Lower Cost Carbon Fiber Precursors
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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:	FY 07-10	$1139K
	FY11	$ 150K

Project Start: June 2007
Project End: Sept 2011
90+% Complete

Accomplishments - Textile Precursors

FISIPE

Conversion research at ORNL

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

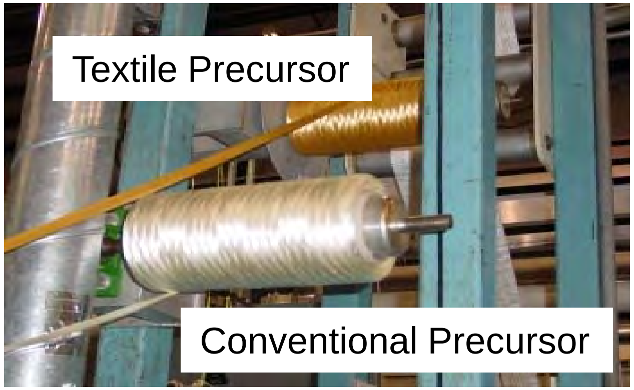
Began: January 2007   Partner: FISIPE (PT)

FISIPE uses a VA co-monomer

Guided FISIPE choosing a polymer composition and in installing the chemical bath which was 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.

Textile Precursors

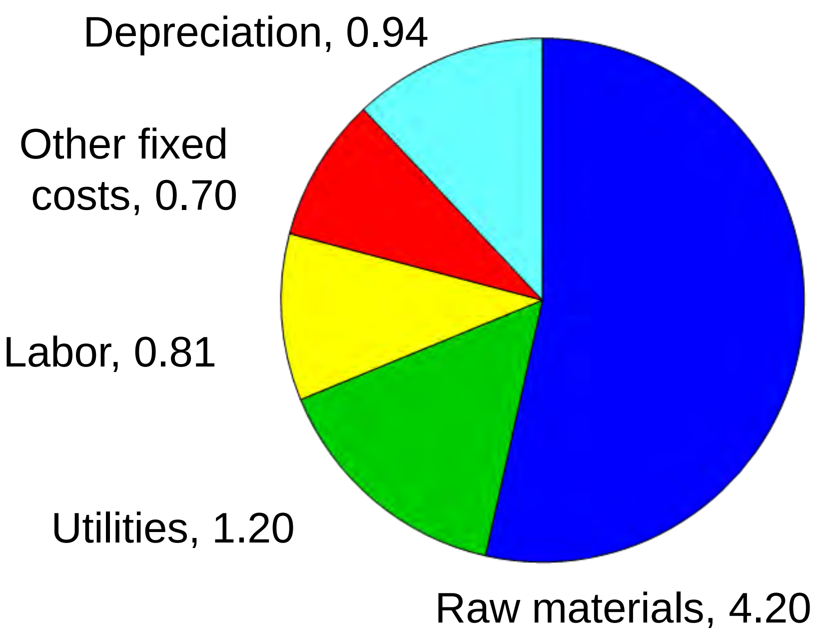


Textile PAN_VA Co-monomer - Formulation proprietary to FISIPE - 26,600 filament tow size

Chemically treated with a proprietary solution treatment at “normal” processing temps

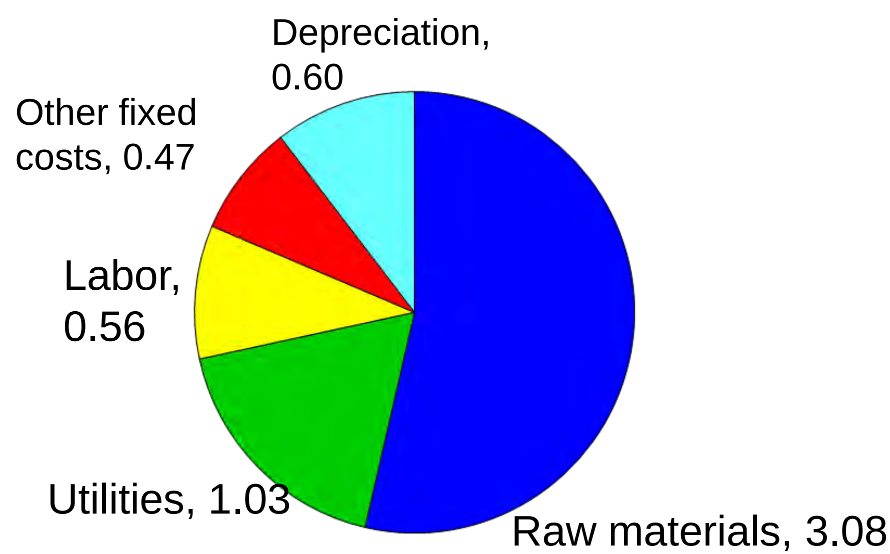
Oxidized and Carbonized using both the Precursor Evaluation Line and the Pilot Line

High Volume Baseline
24 MM lb/YR CF Plant
Conventional PAN Precursor



Total: $7.85/lb

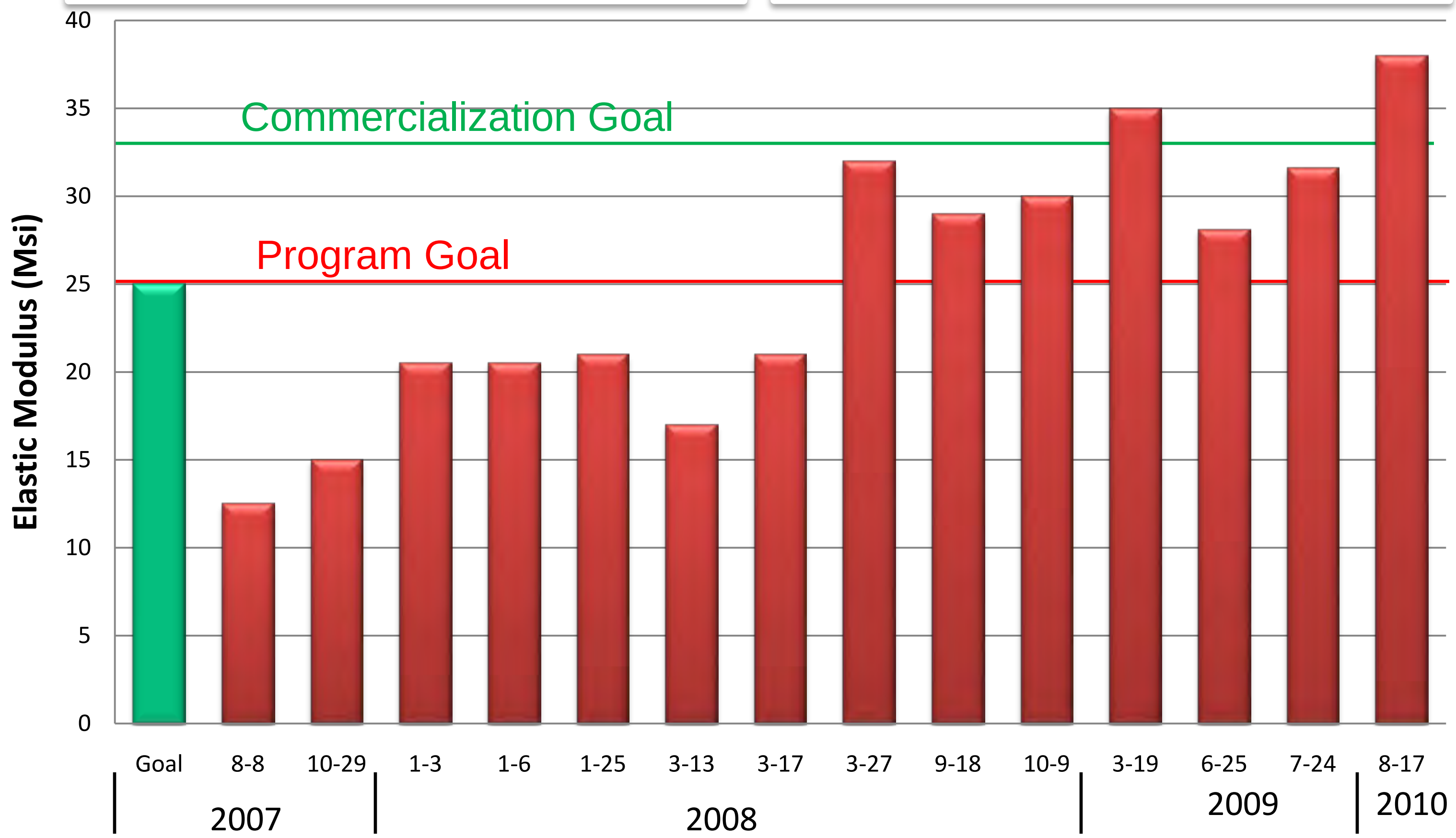
Textile Precursor
27.5 MM lb/YR CF Plant



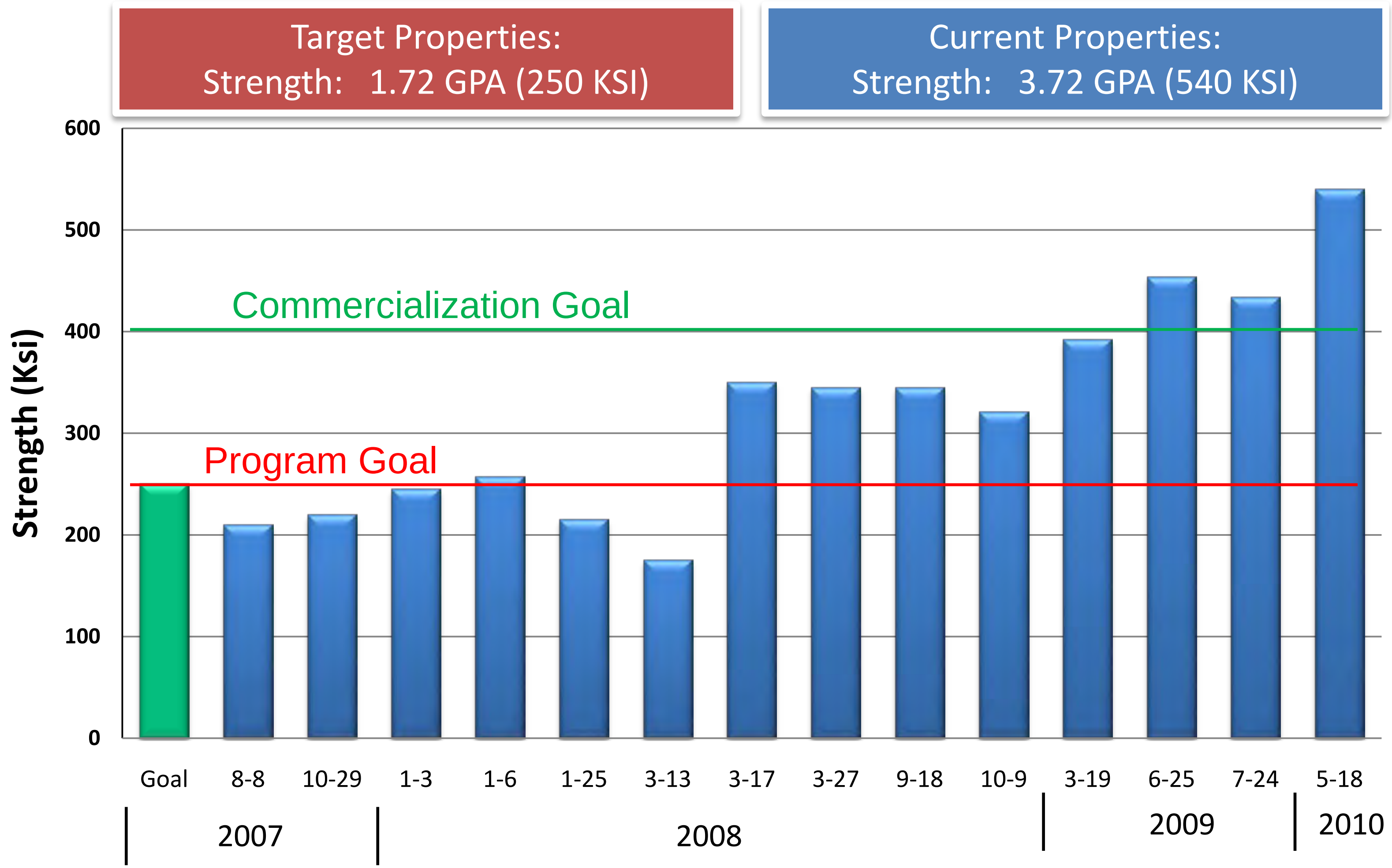
Total: $5.74/lb

Mechanical Properties – Modulus

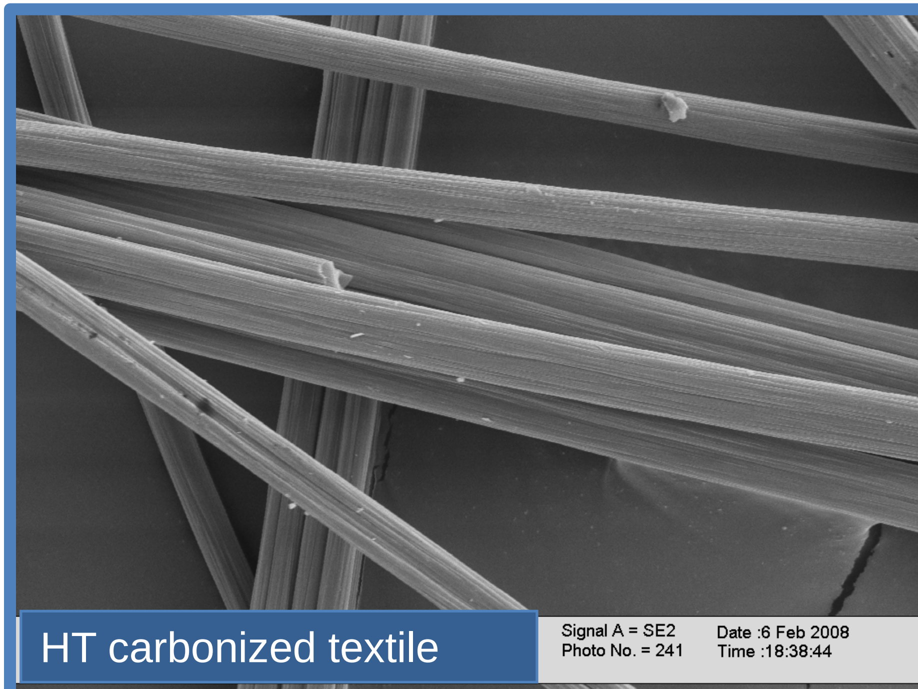
Target Properties:	Current Properties:
Modulus: 172 GPA (25 MSI)	Modulus: 261 GPA (~38 MSI)



Mechanical Properties – Strength



Scanning Electron Micrographs



This Year the ability to spin circular fibers was achieved and incorporated in the production line.

Textile Precursors – What is Happening

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.

FISIPE has installed a pilot scale production line to produce sample quantities of finished carbon fiber.

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 precursor 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 Start: June 2009
Project End: Sept 2012

Collaborative Partnerships: Large Proprietary CRADA funded through Industrial Technologies Program

Polyolefin Precursors

Polyolefin-based carbon fibers offer:

– Significant cost/performance benefit through
  - High carbon yield
  - Low raw material cost
  - Possibility of using recycled raw materials
  - Ease of precursor fiber handling and processibility

Compared to Other Precursors

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

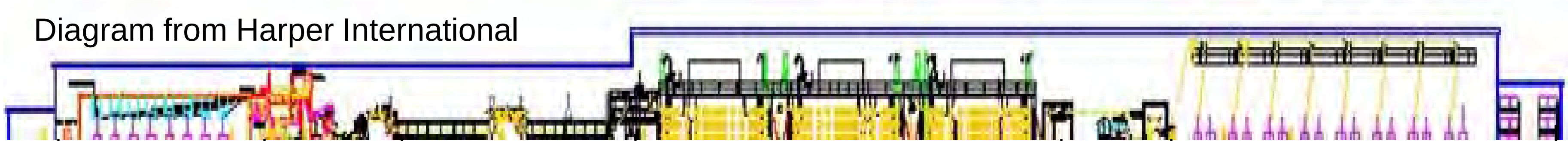
* Ongoing work
** Hexcel work (2004)

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

80 – 120 min Oxidative Stabilization replaced by a 30 - 40 min functionalization.

Polyolefin Precursors – Cost Potential

Diagram from Harper International



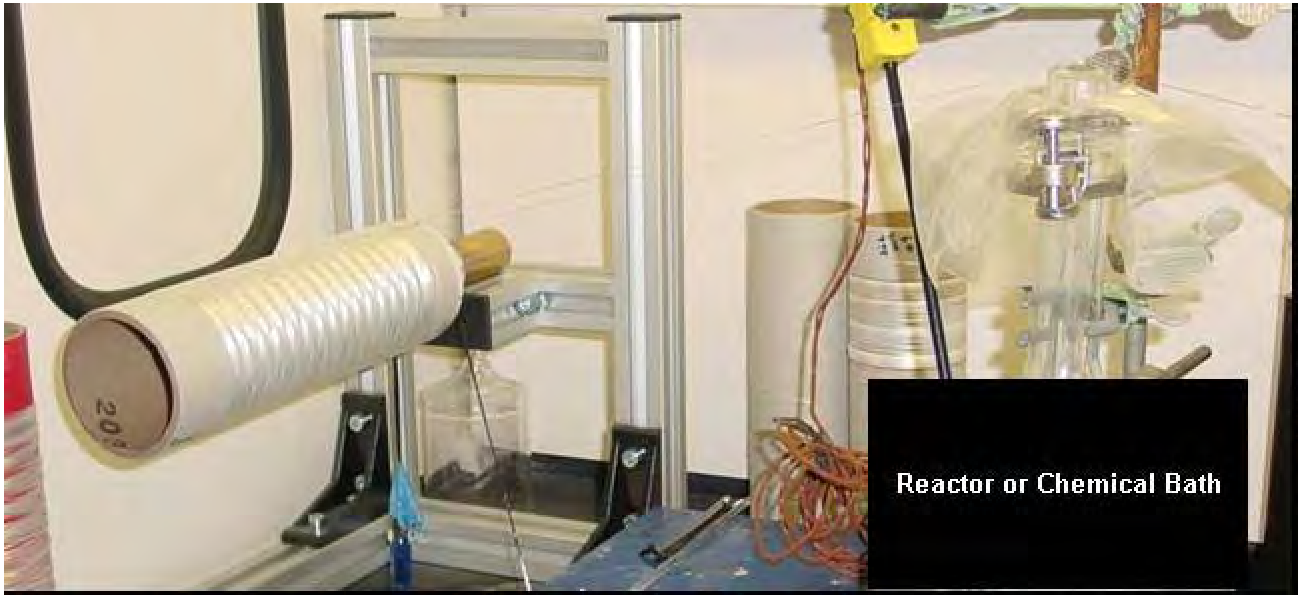
	Spooling & Packaging	Surface Treatment	Carbonization/ Graphitization	Stabilization & Oxidation		Precursors
	$0.61	$0.37	$2.32	$1.54	Baseline Today - $9.88	$5.04
	$0.41	$0.33	$1.48	$0.99	High Volume - $7.85	$4.64
High	$0.41	$0.33	$1.48	$0.20	$3.32	$0.90
Low	$0.41	$0.33	$1.25	$0.10	$2.74	$0.65

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

LLDPE Functionalization – FY'10
Chemical Bath Set-up

- 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.



Virgin fiber　　Chemical bath

Functionalized fiber spooling

Continuous fiber functionalization made operational in early FY'10

Set up semi-continuous functionalization module

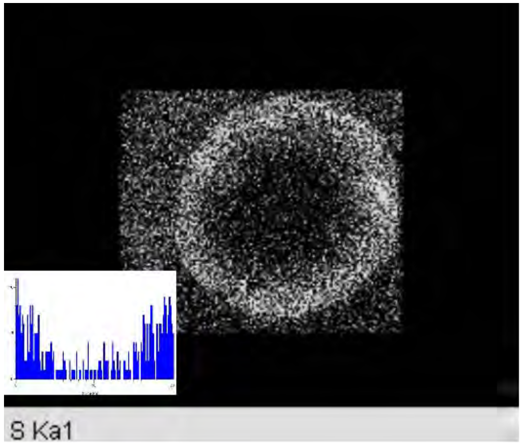
Properties of Fibers from Polyolefins

Materials

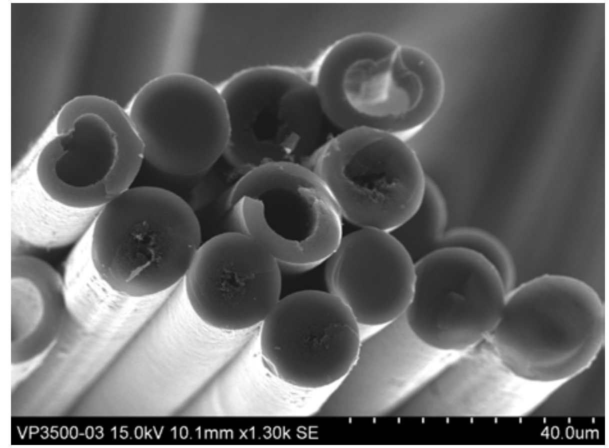
Tensile properties of polyethylene fibers and their carbonized filaments.					
Fiber type	Filament Diameter (μm)	Max. Filament Stress (ksi)	Max. Modulus. (Msi)	Ultimate elongation (%)	Remarks
Precursor-1	16	14	0.02	190	Resin-1
Precursor-2	16	20	0.06	120	Resin-1
Precursor-3	16	25	0.10	115	Resin-1
Precursor-4	19	22	0.15	100	Resin-2
Stabilized-1	21	10	0.20	25	From precursor-1
Stabilized-2	19	8	0.20	17	From precursor-2
Stabilized-4	28	7	0.20	12	From precursor-4
Carbonized-1	15	92	4	1.6	Difficult to process under tension
Carbonized-4	15	160	15	1.1	Carbonized under specific conditions

Met Sept 2010 milestone: **15 Msi modulus and 150 ksi strength in polyolefin-based CF**

Challenges in functionalization



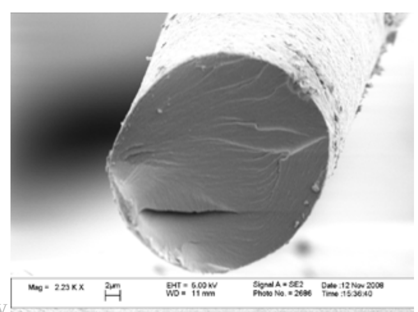
(a)

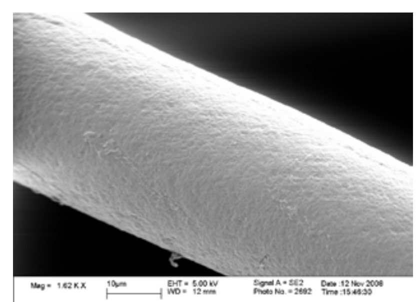


(b)

Figure (a) Mapping of elemental S on the fiber cross-sections during EDS study in a scanning electron microscope (SEM) and quantitative linescan of elemental S across the filament diameter (inset) and (b) carbonized filaments from such stabilized fibers with no core or weak amorphous core.

- Hollow cores in many of the fibers cause week mechanical properties.
- Optimal temperature range for accelerated functionalization of LLDPE fibers is identified.
- Degree of functionalization is critical for CF properties.
- Smaller diameter filaments are being studied now.





Milestones

- GATE Milestone FY'09: Spin modified polyolefin-based filaments and demonstrate conversion via accelerated sulfonation route. Completed
  - We have demonstrated a functionalization time (<60 min) that is significantly less than the residence time for prior work which produced 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 Completed
- 15 MSI Modulus

Gate Milestone FY'11: Meet minimum properties

- 200 KSI Strength
- 20 MSI Modulus

Future Goals

- To eliminate inter-filament bonding problem, which has been partially addressed.
- To obtain homogeneous sulfonated fiber without core in carbonized fiber (can be controlled by precursor type and morphology)
- To meet FY'11 milestone of 200 ksi strength and 20 Msi modulus.
- It is anticipated that at the end of FY'12 researchers will be able to demonstrate target properties (250 KSI and 25 MSI).

Lignin Precursors – Purpose, Barrier, Approach

Purpose: Develop the lowest cost potential carbon fiber precursor from a renewable resource. It has never been done achieving moderate properties.

Barriers: Three minimum criteria for process development work on a lignin material:

1. Meets the purity specifications for melt spinning
2. Can be readily melt spun into precursor fibers 10 µm in diameter
3. Is available in the quantities necessary (kilograms)

Approach:

1. Identify appropriate lignin chemistry, purity levels and co-polymer compositions.
2. Develop the capability to melt spin or solution spin the precursor yielding a handleable fiber.
3. Develop the conversion protocol for any potential forumulations.

Budget: $ 900K FY11

(On hold pending program direction)

Project Start: June 2004
Project End: TBD

Collaborative Partnerships: ITP funded collaborative projects for developing other lignin fiber applications.

Status of Lignin-based Carbon Fiber Project

Only one lignin material meets these three criteria: the Alcell™ hardwood lignin furnished by "Lignol Innovations," Vancouver, Canada (operating pilot scale biorefinery).

- Produced by "Repap Enterprises" 20 years ago! (120 tons in cold storage)
- Produced through Organosolv™ pulping of waste hardwood for paper manufacture
- Not produced with carbon fiber in mind!
- Mainstay of lignin carbon fiber project for last 3 years,
- Chemistry of the Alcell lignin not suitable for production of carbon fiber meeting the target mechanical properties for automotive lightweighting.
  (but is suitable for carbon fiber for other applications)

Mechanical Properties of Alcell Hardwood Lignin-based Carbon Fiber

Tensile Strength: 155 Ksi (62% of Target 250 Ksi)
Modulus: 10-12 Msi (40-48% of Target 25 Msi)

Missed October Milestone (150 Ksi/15 Msi): Revised Plan Being Developed

* 10 kg sample of high purity, organosolv-pulped softwood lignin material received from Lignol Innovations on February 8. This is probably the first organosolv-pulped softwood lignin produced worldwide, at least in significant quantity. Evaluation pending.

Status of Lignin-based Carbon Fiber Project

Materials

Does this mean that the target carbon fiber properties for automotive use cannot be obtained with a lignin-based system ?? NO !!

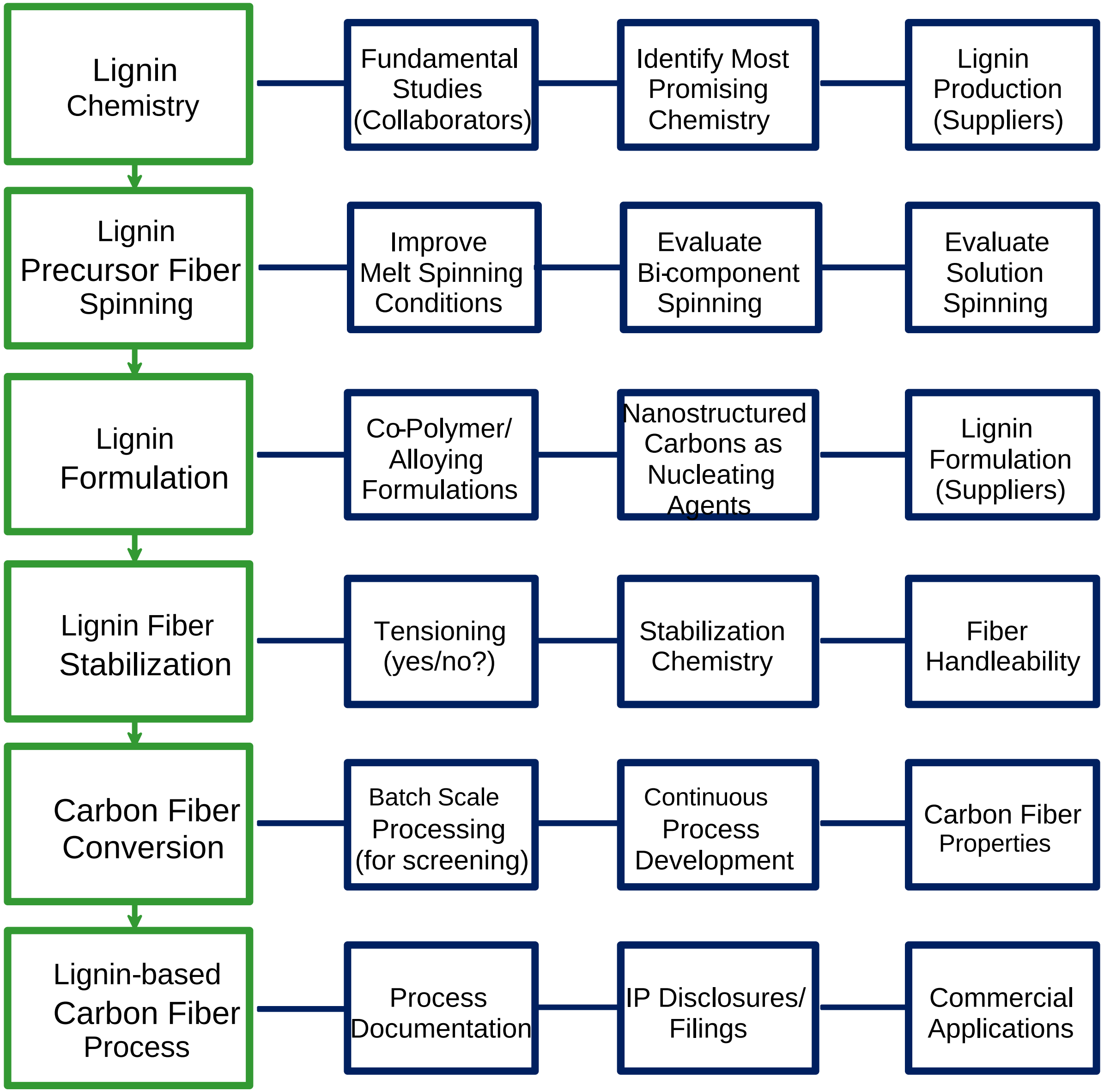
It means that although we have developed some understanding of lignin chemistry as it relates to carbon fiber production, we still have much more to learn about what is a complex system, especially the role of lignin chemistry and how to tailor it for carbon fiber production, and the fundamental mechanisms by which lignin fiber crosslinks (stabilizes) and carbonizes.

Note: During the development of PAN-based carbon fibers, it took roughly ten years to reach the engineering properties achieved to date for lignin-based carbon fiber!

Path Forward:

The overall path forward to reach target engineering properties is summarized in the next slide. Main thrust: Understand the Chemistry.

Path Forward – Process Focus Areas and Research



Path Forward – Lignin Chemistry

Materials

Objective: Obtain both the melt spinnability of organosolv-pulped hardwood lignin and the crosslinking characteristics of Kraft-pulped softwood lignin in a <u>single lignin material</u>

Lignin Chemistry

Research area	Partner	Status
Organosolv-pulped, switchgrass lignins. Isolation conditions. Tailoring of chemistry. Deconstruction-reconstruction: synthesis of more linear and polyaromatic derivatives.	University of Tennessee Knoxville, TN (Tim Rials, Joe Bozell, Darren Baker)	→ Contract for research work pending
Kraft-pulped, soft and hardwood lignins. Isolation conditions. Tailoring of chemistry. Solid state nmr, Raman, and XPS spectroscopy studies: chemistry of stabilization and carbonization.	IPST at GaTech Atlanta, GA (Art Ragauskas, Yunqiao Pu)	→ Exploratory (gratis) work implemented Dec'10. Funding to be determined
Kraft , organosolv, and steam-exploded lignins. Fundamental studies of thermotropic liquid crystalline phase behavior of lignin; relationship to melt spinning and carbon fiber properties.	VaTech; Blacksburg, VA (Wolfgang Glasser, Scott Renneckar, Justin Barone)	→ Joint research proposal submitted to Sun Grant Program Jan'11
Kraft-pulped, soft and hardwood lignins. Tailoring of properties through control of pulping and Lignoboost™ isolation conditions; enhancement of molecular weight, T_g, T_m.	Innventia Stockholm, Sweden (Peter Axegard, Elisabeth Sjoholm)	→ High purity Kraft softwood lignin received Dec'10. Evaluation underway
Organosolv-pulped, hard and softwood lignins. Tailoring of properties through control of pulping and isolation conditions; enhancement of molecular weight, T_g, T_m.	Lignol Innovations Burnaby, BC, Canada (Ken Pye, Mikhail Balakshin)	→ "Alcell" hardwood lignin mainstay of project since 2007. High purity organosolv-pulped <u>softwood lignin</u> received Feb'11. Evaluation pending
Kraft-pulped, softwood lignin. Tailoring of properties through control of pulping and electrolytic isolation conditions; enhancement of molecular weight, T_g, T_m.	Kruger Wayagamack Trois Rivières, ON, Canada (Jessica Charland Labonté)	→ 1st sample of electrolytically isolated Kraft softwood lignin received Dec'10. High ash content and unsuitable. Kruger refining process.
Switchgrass lignins. Genetic modification of lignin chemistry through manipulation of S/G ratio (ratio of syringyl to guacyl units). Long-term research.	ORNL-BESC and Noble Foundation	→ Long-term research to be negotiated .

High Melt Spinning Speeds Consistently Demonstrated

12-filament fiber spun from Kraft hardwood lignin

- Sustained melt spinning of lignin fiber of target diameter (10 µm) consistently demonstrated at 1500 meters/minute, the maximum speed of the winder on the lab scale equipment
- Both Kraft and Organosolv-pulped lignins (hardwood)
- Almost 3-times speed of commercial mesophase pitch-based fibers; almost 4-times commercial wet spinning speed of PAN-based fibers
- Much higher melt spinning speeds appear within reach; e.g., 5000 meters/minute with appropriate winding equipment

<u>Other Efforts with Lignin</u>

Rigid, High-Temperature Insulation for Si Production Furnaces

Utilization of Lignin-Based Carbon Fiber for Electrical Energy Storage

Manufacture of Nanoporous Carbons for Ultra (Super) Capacitor Applications

HVAC Systems with Energy-efficient CO_2 and VOC Capture

Joint Project between Vehicle Technologies and Hydrogen Storage Team

Purpose: 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. (600-750 KSI)

Barriers: Addresses the need for higher performance low cost fiber for hydrogen storage tanks and energy management structures of automobiles.

Approach:

1. Identify candidate PAN-MA resins.
2. Determine fiber spinning parameters.
3. Determine the production protocol.

Budget: $ 300K FY11
$ 600K FY12
$ 300K FY13

Project End: June 2013

Partnerships: FISIPE, 110% Cost Share

What is the difference between making aerospace and industrial grade carbon fiber?

Materials

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.

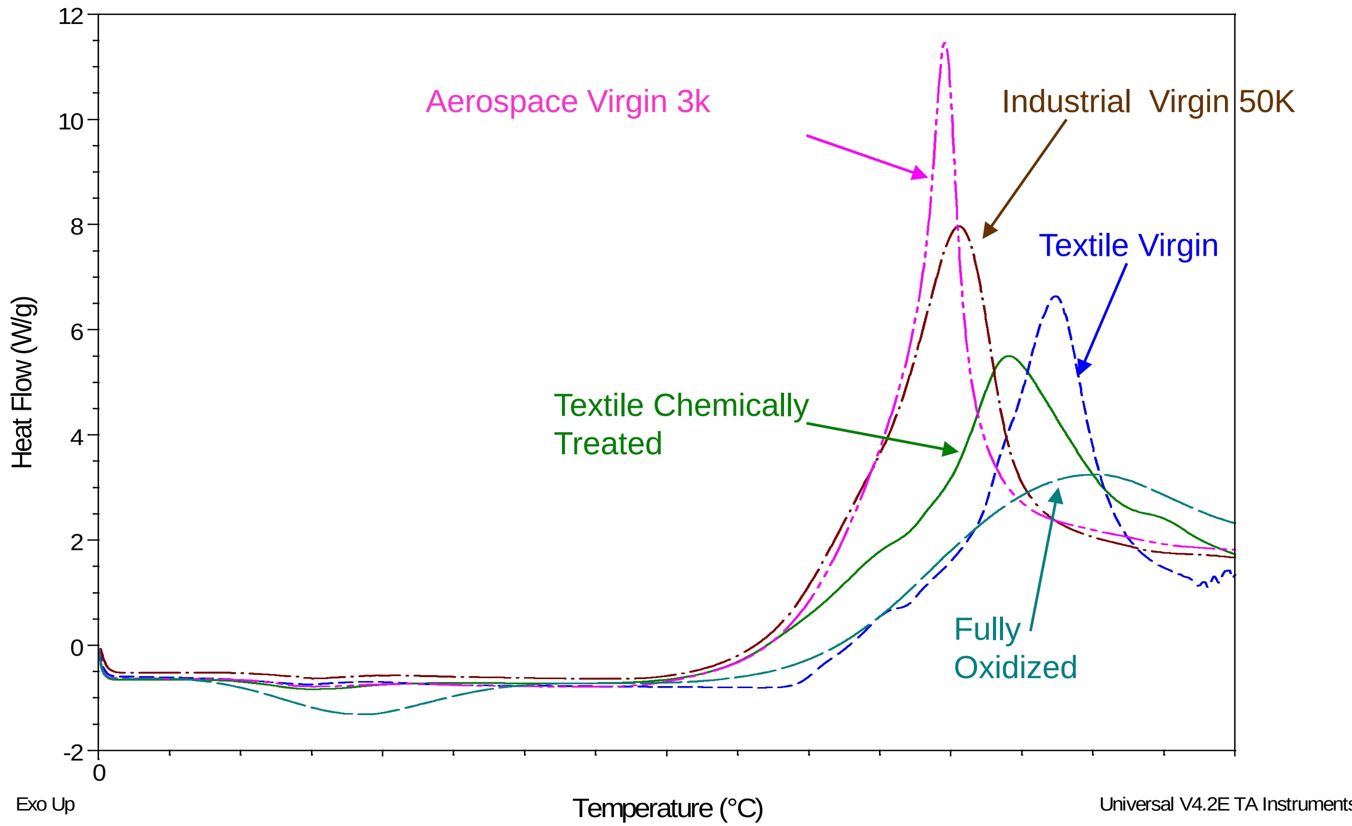
Essentially the same process with slightly different starting materials. Not captured is the fact the CF manufacturers are specialty material makers, not high volume.

What is the difference between making aerospace and industrial grade carbon fiber?

Materials

An higher performance fiber during production has:

1. Less material throughput (smaller tow size).
2. Requires more care in spinning (to get round fibers).
3. Spends longer in oxidation (affects lbs/hr production).
4. And requires higher temperature carbonization (energy $).



Challenges to be Addressed

Materials

Textile PAN that is MA-based

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.

Target Properties:
Strength: 1.72 GPA
(250 KSI)

Current Properties:
Strength: 3.72 GPA
(540 KSI)