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RENEWABLE ENERGY

On the Pathway to Lower-Cost Compressed Hydrogen Storage Tanks

Cassidy Houchins, Matthew Weisenberger, Mike Chung & Sheng Dai

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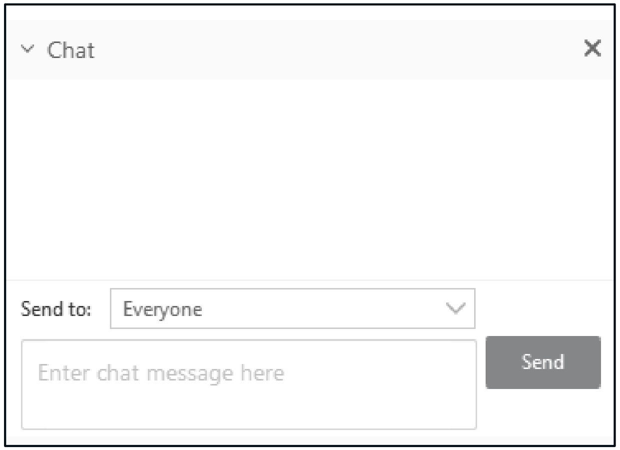
Fuel Cell Technologies Office Webinar

December 17, 2019

This presentation is part of the monthly webinar series provided by the U.S. Department of Energy's Fuel Cell Technologies Office (FCTO) within the Office of Energy Efficiency and Renewable Energy (EERE). Funding for research, development and innovation to accelerate progress in hydrogen and fuel cell technologies is provided by EERE FCTO.

During Q&A session:

Please type your questions to the chat box. <u>**Send to: (HOST)**</u>



On the Pathway to Lower-Cost Compressed Hydrogen Storage Tanks

- Welcome and Webinar Introduction

Ned Stetson
Program Manager – Hydrogen Technologies
DOE-EERE-Fuel Cell Technologies Office

700 Bar Type 4 Storage System Cost Analysis for Light-duty Vehicle Applications

"On the Pathway to Lower-Cost Compressed Hydrogen Storage Tanks—Novel Precursors to Reduce the Cost of High-Strength Carbon Fiber" Fuel Cell Technologies Webinar

17 December 2019

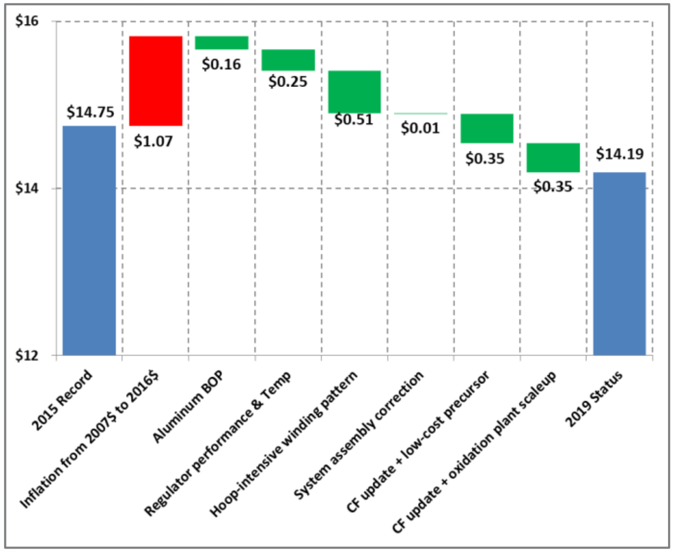
Cassidy Houchins and Brian D. James

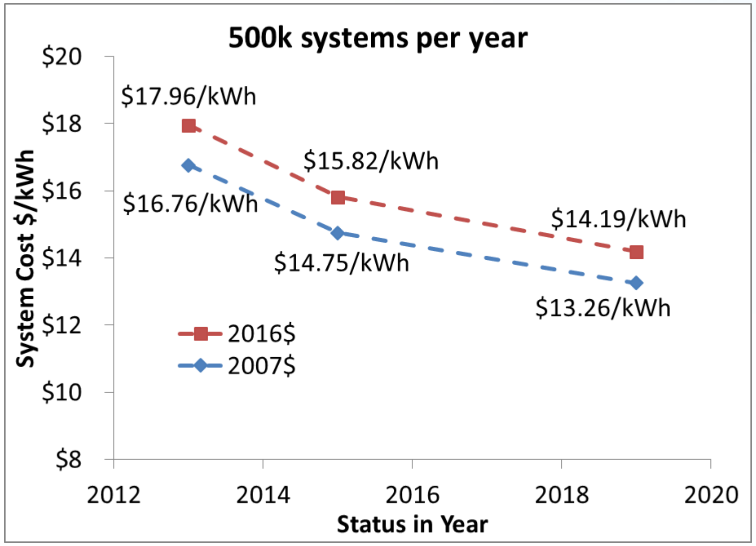
Outline

- High-level storage system cost results presented in the 2019 program record.
- Carbon fiber cost assumptions used in the analysis.
- System cost sensitivity and a pathway to achieve the DOE cost targets.

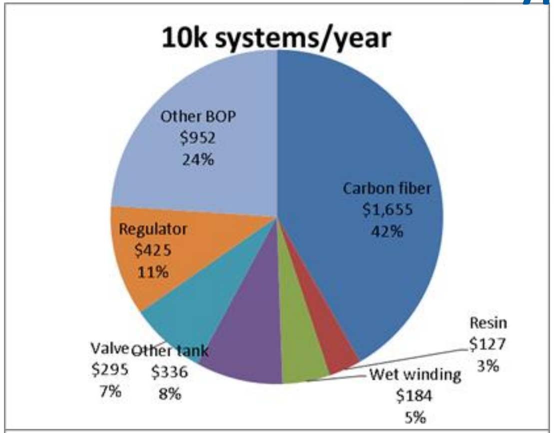
The 2019 FCTO Program Record reflects incremental changes

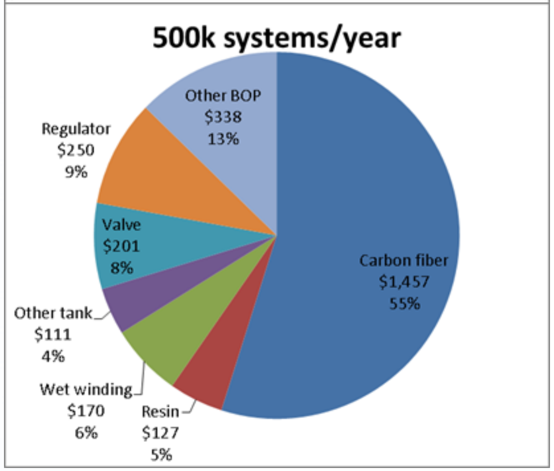
- Changes in design assumptions since the 2015 program record include:
  - Replaced stainless steel Balance of Plant (BOP) components with aluminum.
  - Reduced storage vessel carbon fiber composite mass by employing a hoop-intensive winding pattern.
  - Model adjustments to address gas temperatures, regulator performance, and inflation.
  - Updates to carbon fiber price assumptions.
- Adjusted for inflation, system cost shows a steady trend towards lower cost

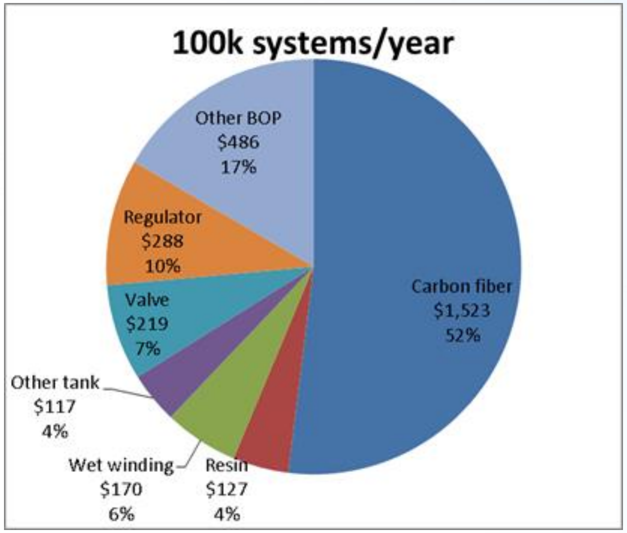




Carbon Fiber Costs Are the Largest Single Item in 700 bar Type 4 Storage at All Production Rates



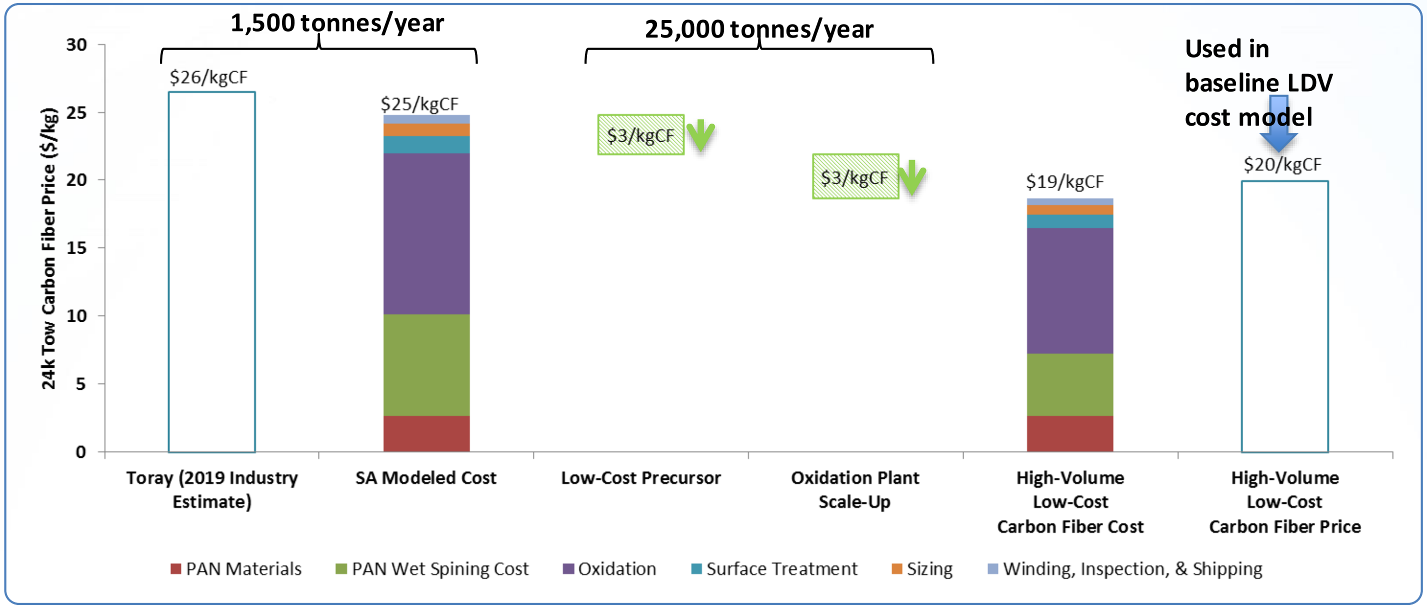




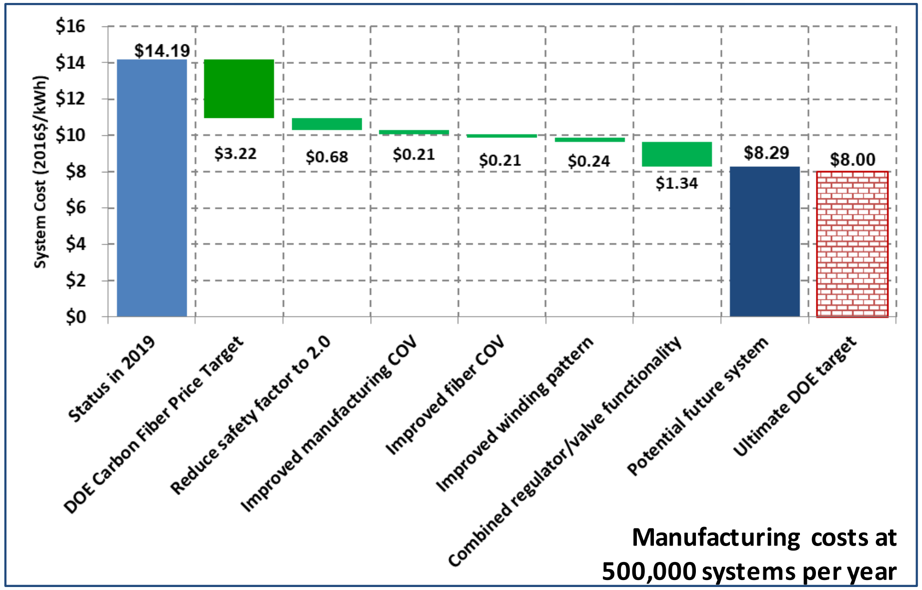
- Carbon fiber continues to represent >50% of the system cost at high volume (100k - 500k/year)
- BOP represents ~40% of the system cost at low volume (10k/year)
- 'Other BOP', which includes mounts, fuel controllers, receptacles, etc., is a large fraction of the total BOP cost low volume

Carbon fiber costs used in high-volume storage system projections assume scaled up precursor and oxidation plants

- Three carbon fiber models (SA, Das, Kline) suggest 24k tow 700 ksi CF cost is ~$24-25/kg
- Industry estimate of T700 is $26/kg so either very small margins or models overestimate costs
- T700 price is compared with costs modeled for a 1,500 tonnes/year plant
- Low-cost precursor cost based on Das capital and operating cost reductions
- Oxidation plant scale-up costs based on assumed capital and operating cost reductions reported by Das and Kline
- High-volume CF price is the T700 price scaled by modeled high and low volume costs 26(19/25)=20



Meeting DOE storage system cost targets will require significant reductions in carbon fiber cost



Category	2019 assumption	Future assumption	Basis
DOE Carbon Fiber Target	$21.48/kg	$12.60/kg	https://www.energy.gov/sites/prod/files/2017/07/f35/fcto_webinarslides_carbon_fiber_composite_challenges_072517.pdf
Safety Factor	2.25	2.0	GTR discussions
Manufacturing COV	3%	1%	Current R&D
Fiber COV	3%	1%	Proposed R&D improvement
Improved winding pattern	90.3 kg	85.8 kg	Based on an assumed reduction of 5% due to winding pattern improvements similar to the hoop intensive approach
Combined valve/regulator	With regulator	No regulator	Assumed all regulator function can be integrated into solenoid valve without increasing the valve price

Note that the order in which cost reductions were applied in this analysis affects the absolute size of each step in the wate rfall chart.

Recap

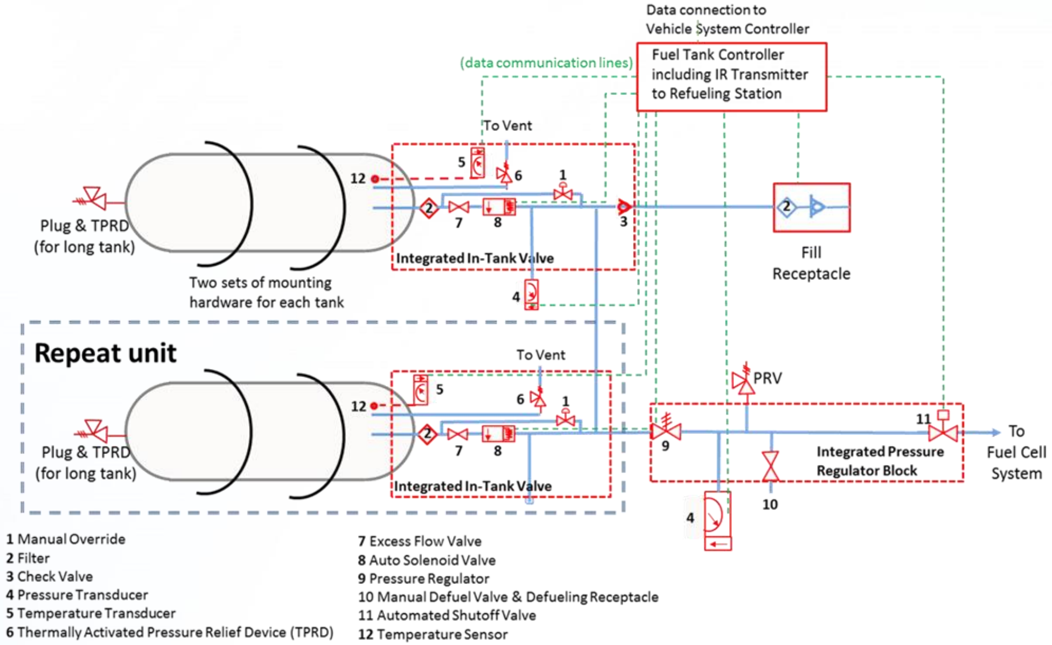
- We reported an updated 700 bar Type 4 light-duty vehicle storage system cost that accounts for changes in
  - Tank boss and fiber winding improvements the reduced system weight and cost
  - Carbon fiber price updates
  - Model adjustments
- Carbon fiber assumptions reflect cost reductions based on lab-demonstrated carbon fiber and high-volume textile process precursors
- Achieving the DOE cost targets require significant reductions in carbon fiber costs

Thanks!

Cassidy Houchins
chouchins@sainc.com

Backup

Key System Assumptions



Usable H_2	5.6 kg
Pressure	700 bar
Empty pressure	15 bar
Temperature	15°C
Carbon fiber	ORNL Fiber
Precursor	PAN-MA
CF Tensile strength	4900 MPa
Safety Factor	2.25
Manufacturing COV	3%
Fiber COV	3%

A complete report of results and assumptions can be found at https://www.hydrogen.energy.gov/pdfs/19008_onboard_storage_cost_performance_status.pdf

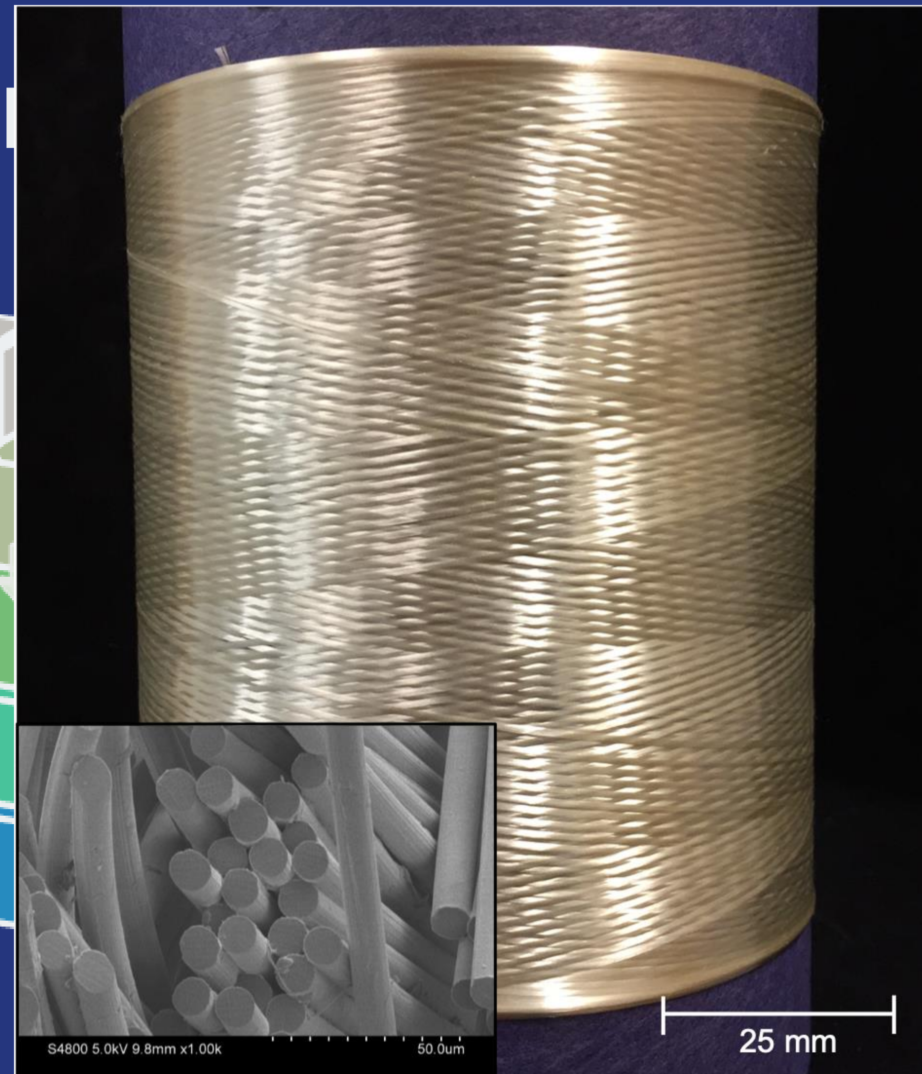
Progress on the Development of Small Diameter Hollow PAN Precursor for Carbon Fibers

Matthew C. Weisenberger*, Nik Hochstrasser, and E. Ashley Morris

University of Kentucky Center for Applied Energy Research
2540 Research Park Drive
Lexington, KY 40511
Phone: (859) 257-0322
Email: Matt.Weisenberger@uky.edu

Carbon Fiber: General

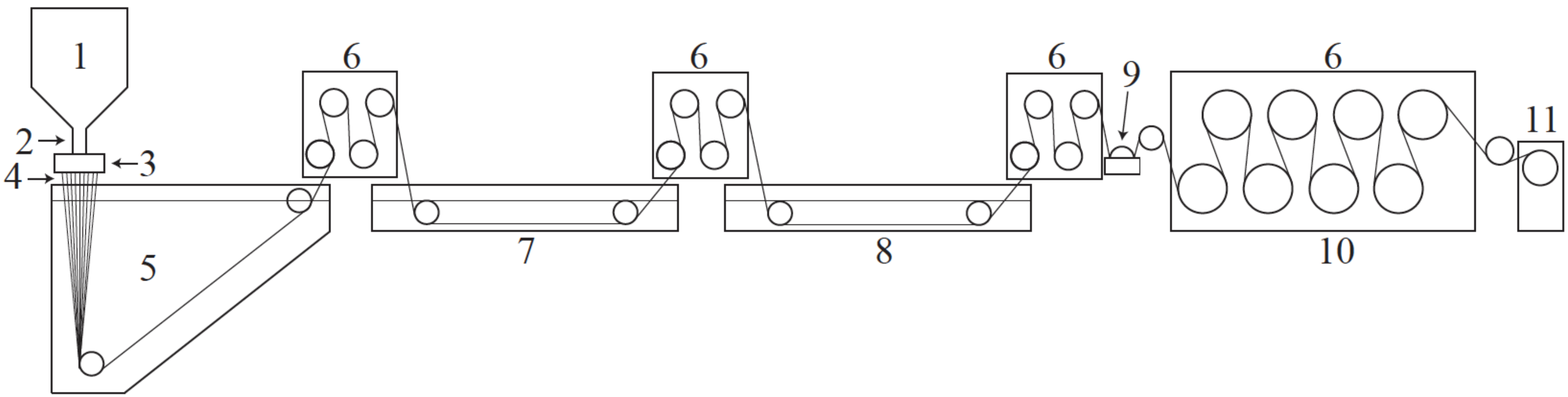
- PAN, pitch, etc. starting material
- Solution, melt, etc. fiber spinning
- Oxidation
- Carbonization/graphitization, sizing
- Composites



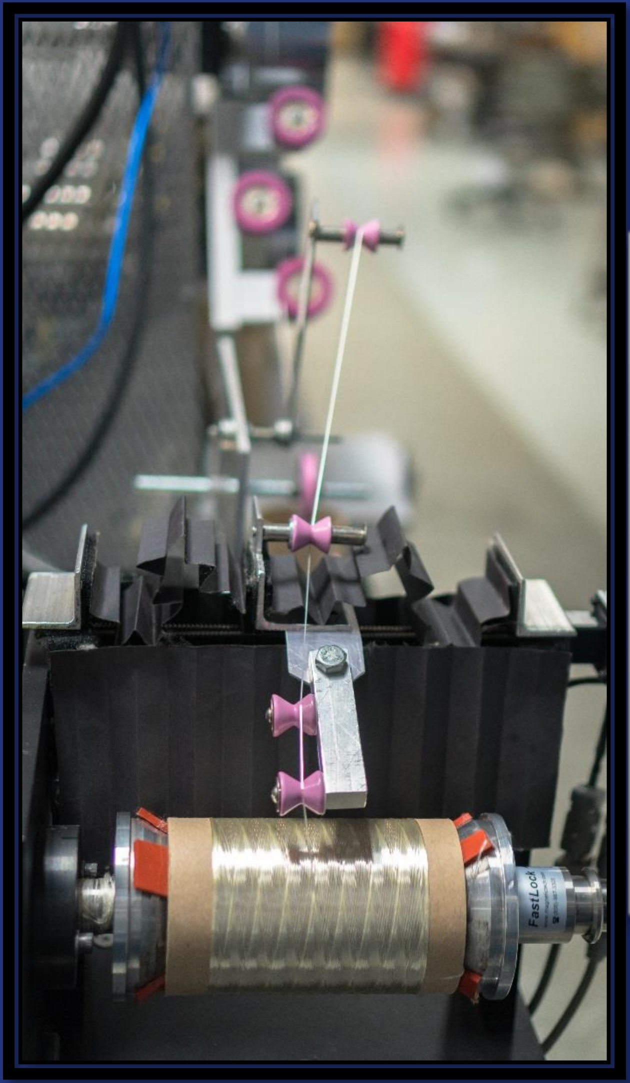
Air Gap Solution Spinning

Google "CAER Fiber"

CAER Fiber Development Facility



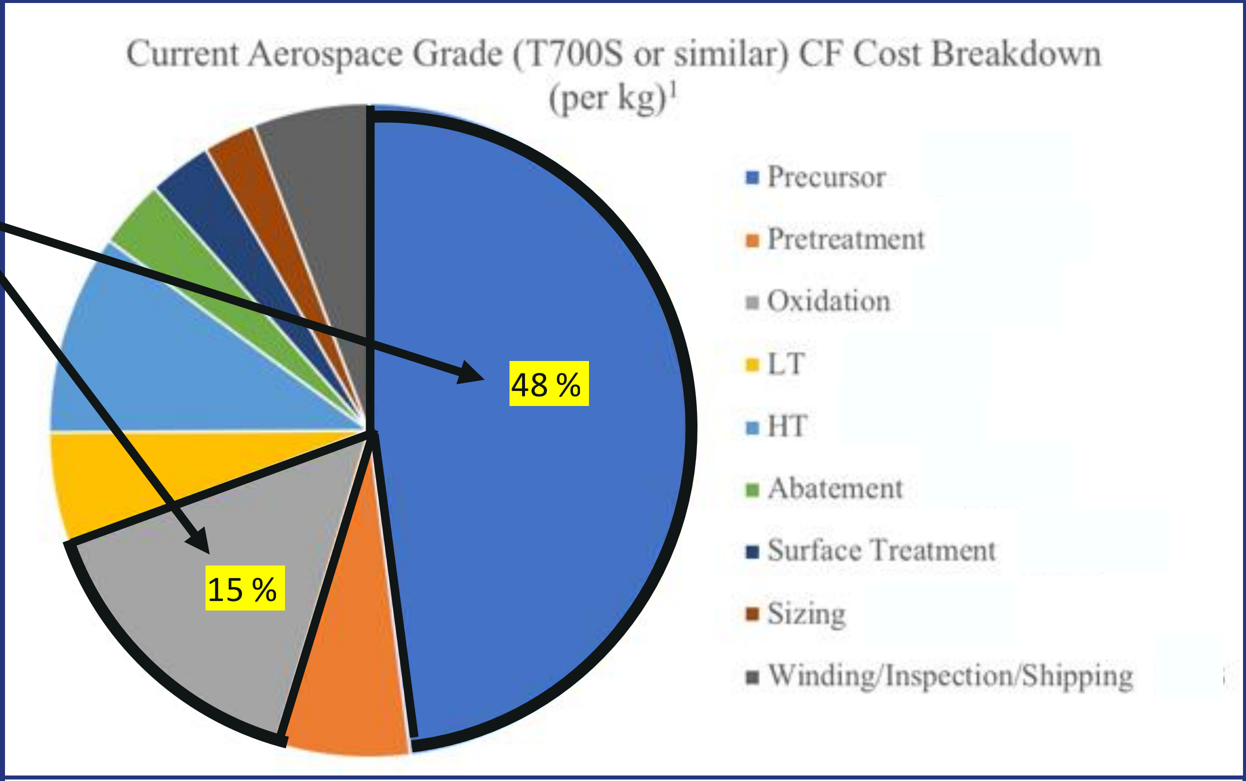
1 - spinning solution
2 - filtration
3 - spinnerette
4 - air gap
5 - coagulation bath
6 - driven rollers
7 - washing bath(s)
8 - stretching bath(s)
9 - spin finish application
10 - drying
11 - traversing takeup



Air-Gap Spinning

Carbon fiber accounts for 62% of the COPV system cost[2]

Largest costs in CF production
- ✓ Precursor manufacture
- ✓ Fiber oxidation



[1]Warren, C. D. Development of low cost, high strength commercial textile precursor (PAN-MA); ORNL: 2014

[2]Ordaz, G., C. Houchins, and T. Hua. 2015. "Onboard Type IV Compressed Hydrogen Storage System - Cost and Performance Status 2015," DOE Hydrogen and Fuel Cells Program Record, https://www.hydrogen.energy.gov/pdfs/15013_onboard_storage_performance_cost.pdf

Hollow Precursor

Cost Savings Approach

1. (Low cost PAN polymer)
2. Use less precursor
    a. Higher specific properties
3. Oxidize faster

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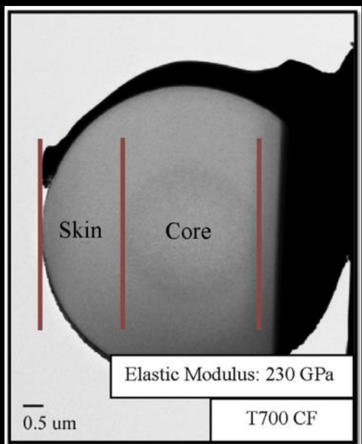
Hollow Fiber: Skin-core

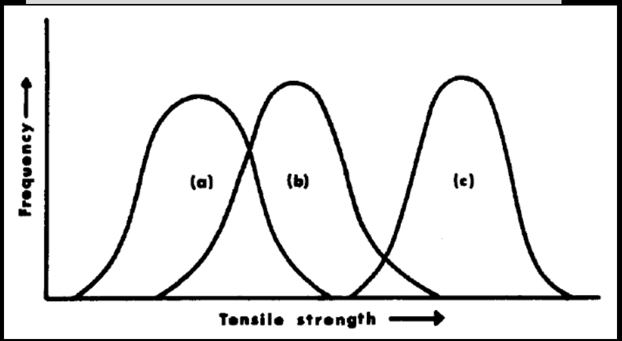
Traditional solid CF
Skin-core structure



Morris, E.A. et al. *Carbon*, 2016. **101**: p. 245-252.

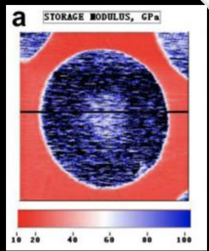
CF tensile strength limited by surface flaws
(internal flaws are less impactful)

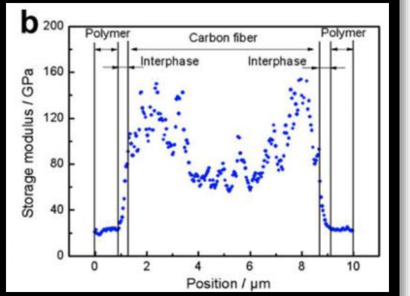
Johnson, J. W.; Thorne, D. J. *Carbon* **1969,** 7, 659 – 661



(a) original surface flaws, (b) internal flaws, (c) surface flaws after etching

External "skin" carries the bulk of the tensile load (T700)





Y. Gu, et al., CARBON 2010, 48 (11), 3229-3235

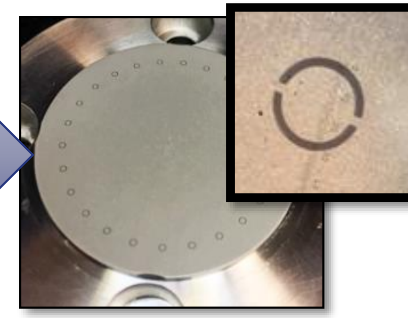
Hypothesis: We can produce a hollow fiber capable of retaining or exceeding the specific tensile strength of T700S

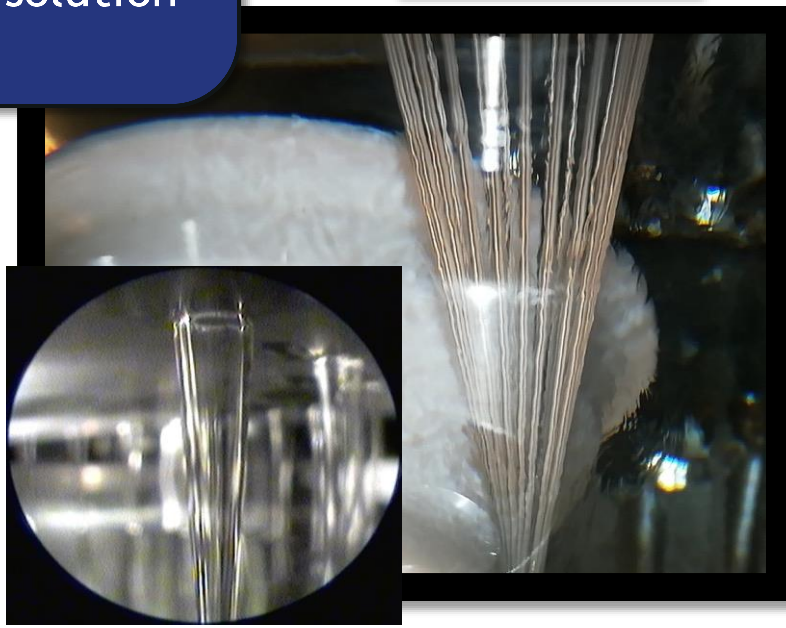
caer.uky.edu

UK Center for Applied Energy Research

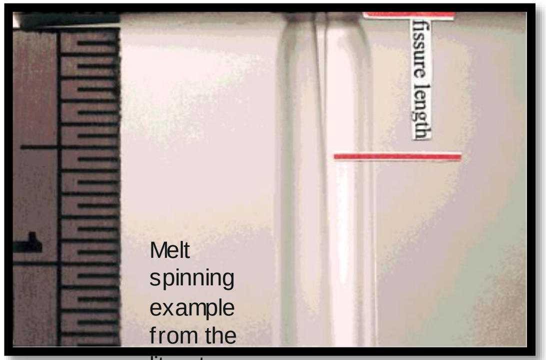
UKY CAER Approach - Hollow Fiber Spinning

- Utilize segmented-arc slip shaped spinneret (traditionally used in melt spinning hollow fiber)
- No sacrificial polymer or bore fluid
- Drop-in scalable for multifilament tow
- Requires PRECISE control during air-gap solution spinning to form a hollow filament





Segments healing in the air gap

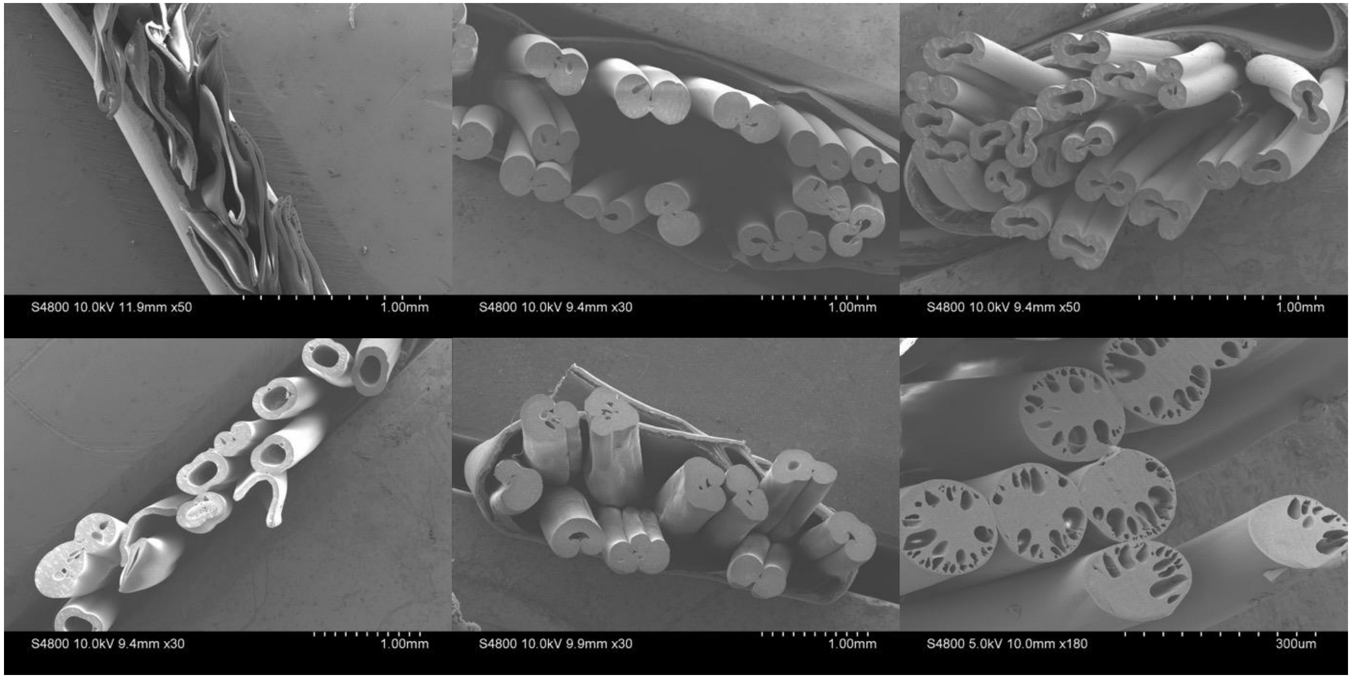


Melt spinning example from the literature

Rwei, S. (2001), J. Appl. Polym. Sci., 82: 2896-2902

Center for Applied Energy Research

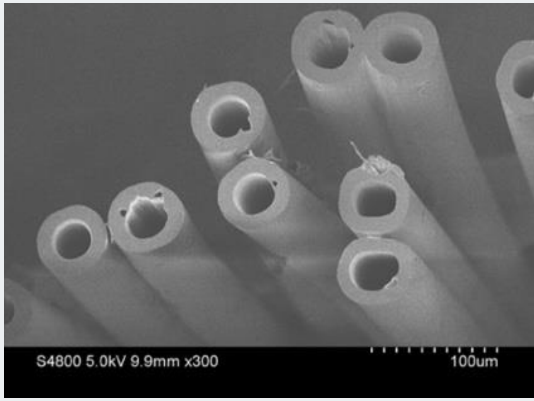
Hollow Precursor Fiber – Initial Results

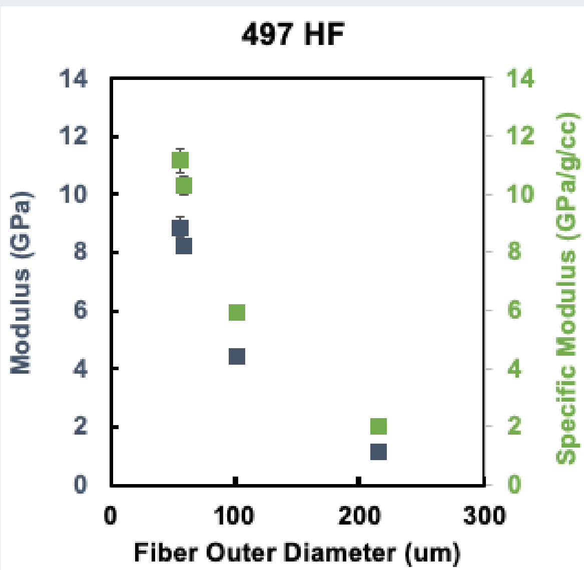


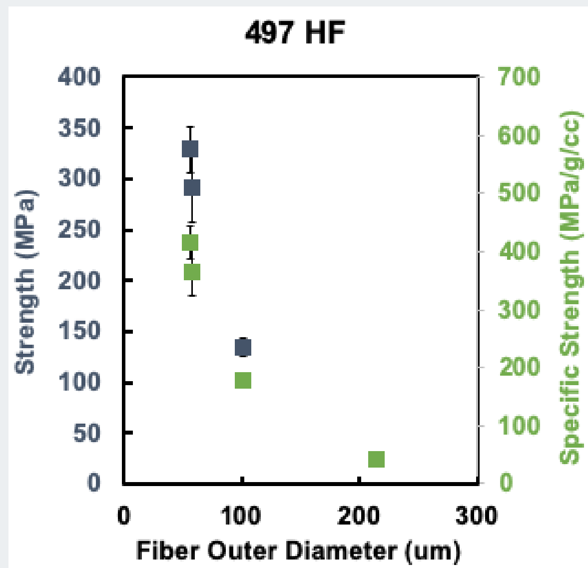
Variables:

- Air gap
- Spin draw
- Dope composition & temp
- Coagulation bath composition & temp

All spinning variables must be carefully understood and controlled to produce hollow filaments utilizing a segmented arc spinneret







UK CAER multifilament continuous tow hollow filaments

25 filaments/tow

average OD = 56 µm

+/- 1.6 µm, N = 10

average ID = 32 µm

+/- 1.3 µm, N = 10

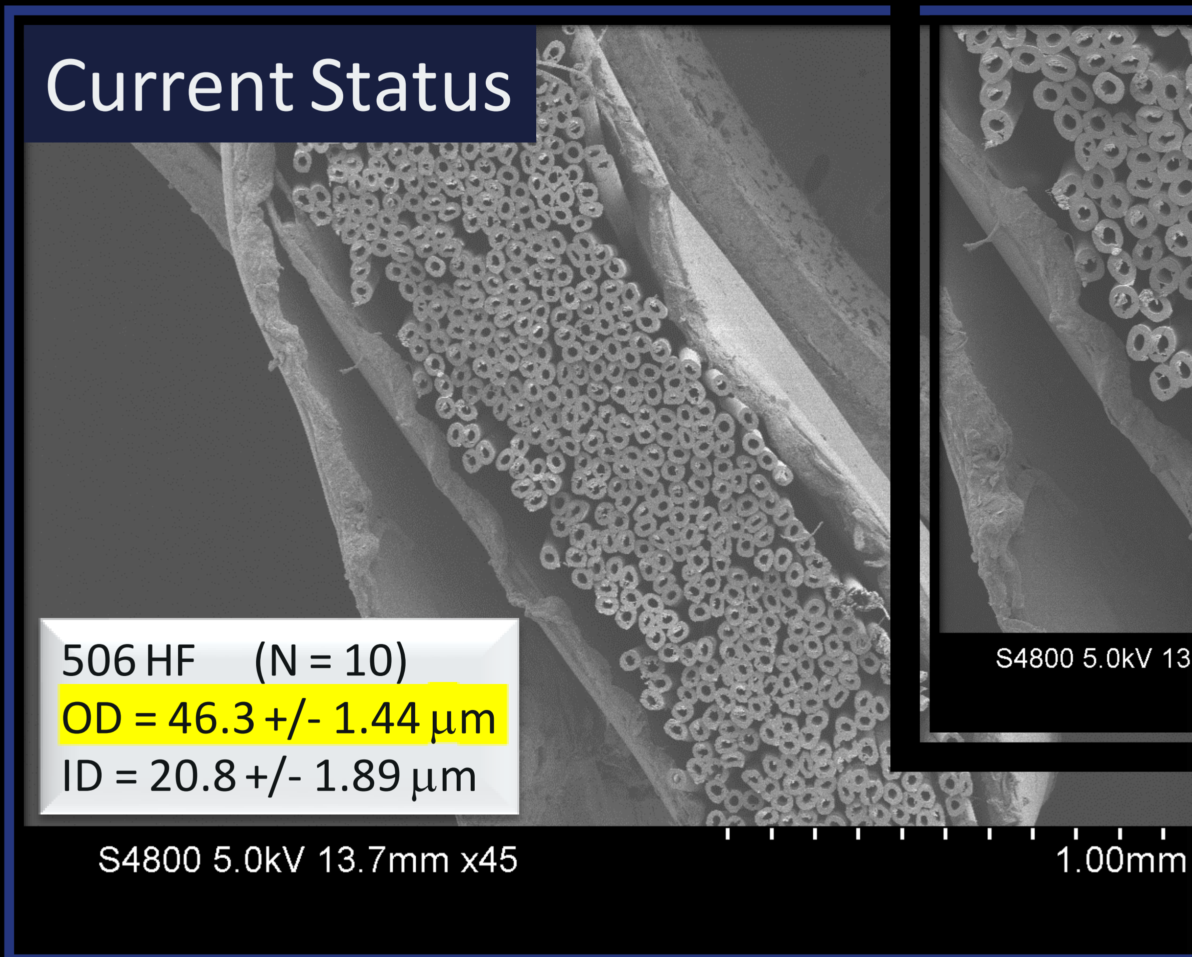
$Density_{OD}$ = 0.75 g/cc

<u>Final Target</u>

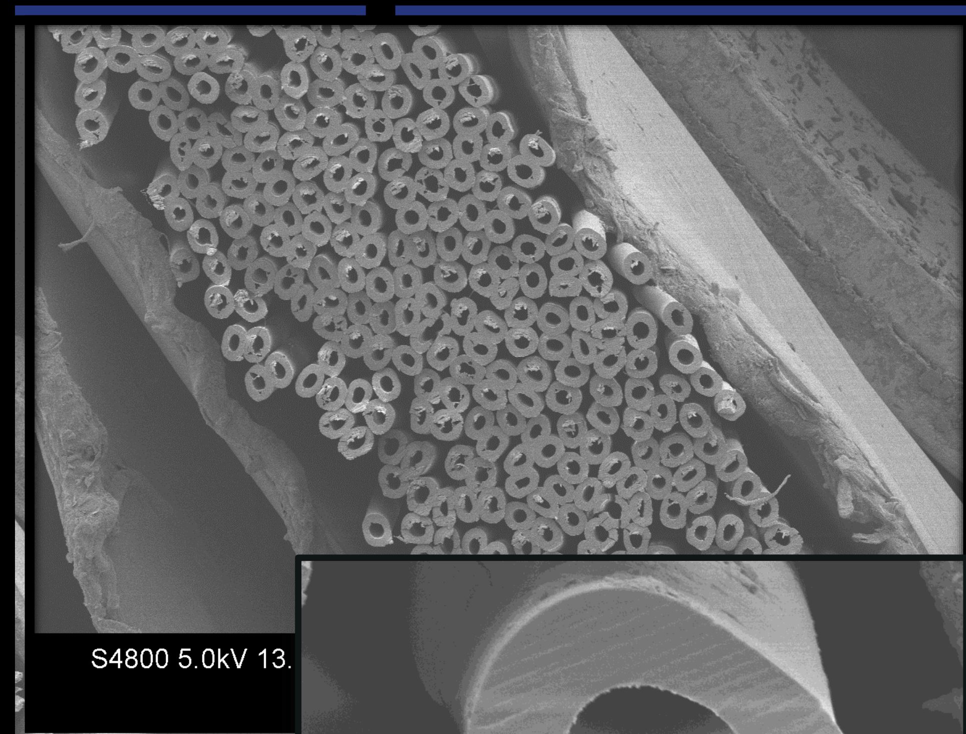
OD = 14 µm

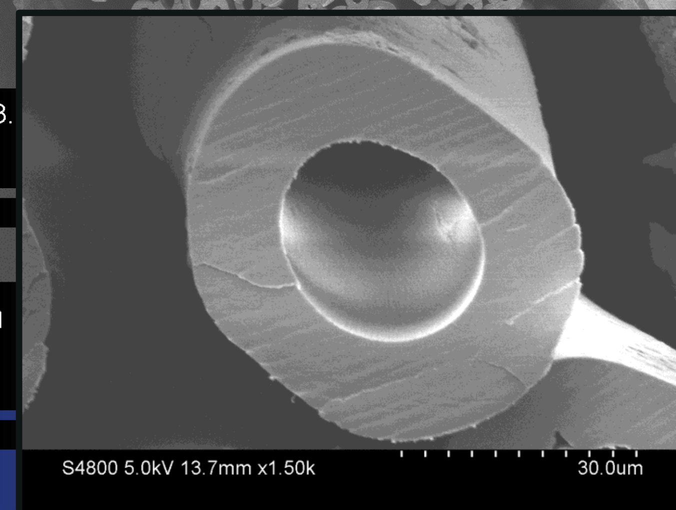
ID = 9.3 µm

Current Status

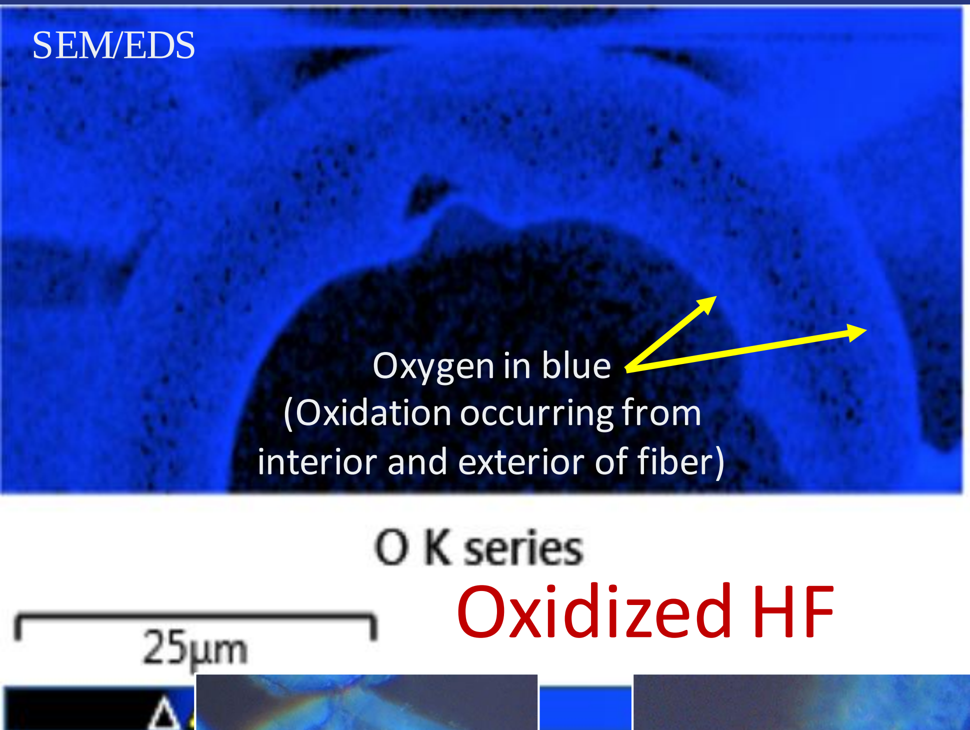


506 HF (N = 10)
OD = 46.3 +/- 1.44 µm
ID = 20.8 +/- 1.89 µm



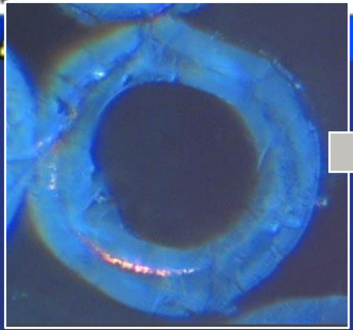


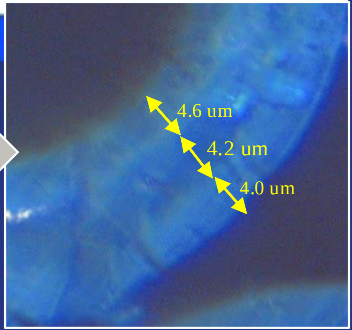
Preliminary Thermal Conversion



Oxidized HF

Polarized
Optical
Microscopy





Carbonized HF

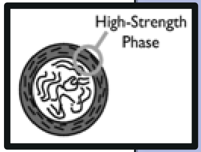
Hollow Fiber Progress - Conclusions

- Demonstrated viability of low-cost precursor polymer in this work
- Developing stable, multifilament continuous tow, HOLLOW FIBER precursor spinning
    - OD = 46.3 +/- 1.44 μm
    - ID = 20.8 +/- 1.89 μm
    - Wall thickness = 12.75 μm
  - Target
    - OD = 14 μm
    - ID = 9.3 μm
    - Wall thickness = 2.35 μm
- Fast oxidation trials are beginning

BASELINE COST
$29.40/kg

Our Work

Non-exclusive, low cost, high quality PAN polymer **"TechPAN"**
CF Cost impact: -13.8%
✓ $25.35/kg



Hollow carbon fibers forego core structure, improve specific properties
CF Cost impact: -15.4%
$20.83/kg*

Hollow fibers oxidize up to 35x faster
CF Cost impact: -29.3%
$12.21/kg*

LOW COST
< $12.60/kg

[1]Morris, E. A., et.al., *Carbon* **2016,** 101, 245-252
[2]Steiner III, S. A., et al., *ACS Appl. Mater. Interfaces* **2013,** 5, (11), 4892-4903

*Equivalent length and performance as 1 kg of solid fiber OD = 7 micron; 44% open area

Thanks

Developing A New Polyolefin Precursor for Low-Cost, High-Strength Carbon Fiber

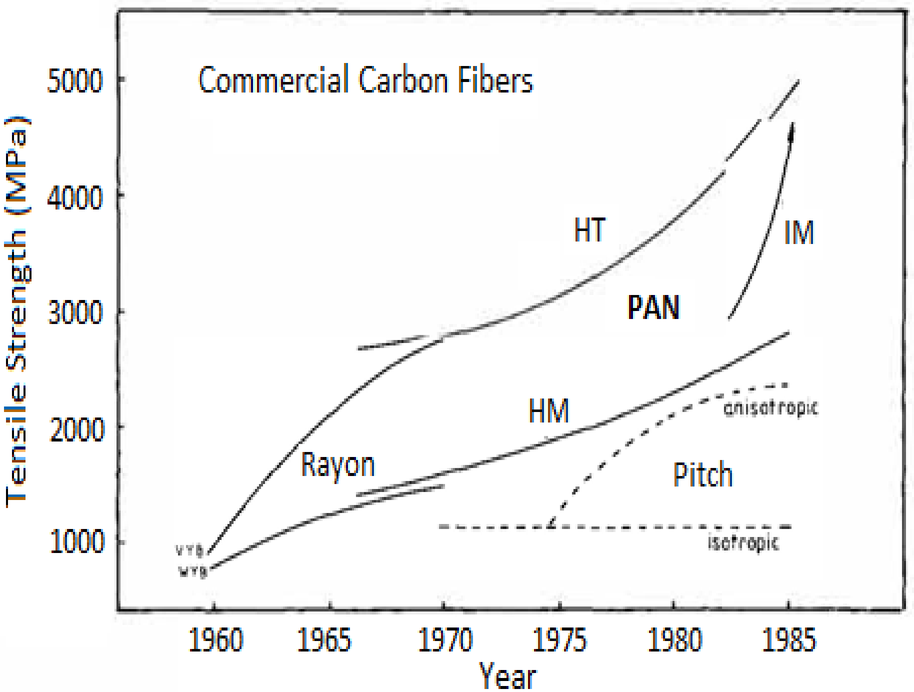
T. C. Mike Chung, Joseph Sengeh, Houxiang Li, and Matthew Agboola

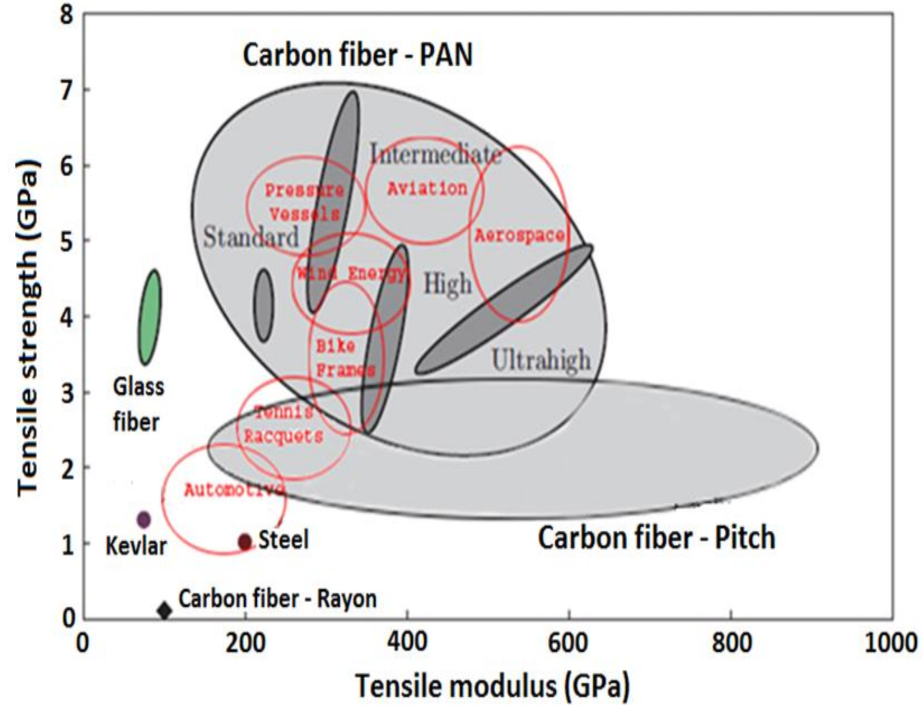
Department of Materials Science and Engineering
The Pennsylvania State University

ORNL Support Team: Dr. Logan Kearney and Dr. Amit Naskar

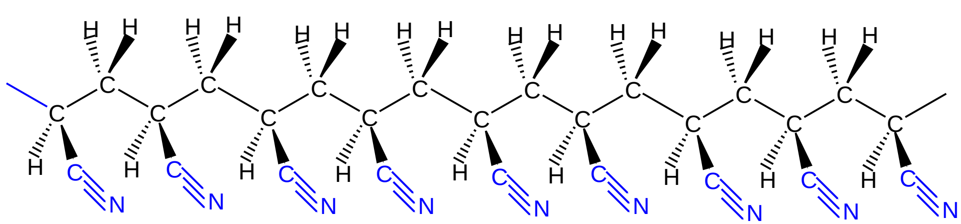
Financial Support: US Department of Energy (EERE) through grant DE-EE0008096.

Relevance: High Tensile Strength Carbon Fibers

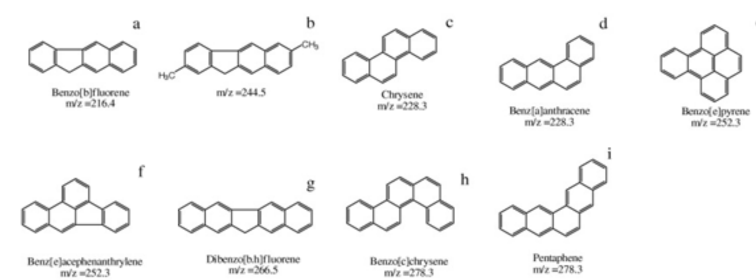




Polyacrylonitrile (PAN)



Pitch (polyaromatic molecules)



Chemical Engineering and Technology 1990, 13, 41-49

Relevance: Current CF production process

PAN Polymer Precursor —(wet spinning + stretching)→ **PAN Fiber**

PAN Fiber —(▲ air)→ **Stabilization** (200-300 ºC in air for 30-120 minutes) + Stretching

Stabilization —(▲ N_2)→ **Carbonization** (1000-2000 ºC in N_2 atmosphere) + Stretching

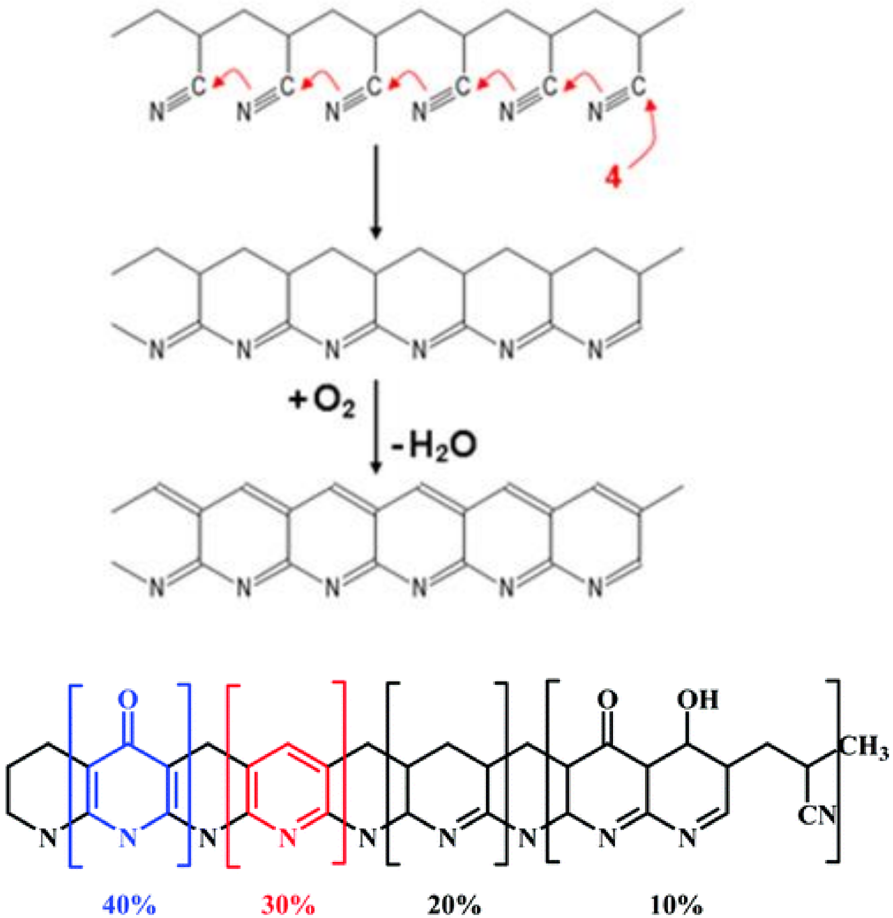
Carbonization → **Surface Treatment & Sizing**

High Cost !

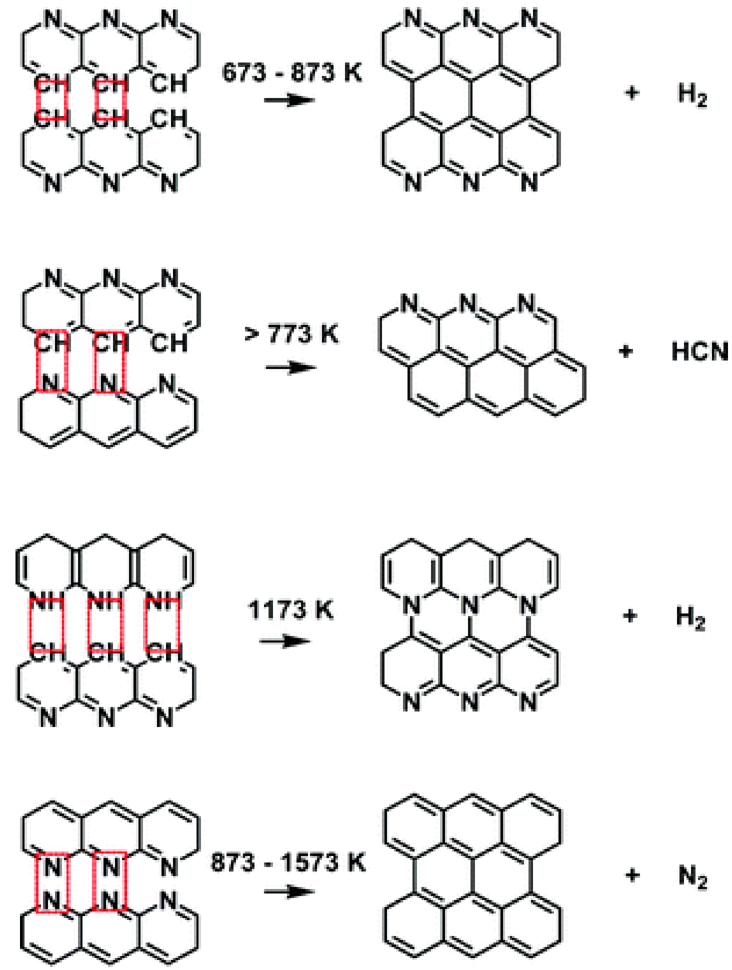
PAN fiber going through oxidation oven

Relevance: PAN thermal conversion chemistry

Stabilization
(200-300 °C)

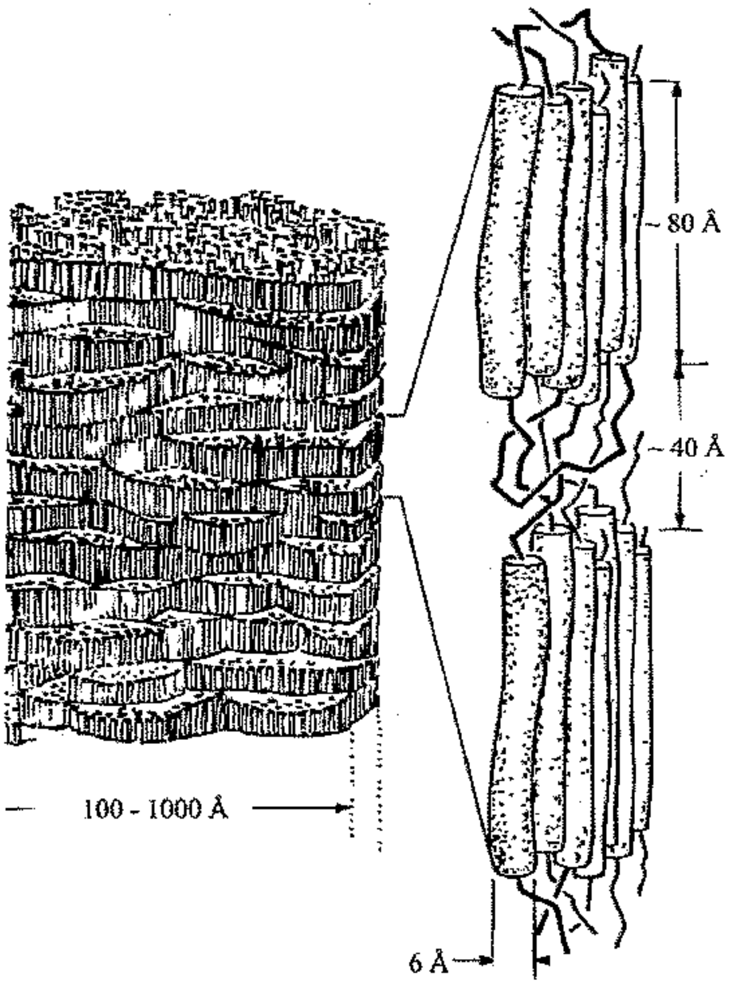


Carbonization
(1000-2000 °C)



Overall thermal conversion with a low yield <50%

Relevance: Morphology of high tensile strength CFs



Crystallite size and shape (nano-polycrystalline)

Orientation of basal line

Order-disorder ratio

Structure defects (voids)

Fiber diameter

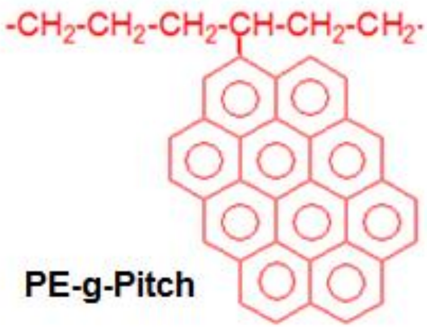
- *Carbonization under mechanical stretching (tension)*
- *Control heating and winding rates*

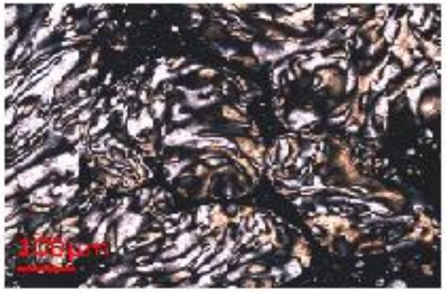
Approach: New polymer CF precursor (PE-Pitch)

- Polyethylene (PE) copolymer with Pitch moieties (side groups)
- Melt-spinning in forming precursor fibers
- One-step C conversion under inert atmosphere
- PE with Reactive side groups that can engage facile thermal-induced stabilization reactions at 300-400 ^{o}C range
  - Crosslinking/conjugation chain structure
  - No external reagent required
  - No by-product formed
- High overall C yield (>80%)

Accomplishments: PE-Pitch Precursor (Mesophase)

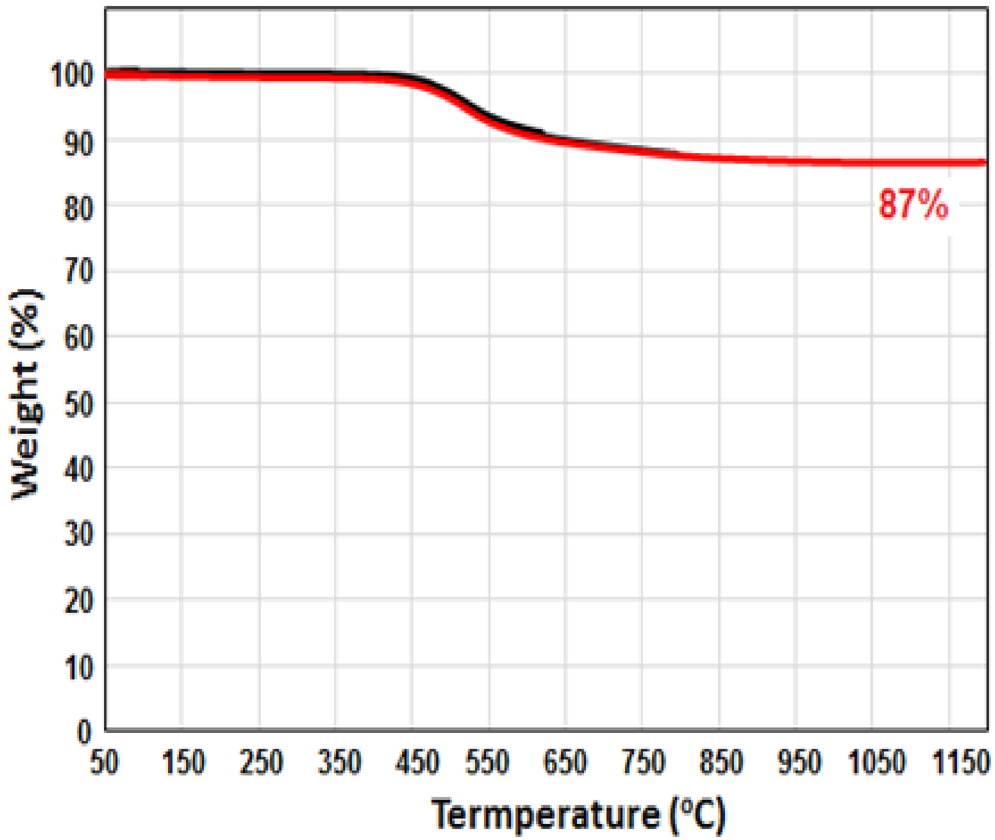
Mesophase PE-Pitch Precursor





Mesophase

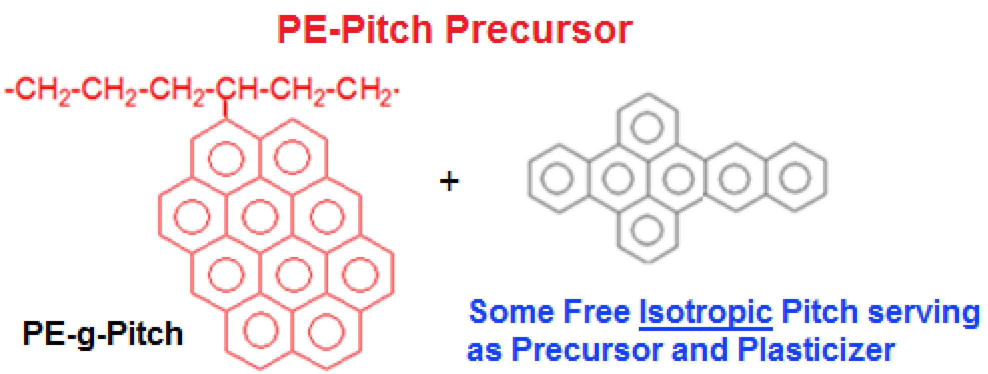
TGA curve under N_2

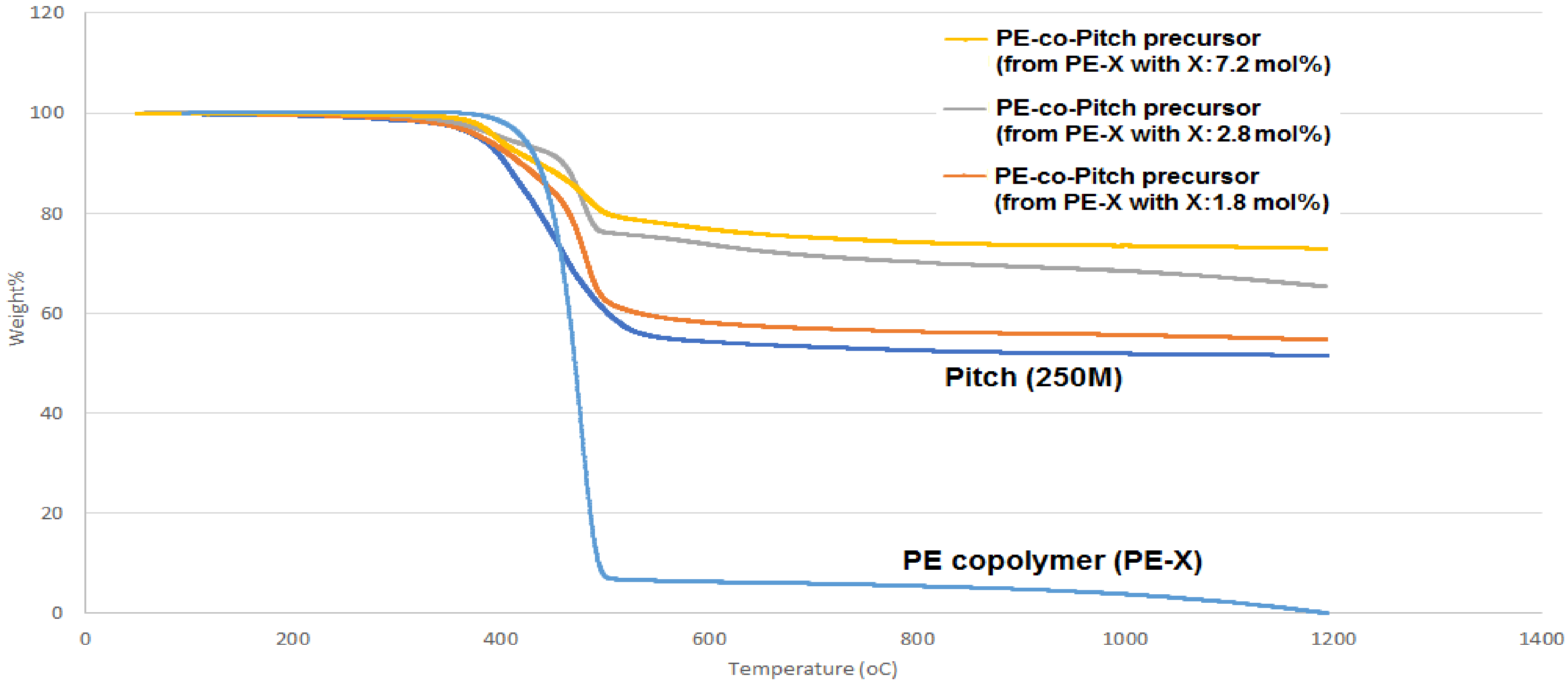


One step C conversion under N_2 atmosphere with high yield (87%)

The resulting mesophase PE-Pitch precursor shows high melt-viscosity

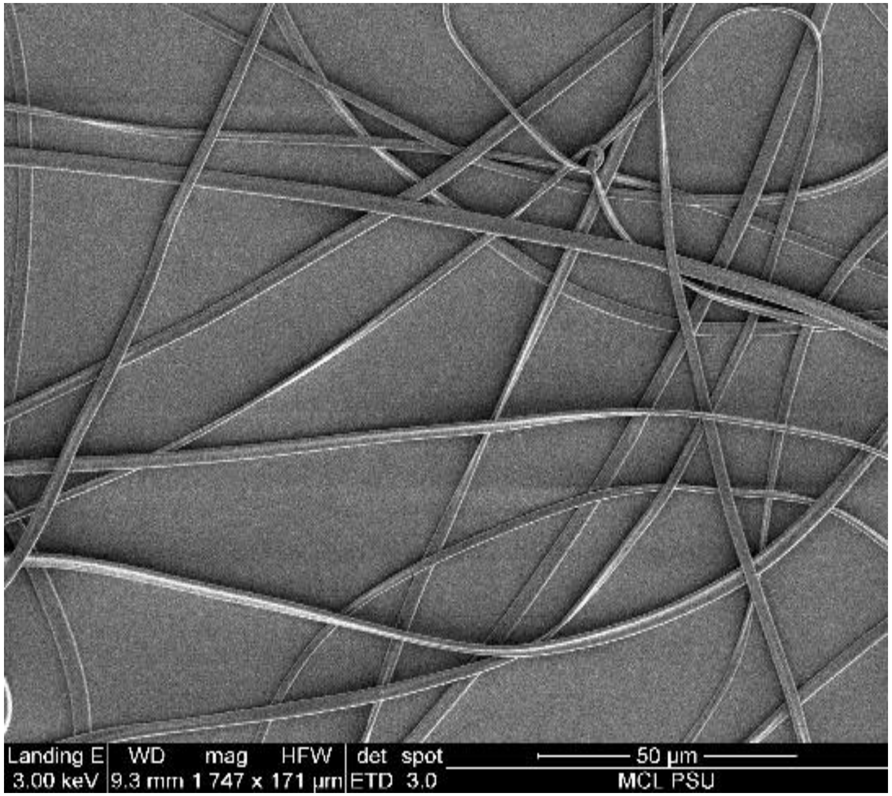
Accomplishments: PE-Pitch precursor (Isotropic phase)

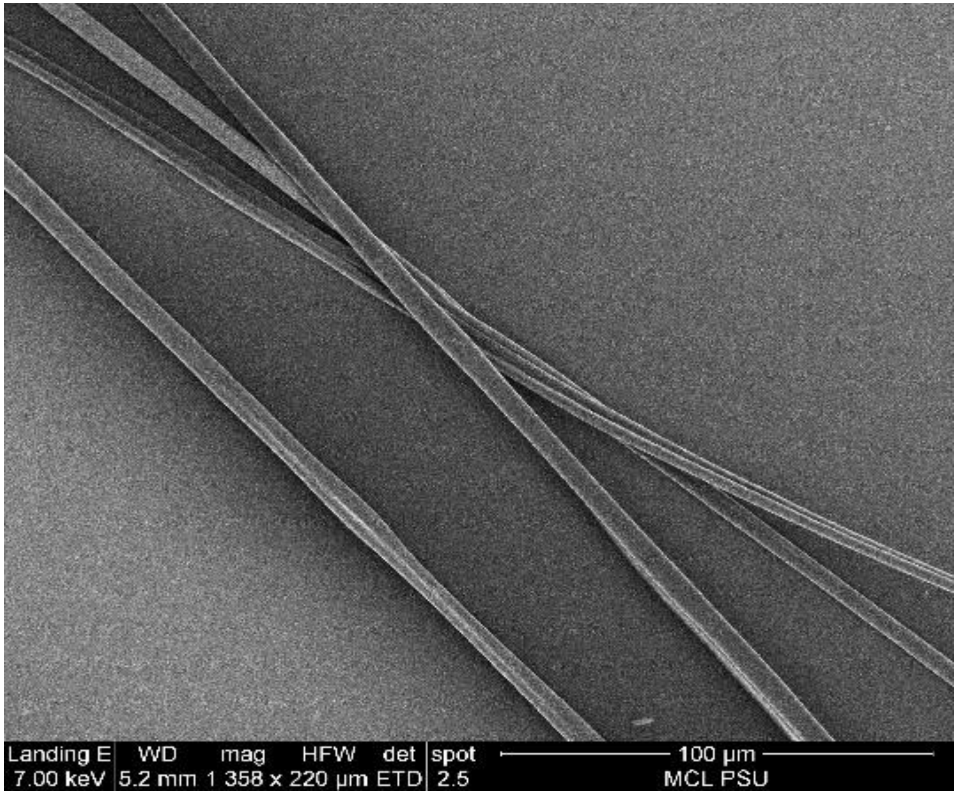




PE-Pitch precursors show higher C yield than both starting PE-X and Pitch

Accomplishments: SEM Micrographs of Electrospun Pure PE-Pitch (mesophase) Precursor Fiber





Dry-spinning from 30 wt% polymer solution in toluene solvent

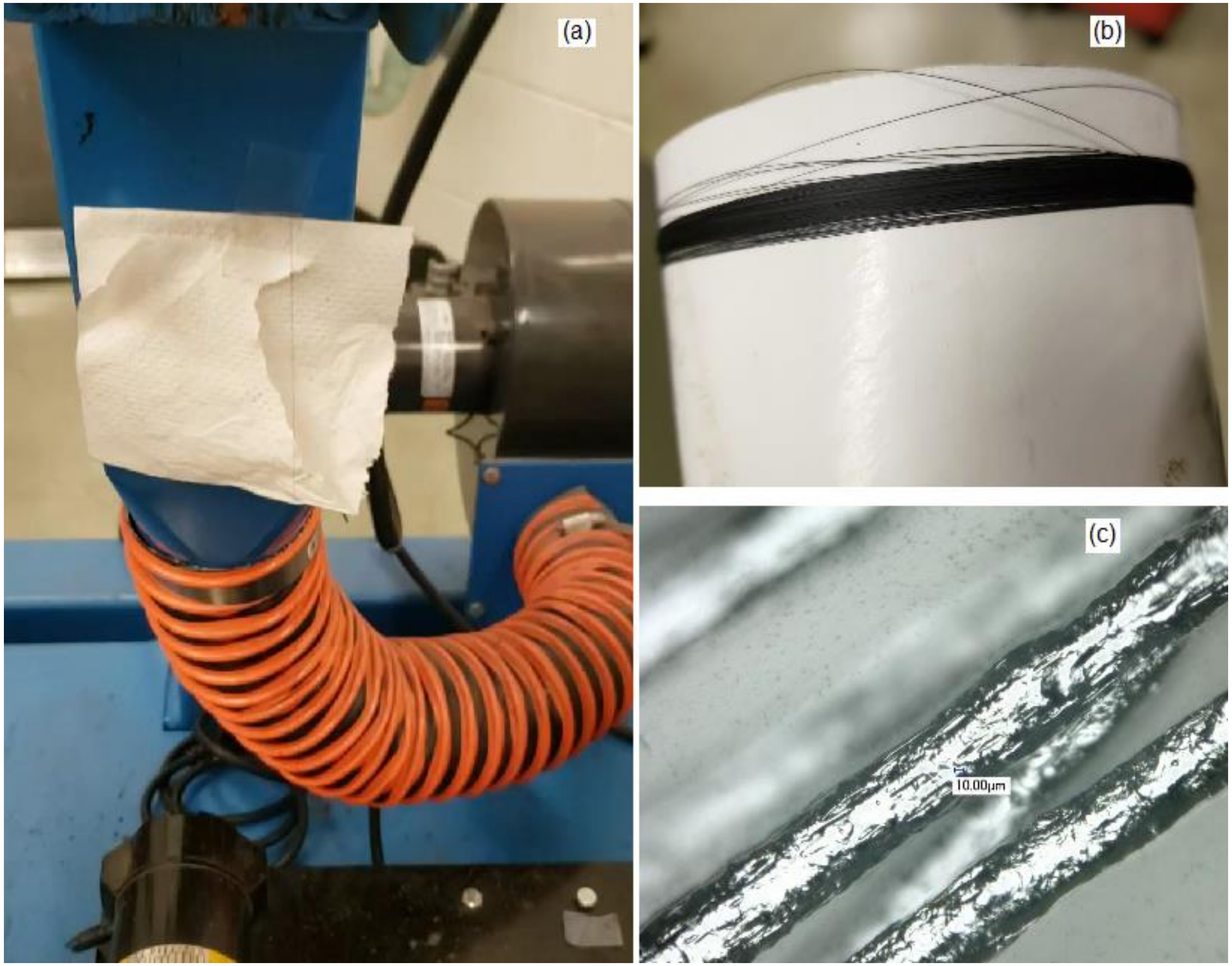
Accomplishments: Melt-spun PE-Pitch (isotropic) fibers (Penn State Facility)

Filabot desktop filament extruder (die diameter : 1 mm)

Spun PE-Pitch precursor fibers (fiber diameter: 500-800 μm)

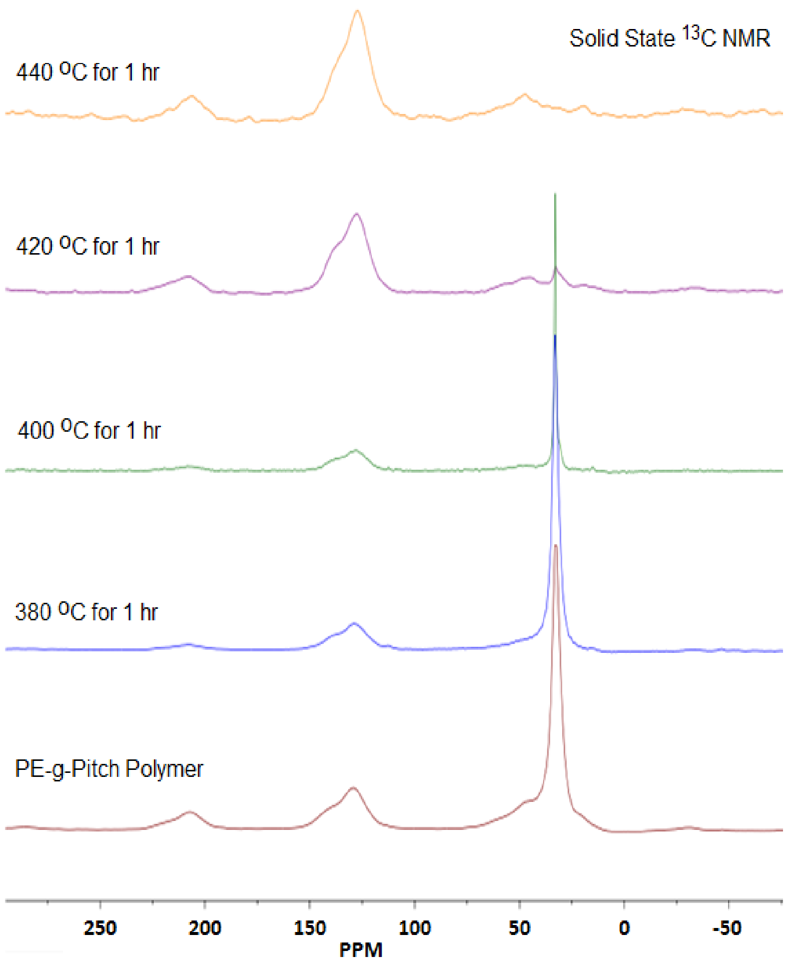
Samples 3, 4, and 5 PE-Pitch precursors (with some free pitch) were melt-extruded at 310-330 °C to produce precursor fibers with smooth surface and uniform fiber diameter (500-800 mm), and good mechanical strength.

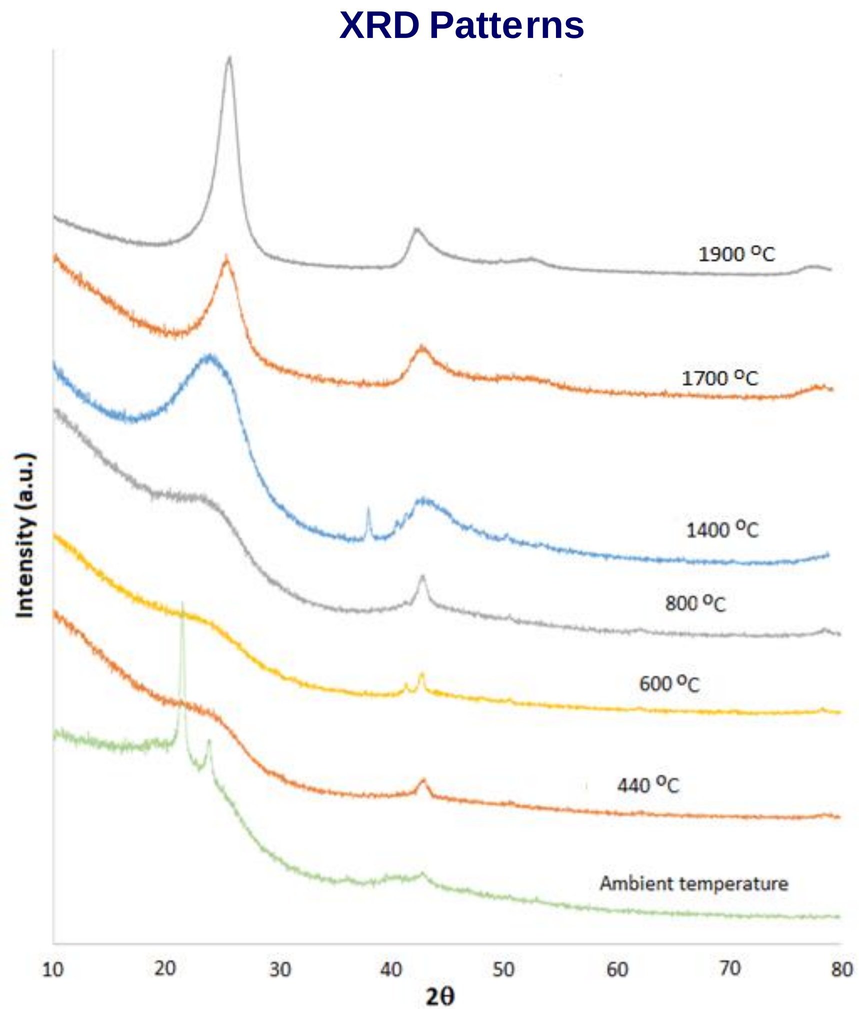
Accomplishments: Melt-spun PE-Pitch (isotropic) fibers (ORNL facility)



PE-Pitch precursor (Sample 4) was spun continuously by ORNL laboratory-scale single-filament spinning apparatus. The fiber diameter is about 30 μm.

Accomplishments: ^{13}C NMR and XRD spectra of PE-Pitch fiber during thermal conversion to CFs under N_2

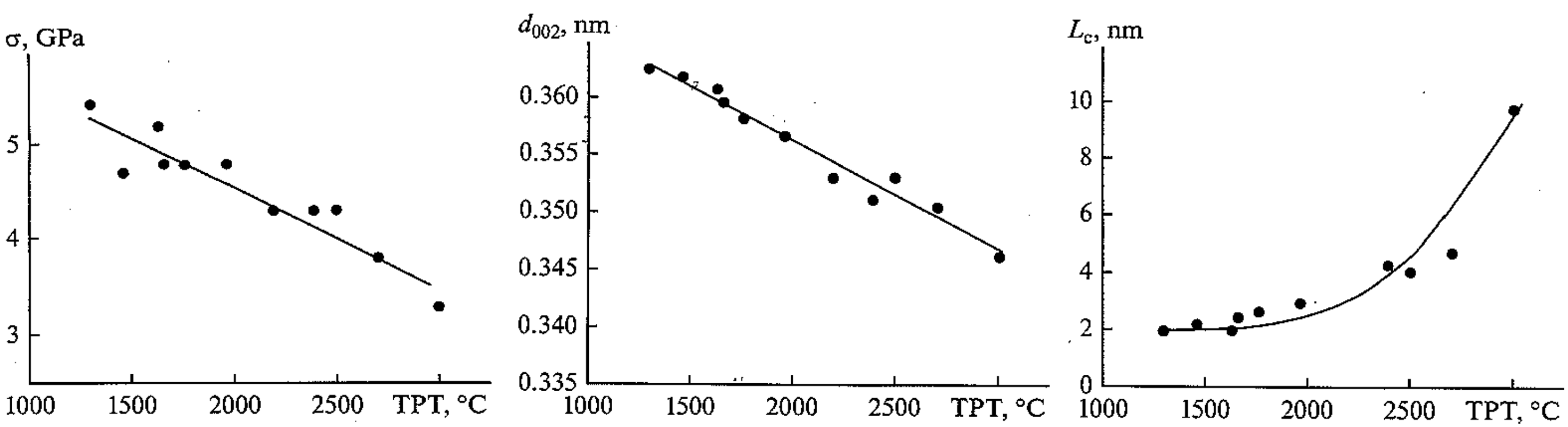




PE polymer chain is conversed to aromatic structure at 400-440 °C under N_2

Accomplishments: XRD comparison between PE-Pitch and PAN based Carbon Fibers

	PE-Pitch based Carbon Fiber			PAN based Carbon Fibers*	
Temperature (°C)	D_{002} interlayer spacing (nm)	Lc (nm)	La (nm)	D_{002} interlayer spacing (nm)	Lc (nm)
1400 (Sample 6)	0.3687	1.2956	3.4987	0.364	2.0
1400 (Sample 4)	0.3708	1.2968	4.6150	0.364	2.0
1700 (Sample 4)	0.3549	1.6697	5.9562	0.357	2.5
1900 (Sample 4)	0.3524	3.9405	6.9944	0.351	3.1
1500 (Sample 1)	0.3674	1.5774	5.1327	0.361	2.0
1700 (Sample 1)	0.3500	2.5778	6.2958	0.357	2.5
1900 (Sample 1)	0.3480	3.2731	7.4849	0.351	3.1

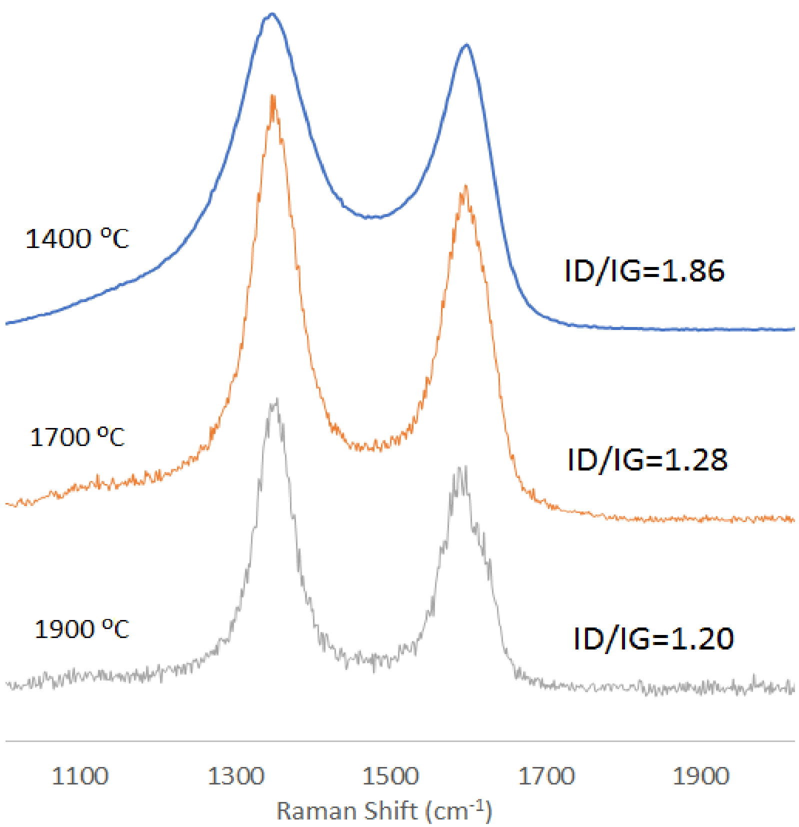


* Inorganic Materials: Applied Research **2018**, 9, 890-899

Raman Spectra of Resulting Carbon Fibers
(carbonization at 1400, 1700, 1900 °C for 1h under N_2)

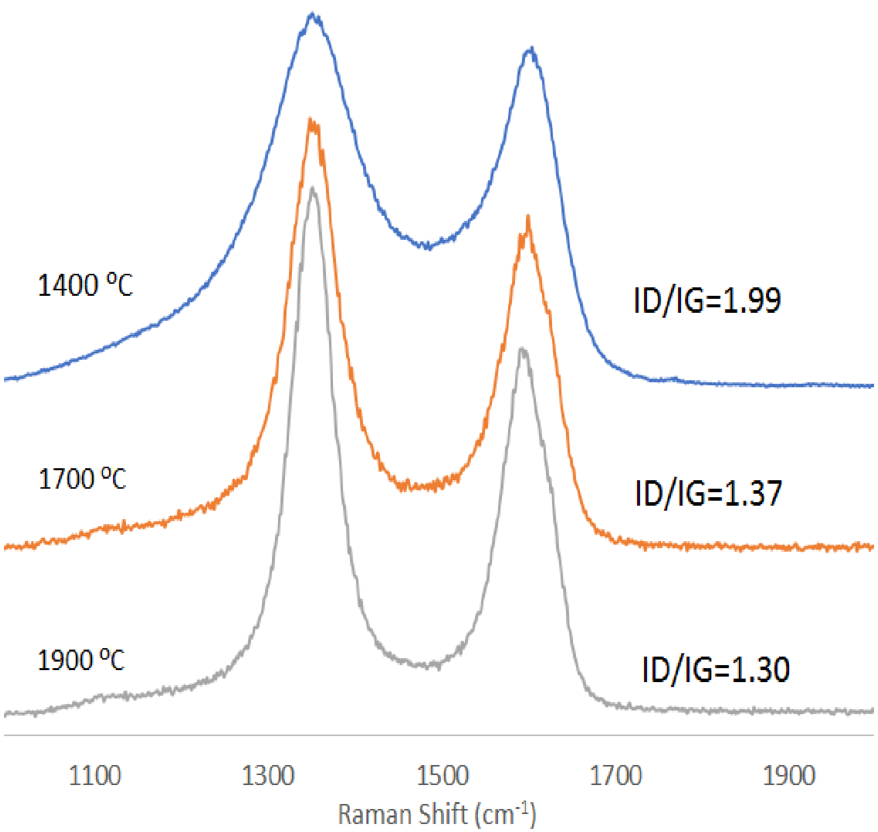
From PE-g-Pitch precursor with 79% free Pitch (Sample 1)

D band G band



From PE-Pitch precursor with 40% free Pitch(Sample 4)

D band G band



The integrated intensity ratio ($R=I_D/I_G$) for PAN-based carbon fibers is about 1

Summary

In this research project, we have developed <u>a new class of polymer precursors</u> based on a PE-g-Pitch graft copolymer containing PE backbone and Pitch side chains with some free Pitch molecules (serving as plasticizer and also precursor).

Several potential benefits of this PE-Pitch precursor over current PAN precursor.

1. **Low material cost: inexpensive PE and Pitch**
2. **Low processing cost: melt-spinning process**
3. **Low thermal conversion cost: one-step heating under N_2**
4. **Uniform thermal conversion from fiber core to the surfaces**
5. **High carbon conversion yield**
6. **Resulting similar nano-polycrystalline carbon fiber morphology**

Future Research: Thermal conversion under tension (stretching) to align graphene nano-crystals (order phase) and C chains (disorder phase) along the fiber direction and reduce structural defeacts (voids).

Novel Plasticized Melt Spinning Process of PAN Fibers Based on Task-Specific Ionic Liquids

Sheng Dai
Email: dais@ornl.gov
Phone: 865-576-7307

Oak Ridge National Laboratory

Dec. 17, 2019

Project ID: ST148

Collaboration and Coordination

Project Team

Dr. Sheng Dai
Oak Ridge National Laboratory
Ionic liquids, carbon materials, and their energy-related applications

Dr. Huimin Luo
Oak Ridge National Laboratory
Ionic liquids and their energy-related applications

Dr. Halie Martin
University of Tennessee-Knoxville
Postdoctoral Research Associate responsible for polymer characterization

Dr. Richard T. Mayes
Oak Ridge National Laboratory
Carbon materials and their energy-related applications

Dr. Amit Naskar
Oak Ridge National Laboratory
Carbon materials and their energy-related applications

Dr. Gabriela Gurau
525 Solutions, Inc.
Ionic liquids and their scale-up synthesis

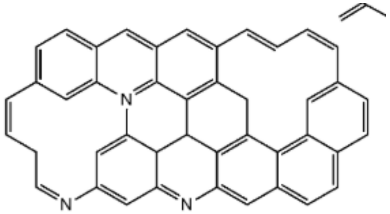





Introduction

- The CF industry is a continuously growing area of research.
- Commercial carbon fiber (CF) has exceptional mechanical properties.
- Carbon fiber are prepared from a variety of precursor materials.
  - **polyacrylonitrile (PAN)**, mesoporous pitch, rayon
- PAN-based carbon fiber dominates consumption, accounting for nearly 90% of all sales.
  - Correlation between CF structure and CF properties is not fully developed.

Boeing 787 Dreamliner

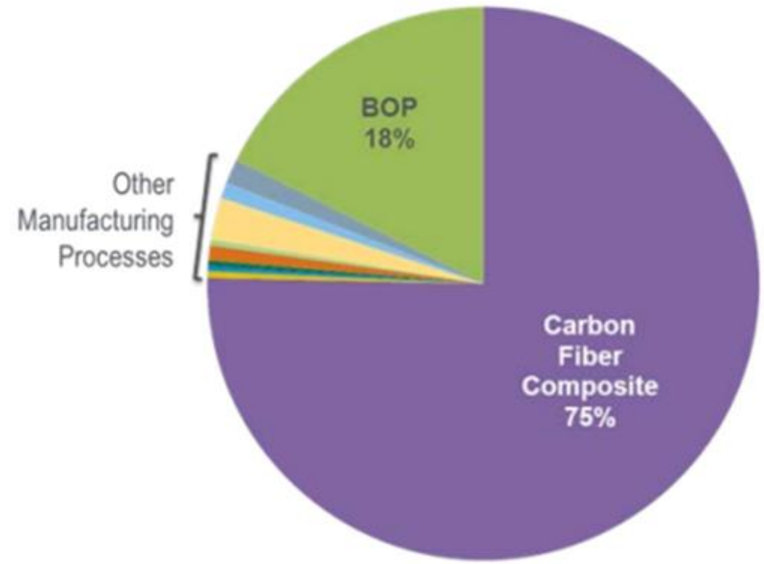


Chemical Structure of PAN-based CF

Angew. Chem. Int. Ed. 2014, 53, 5262 – 5298
Carbon 93 (2015) 81 –87

Carbon Fiber Composites for Hydrogen Storage Systems

- Hydrogen storage R&D focuses on lowering the cost for fuel cell and hydrogen storage systems.
- Hydrogen is currently stored in Composite Overwrapped Pressure Vessels at 700 bar (~10,000 psig) based on carbon fiber technology.
- The production of carbon fiber composites dominates the cost for hydrogen storage.

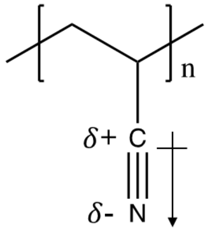


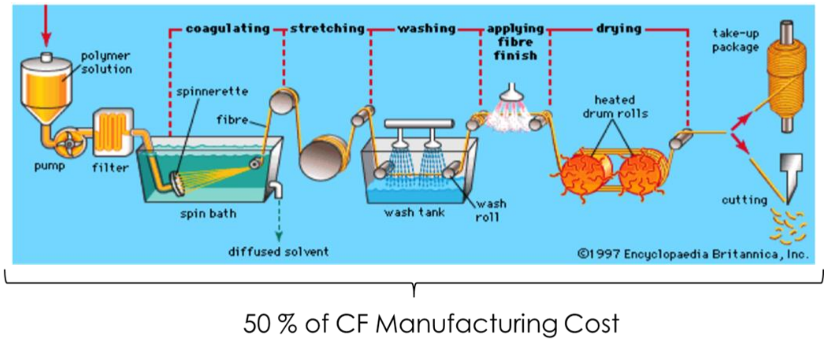
Systems Analysis sub-program cost analysis of a 700-bar Type IV hydrogen storage system shows >75% of cost is in the filament wound carbon fiber composite layer.

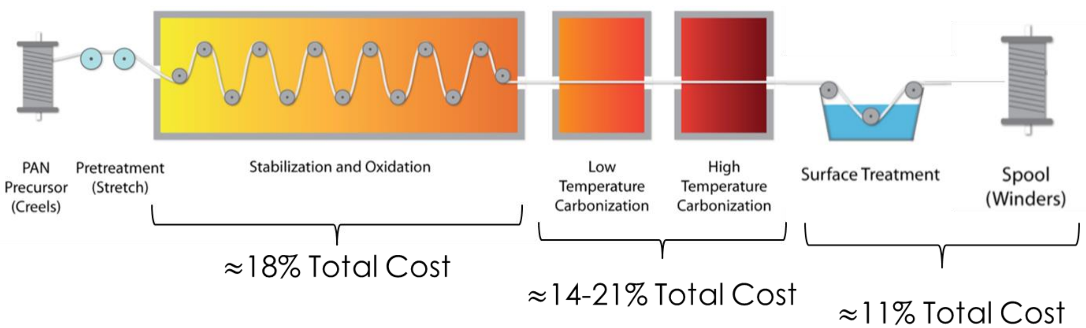
https://www.hydrogen.energy.gov/pdfs/15013_onboard_storage_performance_cost.pdf

PAN-Based CF Precursors

- PAN has an intense dipole moment of nitrile groups.
  - Results in strong interchain and intrachain interactions
- Wet spinning is the preferred method for the manufacturing of PAN precursors.
  - Internal Plasticization i.e. PAN-based copolymers
  - *External Plasticization*
  - <u>MUST</u> use highly polar solvents
  - Concentration of polymer ranges from 10-20 wt%
  - Coagulation bath determines morphological structure
- **Main Barrier:** *PAN polymer degrades/crosslinks before melting.*







Warren, C. D., "Carbon Fiber Precursors and Conversion", Oak Ridge National Laboratory, Department of Energy Physical -Based Storage Workshop: Identifying Potential Pathways for Lower Cost 700 Bar Storage Vessels, August 24, 2016.

Objective & Relevance

- Objective: The overarching goal of our project is to develop a novel plasticized melt-spinning process to replace the current solution spinning process based on nonvolatile task-specific ionic liquids (ILs). The four underpinning research tasks we aim to accomplish in our project are:
  - to investigate how the molecular structures of ILs dictate plasticizing interactions with PAN for controlling glass transition temperatures and rheological properties of PAN-IL composites,
  - to study how the chemical interactions of ILs with PAN can be used to control the cyclization degree in intermediate ladder structures
  - to integrate the information gained from the above two tasks to develop IL-assisted melt spinning systems
  - demonstrate considerably enhanced production efficiencies and improved structural properties of PAN fibers.

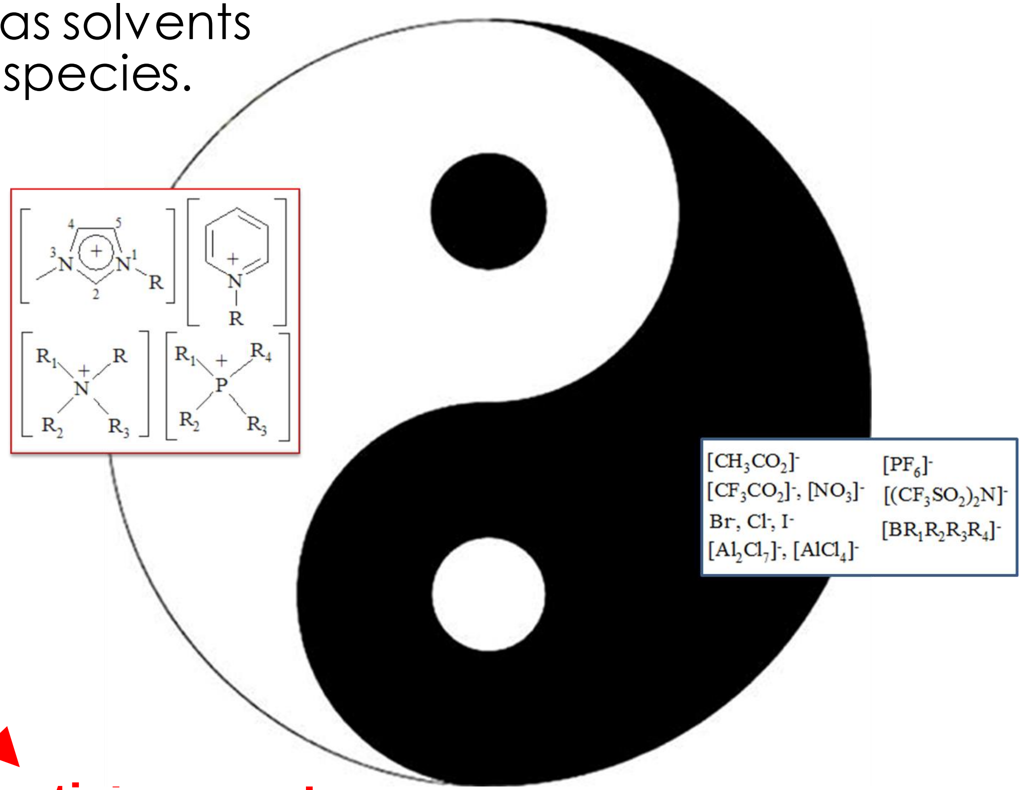
- Relevance to Barriers and Targets
  - The ability to melt-spin the PAN into fibers has been identified as a significant cost-driver for high strength carbon fiber production.
  - The fiber production has a direct correlation to the costs of a hydrogen storage system where the carbon fiber cost is 75 % of the total system cost
  - To replace the current solution spinning process with a novel plasticized melt-spinning process based on nonvolatile task-specific ionic liquids (ILs)

Why Ionic Liquids for Melt Spinning Production of PAN Fibers?

Ionic systems consisting of salts that are liquid at ambient temperatures can act as solvents for a broad spectrum of chemical species.

- *Ionicity (Polar)*
- *Nonvolatility*
- *Thermal Stability*
- *Nonflammability*
- *Tunable Hydrophobicity*
- *Wide Liquid-Phase Temperature*
  (-100°C to around 300°C)

- *Wide Electrochemical Window*
- *Tunable Lewis Acidity*

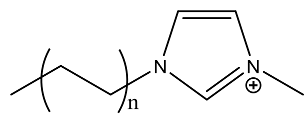


Ma, Yu, Dai, *Adv. Mater.* **2010**, *22*, 261

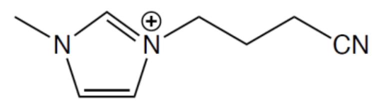
Ideal as plasticizers and designer solvents

Down-selection of ILs for plasticization studies based upon melt temperature suppression

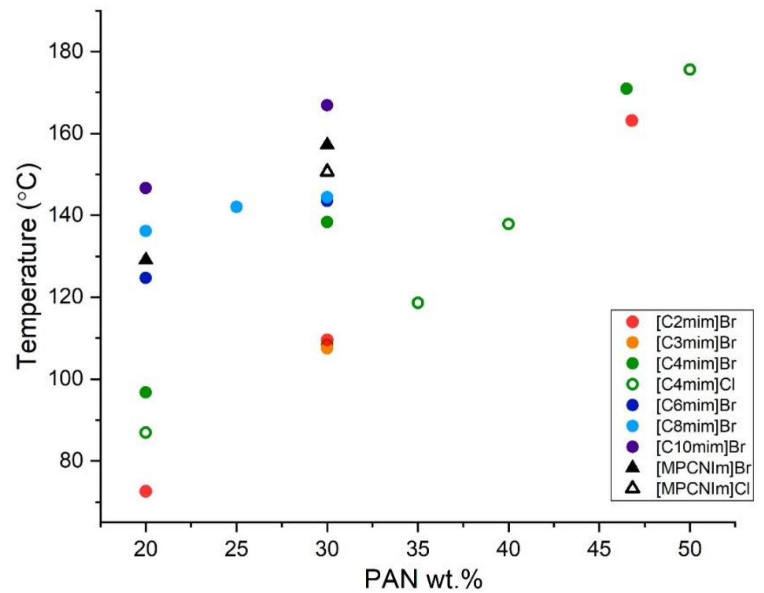
- Ionic liquids as a plasticizer to suppress the melting temperature of PAN
  - **Melting temperature for PAN-IL composites are greater than 100 °C lower than neat PAN (~325 °C)**
- Generally, for a given PAN wt.% as the carbon chain length is increased for $[C_n mim]^+$ the melting temperature is increased.
- Chloride anions suppresses the melting temperature greater than bromide anions for a given cation
- As the PAN concentration is increased the more energy it takes to disrupt the crystalline phases of the polymer chains



$[C_n mim]^+$

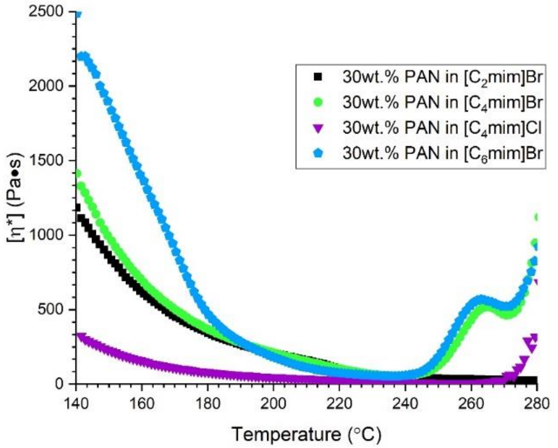


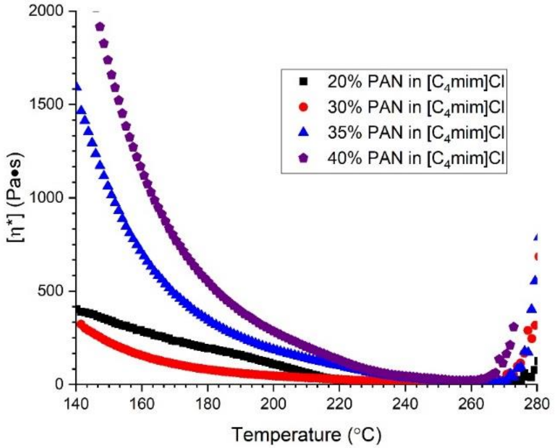
$[MPCNIm]^+$



Demonstration of melt viscosity of PAN-IL composites

- Rheological properties of the PAN-IL composites can determine the "melt spinnability"
- Viscosity curves are a superposition of two different effects
  - Viscosity first decreases when the molecular activity is increased.
  - Viscosity increases when PAN begins to crosslink/cyclizes.
- As the carbon chain length is increased the initial viscosity is also increased.
- As the PAN concentration is increased for a given IL the viscosity also increases.



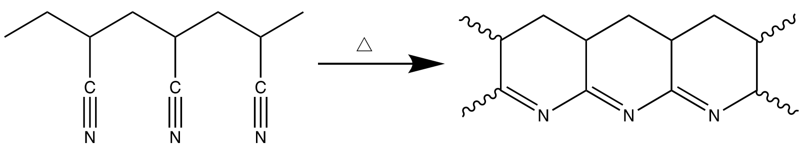


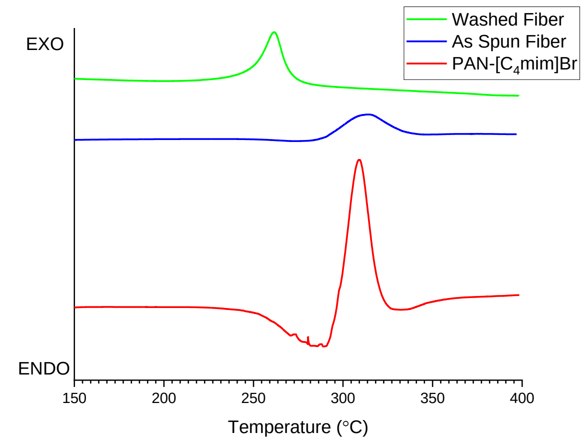
Demonstration of Melt Spinning PAN Fibers

- Fiber spinning experiments were performed on a melt extruder
- Melt extruder is ideal for small sample sizes
  - 3-5 total grams of material
- Initial testing parameters are:
  - Rotor ≈ 150-160 °C
  - Header ≈ 150-170 °C
  - Rotational speed ≈ 90 RPM
  - Take up speed ≈ 60 ft/min
- 30 wt.% PAN in 5 different IL
  - [C_3mim]Br, [C_4mim]Br, [MPCNIm]Br, [C_4mim]Cl, [MPCNIm]Cl

PAN Fiber Precursors Characterization

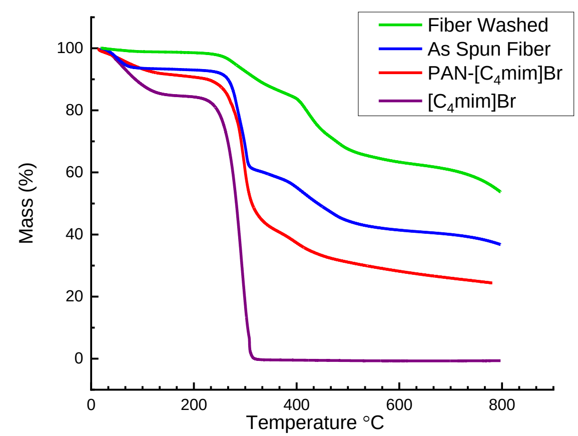
- DSC shows the as-spun fiber exhibits a smaller, wider exotherm compared to composite.
  - DSC of washed PAN fibers elude to stabilization process





- Carbon yield increases from the melt to over 50 wt.% for the washed PAN fibers.
  - Higher carbon yield indicates an increase in crystallinity
  - Weight loss intervals correspond to stabilization process and low temperature carbonization

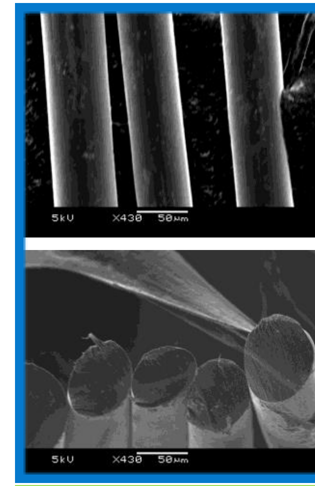
Ionic liquid	PAN (%)	Carbon yield (%)		
		Melt	As Spun Fiber	Washed Fiber
PAN	100	33.4	31.4	----
C_3Br	30	20.6	44.4	53.7
C_4Br	30	24.4	36.8	53.8
C_4Cl	30	13.1	29.3	45.0
CNBr	30	26.5	38.4	58.5
CNCl	30	21.0	33.1	52.2

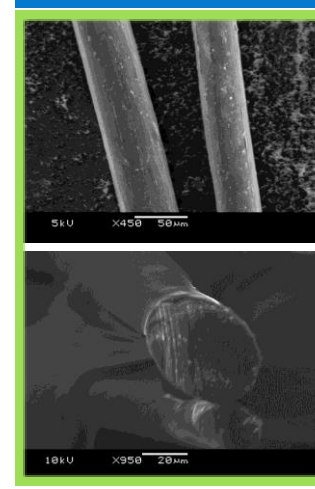


Morphology/Size of PAN Fiber Precursor

- Fiber spinning is not only responsible for the chain alignment but for the morphology of the fiber.
- Both surface and sub-surface morphology can affect the tensile strength.
- Surface of fibers are relatively smooth, and the cross sections do not reveal any voids or defects.
- Commercial CF has a diameter range of 5-20 μm.

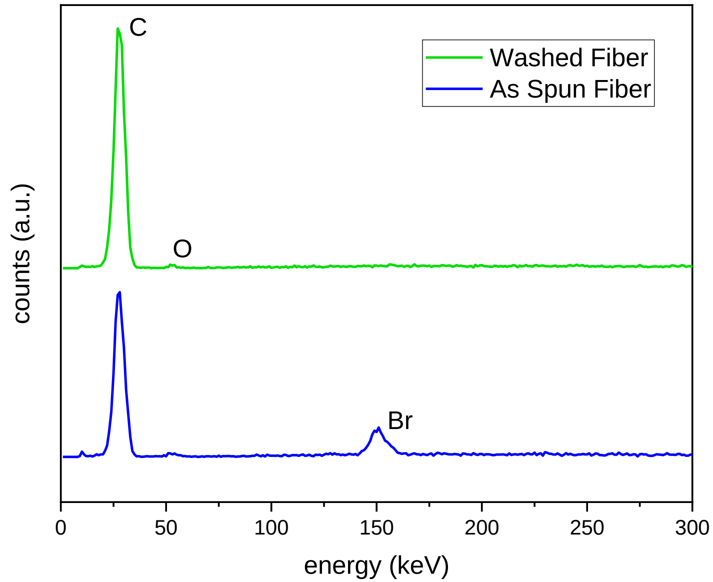
Ionic liquid	PAN (%)	As Spun Fiber Diameters (μm)	Washed Fiber Diameters (μm)
$[C_3mim]Br$	30	56.2 +/- 0.16	53.4 +/- 7.6
$[C_4mim]Br$	30	56.8 +/- 2.00	45.6 +/- 7.9
$[C_4mim]Cl$	30	54.7 +/- 0.08	45.3 +/- 8.7
[MPCNIm]Br	30	59.6 +/- 0.25	47.9 +/- 14.1
[MPCNIm]Cl	30	53.4 +/- 0.17	48.6 +/- 10.4

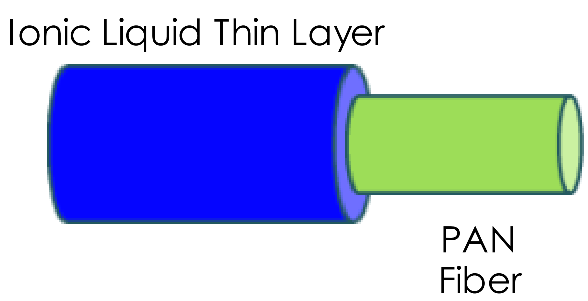




Morphology/Size of PAN Fiber Precursor

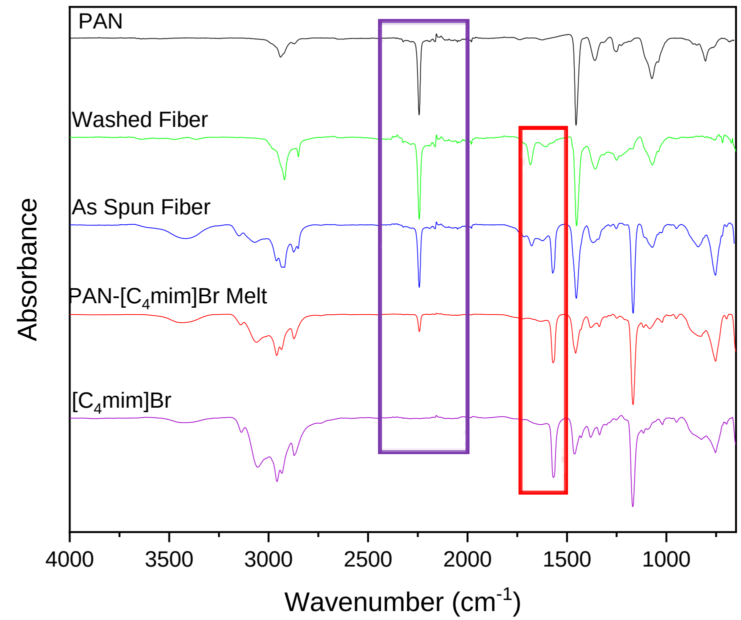
- EDS characterizes the elemental composition of the surface of the fibers.
- As spun fiber have a thin coating of ionic liquids on the surface.
  - Denoted by a bromide or chloride elemental response.
- Washed fibers show no evidence of IL on surface
  - Accounts for the smaller fiber diameters.

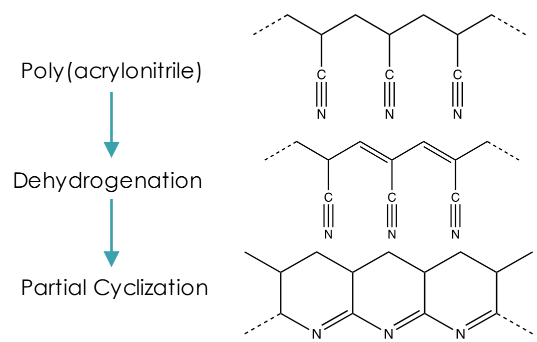




Functional Group Characterization of Fibers

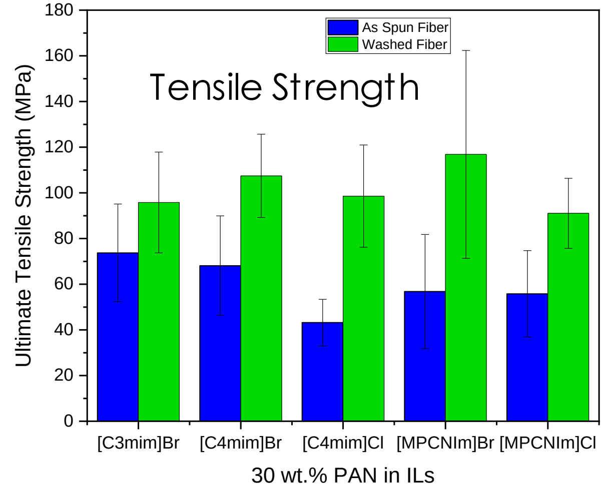
- FTIR was used to analyze the functional groups of PAN through out the fiber processing.
- PAN has a dominate IR band at 2240 cm^{-1} → C≡N stretching modes.
  - Intensifies throughout the fiber spinning process.
  - C≡N neighbor distance decreases
- As-spun fibers and washed fibers have formation of 2 new IR bands.
  - 1610 cm^{-1} → C=C and C=N vibrations, N-H stretching
  - 1680 cm^{-1} → C=O bending (oxygen uptake)
- ***PAN fibers are partially cyclized!***

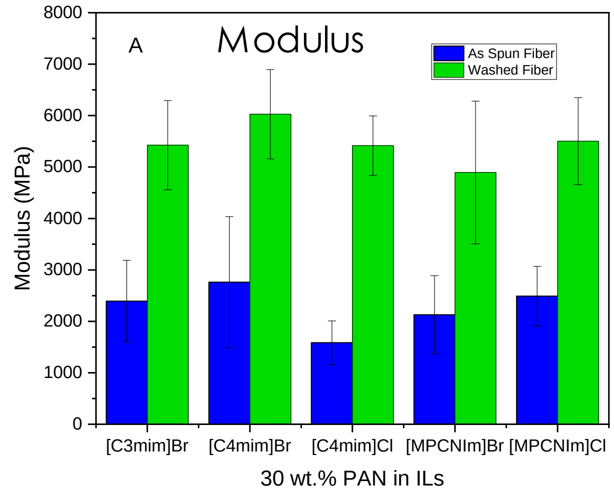




Mechanical Performance of PAN Fiber Precursors

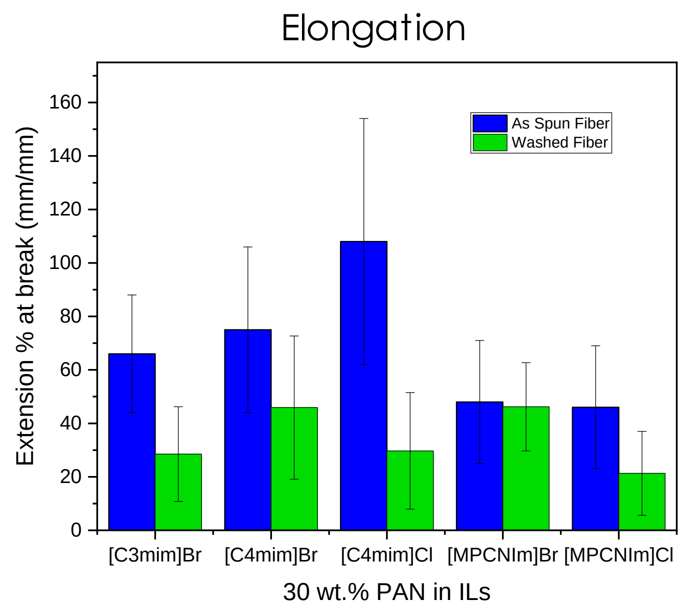
- The changes in mechanical properties of the as spun fibers and washed fibers are shown.
- Tensile strength is the stress needed to break a sample.
  - Tensile strength increases with the removal of ILs from fibers.
  - Amorphous regions dominate structure in as spun fibers
- The modulus shows the rigidity/stiffness of fibers.
  - The modulus increases with the removal of the ILs form the fibers.
  - Comparative to literature values for PAN precursors





Mechanical Performance of PAN Fiber Precursors

- Why are the mechanical properties of the washed fibers higher than the as spun fibers?
- The as spun fibers are able to be stretched or elongated upwards of 100% of its original length.
  - Ionic liquids are acting as a lubricant stretching the amorphous region of the polymer chains.
- Removal of ionic liquids result in a decrease in fiber extension.
- *Fibers are in favor of stretching or drawing while in the presence of the ionic liquids.*



OAK RIDGE
National Laboratory

Summary

- The melting temperature of PAN has been demonstrated to be suppressed by over 100 °C by the addition of ionic liquids.
  - Ionic liquids containing chloride anions had a greater effect on the decrease in melting temperatures.
  - Lower production temperatures decreases cost of carbon fiber production.
- Demonstrated the ability to successfully melt spin uniform and homogeneous PAN fibers.
  - Utilizing benchtop melt extruders allows us to determine the processability before scaling up.
  - Surface of fibers are smooth and without defects.
- Preliminary experiments show that the PAN fibers can be stabilized at lower temperatures with carbon yields > 50 %.

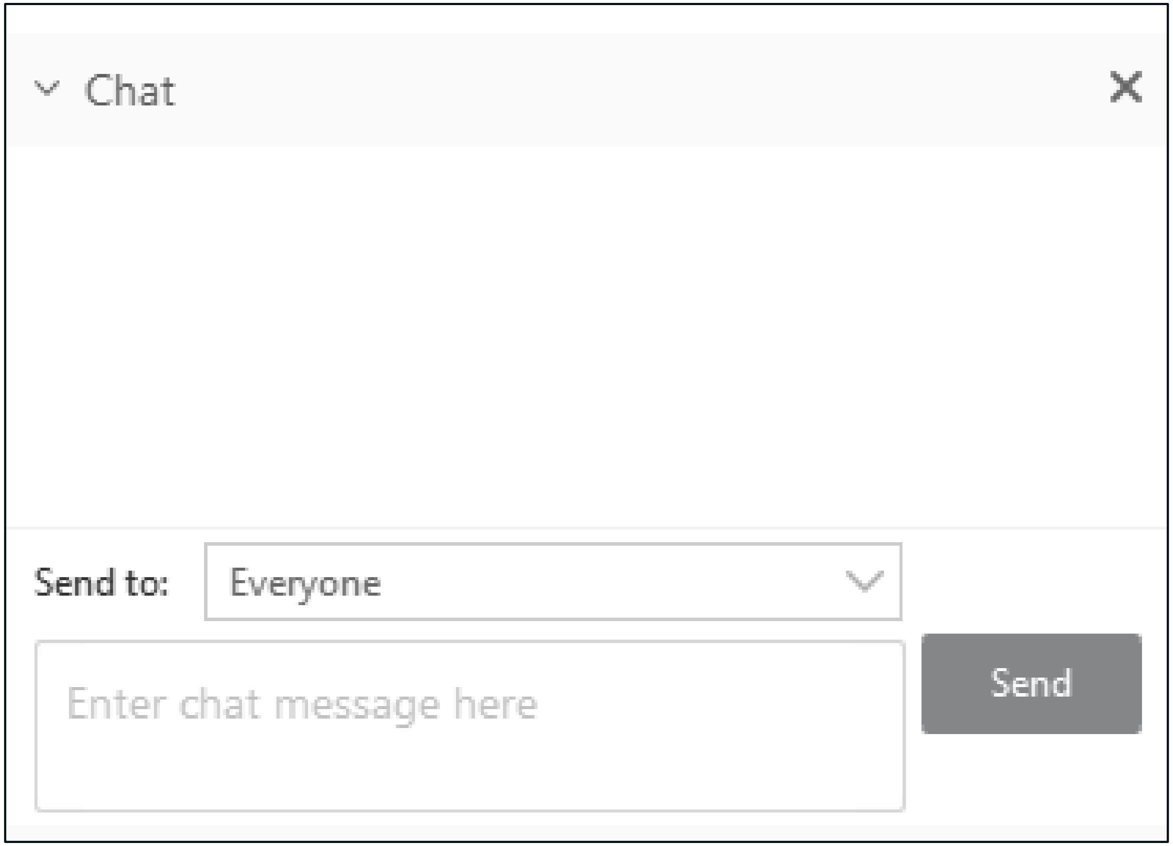
Angew. Chem. Int. Ed. **2014**, *53*, 5262 – 5298

Acknowledgements

U.S. DOE Office of Energy Efficiency and Renewable Energy (EERE) (Program Manager: Bahman Habibzadeh)

Question and Answer

- Please type your questions to the chat box. **Send to: (HOST)**



Thank you

Cassidy Houchins
chouchins@sainc.com

Sheng Dai
dais@ornl.gov

Matthew Weisenberger
matt.weisenberger@uky.edu

Mike Chung
chung@psu.edu

Eric Parker
DOEFuelCellWebinars@ee.doe.gov

Ned Stetson
Ned.stetson@ee.doe.gov

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