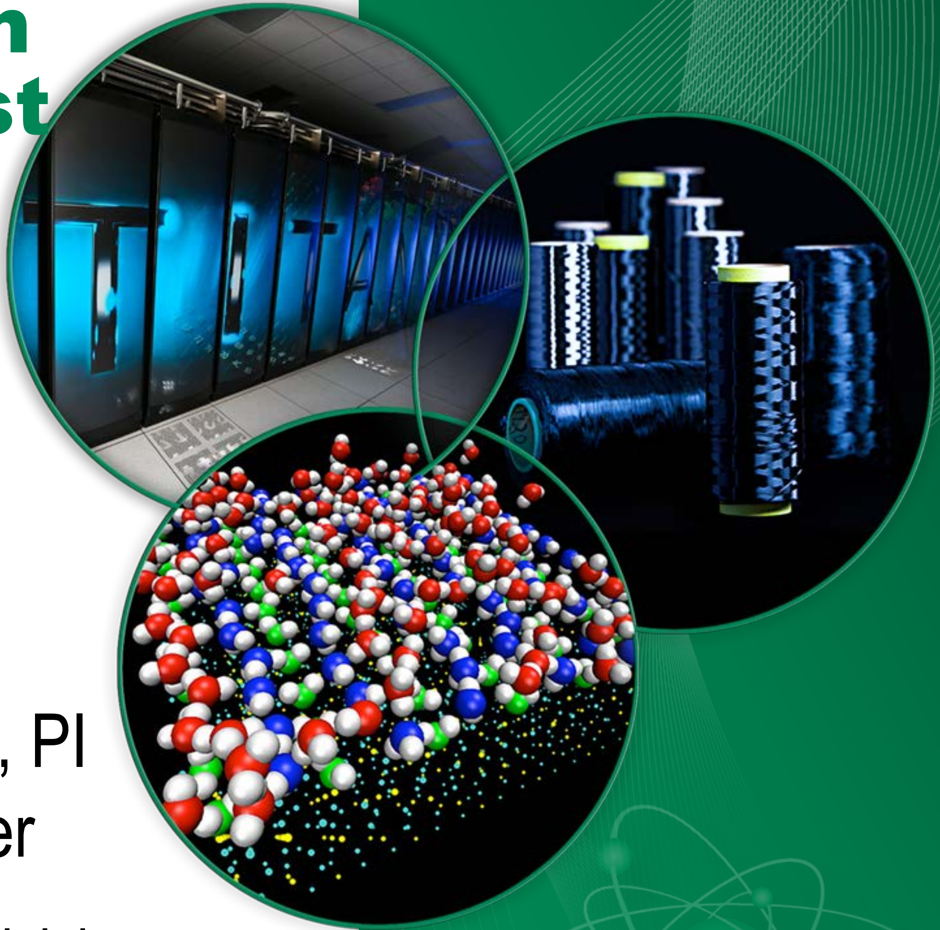
Melt Processable PAN Precursor for High Strength, Low-Cost Carbon Fibers



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Merit Review 2015

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Project ID: ST093

Overview

- **Timeline**
  - Phase I completed 9/2013
  - Phase II Start: 10/2013
  - Phase II End: 09/2016
  - ~35% complete at submission

- **Budget**
  - FY15 $400K

- **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**

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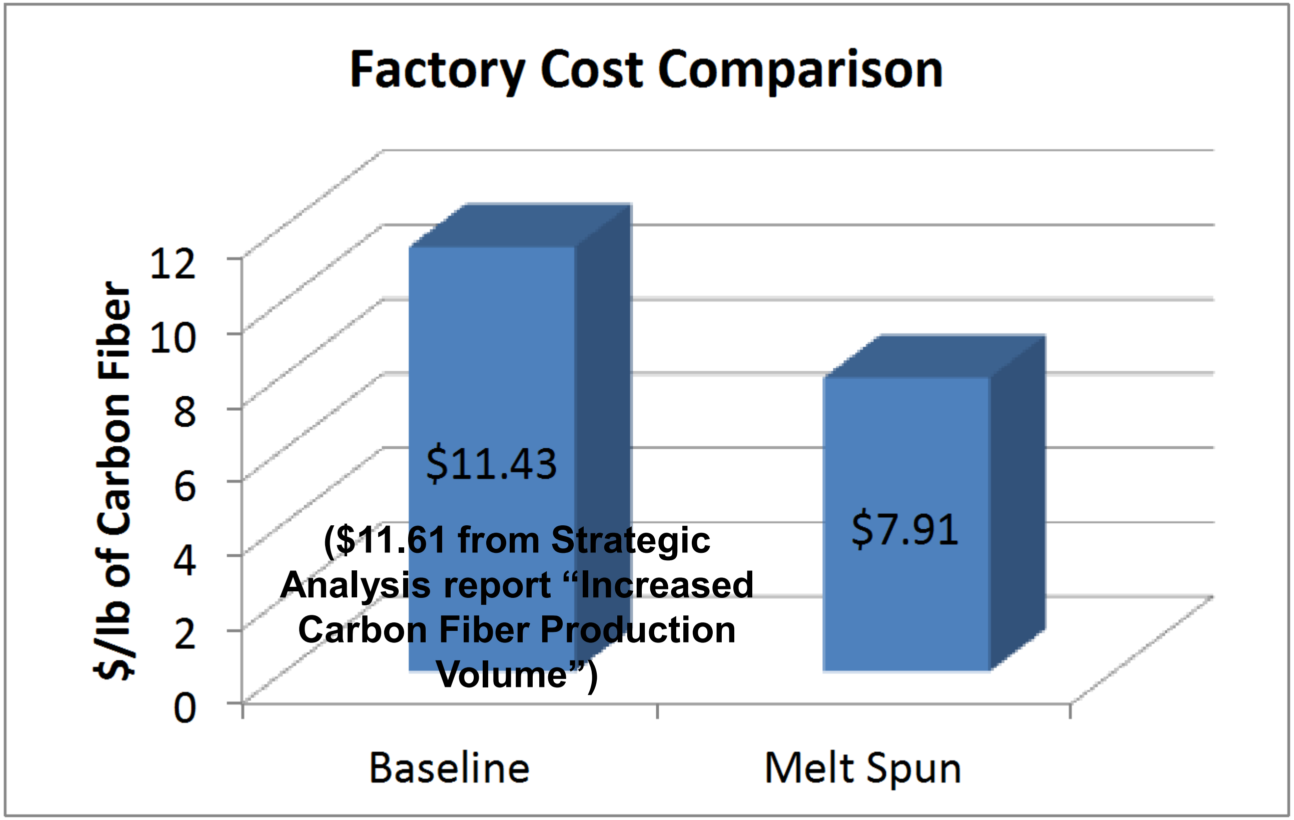
Potential CF Cost Matrix

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.**

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-MA 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

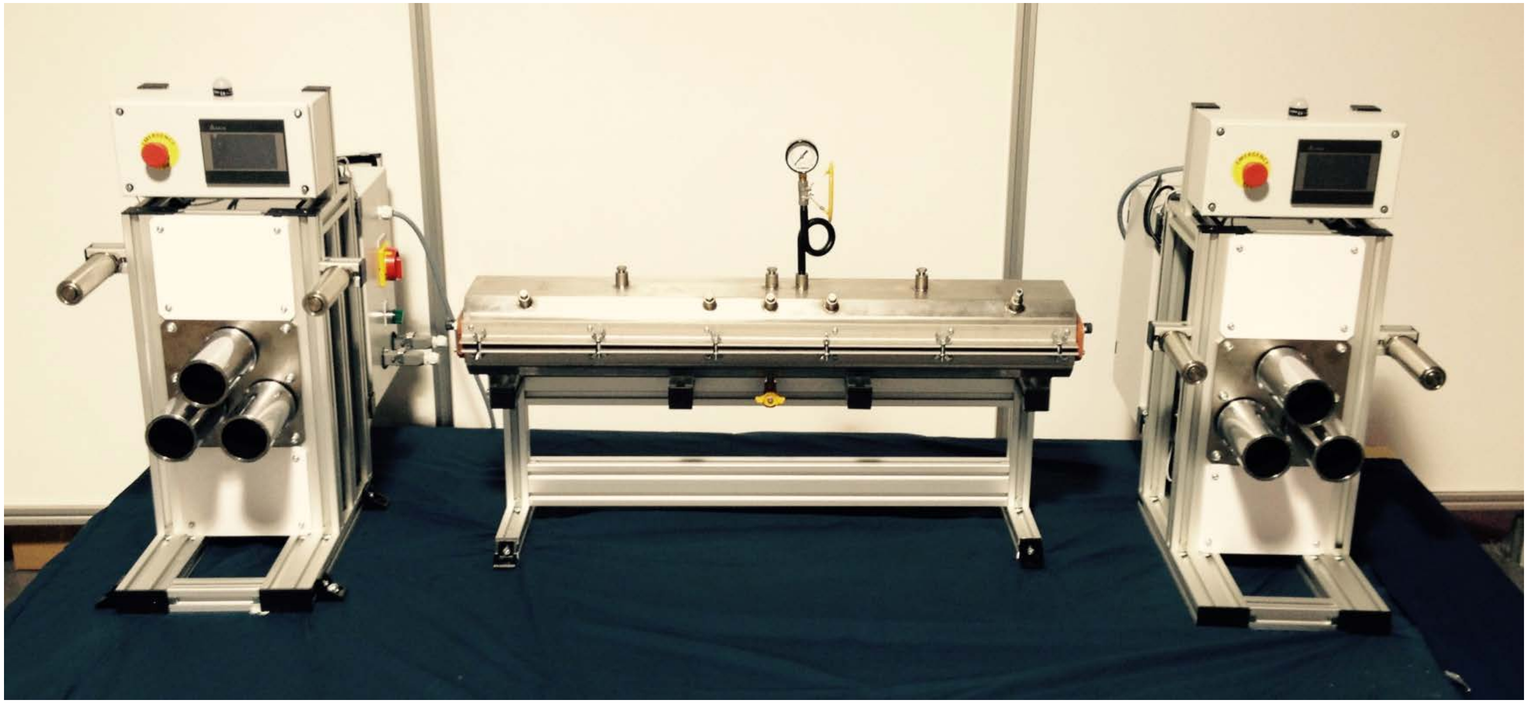
Sample ID	Initiator (mol %)	Activator (mol %)	Start Temp - Max Temp (°C)	Reaction Time	AN/MA wt/wt (NMR)	SEC M_w (kg/mol) - PDI	Recovered Yield	IV (SEC) DMAC-0.1M LiCl-50°C
MJ-162	0.116	0.0630	40-52 (too hard to control exotherm)	20 h	96/4	82-2.2 (DMAc)	60%	0.62
MJ-02-01	0.116	0.0473	40-56	21 h	95/5	152-1.8 (DMAc)	94%	1.1
MJ-02-04	0.116	0.0315	40-47	24 h	95/5	143-1.7 (DMAc)	88%	1.0
MJ-02-07	0.116	0.0200	40-41	46 h	96/4	insoluble	low	--
MJ-02-57	0.116	0.0315	40	24h	96/4		99%	
MJ-02-04	0.116	0.0315	40-47	24 h	95/5	143 - 1.7 (DMAc)	88%	1.0
MJ-02-33	0.116	0.0315	40-41	16h	93/7	200 - 1.8 (DMAc)	60%	
MJ-02-11	0.116	0.0315	40-46	23h	91/9	130/141 – 1.9/1.6 (DMAc)	97%	0.63
MJ-02-59	0.116	0.0315	40-44	24h	91/9		93%	
MJ-02-14	0.116	0.0315	40-41	19 h	87/13		83%	
MJ-02-16	0.116	0.0315	40-55	24 h	81/19		94%	

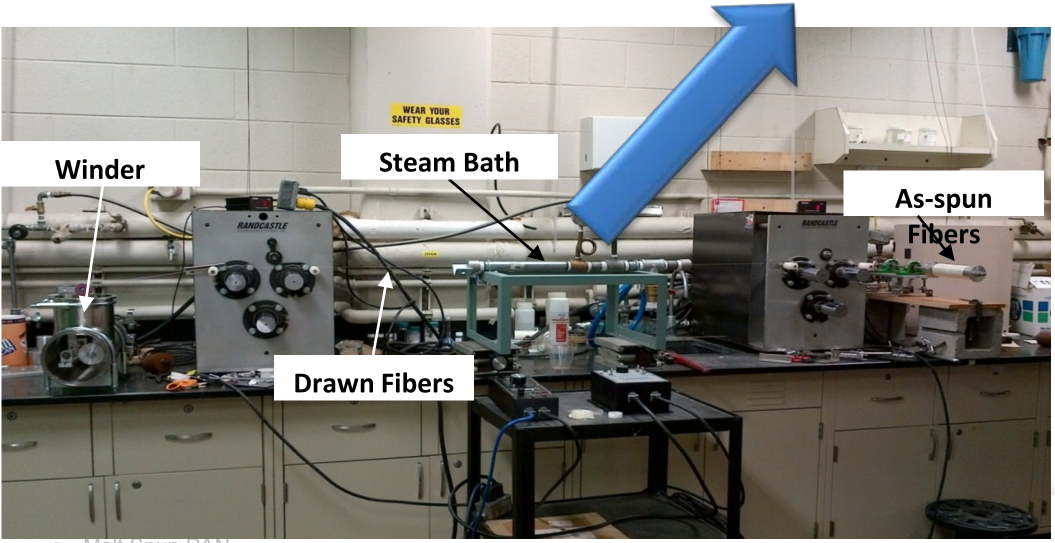
Approach – Melt Spinning

- Continued producing small amounts of filaments in rheometer to advance melt spinning knowledge and experience
  - Characterization of molecular weight effects on processing/properties
  - Provision of precursor to continue conversion development
  - Establishing more consistent rheological background and approach for material/process down-selection
- Evaluation of various plasticizers and effects

- Installed new 5/8-in extruder to replace rheometer
  - Sized to produce adequate quantities of precursor without overwhelming capability to produce dope
  - Can take advantage of existing equipment for initial experiments while allowing for upgraded capabilities as program progresses

Approach – Hot Fiber Drawing





- Significantly improved tension control and less fiber damage
- Improved fiber heating
- More flexible operations

FY15 Milestones

Milestone	Property/Metric	Deliverable	Date	Status
2	Upgraded equipment received, installed, and producing precursor with greater than 100 filaments and continuous lengths >100m.	Documentation in quarterly report.	~~12/31/14~~ 6/30/15	Powder spinning and moisture retention problems have delayed progress. New date proposed.
3	Upgraded equipment received, installed, and producing precursor converted to carbon fiber achieving 25 Msi modulus and 300 ksi strength with 25-50m tow.	Test results reported	~~3/31/15~~ 8/15/15	New date proposed due to problems in spinning.
4	Updated economic model completed for chemistry and process parameters to support Go/No-Go Decision.	Assumptions and results outlined in quarterly report.	~~6/30/15~~ 9/30/15	New date proposed to have adequate data.
5	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.	~~9/30/15~~ 10/31/15	Will likely need to reschedule.

Accomplishments and Progress

- Completed transition from PAN-VA to PAN-MA work other than using PAN-VA to checkout and adjust machine parameters while saving key developmental materials
- Capillary rheometer studies have allowed us to down-select and order specific PAN-MA molecular weight and concentration compounds
- Although conversion has been problematic at small quantities, work with spinning precursor in capillary rheometer continues to show improving precursor properties comparable to similar precursor reported by others, i.e.:
  - Work reported in Georgia Tech thesis (shown for comparison at right), and
  - Data provided on BASF melt spun fiber prior to any drawing (not cleared for public release)

Sample Name	AN % (wt%)	IV[b] (dL/g)	Mv[c] (kg/mol)	Precursor Fiber		Carbon Fiber	
				Strength (Ksi)	Modulus (Msi)	Strength (Ksi)	Modulus (Msi)
VT 04-14A	93	1.96	162	62.4	1.70	169.8	20.7
VT 04-14B	93	1.96	162	64.3	1.80	200.3	25.9
GT 93-265	93	2.72	250	60.3	1.62	333.5	31.0
GT 93-170	93	1.94	160	60.3	1.91	362.5	30.5
GT 93-106	93	1.37	100	57.4	1.87	246.5	25.1
GT 93-074	93	1.05	70	42.6	1.31	290.0	25.1
GT 97-149	97	1.76	140	56.0	1.77	304.5	26.4
GT 97-106	97	1.37	100	54.4	1.68	319.0	27.7

Accomplishments and Progress

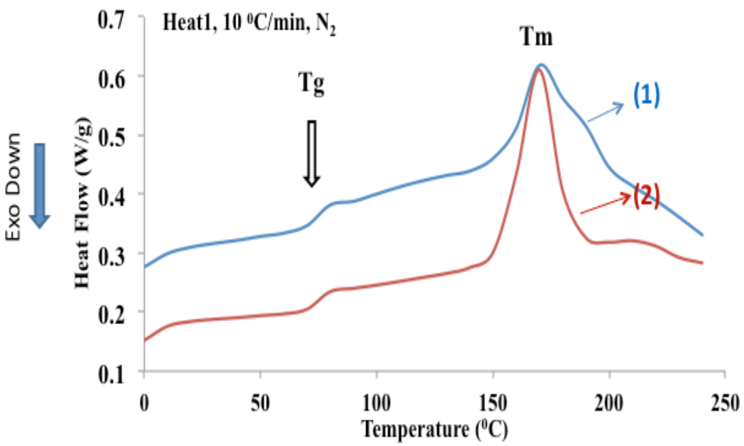
- Extensive study of plasticizer approaches focusing on water as primary means of significant suppression of melt temperatures

	SampleID	AN:MA (wt%) By 1H NMR	M_w (Kg/mol) By SEC[a]	PDI	T_g (°C)	T_m(°C)
(1)	MJ-02-11	91:9	130	1.9	69	155
(2)	MJ-02-33	93:7	200	1.8	73	160
(3)	E22B	93:7	222	3.1	73	160
(4)	MJ-02-04	95:5	143	1.7	73	170

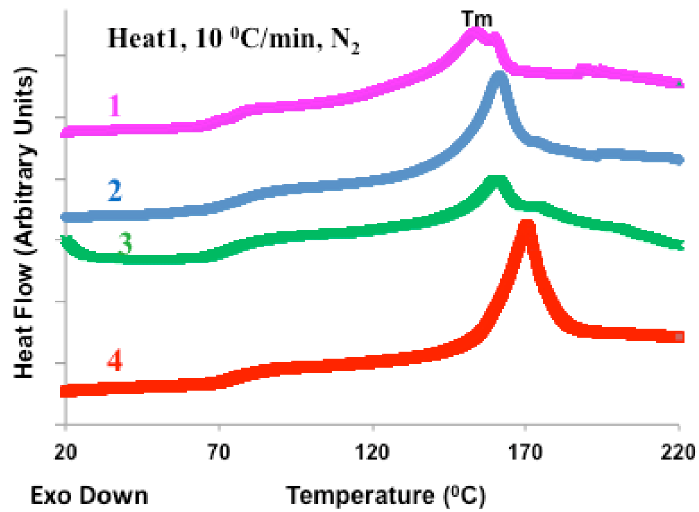
[a] run in DMAC with 0.1 M LiCl

PDI is polydispersity index

	SampleID	T_g (°C)	T_m (°C)	Mol% water
(1)	MJ-144+ 15 wt%Water	74.4	171.2	35
(2)	MJ-144 + 20 wt%Water	73.2	170	43



96/4 wt/wt acrylonitrile to methyl acrylate) blended with 15 wt % of water (blue) and 20 wt % of water (red).



Blends of copolymers with varied acrylonitrile to methyl acrylate ratios and 25 wt% water

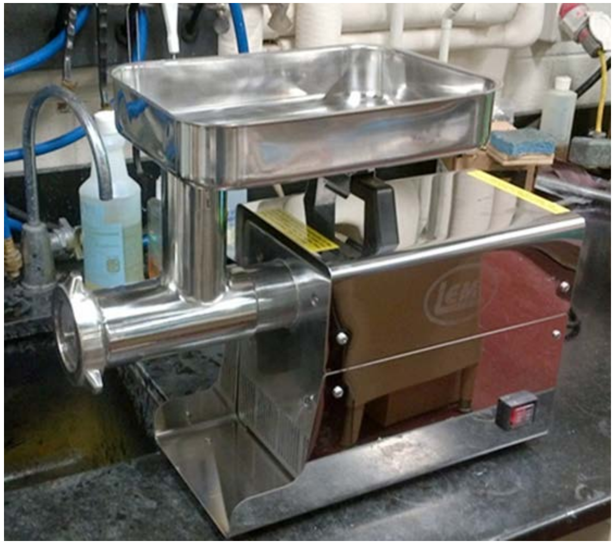
Accomplishments and Progress

- Spinning scale-up has been much more difficult than anticipate although the team strongly feels problems are surmountable engineering issues:
  - Powder feed bridging
  - Pelletization to adequate structural integrity without cross-linking
  - Maintaining water plasticizer while extruding

We are working a number of approaches in parallel, but are now focused on spinning pellets!

AEX-10 Pasta Maker

Utilizing best features of both systems to mix & compress dope produces the best pellets



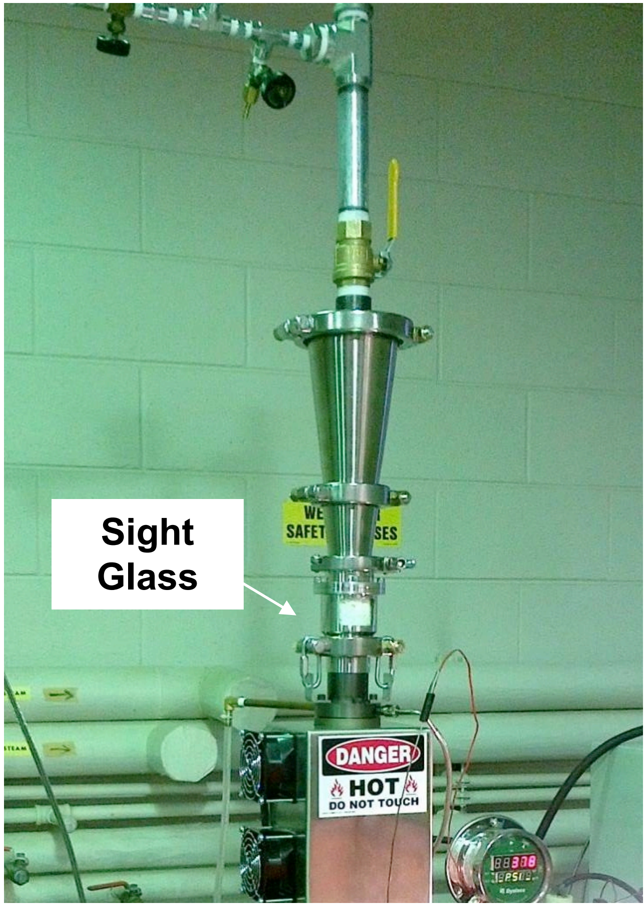
LEM #12 Meat Grinder

Accomplishments and Progress

- Multiple modifications to enhance feeding and sealing in plasticizers

Pressurized Hopper

Pressurized Hopper & Stirrer

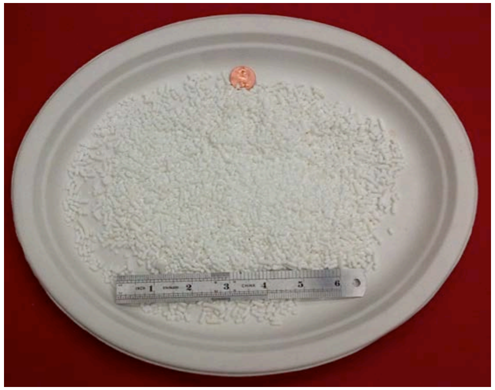


Pressurized Hopper with Sight Glass

Accomplishments and Progress

- …but after a number of frustrating months, we are beginning to see success in the scale-up:

Wet strands for pellets



Pellets for spinning

First Extrusion!!! (Without pressure Chamber)

Large precursor filaments

Response to Previous Year Reviews

- Comments on Project Approach and Relevance/Impact
  - We agree with the reviewer comments in that this is a good fit with overall program goals and will have significant industrial impact.
  - We also agree that much of the spinning has involved trial and error; however, the formulation work has been investigated systematically and with baseline established, spinning can be optimized more systematically.
- Comments on Progress
  - The team has enhanced internal planning including risk and mitigation plans
  - *Consultant under contract with previous BASF spinning experience*
  - An economic model focused on melt spinning is being established
- Comments on Collaboration
  - We concur that we have a good team and are already getting some dope externally
  - We are in frequent communication with potential implementers of *this* technology.
  - Our intention is to formally pursue collaboration with carbon fiber producers and/or associated equipment suppliers with better baseline technology established

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
  - Finding lowest practical pressurization level
  - 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
- 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 ARPA programs***
- Numerous potential ***technology implementers*** are in frequent contact

Future Work – Key FY 16 Milestones

Milestone	Property/Metric	Deliverable	Date	Status
6	Precursor produced and converted to carbon fiber achieving 25 Msi modulus and 425 ksi strength with >100m tow.	Test results reported, 10m demo sample provided to sponsor.	12/31/15	On schedule.
8	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.	3/31/16	On schedule.
9a	Draft of final economic model updated and supplied to sponsor to include near final data and estimated materials and processes cost projections.	Draft provided to sponsor for discussion, feedback, and modification prior to inclusion into final report.	6/30/16	Additional milestone added at sponsor request.
10	Precursor produced and converted to carbon fiber achieving 30 Msi modulus and 650 ksi strength with >100m tow.	Test results reported, 10m demo sample provided to sponsor.	9/30/16	On schedule.
11	Final report draft completed and issued.	Final report draft issued to sponsor. Including technical progress, economic projections, outstanding technical issues assessed, and technology transfer plan proposed.	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.
- **Assistance being provided by consultant directly involved with spinning at BASF**

Future Work

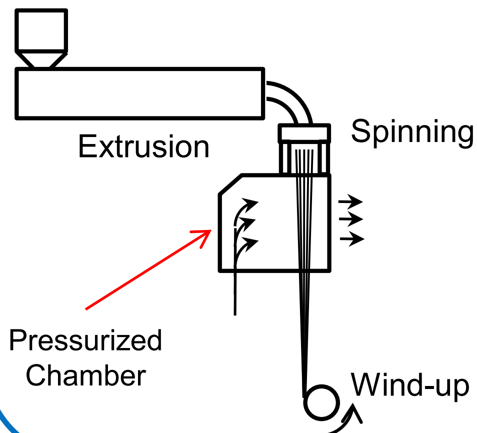
- **Now that feasibility has been demonstrated,** the main two tasks ahead of us are the refinement and scale-up of the process to demonstrate technology and process economics justify investment risk**.**

BACKUP SLIDES

Melt Spinning vs. Wet Spinning

Advanced Technology (for PAN)

Melt-processing

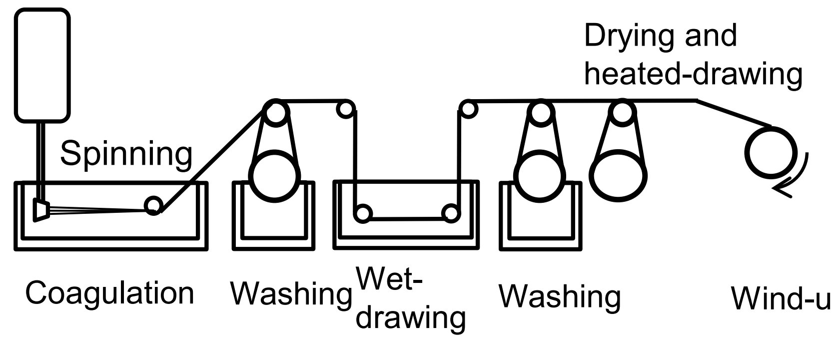


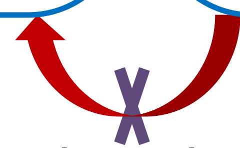
- Low production cost
- High production rate
- Environment-friendly

Current Technology

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

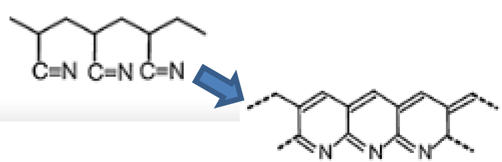
Solution-processing





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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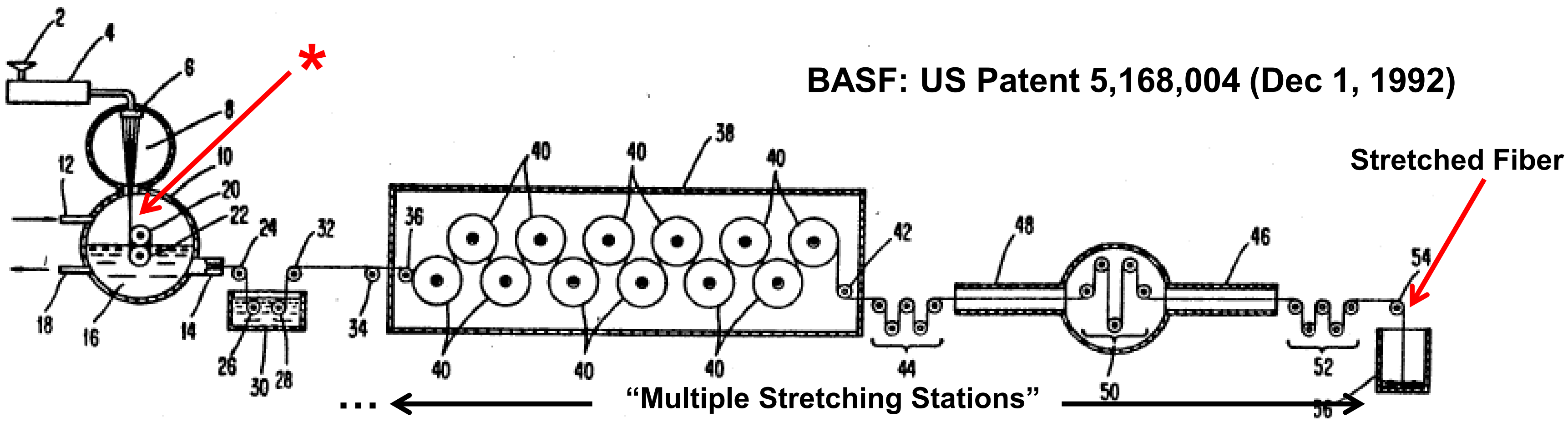

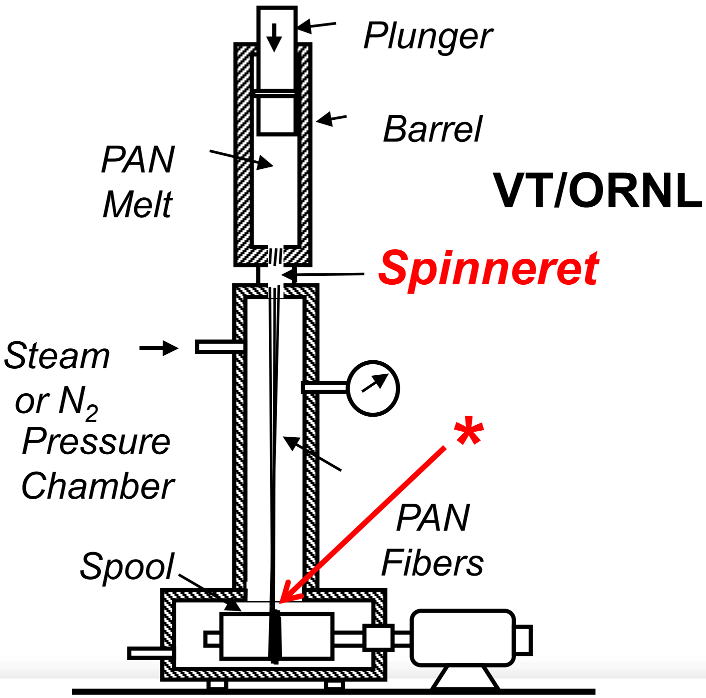

*** As-spun condition at this point**

- **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**

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.