Carbon Fiber R&D for Hydrogen Infrastructure Technologies

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Welcome Slide – Introduce Yourself

- Amit Naskar
- Oak Ridge National Laboratory
- Distinguished R&D Staff and Group Leader
  - Areas of research include carbon fibers, carbon precursors, sustainable polymers, composites, and characterization polymer structure and dynamics.
  - Ph.D. in Rubber Technology from the Indian Institute of Technology, Kharagpur, India and conducted post-doctoral research at Clemson University, SC before joining ORNL in 2006.
  - Published more than 120 journal articles, 1 edited book, and has 35 issued US patents.
  - He is the lead inventor of the ORNL's technology for conversion of polyolefin fibers into carbon fibers, sustainable polymer formulations for composites, and tailored carbon morphology for energy storage applications.
    - Distinguished Achievement Award (2020) from DOE (EERE-VTO) in recognition of extraordinary expertise in leading alternative precursors R&D to achieve low-cost carbon fiber.
    - Distinguished Inventor Honored by Battelle Memorial Institute (2019)
    - Inventor of the Year, 2017, award at ORNL.

Cost-effective high pressure compressed gas storage is critical for widespread utilization of hydrogen in vehicles

CF cost accounts for approximately 50% of total vehicle high pressure storage system cost

- The baseline 700+ ksi commercial fiber in high pressure storage ranges from $26-30/kg CF
- To meet the DOE targets for hydrogen storage on board vehicles, CF cost would need to be reduced to approximately $13-15/kg CF.

Cost of CF includes the cost of the precursor fiber and the cost of converting the precursor to CF

- Cost reductions will be required in both the precursor and conversion processes.
- DOE has previously supported R&D on novel advanced conversion processes with potential to enhance low-cost, high-strength CF and lower cost precursors, but very little focused research on
  - *Advancing the lower cost precursor capability towards higher performance fiber and/or*
  - *Developing new chemical formulation approaches specifically targeting higher performance at lower cost.*

Image source:
Chris Wilson et al.
Hexagon

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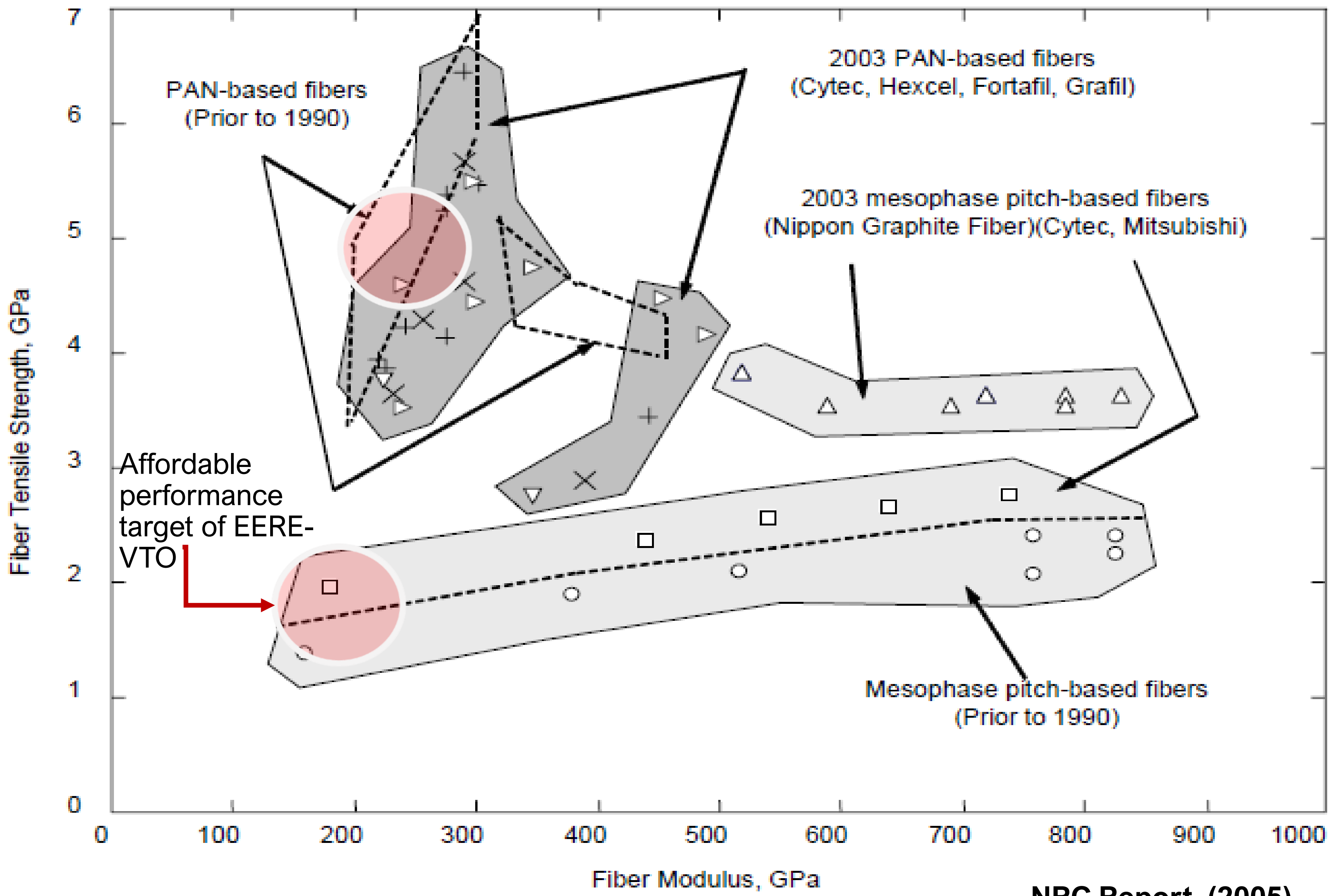
State-of-the-art Carbon Fibers and Properties



NRC Report, (2005)

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Carbon Fiber Production Cost Breakdown:

≈50% Precursor

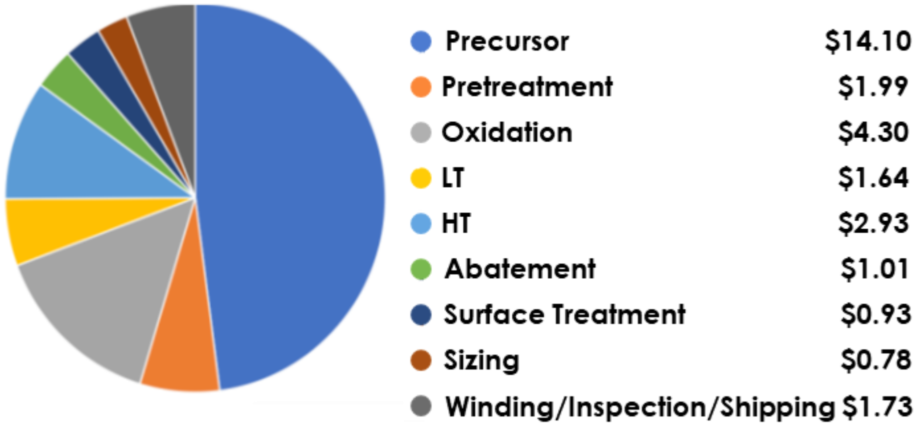
a) Polymer synthesis:

- State-of-the-Art: Predominantly acrylonitrile, cost dependent on supply chain health, feedstock prices, economic conditions
- Innovation: Moderate reductions in AN content through comonomer incorporation; improved synthetic yield

b) Filament Spinning:

- State-of-the-Art: Costs associated with processing solvents, coagulations media, and costs of running equipment
- Innovation: Process-inspired precursor which improves polymer loading by 67%, reducing process solvent, coagulation media consumption; air gap spinnable precursor improves line speeds by 78%

Current Aerospace Grade (T700S or similar) CF Cost Breakdown (per kg)[1]



≈50 % Thermal Conversion & Post Treatment

a) Oxidation/Stabilization:

- State-of-the-Art: Process requires long exposure to elevated temperatures to promote cyclization of AN units
- Solution: Improve accelerant chemistry/content to enable cyclization at lower temperatures; Stabilization process redesign reduces oxidation times by 25%

b) Carbonization: high temperature phases

- LTC: Low Temperature Carbonization
- HTC: High Temperature Carbonization

c) Post-carbonization Treatment(s):

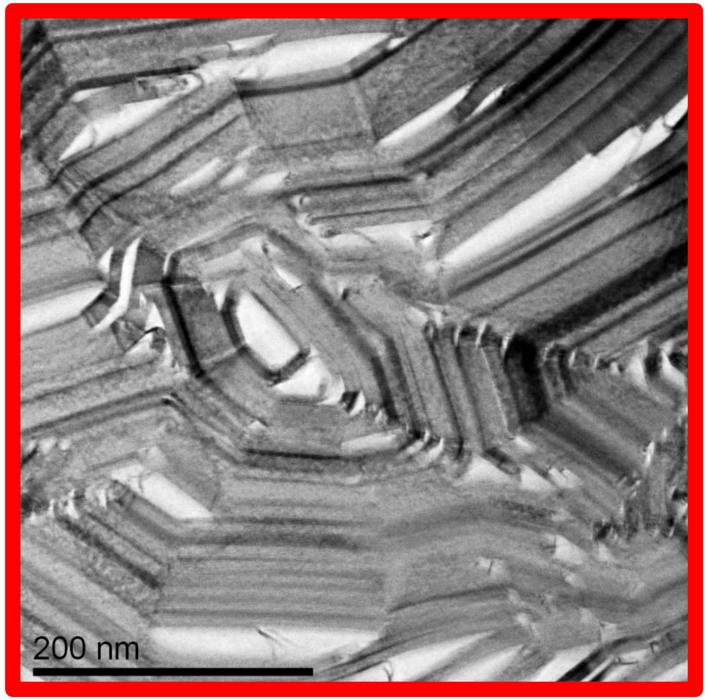
- State-of-the-Art: Multi-step process (surface treatment and sizing), essential in transferring load from matrix to CF reinforcing phase
- Innovation: Single-step treatment process; better load transfer to CF (enabling reduction in CF used)

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

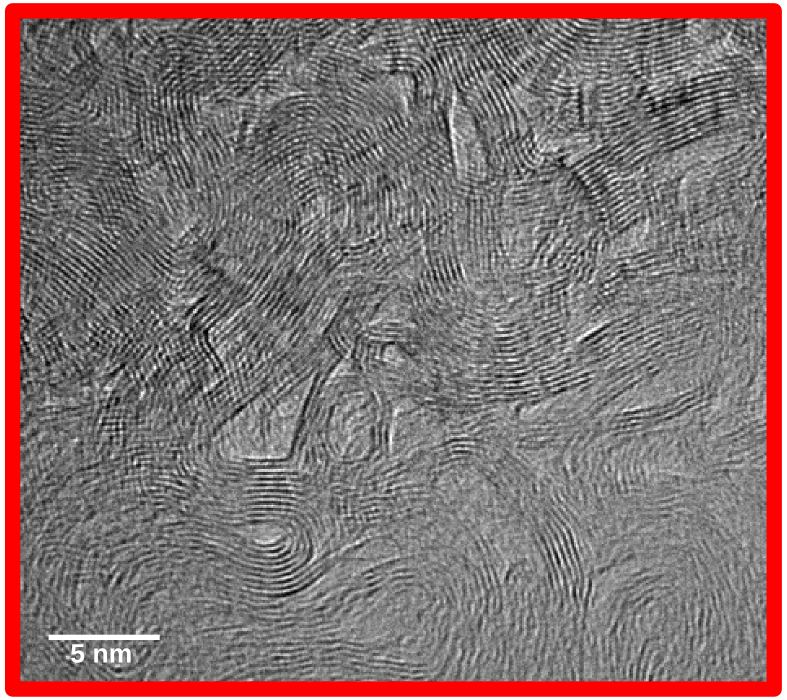
Microstructure-informed conversion

Transmission electron microscopy elucidates microstructural implications of processing parameters to optimize processing and target performance

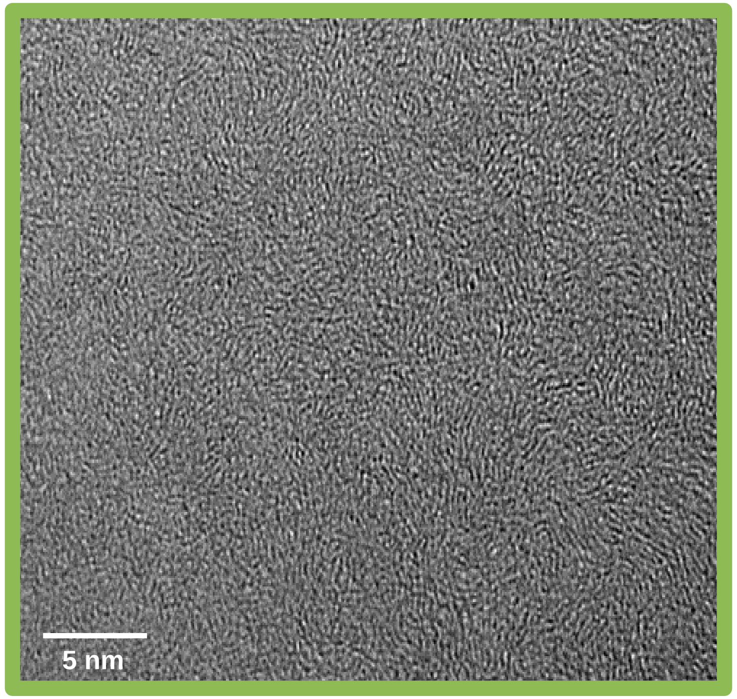
Increased brittle behavior



TEM image corresponding of the cross section of K1100 carbon fibers



TEM image of the cross section of a high modulus PAN-based carbon fiber



TEM image of the cross section of high strength PAN-based carbon fibers

Improved break strength performance

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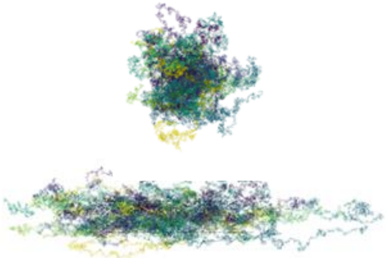
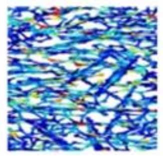
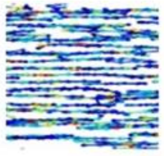
Polymer Precursor derived carbon. Editors: Naskar AK, Hoffman WP, Volume 1173, American Chemical Society Symposium Series Publication, Chapter 10, pp 215-232 (2014).

Precursors: Disordered molecules to performance materials

Comprehensive capability for precursor design and thermal processing





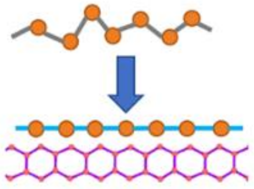


Solution/Melt Processing

- Rheology
- Thermal stability

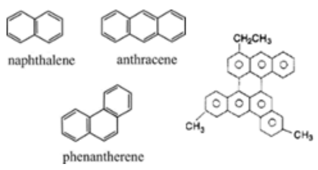
Microstructure

- Crystallinity
- Orientation
- Porosity



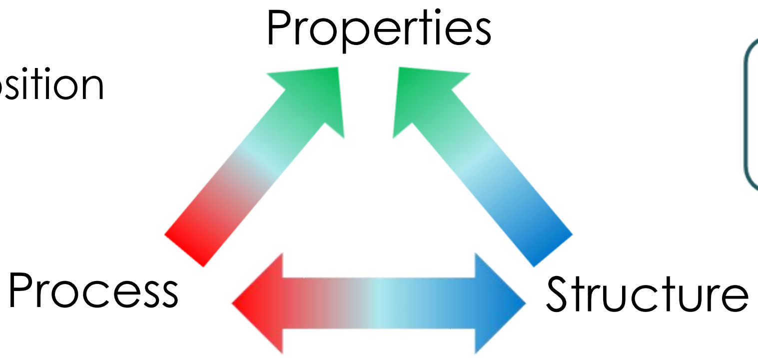
Constructive Oxidation

- Thermal relaxations
- Network formation



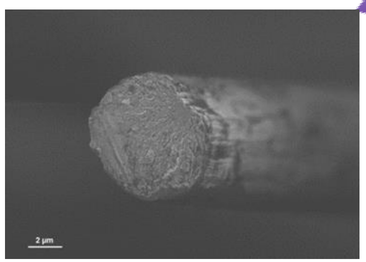
Molecular Structure

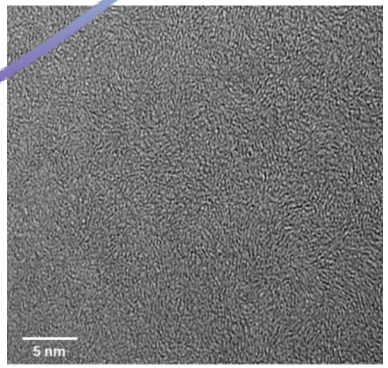
- Molecular weight
- Chemical composition
- Dispersity
- Dipole disruption



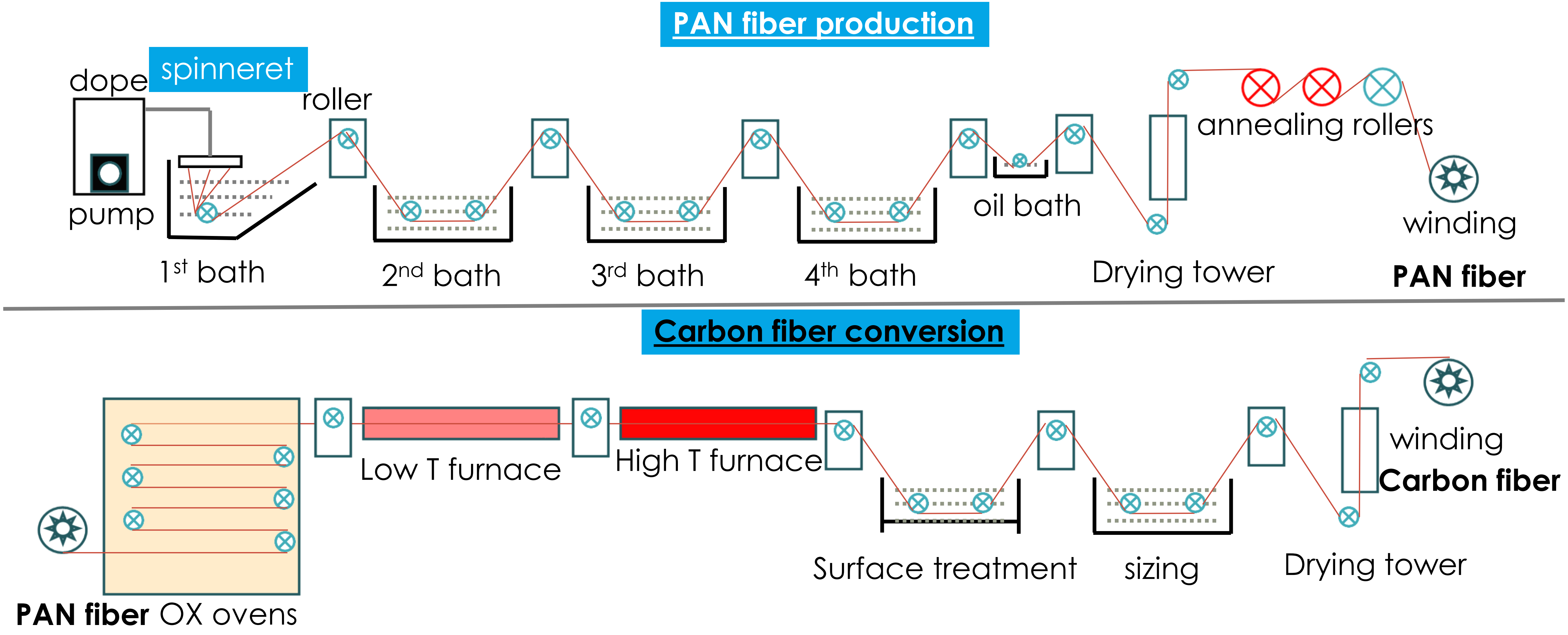
Carbonization

Performance Carbon Products





Precursor spinning and carbon fiber conversion

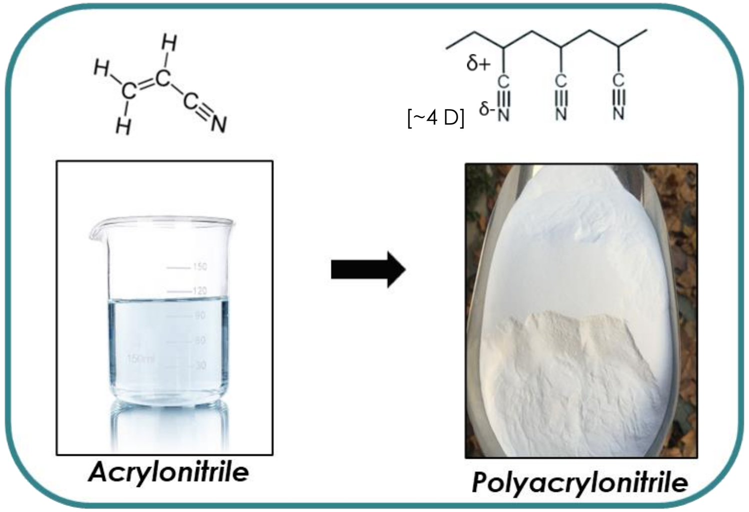


ORNL carbon fiber R&D lines have separate units, enabling more control at each step with minimal materials needed.

Outline: towards 700 ksi 35 msi CF with $15/kg

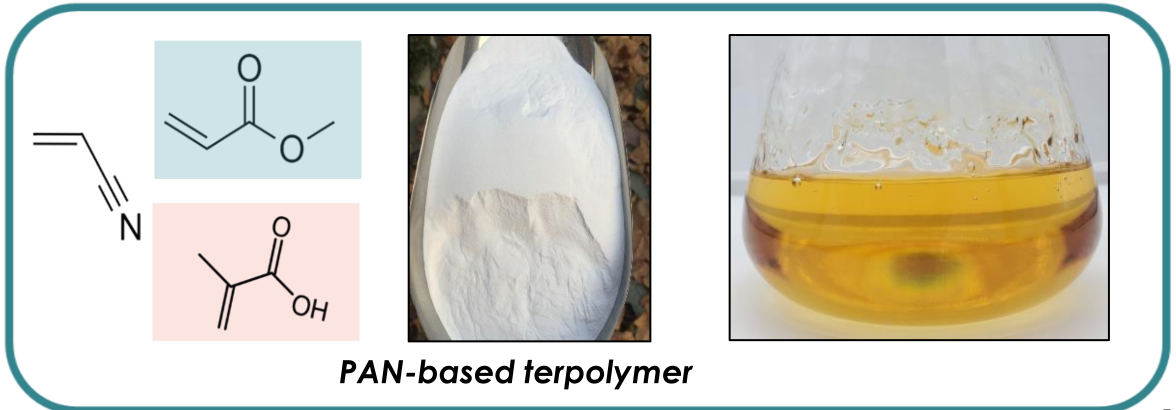
- ORNL Precursor development enables fundamentally informed precursor design starting at the monomer scale
- Plate/extensional rheology characterization capabilities for precursor solution/gel optimization
- Spinning
  - Commodity-grade copolymer wet spinning
  - Air gap wet spinning
- Faster Stabilization and carbonization
- Carbon fiber characterization
- Surface treatment and sizing

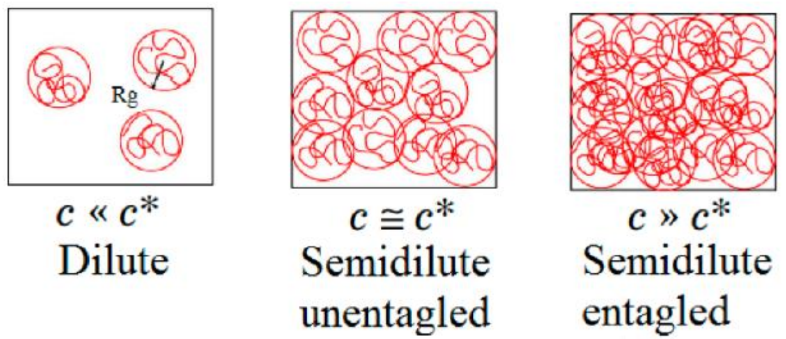
Designing a PAN-based terpolymer to improve structure, processing, and properties

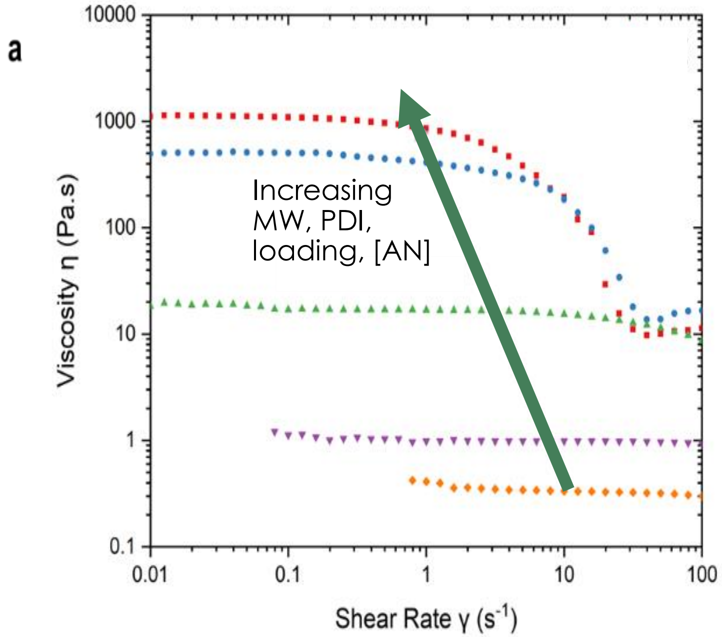


Highly electronegative nitrile group increases partial dipole interactions, limiting mass loading, spinnability in PAN dopes

Comonomer/accelerant incorporation into precursor chain facilitates increased polymer loading







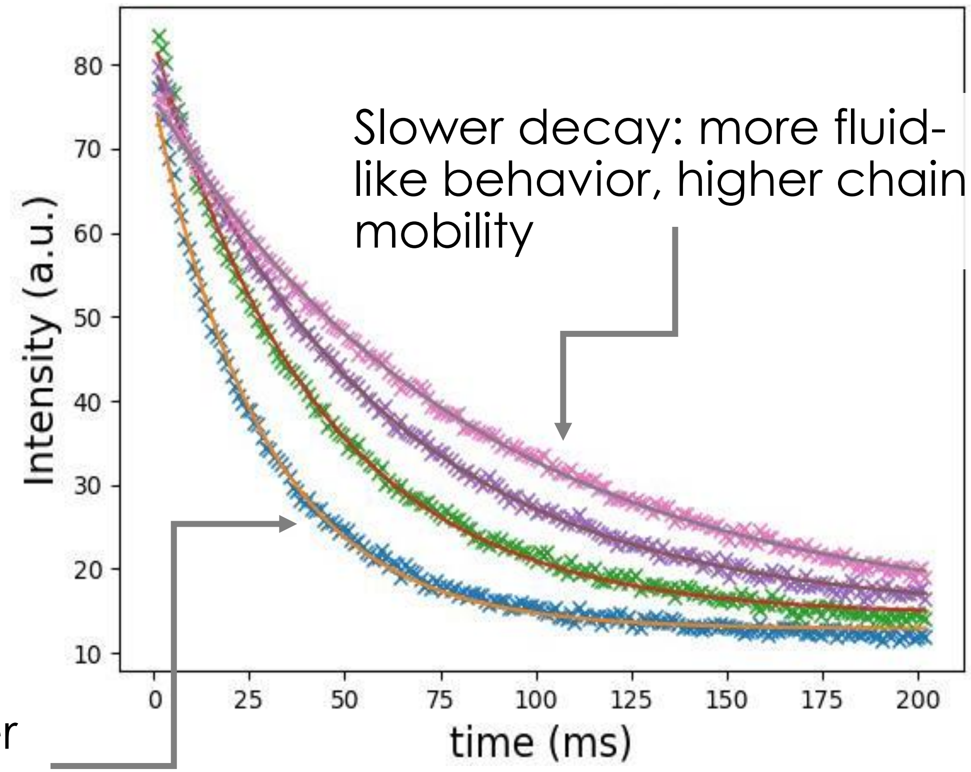
Ideal concentration ranges need to be tuned for every polymer formulation and Mw.

Probing polymer-solvent, polymer-polymer interactions

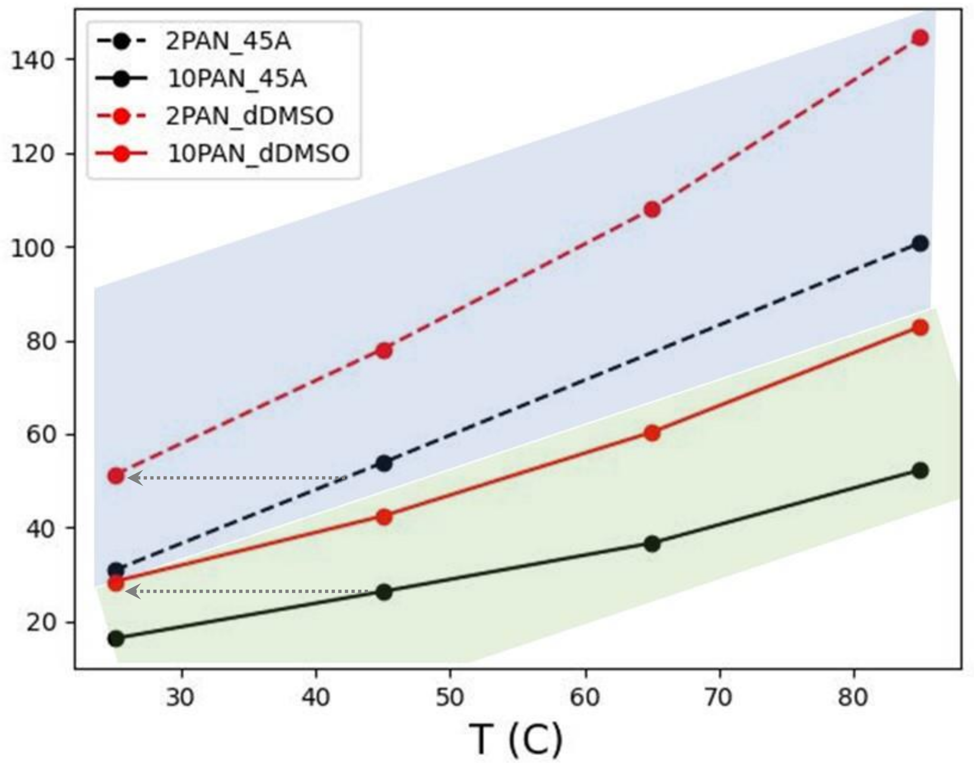
With respect to comonomer selection, what solvent-polymer pairs are optimal?
How does polymer solid content influence chain mobility?

Probing sub-chain relaxation behavior of dope

$$I = I_0 * e^{-\frac{t}{t_2}}$$



Faster decay (smaller T2 value): more rigid behavior



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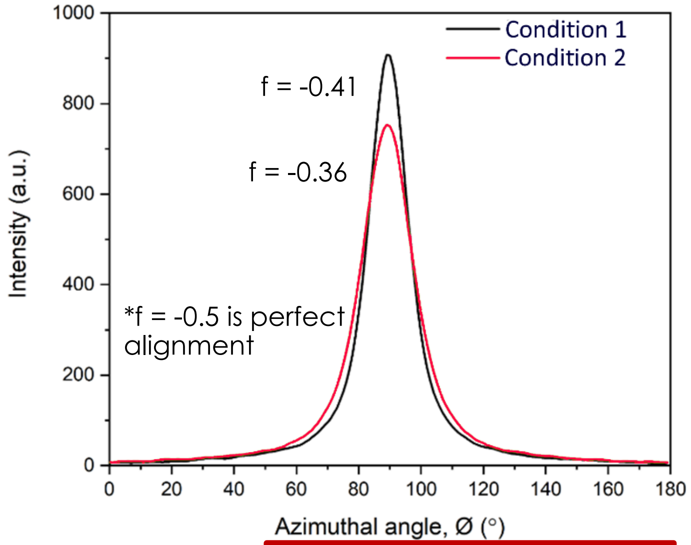
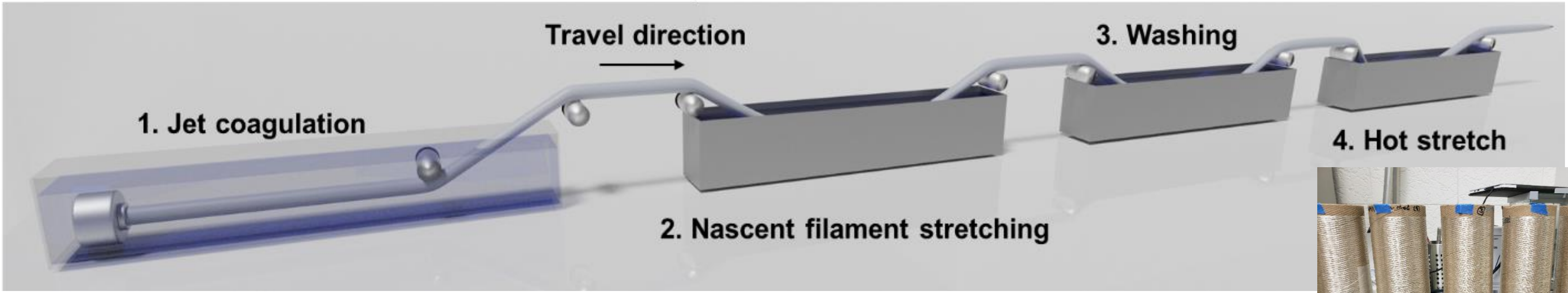
Fiber spinning: Inducing order via flow and deformation



$$f = \frac{3 < \cos^2(\phi) > -1}{2},$$

High degree of alignment is essential for good carbon fiber properties.

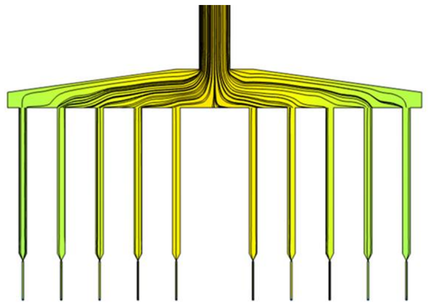
Simulated polymer chain configuration during drawing



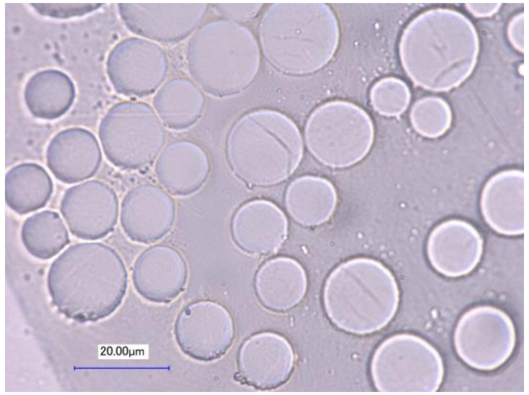
Ferralis et al. (Unpublished)

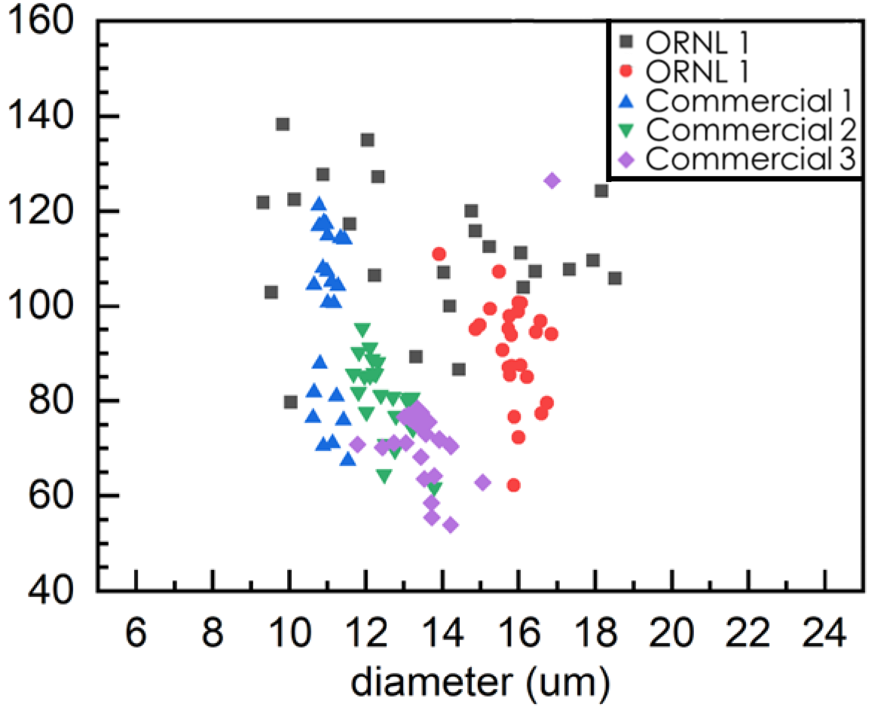
Leveraging computation for improved processing and coefficients of variance

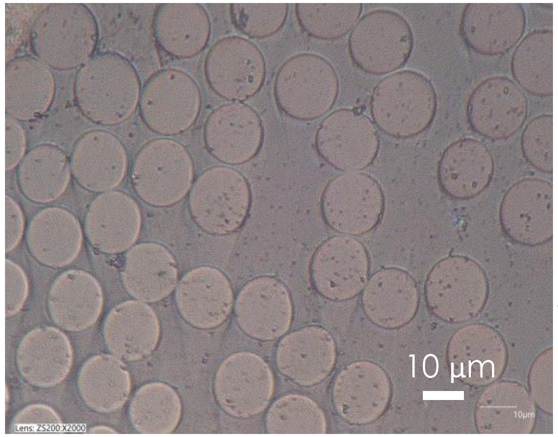
- Comsol simulation of the spinning process (from pump to hole ends of the spinneret) shows temperature gradient radially across the spinneret.
- Viscosity dependence on temperature causes non-uniform flow distribution among the spinneret holes.
- Stabilization and carbonization problems with PAN fibers with varied diameters.



Temperature drops from center to rim







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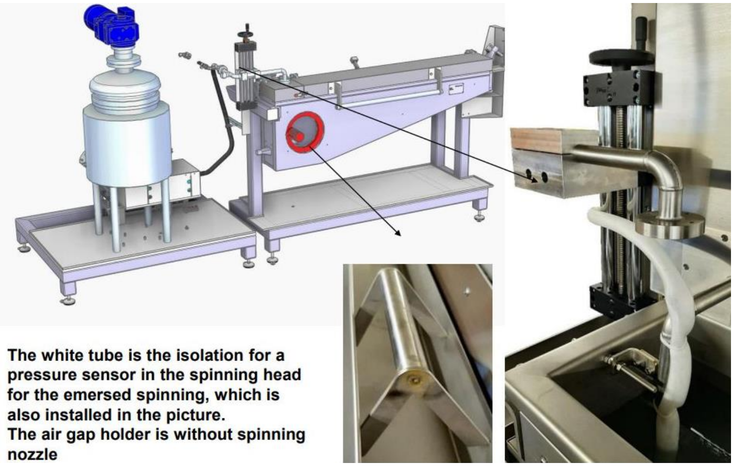
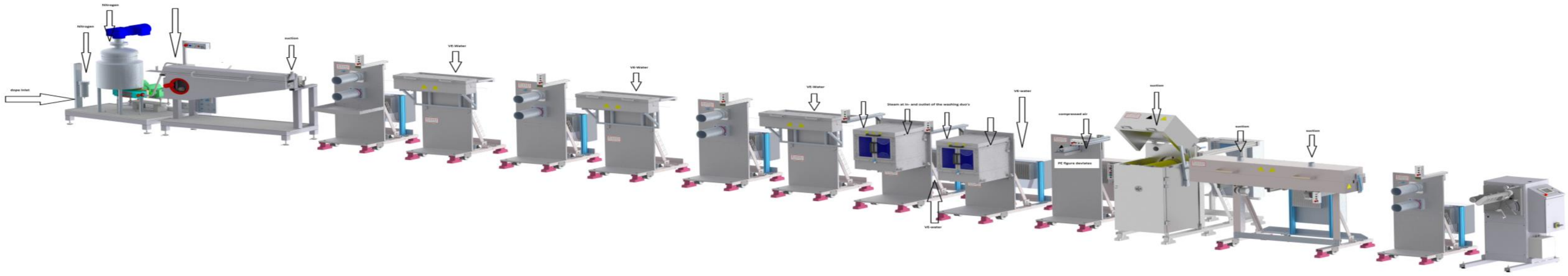
ORNL is establishing state-of-the-art carbon precursor manufacturing capability



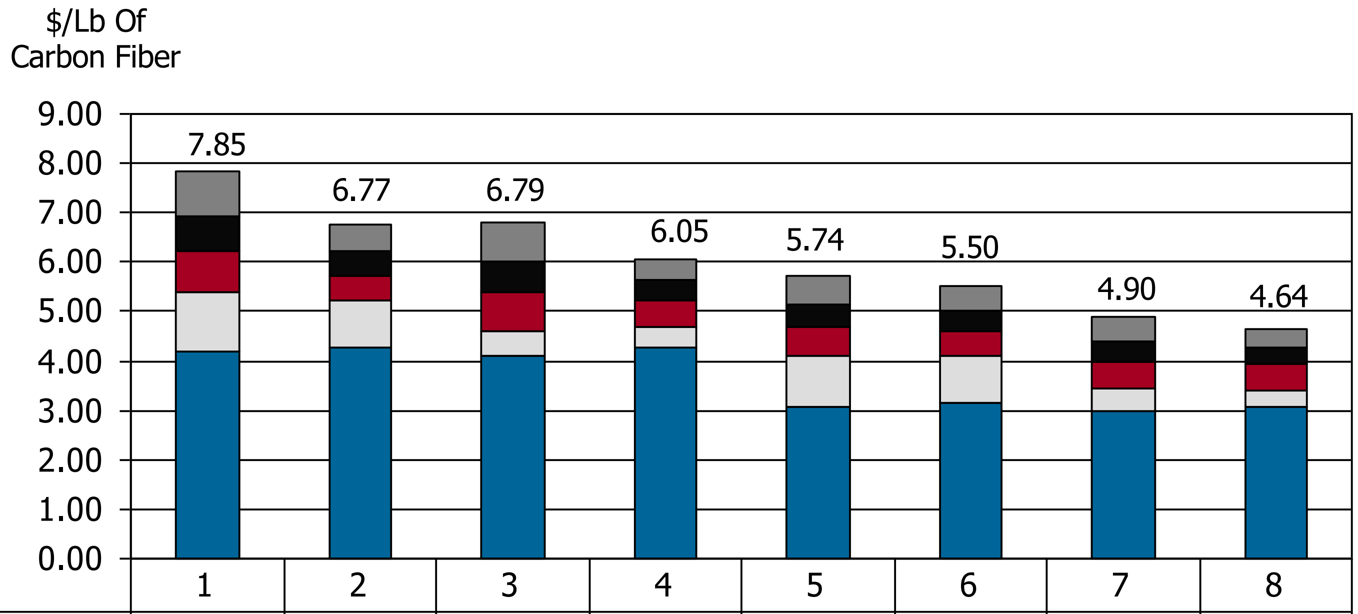
Polymer gel dispensing option allows formation of highly oriented macromolecule in fibers

A new solution spinning line will be installed for carbon precursor fiber research and development

- Precursors with higher dimensional stability and high carbon yield
- Coagulation bath with externally controlled environment
- New fiber heat setting capability for other structural fiber R&D
- Modular carbonization/conversion strategy already demonstrates high yield large diameter carbon fiber with properties (4+ GPa strength) acceptable for vehicles and pressure vessel applications



Prior carbon fiber manufacturing cost model for various cases investigated at ORNL (from a report by Kline and Company, January 2007).



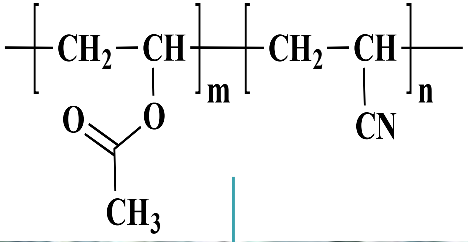
	1	2	3	4	5	6	7	8
Depreciation	0.94	0.55	0.78	0.43	0.60	0.47	0.49	0.36
Other Fixed	0.70	0.48	0.61	0.41	0.47	0.41	0.42	0.34
Labor	0.81	0.53	0.80	0.53	0.56	0.53	0.56	0.53
Utilities	1.20	0.93	0.49	0.40	1.03	0.92	0.44	0.33
Raw materials	4.20	4.28	4.11	4.28	3.08	3.17	2.99	3.08

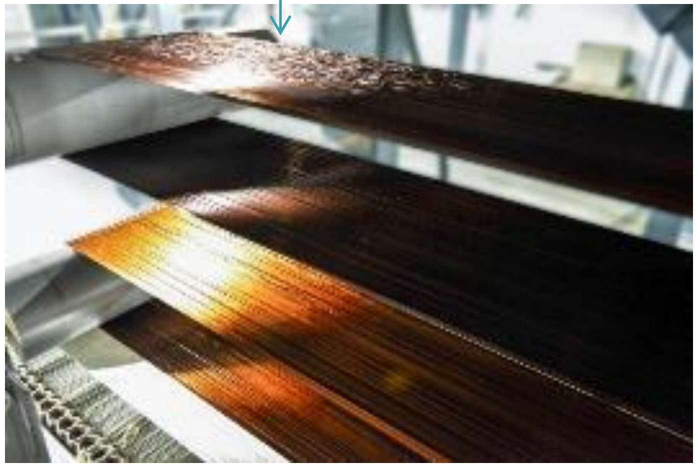
Raw materials Utilities Labor Other Fixed Depreciation

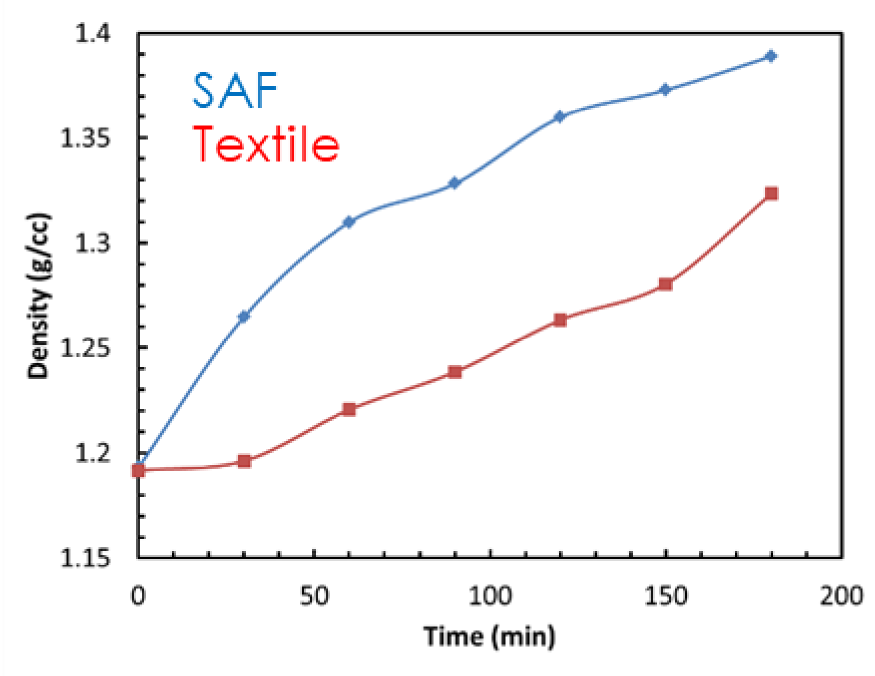
Key
1-Baseline (CF-PAN)
2-Plasma oxidation (PO)
3-MAP carbonization (MAP)
4-CF-PAN with PO & MAP
5-Textile PAN (TP)
6-TP & PO
7-TP & MAP
8-TP with PO & MAP

High Throughput Conversion of Commodity Precursor

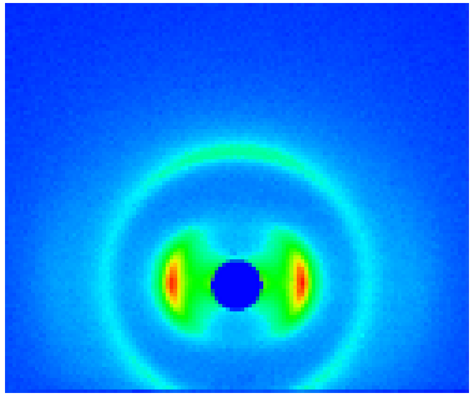
ORNL successfully produced and licensed the technology for conversion of unmodified, alternative textile-derived carbon fiber based on solution-spun PAN copolymer precursor fiber.







Lack of accelerants allows slow oxidation kinetics which favors high throughput conversion.



Jackson and Naskar, **U.S. Patent No. 10,961,642 (2021) and 10,407,802 (2019).**

CF conversion work focuses on process energy efficiency

The Precursor Evaluation System for oxidizing and carbonizing very small research and development tows from 100 filaments up to 24,000 filaments in order to evaluate processability and project performance capabilities for advanced carbon fiber formulations is shown in one of ORNL's research laboratories.

Overview of 1-ton-per-year pilot line (at 4X Technologies) for fully integrated conversion of 1-4 carbon fiber tows to demonstrate conversion recipes and resulting fiber improvements.

Advanced conversion method accelerates precursor oxidation

ORNL demonstrated that alternative textile equivalent acrylic precursor was able to meet achieve 600ksi tensile strength in single filament testing while also utilizing the advanced oxidative stabilization process.

Fv #	Diameter (µm)	Diameter Calculated	Density (g/cc)	Break Stress (Ksi)	Modulus (Msi)	Strain (%)
3201 Pre	12.70 (0.74)	12.62	1.1787 (.0001)	59.71 (5.64)	1.29 (0.14)	18.08 (1.78)
3591 ox	8.32 (0.23)	8.06	1.3634 (.0002)	40.11 (2.10)	1.13 (0.03)	18.93 (2.16)
3621*	4.82 (0.29)	4.82	1.7761 (.0007)	582.30 (75.35)	34.33 (0.61)	1.63 (0.19)
3622	4.66 (0.26)	4.82	1.7738 (.0005)	617.26 (66.79)	35.55 (0.63)	1.67 (0.16)
3623	4.54 (0.21)	4.77	1.7781 (.0084)	580.06 (68.15)	35.78 (0.97)	1.57 (0.17)
3624	4.63 (0.27)	4.79	1.7690 (.0079)	605.73 (49.47)	35.34 (0.95)	1.64 (0.11)
3625	4.76 (0.24)	4.82	1.7746 (.0005)	592.07 (67.97)	34.04 (0.71)	1.67 (0.16)
3626	4.82 (0.24)	4.89	1.7717 (.0003)	589.02 (57.51)	32.96 (0.61)	1.71 (0.14)

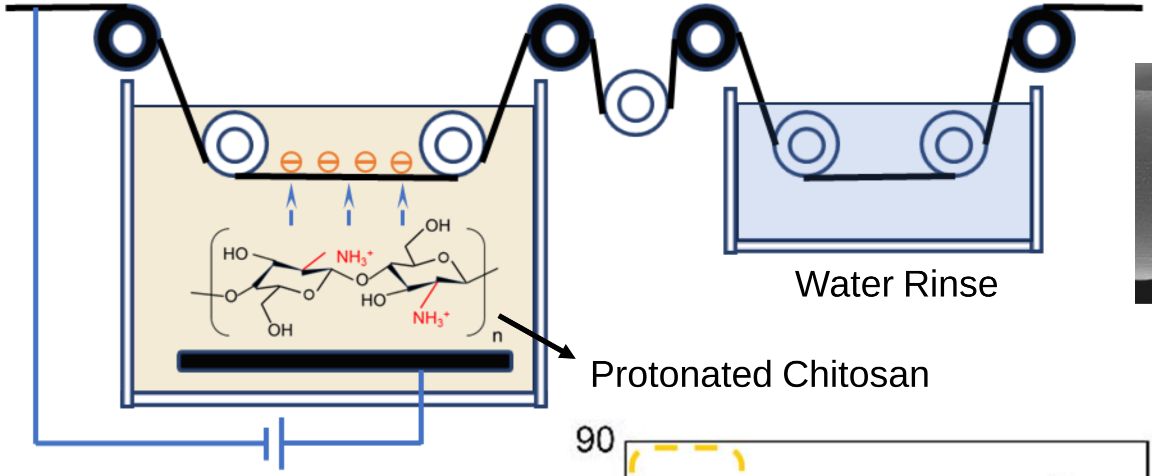
Accelerant containing precursors meets 700 ksi strength goal via advanced oxidation

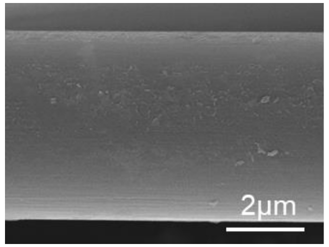
Fv #	Diameter (µm)	Diameter Calculated	Density (g/cc)	Break Stress (Ksi)	Modulus (Msi)	Strain (%)
3711	11.00 (0.26)	10.83	1.181	102.59 (14.88)	2.16 (0.04)	11.42 (1.53)
3705	10.11 (0.83)	10.39	1.3416	57.13 (7.04)	1.69 (0.20)	13.18 (1.82)
3699	6.00 (0.24)	6.18	1.8142 (.0010)	641.09 (123.60)	36.33 (1.81)	1.68 (0.30)
3700	6.15 (0.36)	6.10	1.8128 (.0004)	570.26 (139.17)	35.56 (2.07)	1.54 (0.32)
3701	5.96 (0.22)	6.09	1.8126 (.0004)	669.85 (107.09)	37.44 (1.67)	1.70 (0.24)
3702	6.07 (0.29)	6.13	1.8076 (.00030	623.84 (162.17)	37.79 (2.91)	1.57 (0.34)
3703	5.88 (0.30)	6.39	1.8028 (.0004)	655.46 (125.77)	38.78 (3.49)	1.62 (0.26)
3704	5.83 (0.28)	6.37	1.8031 (.0004)	735.29 (126.19)	41.37 (3.28)	1.70 (0.21)
3707	6.47 (0.27)	6.59	1.8018 (.0005)	608.32 (104.09)	32.36 (1.58)	1.81 (0.33)
3708	6.36 (0.24)	6.54	1.8007 (.0021)	667.02 (95.11)	35.22 (1.36)	1.81 (0.23)
3709	6.22 (0.23)	6.48	1.8014 (.0004)	632.58 (116.86)	34.61 (1.34)	1.75 (0.30)
3710	6.52 (0.26)	6.53	1.8031 (.0003)	606.12 (92.86)	32.25 (1.69)	1.80 (0.24)

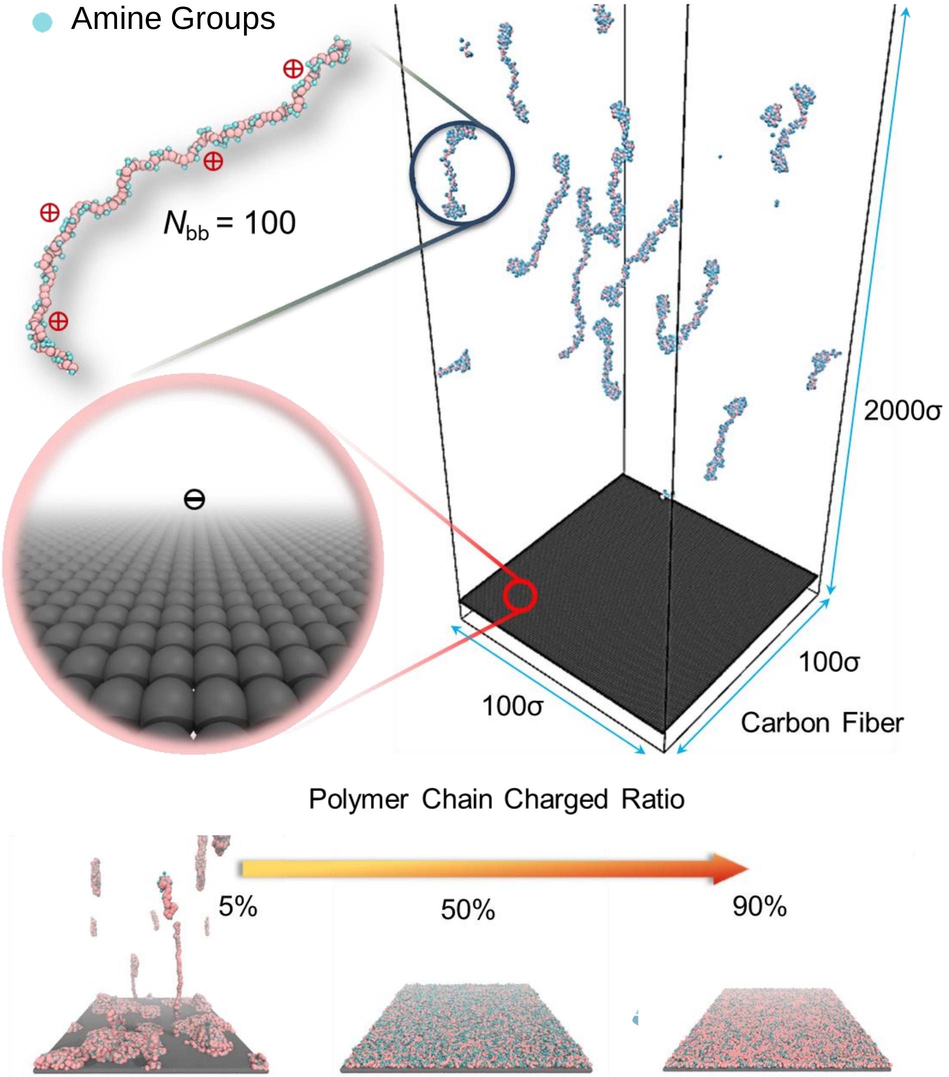
Variation in process parameters helps us understand importance of combined influence of process variables

Electrophoretic Deposition for Controlling Interfacial Properties of Carbon Fiber

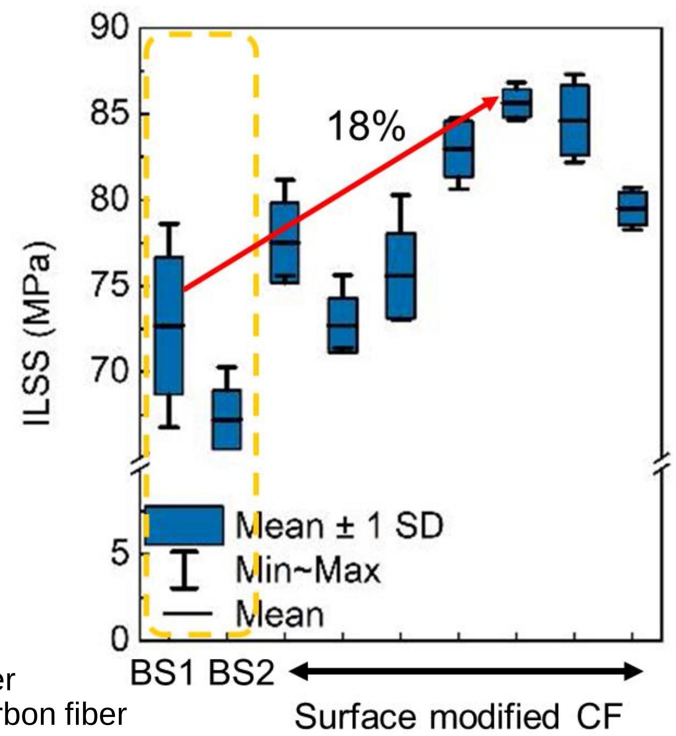
- A rapid, energy-efficient, and sustainable deposition process has been developed for carbon fiber (CF), suitable for a wide range of polymer composites.
- The coating layer can be reversibly removed, offering the potential for recycling CF-polymer composites.







Increased ILSS with increased electrophoretic deposition

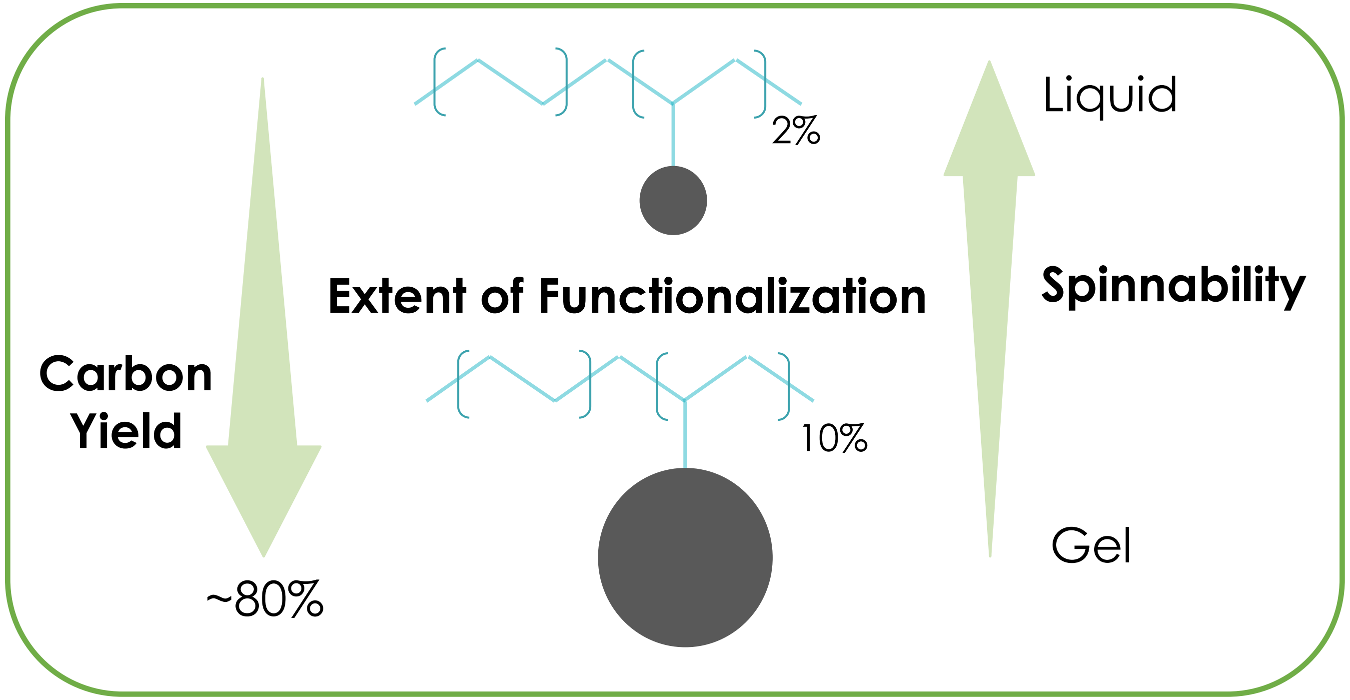


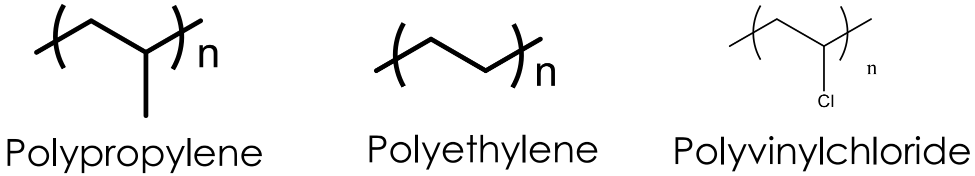
BS1: untreated carbon fiber
BS2: commercial sized carbon fiber

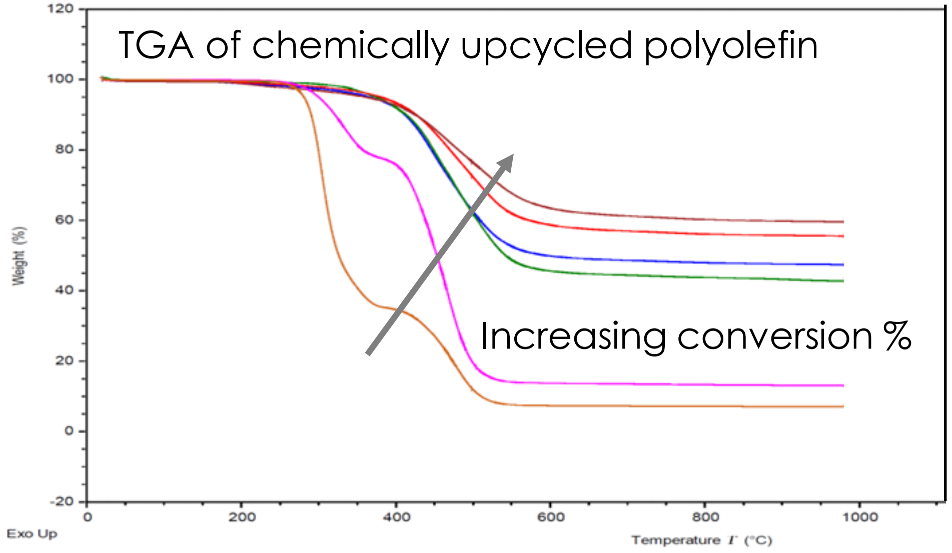
Naskar, Yu, Zhou, and Bowland, **US Patent Application No. 18/373,628** (Filed on Sep. 27, 2023).

Novel precursor designs

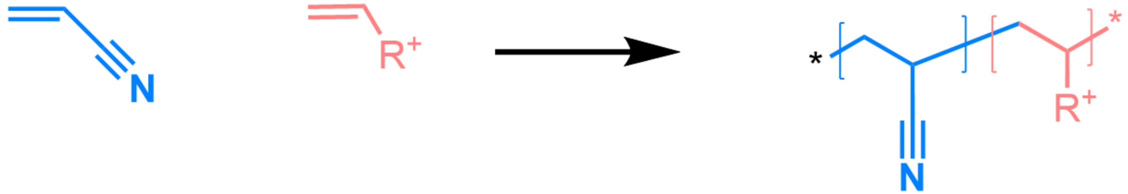
Polymer waste to carbon fiber: Utilize selective functionalization to attach reactive moieties to commodity polyolefin substrates for conversion to carbon fiber







Melt spinnable PAN: Utilize selective functionalization to attach reactive moieties to commodity polyolefin substrates for conversion to carbon fiber



Incorporation of low-cost co-ionomer reduces glass transition by interrupting dipolar interactions

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Carbon Fiber R&D at ORNL (Bench-scale to CFTF scale)

Laboratory R&D Projects

CFTF Projects

- Establish and perform collaborative R&D projects to reduce technical uncertainties
- Investigate CF intermediate forms and technical challenges in composite applications
- Investigate potential alternative CF precursors
- Establish artificial intelligence-based framework and correlate process data to product characteristics
- Investigate and develop in-process measurement, sensing and control methods

Industry Adoption

TRL 1-3

TRL 3-7

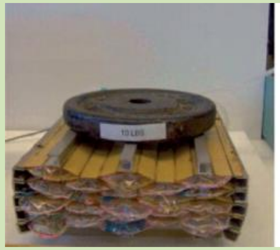
TRL 8-9

Resilient and Multi-Functional Composites: Potential for AI Guided Composite Manufacturing Methods

BEFORE

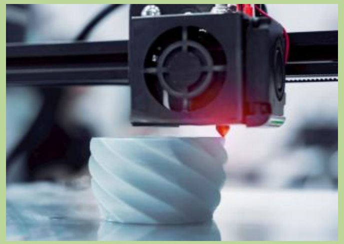
- Multimodal sensing
- New SHM/ NDI tool for sensing
- Condition assessment

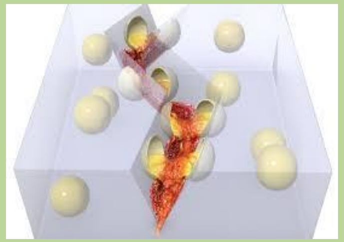
DURING



- Damage resistant
- Variable stiffness
- Structural control

AFTER





- Self-healing
- Rapid replacement
- Additive manufacturing

Multifunctional Composite for Passive Sensing and *In Situ* Damage Identification with Enhanced Mechanical Performance

Multifunctional materials

Applying the methodology in CF filament winding

S. Gupta and C. Bowland

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