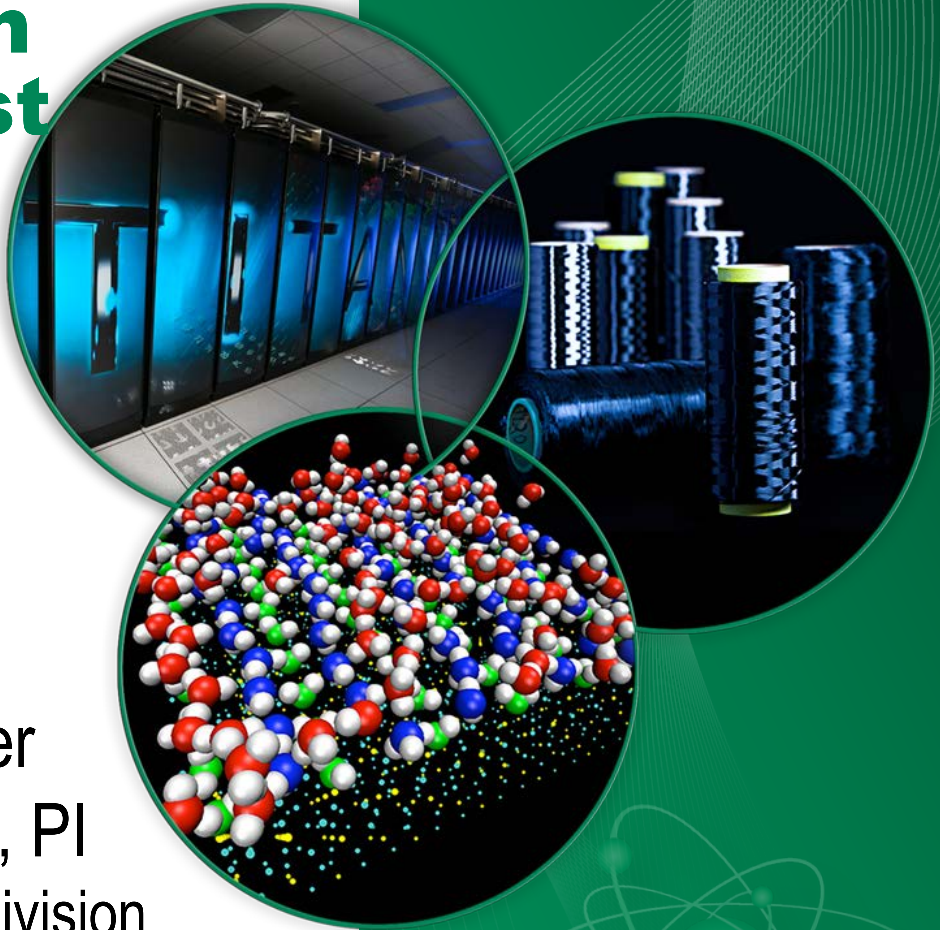
Melt Processable PAN Precursor for High Strength, Low-Cost Carbon Fibers



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Merit Review 2016

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Project ID: ST093

U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY

MANAGED BY UT-BATTELLE FOR THE U.S. DEPARTMENT OF ENERGY

Overview

- **Timeline**
  - Phase I completed 9/2013
  - Phase II Start: 10/2015
  - Phase II End: 09/2018
  - ~25% complete at submission
- **Budget**
  - FY16 $550K
- **Other Key Participants**
  - Leistritz contracted for alternative spinning approaches
  - Former BASF employee Mark Cauthen consulting
  - FISIPE contracted for PAN material
- **Barriers**
  - High cost of high strength carbon fibers (CF)
  - CF account for ~65% of the cost of the high pressure storage tanks
- **Partners**
  - ORNL (Project direction and carbon fiber conversion)
  - Virginia Tech (VPI)
    - Don Baird (precursor spinning)
    - Judy Riffle (precursor chemistry)

Relevance

- Objective: Significantly reduce the manufacturing cost (>25%) of high-strength CF's via:
  - Introduction of high quality PAN precursor ***melt spinning*** techniques for practical application
  - Development of alternative formulations for advanced precursors capable of being melt spun in high volumes
  - Development/demonstration of appropriate conventional and/or advanced CF conversion technologies
  - Advance properties, scaling, and overall economics to meet high pressure storage targets

Phase II approach with continuous processing allows the team to focus on engineering larger-scale demonstration beyond bench-scale "science" of Phase I

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

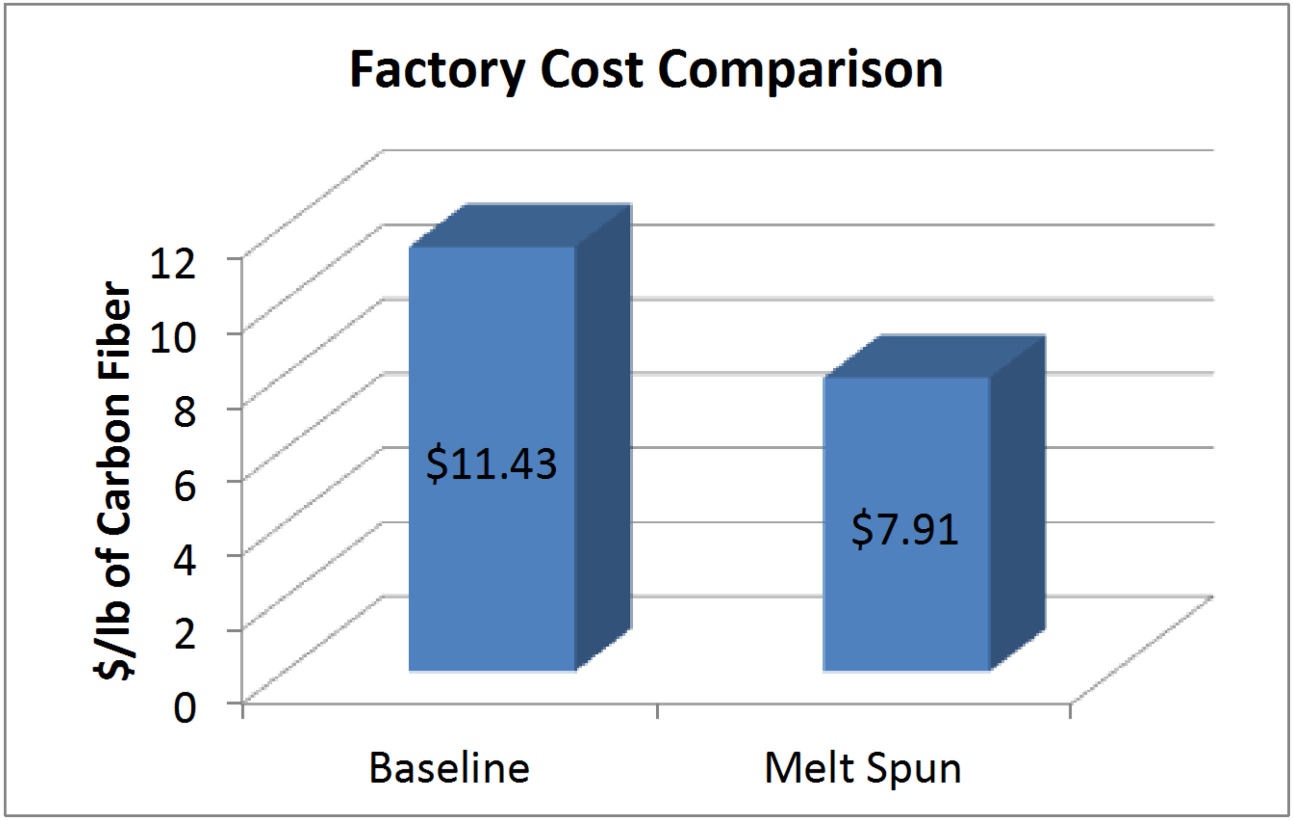
- BASF* developed melt-spun PAN precursor in the 1980s.
  - CF's were qualified for B2 bomber
  - Demonstrated 400 to ~600** KSI fiber strength and 30 – 40 MSI modulus; even better properties were thought to be achievable
  - AN content was 95% - 98% (consistent with high strength)
- Lower production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

We are recently drawing even more heavily on this experience!

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

Potential CF Cost Matrix

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



Cost benefits from increase in precursor throughput and reduction in solvent handling.

This represents ~31-33% savings in cost.

Model Will Be Updated With Project Findings

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.**

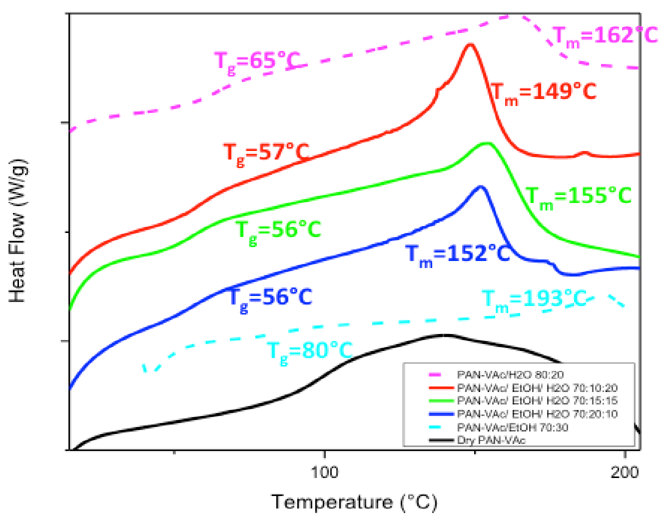
Approach

Phase II provides next step in development from feasibility demonstration in Phase I towards robust pre-production demonstration:

- Utilizing *PAN-MA chemistry* capable of formulation to meet targeted performance (650 ksi strength, 30 Msi modulus)
- Co-monomers, solvents, and plasticizers appropriate for large-scale production
- Utilizing extruder for *continuous spinning*
  - More conducive to achieving process stability
  - Overall production level (>100 filaments X >100m length) is adequate for conversion recipe development
  - Spinning pressure chamber and winding more representative of production processes
- *Hot drawing* for high performance

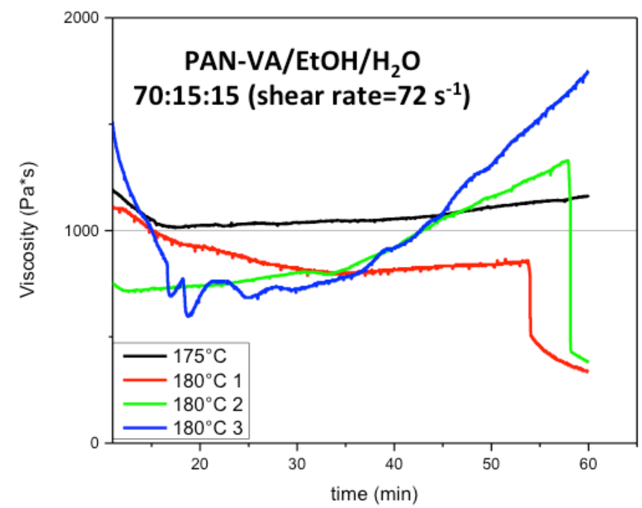
Approach – Precursor Chemistry

- Developing/evaluating preferred methods for preparing PAN compounds at various concentrations, molecular weights, and plasticizer levels
  - Generally higher concentrations of AN and higher molecular weights yield higher properties at the expense of ease in processing
  - Current focus is water as primary plasticizer
- Providing compositional analysis for compounds supplied externally and supporting spinning development



DSC thermograms of PAN/vinyl acetate/vinyl alcohol copolymer containing water and ethanol plasticizers

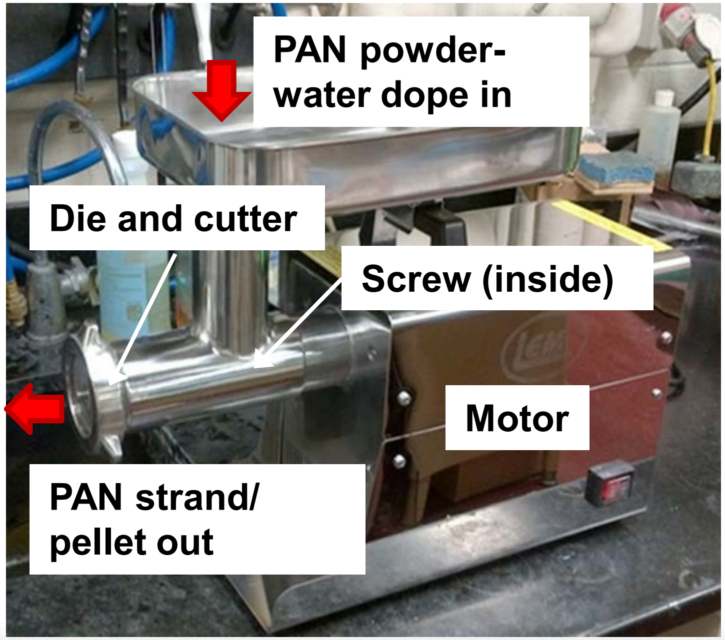
Targets:
Tm <180º C
Stable for
Time > 45 minutes



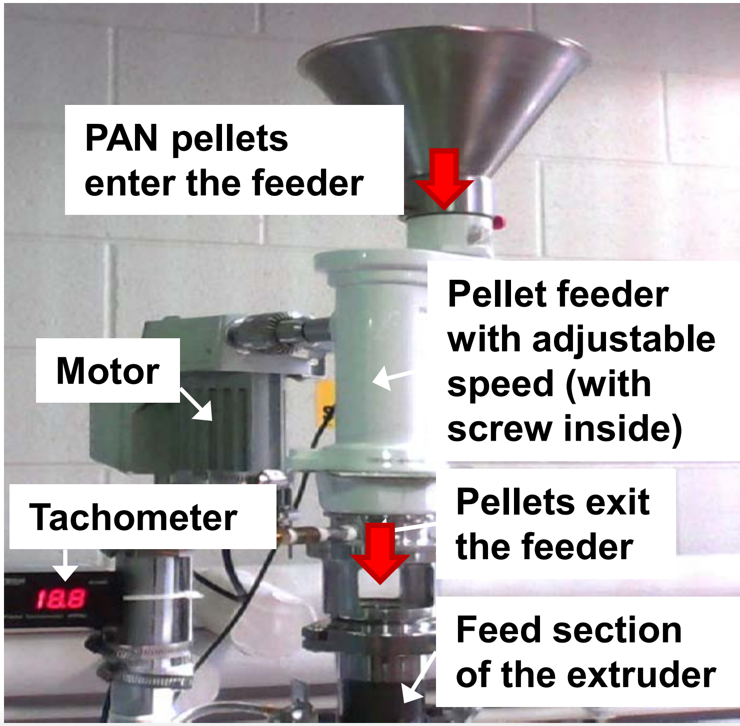
Isothermal melt viscosities of 85% PAN/vinyl acetate/vinyl alcohol/15% ethanol/15% water at 175 and 180° C

Approach – Melt Spinning

- Primary work has been conducted at Virginia Tech with 5/8-inch single screw extruder
  - Sized to produce adequate quantities of precursor without overwhelming capability to produce dope
  - Feeding is difficult, but has become manageable
  - Retention of moisture for plasticization at spinning temperatures is key issue



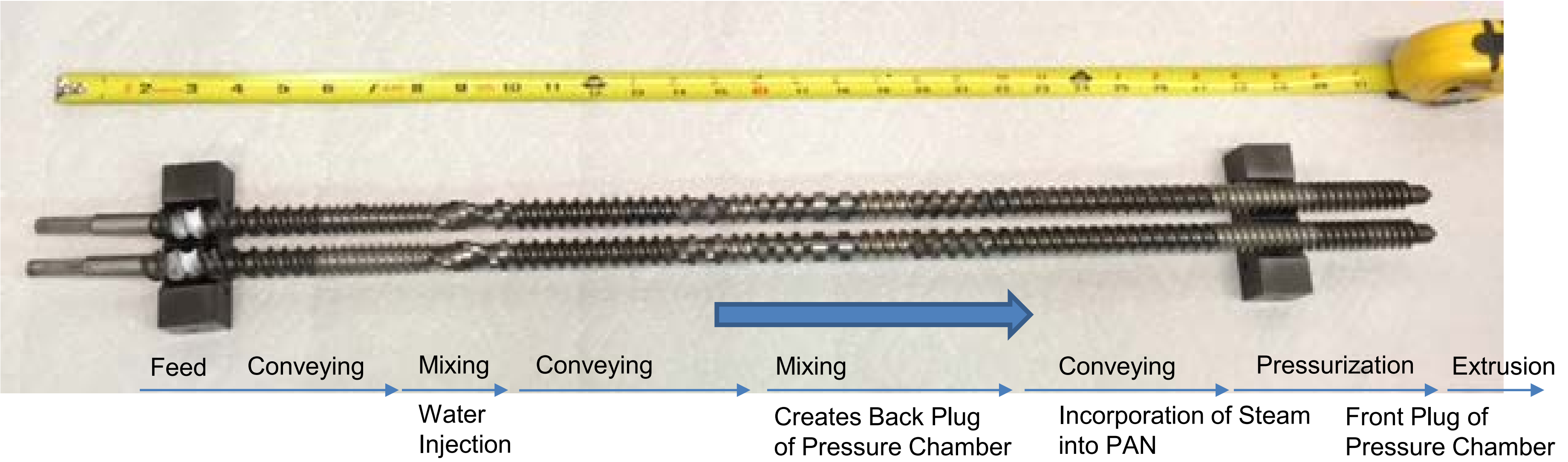
Meat Grinder for Pellets



Improved Feeding and Moisture Retention at Extruder

Risk Mitigation - Melt Spinning with Twin-Screw Machine

- Recently added spinning trials at Leistritz to investigate potential benefits of twin-screw approach
  - Modular construction allows rapid change-out of screw types overall and sections of the screw along the length as well as adjustment of screw length and barrel.
  - Production rates are more tunable in optimizing conditions.
  - Leistritz extruder modules have ports available for downstream injection of 2nd and 3rd phases - powder can be fed dry and the plasticizers then injected downstream.



FY16 Milestones

Milestone	Property/Metric	Deliverable	Date	Status
2	Based on results of continuing trials with PAN/VA process development materials, down-select processing conditions and water/plasticizer formulations and demonstrate spinning of >100 filament tows of length >10m.	Documentation in quarterly report.	12/31/15	Completed as demonstrated in spinning trials on 2/29/16 and achieved even more conclusive results on 3/22/16.
3	Successfully spin AN/MA formulated with the best plasticizer system to reach filament diameter (<20 microns), and 100 filaments in a tow of 25 to 50 m.	Documentation in quarterly report.	3/31/16	Recent progress indicates this may be achievable in April or May.
5	Go/no-go decision point based on Demonstrated production of precursor fibers with greater than 100 filaments and continuous lengths >100m, and with the following characteristics: •PAN/MA copolymer with 93 mol-% or more AN, •Average diameter of 18 microns or less, •Tensile strength of >40ksi, •Elongation of >6.5%, And weight per length variation of <10%.	Test results reported, 10m demo sample provided to sponsor.	6/30/16	Chances have improved with recent progress and new approach of working alternative/multiple spinning options.
6	Demonstrate production of converted carbon fiber achieving 22 Msi modulus and 250 ksi strength with 25-50m tow.	Test results reported	9/30/16	Likely depends on success of alternative plans.

Accomplishments and Progress

- Successfully completed milestone: Down-selected processing conditions and water/plasticizer combinations for PAN/VA formulations and demonstrated spinning of >100 filament tows of length >10m.
- Approaching minimum requirements for next milestone: Spin AN/MA formulated with the best plasticizer system to reach filament diameter (<20 microns), and 100 filaments in a tow of 25 to 50 m.

Sample Meeting PAN/VA Milestone

Sample Approaching Requirements for PAN/MA Milestone

Accomplishments and Progress

- Extensive study of plasticizer approaches focusing on water as primary means of significant suppression of melt temperatures
- Water and various solvents work together to suppress melt temperature more than either component by itself

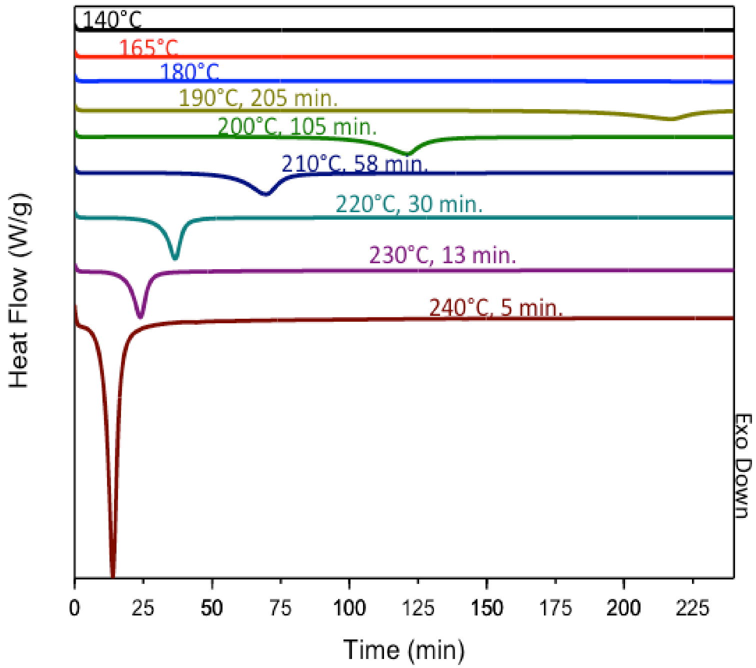
70 wt% PAN-MA/20 wt% H2O	+ 10 wt% DMF	+ 10 wt% Ethanol	+ 10 wt% Adiponitrile	+ 10 wt% Acetonitrile
Tm 156° C	Tm 149° C	Tm 148° C	Tm 145° C	Tm 142° C

60 wt% PAN-MA/20 wt% H2O	+ 20 wt% DMF	+ 20 wt% Ethanol	+ 20 wt% Adiponitrile	+ 20 wt% Acetonitrile
Tm ~156° C	Tm 144° C	Tm 149° C	Tm 133° C	Tm 123° C

- Team is revisiting potential use of acetonitrile as it is considered modestly toxic in small doses and currently NOT classified as a carcinogen.

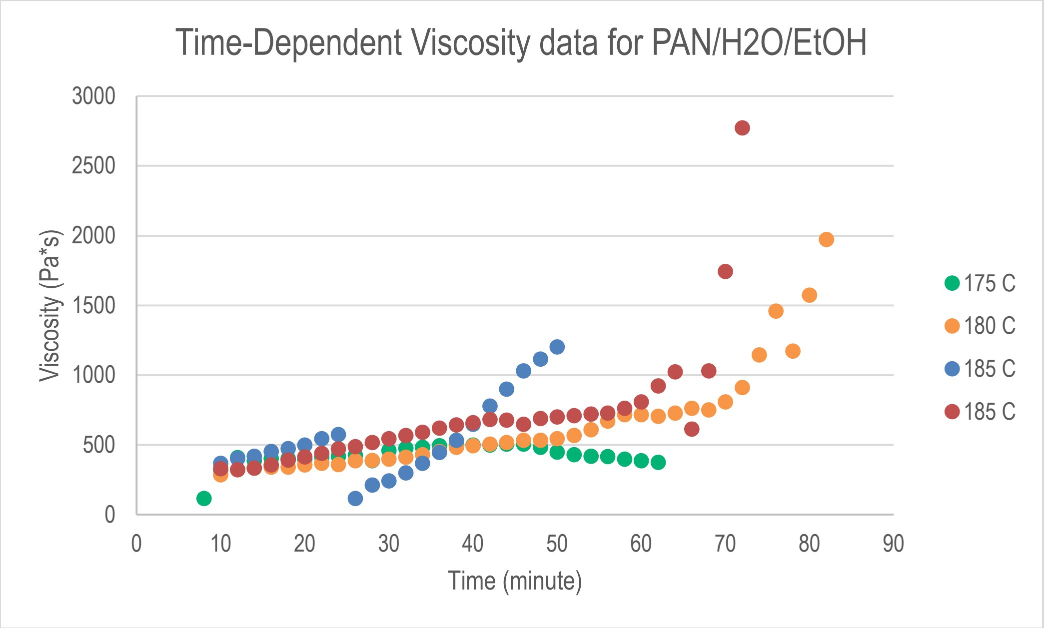
Accomplishments and Progress

- Focal formulations appear both thermally and rheologically stable at "spinnable" conditions



Isothermal analysis of PAN/MA/acetonitrile/water 70/10/20 wt/wt/wt over 4 hours

Time Dependent-Viscosity data at 161 s^{-1} obtained with the small capillary, using PAN-VA/EtOH/Water (70/15/15 wt%)



Targets: Tm <180° C
Stable for Time > 45 minutes

Response to Previous Year Reviews

Reviewer comments were largely focused in the 3 areas addressed below:

- Insufficient Progress in Spinning
  - The team continues to enhance with even more frequent teleconferences, assessments, and reporting including risk and mitigation plans
  - Consultant under contract with previous BASF spinning experience
  - ***Most recently Leistritz has been brought onboard to evaluate alternative approaches in spinning.***
- Consideration of Additional Carbon Fiber Manufacturer Involvement
  - We continue to make our interest/activities in this area public and talk with carbon fiber manufacturers who always appear technically interested.
  - Existing manufacturers, however, are careful not to expose their level of business interest at this point so we have been more focused on getting expertise from other sources such as organizations having direct expertise where needed in spinning such as Leistritz and Randcastle.
- Adequacy of Resources
  - We also are concerned about the level of resources available currently and projected for the near future, but understand the reluctance to invest more heavily until more progress is demonstrated.

Remaining Challenges and Barriers

- Success requires innovative chemistry and processing developments combining
  - Precursor formulation that can be *consistently* spun and meet property targets
  - Choice of plasticizers that facilitate spinning without detriment to properties
  - Finding lowest practical pressurization level with adequate plasticizer retention
  - Conversion process optimized for performance and economics
- Each of the above steps is independently challenging, but all are interdependent
- Coordination is critical for effective integration and optimization

Collaborations

- ***Virginia Tech*** provides critical spinning and chemistry resources
- Long-time partners in related projects contribute to materials and hardware development and implementation
  - ***Izumi International*** customizes fiber handling equipment to ORNL specs
  - ***ReMaxCo*** provides unique heating, instrumentation, and data acquisition systems
  - ***FISIPE*** supplies polymer dope and advises on dope production alternatives
- ORNL has recently brought in **Leistritz** to augment spinning options to enhance probability of success
- Past participants in ***BASF*** melt spinning initiative continue to provide advice while a new resource from that program is now on-board as consultant
- This program ***leverages*** investments from related ***DOE and DARPA programs***
- Numerous potential ***technology implementers*** are in frequent contact

Key Future Milestones

Milestone	Property/Metric	Deliverable	Date	Status
9	Go/no-go decision point based on precursor produced and converted to carbon fiber achieving 25 Msi modulus and 400 ksi strength with >100m tow.	Test results reported, 10m demo sample provided to sponsor.	6/30/17	Currently considered achievable
10	Updated economic model completed for chemistry and process parameters	Assumptions and results outlined in quarterly report.	9/30/17	Currently considered achievable
12	Initial tests completed to directly compare advanced conversion property results with conventional conversion property results to estimate cost versus benefits of continuing advanced conversion work in this project versus deferral to later project(s)	Results and recommendations provided to sponsor in letter report.	3/15/18	Currently considered achievable
13	Go/no-go decision point based on precursor produced and converted to carbon fiber achieving 30 Msi modulus and 550 ksi strength with >100m tow.	Test results reported, 10m demo sample provided to sponsor.	3/31/18	Currently considered achievable
16	Precursor produced and converted to carbon fiber achieving 33 Msi modulus and ≥650 ksi strength with >100m tow.	Test results reported, 10m demo sample provided to sponsor.	9/30//18	Currently considered achievable

- Pathway assumes successful iteration of previously described approach

Project 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 work by BASF that is not appropriate for today's environment.
- Innovative chemical and processing improvements are required.

Technical Accomplishments

- **Feasibility has been demonstrated. Recent work has made significant progress in working towards demonstration of a scalable, economic process that can meet property requirements.**

Collaboration and Coordination

- ORNL worked closely with Virginia Tech and others in the industry to get to this point.
- **Additional partnership arrangements are being sought, most recently Leistritz has been brought onboard to evaluate alternative approaches in spinning.**
- Assistance being provided by consultant directly involved with spinning at BASF

Future Work

- **Now that feasibility has been demonstrated,** the main two tasks ahead of us are the refinement and scale-up of the process to demonstrate technology and process economics justify investment risk**.**

BACKUP SLIDES

Melt Spinning vs. Wet Spinning

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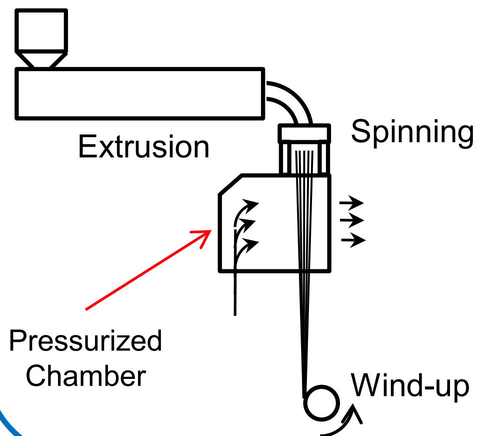
Advanced Technology (for PAN)

Melt-processing

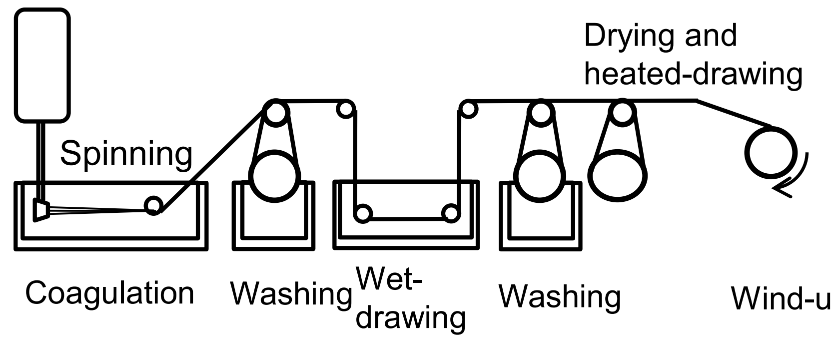


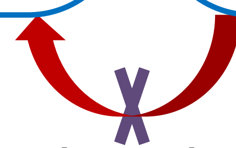
- Low production cost
- High production rate
- Environment-friendly

Current Technology

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

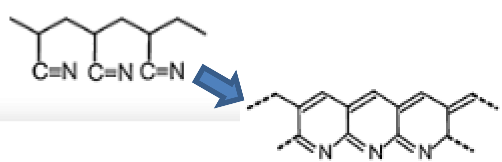
Solution-processing





Why not for PAN-based precursor fiber?

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



(Crosslinking)

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

Encyclopedia of Polymer Science and Technology.

Filament Generation System Comparison BASF vs. VT/ORNL

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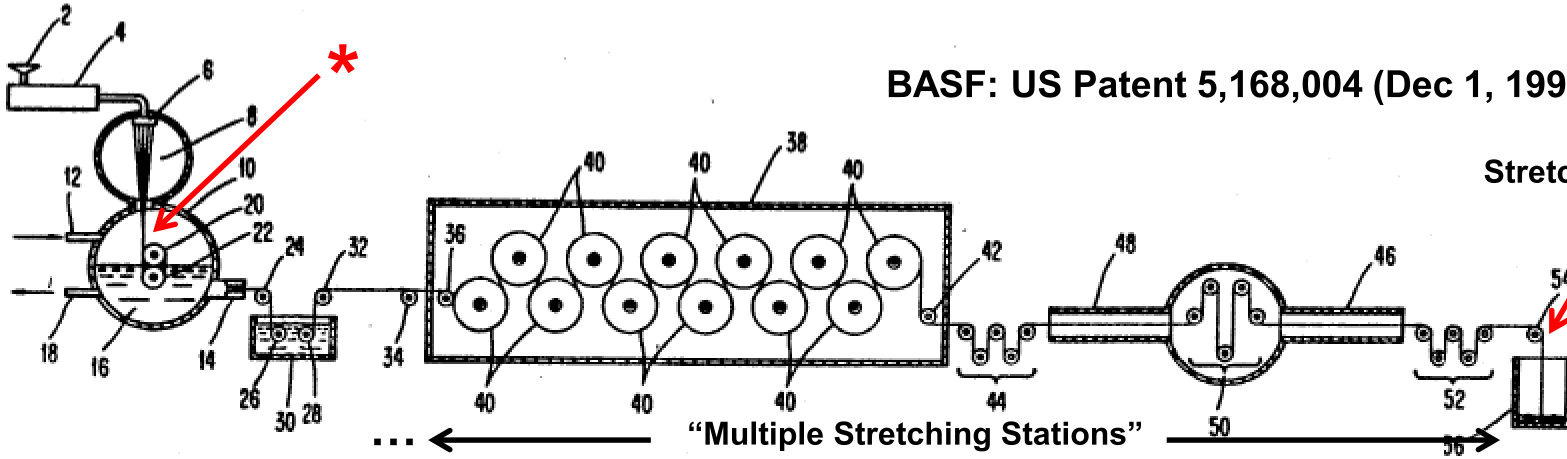
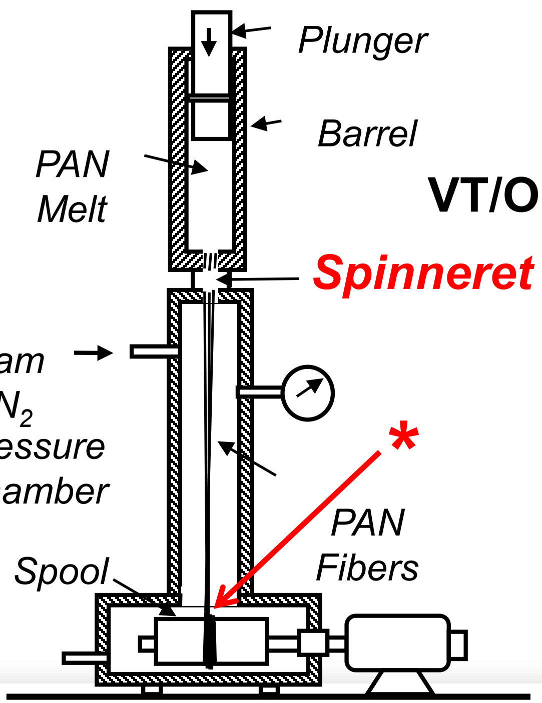
BASF: US Patent 5,168,004 (Dec 1, 1992)



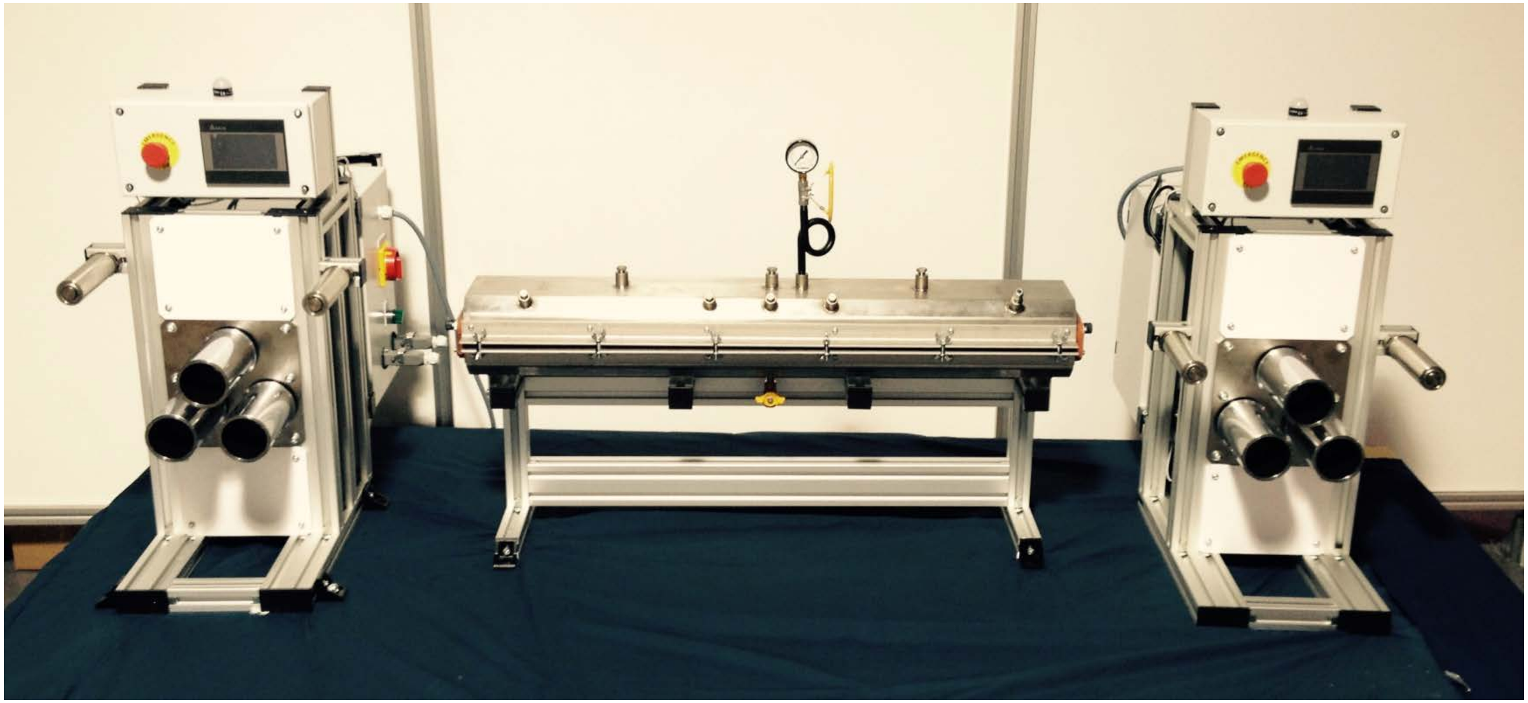


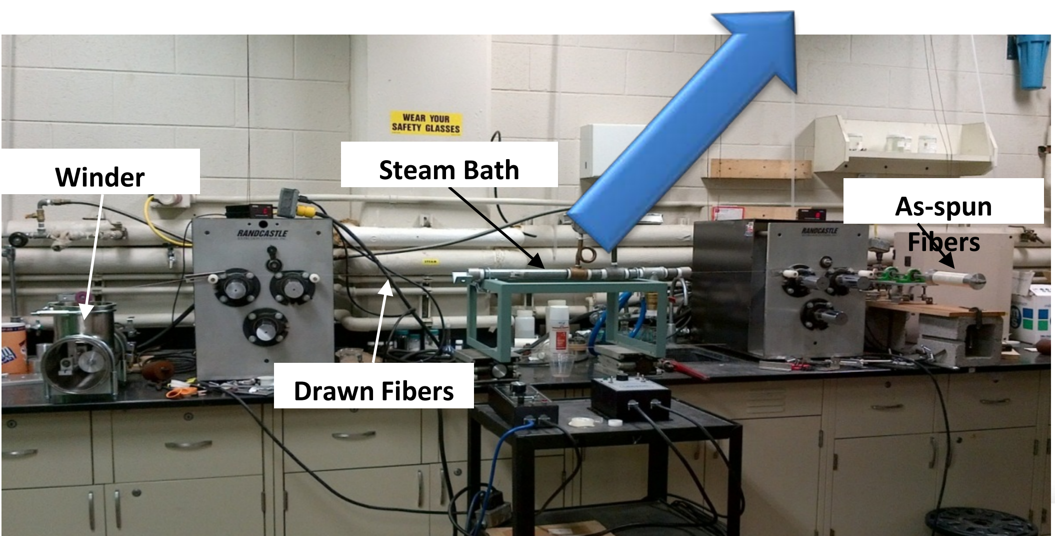
VT/ORNL

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

- **We originally attempted to do all drawing in a single step in the pressure chamber vs BASF added subsequent drawing steps at the end of spinning**
- **Adding a discrete drawing stage after spinning allowed us to separate spinning and drawing and better concentrate on each independently**

Approach – Hot Fiber Drawing





- Significantly improved tension control and less fiber damage
- Improved fiber heating
- More flexible operations while retaining earlier capabilities

ST093

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

Best Carbonized ORNL/VT PAN Fiber Data

Progressing

Sample name	Diameter [µm]	Peak stress [ksi]	Modulus [Msi]	Strain [%]
VT_201201	Could not be unspooled			
VT_201203	11.58	76.5	16.1	0.52
VT_201205	10.55	77.4	6.2	1.67
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.