Melt Processable PAN Precursor for High Strength, Low-Cost Carbon Fibers

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Merit Review 2013
Status as of end of March 2013

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Project ID: ST093

U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY
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Overview

- **Timeline**
  - Start 2007
  - Project End date: 2015
  - ~33% completed
- **Budget**
  - FY11 $150K
  - FY12 $200K
  - FY13 $250K
- **Barriers**
  - High cost of high strength carbon fibers (CF)
  - CF account for ca. 65% of the cost of the high pressure storage tanks
- **Partners**
  - ORNL (Host side)
  - Virginia Polytechnic Institute (Virginia Tech – VT)
    - Prof. Dan Baird
    - Prof. J. McGrath

Relevance

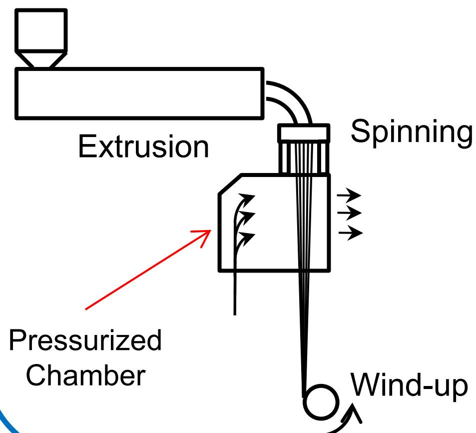
- Objective: to reduce the manufacturing cost of high-strength CF’s by means of:
  - Significant reduction in the production cost of the PAN-precursor via hot melt methodology
  - The utilization of PAN-VA polymer (vinyl acetate, not – MA, methyl acrylate).

This melt-spun PAN precursor technology has the potential the reduce the production cost of the high strength CF’s by ~ 30% [Kline Study, 2007].

Melt Spinning vs. Wet Spinning

Advanced Technology (for PAN)

Melt-processing

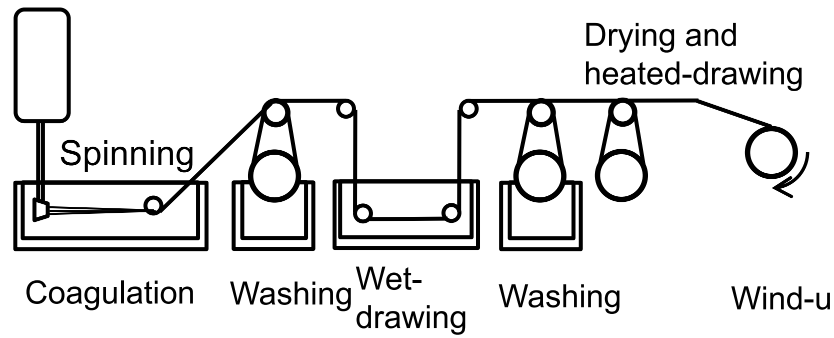


- Low production cost
- High production rate
- Environment-friendly

Current Technology

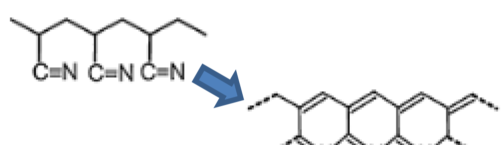
- **Capital intensive**
- **Solvent typically highly corrosive**
- **Significant solvent plant hold-up**

Solution-processing



Key technical issue:
Improve PAN melt stability by reducing the melt temperature ™ below the degradation temperature.

Why not for PAN-based precursor fiber?



(Crosslinking)

Rawwendaal, Polymer Extrusion, 4th Ed., 2001.

Encyclopedia of Polymer Science and Technology.

Technical Accomplishments FY11/12

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Hardware and Processing Comparison (Previously Presented)

VT/ORNL

	Nozzle Orifice Diameter (um)	Dope Filtration (um mesh)	Filament Draw-Ratio	Filament Voids	Filament Diameter (as-spun, um)
Initial	330/254	No filtration	3	Porosity Present	>100
	110	10 (2010)	From 2010 5/6	Porosity ≤1% vol	15 – 30 (40) (some variation)
	55 (11/2011)	5 (12/2011)			

VT/ORNL technology uses benign solvents, resulting in higher chamber pressure than BASF process.

The starting point for this project was based on 1980s BASF prior work.

BASF

Nozzle Orifice Diameter (um)	Dope Filtration (um mesh)	Filament Draw-Ratio	Filament Voids	Generated Filament (as-spun, um)
55 - 65	Not Indicated ("substantially homogeneous melt", patent indication)	6	Visible voids ≤ (0.1 - 0.2 um)	30 – 45 (50)

Presented in last Merit Review

Technical Accomplishments FY12/13

THEN

Carbonized ORNL/VT PAN precursor (CF)

First round of results were discouraging.

Date of carbonization	Sample name	diameter [μm]	Peak stress [ksi]	Modulus [Msi]	Strain [%]
Feb. 2012	VT_201201	Could not be unspooled			
Apr. 2012	VT_201203	11.58	76.5	16.1	0.52
Jun. 2012	VT_201205	10.55	77.4	6.2	1.67

Issues:

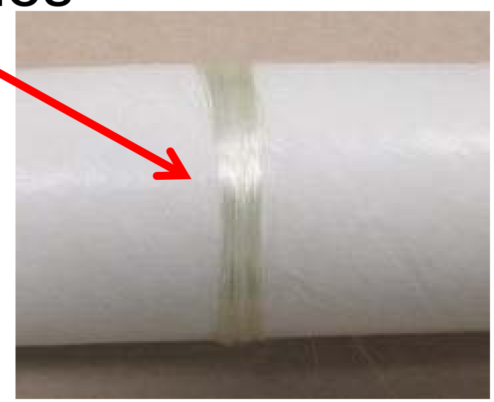
- Originally could not unspool fiber until Apr 2012.
- Impurities in dope due to improper level of filtration.
- Inadequate spinning equipment.
- No post-treatment equipment.
- Stretching was performed only during oxidation stage of conversion into carbon fiber.

Thus – low mechanical properties!

Technical Accomplishments FY13

- **Improvement in the filament generation system:**
  1. **Incorporation of a finer filtration system for polymeric dope.**
     - **Solid impurity in the PAN dope lead to clogging of the spinnerets and/or filament breakage. A fine 5 µm filter screen was installed.**
  2. **Fabrication of new spinnerets with small holes.**
  3. **Redesign of the pressure chamber and fiber take-up device.**
     - **Initially the filaments were being wound on top of each other (statically), making tow unwinding impossible (interfilamentary entanglement).**

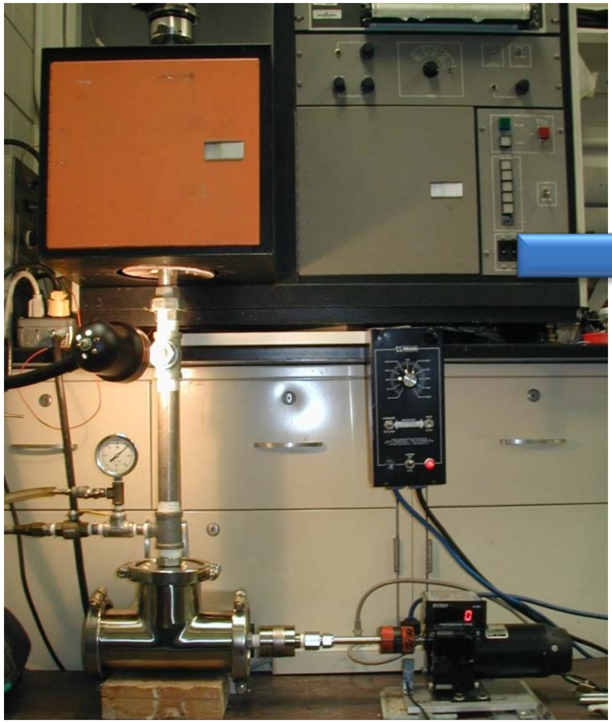
Examples

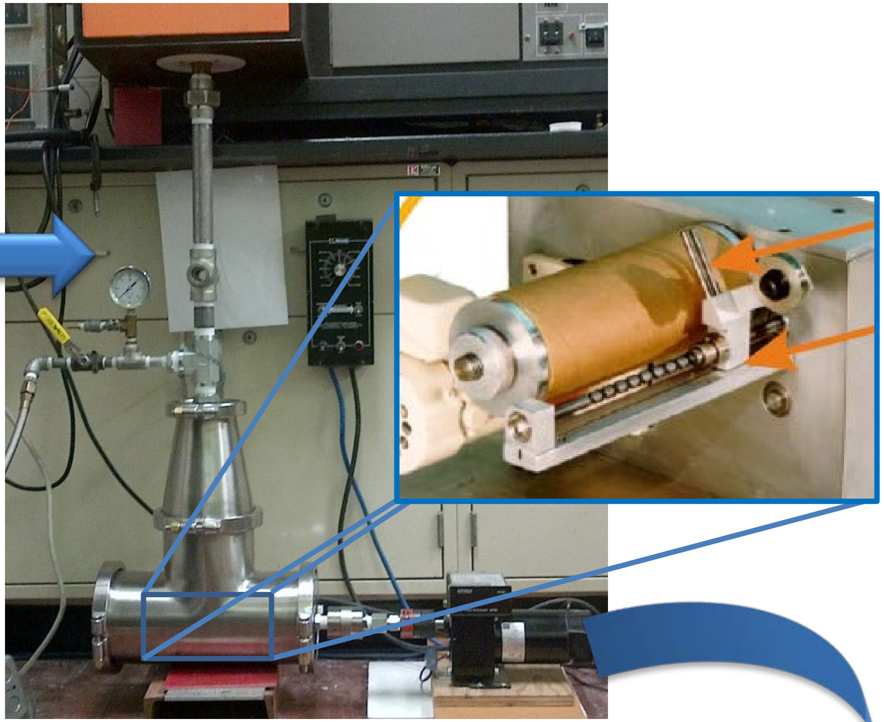


- **To solve this problem, a new take-off device with traverse fiber guide was designed and installed inside the chamber. However, it was also necessary to enlarge the pressure chamber itself.**

Technical Accomplishments FY13

Newly improved fiber spinning system.

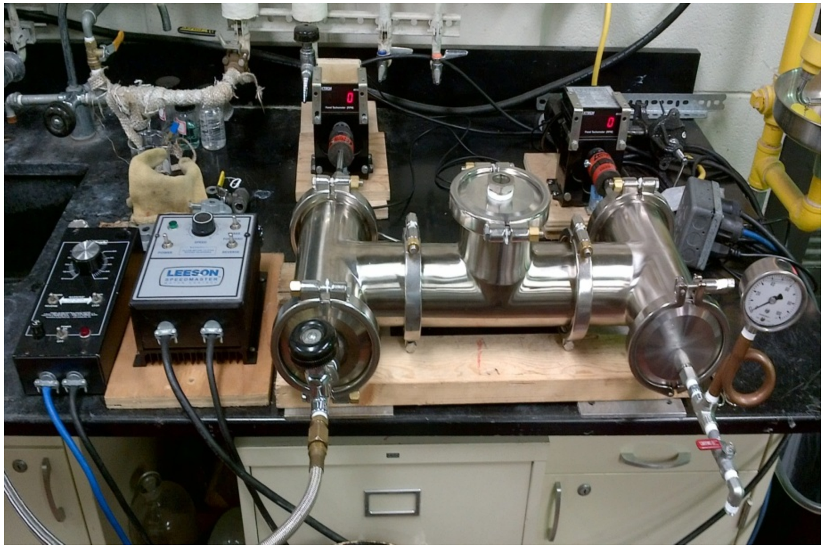




Melt spun fibers generated with new system/winder with traverse fiber guide.

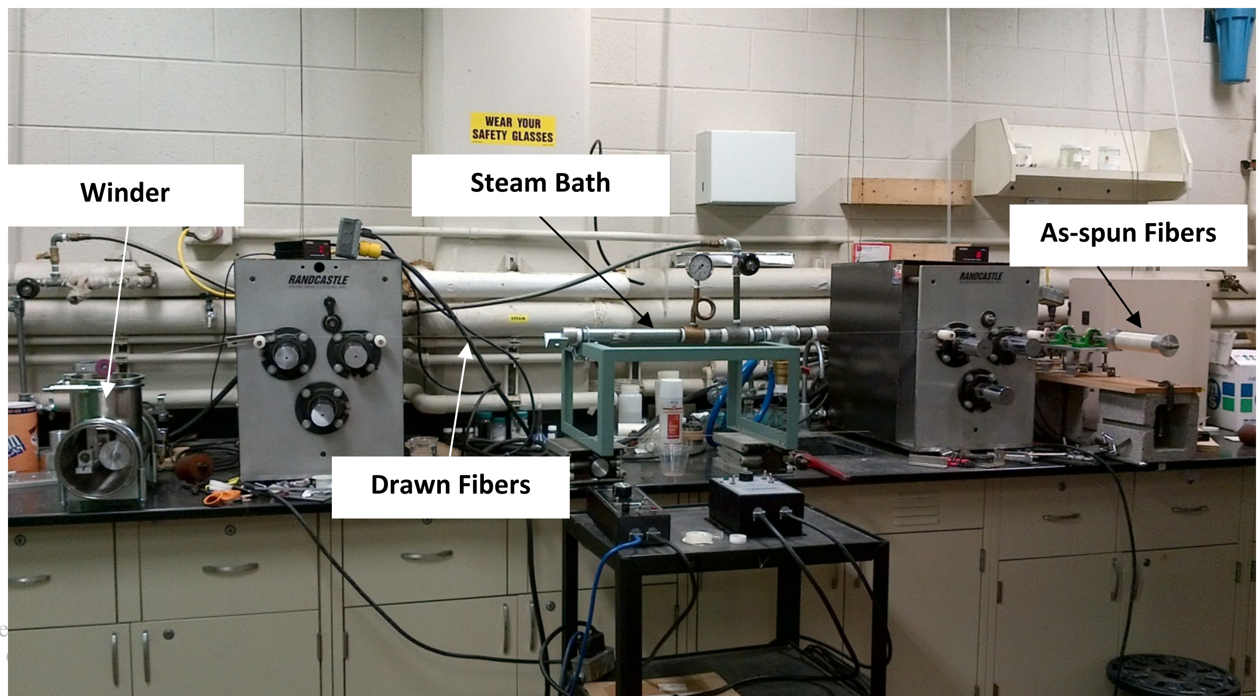
Technical Accomplishments FY13

Precursor Post Treatment Stages

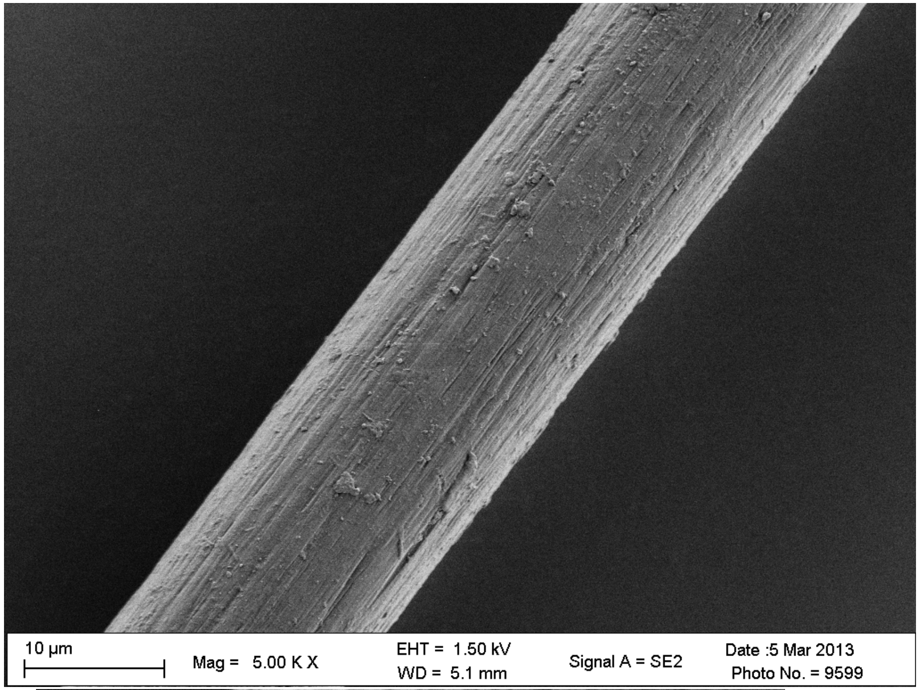


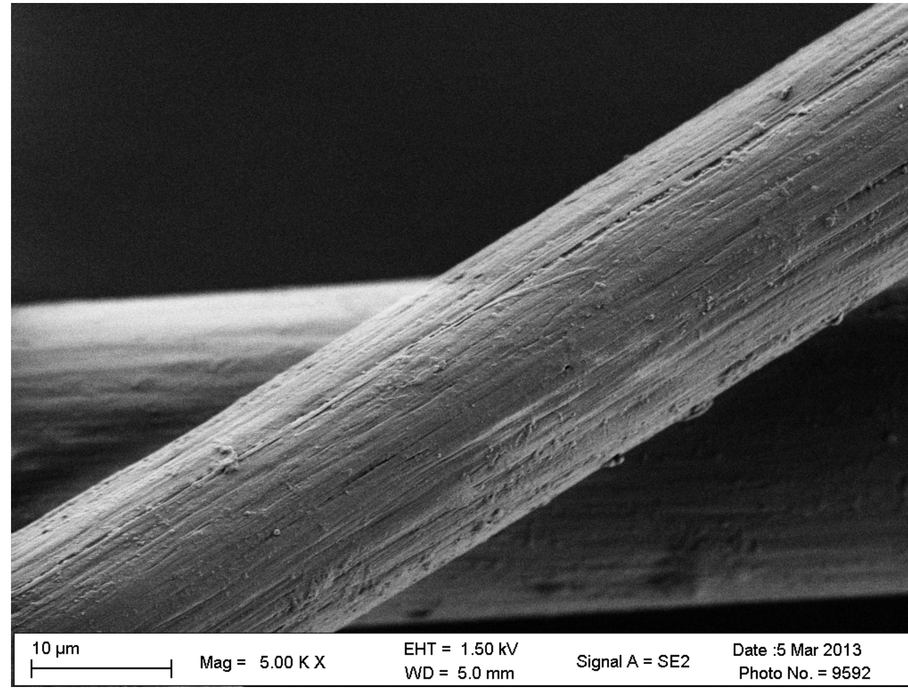
Left: Initial steam chase with a basic two-roller system. Stretching is achieved by differential rpm on each roller. (batch system)

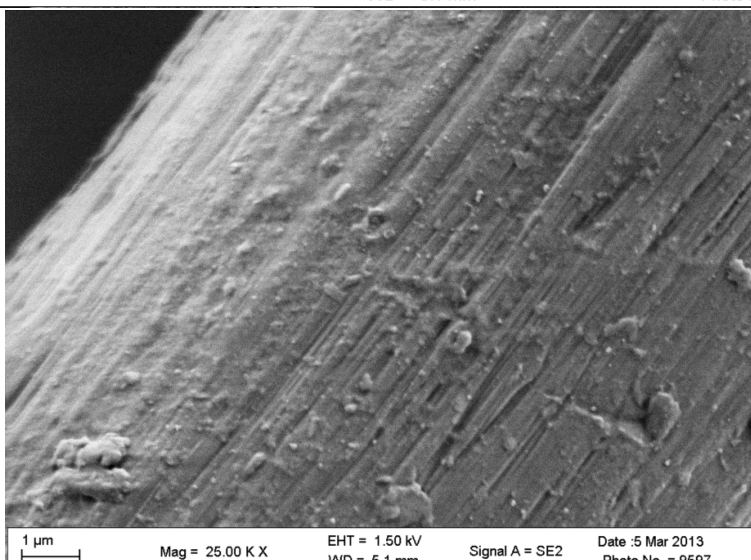
Below: A continuous stretching system with an inline steam bath.



Technical Accomplishments
ORNL/VT Stretched PAN Precursor
Dec 2012



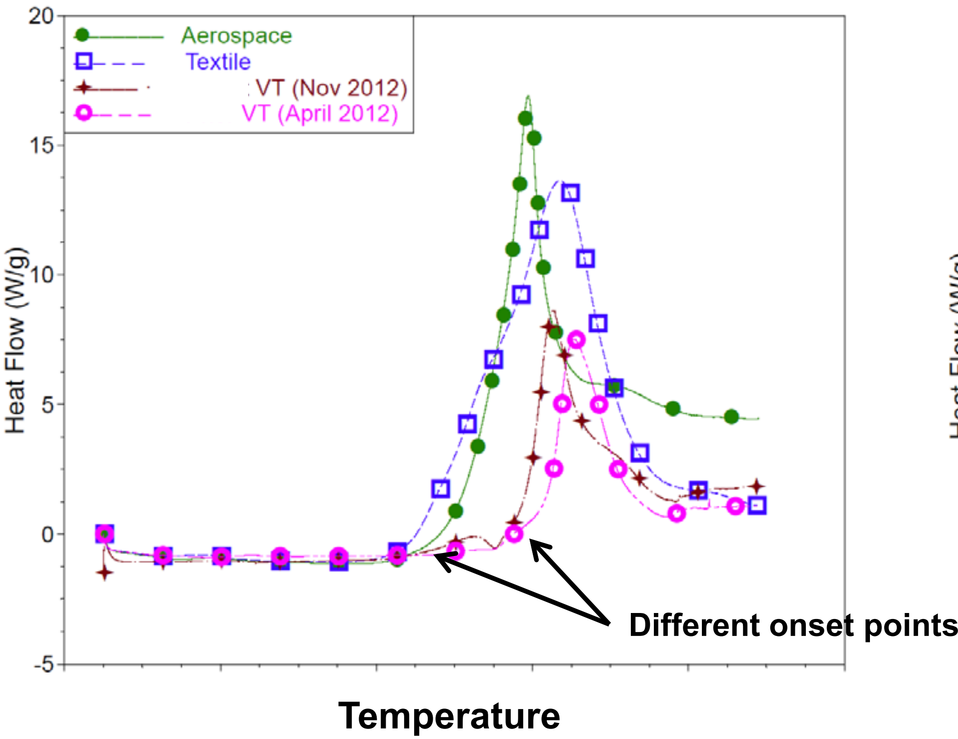


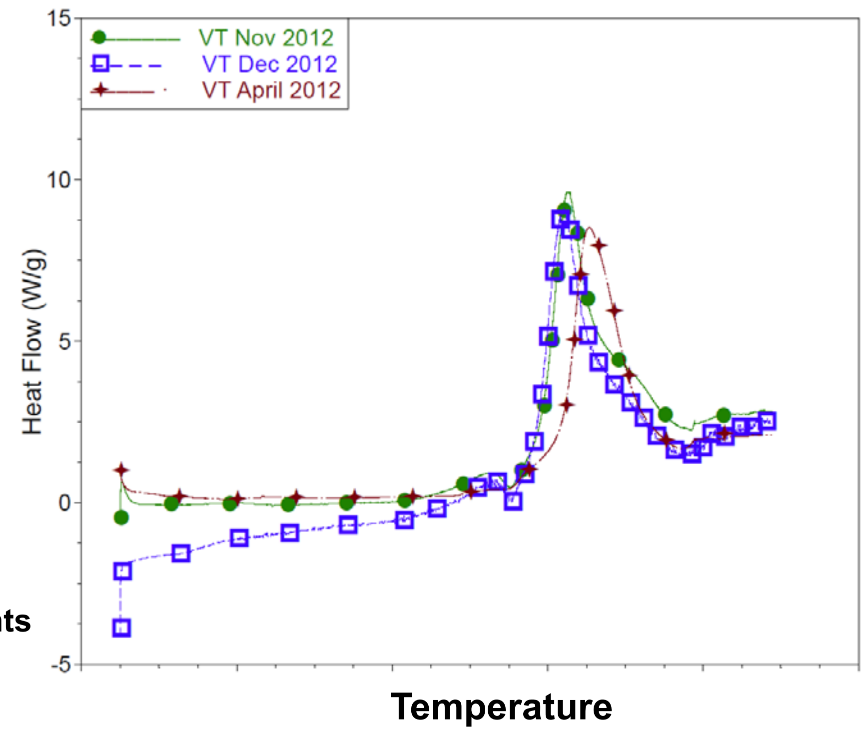


- Precursor with very well aligned external fibril structures.
- No external pores
- In general, matches PAN precursor characteristics

Technical Accomplishments FY13

DSC Thermograms for VT/ORNL PAN Fiber





While there are some differences between exothermic behavior of melt-spun PAN fibers and wet-spun PAN commodity-grade fibers, the potential for conversion of the VT/ORNL fibers is there. (Qualitative comparison of the shape and characteristics of the DSC thermal curves show good similarities).

Progress Status FY12/13

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PAN Precursor Filaments Mechanical Property Comparison

PAN BASED PRECURSORS				MECHANICAL PROPERTIES (Standard deviation between parentheses)				
Components	Name	Type of sample	Tow	Fiber diameter, µm (SD)	Peak stress, KSI (SD)	Modulus, MSI (SD)	Strain at break, % (SD)	
Industrial precursors								
AN/VA	FISIPE	Low Grade Textile	26k	14.15	54.2 (8.5)	0.5 (0.1)	15.7 (0.9)	
AN/MA	COURTAULDS	Commodity	50k	11.7	73.5 (10.5)	1.5 (0.4)	11.21 (1.36)	
AN/MA	Aerospace	Aerospace	3k	12.9	76.6 (5.6)	1.7 (0.2)	10.53 (0.76)	
ORNL/VT Achievements								As-Spun No Post-treatment (no secondary stretching)
Presented in Merit Review 2012	PAN-VA_12%H2O		3/2010	67.1 (3.1)	37.6 (3.7)	1.0 (N/M)	11.89 (1.16)	
	PAN-VA(II)_12%H2O		7/2010	53.8 (4.8)	35.3 (4.0)	1.0 (N/M)	10.76 (1.08)	
	PAN-VA		11/2011	30-40	45.3 (5.72)	1.2 (0.15)	8.84 (0.67)	
VT May 2012 Precursor			5/2012	23.5*	33.90	1.18	8.97	With Post-treatment – secondary stretching
FY13: VT Nov 2012 Precursor			11/2012	21.5*	51.60	1.90	10.40	
FY13: VT Dec 2012 Precursor			12/2012	20.2*	60.70	2.10	9.60	

*Diameter range averaged 15-23 um

Progress Status FY12/13

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Carbonized ORNL/VT PAN precursor (CF)

NOW

2nd round better: Highlighted values surpass March Milestone

Progressing

Date of carbonization	Sample name	diameter [µm]	Peak stress [ksi]	Modulus [Msi]	Strain [%]
Feb. 2012	VT_201201	Could not be unspooled			
Apr. 2012	VT_201203	11.58	76.5	16.1	0.52
Jun. 2012	VT_201205	10.55	77.4	6.2	1.67
Mar. 2013	VT_20121129_S4_A	8.20 (1.19)	143.7 (44.1)	20.1 (1.8)	0.70 (0.2)
	VT_20121129_S4_B	9.65 (1.19)	132.1 (44.9)	17.1 (0.8)	0.7 (0.2)
	VT_20121129_S4_C	9.49 (1.27)	122.1 (33.2)	14.2 (2.4)	0.8 (0.2)
	VT_20121129_S5_A	8.24 (1.30)	129.3 (48.2)	26.8 (8.6)	0.5 (0.3)
	VT_20121129_S5_B	8.81 (1.35)	132.1 (42.1)	21.6 (8.8)	0.7 (0.3)
	VT_20121129_S6_A	8.34 (.12)	198.7 (70.5)	23.6 (.85)	0.81 (0.3)
	VT_20121129_S6_B	7.34 (.74)	222.4 (84.0)	22.4 (2.6)	0.94 (0.3)
	VT_20121129_S7_A	**8.04 (.79)**	**261.4 (67.2)**	**25.3 (3.1)**	**1.0 (0.2)**
	VT_20121129_S7_B	7.24 (.96)	212.0 (31.8)	20.8 (1.1)	1.0 (0.1)
	VT_20121129_S9_A	7.01 (1.03)	104.0 (1.7)	25.5 (2.8)	0.4 (0.0)
	VT_20121129_S9_B	6.91 (.74)	215.7 (113.2)	27.0 (2.5)	0.8 (0.4)

Standard Deviation in parenthesis

Better: diameters, post-spin stretching capabilities, mechanical properties.
Sample **S7_A** (**in bold**) *surpasses* the September 2013 milestone as well.

Technical Accomplishments FY13

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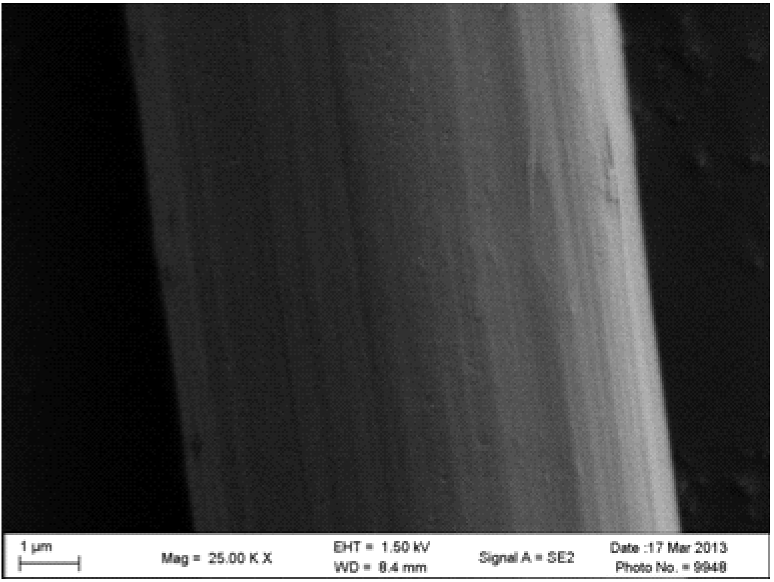
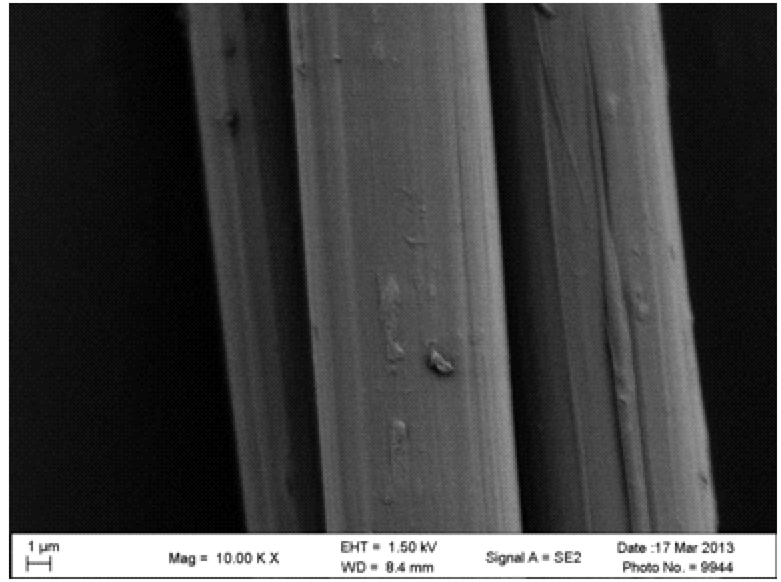
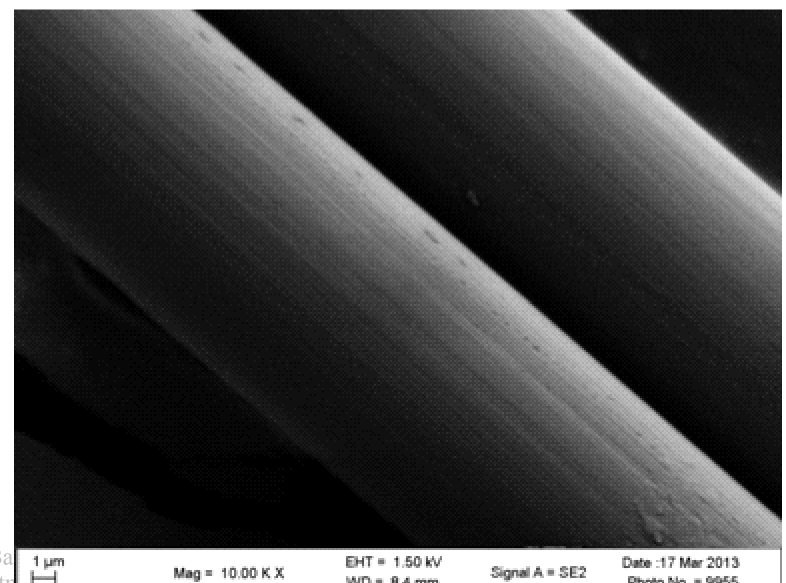
ORNL/VT Carbonized PAN Fiber/Carbon Fiber





Sample II

Sample III



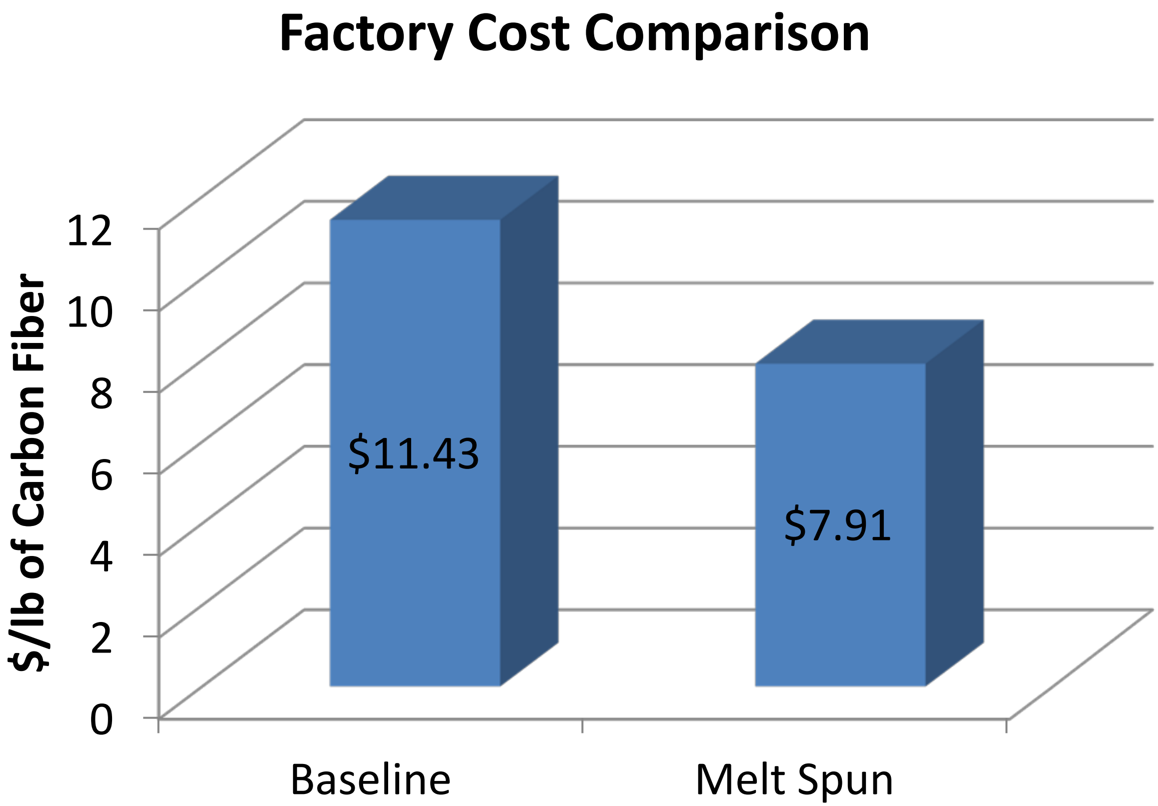
- Very good outside surface.
- No detectable damage.
- No notching or cracking perpendicular to length.
- Fibers show typical diameter for carbon fiber.

FY13 Milestones
Precursor Development

Task No.	Title	Milestone/Deliverable Description	Planned Completion Date
1	Spinning of 10m tow	Demonstrate spinning of a 10-m sample tow of ~10-12 micron fibers from high molecular weight (>200,000 MW) dope that can be easily spooled and de-spooled.	01/2013 **Completed**
2	Conversion into Carbon Fiber	Conversion of above sample at ORNL's Precursor Development System and yielding 15 Msi modulus and 150 ksi strength.	03/2013 **Completed**
3	Spinning of 10m 0.1k tow	Demonstrate spinning of a 10-m continuous ~100 filament tow of ~10-12 micron fibers from high molecular weight (>200,000 MW) dope that can be easily spooled and de-spooled for conversion at ORNL's Precursor Development System and yielding 20 Msi modulus and 200 ksi strength.	09/2013 **In Progress, Partially Met**

Potential CF Cost Matrix

Estimated Cost Savings of Finished Carbon Fiber Based on Implementation of This Technology



The main benefit is the increase in throughput of the precursor production.

This represents ca. 31-33% savings in cost.

***Factory cost* is the manufacturer's cost to produce finished CF's. These cost estimates are derived primarily from the 2007 Kline reports and are based on petrochemical prices in CY2007Q1. Estimates based on oil at $60/bbl.**

Conclusions

- **After successful introduction of the post-spinning stretching, filaments acceptable for carbonization were achieved.**
- **In spite of all the technical difficulties encountered over the course of this project, significant breakthrough was achieved this year by carbonizing the first stretched fiber samples of PAN precursor.**
- **All work to date was accomplished with vinyl acetate (VA) as the comonomer. Any comparison has to be made with other VA-based precursor or carbon fiber.**
- **Two FY13 milestones were met (January and March 2013). The September 2013 milestone is already partially met.**

Future Work

- **Rest of FY13**
  - **Conversion of PAN filaments (processed with different parameters) into carbon fibers**
  - **Consideration towards scalability, more and longer filaments and/or tows**
  - **Outline fundamentals towards the production of tows with longer length and higher filament count**

- **Future**
  - The results of the work to date will need to be verified with a different comonomer (MA). In addition, further increase the mechanical property values, and make the move towards scaling up will be necessary.
  - **As indicated in the last AOP, the intended mechanical property targets are:**

Modulus, Msi	Tensile Strength, ksi	Estimated Date
25	300	March, 2014
30	450	September, 2014
33	600	September, 2015

Summary

Relevance

- This technology will increase the throughput in the production of PAN precursor and will definitely decrease the cost of precursor production.

Approach/Strategy

- This work was based on prior abandoned work by BASF.
- To make possible the hot melt spinning of PAN precursor, innovative technical and chemical improvements were required.

Technical Accomplishments

- Feasibility was demonstrated after significant challenges and effort.

Collaboration and Coordination

- ORNL worked closely with two departments at Virginia Tech –Chemistry Dept. – Prof. James McGrath for polymeric alterations/modifications and Chemical Eng. Dept. – Prof. Don Baird for rheology and filament spinning/generation.

Future Work

- Now that feasibility has been demonstrated, the main two tasks ahead of us are the refinement and scale-up of the process. For this reason, this project requires a reevaluation of the tasks as a function of the current allocation of resources.

Thanks

Questions?

TECHNICAL BACKUP SLIDES

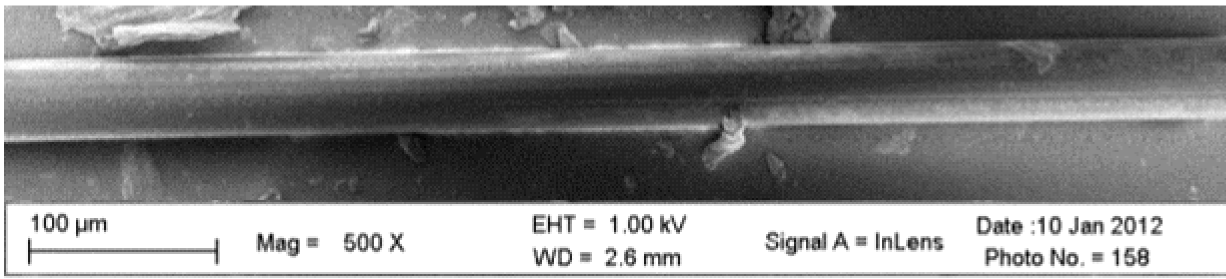
Melt-Spun PAN Precursor has a history of prior R&D

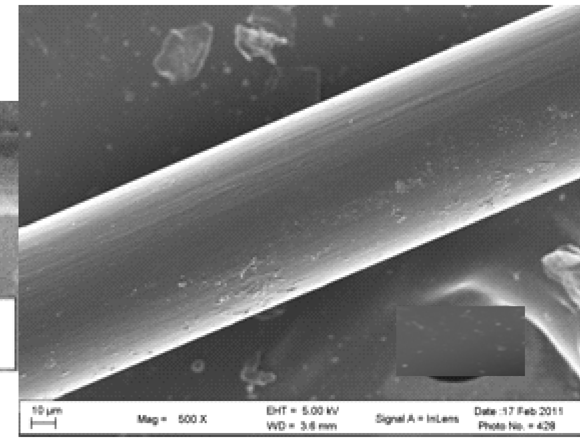
- BASF* developed melt-spun PAN precursor in the 1980s.
  - CF's were qualified for B2 bomber
  - Demonstrated 400 to ~600** KSI fiber strength and 30 – 40 MSI modulus; even better properties were thought to be achievable
  - AN content was 95% - 98% (consistent with high strength)
- Lower production cost than wet-spun fibers by ~30%.
  - Typical precursor line speed increased by ≥ 4X at winders
- Program was terminated in 1991 due to CF market collapse at cold war's end, a forecasted long (~ 10 yr) recovery period, and solvent issues (acetonitrile, nitroalkane).
- This work has produced various US patents and publications.

*ACC: American Cyanide Company
**DOE programmatic requirement: ≥650 KSI

Technical Accomplishments FY13

- **Incorporation of post-spinning treatment (stretching):**
  - **As-spun, the generated filaments have large diameters (25-40 µm)**





- **Matches the range of as-spun filament diameter of the prior work.**
- **Fibers are too big for conventional oxidation.**
- **Fibers indicates a low level of molecular orientation.**

Thus,
A post-treatment stage is necessary to improve the quality of the fiber.
(The prior R&D work had this post treatment stage as well.)
After this stretching treatment, the prior-work diameter was matched.

Filament Generation System Comparison BASF vs. VT/ORNL

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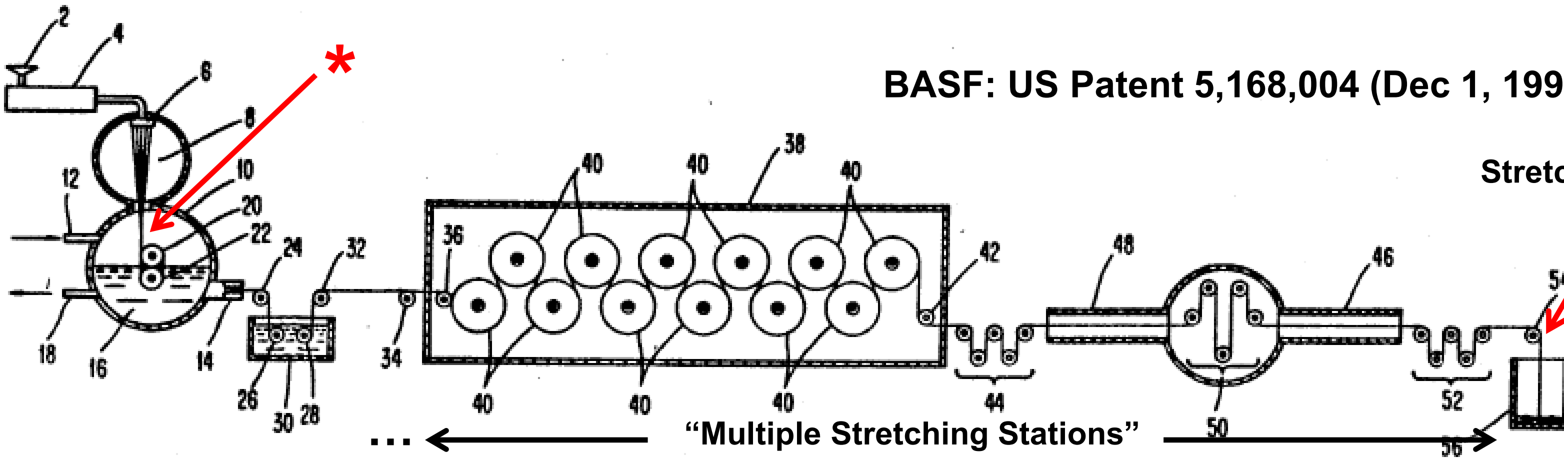
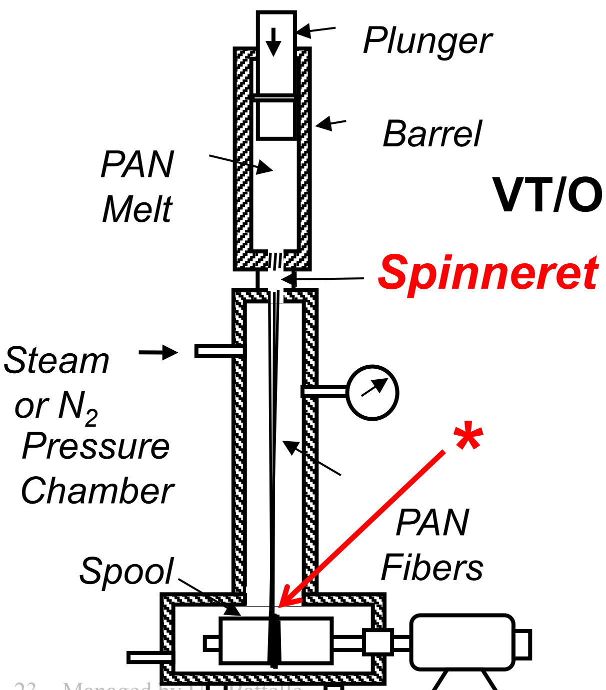
BASF: US Patent 5,168,004 (Dec 1, 1992)





VT/ORNL

*** As-spun condition at this point**

- **The as-spun BASF fiber are subjected to typical stretching post-treatment after spinning resulting in a tensile strength in the range of 75-90 ksi.**
- **Initially, VT/ORNL fibers were as-spun only. They are not yet subjected to stretching post-treatment.**

Technical Accomplishments FY13

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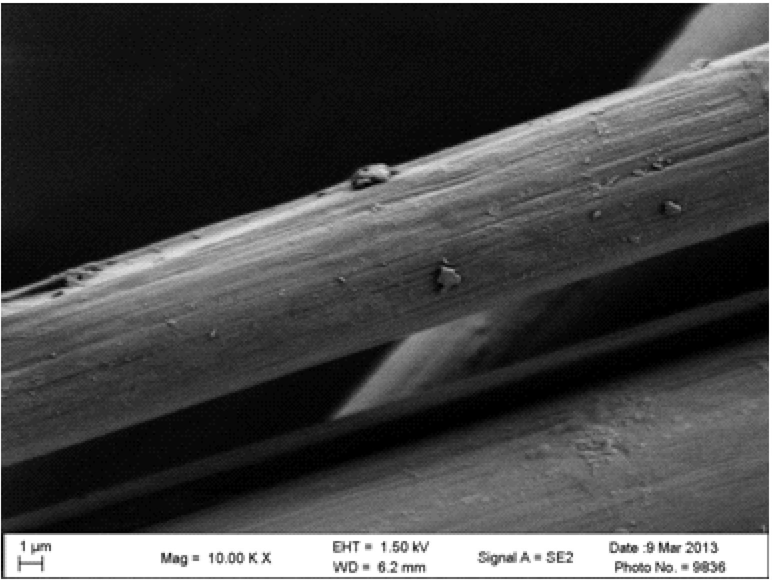
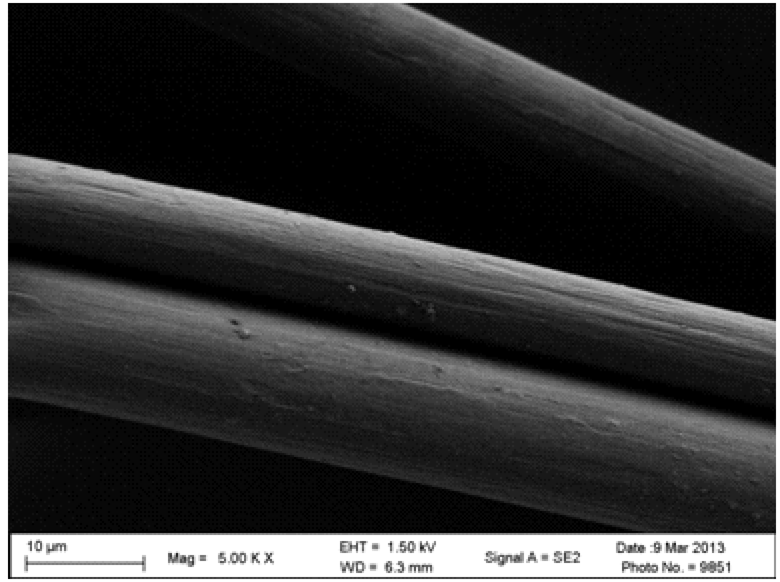
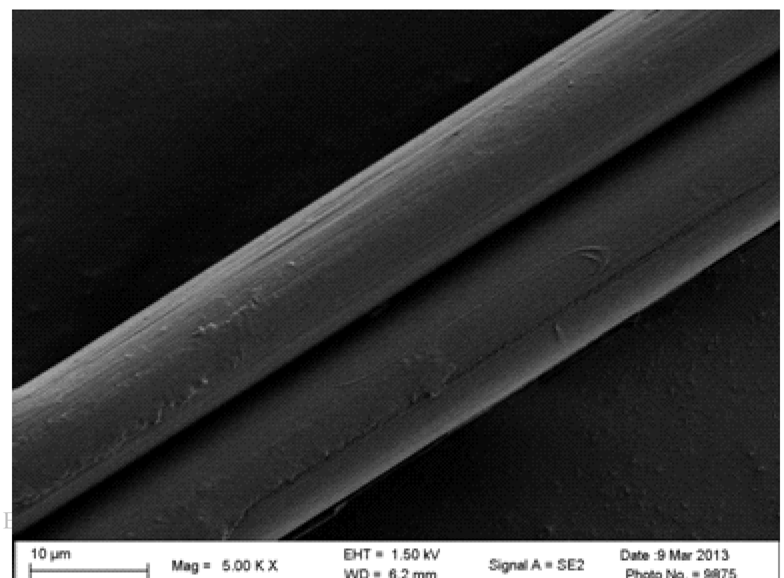
ORNL/VT Oxidized PAN Fiber (prior-stretched precursor)

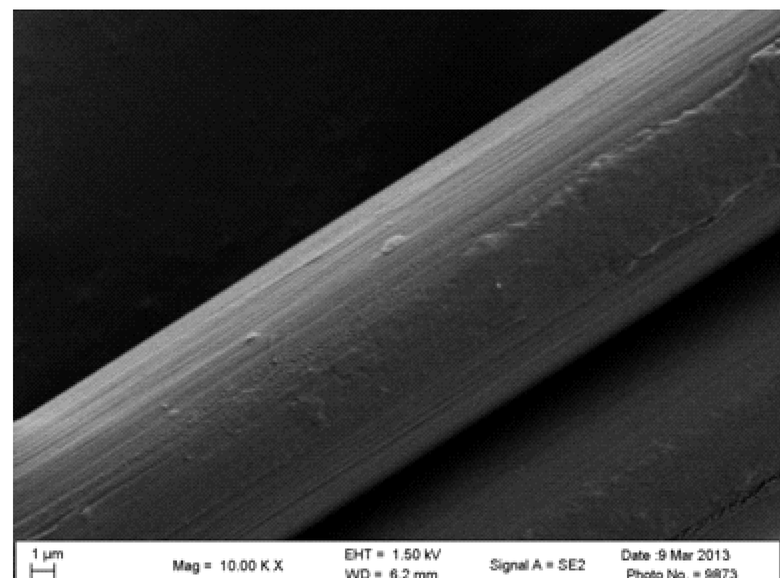




Sample 2

Sample 5





Unique ORNL Capability

- **Precursor Evaluation System (PES)**
  - Designed for development of conventional processing recipes with limited quantities of precursor
  - Residence time, temperature, atmospheric composition, and tension are independently controlled in each oven or furnace
  - Can process single filament up to thousands of filaments
  - Precise tension control allows tensioned processing of ~20-filament tows
  - Single stage or multiple stage evaluation during conversion

- **Conventional Pilot Line (PL)**
  - 1:20 scale of a commercial grade production line
  - Capacity for 8 tows
  - Upgrades underway for automated operation and production of high strength CF
  - Unique capability among FFRDC's and universities

This high strength CF project is benefiting from a decade of prior development in CF R&D at ORNL