Advanced Oxidation & Stabilization of PAN-Based Carbon Precursor Fibers

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Status as of early March 2012

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Project ID: LM006

Project Overview

Timeline

Phase **I**
- Start 2004
- End 2011

Phase **I** completed

Phase **II**
- Start 2011
- End 2015

Budget

- FY 2012: $2,000K

Barriers

- Barriers addressed
  - High cost of carbon fiber
  - Inadequate supply base for low cost carbon fibers
  - High volume manufacturing of carbon fiber
  - Long conventional processing times for oxidative stabilization are the bottleneck in production

Partners

- ORNL (Host site), carbon fiber expertise, characterization
- ReMaxCo Technologies (Experimental site), atmospheric plasma and hardware development.

Presentation Outline

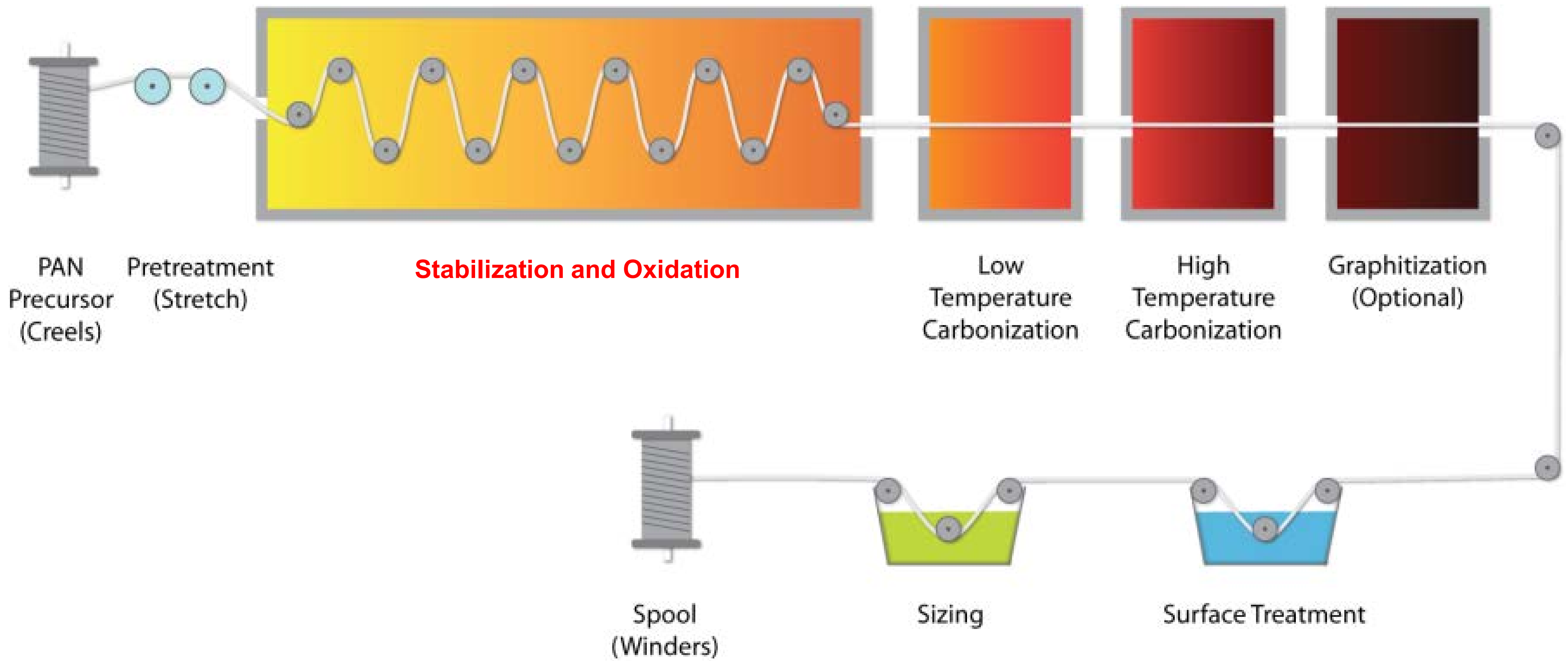
- Project Objectives
- Background
- Approach
- Milestones
- Phase I Technical Accomplishments
- Phase I Results
- Phase II Technical Accomplishments
- Phase II Results
- Future Work
- Conclusions

Project Objectives

- **Phase I: Produce multiple tows of carbon fiber meeting minimum program specifications using oxidation residence time of 40 minutes or less.**
  - Oxidative stabilization is the bottleneck in the production process often requiring 90 to 120 minutes. By developing a 2-3X faster oxidation process, higher throughput and significant cost reduction can be achieved. Completed.
  - JOULE Milestone was completed successfully in 04/2011.
- **Phase II: Demonstrate Phase I capability at pilot scale.**
  - This will involve multiple tows and larger tows at less than 35 min residence time (increased throughput).
  - This phase is in progress.

Background

Conventional PAN Processing



Typical processing sequence for PAN –based carbon fibers

Major Cost Elements	
Precursor	43%
Oxidative stabilization	18%
Carbonization	13%
Graphitization	15%
Other	11%

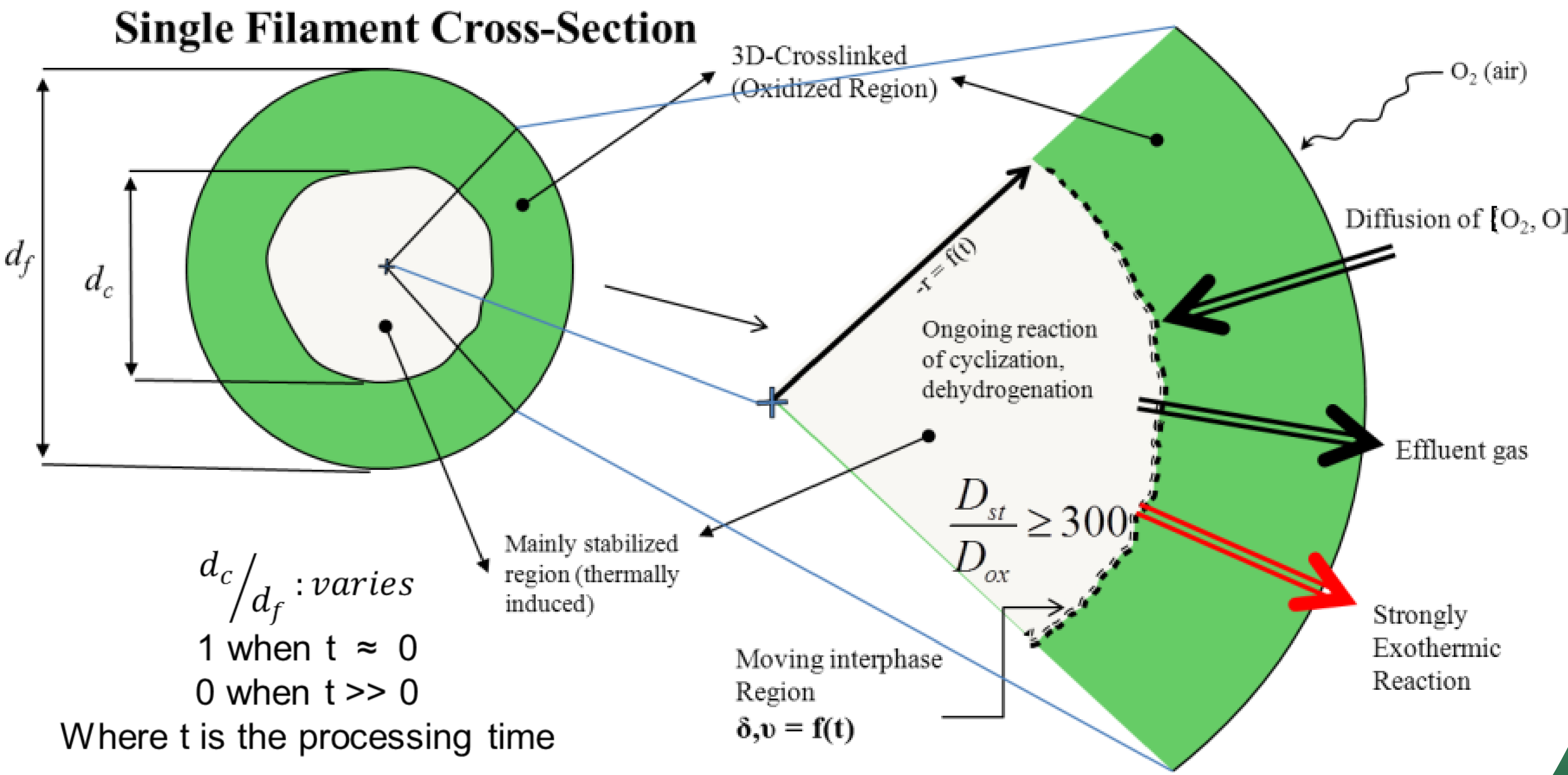
Automotive cost target is $5 - $7/lb

Tensile property requirements are 250 ksi, 25 Msi, 1% ultimate strain

ORNL is developing major technological breakthroughs for major cost elements

Approach: Reduce PAN-Oxidation

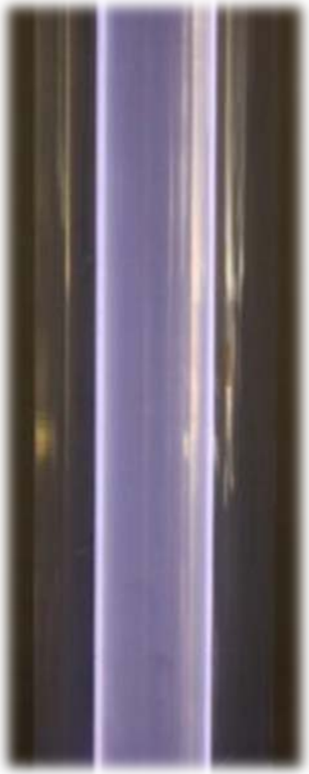
Two Zone Morphology



- **Diffusion of oxygen to reactive sites is restricted, sequent reactions follow more slowly**
- **The limiting factor in the oxidative processing is the diffusion-controlled phase**

Approach: Plasma-Based Oxidation

- Addresses diffusion-controlled stages of conventional oxidation
- Driven by non-thermal atmospheric pressure plasma processing versus more commonly thermal plasmas.
- After carbonization – good physical, morphological, and mechanical properties.
- Residence time reduced by 2 - 3X (single and multiple small tow)
- Fiber core more highly oxidized (digestion profiles)
- System design improvements and scale-up underway



Plasma Discharge Device

Milestones

Date	Milestone	Status
March 2011	Demonstrate plasma oxidation of large tows (≥ 24K) achieving densities larger than 1.35 gr/cm^3.	Complete
September 2011	Report experimental data in large tow (>3k, commodity or aerospace) of plasma oxidized and conventionally carbonized, achieving programmatic mechanical properties (250 KSI & 25 MSI, 1%).	Complete
January 2012	Plasma oxidize three 3K filament tows simultaneously in less than 35 minutes that, after carbonization, yield fiber in excess of the minimum program goals of 250 ksi strength and 25 Msi modulus	Complete
May 2012 GO/NO GO	Develop the processing protocol to plasma oxidize a single textile grade precursor tow with a filament count larger than 20K filaments at half of the conventionally required residence time and achieve carbonized fiber properties in excess of the minimum program goals of 250 ksi strength and 25 Msi modulus.	In progress
August 2012	Complete design of the Multiple Tow Reactor 2 as the next scale-up step in the plasma oxidation. (Initial design completed; runs from first module will complete design)	In progress

Technical Accomplishments

Major Apparatus Transition (Phase I)

- Over the course of this research program, the plasma methodology has progressed from direct exposure, to remote exposure, to close proximity indirect exposure. The latter method was developed as a new processing technique to address several challenges with the previous methods, which was resulting in fiber damage and poor mechanical properties. Valuable lessons learned from the MTR1 were incorporated into this technique.

- The original design used conduction heating and remote plasma treatment, while the new design uses convection heating and a different plasma processing technique (Close Proximity Indirect Exposure [CPIE] Plasma).

- The resulting fiber properties of the new method were far superior to the original one. The resulting mechanical properties of the carbonized fiber of 75% of the initial tests (during optimization) exceeded the minimum program requirements.

- During this transition, an improved chemistry was developed that allows for a reduced consumption of oxygen supply to the reactor.

Technical Accomplishments

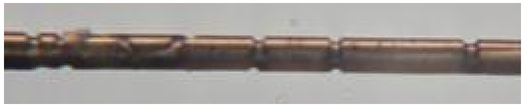
Major Apparatus Transition (Phase I)

Multiple Tow Reactor 1

- **RE/Multiple Tow Reactor 1 (MTR1)**

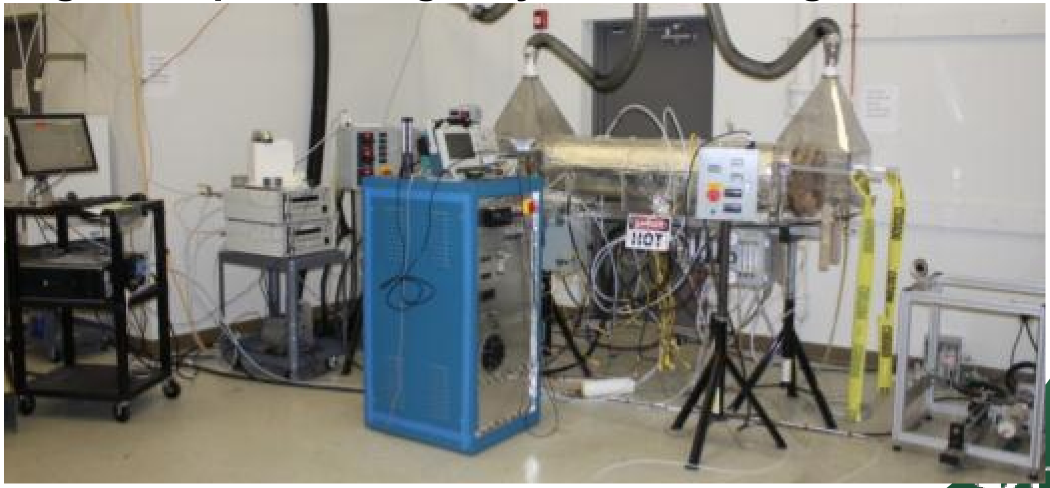
This reactor was designed for simultaneous processing of up to 6 tows continuously. Utilizes remote exposure (RE) plasma method. Initial work of simultaneous processing was performed here.

E.g. of fiber damage: (extreme example)



- **CPIE/SMR2**

This reactor was designed as dual use between plasma-based surface treatment as well as oxidation. Adapted for use with new CPIE plasma method. Designed for single tow processing only. Fiber damage eliminated.



Close Proximity Indirect Exposure Reactor

Select Phase I Results (Single Tow)

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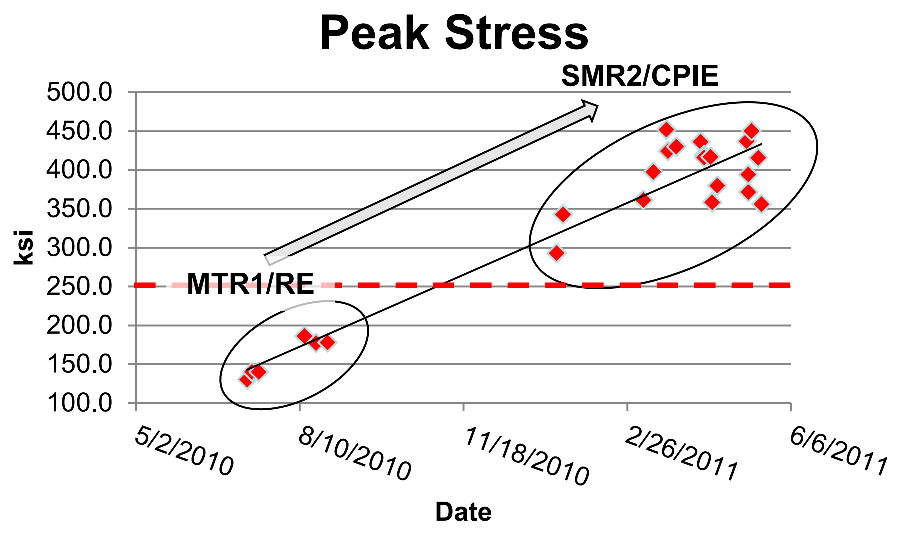
	Oxidized						Carbonized				
Sample	Date Oxidized	Fiber Diameter (um)	Peak Stress (ksi)	Modulus (Msi)	Strain @ Break (%)	Res Time (min)	Date Carbonized	Fiber Diameter (um)	Peak Stress (ksi)	Modulus (Msi)	Strain @ Break (%)
SR374	7/9/2010	13.5	28.2	0.9	8.2	77	7/16/2010	8.59	130.0	20.3	0.61
SR376	7/12/2010	13.6	35.2	1.1	11.6	77	7/28/2010	9.3	140.1	21.2	0.65
SR381	7/16/2010	13.5	26.4	0.9	5.7	77	7/29/2010	9.4	139.8	18.7	0.73
SR408	8/13/2010	13.0	35.7	0.8	12.4	77	9/24/2010	7.78	186.0	23.2	0.75
SR415	8/20/2010	13.0	35.4	0.6	13.9	77	11/3/2010	8.84	176.8	23.9	0.74
SR419	8/27/2010	12.7	37.7	1.0	13.9	77	10/14/2010	8.96	177.8	20.9	0.83
SR442	1/18/2011	13.2	42.1	1.1	11.9	120	2/2/2011	6.95	342.5	35.6	0.93
SR460	3/8/2011	11.3	49.1	1.56	11.6	60	3/23/2011	7.2	361.2	31.7	1.09
SR466	3/14/2011	11.0	45.3	1.49	7.6	45	4/4/2011	6.99	397.5	35.5	1.07
SR472	3/22/2011	10.8	51.4	1.59	10.0	45	4/4/2011	6.95	451.6	34.9	1.20
SR473	3/23/2011	11.5	53.1	1.53	12.5	30	4/1/2011	7.62	423.9	27.7	1.39
SR478	3/28/2011	11.5	56.2	1.59	12.0	35	4/8/2011	7.5	429.7	29.0	1.38
SR485	4/12/2011	11.9	49.2	1.64	15.6	30	4/21/2011	7.12	436.2	30.5	1.30
SR488	4/14/2011	11.3	48.3	1.46	13.2	45	5/4/2011	7.11	418.9	31.4	1.25
SR489	4/14/2011	10.7	50.3	1.55	9.9	45	5/4/2011	6.51	415.8	34.8	1.11
SR491	4/18/2011	9.6	54.5	1.8	10.2	45	05/05/11	6.1	416.6	36.3	1.06
SR492	4/19/2011	11.2	46.9	1.4	13.2	45	05/05/11	7.1	358.3	32.3	1.05
SR494	4/22/2011	11.6	60.4	1.4	15.4	20	05/05/11	6.9	379.6	29.4	1.20
SR498	05/10/11	12.2	38.4	1.3	11.4	30	06/03/11	6.9	436.7	32.9	1.23
SR499	05/11/11	11.9	37.1	0.9	9.4	30	06/03/11	7.1	371.5	31.6	1.10
SR500	05/11/11	11.4	36.0	1.5	7.7	30	06/06/11	6.6	394.0	34.4	1.08
SR502	05/13/11	11.9	39.9	0.7	12.1	30	06/07/11	6.6	449.9	34.0	1.21
SR505	05/17/11	11.2	39.9	1.3	13.0	30	06/02/11	5.9	415.3	36.8	1.05
SR506	05/19/11	12.7	33.8	1.0	12.8	30	06/03/11	7.4	355.7	30.7	1.09

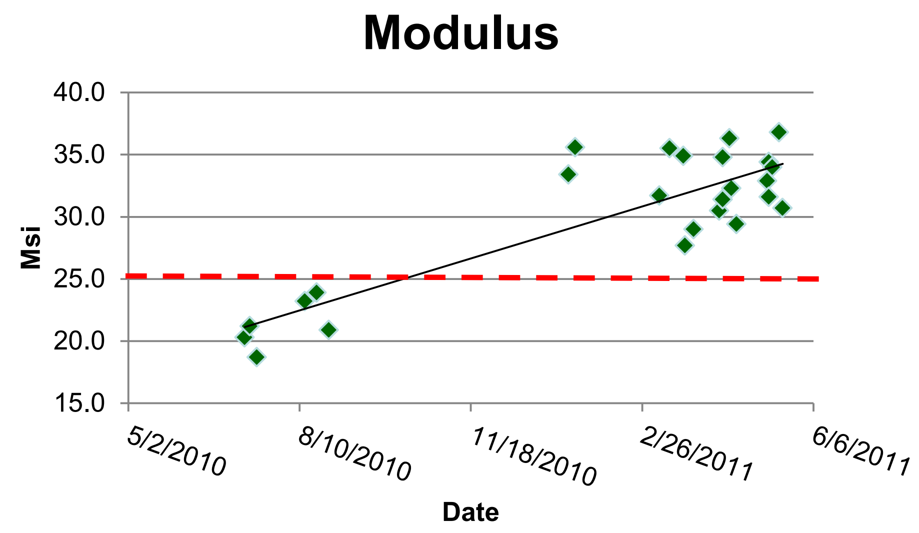
RE/MTR1 Method

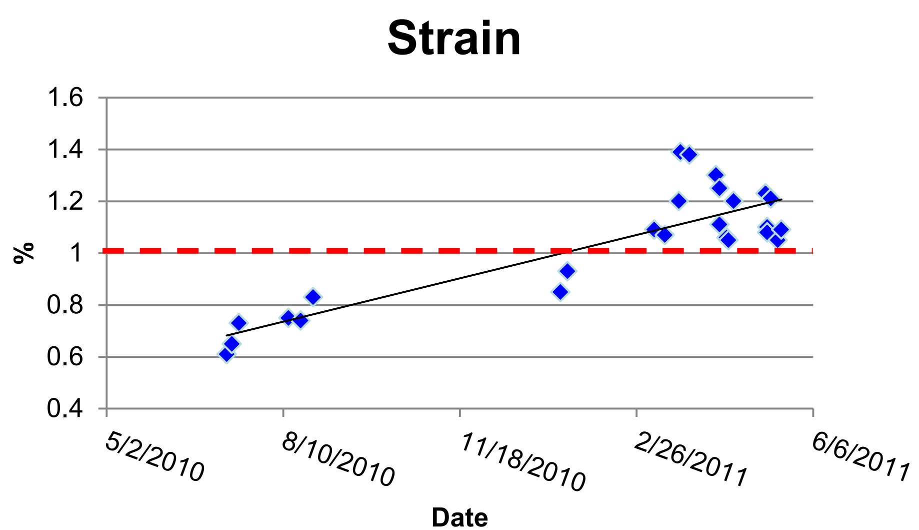
CPIE/SMR2 Method

Select Phase I Results (Single Tow)

Phase 1 Select Mechanical Properties (Chronologically)







- Graphical representation of previous tabled data.
- These graphs illustrate the dramatic difference between the RE and CPIE methods, and the overall progress made.
- Red dashed line are program minimum requirements. (250ksi, 25Msi, 1%)

More Phase I Results (Single Tow)

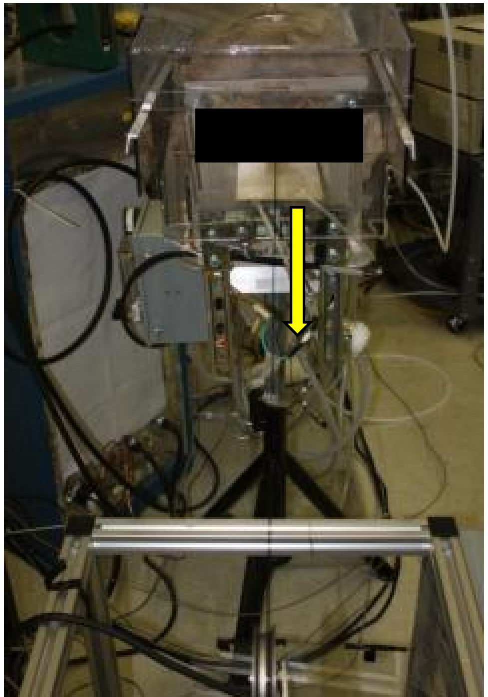
CPIE/SMR2 Method

	Oxidized					Carbonized					
Sample	Date Oxidized	Fiber Diameter (um)	Peak Stress (ksi)	Modulus (Msi)	Strain @ Break (%)	Date Carbonized	Fiber Diameter (um)	Peak Stress (ksi)	Modulus (Msi)	Strain @ Break (%)	
SMR470	3/21/2011	11.4	41.4	1.48	8.4	4/1/2011	7.4	340.2	32.6	0.98	
SMR471	3/22/2011	11.6	48.2	1.48	14.5	4/1/2011	7.62	279.5	30.4	0.87	
						4/4/2011	7.80	276.2	28.7	0.9	
SMR472	3/22/2011	10.8	51.4	1.59	10.0	4/4/2011	6.95	451.6	34.9	1.20	
SMR473	3/23/2011	11.5	53.1	1.53	12.5	4/1/2011	7.62	423.9	27.7	1.39	
						4/5/2011	7.06	362.5	32.6	1.03	
SMR474	3/23/2011	11.3	57.4	1.59	13.2	3/24/2011	~	~	~	~	Breakage
						3/24/2011	~	~	~	~	
SMR475	3/24/2011	11.6	50.2	1.47	13.4	4/11/2011	7.78	280.6	28.0	0.96	
						4/11/2011	7.77	303.7	27.3	1.06	
SMR476	3/24/2011	11.8	46.5	1.52	13.1	4/21/2011	7.27	198.3	31.3	0.61	
						4/13/2011	~	~	~	~	
SMR477	3/25/2011	11.7	52.5	1.49	10.3	4/11/2011	~	~	~	~	Breakage
						4/11/2011	~	~	~	~	
SMR478	3/28/2011	11.5	56.2	1.59	12.0	4/8/2011	7.29	378.5	29.4	1.23	
						4/8/2011	~	~	~	~	Breakage
						4/8/2011	~	~	~	~	
						4/8/2011	7.5	429.7	29.0	1.38	
SMR480	3/29/2011	11.9	51.6	1.47	14.7	5/4/2011	7.57	268.4	28.8	0.9	
						5/4/2011	6.95	336.6	34.4	0.93	

- Snapshot of chronological progression of testing.
- ~ shows where breakage has occurred on occasion (highlighted in orange).

Technical Accomplishments

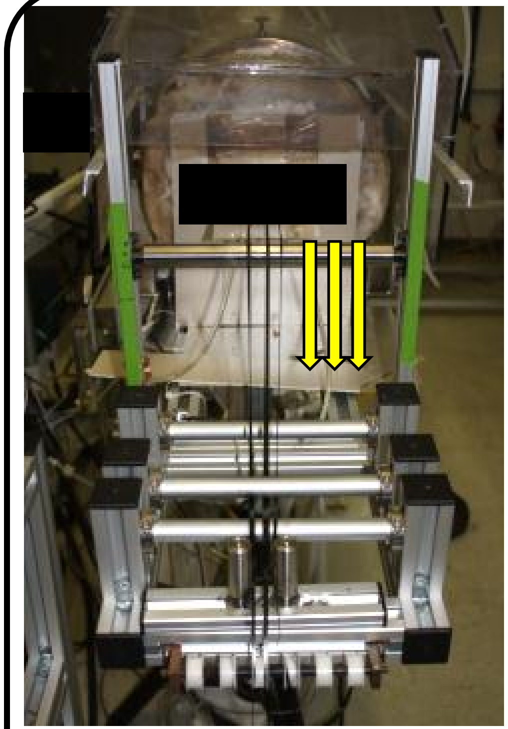
New Method Implementation in SMR2 (Phase I to II)

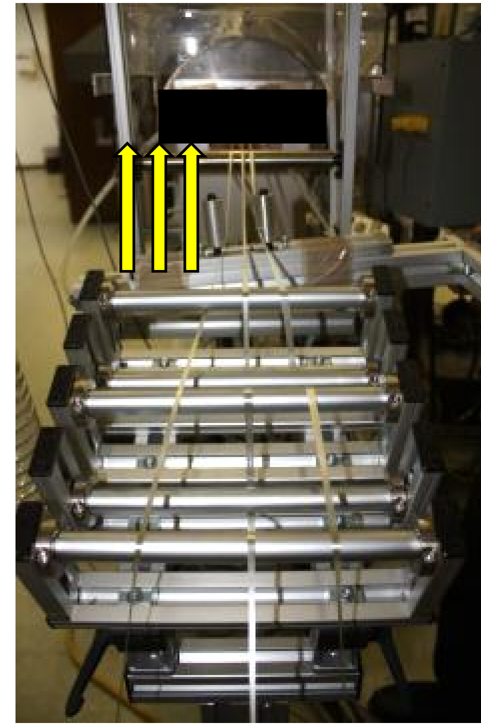


Phase I:
New CPIE Method for one tow

Oxidized Fiber Exit Port

Precursor Entrance Port





Oxidized Fiber Exit Port

Precursor Entrance Port

Phase II:
New CPIE Method with three tows simultaneously. (Fiber handling equipment cannot be shown).

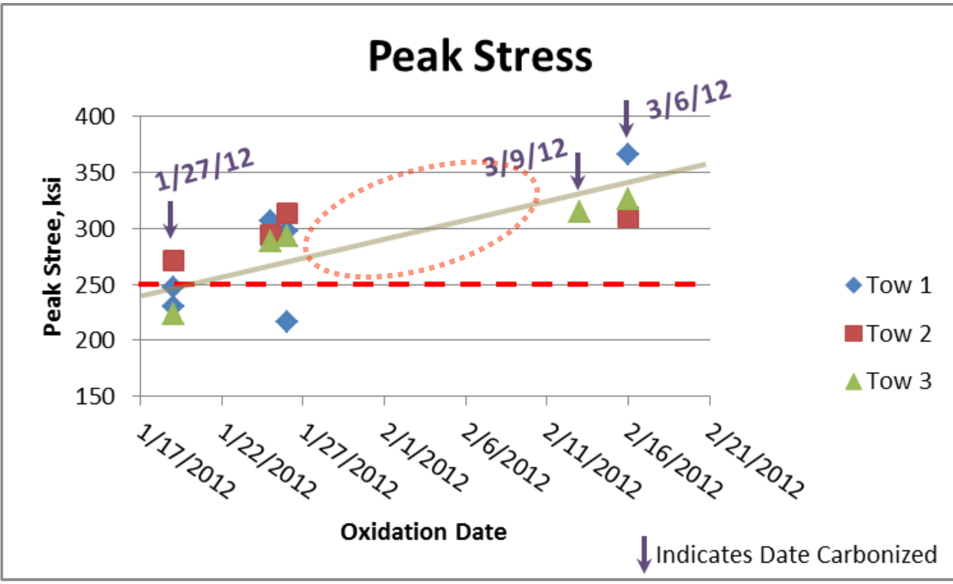
Technical Accomplishments

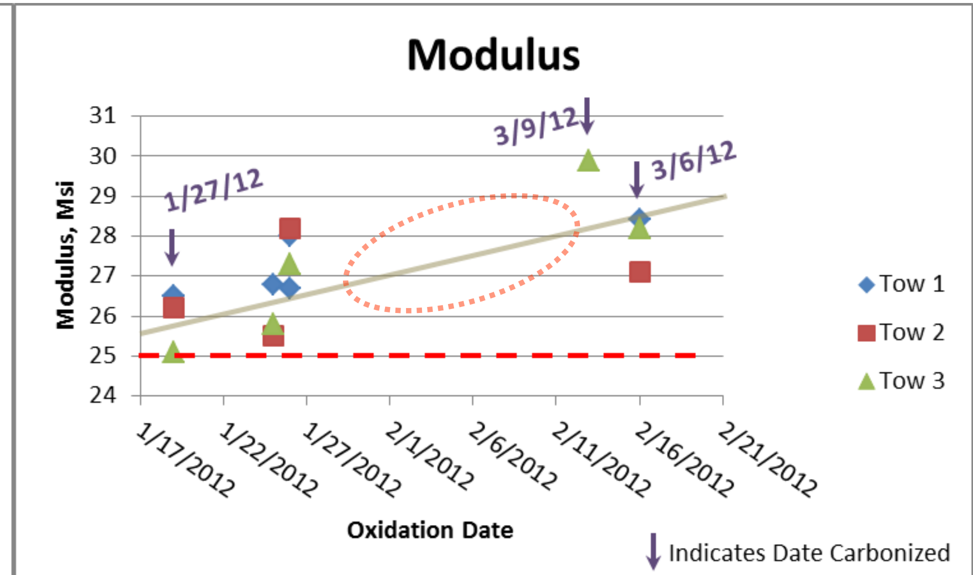
Multiple Tow Processing with CPIE (Phase II)

- Phase II work began November 18, 2011 (FY12).
- The initial CPIE/SMR2 method/apparatus was not designed for processing multiple tows – required modifications were completed late 2011.
- In addition to reactor modifications, new fiber handling equipment had to be designed, built, and delivered by a vendor for multiple tow processing. This caused some delay, but was necessary based on lessons learned from multiple tow processing in the MTR1 (at this moment, each tow requires individual handling).
- Schedule for fiber handling equipment (to obtain a 4-position creel and 3-position winder):
  - Design start: 6/2011
  - PO issued by ORNL: 8/11/2011
  - Equipment delivery to ORNL: 12/19/2011
  - Received Onsite: 01/10/2012
- Start of multiple tow experimentation began 01/11/2012.
- First sample set delivered to ORNL for evaluation on 1/19/2012.

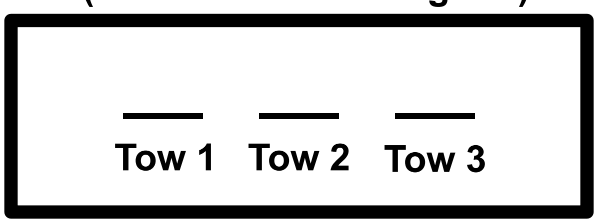
Phase II Initial Results (Multiple Tows) LM006

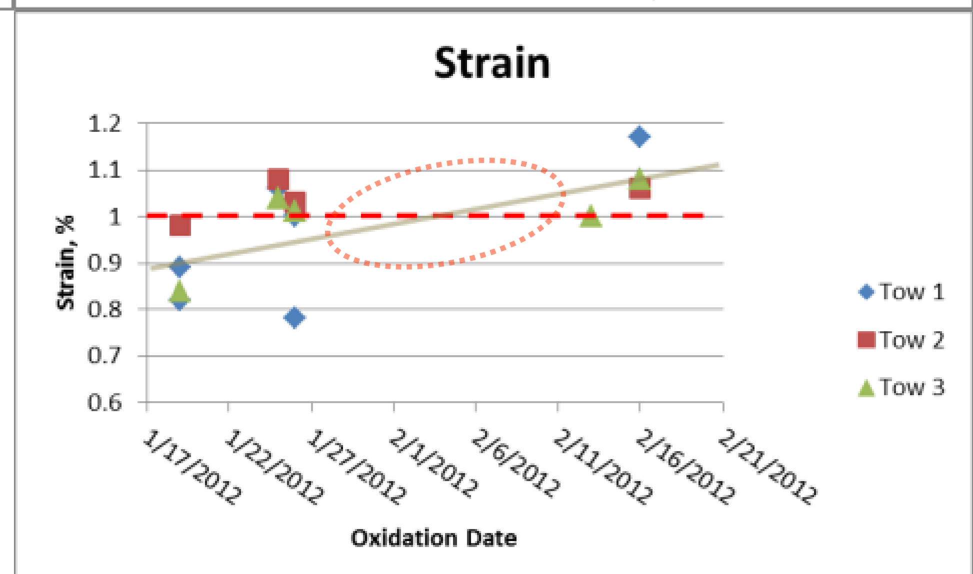
Phase II Mechanical Properties (Chronologically)





Exit End of Reactor
(tows shown coming out)





- All with 32 minute residence time for CPIE plasma oxidation.
- Dotted circled region shows that samples were oxidized during this time, but the mechanical analysis is still ongoing.

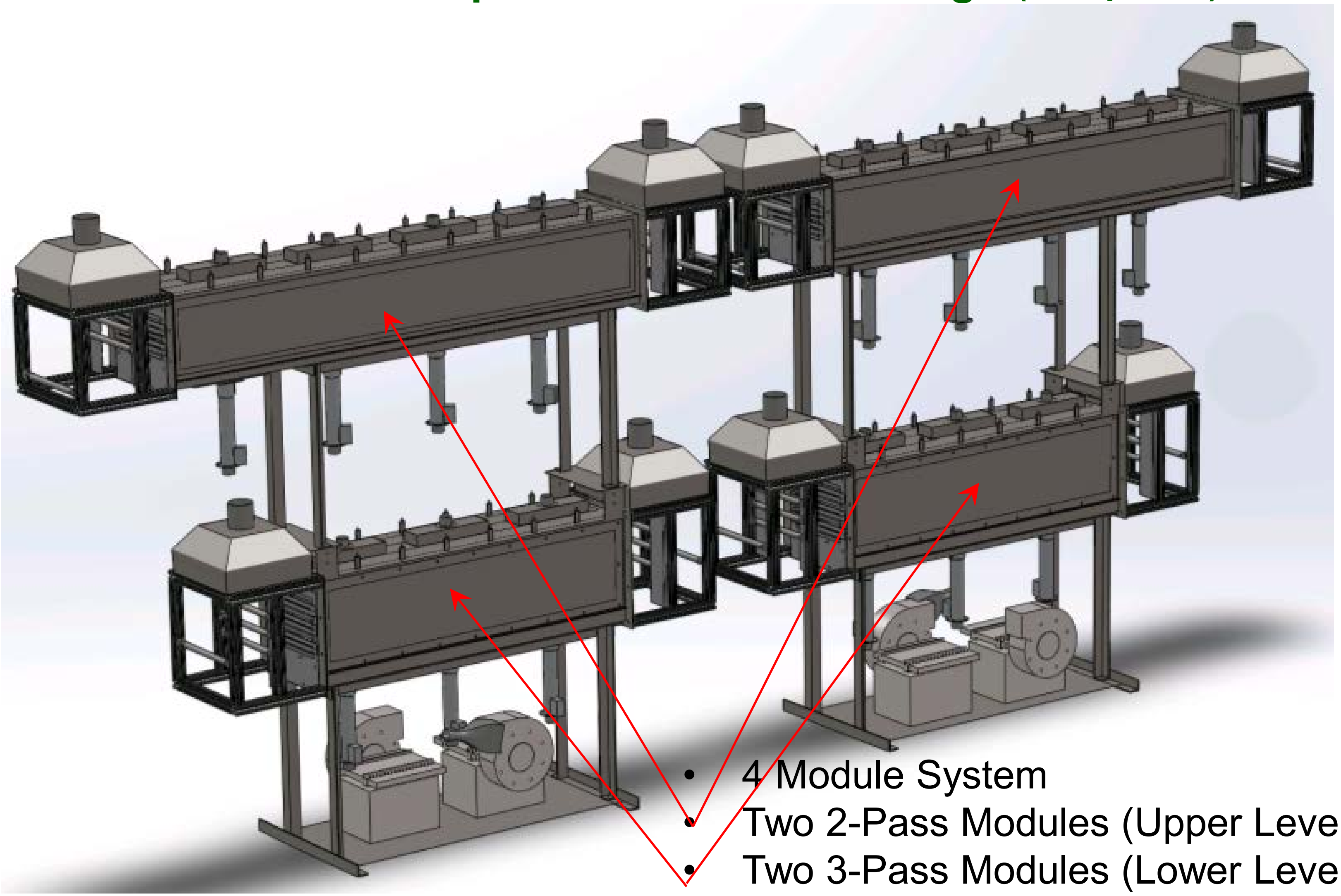
Technical Accomplishments

Multiple Tow Processing with CPIE (Phase II)

- Further fiber damage analysis using specific process chemistries has been completed to isolate cause and effect.
- January milestone completed on schedule.
- Design of MTR2 is complete. Construction has begun.
  - First module (short 3-pass) is scheduled to be delivered in March/April
  - Overall system will incorporate four separate modules.
  - Design meets floor space requirements for integration into ORNL's Small Pilot Line (SPL). Also minimizes fiber dwell time outside modules.
- Patent has been filed (July 2011) covering new CPIE processing method and apparatus (ORNL-ID 2626).
- Multiple tow fiber handling equipment is installed and operational.
- Investigations have begun with applying plasma oxidation methods to alternative precursors.

Technical Accomplishments

Multiple Tow Reactor 2 Design (Completed)



- 4 Module System
- Two 2-Pass Modules (Upper Level)
- Two 3-Pass Modules (Lower Level)
  - First module to be built for design validation
- Anticipate residence time of 20-30 minutes.

Future Work

- **Rest of FY12**
  - **Complete construction of MTR2.**
  - **Commission MTR2 into operation for full experimentation of multiple tow CPIE at high line speeds.**
  - **Complete adaptation of CPIE process to large tow textile PAN.**
  - **Complete Go/No Go milestone**
- **FY13**
  - **Verify continuous operation capabilities of MTR2**
  - **Process multiple tows of large textile grade PAN.**
  - **Obtain scaled energy consumption data**

Date	Milestone
May 2012 Go/No Go	Develop the processing protocol to plasma oxidize a single textile grade precursor tow with a filament count larger than 20K filaments at half of the conventionally required residence time and achieve carbonized fiber properties in excess of the minimum program goals of 250 ksi strength and 25 Msi modulus.
August 2012	Complete design of the Multiple Tow Reactor 2 as the next scale-up step in the plasma oxidation.

Date	Milestone
May 2013	Complete construction of the Multi-Tow Reactor 2 for plasma oxidation of multiple tows of lower cost, commodity precursor fibers.
September 2013	Plasma oxidize three to five 20,000+ filament textile precursor tows simultaneously in less than 35 minutes that, after carbonization, yield fiber in excess of the minimum program goals of 250 KSI strength and 25 MSI modulus.

Long Term Milestones/Deliverables

- Demonstrate plasma oxidation of multiple tows of textile precursor
- Demonstrate program property requirements satisfied, with low variability, in processing multiple large tows in MTR2.
- Optimize oxidation reactor module hardware and controls as required
- Review and update key technical and economic drivers for this technology specifically including residence time, projected equipment costs, and energy consumption per unit mass (go/no-go decision gate)
- Deliver, install, and commence operations of plasma oxidation reactor in the ORNL Small Pilot Line (SPL). Evaluation needed both as standalone unit, and incorporated inline with ORNL SPL.
- Deliver equipment specification for a plasma oxidation module for an advanced technology/demonstration pilot line (principal project deliverable) appropriate for integration with the Carbon Fiber Technology Facility currently being constructed.

Summary and Conclusions

- Achieved a major technological breakthrough in FY11, developing a new oxidation method and apparatus with dramatic improvements at all levels.
- Project on schedule – all milestones have been met to date. Research team is committed to meet all future programmatic milestones.
- Phase I completed. Phase II commenced Nov 2011.
- MTR2 anticipated fully operational July 2012.
- Materials compatibility testing to determine optimal construction materials of future furnaces is ongoing (not presented here).
- This work directly supports petroleum reduction via improved fuel economy from vehicle weight reduction
- This work addresses the barrier of carbon fiber cost
- The approach is to develop a revolutionary new method for converting carbon fiber, which offers much higher potential for achieving significant cost reduction than evolutionary improvements to existing conversion technology
- Process and equipment scaling, as well as textile PAN adaptation, will constitute the majority of future work.

Backup Materials

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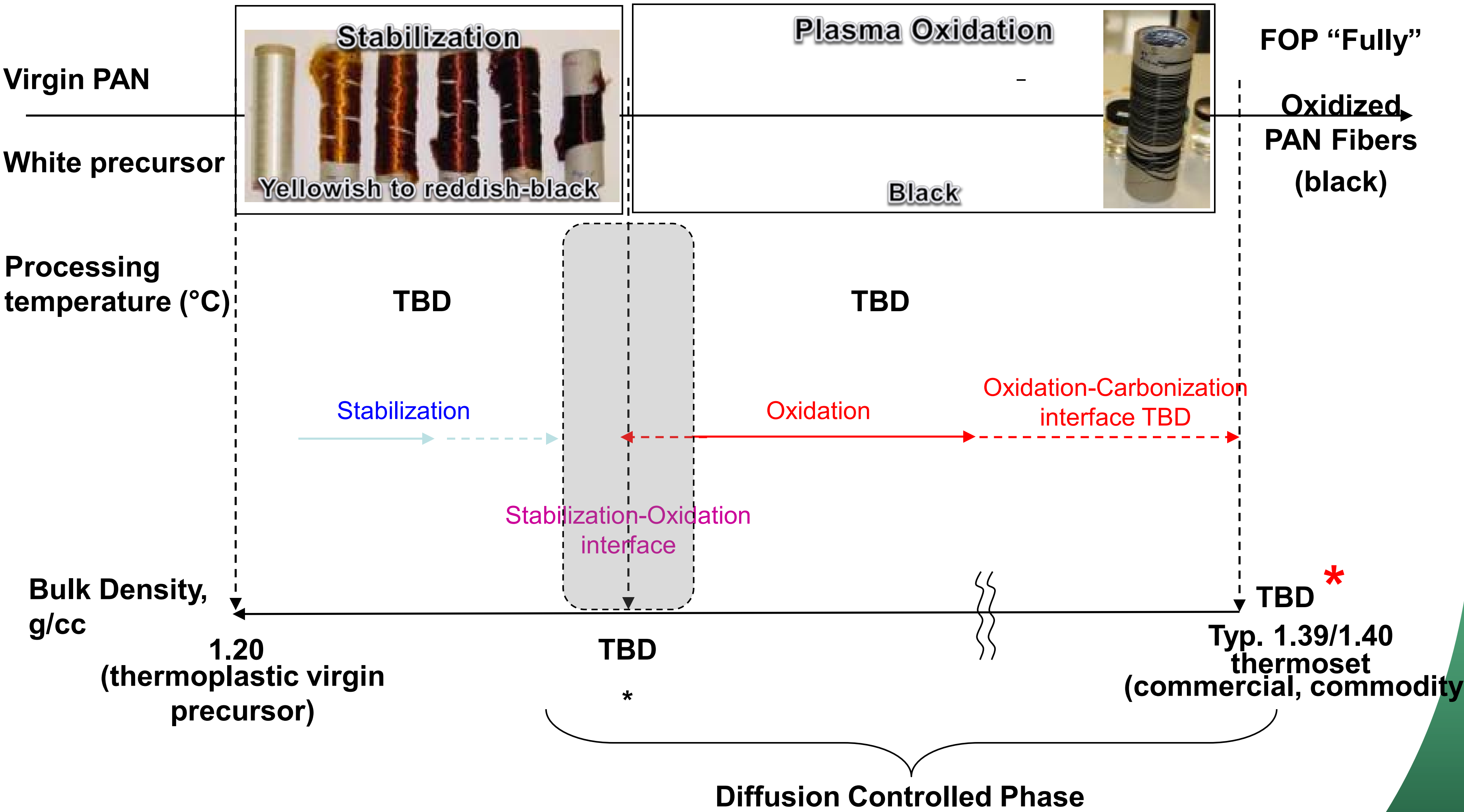
Oxidation Interfaces



Chronological Textile PAN Progress

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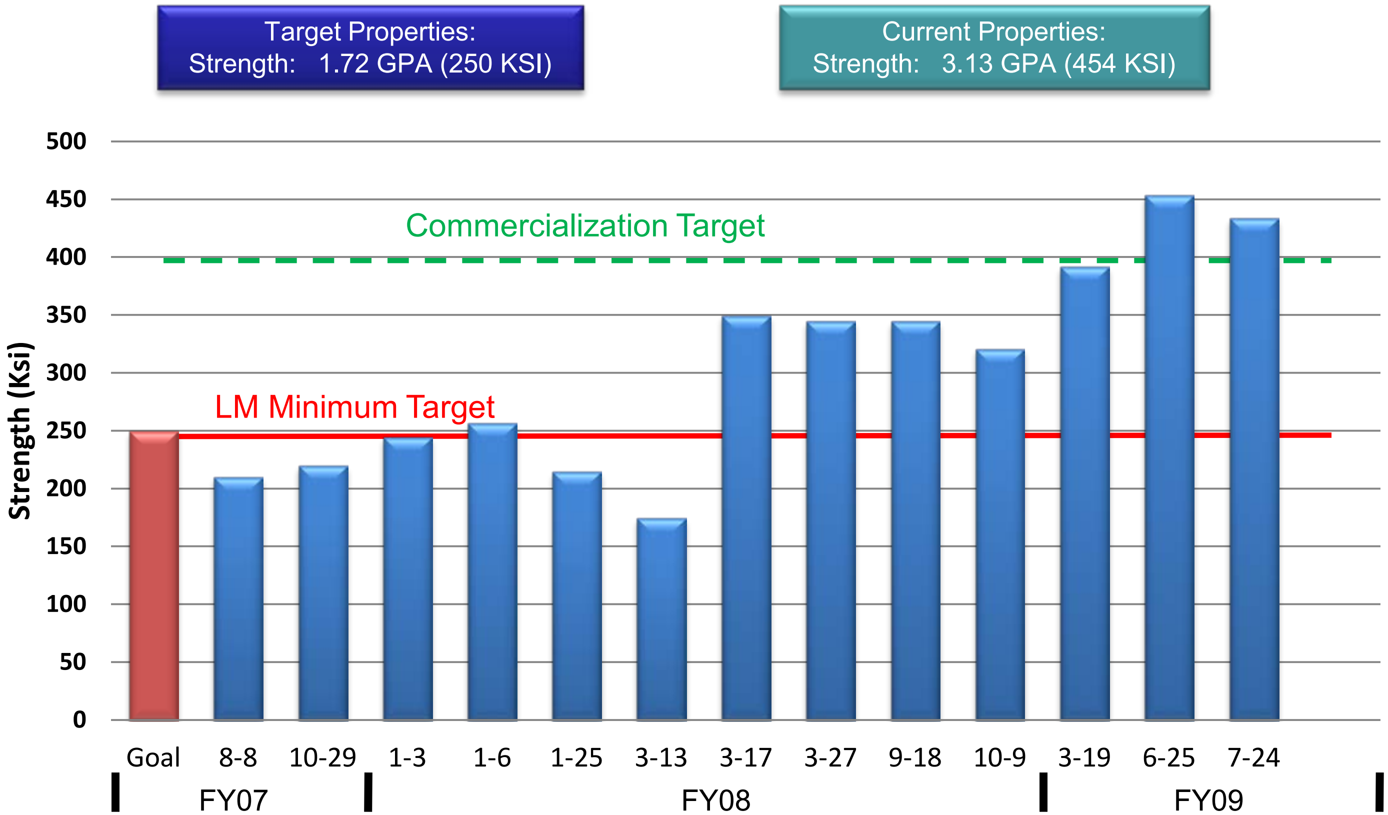
Conventional Conversion/Analysis of two PAN Precursors

As a reference, it took over two years to find the proper conversion conditions for the textile precursor. For the aerospace fiber, this time was reduced significantly (~3 months).



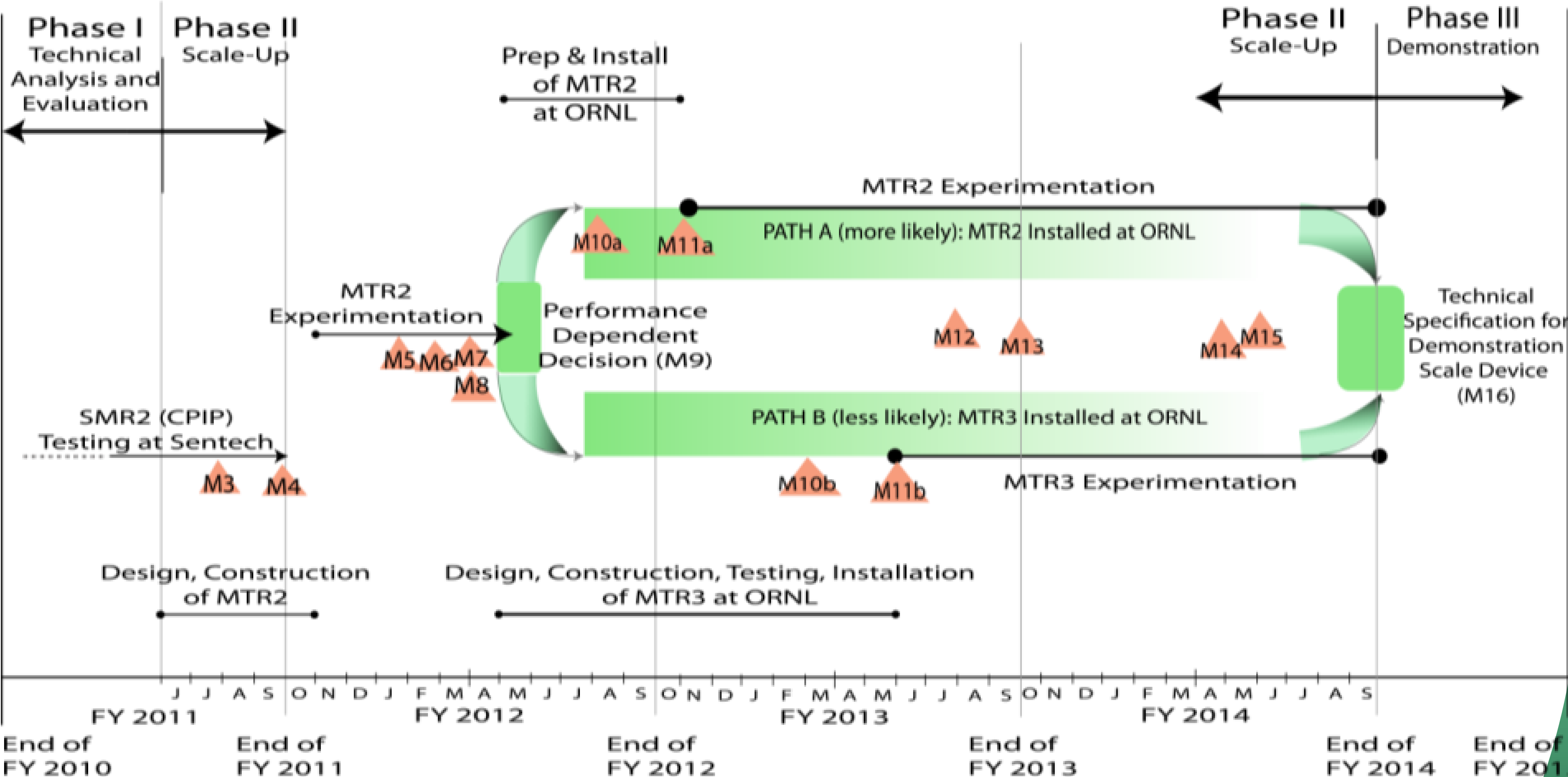
Phase II Initial Results (Multiple Tows) LM006

Phase II Mechanical Properties (Chronologically)

	Oxidized					Carbonized				
Sample	Date Oxidized	Fiber Diameter (um)	Peak Stress (ksi)	Modulus (Msi)	Strain @ Break (%)	Date Carbonized	Fiber Diameter (um)	Peak Stress (ksi)	Modulus (Msi)	Strain @ Break (%)
SR562 Fiber 1	1/19/2012					2/9/2012	8.08	216.6	25.7	0.81
						2/9/2012	7.75	165.7	27.5	0.59
						2/1/2012	8.05	205.3	25.0	0.78
						2/2/2012	7.83	230.1	26.5	0.82
						2/1/2012	7.80	220.4	26.0	0.80
SR563 Fiber 1	1/19/2012					1/27/2012				
						1/27/2012	7.82	247.2	26.5	0.89
						1/27/2012	8.53	188.5	23.5	0.77
SR563 Fiber 2	1/19/2012					1/27/2012	7.79	271.6	26.2	0.98
						1/27/2012	8.10	222	24.8	0.84
						1/27/2012	7.99	261.7	25.5	0.96
SR563 Fiber 3	1/19/2012					1/27/2012	8.15	217.2	24.7	0.84
						1/27/2012	8.31	206.7	23.8	0.83
						1/27/2012	8.03	222.7	25.1	0.84
SR566 Fiber 1	1/25/2012					1/30/2012	8.18	144.0	23.8	0.59
						2/3/2012	7.73	306.5	26.8	1.06
						2/6/2012	7.74	251.5	27.0	0.88
						2/3/2012	7.66	246.5	27.1	0.86
SR566 Fiber 2	1/25/2012					1/31/2012	7.99	236.7	25.4	0.88
						2/2/2012	7.93	294.4	25.5	1.08
						1/31/2012	7.98	221.4	26.5	0.80
						2/8/2012	7.74	247.2	27.7	0.84
SR566 Fiber 3	1/25/2012					1/31/2012	8.35	249.5	24.3	0.97
						2/7/2012	7.89	217.3	25.6	0.81
						2/6/2012	7.81	288.7	25.8	1.04
						2/10/2012	7.58	241.1	29.1	0.79
SR567 Fiber 1	1/26/2012									
						2/7/2012	7.83	206.5	26.8	0.73
SR568 Fiber 1	1/26/2012					2/9/2012	7.95	214.0	25.6	0.80
						2/8/2012	7.68	216.6	26.7	0.78

All with 32 minute residence time for CPIE plasma oxidation.

Oxidized mech data yet to be determined. Additional test results are forthcoming.


Phase I
Technical Analysis and Evaluation
Phase II
Scale-Up
Prep & Install of MTR2 at ORNL
Phase II
Scale-Up
Phase III
Demonstration
MTR2 Experimentation
PATH A (more likely): MTR2 Installed at ORNL
M10a
M11a
MTR2 Experimentation
Performance Dependent Decision (M9)
M5 M6 M7
M8
M12
M13
M14 M15
Technical Specification for Demonstration Scale Device (M16)
SMR2 (CPIP) Testing at Sentech
M3
M4
PATH B (less likely): MTR3 Installed at ORNL
M10b
M11b
MTR3 Experimentation
Design, Construction of MTR2
Design, Construction, Testing, Installation of MTR3 at ORNL
J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M A M J J A S
FY 2011
FY 2012
FY 2013
FY 2014
End of FY 2010
End of FY 2011
End of FY 2012
End of FY 2013
End of FY 2014
End of FY 2015