Composite Overwrapped Pressure Vessels Material Development

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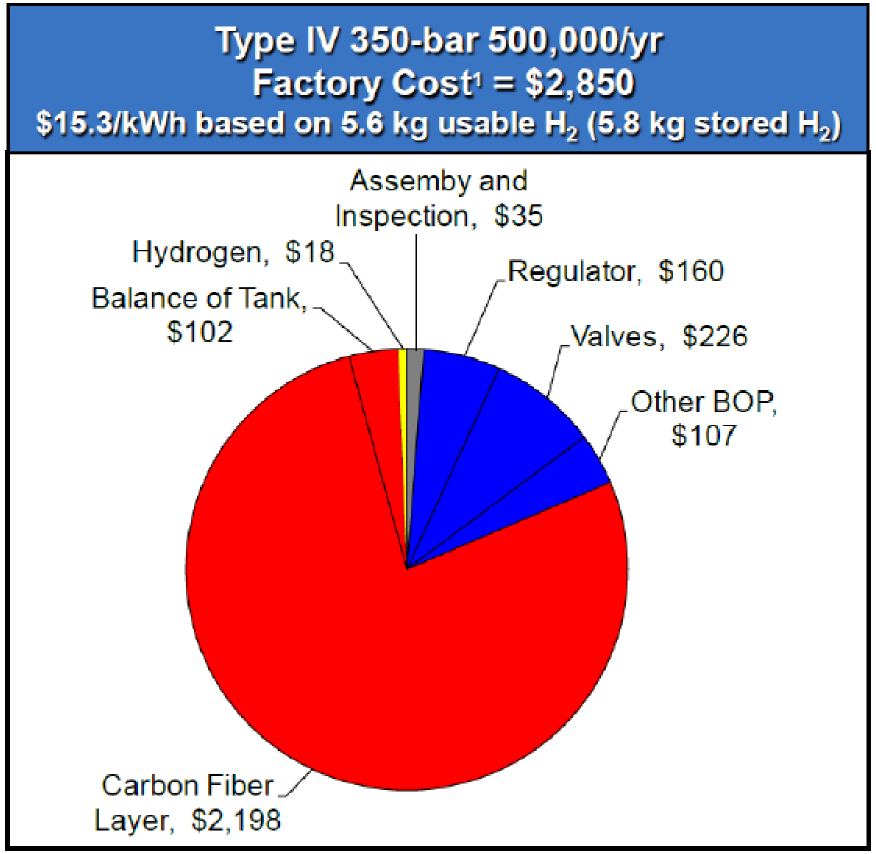
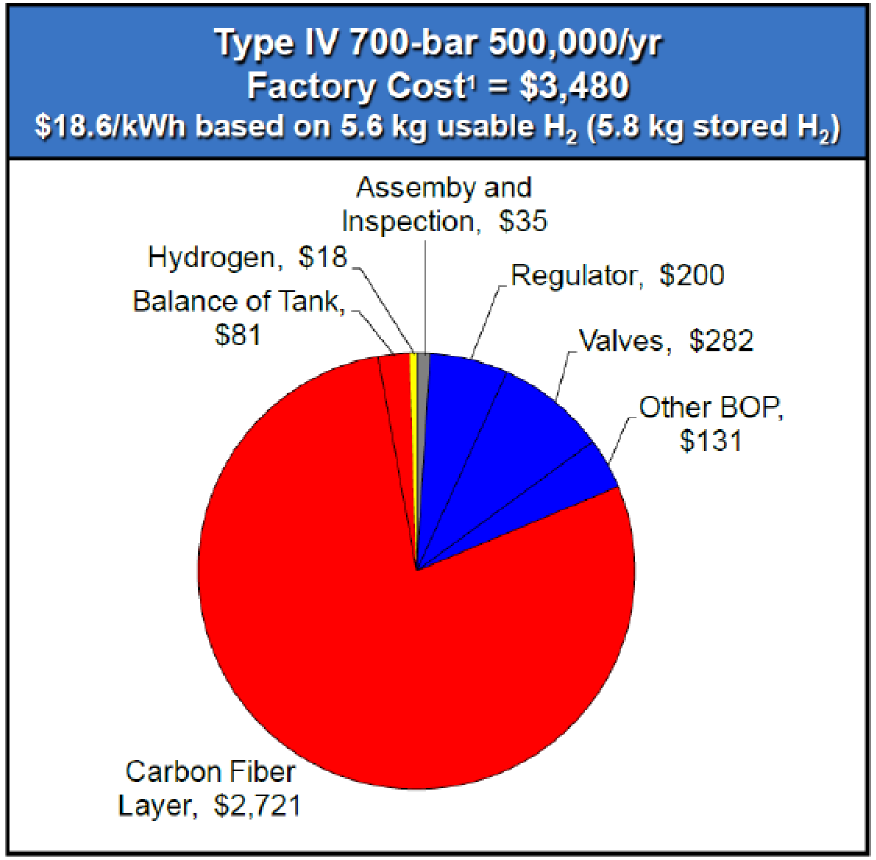
Hydrogen Storage Tank – Cost Analysis



Type IV 350-bar 500,000/yr
Factory Cost[1] = $2,850
$15.3/kWh based on 5.6 kg usable H_2 (5.8 kg stored H_2)

[1] Cost estimate in 2005 USD. Includes processing costs.



Type IV 700-bar 500,000/yr
Factory Cost[1] = $3,480
$18.6/kWh based on 5.6 kg usable H_2 (5.8 kg stored H_2)

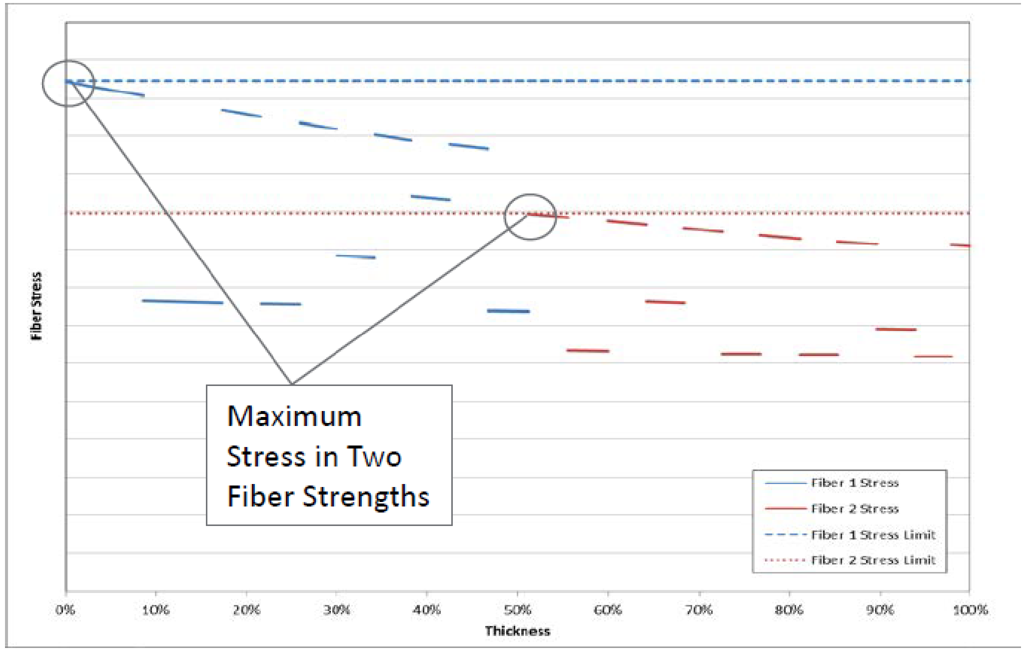
[1] Cost estimate in 2005 USD. Includes processing costs.

Carbon fiber composite layer shares the significant cost (75-80%) of the hydrogen fuel system

Low-cost carbon fiber (LCCF) is needed for Hydrogen or CNG storage tank

Simmons et al. AMR presentation 2013

Technical Accomplishment – Alternate Fiber Placement and Multiple Fiber Types



Maximum Stress in Two Fiber Strengths

Fiber Properties

Material Property	E-Glass	T300	T700	T720	T800
Tensile Strength [ksi]	350	512	711	850	850
Tensile Modulus [Msi]	12.0	33.4	33.4	38.7	42.7
Fiber Count [x1000]	2	12	24	24	24
Yield [ft/lb]	1341	1862	903	1367	1446
Density [lb/in3]	0.093	0.064	0.065	0.065	0.065

Single Fiber Designs

Evaluation Criteria	T300	T720	T800
Percent Change in Cost	+19%	+9%	+63%
Percent Change in Mass	+59%	-30%	-30%

Combinations of Modulus and Strength Fiber Designs

Evaluation Criteria	Hybrid Modulus Design	Hybrid Strength Design
Percent Change in Cost	+38%	-1%
Percent Change in Mass	-34%	-23%

Low and High Angled Helical Combinations

Evaluation Criteria	Mild Tailoring	Aggressive Tailoring
HAH Percent Change in Cost	-3%	-14%
HAH Percent Change in Mass	-3%	-14%
LAH Percent Change in Cost	-7%	-16%
LAH Percent Change in Mass	-7%	-16%

Simmons et al. AMR Presentation slide #24, 2013

- ❑ COV in fiber properties plays significant role in this cost analysis.
- ❑ LCCF must have consistent properties.

HEXAGON
LINCOLN

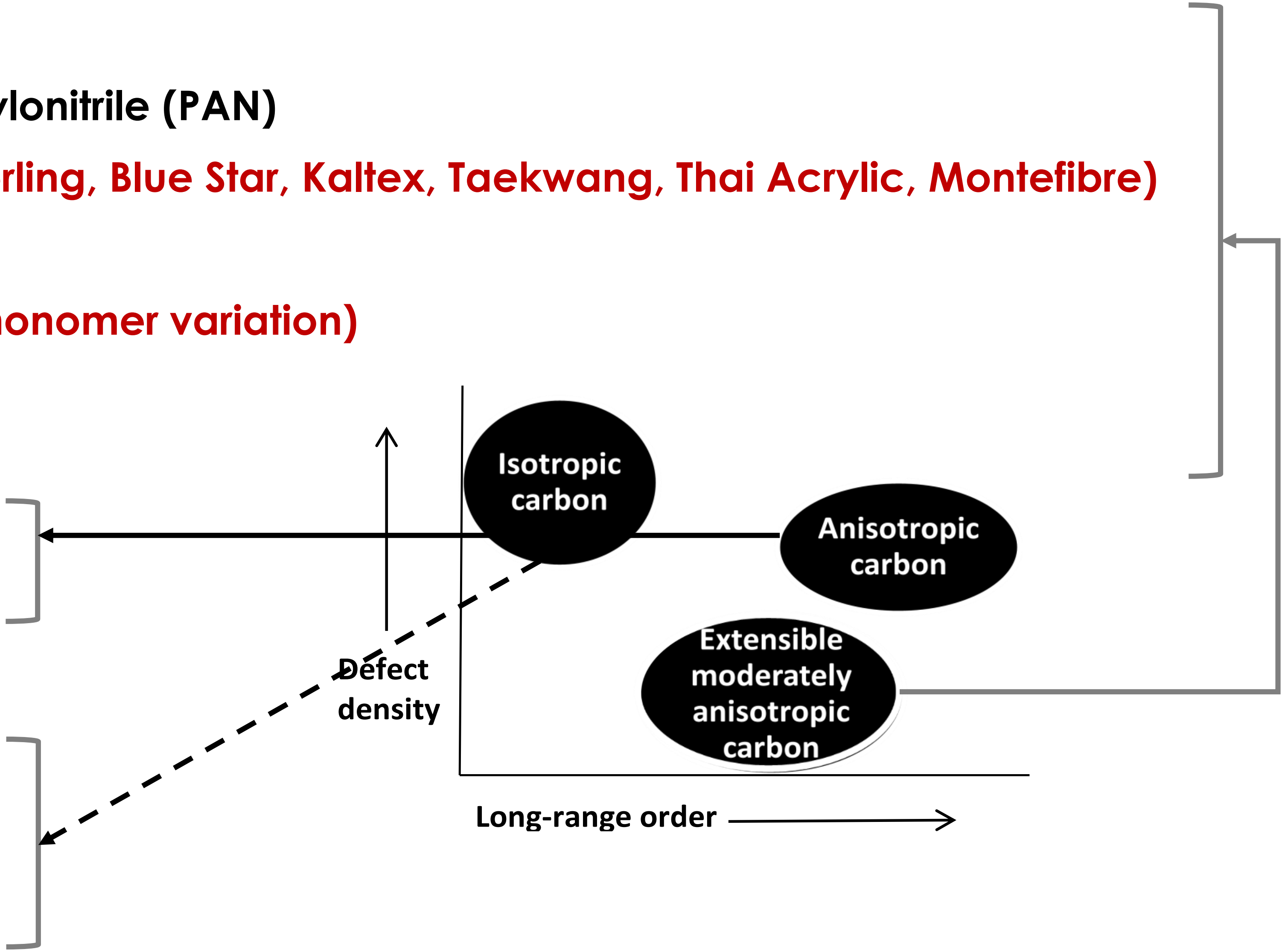
Gains in cost and mass savings up to 16% through controlled fiber placement

Outline

- Update on research status and future affordability perspective on the US manufactured carbon fibers
- Interfacial engineering of carbon fiber composites
- Devising composite tanks with health monitoring tools
- Thermoplastic liners and studies to reduce permeability

Globally studied precursor candidates

- Specialty acrylic fibers (SAF)
  - High molecular weight polyacrylonitrile (PAN)
- Textile and PAN Variants (FISIPE, Sterling, Blue Star, Kaltex, Taekwang, Thai Acrylic, Montefibre)
  - Renewable acrylonitrile
  - Variant PAN compositions (comonomer variation)
- Melt-processible PAN precursors
- Polyolefin (polyethylene)
- Pitch precursors
  - Mesophase synthesis
- Natural gas (for CNT yarn)
- Cellulosic precursor
- Lignin (MeadWestvaco/GrafTech)
- Spider silk



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

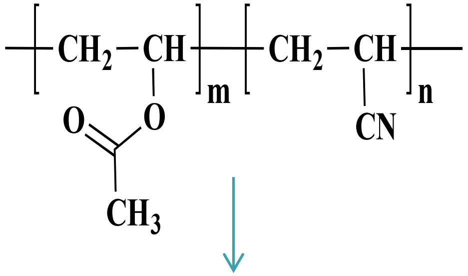
MRL 1-2

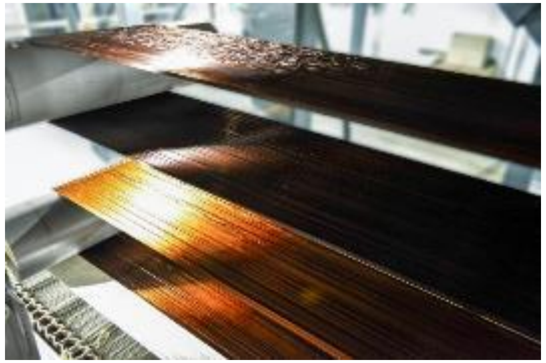
MRL 3-7

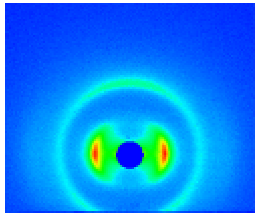
MRL 8-9

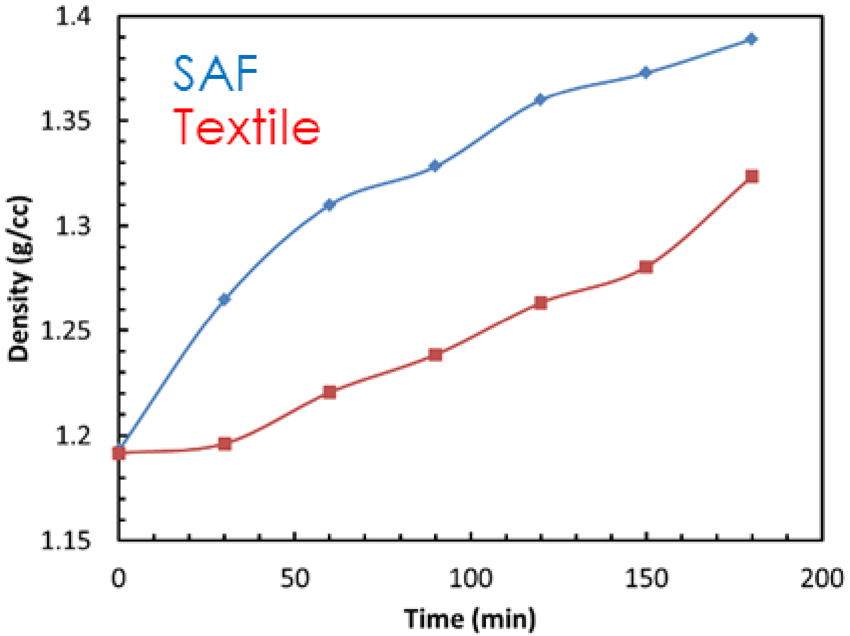
Conversion of Alternative Textile Precursor

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.

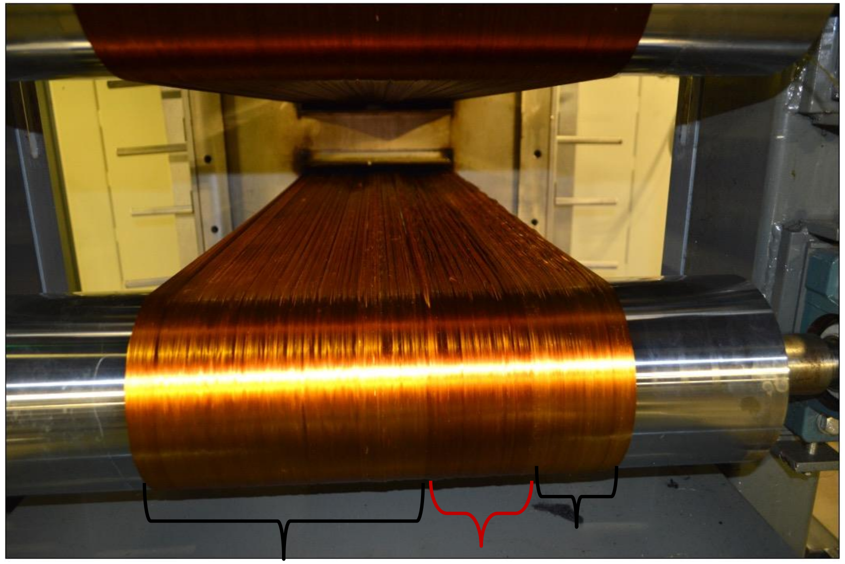
Types of Fibers Produced:

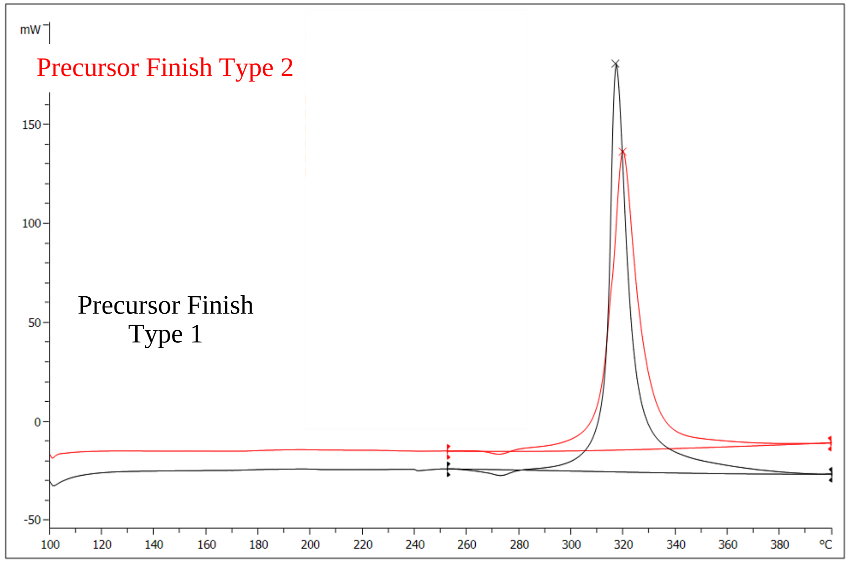
~500 ksi, 33 Msi
~450 ksi, 39 Msi
~400 ksi, 36 Msi

~625 ksi, 50 Msi (from SAF and controlled carbonization)

Precursor treatment and finish can affect properties

- Chemical impact on oxidation time and state may not be significant.
- The applied spin finish can generate defects (on precursor fiber surfaces).

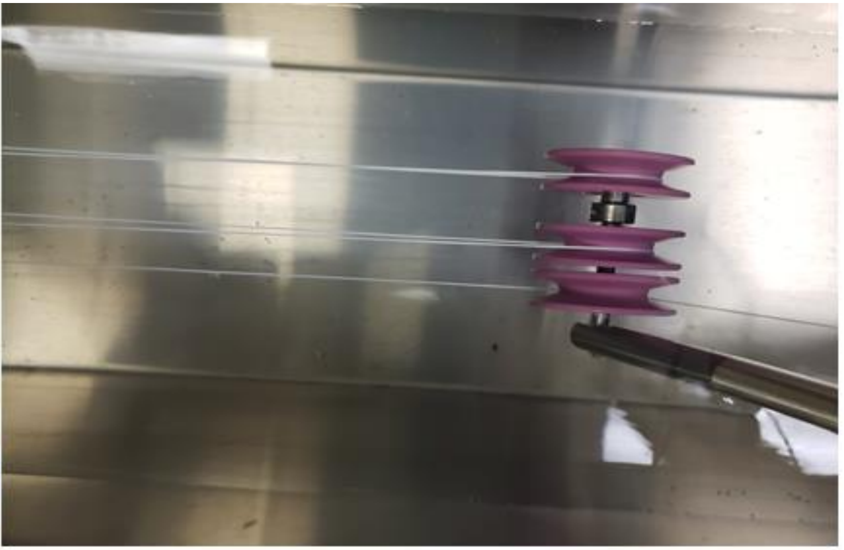


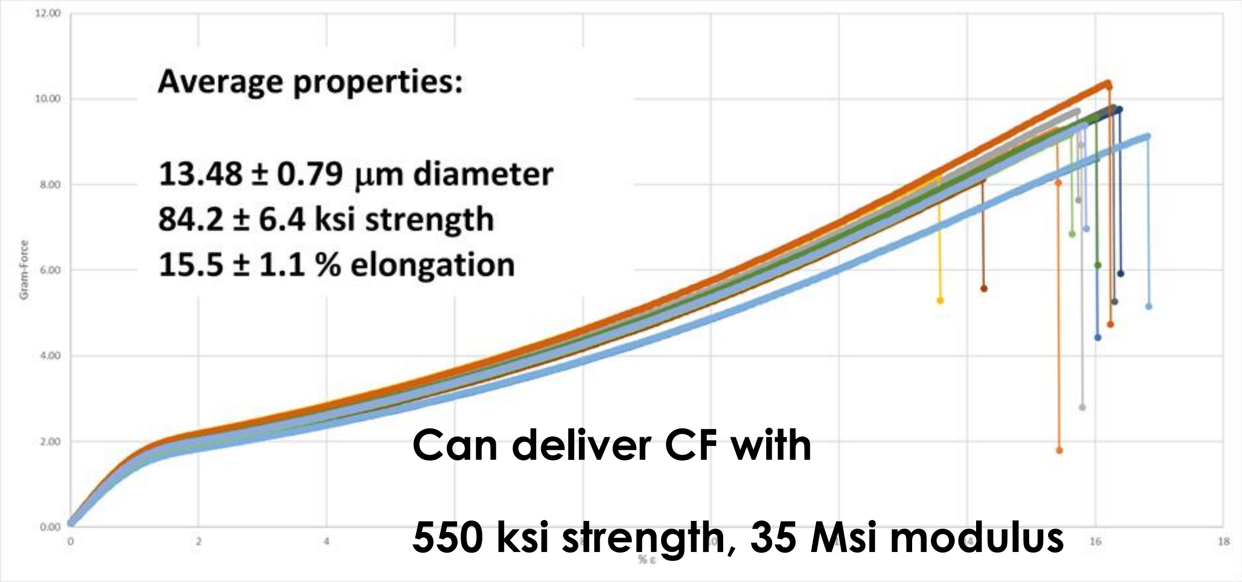


Carbon Fiber A		
Property	**Precursor Finish Type 1**	**Precursor Finish Type 2**
Tensile Strength (ksi)	457	369
Tensile Modulus (msi)	39	36
Elongation (%)	1.18	1.06
CF Density (g/cc)	1.7651	1.7573

Lab-scale PAN Spinning: Variation in Properties

Coagulating jet



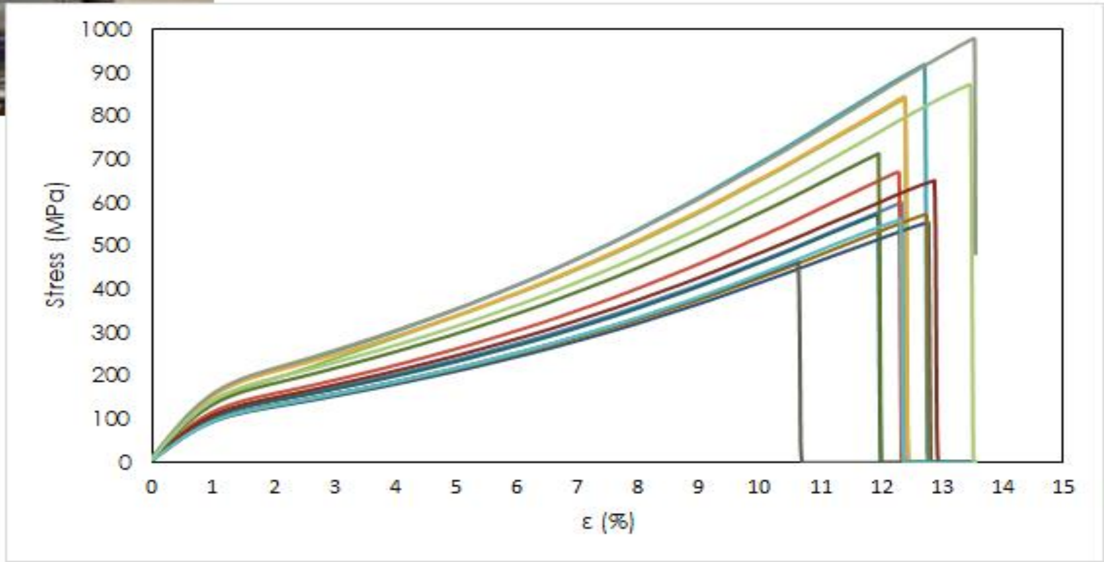


Average properties:

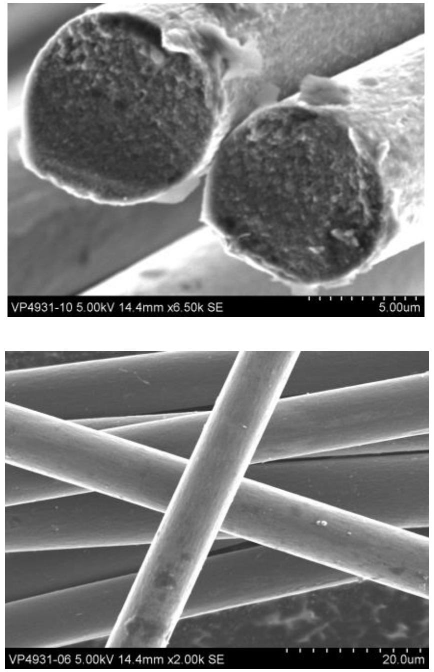
13.48 ± 0.79 μm diameter
84.2 ± 6.4 ksi strength
15.5 ± 1.1 % elongation

Can deliver CF with

550 ksi strength, 35 Msi modulus



Continuous processing of PE was demonstrated



300 ksi (2.0 GPa) tensile strength and 30 Msi (200 GPa) tensile modulus in carbonized filaments were observed.

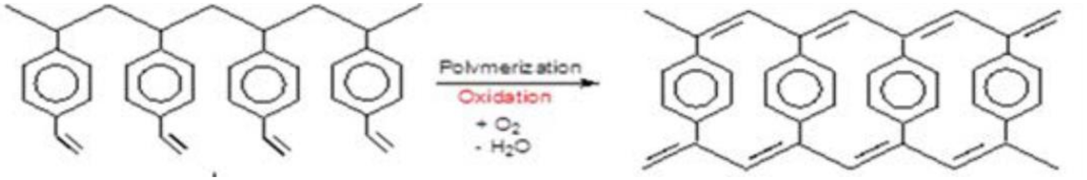
- Fully functionalized PE fibers are brittle in nature. Handling of tow was improved in the modified sulfonation reactor.

- The issue of inter-filament bonding during thermal treatment was identified as one of two major obstacles. After undertaking numerous studies, optimized fiber treatments were identified and inter-filament bonding even with small diameter fibers has been eliminated.

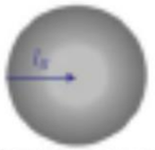
Ongoing LCCF R&D Projects Sponsored by FCTO

- Novel Plasticized Melt Spinning Process of PAN Fibers Based on Task-Specific Ionic Liquids (ORNL; PI: Sheng Dai)
  - Ionic liquids enable melt-processing of PAN and higher carbon yield

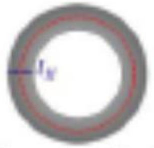
- Developing A New Polyolefin Precursor for Low-Cost, High-Strength Carbon Fiber (Penn State; PI: Mike Chung)
  - High-yield polymeric char forming fibers as carbon precursors



- Precursor Processing Development for Low-Cost, High-Strength Carbon Fiber for Composite Overwrapped Pressure Vessel Applications (Univ. Kentucky; PI: Matthew C. Weisenberger)
  - Designed carbon fiber morphology for enhanced composite performance

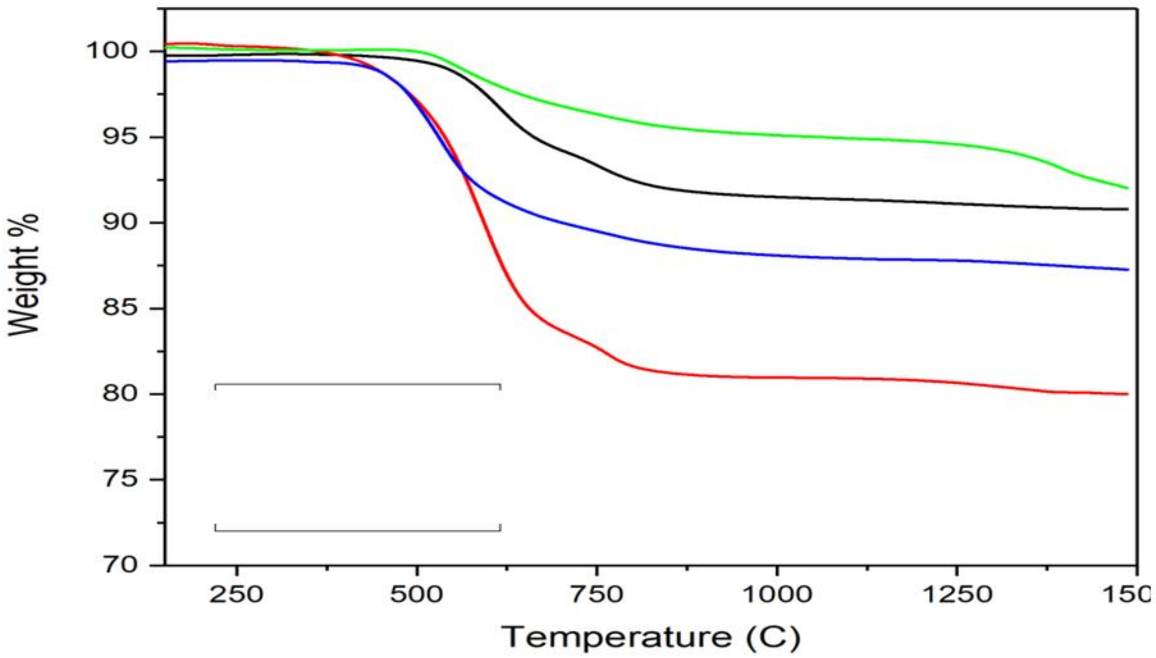


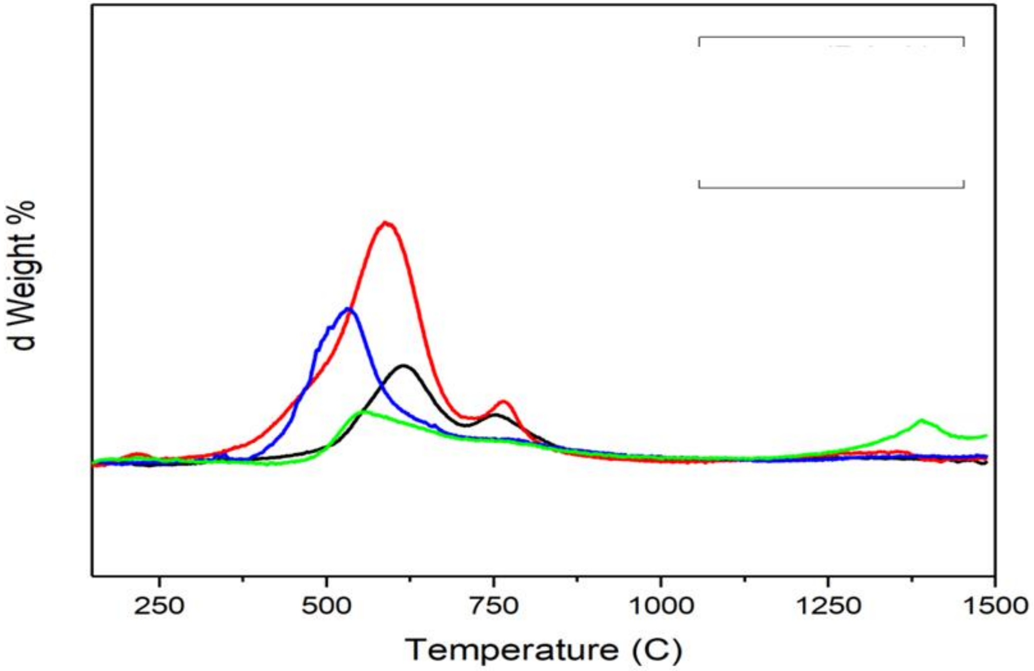
Conventional precursor fiber (14 micron diameter)
l_D = 7 um



Hollow precursor fiber (14 um OD, 9.3 um ID)
l_D = 1.175 um

New hybrid melt-processable precursor offer excellent opportunity for extensive study

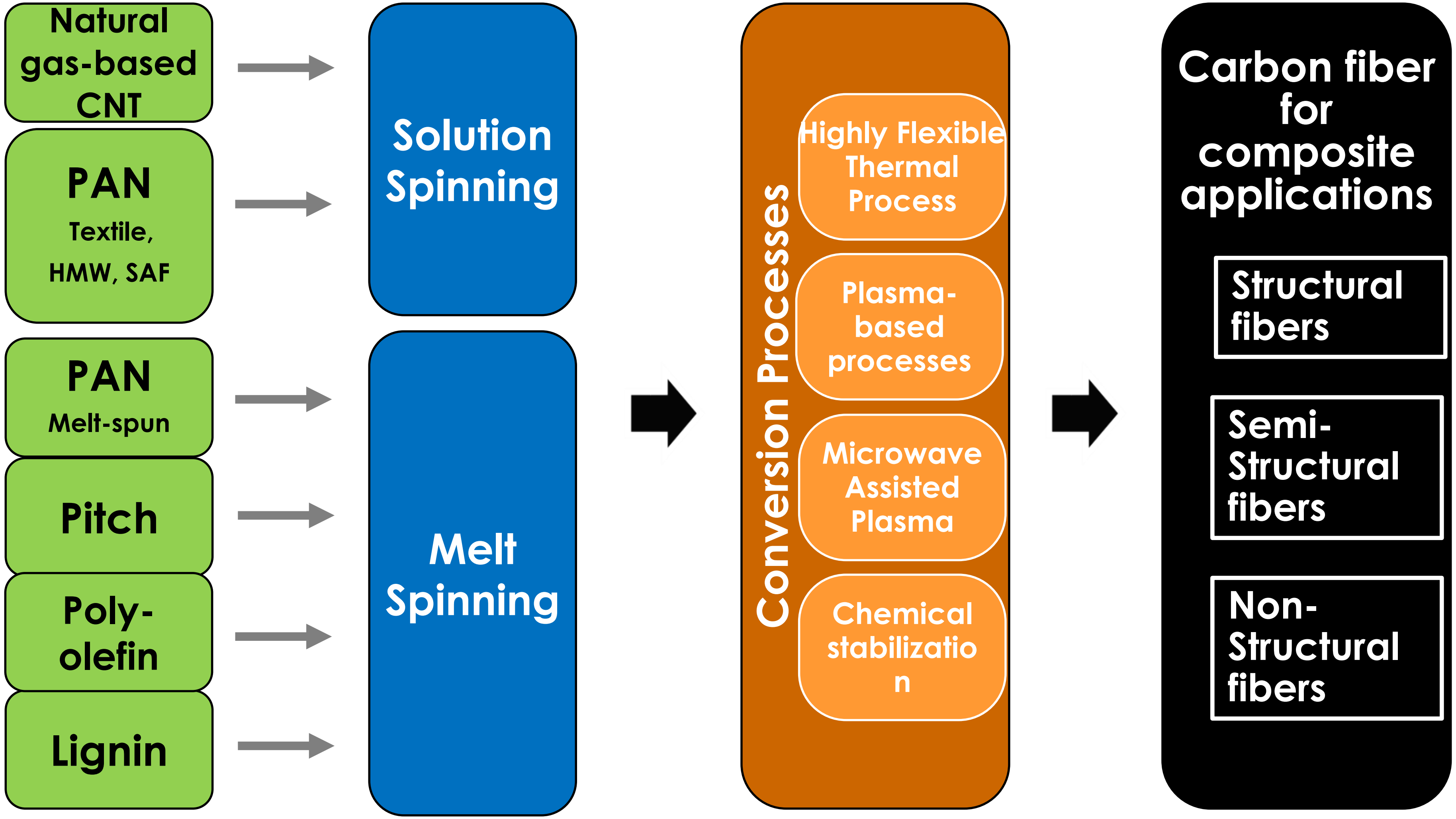




New high-yield carbon precursors have the potential to change the manufacturing methodology. (Penn State University: Prof Chung)

Rice University is working on natural gas derived CNT fiber with 4 GPa tensile strength.

Precursors and associated conversion option



Natural gas-based CNT

PAN
Textile,
HMW, SAF

PAN
Melt-spun

Pitch

Poly-olefin

Lignin

Solution Spinning

Melt Spinning

Conversion Processes

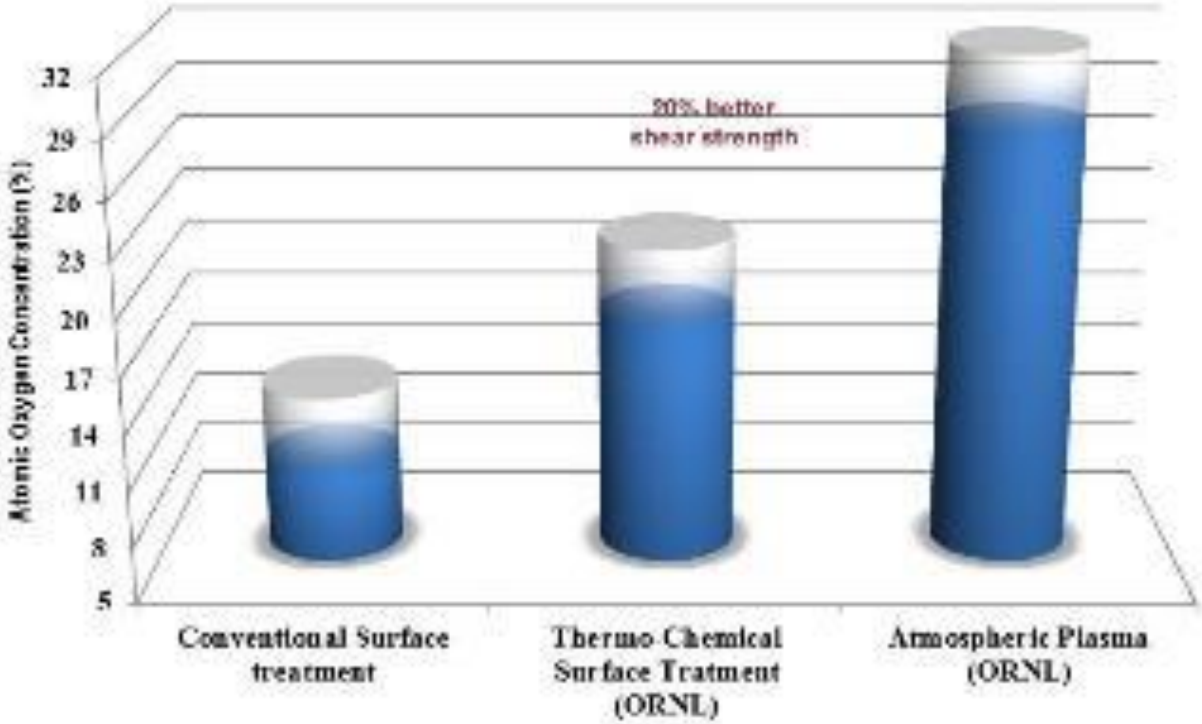
- Highly Flexible Thermal Process
- Plasma-based processes
- Microwave Assisted Plasma
- Chemical stabilization

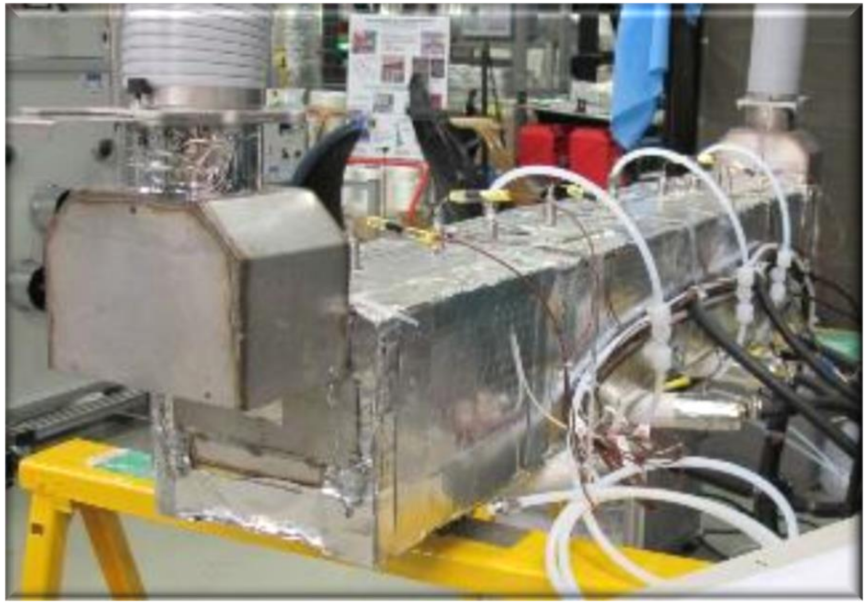
Carbon fiber for composite applications

- Structural fibers
- Semi-Structural fibers
- Non-Structural fibers

ORNL has established precursor fiber manufacturing and conversion capability for all probable precursors. However, the conversion of these variant carbon precursors (fibers) requires different approaches

Carbon Fiber Manufacturing –Surface Treatment Surface Engineering is Critical to Composite Properties





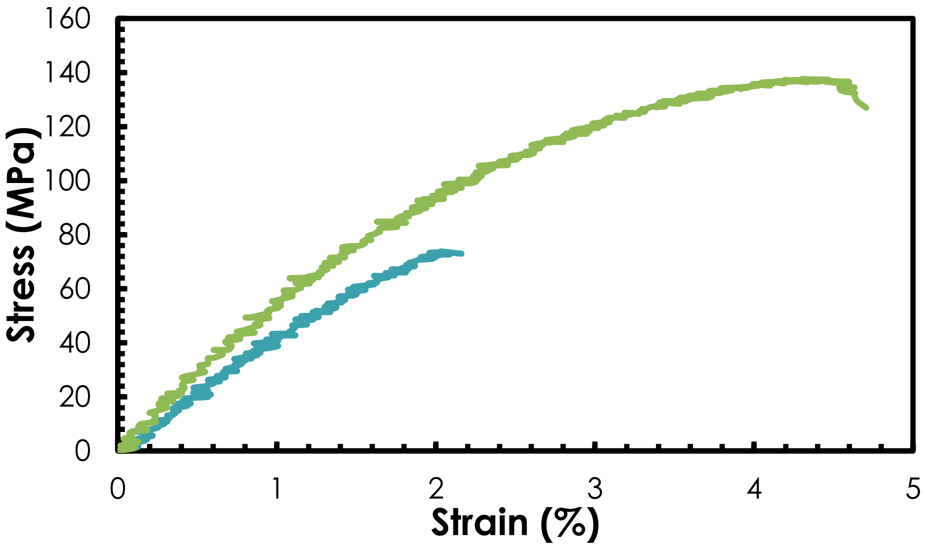
1 tpy dry surface treatment module

- Current CF post-treatment not tailored for commodity resins
- SBS strength increased by 40+% with proper fiber surface engineering

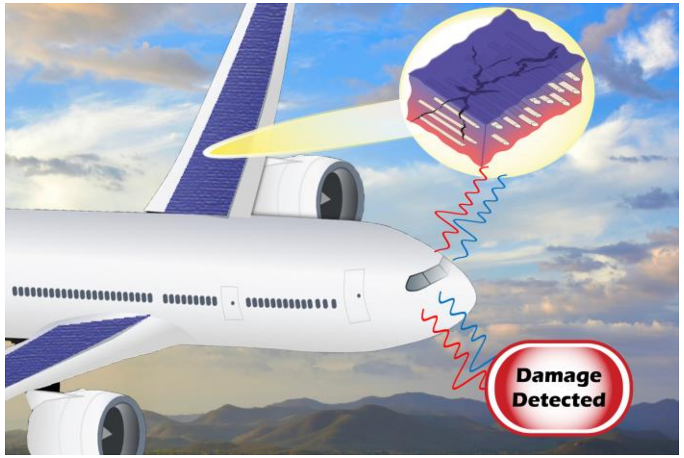
Better understanding of the hierarchical interactions between a polymer matrix and large-diameter fiber reinforcements is needed

Enables designing interphases in composites via targeted interfacial chemistry, scattering tools, and large-scale simulations to unravel correlations between structural properties, rheology, interfacial stability, and dynamics.

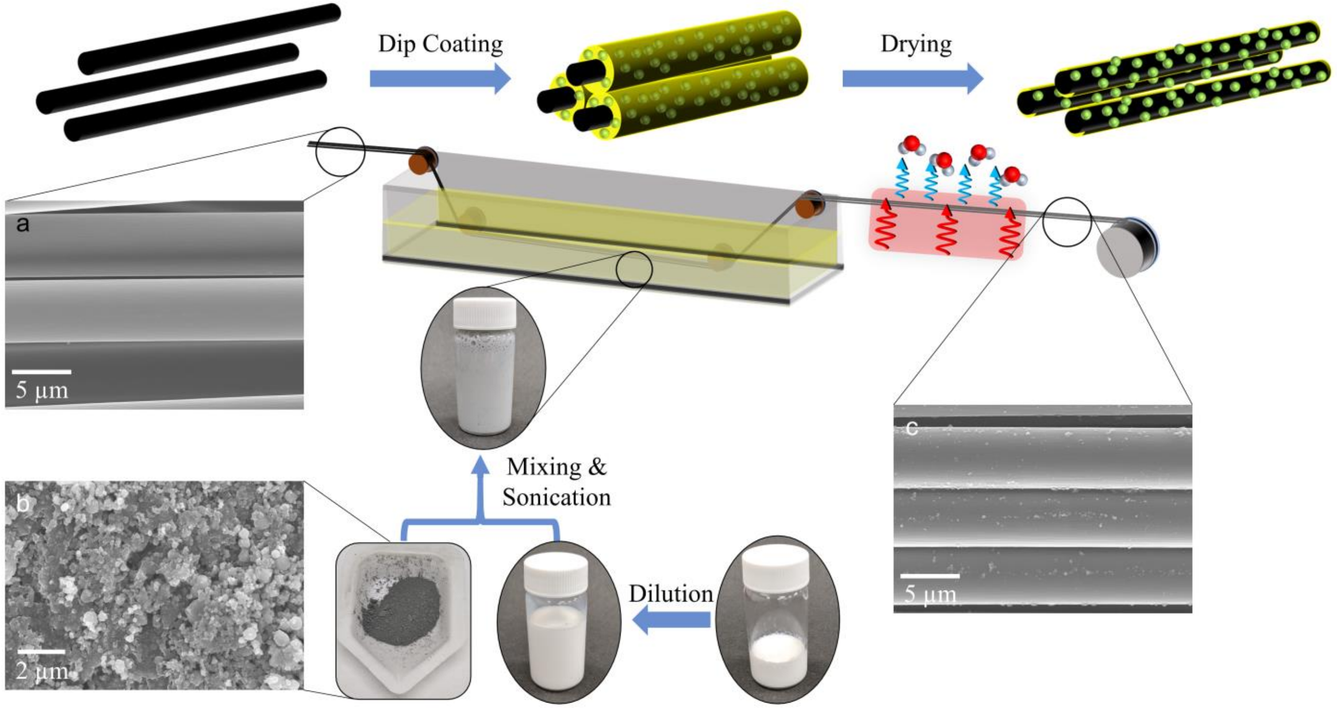
Relative tensile strength of TP matrix composites with the use of **untreated CF** vs. **treated CF**.

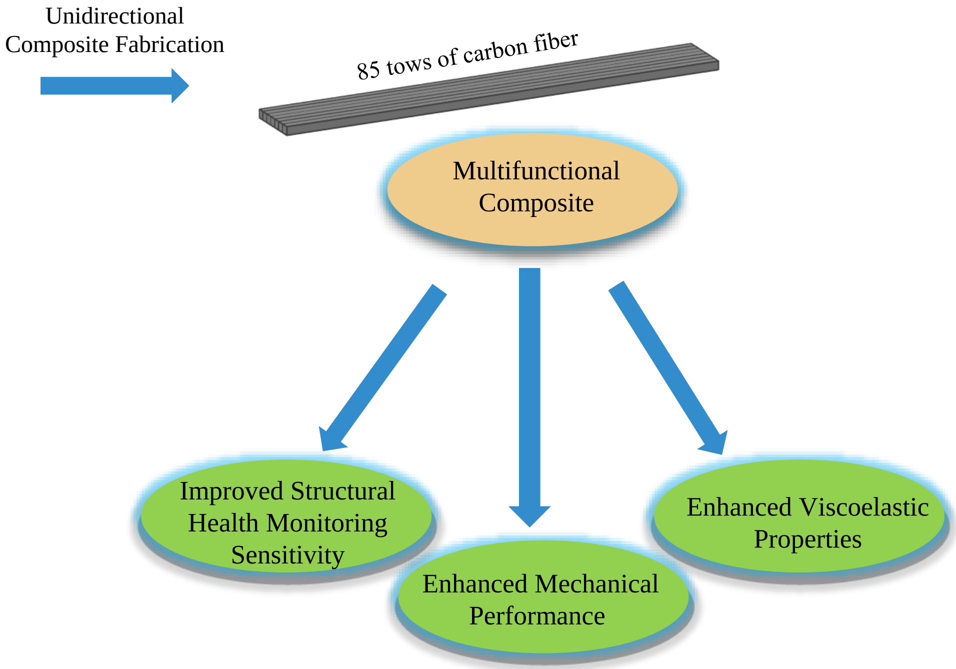


Nanoparticles in Fiber Sizing: Self Sensing



- Integrated SiC nanoparticles onto carbon fiber surface through a continuous feed-through dip coating process of fiber tows
  - Utilized commercially-available epoxy sizing and SiC nanoparticles
  - Mechanically mixed nanoparticles in the epoxy sizing solution (at different epoxy and nanoparticles concentrations)
  - Combined fiber tows in an epoxy matrix to generate a unidirectional composite
- Goal: Use the piezoresistive behavior of SiC to enhance the structural health monitoring capabilities of the composite while maintaining mechanical performance




Unidirectional Composite Fabrication

85 tows of carbon fiber

Multifunctional Composite

Improved Structural Health Monitoring Sensitivity

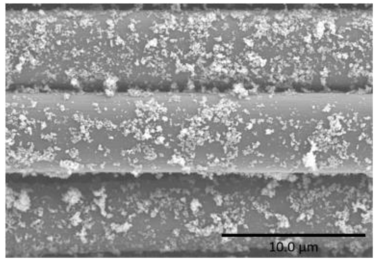
Enhanced Mechanical Performance

Enhanced Viscoelastic Properties

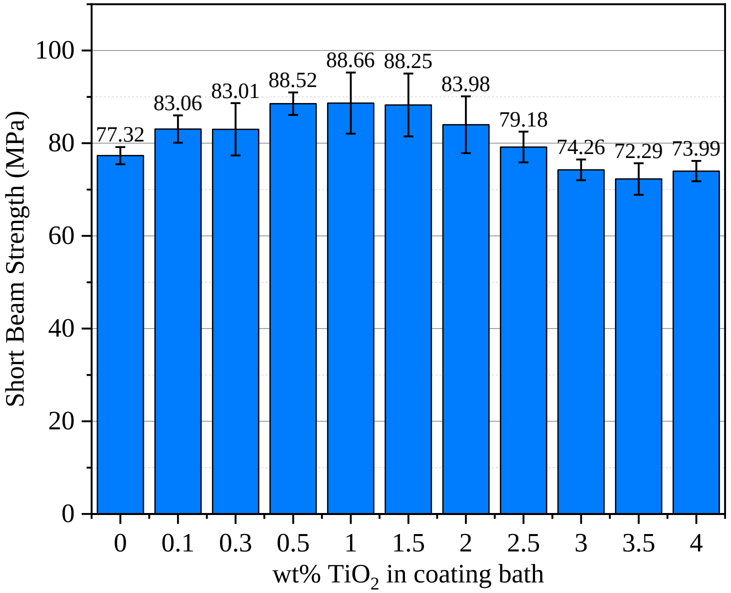
Bowland et al ACS Applied Materials and Interfaces (2018)

Next Generation Self-Sensing Multifunctional Composites via Embedded Nanomaterials

Method to integrate ceramic nanoparticles into composites

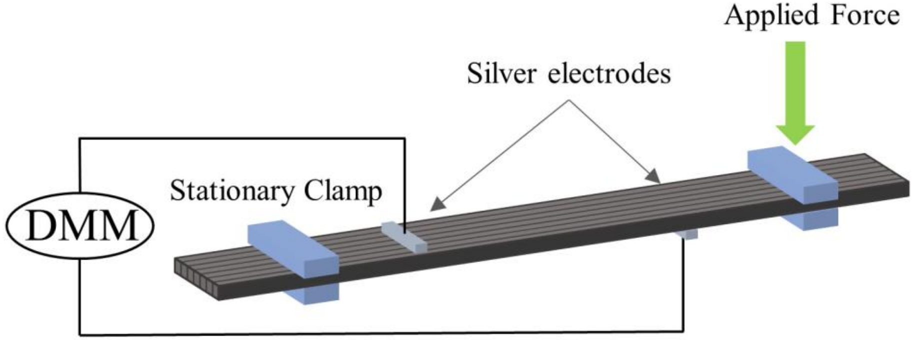


Pinning effect causes 10-15 % improvement in interlaminar shear strength in the composites

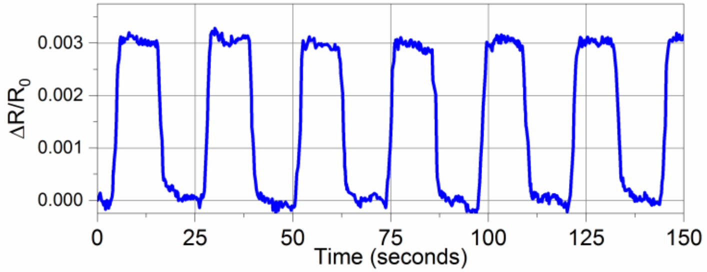


Damping loss factor increases:
1:10: **130-257%**
1:40: **65-147%**

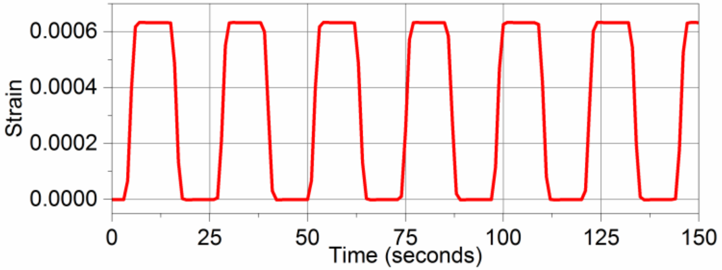
Out-of-plane through thickness variation of composite resistivity was monitored during dynamic mechanical forces



Electrical Resistance Response



Mechanical Input



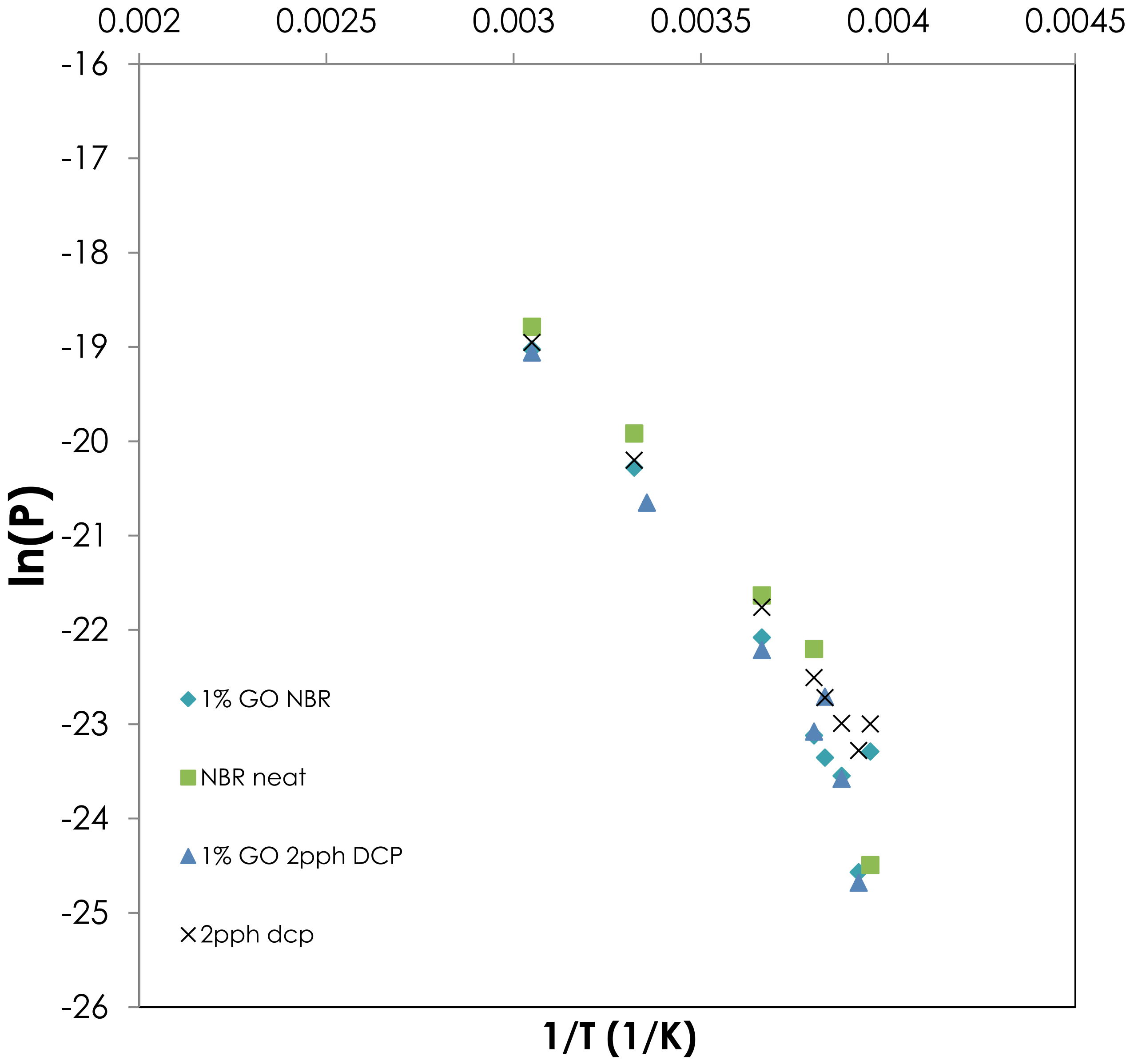
COPV liners based on blow-molded plastics

Barrier properties can be enhanced without affecting its processability.

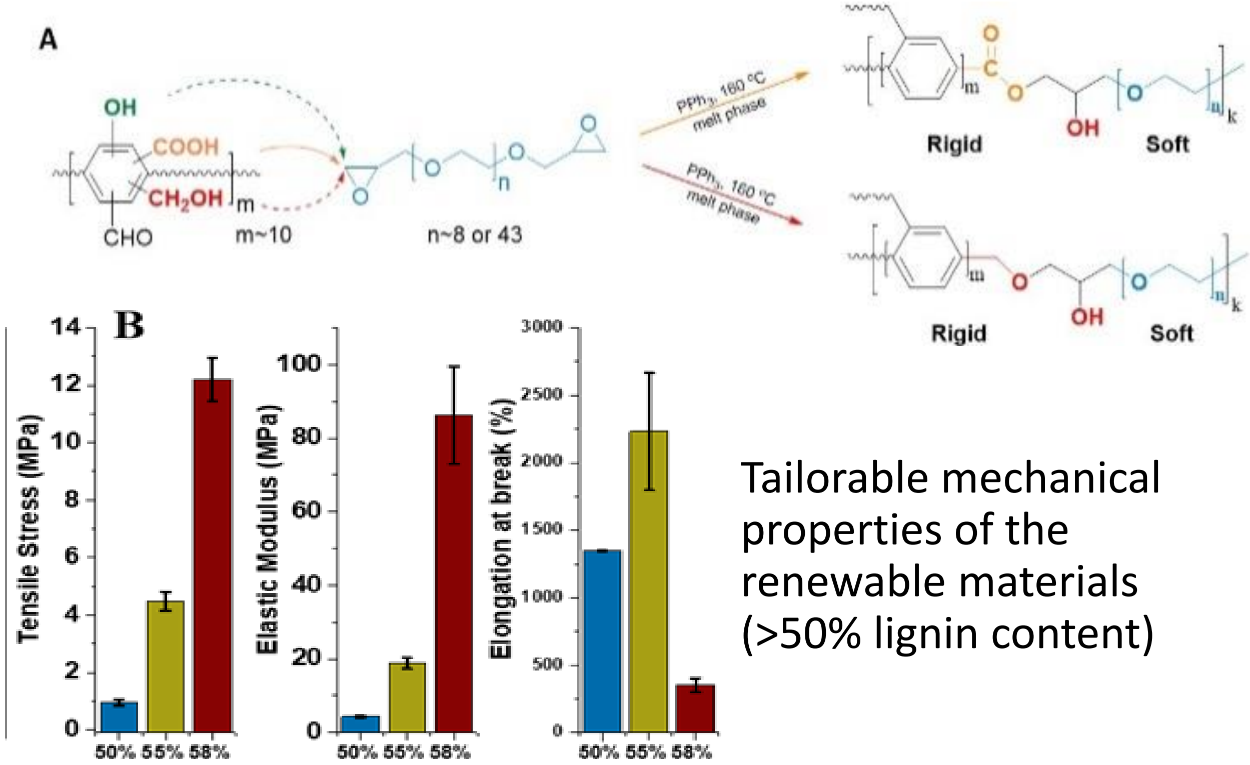
A malleable not-completely-crosslinked nitrile rubber gel filled with additives exhibits reduced permeability data compared to its unfilled control.

Materials for liner:

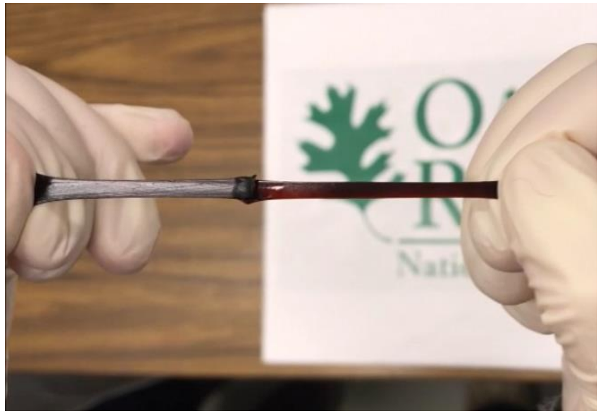
HDPE
POM



A Tough, Self-Healing Elastomer



Tailorable mechanical properties of the renewable materials (>50% lignin content)



Exhibits instant healing in elastomers or thermal bondability in high lignin content plastic material.

Cui et al. **ACS Macro Letters** 7, 1328-1332 (2018)

Significance and Impact

Renewable materials are being examined as chemicals, materials, and fuels. Here, we developed a simple method to obtain a beneficial chemical, structurally like 3,4-dihydroxyphenylacetic acid (DOPAc), from the natural phenolic polymers from industrial waste-stream. The multifunctional polyphenol oligomers exhibit the potential to serve as an alternative for the traditional chemicals in many applications.

Research Details

A new, stretchy, plant-derived material that outperforms the adhesiveness of the natural chemical that gives mussels the ability to stick to rocks and ships. This bio-based material—composed of functional polyphenol and epoxy—can self-heal and elongate up to 2,000%. To achieve these results, researchers developed a unique method to extract a specific form of lignin. The resulting molecular structure creates a super-sticky, highly elastic material that can heal quickly, where broken, through hydrogen bonding.

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- Update on research status and future affordability perspective on the US manufactured carbon fibers
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