

Integrated Computational Materials  
Engineering (ICME)

# **Predictive Tools Development for Low Cost Carbon Fiber for Lightweight Vehicles**

- 2019 Annual Merit Review -



PI / Presenter: Xiaodong (Chris) Li, University of Virginia  
June 11, 2019

**Project ID: MAT124**

This presentation does not contain any proprietary, confidential, or otherwise  
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# Overview

## Timeline

- Start Date: October 1, 2017
- End Date: September 30, 2020
- Percent Complete: 55%

## Budget

- *Total* Project Funding: \$4,408,032
  - \$3,000,000 Federal
  - \$418,032 Cost Share
  - \$990,000 LightMat Consortium
- *FY 2019* Funding: \$1,463,645
  - \$993,301 Federal
  - \$140,344 Cost Share
  - \$330,000 LightMat Consortium

## Partners

- University of Virginia (*Lead*)
- Pennsylvania State University
- Oak Ridge National Laboratory
- Solvay S.A.
- Oshkosh Corporation

## Barriers

- Reduction of vehicle weight necessitates lower-density materials with suitable mechanical properties, low-cost carbon fiber
- Development of a calibrated ICME predictive tool that can identify & optimize fiber processing parameters
- Extend the ICME framework to encompass synthesis and characterization of fibers based on alternative precursors and novel manufacturing processes

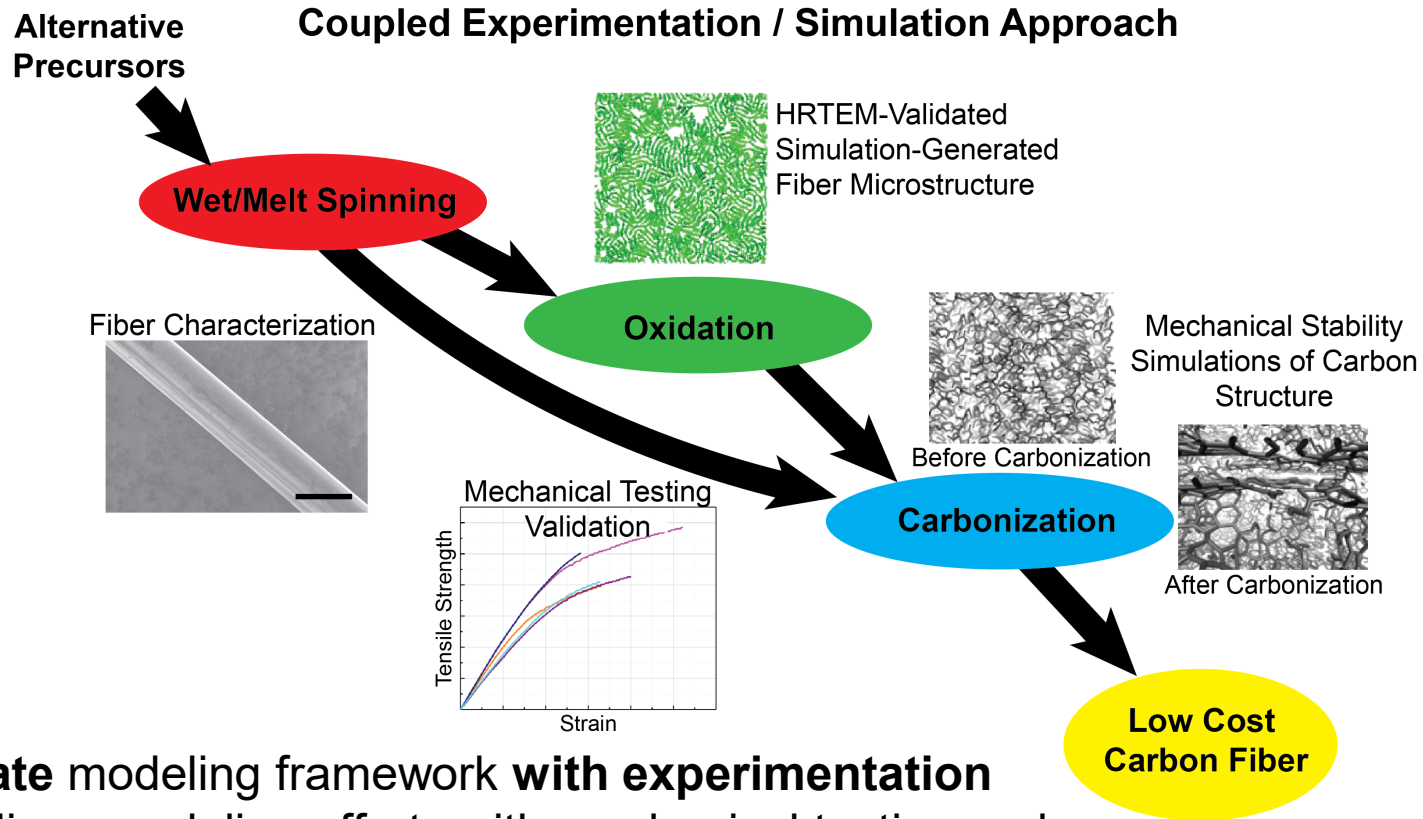
Source: 2017 U.S. DRIVE MTT Roadmap Report, Section 3

# Relevance

- **Objective:** To demonstrate CF precursor technology and processing techniques capable of achieving the following:
  - Cost  $\leq$  \$5/pound
  - Strength  $\geq$  250 Ksi (1.72 GPa)
  - Modulus  $\geq$  25 Msi (172 GPa)
  - Strain  $\geq$  1%
- This objective will be accomplished through the ICME framework, **coupling simulations and targeted experimentation** to evaluate alternative precursors for suitability to manufacture low-cost CF
  - First year objectives met with a demonstration of accurate ICME framework analysis of PAN fibers (less than 15% error margin)
  - Second year objectives are nearly met, including extension of ICME framework to alternative precursors and identification of a low cost alternative to PAN
  - Third year objectives are to conduct scalability studies to predict industrial scale productivity and cost savings with the alternative fiber
- **Impact** - Achieve significant vehicle weight reduction and develop high-strength material systems with low-cost carbon fiber
  - Demonstrate a testbed technical framework to enable at-scale production

# Technical Objectives

- Assemble framework to **model conversion of fibers** and **predict properties**
  - Model individual processing steps, including oxidation and carbonization, to predict coupled thermal-chemical-mechanical fiber transformation
  - Identify a **low-cost alternative precursor** to PAN



- **Validate** modeling framework **with experimentation**
  - Mirror modeling efforts with mechanical testing and chemical characterization of fibers before and after each processing step

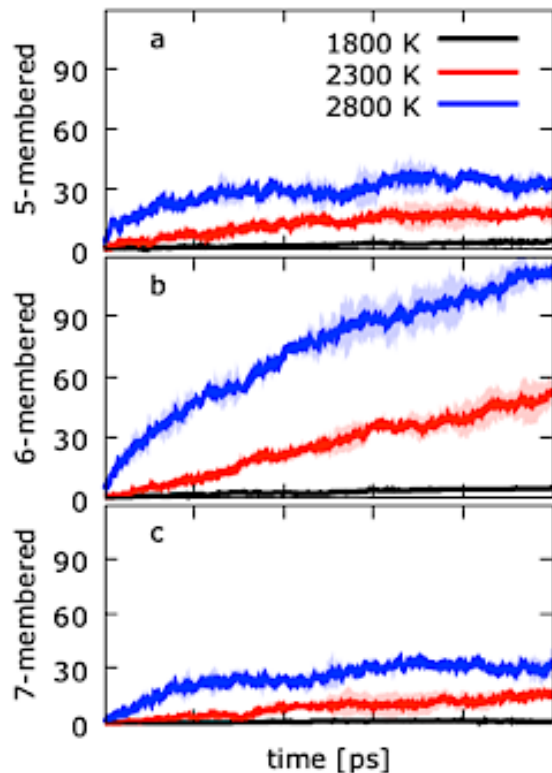
*Any proposed future work is subject to change based on funding levels.*

# Approach and FY19 Milestones

- The project is on track to meet FY19 milestones

Date	Milestone	Status
September 30, 2018	<b>FY18 Go/No Go:</b> Accurate prediction of PAN-fiber properties. Simulations will estimate PAN-based fiber properties (strength, modulus, strain) within a 15% error margin.	<b>Met</b>
September 30, 2019	<b>M1:</b> Statistical analysis of alternative precursor oxidation, baseline reference for validation of simulation predictions, and exploratory investigation and mechanical testing of low-cost alternative fibers.	<b>On-Track 80%</b>
September 30, 2019	<b>M2:</b> Chemical conversion of alternative carbon fibers and verification through direct comparison with M1. Milestone will be met if simulations identify resultant properties within 15% error margin.	<b>On-Track 60%</b>
September 30, 2019	<b>M3:</b> Large-scale simulations of fiber mechanics to predict resultant properties with verification through comparison with M4. Milestone will be met if simulations identify properties within 15% error margin.	<b>On-Track 60%</b>
September 30, 2019	<b>M4:</b> Synthesis and evaluation of prototype carbon fibers produced via alternative precursors. Characterization and mechanical testing of alternative fibers to track progress toward DOE targets.	<b>On-Track 60%</b>
September 30, 2019	<b>FY 19 Go/No Go:</b> The ICME framework shall identify at least one potential alternative precursor yielding a carbon fiber that is projected to meet cost, strength, modulus, and strain requirements.	<b>On-Track</b>

# Innovative Approach & Strategy

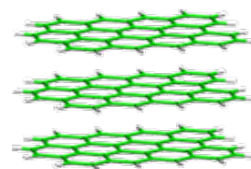


ReaxFF-predicted ring production of oxidized PAN during carbonization (PSU).

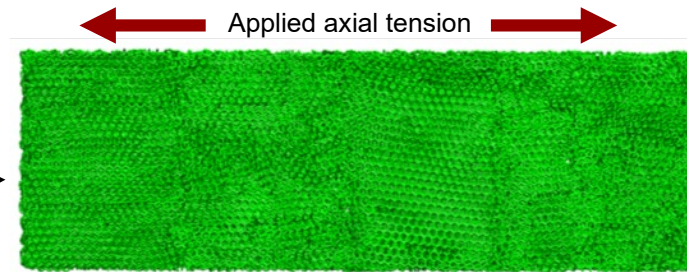
**Continuous feedback** then optimizes the simulations and reduce error

Coupled simulation-experimentation approach provides **closed-loop feedback** and verification of the ICME framework

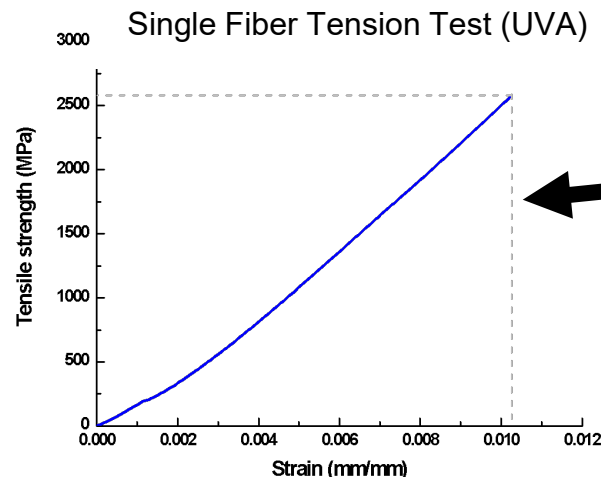
ReaxFF simulations probe the effect of temperature, heat rates, fiber tension, etc. on resultant **fiber chemical structures**. Resulting structure provides input to AIREBO MD simulations of fiber mechanics.



Polymer ladders aligned along axis



Ring microstructure built up into 3D fiber for mechanical test simulations (UVA).

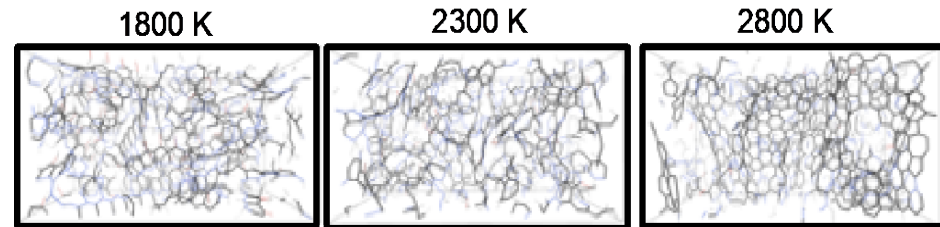


MD simulation results are directly compared with experimentation to **validate property predictions**

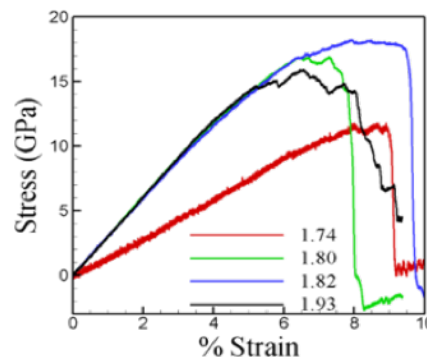


# Technical Accomplishments - FY18 / Year 1

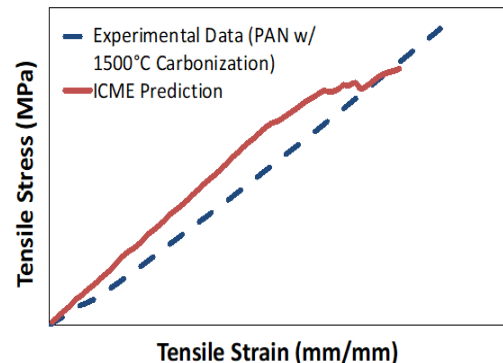
- In FY18, we established and validated the ICME framework with **PAN-based fibers**
- ReaxFF simulations provided chemistry inputs to mechanics model
- AIREBO simulations then predicted fiber strength and strain based on an ideal microstructure
- Griffith's law strength correction was used to account for SEM/XCT-measured pore size
- Resulting property predictions agreed with experimental properties within 13% error margin



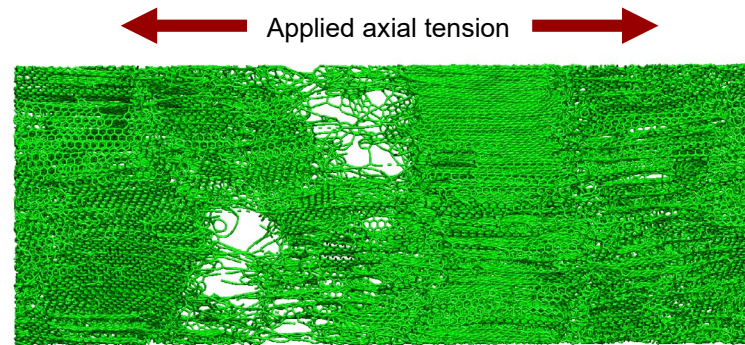
ReaxFF simulation of PAN ring production during carbonization at different temperatures (PSU).



Large-scale MD simulations provide predictions of critical fiber mechanical properties for comparison with lab/pilot-scale production (UVA).



Final ICME predictions and experimental measurements for PAN-based fiber.

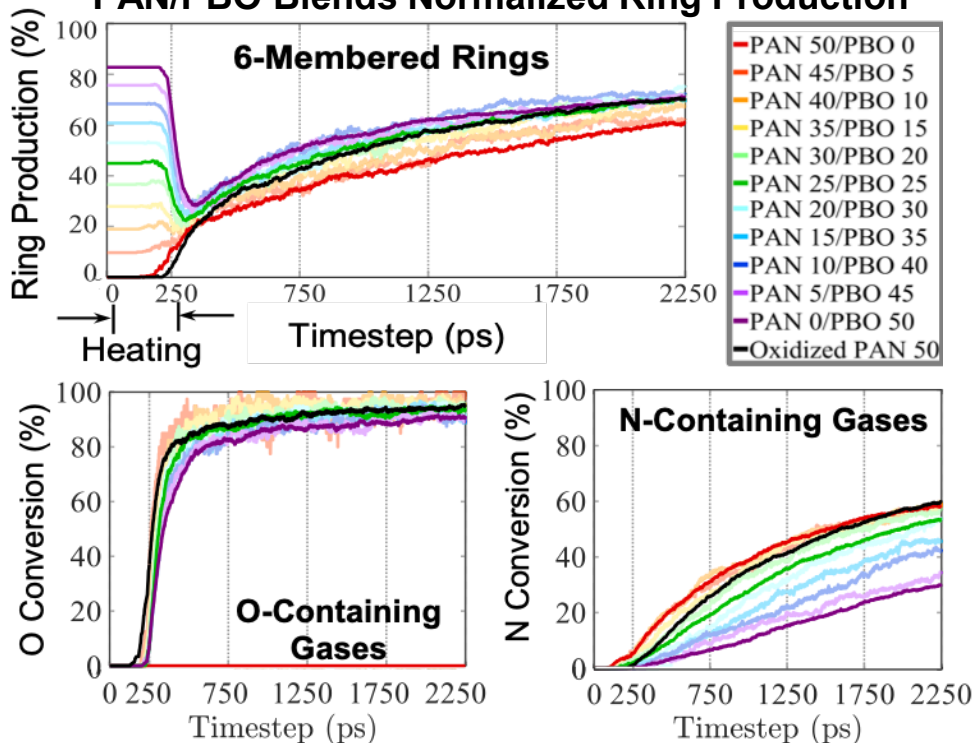


	Experimental Measurement	ICME Prediction	Percent Difference
<b>Strength</b>	3827 ± 88 MPa	4203 MPa	9.8 %
<b>Strain</b>	1.54 ± 0.003 %	1.71 %	12.9 %
<b>Modulus</b>	276 ± 5 GPa	297 GPa	7.6 %

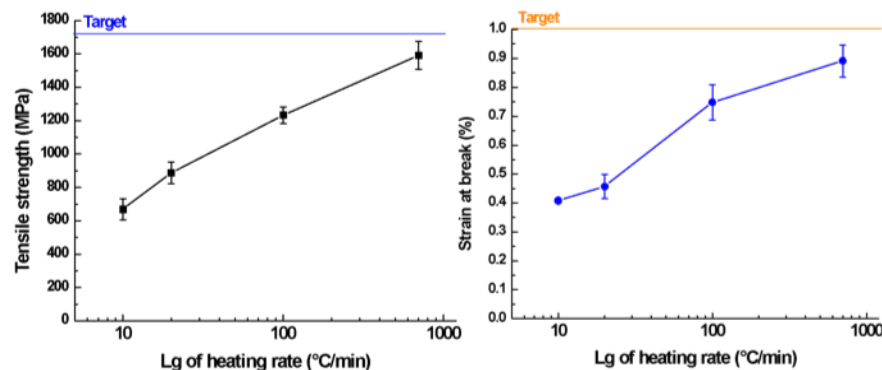
# Technical Accomplishments - FY19 / Year 2

- In FY19, we aim to (1) update and strengthen the ICME framework for **non-ideal, realistic microstructures** and (2) extend this successful framework to identify a low-cost **alternative precursor**
- We considered
  - Multiple precursors: PBO, PBO/PAN blends, polyethylene (PE), nylon
  - Multiple procedures: heating/cooling rates, treatment temperatures, fiber tension/drawing speed
  - Precursor additives: graphene

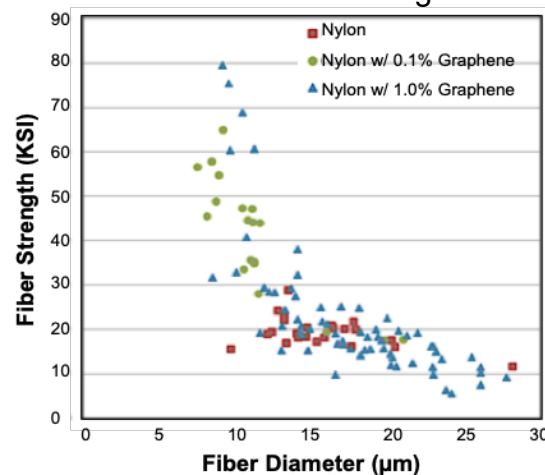
## PAN/PBO Blends Normalized Ring Production



ReaxFF simulations of PAN/PBO blends were used to track ring production and gauge the importance of oxygen and nitrogen containing groups to successful fiber conversion (PSU).



Increasing heating rate during carbonization of PBO fibers enhanced strength and strain (UVA).



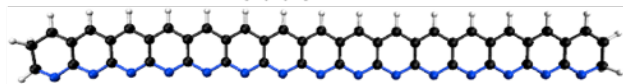
(Left) Study demonstrating an increase of strength with fiber diameter and added graphene content (ORNL).



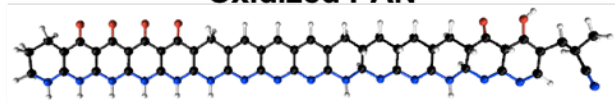
# Technical Accomplishments - FY19 / Year 2

- What role does **polymer alignment** and fiber tension play during fiber conversion?

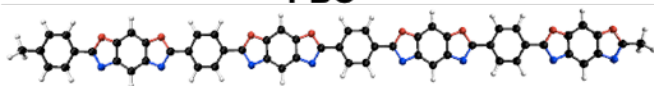
**Ladder PAN**



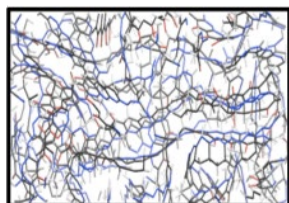
**Oxidized PAN**



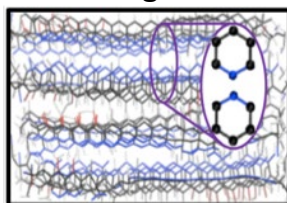
**PBO**



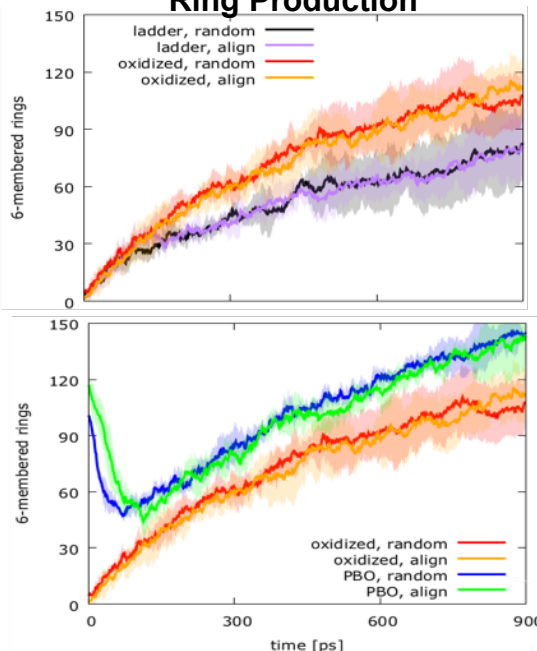
**Random**



**Aligned**

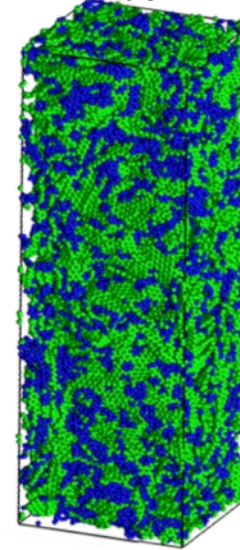


**Ring Production**

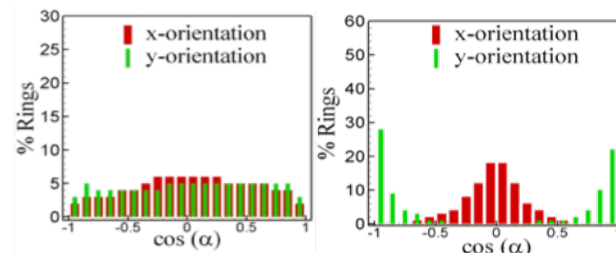
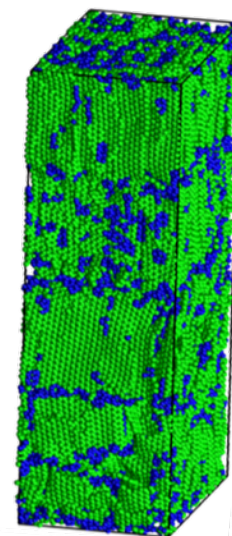


**Mechanics Model Polymer Alignment**

**Random**

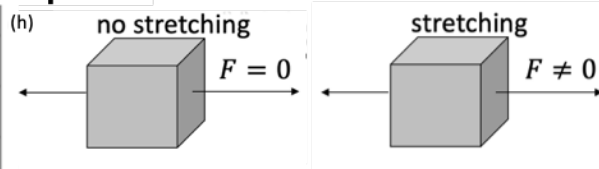
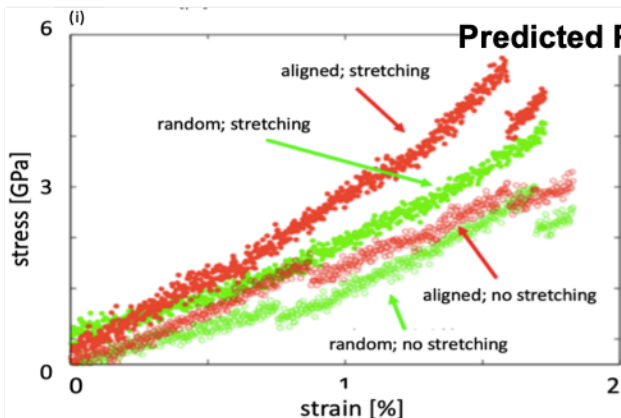


**Aligned**



This aligned polymer structure is translated to large-scale MD simulations to predict mechanical properties (UVA).

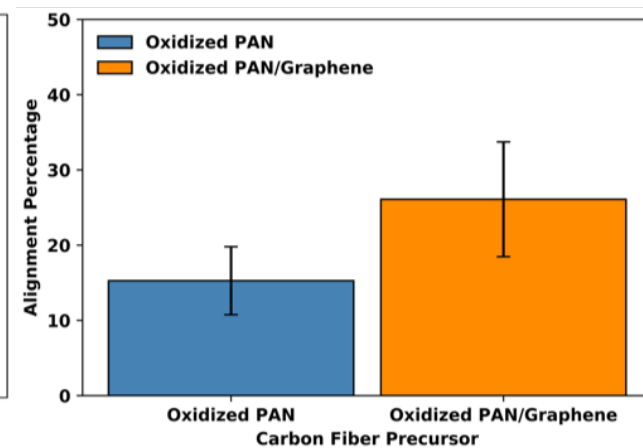
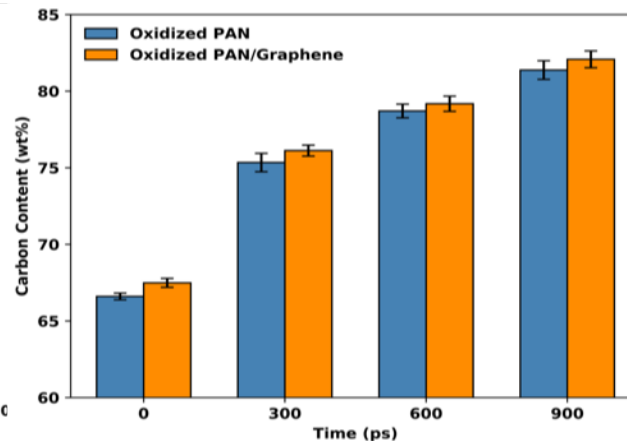
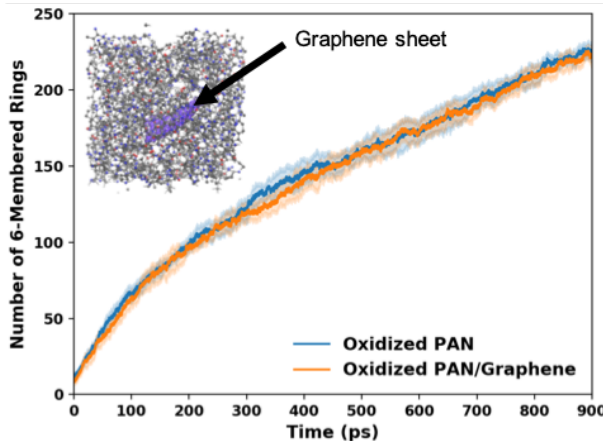
**Predicted Properties**



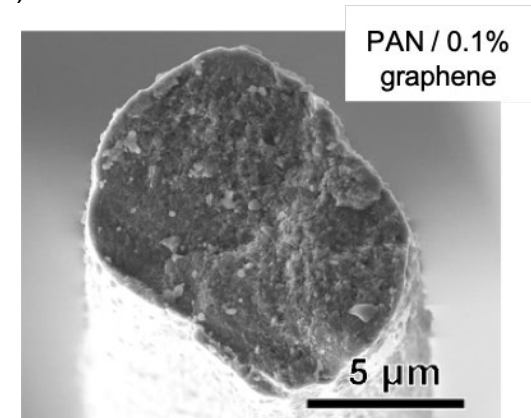
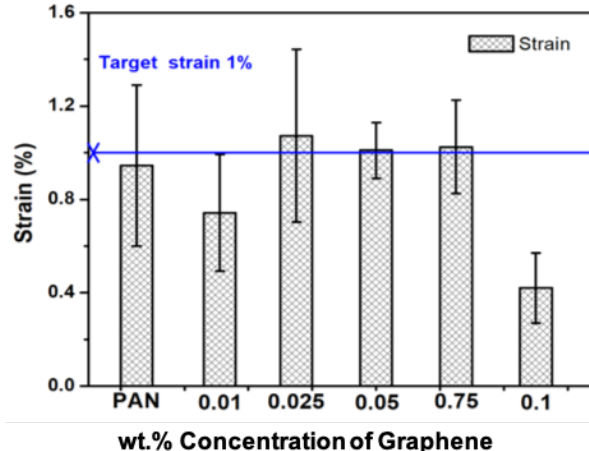
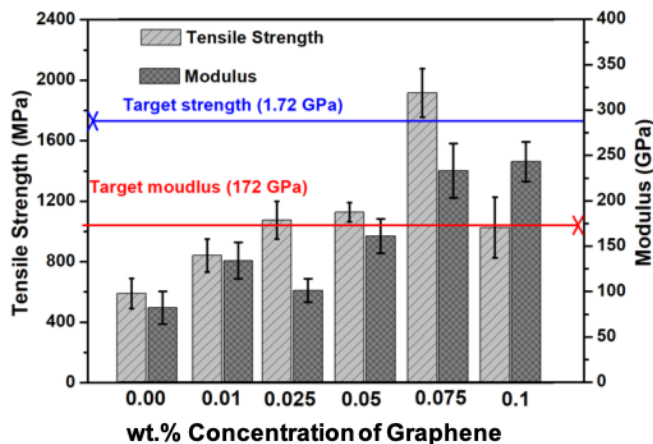
These simulations predict higher strength in stretched fibers with aligned polymer chains (PSU).

# Technical Accomplishments - FY19 / Year 2

- What are the benefits and disadvantages of using **nanoadditives**, like graphene?
- Graphene is easily applied by coating the precursor pellets with graphene solution



ReaxFF simulations show graphene contributes to significant alignment of the fiber microstructure but does not benefit carbon ring production despite higher carbon content (PSU).

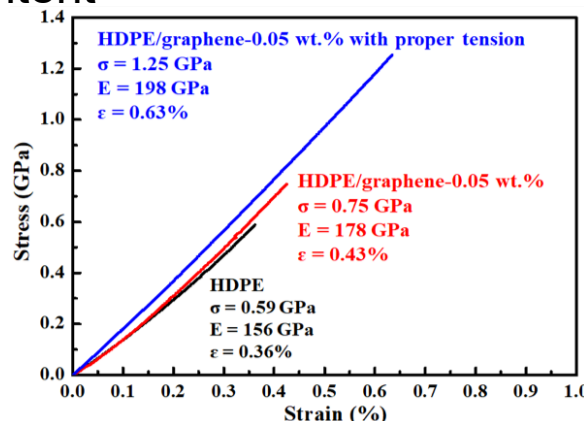
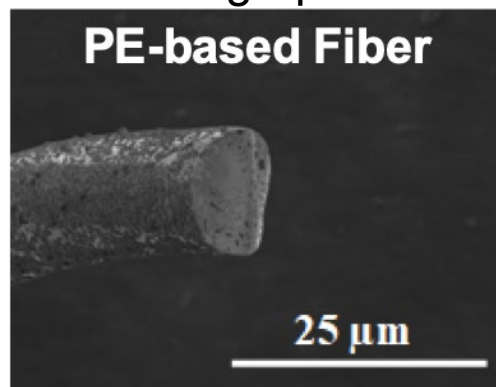


Optimized graphene content has been shown to **significantly enhance** the properties of PAN-based fiber (UVA).

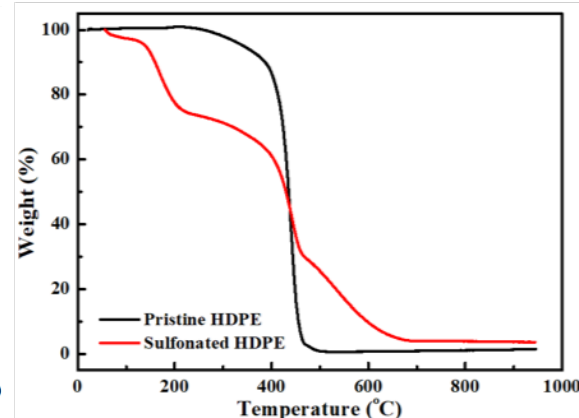
PAN-based fiber with 0.1 wt% added graphene (UVA).

# Technical Accomplishments - FY19 / Year 2

- The most attractive alternative precursors are polyethylene and nylon with added graphene content



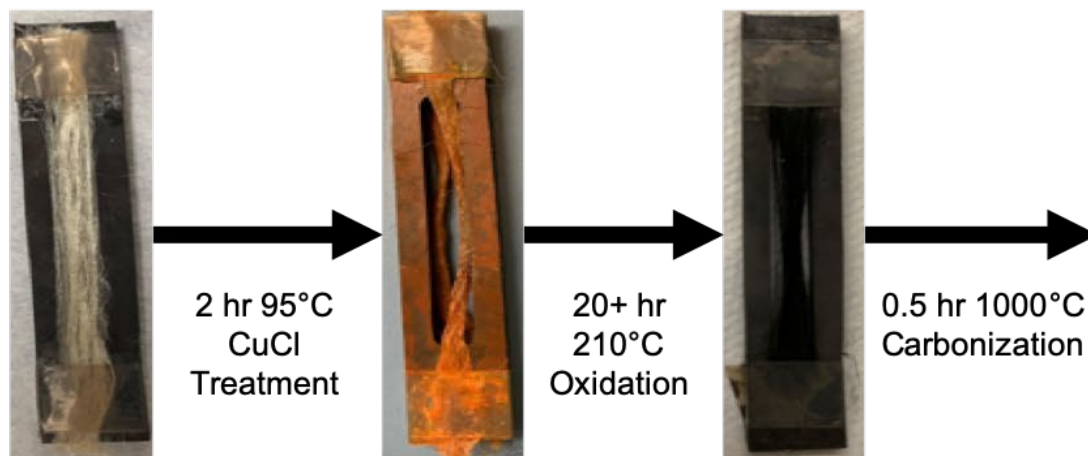
PE fiber properties fell below the DOE target but exhibited significant improvements with added graphene and proper tension (UVA).



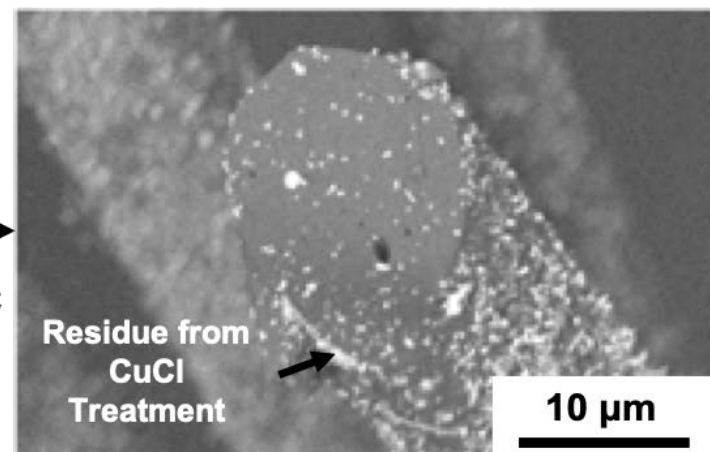
Thermogravimetric analysis of PE fibers before and after sulfonation (UVA).

## Nylon/Graphene Precursor

## Treatment Procedure for Nylon Fibers



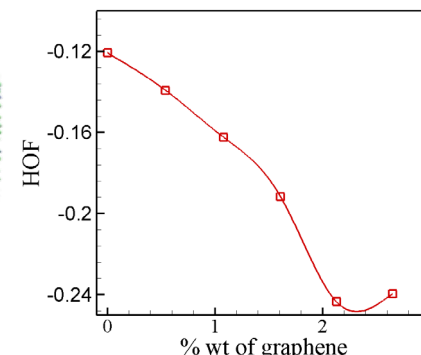
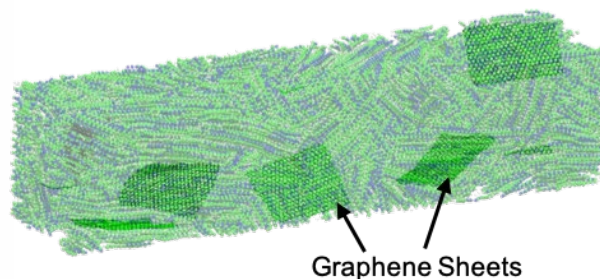
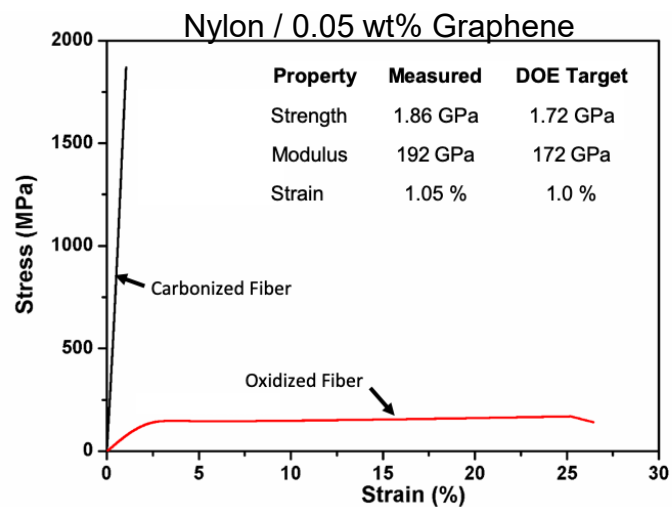
## Carbonized Nylon Fiber





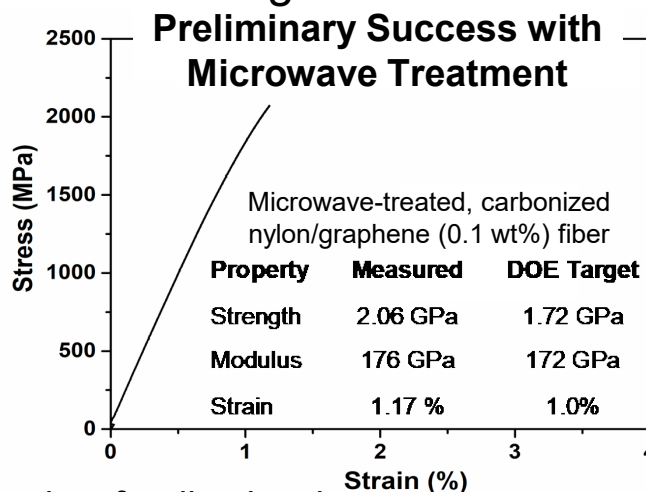
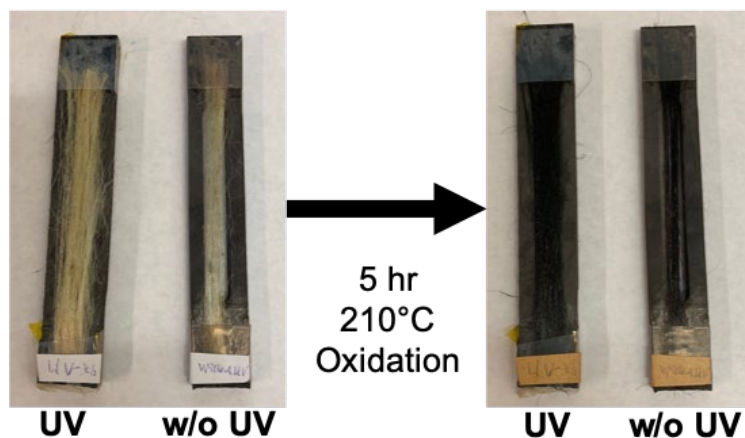
# Technical Accomplishments - FY19 / Year 2

- Nylon/graphene fibers have repeatedly met DOE mechanical property targets



MD simulations support experiments, indicating graphene acts to align polymers to enhance mechanical properties. Higher HOF magnitude corresponds to greater alignment of polymers (UVA).

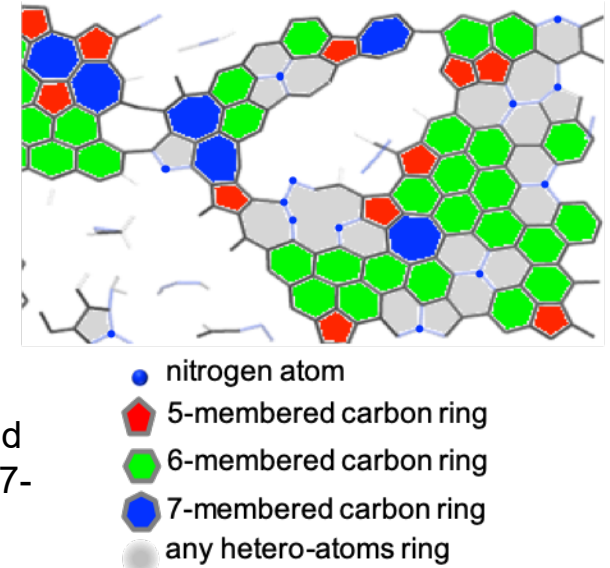
- Nylon, as a precursor, is much cheaper than PAN but requires >20 hour oxidation treatment. We are implementing **UV** and **microwave treatments** to dramatically shorten the oxidation treatment to achieve cost target.



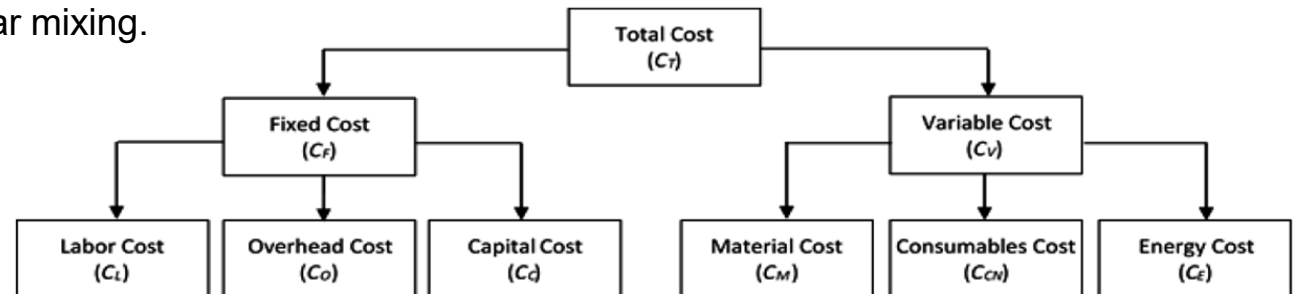
(Left) Preliminary success with a nylon/graphene fiber after a 700 W, 8 min microwave treatment and **only 5-hour oxidation** (UVA).

# Responses to Previous Year Comments

- “Relatively important elements related to embedded flaws in the atomic structure and whether [they are] stochastic in nature or a result of precursor chemical makeup and contamination would appear to be an important consideration to bake into a model/simulation.”
  - The benefit of ReaxFF simulations is the capability to integrate realistic chemistries into the modelling. Simulations are repeated to evaluate statistical trends and to predict defects, such as 5-, 7-membered ring formation, the degree of alignment of chemical structure, differing chemical bonds, etc.
- “The reviewer recommended there should be more emphasis placed upon [cost] component of the work.”
  - While the first year of the project focused on building a baseline ICME framework, in this second year, we have increased our consultation with Solvay and Oshkosh to project the costs of fiber project. According to industry, the key to effective cost management is to lower the cost of the precursor and processing time. In FY20, we will work with Solvay and Oshkosh to quantify the cost of scaled up production of the identified alternative fibers. Graphene is also a cheap additive produced from graphite via shear mixing.



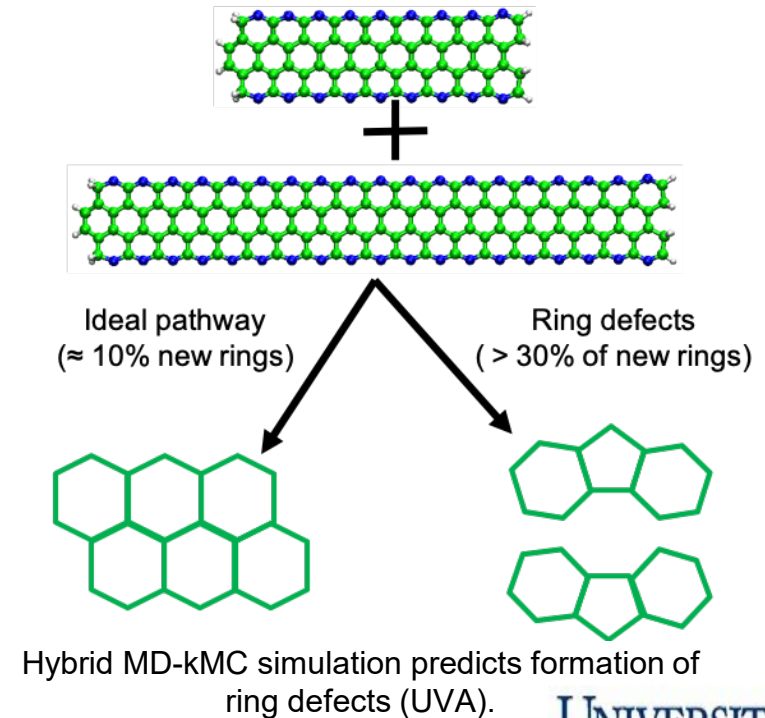
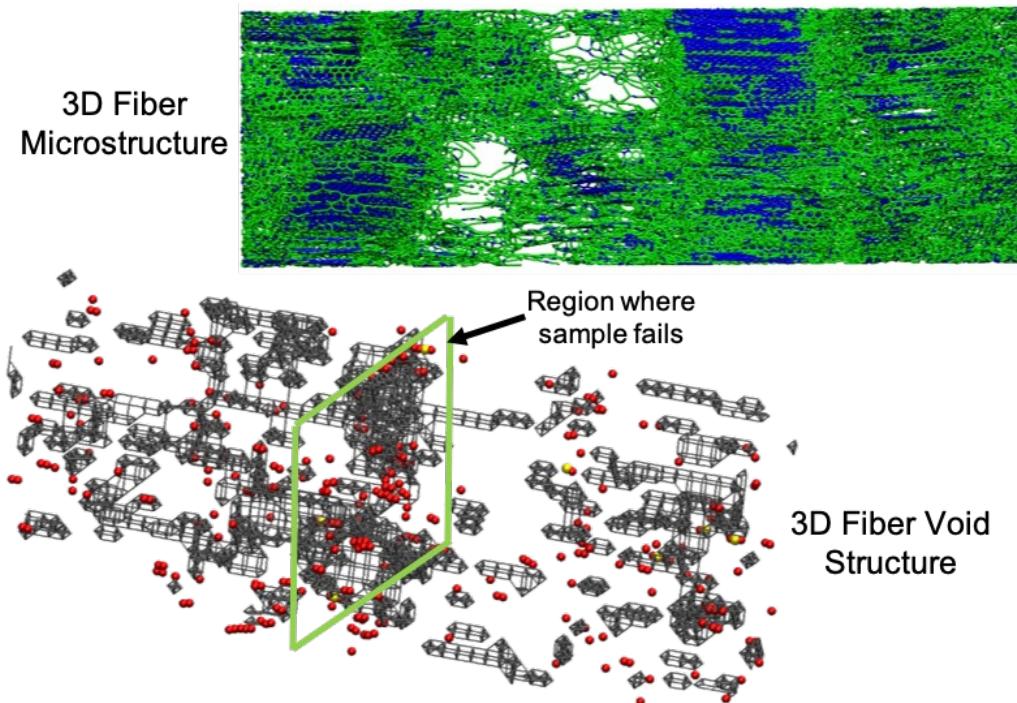
(Right) Gill, et al., Cost Estimation Model for PAN Based Carbon Fiber Manufacturing Process, 2016.





# Responses to Previous Year Comments

- “One issue moving forward [is] the heterogeneity of the precursor. The reviewer stressed that care must be taken to quantify the amount of imperfections tolerated in each step.”
  - ReaxFF and large-scale AIREBO simulations account for the heterogeneity of the precursor and carbon fiber; these simulations quantify the population of defects and specifically search for ways to minimize defects to suggest optimized production techniques. For example, AIREBO simulations report a Herman’s Orientation Factor as a measure of the alignment of precursor molecules within the fiber and relate this to strain.



Voids (gray) within the AIREBO MD simulation were tracked, showing large concentration associated with the location of fracture (UVA).



# Collaboration and Team Coordination



- **UVa Co-PI Zhigilei & Penn State Co-PI van Duin** — Subcontractors
  - Developing simulations of the chemical conversion of precursor fibers and large-scale MD simulations of fiber chemical-mechanical behavior
- **Oak Ridge National Laboratory** — Subcontractor
  - Experimental analysis of alternative precursors and large-scale pilot runs
- **Solvay S.A.** — Subcontractor
  - Provides PAN fiber for baseline testing, industry guidance on fiber characterization techniques and fiber cost analysis, and operates pilot—scale production of fibers derived from PAN and alternative precursors
- **Oshkosh Corporation** — Subcontractor
  - Industry insight on unique constraints and priorities for technology transfer from research laboratory to industrial production

# Remaining Challenges and Barriers

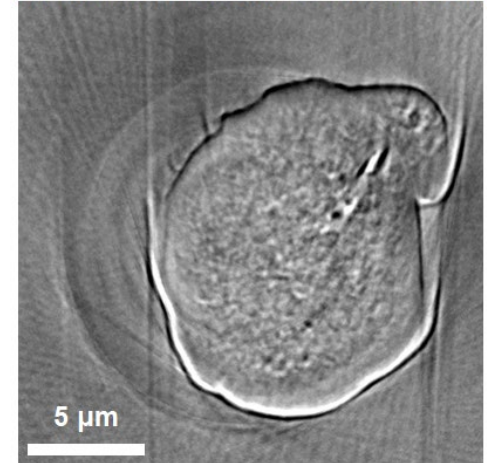
## Key Challenges

- **Challenge:** Limitation of lab-scale production techniques
  - Fibers have tendency to adhere together -> UVA uses heat treatment with steady air flow to help maintain individual fibers
- **Challenge:** Compatibility of PAN-ICME framework to alternative precursors (Nylon, PE, etc.)
  - ReaxFF simulations are being used to identify the chemical structure of these precursors through carbonization and will provide input structure for MD mechanics simulations
  - AIREBO simulations tend to overpredict strength due to artificial strain hardening and underestimated void volume -> UVA is using X-ray tomography to quantify fiber void volume
- **Challenge:** Nylon requires a 20+ hour stabilization treatment, which poses cost challenges
  - UVA has UV equipment and is performing statistical analysis of varied UV exposure and stabilization treatments to identify optimal procedure to maximize properties while reducing or eliminating this stabilization stage
  - Literature studies of UV treatment of PAN and lignin fibers show significant reductions of the stabilization stage
  - UVA is also conducting microwave thermal stabilization treatments as an alternative approach; preliminary work achieved target properties after 5 hour oxidation

0.1 wt% Graphene content

Smaller, fewer voids.

Fine interior texture (75-150 nm void size)



XCT scan of PAN/Graphene fiber acquired at National Synchrotron Light Source at Brookhaven Nat. Lab. (UVA / DE-SC0012704).

# Proposed Future Research

## Future Work

- **FY19** - Framework adapted to predict alternative fiber precursors
  - Continue efforts to optimize Nylon and PE fiber production (treatment duration, temperature, graphene content, etc.)
  - Complete investigation of UV and microwave treatments to reduce oxidation stage of Nylon fibers
  - Investigate pre-treatment of the Nylon precursor with CuCl
  - Confirm downselection of alternative precursors: PE and Nylon with added graphene content
- **FY20** - Computational framework integrated into testbed with 15% accuracy of production scaling strategies
  - Scalability/economics study of carbon fiber production
  - Detailed cost analysis with Solvay and Oshkosh
  - Finalize ICME framework with ReaxFF and AIREBO simulations
  - Complete mechanical testing and characterization of pilot-scale produced alternative fibers to validate ICME framework

# Summary

- The baseline **ICME framework has been established**:
  - **ReaxFF simulations** model the carbonization of the fiber, predicting the chemical structure, gas outputs, polymer alignment, etc.
  - These properties provide inputs to the **large-scale mechanics simulations**, which predict void size and distribution, polymer alignment, fiber strength, and strain
  - Preliminary ICME predictions have been validated with experimental work with PAN-based fiber
- On-going work is focused on identifying an alternative, low-cost precursor
  - ReaxFF simulations **predict ideal chemistries** for efficient carbonization
  - MD simulations **extend these chemistries to mechanical properties**
  - Experimental analysis of these chemistries has identified two promising alternatives: Nylon and PE fibers with added graphene content
  - **Nylon/Graphene fibers have met DOE mechanical property targets**

Property	w/o Micro. Trt	w/ Micro. Trt	DOE Target
Strength	1.86 GPa	2.06 GPa	1.72 GPa
Modulus	192 GPa	176 GPa	172 GPa
Strain	1.05 %	1.17 %	1.0 %

- Future work will generate a detailed industry cost analysis via pilot-scale production of the alternative fibers

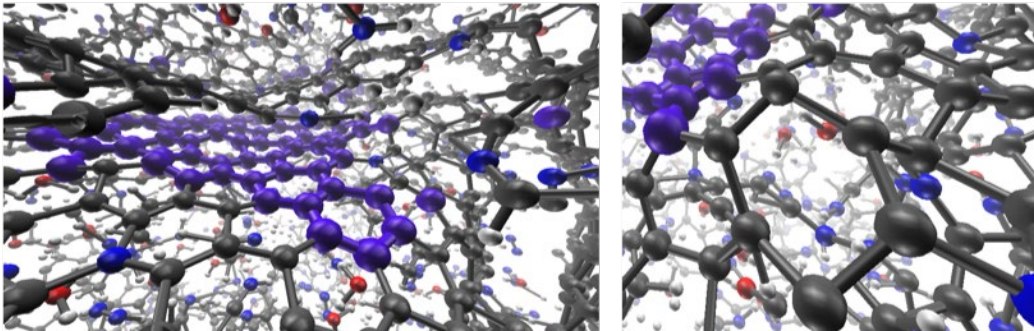
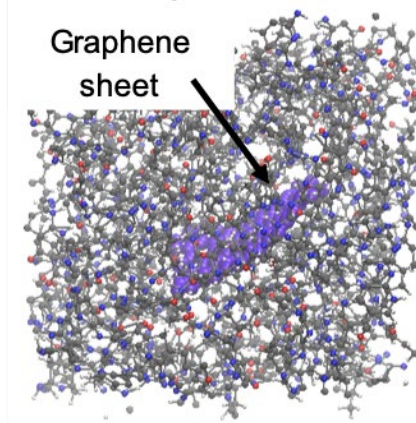
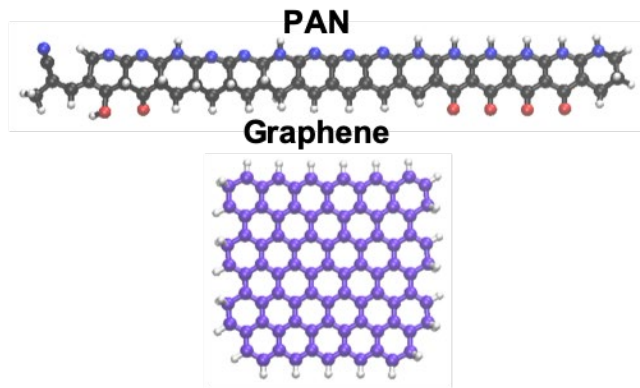
*Any proposed future work is subject to change based on funding levels.*



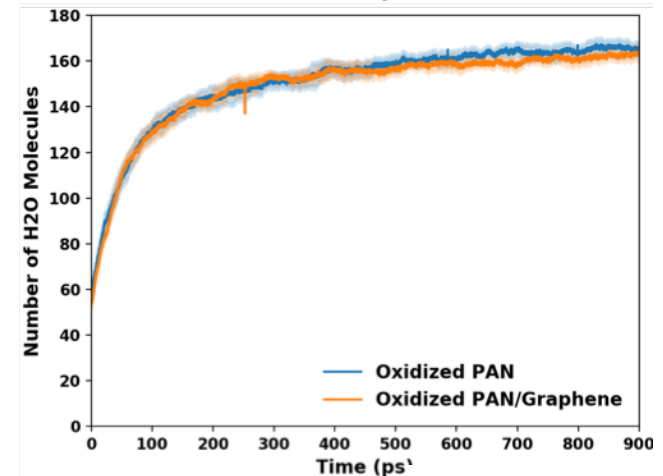
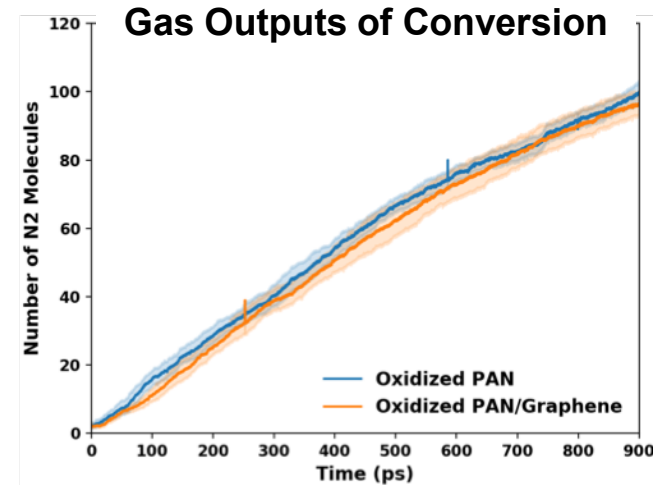
# Technical Backup Slides

# Technical Backup Slides - ReaxFF Simulations

- ReaxFF simulations provide critical insight into the chemical evolution of the precursor during carbonization, particularly the effect of added graphene content



Formation of 5-, 6-, and 7-membered rings occur at the edges of the graphene sheet (PSU)



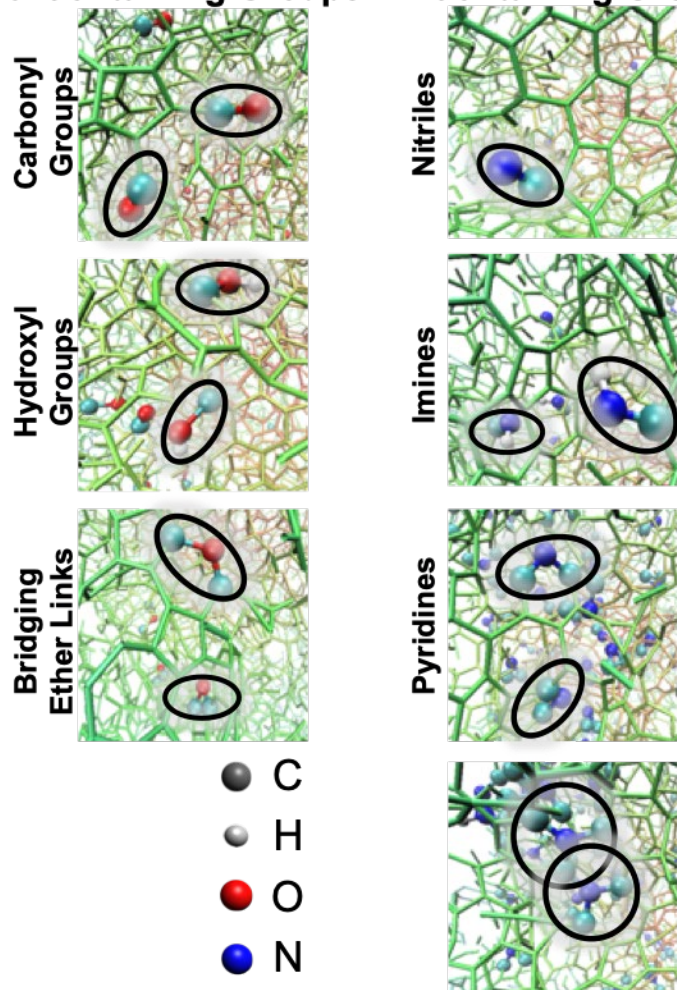
Graphene does not affect molecule production during carbonization (PSU)

# Technical Backup Slides - ReaxFF Simulations

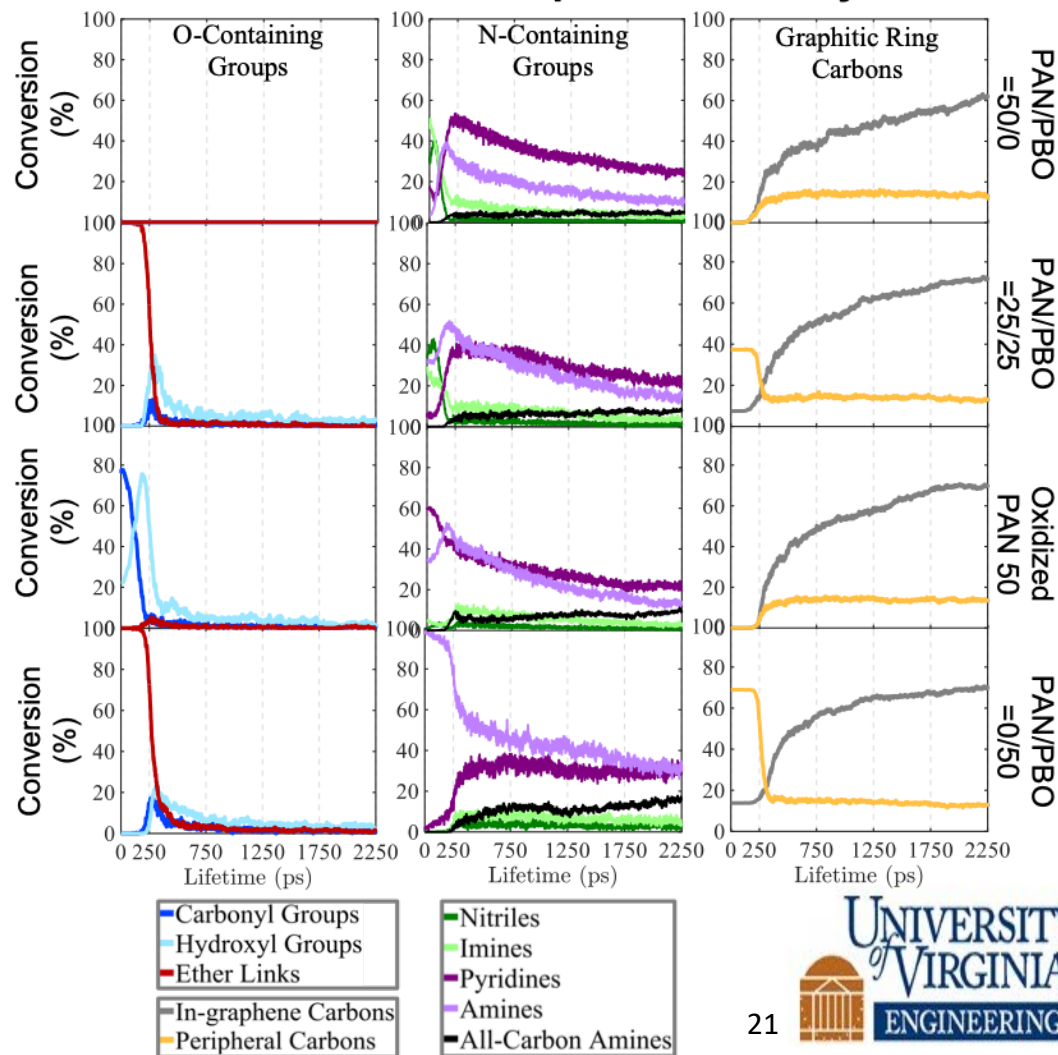
- Using ReaxFF, we found that oxygen-containing groups are more efficient in improving the graphitization process, achieving greater conversion percentages.

## Functional Group Search

### O-Containing Groups    N-Containing Groups



## Functional Group Lifetime Analysis

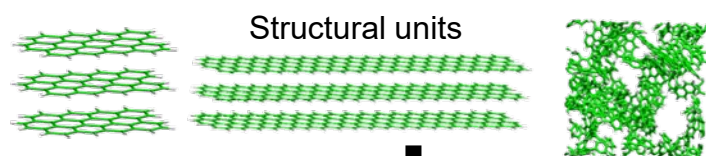




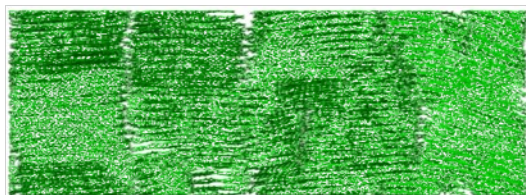
# Technical Backup Slides - Fiber Mechanics Model

- AIREBO simulations translate the ReaxFF-modeled chemical structure to mechanical properties and predict microstructural variation
- Simulations reveal direct correlation between degree of graphitization, fiber alignment, and modulus

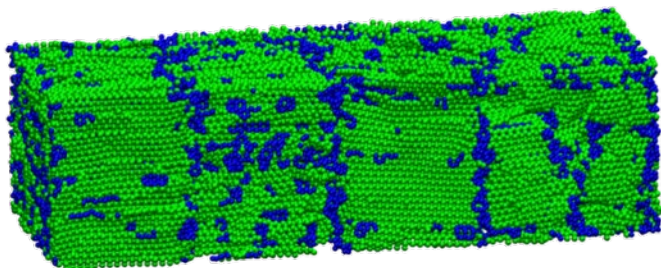
## Microstructure Generation



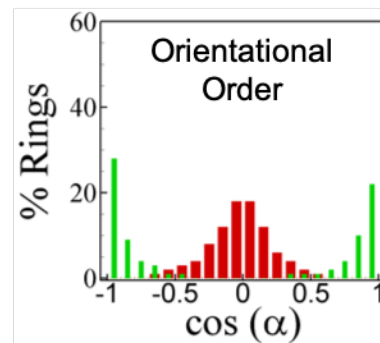
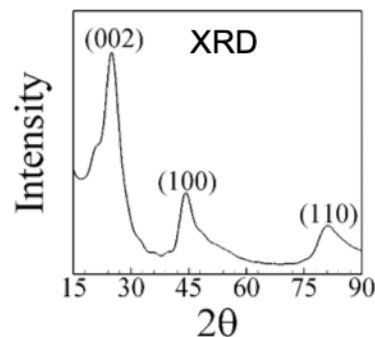
Build atomistic model



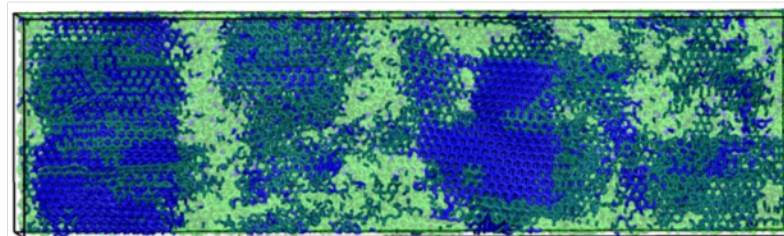
Reactive atomistic simulations for 3D microstructure



## Microstructure Characterization

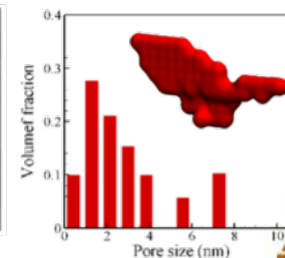
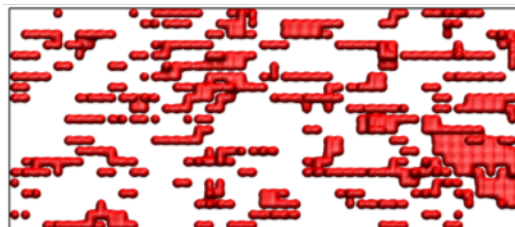


Polymer alignment quantified via Herman's orientation factor for rings



Degree of graphitization

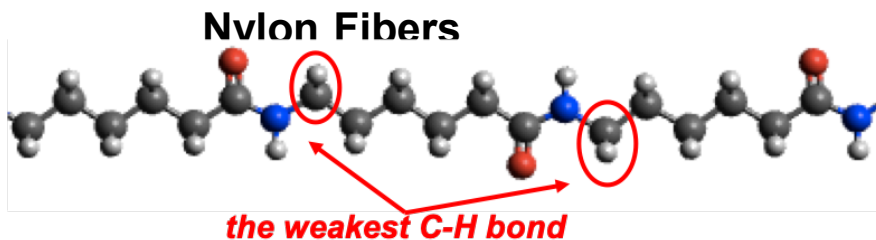
Graphite flakes shown by blue color



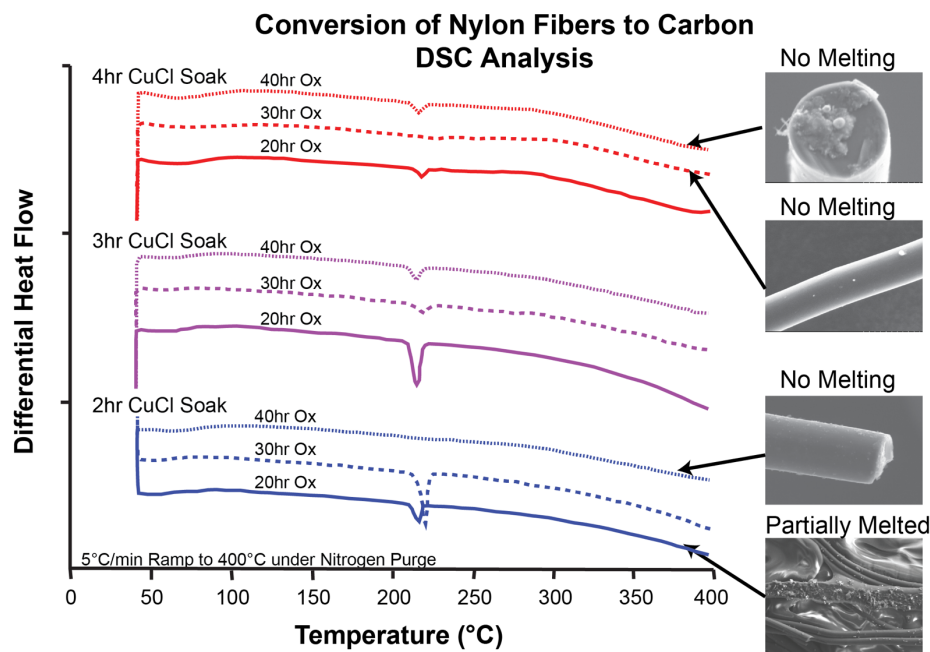
Pore size distribution

# Technical Backup Slides - Process Optimization

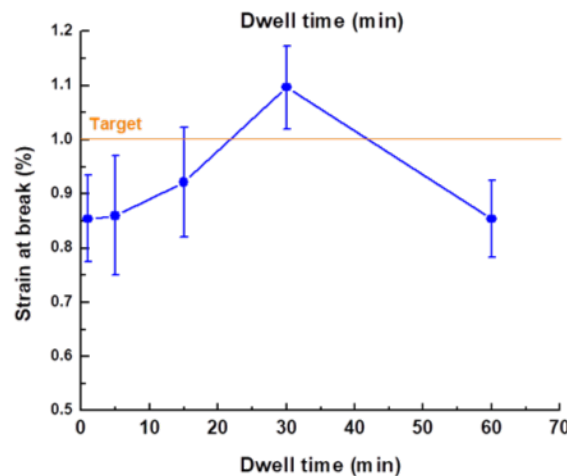
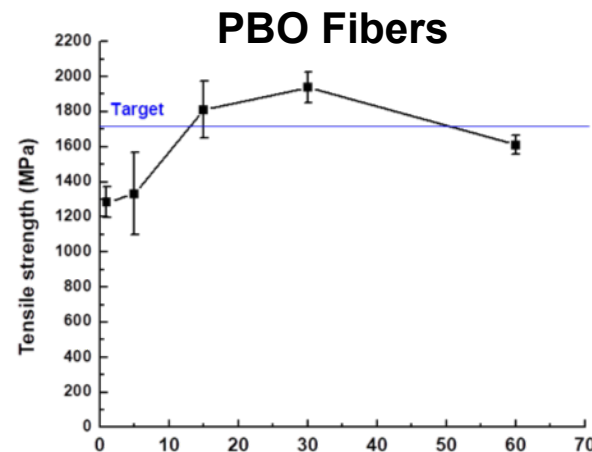
- Small-scale production, at UVA and ORNL, has been used to optimize the fiber production of PAN, PBO, Nylon, and PE fibers



DFT data reveal that CuCl can be efficient stabilizing species for Nylon due to destabilizing the hydrogen bonds via promoting the coordination complexes (PSU).



Parametric study of CuCl treatment to identify optimal stabilization procedure for Nylon fibers to render fiber infusible and avoid melting (ORNL).

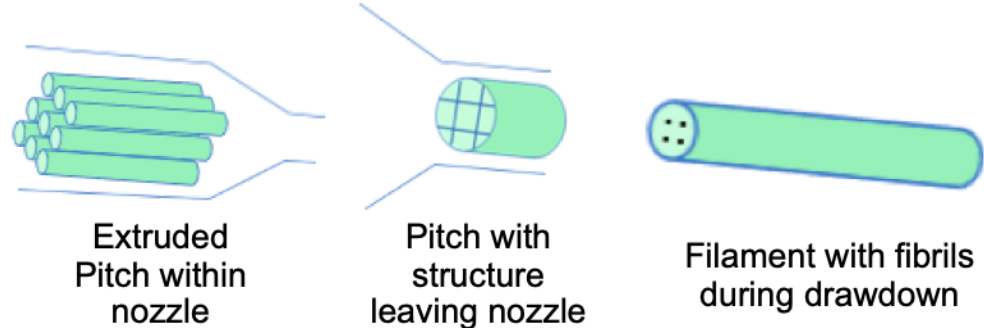
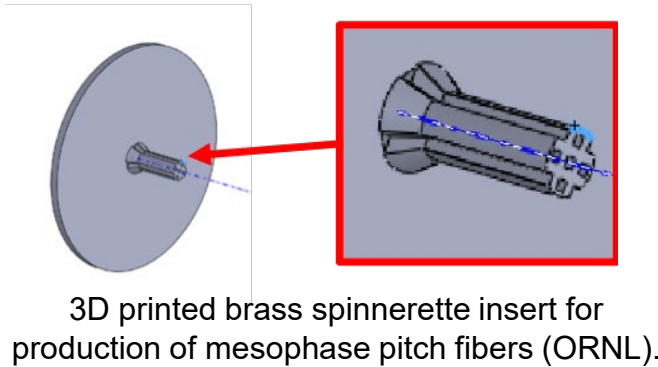


Optimization of carbonization dwell time of PBO fibers (UVA),

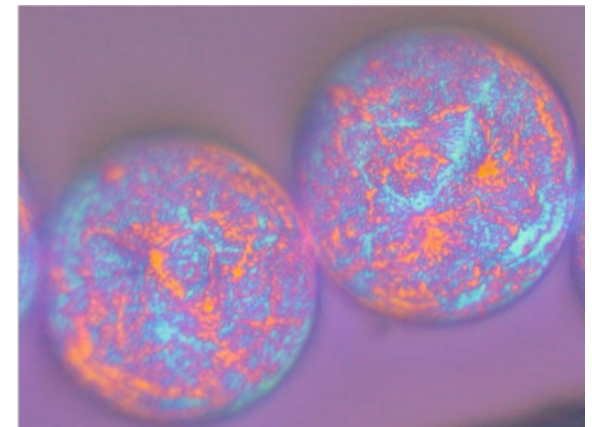
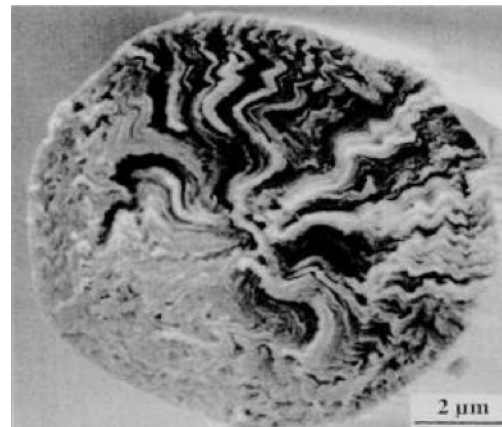
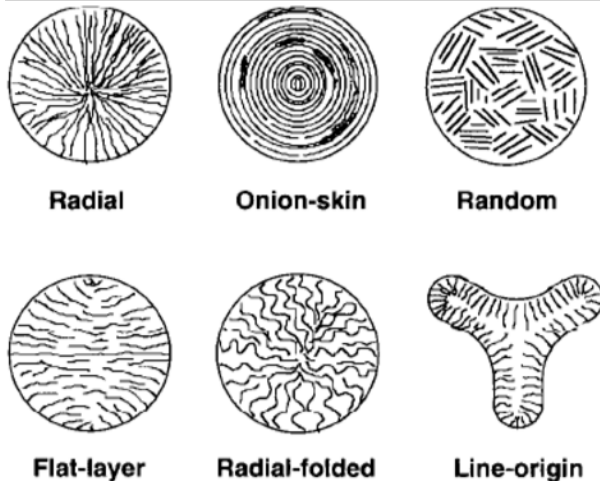


# Technical Backup Slides – Fiber Microstructure

- ORNL is also investigating the role of fiber microstructure on resulting properties using mesophase pitch fibers; this work will inform future fiber structural design



The spinnerette introduces fibrils within the pitch fiber, creating a controlled microstructure, which will be tested to evaluate effect on mechanical properties (ORNL).



(Left) Schematics of documented fiber/graphitic structure observed by Fathollahi and White and (right) SEM of graphitic structure in pitch fiber (J. of Rheology, 1994; Biennial. Conf. on Carbon, San Diego, 1995).

Preliminary polarized light images of first pitch fibers produced via new spinnerette indicate new fiber microstructure (ORNL).