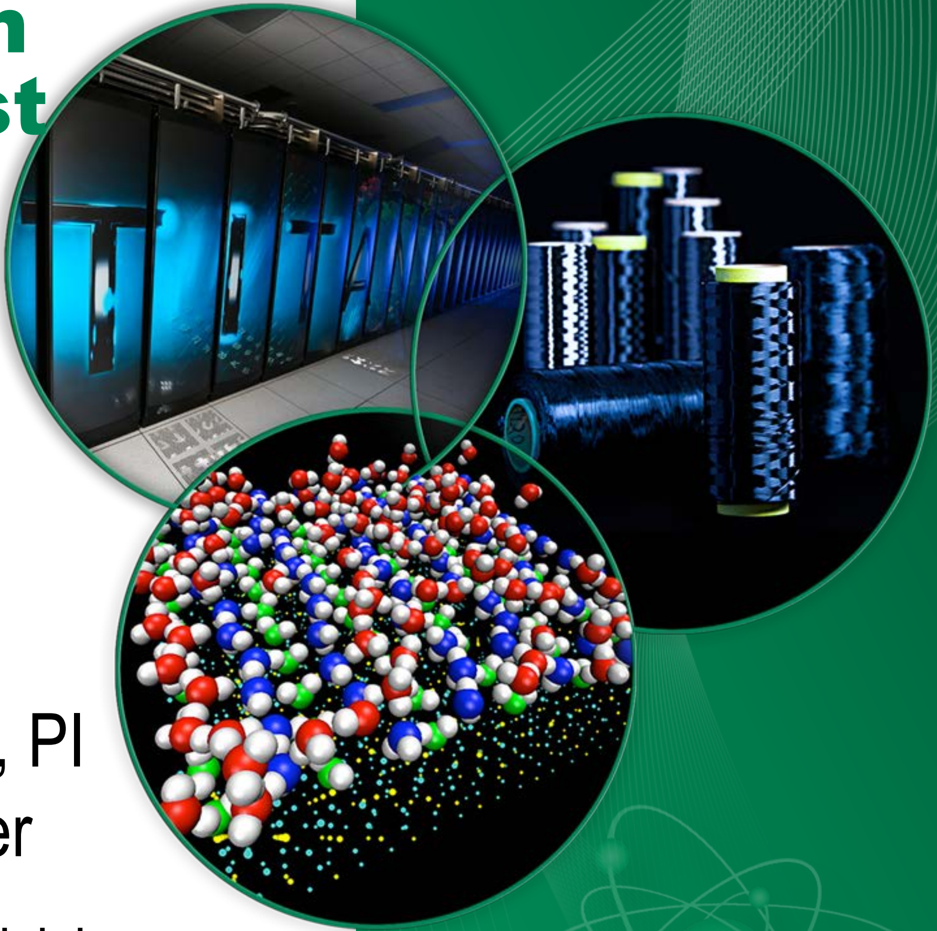
Melt Processable PAN Precursor for High Strength, Low-Cost Carbon Fibers



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Merit Review 2014

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Project ID: ST093

Overview

- **Timeline**
  - Phase II Start: 10/2013
  - Phase II End: 9/2016
  - ~15% complete at submission
- **Budget**
  - FY13: $600K (for Phase I completion and Phase II equipment)
  - FY14: $200K
  - Total DOE Project Value: $1,595K
- **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)
    - James McGrath/ Sue Mecham (precursor chemistry)

Relevance

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

Capabilities upgrades recently initiated in Phase II allow work to move beyond bench-scale "science" towards engineering larger-scale demonstration

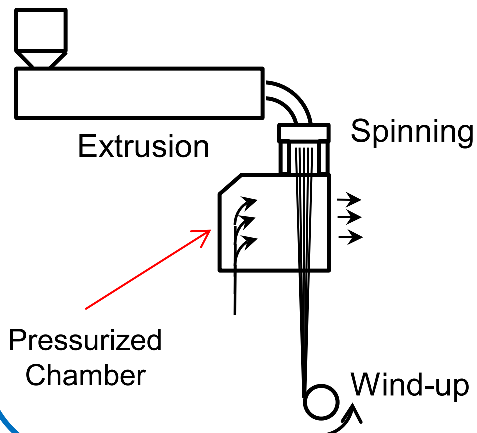
Melt Spinning vs. Wet Spinning

Advanced Technology (for PAN)

Current Technology

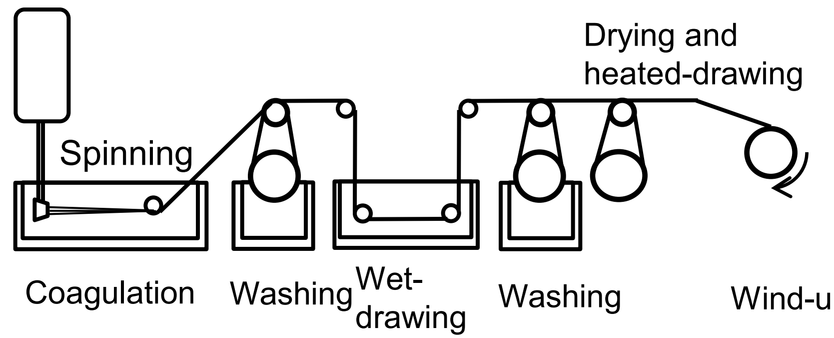
- Capital intensive
- Solvent typically highly corrosive
- Significant solvent plant hold-up

Melt-processing



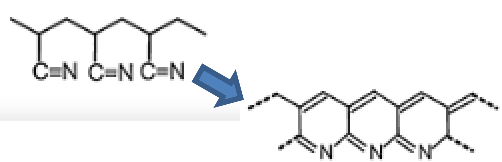
- Low production cost
- High production rate
- Environment-friendly

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.

Approach

Phase I study successfully demonstrated feasibility, but team was extremely limited in going forward:

- Utilized PAN-VA chemistry likely not capable of meeting targeted performance
- Co-monomers utilized in PAN formulation not appropriate for production
- Capillary rheometer utilized for spinning produces very small quantities
  - Achieving process stability difficult if not impossible
  - Overall production level (~12 filaments X 25-50m MAX length) inadequate for conversion needs
  - Spinning pressure chamber and winding inadequate
- Rudimentary hot drawing not suitable for high performance
- Conversion experiments limited by precursor quantities/quality available

Approach – Precursor Chemistry

Chemistry work deferred in Phase I to focus on spinning and conversion feasibility demonstration is now restarted

- Moving back from PAN-VA to PAN-MA
- Moving to higher molecular weight
- Evaluating more attractive co-monomers and alternative plasticizers

	AN/MA ^{1}H NMR (wt %)	M_w (g/mol)	T_g [b] (^{0}C)		T_m (^{0}C)		Melt extrusion at "T_m"
			Control	Blend	Control [c]	Blend[b]	
(1)	93/7	240,000	100	96	288	213	X
(2)	88/12	137,000	91	88	238	201	√
(3)	95/5	65,700	88	85	307	221	√

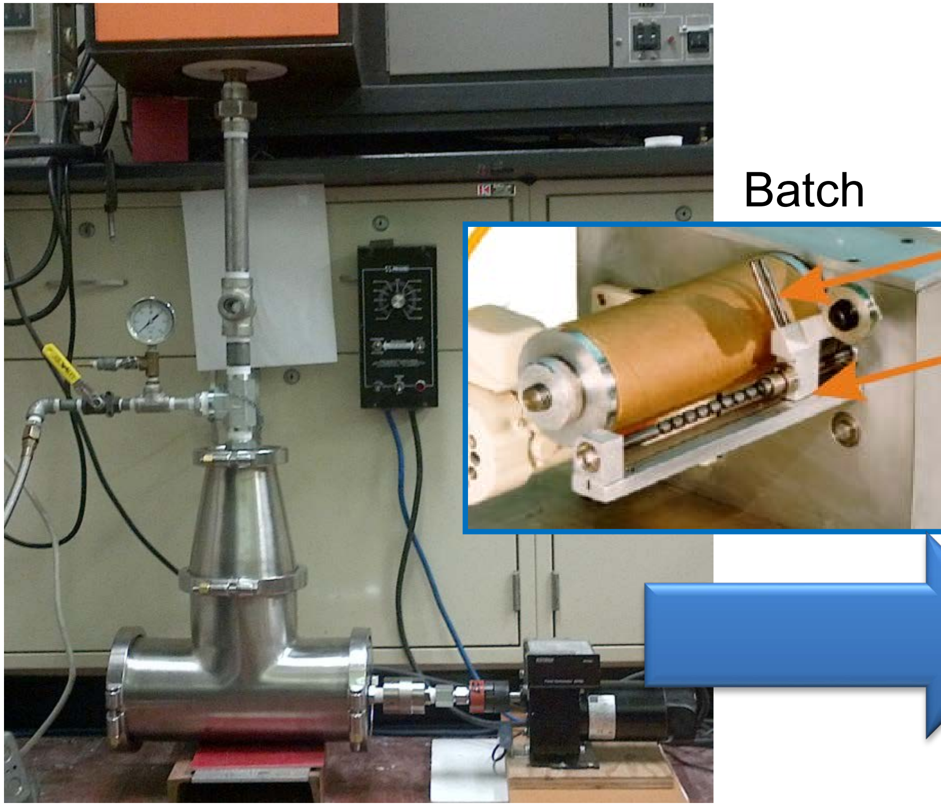
Approach – Melt Spinning

- Produced small amounts of filaments from PAN-VA demo formulations in rheometer to advance melt spinning knowledge and experience
  - Characterization of molecular weigh effects on processing/properties
  - Provision of precursor to continue conversion development
  - Evaluation of various plasticizers and effects
- New 5/8-in extruder to replace rheometer
  - Sized to produce adequate quantities of precursor without overwhelming capability to produce dope
  - Ordered 12/13
  - Delivery delayed until May (was expected April 2014)

Polymer	Plasticizer 1	Plasticizer 2	Spinning Temp (°C)	Quality of As-Spun Fibers	Max. Draw Ratio
PAN/VA	Water-20%	None	185~190	Good	2.0
PAN/VA	Water-12%	Acetonitrile-12%	165	Good	6.0
PAN/VA	Water-12%	SP-A-12%	170	Marginal	2.0
PAN/VA	Water-12%	SP-B-12%	160~170	Marginal	2.0
PAN/MA	Water-24%	None	190~195	Good	1.7
PAN/MA	Water-12%	Acetonitrile-12%	170	Good	3.0
PAN/MA	Water-12%	SP-A-12%	185	Marginal	1.5
PAN/MA	Water-12%	SP-B-12%	190	Marginal	TBD

- Experiments and design work supporting
  - Spin pack specification
  - Final spinneret acquisition

Approach – Melt-Spinning (cont)

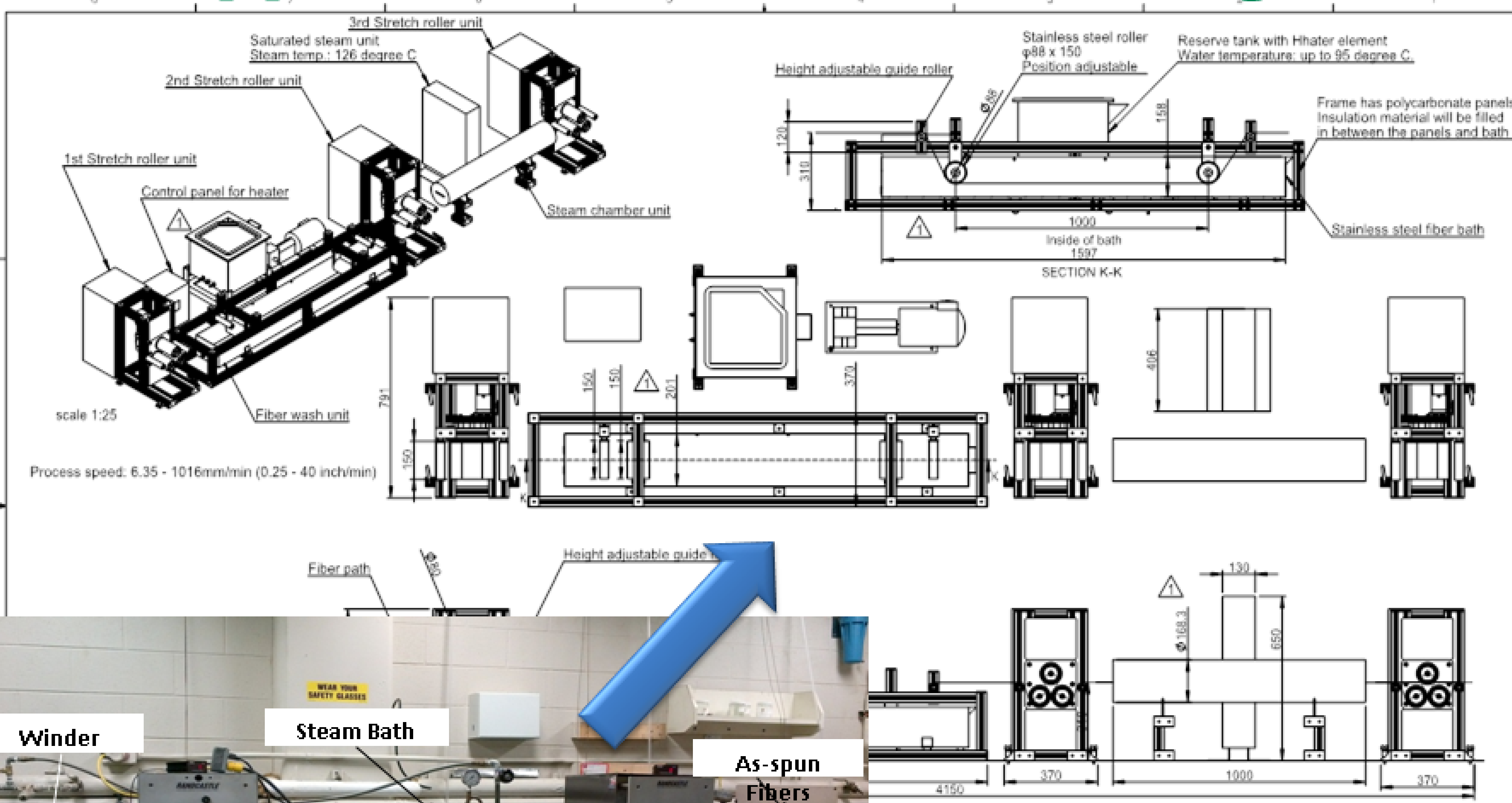


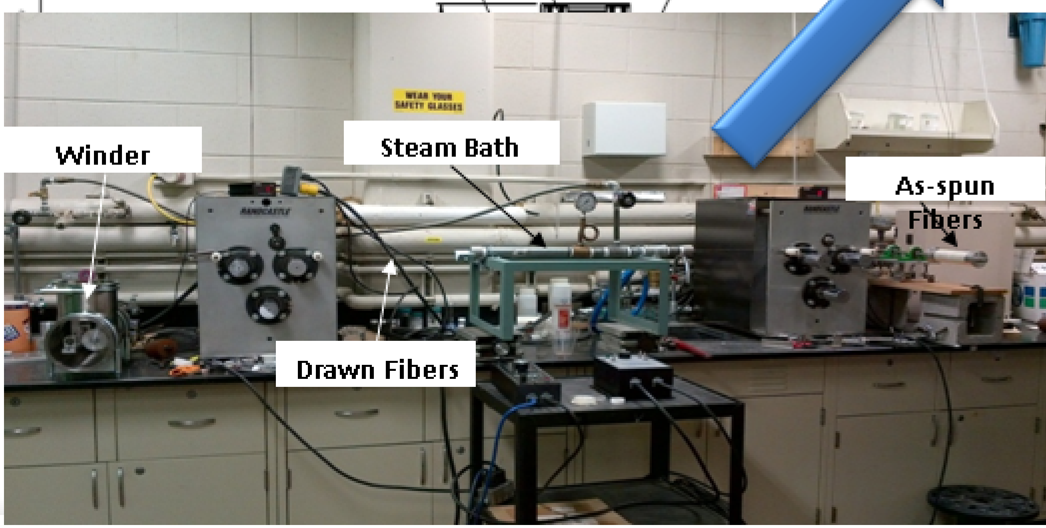
Batch

Continuous processing with new extruder/ pressure chamber:

- Allows more time/material to achieve spinning stability
- Provides significantly longer tow with more filaments for conversion

Approach – Hot Fiber Drawing





Flexible drawing system will provide enhanced orientation control between spinning and conversion

FY14 Milestones

Milestone	Property/Metric	Deliverable	Date	Status
1	Extruder modification and upgraded spinneret design completed.	Equipment on order.	12/31/13	Extruder is on order and thus primary portion of milestone is complete. Spinneret design is continuing.
2	Precursor produced and converted to carbon fiber achieving 25 Msi modulus and 300 ksi strength with 25-50m tow.	Test results reported	3/31/14	Anticipate April completion.
3	Upgraded equipment (Milestone 1) received, installed, and producing precursor meeting 25 Msi and 300 ksi in carbon fiber in >100m length.	Test results reported.	6/30/14	Now in jeopardy due to extruder delay. Working with VPI and manufacturer to solidify delivery date and options.
4	Go/no-go decision point based on precursor produced and converted to carbon fiber achieving 25 Msi modulus and 375 ksi strength with >100m tow.	Test results reported, 10m demo sample provided to sponsor.	9/30/14	On schedule.

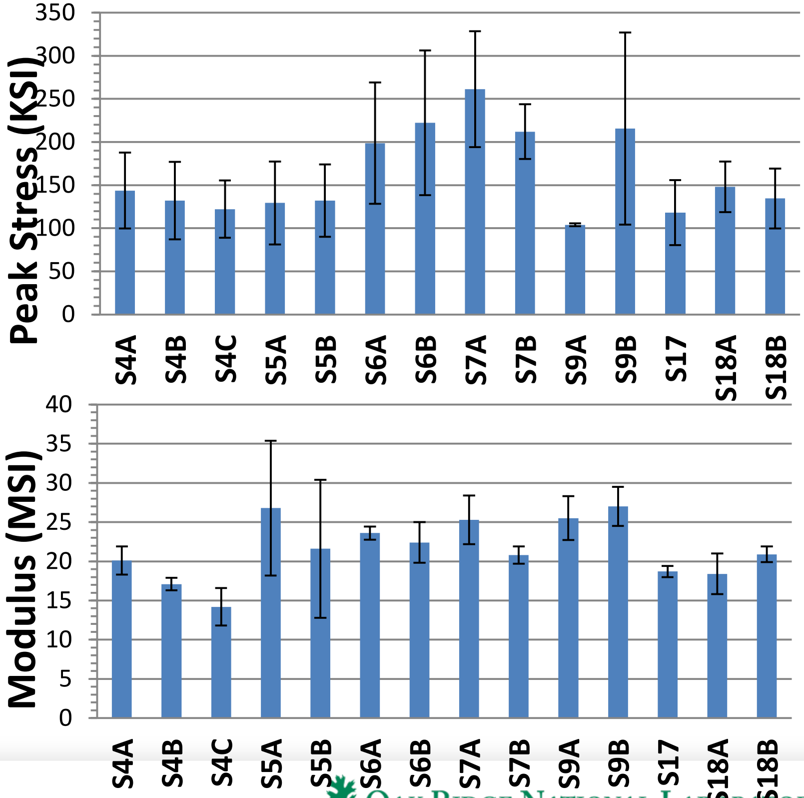
Accomplishments and Progress

- Working towards consistently meeting 3/31/14 milestone for strength and modulus.
- Process parameters have been reviewed and are being better formalized

Precursor format is becoming more uniform

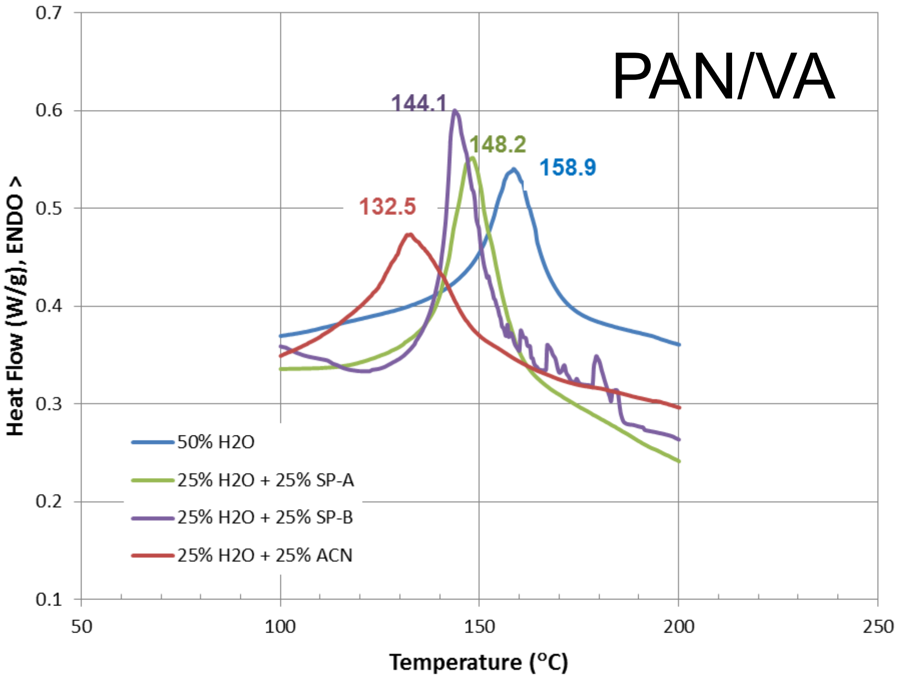
Results show promise, but are highly variable at small scale

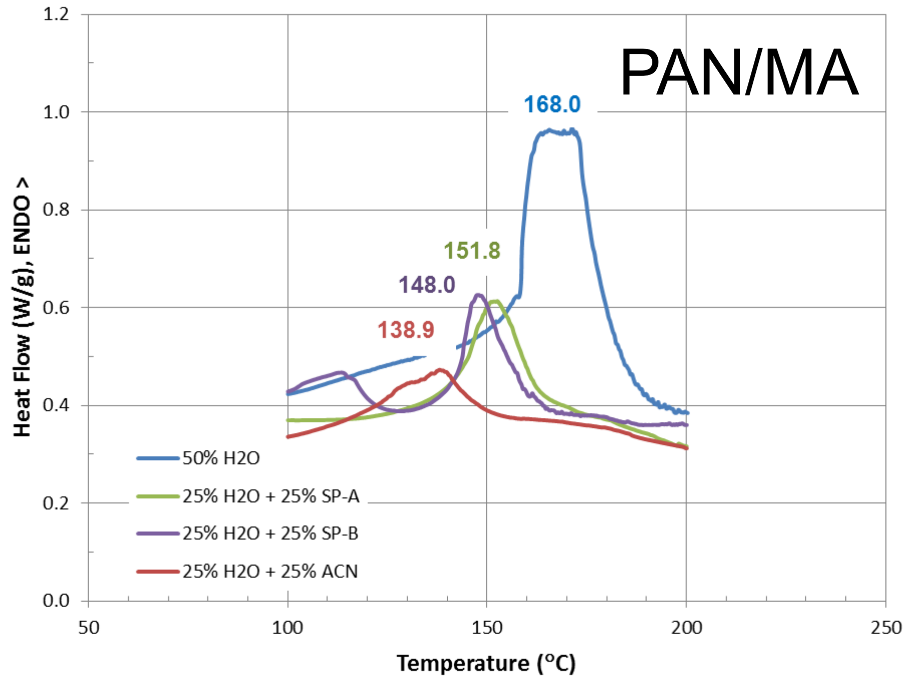
Carbonized Fiber Properties



Accomplishments and Progress

- Expanding plasticizer options as shown by significant suppression of melt temperatures versus plasticizer/plasticizer concentration





Accomplishments and Progress

Example of Spun Polymer PAN/VA (Textile)							
Sample ID	**Spinning Date**	**As-spun Draw Ratio**	**2nd Stretch Draw Ration**	**Fiber Diameter (µm)**	**Peak Stress (Ksi)**	**Modulus (Msi)**	**Strain at Break (%)**
VT 11-12	11/8/12	1.6	4.2	20.54	51.6	1.9	10.4
VT 12-12	11/8/12	1.6	6.2	19.49	62.2	2.3	9.6
VT 04-13	4/8/13	1.7	5.0	17.42	69.5	1.9	9.2
VT 03-14	3/13/14	1.7	4.4	17.75	54.6	1.6	8.59

*Plasticizer for all samples; Water and Acetonitrile

- Recent data regression due to material history misunderstanding

Conversion of Spun Polymer PAN/VA (Textile)							
Precursor .	**Spinning Date**	**Carbon Fiber ID by VT**	**Carbon Fiber ID by ORNL**	**Fiber Diameter (µm)**	**Peak Stress (Ksi)**	**Modulus (Msi)**	**Strain at Break (%)**
VT 11-12	11/8/12	S3A	VT_20121129_S3_A	8.70	86.5	20.7	0.42
VT 11-12	11/8/12	S3B	VT_20121129_S3_B	7.88	191.8	23.2	0.81
VT 11-12	11/8/12	S4A	VT_20121129_S4_A	8.20	143.7	20.1	0.70
VT 11-12	11/8/12	S4B	VT_20121129_S4_B	9.65	132.1	17.1	0.70
VT 11-12	11/8/12	S4C	VT_20121129_S4_C	9.49	122.1	14.2	0.80
VT 11-12	11/8/12	S5A	VT_20121129_S5_A	8.24	129.3	26.8	0.50
VT 11-12	11/8/12	S5B	VT_20121129_S5_B	8.81	132.1	21.6	0.70
VT 11-12	11/8/12	S6A	VT_20121129_S6_A	8.34	198.7	23.6	0.81
VT 11-12	11/8/12	S6B	VT_20121129_S6_B	7.34	222.4	22.4	0.94
VT 11-12	11/8/12	S7A	VT_20121129_S7_A	8.04	261.4	25.3	1.00
VT 11-12	11/8/12	S7B	VT_20121129_S7_B	7.24	212.0	20.8	1.00
VT 11-12	11/8/12	S9A	VT_20121129_S9_A	7.01	104.0	25.5	0.40
VT 11-12	11/8/12	S9B	VT_20121129_S9_B	6.91	215.7	27.0	0.80
VT 04-13	4/8/13	S17	VT17 15g_15g	7.99	118.1	18.7	0.62
VT 04-13	4/8/13	S18A	VT18 10g_10g	8.87	147.9	18.4	0.74

Additional Accomplishments and Progress

- Chemistry
  - Characterization of rheological effects vs increasing molecular weight driving progress towards new PAN-MA formulations

    in conjunction with:

  - Multiple alternative plasticization techniques have been and are being evaluated to facilitate spinning
- Spinning
  - Pressure chamber, spin pack, and spinneret designs nearing completion
  - Capability for pelletizing PAN dope being implemented
- Conversion
  - Hot drawing capability being acquired
  - Formulation/spinning/drawing/conversion relationships being established

Collaborations

- Virginia Tech continues to be principal partner in science and technology development phases
- Customized "model" PAN compounds have been supplied by FISIPE
- Suppliers for larger quantities of PAN-based dope have been identified (FISIPE, Akron Polymer Systems, etc.) for use as formulations are resolved and need arises
- Background and consultation have been supplied by past participants in BASF melt-spun program
- In related projects, industrial participation is being solicited for advanced oxidation and carbonization development
- Additional partnerships at this time may compromise longer-term options

Response to Previous Year Reviews

- Comments on Project Approach
  - Reviewers provided positive comments on overall approach and team arrangements along with suggestions for updating the cost model, moving from PAN-VA to PAN-MA, and correlating porosity with properties.
  - Cost model will be updated during 2014, transition from VA to MA is in progress, and porosity mitigation will always be a portion of processing considerations.
- Comments on Progress
  - Reviewers acknowledged enhanced progress over previous years along with suggesting addressing barriers better and clarifying connection of progress with DOE targets.
  - Phase II milestones demonstrate needed progress to meet targets. Technology barriers and participant resource limitation barriers are also addressed in Phase II.
- Comments on Collaboration
  - Existing collaboration is acknowledged as very effective, but team is encouraged to seek additional partners.
  - Less evident partners have been identified and additional partners are being sought in several areas.

Remaining Challenges and Barriers

- Success requires innovative chemistry and processing developments combining
  - Precursor formulation that can be spun and meet property targets
  - Choice of plasticizers that facilitate spinning without detriment to properties
  - Development of spinning into chamber pressurized at lowest level practical to achieve robust, cost-effective process
  - Conversion process optimized for performance and economics
- Each of the above steps is independently challenging, but all are interdependent
- Coordination is critical to make significant technology leaps in each area that can be effectively integrated and optimized together

Future Work – Key FY 15/16 Milestones

Milestone	Property/Metric	Deliverable	Date	Status
5	Updated economic model completed for chemistry and process parameters demonstrated in Milestone 4.	Assumptions and results outlined in quarterly report.	12/31/14	On schedule.
6	Precursor produced and converted to carbon fiber achieving 30 Msi modulus and 400 ksi strength with >100m tow.	Test results reported, 10m demo sample provided to sponsor.	3/31/15	On schedule.
8	Go/no-go decision point based on precursor produced and converted to carbon fiber achieving 30 Msi modulus and 500 ksi strength with >100m tow.	Test results reported, 10m demo sample provided to sponsor.	9/30/15	On schedule.
11	Draft technology transfer plan completed.	Plans for scale up and transfer of technology leading to commercialization presented to sponsor for comment.	6/30/16	On schedule.
12	Precursor produced and converted to carbon fiber achieving 33 Msi modulus and ≥650 ksi strength with >100m tow.	Test results reported on milestone and 10m demo sample provided to sponsor.	9/30/16	On schedule.

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

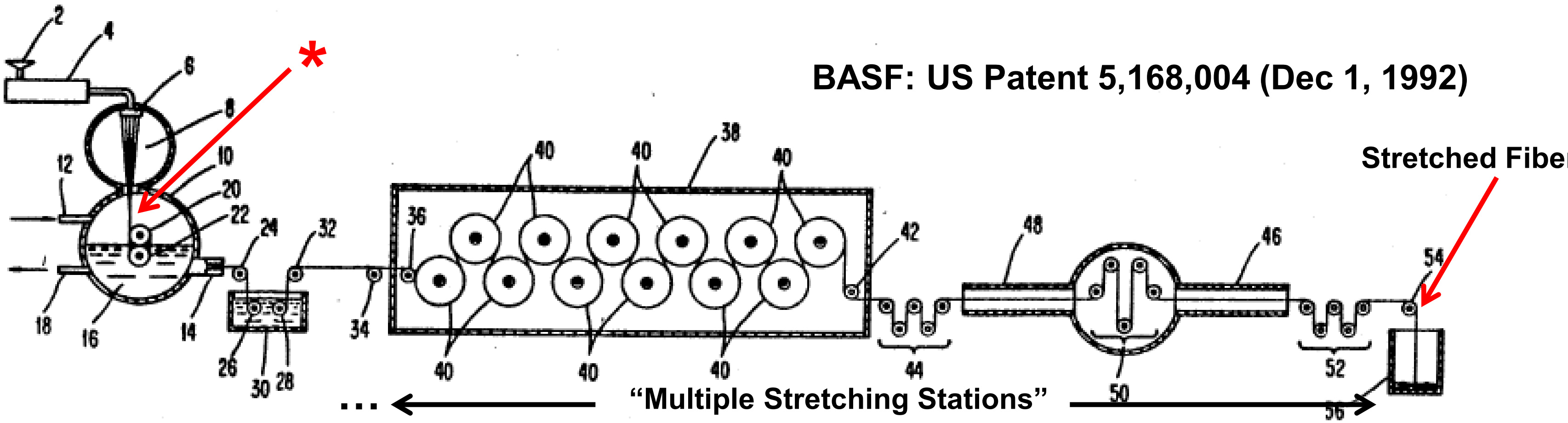
- ORNL worked closely with Virginia Tech and others in the industry to get to this point.
- Additional partnership arrangements are being sought.

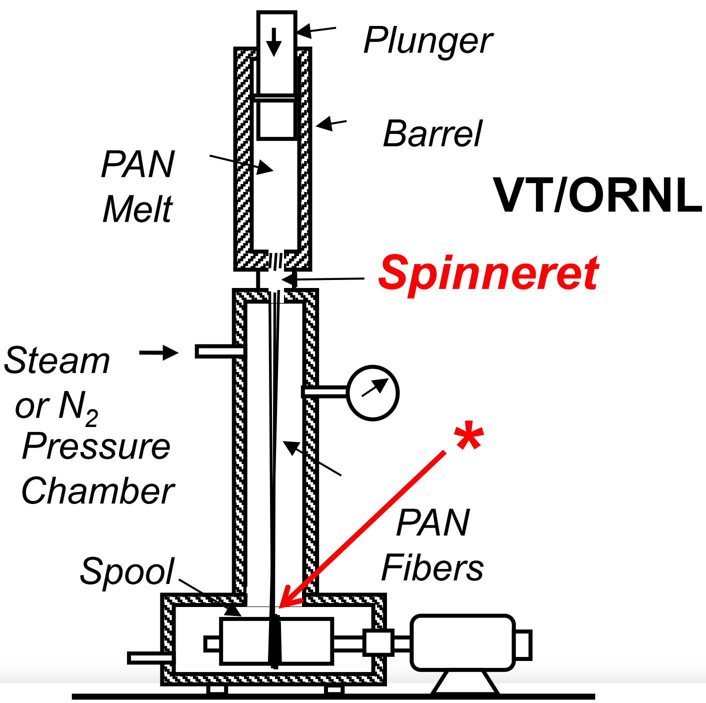
Future Work

- **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 TECHNICAL SLIDES

Filament Generation System Comparison BASF vs. 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.**

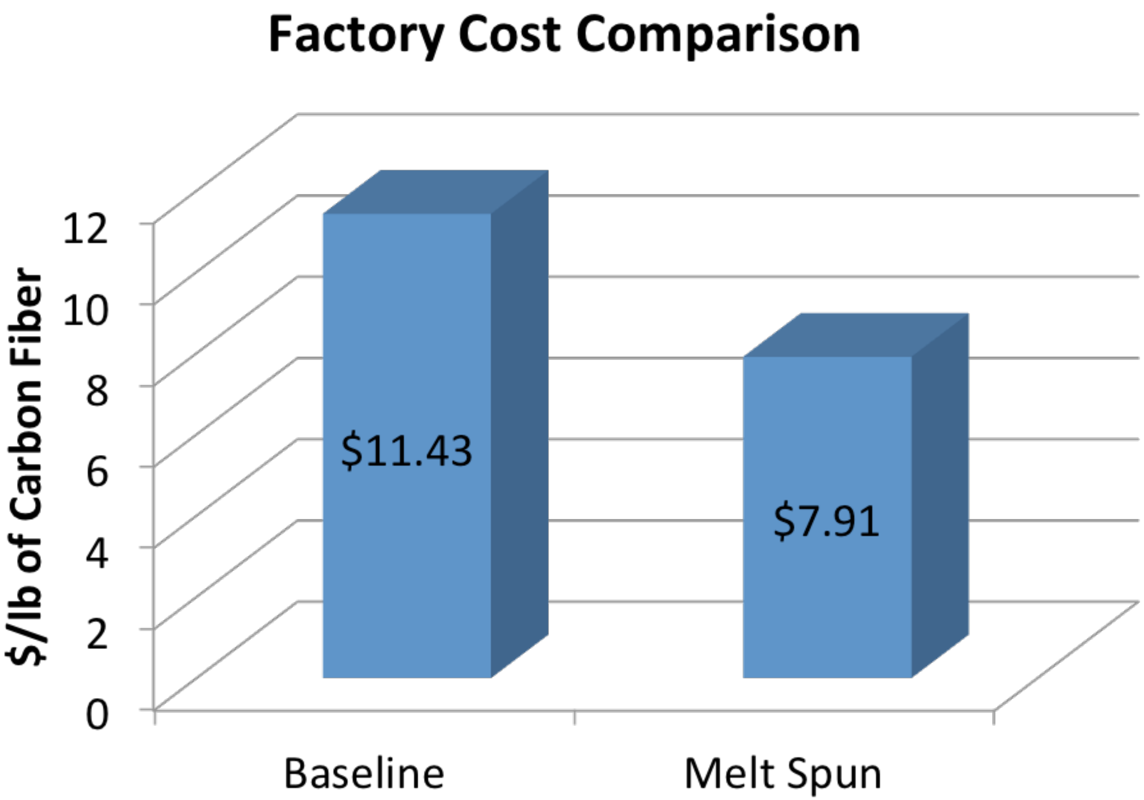
Melt-Spun PAN Precursor has a history of prior R&D

- 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**

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.

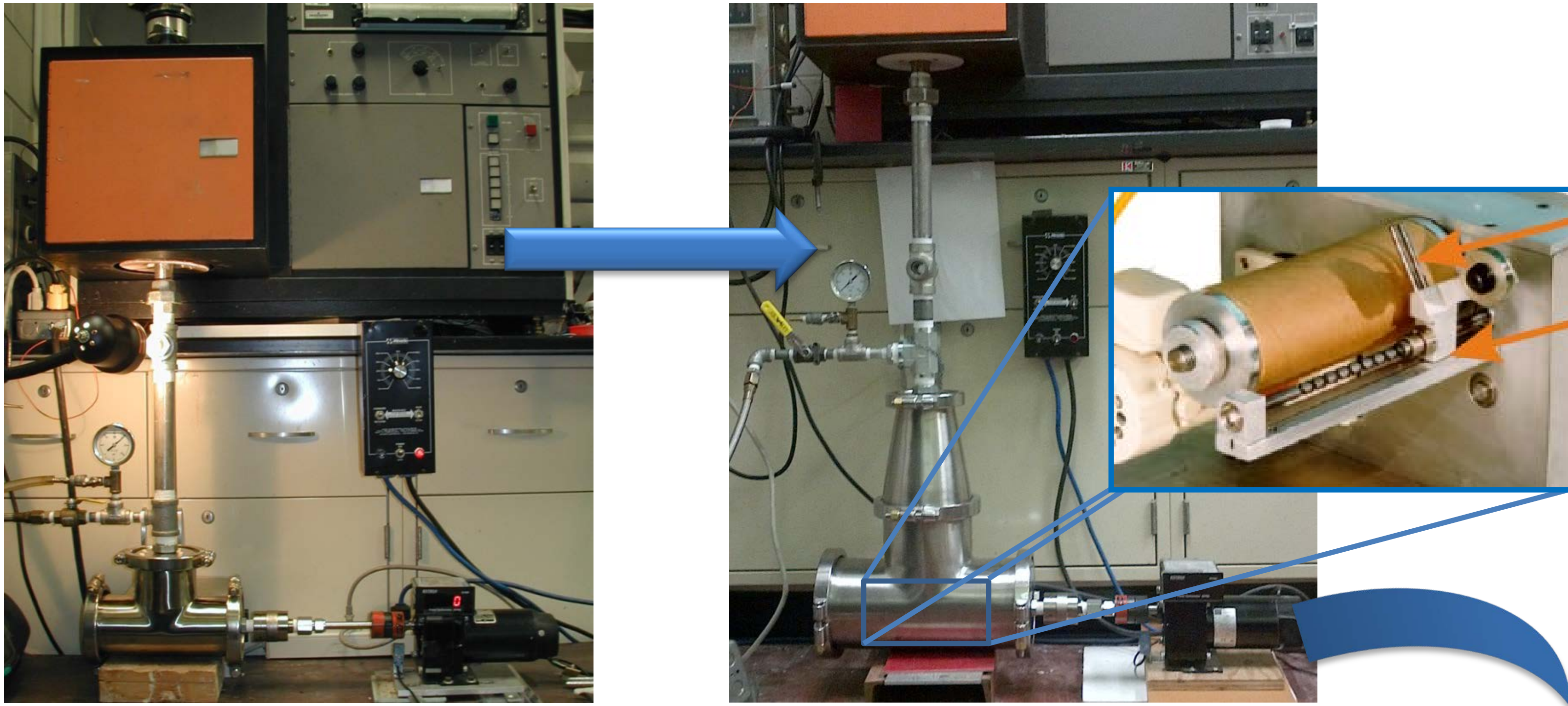
This represents ~31-33% savings in cost.

Model Currently Being Updated

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.**

Technical Accomplishments

Newly improved fiber spinning system.



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

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.