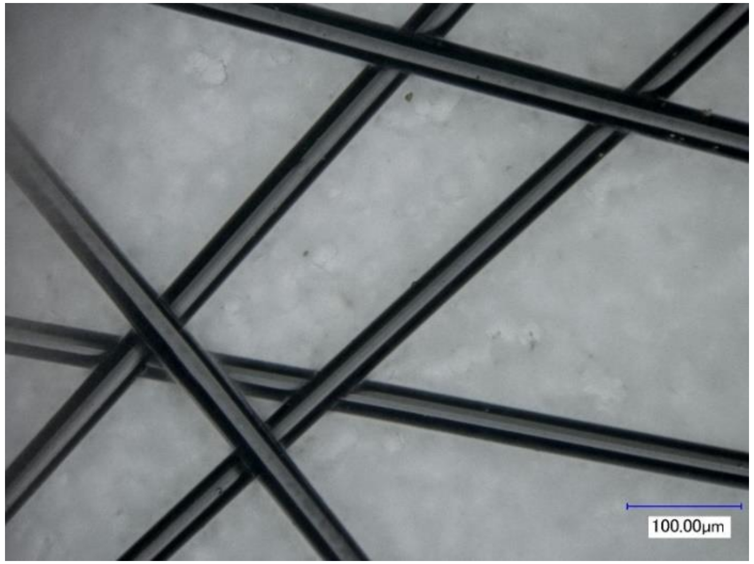
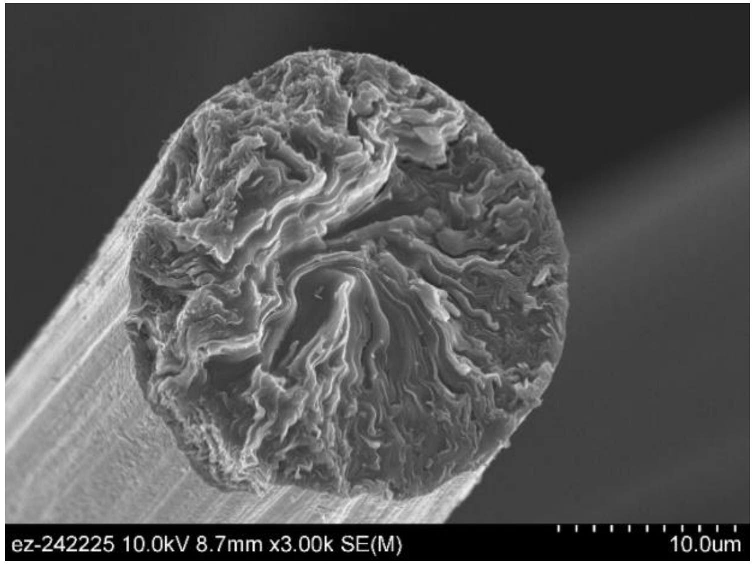
Integrated Computational Materials Engineering (ICME) Predictive Tools for Low-Cost Carbon Fiber





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Stacey McKinney/Brett Johnston (Koppers),
Charlie Atkins/Jim Dietz (RAMACO),
Ray Fertig (UW)

Project ID #: MAT125 **June 22, 2021**

Overview

Timeline:

Start: October 2017

End: July 2021 (3 month no-cost extension 2018, 7 month no-cost extension in 2020 **COVID**)

Completion: 85%

Budget:

Total: $5,242,820

DOE Share: $3,745,413

Cost Share Total: $1,497,407 (28.6%)

FY	DOE Share	Cost Share
2018	$1,021,685	$792,199
2019	$821,245	$353,384
2020	$852,483	$351,825

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)

Southern Research Institute (SRI)

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

-USDRIVE Materials Technical Team Roadmap, October 2017

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

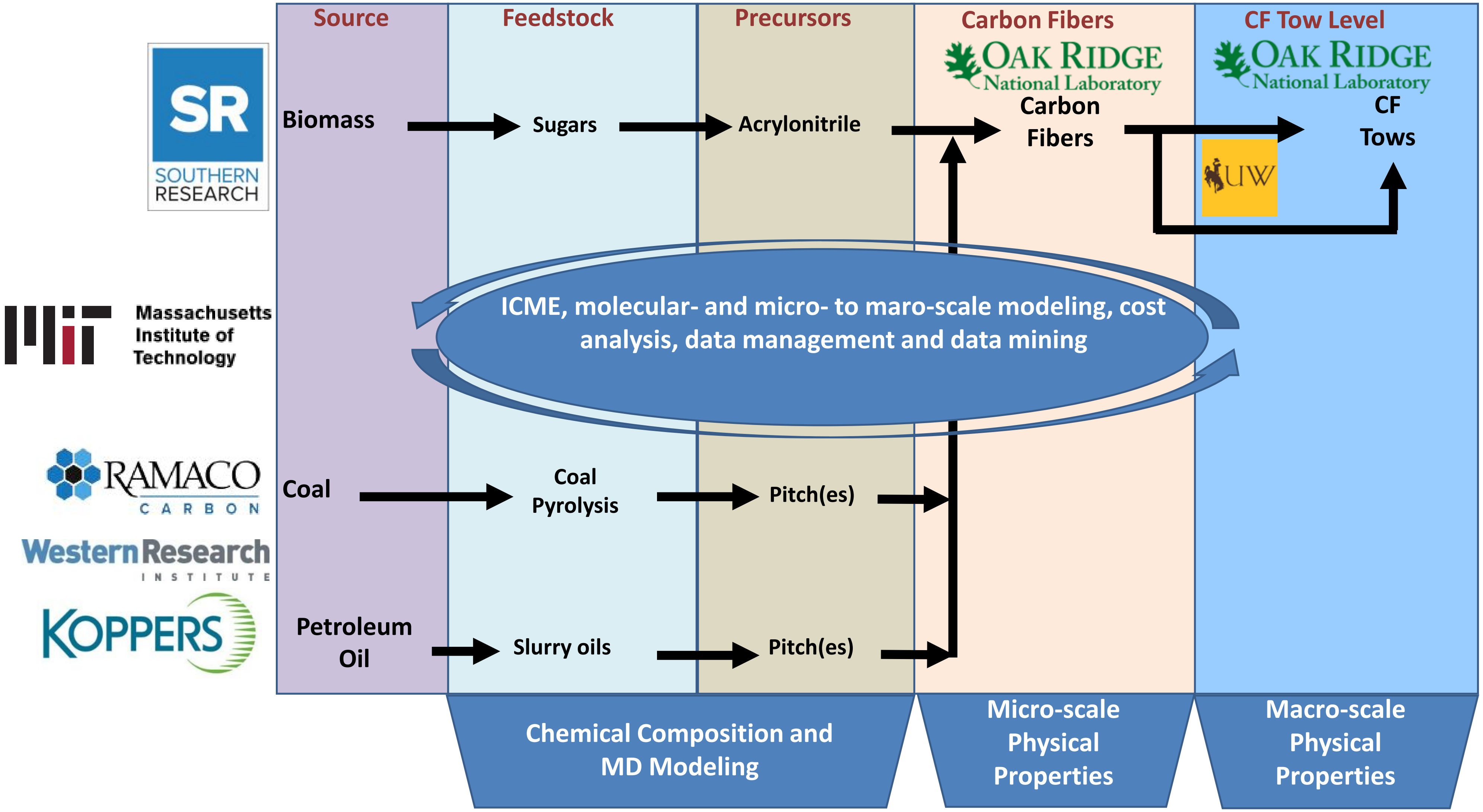
Milestones

Budget Period, FY	Milestones (M) and Go/No-Go (GNG) Decisions	Status
1, 18	M: Major subcontracts executed	Completed
1, 18	M: Raw Material feedstock verified as acceptable to process into CF	Completed
1, 18	M: Precursor verified as acceptable to make CF	Completed
1, 18	GNG: CF strength and cost coals achieved	Completed
2, 19	M: Verify Macro-level finite element models, tow mechanical properties, +/- 15%	Completed
2, 19	M: Micro-level models validated, +/- 15%	Completed
2, 19	M: Establish CF tow strength-weight ratio, 30-15% less than steel	Completed
2, 19	M: Rank precursors and CF vs. DOE goals using machine learning	Completed
2, 19	GNG: Scaled up precursors produce CF with strength and cost goals	Completed
3, 20	M: Validation of integrated micro-macro models, +/- 15%	On Target (June)
3, 20	GNG: Verify CF still meet strength and cost goals	On Target (June)
3, 20	M: CF meet automotive strength-weight ratio target	Completed
3, 20	M: Validation of macro-level models	On Target (July)

Go/No Go: Meets DOE strength 250 Ksi (modulus 25 Msi, Elongation >1%) and < $5/lb for scaled up batches of precursor material

Budget Period 3: down-selected for bio-ACN and PP

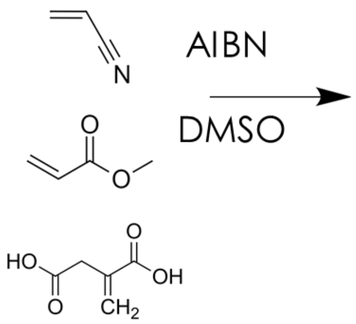
Approach

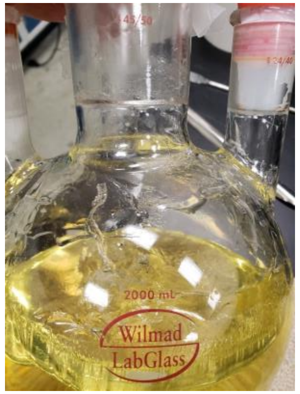

Source
Feedstock
Precursors
Carbon Fibers
CF Tow Level
OAK RIDGE National Laboratory
OAK RIDGE National Laboratory
SR SOUTHERN RESEARCH
Biomass
Sugars
Acrylonitrile
Carbon Fibers
CF Tows
UW
Massachusetts Institute of Technology
ICME, molecular- and micro- to maro-scale modeling, cost analysis, data management and data mining
RAMACO CARBON
Coal
Coal Pyrolysis
Pitch(es)
Western Research INSTITUTE
KOPPERS
Petroleum Oil
Slurry oils
Pitch(es)
Chemical Composition and MD Modeling
Micro-scale Physical Properties
Macro-scale Physical Properties

Accomplishments for FY 2020

Multi-liter Bio-acrylonitrile (bio-ACN) (Task 3.6.3)

Bio-polyacrylonitrile (bio-PAN) scale up synthesis

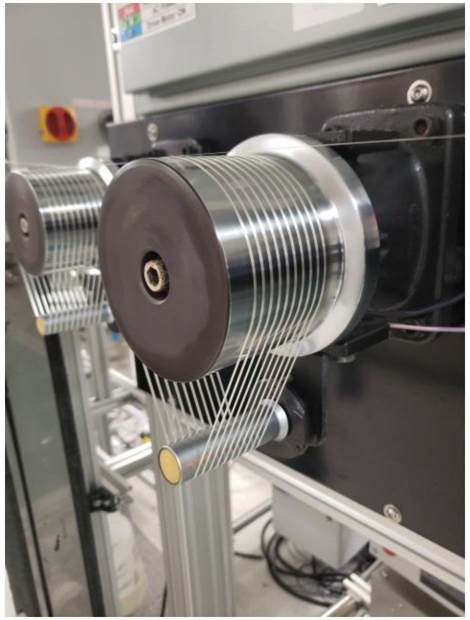




Monomer reactivity verified

Terpolymer concentrate: ~ 2 L

Bio-PAN spinning

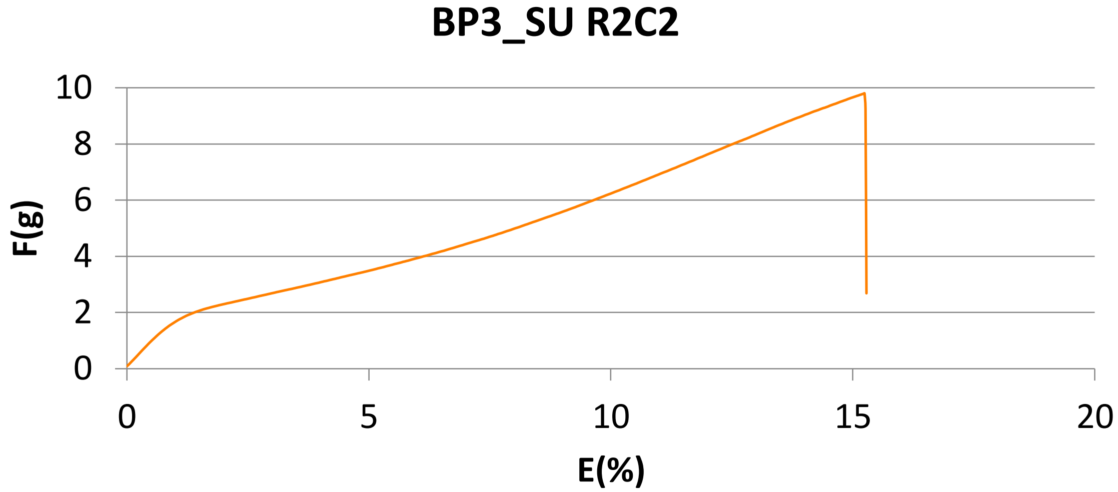


Accomplishments for FY 2020

Bio-PAN, 125-150 m, 1000 filament tow

Air

Δ

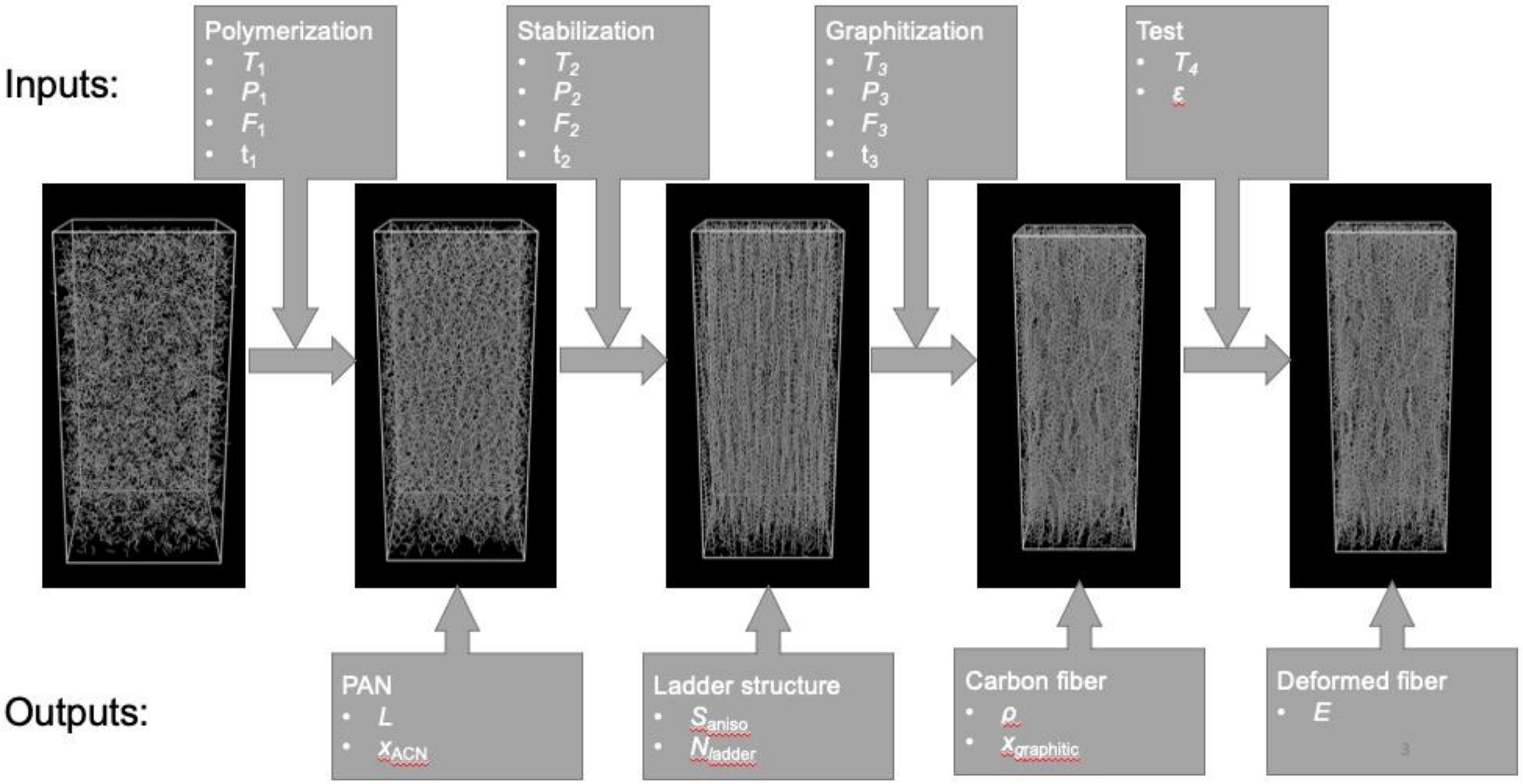


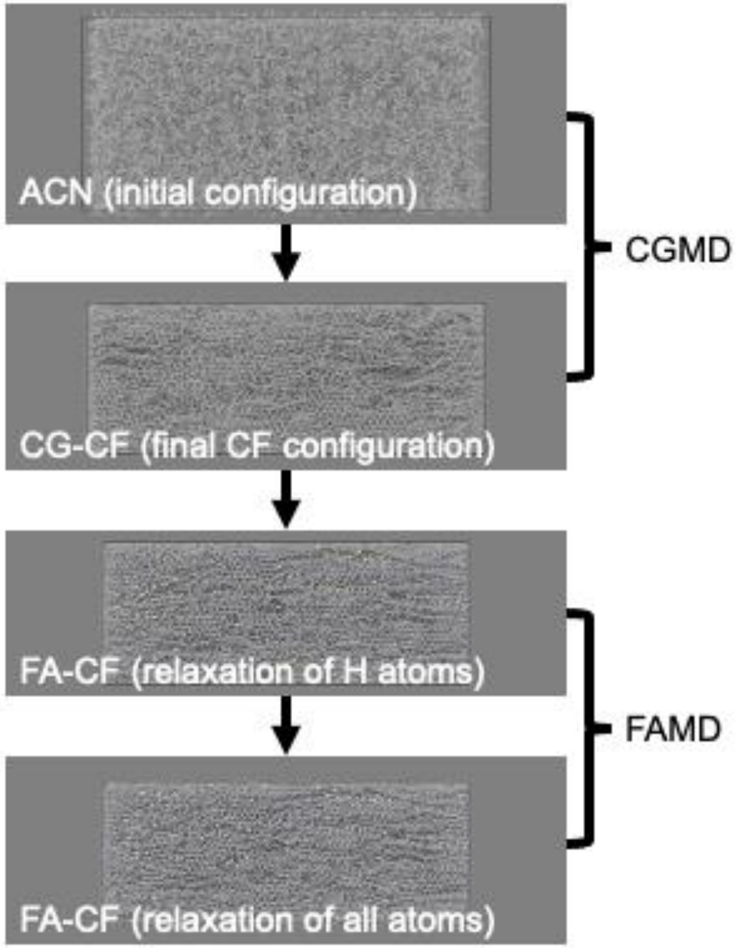
Break Stress (ksi)	Diameter (µm)	Strain (%)
90.6 ± 8.7	13.6 ± 1.4	14.9 ± 1.1

-Fibers after stabilization are high quality
-Carbonization is completed
-Testing expected to meet DOE Targets

Accomplishments for FY 2020

Bio-PAN Modeling, Coarse-Grained (CG) Refined by Fully Atomistic (FA) (Task 3.1/3.3)

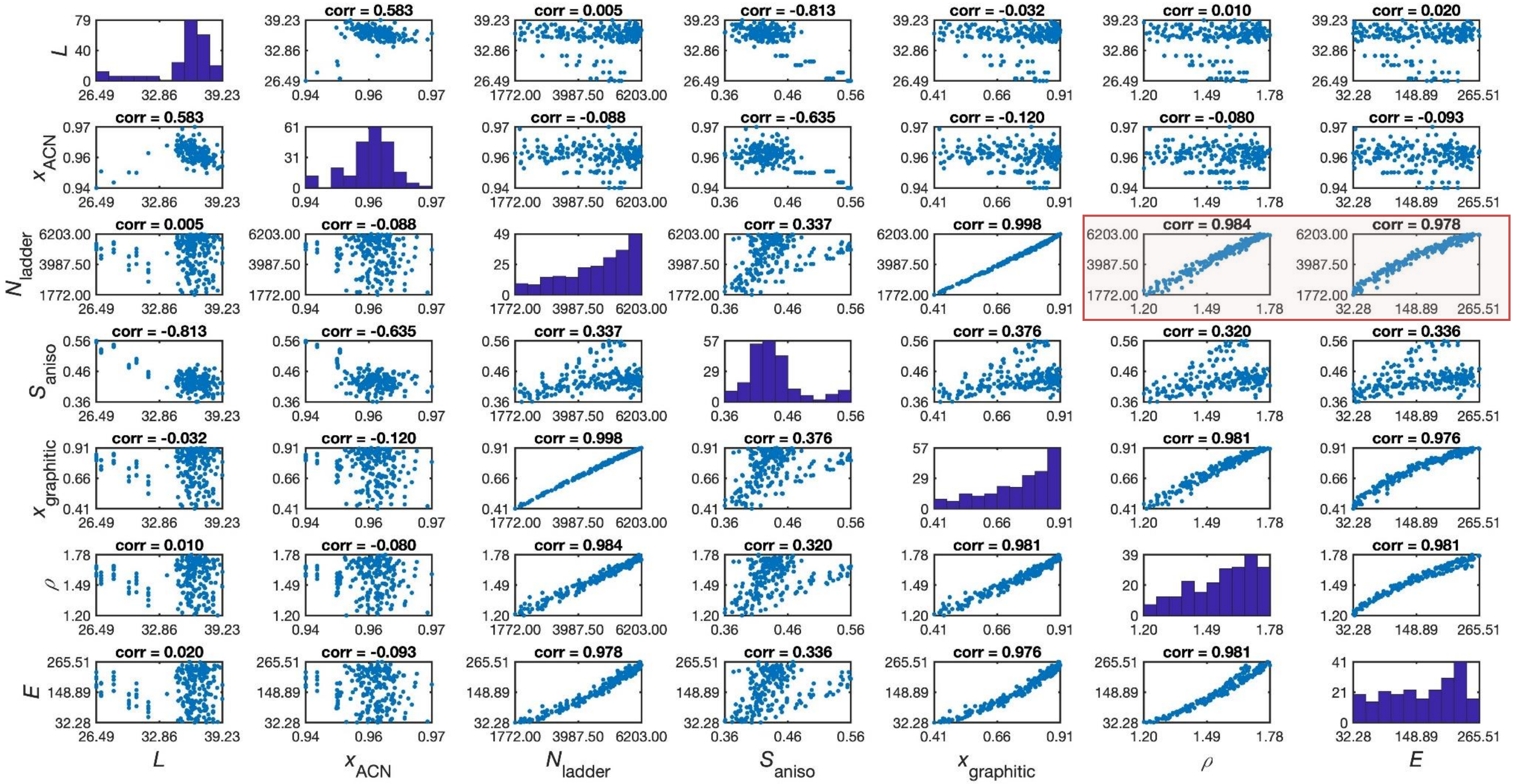




-Conversion of GC to FA allows better prediction of elastic properties and stress-strain relationship

Accomplishments for FY 2020

Bio-PAN Modeling, Coarse Grained (CG) Refined by Fully Atomistic (FA) (Task 3.1/3.3)



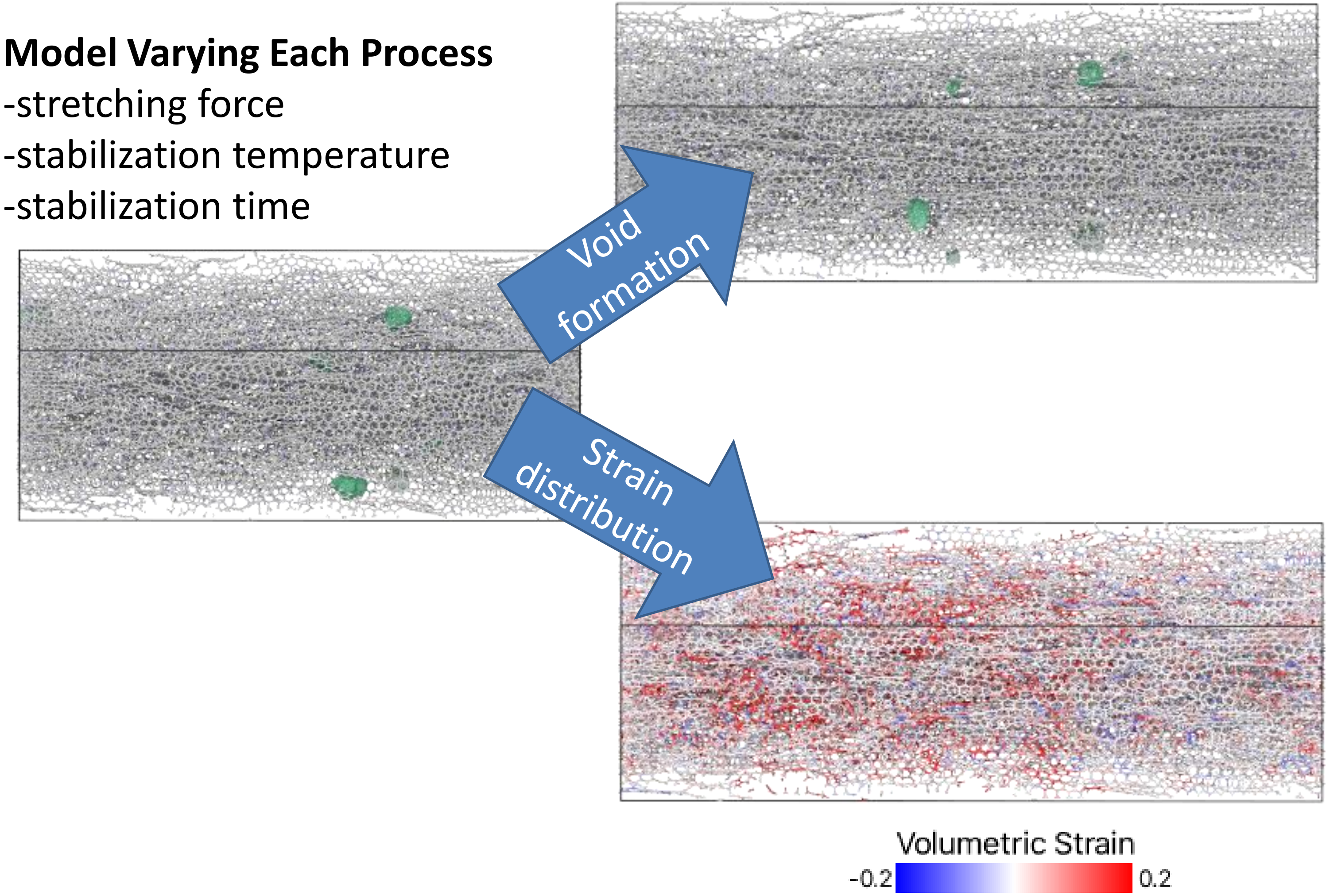
-Many predictive models for many different parameters
-Correlations between molecular structure and physical properties (density) and elastic properties (modulus)

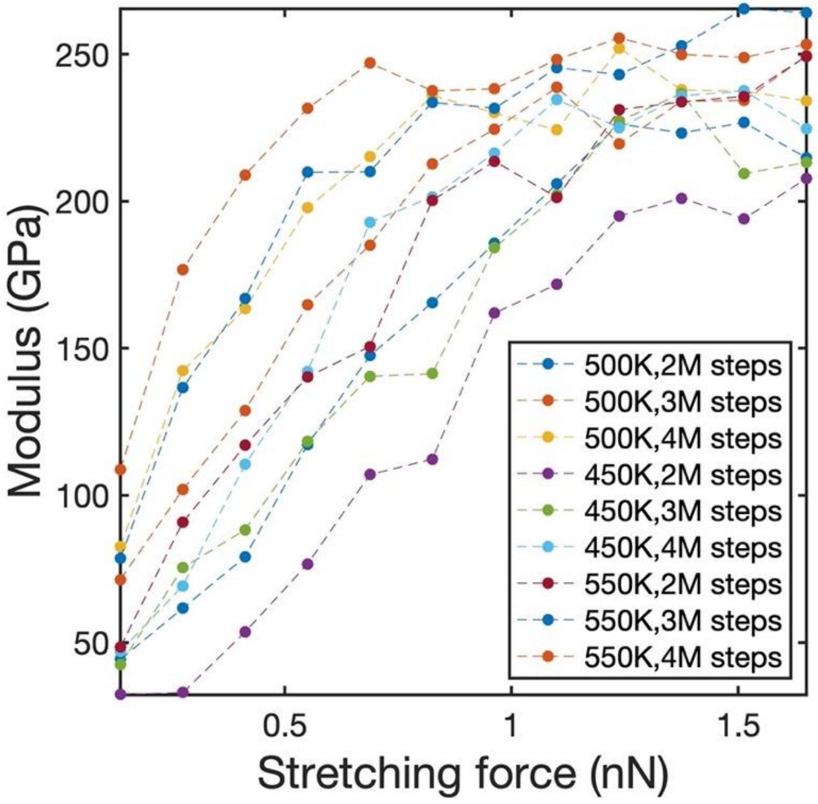
N_{ladder} = # of new bonds from stabilization
$\chi_{graphitic}$ = Fraction of aromatic content
ρ = Density
E = Young's modulus
χ_{ACN} = Mole fraction of bio-ACN
S_{aniso} = x component of radius of gyration as alignment measurement
L = Average chain length of bio-PAN

Accomplishments for FY 2020

Bio-PAN Modeling, Processing Validation (Task 3.1/3.3)

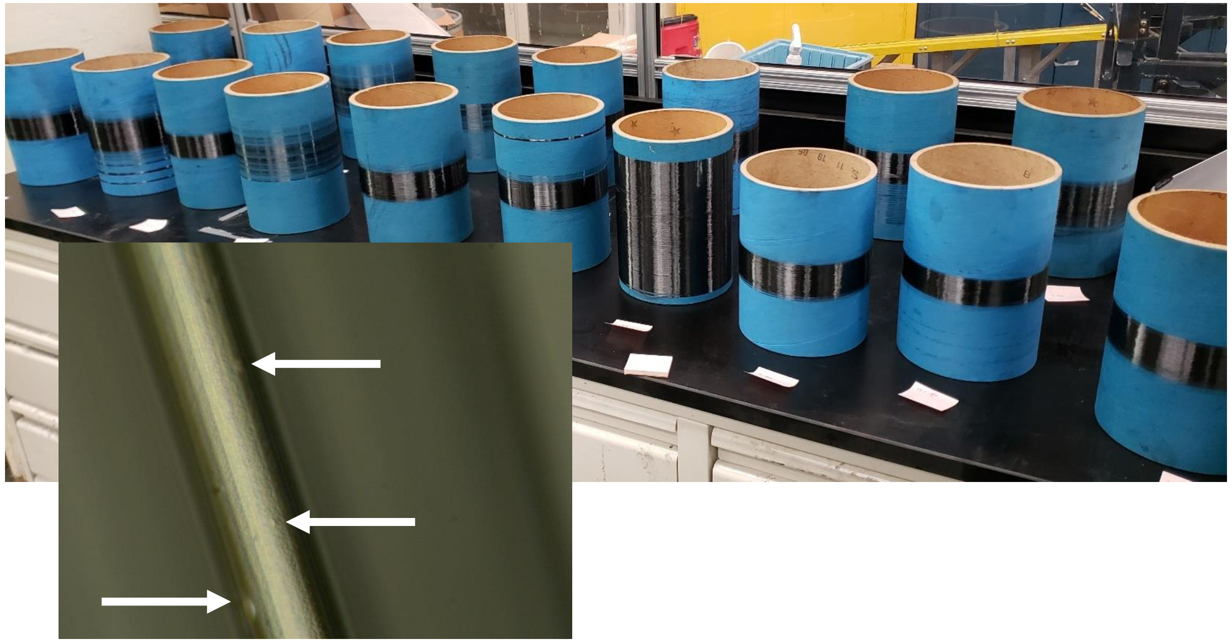
Model Varying Each Process
-stretching force
-stabilization temperature
-stabilization time





Accomplishments for FY 2020

Petroleum Pitch (Task 3.6.1/3.6.2)



Multifilament Spinning Multi-Kg Batches

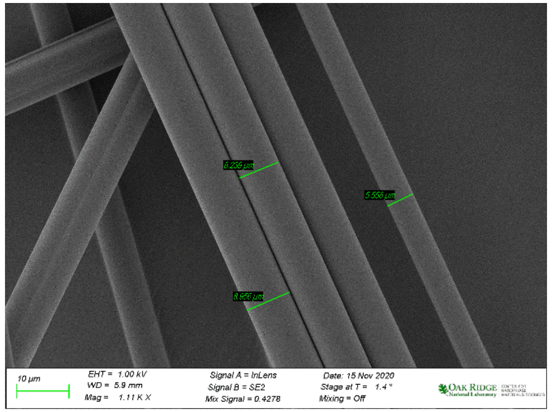
Sample	Break Stress (ksi)	Diameter (µm)	Modulus (Mpsi)	Strain (%)
Koppers **SP297**	225.7	17.46	24.69	0.92
Koppers **SP300**	258.8	23.35	22.07	1.21

Filtered vs. Unfiltered (2-3 % Primary QI) Isotropic PP

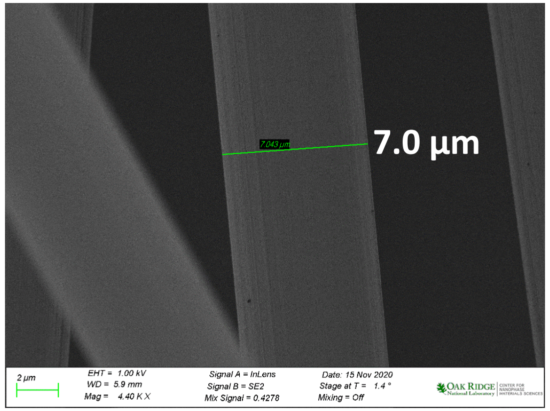
Sample	Break Stress (ksi)	Diameter (µm)	Modulus (Mpsi)	Strain (%)
WRI **Filtered SP308**	299.56	7.40	18.74	1.43
WRI **Unfiltered SP308**	172.8	16.9	24.9	0.73

-Smallest diameters: unfiltered 12-16 µm, filtered 7-10 µm
-Primary quinoline insolubles reduces strength and % elongation

Filtered – as spun

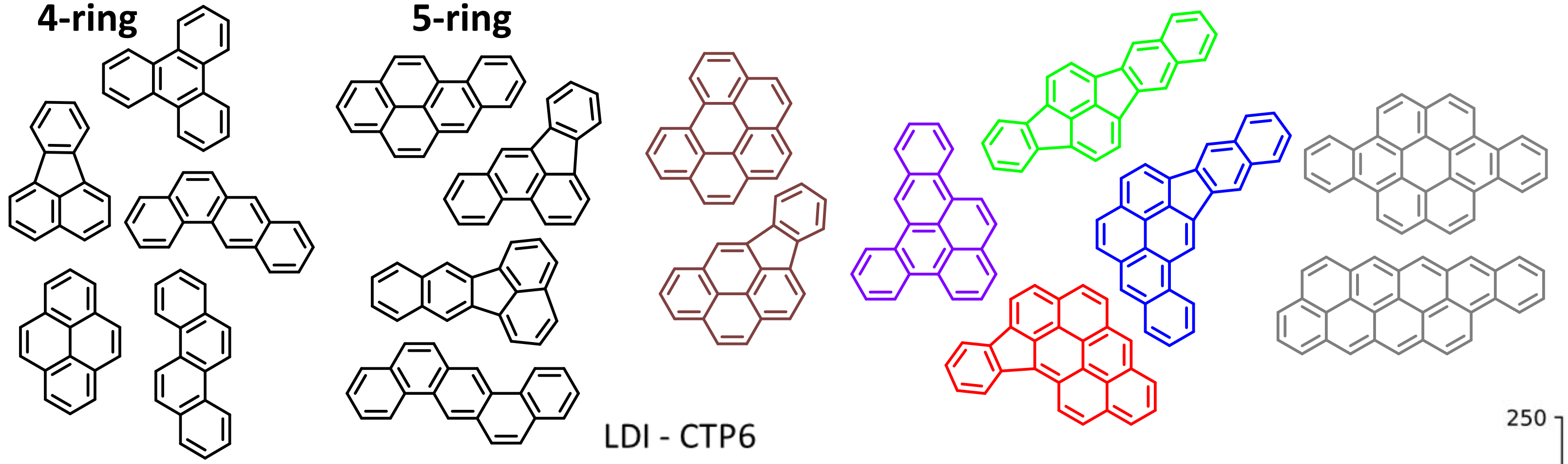


Filtered – CF



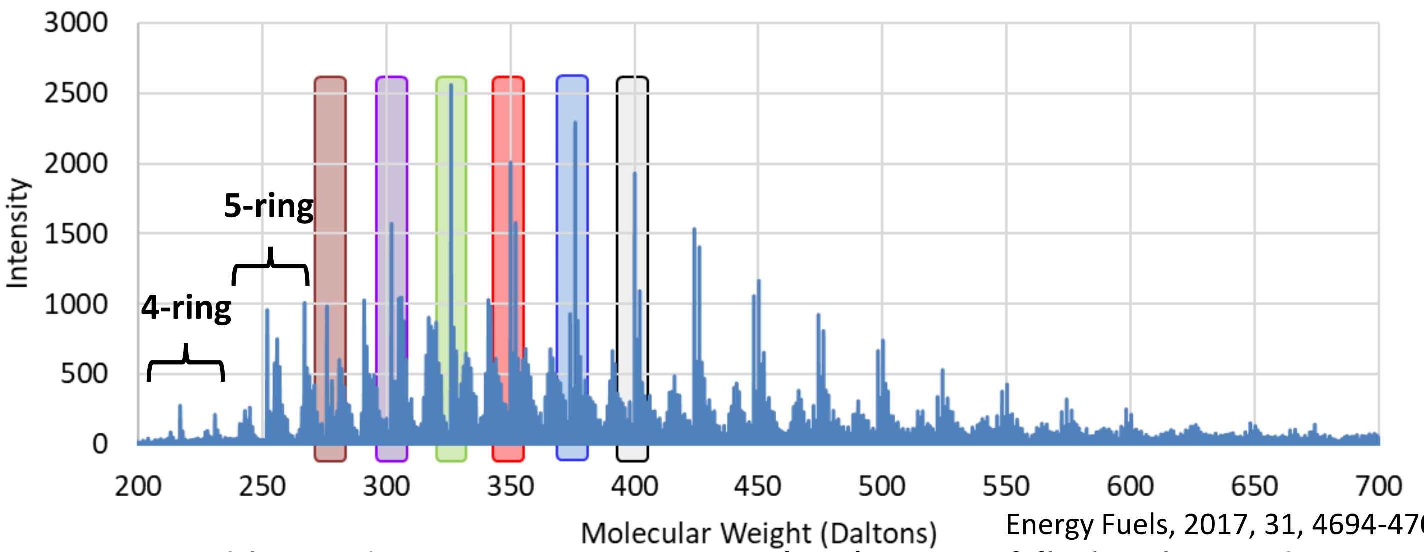
Accomplishments for FY 2020

Petroleum Pitch Modeling (Task 3.1/3.6.1.1/3.3.2) A Step Back to Coal Tar Pitch (CTP)

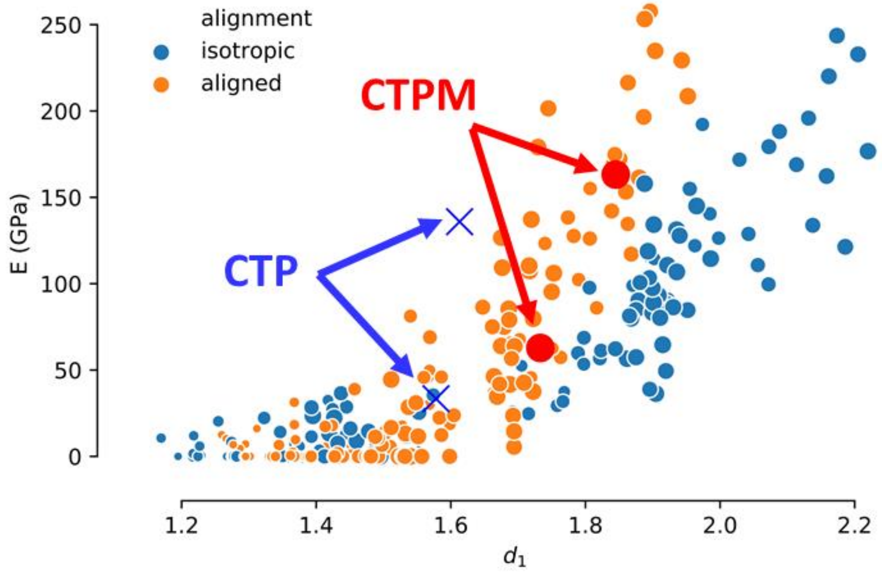


- Worked with a set of representative proxy molecules
- Varied size, alignment, degree of H-removal
- Models validated with CTPM CF

LDI - CTP6



Energy Fuels, 2017, 31, 4694-4704



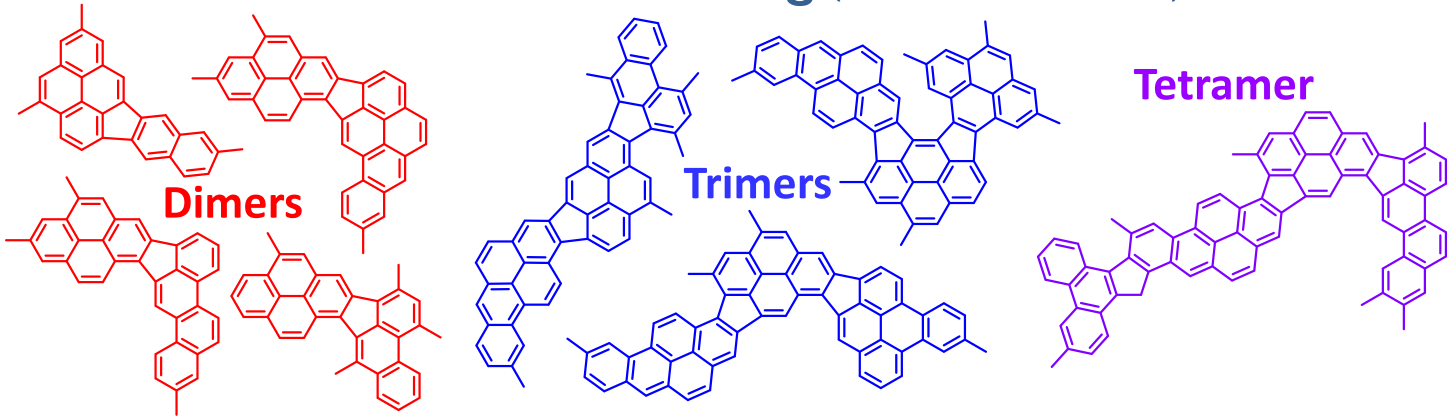
GC-MS and laser desorption ionization (LDI) time of flight showed > 4 rings

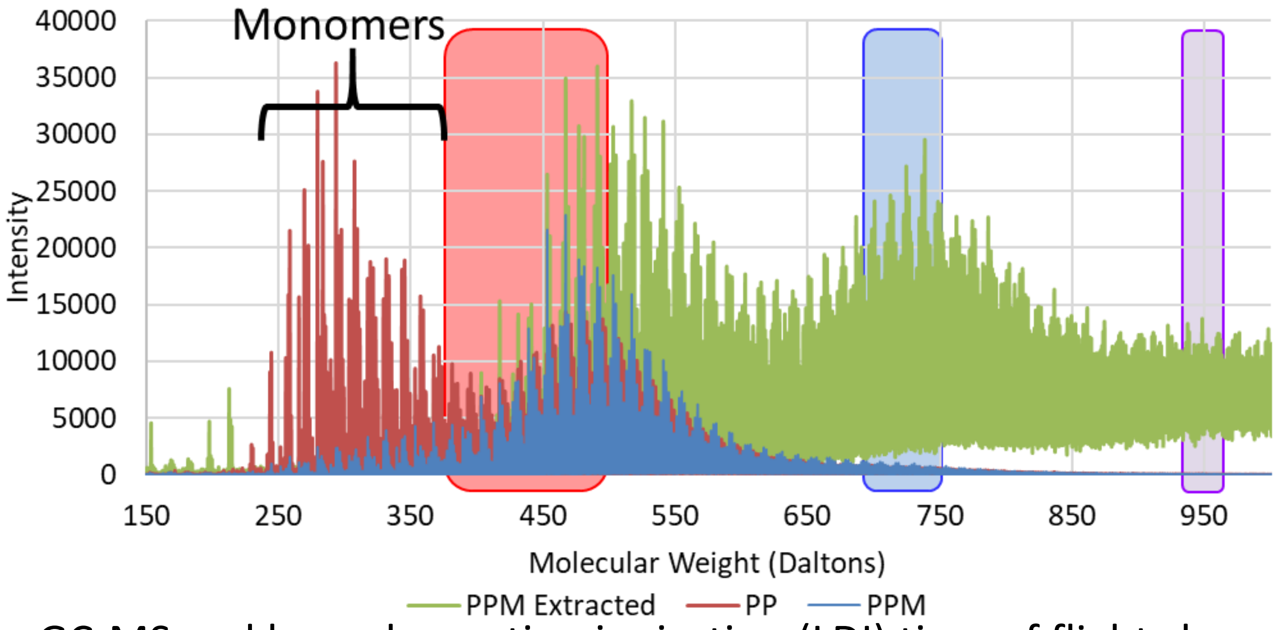
Accomplishments for FY 2020

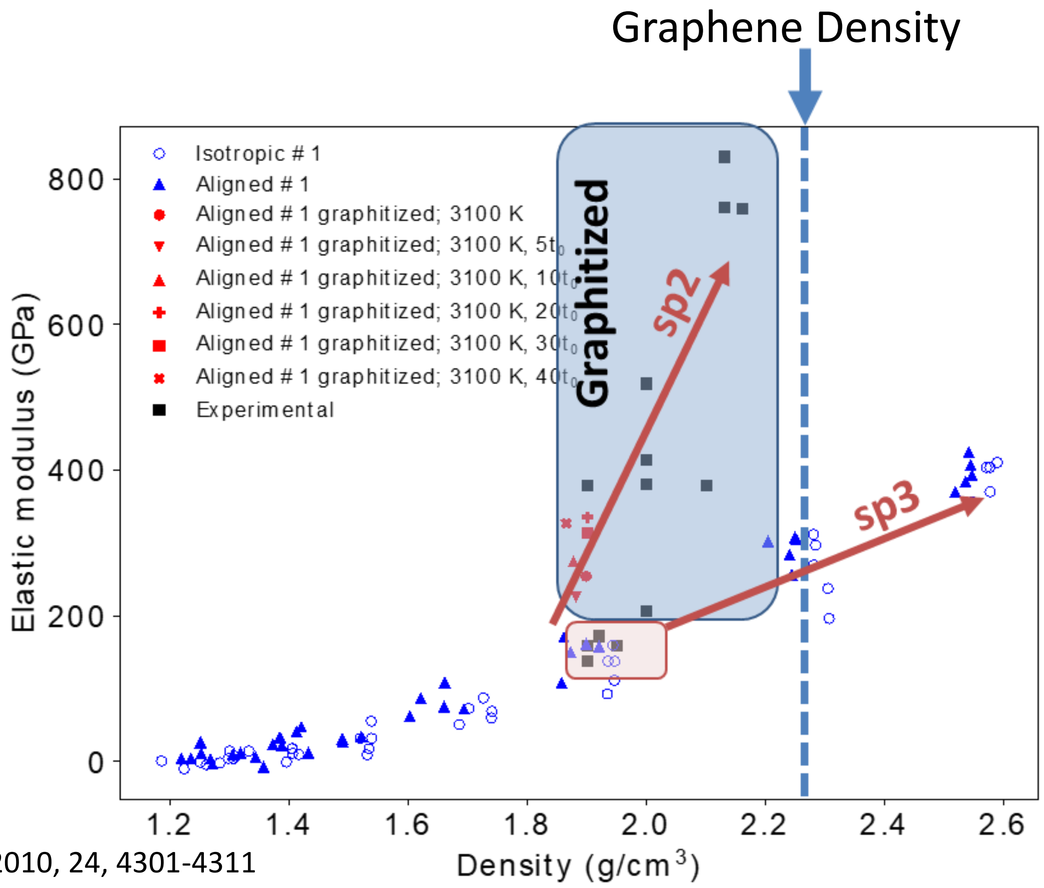
Petroleum Pitch Modeling (Task 3.1/3.6.1.1/3.3.2)

-Models validated with carbonized commercial PP CF data

-Closer agreement with graphitized CF







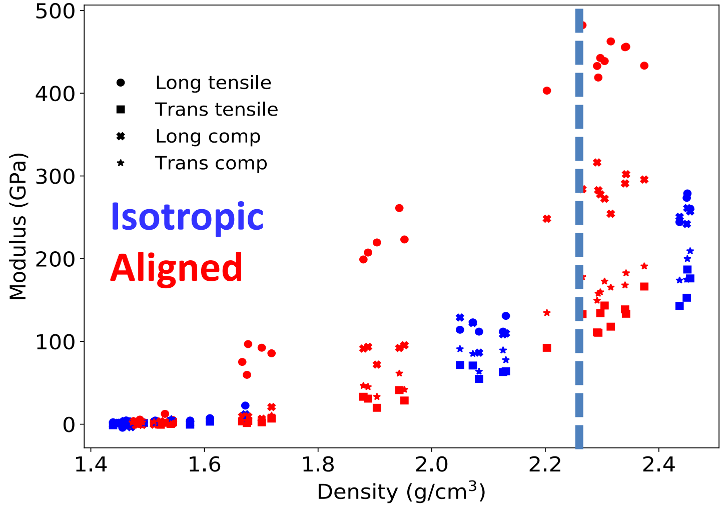
Energy Fuels 2010, 24, 4301-4311
Carbon 2014, 79, 265-273
Carbon 2020, 161, 456-465

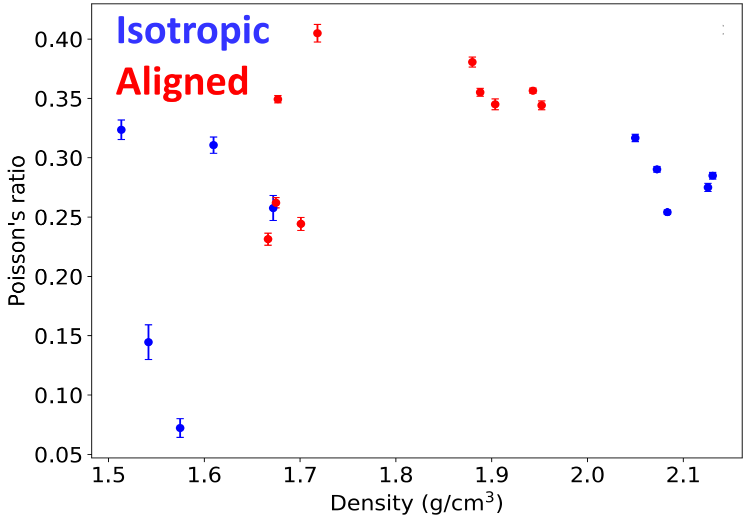
GC-MS and laser desorption ionization (LDI) time of flight showed > 4 rings

Western Research INSTITUTE

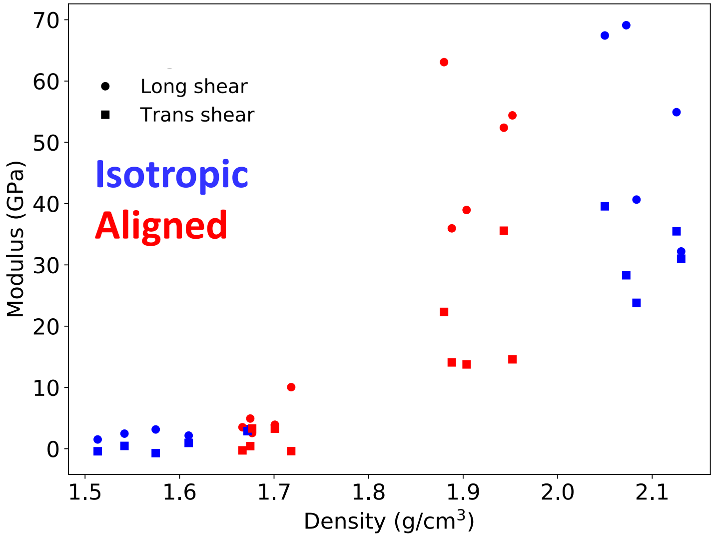
Accomplishments for FY 2020

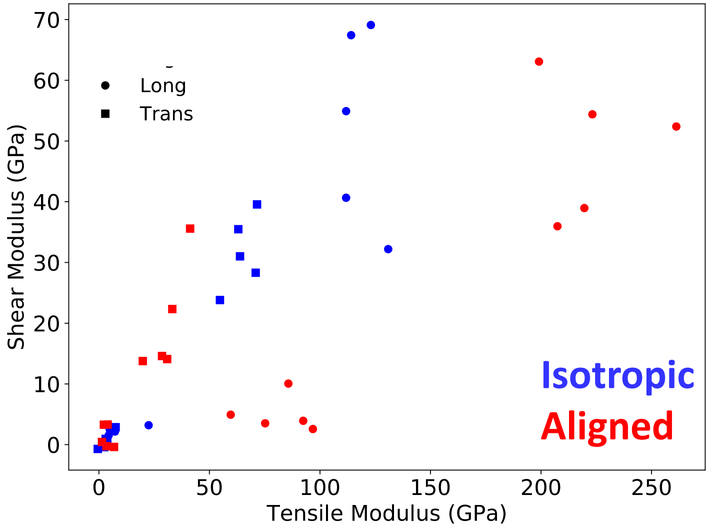
Petroleum Pitch Predictive Atomistic Modeling CF Elastic Properties (Task 3.1/3.3)





-Molecular level computation investigation of isotropic or aligned molecules on various mechanical properties and density



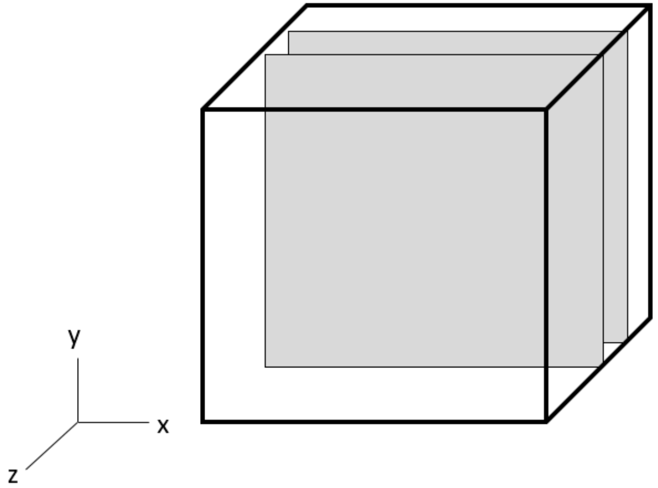


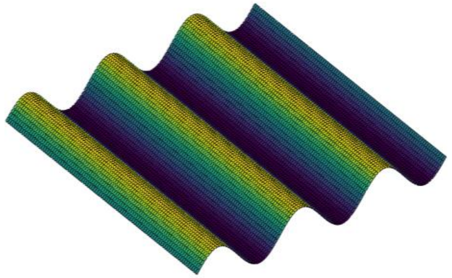
Accomplishments for FY 2019

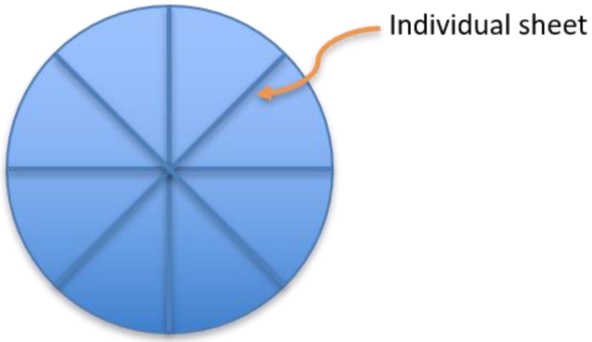
Macro- and Micro Modeling Integration (Task 3.3)

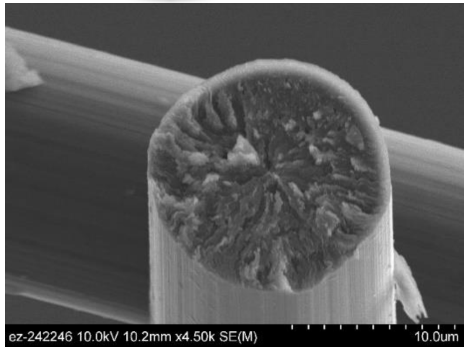
Macro-level models validated in BP2, awaiting tows of current CF samples to complete analysis (Task 3.5)

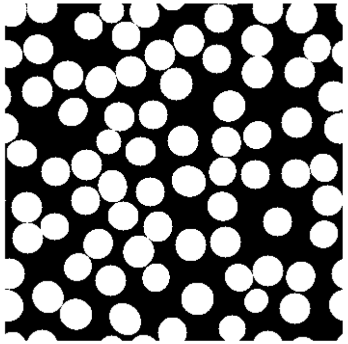
MIT Micro-level Data (Aligned Carbon Sheets) → Wavy Sheet Model (Neural Network) → Radial Sheet Model (Neural Network) → Tow-Level Macro-Model (Neural Network)









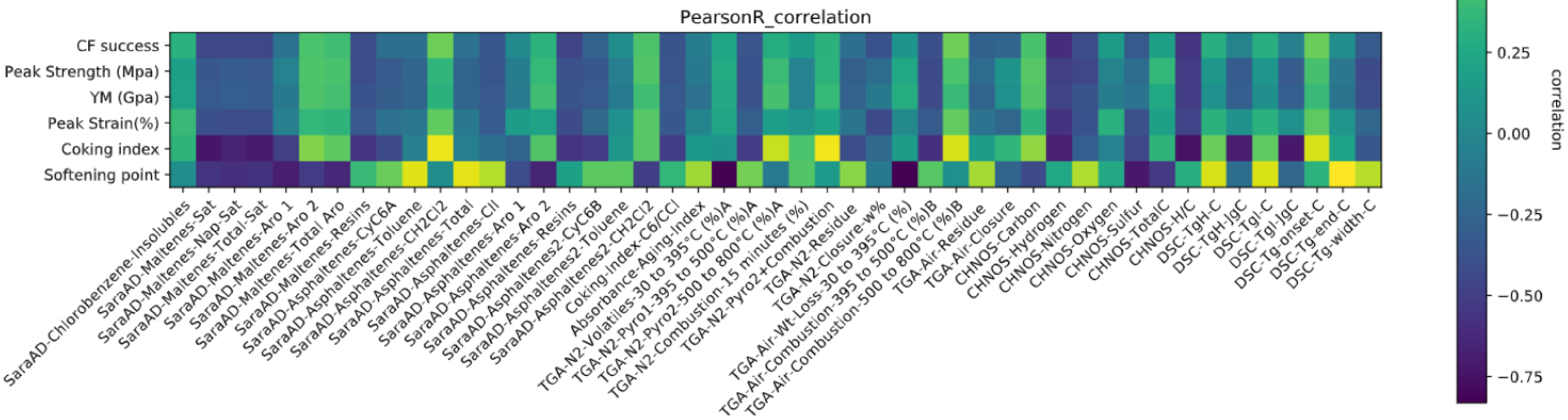


-All individual steps are nearly completed
-Validation is in progress

Accomplishments for FY 2020

Machine Learning (Task 3.2)

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



- **Holistic**: Models including all characterization and processing parameters
- **Targeted**: Models using highly correlated characterization and processing parameters

Accomplishments for FY 2020

Machine Learning (Task 3.2)

Coded Processing/Synthesis Parameters

Diameter (μm)

Break Stress (Ksi)

Modulus (Msi)

Strain (%)

Specimen	C1	C2	C3	C4	C5	C6	C7	C8	C9	P1	P2	P3	CF
2194	0.03	0.29	0.25	0.10	1.00	0.33	0.10	0.10	20.32	127.18	20.86	0.64	1
2201	0.03	0.29	0.25	0.10	1.00	0.33	0.10	0.10	19.88	96.48	20.22	0.50	1
2221	0.03	0.29	0.25	0.40	1.00	0.33	0.10	0.40	24.16	103.20	22.02	0.49	1
2246	0.03	0.29	0.25	1.00	1.00	0.33	0.10	1.00	23.46	159.81	22.17	0.74	1
2247	0.03	0.29	0.25	1.00	1.00	0.33	0.10	1.00	24.00	149.00	23.12	0.67	1
2282	0.14	0.29	0.25	0.10	1.00	0.33	0.10	0.00	20.20	177.98	21.65	0.83	1
2202	0.03	0.43	0.25	0.10	1.00	0.33	0.10	0.10	23.65	146.05	24.77	0.61	1
2223	0.03	0.43	0.25	0.40	1.00	0.33	0.10	0.40	23.81	145.58	22.37	0.67	1
2250	0.03	0.43	0.25	1.00	1.00	0.33	0.10	1.00	21.92	86.65	16.78	0.47	1
2307	0.43	0.43	0.25	0.10	1.00	0.33	0.10	0.10	19.99	197.57	20.72	0.95	1
2206	0.03	0.57	0.25	0.10	1.00	0.33	0.10	0.10	23.13	91.30	21.43	0.46	1
2225	0.03	0.57	0.25	0.40	1.00	0.33	0.10	0.40	22.58	63.58	0	0.34	1

-Algorithm used by ORNL to encrypt processing parameters for export control
-ML is performed on the encrypted data

Accomplishments for FY 2020

Cost Estimation (Task 3.4)

Consolidated Production Costs

OpEx Item/ Source	ACN, petro-based	Bio-ACN, SRI	Petro Pitch - ACP
Raw Material Charge/ kg carbon fiber	$9.70	$1.99	$4.41
Energy, $/ kg	$1.62	$1.62	$1.32
M&R Expense (8% of Inv.), $/ kg	$1.20	$1.19	$0.88
Direct Labor Expense @$30/hr), $/ kg	$1.74	$1.74	$1.74
Site Overheads (50% of Directs), $/ kg	$0.87	$0.87	$0.87
12% Capital Charge, $/ kg	$0.82	$0.82	$0.60
Total OpEx/ kg carbon fiber	$15.94	$8.23	$9.81
Total OpEx/ lb carbon fiber	$7.23	$3.73	$4.45

On an equal quality basis, carbon fiber production by either bio-ACN or petroleum pitch production can achieve the project $5.00 per pound cost goal.

Excerpt from A Techno-economic Assessment for the Production of Carbon Fiber from Selected Alternative Raw Materials, Ramaco Carbon, 6 May 2021

Response to Previous Year Review Comments

Reviewers: Clarity for techno economic analysis (TEA) details including any supply chain issues that can affect carbon fiber cost

Response:

Bio-ACN to PAN-based CF

- Biomass sugar represents 80% of raw material costs. A 20% cost increase would increase carbon fiber cost by 9%, or to $4.06 per pound.
- The co-product credits reduce raw material costs by more than 70%. A propylene glycol price drop of 20%, would increase carbon fiber cost by 14%, or to $4.25 per pound.
- Capital investment is too high to attract investor interest.

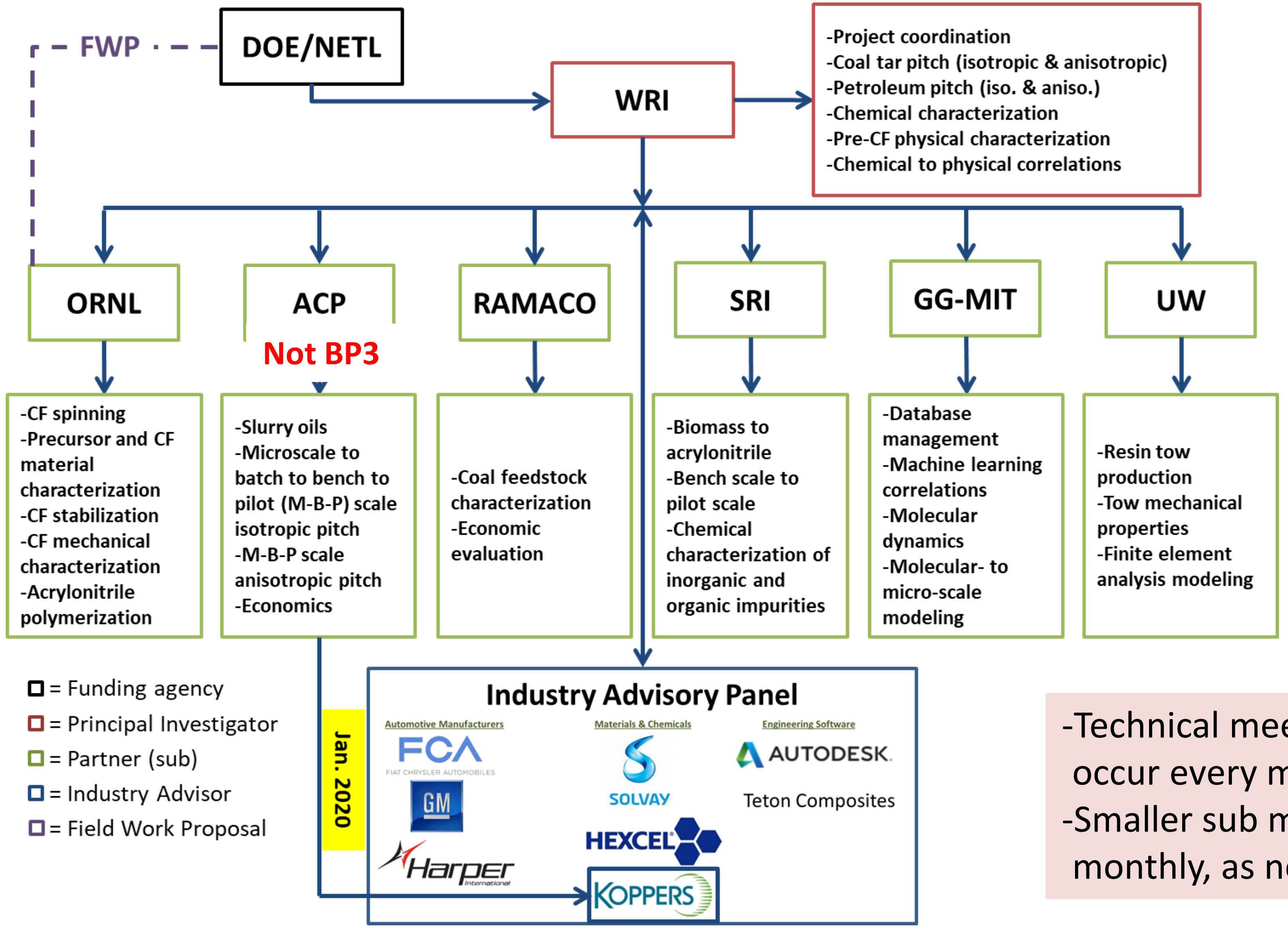
Decant oil to pitch-based CF

- At only 15% of the input cost of mesophase pitch, a 20% increase in residual fuel prices increases carbon fiber prices by 1.3%, or to $4.51 per pound.
- Attempting to maximize yields in production of mesophase pitch, equipment fouling occurs and reduces availability.
- Capital investment is too high to attract investor interest.

Reviewers: The reviewer would also like to see validation of the developed model(s) to make the predictions central to the outcomes, including for the atomistic and micro modeling completed

Response: Some examples of validation for CTP and bio-PAN and a degree of predictability are shown in the presentation. Developing a fully predictable model that is validated would require more data and effort beyond the current program. Validation for petroleum pitch mesophase CF was performed using literature data available on commercial fibers.

Partnerships / Collaborations



-Technical meetings for all occur every month
-Smaller sub meetings also monthly, as needed

Remaining Challenges and Barriers

Further Model Refinement

-PP and CTP and their mesophases contain thousands of different molecules: additional molecule sets with variation in size, shape, alkyl substituents, heteroatoms and functional groups need evaluated for PP to understand limitations on what molecules make better or worse mesophase and resulting CF, should be validated from chemical characterization data

-Additional reaction pathways should be investigated for CTP, PP and bioPAN systems, especially for oxidation reaction and kinetics during stabilization to check the sensitivity to molecule features and functional groups, addition of additives

-CF crystalline properties may need to be included in the micro-macro level integration

Further Model Validation

-More CF samples with a wider range of properties, especially out side the window of the DOE targets, would add additional meaning to the models and further improve their predictive capabilities

-Additional materials and data sets are needed to further refine and validate the micro- to macro-level modeling

Wider Set of Feedstocks and Precursors

-Mesophase pitch can be made from Lewis acid catalyzed reactions with smaller aromatic molecules, from air blown pitches, from hydrogenated materials, from ethylene cracker bottoms and many other aromatic feedstocks the molecular features of the feedstocks and CF precursors should be studied in light of the current effort to further understand limitations, differences and similarities of primarily aromatic feedstocks and precursors.

-After understanding limitation of primarily aromatic materials more diverse molecules should be investigated

Export Control

-Further methods need to be developed to handle sensitive data to make models for CF processing accessible

Proposed Future Research*

CF, Modeling and Database, Resins, Economics

CF Production and Characterization

-Additional work on PP, CTP, blends and other materials suitable for multi-filament CF with < 20 µm diameters
-More work to understand scaled up multi-filament CF production variations
-Morphological characterization and mechanical testing of fibers from various precursor materials

Modeling and Database

-Further development of oxidative stabilization models moving towards graphitic domains
-Advancing model integration: molecules → mesogens → stabilization → graphitic domains → CF → tow level
-Additional validation of model simulations with actual material properties, including graphitization
-Additional building up the database with more divers materials and CF to further refine and optimize machine learning

Resin CF Tow Fabrication and Marco-scale Modeling

-More work on characterization and integration of the CF morphology into tow level FEA modeling

Economic Evaluation

-Performance and economic evaluation of other 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-level resin composites

-Develop 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

-Biomass (sugar) derived bio-ACN, CTP mesophase and PP mesophase meet DOE targets, PP mesophase and bio-ACN down selected for further scaleup

-Characterize the chemical and physical properties of these materials at different production stages to build predictive models

-Integrate micro- and macro-scale models to predict tow-level properties from feedstock/precursor molecules and processing

Accomplishments

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

-Production of scaled up multi-filament CF from bio-ACN (liters) and PP mesophase (kilograms)

-Production of scaled up bio-PAN CF that met DOE requirements and PP mesophase that met targets within error

-Molecular level models for CTP, PP and bio-PAN that have predictive capabilities for CF performance

-Integration of models to go from the molecules to CF tow-level resin composite properties using neural networks and FEA

-Targeted methods were developed for ML to provide chemical and physical relationships

-Method to encrypt and deal with potentially sensitive export controlled data

Future Research

-Further refinement of models

-Further validation of models with produced CF

Technical Back-up Divider Slide

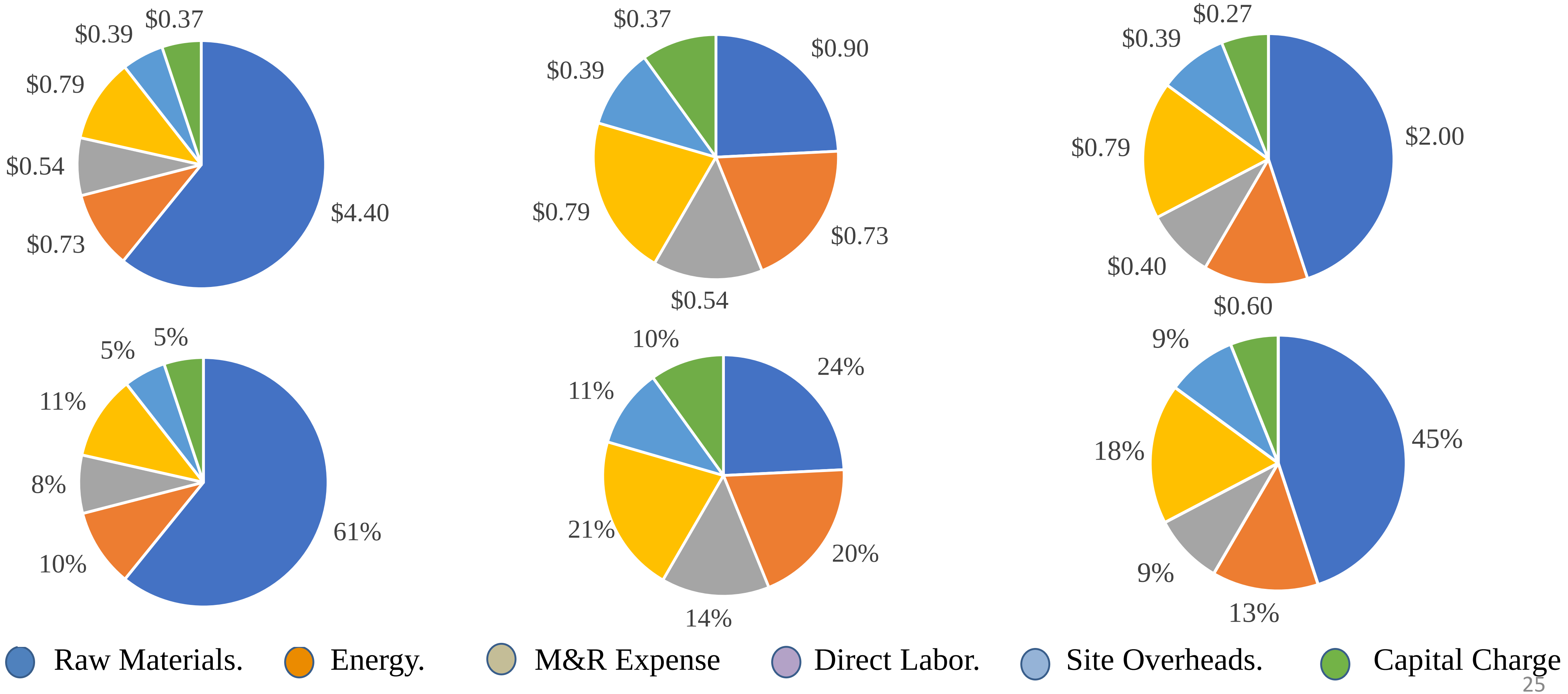
Technical Back-up Slides

Excerpt from A Techno-economic Assessment for the Production of Carbon Fiber from Selected Alternative Raw Materials, Ramaco Carbon, 6 May 2021

Petroleum PAN-based Fibers, $/lb

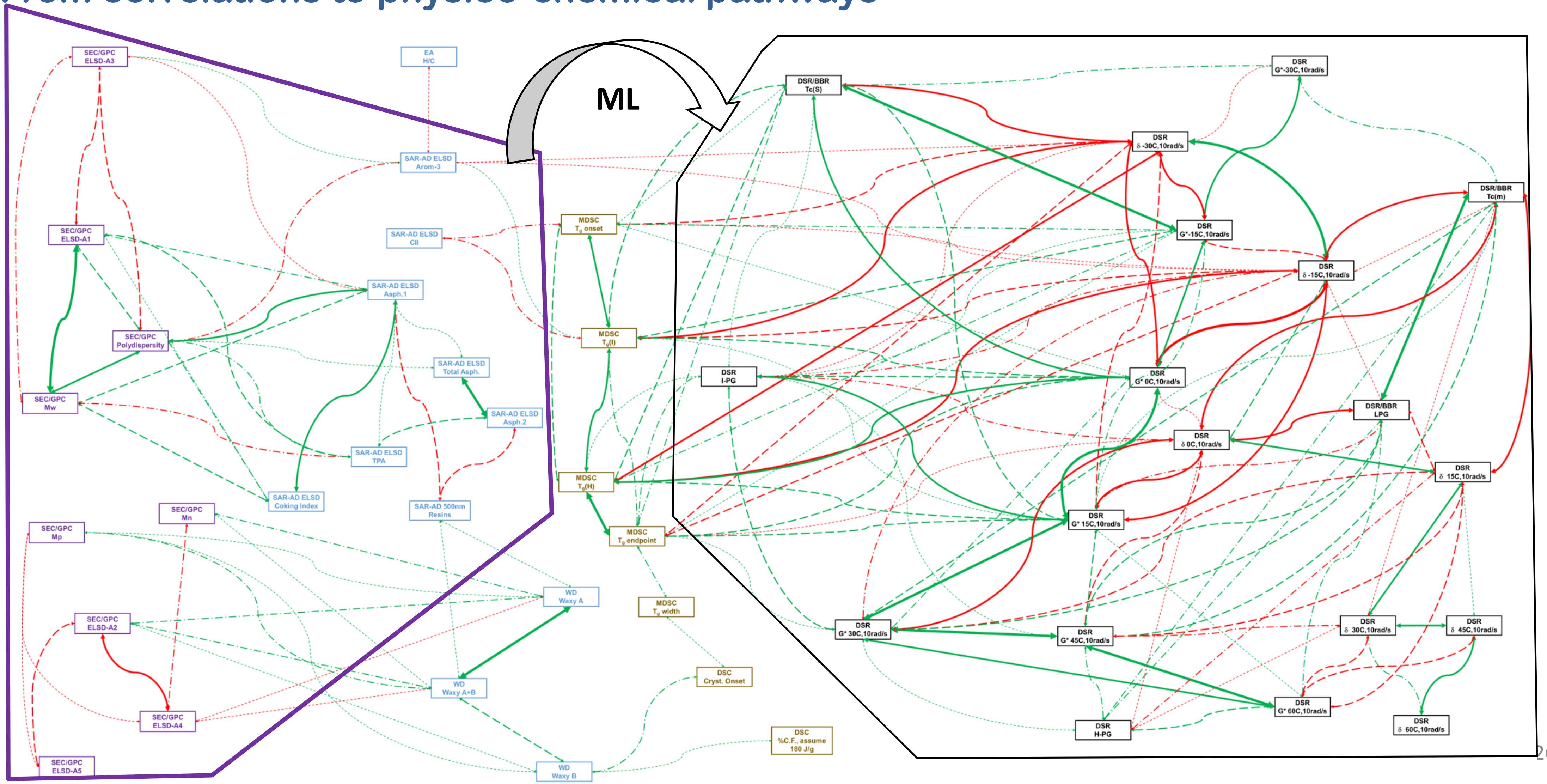
Bio-ACN PAN-based Fibers, $/lb

Petroleum Pitch-Based Fibers, $/lb



Technical Back-up Slides

From correlations to physico-chemical pathways



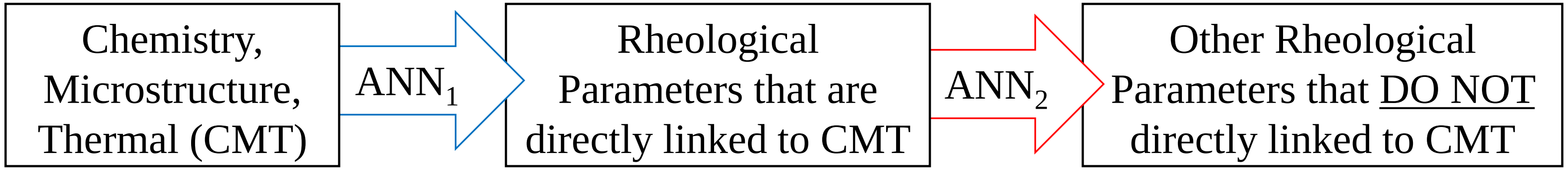
Technical Backup Slides

From correlations to physico-chemical pathways

Targeted (27 parameters) vs. holistic (60 parameters);

55% reduction in the input layer size.

Sum of Square Errors	Holistic	Targeted
Cont. H-PG	200	39
Cont. I-PG	33	12
Cont. L-PG	38	76
Tc(m)	47	79
Tc(S)	80	58
Total	398	264



Stepwise Approach

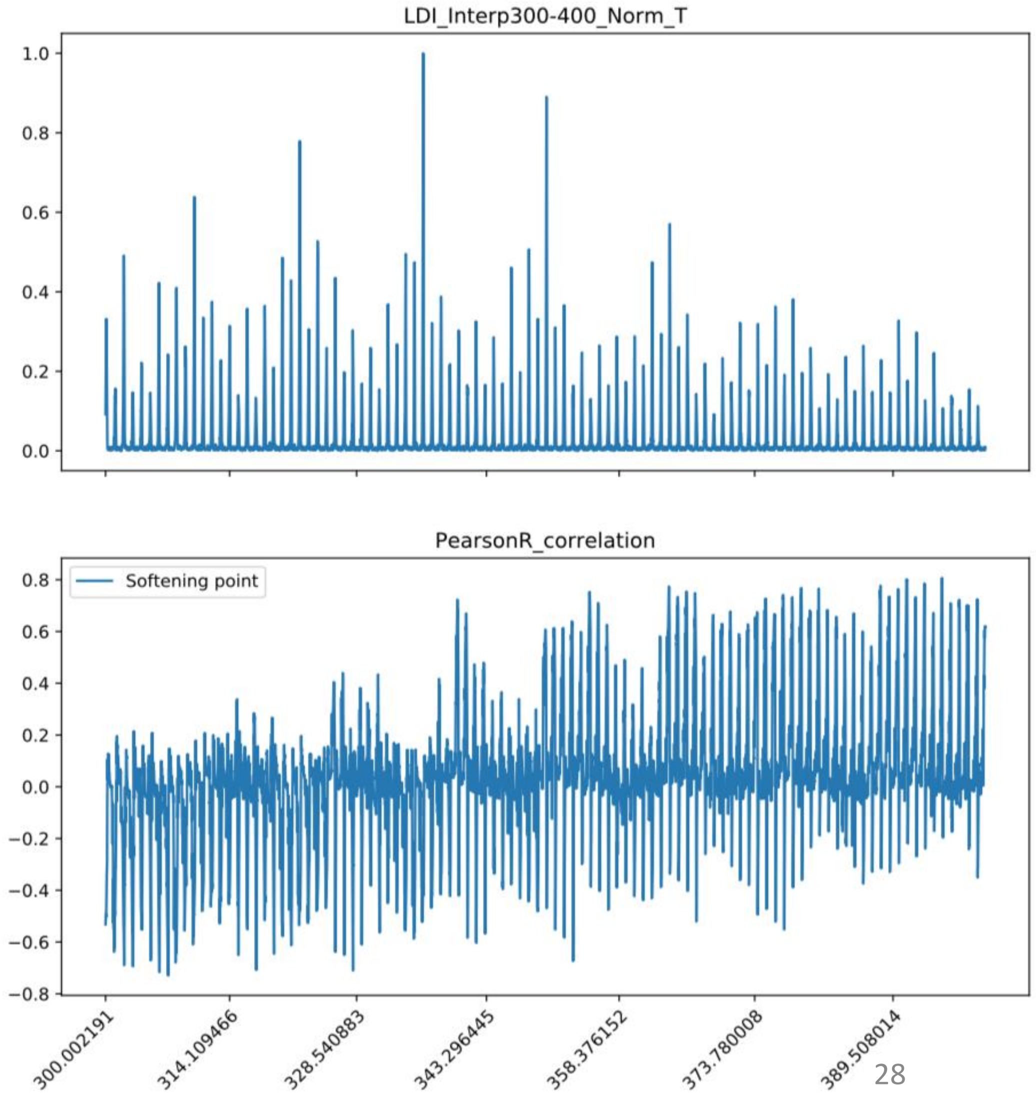
Western Research INSTITUTE

Technical Backup Slides

Identification of Predictive Parameters from Raw Data

- Highly convoluted/complex data cannot be easily used directly in ML
- Establishment of robust correlations with predictors (softening point, for example) is possible

- Example: Increasing softening point:
    - higher amounts of molecular systems with MW>350 D
    - Lower concentrations of mol. Systems with MW<350 D

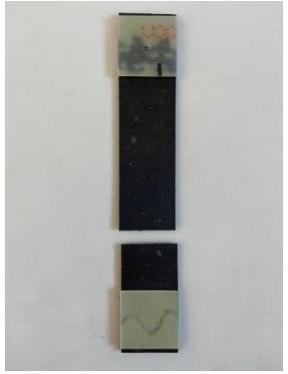


Technical Backup Slides

CF Resin Composites and Macro-Modeling – University of Wyoming

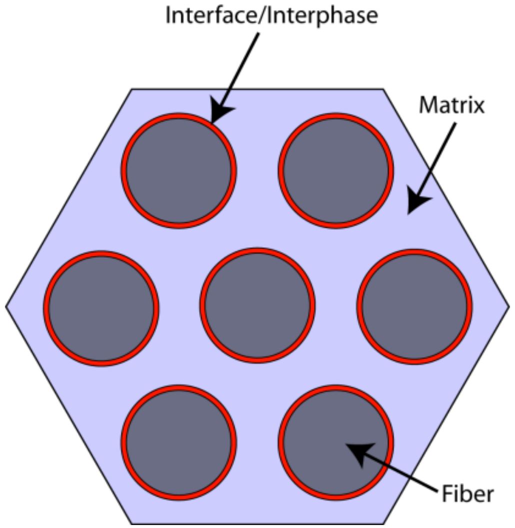
Tensile Testing

90 ° Tensile

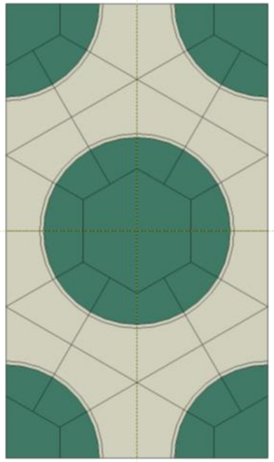


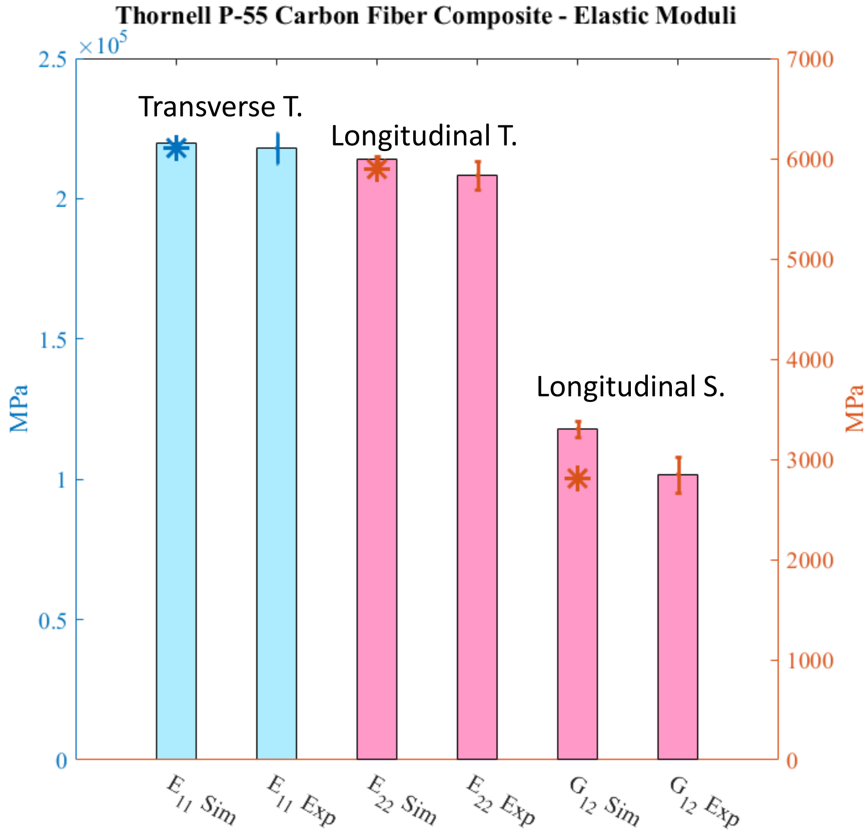
45 ° Tensile

Hexagonal Packing



Representative Volume Element





Models are within ±15%