Lower Cost Carbon Fiber Precursors

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U.S. DEPARTMENT OF ENERGY

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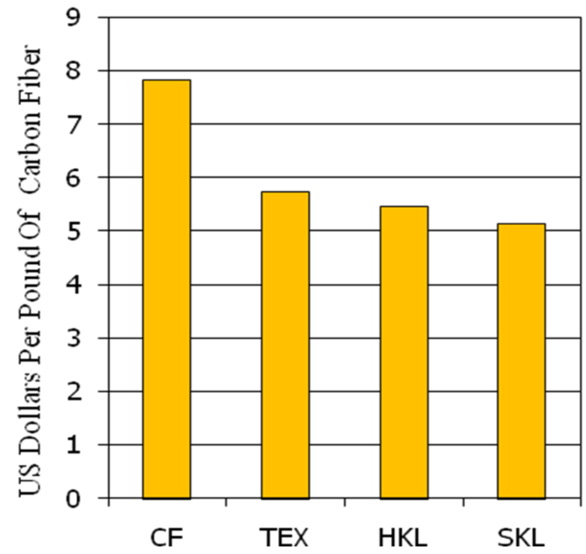
Carbon Fiber Costs (2. Precursors)

More Affordable Precursors are Needed

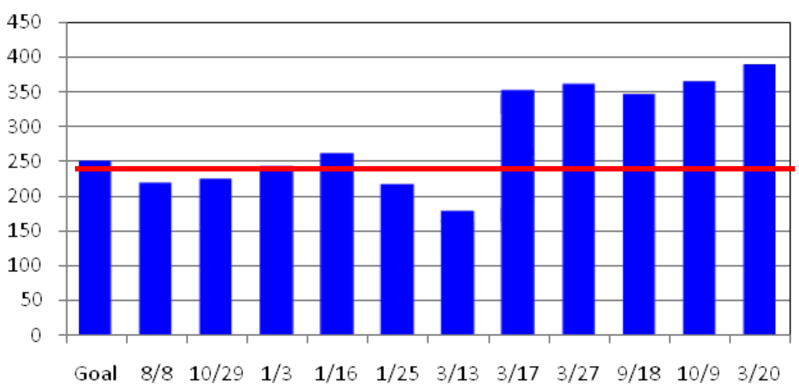
Alternative Precursors and Conventional Processing



<u>3 Current Precursor Options</u>

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

Carbonized Textile Precursor



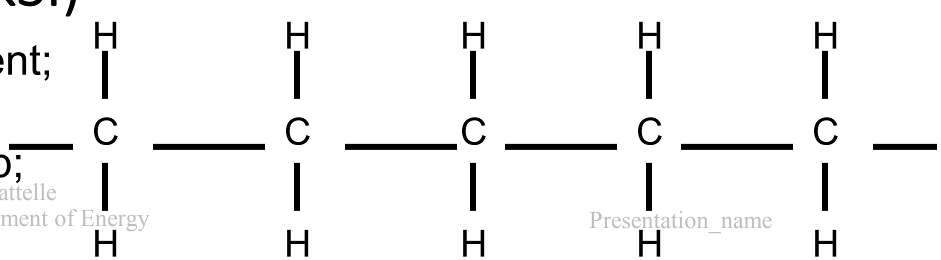
Tensile Strength (KSI)

Current Carbonized <u>Textile Properties:</u>
Strength: 400 KSI
Modulus: 35 MSI

Processed Precursor Fibers from a Hardwood/Softwood Lignin Blend.

PE:

86% C Content;
65-75% Yield
$0.50-$0.75/lb;
Melt Spun



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:

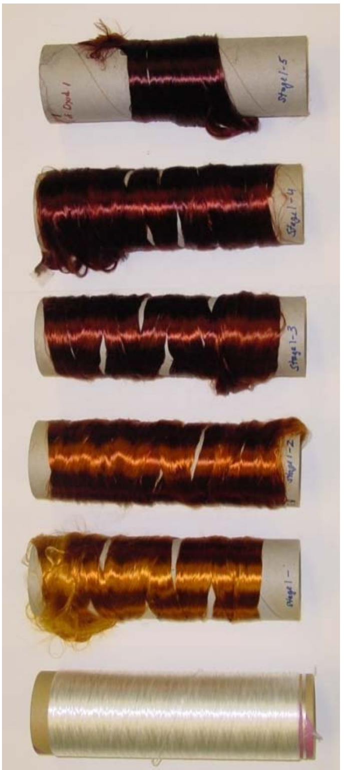
1. Complete previous effort by scaling to the CF production line.
2. Assist CF converters with processing protocol.
3. Optimize processing protocol for improved properties.
4. Incorporate modification in CF demonstration line.

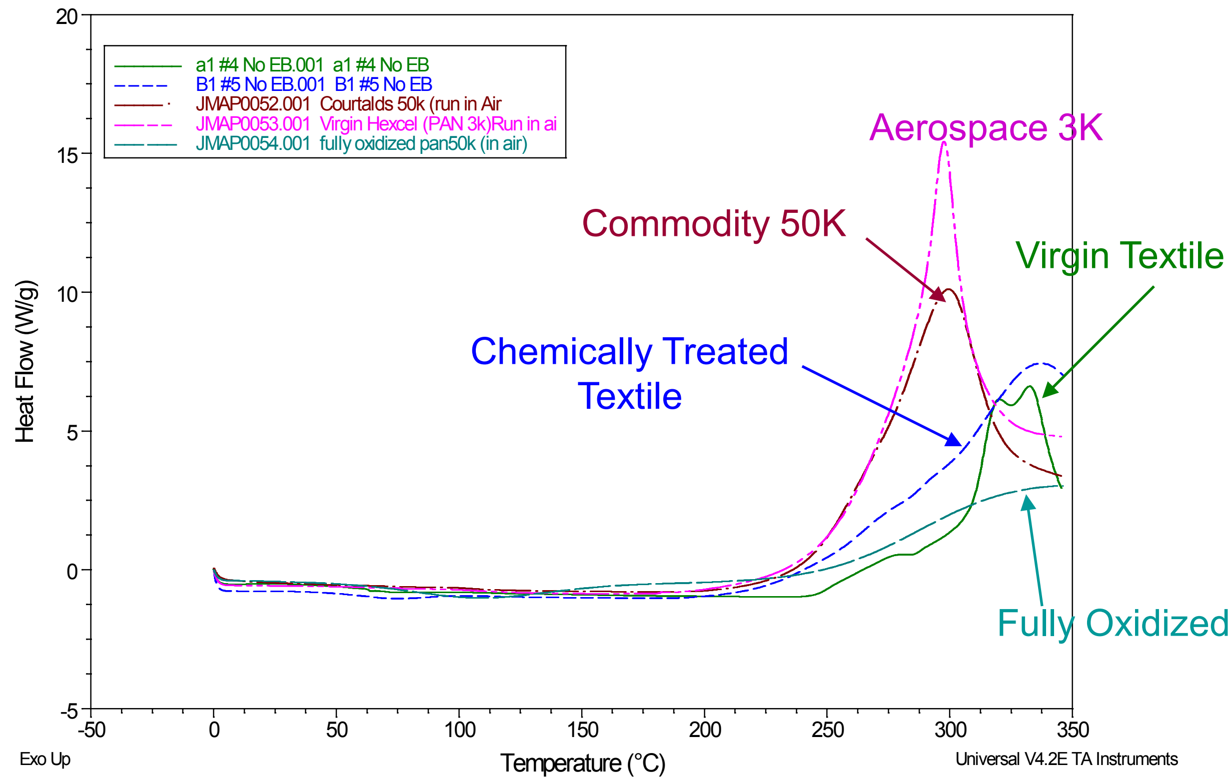
Budget: $ 150K

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.

Accomplishments - Textile Precursors

FISIPE

Conversion research at ORNL

Precursor → Stabilization Oxidation → Low Temperature Carbonization → High Temperature Carbonization

Began: January 2007   Partner: FISIPE (PT)

FISIPE uses a VA co-monomer

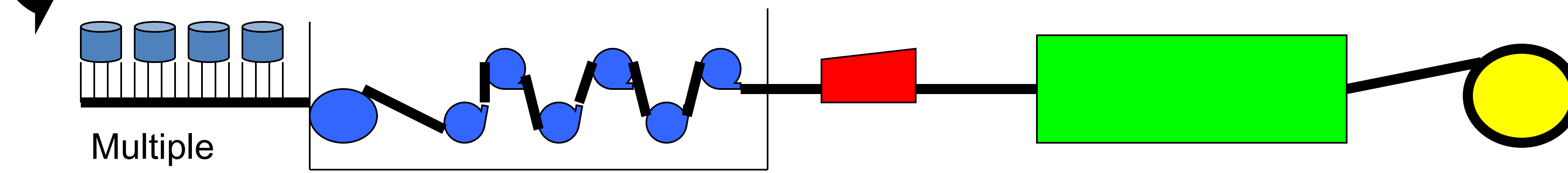
Guided FISIPE choosing a polymer composition and in installing the chemical bath which installed in their pilot line facility and also in optimizing the chemical pretreatment.

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.

Textile Precursors

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



Multiple Spinnerettes

Solvent Extraction, Washing and Tensioning

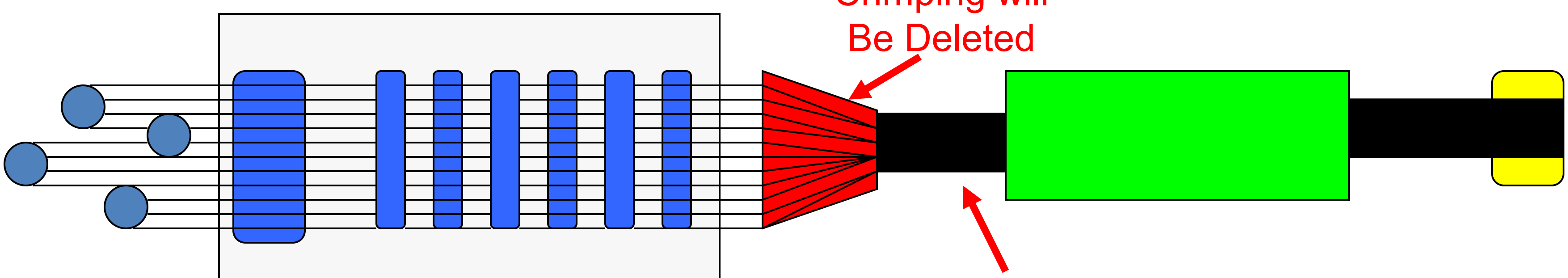
Crimping

Drying with Tension

Spooling or Bailing in Bulk

Slightly Modified versions of polymer selected

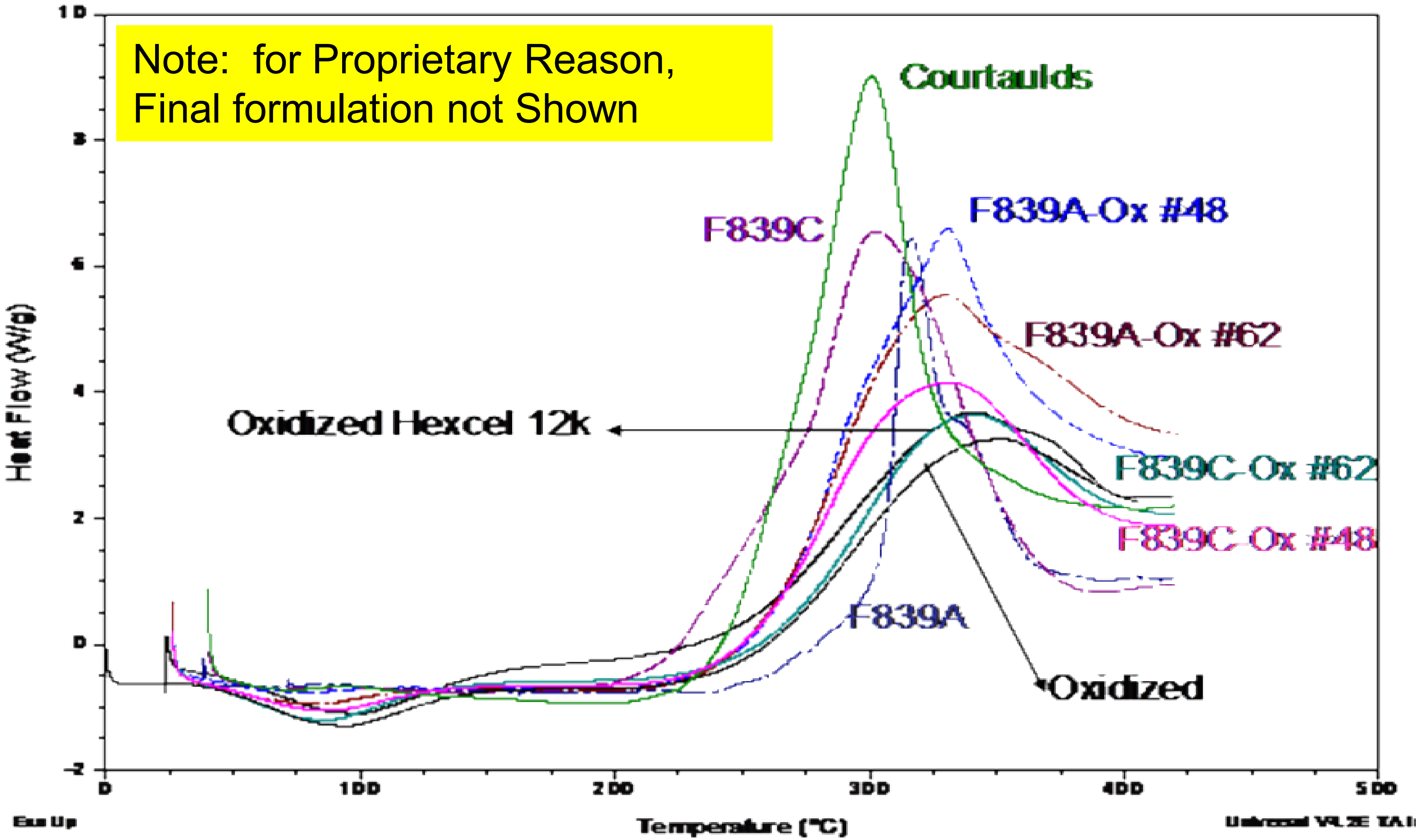
Gathering during Crimping will Be Deleted



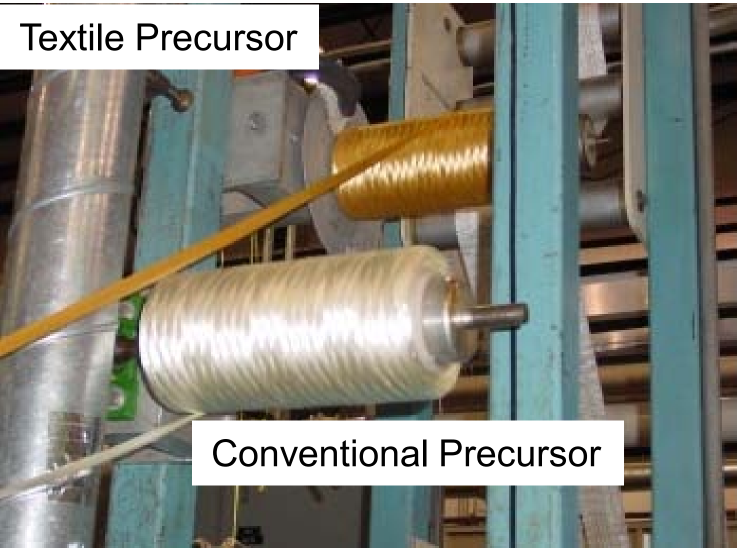
Chemical Pretreatment

Textile Precursors

1st Potential textile formulations were evaluated:

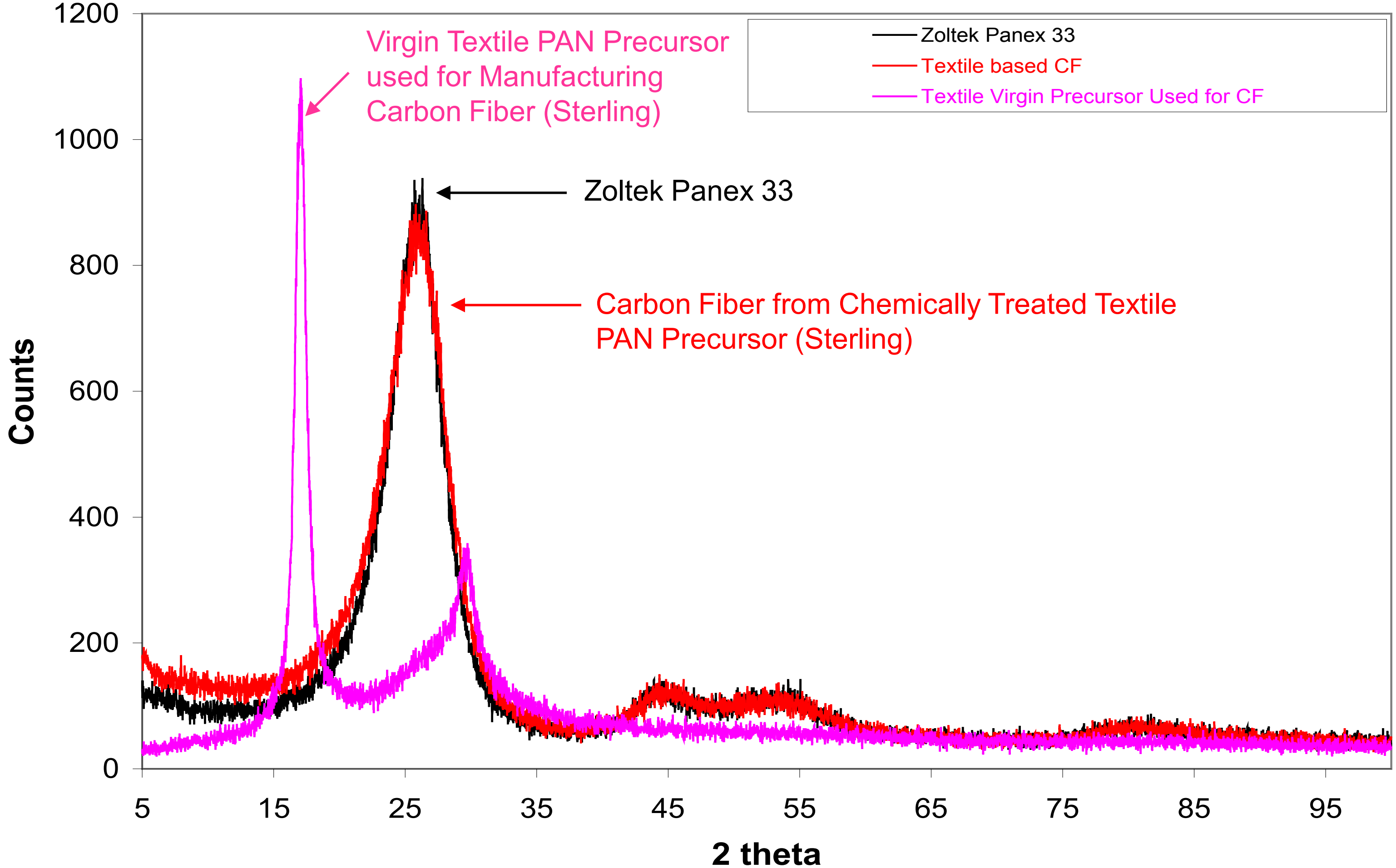


Textile Precursors



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

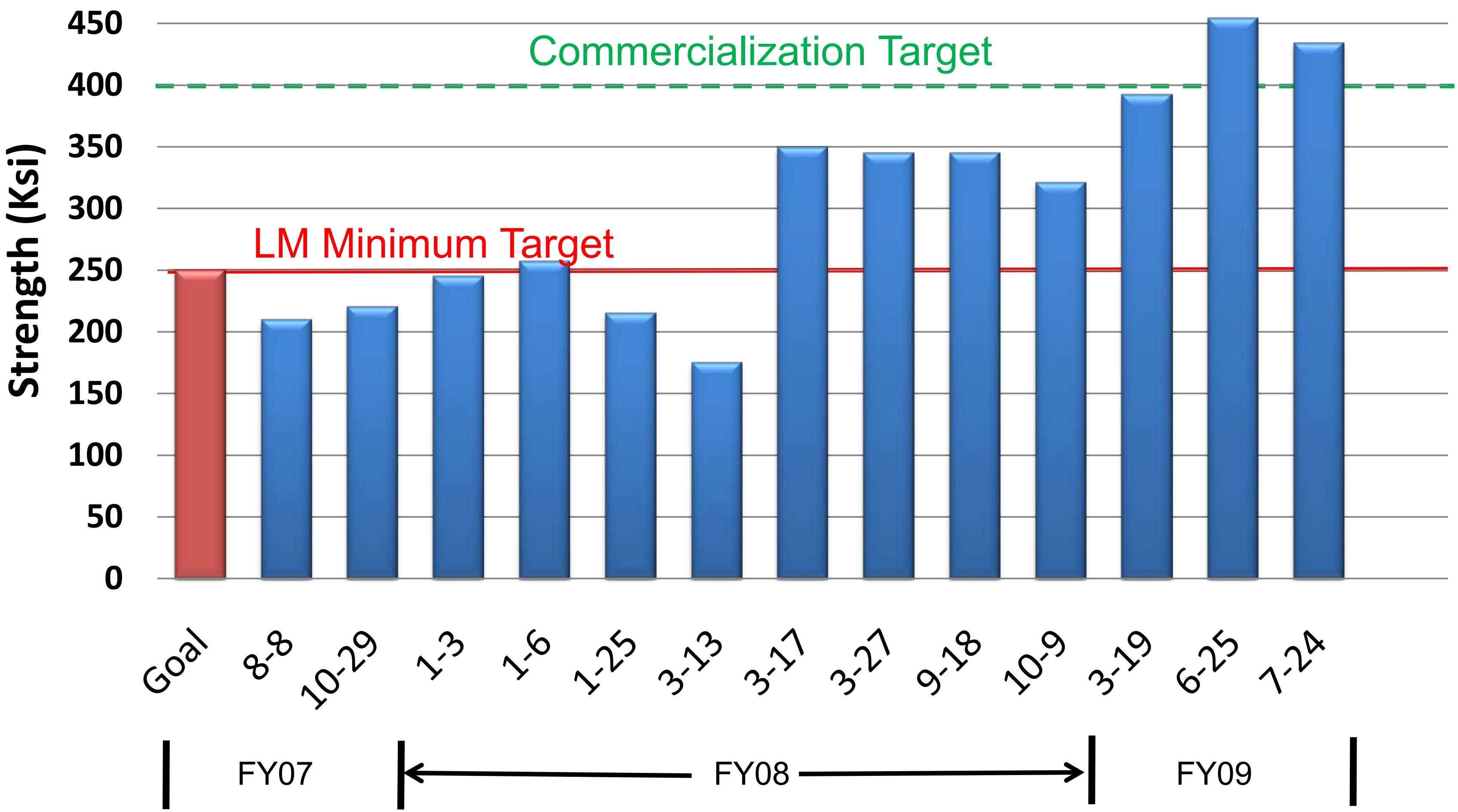
Wide Angle XRD Profiles: Comparison Between Commercial Panex 33 and Textile Grade Carbon Fiber



Mechanical Properties – Strength

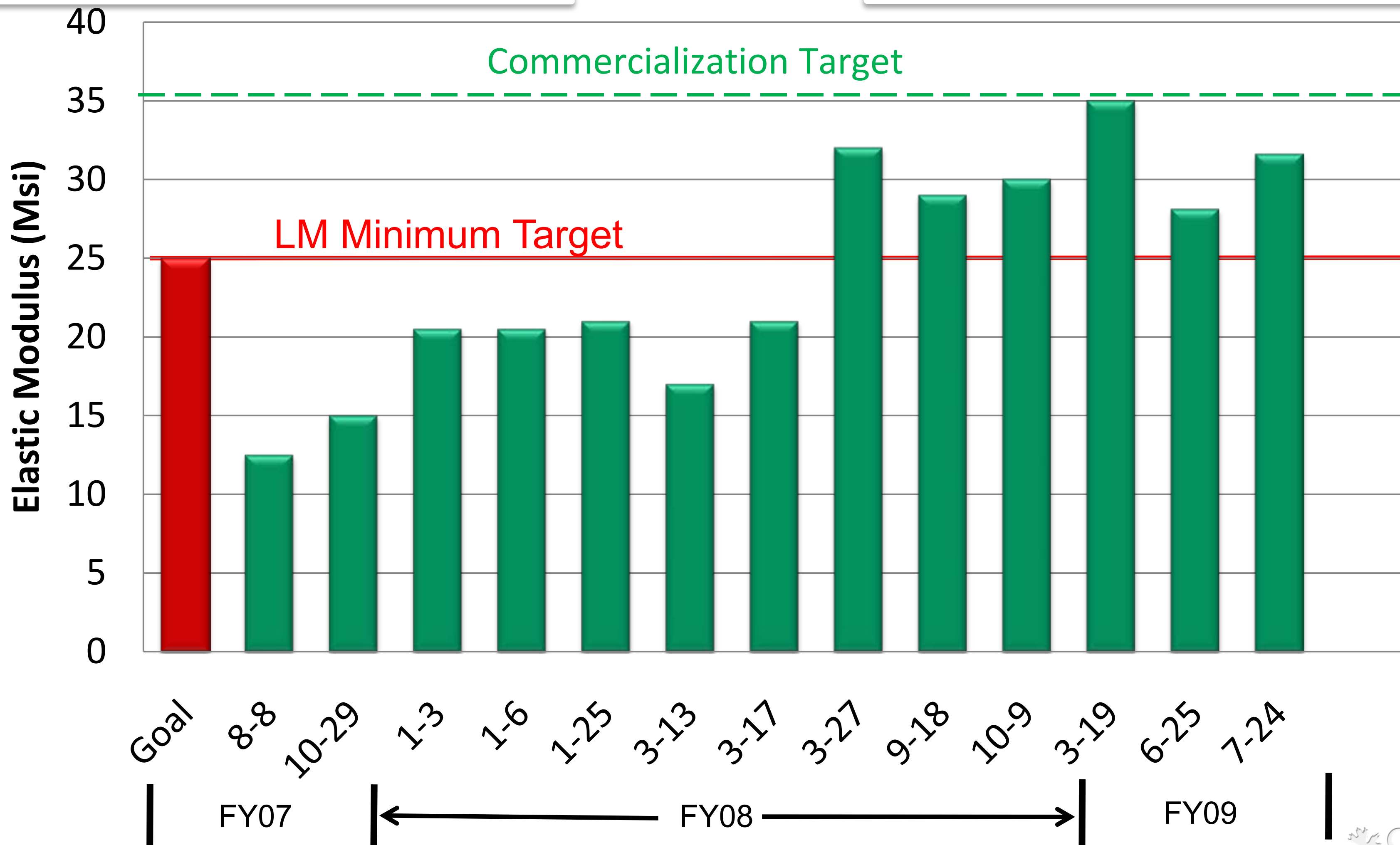
Target Properties:
Strength: 1.72 GPA (250 KSI)

Current Properties:
Strength: 3.13 GPA (454 KSI)



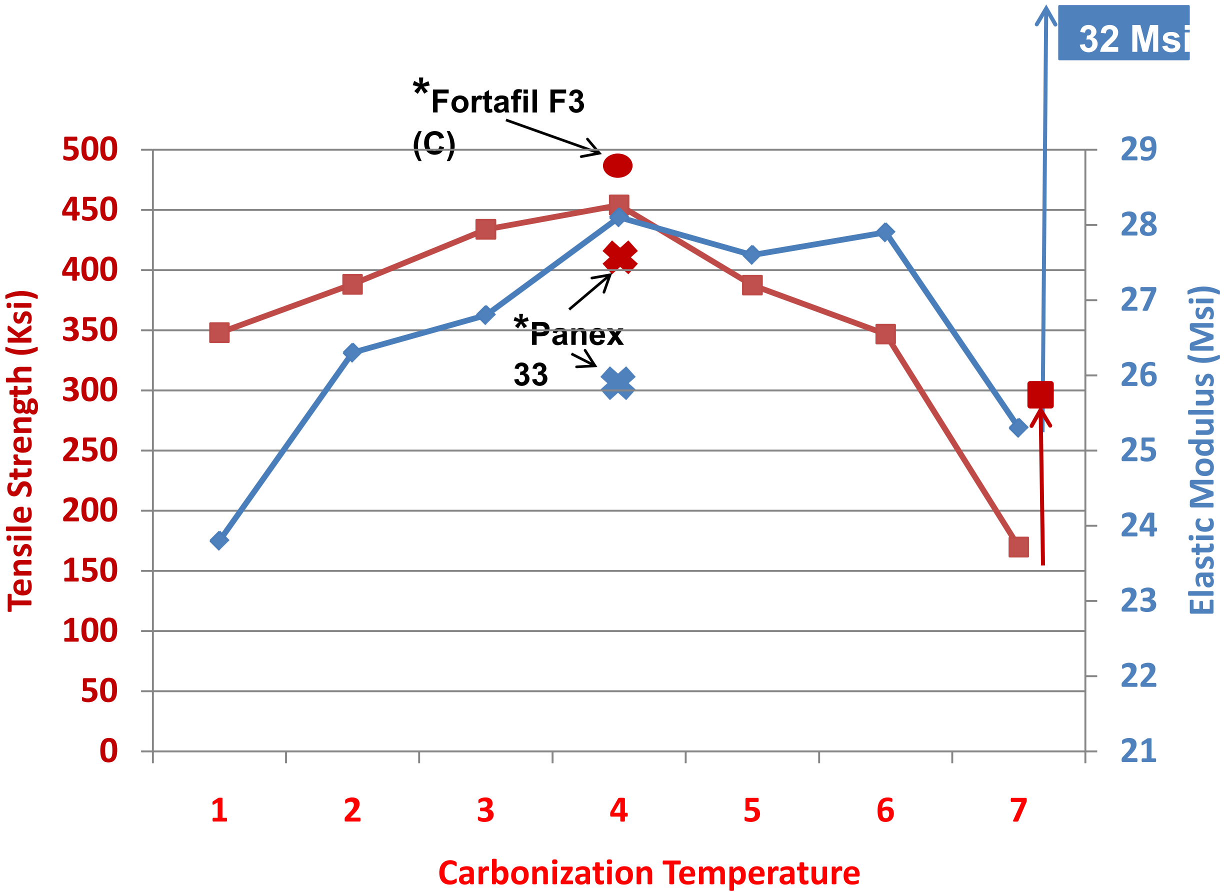
Mechanical Properties – Modulus

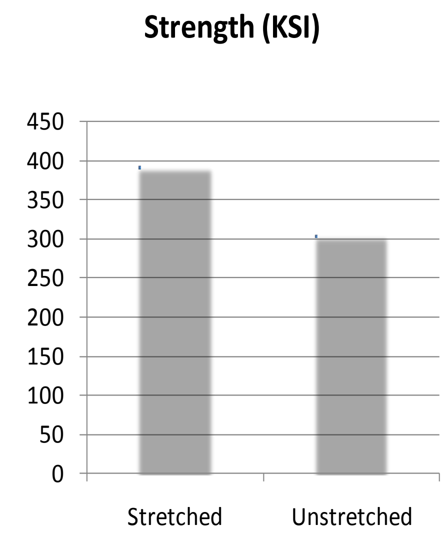
Target Properties:	Current Properties:
Modulus: 172 GPA (25 MSI)	Modulus: 220 GPA (~32 MSI)

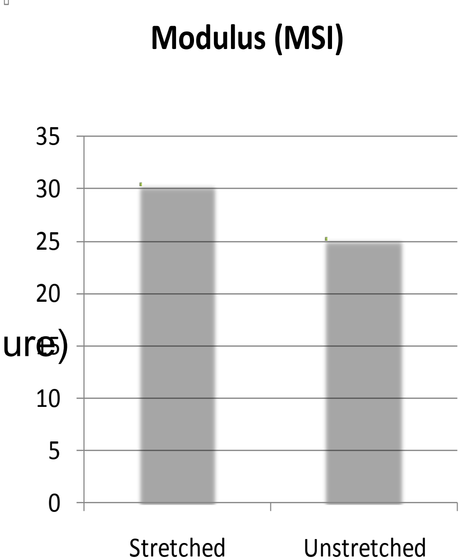


Strength/Modulus vs. Temp – Textile Precursor

Materials



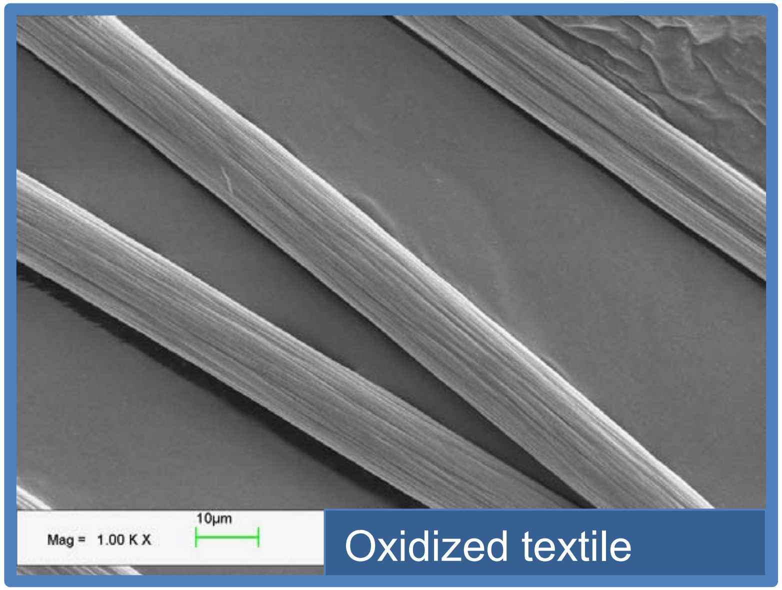


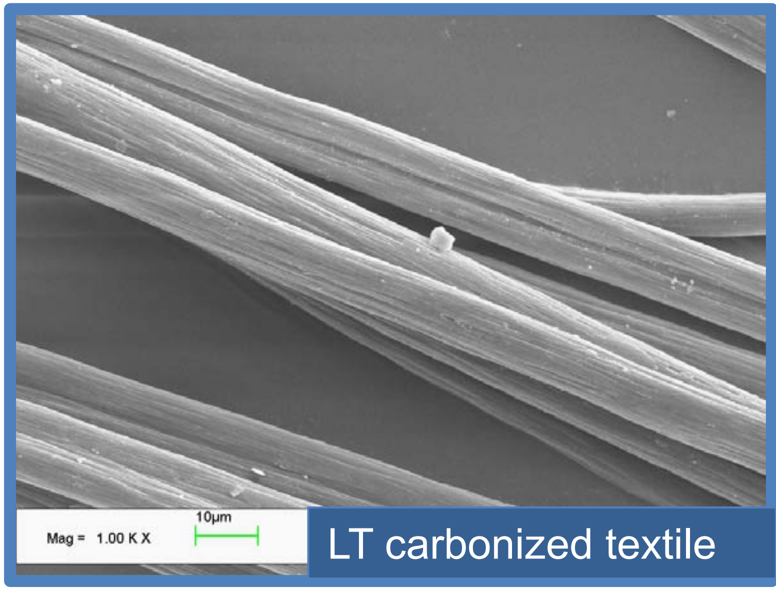


Based on broom straw test method measured in our labs (Not from Co. brochure)

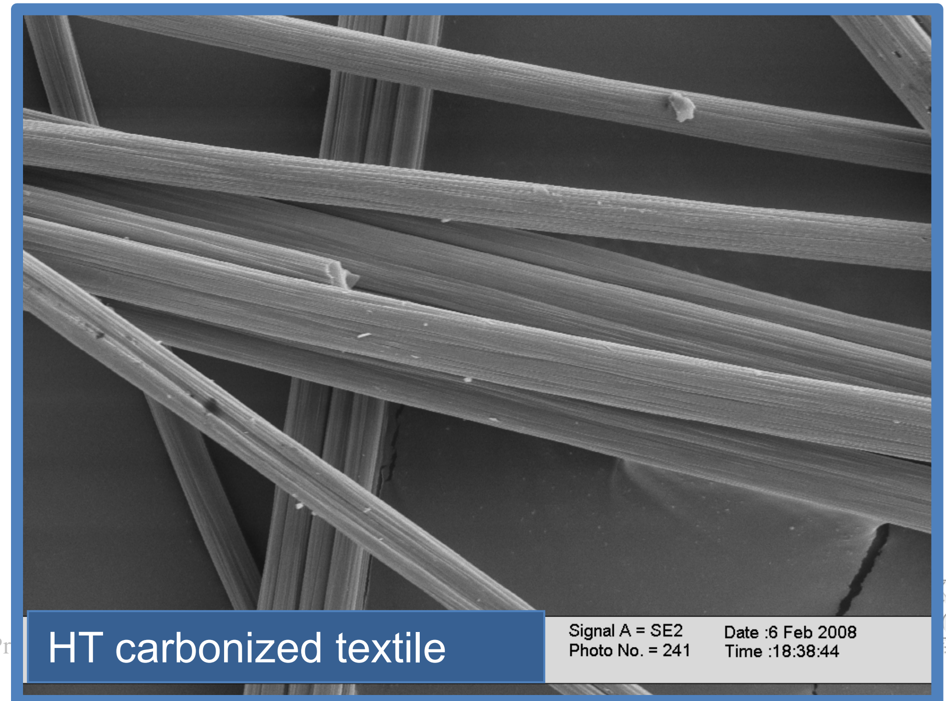
Final Properties Depend upon:
Time – Temperature - Tension

Scanning Electron Micrographs





This Year the ability to spin circular fibers was achieved.



Textile Precursors – What is Happening and Left Undone

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

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.

Publications

Papers:

1. **“**FreedomCAR and Low Cost Carbon Fiber for Automotive Applications,” Low Carbon Generation, 3M innovation Centre, London, UK , 9 February 2008.

2. “The Development of Lower Cost Carbon Fiber Technologies for Automotive Applications”, Proceedings of The Global Outlook for Carbon Fiber 2007, San Diego, CA, 23-25 October 2007.

3. “A Comprehensive Research Program to Develop Commodity Grade, Lower Cost Carbon Fiber”, To be published in the proceeding of the ACMA Breaking New Ground: Structural Composites Applications in Defense, Infrastructure, Transportation and Corrosion-Prevention, University of Alabama-Birmingham, 4-6 March 2008.

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.

5. “Future Lower Cost Carbon Fiber for Autos: International Scale-up & What is Needed”; Proceedings of the 2008 SPE Composites Conference; September 16, 2008; Detroit, MI.

6. “Investment in the Carbon Fibre Business for Commercial Grade Low Cost Composites”; Proceedings of the Carbon Fibre 2008 Conference; September 30 – October 2, 2008; Hamburg, Germany.

7. “Development of Lower Cost Carbon Fiber for High Volume Applications”; Proceedings of the Composites + Polycon 2009 Conference; January 15-17, 2009; Tampa, FL.

8. “Novel Precursor Materials and Approaches for Producing Lower Cost Carbon Fiber for High Volume Industries”, To be presented at and published in the proceedings of 17th International Committee on Composite Materials ICCM-17, July 27-31, 2009, Edinburgh, Scotland, UK.

Polyolefin Precursors – Purpose, Barrier, Approach

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/functionalize 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 Precursors

Polyolefin-based carbon fibers offer:

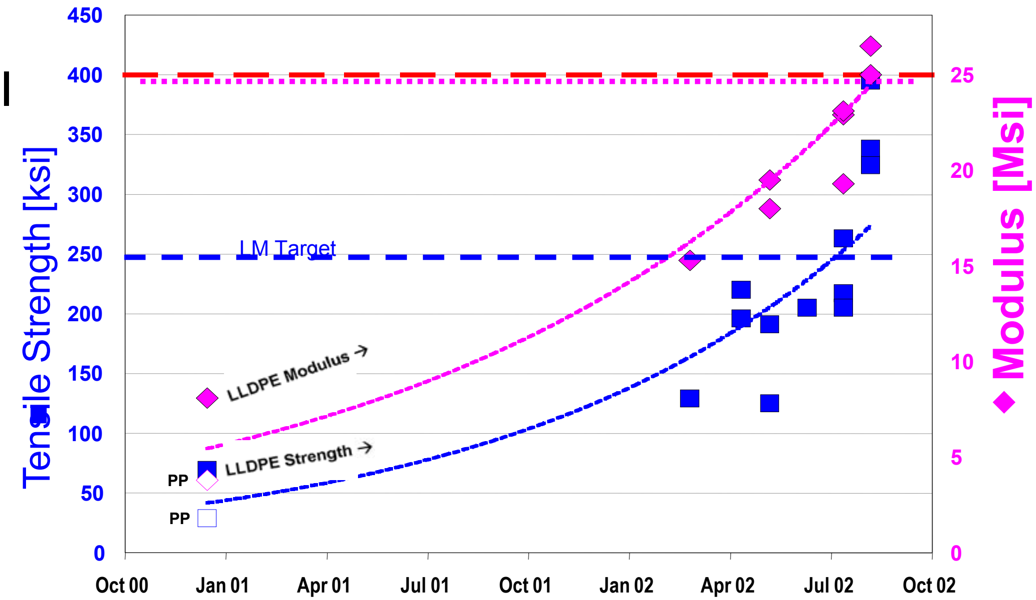
- Significant cost benefit through
  - High carbon yield
  - Low raw material cost
  - Possibility of using recycled raw materials
  - Ease of precursor fiber handling and processibility
- Performance/property benefits
  - Potentially higher properties than those are achievable with other LCCF precursor 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.

Polyolefin Precursors

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

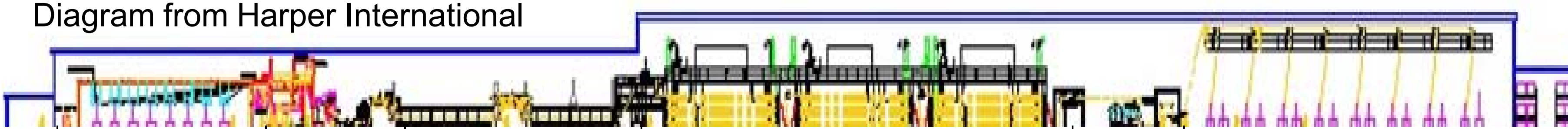


Dr. Naskar has developed a 1 hour sulfonation process that is:

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

Diagram from Harper International



Spooling & Packaging	Surface Treatment	Carbonization/ Graphitization	Stabilization & Oxidation		Precursors
$0.61	$0.37	$2.32	$1.54	Baseline Today - $9.88	$5.04
$0.41	$0.33	$1.48	$0.99	High Volume - $7.85	$4.64

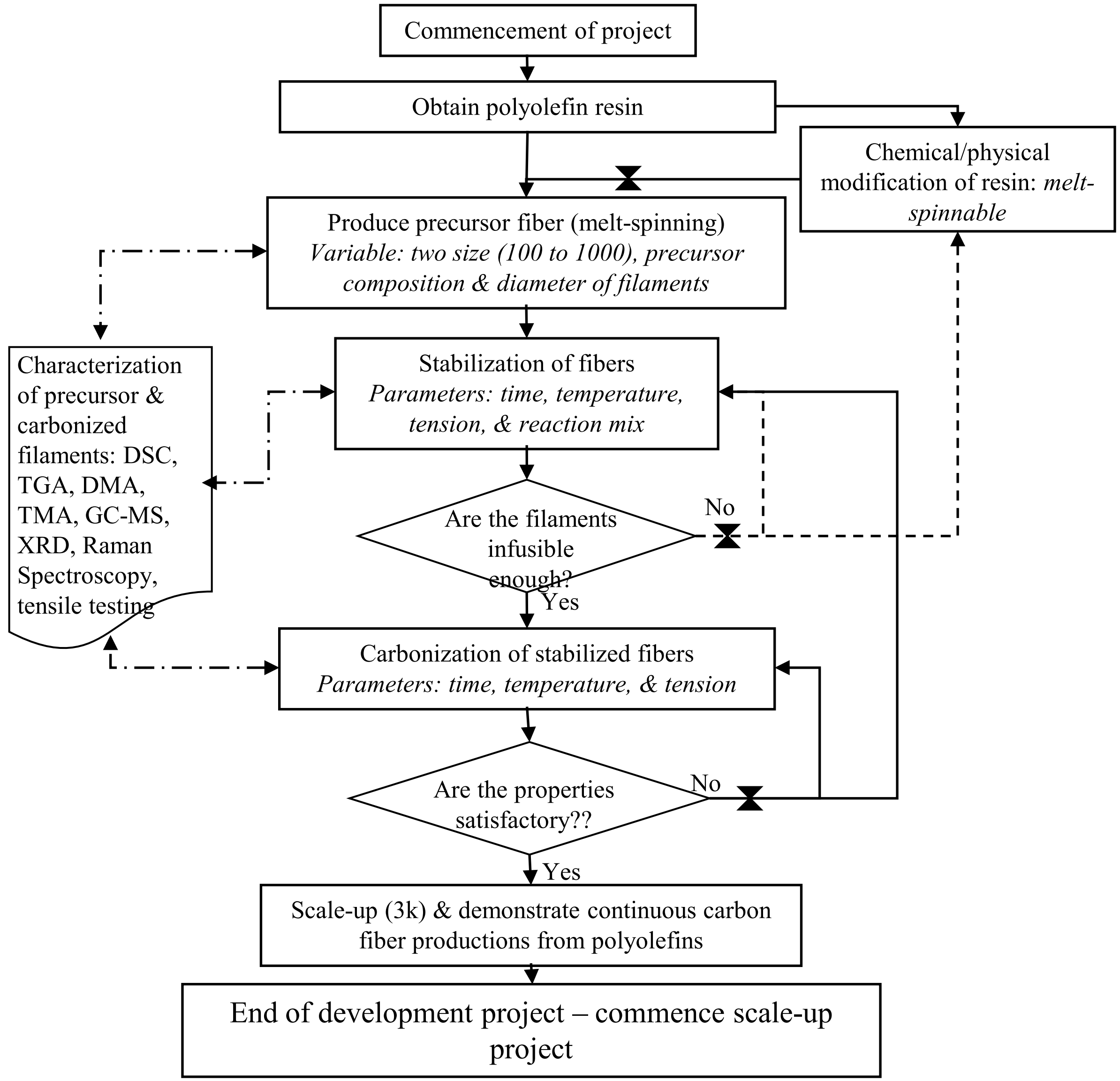
Precursor type	Yield (%)		$/lb (as-spun)	Melt-spinnable	Best achieved properties		Problem
	Theoretical	Practical			Strength (KSI)	Modulus (MSI)	
Conventional PAN	**68**	**45-50**	**>4**	**No**	**500-900**	**30-65**	**High cost**
Textile PAN*	**~ 68**	**45-50**	**1-3**	**No**	**300-400+**	**30**	**High variation in properties**
Lignin*	**62-67**	**40-50**	**0.40 - 0.70**	**Yes**	**160**	**15**	**Fiber handling, low strength & slow stabilization step**
Polyolefin**	**86**	**65-80**	**0.35 - 0.5**	**Yes**	**380**	**30**	**Slow stabilization (sulfonation) step**

* Ongoing work
** Hexcel work (2004)

↑ High ↑ Yield — ↑ Inexpensive — ↑ ↑ Properties Proven At Small Scale — ↑ Obstacle Addressed

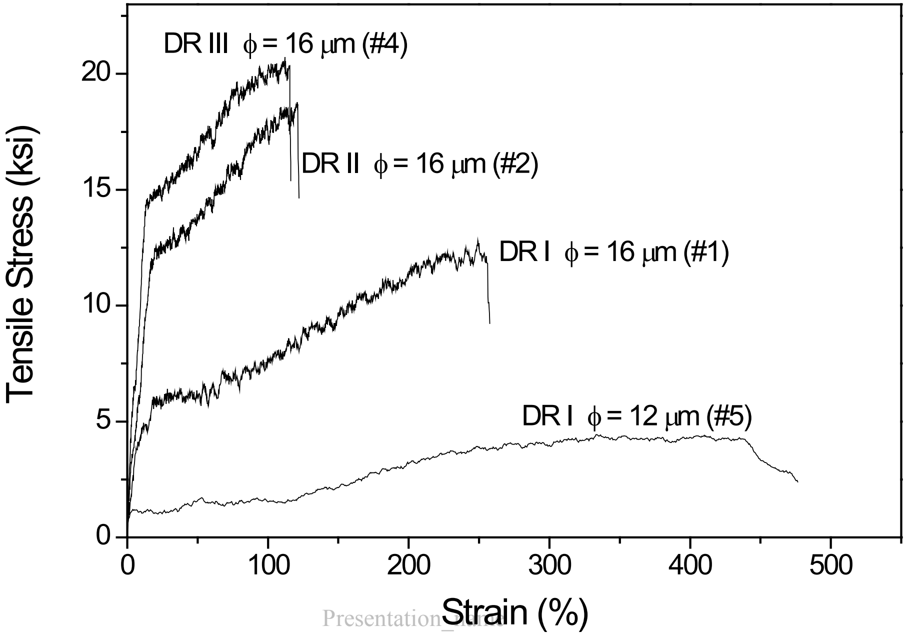
Eliminating Oxidative Stabilization Reduced conversion time to 15 – 30 minutes

Flow Diagram of Work



Precursor Production

- 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.



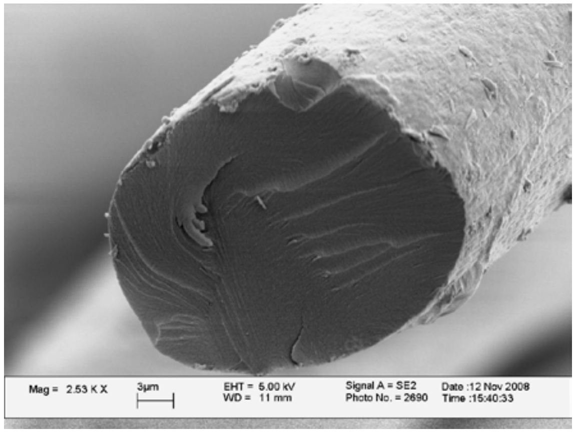
Properties of Precursor Fibers

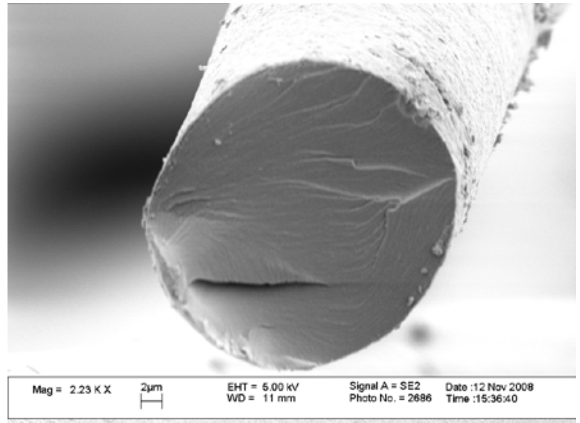
Tensile properties of the neat and functionalized fibers.

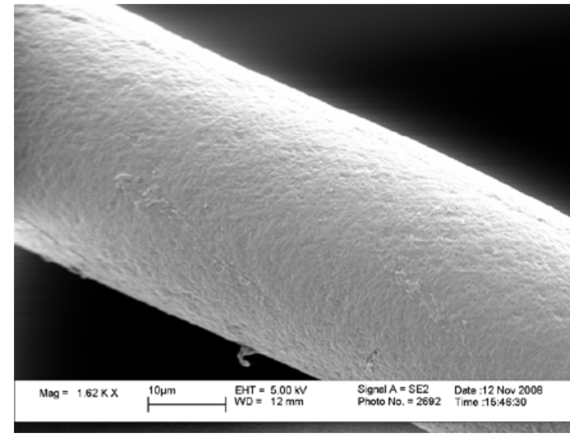
Fiber Sample	Tensile Strength (MPa)	Tensile Modulus (GPa)	Ultimate Elongation (%)	Yield Stress (GPa)
R1	98 ± 14	0.16 ± 0.06	187 ± 24	42 ± 8
R2	138 ± 27	0.41 ± 0.12	117 ± 48	77 ± 14
R3	169 ± 23	0.63 ± 0.09	115 ± 27	116 ± 13
R2S1	91 ± 12	0.83 ± 0.41	29 ± 3	-
R2S2	78 ± 10	1.19 ± 0.46	18 ± 3	-

- Increase in draw ratio increases filament strength and modulus and lowers ultimate elongation.
- Functionalization increases modulus (3 fold) and lowers both strength and elongation.

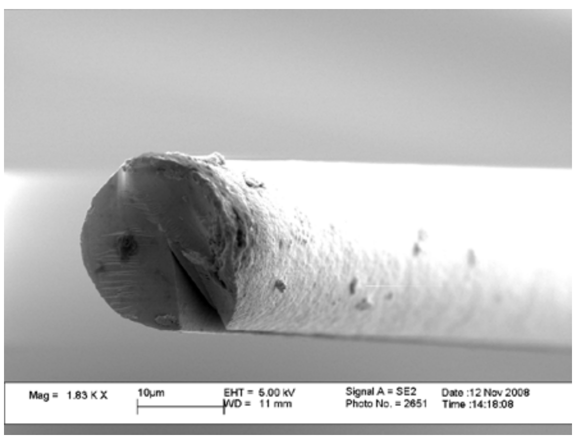
SEM-Micrographs of LLDPE-Based Fibers

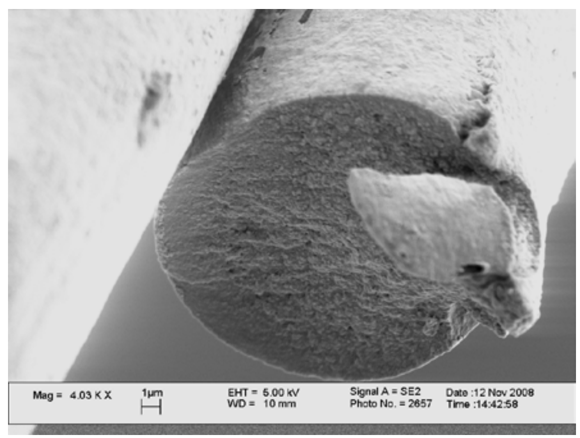


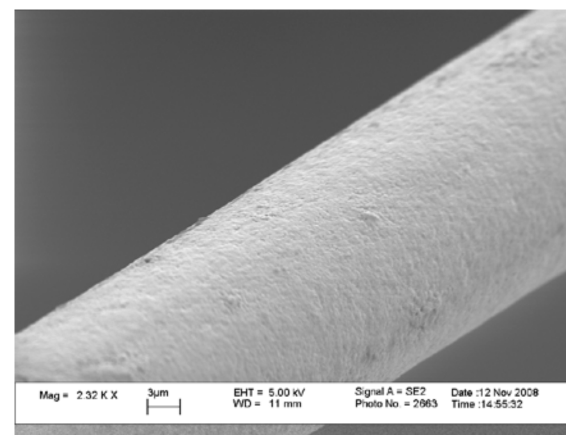




SEM micrographs of stabilized by new method - < 1hour residence time





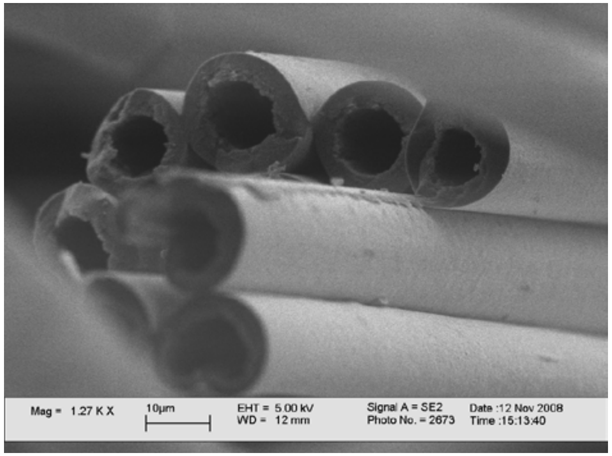


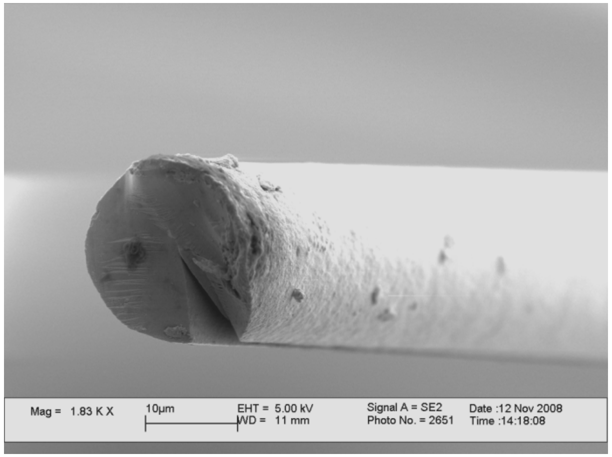
SEM micrographs of carbonized (Run-II) fibers

- 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

Future Direction

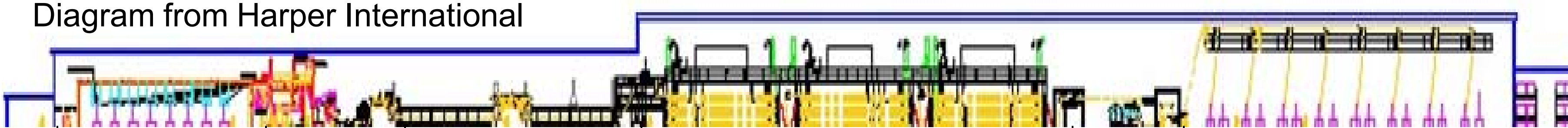
- To date the researchers have demonstrated accelerated stabilization of polyolefin precursor fibers.
- Earlier work required prolonged functionalization (6-10 h) to obtain good carbon fiber (380 KSI and 28 MSI). In this work it has been demonstrated that stabilization can be achieved within 1 h period. 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.

Conclusion

- 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

Diagram from Harper International



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	$0.41	$0.33	$1.48	$0.99	High Volume - $7.85	$4.64
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

	Large tow CF Precursor	Small tow (<24k) CF Precursor	Textile Precursor	Polyolefin Precursor
As-Spun Fiber ($/lb)	$ 3-5	$ 4-6	$ 2-3	$ 0.50 - $ 0.60
Carbon Yield	~45%	~50%	~50%	65 - 80%
Precursor Cost ($ /lb CF)	$ 6.5-11	$ 8-12	$ 4-6	$ 0.65 - $ 0.90
Stabilization	85 - 120 min	75 -100 min	75 - 100 min	60 min **
Carbonization	Same	Same	Same	Same

LM004

Questions?