Filament Formation and Melt Spinning of Coal-Derived Mesophase Pitch for Carbon Fiber Production

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Summary

- Introduction
  - Importance of this research
  - Research Questions
- Overview
  - Explanation of concepts
  - Methods
- Results
- Conclusion

Introduction

Converting Coal-Derived Byproducts into Value-Added Products

- Coal tar pitch derived

- Heat soaking
- Inert atmosphere

- Melt spinning
- Thermal conversion

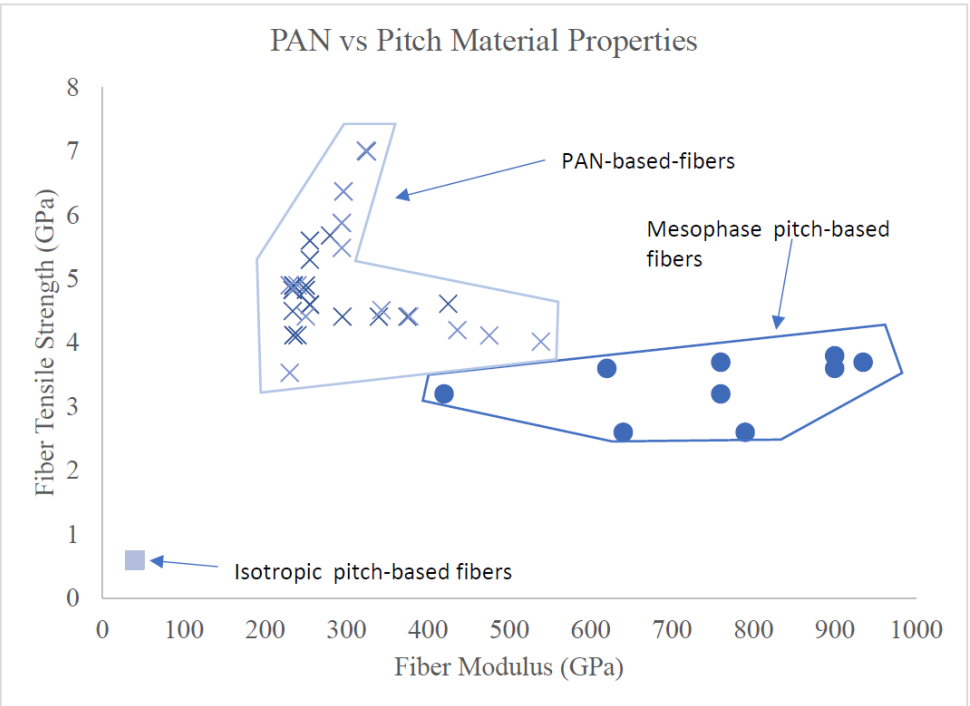
- Carbon-composites

Polyacrylonitrile (PAN) Carbon Fibers

- High tensile strength
- Solution spinning
- Tension required during thermal conversion
- Carbon yield: ~50% yield by weight
- Currently lower priced carbon fiber

Mesophase Carbon Fibers

- High modulus and thermal conductivity
- Melt spinning
- No tension required during thermal conversion
- Carbon fiber yield ~80% by weight
- Lower cost potential

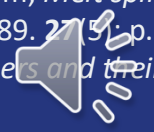


Toray, "Toray Composite Materials America, Inc." https://www.toraycma.com/page.php?id=661

Challenges in Mesophase Pitch Spinning

- Limited processing window at elevated spinning temperatures (as high as 400ºC)
  - Viscosity increases with time
- Short time-scale to draw filament
- High tensile stress experienced in as-spun fiber during melt draw
  - Mesophase pitch: 10-25% of ultimate strength [1]
  - Nylon: 1% of ultimate strength [2]
- Brittle “green” or “as-spun” fibers
- Not all pitches are equal
  - Differences in chemistry, mesophase content, impurities, etc.

[1] Edie, D. and M. Dunham, *Melt spinning pitch-based carbon fibers.* Carbon, 1989. 27(5): p. 647-655.
[2] Morgan, P., *Carbon fibers and their composites*. 2005: CRC press.



Research Question:

- What factors determine spinning stability for mesophase pitch?
- Hypotheses
  - Filament breakage is caused by discontinuities in the viscosity during the melt spinning process. Causes of viscosity discontinuity in mesophase pitch include:
    - Isotropic pitch
    - Gels

Overview

Isotropic vs Mesophase Pitch

Isotropic Pitch

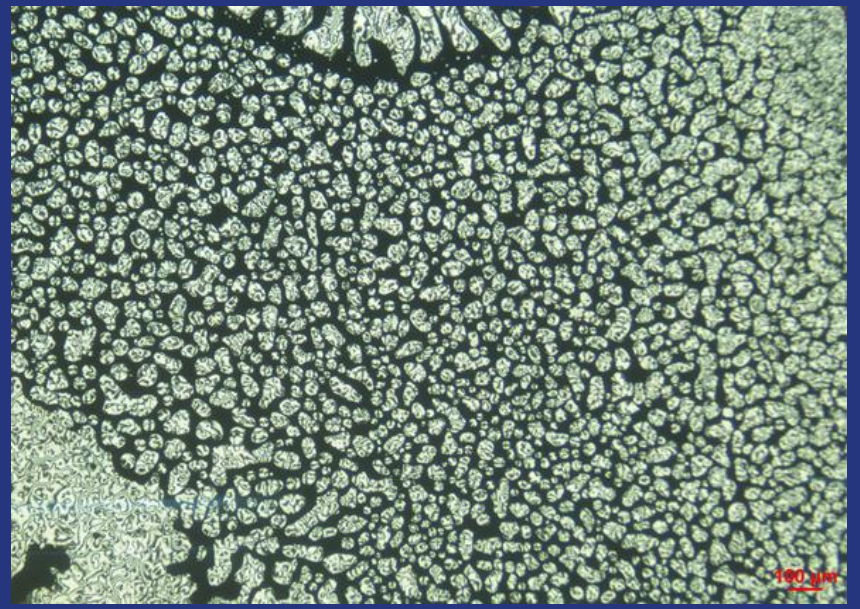
- Smaller aromatic molecules that are arranged in random order
- Non-graphitizable carbon

Isotropic Pitch
Polarized Optical Micrograph

- Time
- Temperature
- Inert Atmosphere

Mesophase Pitch

- Anisotropic
- Larger stacked aromatic molecules
- Graphitic structure with thermal conversion above 2000°C



Mesophase Pitch
Polarized Optical Micrograph

Comparison of rheological properties

- Isotropic pitch: Newtonian fluid
- Mesophase: shear thinning
- Differing rheological properties → instabilities during filament formation

Isotropic Pitch [3]

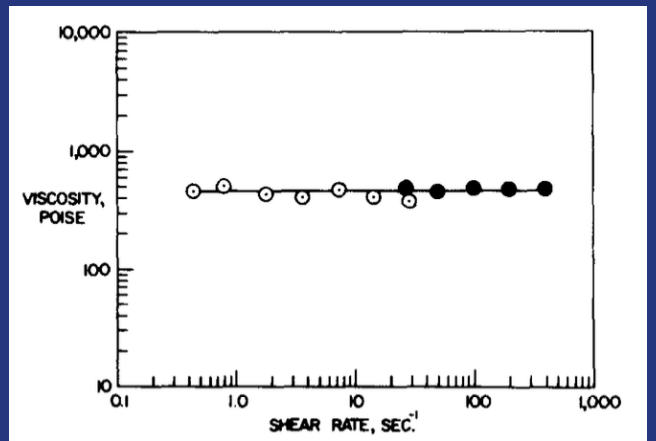


Fig. 5. Viscosity vs shear rate for Sample 10. ⊙, modified Haake viscometer at 194 ± 1°C; ●, Seiscor/Han rheometer at 192 ± 0.1°C.

Mesophase Pitch [3]

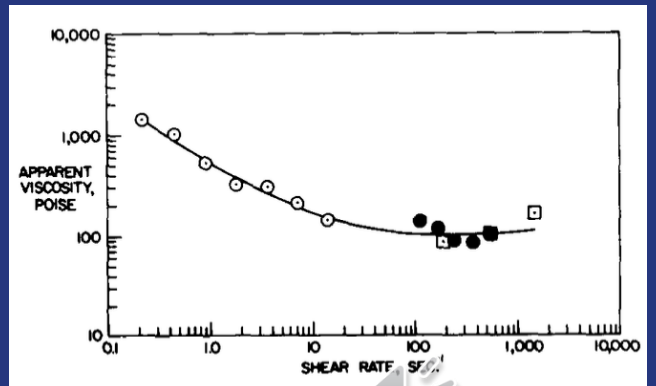
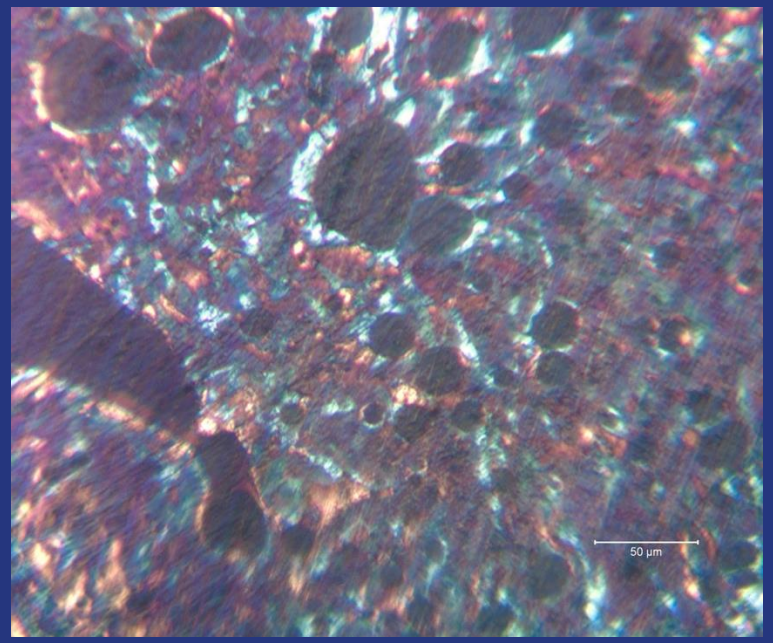


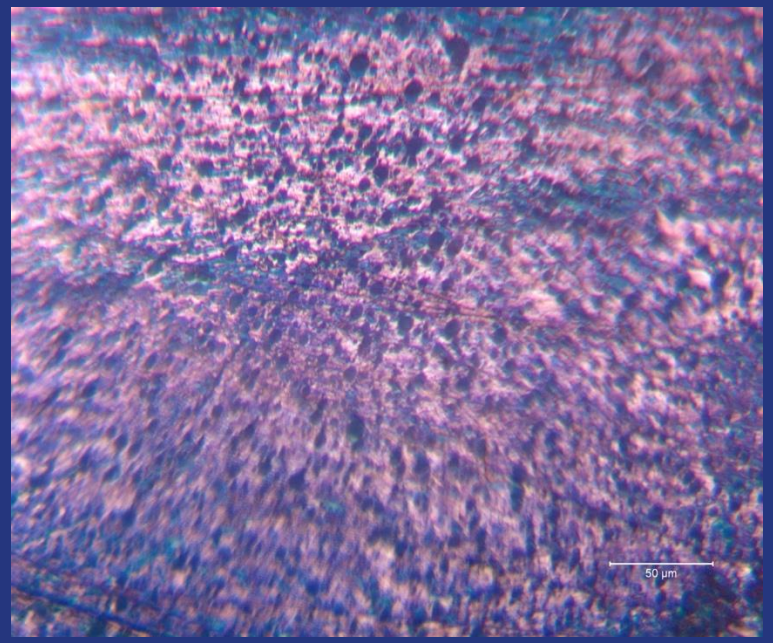
Fig. 7. Apparent viscosity vs shear rate for Sample 11. ⊙, modified Haake viscometer at 326 ± 1°C; ⊡, Instron rheometer at 327 ± 1°C; ●, Seiscor/Han rheometer at 328 ± 0.1°C.

[3] Nazem, F. (1982). "Flow of molten mesophase pitch." Carbon **20**(4): 345-354.

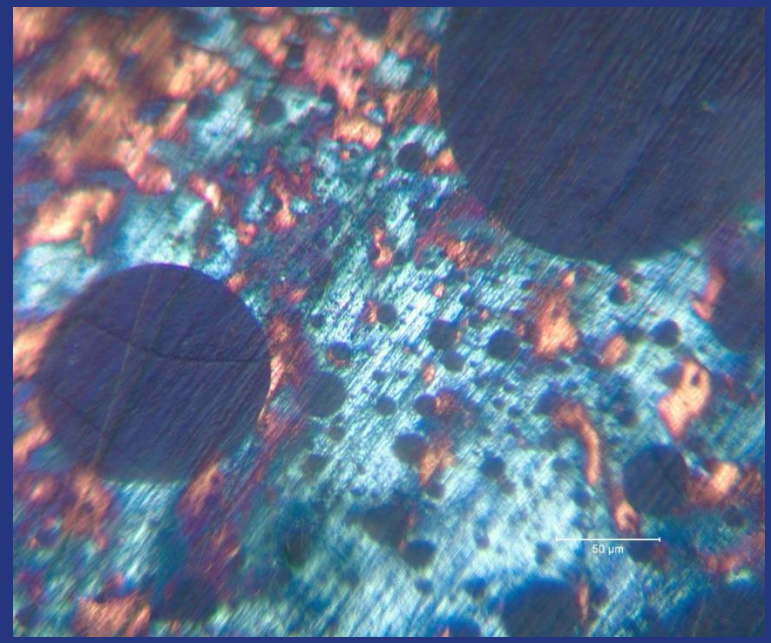
Phase Separation (coalescence) with time



Pre-Mixing



High-Shear Mixed



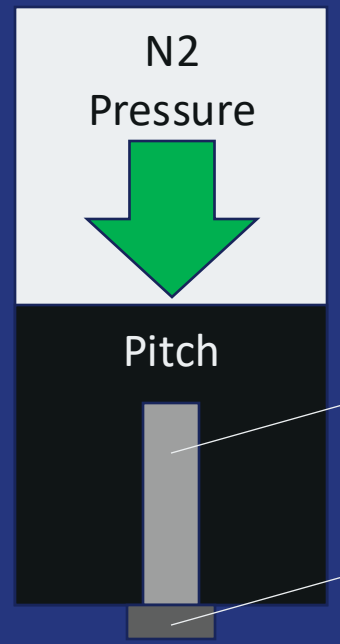
Re-Heated With Time
At Spinning Temperature

Experimental Methods: Instruments

Capillary Rheometer

Pressure Analysis

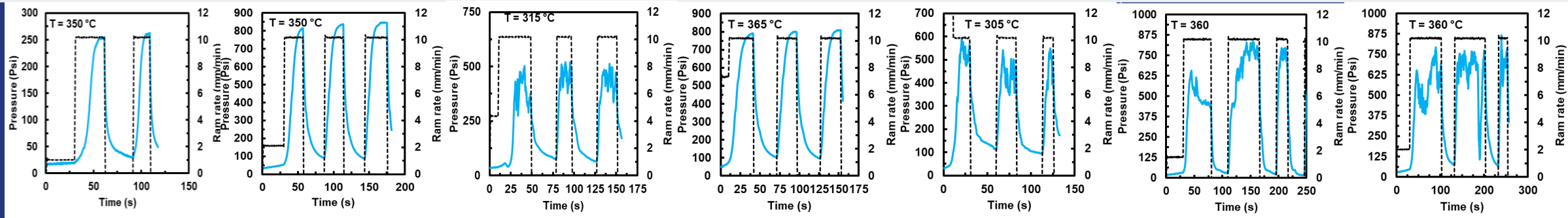
Single Filament
Pressure Spinning

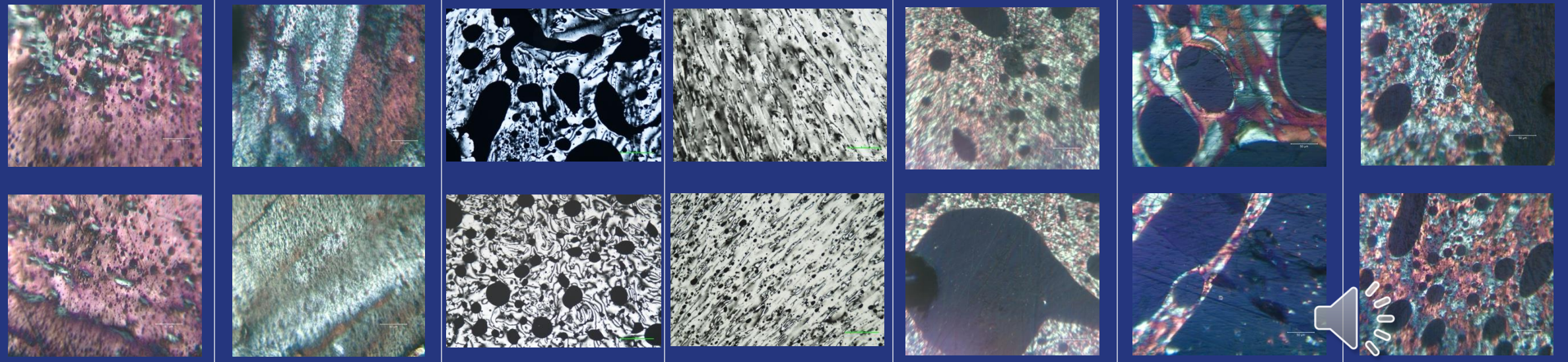


Spinning Durations

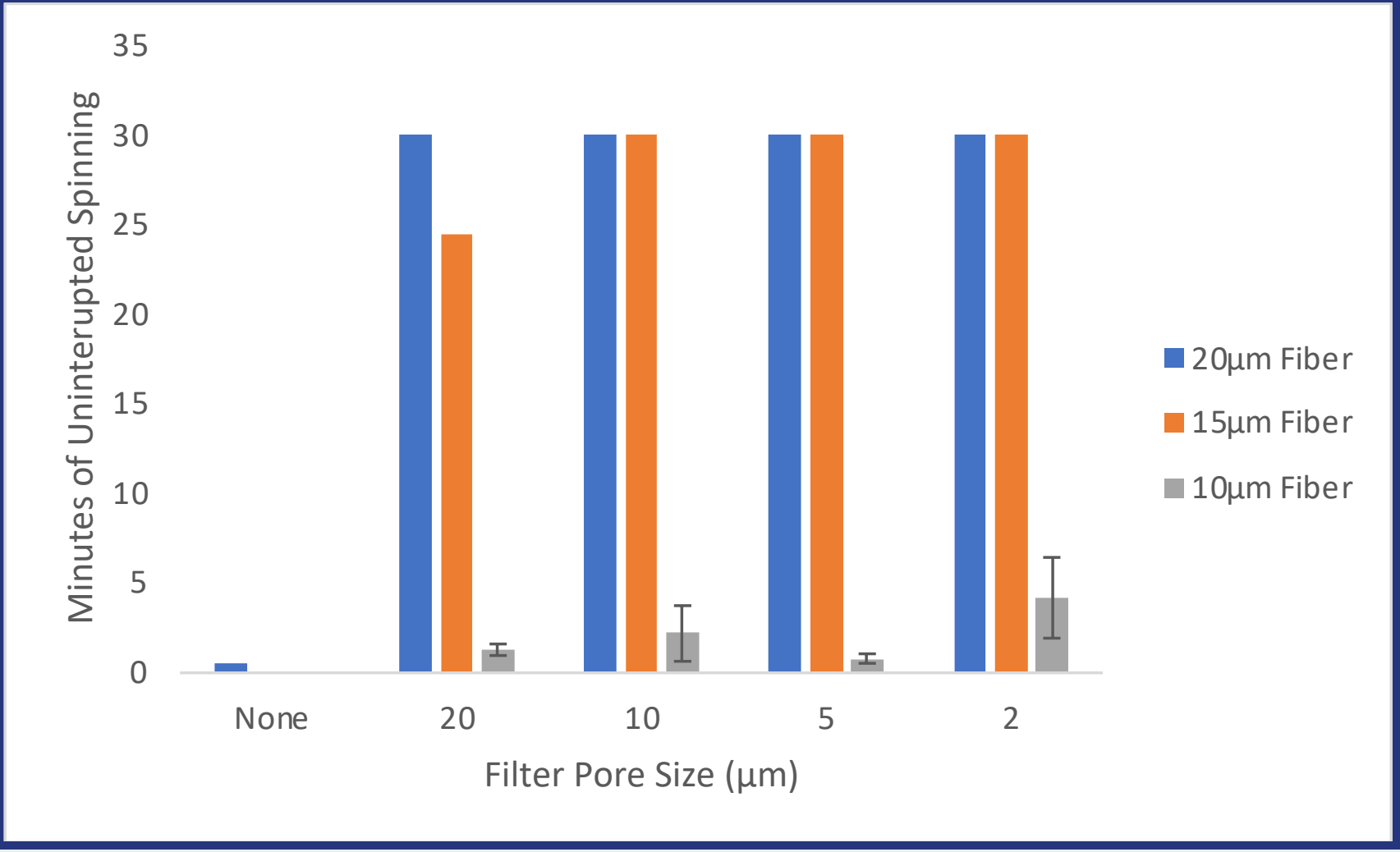
Results

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7
Tsp (°C)	297	299	279	314	272	306	310
Mesophase %	65	62	79	90	53	62	60

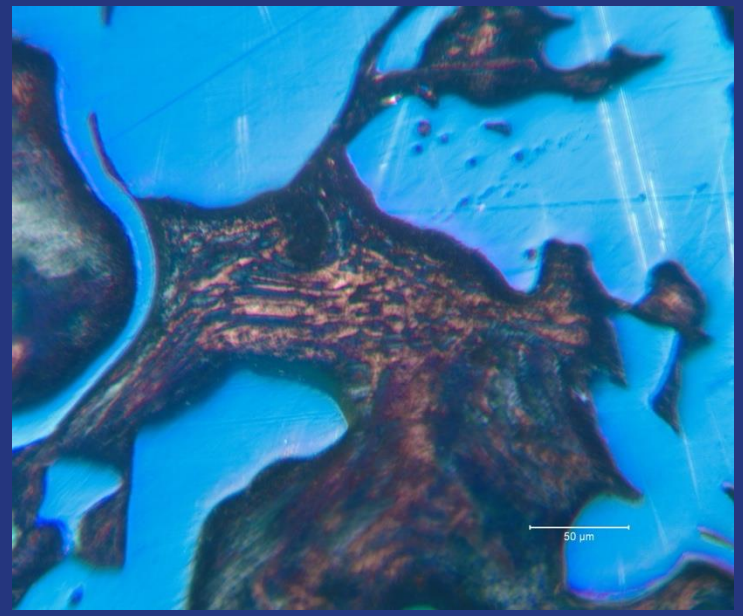




Effects of Filtration

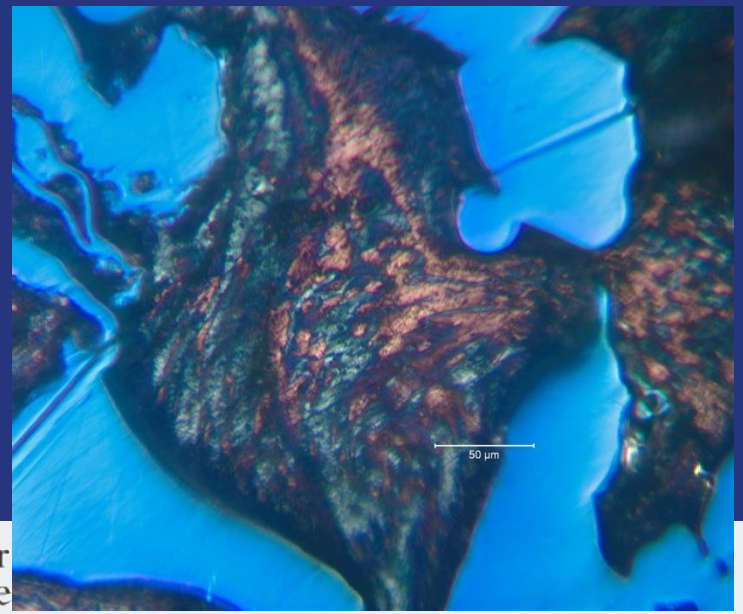


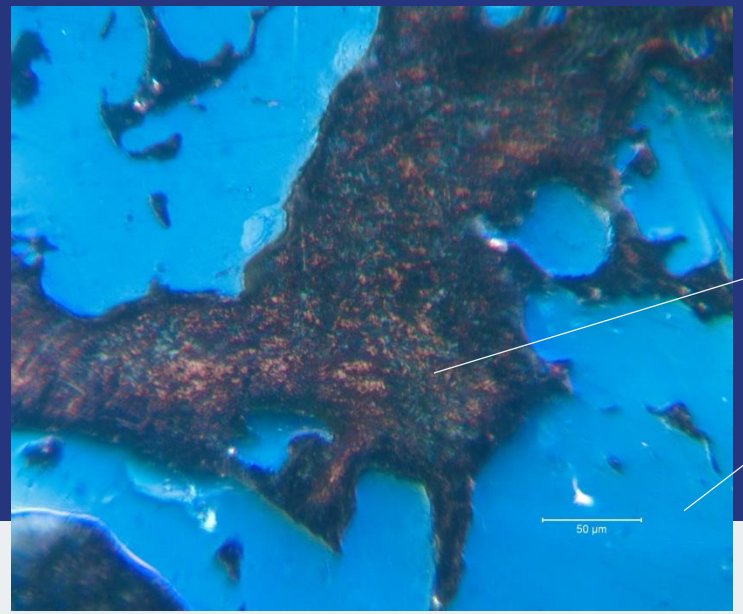
Filter Analysis



Fresher Filter

Plugged Filter





Conclusions

- Small isotropic binder size is essential to have stable spinning
- Role of Filtration
  - No filter → heavily decreased spinning duration
  - Decreased filter pore size→ negligible change in spinning duration
- Plugged filter shows slightly lower OTI

Future Work

- Coalescence
  - Analyze the amount of time it takes for the samples to phase separate
- Filtration
  - Use larger filter size to determine the size of problematic particulates
  - Analyze composition of pitch in the filters
    - LDI mass spectrometry, RAMAN mapping, etc.

Acknowledgement

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