Kinetics Driven Approach to Understanding Void Formation During Carbonization

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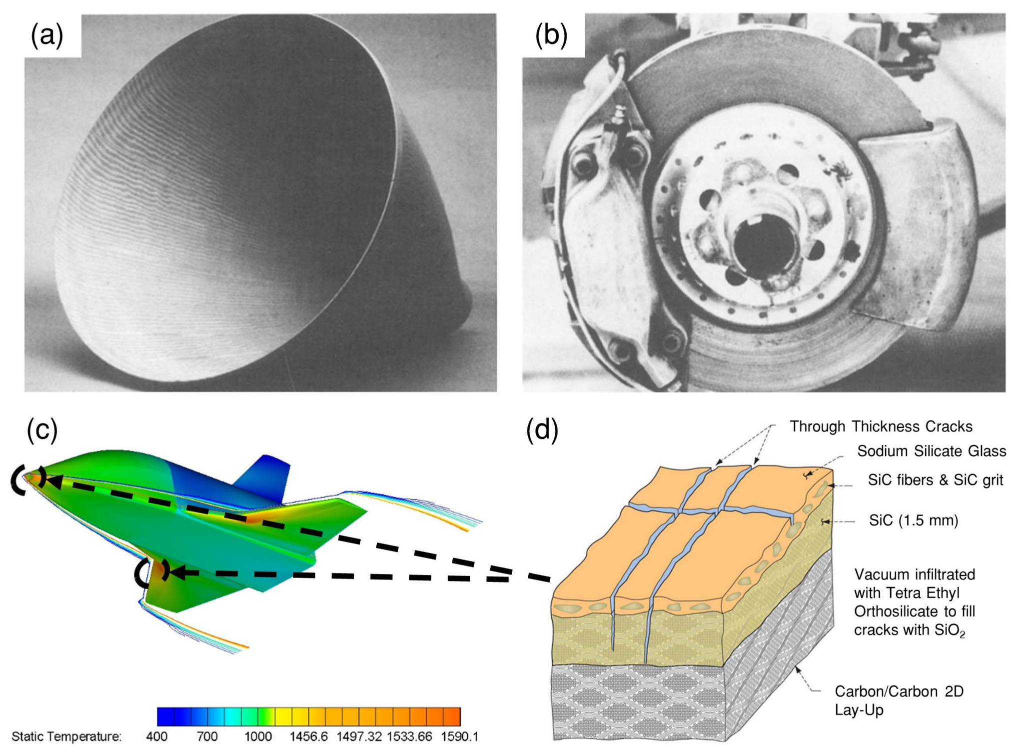
Introduction

Carbon - carbon composites (CCCs) are a unique form of carbon-fiber reinforced materials that exhibit:

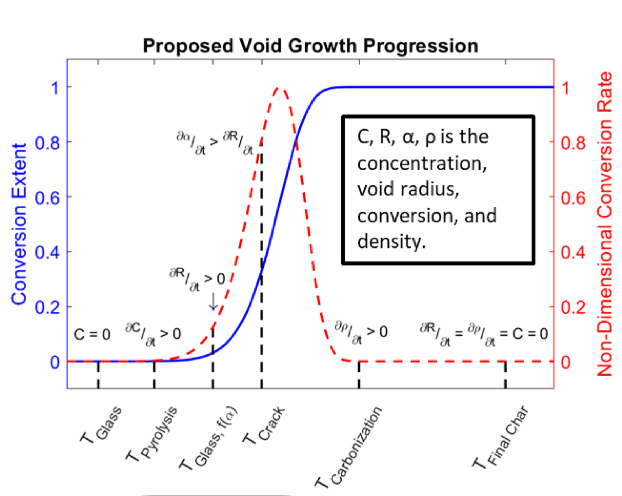
- Exceptional Strength at high temperatures
- High Fracture Toughness
- Excellent frictional properties



(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.

Research Overview

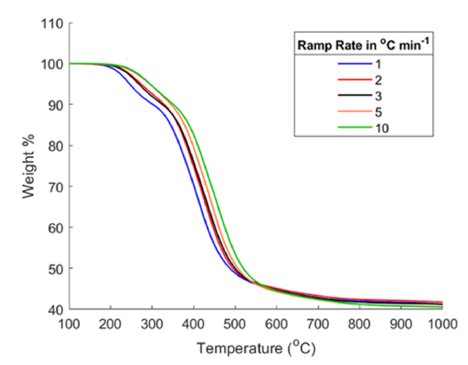
The goal is to characterize material properties as a function of the conversion to predict void formation phenomenon through kinetic modeling. The current results have resulted in the following hypothesis:

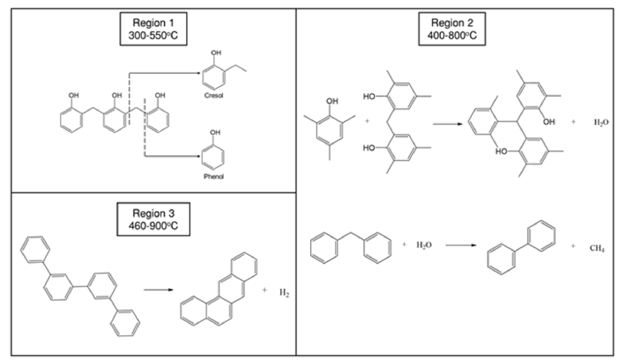


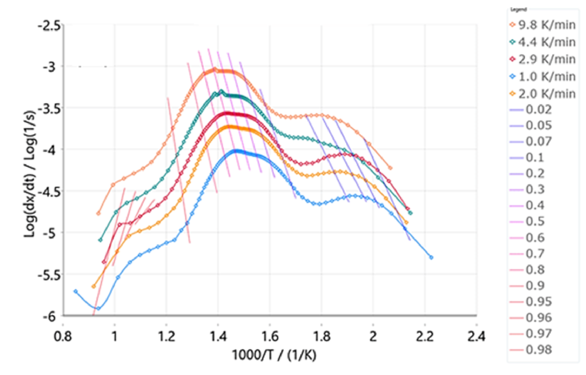
1. Initial void growth functions like nucleation and growth of voids in polymers above their glass transition temperature (T_G)
2. The T_G is shifted to higher temperatures as the decomposition proceeds
3. At a finite conversion, T_G is shifted sufficiently high to prevent further void growth. Instead, cracks are formed to relieve the stresses caused by internal gas pressure

Technical Approach

The purpose of the kinetics-designed multistage decomposition experimental approach was to track void progression as a function of the material conversion from polymer to a carbon-rich matrix.





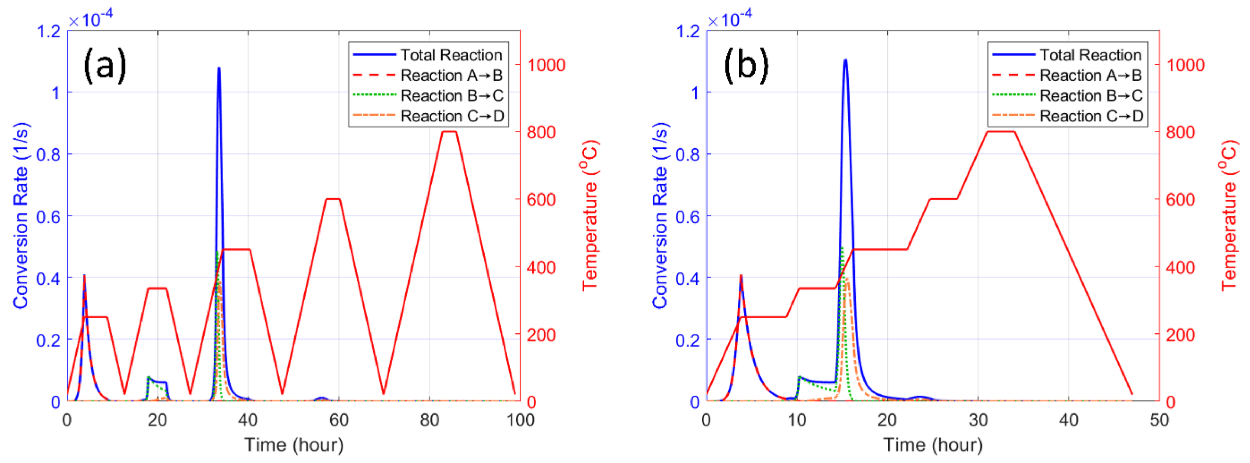


$$\frac{\partial \alpha}{\partial t} = \sum_i w_i f(\alpha)^n \left[A_i \exp\left(-\frac{E_a}{RT}\right)\right]$$

Friedman's Analysis (**bottom left**) is performed under the data gleaned from thermogravimetric analysis (**top left**) and using assumptions about the reaction pathaway (**top right**)

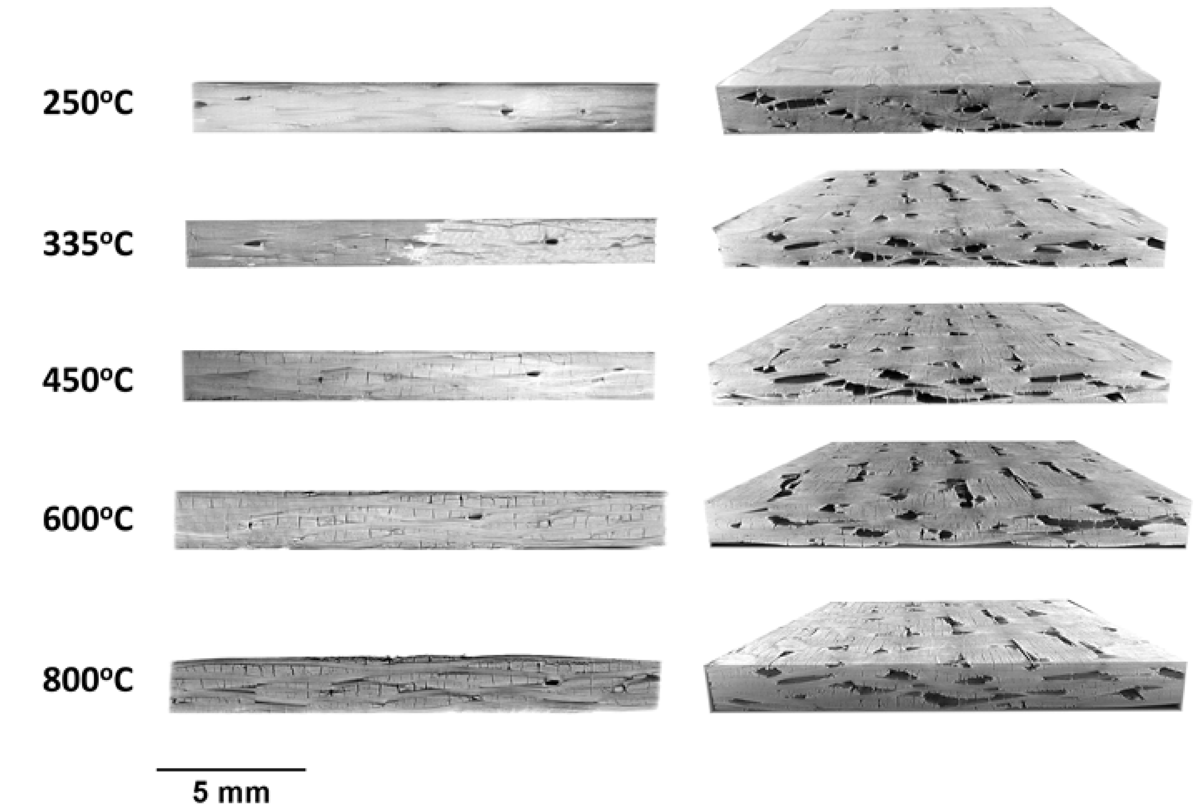
- Slope of the line is a function of activation energy ($\mathbf{E_a}$)
- The intercept a function of the pre-exponential function (**A**) and the reaction order (**n**)
- And the weight of the reaction (**w**) in the equation is found through optimization

Using the above kinetic model, the individual reactions were separated to be able to couple their influence with the evolution of the microstructure.

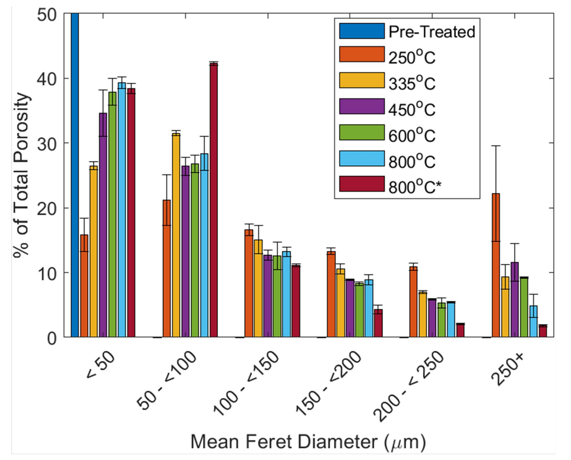


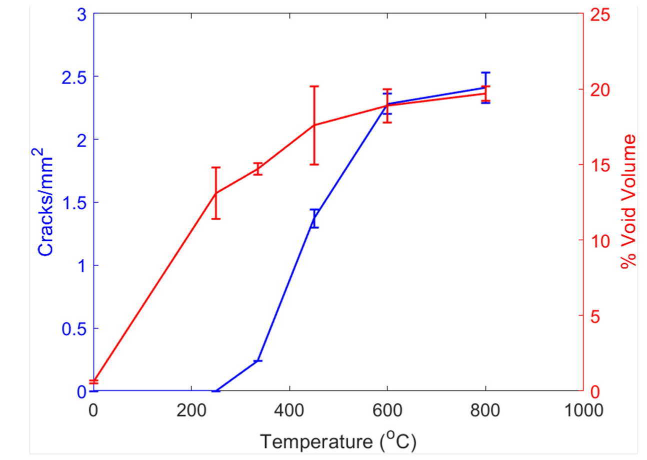
The above heat treatment cycles provided statistically similar data which led to the assertion that despite the cooling process the step-wise decomposition closely resembled in-situ void growth progression.

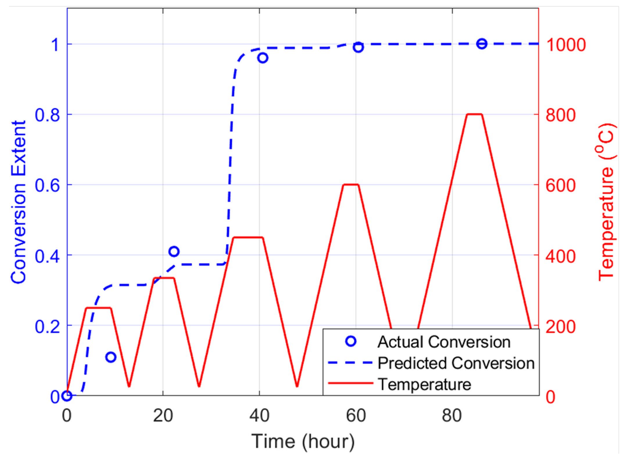
Results and Discussion



Using the volumetric data generated from Micro-CT analysis the following quantitative data was produced through utilizing Dragonfly and the facilities at the Advanced Material Characterization Laboratory.







Quantitative analysis of composite properties:

a) histogram of mean ferret diameters with increasing temperature with the scale adjusted to highlight samples which have been heat treated. 800ºC* indicates sample with no cooling.

b) Crack density (C/mm^2) measured on the XZ plane and the void volume with increasing temperature

c) Measured extent of conversion of the composite sample overlayed over the conversion extent predicted by kinetic analysis

Temperature (ºC)	Void Volume %	% Of Voids Interconnected	Average Void Diameter (µm)	Maximum Void Diameter (µm)	Crack Density (Cracks mm^{-2})
Original Sample	0.3 ± 0.1	-	<10	<10	-
250	13.1 ± 1.7	7.64	143.86	348.79	-
335	14.7 ± 0.4	90.32	122.49	371.58	0.239± 0.001
450	17.6 ± 2.6	98.76	122.25	394.10	1.37±0.07
600	18.9 ± 1.2	99.35	98.91	407.24	2.28±0.08
800	19.7 ± 0.5	99.78	92.91	433.51	2.41±0.12
800*	22.0 ± 0.5	97.98	71.32	472.93	2.61 ± 0.19

Conclusions

- Low pore interconnectivity, and void penetration depth, in the first reaction step indicates that at the early stages of the reaction gas transport is primarily through diffusion.
- The average void diameter is strongly influenced by the early stages of the reaction which suggests that the conversion rate in this temperature regime is an important parameter.
- There was an increase to pore interconnectivity as a function of increasing crack density as transverse cracks provided a pathway from the surface to the centermost voids.

Future Work

- Quantify the influence of material conversion, from resin to carbon, on the thermo-mechanical properties of the matrix.

Acknowledgements

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