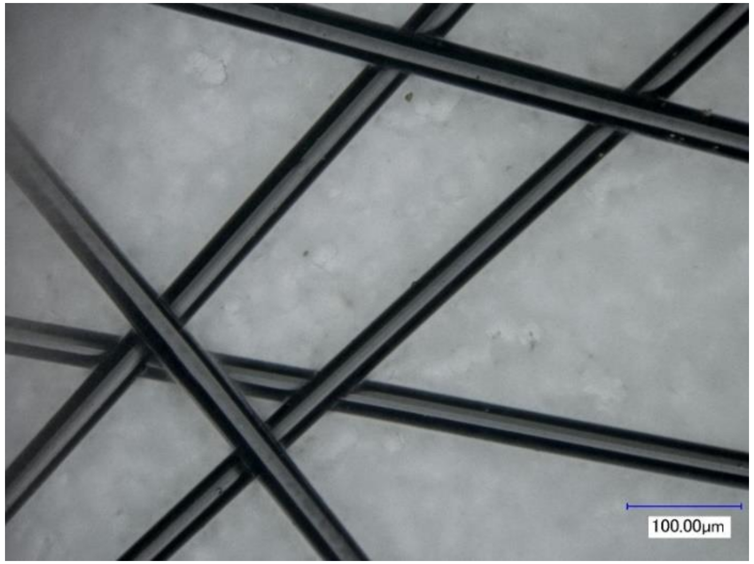
Integrated Computational Materials Engineering (ICME) Predictive Tools for Low-Cost Carbon Fiber



Western Research INSTITUTE

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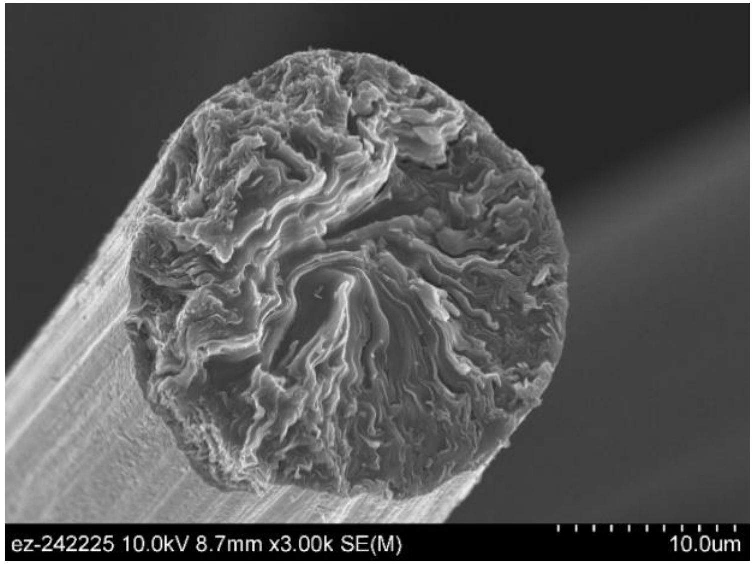


Project ID #: MAT125 June 3, 2020

Overview

Timeline:

Start: October 2017 (3 month no-cost extension in 2018 putting BP1 end December 2019)
End: June 2021 (6 month no-cost extension in 2019 putting BP2 end June 2020)
Completion: 65%

Budget:

Total: $5,242,820
DOE Share: $3,745,413
Cost Share Total: $1,497,407 (28.6%)
FY 2018 DOE Share: $1,371,684 / FY 2018 Cost Share: $792,199
FY 2019 DOE Share: $821,245 / FY 2019 Cost Share: $353,384

Barriers (US Drive Material Technology Roadmap for CF Composites)

-Low-cost high-volume manufacturing of CF of appropriate mechanical properties for vehicles
-Low-cost CF starting materials to make larger utilization of CF in more vehicle components
-Predictive modeling from the molecules of starting materials to CF properties

Partners with WRI

Oakridge National Laboratories (ORNL)
Massachusetts Institute of Technology (MIT), Jeff Grossman Group
Southern Research Institute (SRI)
Advanced Carbon Products, LLC (ACP)/ Koppers
University of Wyoming (UW)
Ramaco Carbon, LLC (RAMACO)
Solvay Composites - Industry Advisor

Relevance & Objectives

Overall Objectives

-Develop an integrated computational materials engineering (ICME) suite capable of predicting select mechanical properties of carbon fiber (CF) tow all the way down to the feedstock molecules

-Provide a map of common high-volume low-cost major feedstocks from petroleum, coal and biomass relative to CF production and end CF mechanical properties

Technical Targets

-ICME: ≥ 15% of predicted properties

-Mechanical properties of CF resin: strength (250 Ksi), modulus (25 Msi), strain (1%)

-Cost: ≤ $5 lb

Impact

-Reduction in vehicle mass

- Less fuel/energy consumption, and less wear on transportation infrastructure (roads, bridges, parking lots, tollways, etc.) and load bearing vehicle components

-Accelerate sustainable implementation of affordable light weight CF in vehicle use

- Achieving the above mentioned objectives, while also providing long term sustainability by providing a portfolio of different materials capable of achieving the same desired properties that mitigates the risks and market fluctuations associated from becoming exclusively dependent on any one high-volume source of feedstock, while being flexible for the future

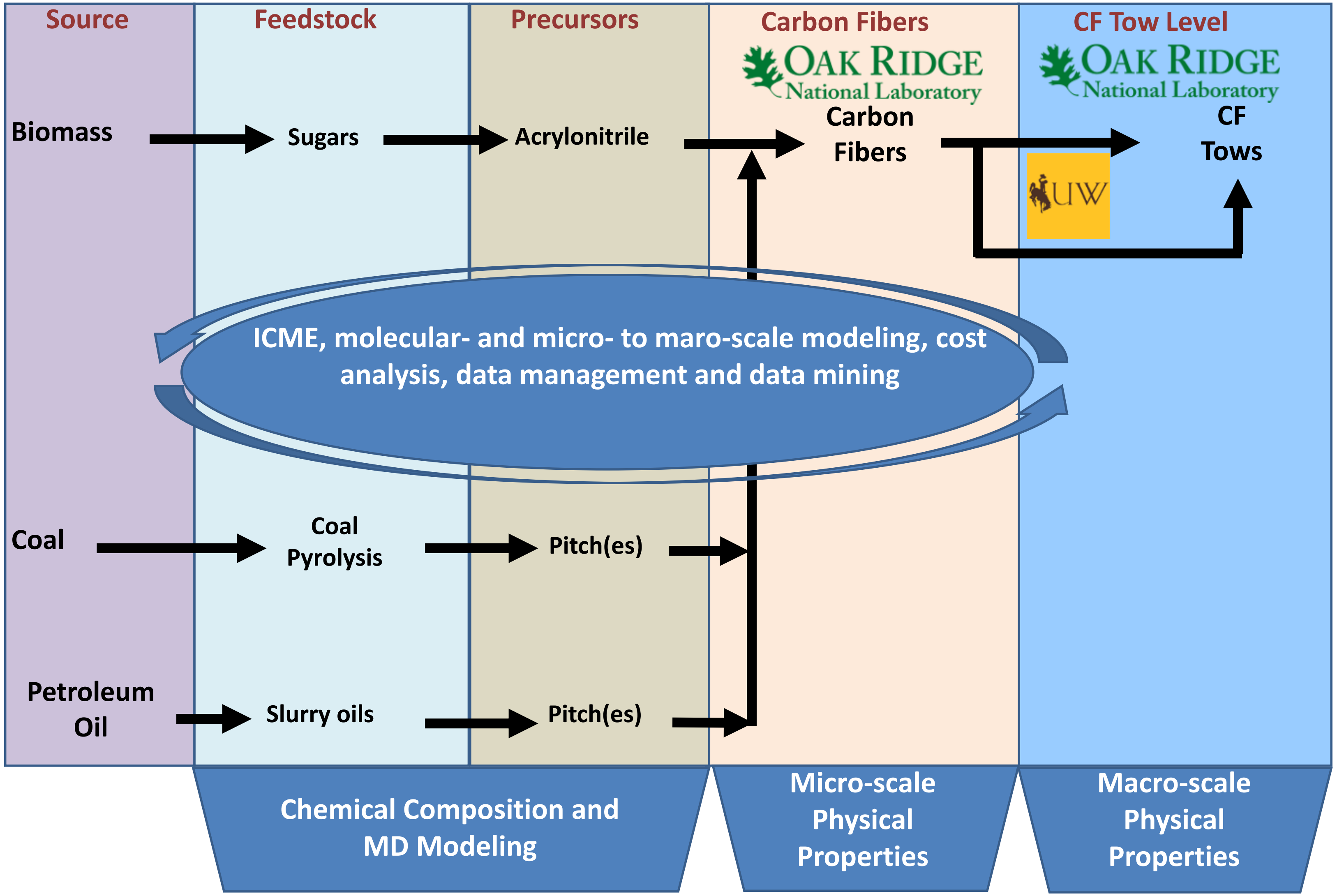
Milestones

Budget Period, FY	Milestones (M) and Go/No-Go (GNG) Decisions	Status (Date)
1, 18	M: Major subcontracts executed	Complete (April 18)
1, 18	M: Raw Material feedstock verified as acceptable to process into CF	Completed (Jan 18)
1, 18	M: Precursor verified as acceptable to make CF	Completed (Nov 18)
1, 18	GNG: CF strength and cost coals achieved	Completed (Dec 18)
2, 19	M: Verify Macro-level finite element models, tow uniaxial creep and mechanical properties, +/- 15%	On Target
2, 19	M: Micro-level models validated, +/- 15%	On Target
2, 19	M: Establish CF tow strength-weight ratio, 30-15% less than steel	On Target
2, 19	M: Rank precursors and CF vs. DOE goals using machine learning	On Target
2, 19	GNG: Scaled up precursors produce CF with strength and cost goals	On Target

FY 2020 Milestones: macro-scale modeling ± 5%, micro-scale modeling ± 5%, CF tow strength to weight ratio is 30 to 50% steel, use machine learning to identify and rank precursor materials and combinations for CF

Go/No Go: Meets DOE strength and < $5/lb for scaled up batches of precursor material

Approach


Source
Feedstock
Precursors
Carbon Fibers
CF Tow Level
Biomass
Sugars
Acrylonitrile
Carbon Fibers
CF Tows
ICME, molecular- and micro- to maro-scale modeling, cost analysis, data management and data mining
Coal
Coal Pyrolysis
Pitch(es)
Petroleum Oil
Slurry oils
Pitch(es)
Chemical Composition and MD Modeling
Micro-scale Physical Properties
Macro-scale Physical Properties

Accomplishments for FY 2019

Bio-acrylonitrile (bio-ACN) – Southern Research

Feedstock
(Sugars)
Wheat Straw
Corn Stove Biomass
Sugar Cane Bagasse
Shorghum Straw
Hybrid Poplar

Impurities (Organic/Inorganic)
(Range of each impurity was mapped)
Organic: furfural, acetic acid, formic acid, acetate, phenolics, aliiphatic acids, aromatic acids, hydroxymethylfuran
Inorganic: SiO_2, Al_2O_3, TiO_2, Fe_2O_3, CaO, MgO, Na_2O, K_2O, P_2O_5, Cl

Intermediate
bio-ACN, ≥99.2%

Impurities
Water and Acetonitrile

CF Production (ORNL)
Bio-ACN/methyl acrylate
153,000 Daltons
Carbonization

Scaled Up CF Properties (ORNL)
CF Diameter 7.74 ± 54.0 (µm)
1512 filament tows
Strength: 328.9 ±54 (ksi)
Modulus: 30 ±1 (Msi)
Strain: 1.11 ±0.15 (%)

Cost: Bio-ACN price driven by sugar price can range from \$0.59 – \$0.93/lb

Accomplishments for FY 2019

Coal Tar Pitch (CTP-Koppers) – Western Research Institute

Feedstock
CTP:
High temperature from metallurgical coal

Impurities (Physical/Chemical)
Physical: primary quinoline-insolubles (coal/coke) 3 – 17 wt%, > 0.22 microns
Chemical: heteroatoms of O (0.9-1.5 %), N (0.9-1.0 %) and S (0.4-1.0 %)

Intermediate
Mesophase Pitch:
1L, 400 °C with flow inert gas, variable times

Properties
Mesophase content: 60-95%
Softening point: 310-330 °C
Carbon residue: 80-95 %
H/C: 0.46-0.49

CF Production (ORNL)
75-85% Mesophase
20 °C Softening Pont
Carbonization

Single Shot CF Mechanical Properties (ORNL)
CF Diameter 17 (μm)
Single filament (scaled up MP)
Strength: 333 (ksi)
Modulus: 40 (Msi)
Strain: 0.95 (%)

Cost: CTP ≈ $0.25-$0.4/lb; filtration, mesophase, side products ≈ $1.5/lb, CF production cost ≈ $3.6/lb, economics are improved from the recycle or selling of mesophase effluent.

Accomplishments for FY 2019

Petroleum Pitch (PP) – Koppers

Feedstock
PP:
Produced from FCC Decant Oil

Impurities (Physical/Chemical)
Physical: quinoline-insolubles (catalyst fines) >0.05 wt%, > 0.22 microns
Chemical: heteroatoms of O (0.61 %), N (0.19 %) and S (0.32 %)

Intermediate
Mesophase Pitch:
Koppers

Properties
Mesophase content: 65-75%
Softening point: 298 °C
Carbon residue: >77 %
Sulfur 0.24 - 0.28

CF (ORNL)
65-75+% Mesophase
298 °C Softening Pont
Carbonization

Single Shot CF Mechanical Properties (ORNL)
CF Diameter 21 (µm)
Single filament (scaled up MP)
Strength: 263 (ksi)
Modulus: 55 (Msi)
Strain: 0.57

Cost: PP mesophase from FCC slurry oil using ACP isotropic and mesophase processes < $1.5/lb, CF production cost ≈ $3.6/lb, mesophase economics are based on petroleum refinery scale process.

Accomplishments for FY 2019

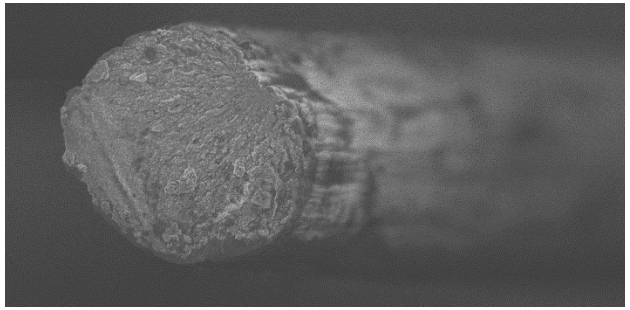
CF Spinning – ORNL

- **Scaled up polymerization of bio-ACN to bio-PAN with methyl acrylate and solution spinning (1512 filament tows)**
  - **Stabilization, carbonization, optical microscopy and mechanical properties**

Bio-PAN

As Spun Fibers

Stabilized & Carbonized CF



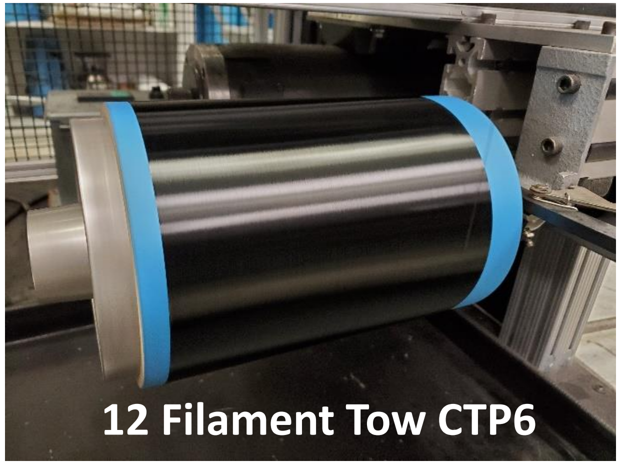
SEM of Bio-PAN CF
7-8 µ diameter
Strength: 328.9 ±54 (ksi)
Modulus: 30 ±1 (Msi)
Strain: 1.11 ±0.15 (%)

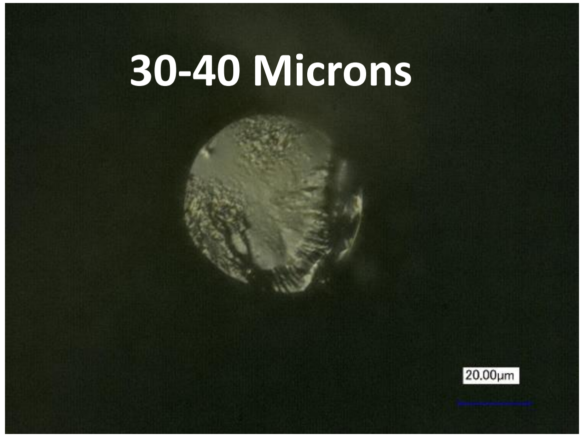
Accomplishments for FY 2019

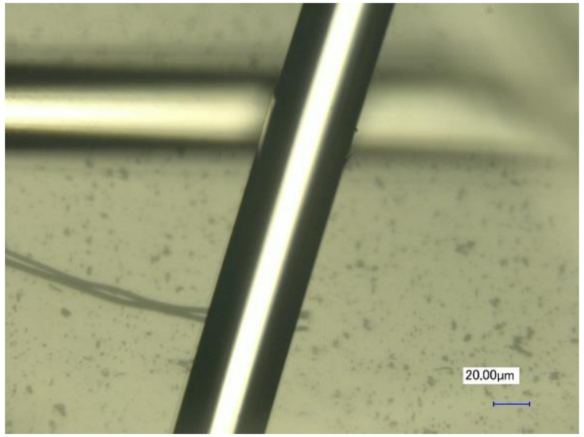
CF Spinning – ORNL

- **Melt-spinning of scaled up batches of CTP and PP mesophase (validation of materials), and scaled up multi-filament melt spinning**

Multi-filament melt spinner

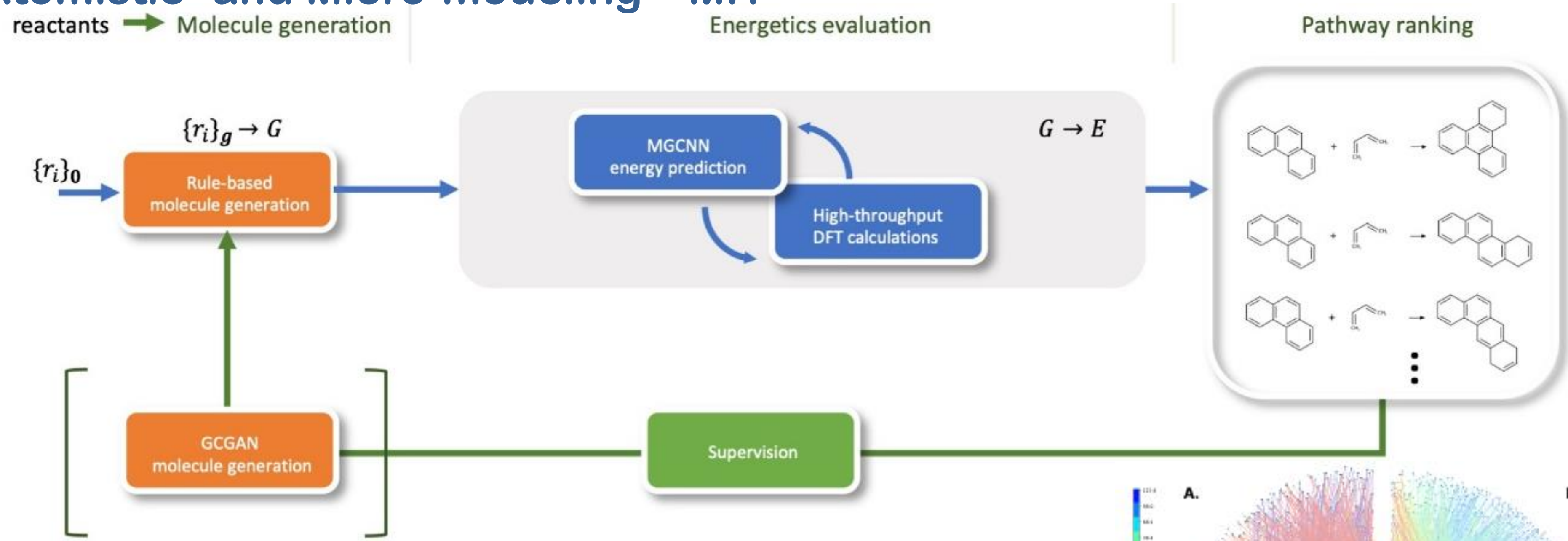


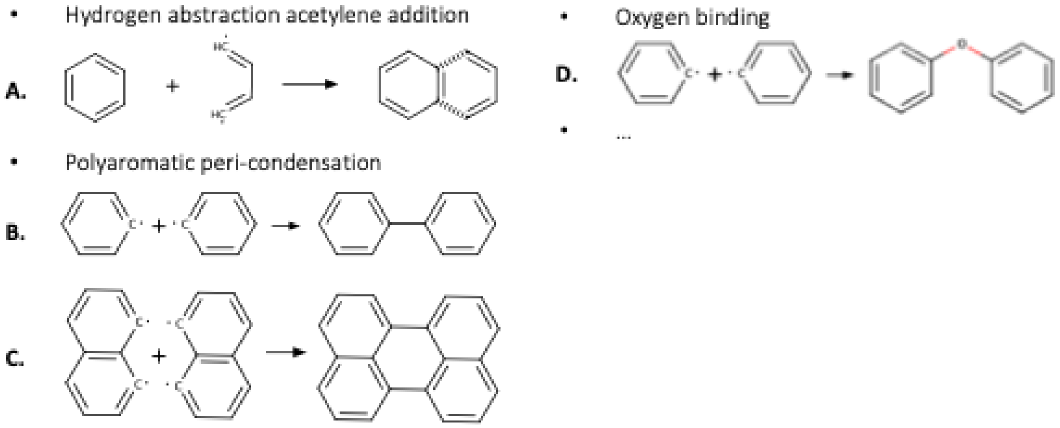


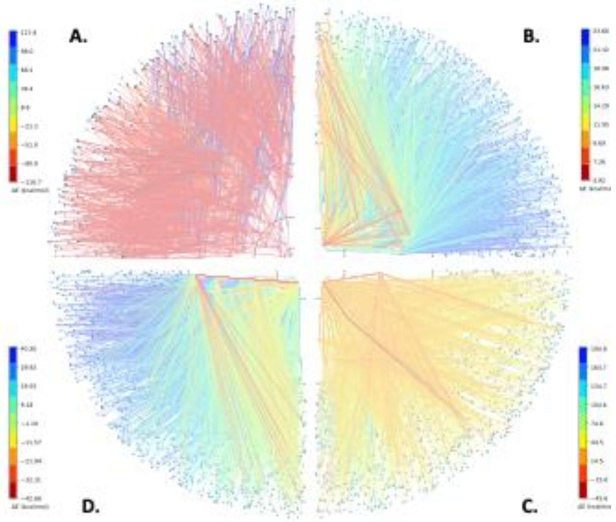


Accomplishments for FY 2019

Pitch Atomistic- and Micro-modeling – MIT







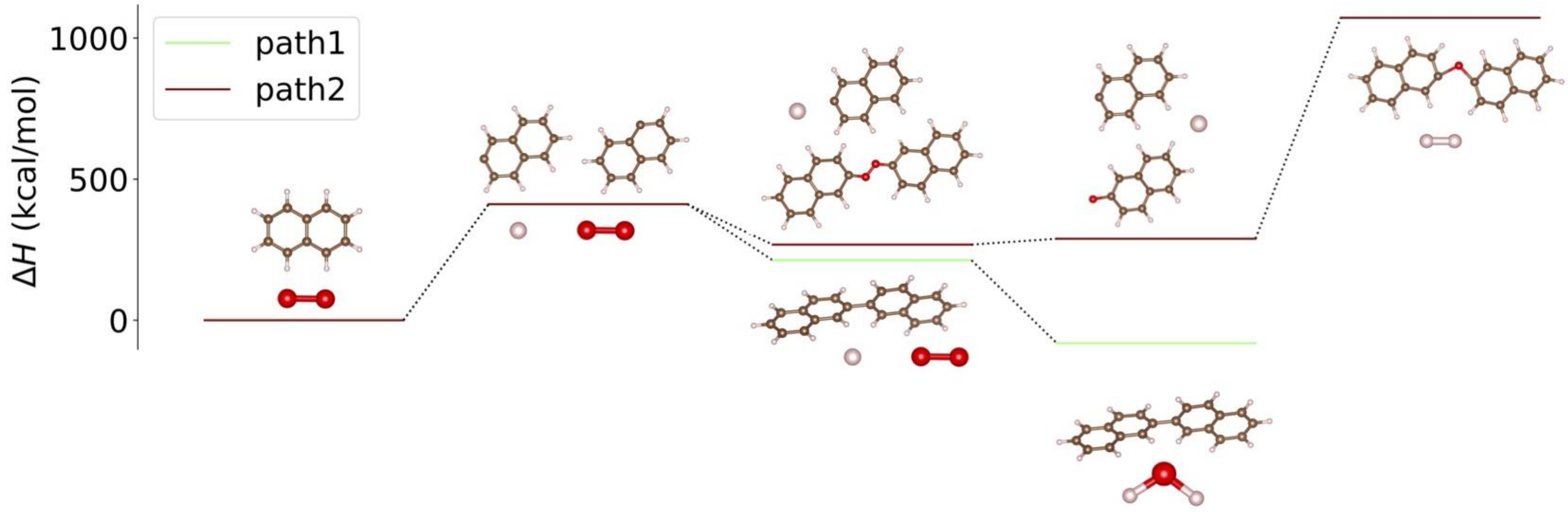
Accomplishments for FY 2019

Pitch Atomistic- and Micro-modeling – MIT

Stabilization (Oxidation): PP oxidizes to significantly take up more oxygen than CTP at the same temperature.

-Investigating effect of alkyl substituent on PP vs. CTP

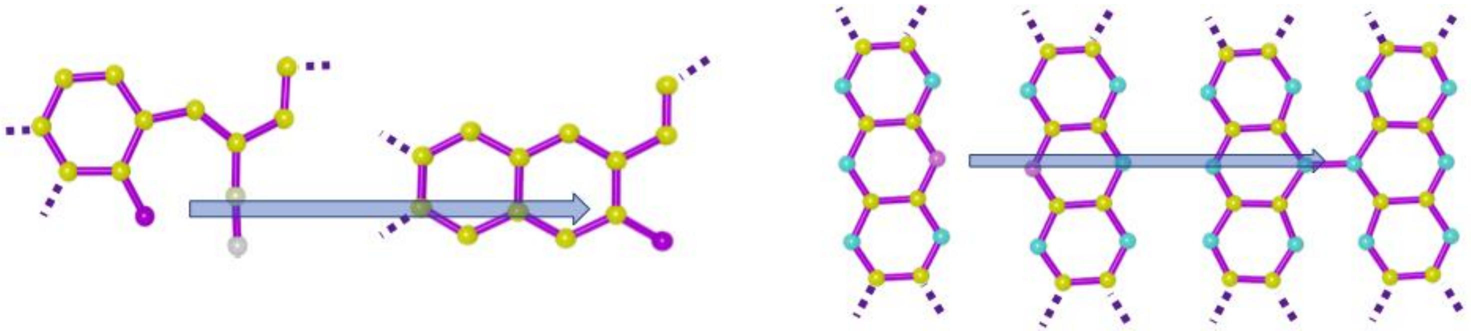
-Investigating differences in solid and volatile products for PP vs. CTP



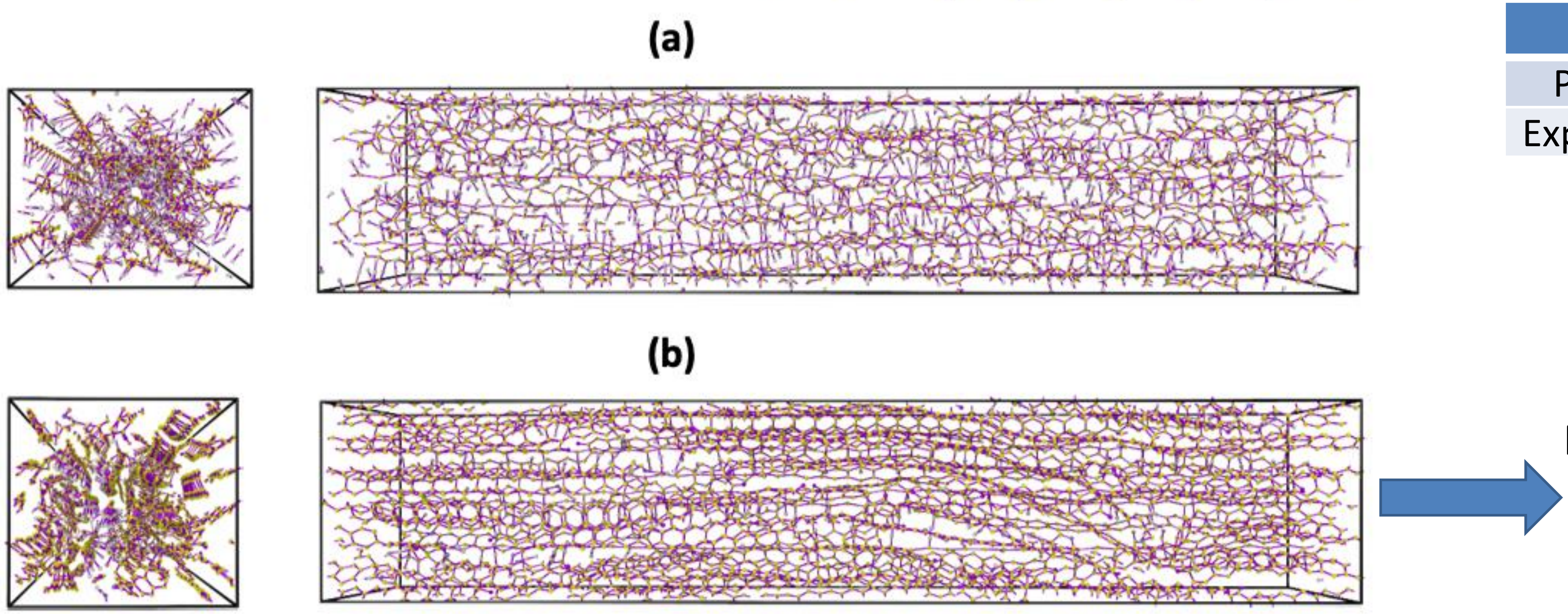
Accomplishments for FY 2019

PAN Atomistic- and Micro-modeling – MIT

Coarse-grained Molecular Dynamics (CGMD)



CGMD	Young's modulus
Predicted	221 GPa
Experimental	231 GPa (Solvay Thornel T-300)

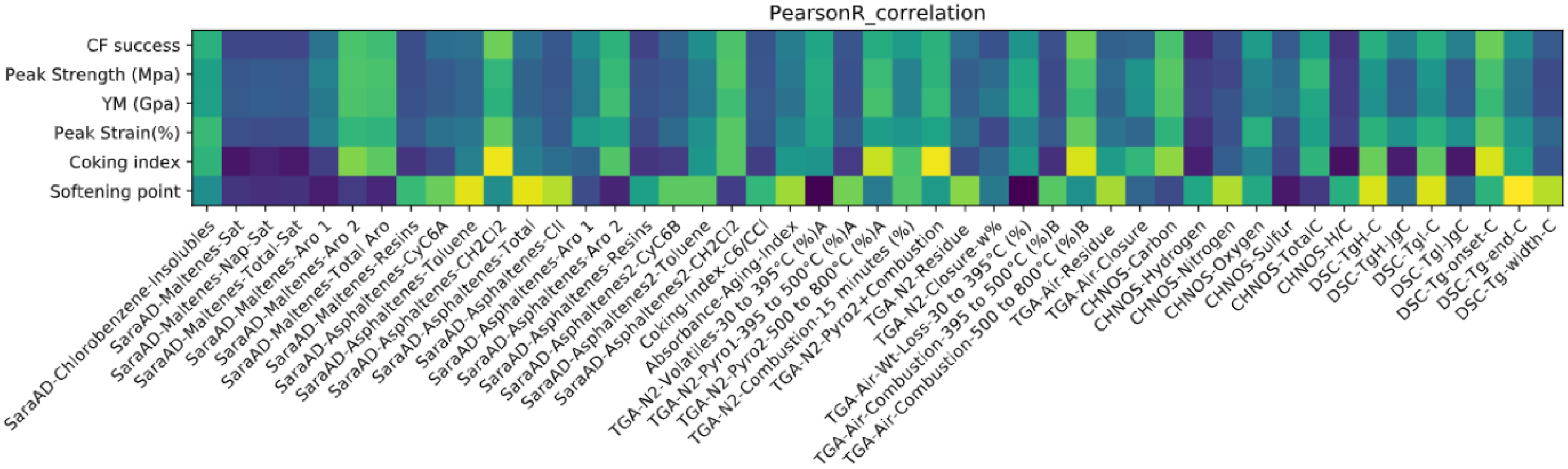


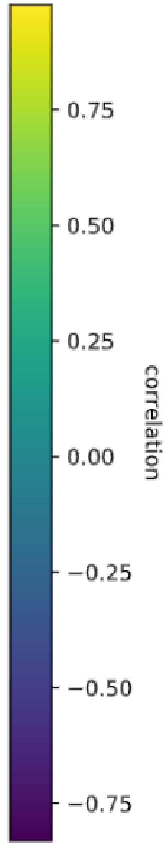
More ordered PAN ladder structure

Accomplishments for FY 2019

Modeling– Machine Learning (WRI/MIT)

Heat Map to Down-Select Most Important Characterization Parameters to Reduce Overfitting





Machine Learning

Physical Input: Softening Point, Optical Microscopy, Differential Scanning Calorimetry, Thermogravimetric Analysis, Insolubles

Chemical Input: SAR-AD^{TM}, LDI-MS, FTIR, Fluorescence Spectroscopy, Elemental Composition

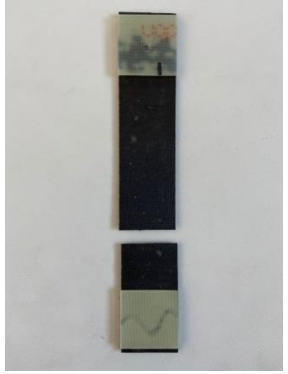
Correlation Output: FTIR, TGA (coking value/carbon residue), Fluorescence, Softening Point

Accomplishments for FY 2019

CF Resin Composites and Macro-Modeling – University of Wyoming

Tensile Testing

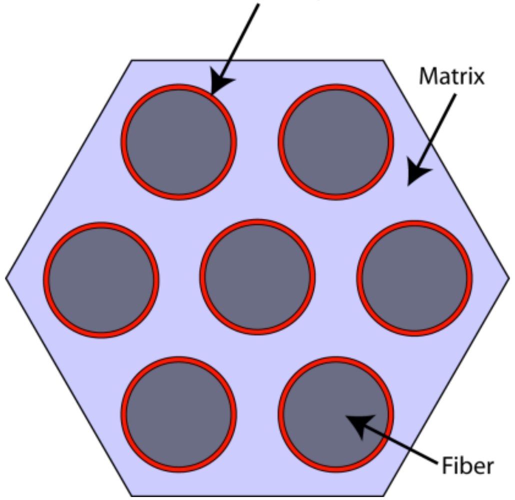
90 ° Tensile



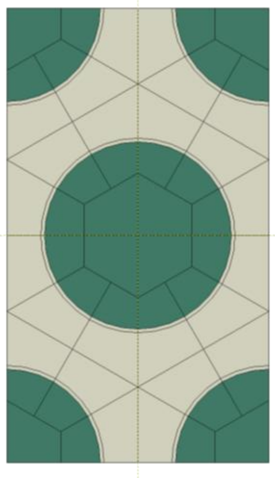
45 ° Tensile

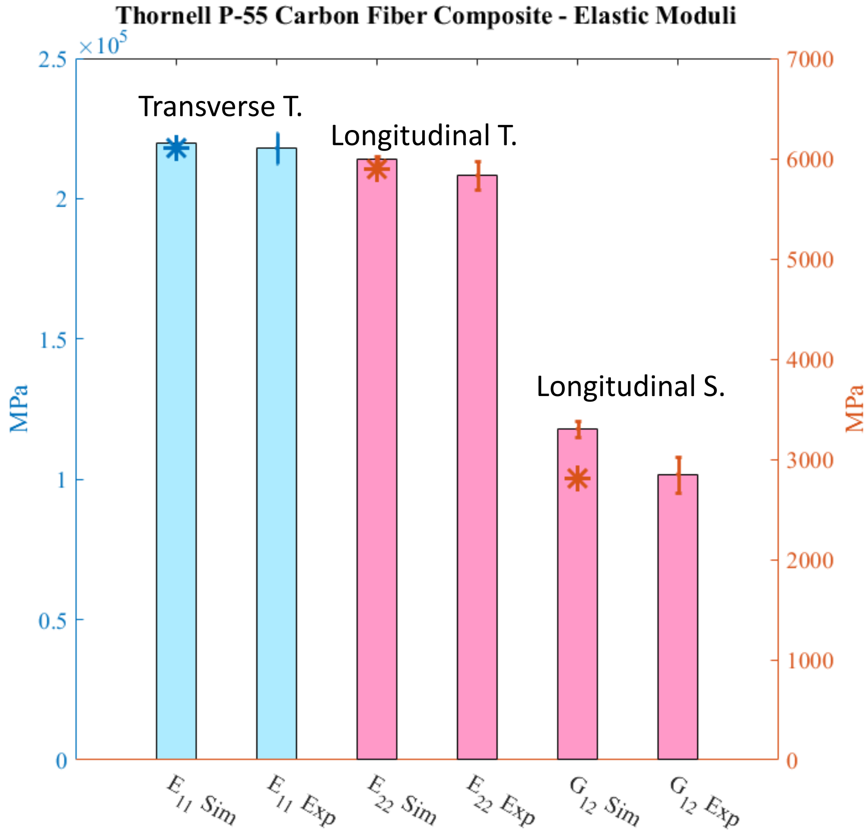
Hexagonal Packing

Interface/Interphase



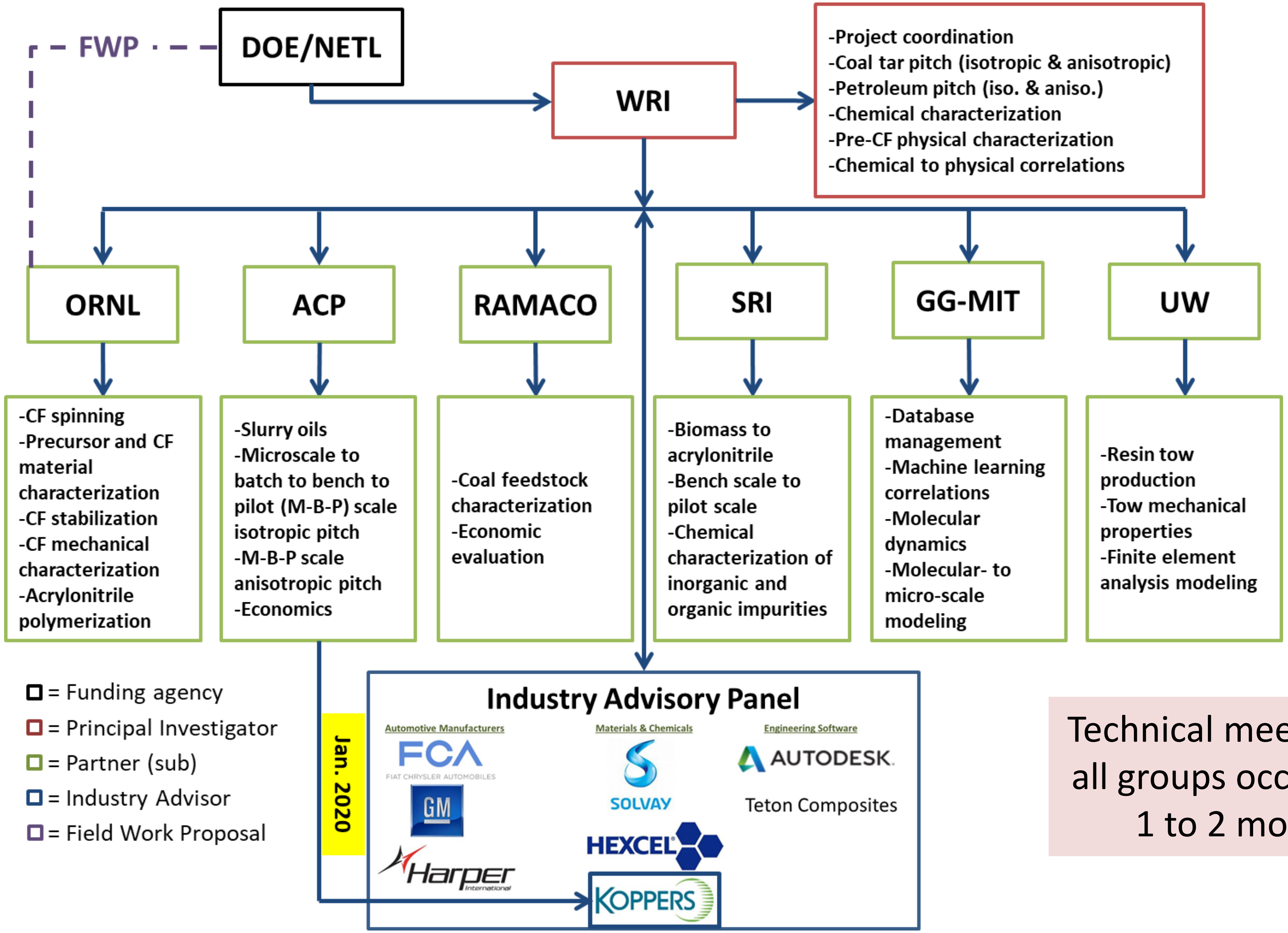
Representative Volume Element





Models are within ±15%

Partnerships / Collaborations



Technical meetings for all groups occur every 1 to 2 months

Response to Previous Year Review Comments

Reviewers: Clarity for techno economic analysis (TEA) details

Response: Sujit Das (Techno economic Analysis of Coal Pitch Carbon Fiber Manufacturing, Carbon 2019, Lexington, KT. July 14-19 2019.) Shows that when considering all the production costs the cost for producing CTP by melt spinning the total cost of production is estimated to be $0.74/lb for labor, $2.54/lb for capital, $0.5/lb for energy and $1.94/lb for mesophase pitch (TOTAL = $5.72). However, this considered graphitized fibers ($0.34/lb) but graphitization is not necessary to produce CF necessary for the current requirements. Also, ACP models show that working at larger scale the production of mesophase pitch can be brought down to a sellable cost of $1.50/lb. Scale up and not applying graphitization this saves $0.78/lb brining the overall cost down to $4.94/lb.

Independent analysis by RAMACO put PP and CTP at about the same cost of $3.56/lb and bio-PAN at $6.56. Production costs for PAN based CF is fundamentally different because of the solution spinning process and strict stabilization and carbonization requirements. We are continuing to work with ORNL to refine these values.

Reviewers: Impurities and their relationship to product variability and elongation

Response: Elongation values slightly < 1% for bio-PAN generated in BP1 may have been partially due to impurities from acetonitrile and water. Each sample of bio-ACN was checked by GCMS to quantify known impurities. A more likely explanation is due to the formulation of the polymer with comonomer. Scaled up batches of bio-PAN for BP2 showed significantly better elongation > 1%.

Regarding, CPT and PP CF, significant characterization of the isotropic pitch and mesophase pitch samples were obtained in BP1, additional characterization of scaled up batches is occurring in BP2. BP1 CF were obtained using a single-shot melt spinner which was prone to higher variability/noise due to a lack of thermal control after the samples left the spinneret. BP2 CF are produced using multi-filament spinner with significantly better thermal controls. This should help determine variability/noise and better links to the effect of impurities. For BP1 SEM analysis were performed on several broken and failed CF samples which showed most of the defects were due to CF spinning and processing.

Proposed Future Research*

Feedstock/Intermediate FY20

Coal Tar Pitch

-Continue scale up of mesophase CTP for CF multi-filament production

-Continue physical and chemical characterization of intermediates/precursors/mesophase from the scaled up products and compare to BP1 materials

Slurry Oil Pitch

-CF multi-filament production

-Continue physical and chemical characterization of intermediates/precursors/mesophase

Bio-acrylonitrile

-Understand variability in bio-ACN product during production in the SR pilot plant

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

Proposed Future Research*

CF, Modeling and Database, Resins, Economics FY20

CF Production and Characterization

-Produce PP and CTP multi-filament CF with < 20 μm diameters

-Scaled up multi-filament CF production, morphological characterization and mechanical testing of fibers from various precursor materials

-Stabilization and carbonization of multi-filament spun fibers to CF

Modeling and Database

-Continue modeling oxidative stabilization move towards graphitic domains

-Integration of: molecules → mesogens → stabilization → graphitic domains → CF

-Verify model simulation properties to actual produced material properties

-Continue to add data to the database and apply and optimize machine learning

Resin CF Tow Fabrication and Marco-scale Modeling

-Resin CF tow-level testing from scaled up multi-filament PP, CTP and bio-ACN CF

-Application of finite element modeling to multi-filament samples

-Feedback to atomistic models and for ML for integration

Economic Evaluation

-Economic evaluation of feedstock/intermediate/precursor materials

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

Summary

Relevance

-Develop ICME tools to predict CF physical properties from the molecular level up through micro-scale CF and macro-scale CF tow resin composites

-Develop a catalogue of materials that can achieve light-weight high-volume CF for use in vehicles at < $5/lb with the following requirements: strength (250 Ksi), modulus (25 Msi) and strain (1%)

Approach

-Assemble a consortium to look at various materials appropriate for CF production from biomass, petroleum and coal

-Characterize the chemical and physical properties of these materials at different production stages

-Correlate properties with the resulting CF properties

Accomplishments

-Chemical and physical characterization of feedstocks/intermediates/precursors/mesophase/CF

-Production of scaled up multi-filament CF from bio-ACN and mesophase CTP

-Production of scaled up bio-PAN CF that met DOE requirements

-Developed models to go from the molecules to CF properties and machine learning (ML) models

Future Research

-Multi-filament production of PP mesophase CF, and multi-filament CTP mesophase refinement

-Further chemical and physical characterization of BP2 materials for modeling and ML

-Optimize atomistic- and micro-models regarding stabilization and carbonization

-Continue to gather tow-level mechanical properties and apply finite element analysis modeling

-Integration of modeling from the atomistic level → tow-level finite element analysis → ML