TWENTY-THIRD INTERNATIONAL CONFERENCE ON COMPOSITE MATERIALS (ICCM23)

Correlation of the Permeability of Carbon/Carbon Composites with the Porosity during the Carbonization Process

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Project Overview

Project Goal

- Optimization of the densification process of Carbon/Carbon composites.

Presented Work

- Development of novel technique for the evaluation of permeability and porosity from one experiment.
- Correlation of permeability and porosity of Carbon/Carbon composites.

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Ph.D. MSE 2022

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Outline

1. Introduction: densification of Carbon/Carbon composites

2. Pyrolysis schedules and materials

3. Permeability of Carbon/Carbon composites
   - Pulse-decay experiment

4. Porosity of Carbon/Carbon composites
   - Micro-computed tomography
   - Pycnometry

5. Correlation of permeability and porosity

6. Prediction of porosity from pulse-decay experiment
   - Quasi-steady state model

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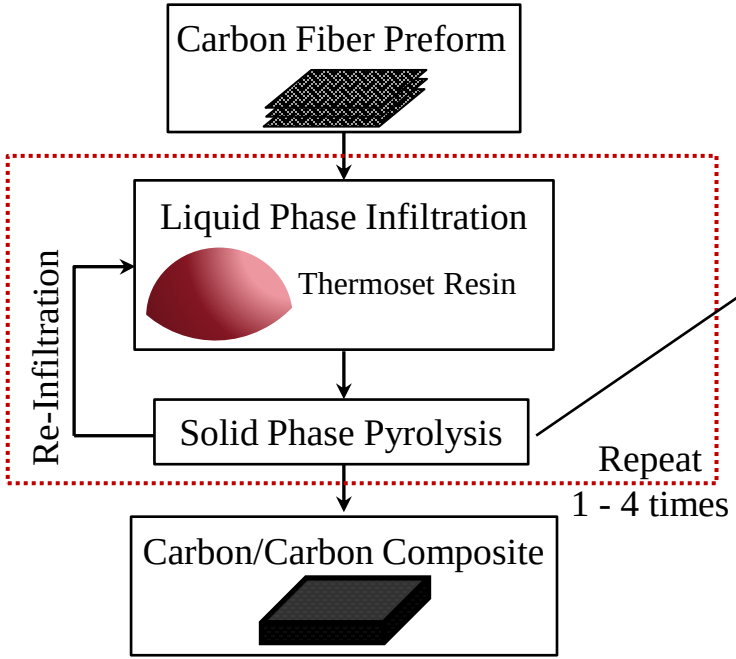
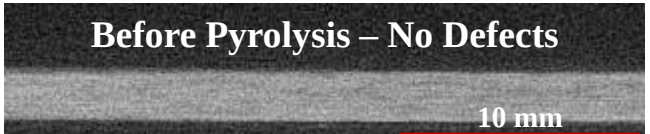
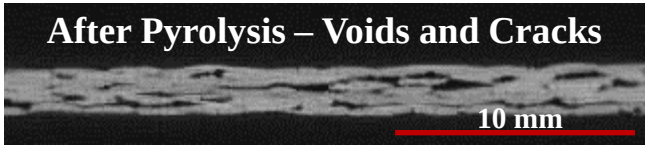
Densification of Carbon/Carbon Composites

Manufacturing of Carbon/Carbon Composites





Matrix Degradation → Shrinkage and Weight Loss



Densification Process

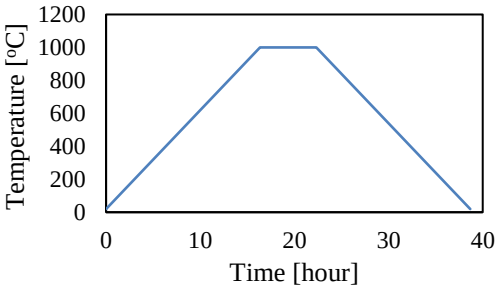
- Repetition Infiltration/Pyrolysis.
- Takes several months to complete.

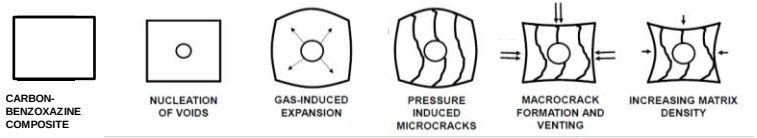
Densification process: Muhammed et al. 2021 *J. Mater. Sci.* DOI 10.1007/s10853-021-06401-3

Optimization of Densification

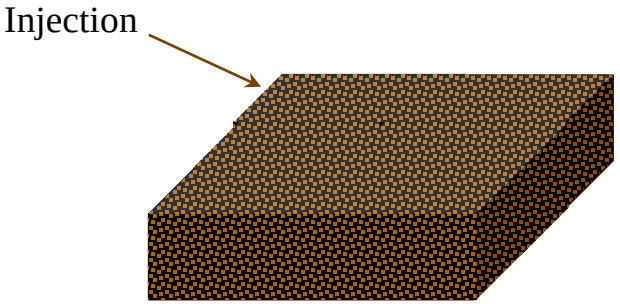
Reduce Densification Time

Tailor Porosity Development with Pyrolysis Schedule





Select Best Parameters for Re-Infiltration



Correlation of permeability with porosity

Void growth: Muhammed et al. 2023 *J. Appl. Polym. Sci.*
Optimization of pyrolysis schedule: Muhammed et al. 2023 *Ceram. Int.* DOI 10.1016/j.ceramint.2023.03.121

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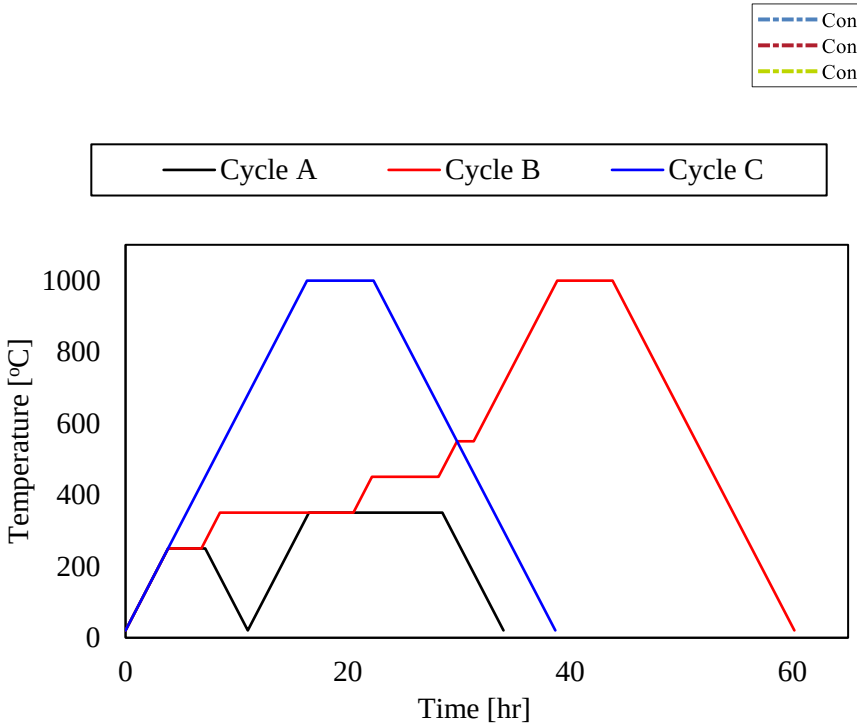
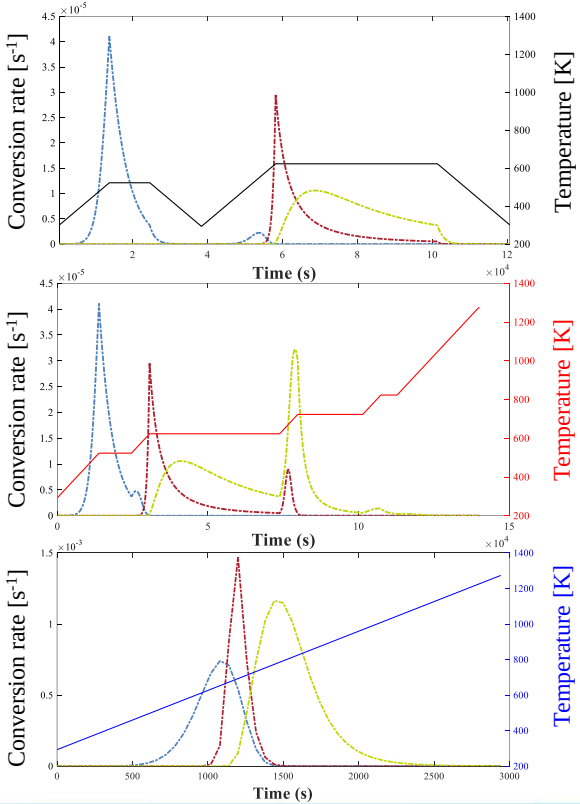
Pyrolysis Schedules and Kinetics of the Reactions





Kinetics of reaction: Muhammed et al. 2022 *J. Mater. Sci.* DOI 10.1007/s10853-022-08007-9

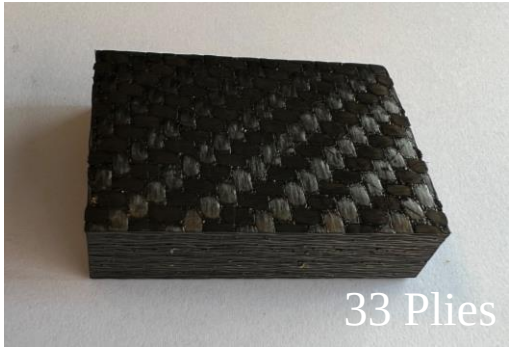
Materials

Laminates

- Matrix precursor → Benzoxazine resin
- Carbon fabric

Samples of Different Thicknesses

- Laminates of 5 plies → 2.1 mm thickness
- Laminates of 33 plies → 12.3 mm thickness



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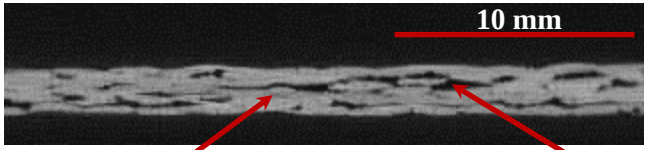
Permeability of Carbon/Carbon Composites

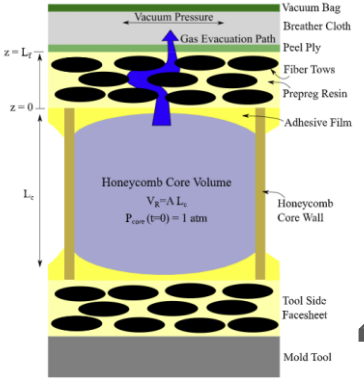
Structure of Carbon/Carbon Composites

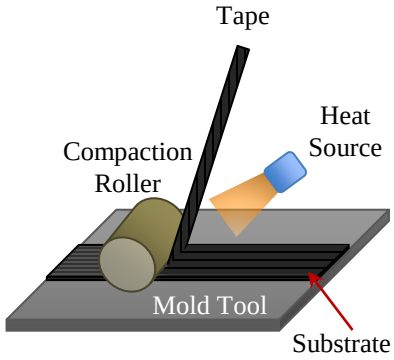


- Flow monitoring experiments not trivial.
- Pulse-decay experiments with air easy and reliable.

Pulse-Decay Experiment for Composites Characterization

- Air evacuation process in sandwich composites[1].
- Effects of lay-up process parameters and post-processing in AFP composites[2].

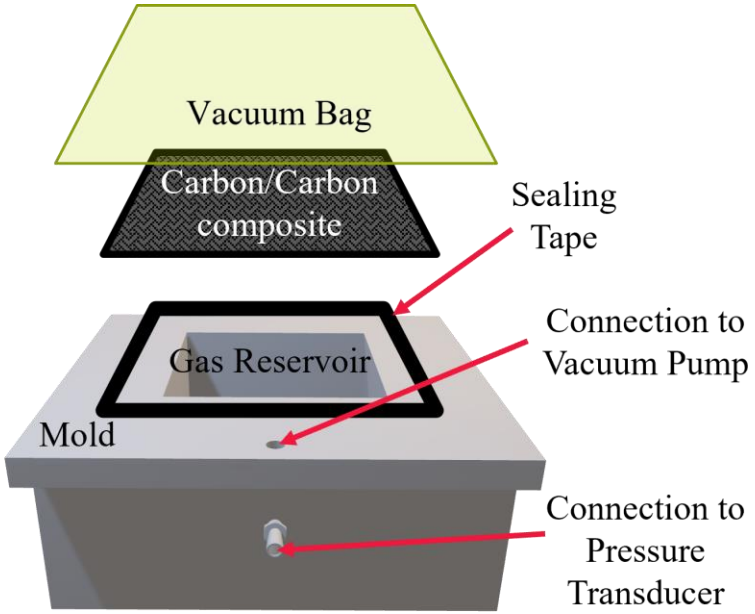


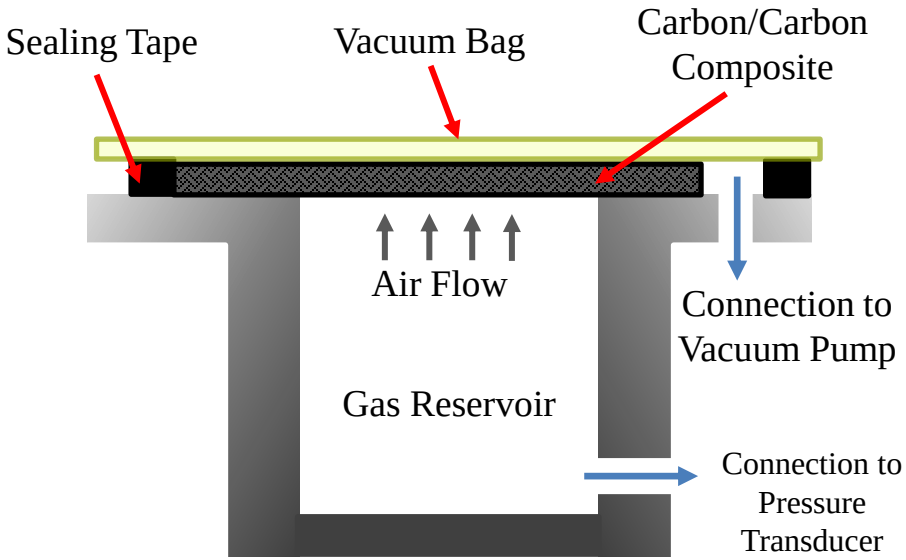


[1] Cender et al. *J. Compos. Mater.* 2022 DOI 10.1177/00219983221115824
[2] Karimi et al. *J. Reinf. Plast.* 2023 DOI 10.1177/07316844231166078

Pulse-Decay Experiment for Air Permeability

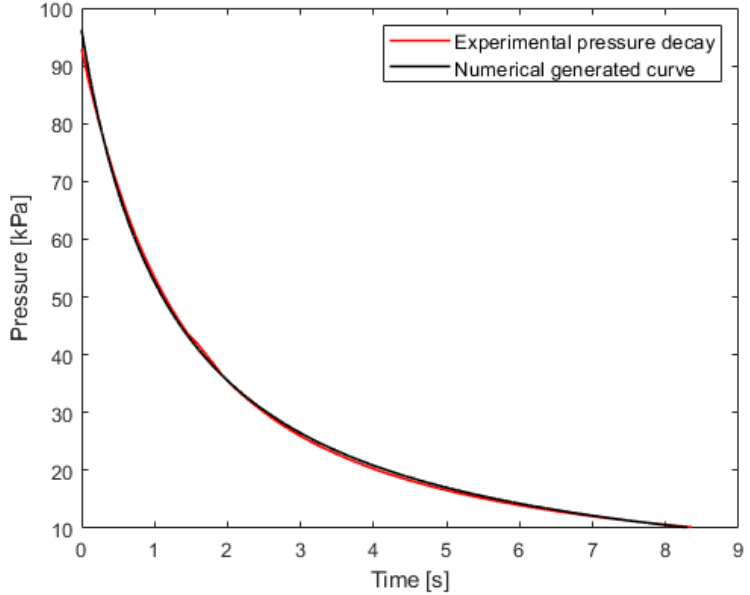
Through-the-thickness experimental set-up for the measurement of air flow





Pressure Decay Curves and Numerical Simulations

- Pressure decays over time: shape of curve depends on unknowns K_i/ϕ and b.
- Generate numerical curve by solving Eq. 1 (non-dimensional form) while optimizing K_i/ϕ and b.



b: Klinkenberg parameter, function of pore diameter only
K_i: intrinsic permeability K_g: permeability to gas
V_R: volume of reservoir A: cross-section of core

$$(1) \quad \frac{\partial P}{\partial t} = \frac{K_i}{\phi \mu} \frac{\partial}{\partial x}\left((P+b)\frac{\partial P}{\partial x}\right)$$

$$(2) \quad K_g = K_i\left(1+\frac{b}{P}\right)$$

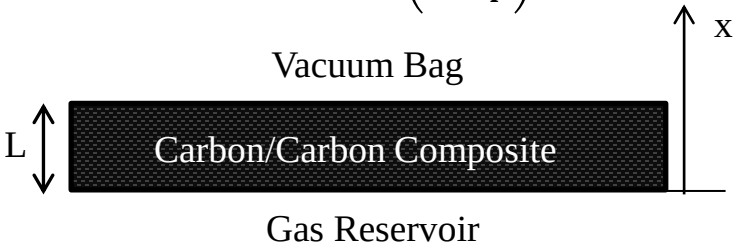
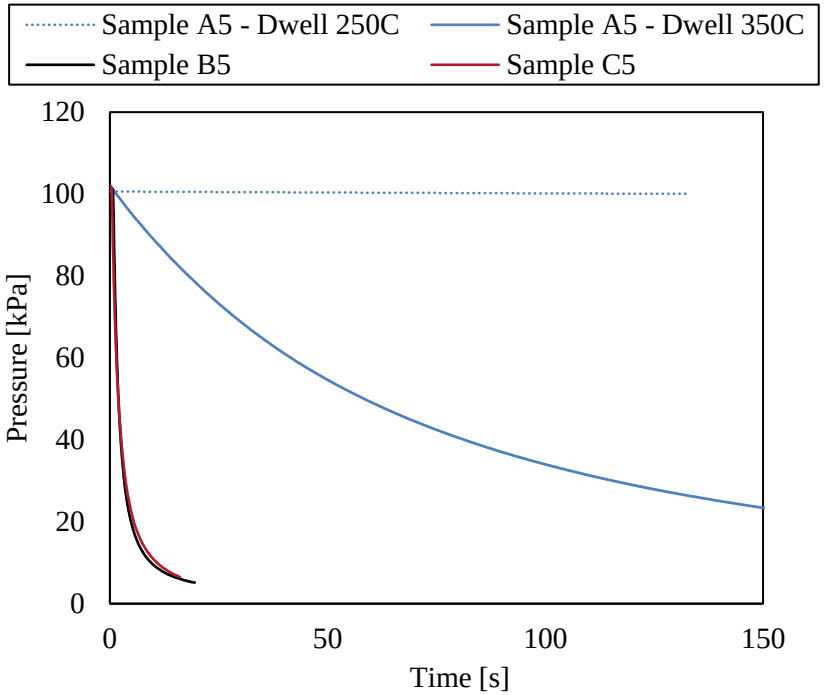
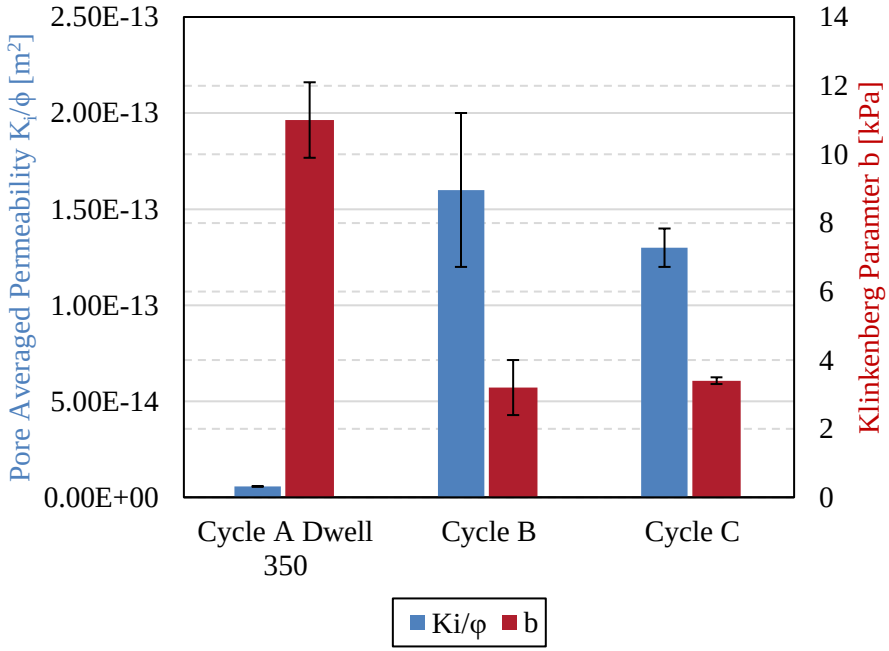


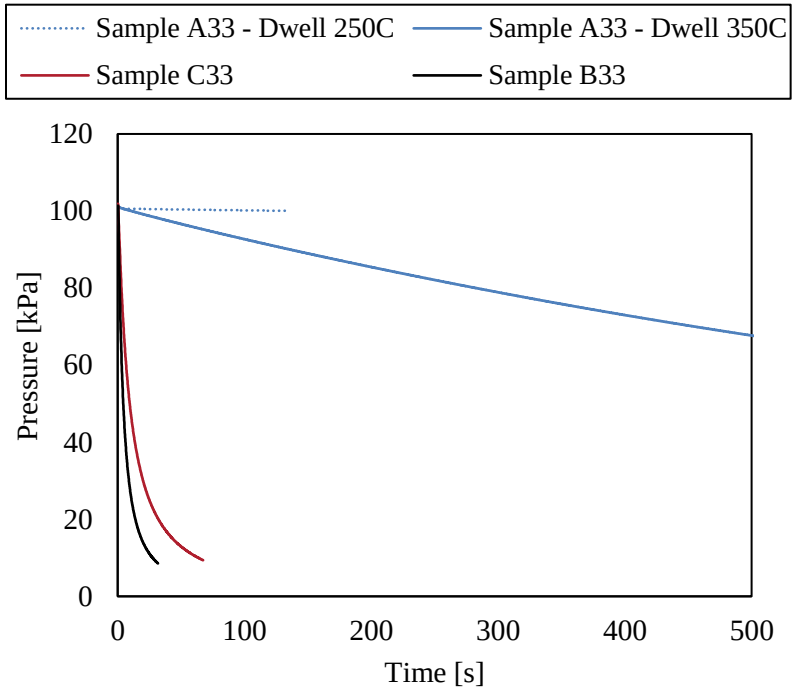
Figure $\hat{P}$ vs $\hat{t}$: Cender et al. *Transport in Porous Media* 2016 (115) 541-562 DOI 10.1007/s11242-016-0784-x

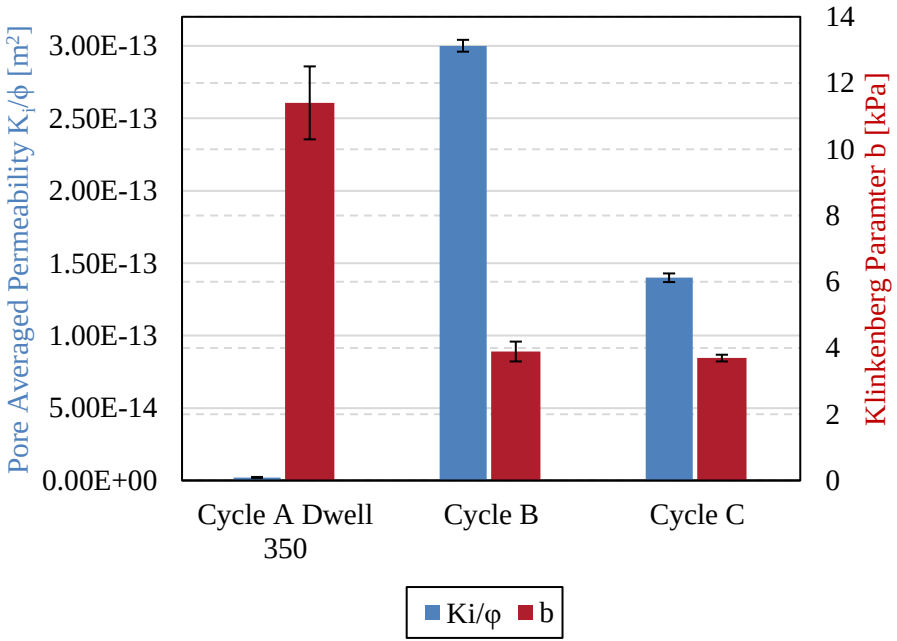
Permeability of Carbon/Carbon Composites – 5 Plies





Permeability of Carbon/Carbon Composites – 33 Plies





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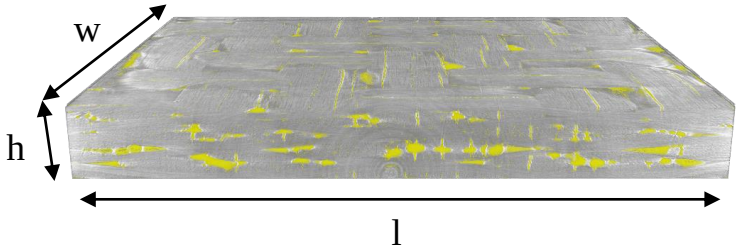
Porosity: X-Ray Computed Tomography

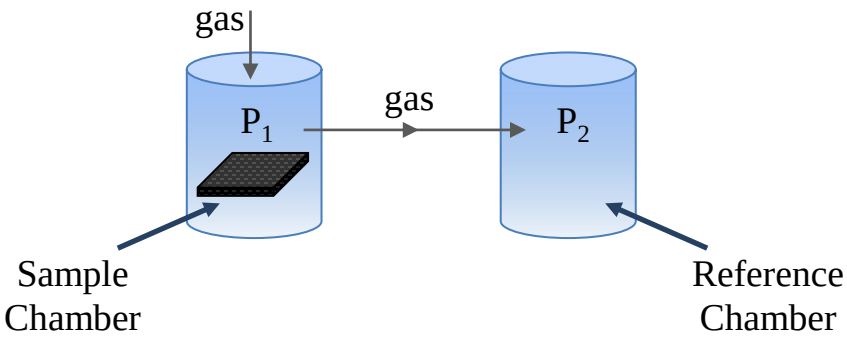
- Otsu's segmentation for the identification of open and closed porosity.
- Possibility to monitor microstructure of same samples tested for permeability.
- Resolution: 90 voxels and 6 voxels (limit on visible pores).



$$\phi_{tot} = \frac{V_{tot}}{V_{sample}} \qquad \phi_{conn} = \frac{V_{conn}}{V_{sample}}$$

V_{tot}: total volume of pores
V_{conn}: volume of connected porosity through-the-thickness
V_{sample}: l*h*w

Porosity: Pycnometry



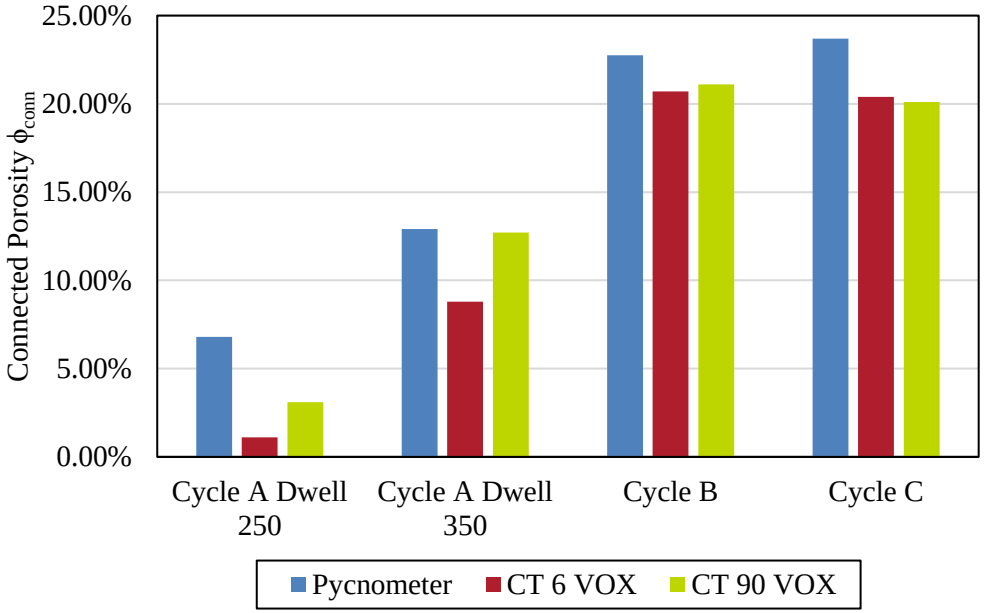
- Measuring gases: Helium and Nitrogen.
- Nitrogen → to measure open porosity.
- Helium → diffuses into closed pores.

$$V_{sample} = V_{sample\ chamber} - \frac{V_{ref.\ chamber}}{\frac{P_1}{P_2} - 1}$$

Comparison Helium and Nitrogen

- Evaluate open and closed porosity

Porosity of Carbon/Carbon Composites – 5 Plies

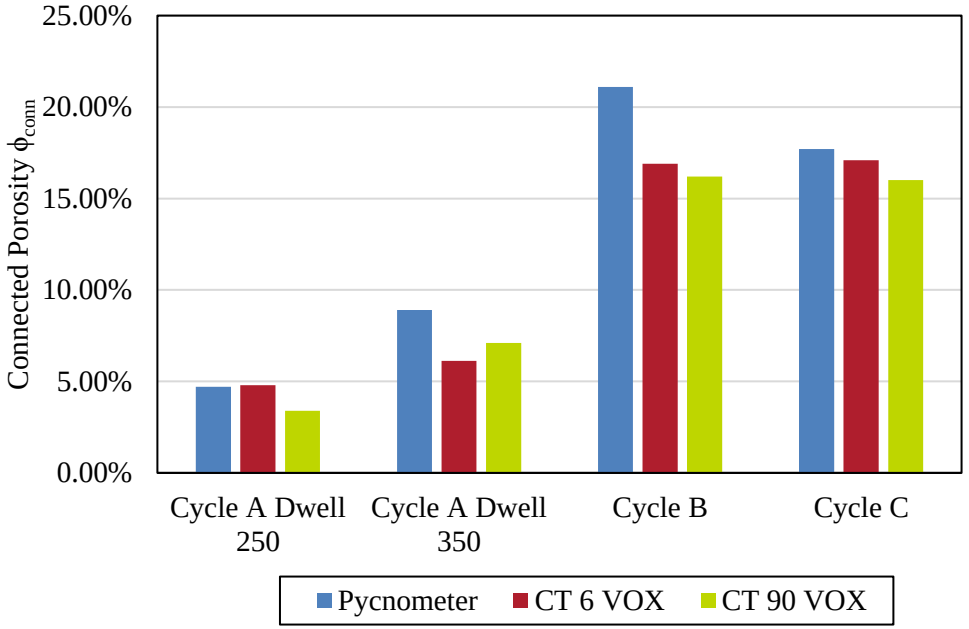


$$\phi_{conn} = \frac{V_{conn}}{V_{sample}}$$

V_{conn}: measured volume of pores connected through-the-thickness (from CT)

V_{sample}: l*h*w

Porosity of Carbon/Carbon Composites – 33 Plies



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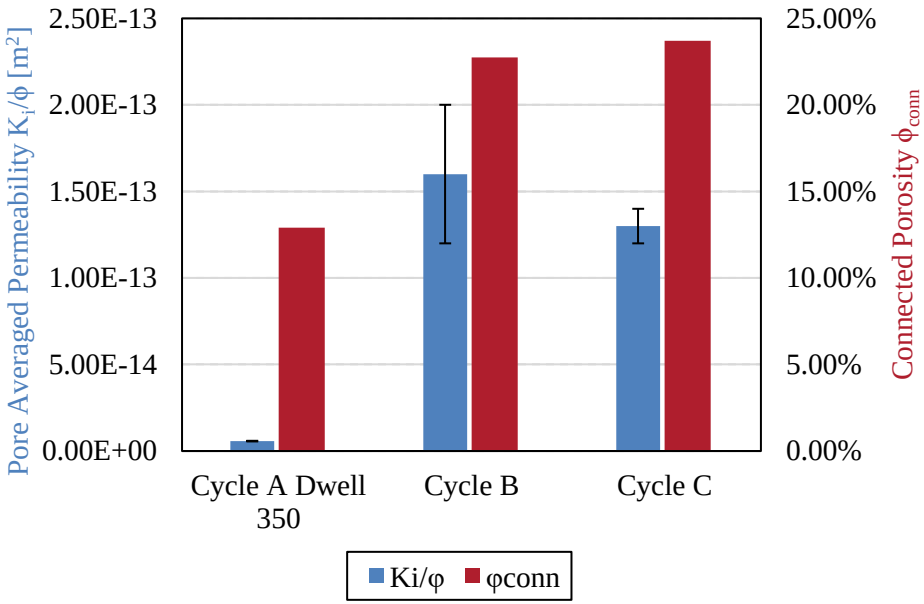
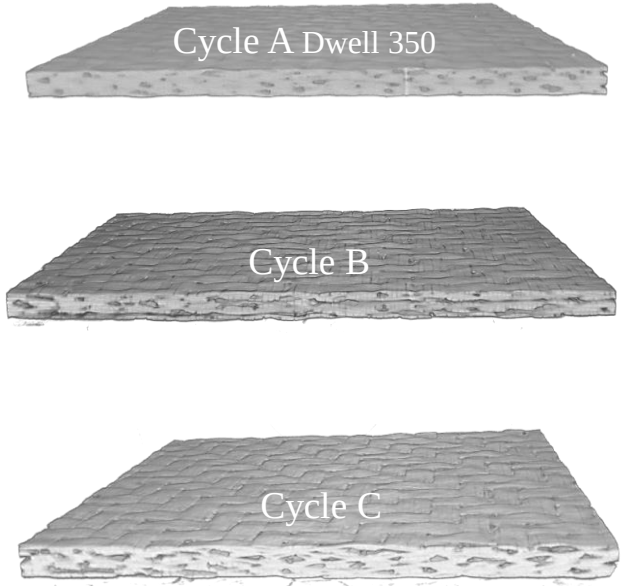
Correlation of Permeability and Porosity – 5 Plies





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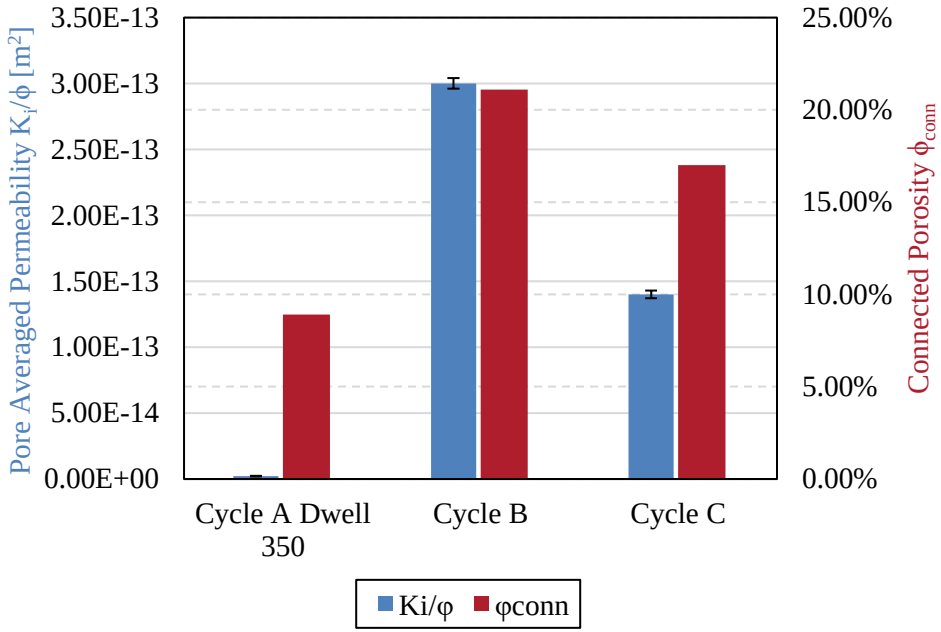

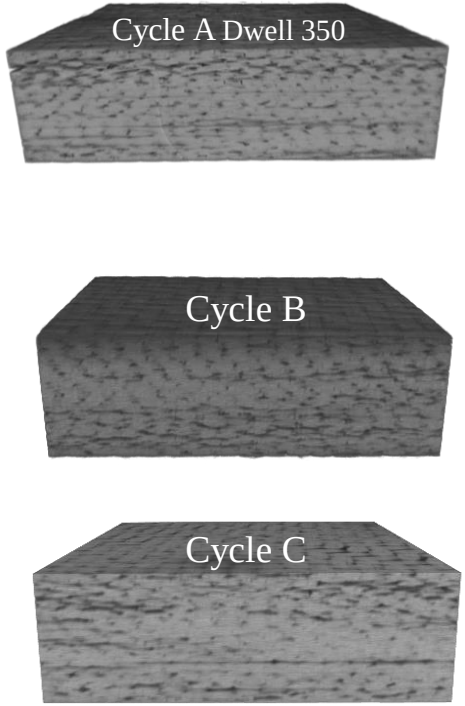

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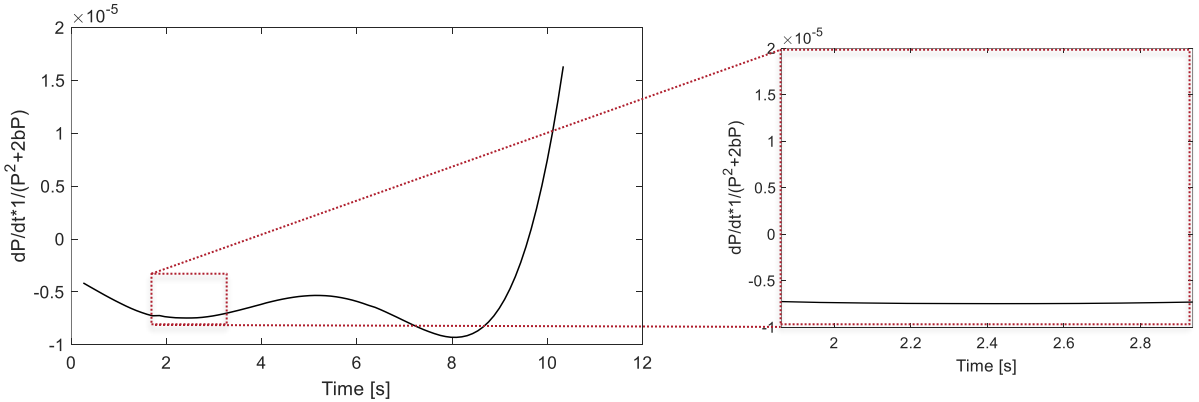
Porosity Predictions: Quasi-Steady State Model

- Small density change in reservoir → Quasi-steady state analysis.

$$K_{is} = -\frac{2\mu_g L_R L_s}{P^2(t) + 2bP(t)} \frac{\partial P}{\partial t}$$

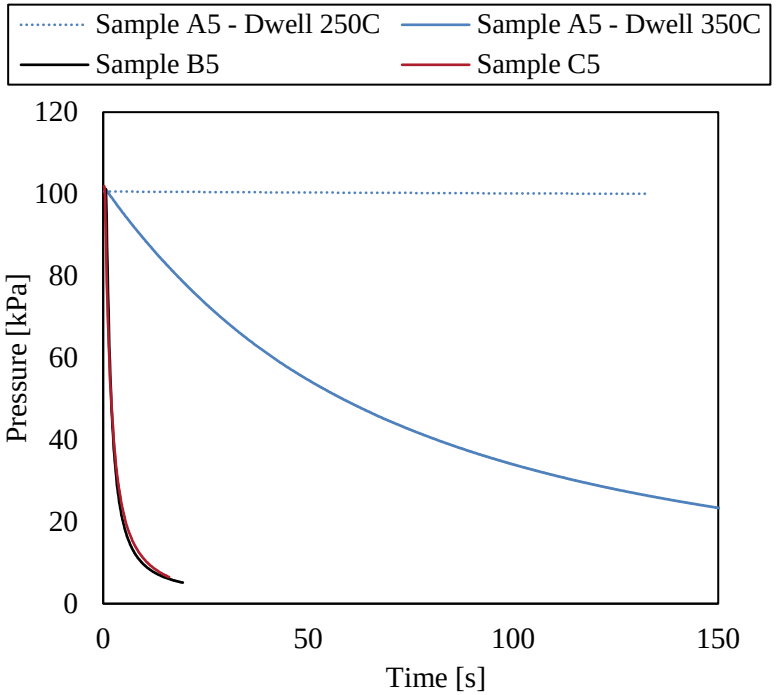
μ_g: gas viscosity
L_s: characteristic length sample
Kis: quasi-steady intrinsic liquid permeability
L_R: characteristic length reservoir
b: Klinkenberg parameter

- Model is valid in interval of constant $\frac{1}{P^2(t)+2bP(t)} \frac{\partial P}{\partial t}$

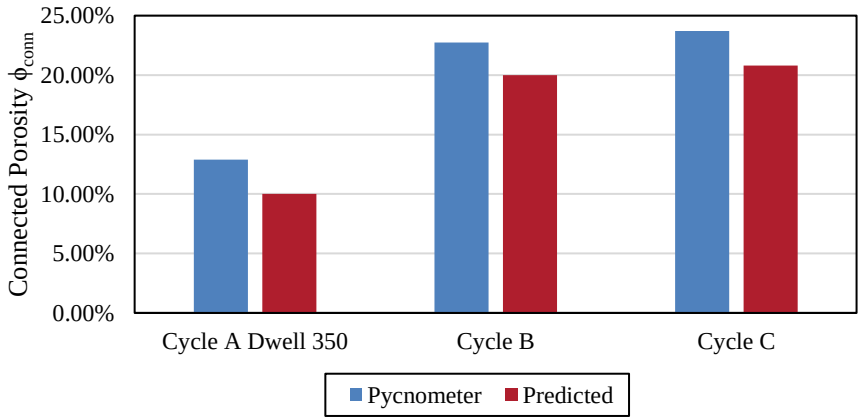


- Model is applied to pressure decay curves.
- Porosity is predicted by comparing K_i/ϕ with K_i.

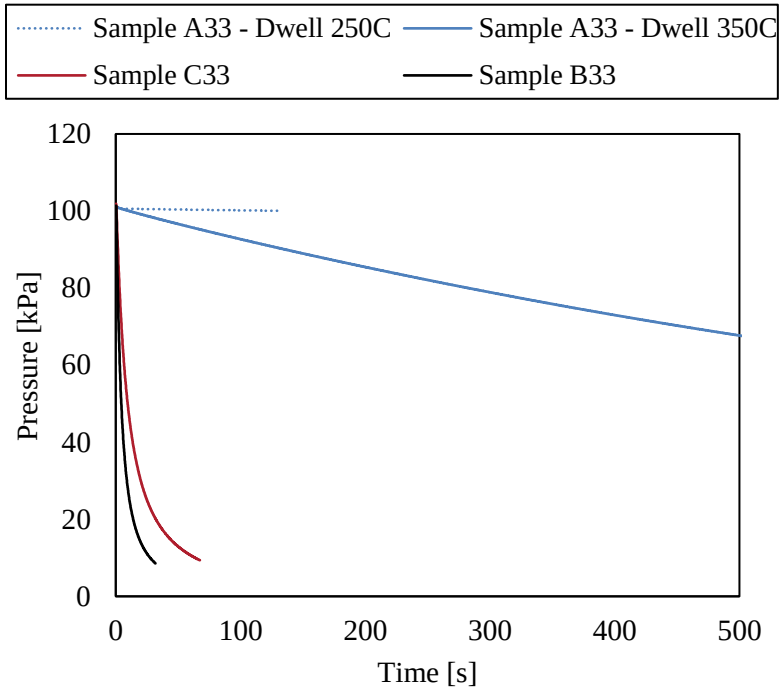
Porosity Predictions with Quasi-Steady Permeability: 5 Plies



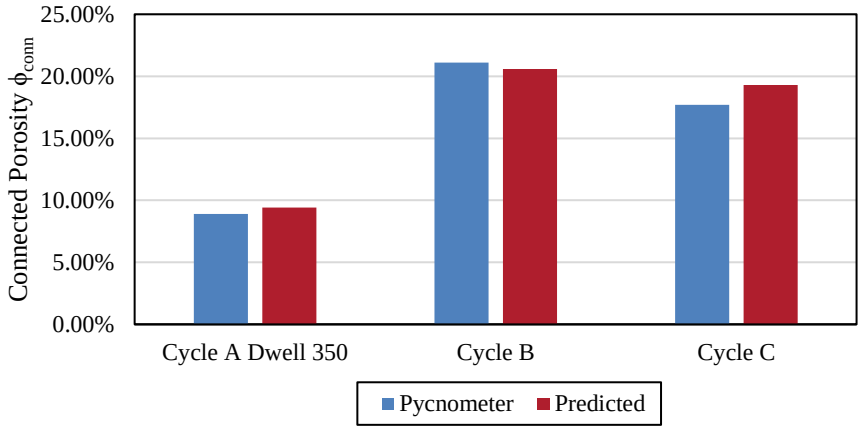
Sample	$\frac{K_i}{\phi}$ [m²]	K_{is} [m²]	Predicted ϕ
Sample A_5 Dwell 350	5.7E-15	5.7E-16	10.0%
Sample B_5	1.6E-13	3.2E-14	20.00%
Sample C_5	1.3E-13	2.7E-14	20.80%



Porosity Predictions with Quasi-Steady Permeability: 33 Plies



Sample	$\frac{K_i}{\phi}$ [m²]	K_{is} [m²]	Predicted ϕ
Sample A_{33} Dwell 350	2.1E-15	2.0E-16	9.4%
Sample B_{33}	3.0E-13	6.2E-14	20.60%
Sample C_{33}	1.4E-13	2.7E-14	19.30%



Conclusions

Pulse-decay test for Carbon/Carbon composites

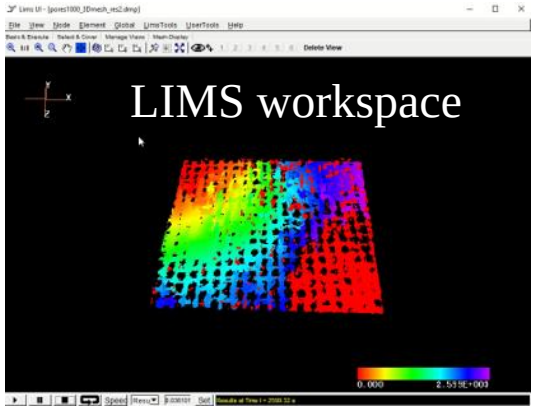
- One experiment to measure both permeability and porosity.
- Time savings: CT and pycnometry measurements not needed.

Correlation of permeability and porosity

- Basis for simulations for optimization of pyrolysis and re-infiltration.

Future Works

- Simulations of gas evacuation during pyrolysis.
- Simulations of re-infiltration process (RTM).
  - Numerical mesh extrapolated from CT scan of physical samples.



Our journal publications on Carbon/Carbon composites

- Densification Process

F. Muhammed, T. Lavaggi, S. Advani, M. Mirotznik, J.W. Gillespie, *Journal of Materials Science* (2021) 56(32):17877–17914
*"*Influence of material and process parameters on microstructure evolution during the fabrication of carbon-carbon composites: a review"

- Kinetics of Degradation Reactions

F. Muhammed, L. Moretti, T. Lavaggi, C. Lam, T. Tao, S. Advani, J.W. Gillespie *Journal of Materials Science* (2022) 57:21915–21934
"Influence of pyrolytic decomposition on the microstructure evolution of benzoxazine-derived carbon-carbon composites"

- Optimization of Pyrolyzing Schedule

F. Muhammed, T. Lavaggi, L. Moretti, S. Advani, J.W. Gillespie, *Ceramics International* (2023) 49(12):19996-20006
"Pyrolysis schedule optimization of benzoxazine-derived carbon/carbon composites through reaction rate optimization"

- Void Growth and Glass Transition Temperature during Pyrolysis

F. Muhammed, T. Lavaggi, S. Advani, J.W. Gillespie, *Journal of Applied Polymer Science* (2023)
"Relating the microstructural and glass transition temperature evolution of a carbon-carbon composite precursor during pyrolysis using thermomechanical analysis"

Thank you!

Questions?