Predicting Char Yield of High-Temperature Resins

Jacob Gissinger* and Kristopher Wise
NASA Langley Research Center

*jacob.r.gissinger@gmail.com
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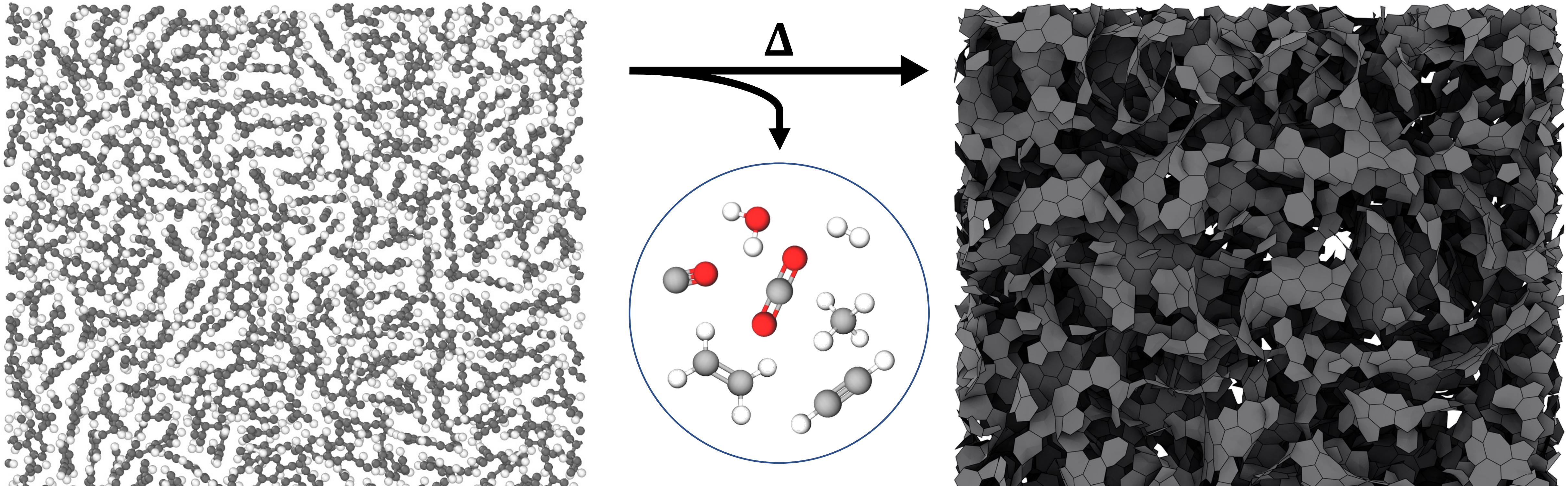


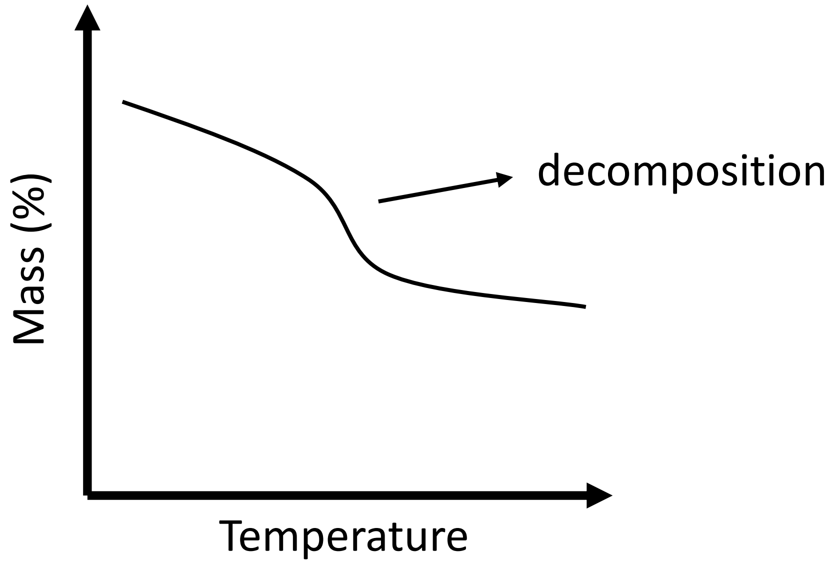
Composites are Pervasive in Aerospace

- Composites have replaced many components of aircraft and spacecraft
- Huge design space: the efficacy of new chemistries is difficult to predict
- Computational screening can help guide us toward next-generation high-temperature resins

Why is Char Yield Important?

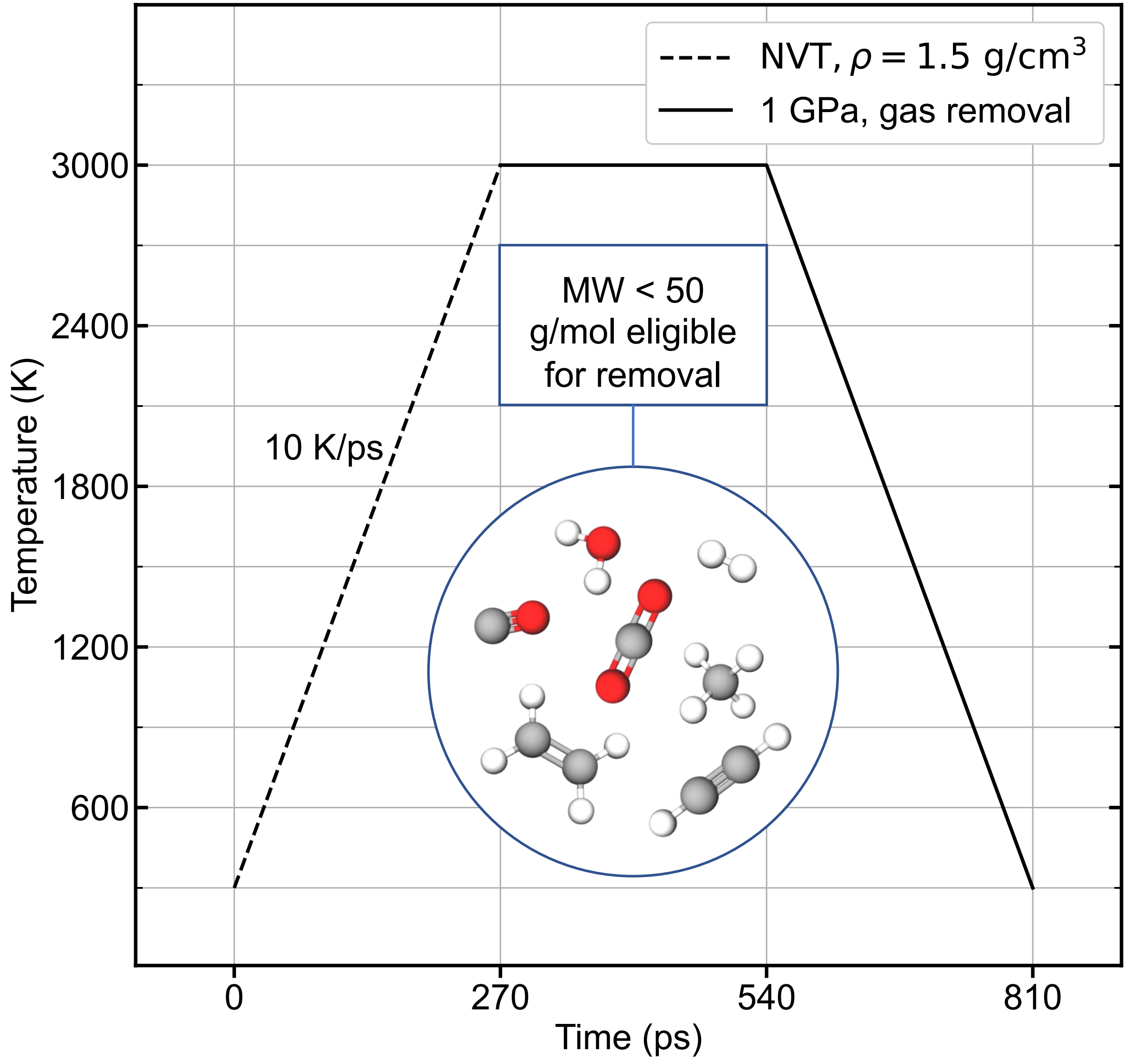
- Char yield is the amount of material left over after being subjected to high temperature pyrolysis
  - Thermogravimetric analysis (TGA) is used to obtain plots of mass vs time and/or temperature (typically ramped up to 800°C -1000°C)
- High char materials require fewer cycles of carbonization and resin infiltration to achieve desired properties

Typical TGA plot



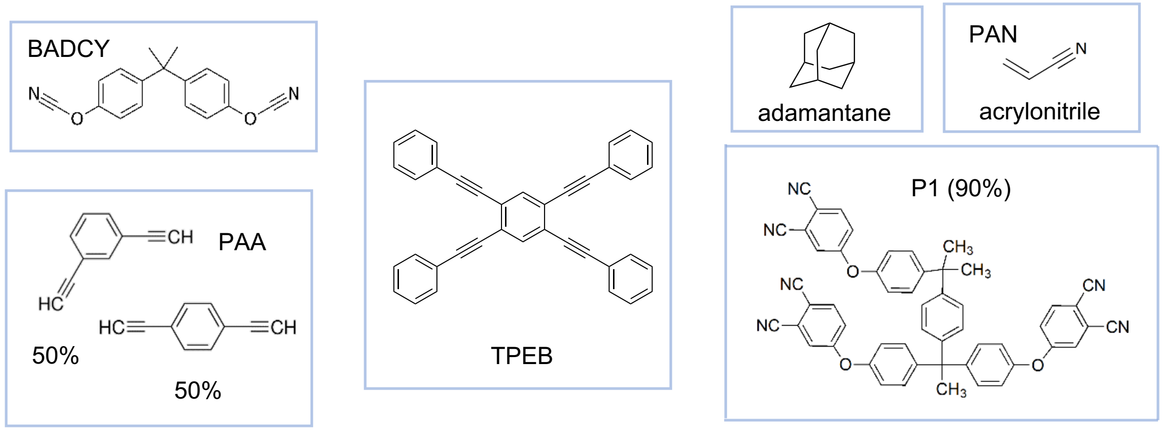
Char Yield Simulation Protocol

- Temperature ramp cycle
  - 300 K - 3000 K at 10 K/ps
  - High temperatures/rates to accelerate reactions
- Anneal at high pressure (1 GPa) to achieve final densities of 1.8 g/cm^3 - 2.0 g/cm^3
- ReaxFF with periodic removal of outgassing products to allow for carbonization and densification
- Initial system size: 36000 atoms

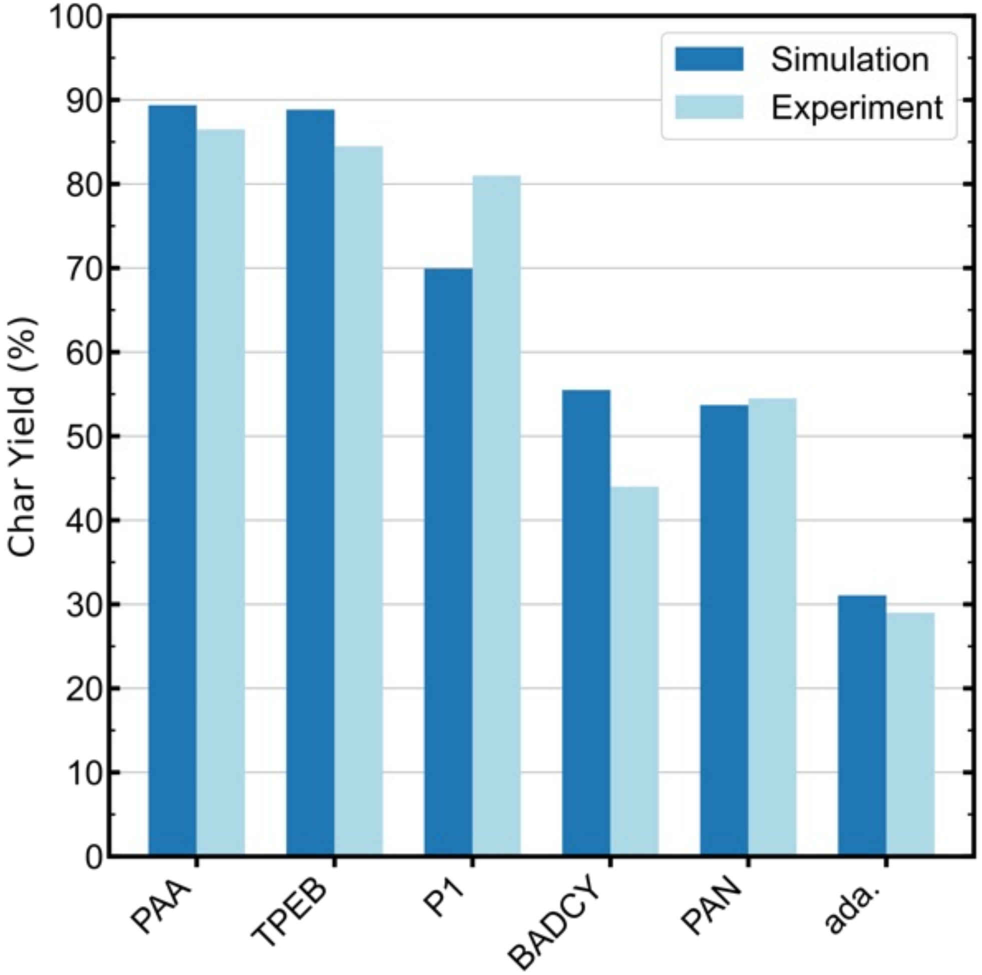


Char Yield Results

- Simulation protocol able to accurately predict char yield trends across a wide range of functional groups, heteroatom content and char yield values
- Chemically specific method
- No assumptions or fitting of experimental results

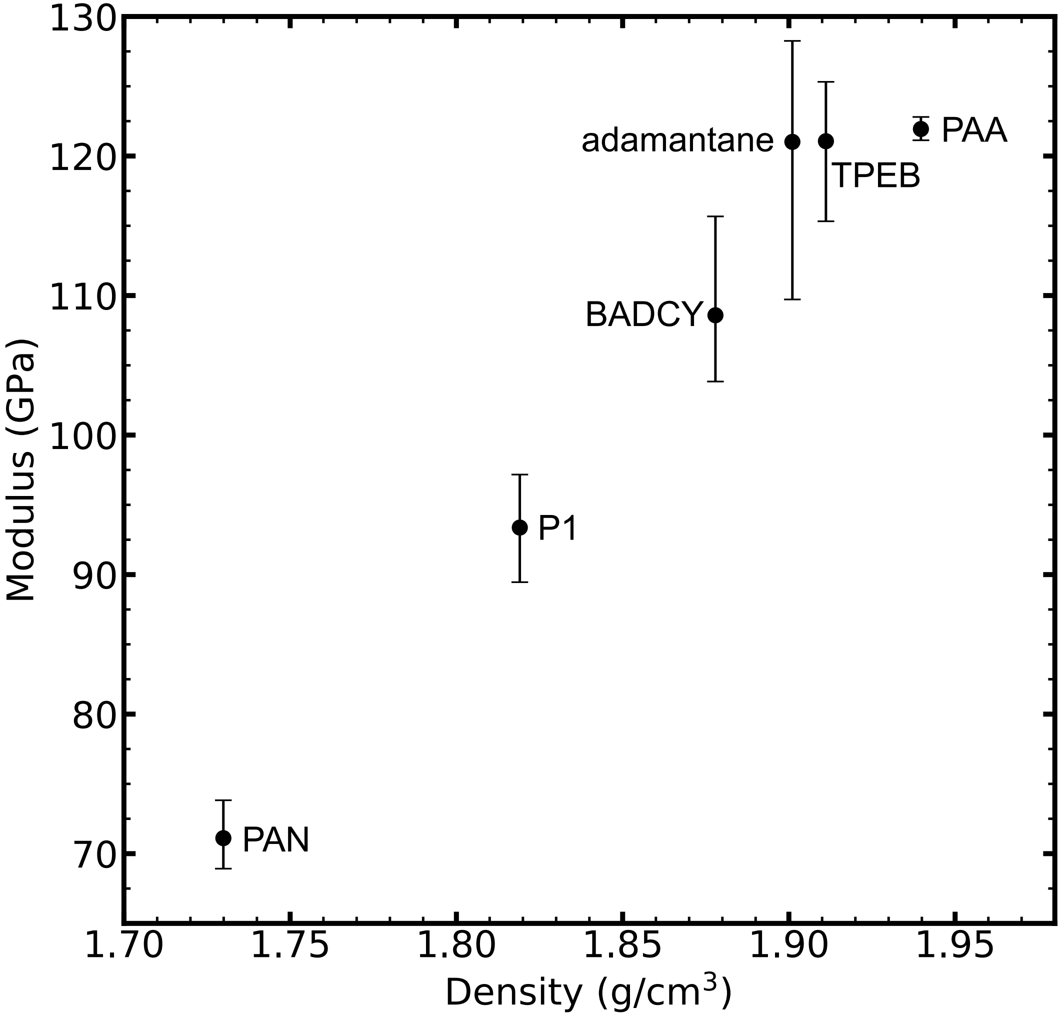


Gissinger et al. "Predicting char yield of high-temperature resins." *Carbon* 202 (2023): 336-347.



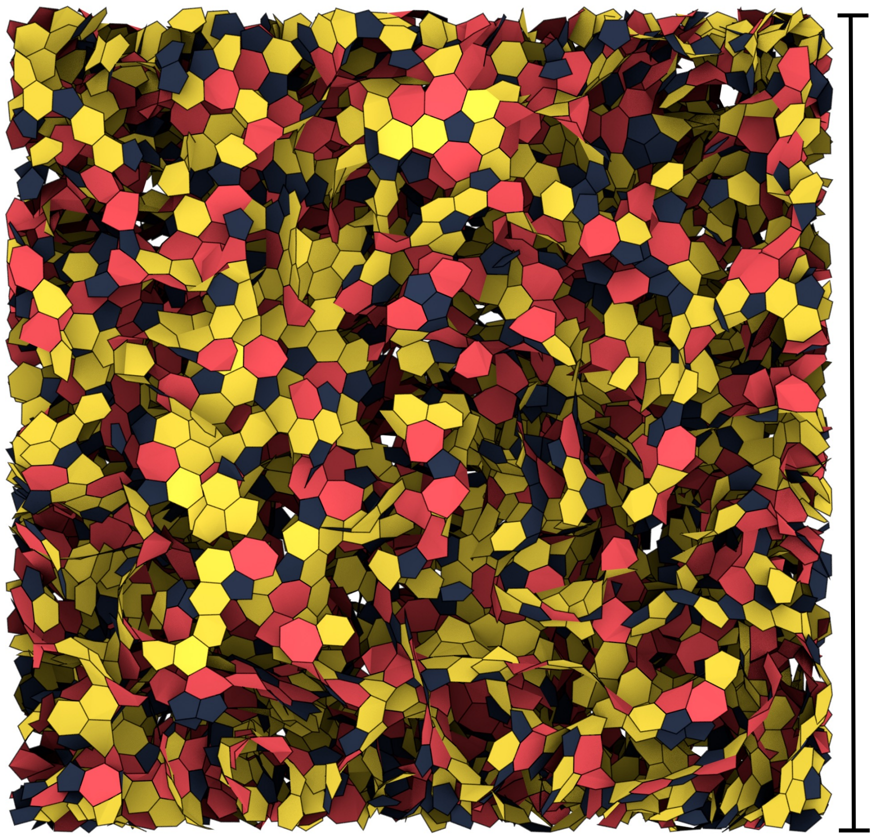
Mechanical Properties

- Nonporous char morphology results in high predicted elastic moduli
- Predicted values in expected range for glassy carbon (~30 GPa @ 1.5 g/cm^3), but far lower than high modulus carbon fibers
- Highlights importance of achieving structures with high density and low defects, porosity



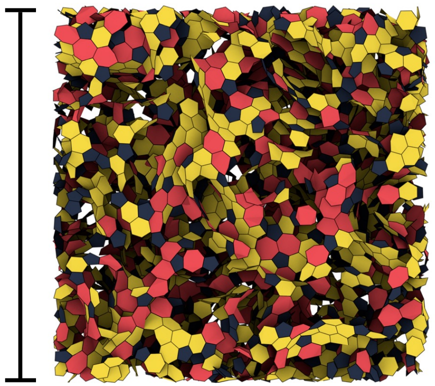
Final Morphology: Ring Distribution

- Final carbonized structure consists primarily of fused five-, six- and seven-membered carbon rings
- Twice as many six-membered rings as other sizes, but rings are well distributed with respect to ring size
- Similar final morphology obtained for lower char yield resins



57.6 A

Polyarylacetylene (PAA)



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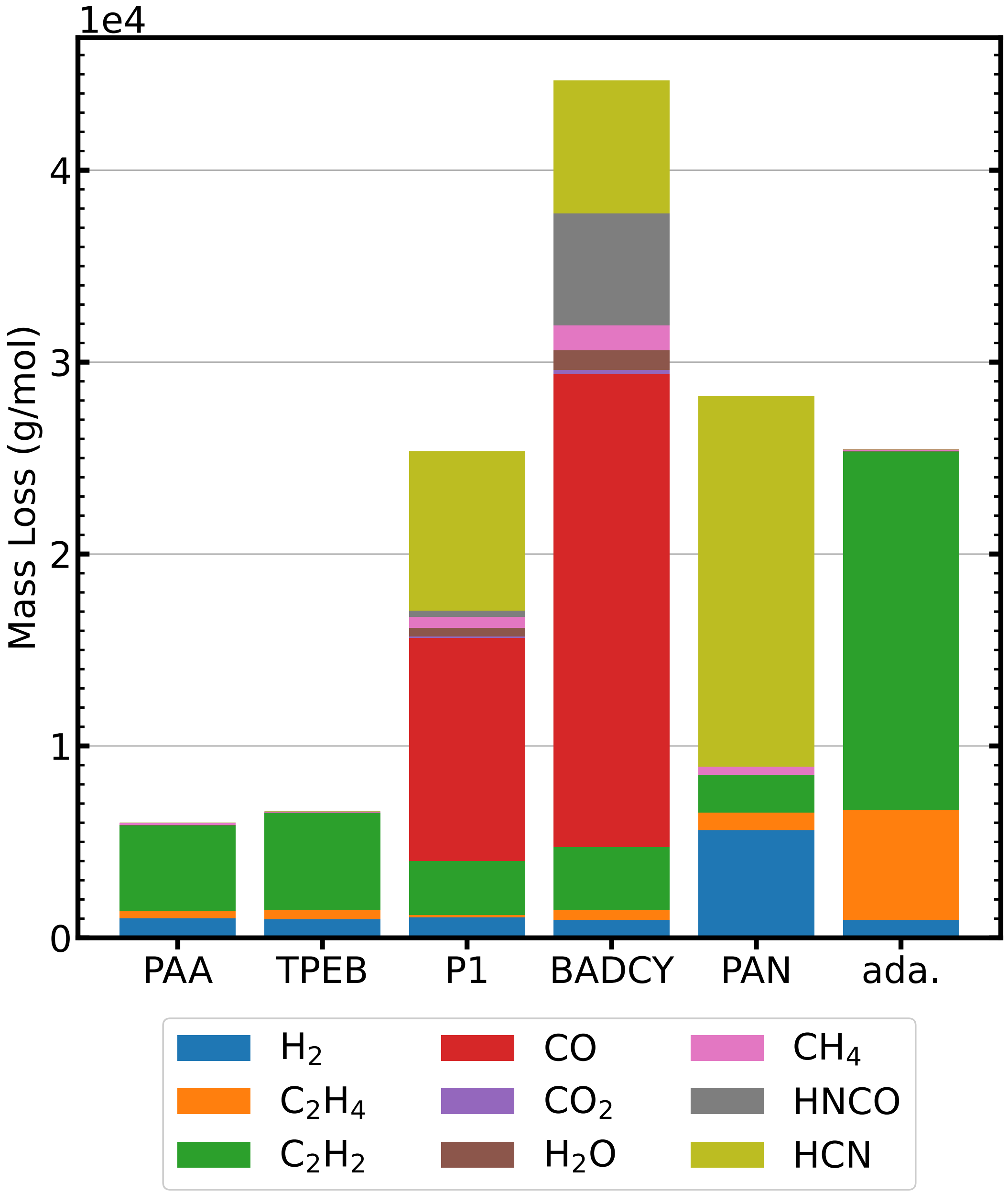
Cyanate ester (BADCY)

Five-membered ring   Six-membered ring   Seven-membered ring

Gissinger et al. *Carbon* 202 (2023): 336-347.

Outgassing Products

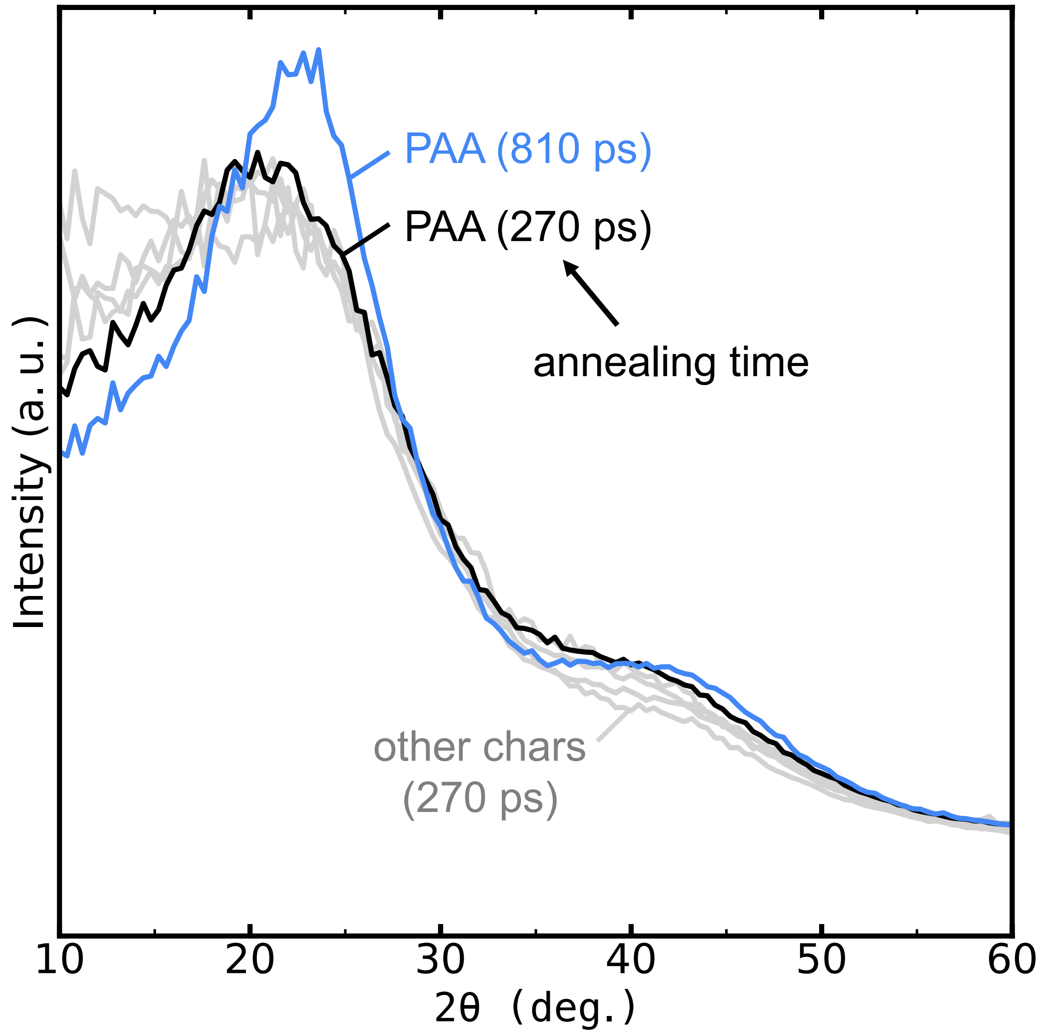
- Protocol keeps track of molecules removed from the system to mimic outgassing
- Primarily CO for oxygen-containing resins (highly stable bond)
- Useful metric to compare to experimental techniques such as TGA-mass spectrometry to confirm the chemistry is being captured accurately



TGA: Thermal Gravimetric Analysis

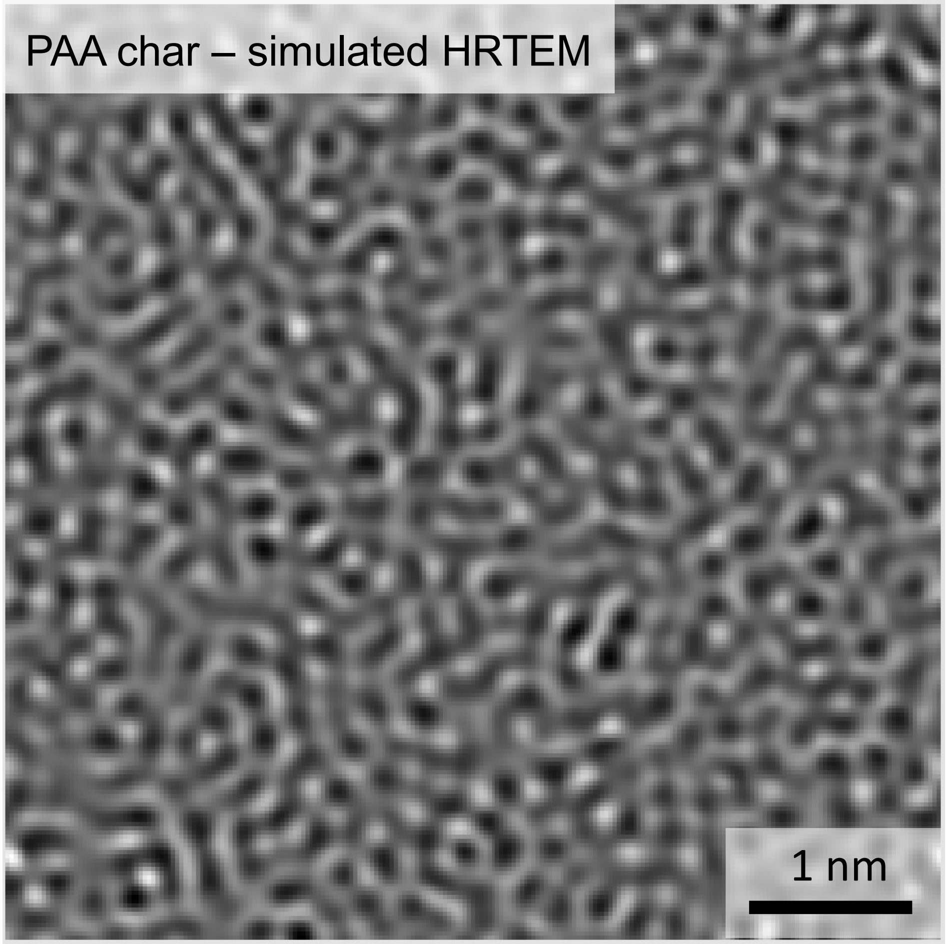
Tools for Direct Experimental Comparison

- Simulated XRD pattern allows for direct comparison with experimental morphologies
- Curve is typical of non-graphitized glassy carbon at lower carbonization temperatures
- The 002 peak, which indicates graphitic structure, notably sharpens after increasing the annealing time

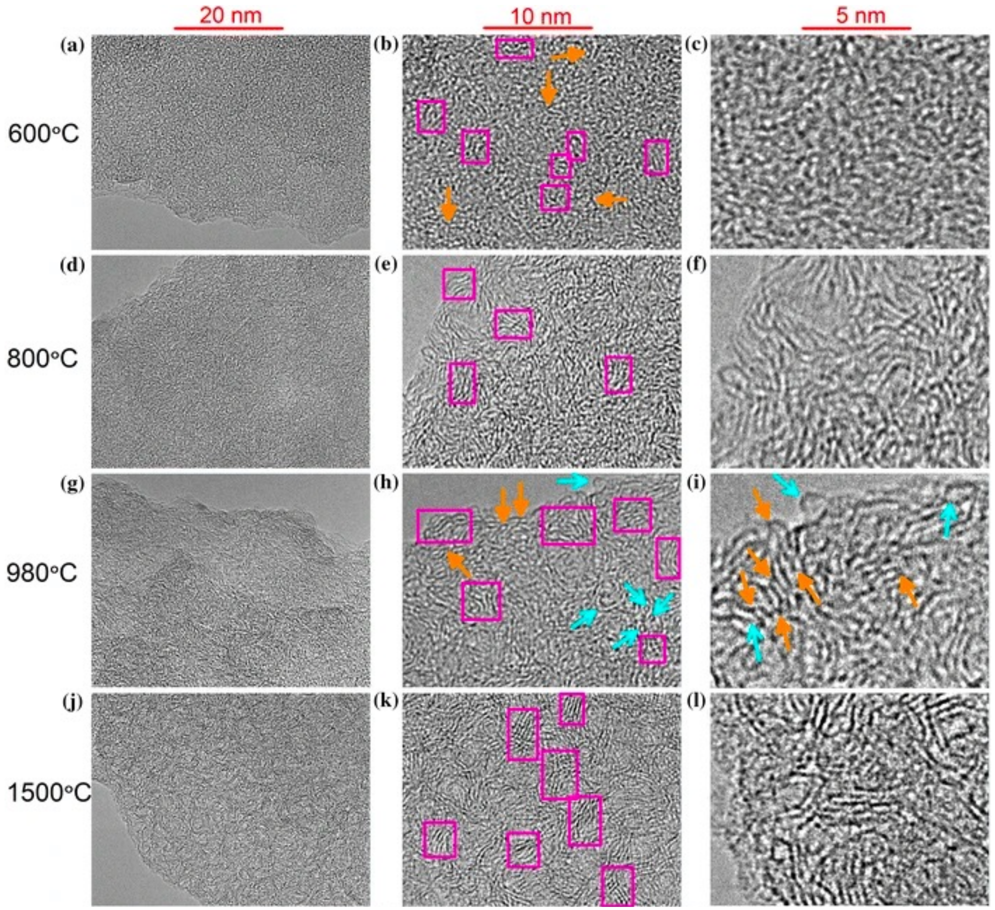


XRD: X-ray diffraction

Simulating high-resolution microscopy



HRTEM: High-resolution transmission electron microscopy



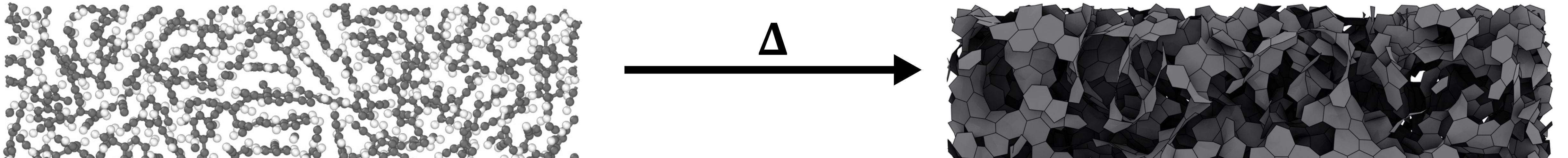
Experimental HRTEM vs. carbonization temperature

Jurkiewicz, Karolina, et al. "Evolution of glassy carbon under heat treatment: correlation structure–mechanical properties." *Journal of materials science* 53.5 (2018): 3509-3523.

Simulated microscopy consistent with non-graphitized glassy carbon at lower temperatures

A Promising Method for Predicting Char Yield

- A chemically specific protocol was developed to predict char yield for high temperature resins
  - No prior knowledge of high-temperature behavior required
- Validated for low, medium and high char yield resins with various chemical structures and number of heteroatoms
- Additional outputs include atomistic structure, composition, morphology, mechanical properties, chemical pathways, outgassing products
- Currently being used to investigate and screen new chemistries



Thank You!

Email: jacob.r.gissinger@gmail.com

References (experimental char yield values):

PAA (polyarylacetylene): Katzman, H. A. et al. DTIC Accession Number ADA302053, 1995.

TPEB (1,2,4,5-tetraphenylethynylbenzene): Jones, K. M. et al. Polymer, 36, 187, 1995.

P1 (phthalonitrile): Hu, Y. et al. RSC Advances, 8, 32899, 2018.

BADCY (bisphenol A dicyanate ester): Wang, Y. et al. Polymer, 77, 354, 2015.

PAN (polyacrylonitrile): Song, C. et al. J Porous Materials, 16, 197, 2009.

Adamantane: Kazanskii, B. A. et al. Russian Chemical Bulletin, 17, 2506, 1968.