Center for Composite Materials
(UD-CCM)

Kinetics Driven Approach to Understanding Void Formation During Carbonization

Faheem Muhammed| 3/30/22

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Advisors: Dr. Gillespie and Dr. Mirotznik

Project Advisors: Dr. Advani and Dr. Heider

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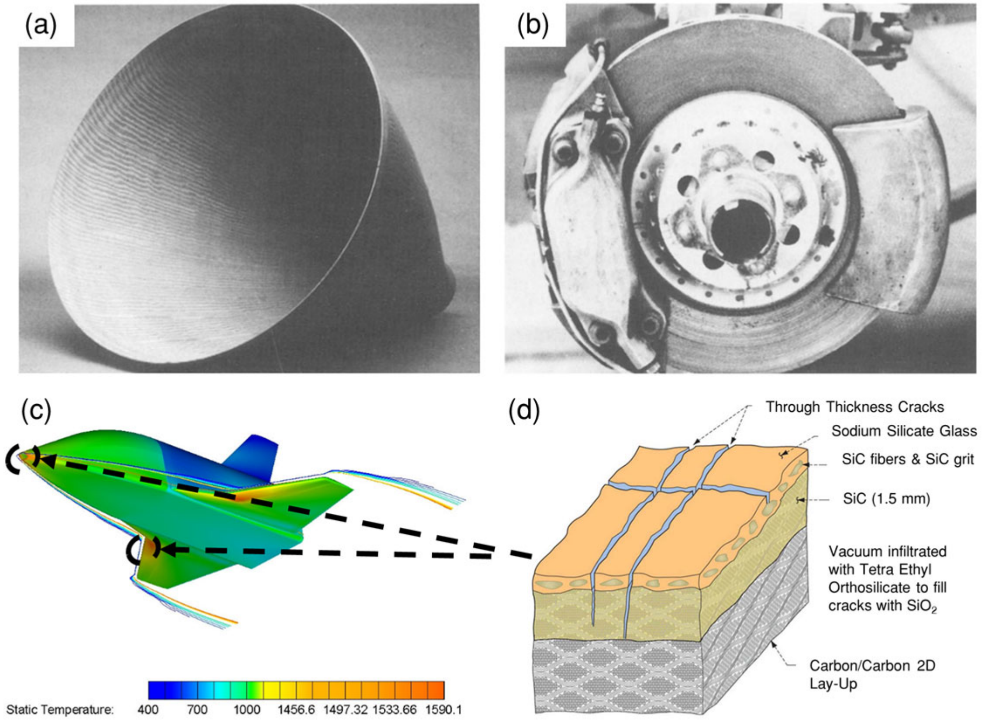
Overview

- Introduction of composite system and methods of manufacturing
- Kinetic analysis and its relation to experimental design
- Proposed mechanisms influencing microstructural properties
- **Composite Microstructural Analysis**
- Concluding Remarks

Carbon-Carbon Composite Background

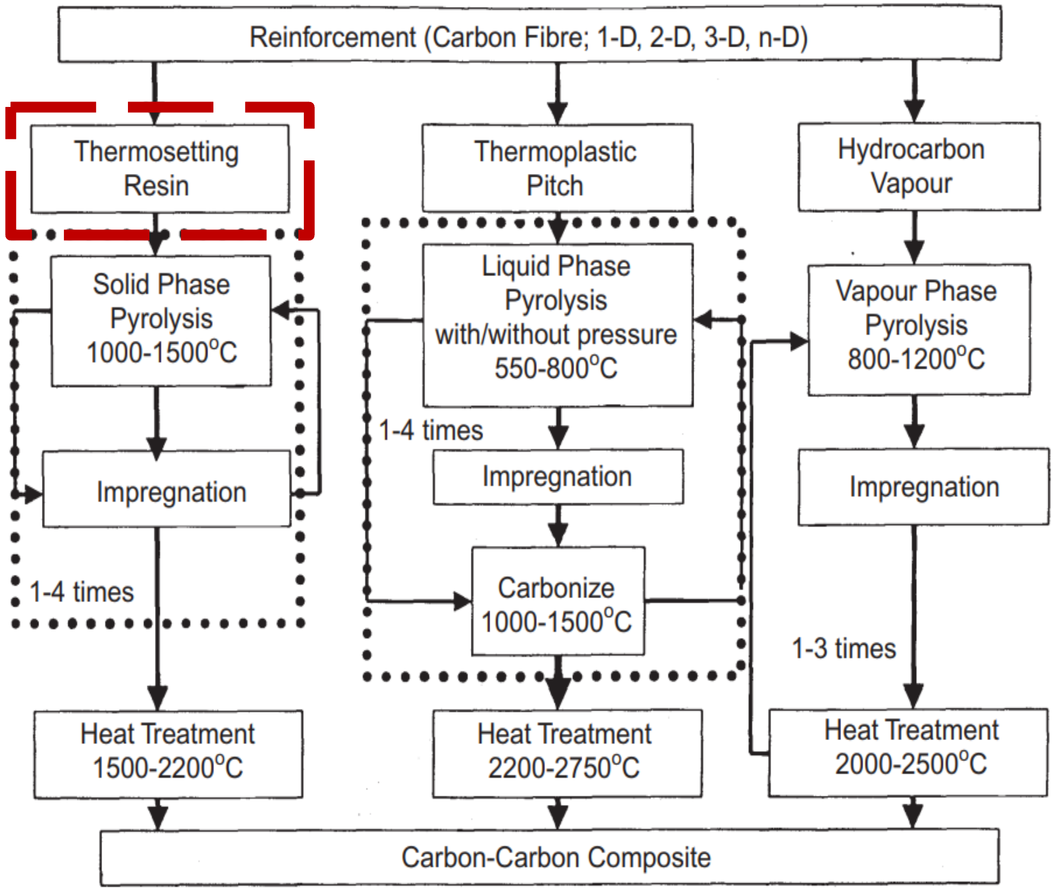
Carbon-Carbon composites (CCCs) are a form of low-density Carbon-Fiber Reinforced composite (CFRCs) where the matrix is purely carbonaceous or graphitic that exhibit:

- Exceptional strength at high temperatures
- Thermal stability in non-oxidizing environments
- High fracture toughness
- Excellent frictional properties



(a) exit cone for MAGE 2 geostationary rocket motor (b) high performance brake assemblies (c) leading edge material for hypersonic vehicles (d) reinforced carbon/carbon (RCC) microstructure deployed in the Space Shuttle Orbiter

Method of Manufacture



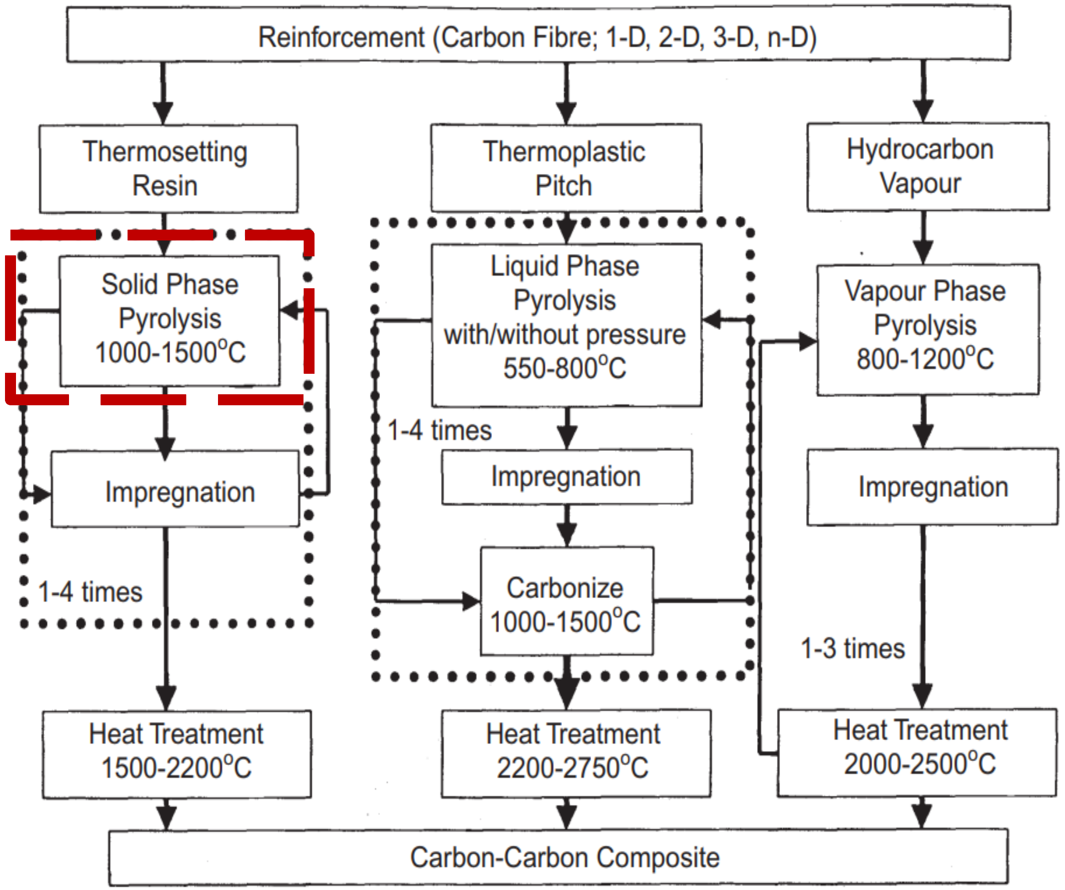
Material Choice

Thermosetting resins grants relatively more flexibility in structural design in comparison to:

- Pitch which requires high pressures for high carbon yields
- Vapor infiltration which is limited in addressable part geometries

F. Muhammed, T. Lavaggi, S. Advani, M. Mirotznik, and JW. Gillespie, "Influence of material and process parameters on microstructure evolution … doi: 10.1007/s10853-021-06401-3

Method of Manufacture



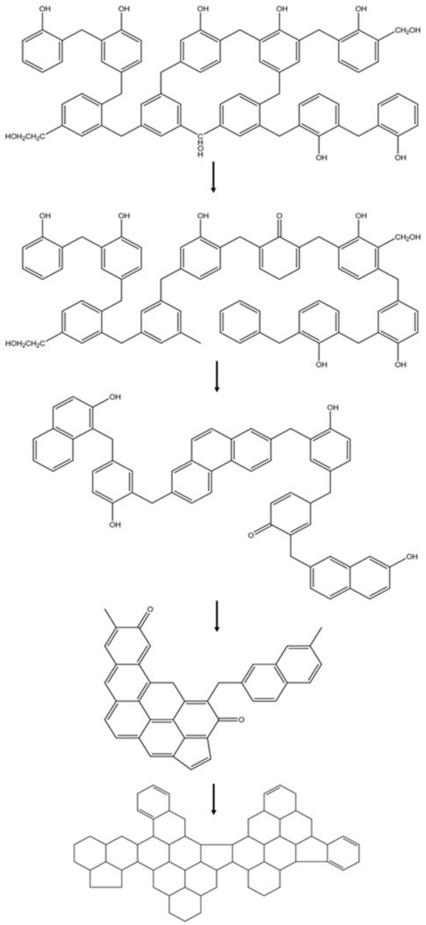
Solid Phase Pyrolysis

Most time intensive process of fabrication as it requires:

- Slow ramp rates to prevent part failure
- Re-iteration to address voids which form in the matrix during thermal decomposition

F. Muhammed, T. Lavaggi, S. Advani, M. Mirotznik, and JW. Gillespie, "Influence of material and process parameters on microstructure evolution … doi: 10.1007/s10853-021-06401-3

Method of Manufacture



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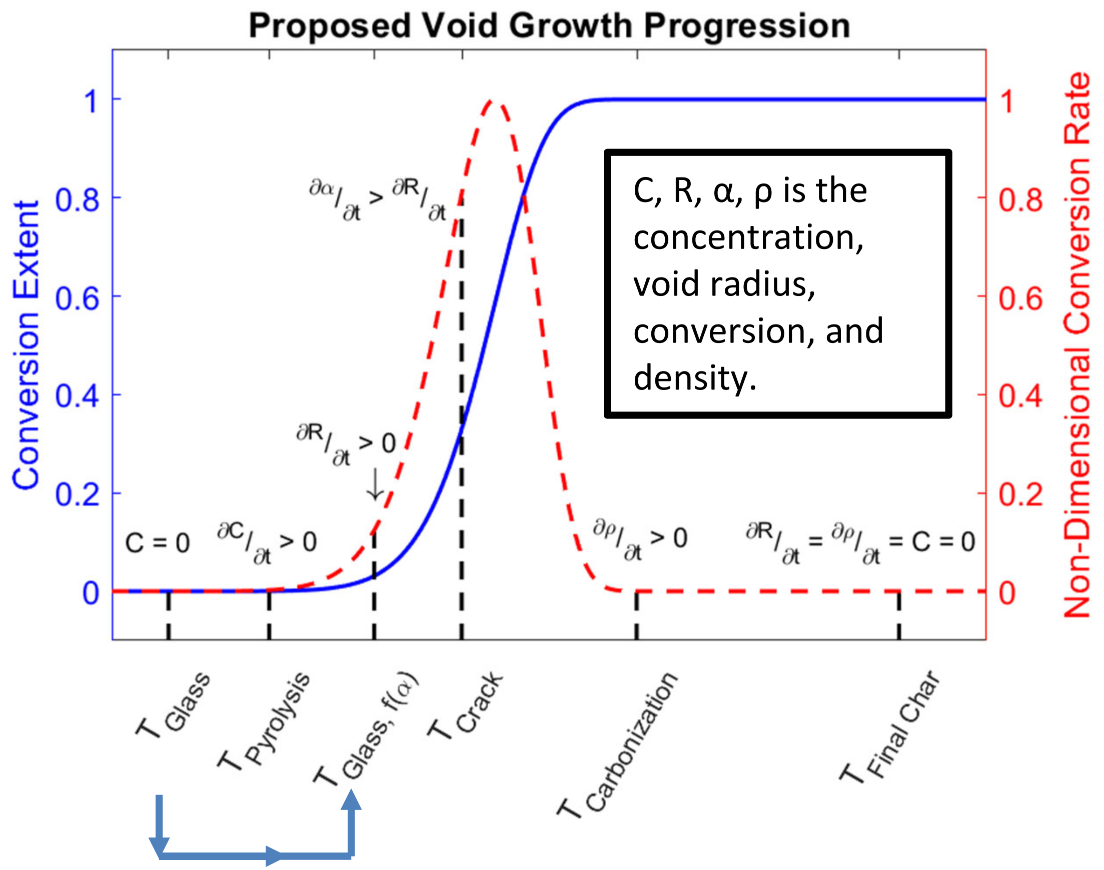
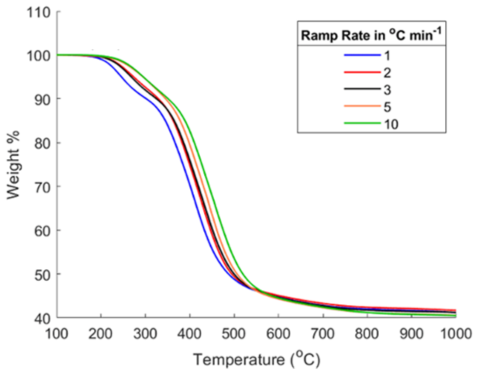
Purpose and Hypothesis

The purpose of the following experimentation is to begin to develop a framework for understanding how the process of carbonization influences the microstructure

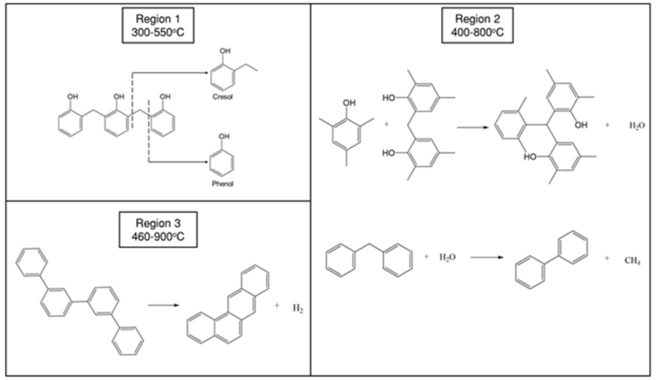
1. Kinetic modeling for conversional properties
2. Microstructural analysis as a function of the properties
3. Designing future work to validate hypothesis



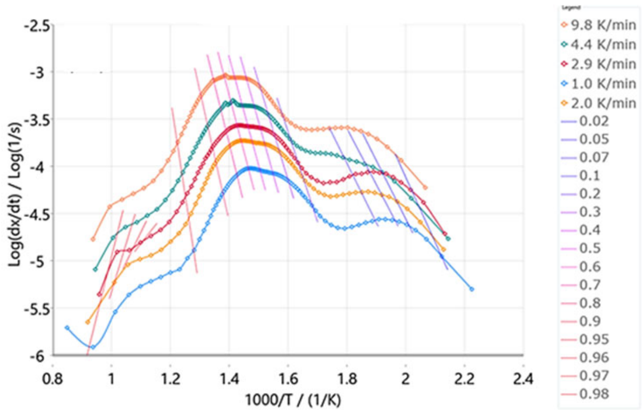
1. Kinetic Modeling of the Polymer



Themogravimetric analysis of polymer matrix



Evolved gas analysis to define reaction regions



Friedman's Analysis

$$\frac{\partial \alpha}{\partial t} = \sum_i w_i f(\alpha)^n [A_i \exp\left(-\frac{E_a}{RT}\right)]$$

- Slope of the line is a (E_a)
- The intercept a function (A) and (n)
- And (w) is found through optimization

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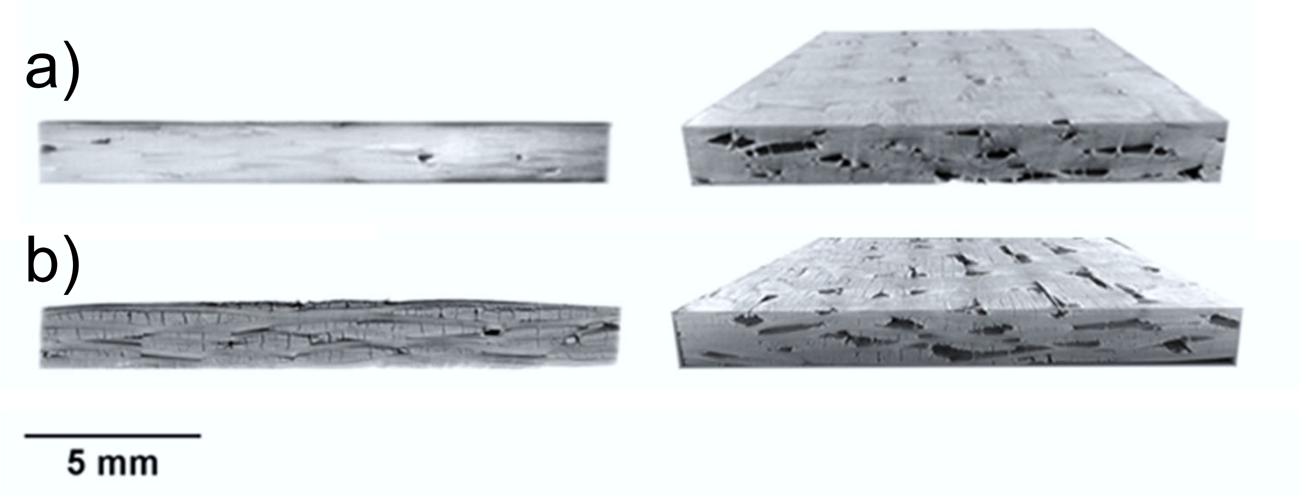
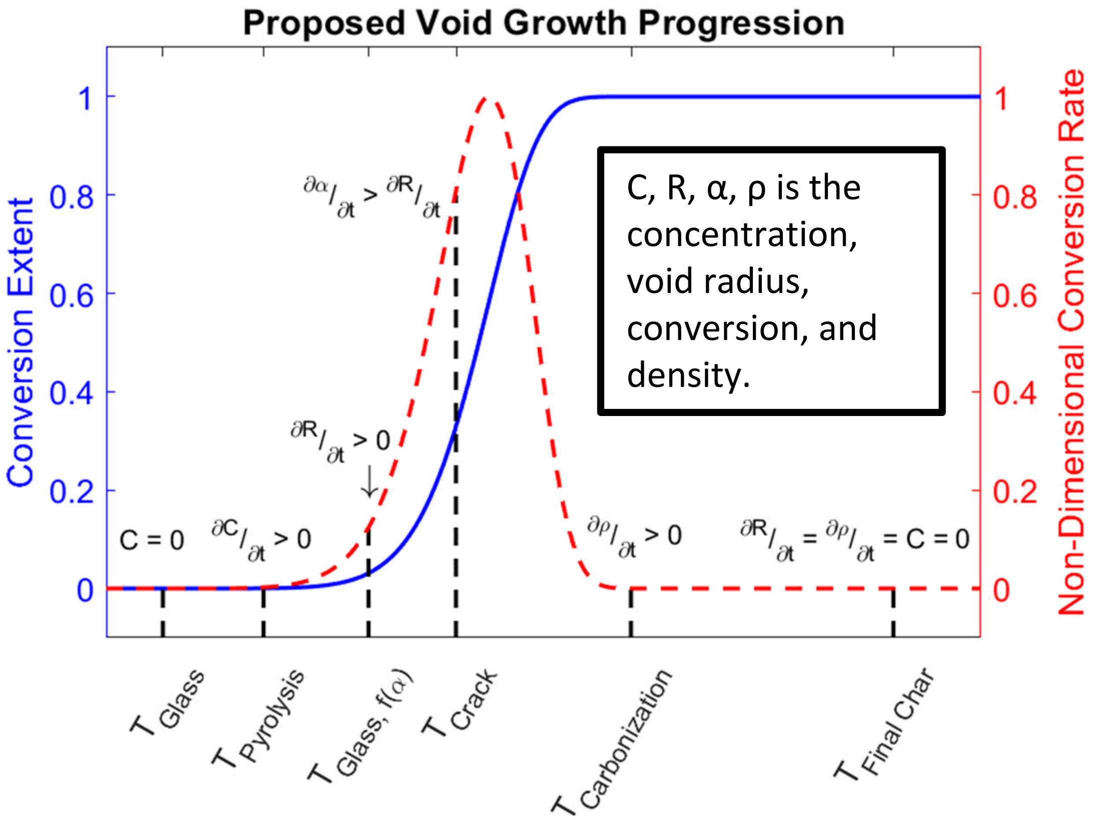
Trick KA, Saliba TE (1995) Mechanisms of the pyrolysis of phenolic resin in a carbon/phenolic composite. Carbon N Y 33:1509–1515. https://doi.org/10.1016/0008-6223(95)0009 2-R

Resulting Microstructure





From Microstructural Characterization:

1. Volumetric Porosity
2. Crack Density on XY/YZ/XZ planes
3. Void Feature Size Distribution

Microstructural Characterization

Porosity

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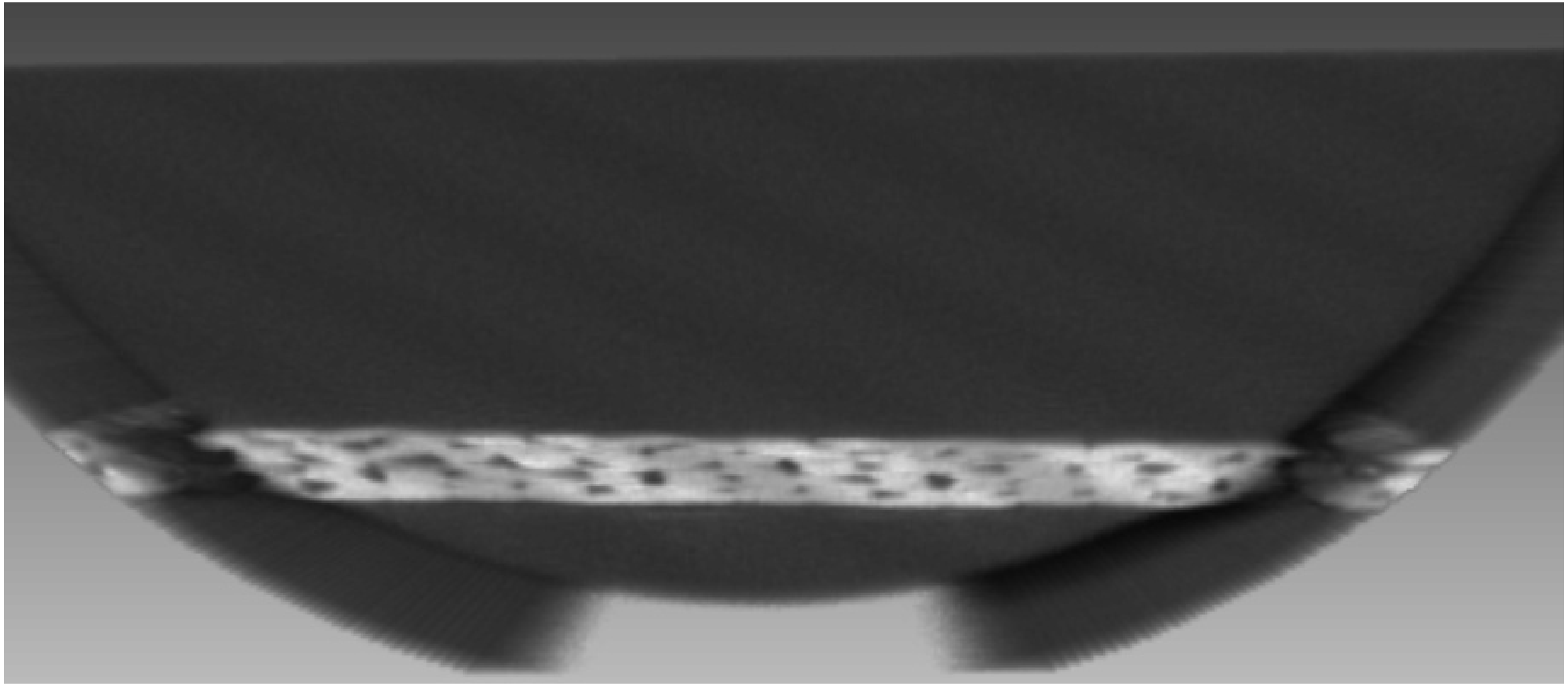
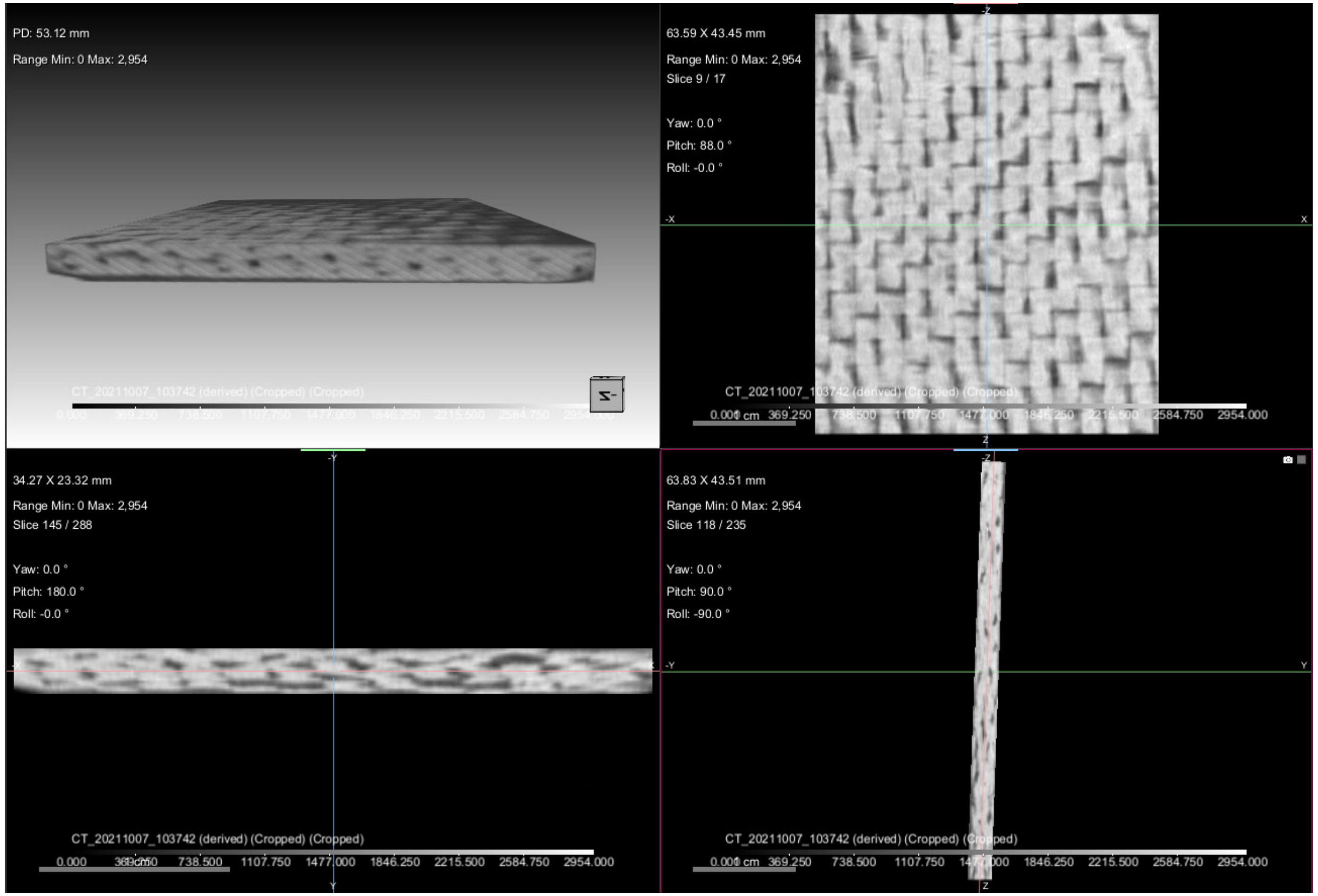
Breakdown of Data Validation

1. Import Image Files or VOX files into Dragonfly
2. Trim to region of interest
3. Window Leveling to partially binarized image
4. Otsu Segmentation to construct void volume
5. 6-Connected Analysis
6. Post Processing

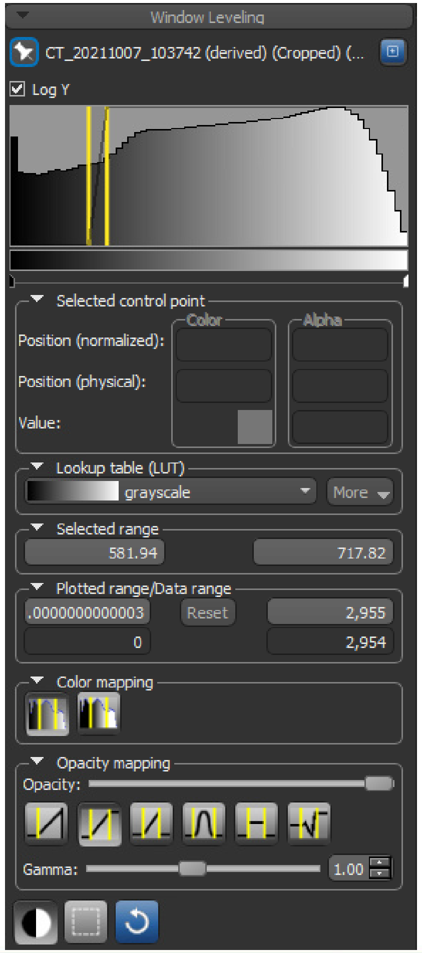
Raw Image Import (90 μm/pixel)

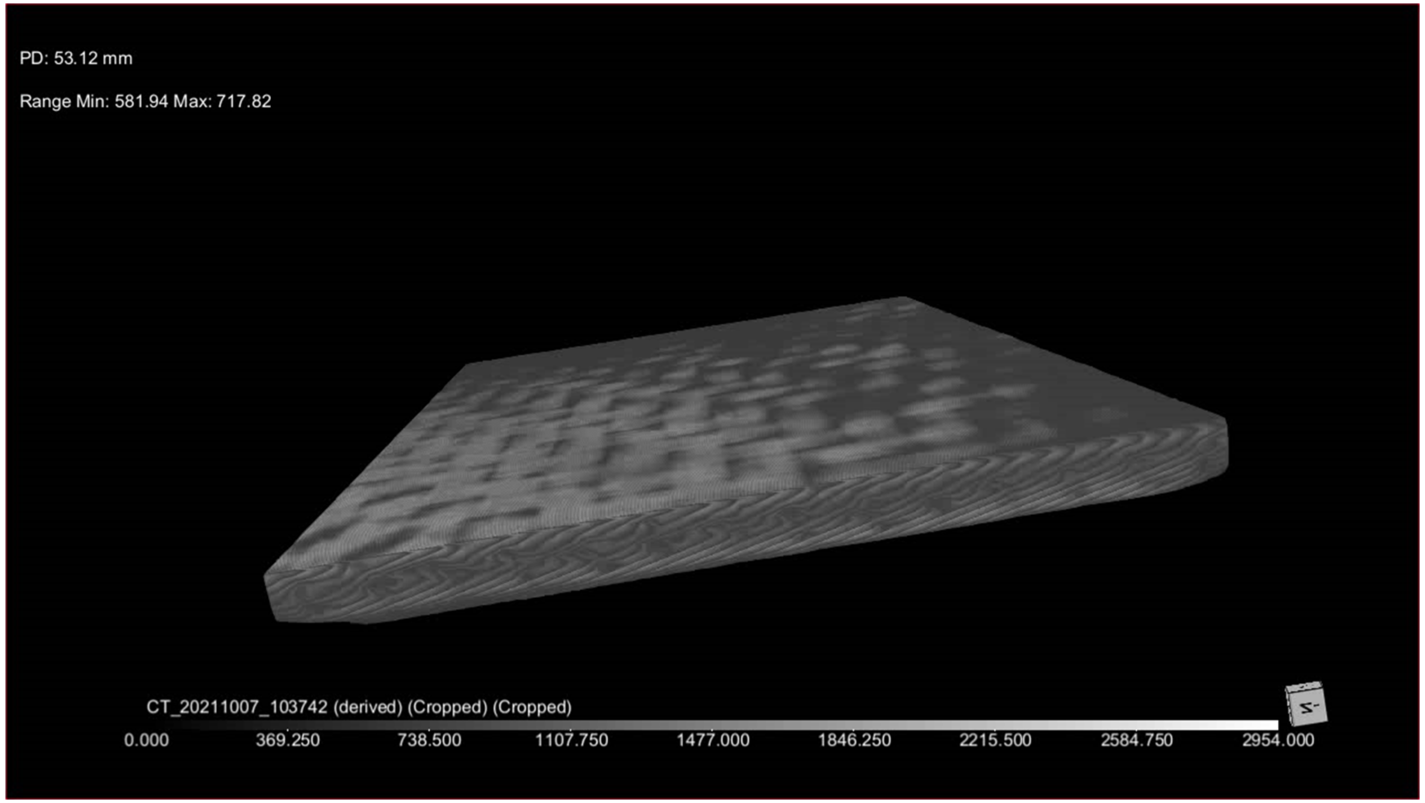


Edge Trimming



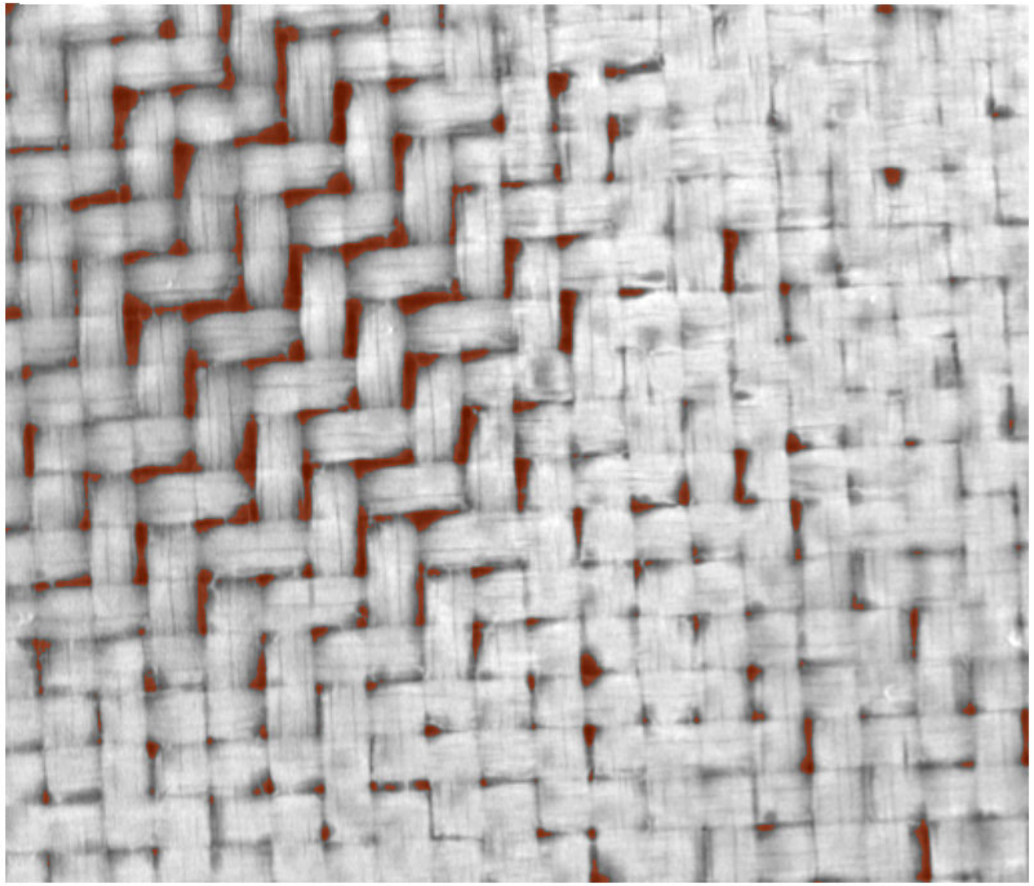
Window Leveling



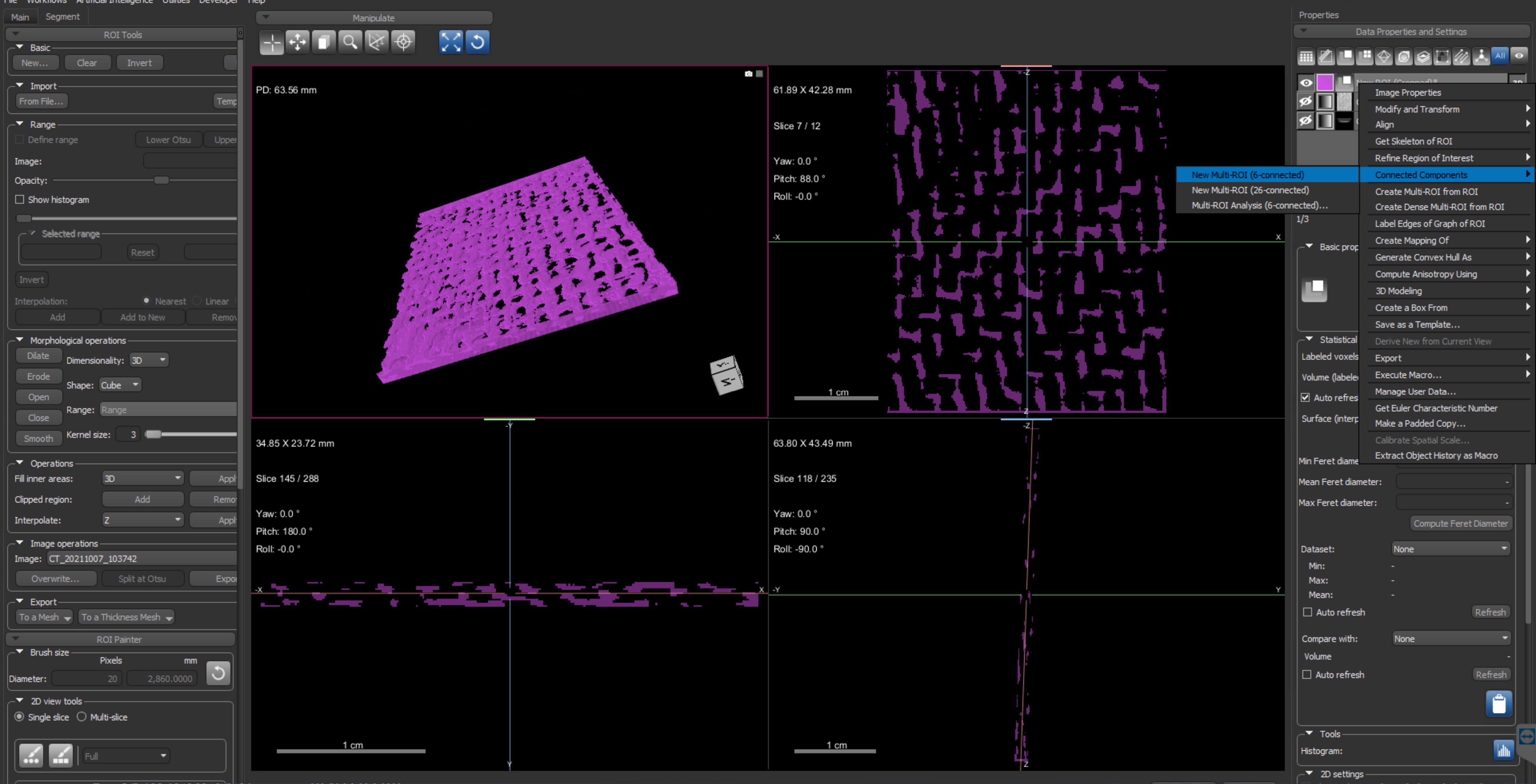


Porosity – X-Ray CT and Segmentation

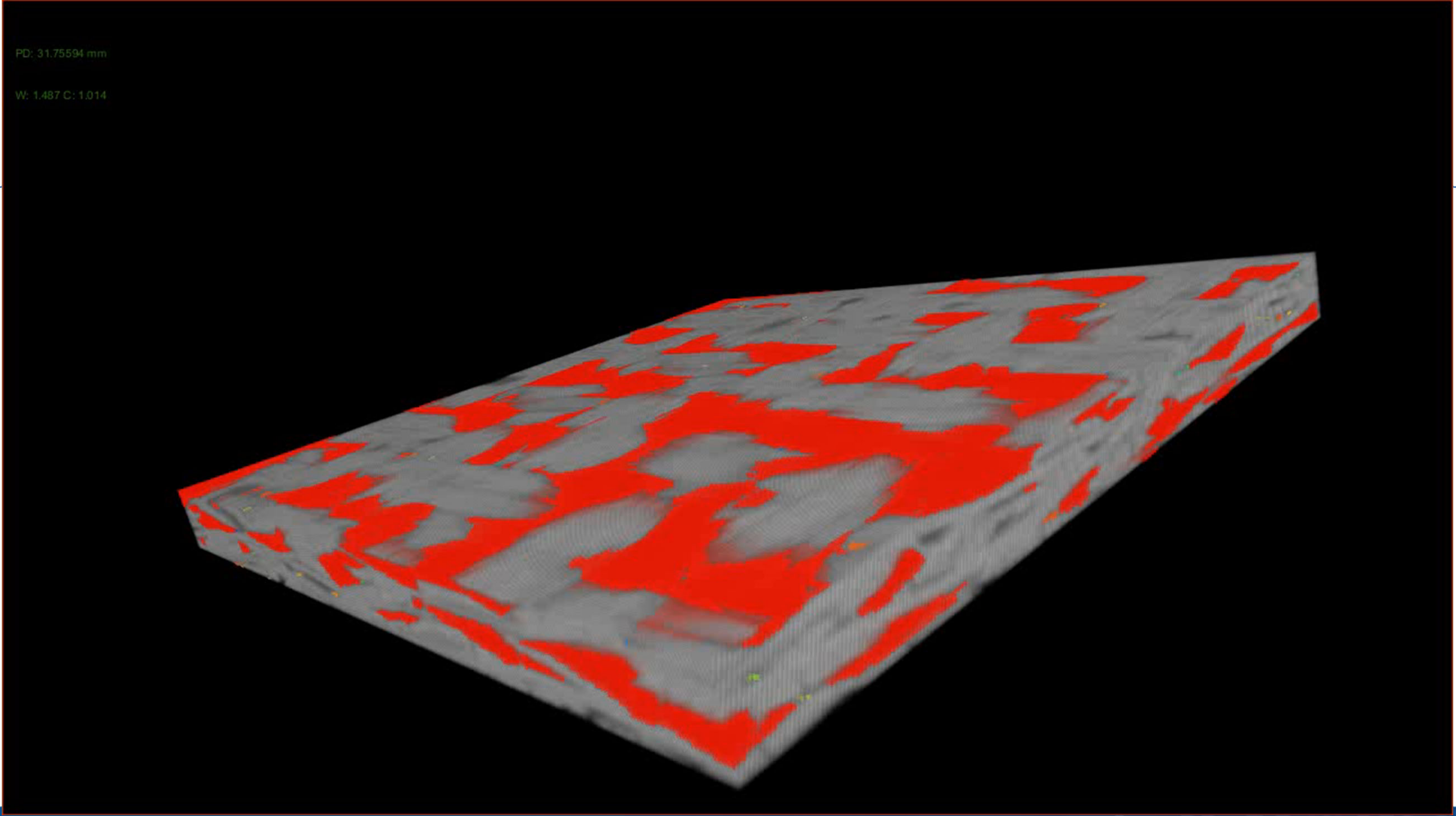
- X-ray CT is used to obtain details on the internal microstructure of the pyrolyzed samples.
- Statistical info on the amount and connectivity of the pores are obtain by segmentation of the CT-scan.
- Otsu's method is used for the thresholding of the images (ORS Dragonfly software).

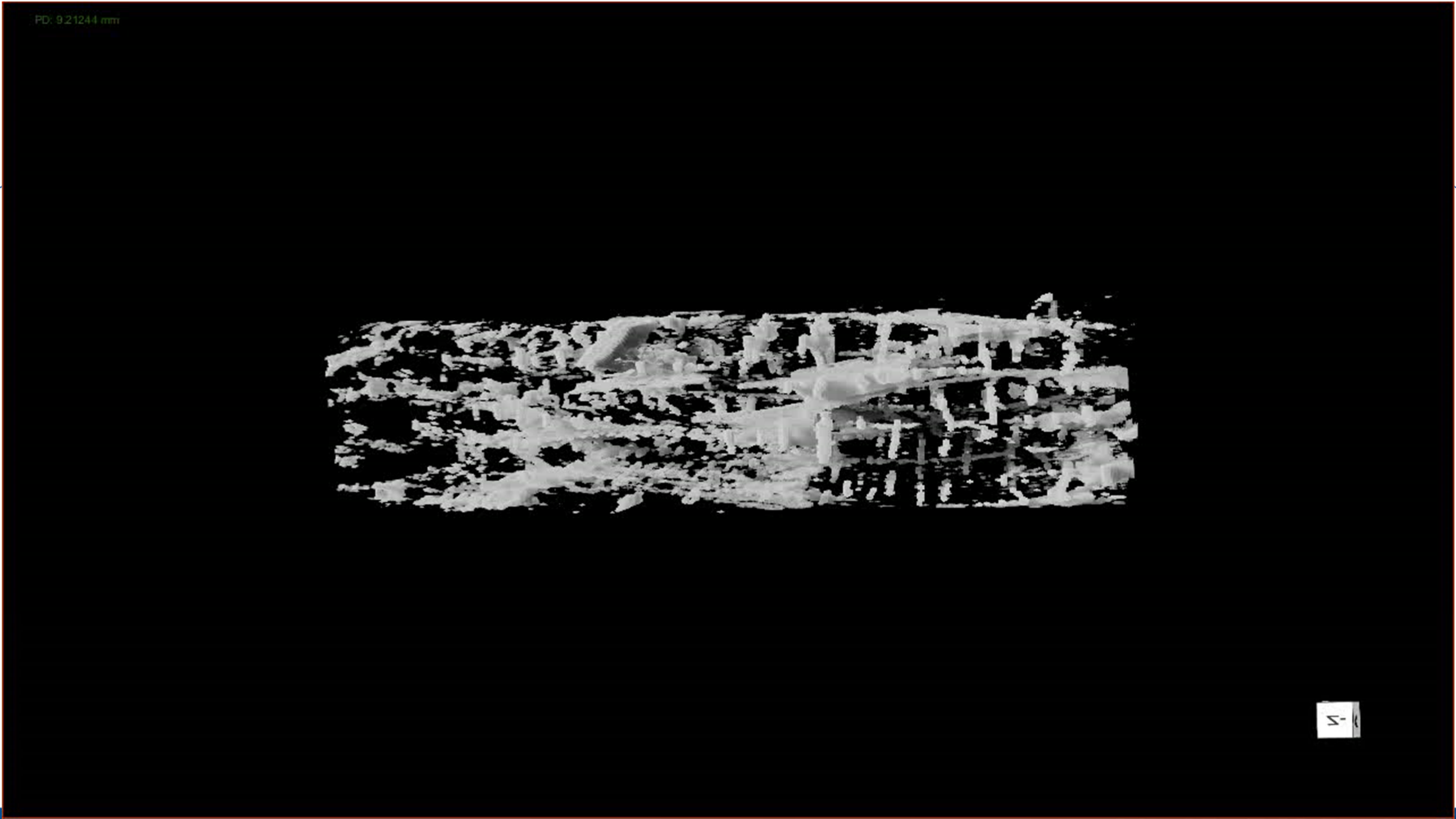


Courtesy of Tania Lavaggi

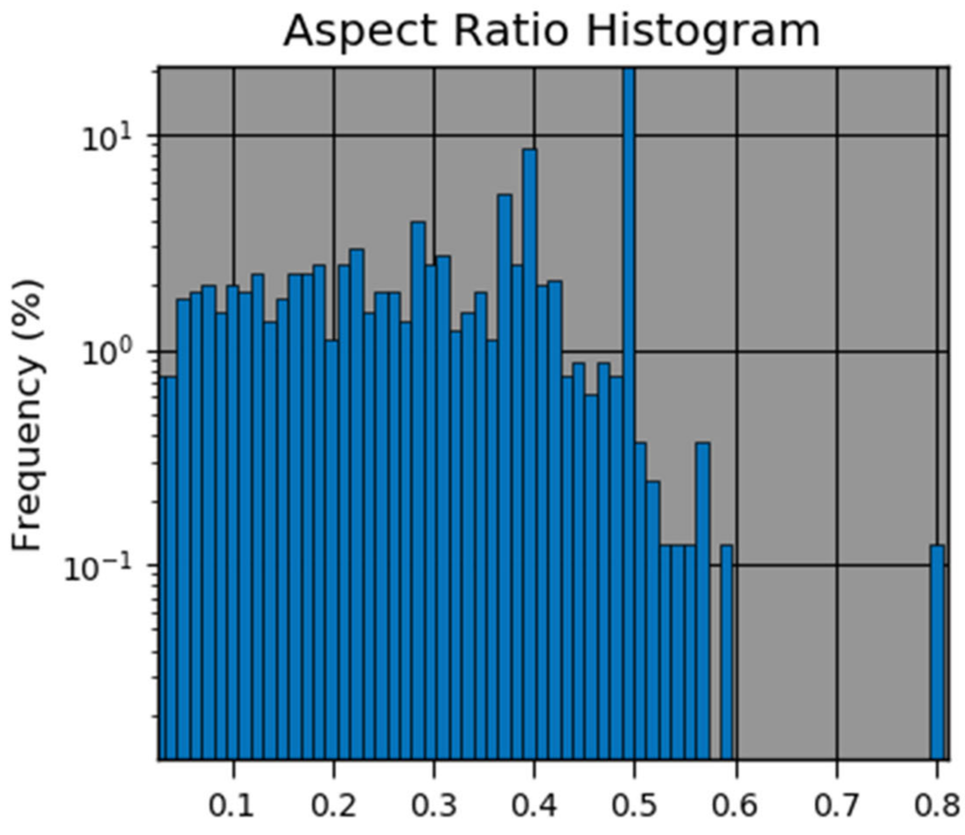


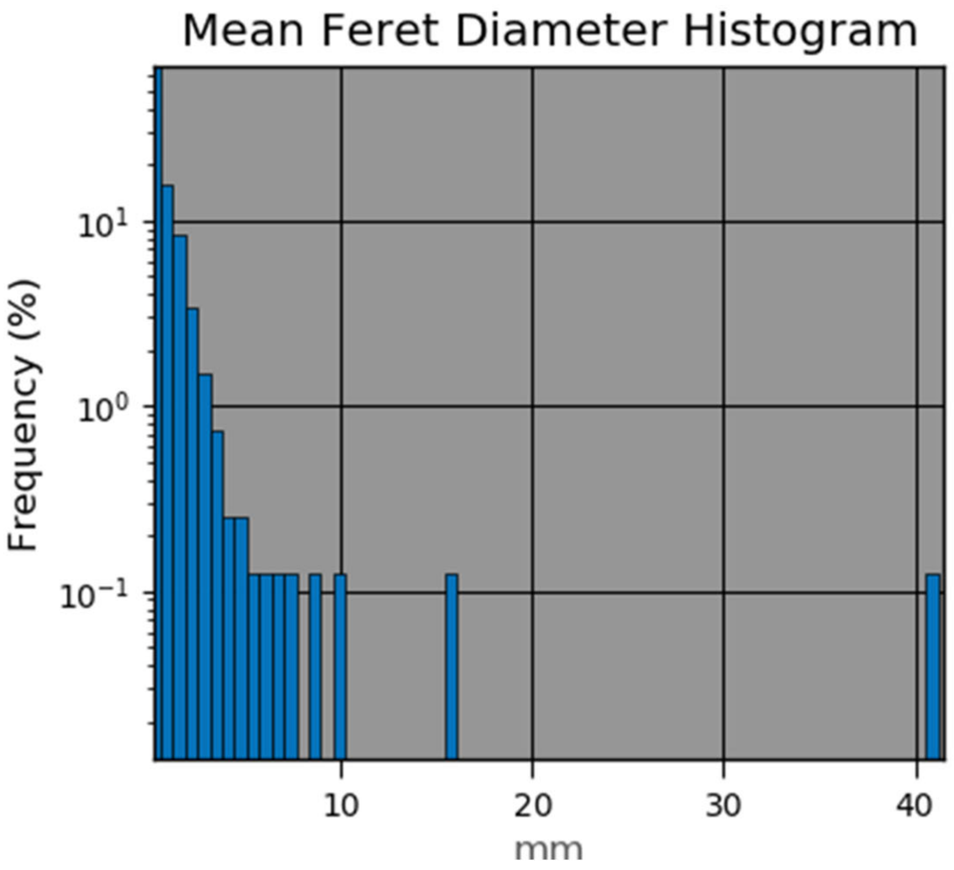
Main
Segment
ROI Tools
Basic
New...
Clear
Invert
Import
From File...
Range
Define range
Lower Otsu
Image:
Opacity:
Show histogram
Selected range
Reset
Invert
Interpolation:
Nearest
Linear
Add
Add to New
Morphological operations
Dilate
Erode
Open
Close
Smooth
Dimensionality: 3D
Shape: Cube
Range:
Kernel size: 3
Operations
Fill inner areas: 3D
Clipped region:
Add
Interpolate: Z
Image operations
Image: CT_20211007_103742
Overwrite...
Split at Otsu
Export
To a Mesh
To a Thickness Mesh
ROI Painter
Brush size
Pixels
mm
Diameter: 20 2,860.0000
2D view tools
Single slice
Multi-slice
Full
Manipulate
PD: 63.56 mm
61.89 X 42.28 mm
Slice 7 / 12
Yaw: 0.0 °
Pitch: 88.0 °
Roll: -0.0 °
1 cm
34.85 X 23.72 mm
Slice 145 / 288
Yaw: 0.0 °
Pitch: 180.0 °
Roll: -0.0 °
1 cm
63.80 X 43.49 mm
Slice 118 / 235
Yaw: 0.0 °
Pitch: 90.0 °
Roll: -90.0 °
1 cm
Properties
Data Properties and Settings
New Multi-ROI (6-connected)
New Multi-ROI (26-connected)
Multi-ROI Analysis (6-connected)...
Image Properties
Modify and Transform
Align
Get Skeleton of ROI
Refine Region of Interest
Connected Components
Create Multi-ROI from ROI
Create Dense Multi-ROI from ROI
Label Edges of Graph of ROI
Create Mapping Of
Generate Convex Hull As
Compute Anisotropy Using
3D Modeling
Create a Box From
Save as a Template...
Derive New from Current View
Export
Execute Macro...
Manage User Data...
Get Euler Characteristic Number
Make a Padded Copy...
Calibrate Spatial Scale...
Extract Object History as Macro
Mean Feret diameter:
Max Feret diameter:
Compute Feret Diameter
Dataset: None
Min:
Max:
Mean:
Auto refresh
Refresh
Compare with: None
Volume
Auto refresh
Refresh
Tools
Histogram:
2D settings


PD: 31.75594 mm
W: 1.487 C: 1.014


PD: 9.21244 mm

Output from Dragonfly





Microstructural Characterization

Data Reduction

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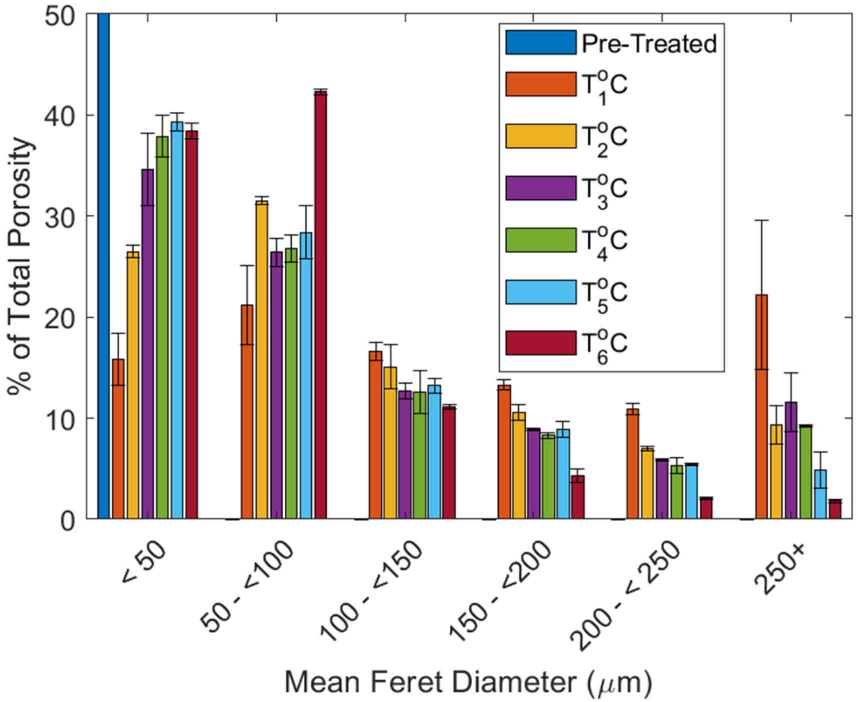
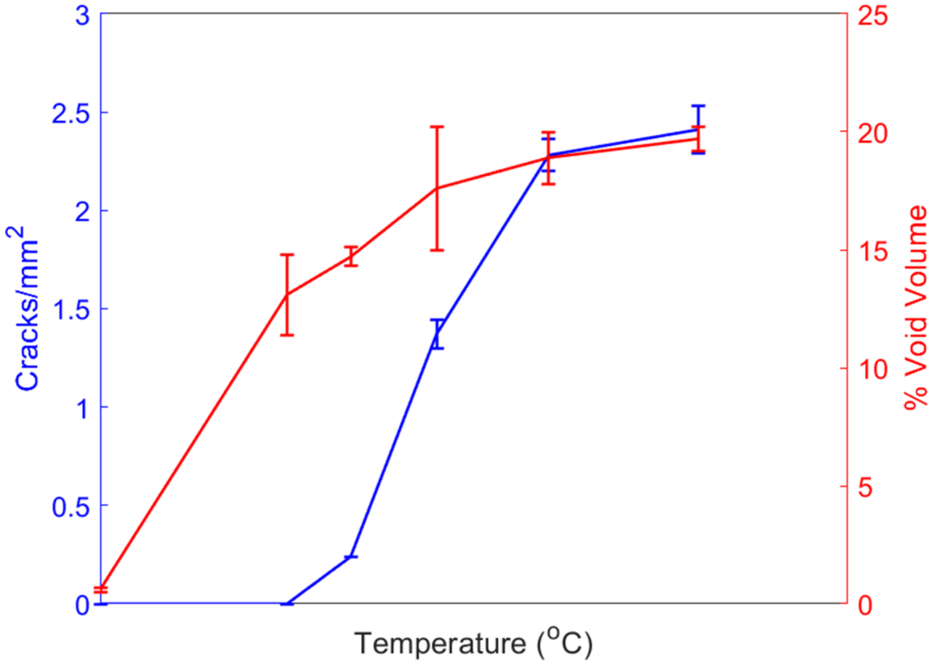
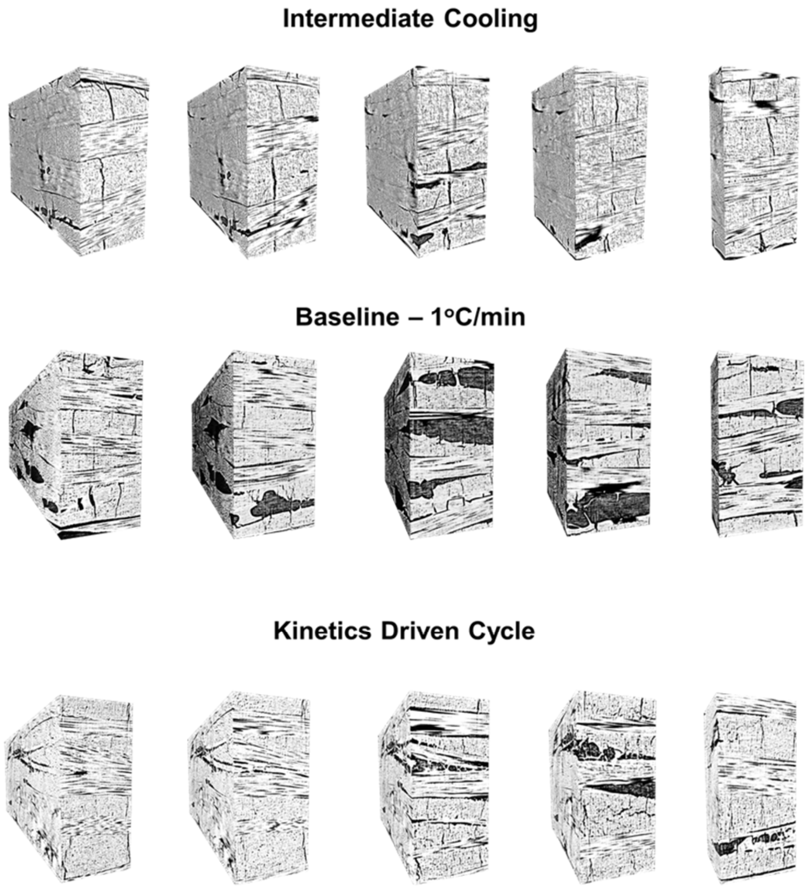
Microstructural Analysis



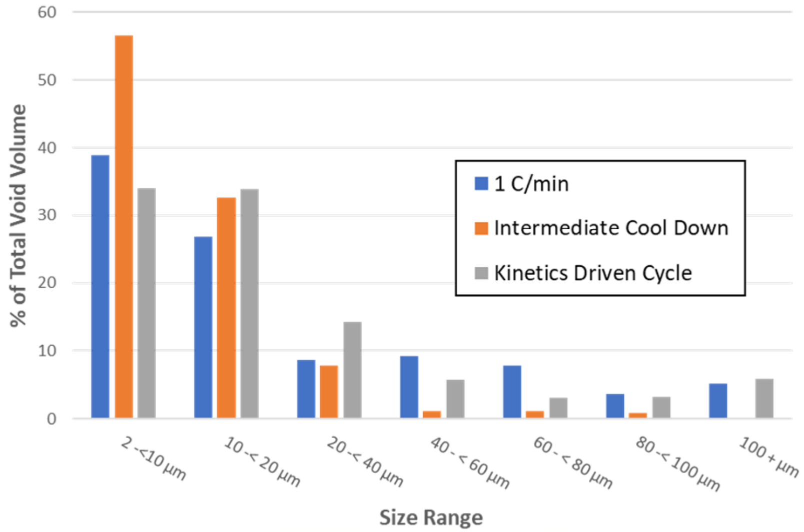


(a) histogram of mean ferret diameters with increasing temperatures. (b) crack density (C/mm^2) measured on the XZ plane and the void volume with increasing temperature.

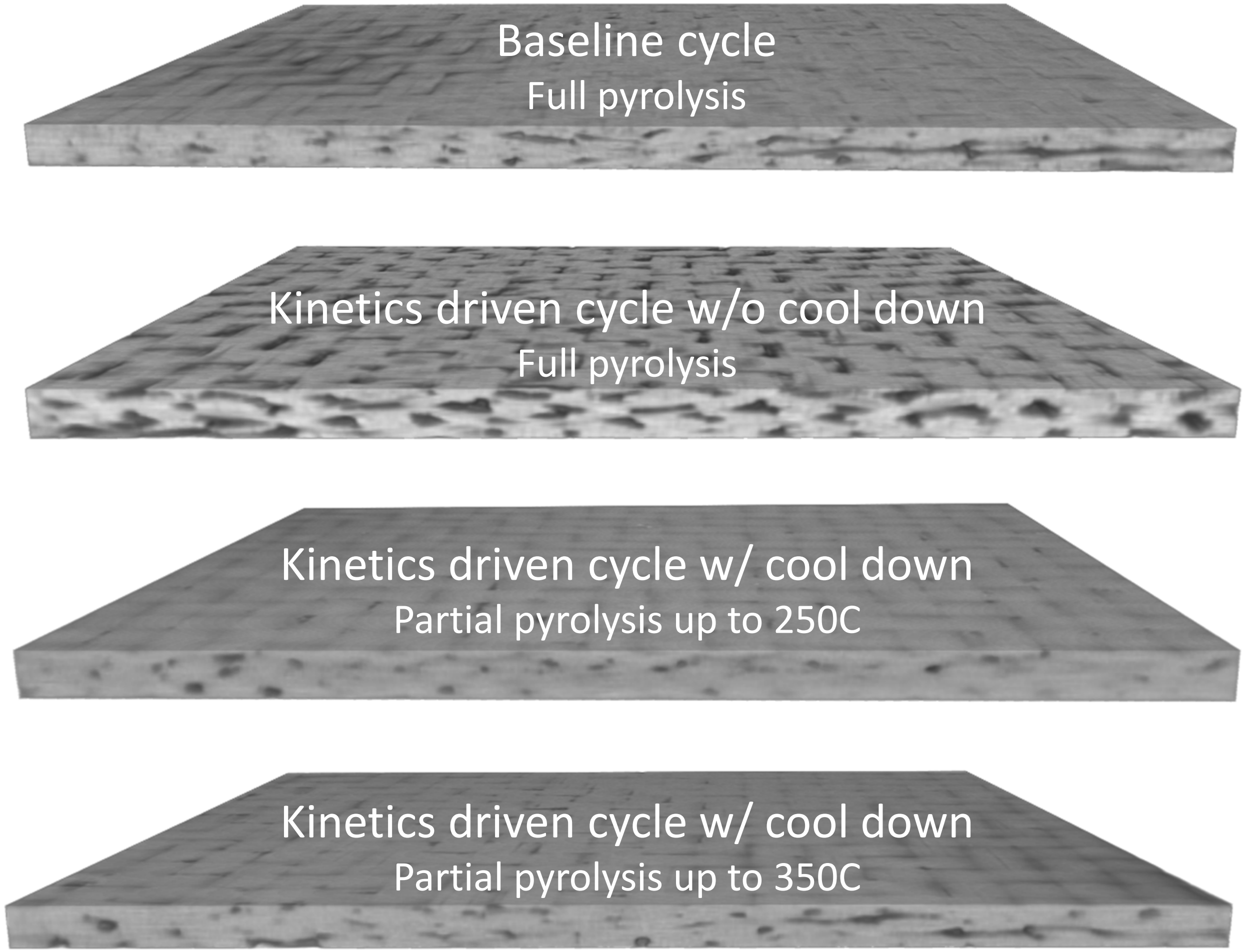
Additional Properties – Open/Closed Porosity



Cycle	Total Porosity %	Open Porosity [%/total]	Closed Porosity [%/total]
Intermediate Cooling to RT	22.34	21.41 [95.8%]	0.93 [4.2%]
Baseline - 1 Cpm	36.35	36.21 [99.6%]	0.14 [0.4%]
Kinetics Driven Cycle	24.85	24.27 [97.7%]	0.58 [2.3%]



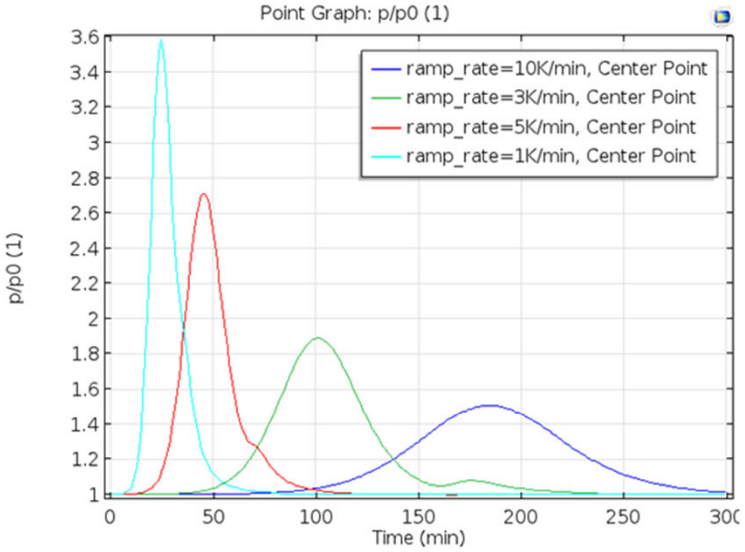
Additional Properties – Comparison of Microstructures

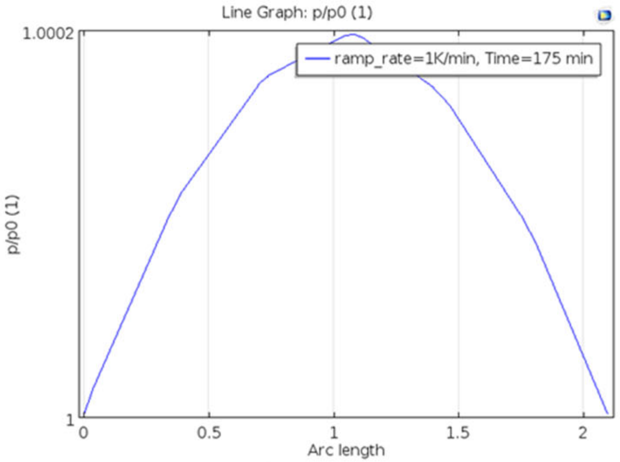


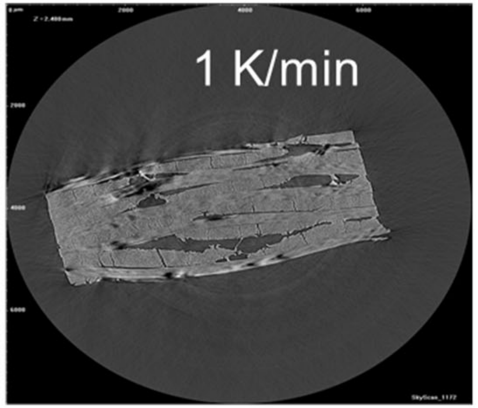
	Porosity
Baseline cycle Full pyrolysis	19.39 % 94.65 % connected
Kinetics cycle w/o cool down Full pyrolysis	22.36 % 98.99 % connected
Kinetics cycle w/ cool down Partial pyrolysis up to 250C	3.25% not connected
Kinetics cycle w/ cool down Partial pyrolysis up to 350C	10.75% 48.96 % connected

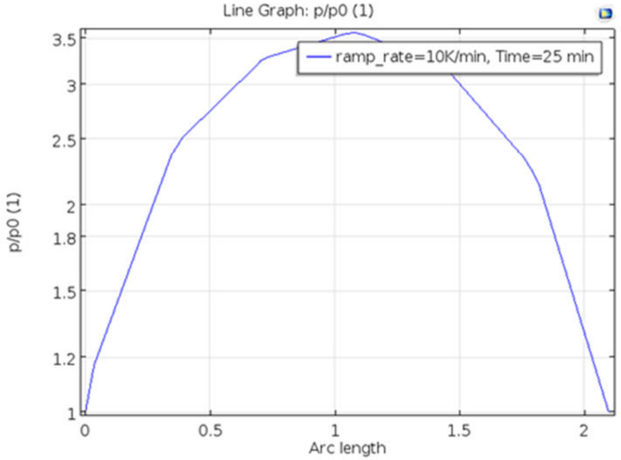
Rigaku CT Scanner at 90 µm.

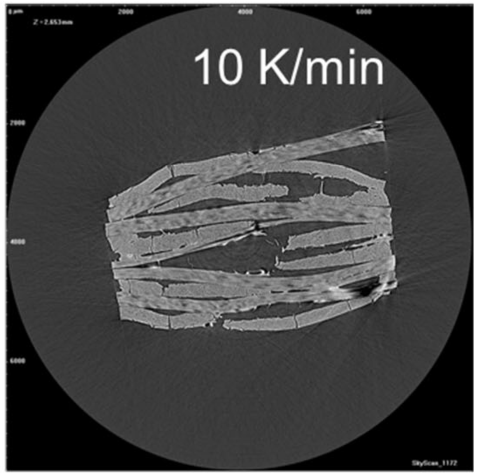
Applications of Data Reduction











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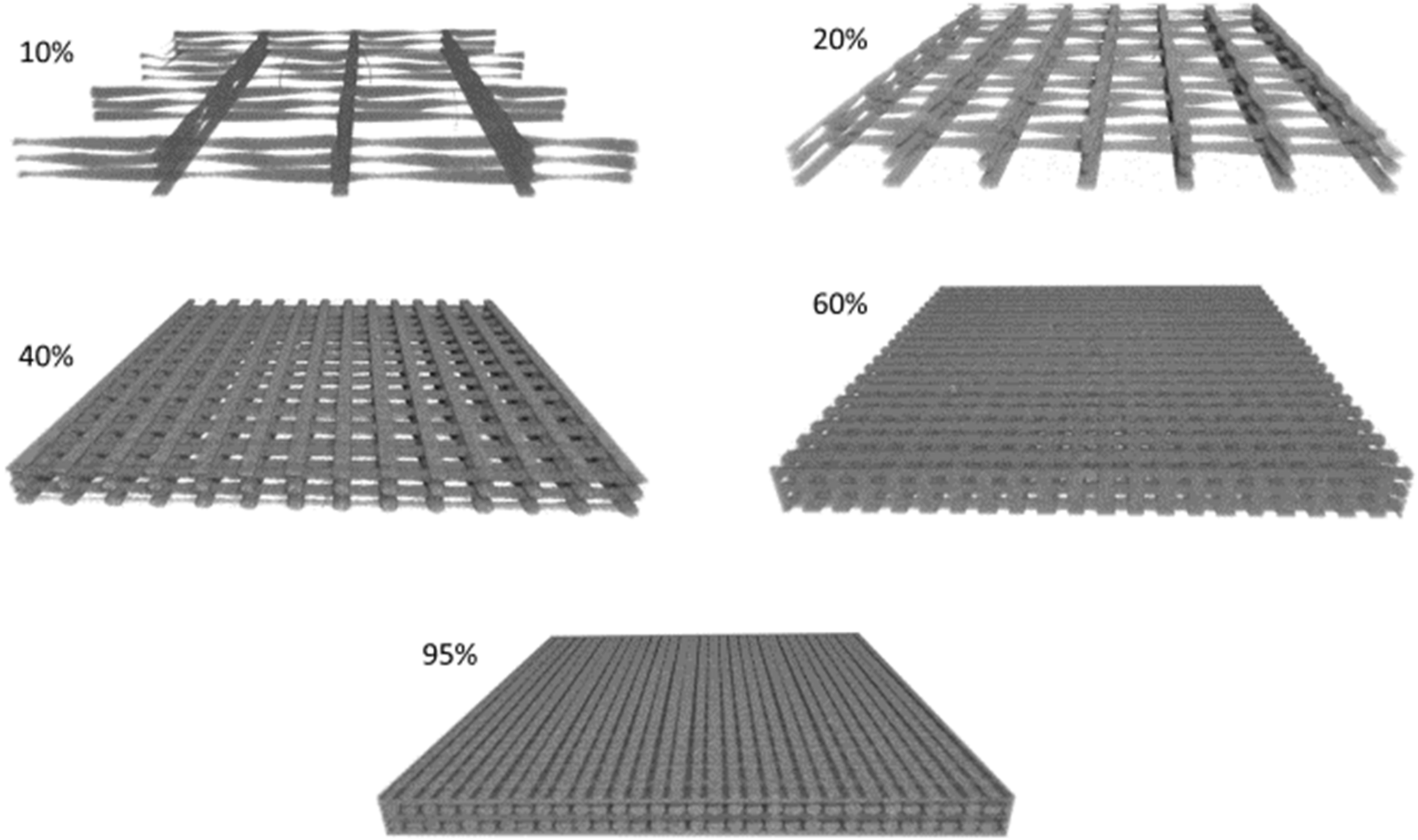
Conclusions

- Porosity evaluation is in line with density measurements that have been done as well as what is predicted by mercury porisometry
- The proposed data reduction parallels carbonization models that are based on intrinsic material properties
- The data generated can be used to guide future experimentation

Acknowledgements

- Dr. L. Moretti and Ms. T. Lavaggi
- Thanks to the Army Research Laboratory for funding my education
- Huntsman chemical corporation for materials and collaborative efforts
- My advisors for their feedback and guidance
- Dr. Sauerbrunn for experimental setup and design

Carbon-Filled Poly Carbonate



Courtesy of Ellen Gupta

Co-Sponsored by: NASA ULI University Leadership Initiative