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

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Status as of Middle March 2013

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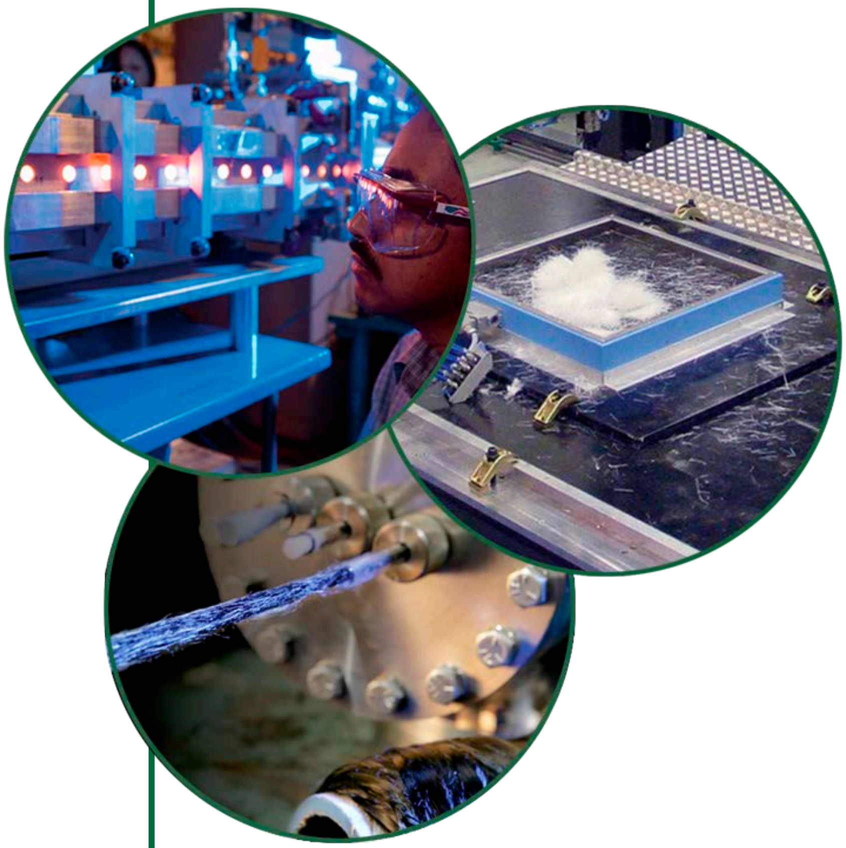

Project ID: ST099

U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY
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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

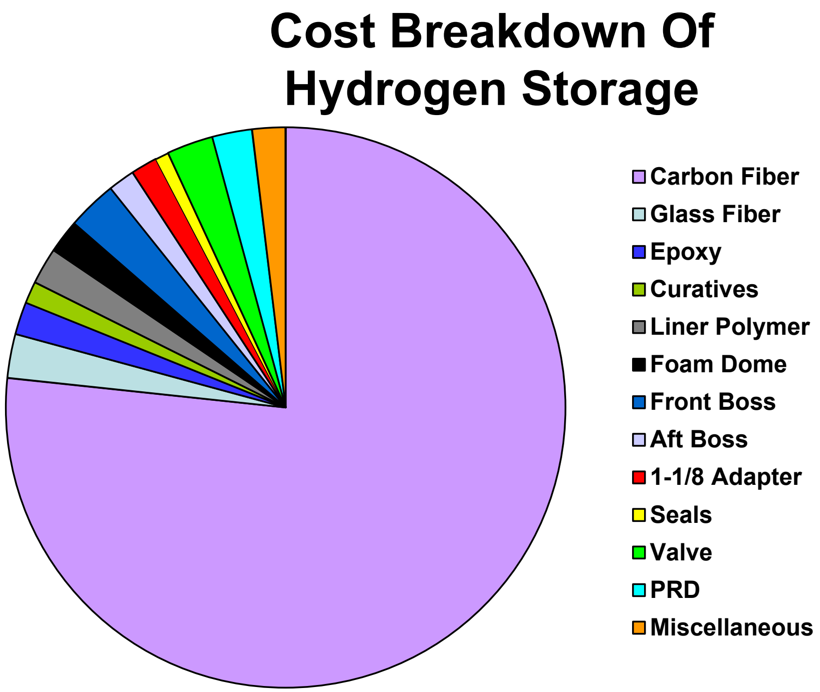
- Barriers addressed
  - High cost of carbon fiber
  - CF accounts for more than 65% of the cost of the high pressure storage tanks.
  - Inadequate supply base for low cost carbon fibers

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

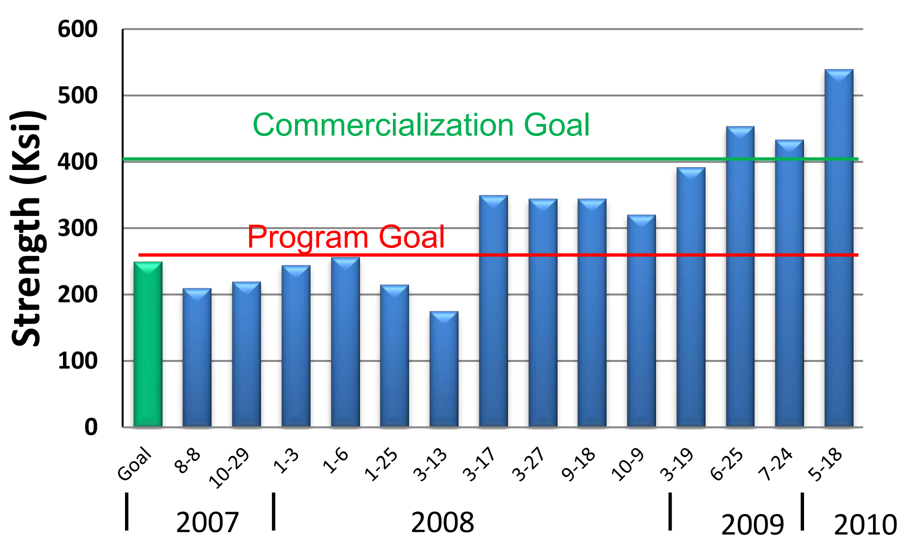
Relevance – Project History

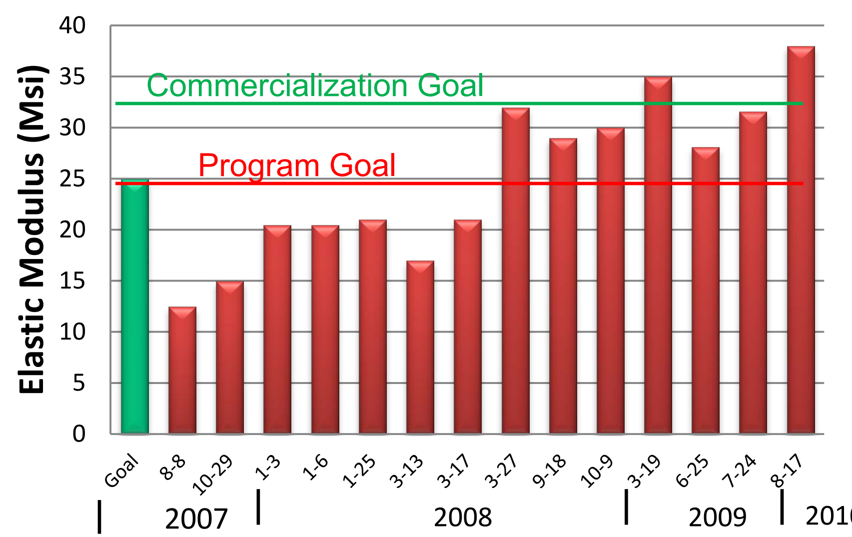
Project built off 2 previous projects funded by Vehicle Technologies.

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:

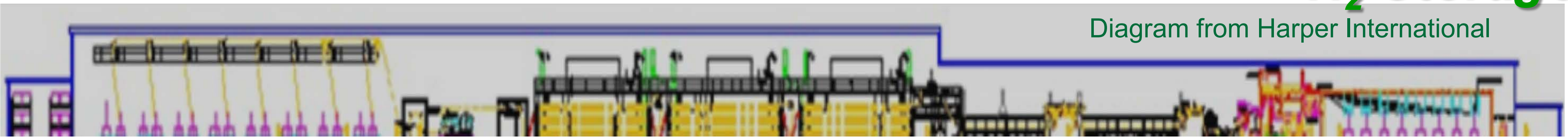
540 KSI and 38 MSI

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	

Above Estimate is for Industrial Grade Fiber

- 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.

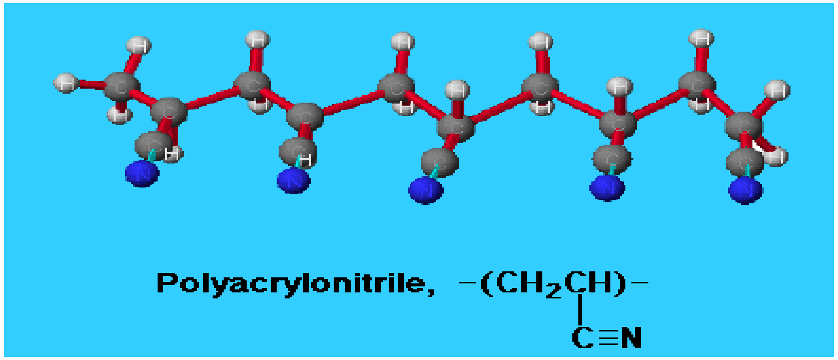
Approach - Milestones

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 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.

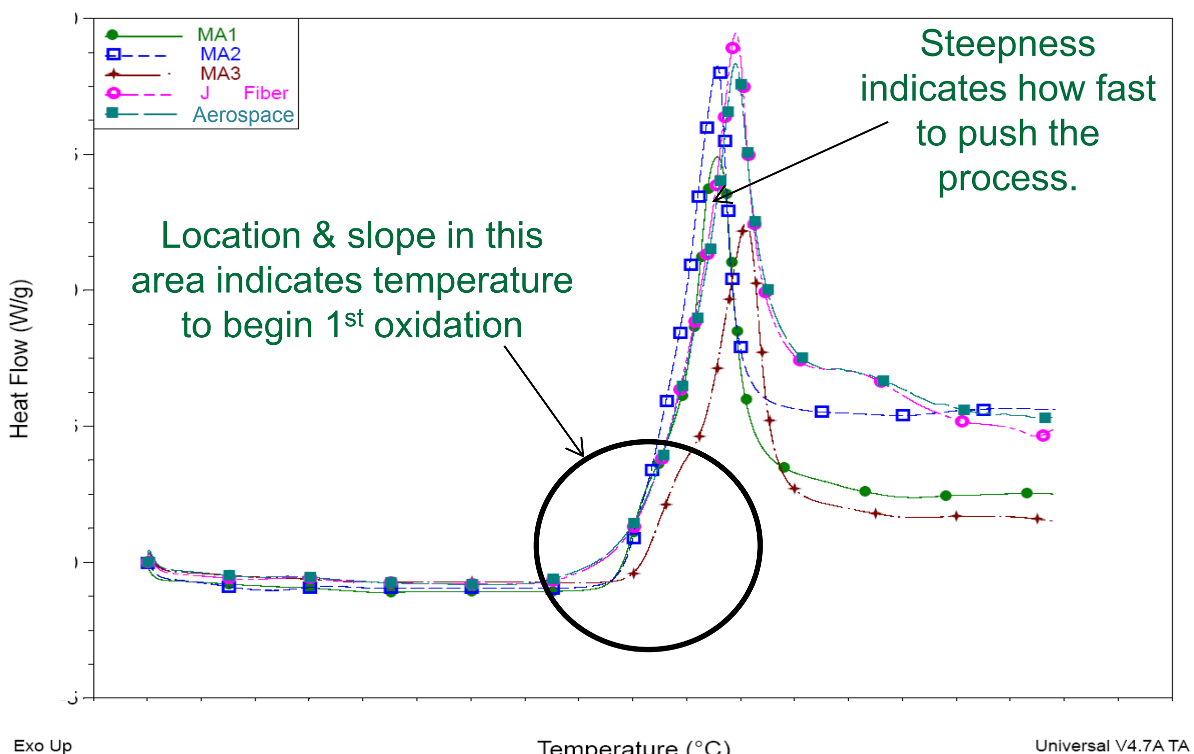
11 polymer compositions sent to ORNL for screening.

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.

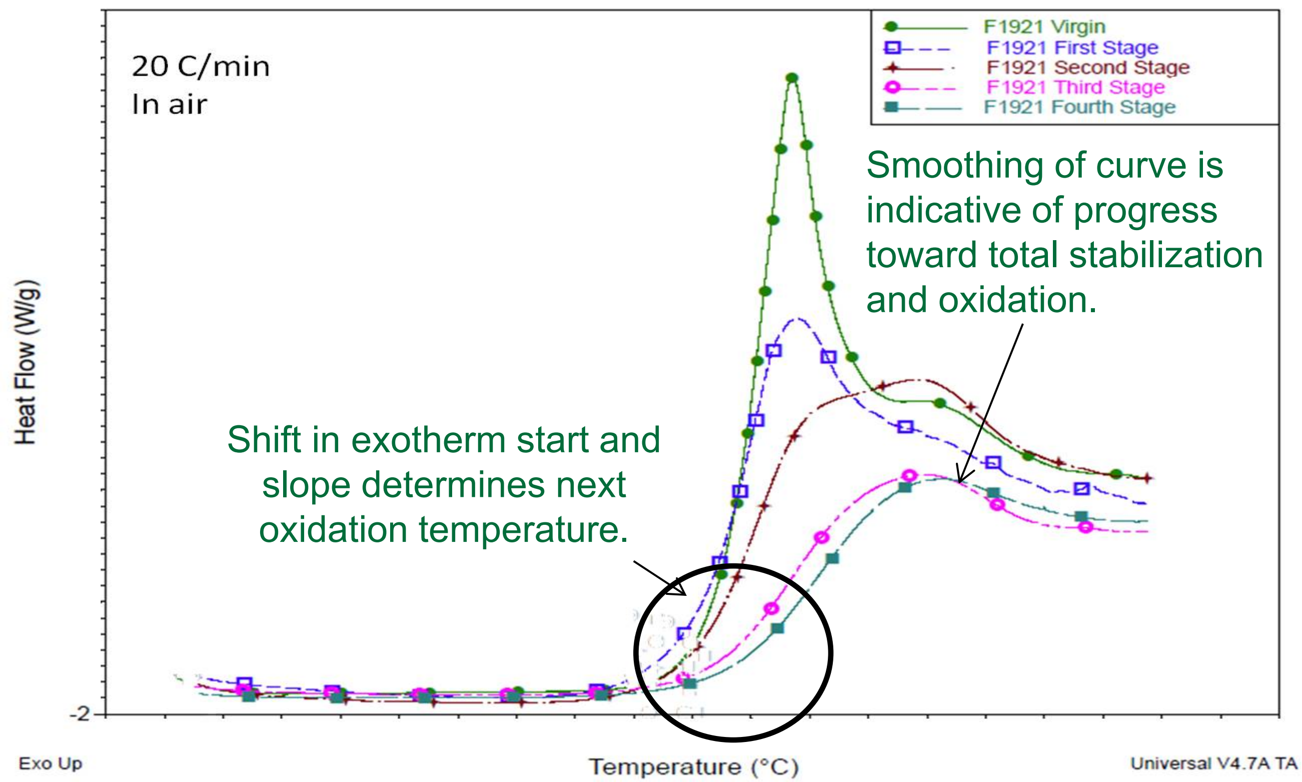
FY12 Status

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.



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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

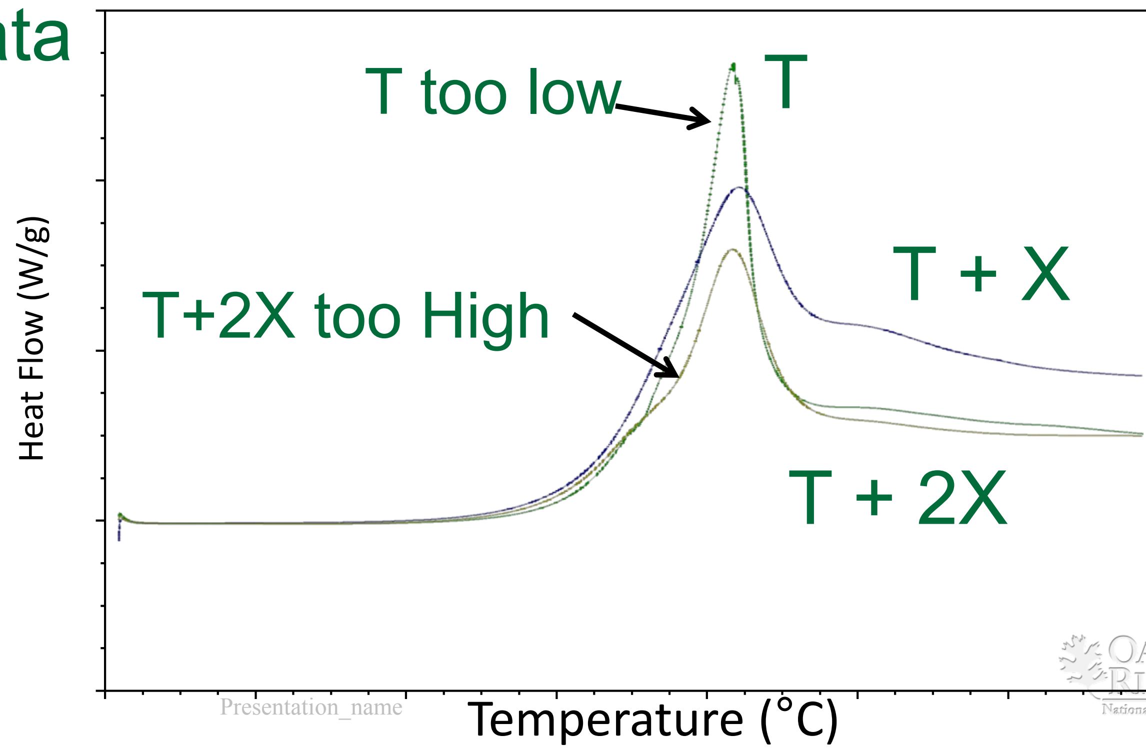
	Oxidation 1	Oxidation 2	Oxidation 3	Oxidation 4
Profile 1	T	T + Y	T + 2Y	T + 3Y
Profile 2	T + X	(T + X) + Y	(T + X) + 2Y	(T + X) + 3Y
Profile 3	T + 2X	(T + 2X) + Y	(T + 2X) + 2Y	(T + 2X) + 3Y

Graphical Comparisons of data in Columns

Graphical Comparisons of data in Columns

Other Important Data

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



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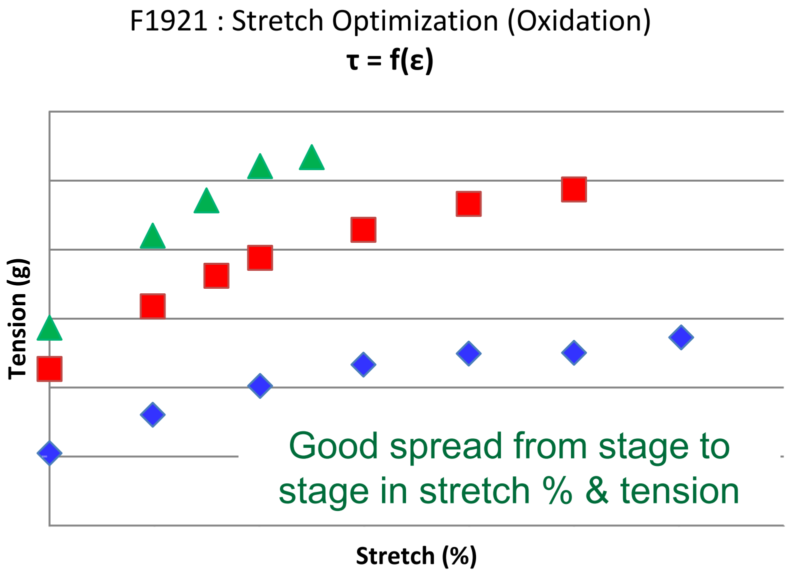
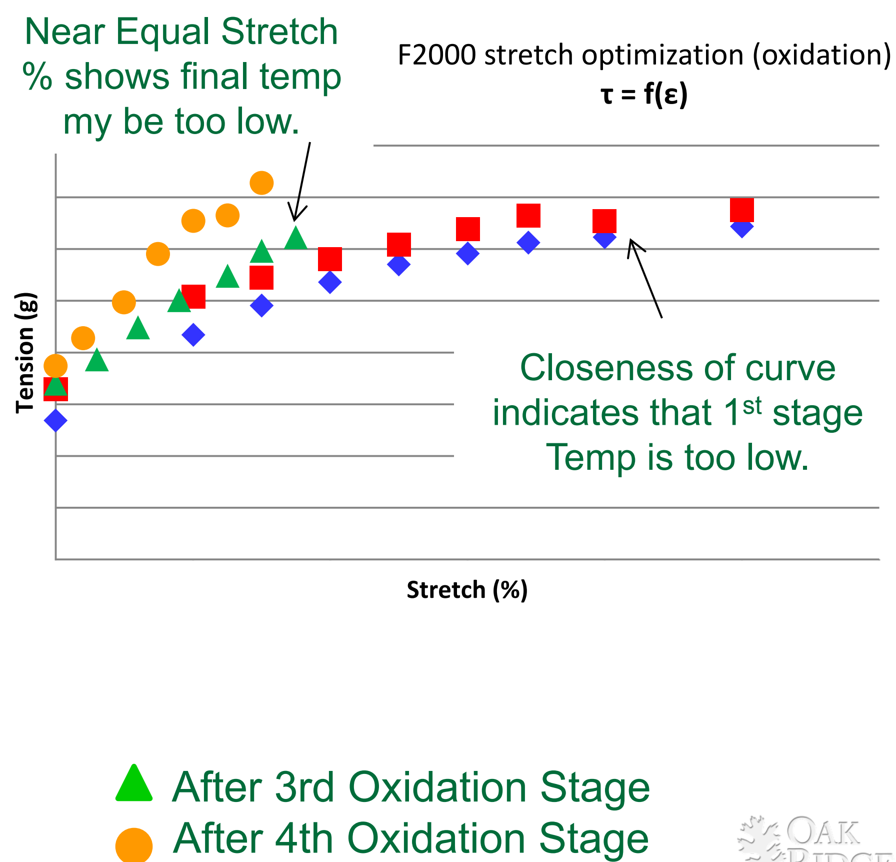
FY13 Status

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.





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FY13 Status – Accomplishments

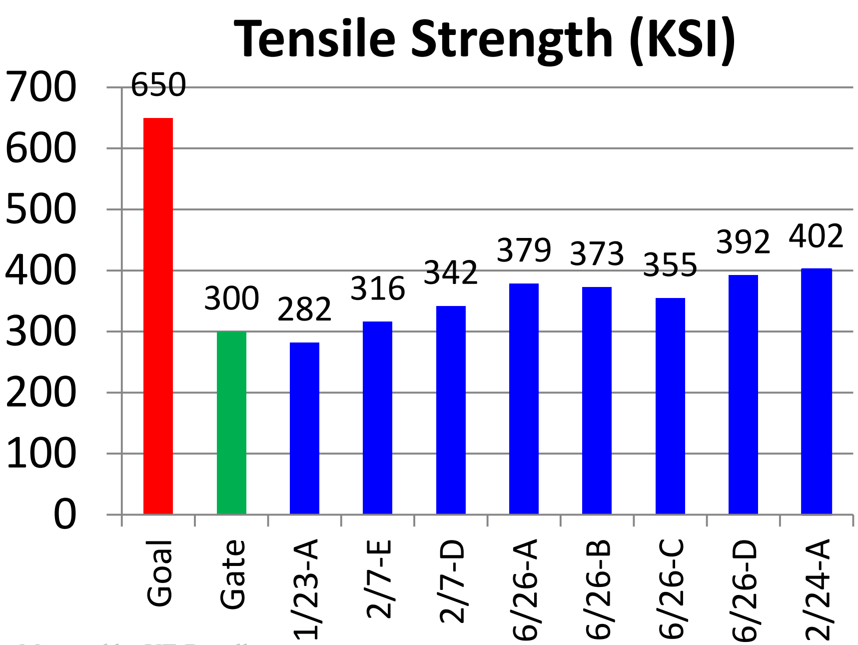
Precursor → Prestretching → Oxidation 1 → Oxidation 2 → Oxidation 3 → Oxidation 4 → Carbonization 1 → Carbonization 2

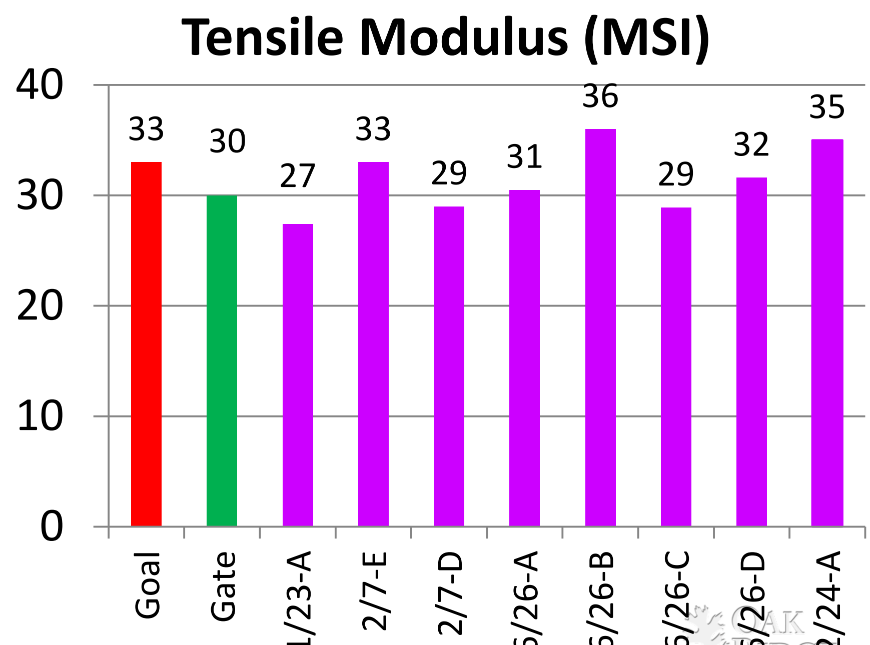
200-300C
80-120 min

400-1800C; 8-14 min

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





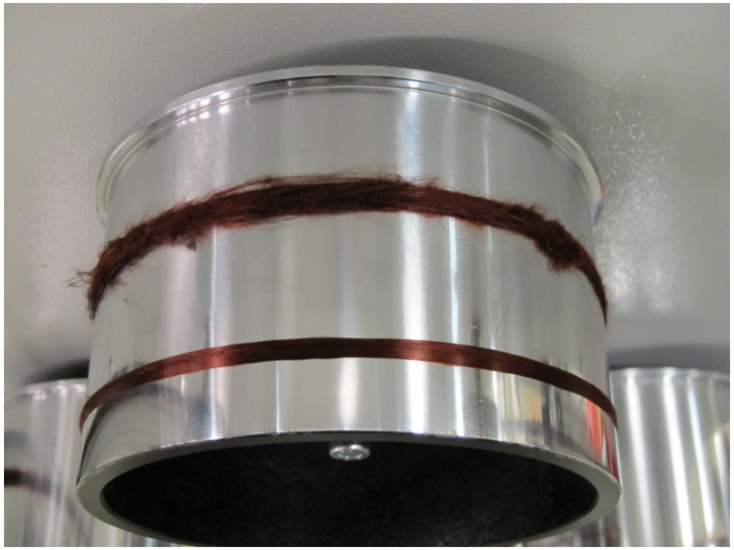
Each data Point Average of 18 tests.

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".

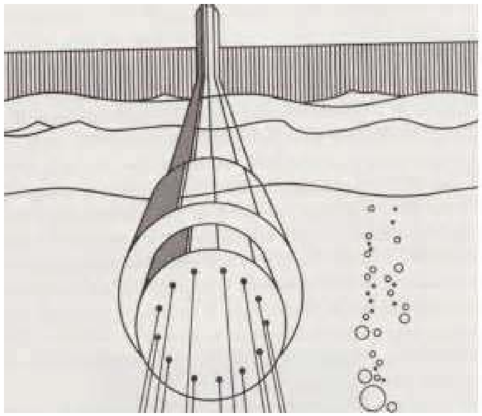
Reduced ability to achieve molecular alignment and optimize fiber properties.

Issue resolved by FISIPE during precursor manufacture.

FY13 Status - Accomplishments

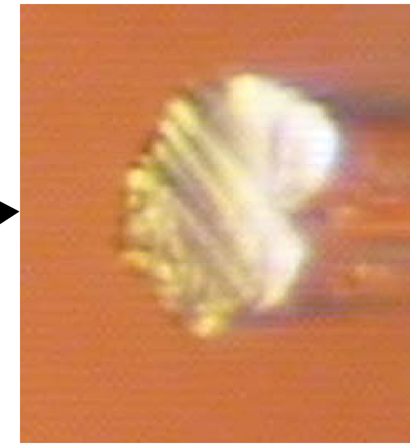
Previous Major Issue:

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

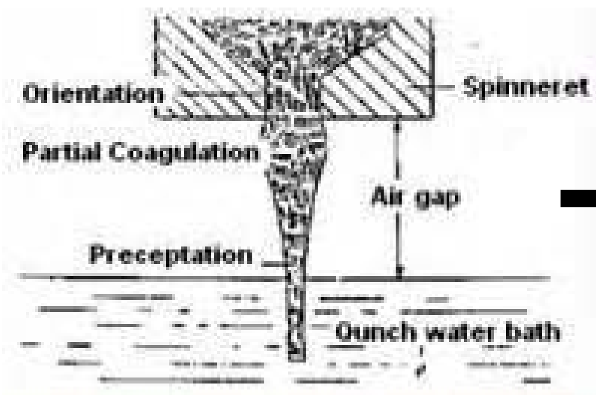


Submersed Solution Spinning

"Kidney Shaped" Textile Fibers



Then



Air-Gap Solution Spinning

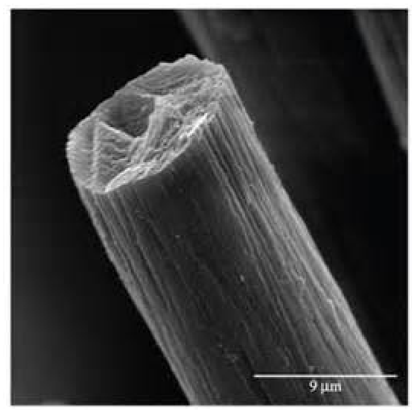
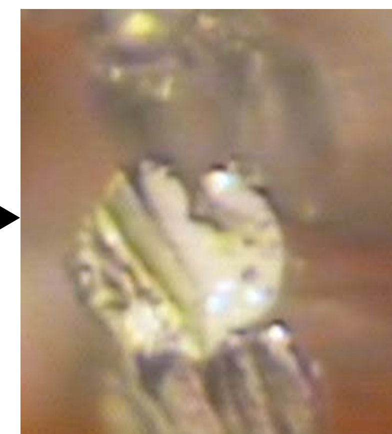


Figure 5. SEM micrograph of commercial oxidized Pan fiber (PANOX)

"Round" Fibers

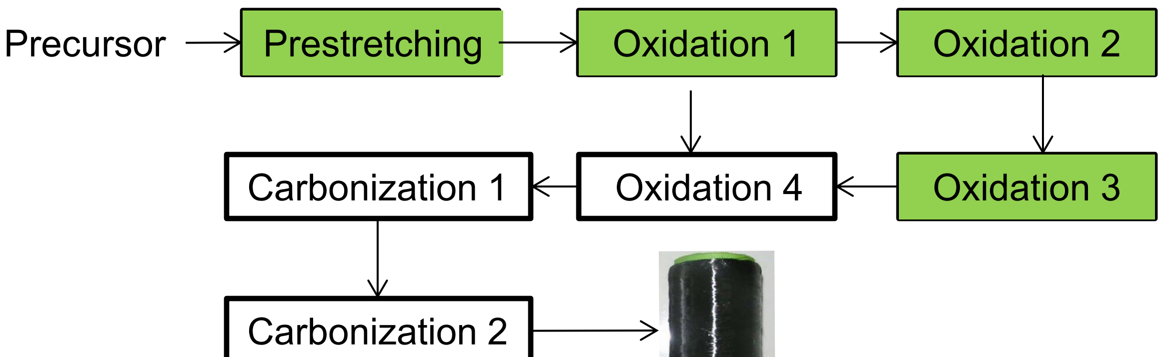


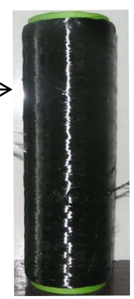
Now

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.