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

## May 13-16, 2013

***Status as of Middle March 2013***


**C. David (Dave) Warren**

Field Technical Manager

Transportation Materials Research

Oak Ridge National Laboratory

P.O. Box 2009, M/S 8050

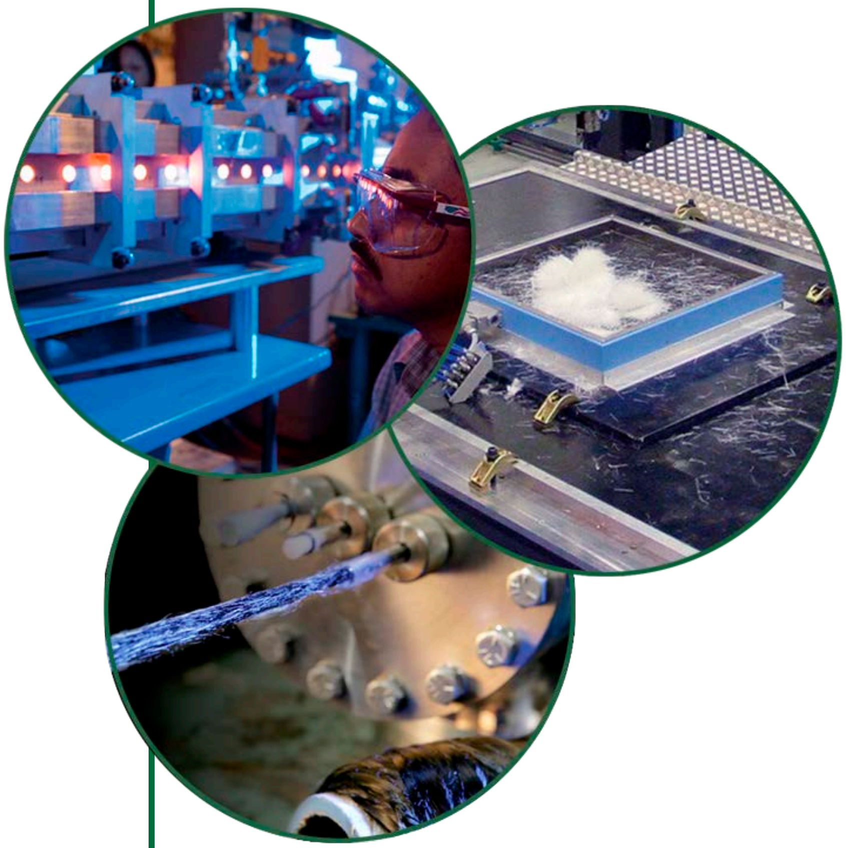
Oak Ridge, Tennessee 37831-8050

Phone: 865-574-9693

Fax: 865-574-0740

Email: WarrenCD@ORNL.GOV



**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 2014
  (Sept 2013-delays)

## Budget

- FY 2011: \$350K
  (\$75k from VT)
- FY 2012: \$300K
- FY 2013: \$300K
- FISIPE Cost Share:
  – \$ 1,277K

No additional cost due to Delays

## 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

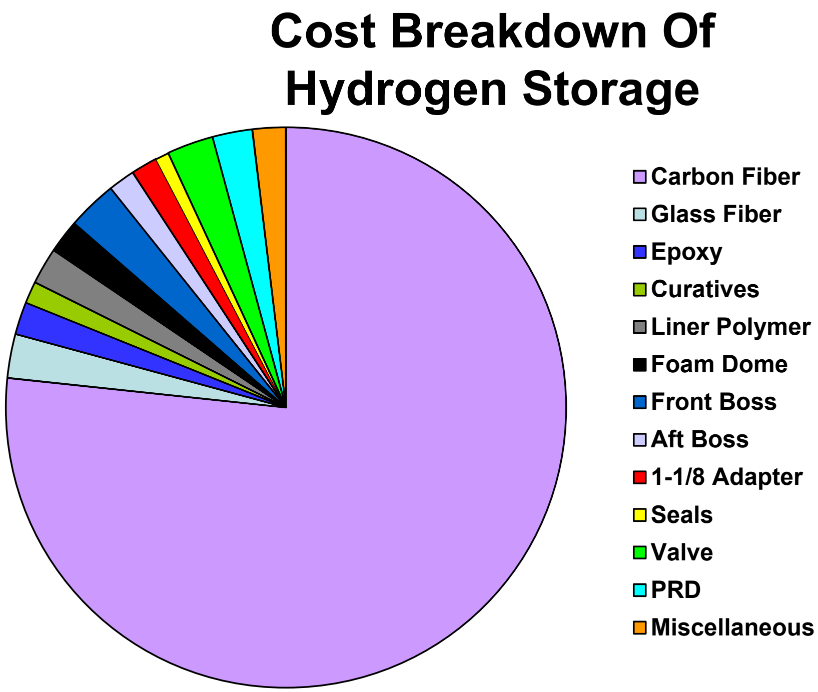
## Partners

- ORNL: carbon fiber conversion, precursor characterization, carbon fiber characterization
- FISIPE: precursor formulation, precursor spinning
- SGL: Carbon Fiber Producer

# Relevance - Background



- The CF material represents a significant portion of the overall cost of pressure vessels (60-80%).
- There is a strong need for a reduction in the cost of CF.
- **Precursor is 55% of the cost of the Carbon Fiber.**
- Target properties: **30-35 MSI Modulus; Strength ~700 KSI.**
- The rapid development of low-cost CF is a commercial/technological necessity.




| | Strength (KSI) | Modulus (MSI) | Estimated Production Costs |
|---|---|---|---|
| Current Market Fibers (Aerospace Grade) | 750 | 38 | \$15-20/lb |
| Project Target | 650-750 | 35-38 | \$10-12/lb |
| Current Status Precursors | 400 | 25-35 | \$10-12/lb |

# Relevance – Project History

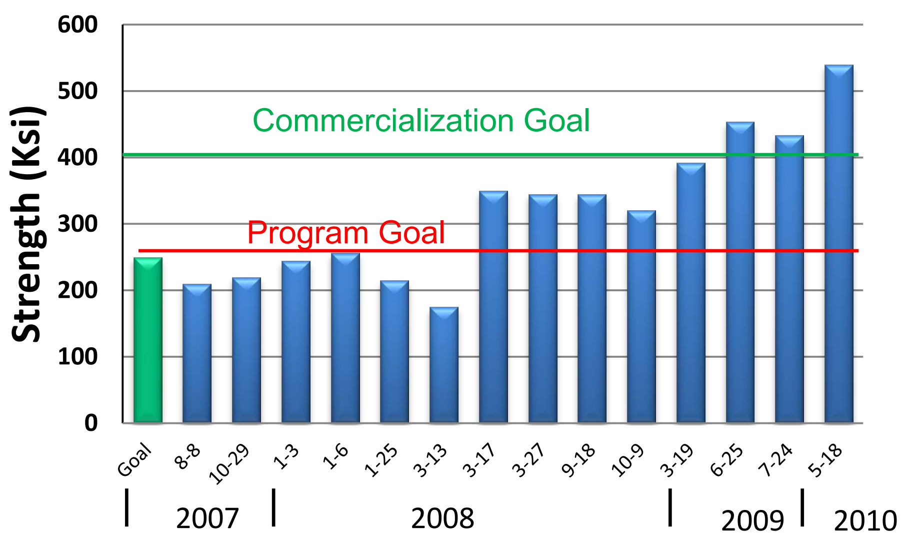
## $H_2$ Storage

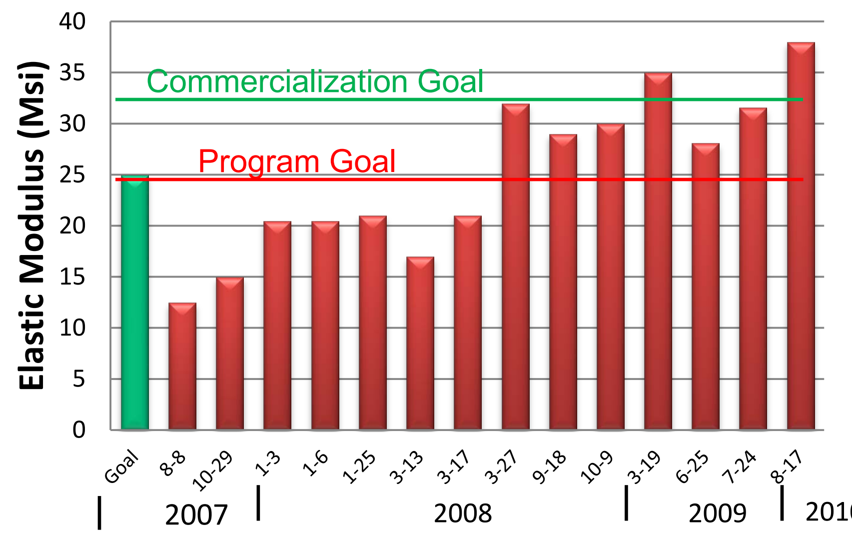
Project built off 2 previous projects funded by Vehicle Technologies.

1st was conducted by Hexcel:

Demonstrated the feasibility of using “textile” grade PAN (carpet and sweater fiber) as a precursor. Utilized fiber from the last US PAN textile mill before it went out of business. Properties: 20 MSI, 240 KSI.

2nd was conducted by ORNL and FISIPE (Lisbon, Portugal): Develop a textile based precursor that uses PAN for vehicle Structural applications.




**Target Properties:**

**250 KSI and 25 MSI**

**Final properties:**

**540 KSI and 38 MSI**

# Approach - Precursor

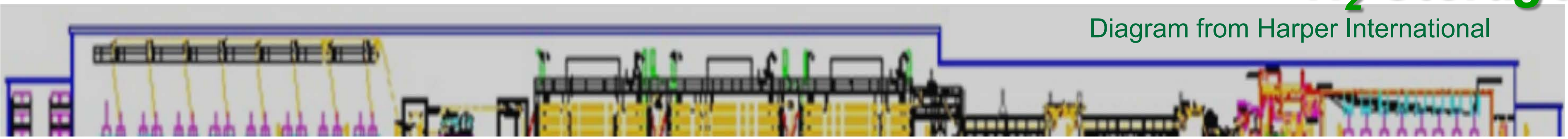


Develop a PAN-MA formulation produced in a textile mill with as few changes to the precursor manufacturing as possible to achieve performance requirements while preserving the high rate, high volume cost advantages of a textile mill.

| Attribute | Industrial Grade | Aerospace Grade | Textile PAN Materials | Textile Grade Precursor | Cost Impact |
|---|---|---|---|---|---|
| Tow Size | 12-80K Filaments | 1-12K Filaments | 500K-1000K Filaments | 500K Pre-Split to 26K | Less material throughput |
| Precursor Content | < 92% AN, MA or VA comonomer | > 92% AN, MA comonomer | <92% AN, VA comonomer | ~92%AN, MA comonomer | Little on raw material; slower oxidation with MA |
| Precursor purity | Can tolerate more impurity | High Purity | Purity not an issue | High Purity | Slower spinning speed |
| Manufacturing | Quicker due to lower AN | Slower due to higher AN | Very High Rate | Very High Rate | Time is money |
| Carbonization | Lower Temp | Sometimes Higher Temp | NA | Lower Temp | Small impact |
| Surface treatment | Same but utility affected | Same | NA | Lower Temp | Same but Utility affected. |

# Approach - Baseline CF Costs (Industrial not Aerospace)






| | Precursors | Stabilization & Oxidation | Carbonization/ Graphitization | Surface Treatment | Spooling & Packaging | |
|---|---|---|---|---|---|---|
| Baseline Today - $10.20 | $5.56 | $1.78 | $1.41 | $0.80 | $0.65 | Recent Model 2012 |
| High Volume Today - $9.35 | $5.23 | $1.62 | $1.27 | $0.72 | $0.49 | |

<u>Above Estimate is for Industrial Grade Fiber</u>

- Project approach is to:
- Build off the FISIPE project to
- Develop a PAN-MA formulation that
- Uses Textile production processes to produce a
- Precursor that yields near aerospace properties
- At Industrial Grade (or below) prices.

Precursor Cost is by far the Greatest followed by Oxidation and Carbonization

Not Captured is that Oxidation is the rate limiting step and thus mass throughput limiting step.

# Approach - Milestones

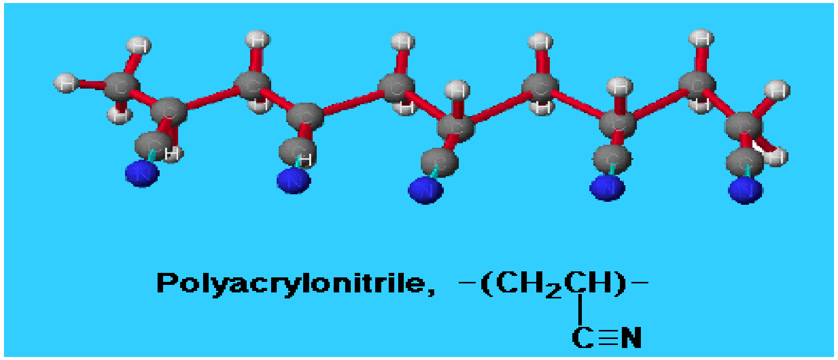
| Date | Milestone | Status |
|---|---|---|
| July 2011 | Down select to most promising precursor formulation based upon test results. | Complete |
| August 2011 | Conduct first chemical pretreatment trials. Deliver DSC curves and written interpretation. Determined not necessary. | N/A |
| September 2012 | Achieve carbonized fiber properties of at least 150KSI strength and 15MSI modulus to demonstrate feasibility. | Complete |
| March 2012<br><br>GATE | Achieve carbonized fiber properties of at least 300 KSI strength and 30 MSI modulus. | Complete |
| October 2012 | Downselect to the most promising precursor for further development. | 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. | Delayed |

# Project Approach



**Approach:**

1. Identify candidate PAN-MA resins.
2. Determine fiber spinning parameters.
3. Improve fiber purity and "roundness"
4. Determine the conversion protocol.
5. Optimize all above parameters.
6. Down Selection from 11 polymers to 3 candidate fibers to 1 final fiber.




## Main Challenges:

1. Adapting high speed processes for higher AN concentration. (2011)
2. Adapting high speed processes to increase precursor purity-minimize defects. (2011-2012)
3. Spinning of round fibers -air gap spinning. (2012)
4. Improving consistency, fiber to fiber and along fibers without sacrificing speed. (2012-2013)
5. Work out conversion protocol.  Time – Temperature – Tension. (2012 – 2013)
6. Optimize all parameters. (2013-2014)

# FY12 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.

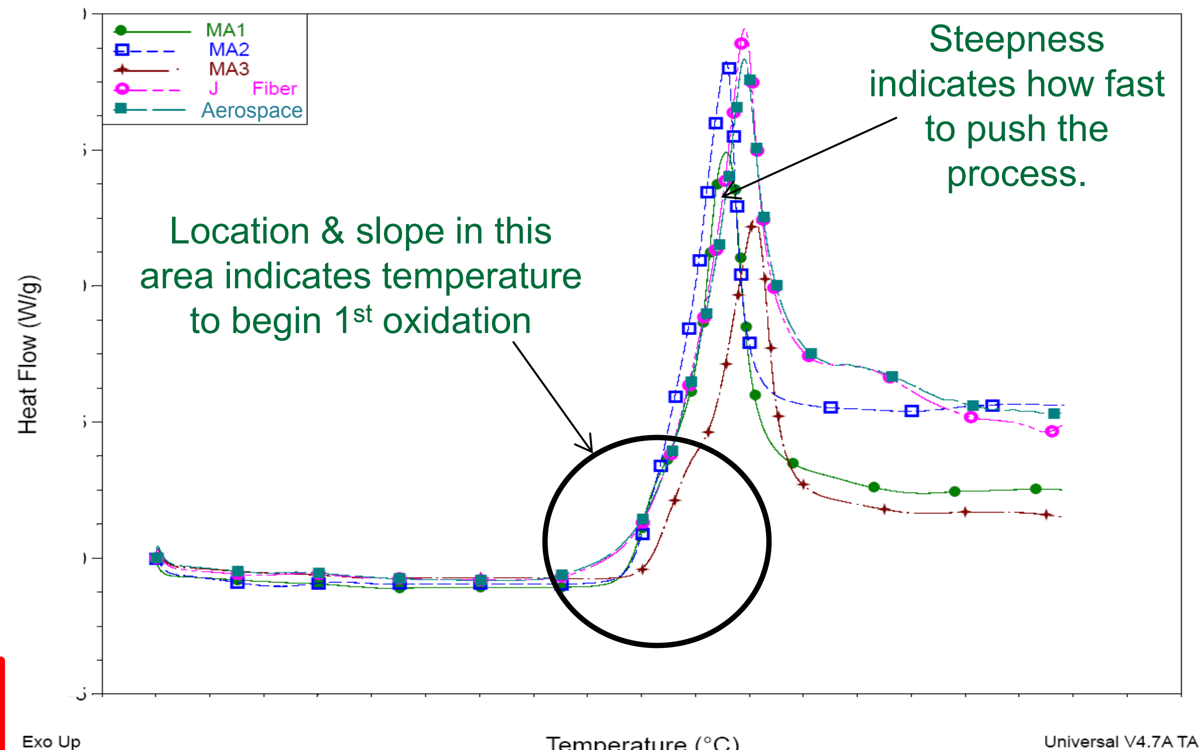
11 polymer compositions sent to ORNL for screening.

3 were selected for further development using various analytical techniques.

## Candidate Precursors

- Produced using textile processes
- Smooth curves (unlike typical textile material)
- Same exotherm behavior as aerospace grade
- According to this MA2 is most like aerospace precursors & should give best properties.

**DSC of 3 FISIPE and 2 Conventional Precursors**




**Note: Axis labels and data values omitted due to export control regulations.**

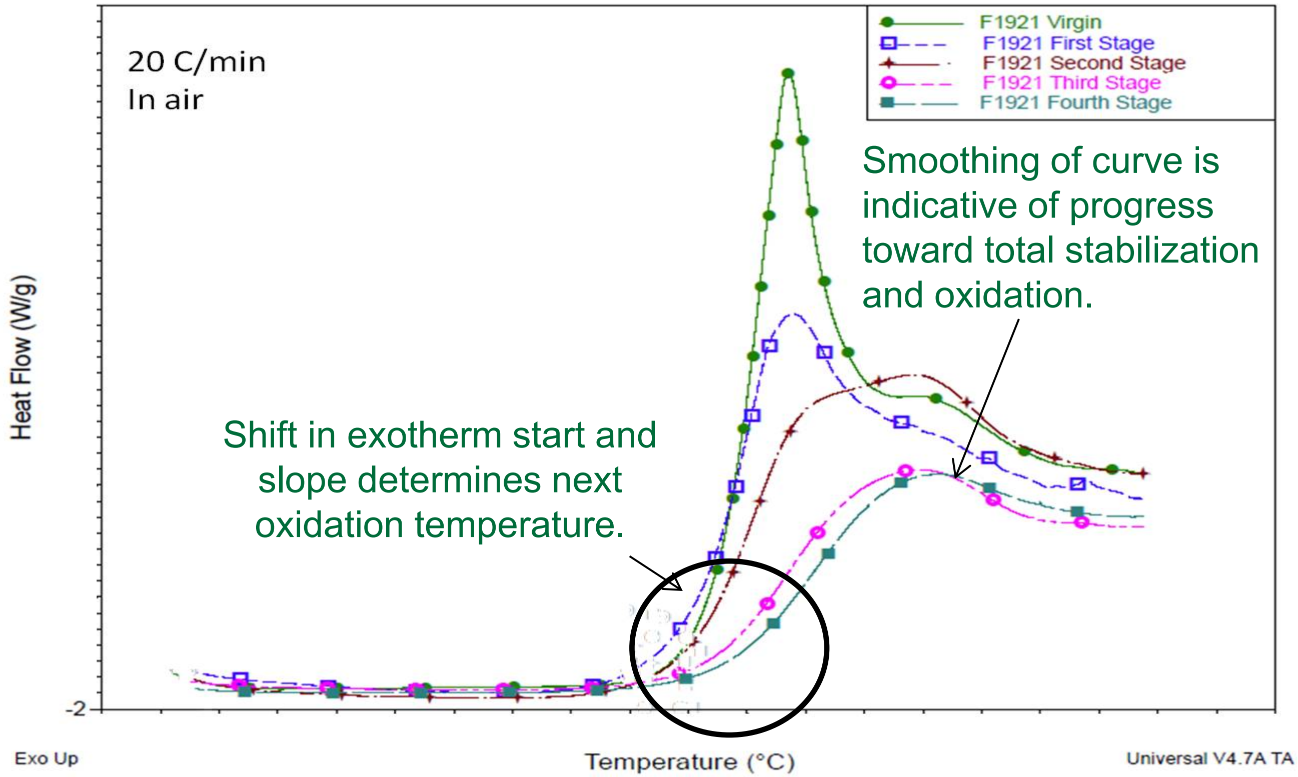
# FY12 Status

F1921 (MA1) formulation was chosen for the first spinning trials. Two more formulations F2000 (MA2) and F2027 (MA3) followed.

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. First trial: 282 KSI, 28.4 MSI with F1921.

The combination of TIME, TEMPERATURE and TENSION (3T) controls the final properties.

More critical in earlier processing stages than later stages.




Note: Axis labels and data values omitted due to export control regulations.

# FY13 Status

Preliminary Conversion Trials were held with all 3 Precursors

Last Major MILESTONE 3/31/12: Achieve properties of at least 300 KSI strength and 30 MSI modulus. (After last year's AMR slides were due.)

Properties from First Round Analysis:
F1921 Precursor: 324.7 KSI; 26.9 MSI
F2000 Precursor: 372.8 KSI; 36.0 MSI
F2027 Precursor: 252.7 KSI; 27.2 MSI

The F2000 Precursor was downselected for further development.

# FY13 Status



Step One Determine Temperatures (Single Stress – Repeated at other Load Levels

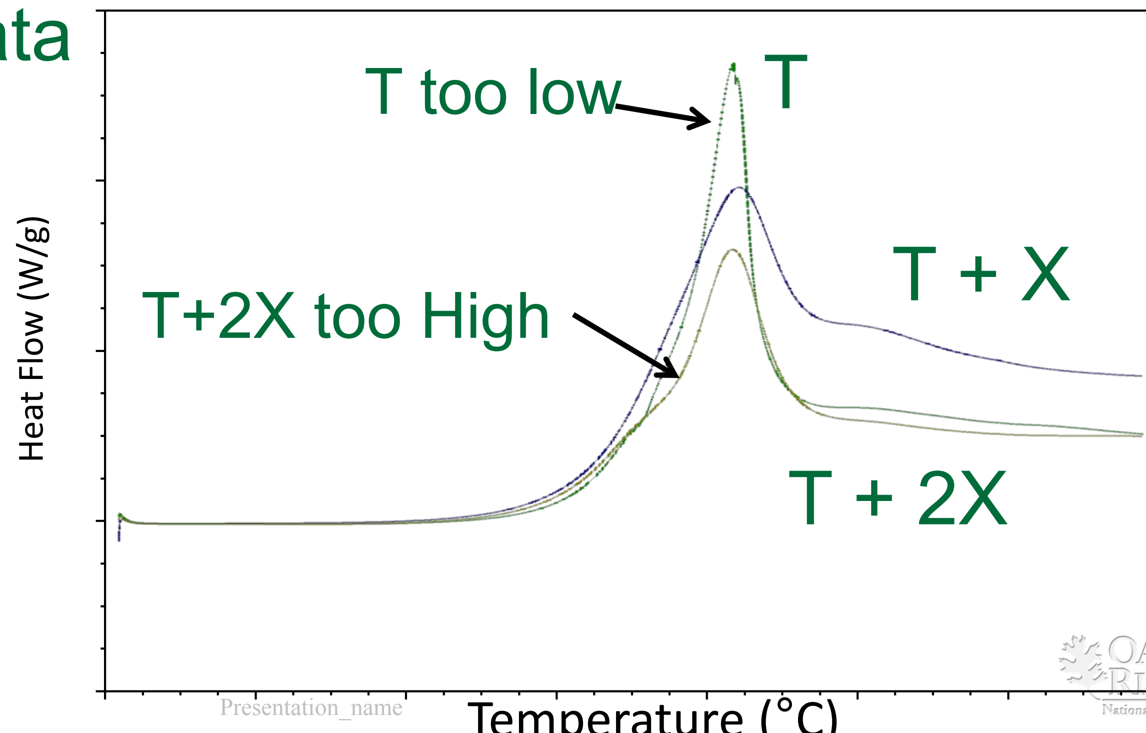
| | Oxidation 1 | Oxidation 2 | Oxidation 3 | Oxidation 4 |
|---|---|---|---|---|
| Profile 1 | T | T + Y | T + 2Y | T + 3Y |
| Profile 2 | T + X | (T + X) + Y | (T + X) + 2Y | (T + X) + 3Y |
| Profile 3 | T + 2X | (T + 2X) + Y | (T + 2X) + 2Y | (T + 2X) + 3Y |

Graphical Comparisons of data in Columns

Graphical Comparisons of data in Columns

## Other Important Data

- Density
- Physical Damage
- Diameter
- Stress-Strain Curve

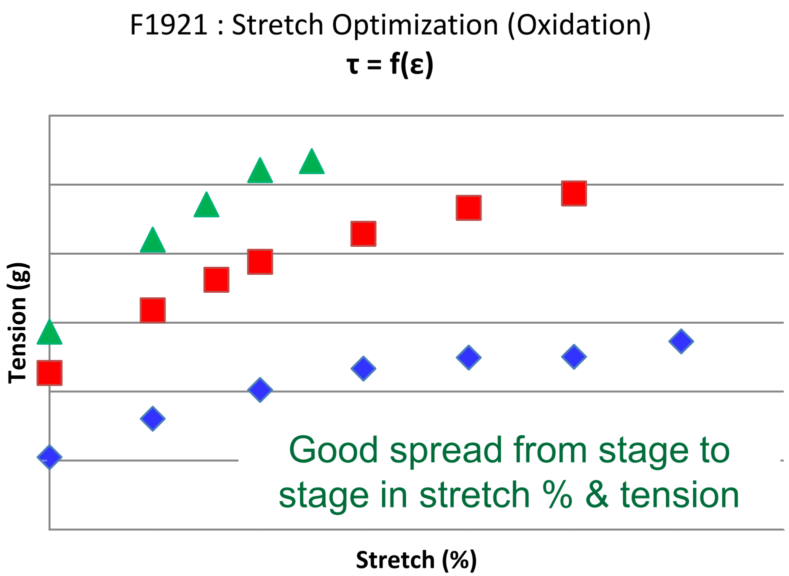


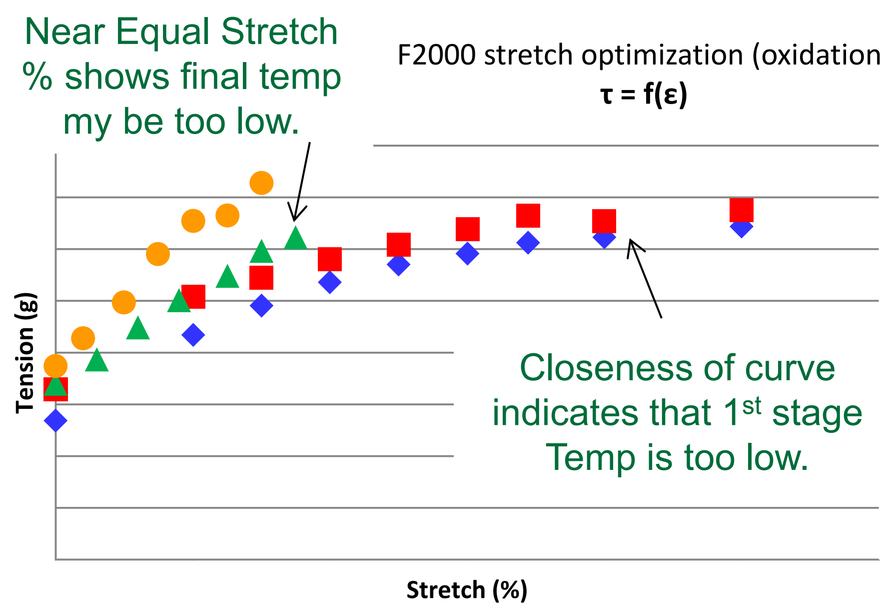

**Note: Axis labels and data values omitted due to export control regulations.**

# FY13 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.  Not an exact science.



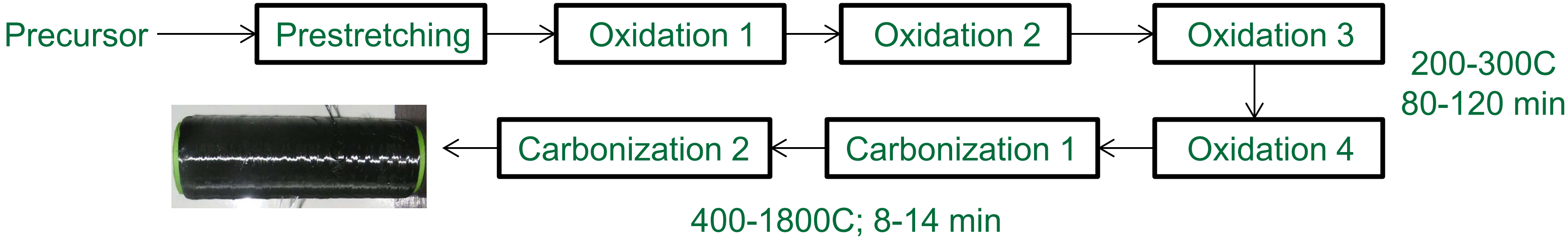




- ◆ After 1st Oxidation Stage
- ■ After 2nd Oxidation Stage
- ▲ After 3rd Oxidation Stage
- ● After 4th Oxidation Stage

**Note: Axis labels and data values omitted due to export control regulations.**

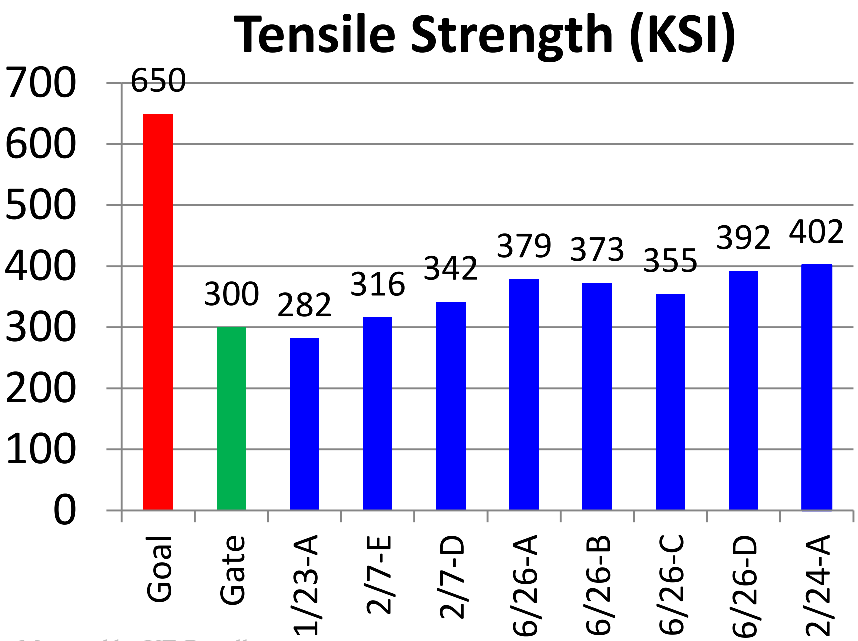
# FY13 Status – Accomplishments

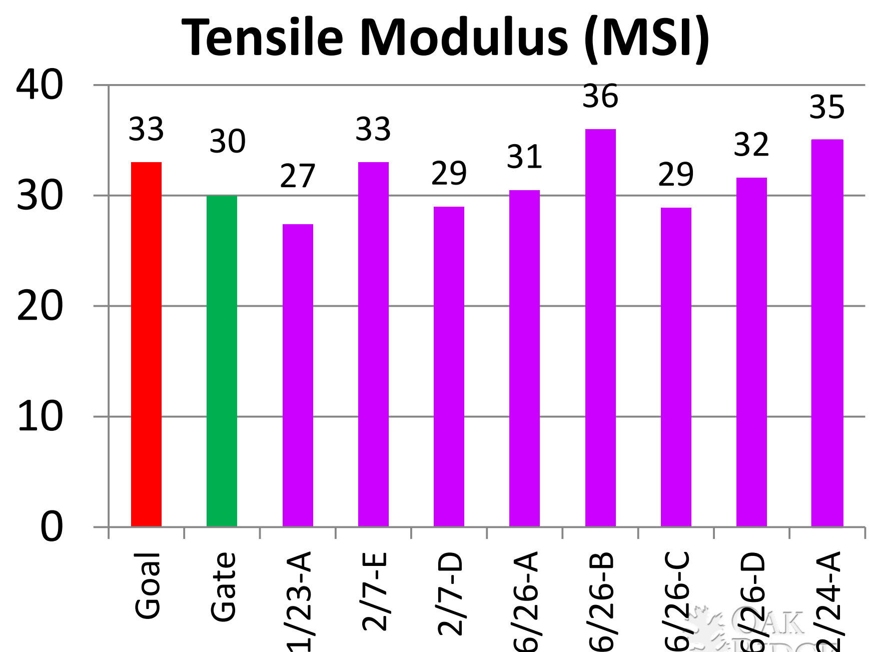





Optimization through iterative optimization of Temperatures, Exposure Times and Tension (Stretch %) in each of 7 stages of conversion. Also through improving precursor purity, precursor homogenity, fiber consistency and fiber roundness.

Current Status: 355-402 KSI, 29-36 MSI




Each data Point Average of 18 tests.

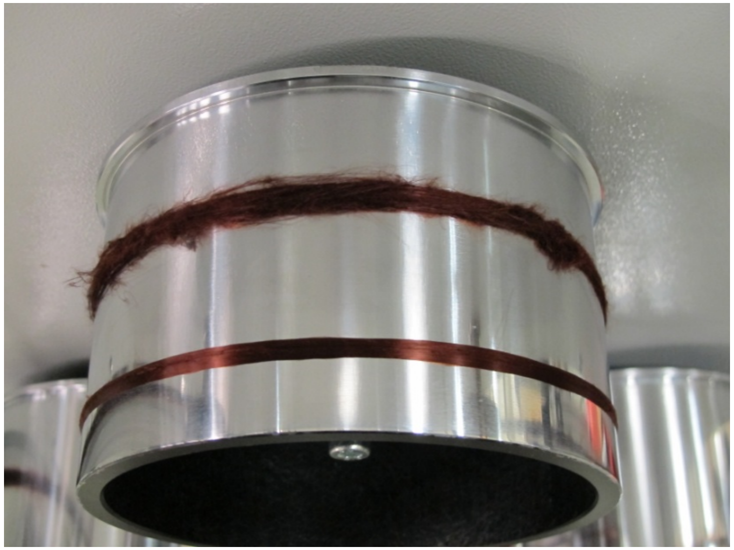
# FY13 Status - Accomplishments



Major Issue:

Fiber fuzzing was limiting stretch, which limits molecular alignment which limits strength. This is due to Underdeveloped Fibers". Even if the small fibers do not cause fuzzing in the early stages, they will in later stages reducing yield and available stretch.

Status: Resolved.



What was happening is that smaller than normal fibers are breaking which creates the "fuzz".

Reduced ability to achieve molecular alignment and optimize fiber properties.

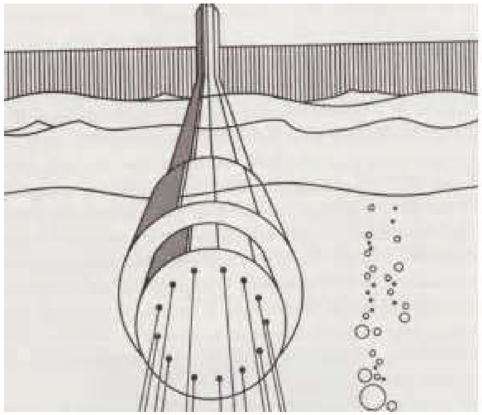
Issue resolved by FISIPE during precursor manufacture.

# FY13 Status - Accomplishments



## Previous Major Issue:

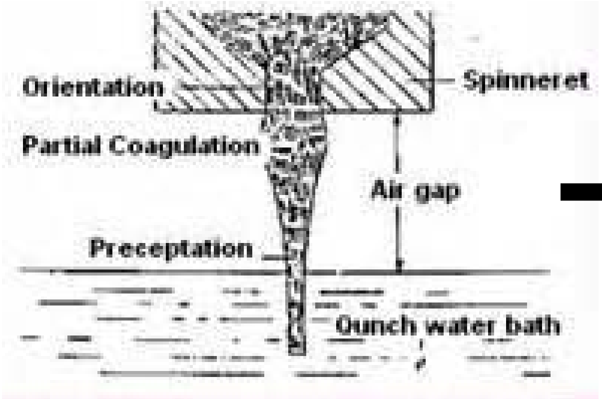
Fibers that are not round. Caused by textile solution spinning and resolved by Air Gap Spinning. Status: Getting better but not fully resolved.



Submersed Solution Spinning

“Kidney Shaped” Textile Fibers

Then




Air-Gap Solution Spinning

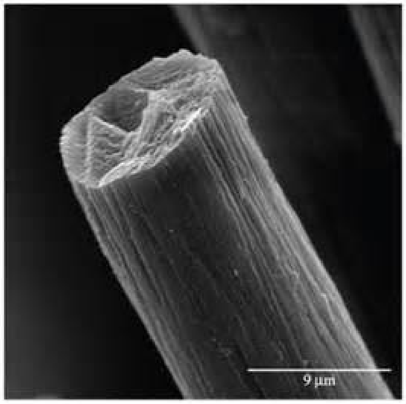



Figure 5. SEM micrograph of commercial oxidized Pan fiber (PANOX)

“Round” Fibers

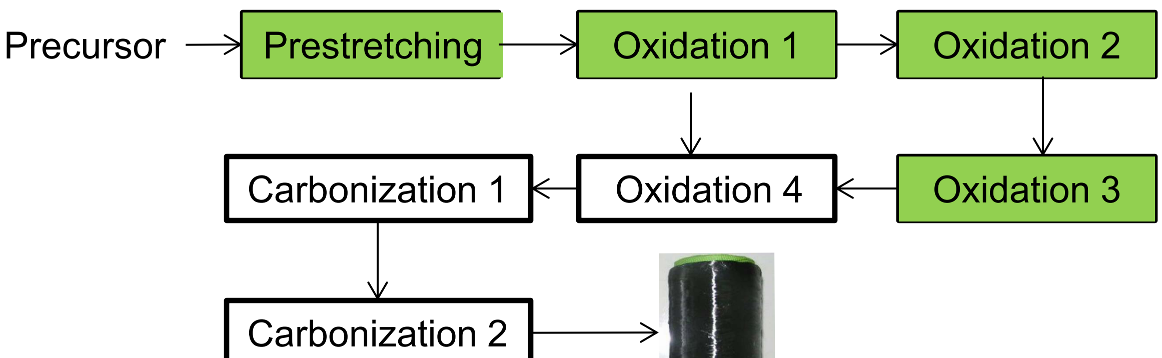
Now

# FY13 - Accomplishments



We were delayed about 4 months waiting on new material from FISIPE. This will delay the final milestone but at no additional program cost.

We have completed optimization of the first 2 oxidation zones and most of the way through the 3rd.




400-1800C; 8-14 min

# Proposed Future Work



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. Scale-up ability to make precursor to an industrial scale (not part of the current program.

# Summary



## Relevance

- Carbon fiber composites make up 60-80% of the hydrogen storage system and the cost of the fiber makes up the majority of that cost.

## Approach/Strategy

- Developing lower cost precursors, building off of previous project, to meet performance requirements while perserving high production rate cost benefits.

## Technical Accomplishments

- Chose 11 Formulations, down selected to 3 candidate fibers and then down selected to1 development system
- Achieved 392 KSI and 36 MSI prior to optimization.
- Almost ½ through optimization

## Collaboration and Coordination

- Building off Vehicle Technologies Work
- FISIPE (Precursor supplier) and SGL Carbon Fibers are partners

## Future Work

- Complete Optimization of current formulation.