Carbon Fiber and Composite Manufacturing for Hydrogen Storage Tanks

Amit Naskar

Oak Ridge National Laboratory

H2-MACH Meeting
Organized by US DOE and National Labs

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Acknowledgements

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Matt Weisenberger, Ashley Morris, University of Kentucky

Amit Goyal, Formerly with Southern Research Institute

T. C. Mike Chung, Penn State University

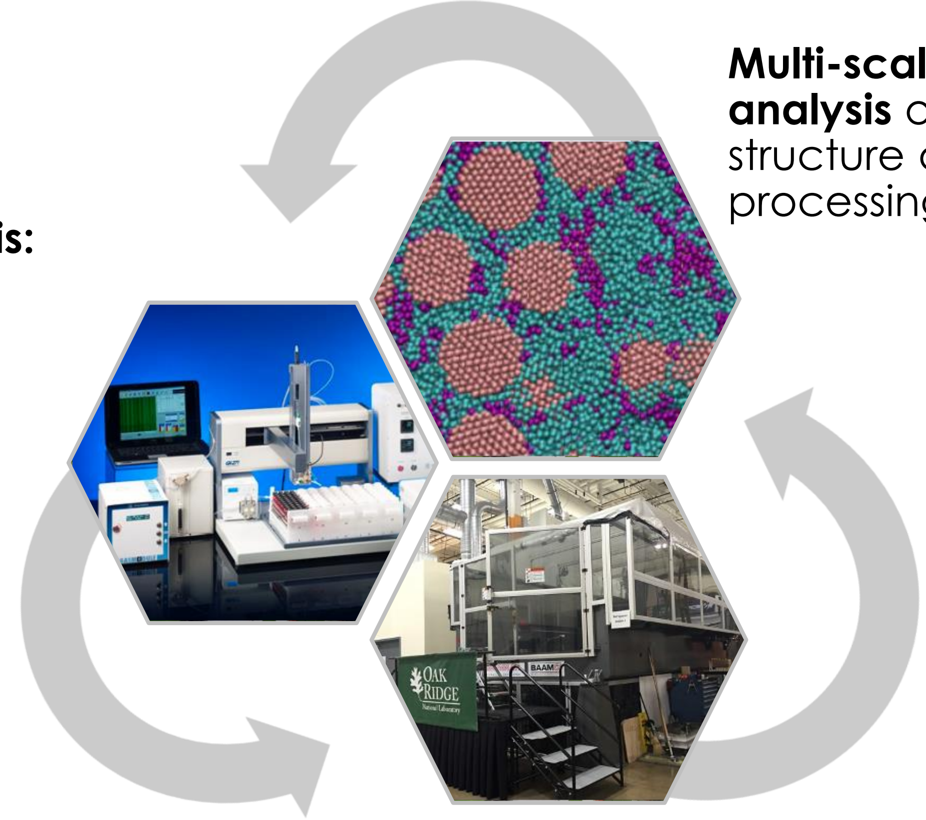
Outline

- Background
- Current state-of-the-art CF precursor candidates
- Approach for significant CF performance enhancement of commodity PAN precursors while retaining inherent textile cost advantages
- Longer term approach with tailoring molecular architecture, high throughput cyclization and formation of high-strength carbonized filaments with controlled morphology for CF performance at lower cost
- Composite with better fiber property translation and tank design optimization
- Multifunctional tank with embedded NDE potential

ORNL Bridges the Gap in Fundamental Polymer Science and Manufacturing of Polymeric Composites

A cross-disciplinary collaborative research team and state-of-the-art R&D capabilities are creating sustainable and innovative polymeric products, processing sciences, and new manufacturing methods for polymer industries.

Synthesis: Building blocks



Multi-scale analysis of structure and processing

(Re)Manufacturing of products at various scales

Composites in High Pressure Storage

- Due to high specific strength capabilities in filament wound format, glass fiber and carbon fiber composites have been utilized for a long time in high pressure gas storage
  - Type 1 – all metal
  - Type 2 – composite overwrapped metal
  - Type 3 – largely composite with a metallic inner liner that bears some load
  - Type 4 – all composite load bearing, typically with polymer (non-load-bearing) liner
    - Liner can be upgraded to a load bearing polymeric liner
- Carbon fiber composites typically require lower safety factor and lower density making CF composites material of choice for weight critical applications such as vehicles

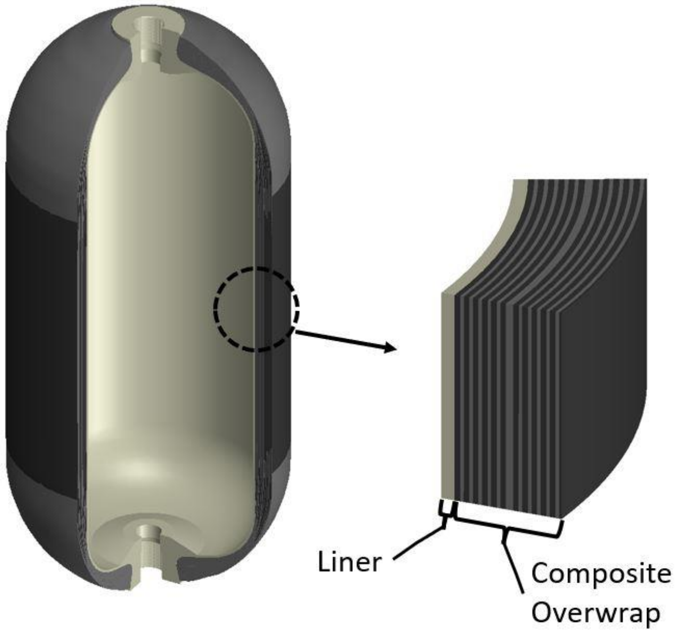
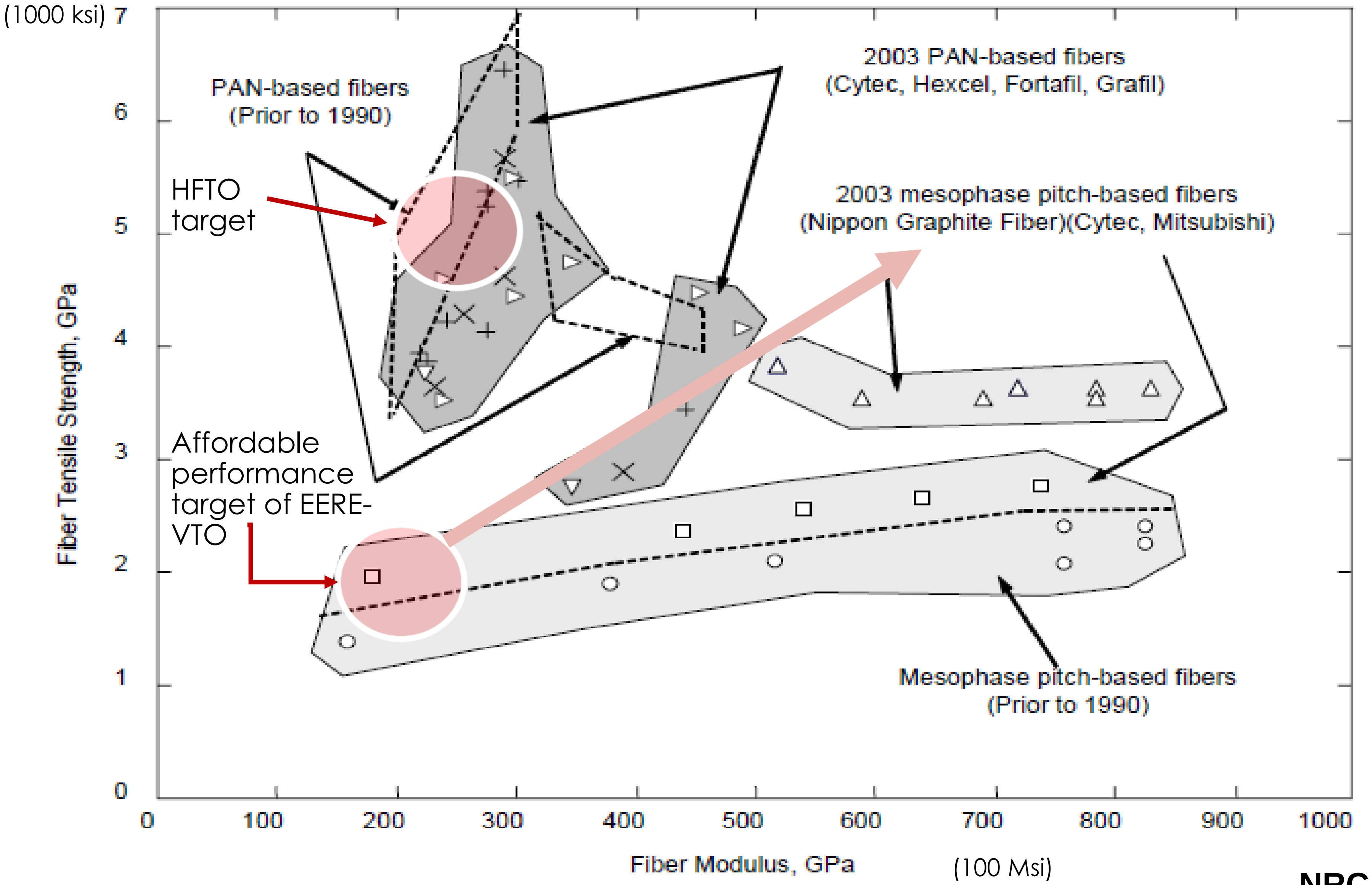


Image source: Dylan Winter, Hexagon

- *CNG tanks are typically 3600 psi (250 bar) max while H2 tanks are typically targeted at 10,000 psi (700 bar)*
- *However, high-strength carbon fiber itself accounts for approximately 65% of the cost of the high-pressure storage H_2 tanks – need for significant cost reduction*
- *New technologies are also needed for enhanced fiber efficiency (load translation efficiency) for minimal CF use.*

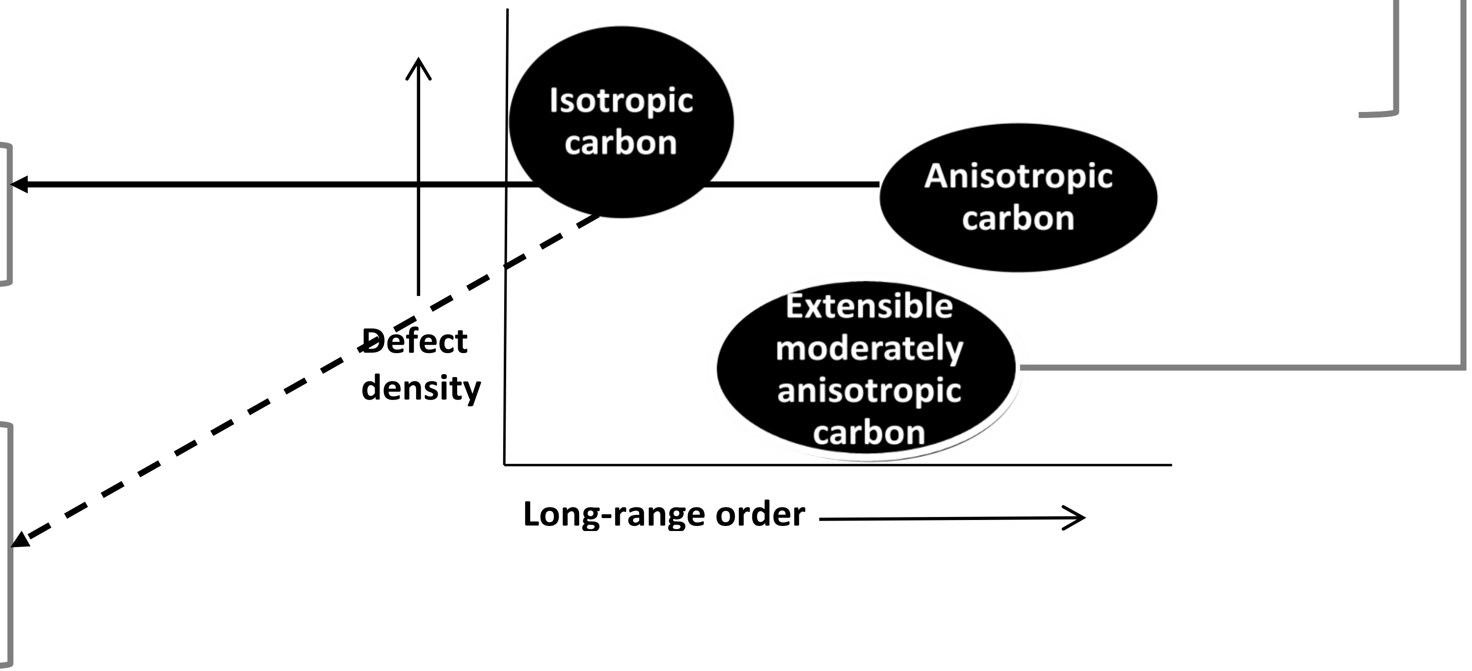
State-of-the-art Carbon Fibers and Properties



NRC Report, (2005)

Carbon Precursor candidates

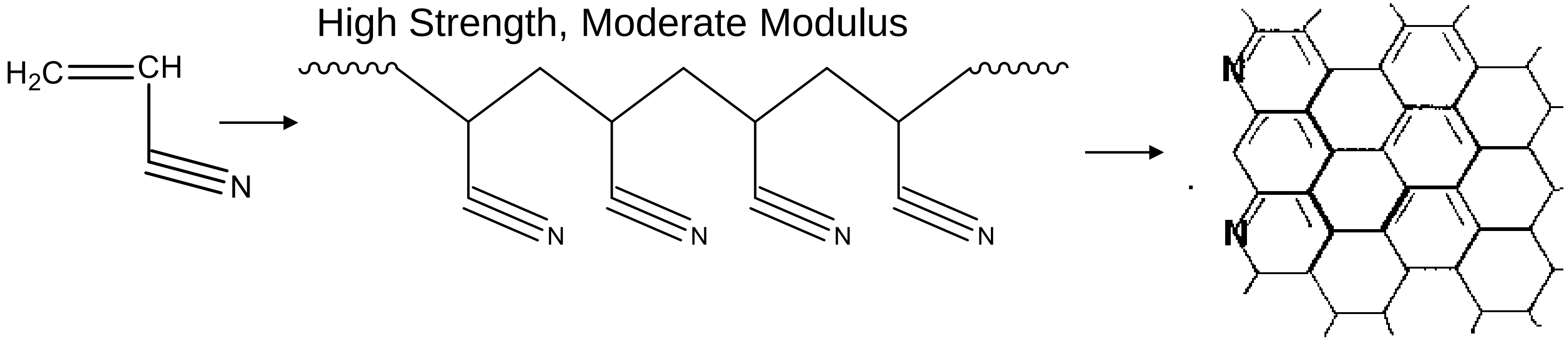
- Specialty acrylic fibers (SAF)
  - High molecular weight polyacrylonitrile (PAN)
- Textile PAN Variants
  - Variant PAN compositions (comonomer variation)
- Renewable acrylonitrile
- Melt-processible PAN precursors
- Polyolefin (polyethylene)
- Pitch precursors
  - Mesophase synthesis
- Natural gas (for CNT yarn)
- Cellulosic precursor
- Lignin (MeadWestvaco/GrafTech)
- Polyamide fibers



Contrasting Chemistries of Carbon Fiber Precursors

High Strength, Moderate Modulus

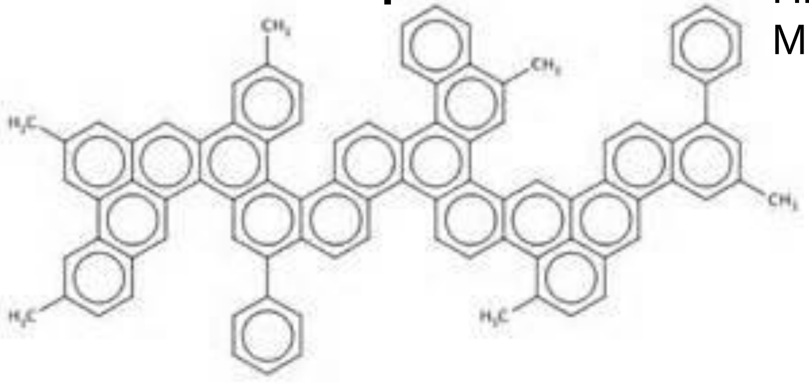
PAN



Chemical yield
~50%

Mesophase Pitch

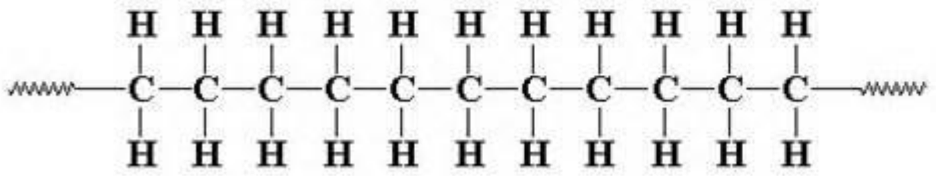
High Modulus,
Moderate Strength



Chemical yield
70-80 %

Polyethylene derivatives

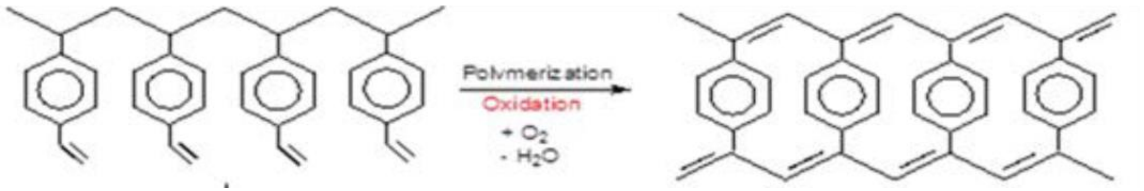
Properties are proven; scalability yet to be demonstrated



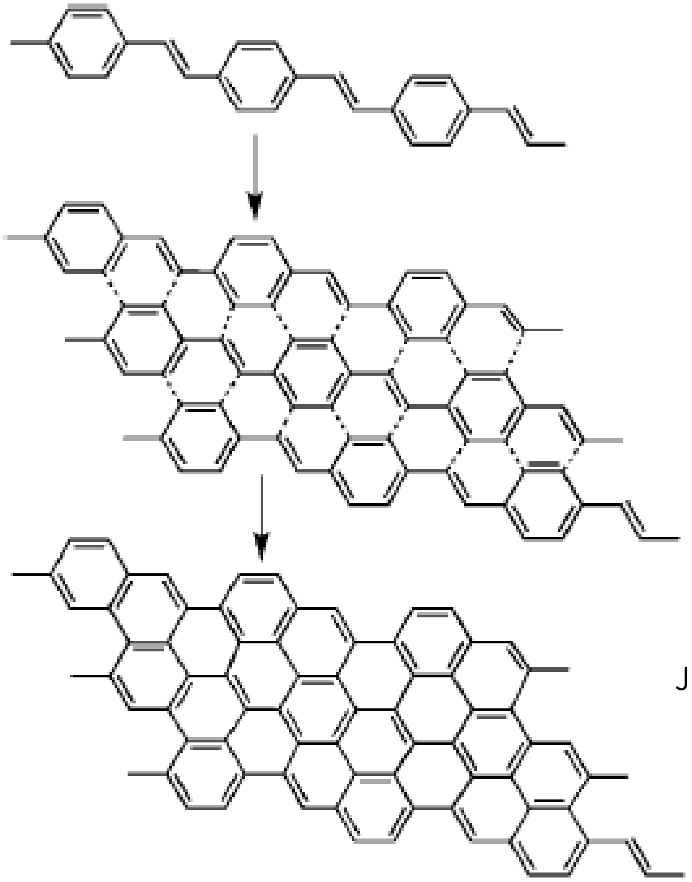
Potential Precursor Candidates

A New Polyolefin Precursor for Low-Cost, High-Strength Carbon Fiber (Penn State; Mike Chung)

- High-yield polymeric char forming fibers as carbon precursors



Synthesis and carbonization of triethylammonium-based poly(p-phenylenevinylene) (PPV) [Universitat Stuttgart; Michael R. Buchmeiser]

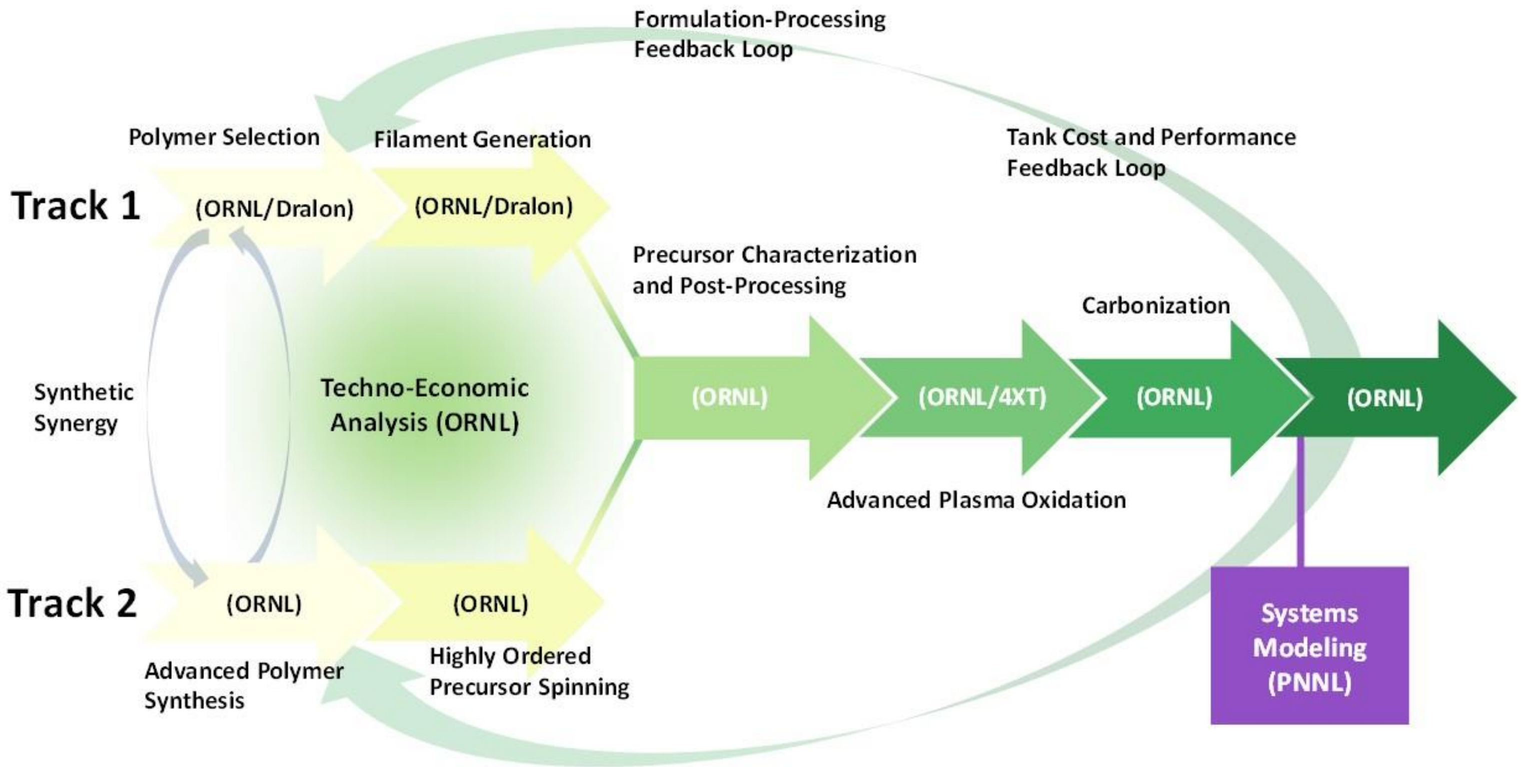


J. Mater. Chem. A, 2013, 1, 13154

Approach and Roadmap of Ongoing Work

Current work utilizes a two-prong approach:

- ***High TRL Track 1***: Translational research with semi-commercially produced commodity-grade polyacrylonitrile (PAN)-based carbon precursor fiber using both conventional and advanced conversion methodologies for cost and performance optimization; and
- ***Low TRL Track 2***: Foundational research to enhance processability of newly synthesized PAN precursors with precise molecular architecture, high throughput cyclization and formation of high-strength carbonized filaments with controlled morphology via optimal conversion technologies to be developed in Thrust 1



Track 1—Accomplishments and Progress (Paulauskas and Norris)

- In related projects, ORNL achieved very good properties with textile precursors.
- It attracted interest from textile producers in working towards goals of bridging key factors previously identified and optimizing towards goals of this initiative.
- This team has demonstrated capability to achieve equivalent or better performance via utilization of larger diameters and/or advanced conversion technologies to drive cost down

Table 1. APO production of various diameter precursor.

Oxidation Method	OPF Density (g/cc)	OPF Diameter (µm)	Oxidation Time (min)
Conventional	1.36	11	60-90
Plasma Oxidation	1.36	11	20
	1.36	16	50*
	1.36	20	84*

*Results from testing with an experimental textile-grade PAN precursor.

Table 2. Performance of APO Precursor after Full Conversion.

Oxidation Method	Data Source	Tensile Strength (ksi)	Tensile Modulus (Msi)	Oxidation Time (min)
Conventional	Mfr. Website*	580	35	60-90**
Plasma	Average (CFTF)	660	36.5	20
	Minimum (CFTF)	640	36	

*These values are published by the CF manufacturer.

Image Source: 4X Technologies

Accomplishments and Progress: Advanced Conversion

Recently demonstrated that alternative textile equivalent acrylic precursor was able to meet key milestone for achieving 600ksi tensile strength in single filament testing while also utilizing the advanced oxidative stabilization process. *(Industry standard impregnated strand data is typically 8-10% higher than average single filament data meaning we are rapidly approaching project performance target of 700ksi.)*

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		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)

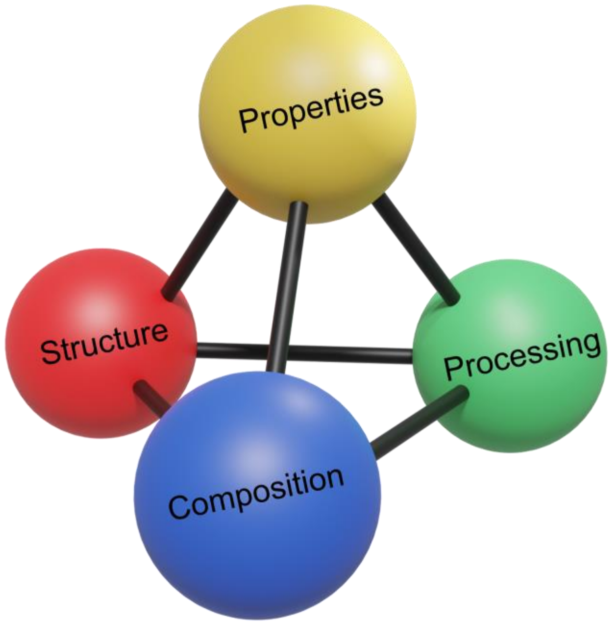
Track 2 – Design motifs in PAN for High-Performance CFs

Polymer design for carbon fibers requires precise control of a multi-variable, inter-dependent phase space

Polymer - MW, PDI, [AN:M_x:M_y] | Precursor Fiber – ε, E, X_c, *f* |OPF – Ø, ρ, *f* → CF Properties

Cost optimized fiber design needs to balance antagonistic materials and process variables

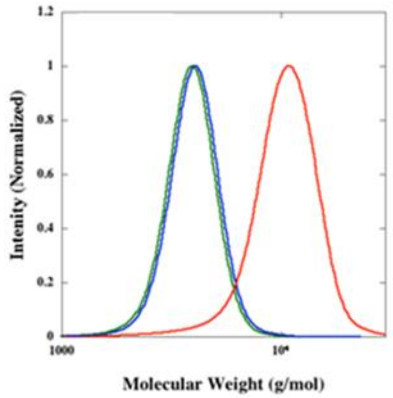
MW and [C] ∝ η ; [C] and Ø ∝ $; [AN] ∝ CED vs $\sigma_{Tensile}$

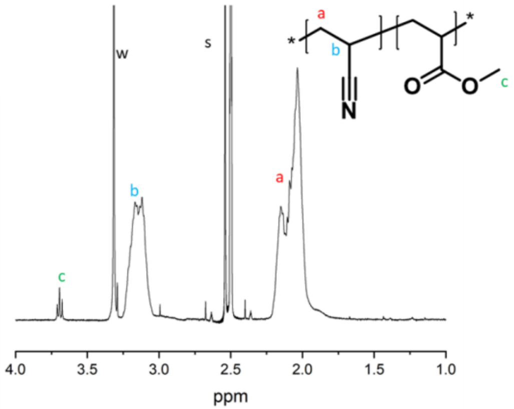


Composition optimization

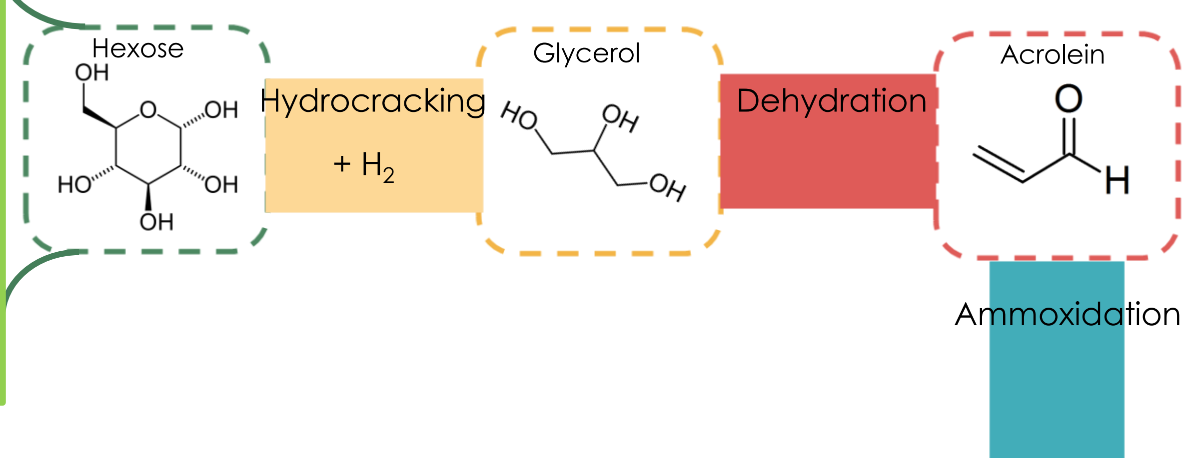
0.1 – 5L Scale
Solution

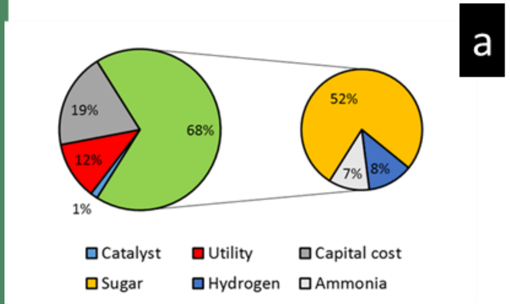
10 -20 L Scale
Dispersion



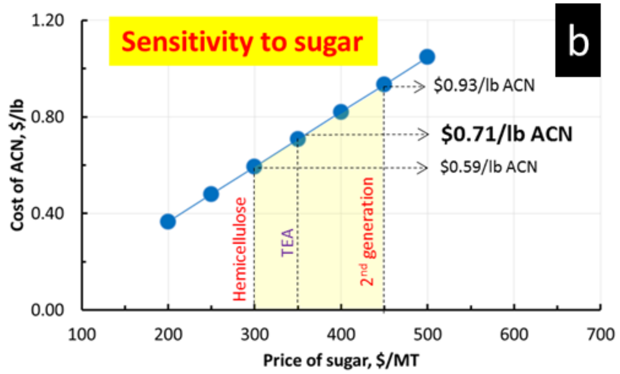


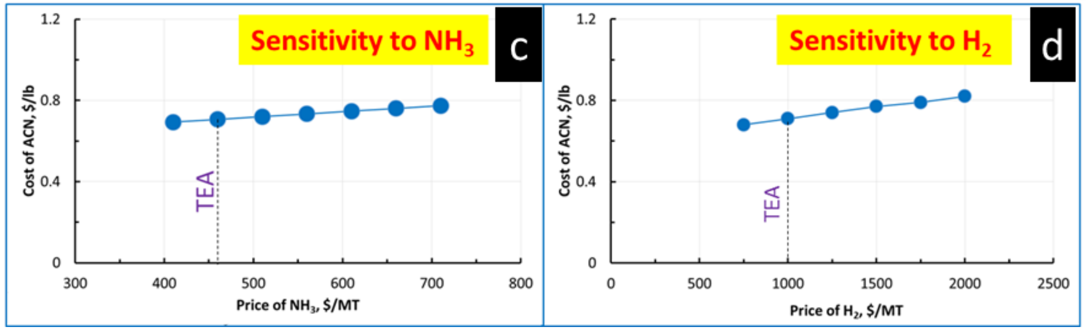
A Drop-in Replacement to Petro-ACN

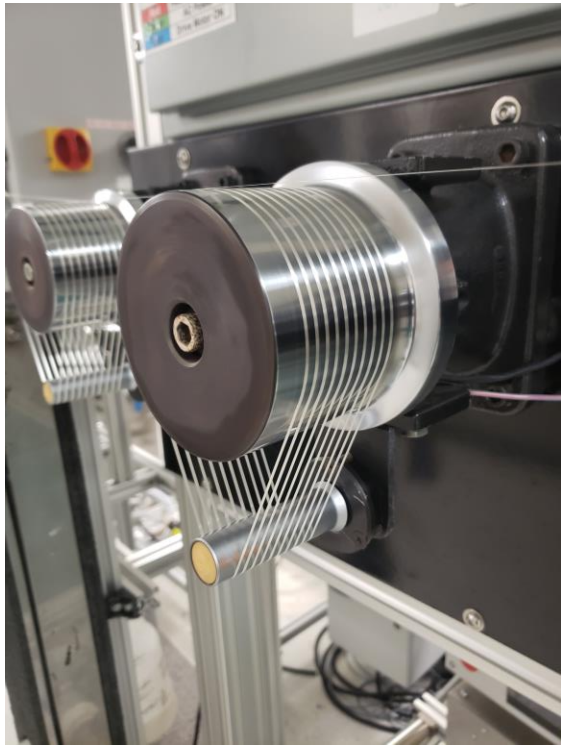


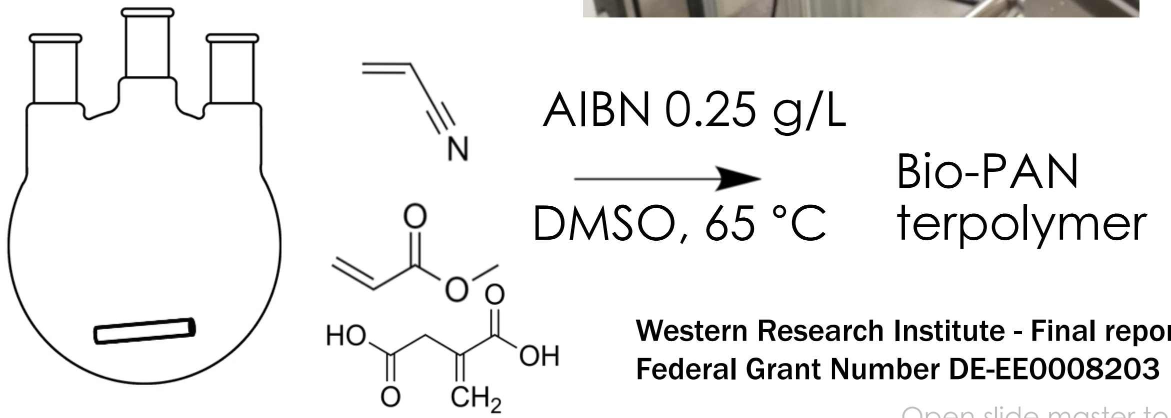


Cost distribution pie chart





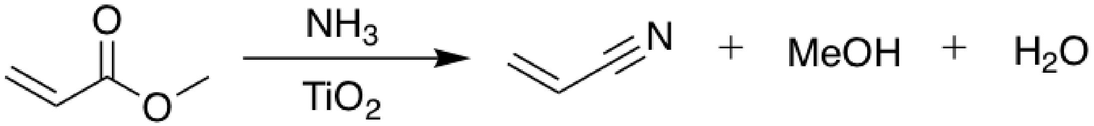




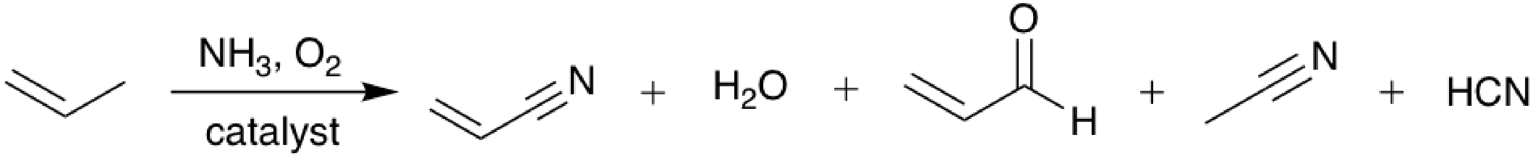
Western Research Institute - Final report:
Federal Grant Number DE-EE0008203

NREL route to manufacture ACN

Nitrilation:
(>98% yield)

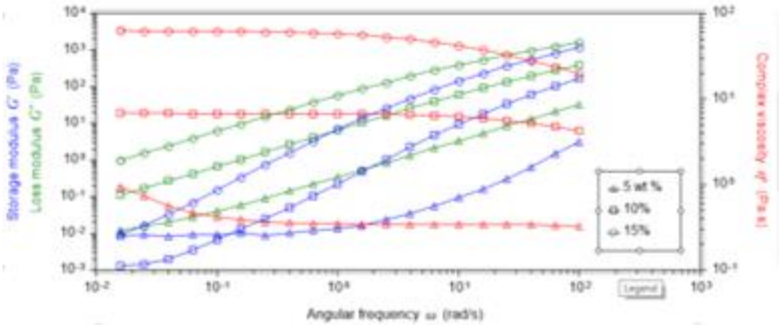


Ammoxidation:
(83% yield)

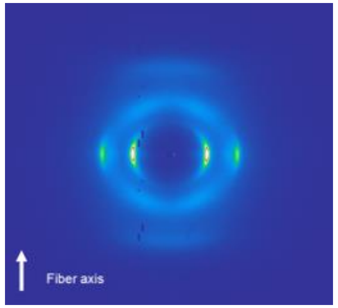


Science **2017,** *358* (6368), 1307-1310.
Green Chemistry **2018**, 20, 5299-5310.

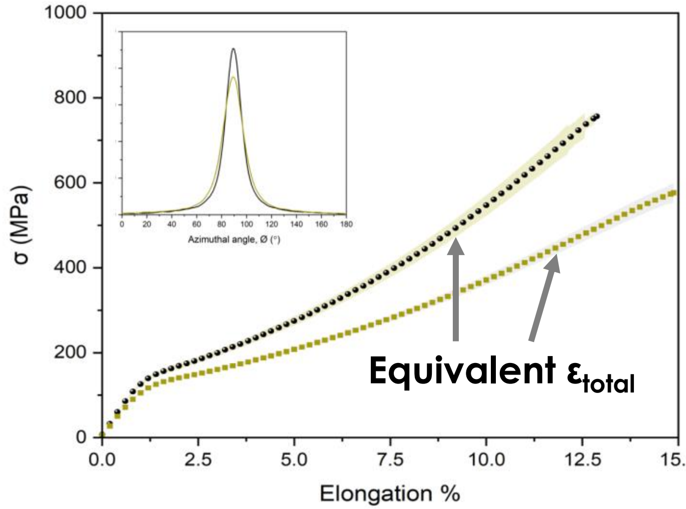
Precursor structure and properties dictate conversion strategy



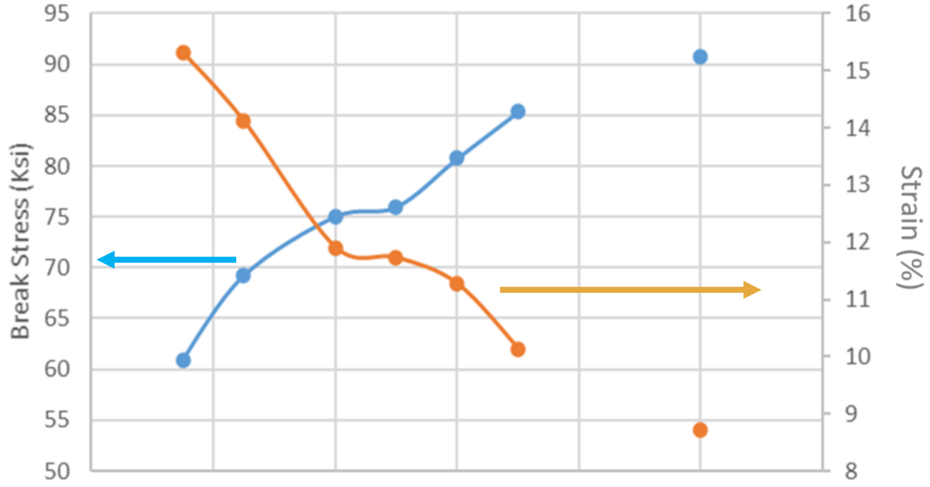
Molecular relaxation dynamics via rheology



2D WAXS
Spinning process – structure evolution



Precursor fiber conditioning can enable a wider range of fiber quality to achieve high performance CF



Macromolecular ordering via secondary deformations

Commodity PAN Composition Delivered 550 ksi strength and 43 Msi Modulus

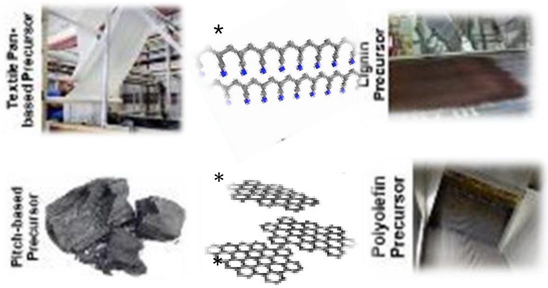
- Acquired baseline textile-based precursor having >10% elongation. Completed characterization of this precursor and initial processing conditions identified; oxidized fiber delivers 1.36 g/cc density
- Developing path for enhanced interfacial interaction between fiber and epoxy matrix.

Sample	%EL at Failure	Break Stress (ksi)	Modulus (Mpsi)
1	1.386071	547.0355	43.22249
2	1.43208	524.4526	36.18613
3	1.47612	513.3752	34.53305
4	1.48415	504.1096	33.69372
5	1.40808	496.985	35.53799
6	1.41415	478.4041	36.46622
7	1.46804	489.3448	33.53422
8	1.41404	495.0222	34.57769
9	1.42608	475.9566	35.20317
10	1.37802	483.3545	35.81152
11	1.45812	484.1576	32.69368
12	1.40402	487.3651	34.1547
13	1.44002	465.8409	34.38446
14	1.38003	486.4044	34.64733
15	1.404218	481.1254	33.65942
16	1.50007	453.2992	32.45328
17	1.402184	481.5163	33.26076
18	1.40802	463.69	33.89963
19	1.380093	466.6139	34.4446
20	1.27205	474.6488	37.02224

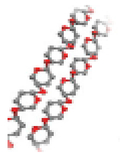
Samples underwent unique oxidation (stretch, temperature), Low temperature conversion (stretch, residence time), and high temperature conversion (stretch, residence time) before being assessed for their final properties, to optimize process. 56 samples processed; top 20 performers shown above.

Scaled-up Research & Development

Material Identification



- Conversion Yield
- Precursor Cost
- Oxidation Time
- Availability
- Precursor Microstructure
- 10s grams - bench scale



*

Fiber Evaluation CF Line

- 1 - 2 tows
- (20k – 80k filaments
- Small Volume
- 100s grams

Pilot scale CF Line

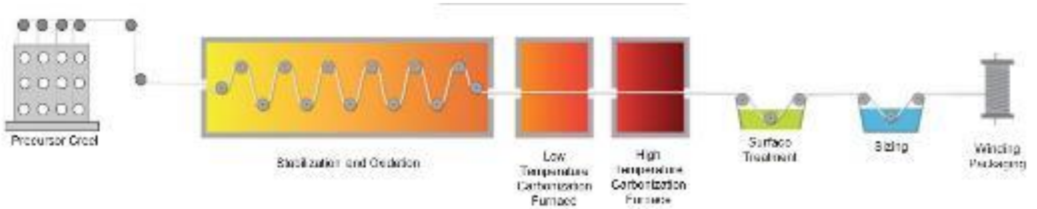
- Capacity for 1-5 tows
- 5k -80k filaments
- Preferred tow size ≥ 3k
- 100s grams – 1 kg

Scale-up CF Line

- 24 tows
- Designed for 3k – 80k tows
- Instrumented research line
- Customizable configuration
- Capacity for additional conversion
- 25 tons/yr capacity

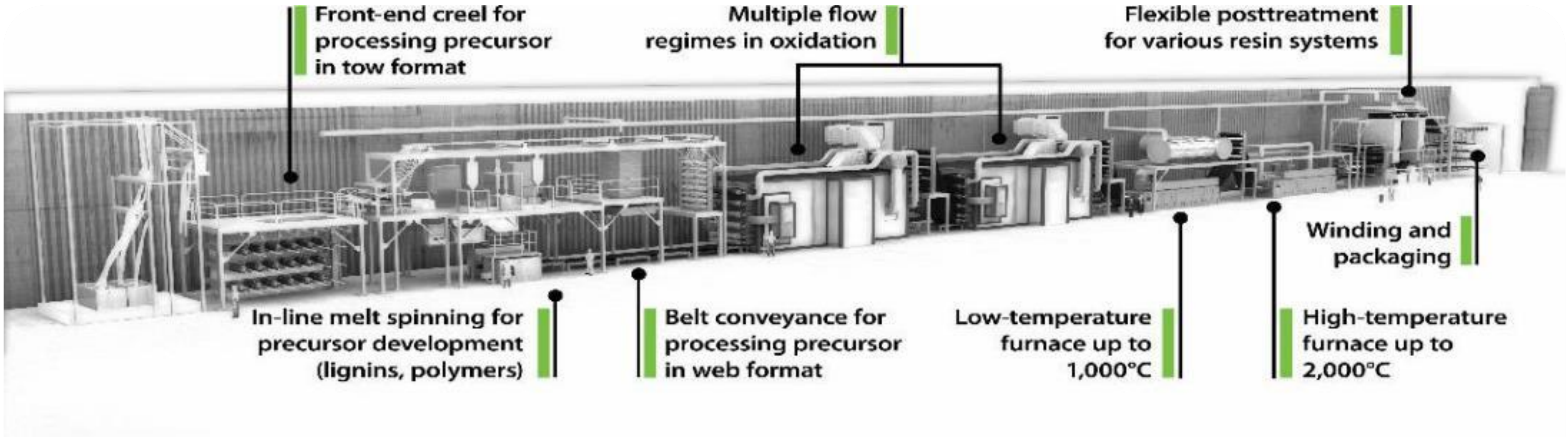
- **ORNL developed a technology to convert textile precursor into carbon fibers**
  - ➢ 4 licenses awarded
  - ➢ comparable tensile properties (especially modulus) to conventional carbon fibers
  - ➢ Demonstrated 2X throughput with a line of sight up to 3X the throughput
  - ➢ lower energy per kg produced
  - ➢ ~$5/lb Target

Commercialization



- Designed for a specific precursor type
- One type of flow distribution
- Defined process condition
- 1500 tons/yr capacity minimum

Carbon Fiber Technology Facility (CFTF)



The Carbon Fiber Technology Facility (CFTF) serves as a national resource to assist industry in overcoming the barriers of carbon fiber cost, technology scaling, and product and market development.

- Demonstrate carbon fiber production using lower-cost precursors and lower energy at semi-production scale.
- Produce low-cost carbon fiber available for evaluation and market development .
- Enable development of domestic commercial sources for production of low-cost carbon fiber.

- Highly flexible, highly instrumented low-cost carbon fiber technology demonstration facility
- Rated capacity 25 tons/year based on 24k PAN tows • Designed for PAN, polyolefins, lignin, and pitch precursors; upgradable for rayon and high-modulus carbon fibers
- Designed for 3k to 80k tows and web up to 300 mm wide x 12.7 mm loft
- Oxidation temperature up to 400°C with airflow configurable to be parallel, cross, or downflow
- Carbonization: Low-temperature carbonization up to 1000°C, High-temperature carbonization to 2000°C
- Post-treatment system designed for compatibilizing fibers with performance or commodity resins

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

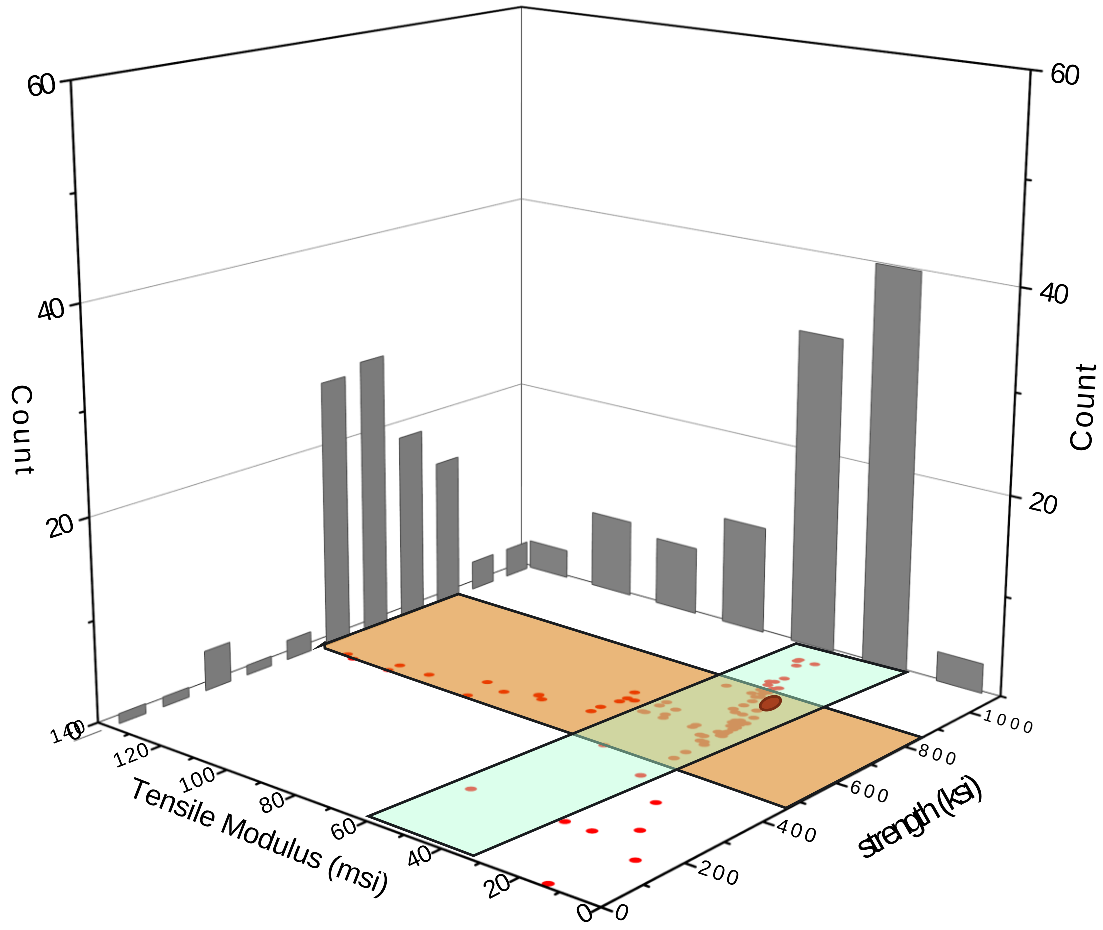
Industry Adoption

TRL 8-9

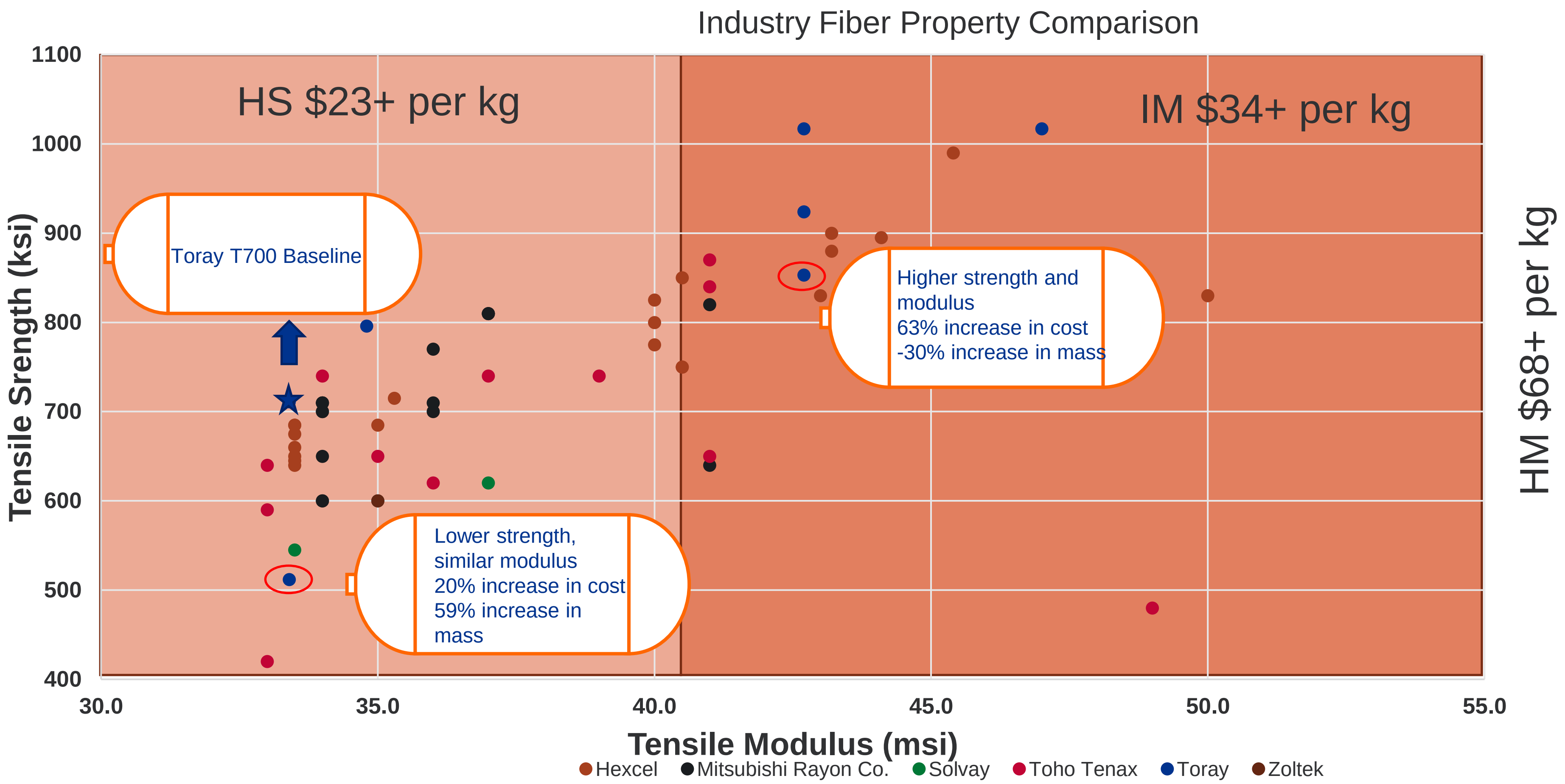
TRL 1-4

TRL 5-7

Most Common Fiber Properties in the Market



Fiber Property Survey with Retail Cost

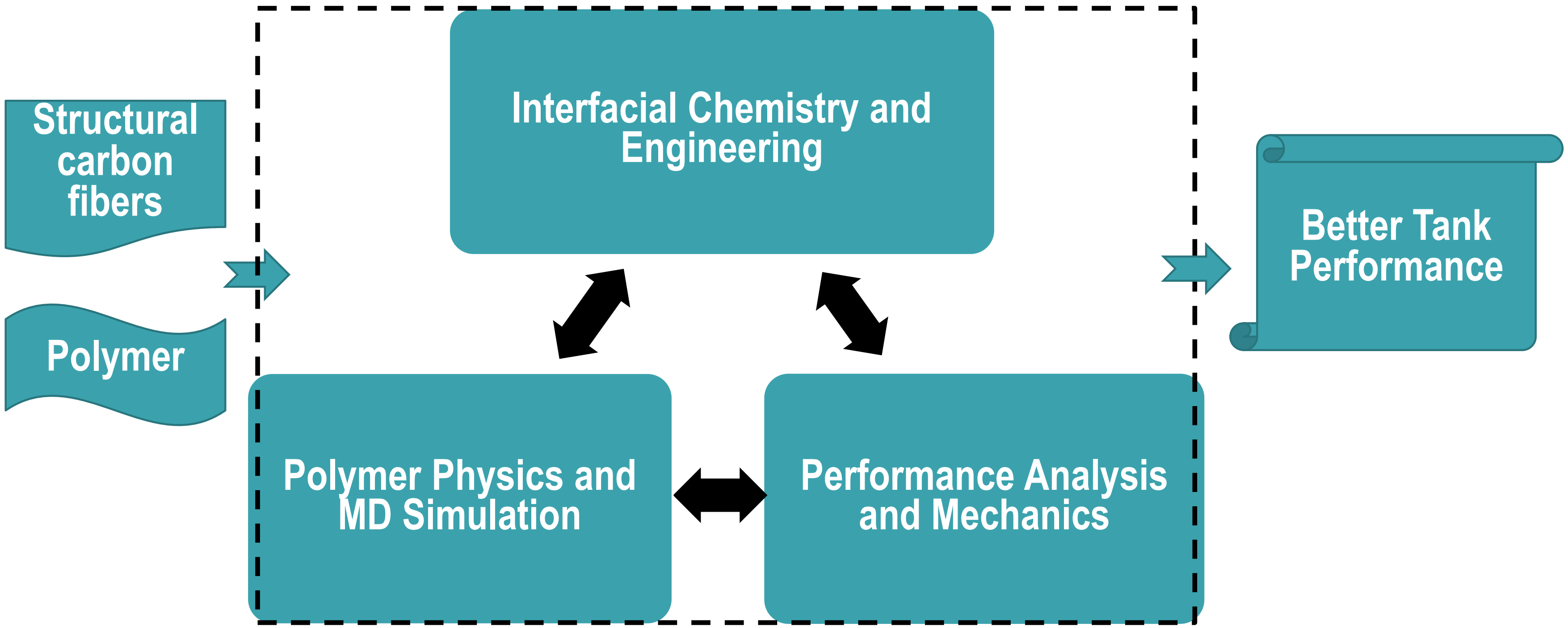


Cost from: Journal of Cleaner Production Volume 223, 20 June 2019, Pages 957-968
https://doi.org/10.1016/j.jclepro.2019.03.156

Kl.simmmons@pnnl.gov

Tailoring polymer matrix and CF can enhance translation of fiber properties in composites

Design of interphases in composites by using targeted interfacial chemistry, scattering, and large-scale simulations is needed to unravel correlations between structural properties, rheology, interfacial stability, and dynamics.



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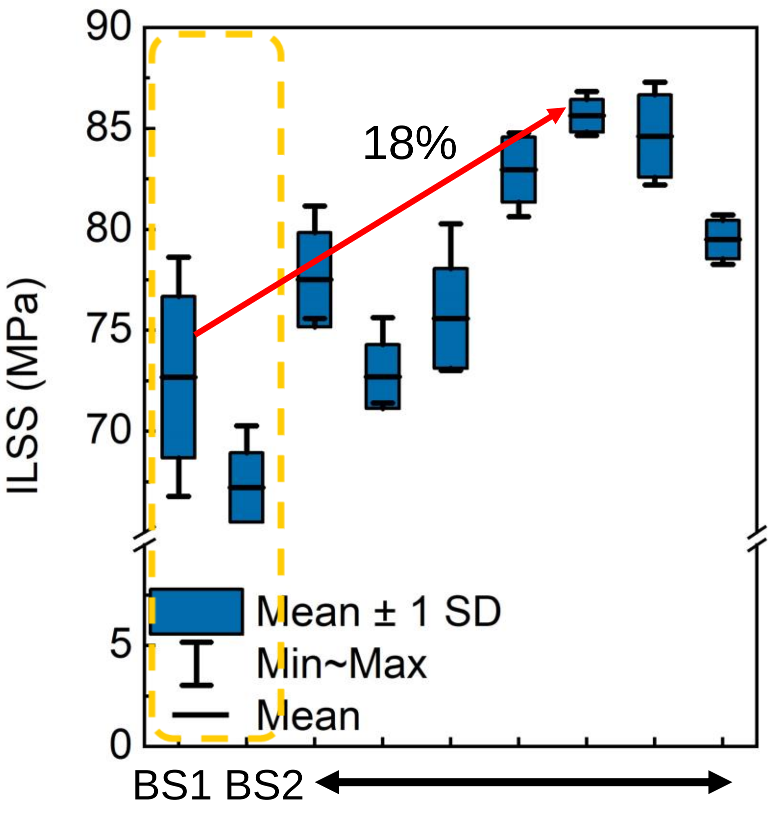
Surface Tailoring of Carbon Fiber

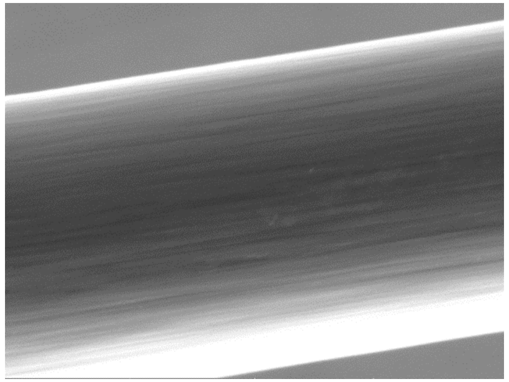
- A sustainable chemistry was applied to improve ILSS with an epoxy matrix. ILSS was measured via short beam shear strength measurement.



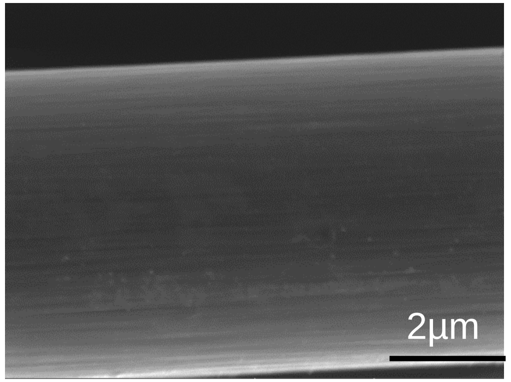
BS1: untreated carbon fiber
BS2: commercial sized carbon fiber

Yu et al. Unpublished data (ORNL)

Untreated CF



Modified CF



Well-dispersed polymer deposition

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

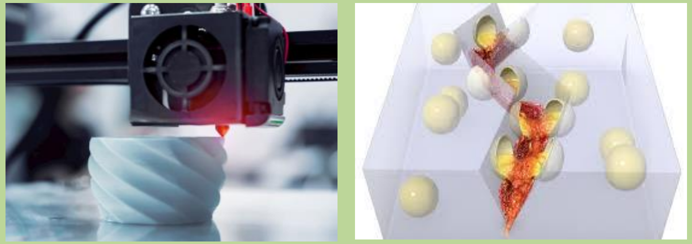
BEFORE

- 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

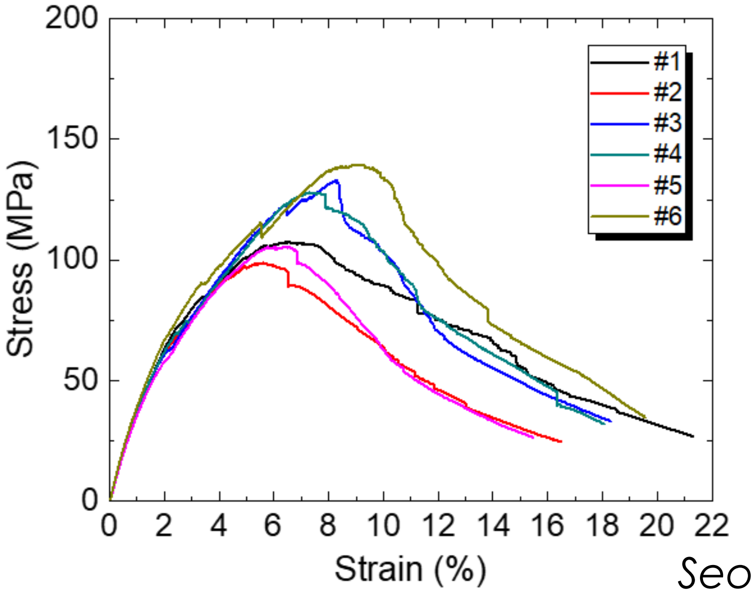
Applying the methodology in CF filament winding

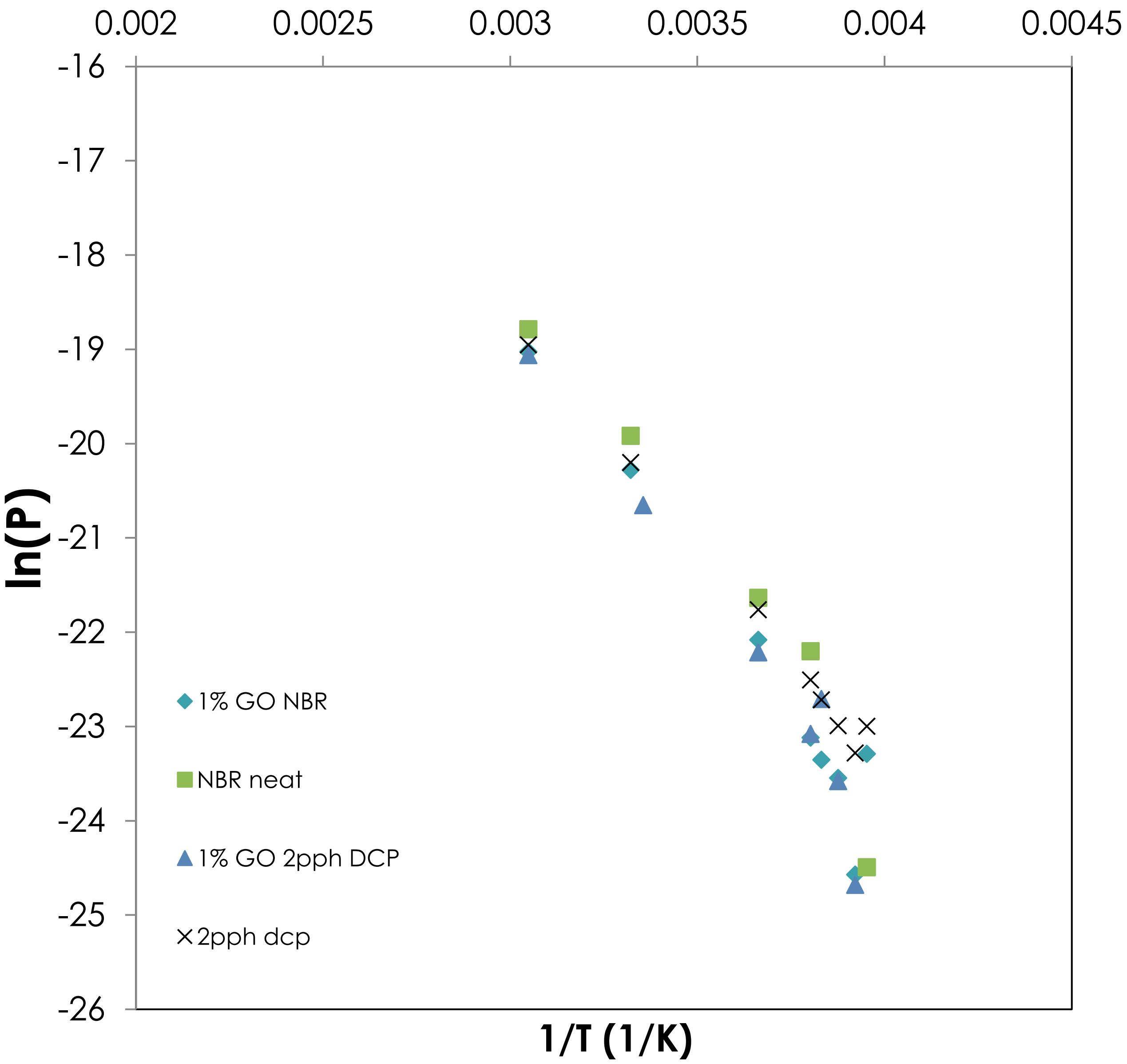
COPV liners based on blow-molded plastics

Barrier properties were enhanced without affecting processability.

A malleable not-completely-crosslinked nitrile rubber gel filled with additives exhibits reduced permeability data compared to its unfilled control.

Materials for liner:
HDPE; POM (current)
New (de/re)manufacturable liner with optimally low plasticization and permeability by H2





Seo et al. Unpublished data (ORNL)

Summary

We reviewed:

- Current state-of-the-art CF precursor candidates
- Near-term methodology for modifying textile PAN precursor approach for significant CF performance enhancement while retaining inherent textile cost advantages
- Longer term precise molecular architecture, high throughput cyclization and formation of high-strength carbonized filaments with controlled morphology for CF performance at lower cost
- Composite with better fiber property translation and tank design optimization are needed
- Composite laminate failure can potentially be predicted without incorporating a separate device