Coal to Carbon Fiber (C2CF)

Continuous Processing for High Value Composites

DE-FE0031796

Matthew Weisenberger
University of Kentucky

U.S. Department of Energy
National Energy Technology Laboratory
Resource Sustainability Project Review Meeting
April 2 - 4, 2024

Center for Applied Energy Research

Disclaimer

- Acknowledgment: "This material is based upon work supported by the Department of Energy Award Number DE-FE0031796."

- Disclaimer: "This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof."

Project Overview

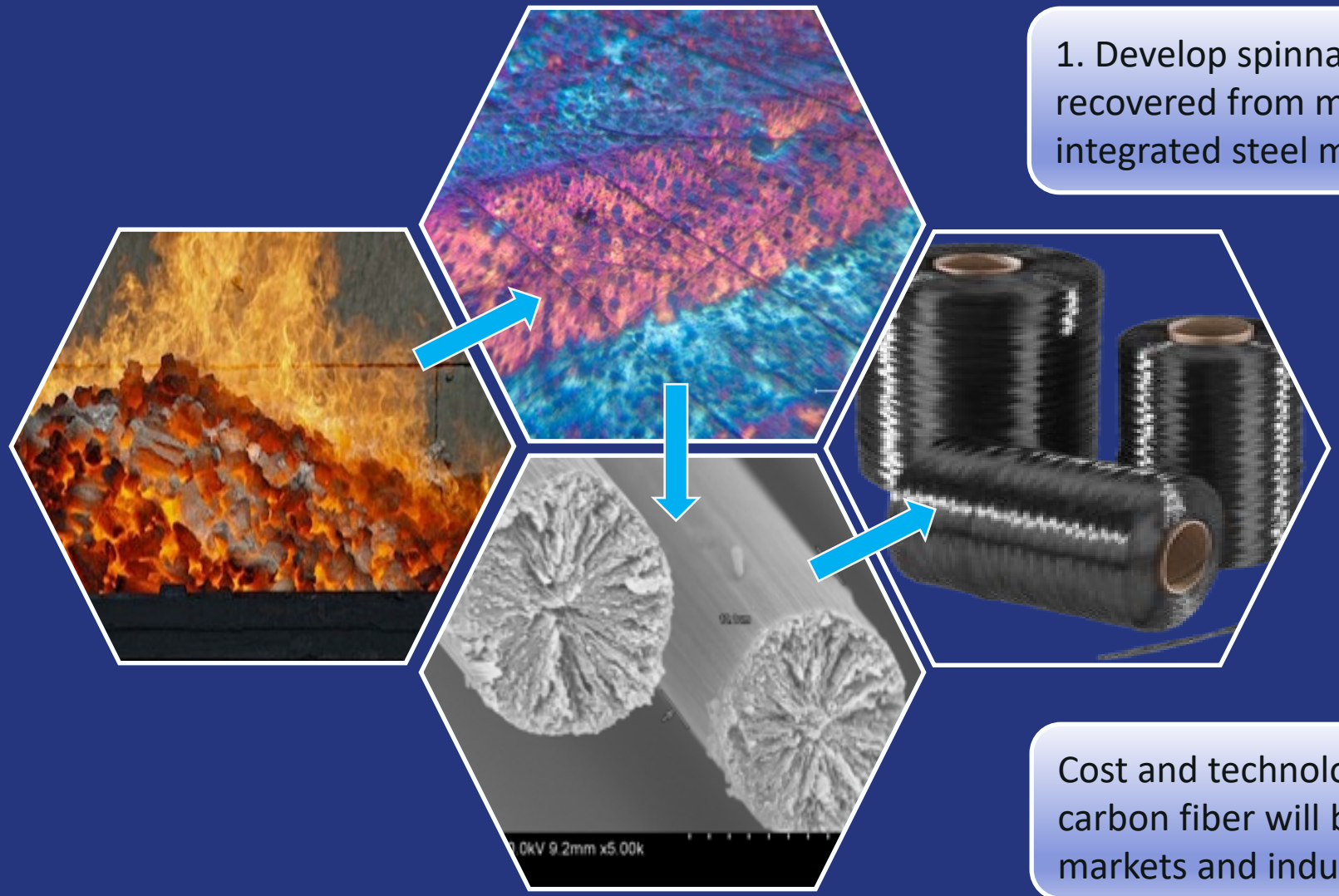
- Funding:
  - *10/01/2019 – 09/29/2024* *with 2 NCTEs to 09/29/2024*
  - *DOE* *$1,475,250* *expended*: $1,419,362*
  - *Cost Share* *$372,721* *(20.2 %)* *expended*: $372,721*

*as of 12/31/2023

- Project Participants:
  - University of Kentucky, Center for Applied Energy Research
    - Koppers Inc. (but not a subrecipient)

C2CF Coal to Carbon Fiber:

Continuous Processing for High Value Composites



OBJECTIVES

1. Develop spinnable mesophase pitch from coal tar recovered from metallurgical coke production at integrated steel mills.

2. Develop stable multifilament melt spinning and continuous thermal conversion

3. Demonstrate prototype composite parts with the carbon fiber.

Cost and technology gap analyses for the carbon fiber will be evaluated, for new markets and industries for US coal.

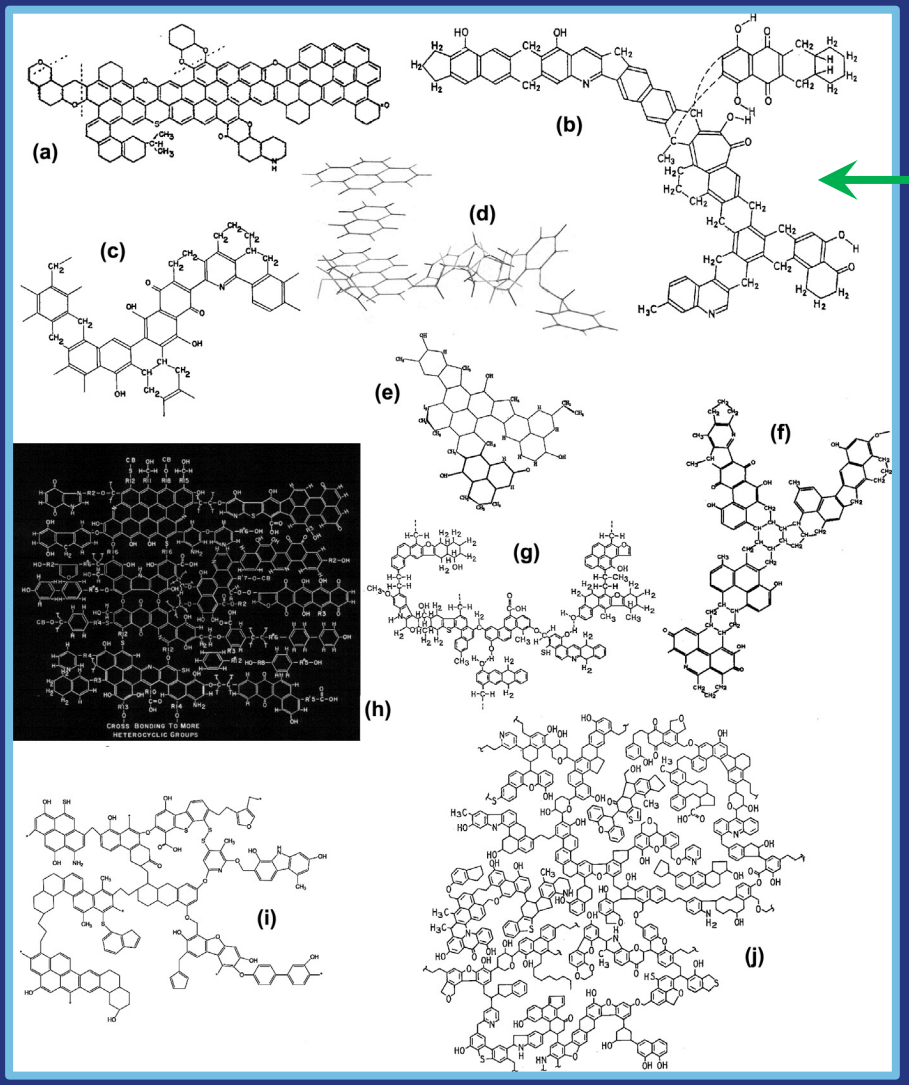
Talk Overview

- Project rationale/background and approach

- Task Updates: Successes & Challenges
  1. What is “spinnable” mesophase pitch?
  2. Single and MULTI filament spinning
     1. Carbon fiber morphology & properties
  3. Simple composites & results

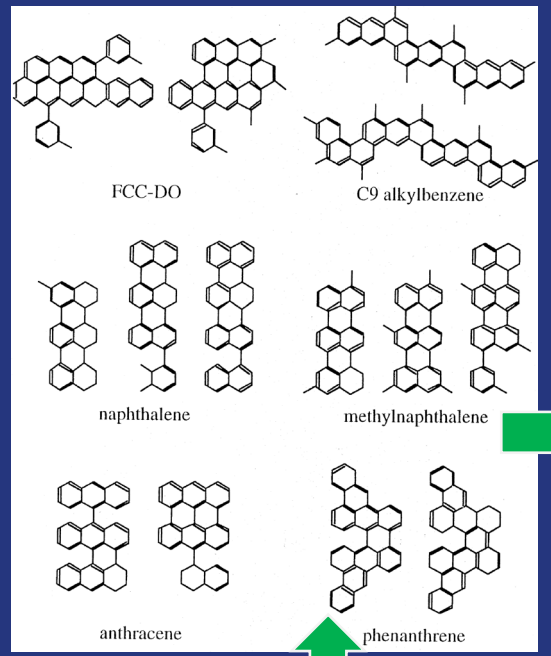
- Update on multifilament spinning stability

Rationale: Source Compounds in Coal



J.P. Mathews, A.L. Chaffee / Fuel 96 (2012) 1–14

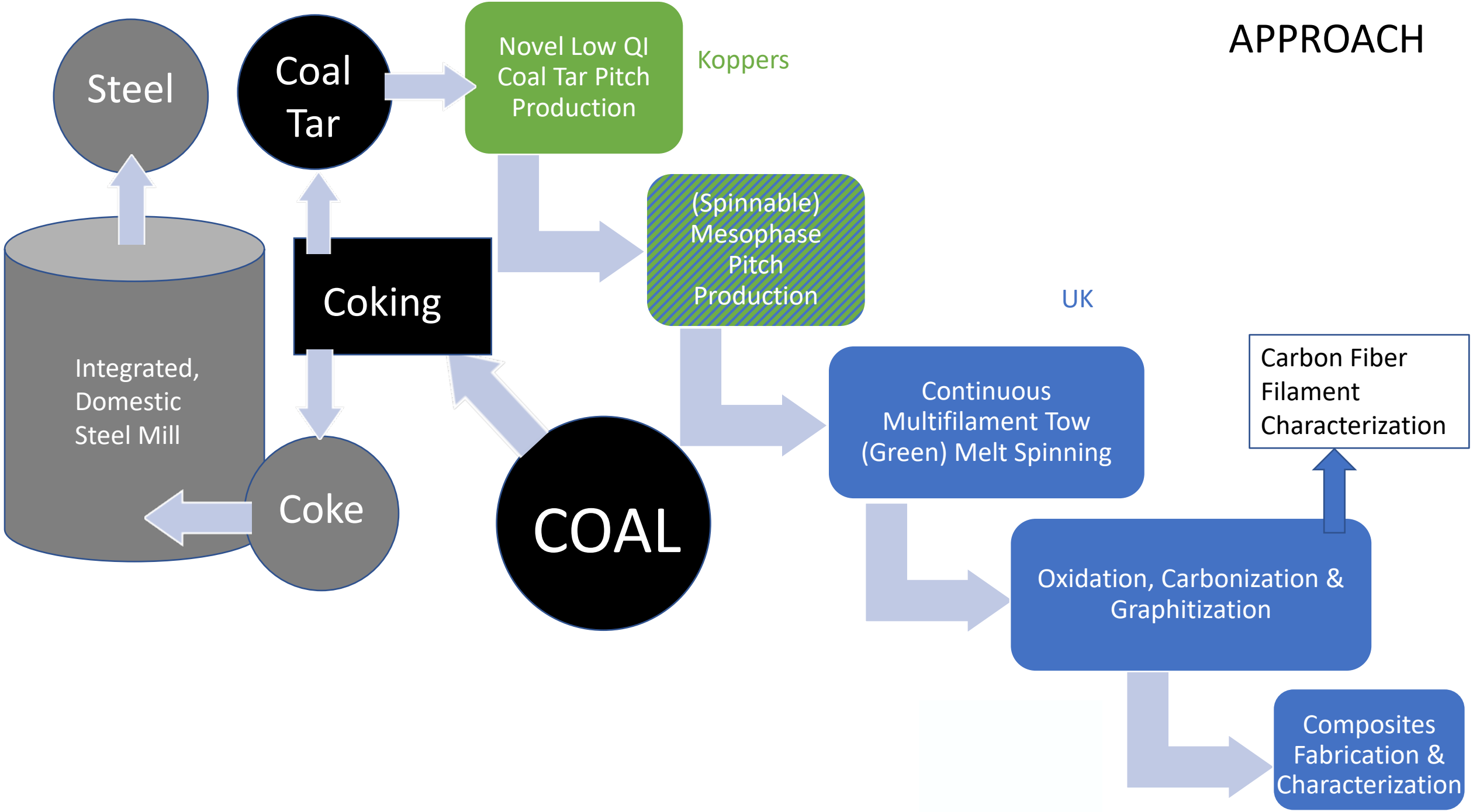
I. Mochida et al. / Carbon 38 (2000) 305 –328



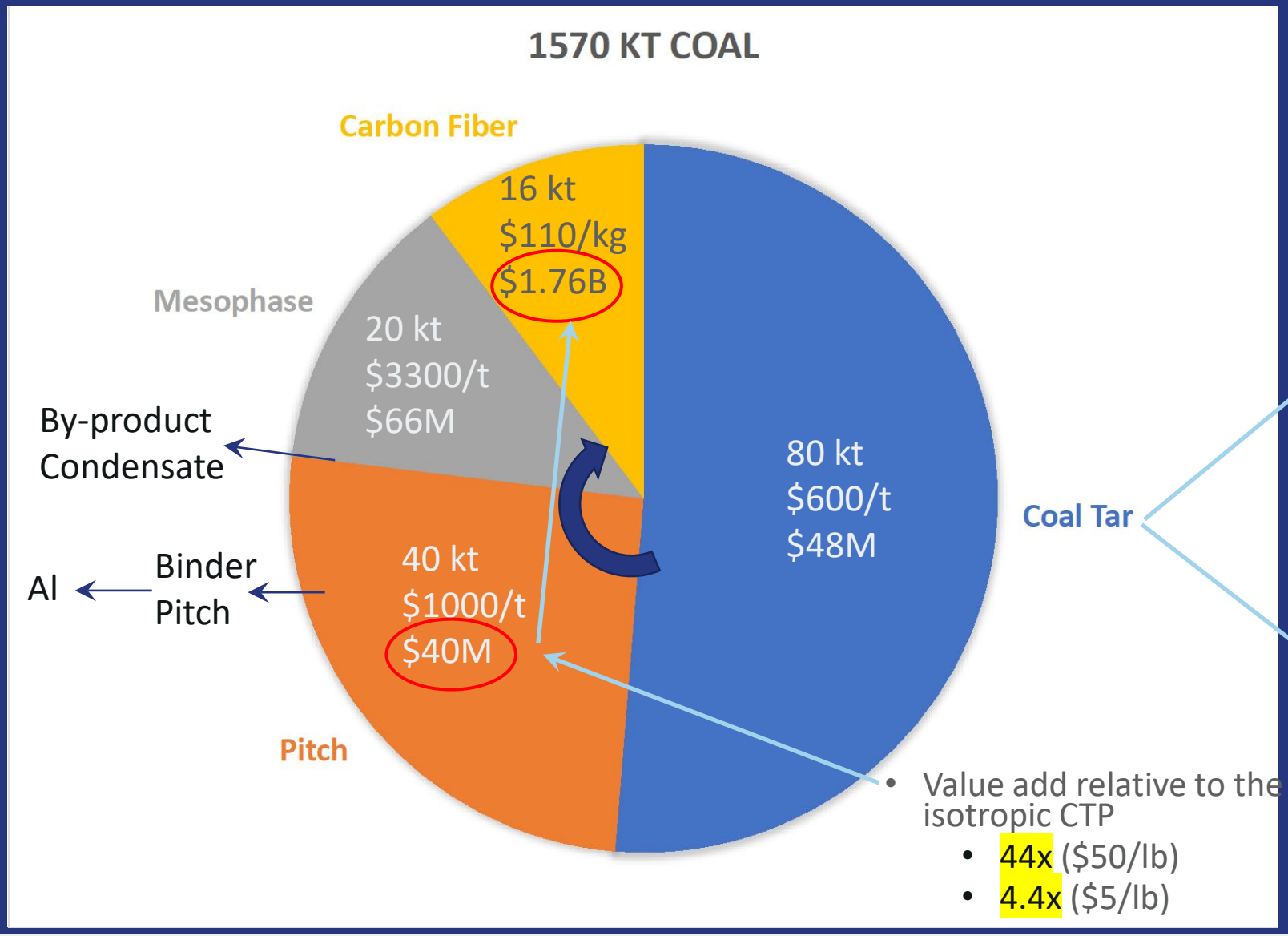
mesophase

Carbon fiber

APPROACH

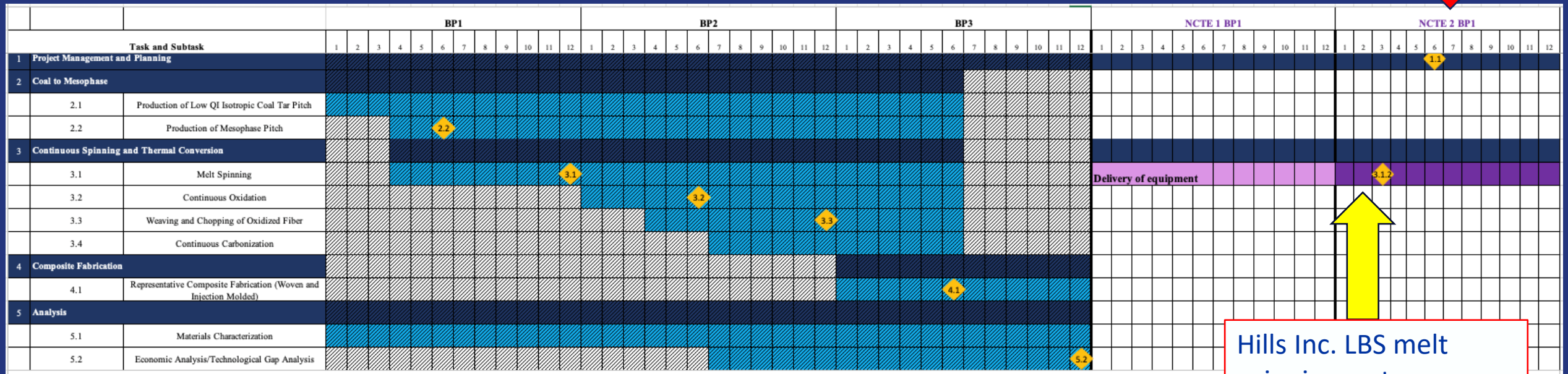

Steel
Coal Tar
Novel Low QI Coal Tar Pitch Production
Koppers
(Spinnable) Mesophase Pitch Production
Integrated, Domestic Steel Mill
Coking
Coke
COAL
UK
Continuous Multifilament Tow (Green) Melt Spinning
Carbon Fiber Filament Characterization
Oxidation, Carbonization & Graphitization
Composites Fabrication & Characterization

Economics: Case Study Value Add



Gantt Chart: Arrival of the Hills Inc. LBS

We are here: April 2024



Hills Inc. LBS melt spinning system delivered to UK CAER

Milestones

2.2: Production of ≥ 1 kg pitch containing ≥ 60% mesophase and a softening point ≤ 315 °C*
3.1: Continuous melt spinning of ≥ 60% mesophase pitch, with ≥ 100 filaments, for ≥ 10 minutes
3.2: Production of non-fused oxidized mesophase pitch fiber with high strain-to-failure
3.3: Demonstrate reproducible, melt spinning of mesophase pitch, with ≥ 100 filaments, for ≥ 10 minutes, with diameters targeting < 20 micron
4.1: Production of composite specimens with a ≥ 10 wt.% (chopped) coal-derived carbon fiber, and report thermal and mechanical properties
5.2: Production of continuous tow coal-derived carbon fiber and fabrication of representative composite specimens. Report mechanical and thermal properties.

3.1.2: Demonstrate reproducible, melt spinning of mesophase pitch, with ≥ 10 filaments, for ≥ 30 minutes, with diameters targeting < 20 micron
1.1: Update the Technological Gap Analysis

Milestone Chart

Task/ Subtask	Milestone Title/Description	Planned Completion Date	Actual Completion Date	Verification method
2.2	Production of ≥ 1 kg pitch containing ≥ 60% mesophase and a softening point ≤ 315 °C	03/31/2020	04/10/2020	Topical Report
3.1	Continuous melt spinning of ≥ 60% mesophase pitch, with ≥ 100 filaments, for ≥ 10 minutes	09/30/2020	11/04/2020	Quarterly Report
3.2	Production of non-fused oxidized mesophase pitch fiber with high strain-to-failure	03/31/2021	03/31/2021	Quarterly Report
3.3	Demonstrate reproducible, melt spinning of mesophase pitch, with ≥ 100 filaments, for ≥ 10 minutes, with diameters targeting < 20 micron	09/30/2021	10/15/2021	Quarterly Report
4.1	Production of composite specimens with a ≥ 10 wt.% (chopped) coal-derived carbon fiber, and report thermal and mechanical properties	03/31/2022	04/06/2022	Quarterly Report
5.2	Production of continuous tow coal-derived carbon fiber and fabrication of representative composite specimens. Report mechanical and thermal properties.	09/30/2022	09/30/2022	Quarterly Report
NCTE 3.2	Demonstrate reproducible, melt spinning of mesophase pitch, with ≥ 10 filaments, for ≥ 30 minutes, with diameters targeting < 20 micron	06/30/2024		Quarterly Report

Tasks Updates

Task 2: Routine Coal Tar to Mesophase

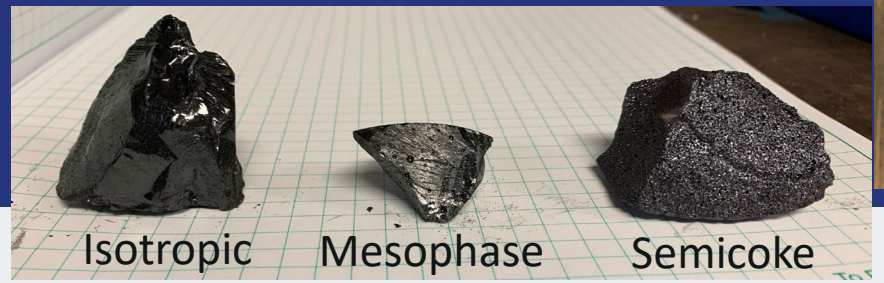
Low QI, isotropic coal tar pitch production

< 1 wt.% QI

T_{sp} ~ 100 ºC

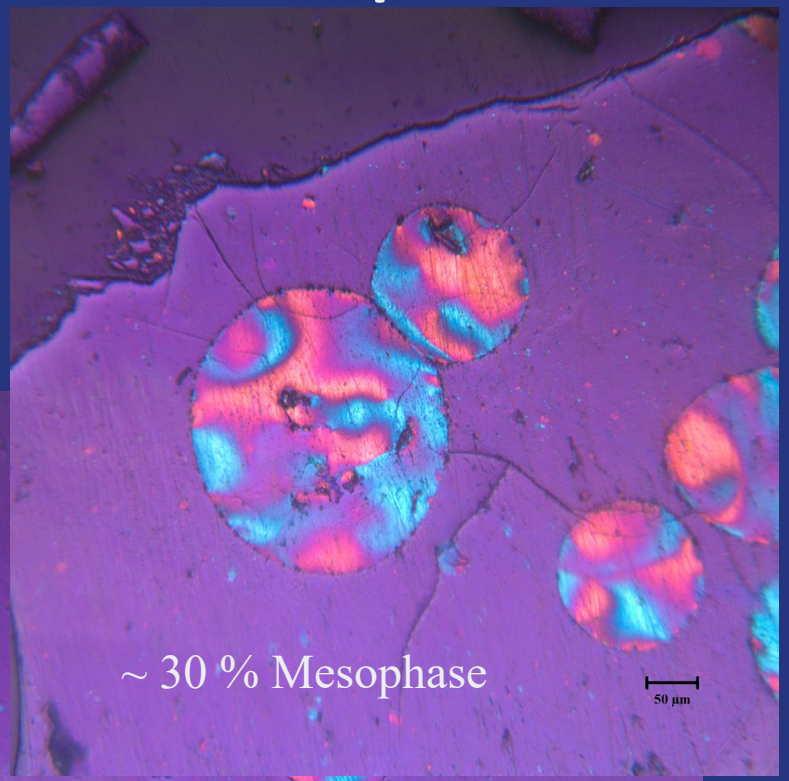
1 kg/batch mesophase production

2 L scale reactor at UK CAER



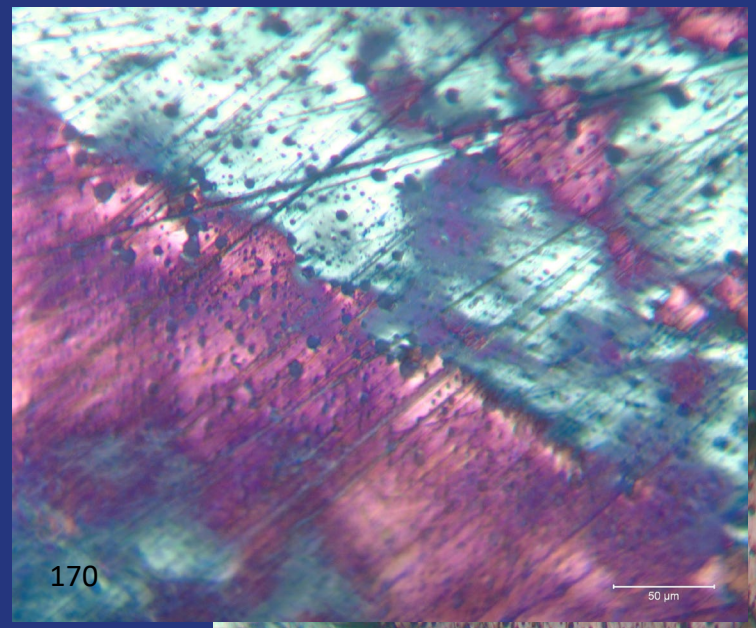
Coal tar derived SPINNABLE mesophase pitch

Development & Counting of Mesophase

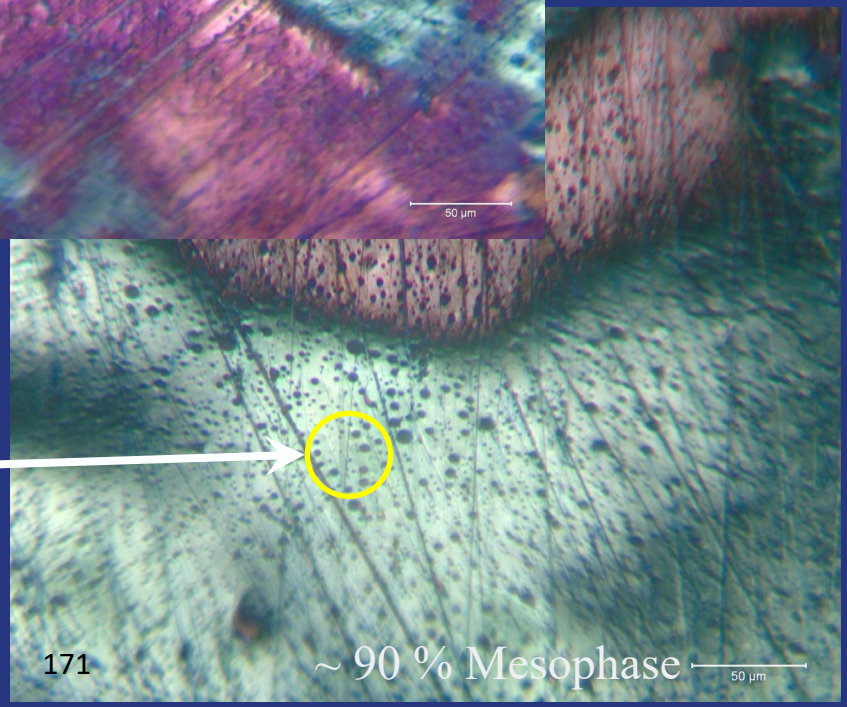


SPINNABLE

- Homogeneous at ~ 10 micron length scale
- T_{sp} < 330 °C
- > 70% Mesophase (flow domain)
- E_a > ~200 kJ/mol

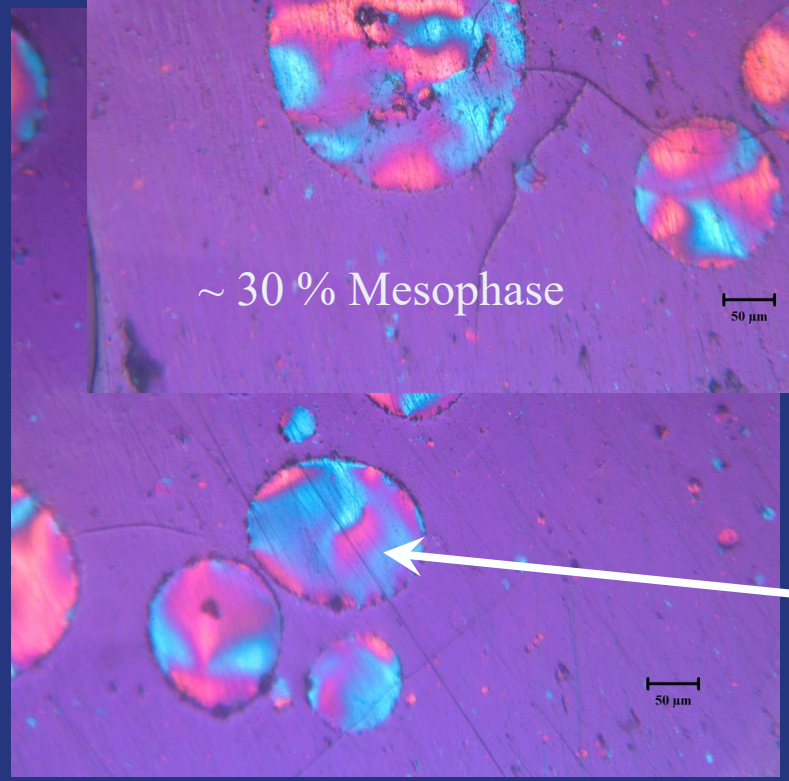


T_{sp} = 296 C
90 – 95% mesophase



Isotropic

Mesophase

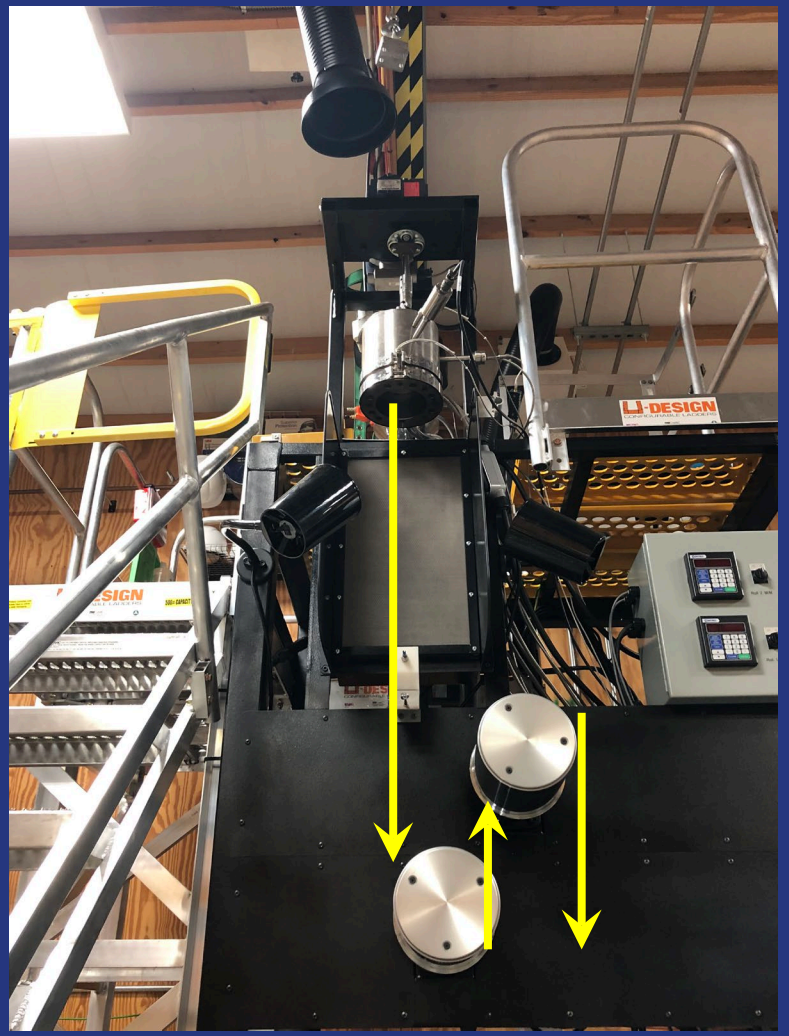


ASTM D4616-95.

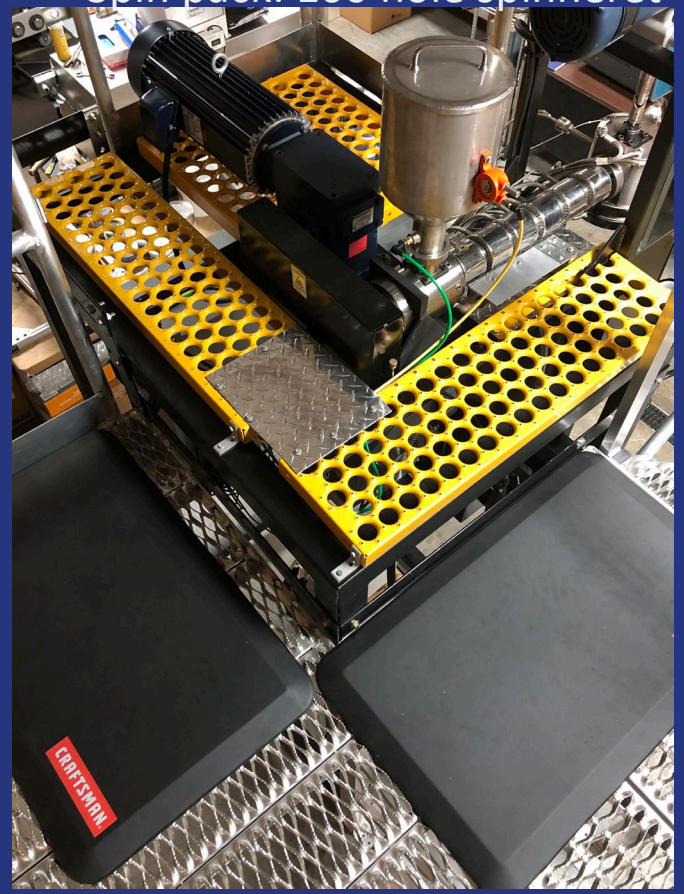
Subtask 3.1 – Melt Spinning AJ

Extruder System

Operational Winter 2021



1” Extruder
Metering pump
Spin pack: 100 hole spinneret



AJ64 Run

25 Filament

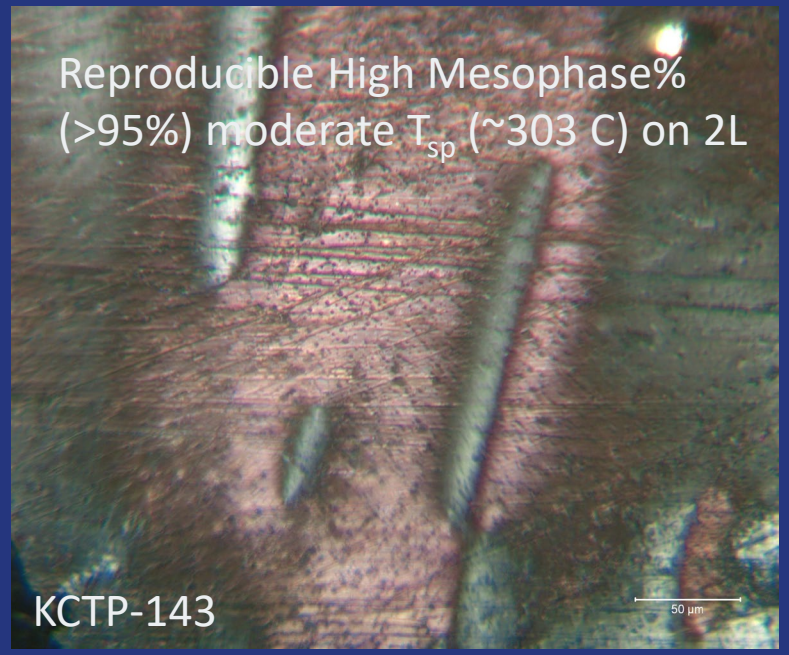
- Pitch: KCTP-143,145,146
- 25-hole 150 μm spinneret
- Newer 0.297 CC/rev metering pump

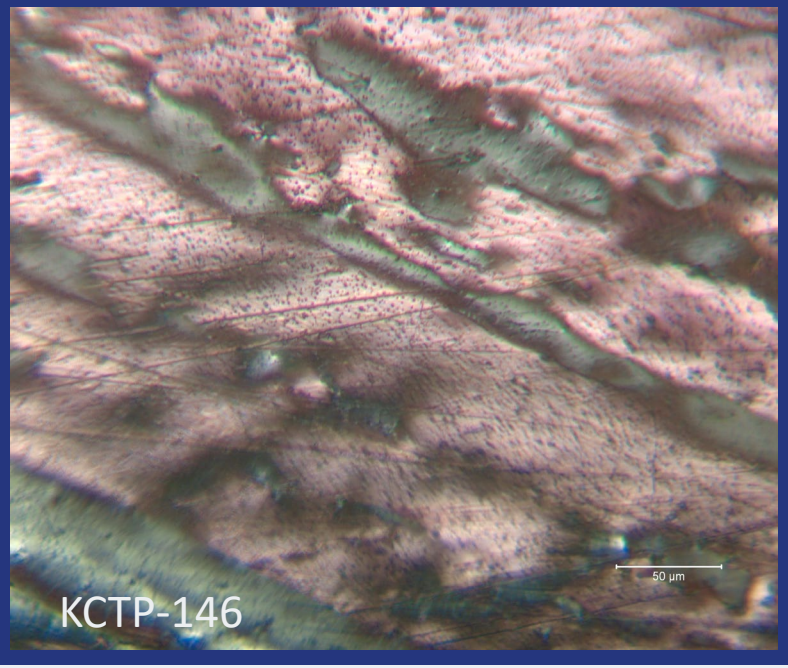
Results

- Able to draw ~30 μm fiber multifilament 10s of min.
- Able to obtain ~20 μm fiber but at only ½ or less filaments
  - Still working on draw processing issues

Keys to improved stability:

- 25-hole spinneret being more manageable
- Improved hole cleanliness
  - (no burnout. Sonication only)
- More accurate flowrate
  - (new metering pump. No burnout)
- Improvement in spinneret face cleanliness during run





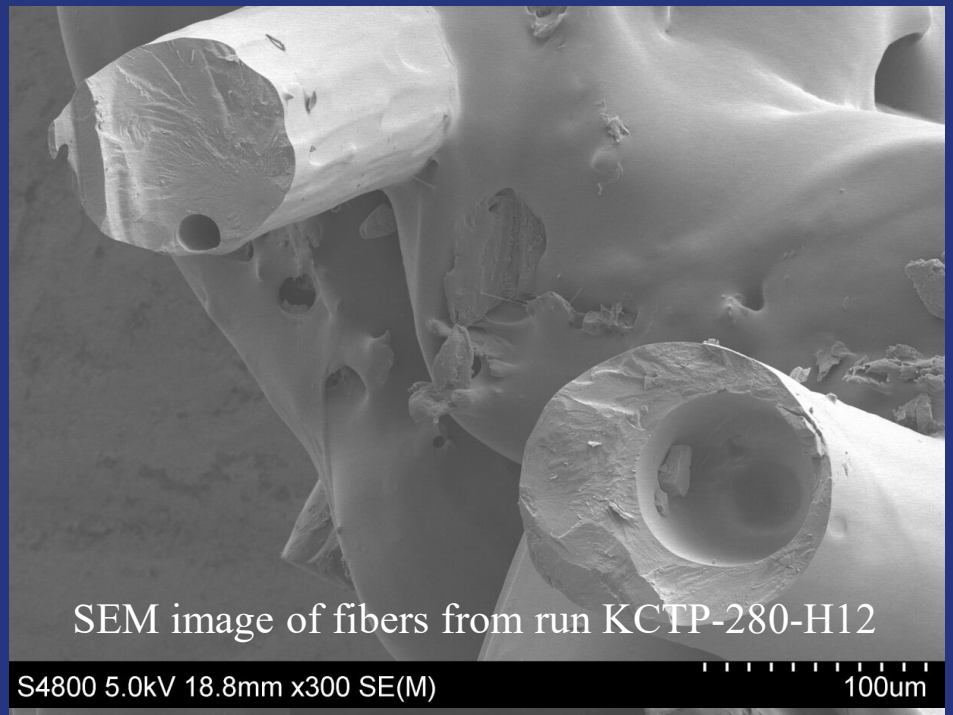
NCTE: Task 3.1 Multifilament Melt Spinning

Hills Inc. LBS

- The LBS machine is a piston-type melt extrusion machine designed to run low volume lab trails with a wide variety of polymers
- Received and installed at CAER late October early November 2024
- 22-hole spinneret
- 150 μm capillary diameter
- L/D = 10
- Load capacity: ~35 g

Hills run KCTP-280-H12

- Poor quality fibers
- Dia. ~ 90 μm
- Bumpy, voids/bubbles



SEM image of fibers from run KCTP-280-H12

SEM image of fibers from run KCTP-280-H12

Two leading hypothesis:

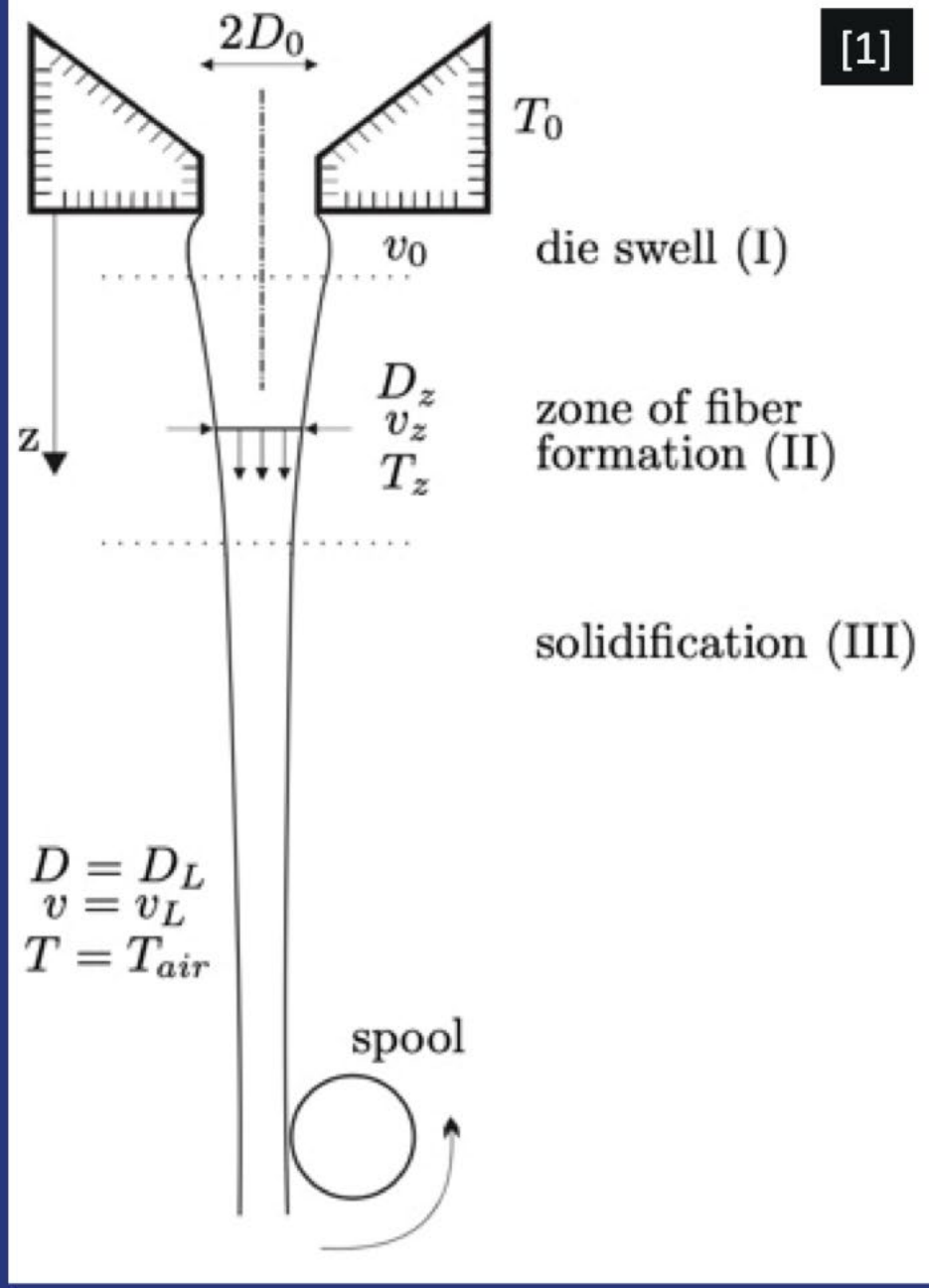
1. Filament is cooling too rapidly as it exits the spinneret, i.e., filament becomes brittle and can not be drawn down

2. Pitch is off-gassing in spinneret and bubbles can only escape out the capillary with the filament causing voids/bumpy fibers

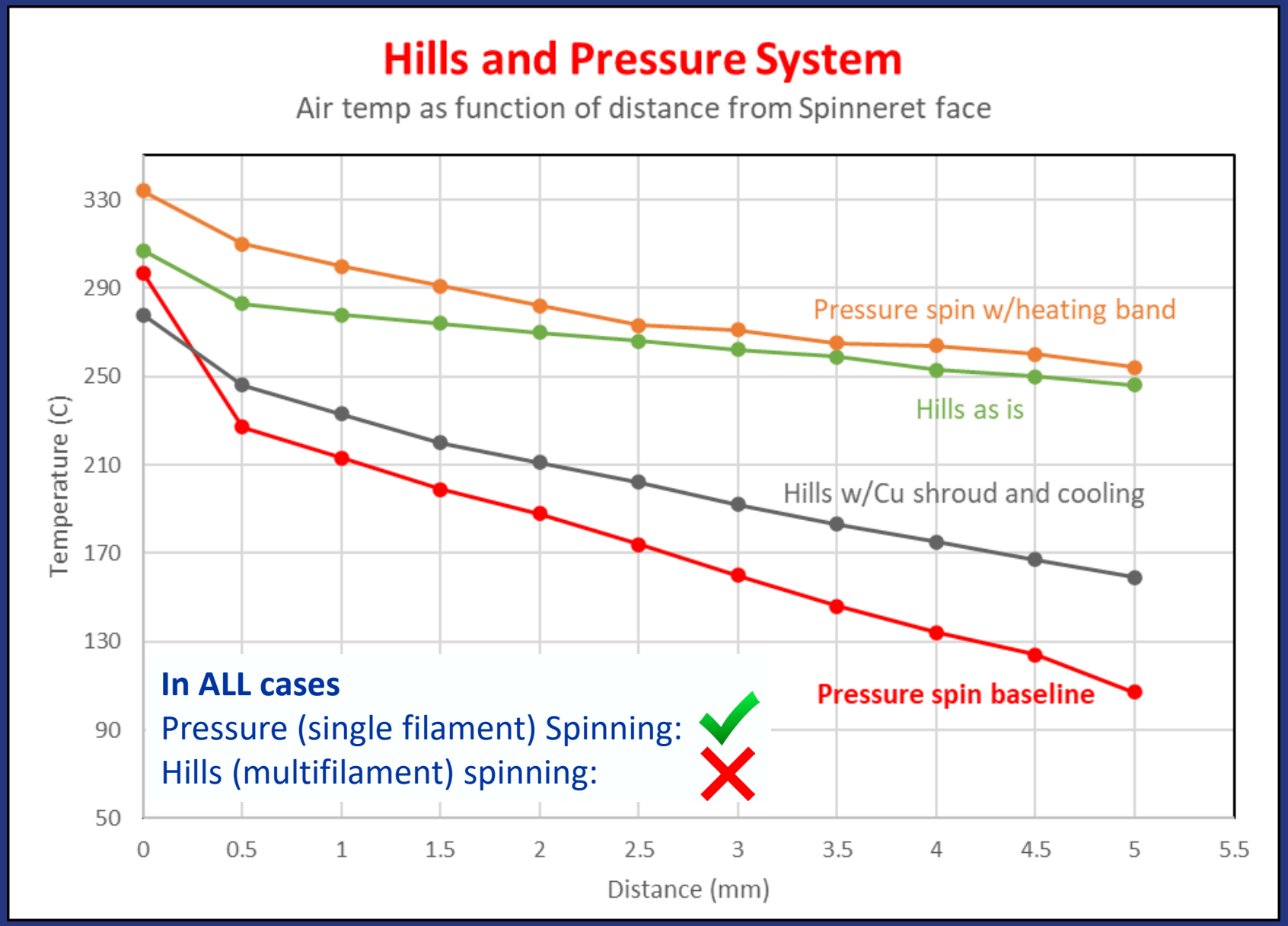
Melt Spinning

$$F = \frac{3\eta Q}{L}\ln(DDR)$$ [2]

- High stress during melt draw
  - Mesophase pitch: 10-25% of ultimate strength [3]
  - Nylon: 1% of ultimate strength [4]
- Factors that induce high stress [3]
  - Decrease spinning temperature
  - Increase air cross-flow



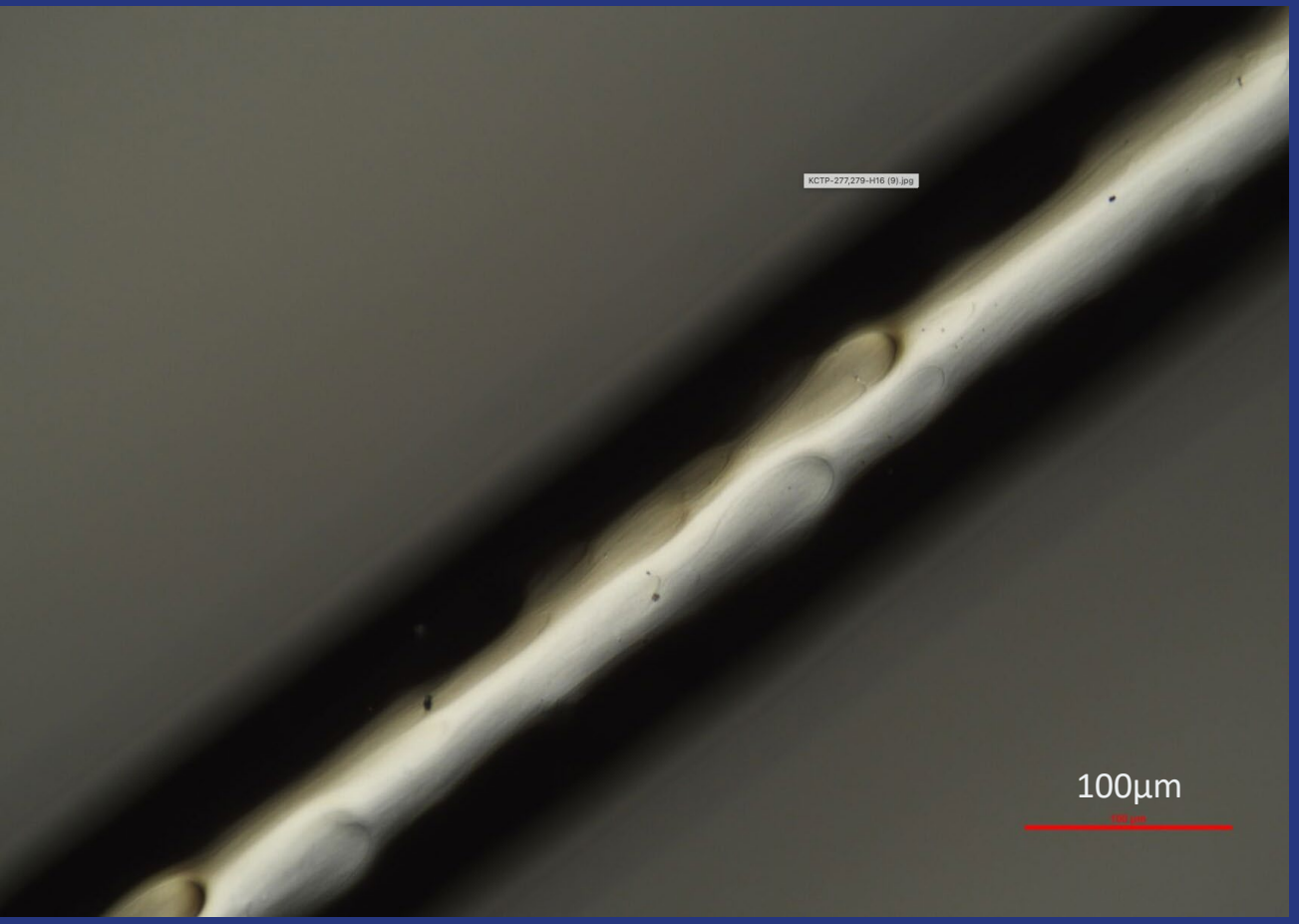
[1] de Souza Mendes, P.R., *Impact of spinning conditions on the structure and tensile properties of mesophase pitch carbon fibers*. 2019, PUC-Rio.
[2] Wagner, M.H., B. Collignon, and J. Verbeke, *Rheotens-mastercurves and elongational viscosity of polymer melts*. Rheologica acta, 1996. **35**(2): p. 117-126
[3] Edie, D. and M. Dunham, *Melt spinning pitch-based carbon fibers.* Carbon, 1989. **27**(5): p. 647-655.
[4] Morgan, P., *Carbon fibers and their composites*. 2005: CRC press.

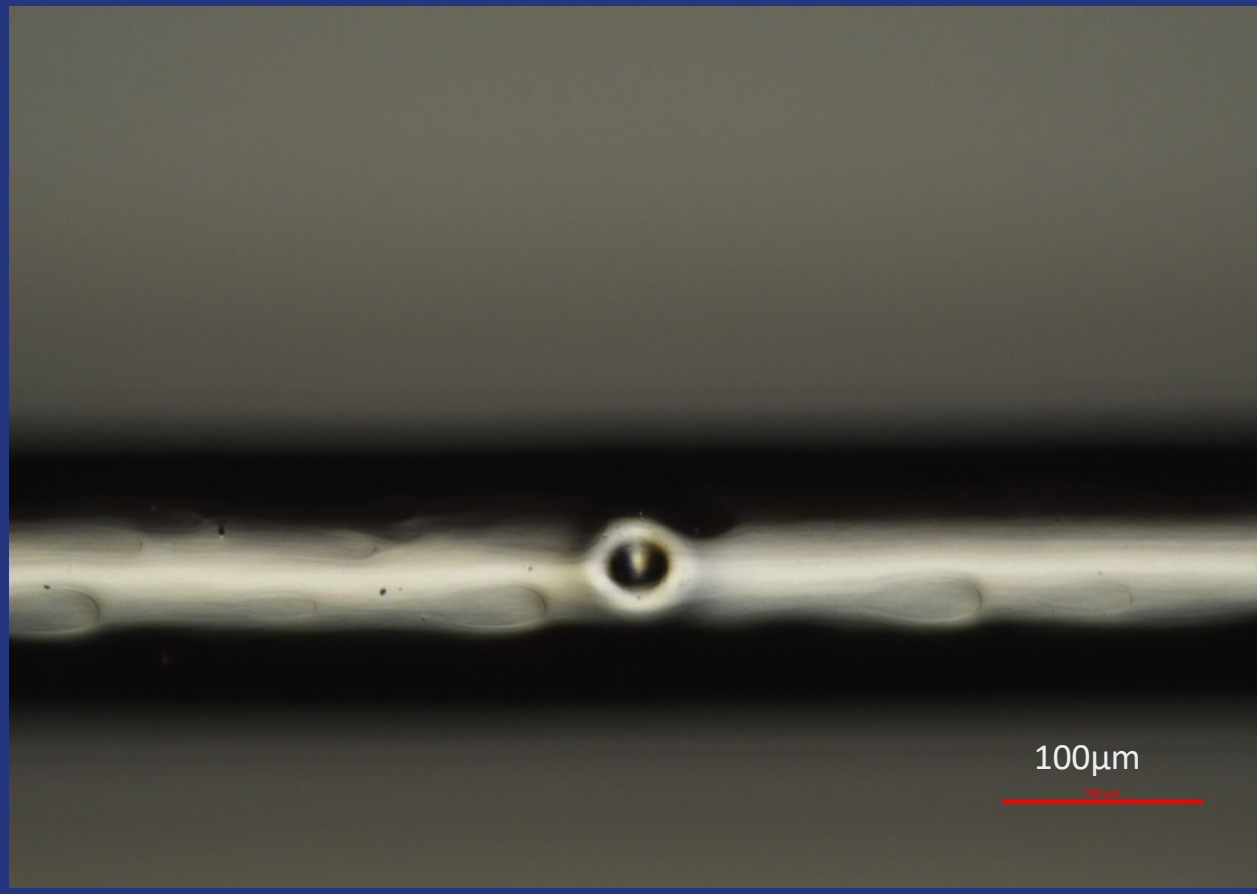


- Pressure spin baseline:
  - Fiber dia. 25 μm
  - Duration indefinitely
- Hills as is:
  - 22/22 filaments
  - Fiber dia. ~ 50 μm
  - Duration ~ 2 min
  - Break – unable to restart
- Hills w/Cu shroud & cooling:
  - 22/22 filaments
  - Fiber dia. ~ 45 μm
  - Duration ~ 2 min
  - 5/22 fibers @ 30 μm for ~ 1min

Hills spinneret showing bubbly/foamy pitch

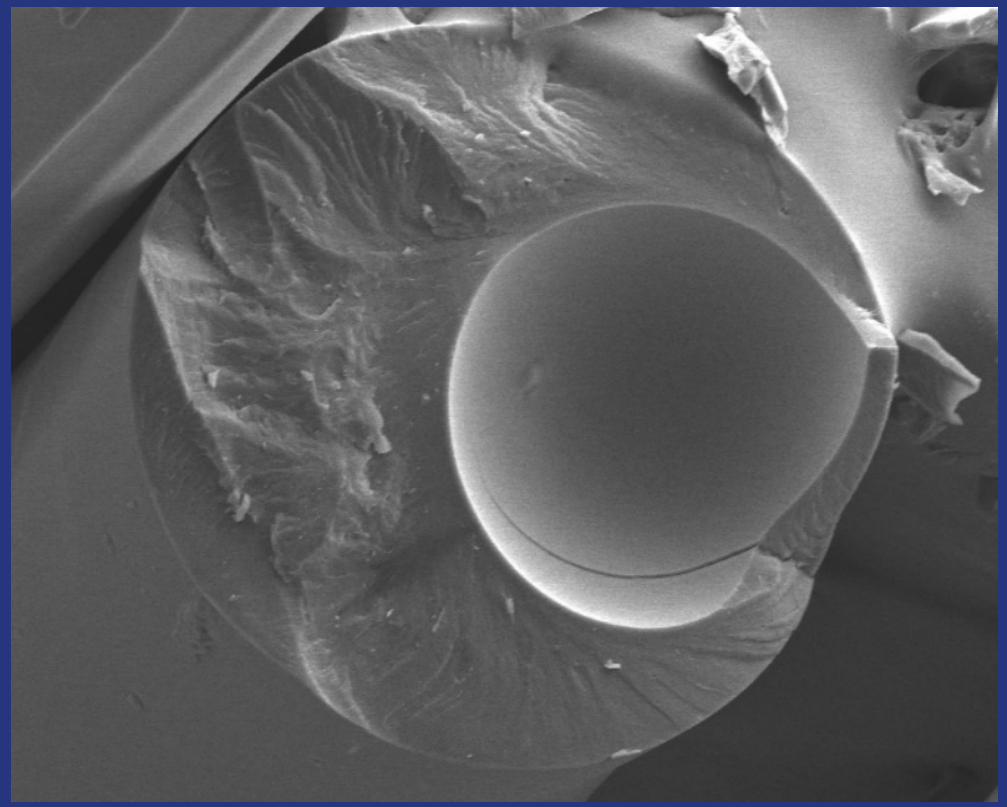
Extrudate from Hills H17 run showing fibers with “tear drop” defects

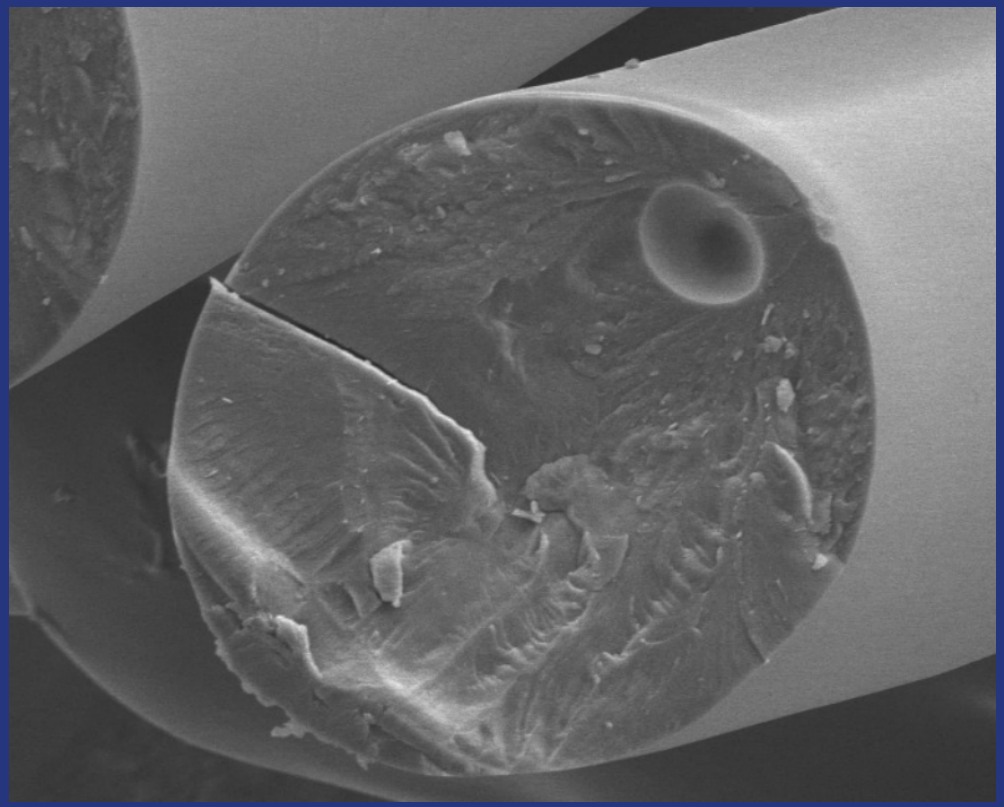




SEM pic of filaments from Hills run H17

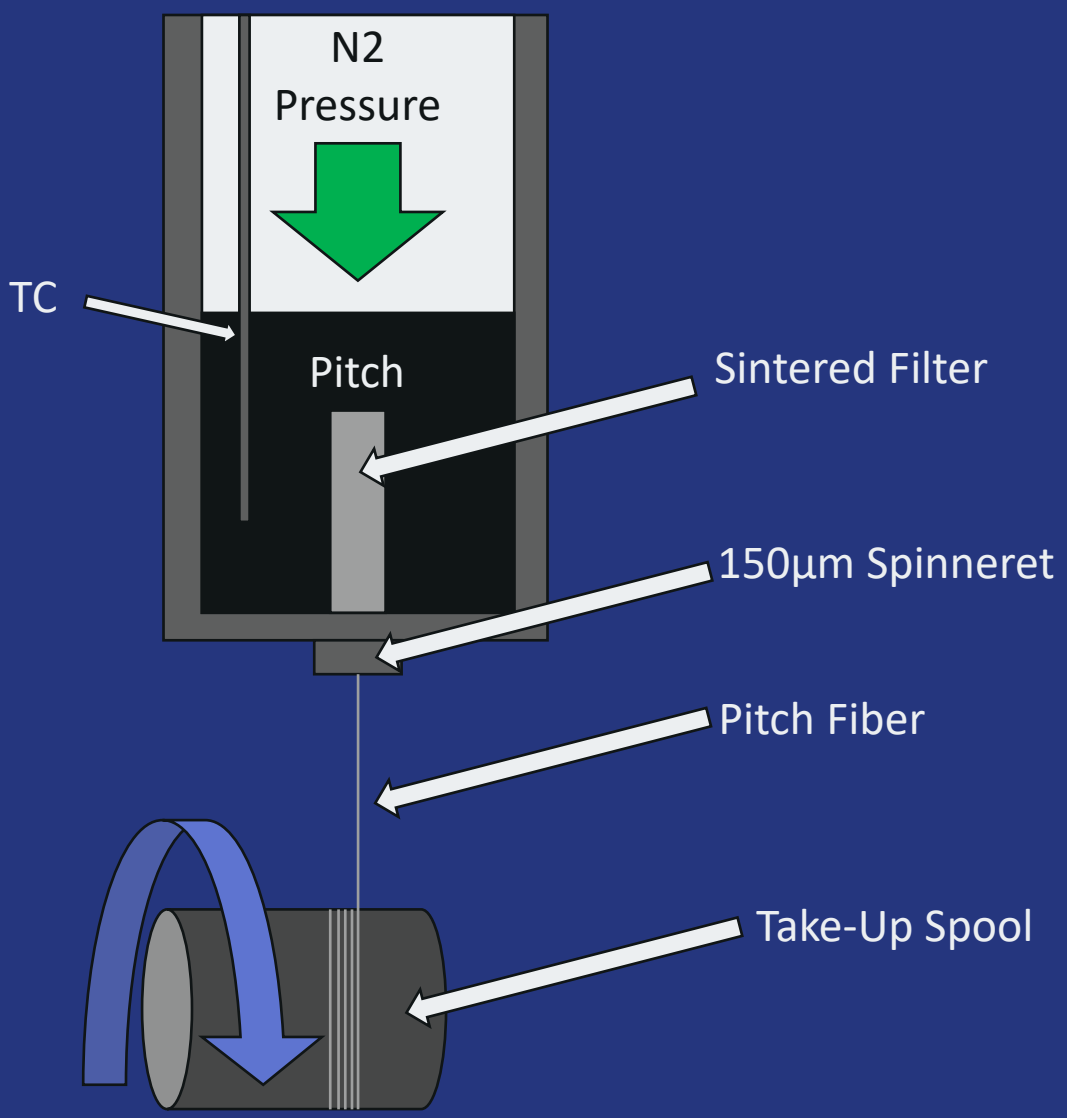
- 2 bubble voids PER 12 filament cross sections
- 17% of random cross sections containing bubble voids

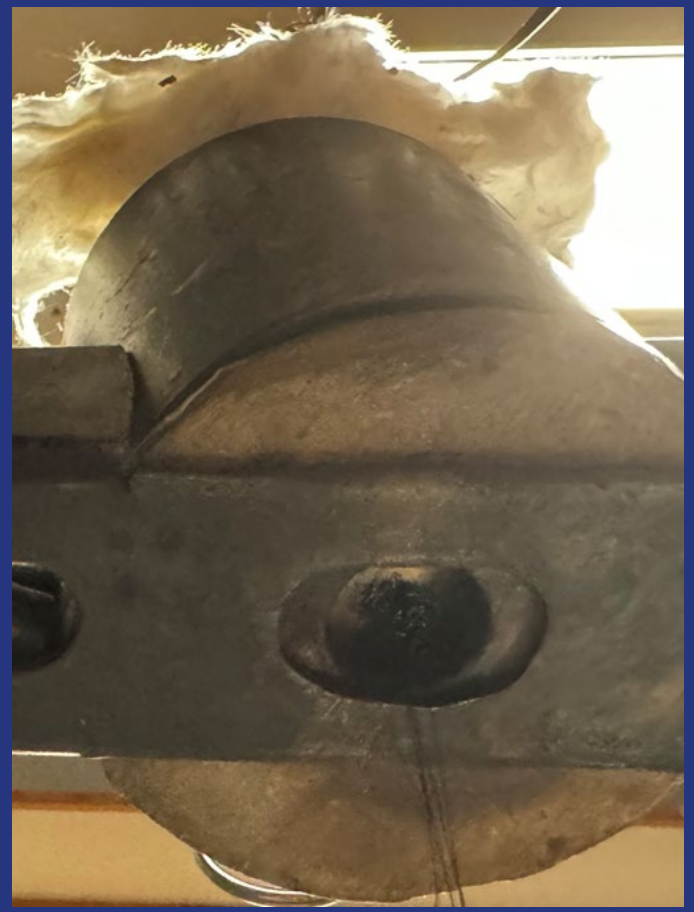




WHY: Pressure spinning apparatus?

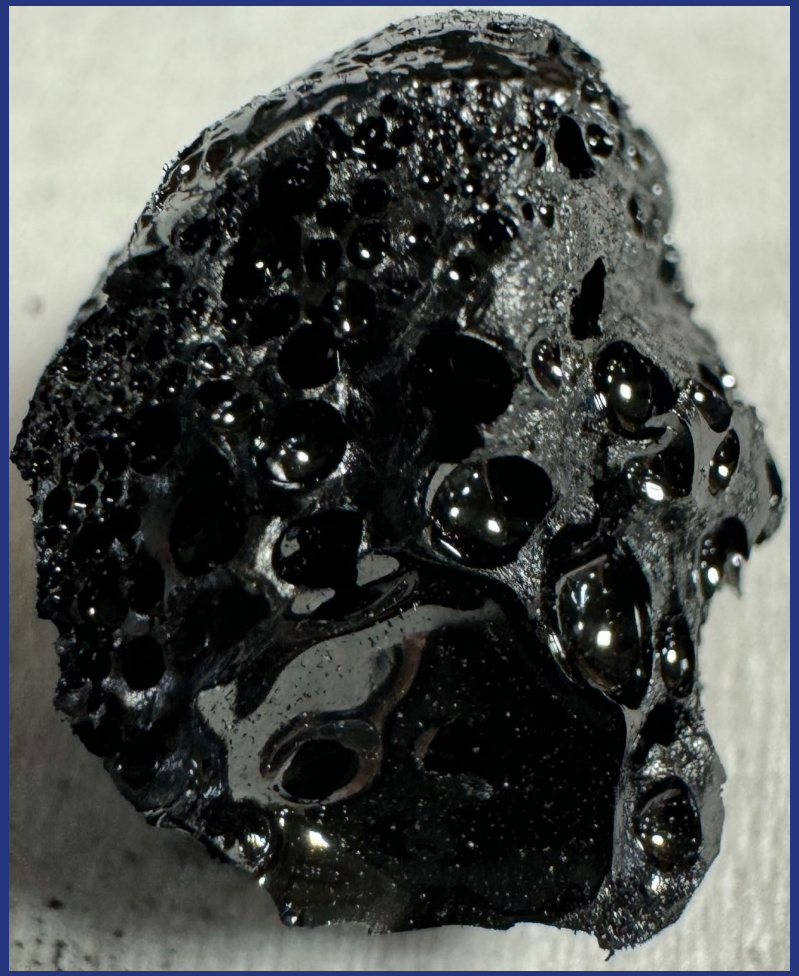
Hypothesis: Quiescent melt

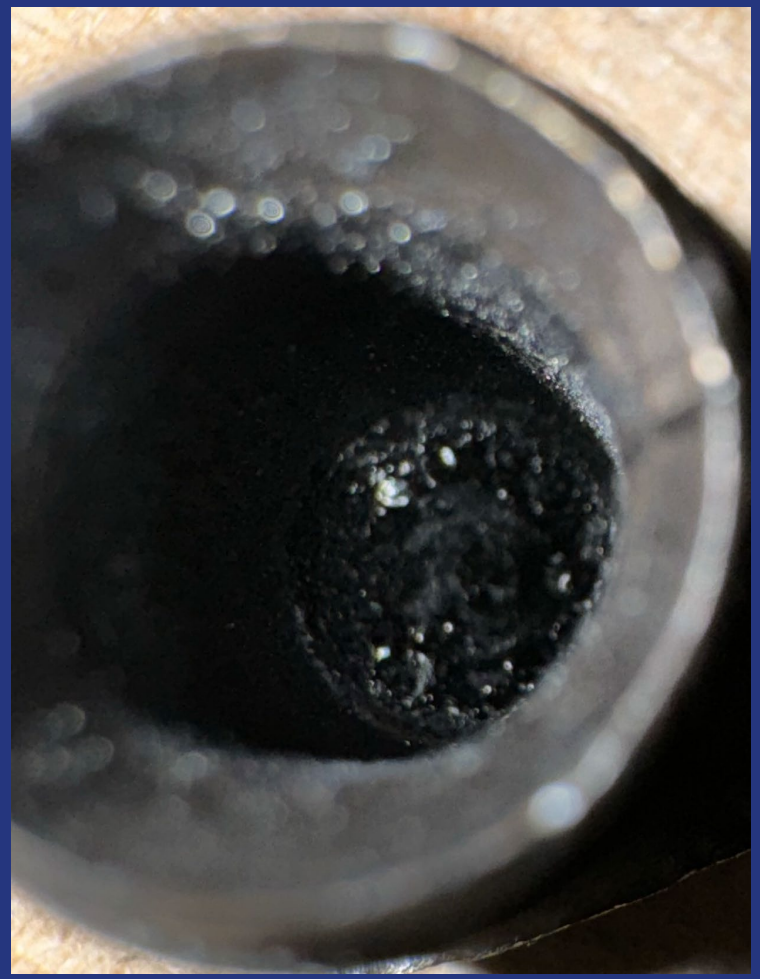


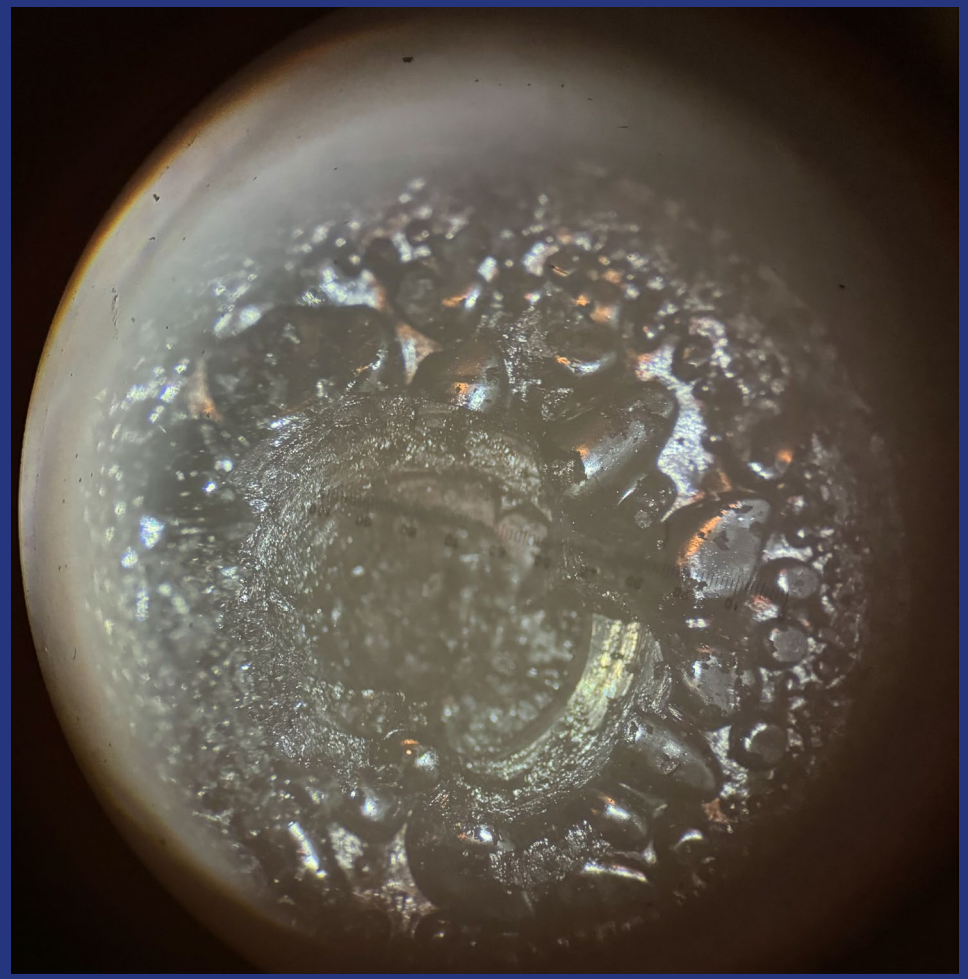


Pressure Spinning Capsule showing bubbly/foamy pitch

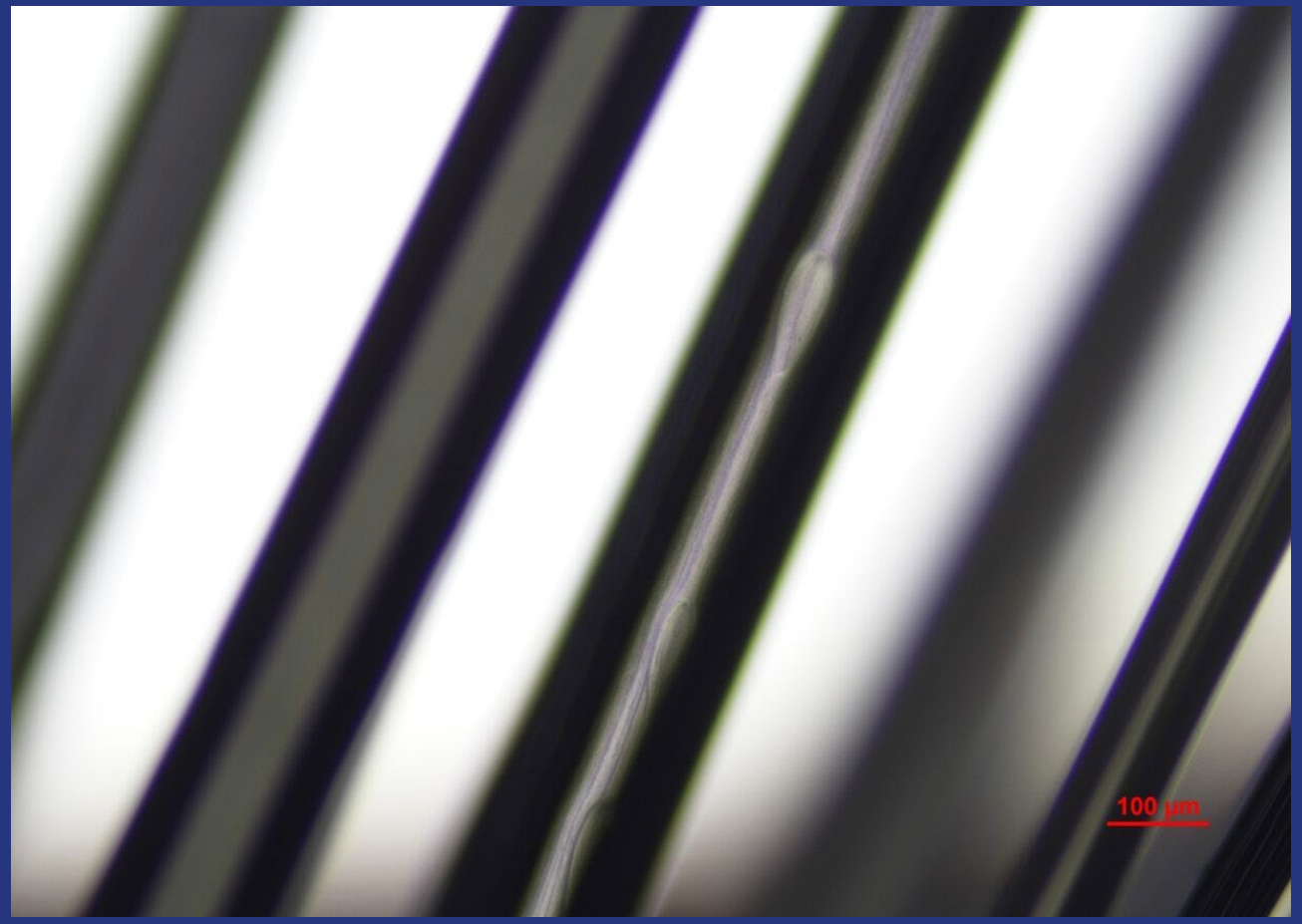
after ~5min of successful spinning ~20um fibers





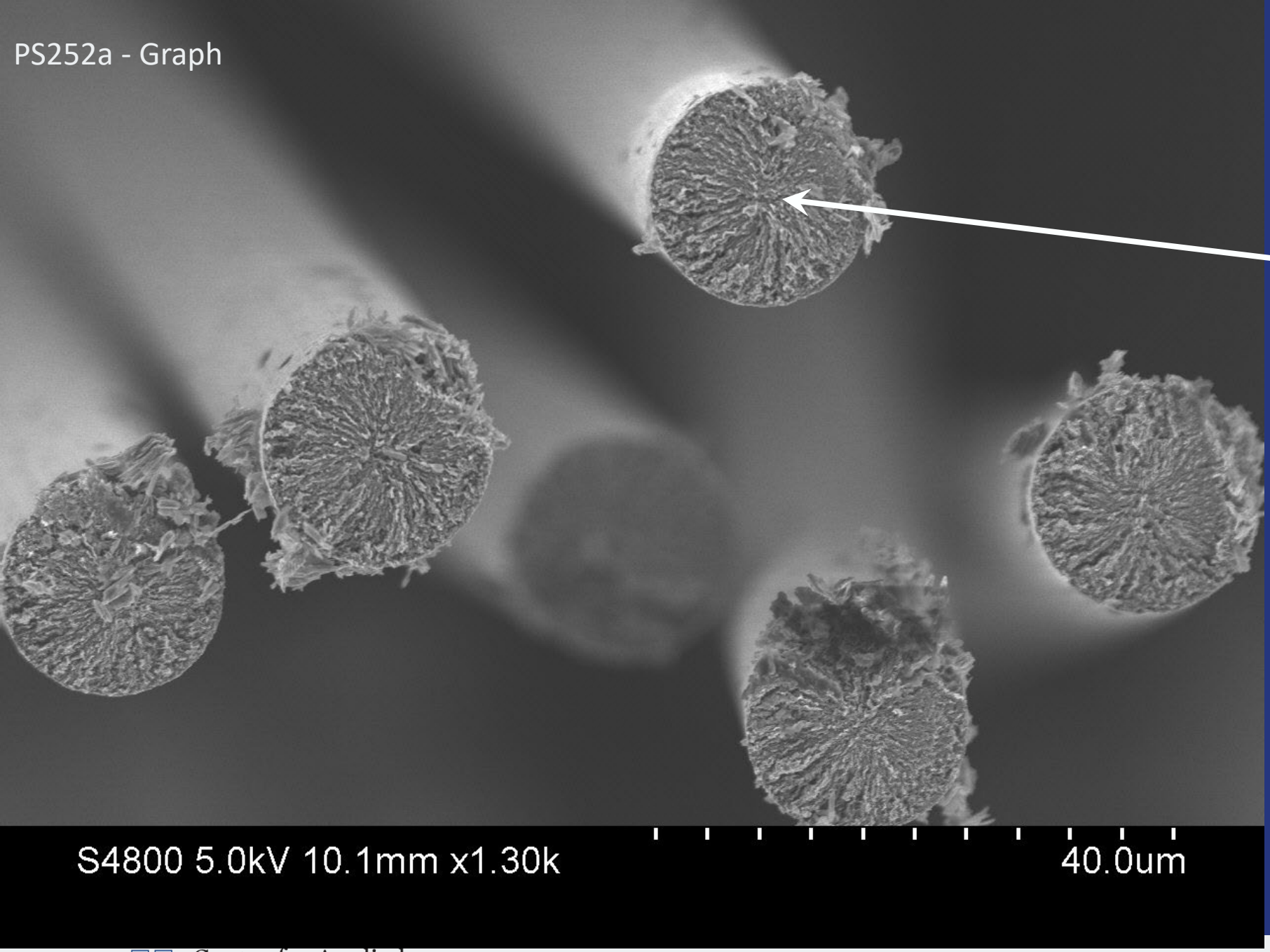


Extrudate from Pressure Spin showing “tear drop” defect - but not on all fibers

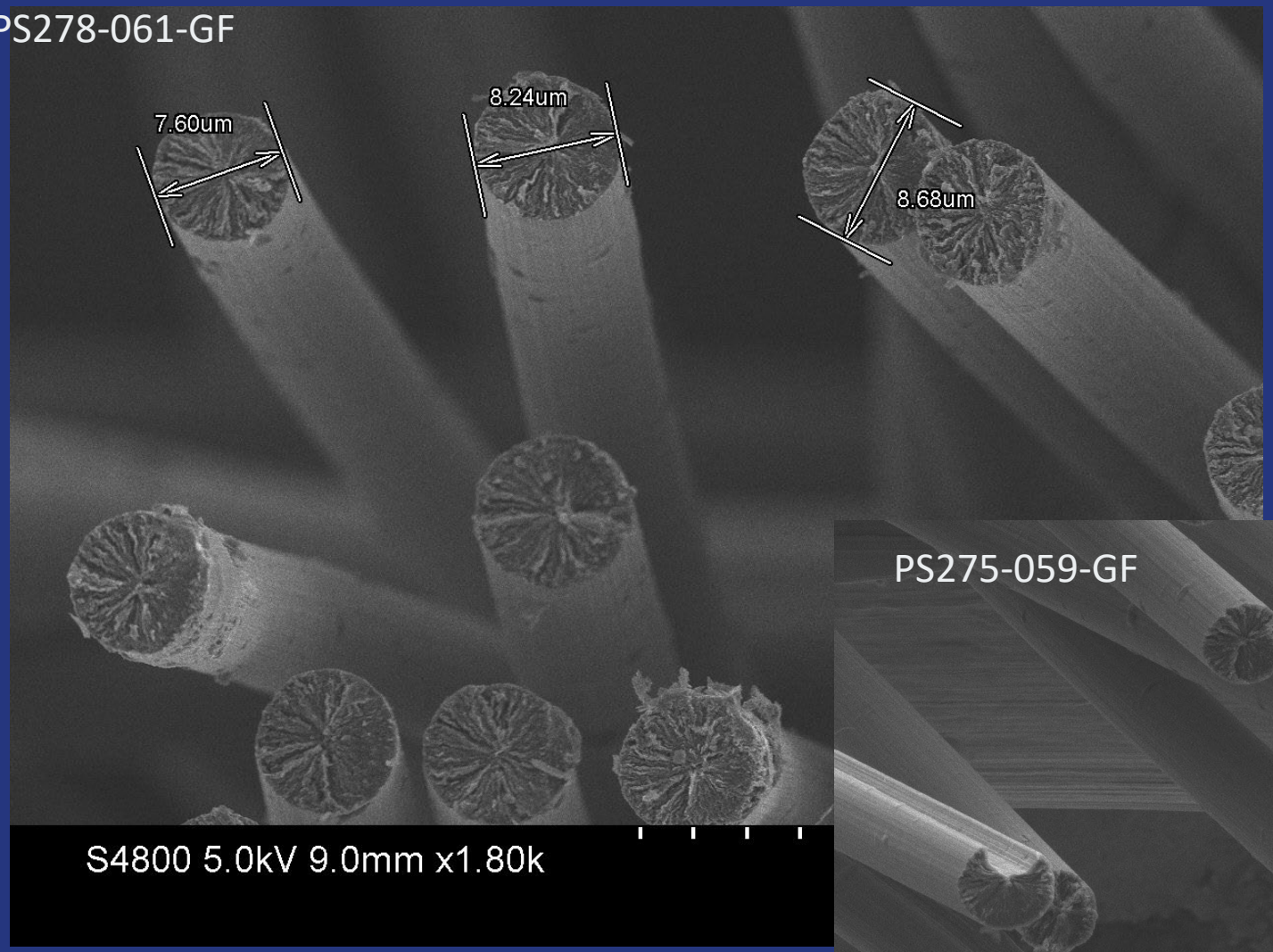


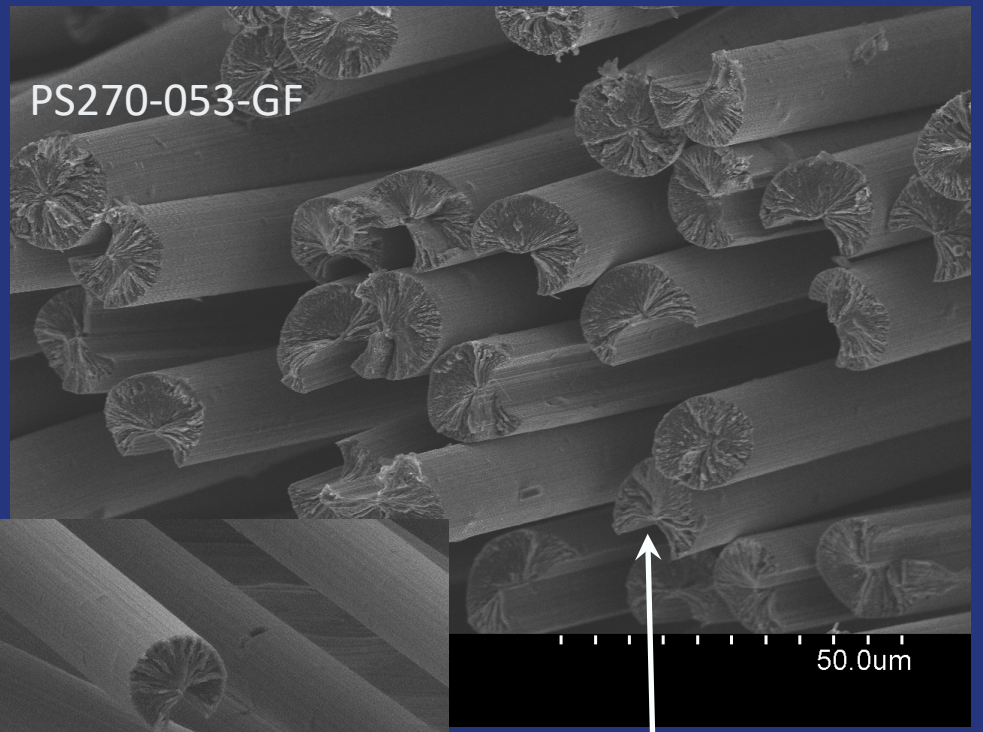
Carbon Fiber Morphologies & Properties

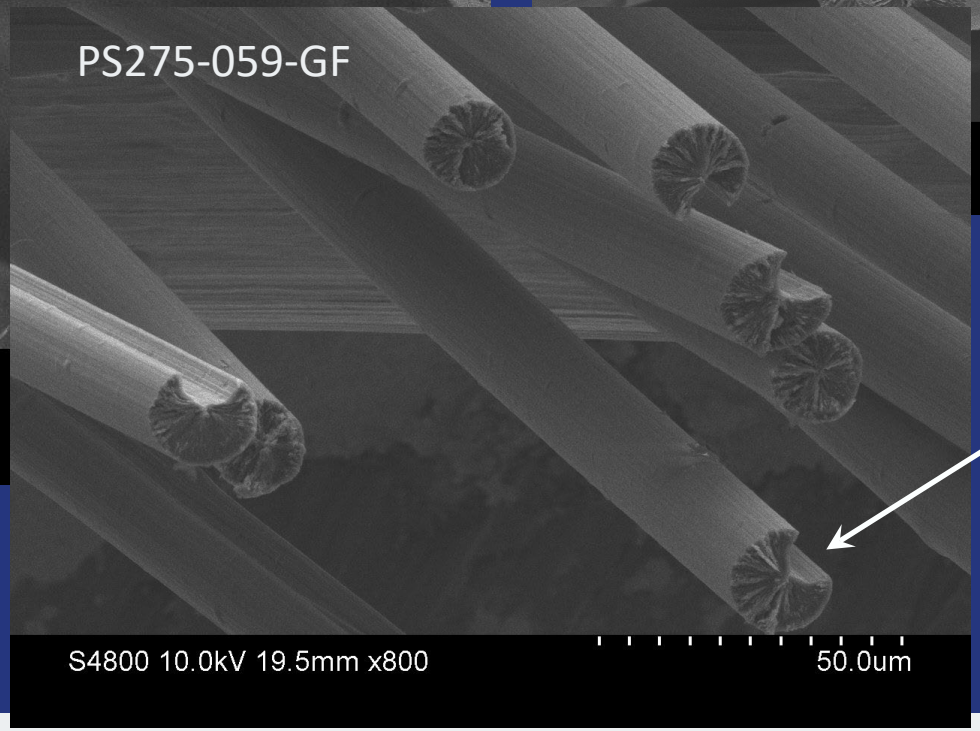
PS252a - Graph



Radial texture of graphitized fibers







Pacman defects

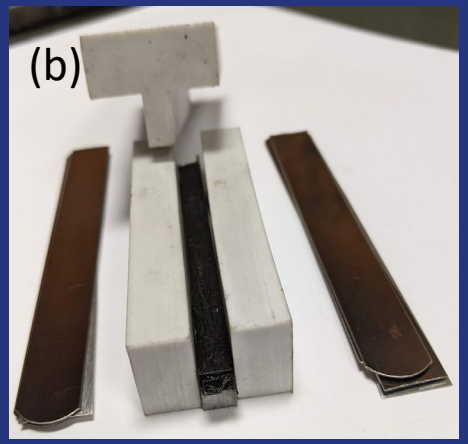
Carbon Fiber Tensile properties (single filament)

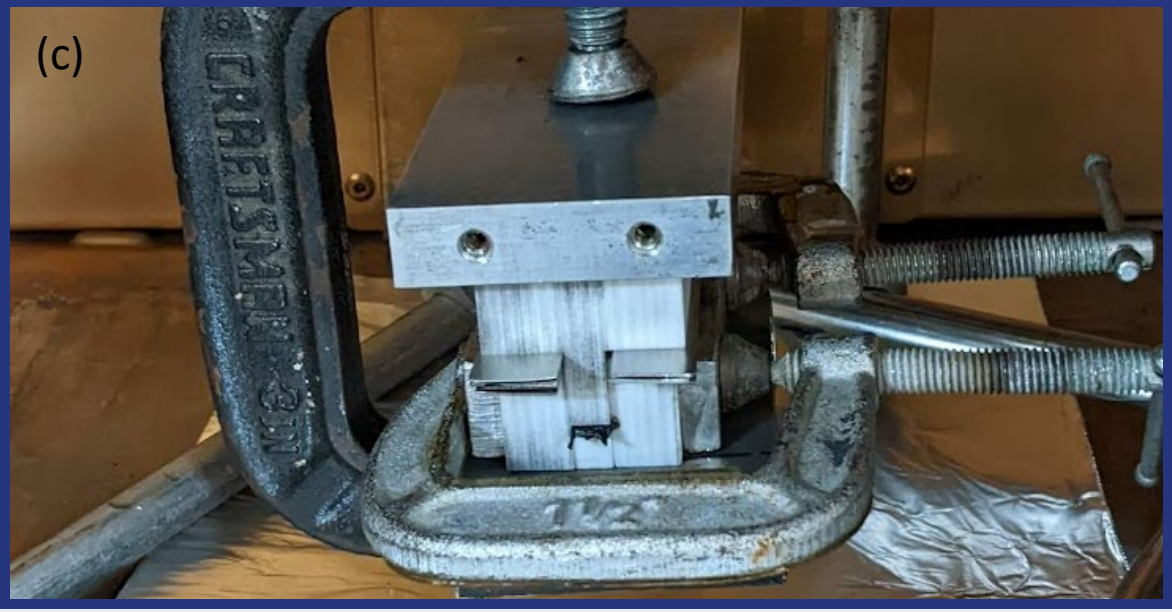
% Mesophase	Fiber	Diameter (um)	Stdev (um)	Stress At Break (MPa)	Stdev (MPa)	Modulus (GPa)	Stdev (GPa)	Strain at Break (%)	Stdev (%)	N	CY %
59.4	PS252a-052-GF671	17.70	0.75	1061	297	624	42	0.17	0.05	40	79
	PS252b-052-GF671	17.62	0.95	1022	379	592	67	0.17	0.06	40	79
77.5	PS253a-053-GF671	15.18	2.21	882	201	609	40	0.14	0.03	40	72
	PS253b-053-GF671	15.18	2.21	902	280	613	61	0.15	0.05	40	80
60.3	PS267a-059-GF678	10.93	0.72	1424	286	542	60	0.26	0.04	48	79
60.3	PS267b-059-GF678	12.90	1.03	1400	366	611	36	0.23	0.05	40	78
77.5	PS270-053-GF678	13.92	1.87	986	240	390*	97	0.26	0.06	40	78
60.3	PS273a-059-GF675	12.23	0.95	1234	328	755	58	0.16	0.04	42	73
60.3	PS275a-059-GF674	15.61	1.52	1145	215	464*	62	0.25	0.05	39	80
60.6	PS278-061-GF676	7.72	0.61	1607	215	448	29	0.36	0.05	40	72

*Pacman defects observed

- Most had moduli ~ 600 GPa (87 MSI)
- Most ~ 80 wt.% carbon yield (CY) from mesophase
- Working to improve strength (strain to failure)

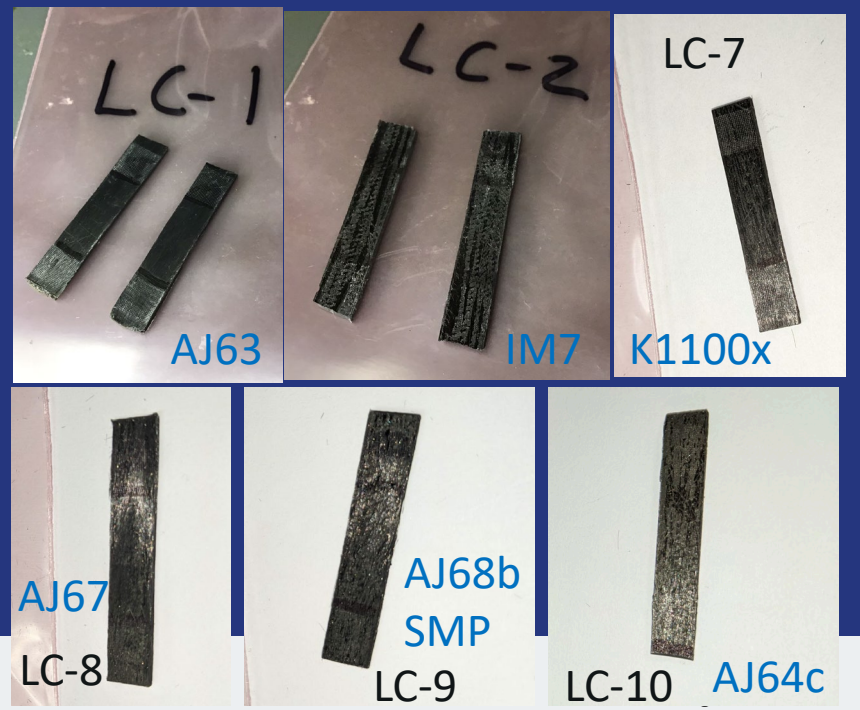
Continuous or “Unidirectional” CF/Epoxy Composites



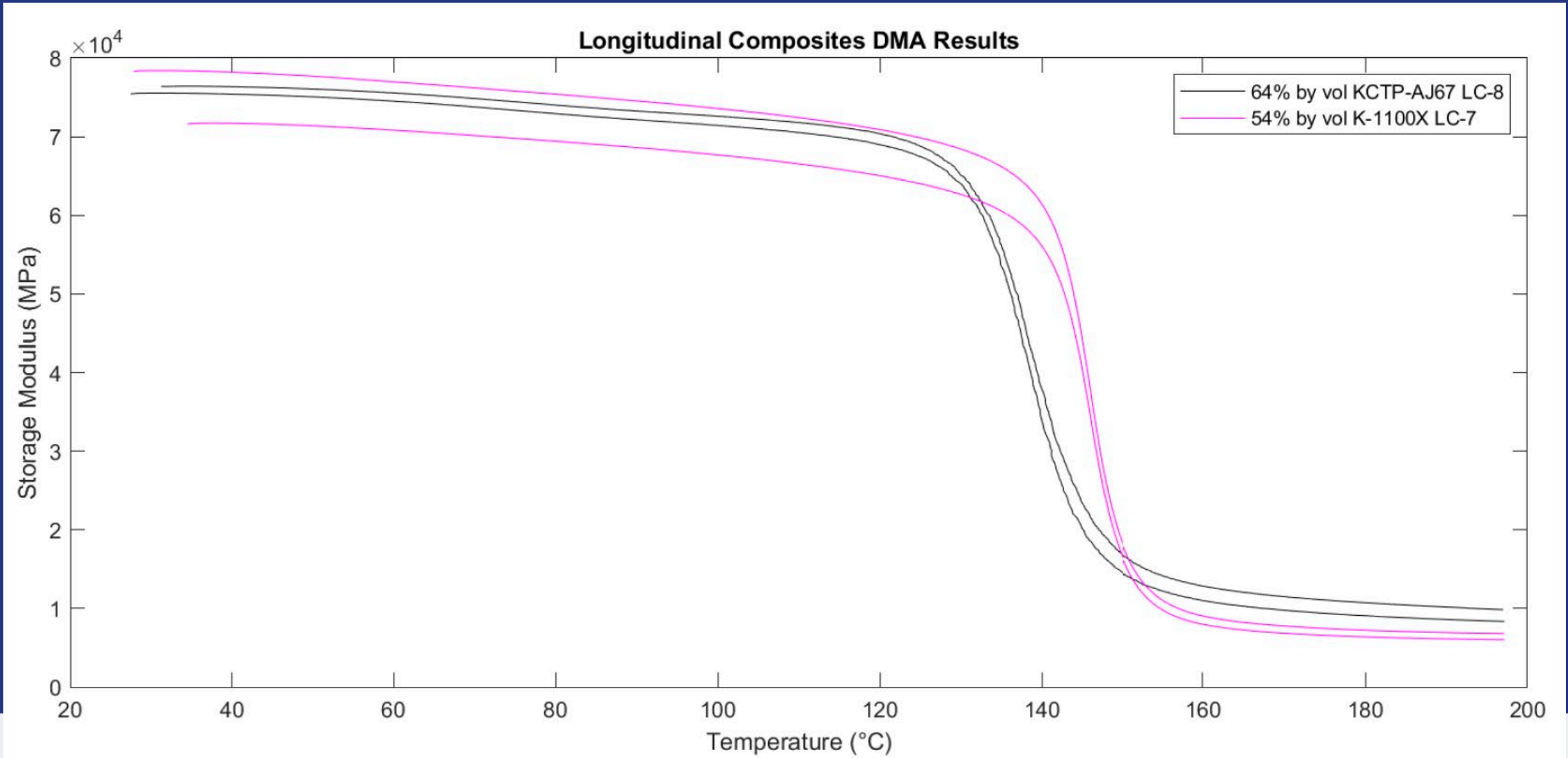


a. Unidirectional bundle of CTM derived carbon fiber is assembled.
b. The glass-filled PTFE mold is shown with a unidirectional carbon fiber/epoxy composite still in it. The upper part of the mold and shims have been removed.
c. The assembled mold in the oven for curing the unidirectional carbon fiber/epoxy composite.

L x W x t: 35.0 x 6.5 x 1.6 mm



Continuous or “Unidirectional” CF/Epoxy Composites



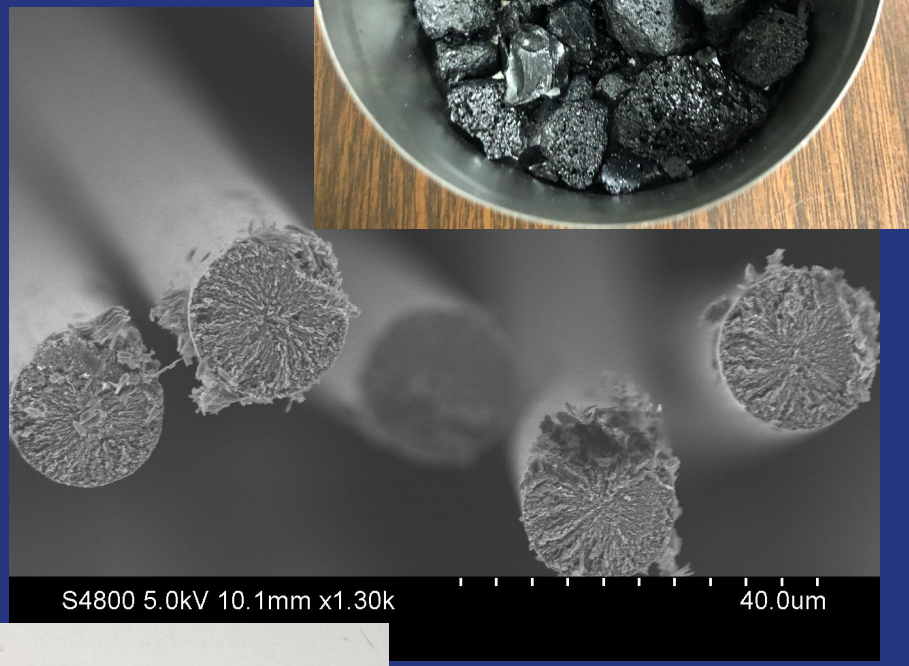
Summary Slide

- Coal tar derived SPINNABLE mesophase production at 1s of kg scale

NCTE
- Multifilament melt spinning
  - Solve the mesophase 'foaming' issue
  - Achieve 30 min stable multifilament spinning

- High modulus carbon fibers demonstrated
  - Moduli at approximately 400 - 600 GPa
    - (58 – 87 Msi)

- Chopped and unidirectional simple composites demonstrated



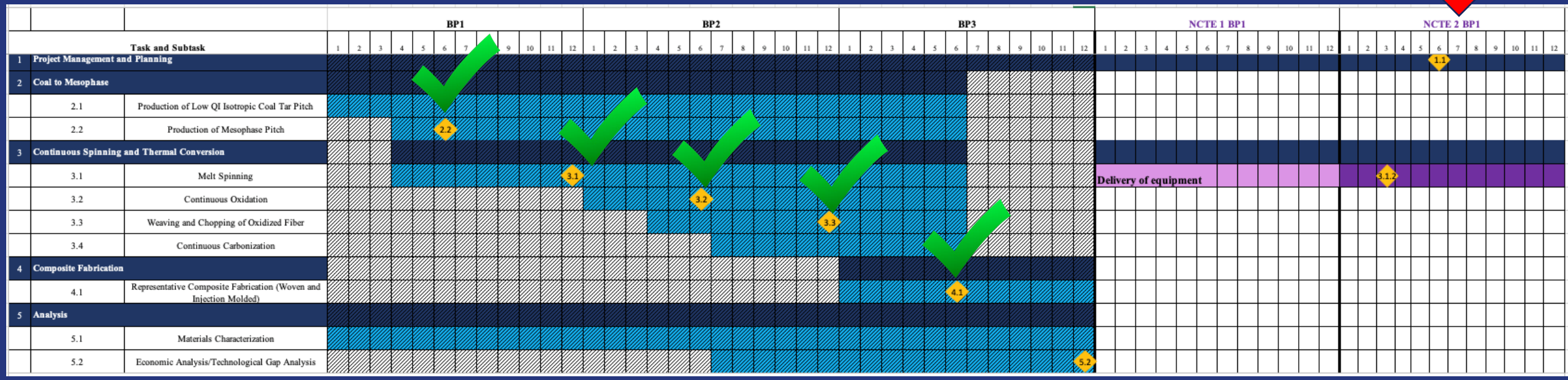
Appendix

Organization Chart

- DOE FECM
  - University of Kentucky, Center for Applied Energy Research
    - PI: Dr. Matthew Weisenberger
    - CoI: Mr. John Craddock, Dr. Ashley Morris
    - Koppers Inc. (not a subrecipient)
      - Supply of low QI isotropic coal tar pitch (precursor to mesophase)
      - Some mesophase processing

Gantt Chart

We are here: April 2024



Milestones

2.2: Production of ≥ 1 kg pitch containing ≥ 60% mesophase and a softening point ≤ 315 °C
3.1: Continuous melt spinning of ≥ 60% mesophase pitch, with ≥ 100 filaments, for ≥ 10 minutes
3.2: Production of non-fused oxidized mesophase pitch fiber with high strain-to-failure
3.3: Demonstrate reproducible, melt spinning of mesophase pitch, with ≥ 100 filaments, for ≥ 10 minutes, with diameters targeting < 20 micron
4.1: Production of composite specimens with a ≥ 10 wt.% (chopped) coal-derived carbon fiber, and report thermal and mechanical properties
5.2: Production of continuous tow coal-derived carbon fiber and fabrication of representative composite specimens. Report mechanical and thermal properties.

3.2: Demonstrate reproducible, melt spinning of mesophase pitch, with ≥ 10 filaments, for ≥ 30 minutes, with diameters targeting < 20 micron
1.1: Update the Technological Gap Analysis