Evaluating Crystallinity in Thermoplastic Composites for Aerospace Applications

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Advanced Polymeric Materials Branch

NASA Glenn Research Center, Cleveland, OH

Presentation overview

Overview of Crystallinity in Thermoplastics

Carbon fiber/PEKK Composites

Regolith/PHB Composites for In-Space Manufacturing

Key Takeaways

Next Steps

Role of Crystallinity in Thermoplastics

Crystalline region

Amorphous region

Highly crystalline regions have…

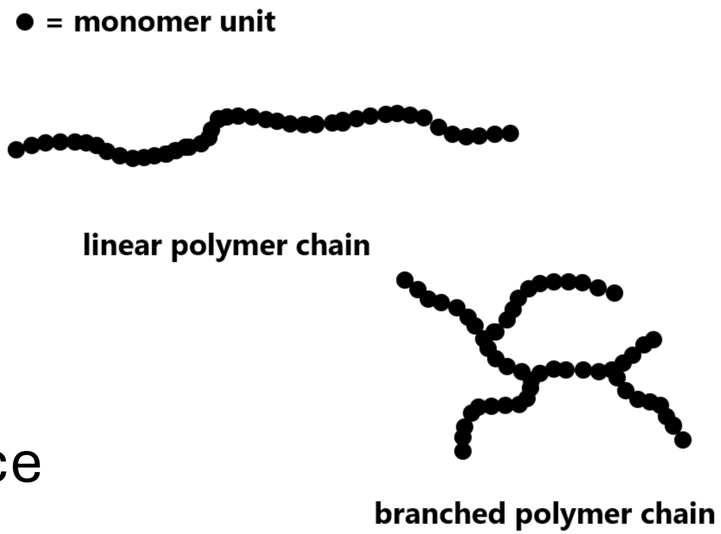
- Increased storage modulus
- Increased chemical resistance
- Increased stiffness and strength
- Increased heat deflection temperature

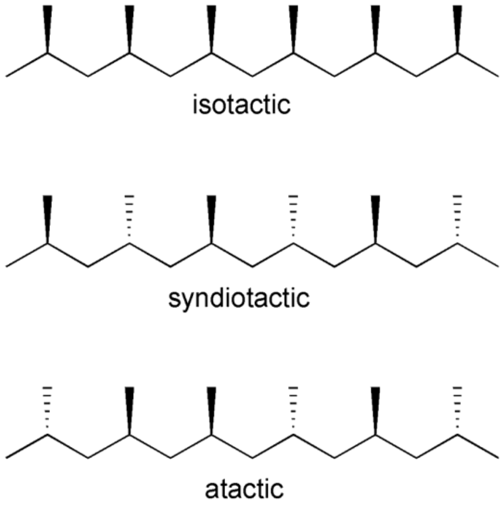
Amorphous regions have…

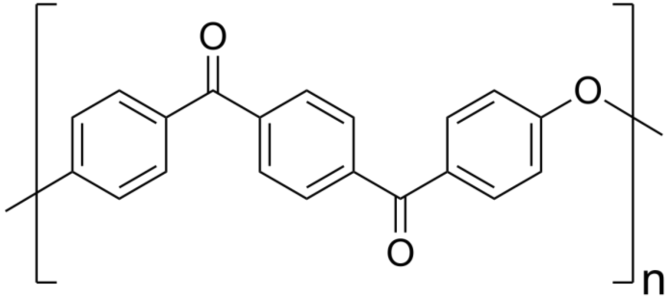
- Increased flexibility
- Optical transparency
- Decreased shrinkage
- Increased gas permeability

Factors Affecting Crystallinity

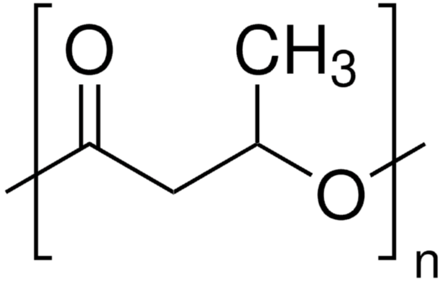
1. **Chemistry and tacticity**
2. **Polymer structure**
3. Mechanical stress and force
4. Thermal processing







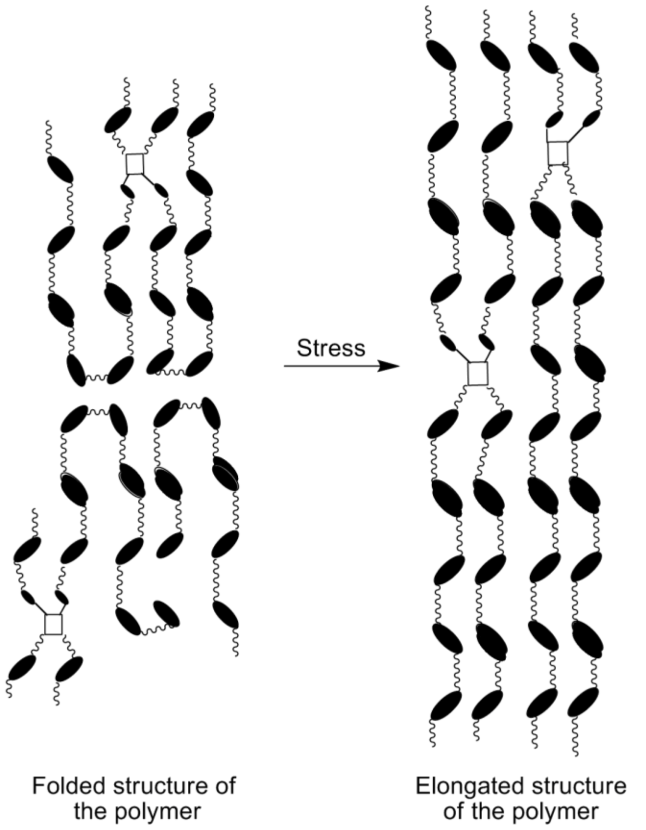
Poly(etherketoneketone) (PEKK)



Poly(3-hydroxybutyrate) (PHB)

Factors Affecting Crystallinity

1. Chemistry and tacticity
2. Polymer structure
3. **Mechanical stress and force**
4. **Thermal processing**



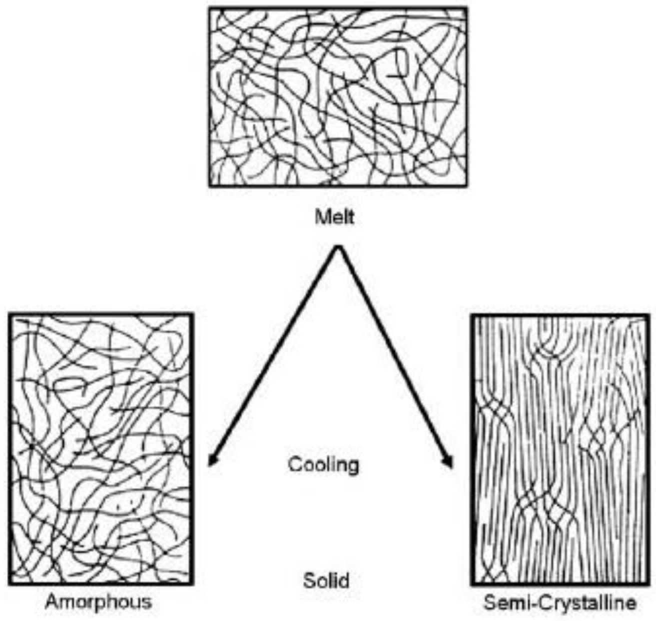


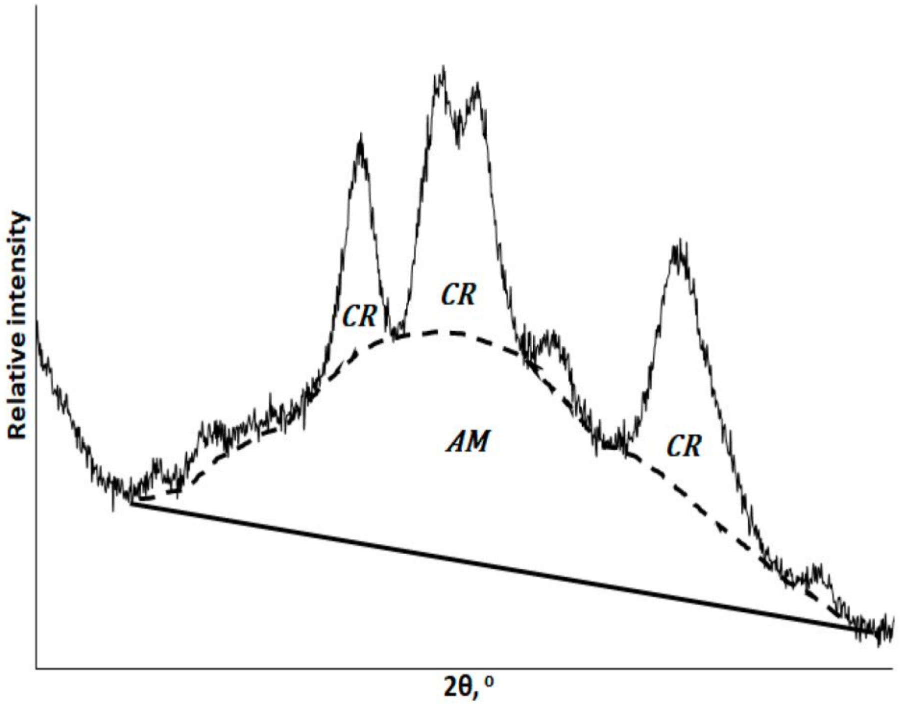
Figure 3.4 Cooling behaviour of materials

Crystallinity is Complex & Composites are Difficult to Evaluate

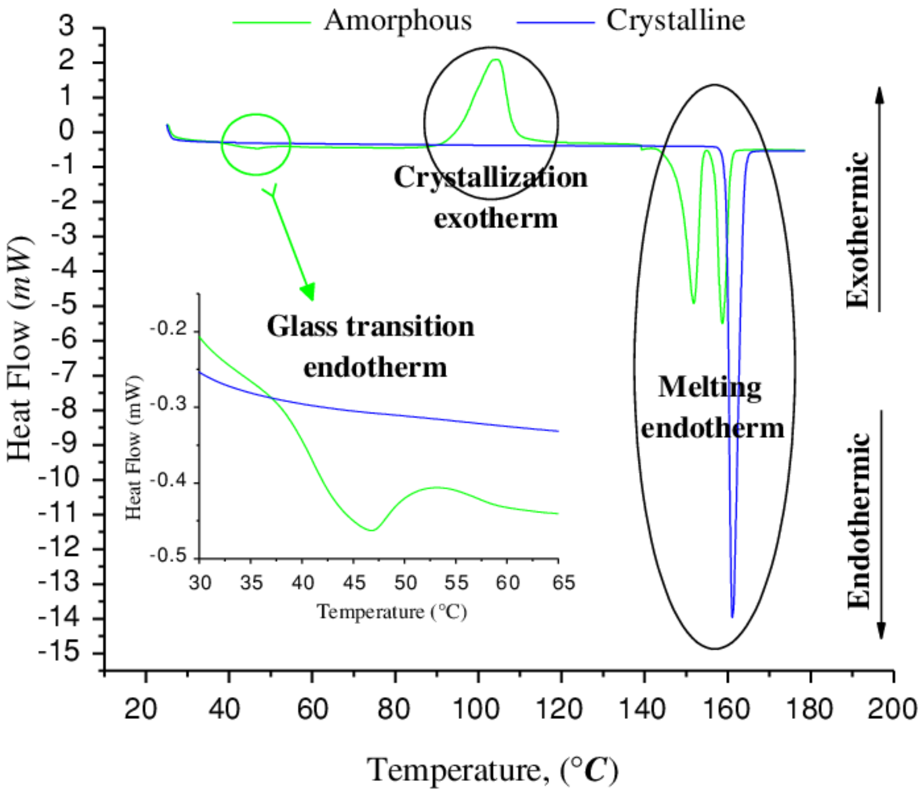
Varied cooling rates and stress exposure

Varied crystallinity profile, varied composite properties

Conventional Methods to Evaluate Polymer Crystallinity

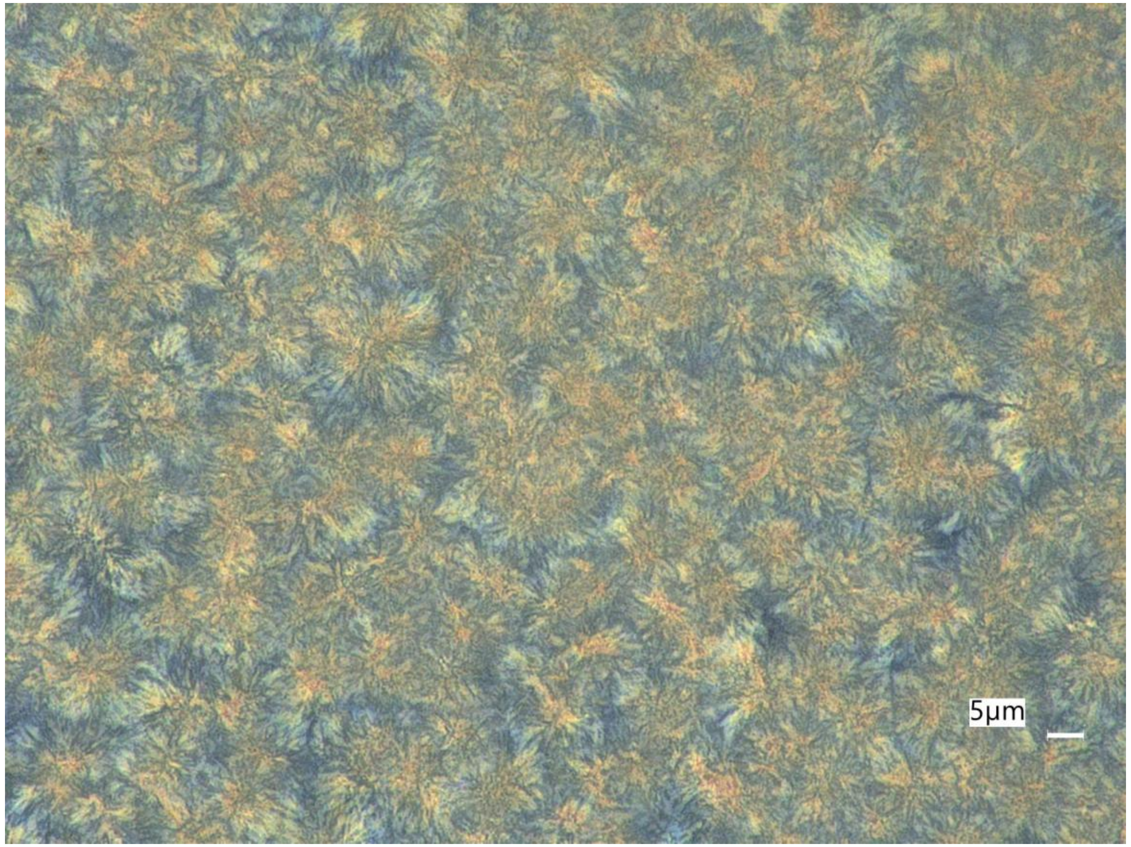


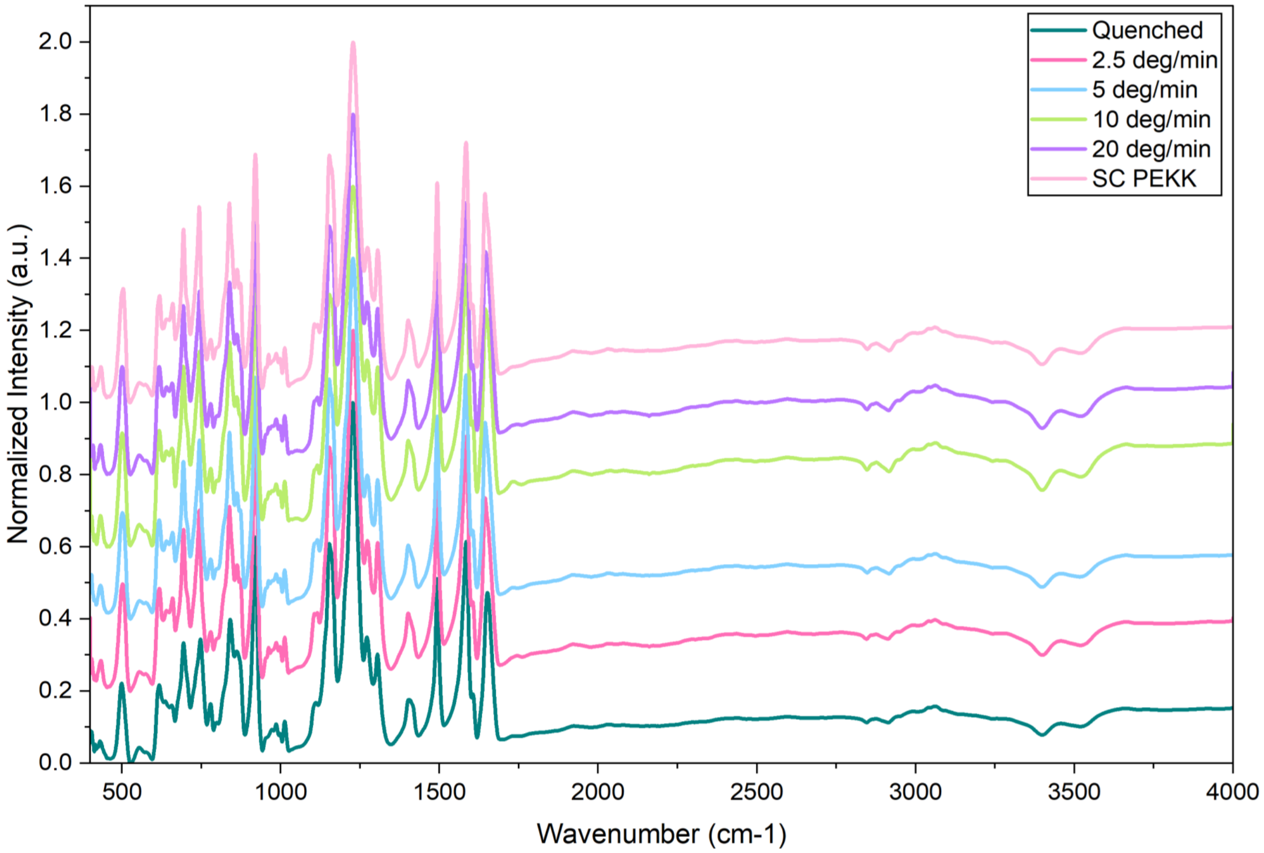
X-Ray Diffraction (XRD)



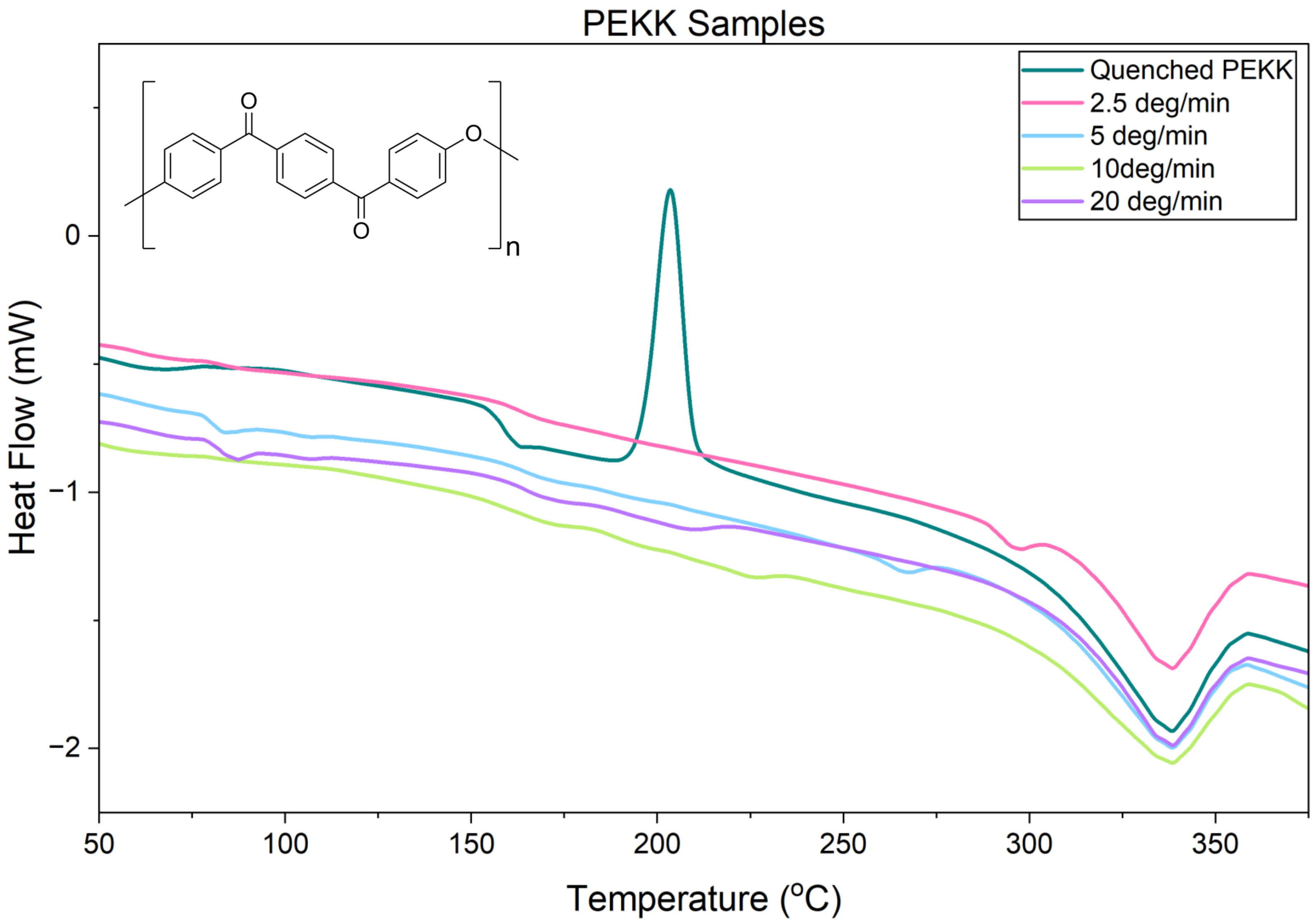
Differential Scanning Calorimetry (DSC)

Polarized Light Optical Microscopy and Fourier Transform Infrared (FTIR) Spectroscopy





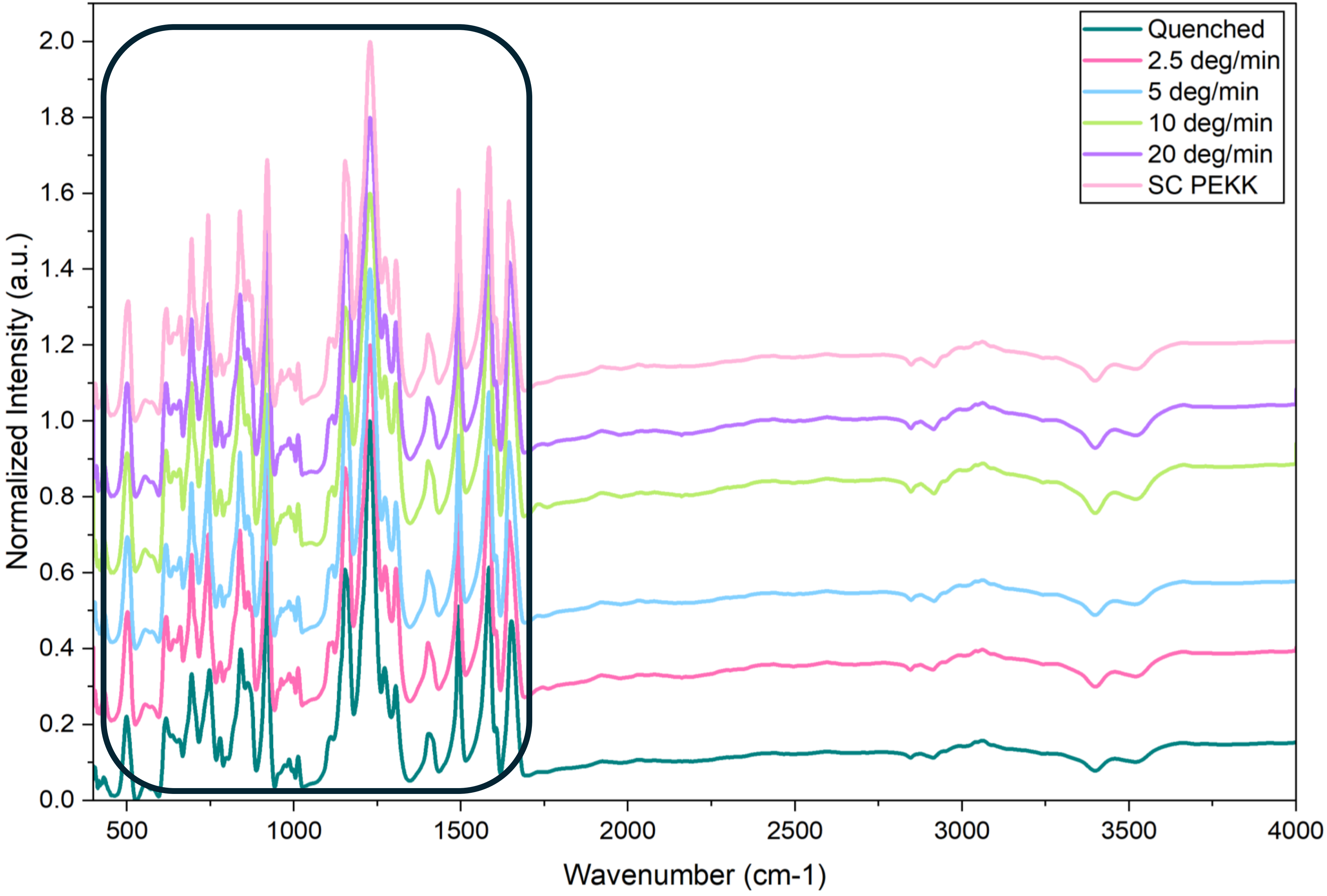
Differential Scanning Calorimetry of PEKK Resin



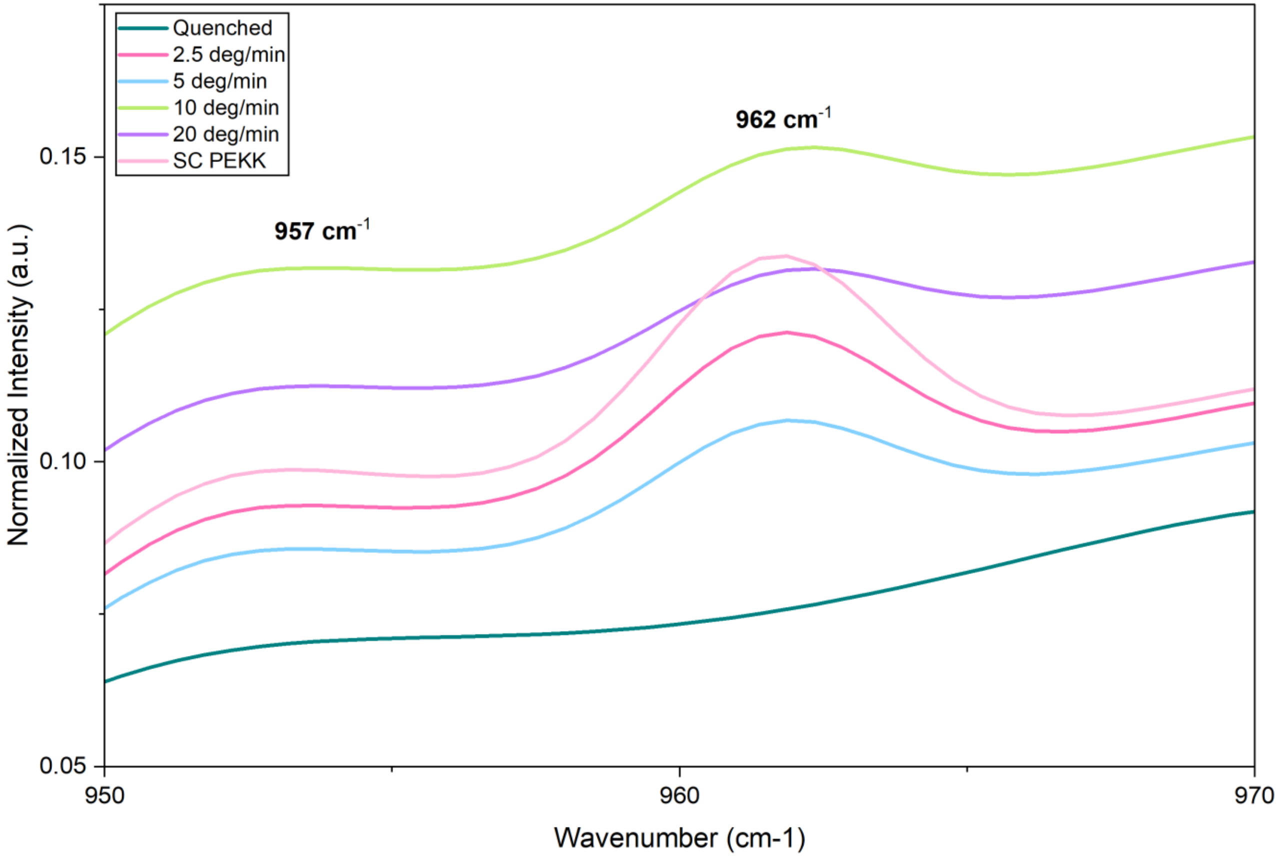
$$X_C = \frac{\Delta H_m}{\Delta H_{100\%}} \times 100$$

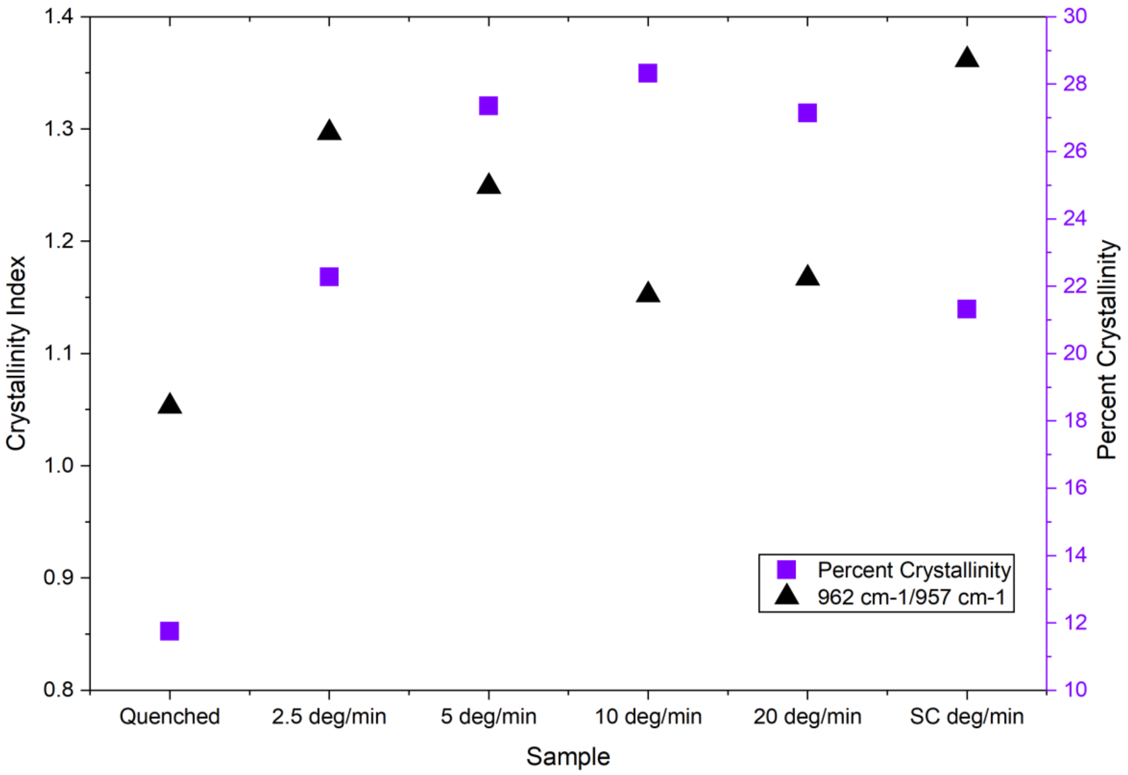
Sample	X_C (%)
Quenched	11.75
2.5 deg/min	22.28
5 deg/min	27.35
10 deg/min	28.32
20 deg/min	27.14

Fourier Transform Infrared (FTIR) Spectroscopy



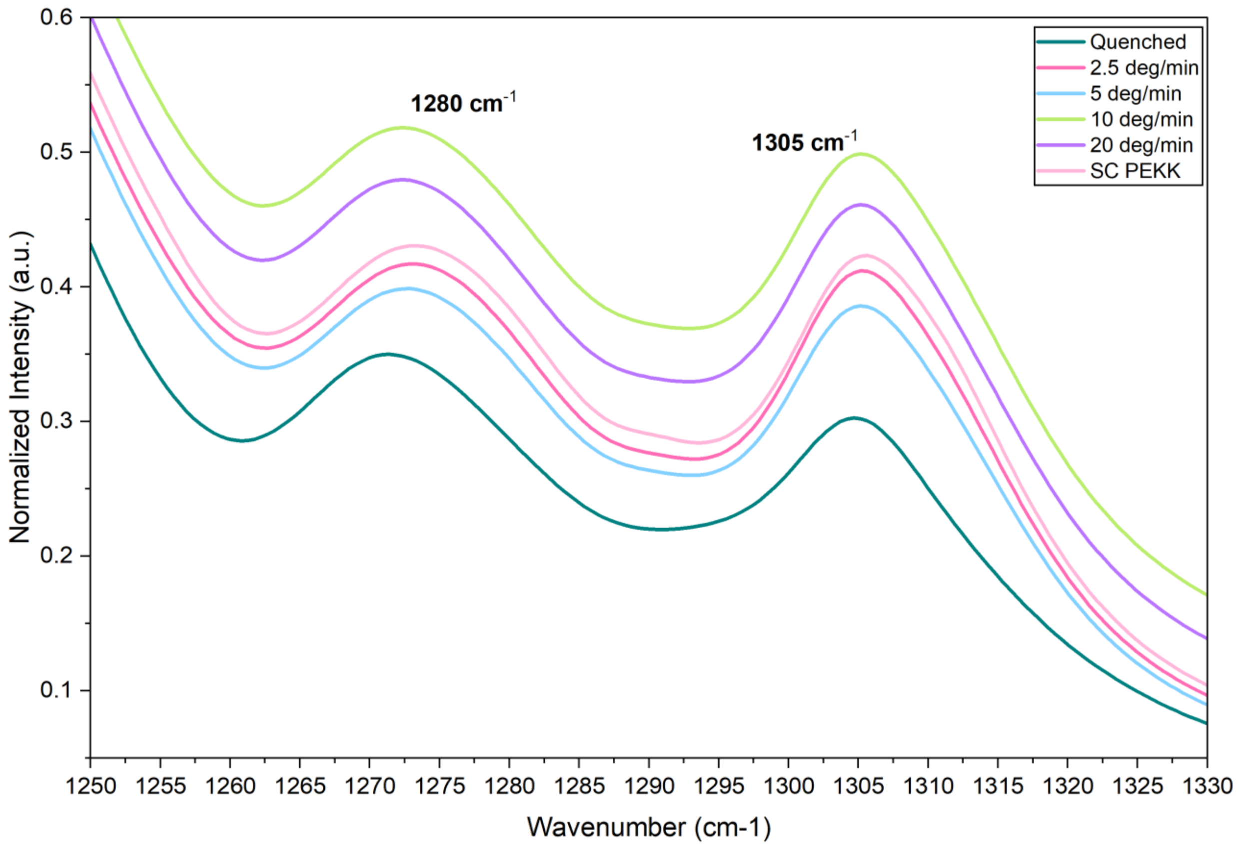
Fourier Transform Infrared (FTIR) Spectroscopy – Crystallinity Index

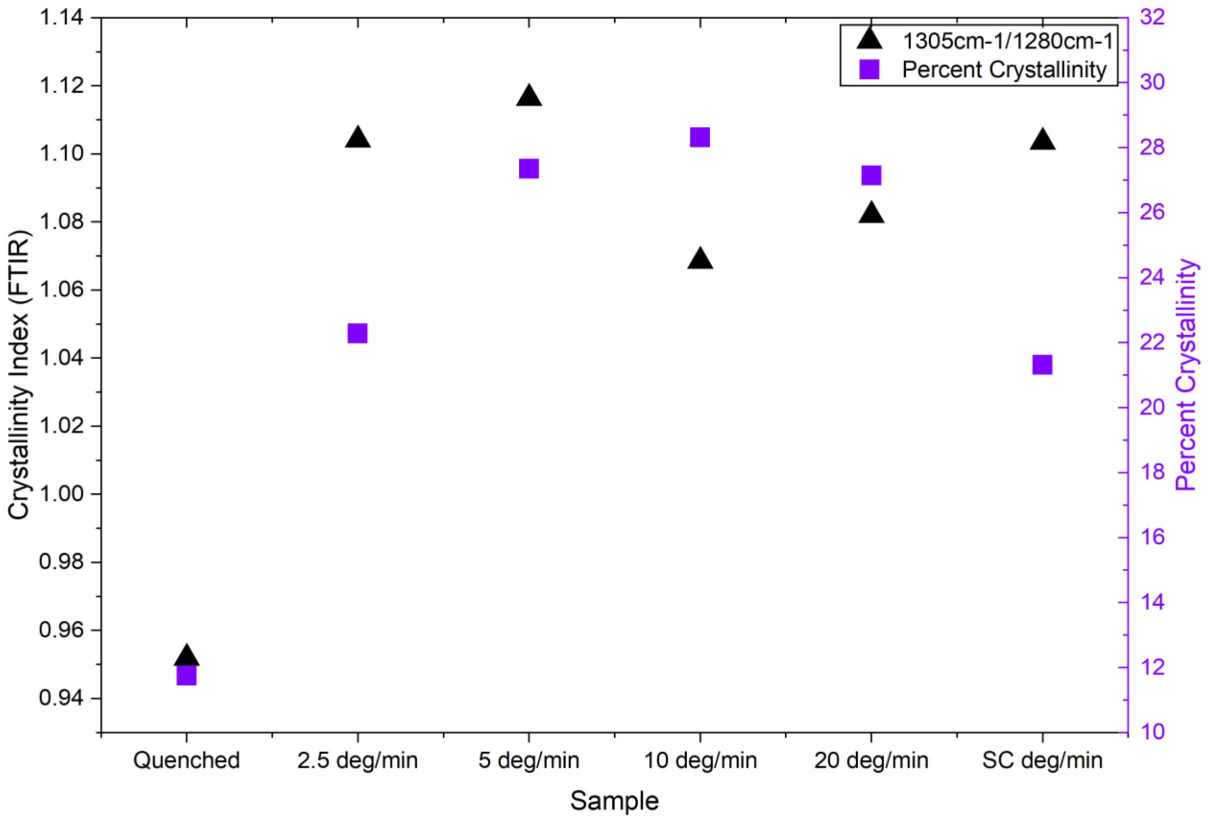




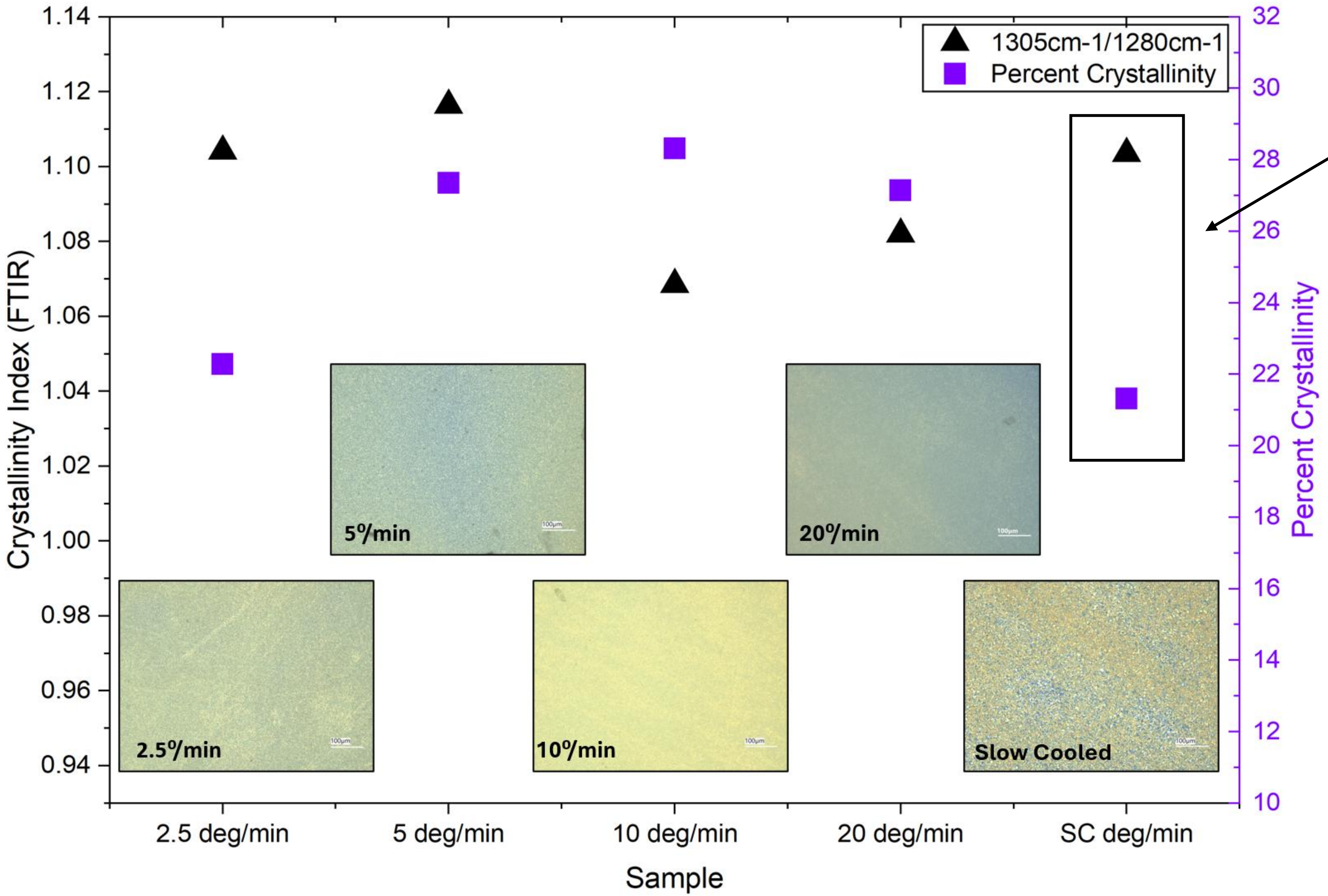
- 962 consistent with aromatic bending, susceptible to crystallinity changes
- 957 corresponds to C-O-C backbone

Fourier Transform Infrared (FTIR) Spectroscopy – Crystallinity Index



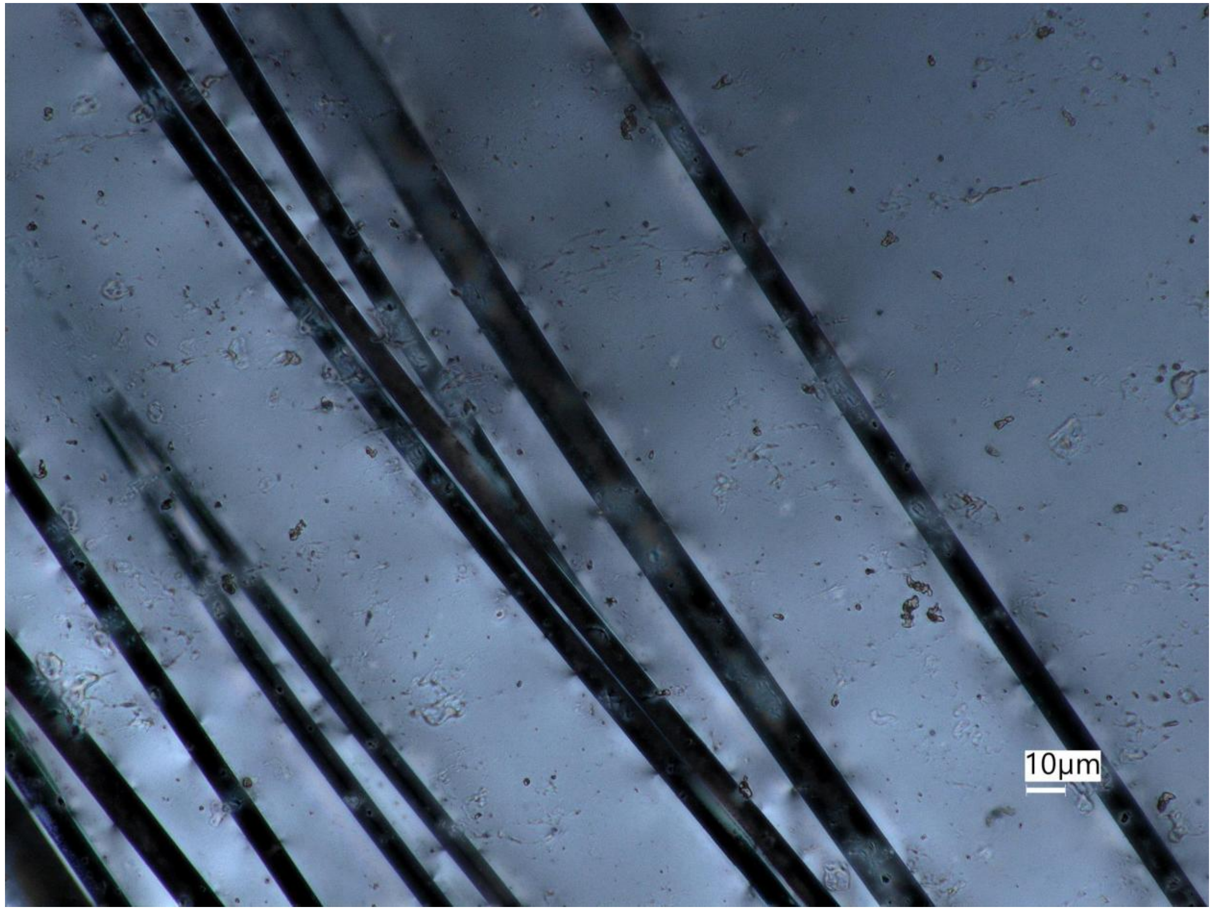


- 1305 corresponds to carbonyl, should increase with higher crystallinity
- 1280 is diphenyl ether groups in backbone and shouldn't change with crystallinity

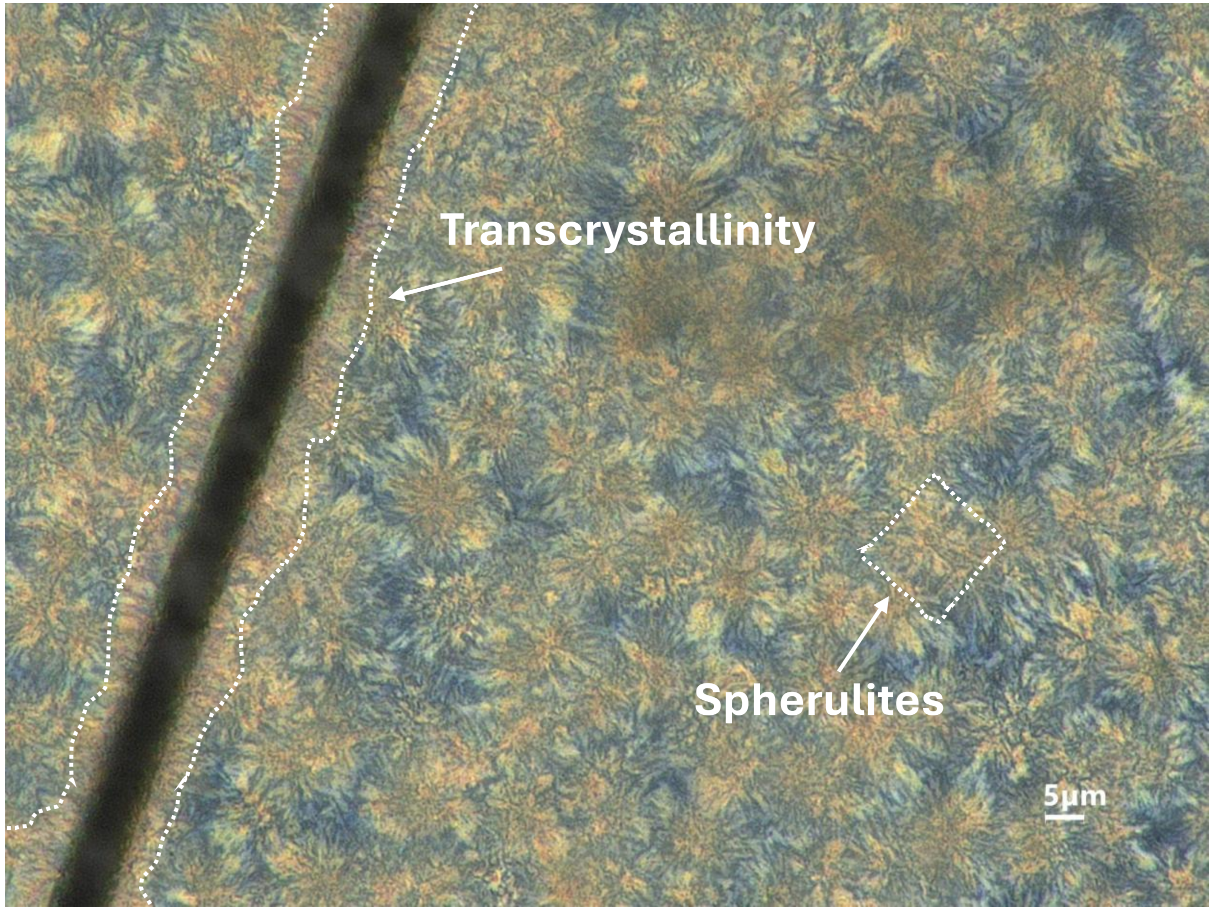


- Generally, saw good agreement with DSC and FTIR data, except for the SC sample
- SC has the largest crystallites, should be the most crystalline – FTIR captured this more effectively than DSC
- Additional experimental validation in progress

Differentiating Crystallites

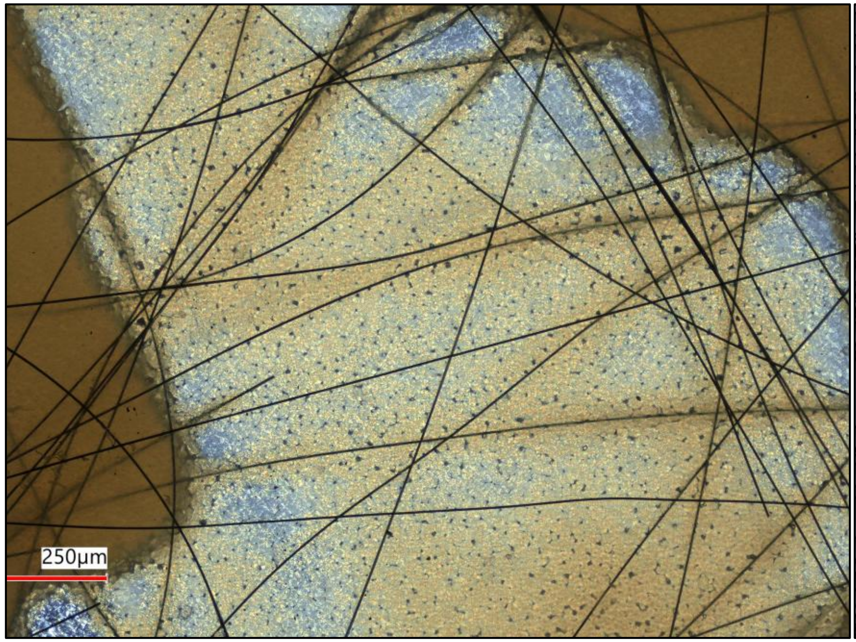


Quenched
X_C: 11.75%

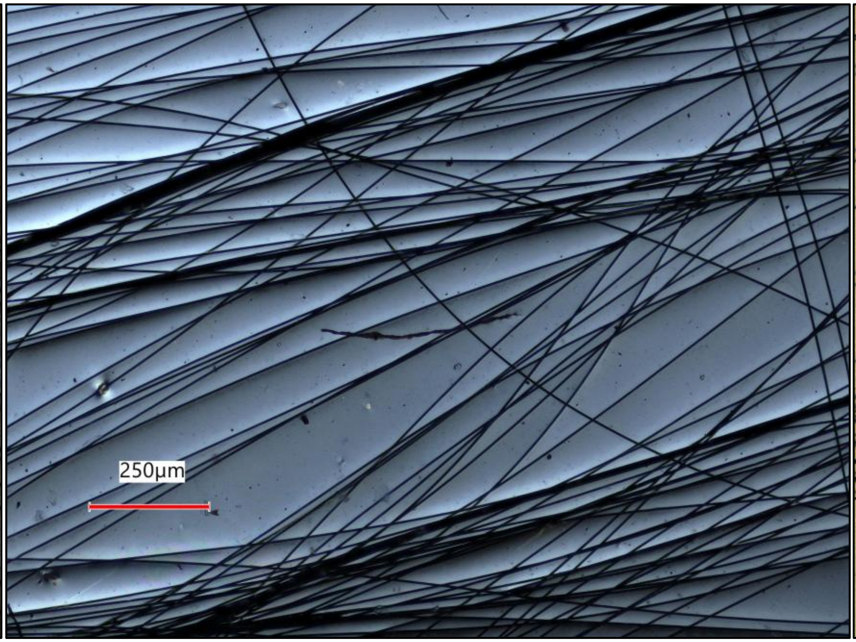


Slow Cooled
X_C: 21.32%

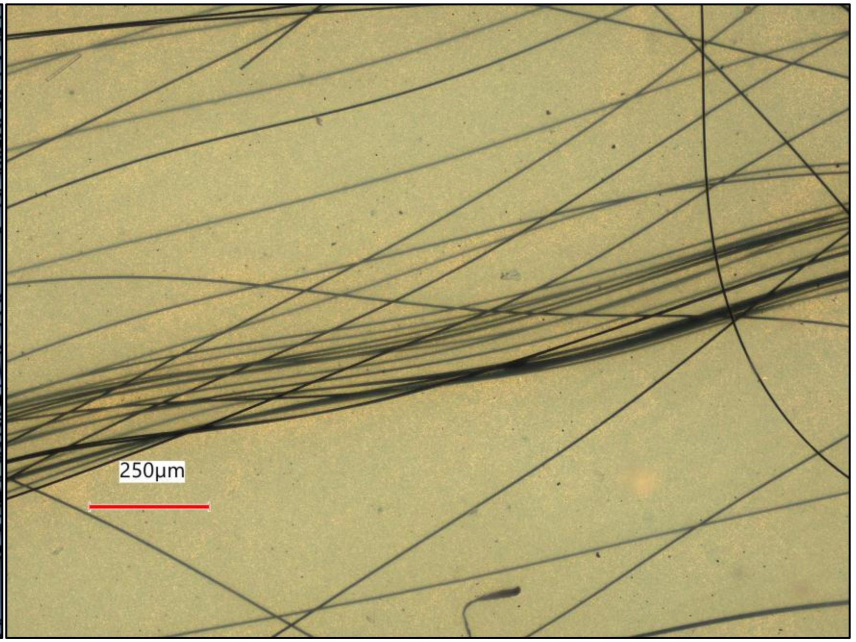
Differentiating Crystallites



Slow Cooled PEKK



Quenched PEKK

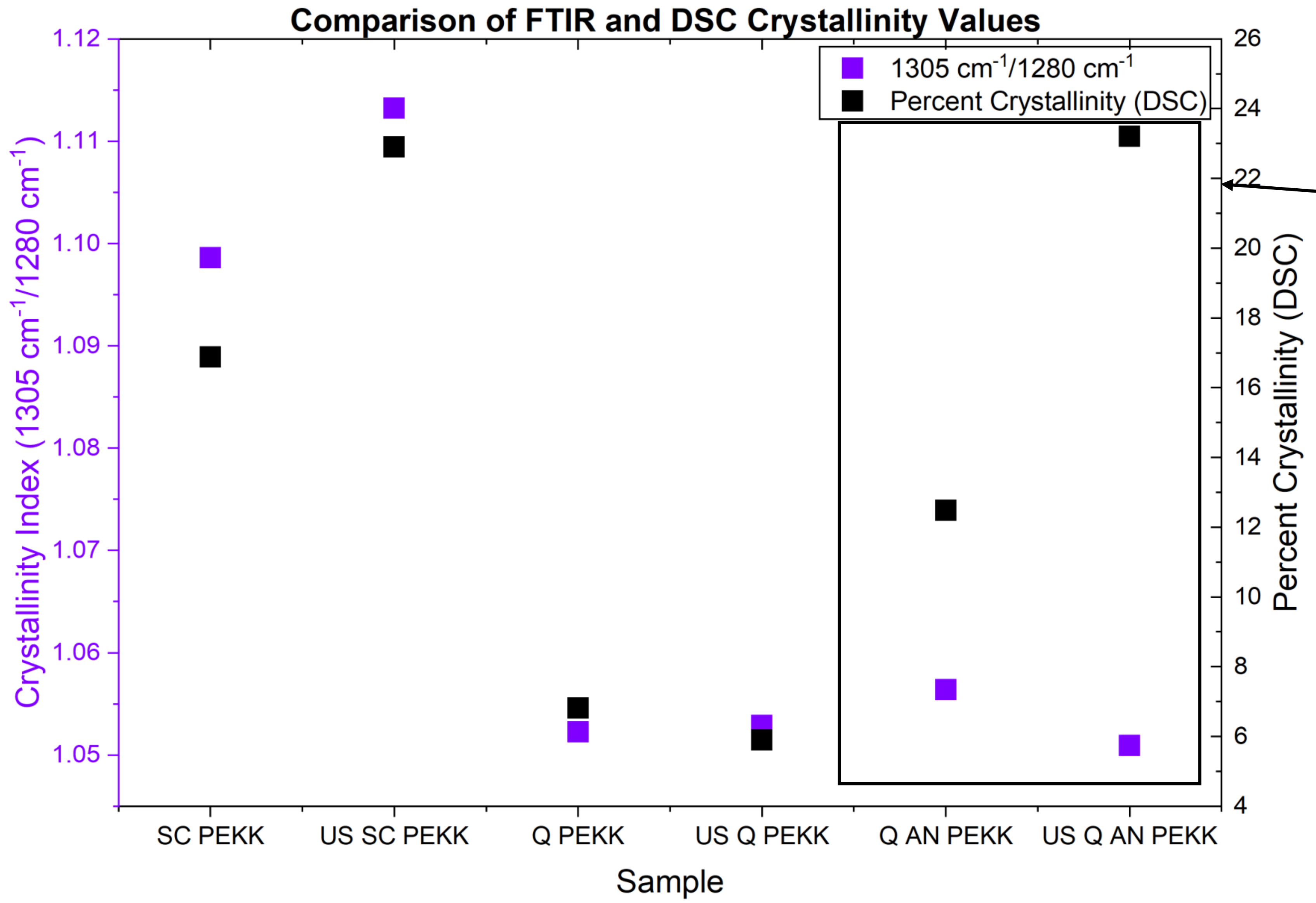


Quenched PEKK
+ Annealed 1h 225°C

Self nucleated, spherulite dominated

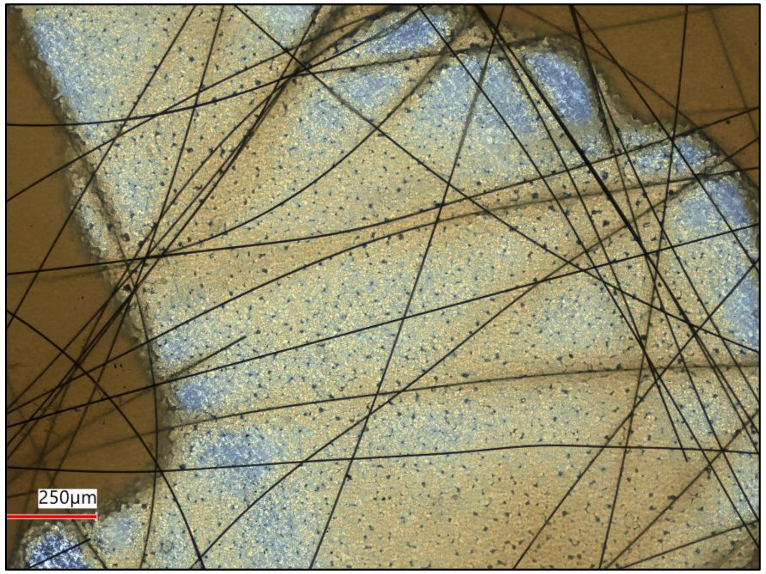
CF nucleated, transcrystalline dominated

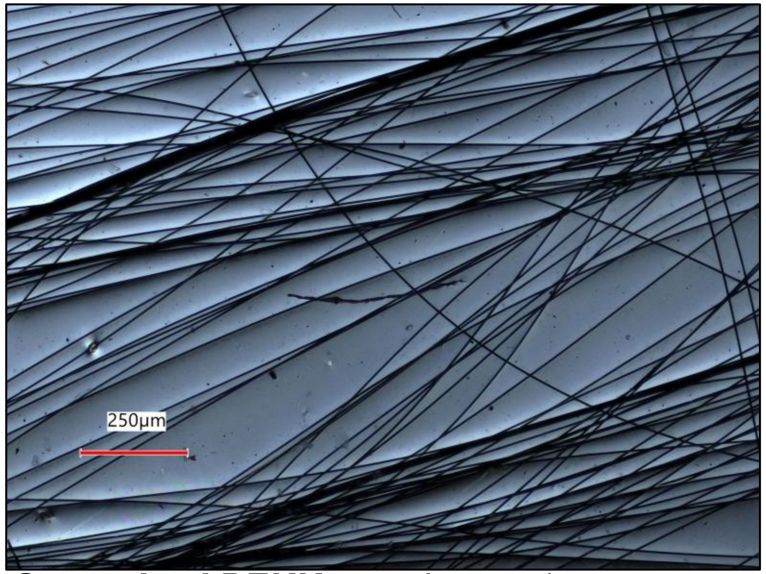
Crystallinity in Ultrasonically Welded Films

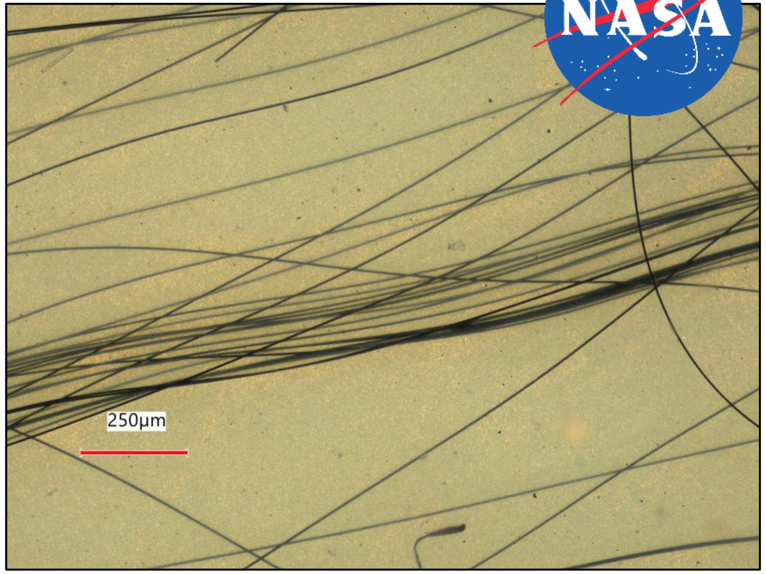


- Overall trend captured in SC and Q samples
- Data between DSC and FTIR for annealed samples differed – compared to optical microscopy

Before welding





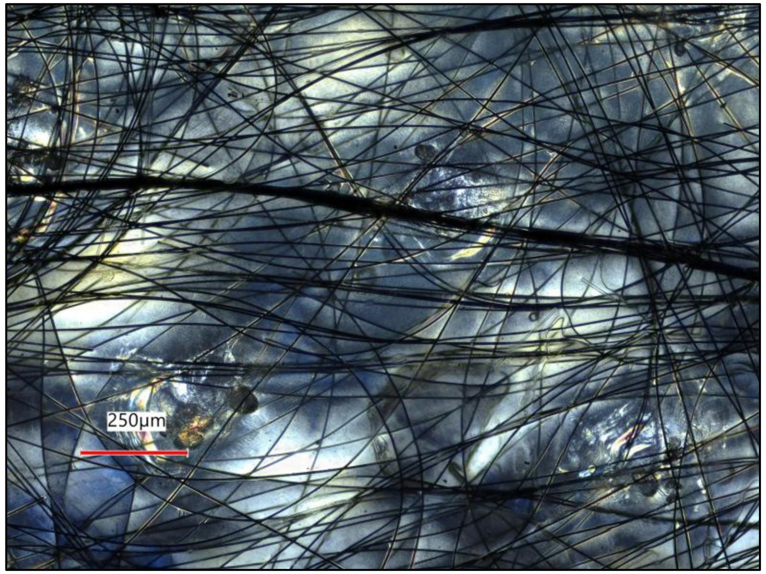


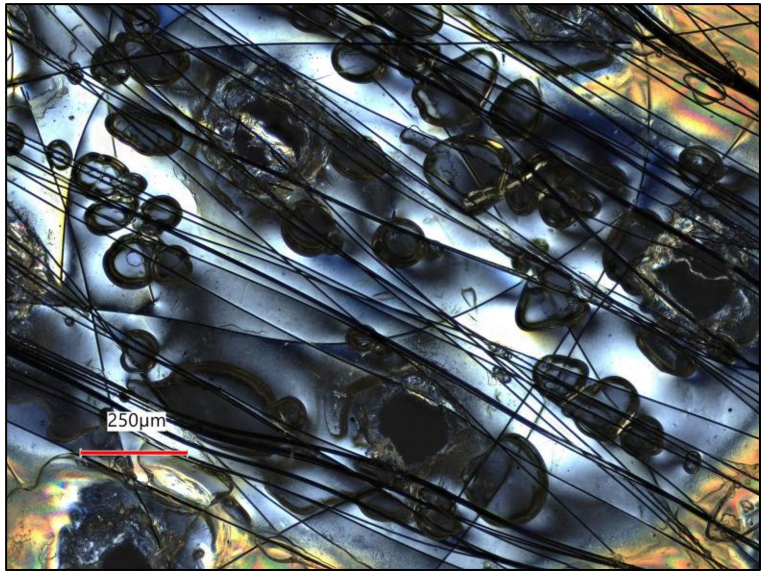
Slow Cooled PEKK: no loss of crystallinity, consistent with both FTIR and DSC data

Quenched PEKK: no change in crystallinity, consistent with FTIR and DSC data

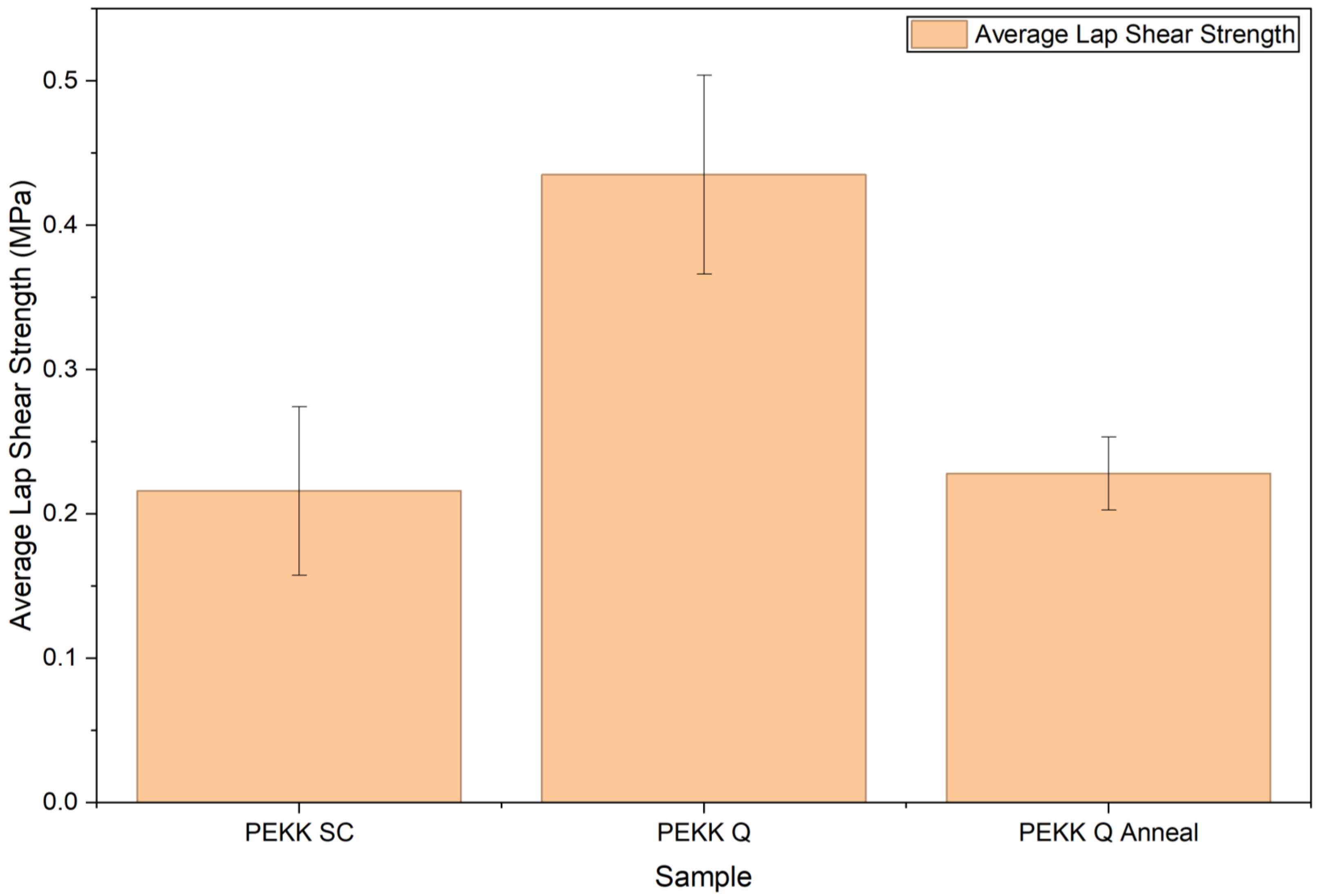
Annealed PEKK: loss of crystallinity in weld area, trend captured by FTIR, not DSC – more sensitive to regional variations

After welding



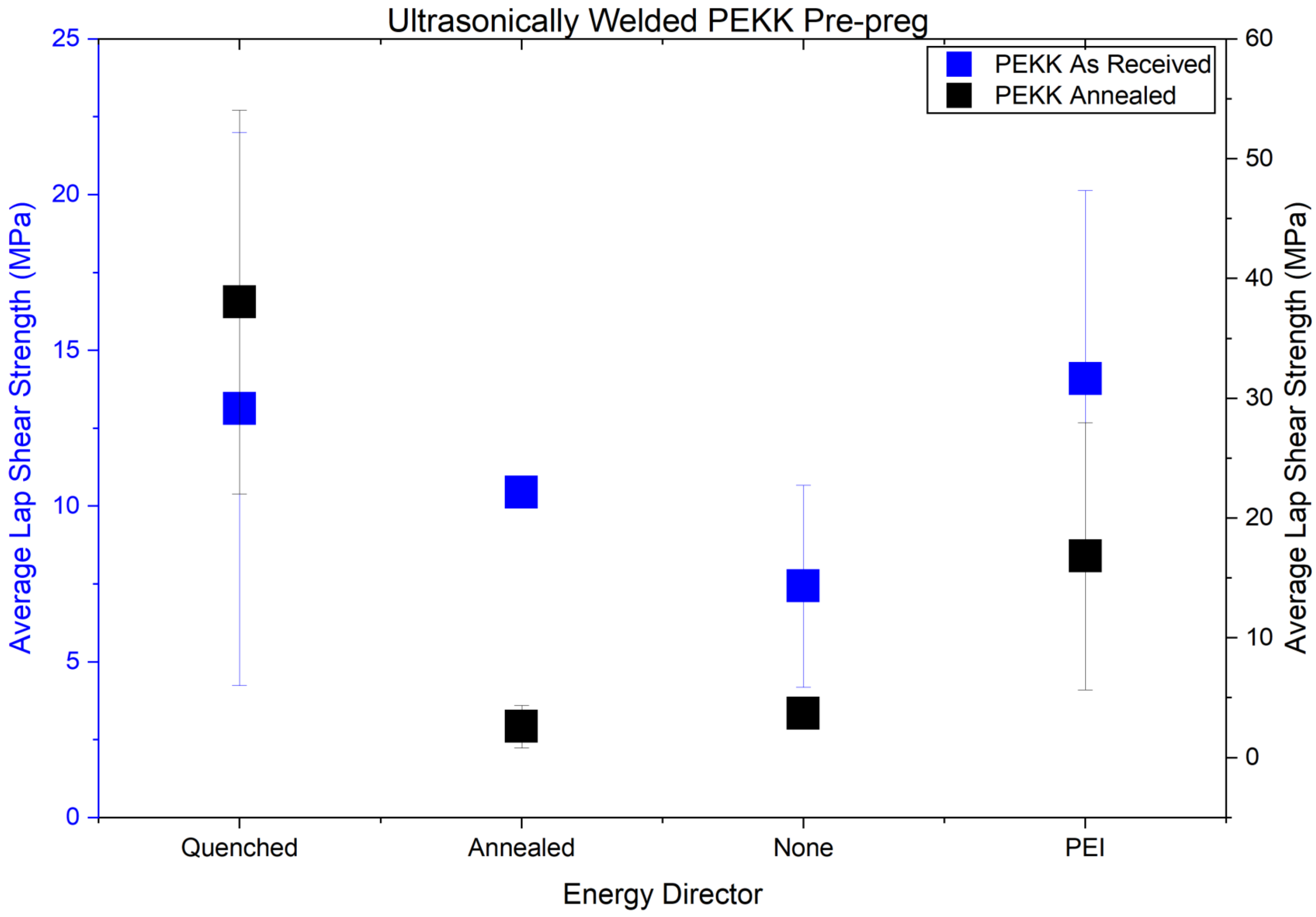


Crystallinity in Ultrasonically Welded Films



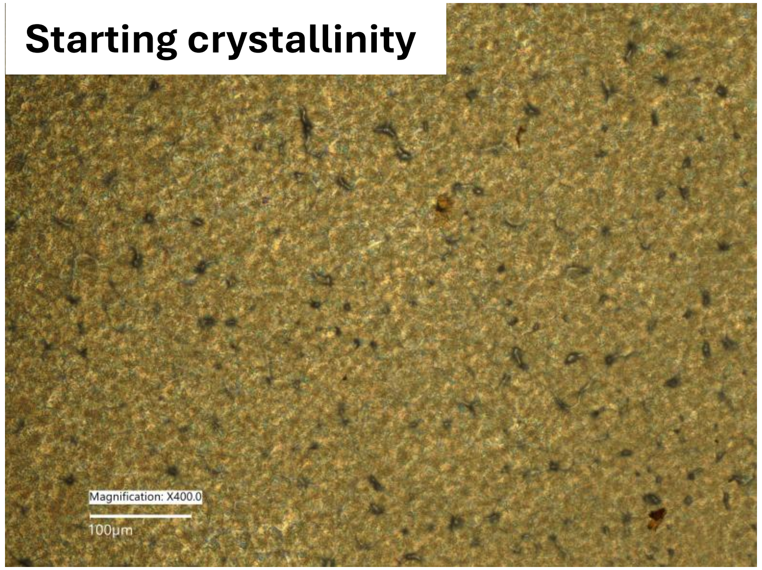
- Key takeaways from initial study: amorphous material much better for ultrasonic welding
- Variations in crystallinity are not always captured by DSC – this is important because crystallinity directly impacts weld strength

Ultrasonically Welded Prepreg w/ Energy Directors

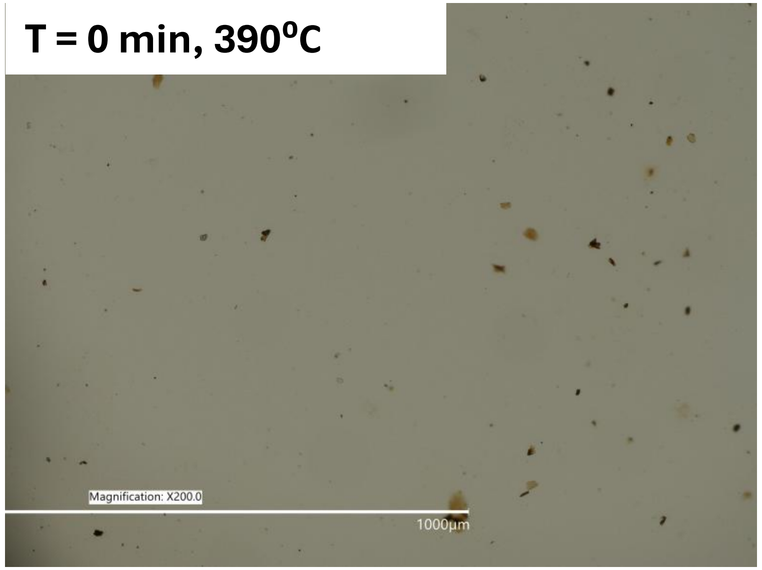


- Lap shear strength stronger when amorphous material is used as an energy director
- Welding crystalline material proved to be challenging, required higher pressures/longer duration – in many cases welding was not possible
- Welding parameters could be further optimized

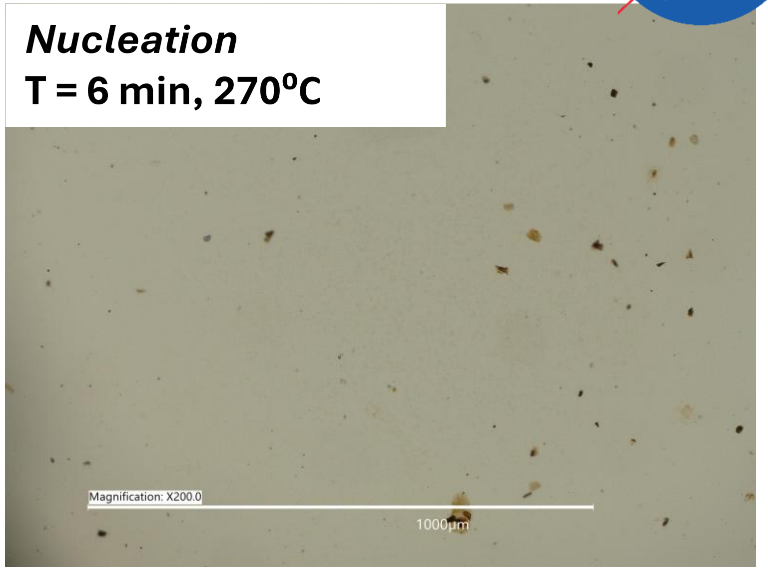
Hot Stage Microscopy – PEKK



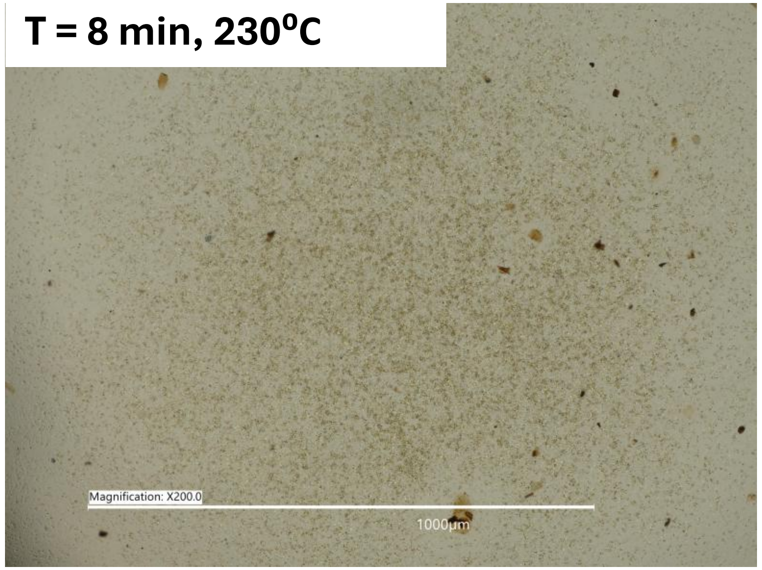
Starting crystallinity



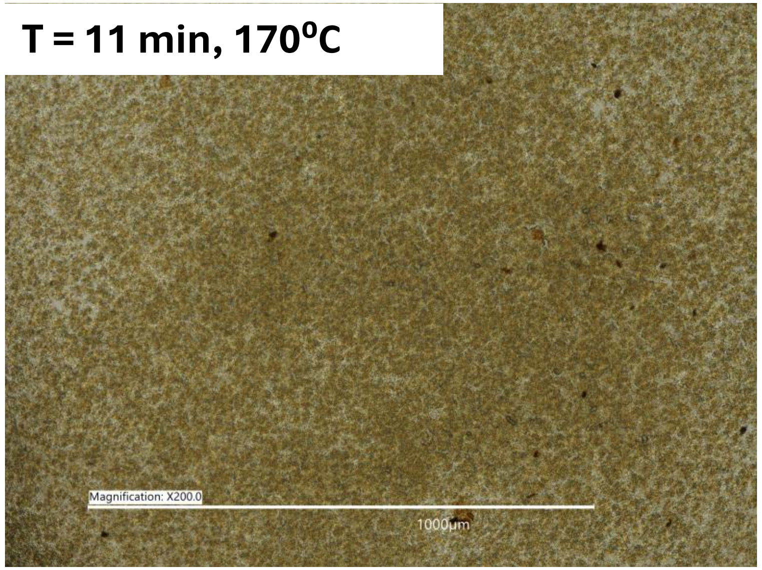
T = 0 min, 390°C



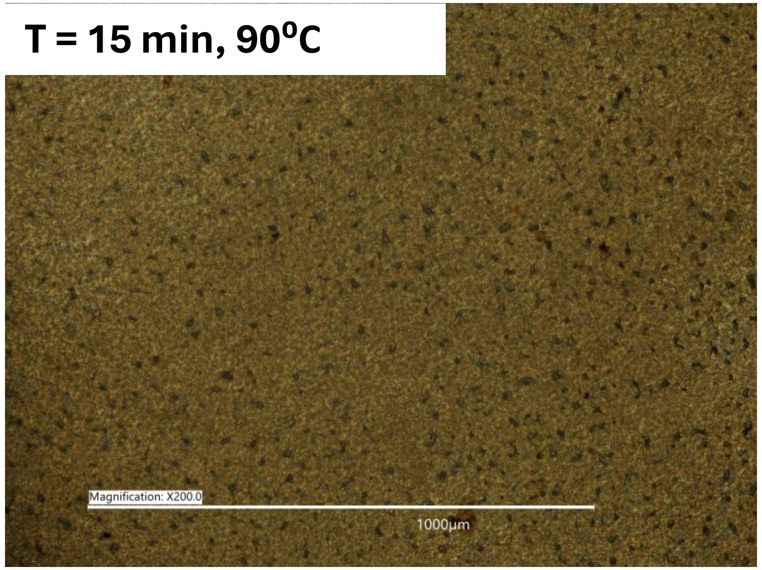
Nucleation
T = 6 min, 270°C



T = 8 min, 230°C



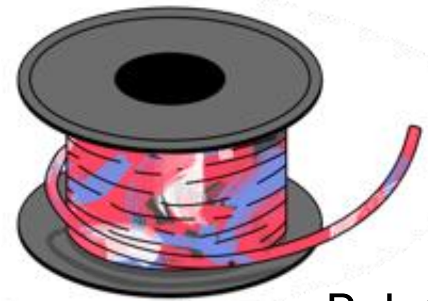
T = 11 min, 170°C



T = 15 min, 90°C

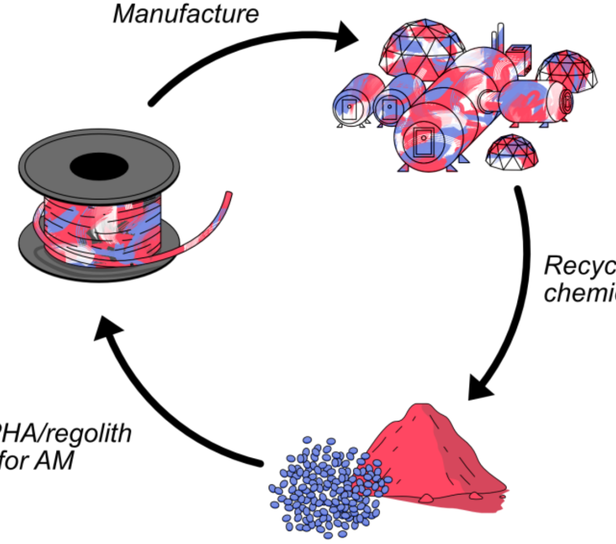
Hot Stage Microscopy Key Takeaways & Ongoing Work

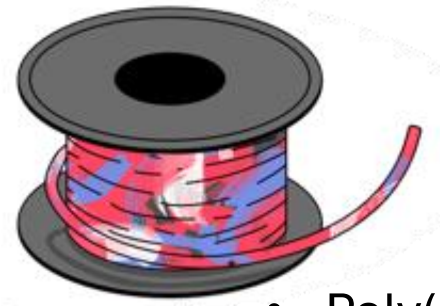
- *Key takeaways*: Self nucleated crystallinity can be efficiently tracked with hot stage microscopy; thick films made it challenging to resolve single layers; PEKK much easier to visualize than LM-PAEK
- *Ongoing work*: Repeating experiment with thinner films, higher resolution, and various cooling rates; experiments with CF embedded films to evaluate fiber nucleation/transcrystallinity; use kinetics/modeling to guide processing



Regolith/PHB Composites

- Poly(3-hydroxybutyrate) (PHB) is a bacterially synthesized resins that use various sources of carbon (including waste products, CO_2, polymers etc.) to create more material
- PHB is highly crystalline but crystallizes very slowly
  - Poor mechanical performance
  - Poor processability





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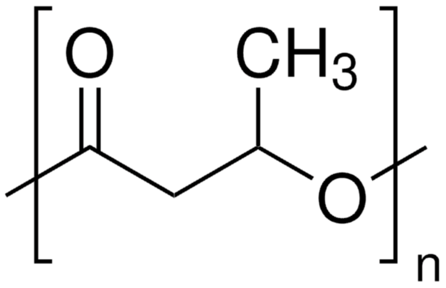
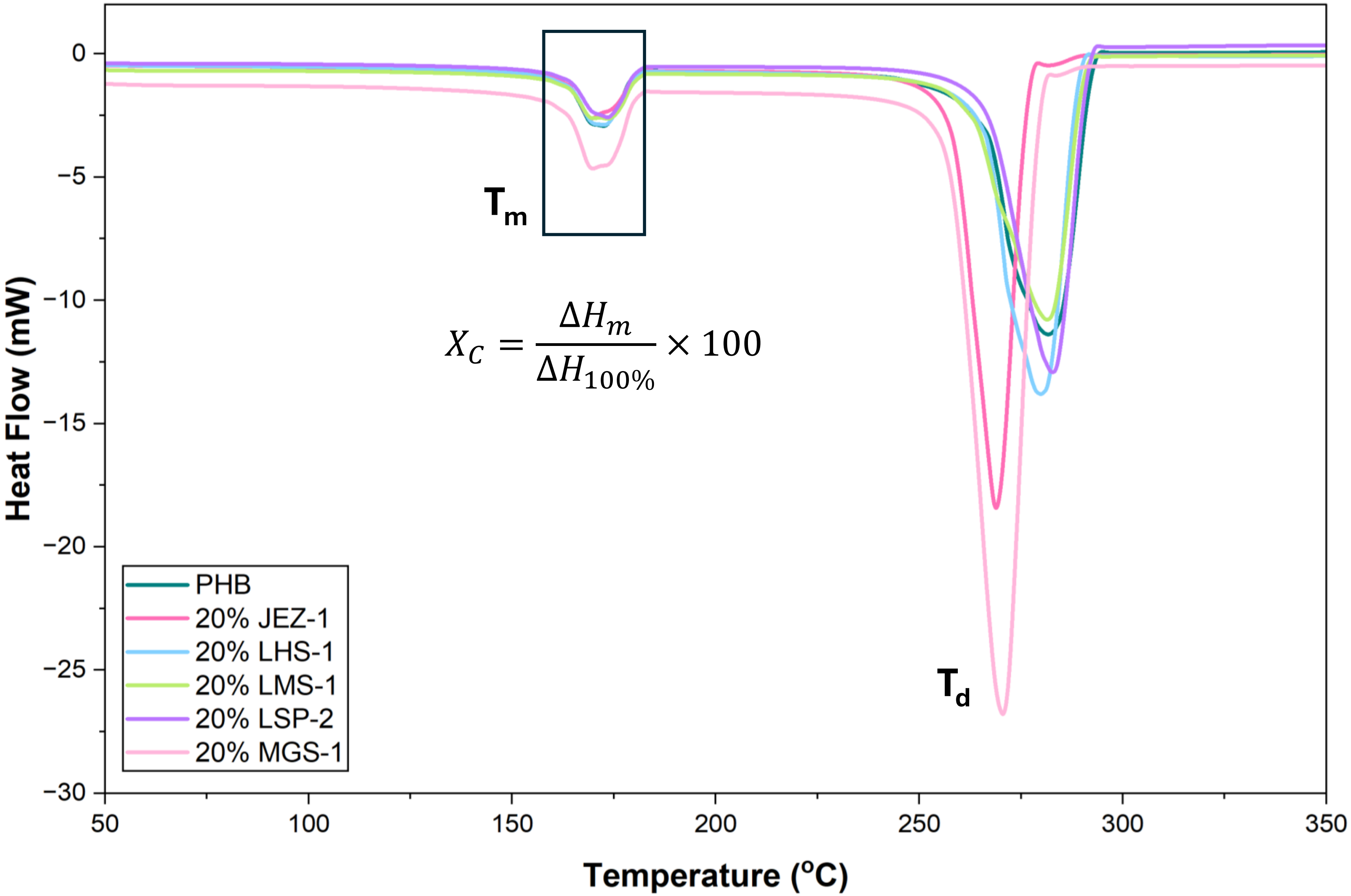
- PHB is highly crystalline but crystallizes very slowly
  - Poor mechanical performance
  - Poor processability
- **Can we use regolith to alter PHB crystallinity?**
- **Does this play a role on material performance?**

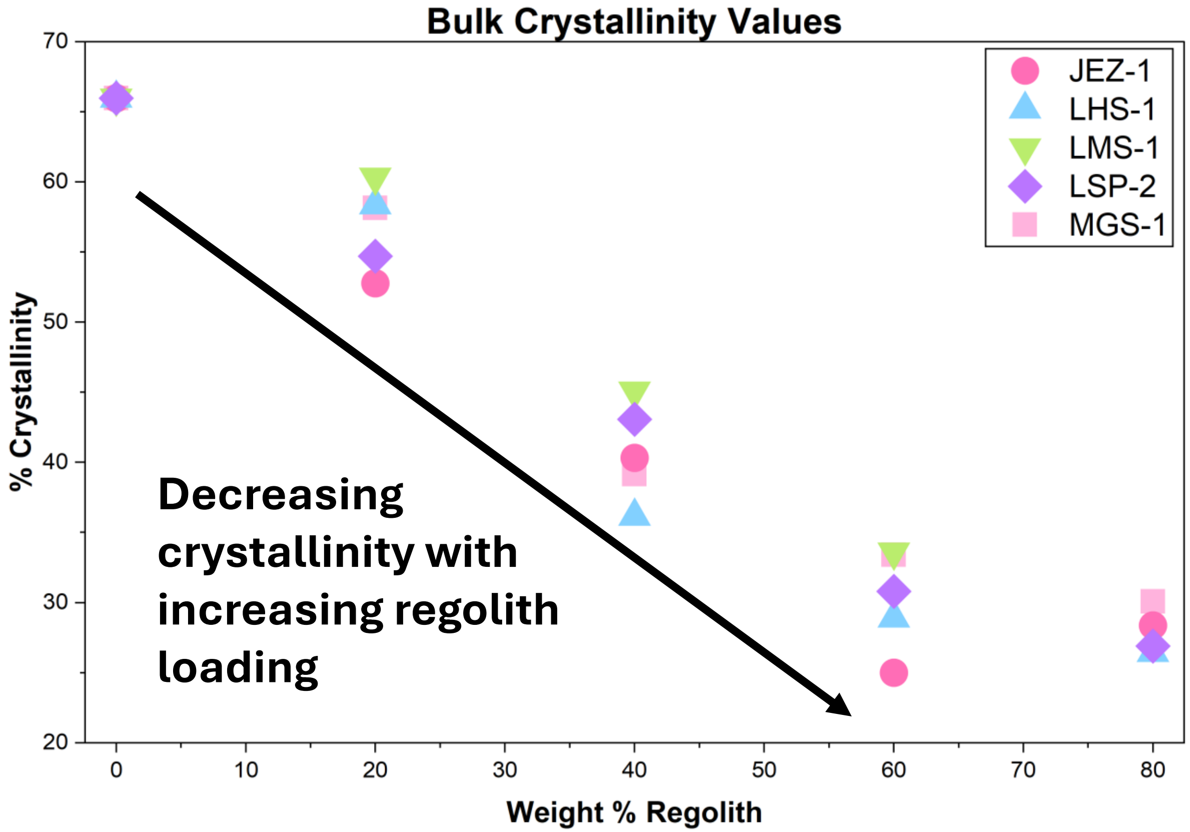


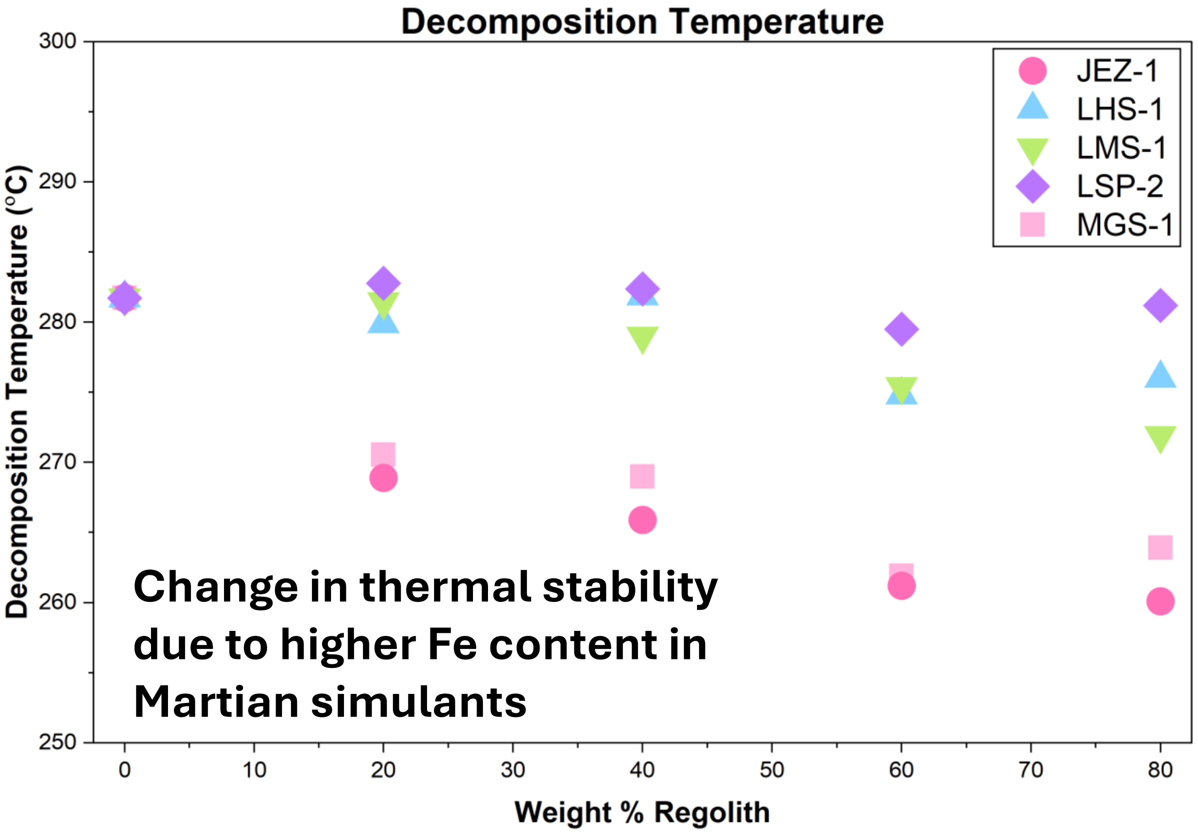
Composites with 20 wt% Regolith



$$X_C = \frac{\Delta H_m}{\Delta H_{100\%}} \times 100$$

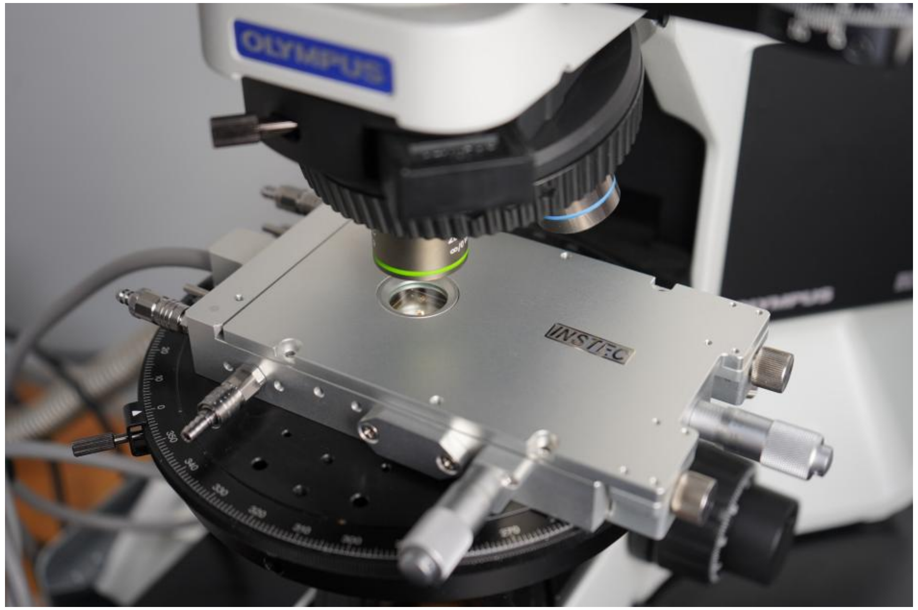
Regolith/PHB Composite Crystallinity – *Bulk Behavior*

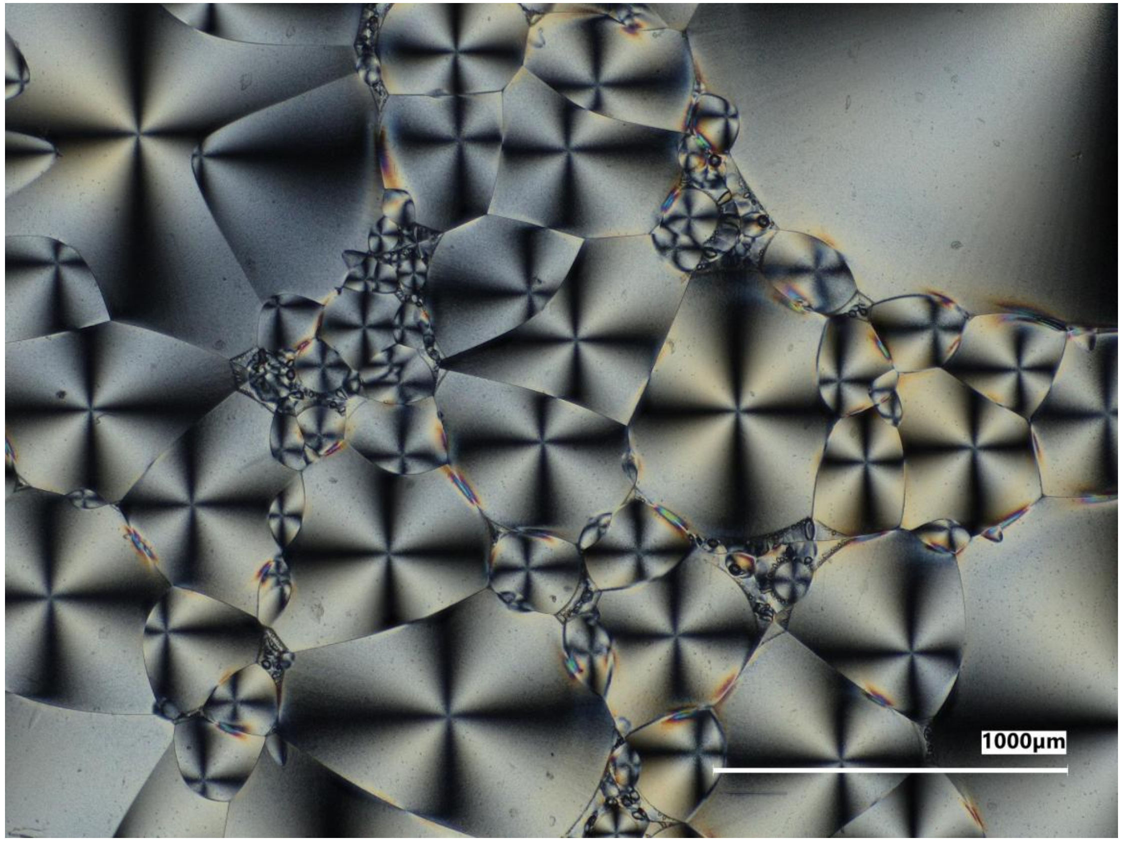




Regolith/PHB Composite Crystallinity – *Cross Polarized Optical Microscopy*

- Captures variations in crystal structure
- Hot stage attachment allows for real-time monitoring of crystallization
  - 20% regolith samples chosen for study

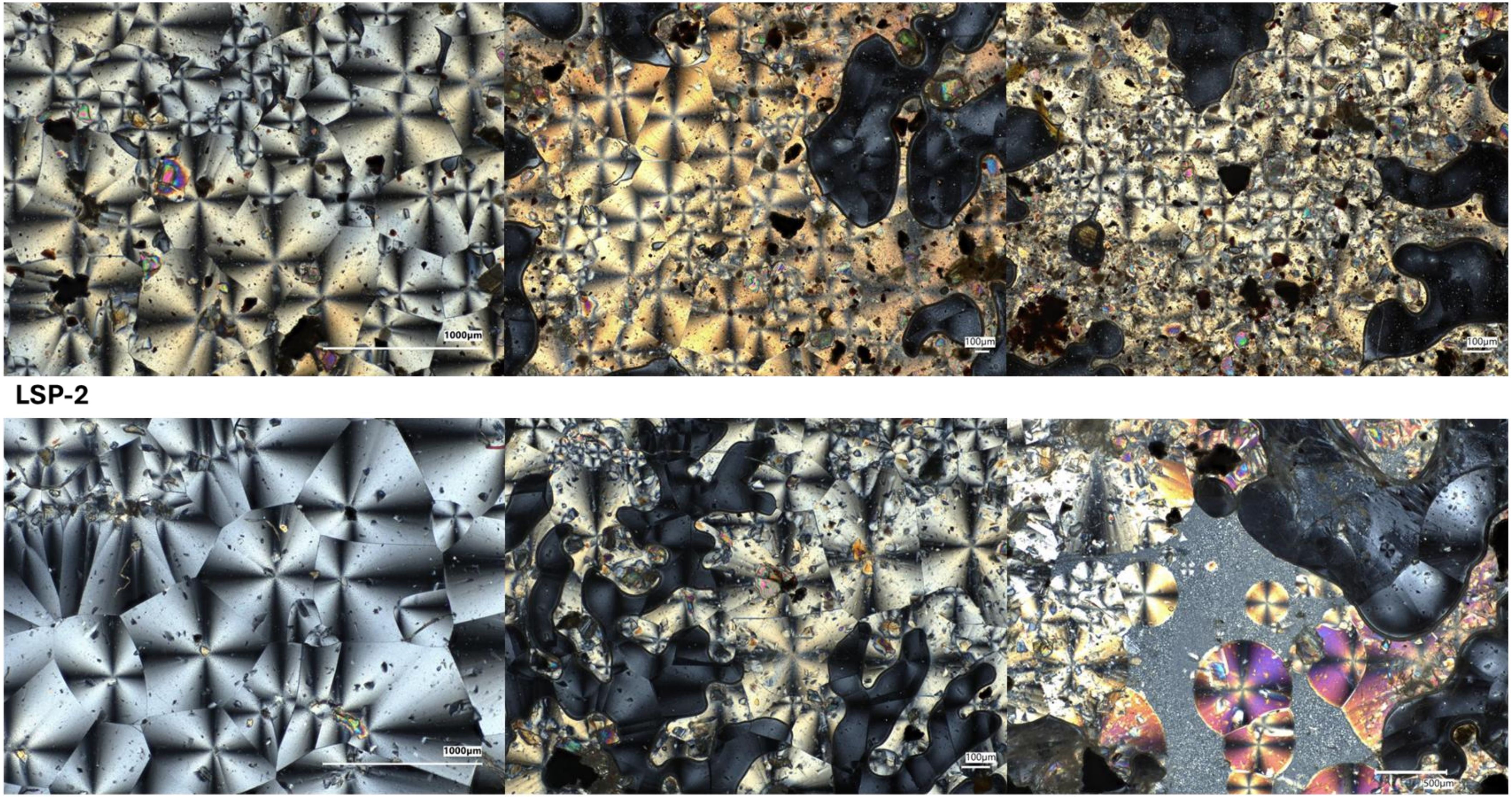




Regolith/PHB Composite Crystallinity – *Effect of Regolith Loading*

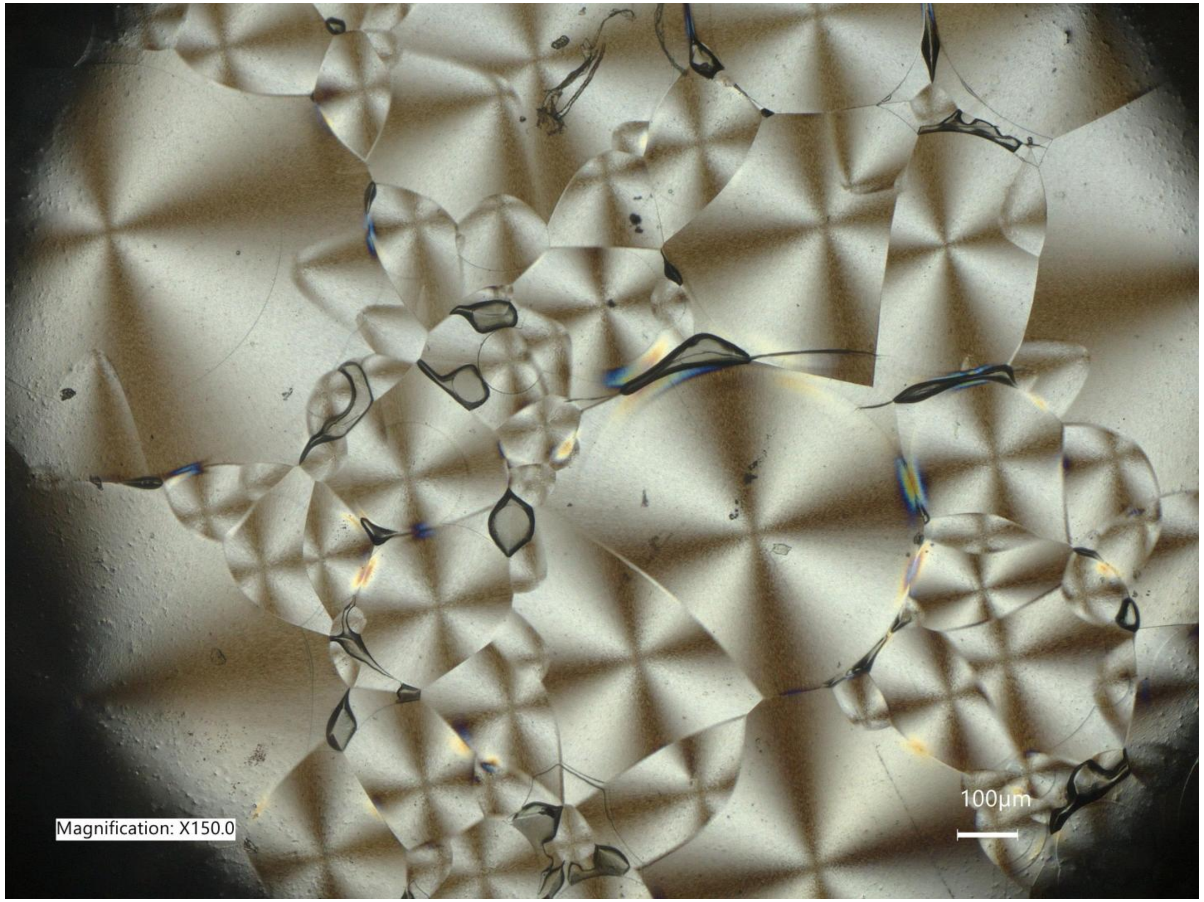
JEZ-1

LSP-2

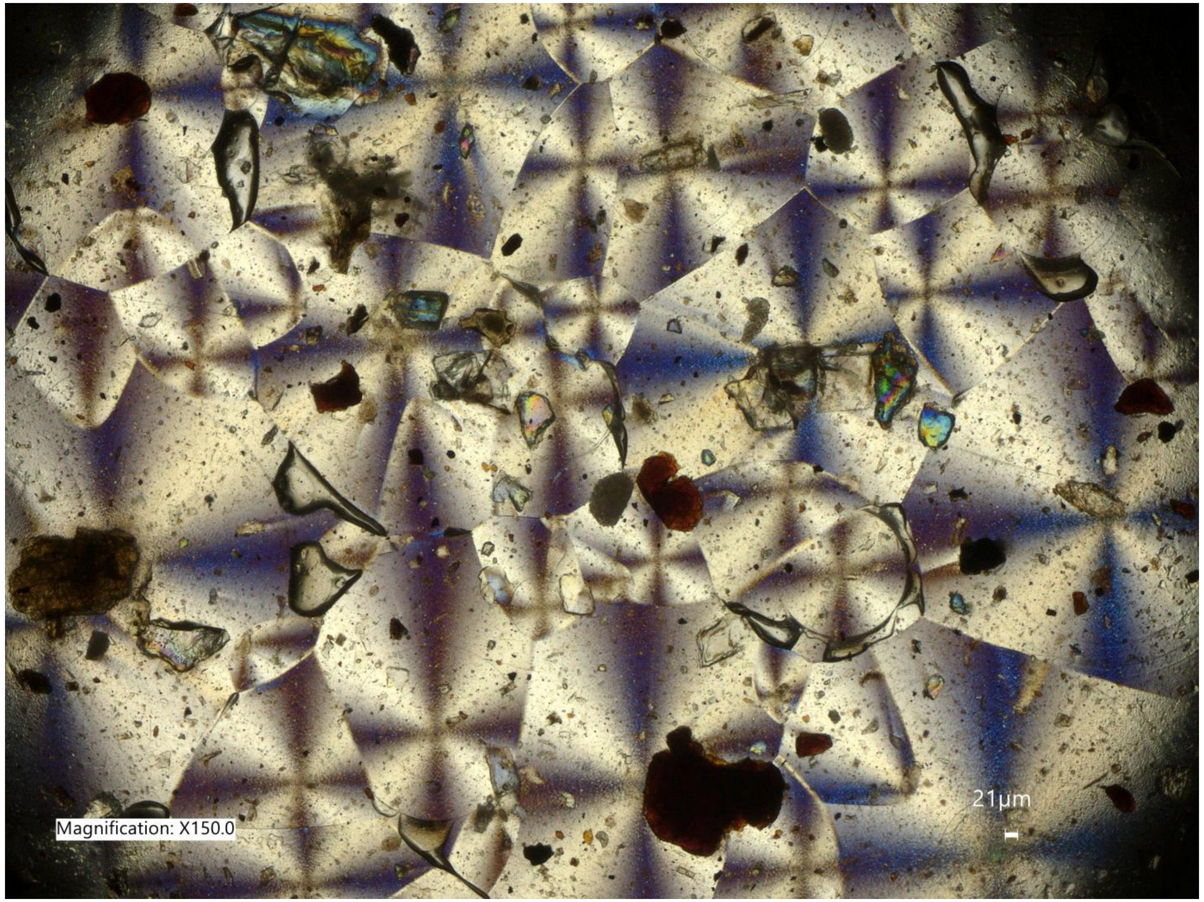


20% **40%** **80%**

Regolith/PHB Composite Crystallinity – *Hot Stage Microscopy*



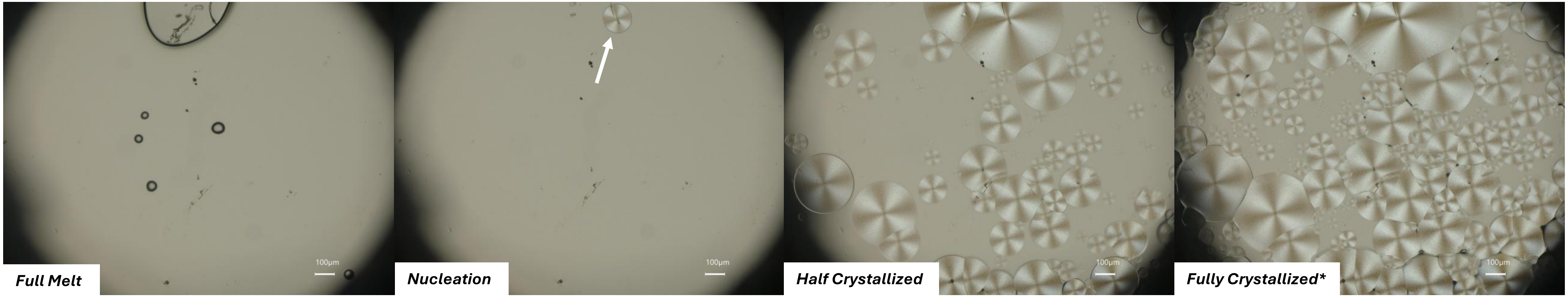
Neat PHB



20 % MGS-1

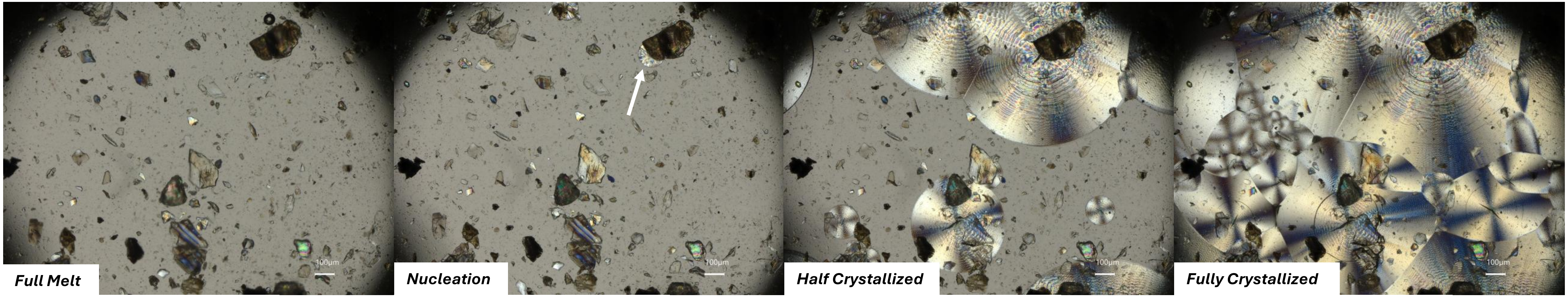
Regolith/PHB Composite Crystallinity – *Hot Stage Microscopy*

(a) Neat PHB



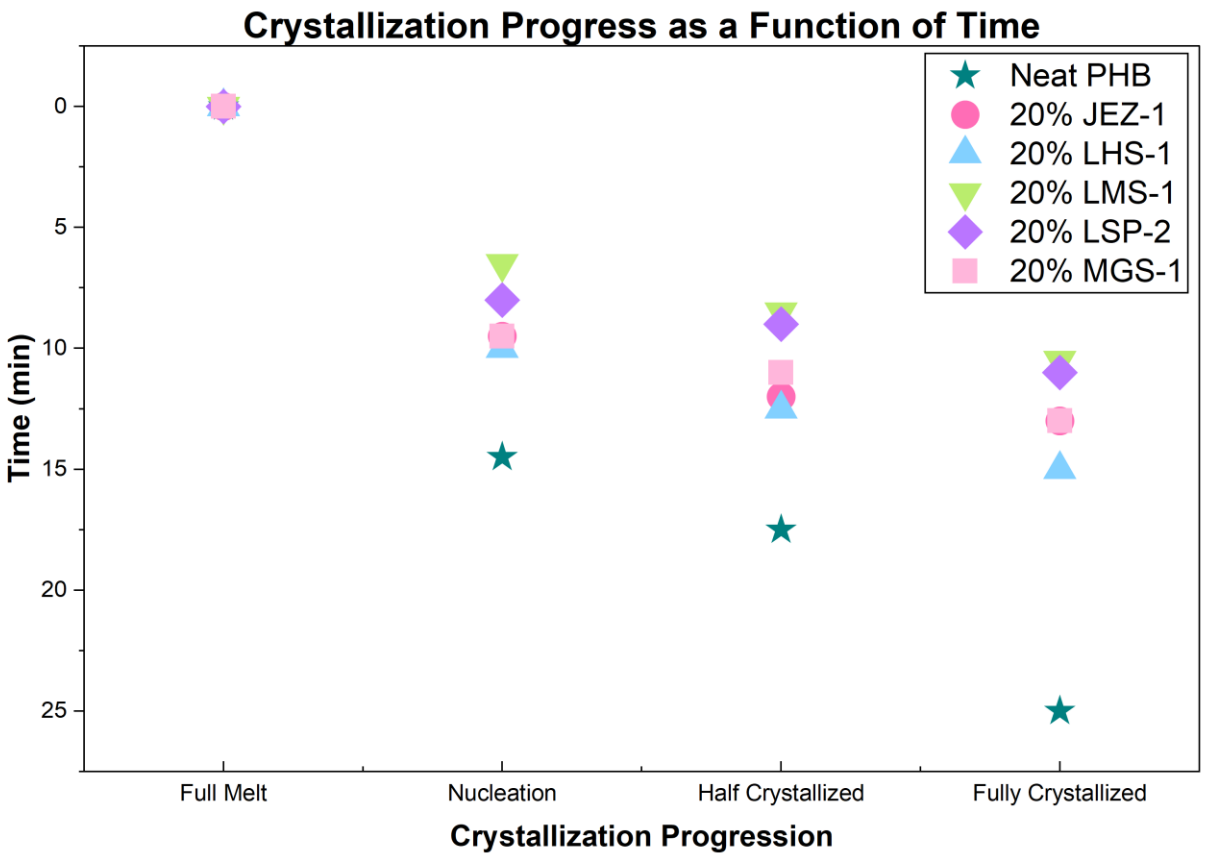
T = 0 min, 190°C | **T = 14.5 min, 45°C** | **T = 17.5 min, RT** | **T = 25 min, RT**

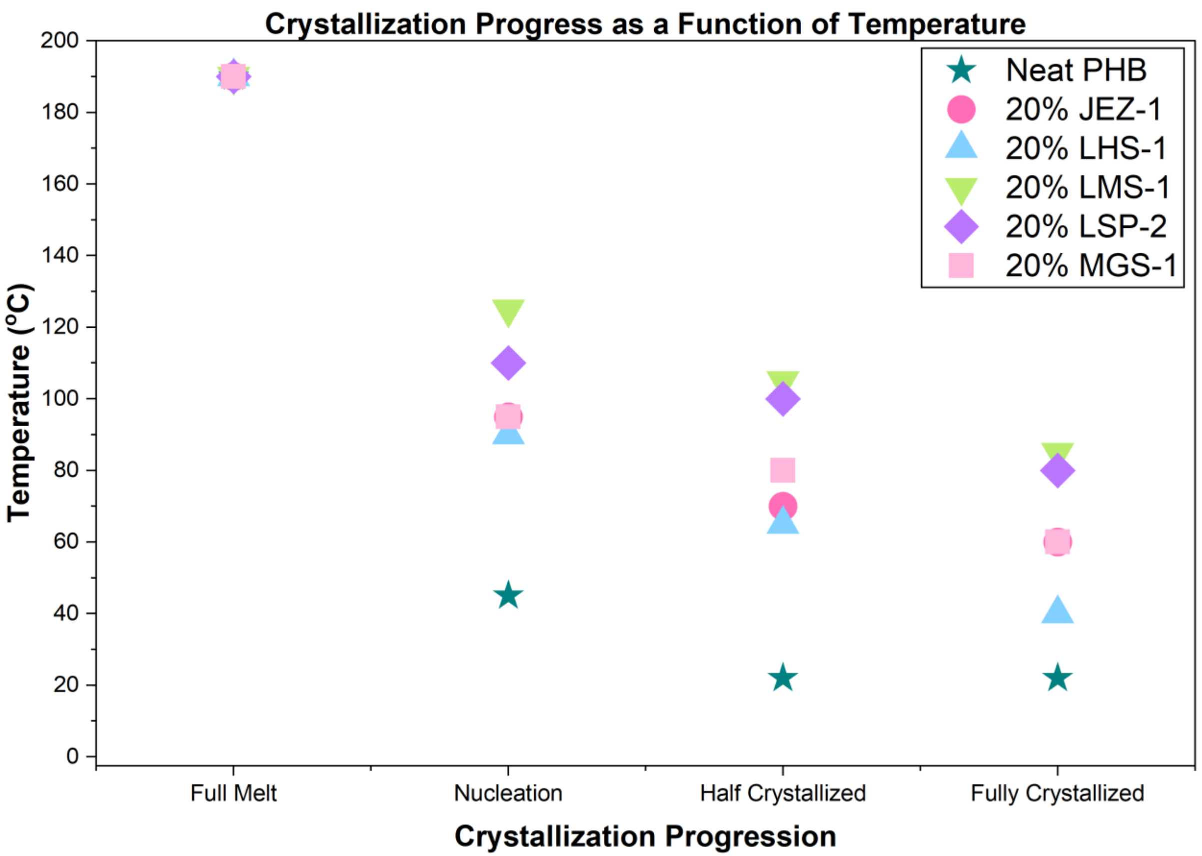
(b) 20% LMS-1



T = 0 min, 190°C | **T = 6.5 min, 125°C** | **T = 8.5 min, 105°C** | **T = 10.5 min, 85°C**

Regolith/PHB Composite Crystallinity – *Hot Stage Microscopy*





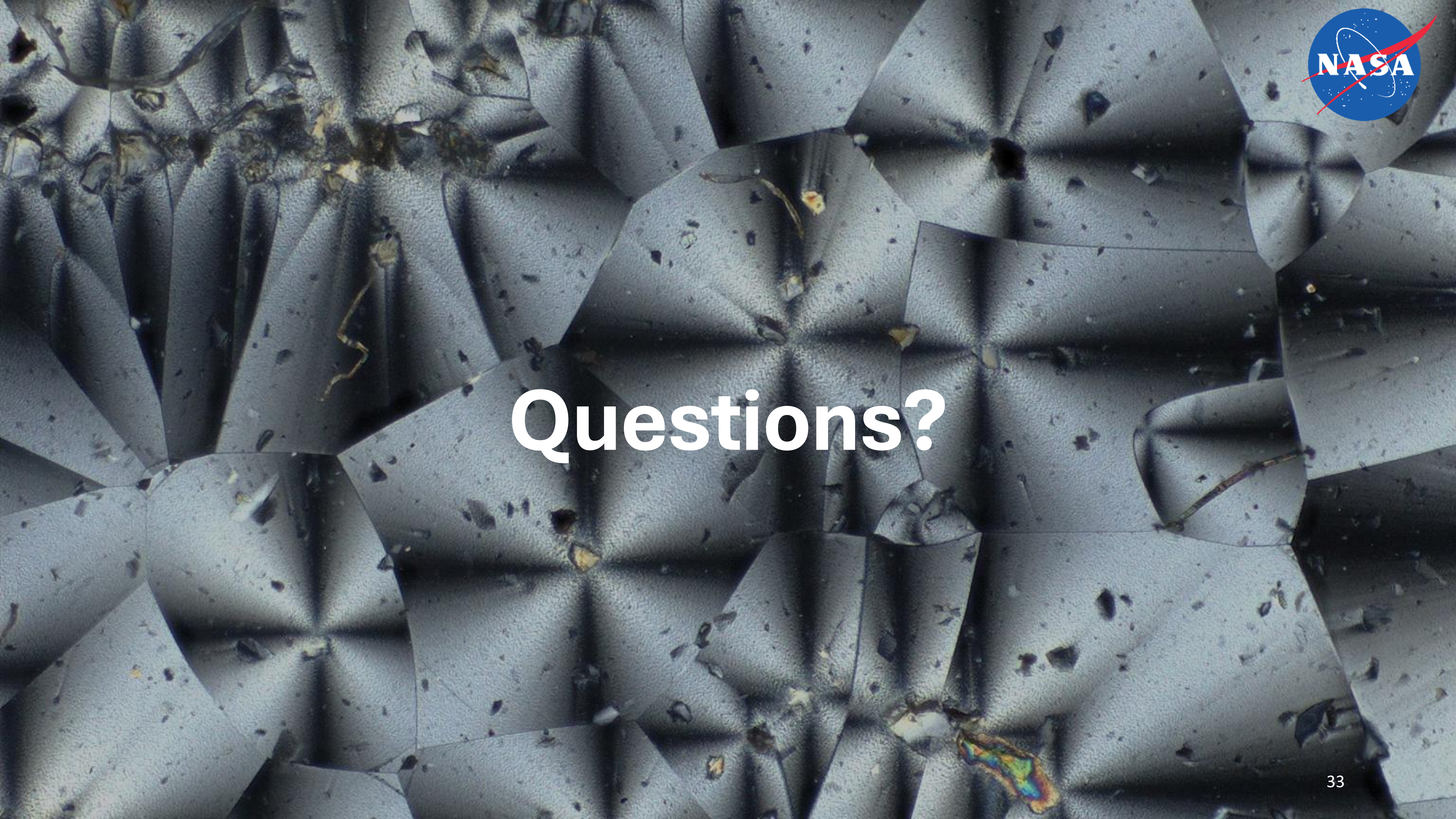
Regolith successfully increased rate of PHB crystallization and decreased overall crystallinity – could be used as in-situ additive!

Key Takeaways

- Assessing the crystallinity of thermoplastic composites is important to produce materials with optimal performance
- DSC is an effective tool for gathering bulk crystallinity profiles; FTIR and POM are effective for analyzing regional variations
- Regolith simulants can be used as an in-situ additive used to vary crystallinity

Key Takeaways & Next Steps

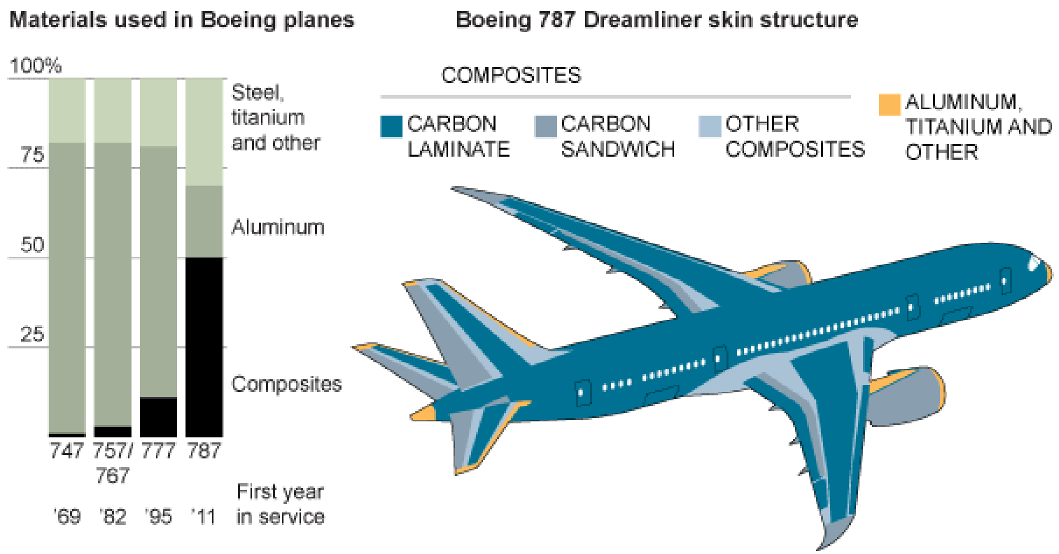
- Assessing the crystallinity of thermoplastic composites is important to produce materials with optimal performance
- DSC is an effective tool for gathering bulk crystallinity profiles; FTIR and POM are effective for analyzing regional variations
- Regolith simulants can be used as an in-situ additive used to vary crystallinity
- **Obtain WAXS and SAXS and compare to other methods**
- **Conduct broader study on the effects of crystallinity on weld strength and performance for in-situ repair**
- **Use fundamental data to guide modeling efforts for predicting material performance**

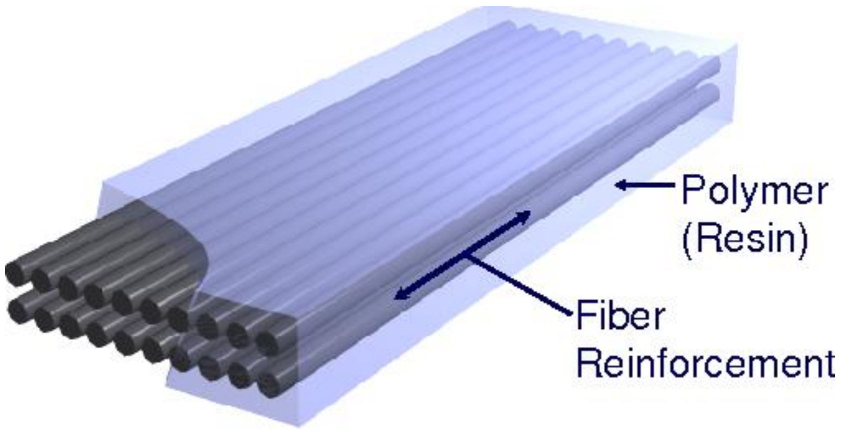


Questions?

Backup Slides

Polymer Composite Use in Aircraft

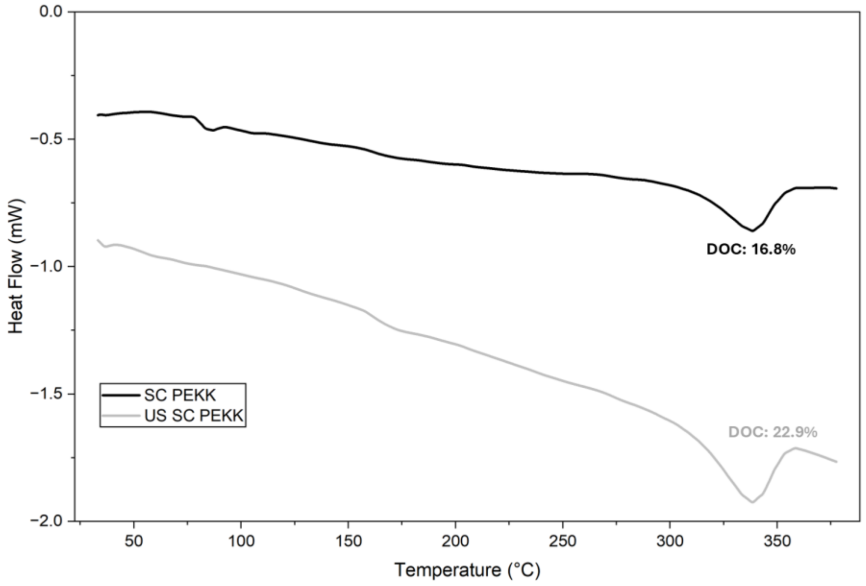


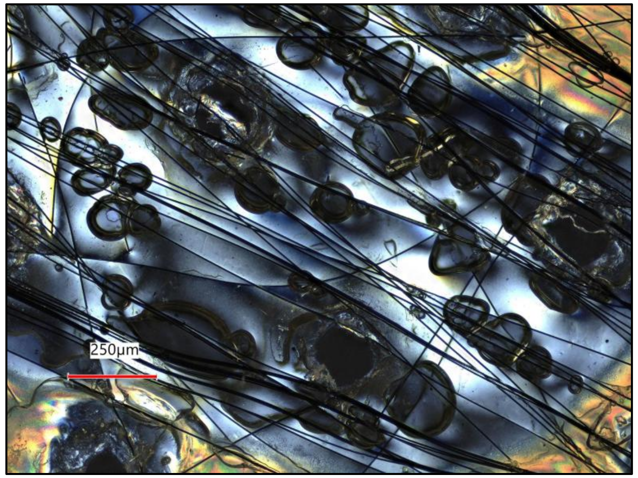


- Thermoset composites are cured in an irreversible reaction using autoclave process
  - *Slow and energy intensive manufacturing and complex repair*
- Thermoplastic composites are consolidated at higher temperatures using compression molding in reversible transition
  - *Potential for efficient repair and increased manufacturing speeds*

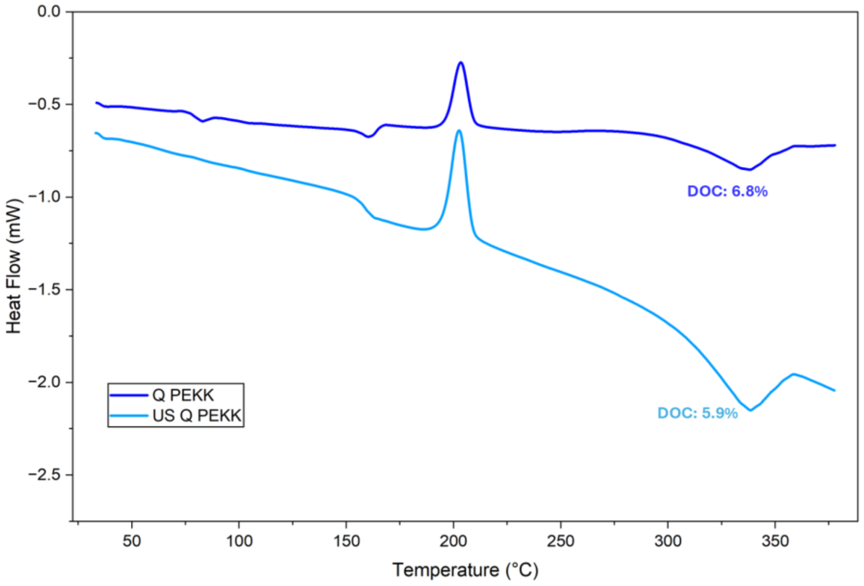
Source: Boeing

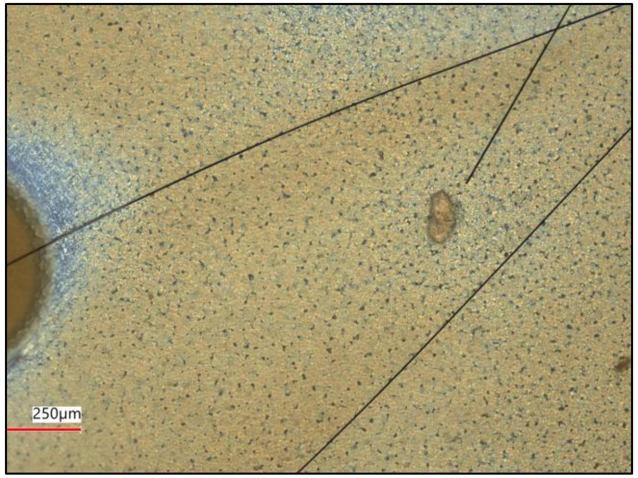
Crystallinity on Ultrasonically Welded Samples



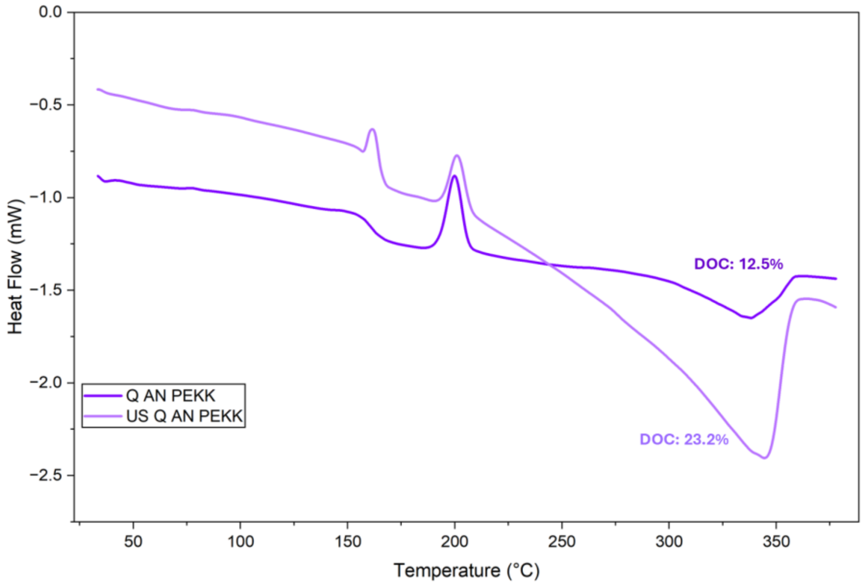


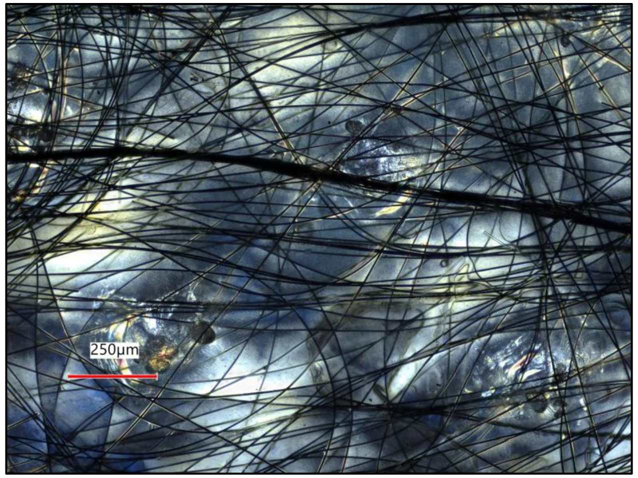
US Annealed





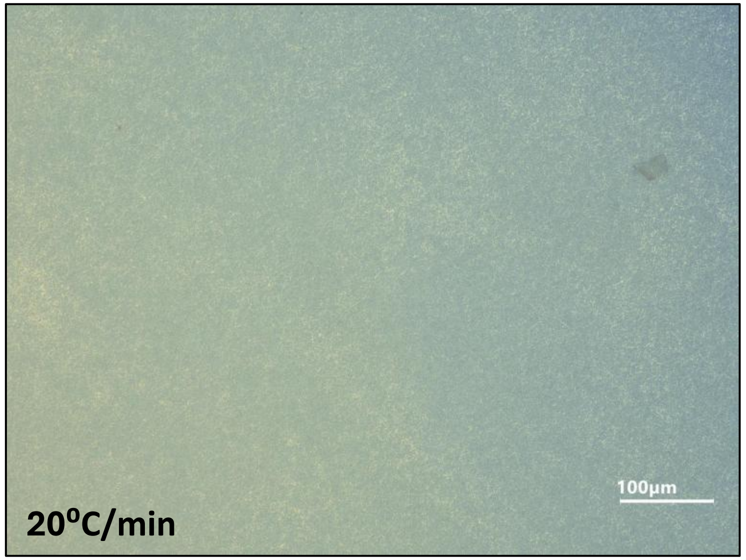
US Slow Cooled

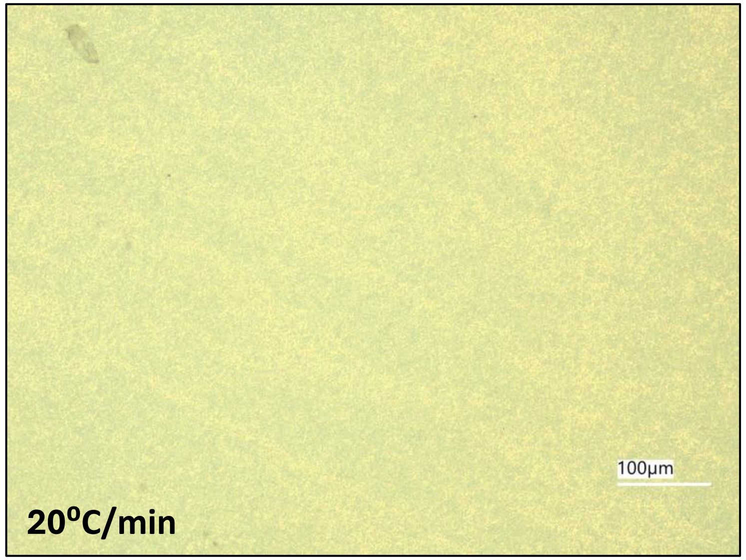


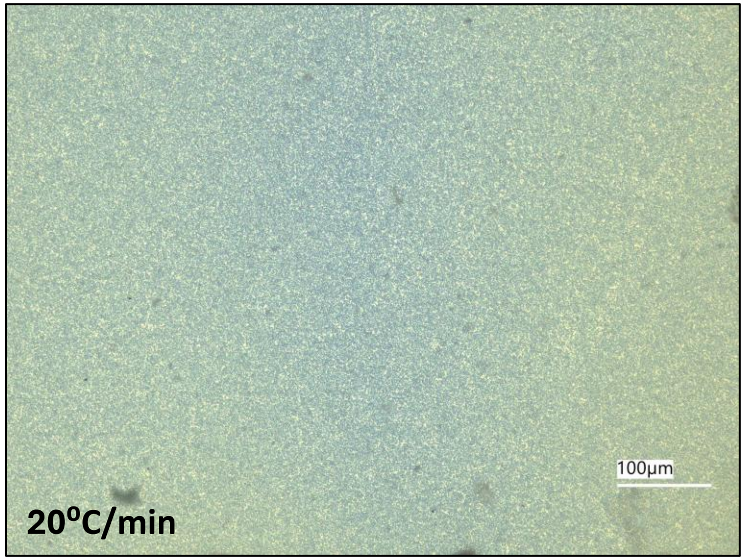


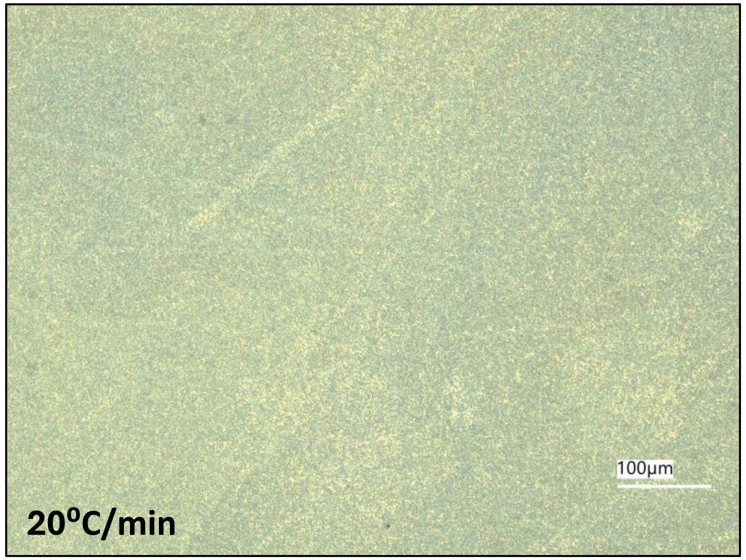
US Quenched

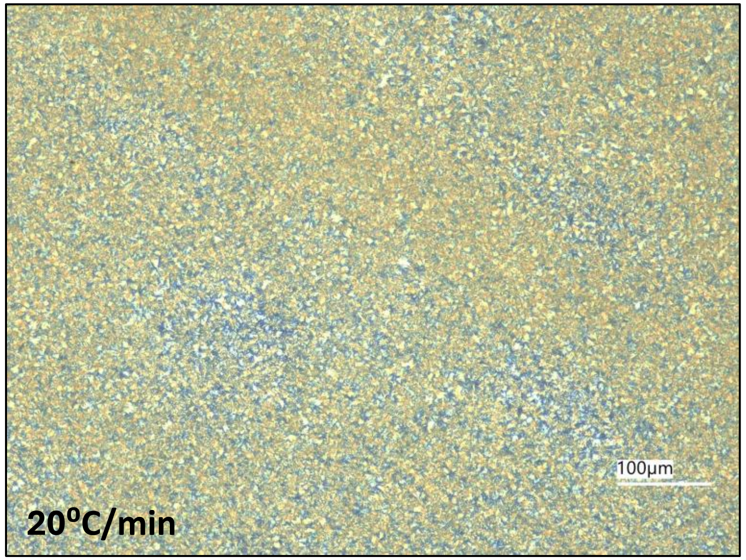
Cross Polarized Light Optical Microscopy





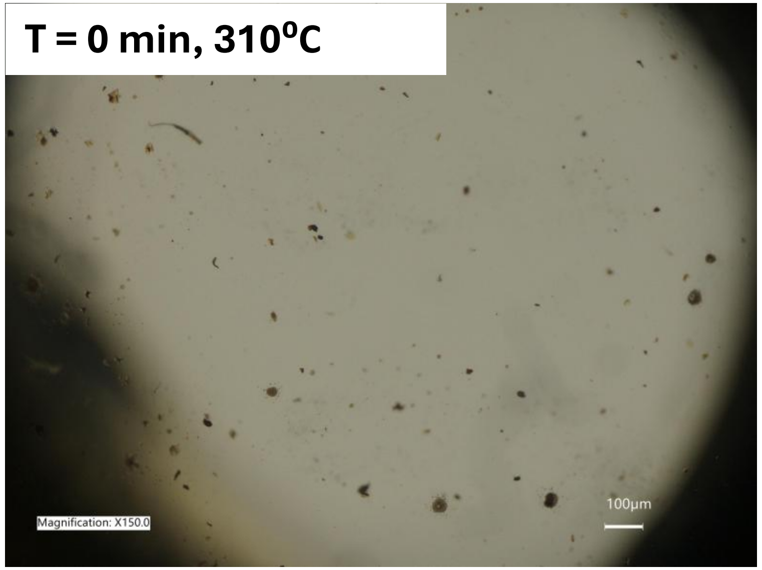




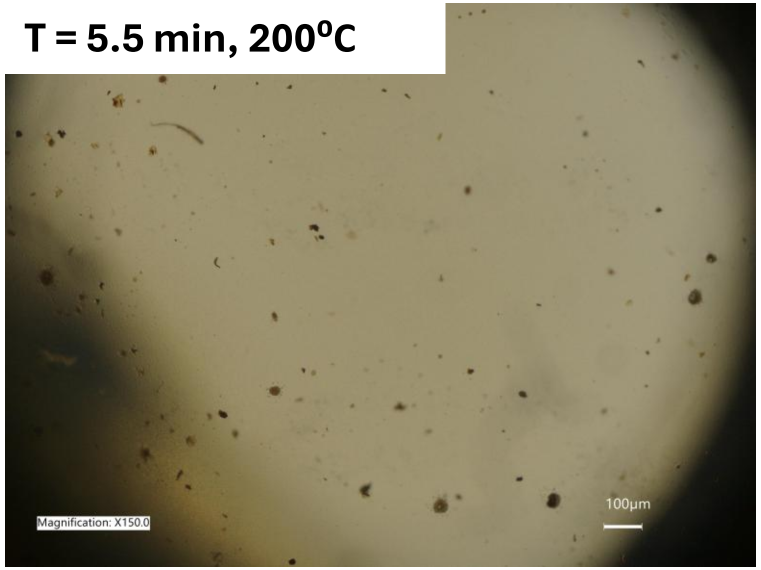


Hot Stage Microscopy – LM-PAEK

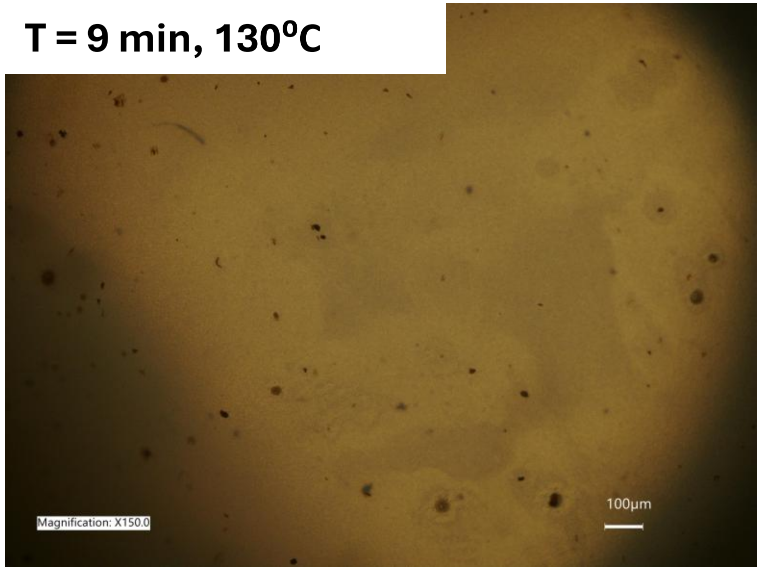
T = 0 min, 310^{o}C



T = 5.5 min, 200^{o}C



T = 9 min, 130^{o}C



- Much smaller crystallites, thicker sample
- Will explore using slower cooling speeds and thinner samples to improve resolution

Regolith/PHB Composite Development

- 5 candidate regolith simulants studied for materials screening from Space Resource Technologies
  - Mars Jezero Delta (JEZ-1)
  - Lunar Highlands (LHS-1)
  - Lunar Mare (LMS-1)
  - Lunar South Pole (LSP-2)
  - Mars Global (MGS-1)
- Design system for as many regions and potential applications as possible