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

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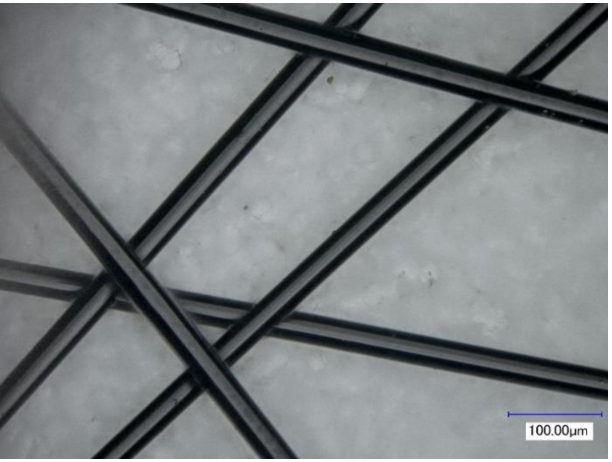

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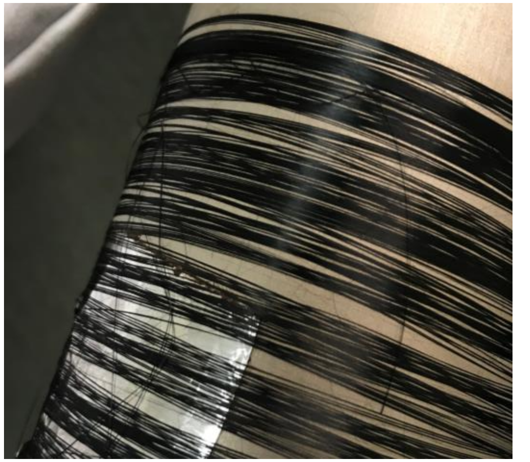

Project ID #: MAT125 **June 11, 2019**

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Overview

Timeline:

Start: October 2017

End: September 2020

Completion: 45%

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

Oak Ridge National Laboratories (ORNL)

Massachusetts Institute of Technology (MIT), Jeff Grossman Group

Southern Research Institute (SRI)

Advanced Carbon Products, LLC (ACP)

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 chemicals

-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

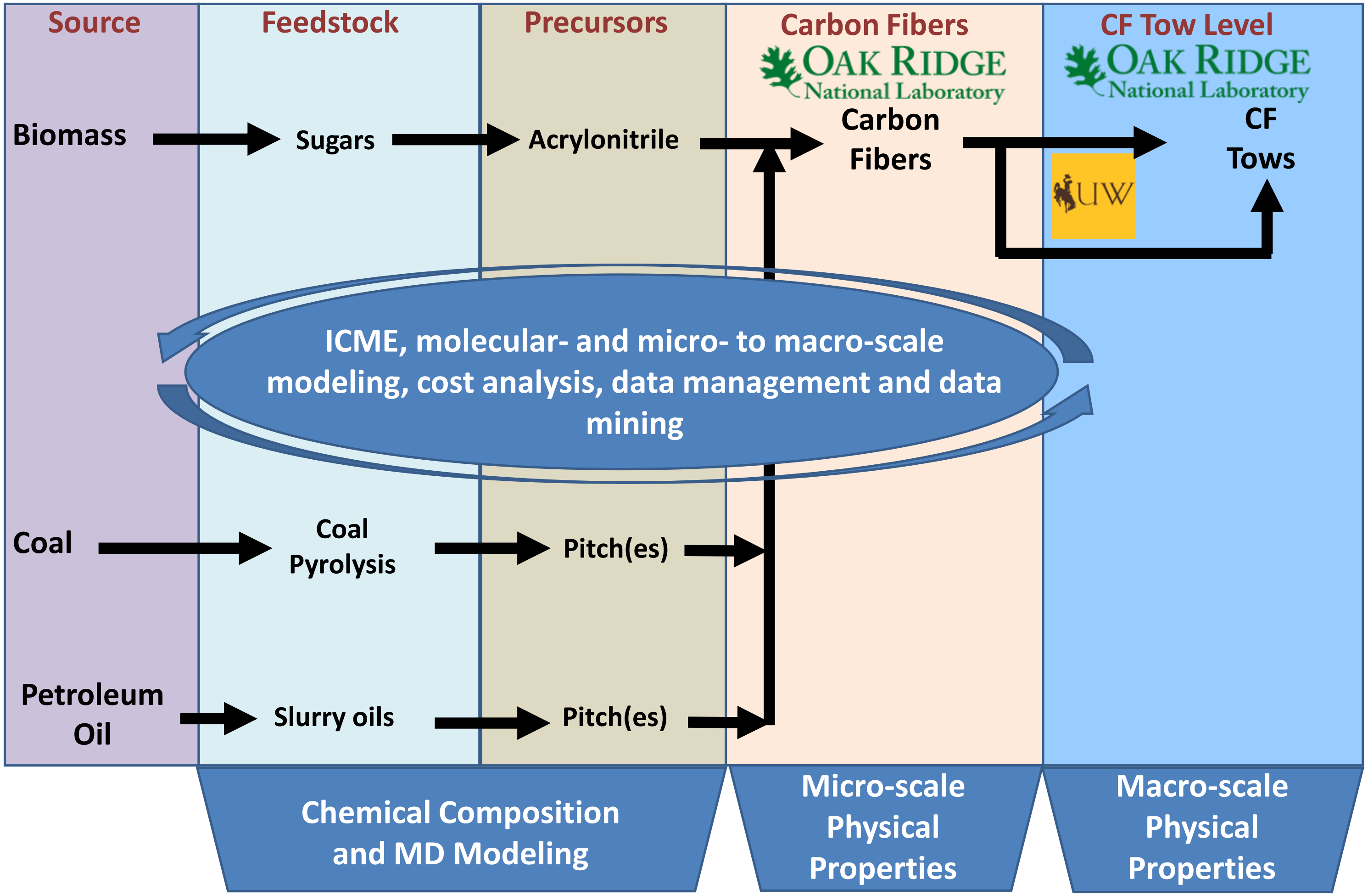
Milestones

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 +/- 30%	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 +/- 15%	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



Southern Research

Massachusetts Institute of Technology

Western Research Institute

Ramaco Carbon

ACP

Accomplishments for FY 2018

Bio-acrylonitrile (bio-ACN) – Southern Research

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

Impurities (Organic/Inorganic)
(Range of each impurity was mapped)
Organic: furfural, acetic acid, formic acid, acetate, phenolics, aliphatic 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 (ORNL)
Bio-ACN/methyl acrylate
153,000 Daltons
Carbonization

CF Mechanical Properties (ORNL)
Strength: 283 ±49 (ksi)
Modulus: 36 ±1.1 (Msi)
Strain: 0.86

Strain acceptable for BP1, but low

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

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Accomplishments for FY 2018

Coal Tar Pitch (CTP) – 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:
410 °C with flow inert gas, variable times

Properties
Mesophase content: 60-95%
Softening point: 320-340 °C
Carbon residue: 80-95 %
H/C: 0.46-0.49

CF (ORNL)
65% Mesophase
320 °C Softening Pont
Carbonization

CF Mechanical Properties (ORNL)
Strength: 361.3 (ksi)
Modulus: 26.5 (Msi)
Strain: 1.17

Cost: CTP ≈ $0.15-$0.3/lb; filtration, mesophase, side products ≈ $0.9-$1.5/lb

Accomplishments for FY 2018

Petroleum Pitch (PP) – Advanced Carbon Products

Feedstock

PP:
Produced from FCC slurry oil in ACP-10 process or M-50

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 (55 %)

Intermediate

Mesophase Pitch:
ACP Process

Properties

Mesophase content: 95-100%
Softening point: 330 °C
Carbon residue: 93 %
H/C: 0.54

CF (ORNL)

95+% Mesophase
330 °C Softening Pont
Carbonization

CF Mechanical Properties (ORNL)

Strength: 347.9 (ksi)
Modulus: 36.6 (Msi)
Strain: 1.18

Cost: PP mesophase from FCC slurry oil using ACP isotropic and mesophase processes < $0.9/lb

Accomplishments for FY 2018

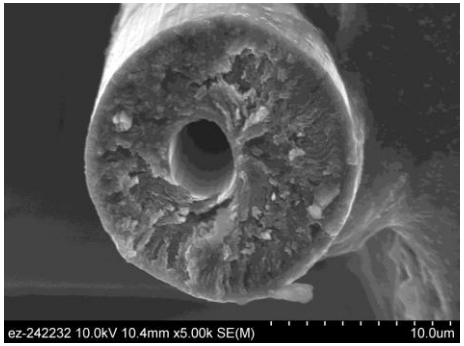
CF Spinning – ORNL

- Melt spinning of isotropic and mesophase CTP, PP and gilsonite samples
- Polymerization of bio-ACN with methyl acrylate and solution spinning
    - Stabilization, carbonization, optical microscopy and mechanical properties of more than 20 different samples

Bio-ACN

As Spun Fibers

Stabilized & Carbonized CF



Defect analysis: example of insufficient stabilization

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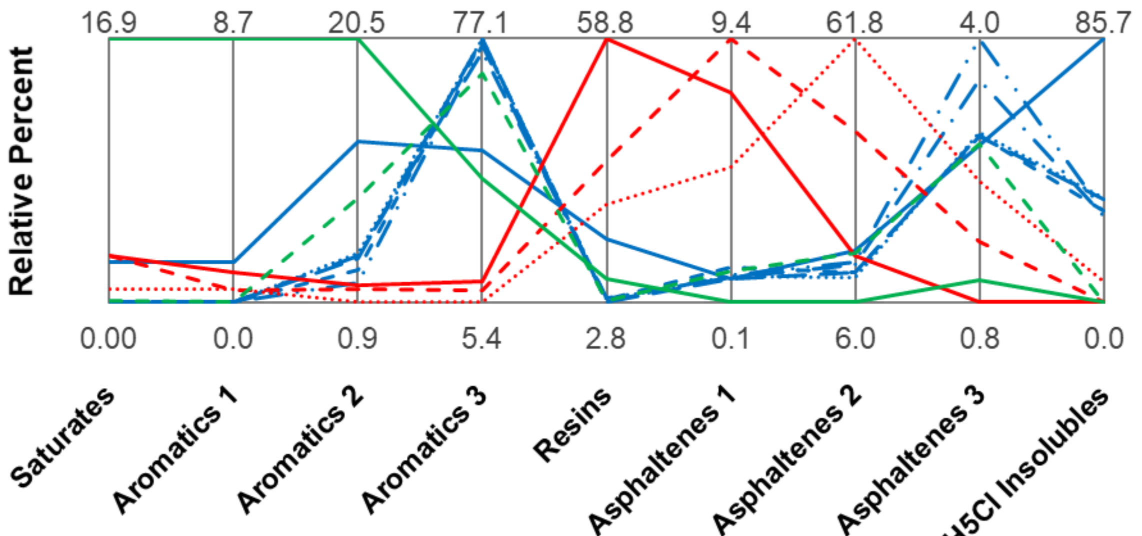
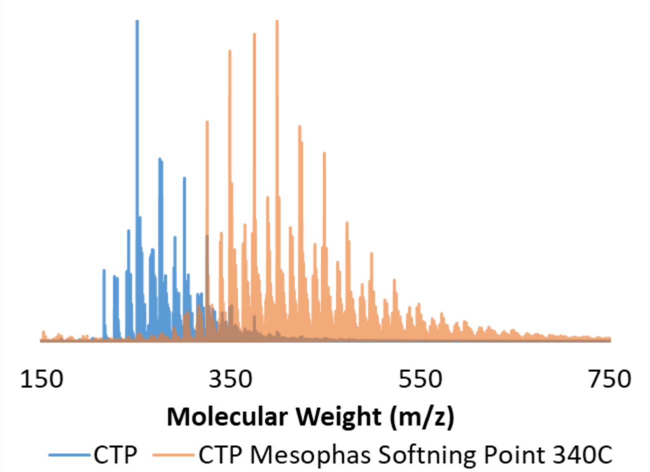
Accomplishments for FY 2018

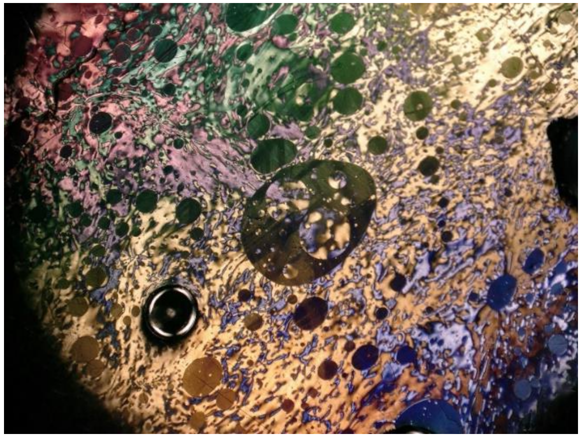
Pitch Characterization – Western Research Institute

SAR-AD^{TM} (Saturates, Aromatics, Resins-Asphaltene Determinator)



Laser Desorption Ionization Mass Spectroscopy (LDI-MS)





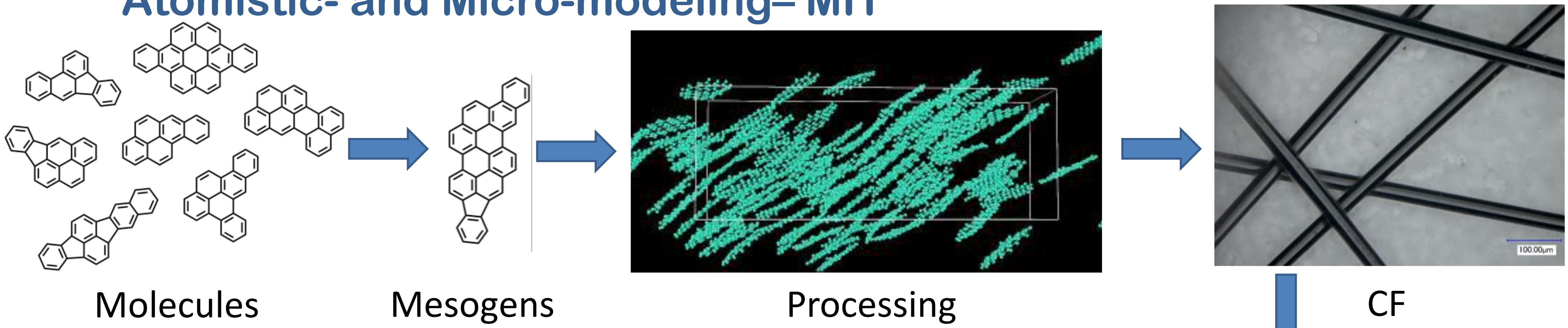
Characterization (for Machine Learning - MIT)

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

Chemical: SAR-AD^{TM}, LDI-MS, Fourier Transform Infrared Spectroscopy, Fluorescence Spectroscopy, Elemental Composition

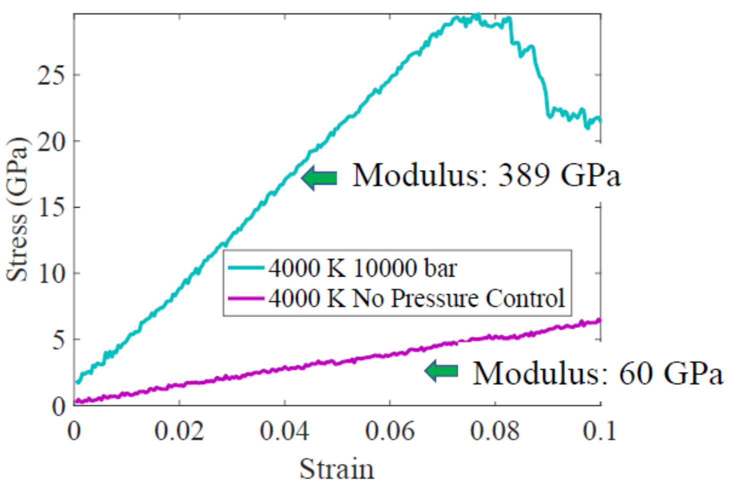
Accomplishments for FY 2018

Atomistic- and Micro-modeling– MIT



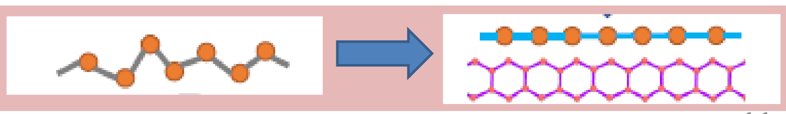
Example Model Results

Molecule	Data Source	Viscosity cP	Density g/cm3	Activation Energy Carbonization KJ/mol
Naphthalene	Model	0.987	0.958	357
	Lit.	0.761	0.963	199-446
Methyl-naphthalene	Model	1.202	0.97	230
	Lit.	1.1	0.972	121-198
50:50 Mixture	Model	1.053	0.972	N/A
	Lit.	N/A	N/A	N/A



Mechanical Properties

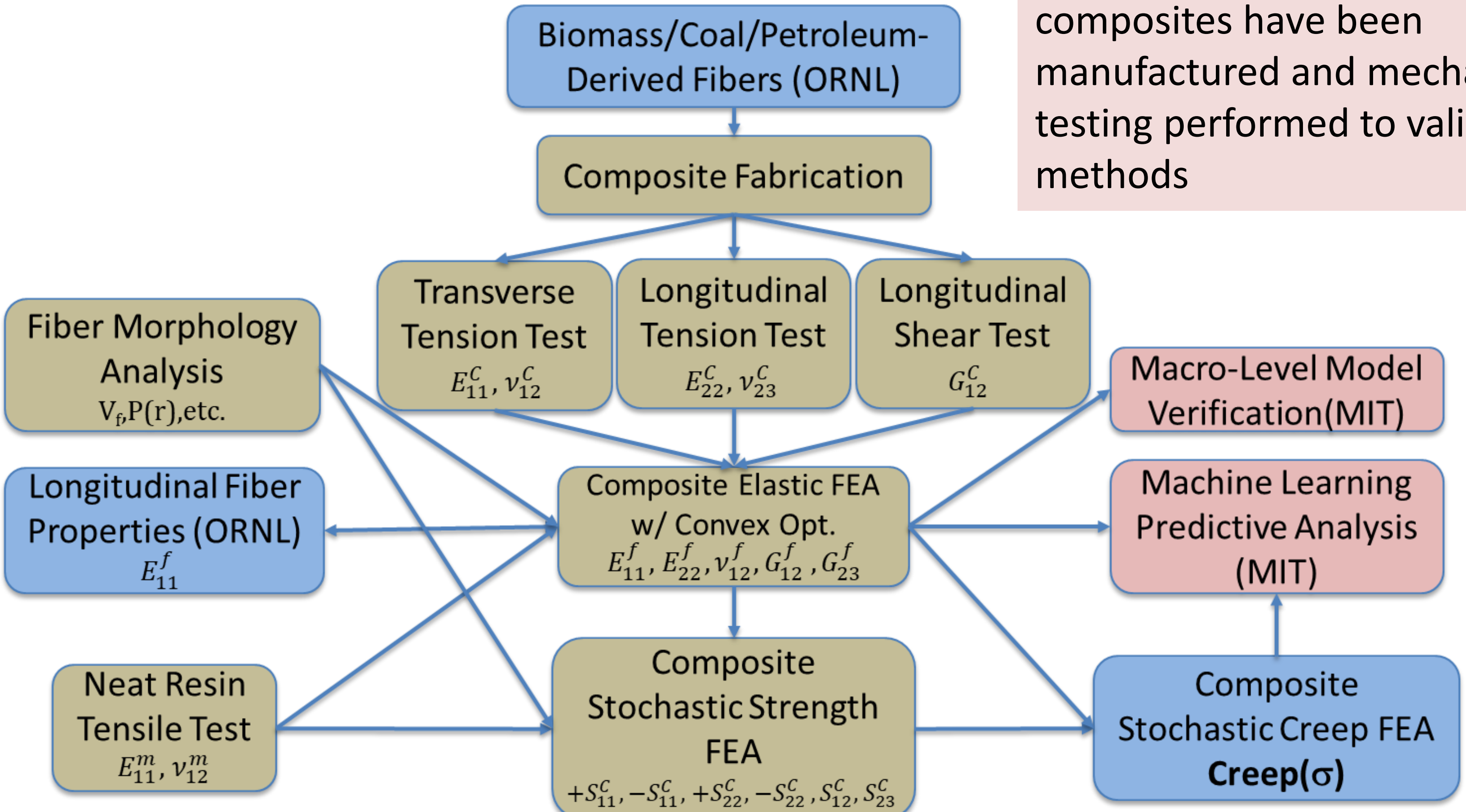
Coarse Grain models, bio-PAN (>70% Predictive)



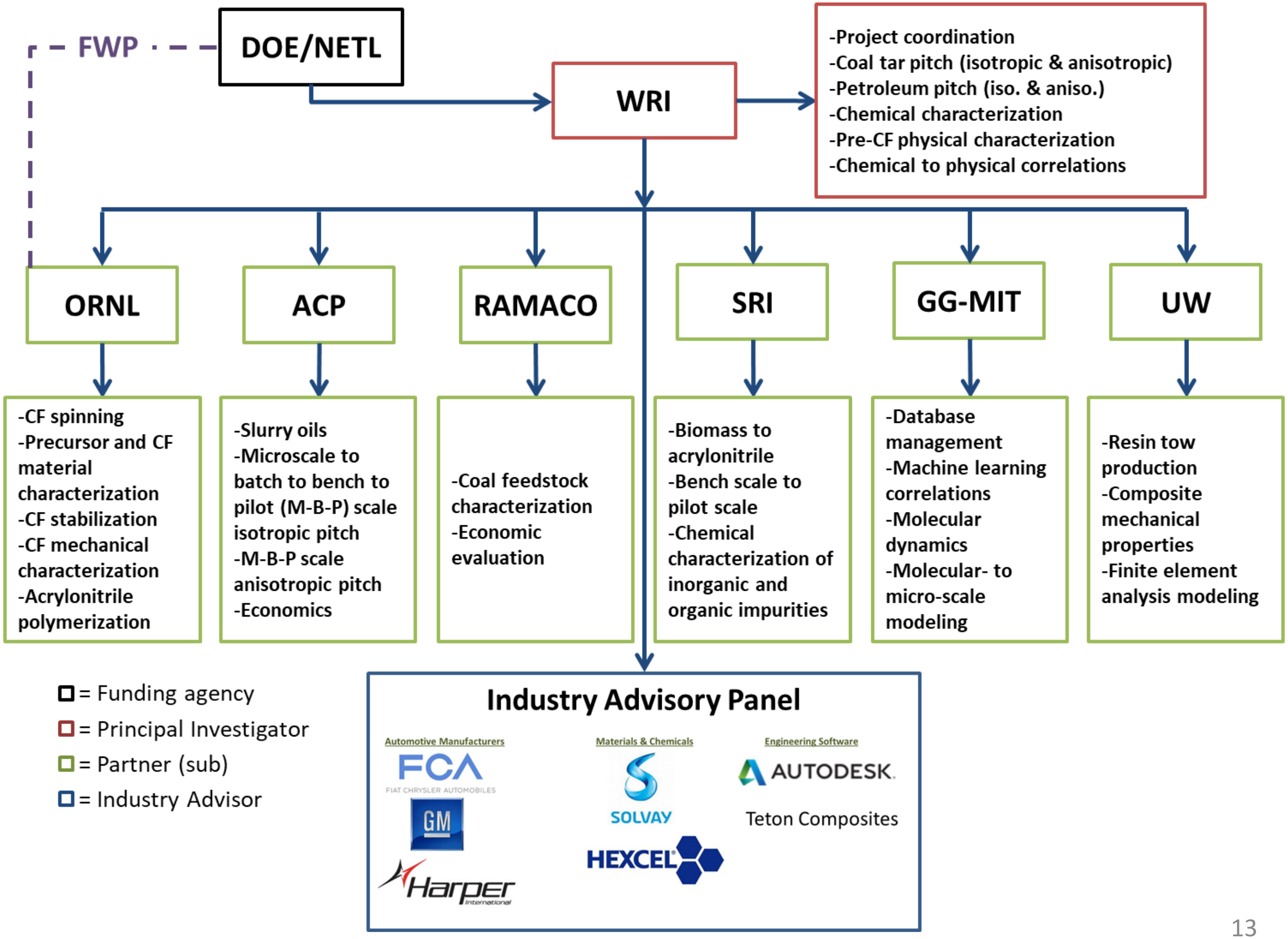
Accomplishments for FY 2018

CF Resin Composites and Macro-Modeling – University of Wyoming

Pitch based commercial CF composites have been manufactured and mechanical testing performed to validate methods



Partnerships / Collaborations



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Proposed Future Research*

Feedstock/Intermediate FY19-20

Coal Tar Pitch and Gilsonite

-Scale up removal of impurities from CTP

-Scale up of mesophase CTP > 2 lb for CF production

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

-Further purification and modification of gilsonite to improve CF performance

Slurry Oil Pitch

-Hot filtration of > 2 lb batches of PP mesophase

-Chemical characterization of ACP-10 isotropic pitch

-Blending of PP isotropic pitch with CTP to produce hybrid mesophase

Bio-acrylonitrile

-Scale up of bio-ACN production

-Optimize polymerization of bio-ACN to produce bio-PAN

-Improve the strain to ≥1%

-Understand variability in bio-ACN product during production

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

Proposed Future Research*

CF, Modeling and Database, Resins, Economics FY19-20

CF Production and Characterization

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

-Stabilization and carbonization of scaled up spun fibers to large batches of CF

-Diagnose CF failure mechanisms and provide strategies to reduce failure

Modeling and Database

-Use modeling to identify the most stable intermediate and precursor molecules

-Model pyrolysis formation of mesogen molecules from starting material molecules

-Model thermal reactions leading to crosslinking due to oxidative stabilization

-Verify model simulation properties to actual produced material properties

-Continue to apply and optimize machine learning

Resin CF Tow Fabrication and Marco-scale Modeling

-Resin and CF tow composite production from scaled up PP, CTP and bio-ACN CF

-Mechanical testing of the tow and resin composite systems

-Application of finite element modeling

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 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 different 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 small quantities of CF from mesophase CTP and PP that met DOE requirements

-Production of bio-ACN that met some DOE requirements

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

Future Research

-Scale up production of PP and CTP mesophase and CF

-Diagnose and troubleshoot CF failure mechanisms

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

-Optimize atomistic- and micro-models

-Produce CF to resin composites from scaled up CF materials to measure mechanical properties and apply finite element analysis modeling

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Response to Previous Year Review Comments

Question 1, Reviewer 2: The reviewer remarked that the approach appears sufficient to address the project. The evaluation of multiple materials should improve the chances for low-cost CF. The reviewer recommended that the project team please play close attention to the tolerance for impurities and/or unwanted phases/defects/impurities. Also, be sure to address the mechanical (tensioning and roller controls) as well as the thermochemical processing steps.

Response: Impurities are being addressed in several ways. Impurities from bio-ACN production in being closely monitored at all stages of production. The most important step is during the final production of the bio-ACN where the concentration of the two main impurities are being quantified and some effects on polymerization have been found if the concentration of these impurities are too great. For CTP, the elemental composition high temperature CTP produced in the US and China show that there are a range of N, O and S heteroatoms but the ranges are not very large. Lower temperature CTP with 6% oxygen showed difficulties in mesophase conversion. The primary impurity in CTP are the primary quinoline-insoluble particles. A series of filtration tests were performed in different solvents and using filters of different porosity. Removal of primary QI at 0.7 microns was found to be sufficient. The primary impurities in FCC slurry oil derived isotropic pitch are catalyst fines. These fines are smaller than CTP QI. A filtration level has been established to be acceptable for producing CF that meets DOE requirements. Microstructure defects in CF are being studied that lead to failure. For the mesophase PP and CTP CF one major pathway of failure deals with voids in the internal structure of the CF due to inadequate diffusion of oxygen into the fibers and incomplete stabilization. Mechanical tensioning and roller control operation are proprietary information. Thermochemical processing steps are also proprietary for CF production and mesophase PP. For mesophase CTP production 410 °C at 4 hrs was found sufficient to produce CF that meets DOE requirements