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

May 17, 2012

Status as of end of February 2012

Dr.–Eng. Felix L. Paulauskas
MS&T Division

Oak Ridge National Laboratory
Phone: 865-576-3785
Email: paulauskasfl@ornl.gov

Project ID: ST093

U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY
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Overview

- **Timeline**
  - Start 2007
  - Project End date: 2015
  - ~20% completed
- **Budget**
  - FY07 $600K
  - FY08 $0
  - FY09 $200K
  - FY10 $200K
  - FY11 $150K
  - FY12 $200K
- **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 application of advanced CF conversion technologies (in) development at ORNL to down selected formulations.**

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].

High Strength CF Projects

- Two well-defined, complimentary high strength CF (HS-CF) projects are ongoing:
  - Short Term (fast track approach):
    - Title: "Development of Low-Cost, High Strength Commercial Textile Precursor (PAN-MA)" Oral Presentation, May 17, 2012 (1:45pm), ST099.
    - Based on alternate chemistry wet-spun textile PAN-based commodity grade previously-developed conversion/technology.
  - Long Term Approach/Disruptive Technology (this project):
    - Title: "Melt Processable PAN Precursor for High Strength, Low-Cost Carbon Fibers."
    - Key technical issue: Improve PAN melt stability by reducing the melt temperature (Tm) below the degradation temperature.
    - Requires thorough basic scientific investigation (new polymer chemistry) to generate the proper polymer feedstock.
    - The precursor filament generation requires a novel technological approach to spinning: proper design of the spinneret integrated with an inline pressurized chamber coupled to an internal take-up winder device.

Melt Spinning vs. Wet Spinning

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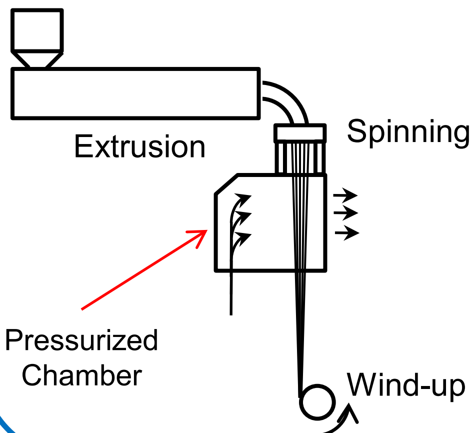
Advanced Technology (for PAN)

Melt-processing

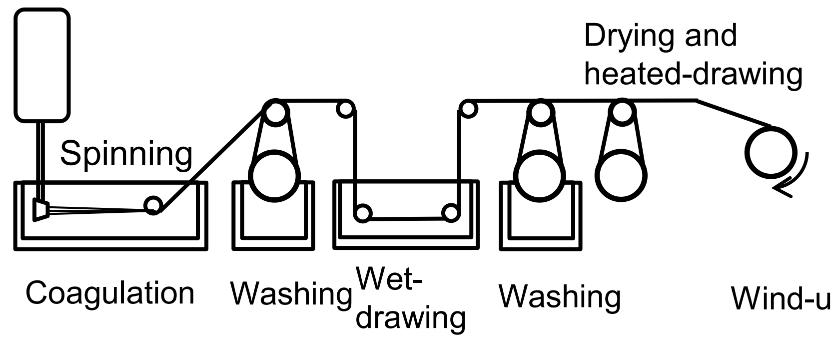


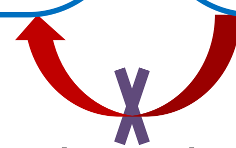
- Low production cost
- High production rate
- Environment-friendly

Current Technology

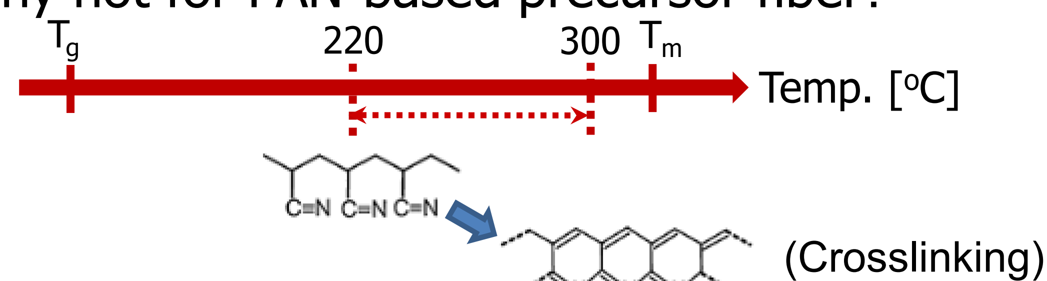
- **Capital intensive**
- **Solvent typically highly corrosive**
- **Significant solvent plant hold-up**

Solution-processing





Why not for PAN-based precursor fiber?



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

Encyclopedia of Polymer Science and Technology.

Melt-Spun PAN Precursor is Partially Proven Technology

- BASF developed melt-spun PAN precursor in the 1980's.
  - 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)
- Significantly 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).
- Various US Patents and publications are available from this initial BASF development time.

*Future HS-CF will need values around 650-700 KSI

Development of new fiber spinning system with multi-hole spinneret

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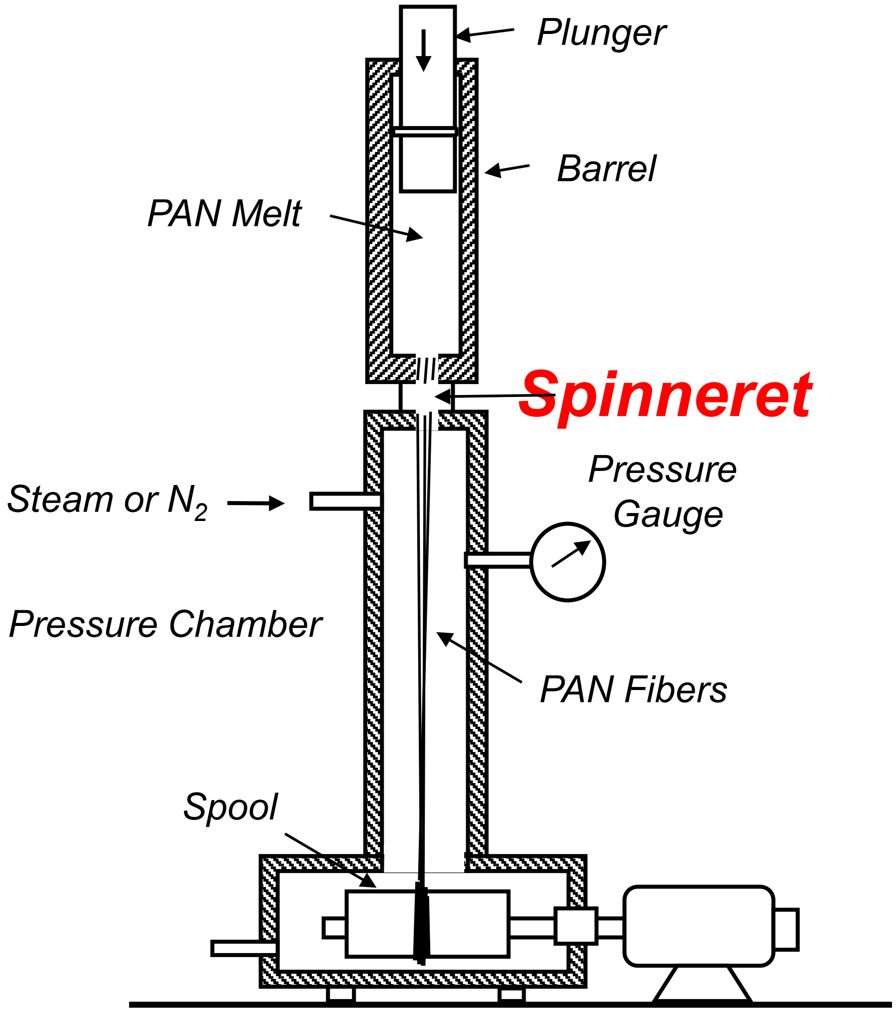
(At Virginia Tech)



Design	Hole No.	Diameter (um)	Work?
1	4	330	Yes
2	10	254	Yes
3	18	110	Yes
4	18	55	Yes

Fiber Take-up Creel Chamber

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(At Virginia Tech)

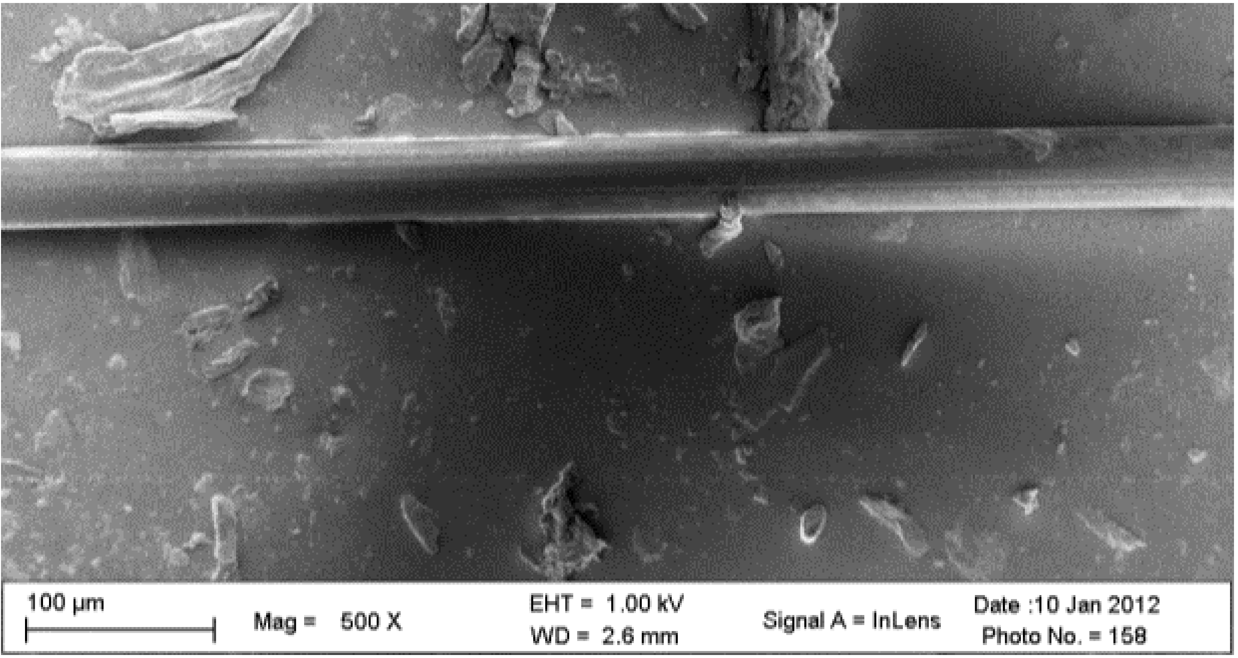
Fiber Images

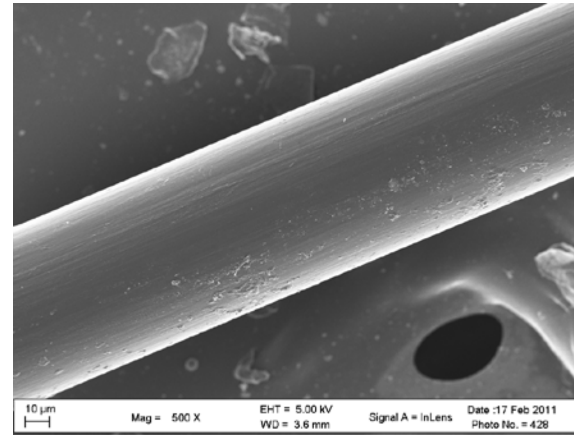
January 2012

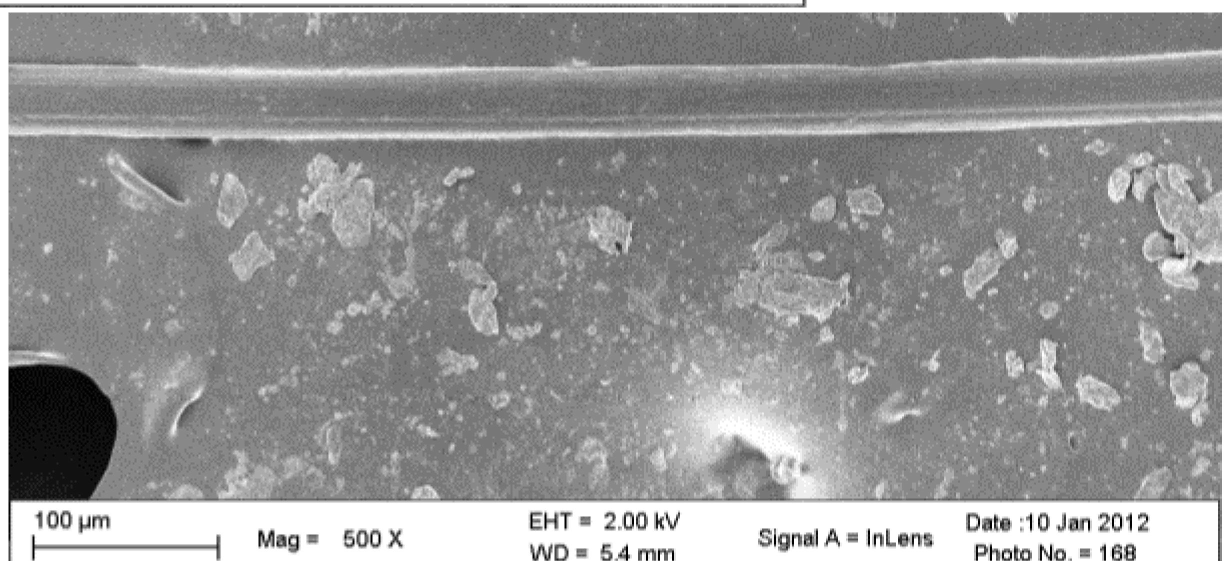
December 2011

(Fiber generated at Virginia Tech)

PAN/VA (II) Various Proportions of H_2O

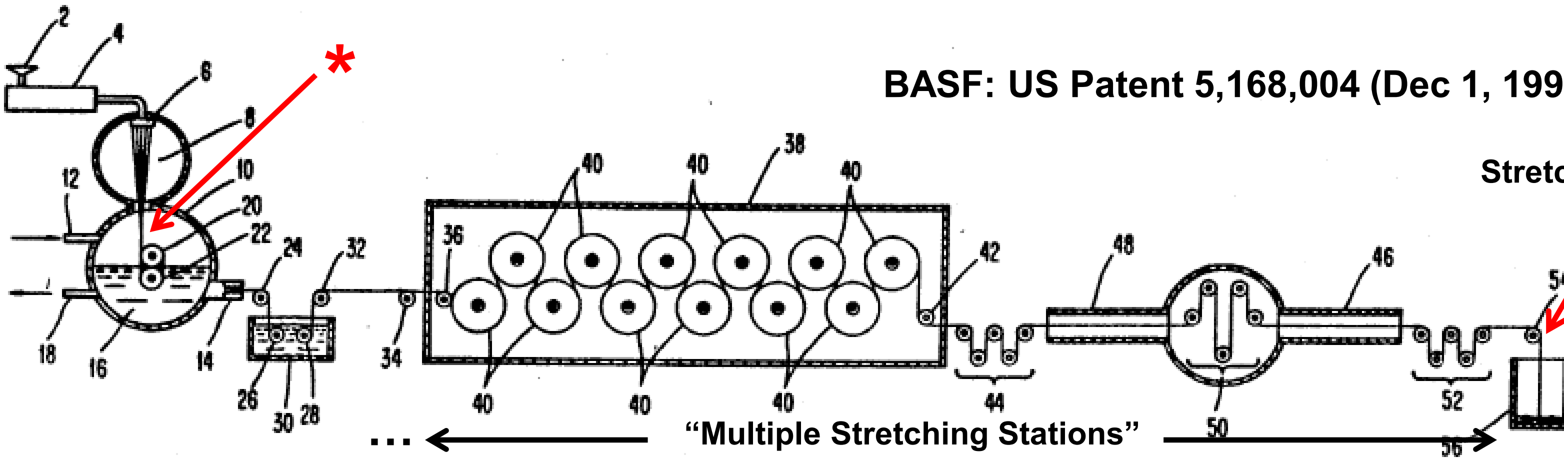


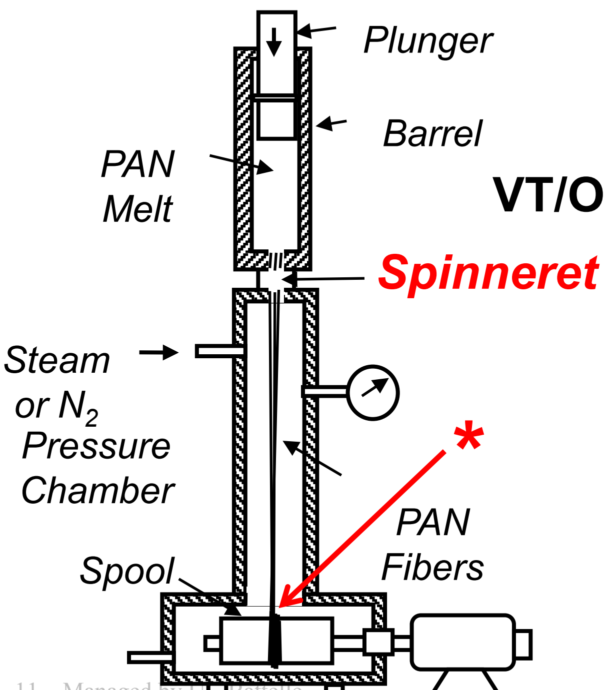




Filament Generation System Comparison BASF vs. VT/ORNL

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.**
- **VT/ORNL are as-spun only. They are not yet subjected to stretching post-treatment.**

Progress Status FY10/11

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PAN Precursor Filaments Mechanical Property Comparison

In spite of the technical challenges of this new melt-spun method, advances have been made in achieving promising mechanical properties.

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				SD – Standard Deviation			
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 (All as-spun)							
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)

BASF's patents do not yield information on mechanical values as spun fiber

DSC Thermograms for VT/ORNL PAN Fiber

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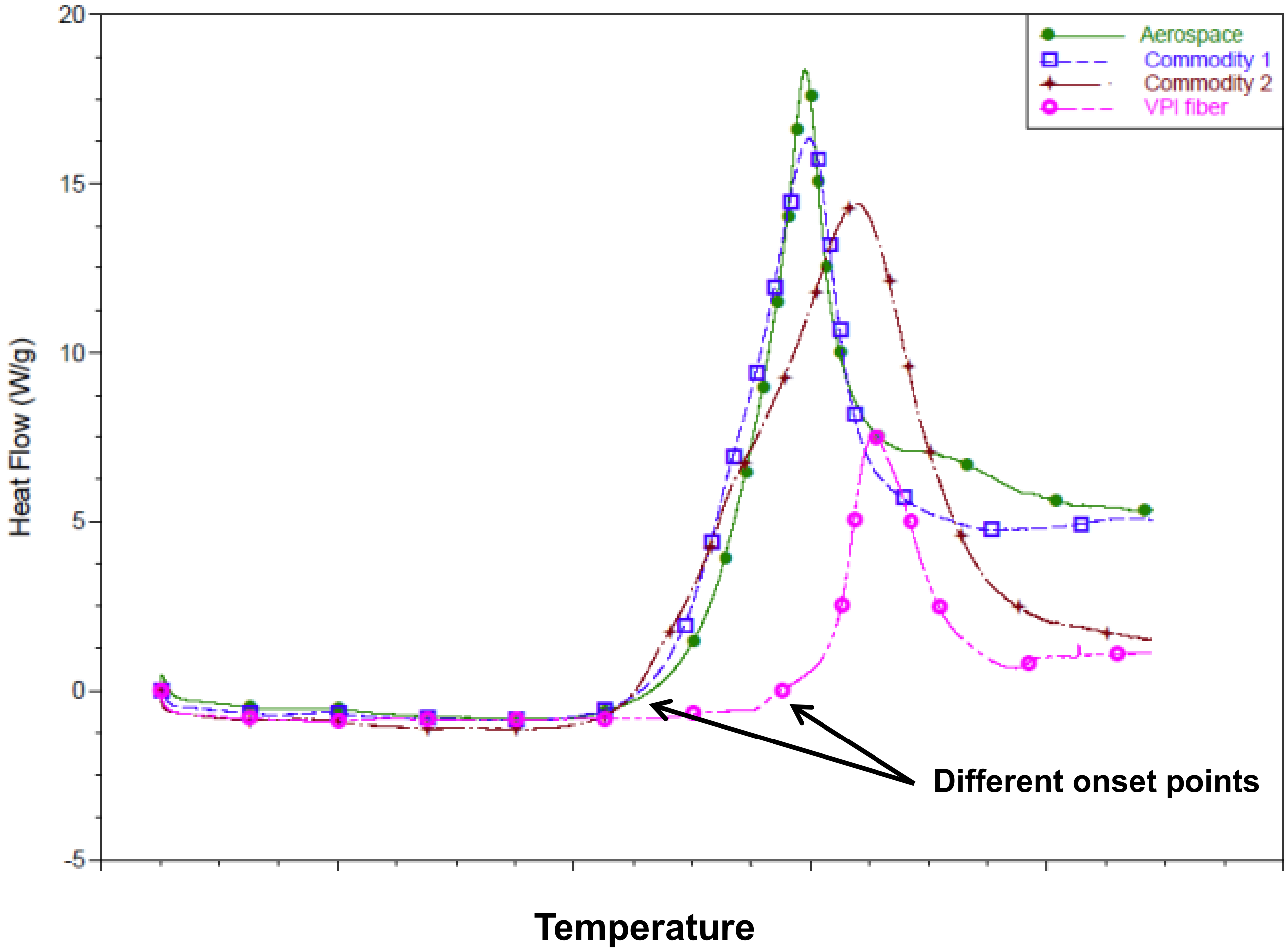


While there are some differences between exothermic behavior of melt-spun PAN fibers and wet-spun PAN commodity-grade fibers, the melt-spun fiber seems acceptable for conversion to carbon fibers.

Technical Accomplishments

Hardware and Processing Comparison

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 1 : 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.

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)	1 : 6	Visible voids ≤ (0.1 - 0.2 um)	30 – 45 (50)

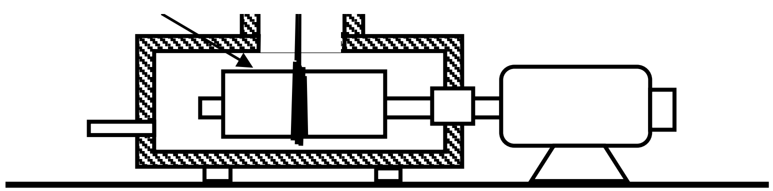
BASF used hazardous organic solvent/plasticizers

Technical Accomplishments

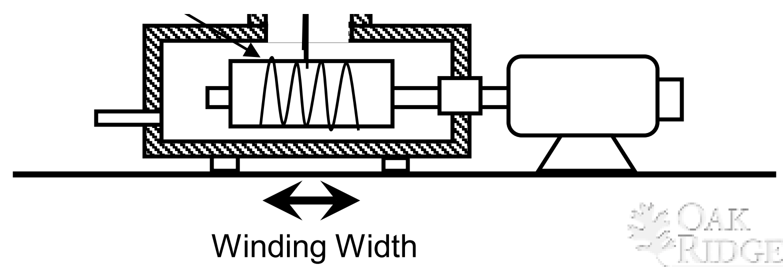
Filament Generation Problematic

- **Initially: Filaments too large, porosity too high, and large variation in filament diameter with enclosed impurities;**
  All Resolved
- **Afterwards, a new challenge arose: The winder system inside the pressurized chamber would tangle on the spool making it impossible to unwind long lengths. At this moment, we are developing/modifying equipment to eliminate this problem (end Feb. 2012).**
- ***At this moment, this issue is why some milestones have not been met in FY12.***

Current Configuration
Fiber clumps on top of itself



Future Configuration
Will permit proper unwinding



Solutions for the Unwinding Problem

- Option 1: Modification and up-grade of the actual VT system
  - Increasing diameter of collecting system (chamber) from ϕ 4” to ϕ 6 (*done*)
  - Incorporation of the reciprocating small winding system (spool and back-and-forth mechanism) only inside the chamber (*in progress*).
  - Testing of hardware, dry-runs (*soon*).
- Option 2: Long term fiber movement specialist (Izumi) has proposed an alternative solution (design is complete). ORNL is prepared to issue a purchase order (PO) to build this device should option 1 be insufficient. Lead time is 1.5 months from receiving PO.

FY11 Milestones
Precursor Development

Task No.	Title	Milestone/Deliverable Description	Planned Completion Date
1	Melt-spinning of ultra-fine PAN precursor fibers	Generate PAN filaments with diameter of 10 – 20 μm drawn from melt stable polymer containing 92 – 95 mol% AN.	01/2011 **Completed**
2	Melt-spinning of multi-filament precursor tow	Make 10-foot or longer “micro-tow” (≥10 filaments) with **uniform** ($\phi \cong 10\ \mu m$) fiber diameter (10 – 20 μm) and porosity of 1 vol% or lower.	06/2011 **Completed, (but filament uniformity not acceptable)**
3	Filament spinning	Achieve melt spinnable PAN copolymers with acceptable/potential characteristics	09/2011 **Completed**

FY12 Milestones
Precursor Development

Task No.	Title	Milestone/Deliverable Description	Planned Completion Date
1	Generation of small tow	Demonstrate spinning of a 50m continuous ~15 filament tow of ~10-12 micron fibers from high molecular weight (>200,000 MW) dope that can be easily spooled and de-spooled.	10/2011 **Incomplete**
2	Conversion into carbon fiber	Conversion at ORNL's Precursor Development System of VT/ORNL precursor and yielding 15 Msi modulus and 150 ksi strength.	12/2011 **Incomplete**
3	Long tows	Demonstrate spinning of a 1,000m 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	04/2012 **Re-evaluation is needed**
4	Conversion into carbon fiber	Conversion of VT/ORNL precursor at ORNL's Precursor Development System and yielding 15 Msi modulus and 150 ksi strength.	06/2012

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

Potential CF Cost Matrix

Estimated Cost Based on Implementation of IP From ORNL Program

Precursor and Conversion	Mill Cost $/lb CF	Mill Cost Savings, %
Baseline – Wet spun PAN precursor conventionally converted	$11.43	0%
Melt spun PAN precursor conventionally converted	$ 7.91	~31%

Mill 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.**

Summary (1)

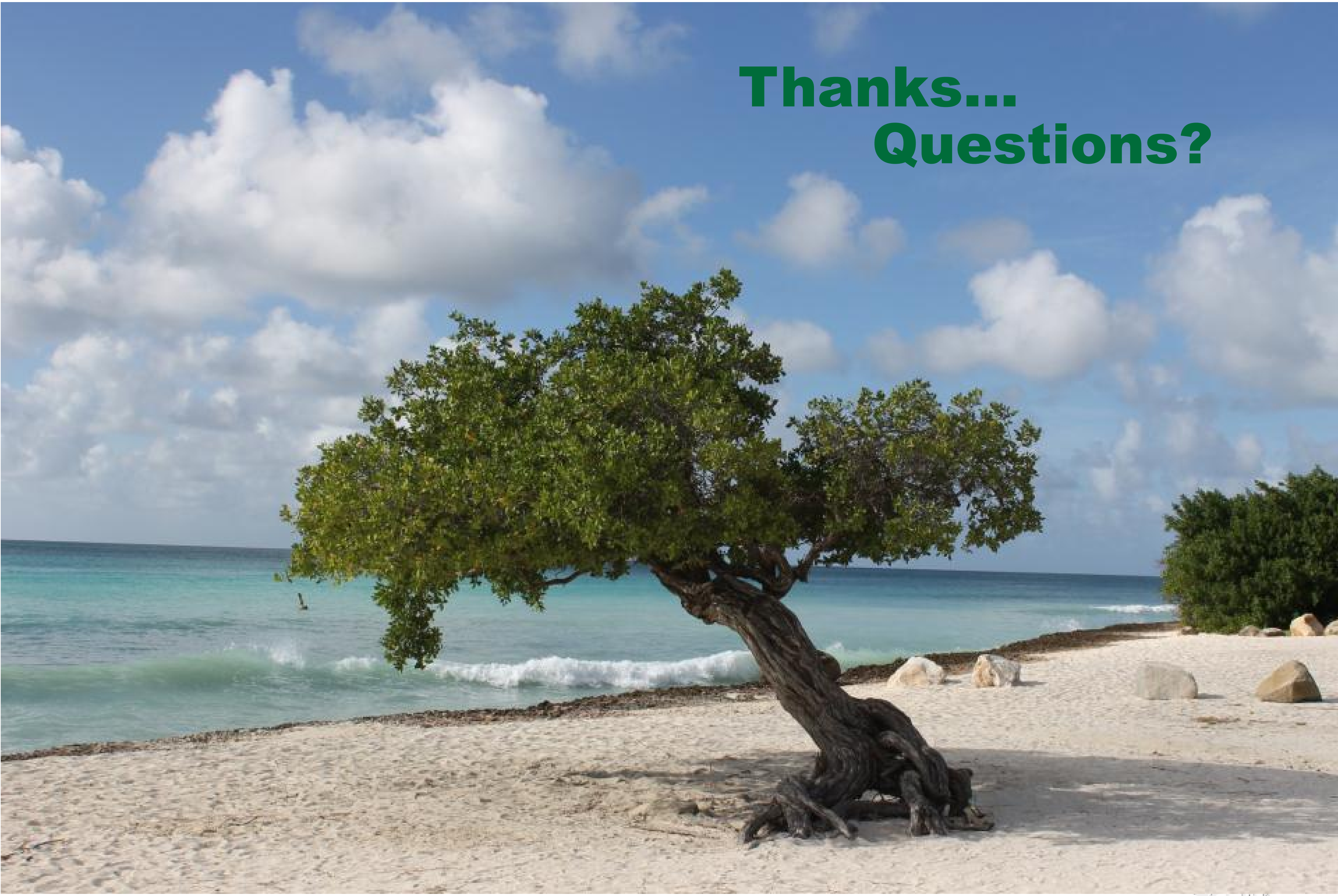
- **Substantial technical progress was achieved in FY11-12:**
  - **Demonstrated initial spinning with a hydrated melt of AN/MA ratio of 95/5.**
  - **Producing the initial small count PAN precursor tows**
  - **Melt spun molecular weight formulations representative of targeted levels in 10 filament tows of 10-30 μm.**
  - **Physical properties and characteristics are approaching commodity grade PAN precursor fibers.**
  - **Porosity must be revisited with each parameter set change.**
- ***With the mechanical properties demonstrated at the precursor level, the actual hurdle is engineering centered (winding under pressure with appropriate pattern to facilitate unwinding).***

Summary (2)

- This VT/ORNL method has achieved comparable filament diameters in a single step compared to the required two or more steps in the BASF system. Thus, the need for a more aggressive schedule for filament post-stretching operation has more flexibility.
- This work aggressively tackles the cost barrier in CF-reinforced pressure vessels with the potential to reduce equivalent CF cost by ~30% leveraging recent and ongoing CF work at ORNL.

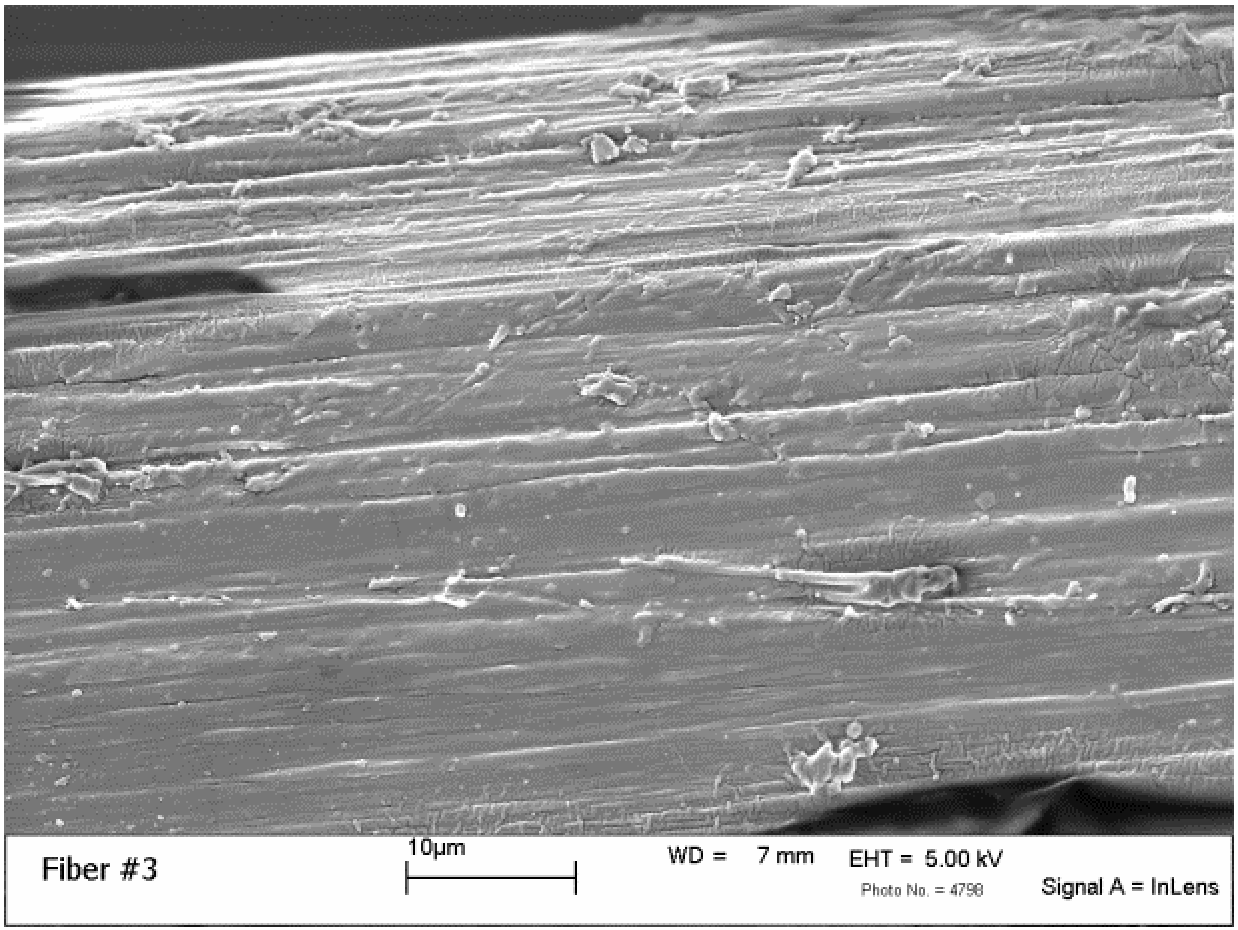
Future Work

- **Rest of FY12**
  - Resolve the problem of proper filament winding inside the chamber
  - Conversion of PAN filaments (processed with different parameters) into carbon fibers
  - Outline fundamentals towards the production of tows with longer length and higher filament count
- **FY13**
  - Improve process efficiency and parameters to achieve a better PAN precursor
  - Consideration towards scalability, more and longer filaments and/or tows
  - Generate filaments/tows with AN/MA (AN≥95%wt)
  - Building on previous efforts by BASF and utilizing project-generated data, develop designs for scaled up hardware

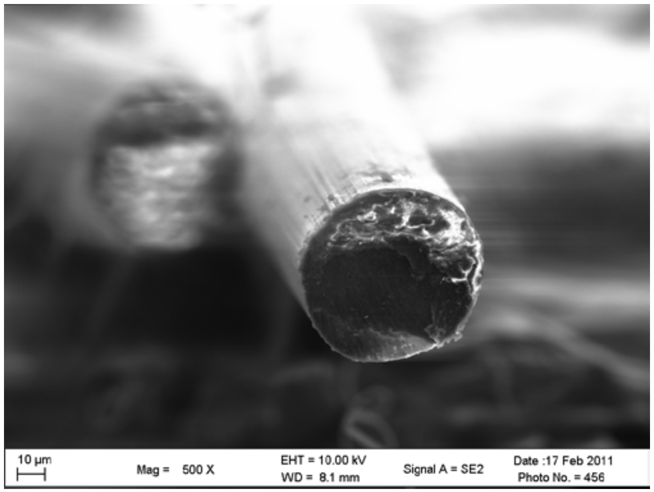

Thanks…
Questions?

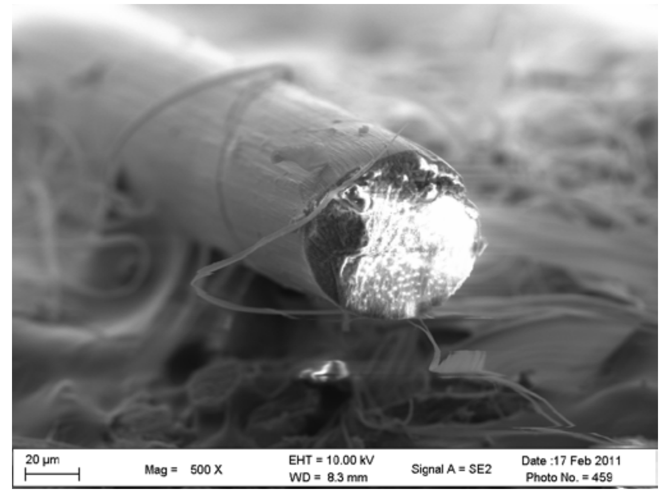
TECHNICAL BACKUP SLIDES

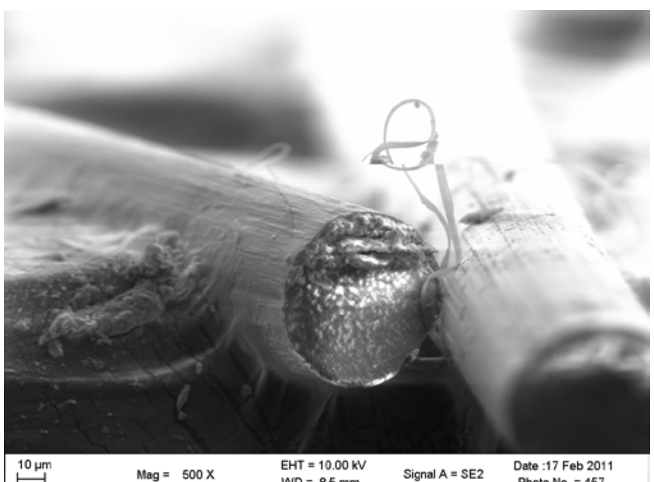
SEM of melt-spun PAN/VA (93 mol% AN) fibers – longitudinal surface

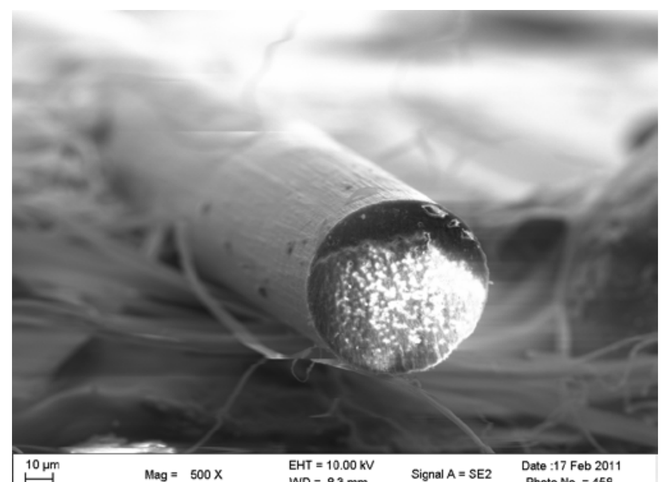


PAN/VA 17% H2O 03/11/2010
X-Section @500x









Technical Accomplishments
Ongoing Precursor Development

An example of ongoing development – the milestone below was completed. However…

Title	Milestone/Deliverable Description	Planned Completion Date	Status
Multi-filament precursor tow	Make > 10-foot long "micro-tow" w ≥ 10 filaments, with 10 – 20 µm filament diameter and ≤ 1 vol% filament porosity	03/2010	**Completed** **Porosity evaluation completed*** **6/30/2011**

…porosity evaluations are an ongoing work that has to be reevaluated when new parametric conditions are established.

Polymer Chemistry Activities Progress Status FY10-11

- **Demonstrated feasibility of using benign plasticizers to melt spin PAN and promote higher degree of drawing**
  - Water
  - Supercritical CO_2 (for now, this approach is on standby)
- **Novel ion-containing comonomers were successfully incorporated and evaluated**
  - Produced high molecular weight "fibrous" materials
  - Contained controlled levels of hydrophilic moieties
  - Assisted in the water and CO_2 melt processing schemes
- **Terpolymers are still under evaluation with PAN/MA**

Project Accomplishments

Progress History FY09-10

- **Demonstrated feasibility of using benign plasticizers to melt spin PAN and promote higher degree of drawing**
- **Novel comonomers were successfully incorporated**
  - **Initially produced: Foamed PAN fibers and high molecular weight "fibrous" materials (4/08)**
- **First (low-quality) fibers were melt spun (2008 to mid 2009)**
- **Produced PAN filaments**
  - **Low quality**
  - **Large diameters ≥ 100 μm**
  - **High porosity**
  - **Mechanical properties below acceptable limits**
  - **Need increased AN content, > 95%**
- **Improvements were needed**