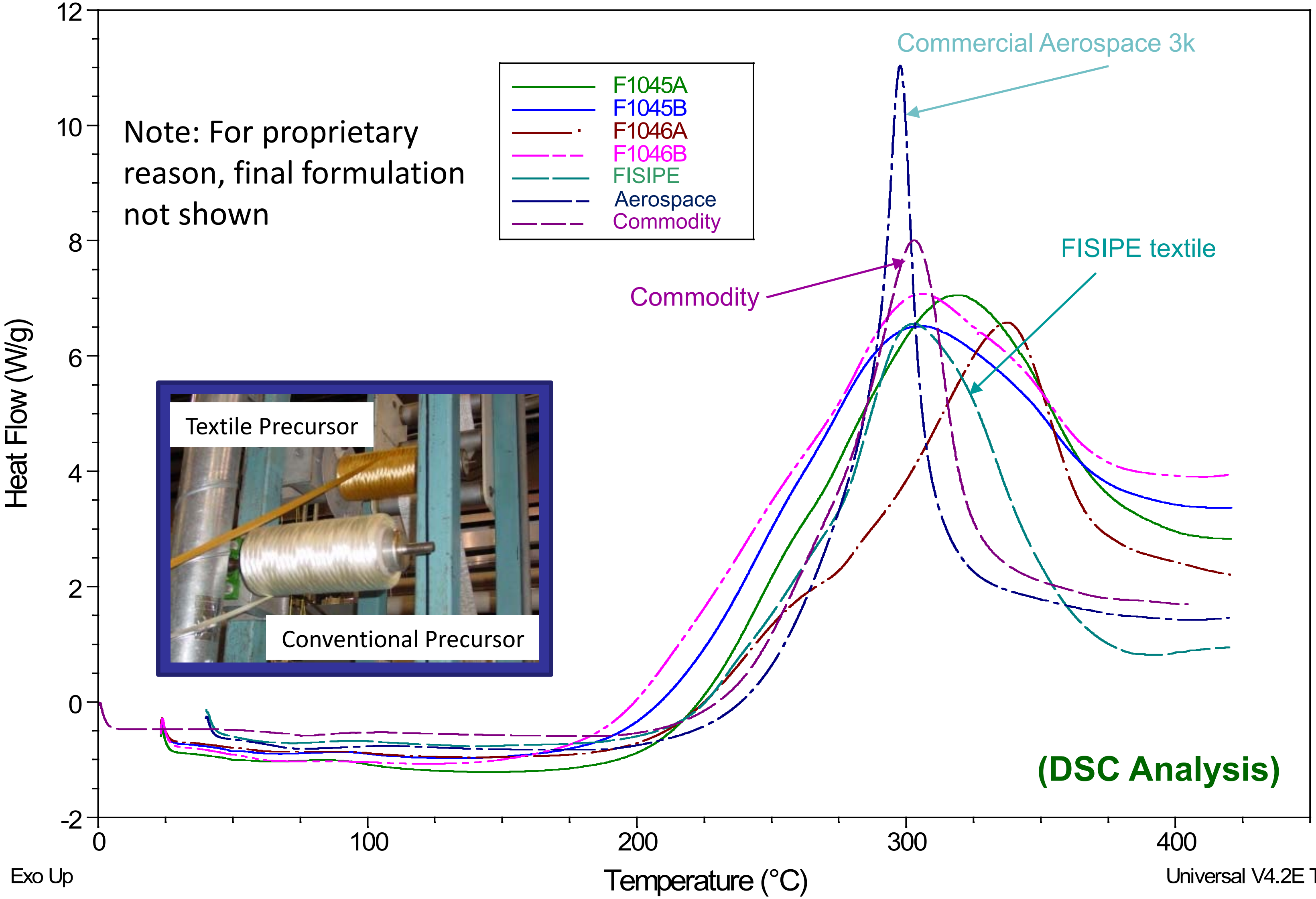


Steepest part of slope determines speed of stabilization.

Location of ramp up start & peak determine oxidative stabilization temp range.

First Textile Formulations

Different types of textile PAN commodity precursors. Historical Data



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Prior Technical Results

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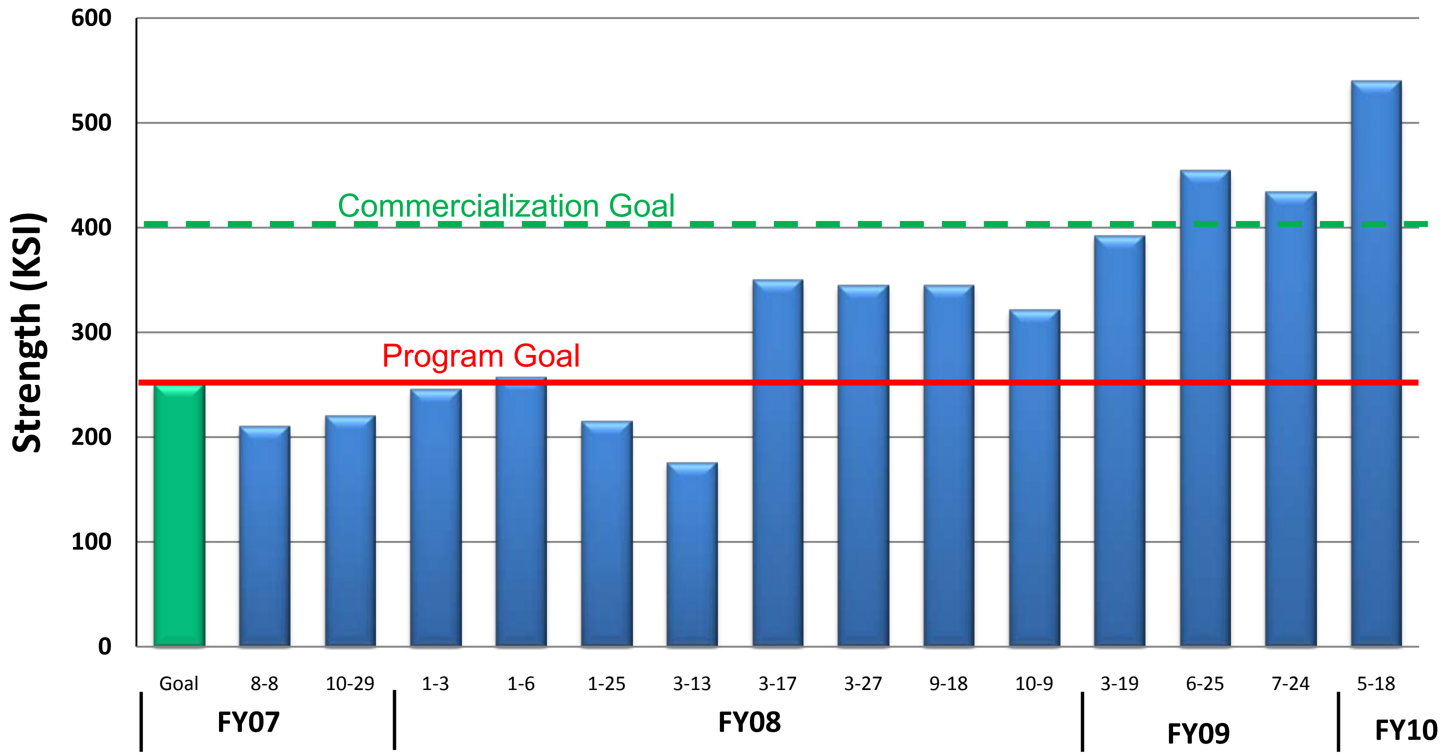
FISIPE Commodity Textile PAN Tensile Strength. Historical Data

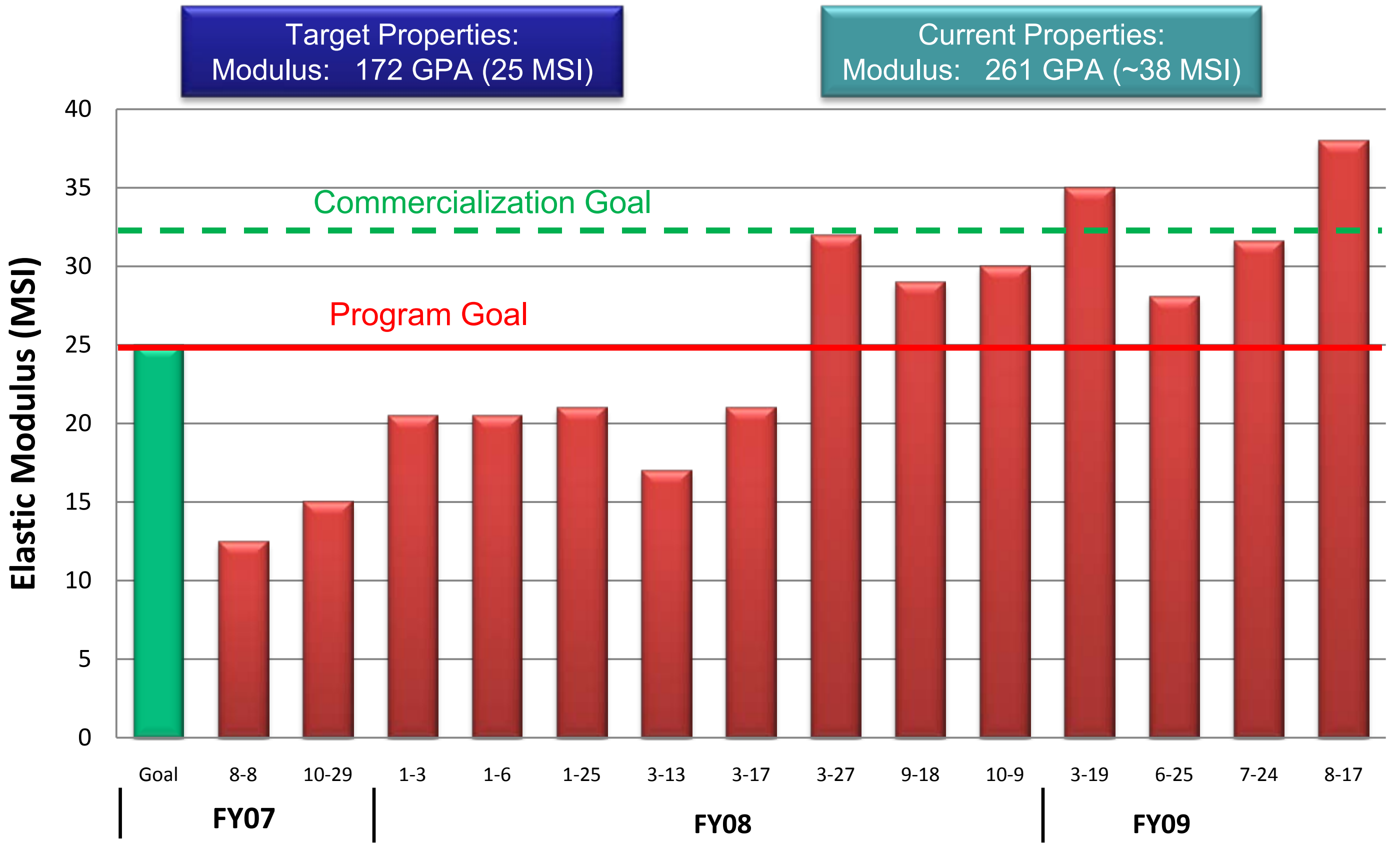
Target Properties:
Strength: 1.72 GPA (250 KSI)

Current Properties:
Strength: 3.72 GPA (540 KSI)



Prior Technical Results

FISIPE Commodity Textile PAN Modulus. Historical Data



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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

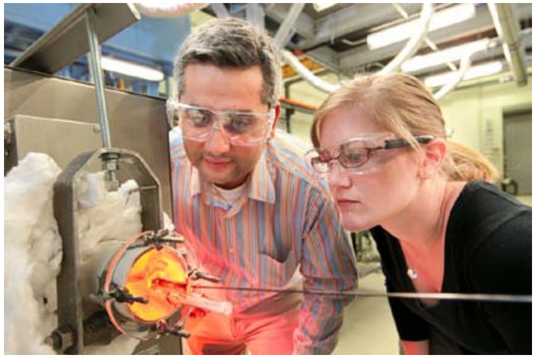
Milestones

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

The dates given are under the assumption that work will commence March 1, 2011.

Leveraging

- **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.



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Unique ORNL Capability

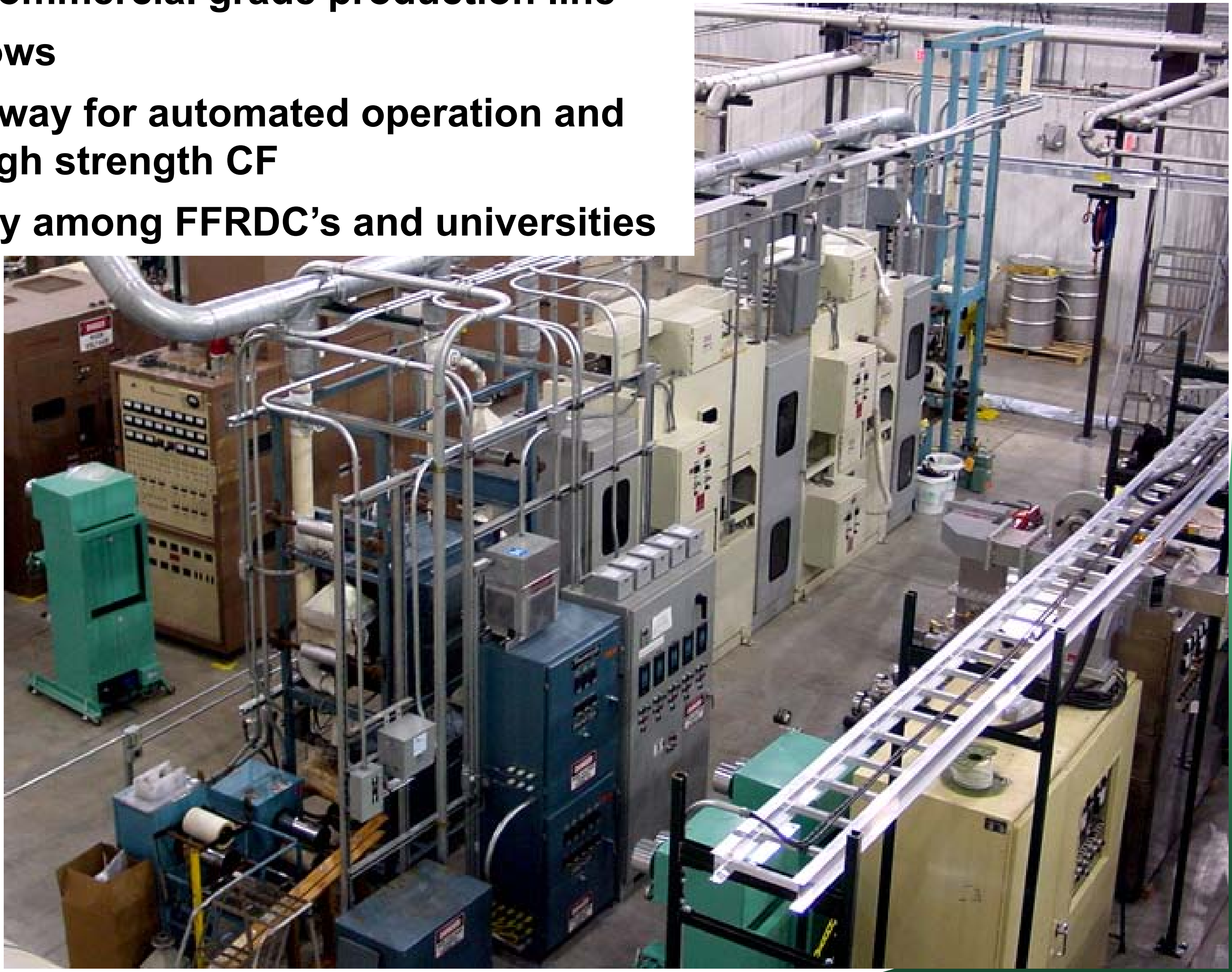
Precursor Evaluation System (PES)

- **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)

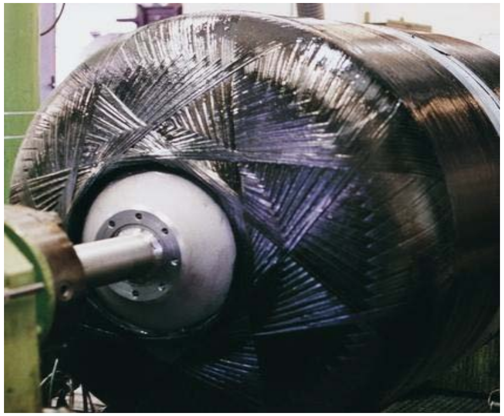
- Prominent acrylic fiber manufacturer (in Portugal)
- ORNL and FISIPIE have already conducted extensive work on commodity grade fibers from textile PAN precursor and are currently evaluating large CF tows.
- FISIPE is aggressively pursuing the development of a new textile pan precursor that may be applicable 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

Date	Milestone
Sept 2011	Deliver CF's with properties of 150 KSI strength and 15 MSI modulus.
Jun 2012	Deliver CF's with properties of 300 KSI strength and 25 MSI modulus.
Sept 2012	Deliver CF's with properties of 500 KSI strength and 33 MSI modulus.
Sept 2013	Deliver CF's with properties of 650 KSI strength and 35 MSI modulus.