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

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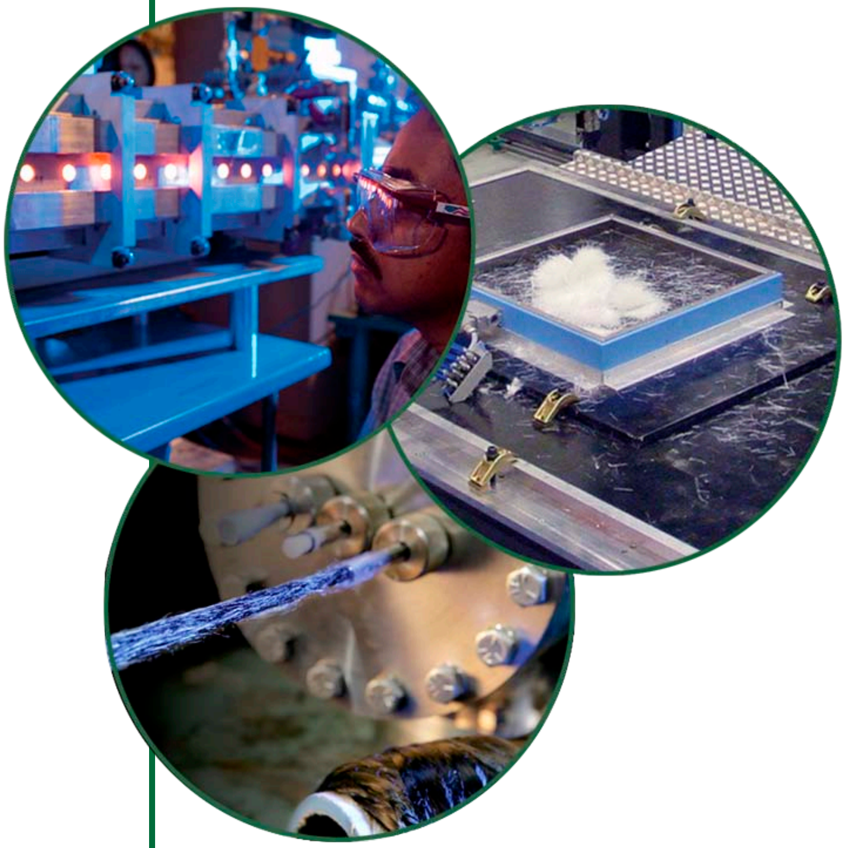

Project ID: ST093

U.S. DEPARTMENT OF ENERGY

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Overview

- **Timeline**
  - Start 2007
  - Project End date: 2015
  - ~55% completed
- **Budget**
  - FY07 $600K
  - FY08 $0
  - FY09 $200K
  - FY10 $200K
  - FY11 $150K
- **Barriers***
  - System Weight and Volume (A)
  - System Cost (B)
  - Materials of Construction (G)
    - High cost of high strength carbon fibers
- **Partners**
  - ORNL (Host side)
  - Virginia Tech - VT

*References "On-board hydrogen storage technical barriers" in the Hydrogen Storage Technical Plan

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].

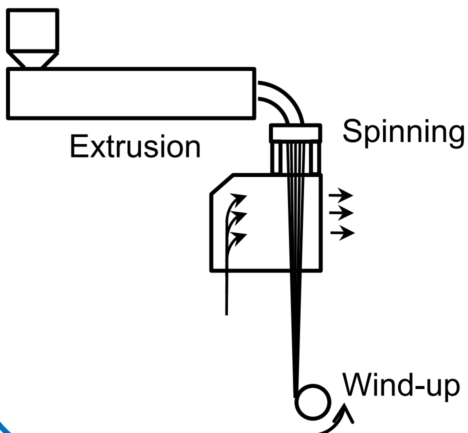
High Strength CF Projects

- **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)", Poster presentation ST099, in MR-2011.**
    - **Based on alternate chemistry melt-spun textile PAN-based commodity grade previously-developed conversion/technology.**
  - **Long Term Approach (this project):**
    - **Title: "Melt Processable PAN Precursor for High Strength Carbon Fibers."**
    - **Key technical issue: Improve melt stability by reducing the wet temperature (Tm) below the PAN 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.**
    - **These two bullets are closely interrelated.**

Melt Spinning vs. Wet Spinning

Advanced Technology

Melt-processing

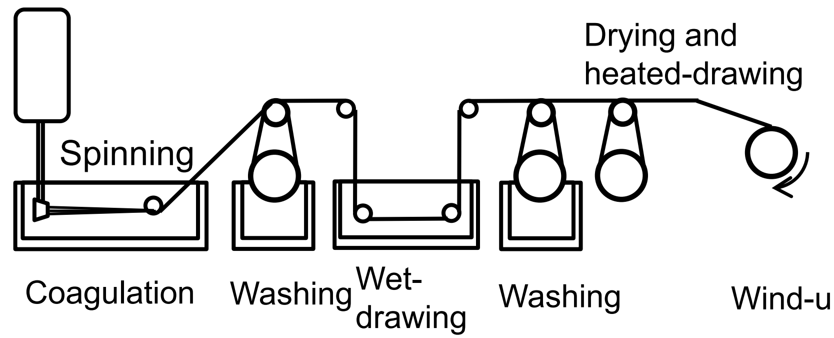


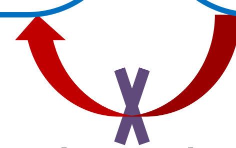
- Low production cost
- High production rate
- Environment-friendly

Current Technology

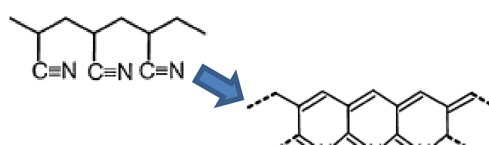
- Capital intensive
- Solvent typically highly corrosive
- Significant solvent plant hold-up

Solution-processing





Why not for PAN-based precursor fiber?



(Crosslinking)

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

Encyclopedia of Polymer Science and Technology.

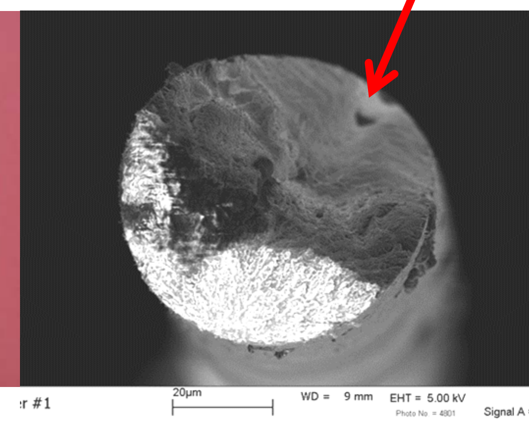
Melt-Spun PAN Precursor is Partially Proven Technology

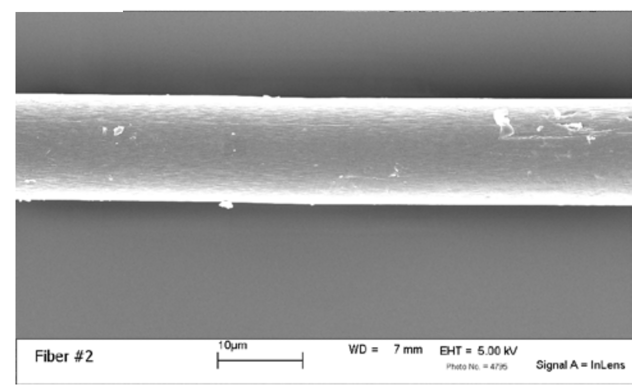
- BASF developed melt-spun PAN precursor in the 1980's.
  - CF's were qualified for B2 bomber
  - Demonstrated 400 to ~600* KSI fiber strength and 30 – 40 MSI modulus; even better properties were thought to be achievable
  - PAN content was 95% - 98% (consistent with high strength)
- Significantly lower 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

Early Project Accomplishments
Progress Status 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.





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
- Novel ion-containing comonomers were successfully incorporated and evaluated
  - Produces high molecular weight "fibrous" materials
  - Contains controlled levels of hydrophilic moieties
  - Assists in the water and CO_2 melt processing schemes
- Lately, terpolymers have been evaluated with PAN/MA

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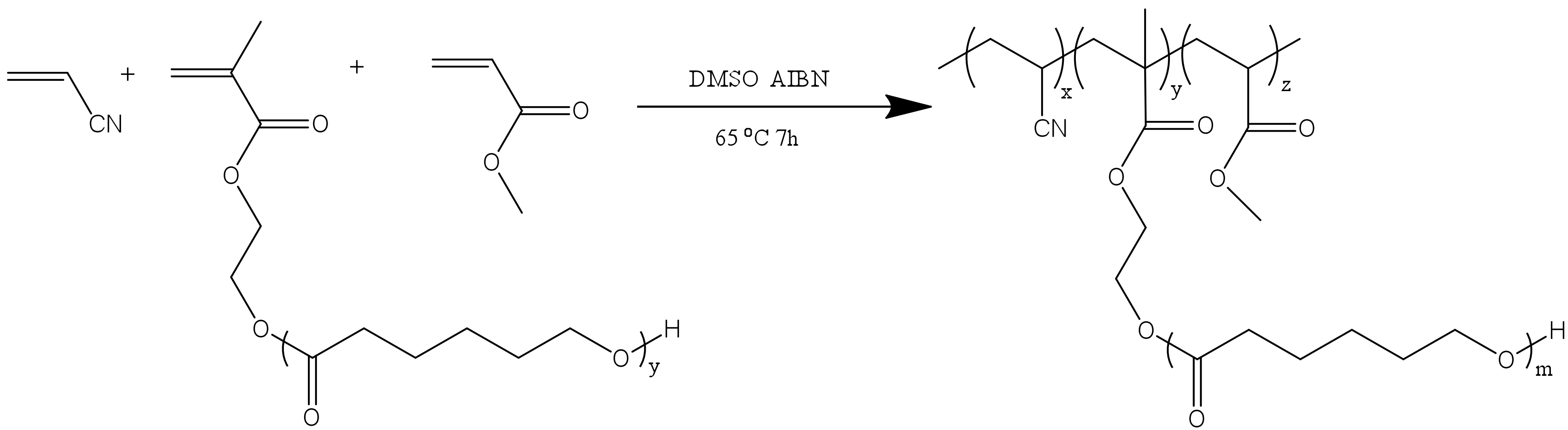
Acrylonitrile/Methyl Acrylate-Poly(Caprolactone)AN-MA-g-PCL Terpolymers; Via Suspension Polymerization May be More Melt Processable



A: 2.48 g PCL 1.24g Methyl Acrylate (MA) (10/5 PCL/MA)
B: 2.48 g MA 1.24 g PCL (10/5 MA/PCL)

AIBN 0.164 g
Dodecyl mercaptan 0.184 g
Acrylonitrile 25 ml (21.05 g) (~85wt%)
DMSO 70 mL

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Melt Spinnability of AN/MA as a Function of Molecular Weight and Composition

Sample No.	Provider	Composition (mol/mol)		IV (dL/g)	Spinnability with hydrated melt
		Nominal	NMR		
1	Aldrich Co.	AN/MA=96/4	90.7/9.3	5.41	Unable to draw fibers
2	Exlan Co.	AN/MA=95/5	92.7/7.3	4.09	Unable to extrude
3	ORNL 6/22/10	AN/MA=95/5	95.0/5.0	1.13	OK

MA: Methyl Acrylate

Progress Status FY10/11 (3)

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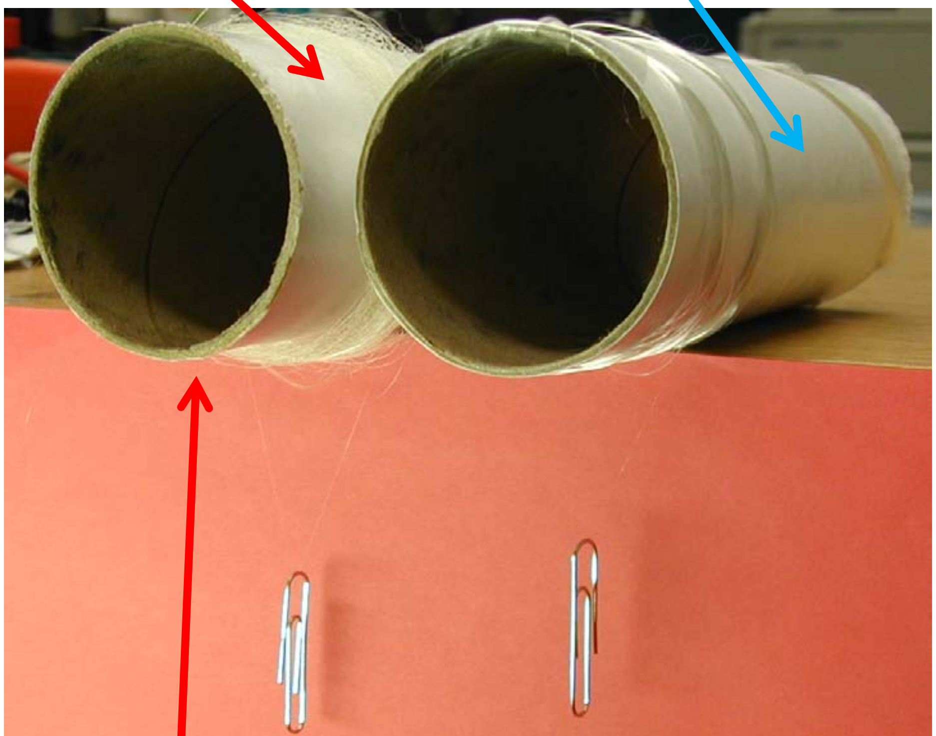
ORNL/VT melt-spun PAN precursor fiber (left) and Commodity commercial wet-spun precursor fiber.

ORNL/VT melt-spun PAN precursor fiber

Commodity-grade, commercial wet-spun PAN precursor fiber.



ORNL/VT melt-spun PAN precursor fiber (left) best achieved diameter so far: 10 um within the overall project.

ORNL/VT melt-spun PAN precursor fiber

- Spinning temperature: 195°C
- Melt water content: 17 wt%
- Number of spinneret holes: 18 Diameter of holes: 0.0022”
- Diameter of finest filament: 15 μm in this sample
- Problem: the hole (and thus the fiber) diameter is not uniform among filaments

Progress Status FY10/11 (2)

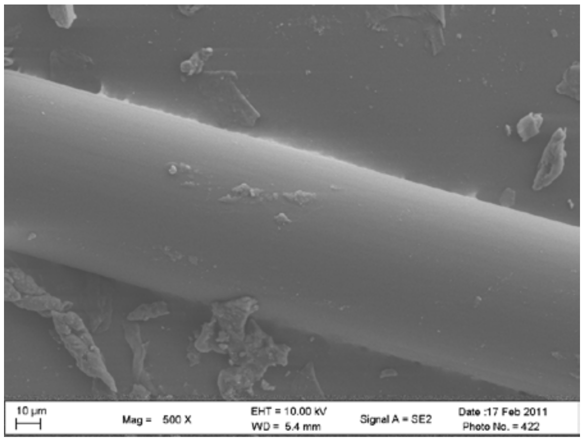
PAN Precursor Filaments Mechanical Property Comparison

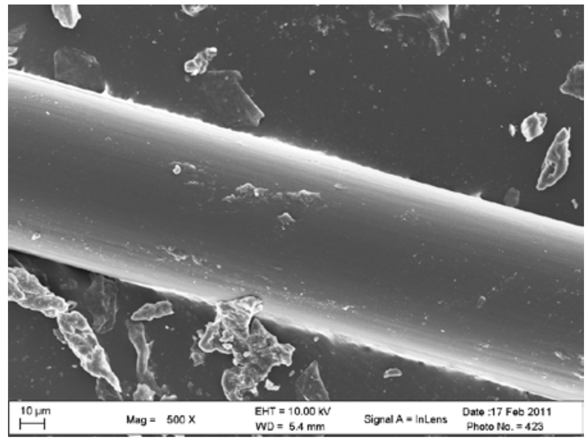
In spite of the technical challenges of this new melt-spun method, advances have been made in achieving promising mechanical properties.

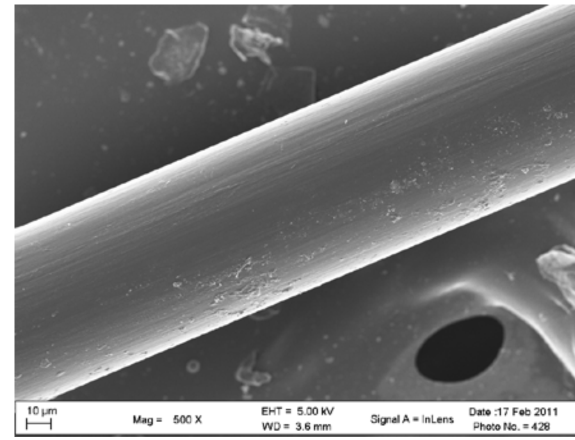
PAN BASED PRECURSORS				MECHANICAL PROPERTIES (Standard deviation between parentheses)			
Components	Name	Type of sample	Tow	Fiber diameter, µm (SD)	Peak stress, KSI (SD)	Modulus, MSI (SD)	Strain at break, % (SD)
Industrial precursors							
AN/VA	FISIPE	Textile	26k	14.15	54.2 (8.5)	0.5 (0.1)	15.7 (0.9)
AN/VA	FISIPE	Textile	26k	13.7	64.9 (5.5)	1.1 (0.2)	14.99 (0.51)
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							
PAN-VA_12%H2O_20100311				67.1 (3.1)	37.6 (3.7)	1.0 (N/M)	11.89 (1.16)
PAN-VA(II)_12%H2O_20100722				53.8 (4.8)	35.3 (4.0)	1.0 (N/M)	10.76 (1.08)

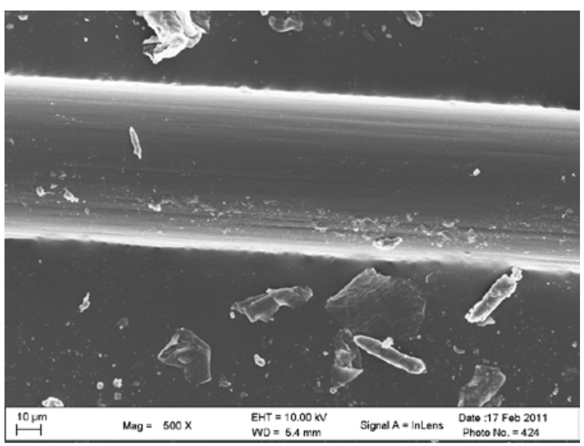
SD – Standard Deviation

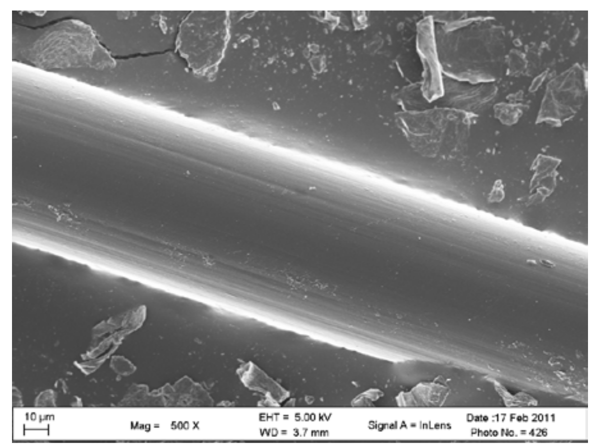
PAN/VA (II) 12% H2O 7/22/2010
Surface @ 500X











FY10 Milestones
Precursor Development

Title	Milestone/Deliverable Description	Planned Completion Date	Status
Melt stable PAN filaments	Single filaments drawn from melt stable polymer with 92 – 95 mol% AN	12/2009	**Completed**
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 in evaluation)**
2nd generation multi-filament precursor tow	Make > 10-foot long “micro-tow” w ≥ 10 filaments, with chemistry	07/2010	**Completed**

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FY 2011 Tasks and Milestones

FY 11 Milestones and Deliverables

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
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
3	2nd generation multi-filament precursor tow with improved mechanical properties	Make 100-foot or longer "micro-tow" (≥100 filaments) which can be used on ORNL's automatic CF conversion line, with mechanical properties about the same or better than that of commercial wet-spun precursor fibers.	09/2011
4		Achieve melt spinnable PAN copolymers with acceptable/potential characteristics	09/2011
5		If acceptable fibers are achieved, performed initial trials of oxidation and carbonization – ***budget permitting***	9/2011

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

Leveraging

- **This high strength CF project is benefiting from a decade of prior development in CF R&D at ORNL:**
  - **Successful development in revolutionary new approaches to precursor and conversion technology.**
  - **Significant intellectual property portfolio in CF has been developed at ORNL.**
  - **Unique physical resources specific to CF R&D**
  - **Access to ORNL's extensive materials processing (PES and PL) and characterization capabilities.**
  - **An extensive network consisting of university and industry partners providing unique strengths and intellectual property contributions in the CF area.**

Cost Modeling

- Kline and Company has been cost modeling CF manufacturing for the Automotive Composites Consortium since 2003
- Kline has completed models on high strength CFs made from wet-spun PAN (baseline) and melt-spun PAN
- Kline's models are fairly rigorous and moderately conservative
- The appropriate use of the Kline model results is for comparison and trending
  - Select the most promising research approaches
  - Identify critical cost sensitivities
  - Establish scaling targets
- Cost is the manufacturer's cost to produce; price is highly dependent on CF market conditions

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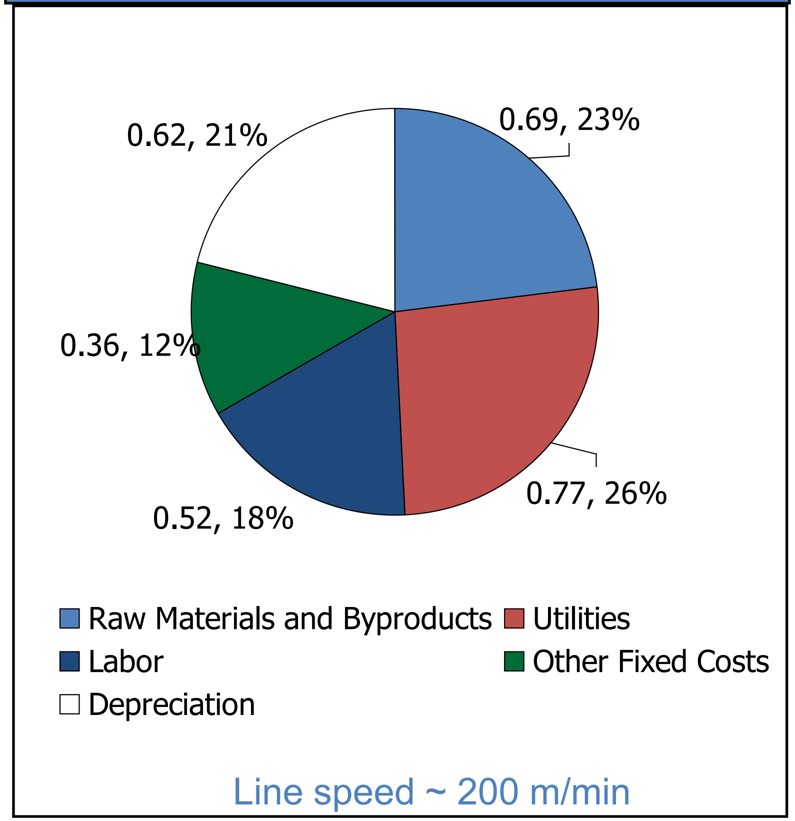
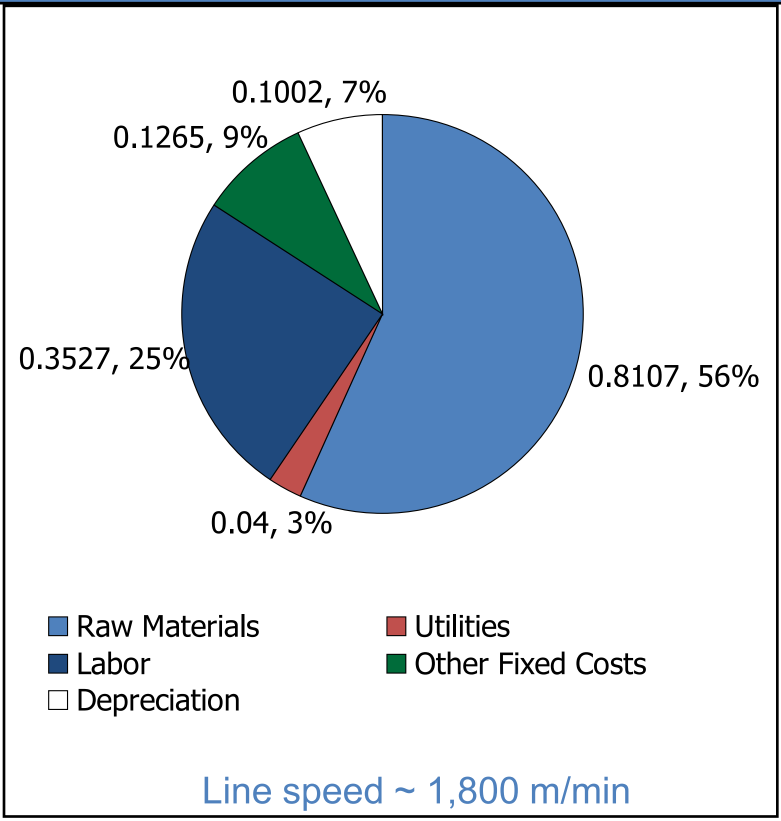
Estimated Precursor Cost

Wet-Spun PAN Cost Structure $2.97/lb of Precursor



3x Melt-Spun PAN Cost Structure $1.43/lb of Precursor



- **Precursor plant scale is 12M lb/yr of precursor fibers. Melt spinning rate is assumed to be 3X that of pitch.**
- **Source: Kline and Company, November 2007; estimates based on oil at $60/bbl**

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

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Future Work

- **Rest of FY11**
  - Continue efforts for the generation of acceptable hot-melt PAN-filaments/tows

- **FY12**
  - Improve process efficiency and parameters to achieve a better PAN precursor
  - Start conversion of these PAN filaments/tows into CF's and their evaluations
  - Consideration towards scalability, more and longer filaments and/or tows
  - Generate filaments/tows with AN/MA (AN≥95%wt)

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Summary

- **Substantial technical progress was achieved in FY10/11:**
  - **Demonstrated initial spinning with a hydrated melt of AN/MA ratio of 95/5.**
  - **Successfully incorporated ion-containing co-monomers and terpolymers into formulation for evaluation.**
  - **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.**
- **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.**

TECHNICAL BACKUP SLIDES

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

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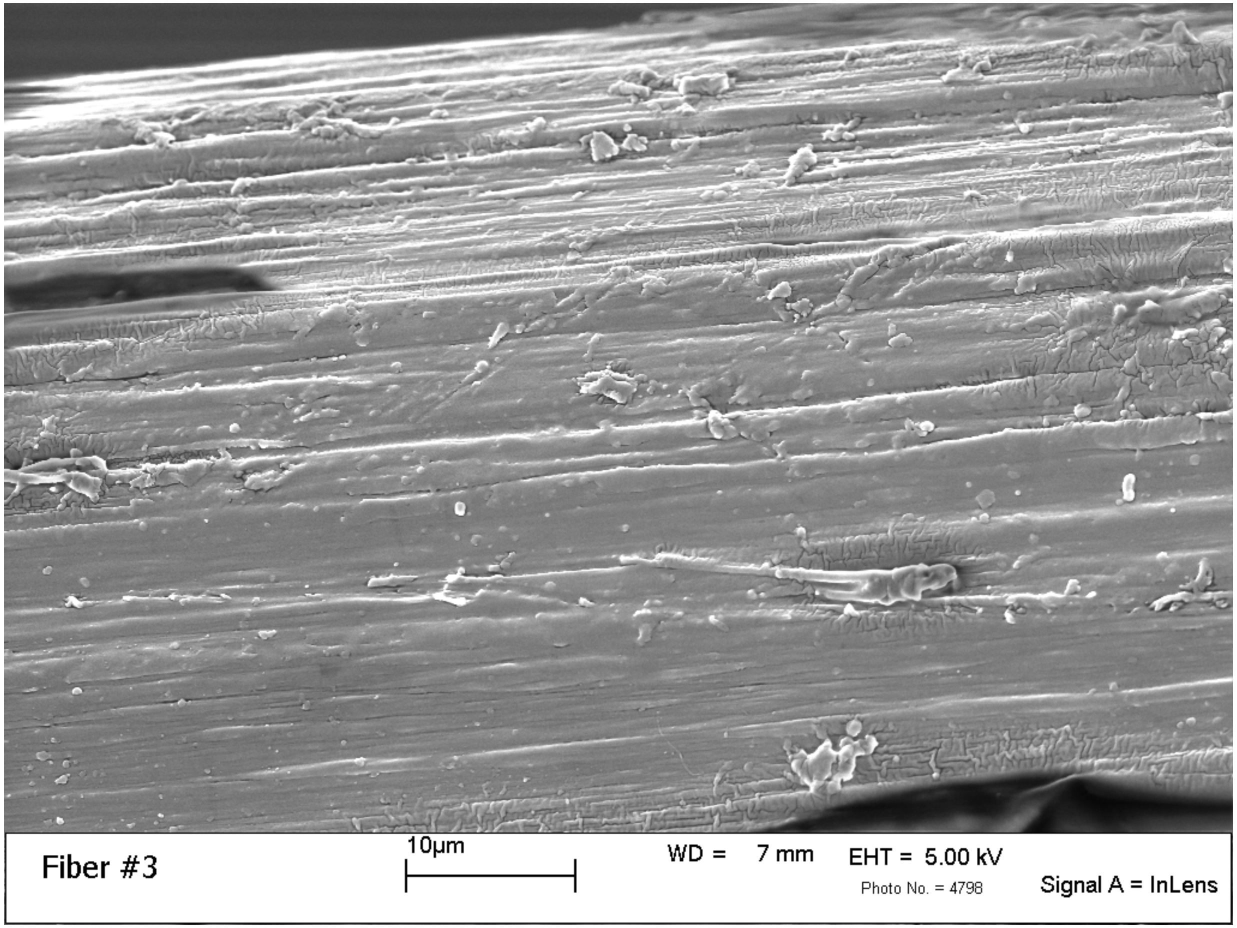

PAN/VA 17% H2O 03/11/2010 X-Section @500x