Ablation Performance of 3D Printed Continuous Carbon Fiber-Reinforced PEEK

September 25, 2020

Hao Wu Ph.D.

KAI, LLC, Austin, TX

www.koo-associates.com

Outline

- The Team
- Overview/Problem
- Technical Approach
- Literature Review
- Project Objective
- Preliminary Results
- Summary
- Acknowledgements

Our Team

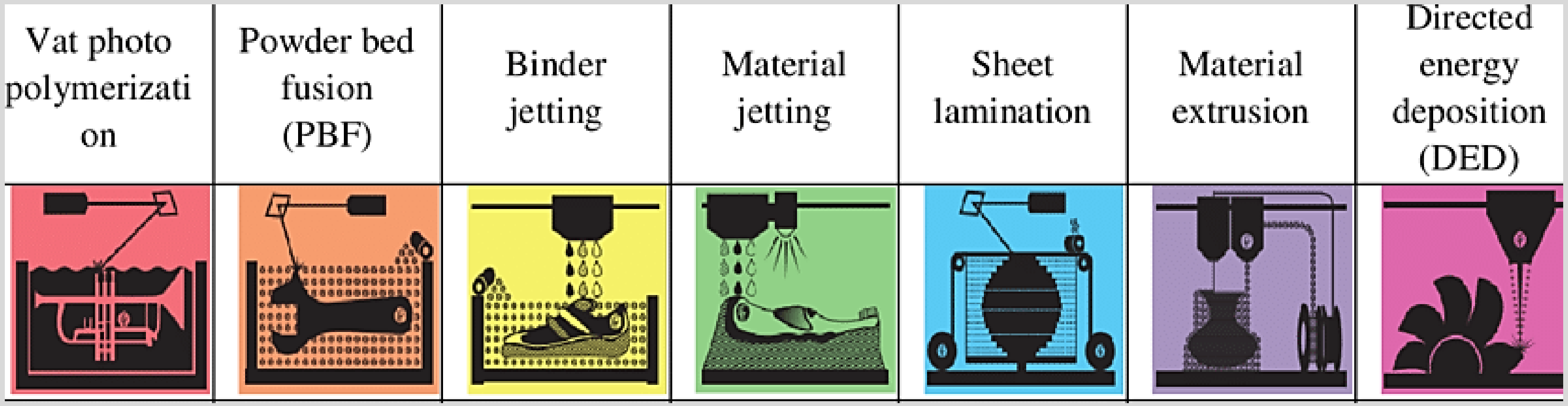
- Hao Wu, Ph.D.
  - Senior Research Scientist and Business Development Manager, KAI, LLC.
- Steven D. Kim, Colin Yee and Yanan Hou
  - Graduate Research Assistant, Texas Materials Institute, The University of Texas at Austin.
- William P. Fahy
  - Research Engineer, KAI, LLC.
- Zack August, Ph.D.
  - Senior Manager, AREVO Inc.
- Zhe Liu,
  - Research Engineer, AREVO Inc.
- Joseph H. Koo, Sc.D.
  - Vice President & Chief Technology Officer, KAI, LLC, and Sr. Research Scientist/Research Professor, & Director, Polymer Nanocomposites Technology Lab, Walker Department of Mechanical Engineering, The University of Texas at Austin

Overview/ Problem

- **Heat shields** are required to protect the vehicle from extreme heating conditions during re-entry.
- The manufacturing of current Thermal Protection Systems (TPS) are **labor intensive**. They are **high cost**, require **long production time**, and there are also **quality issues**.
- The current state-of-the-art manufacturing technology, such as **3D printing** or **additive manufacturing** and **automated production** can potentially solve the current issues of heat shield manufacturing.
- One of the challenges is to develop **TPS materials** that are compatible with AM techniques. If successful, the benefits will be **better performing** TPS at **lower cost** as well as **shorter lead times**.

Additive Manufacturing

KAI



- The current classifications divide AM into **7 categories**.
- More innovations in AM are emerging.
- **Materials** selection is also important.

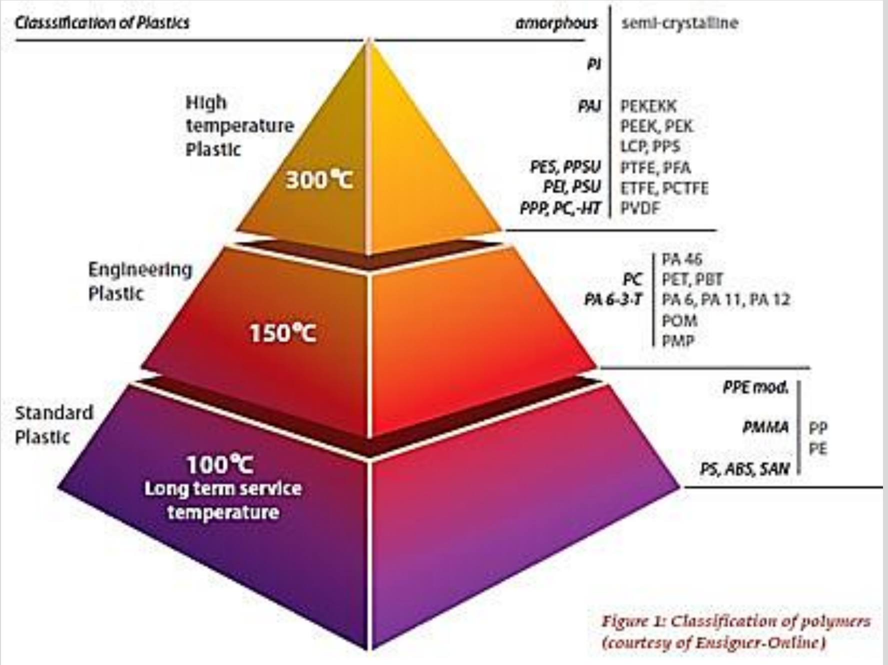
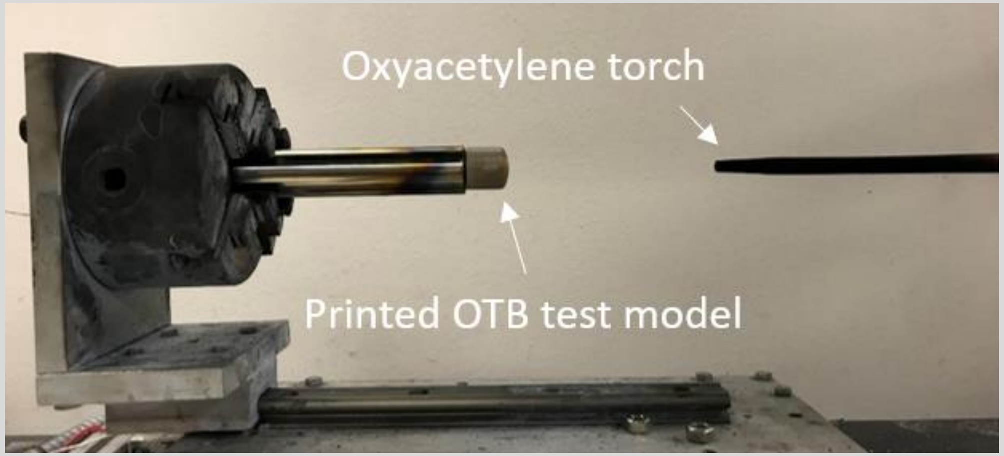
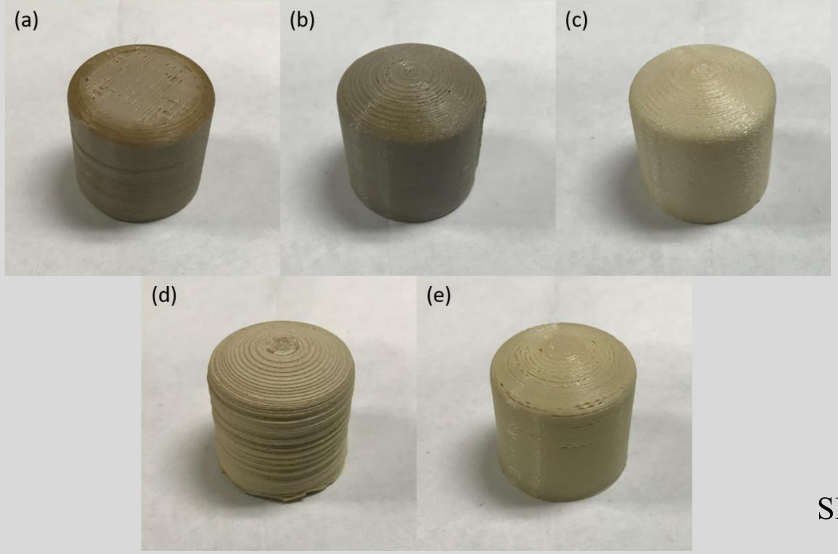


Figure 1: Classification of polymers (courtesy of Ensigner-Online)

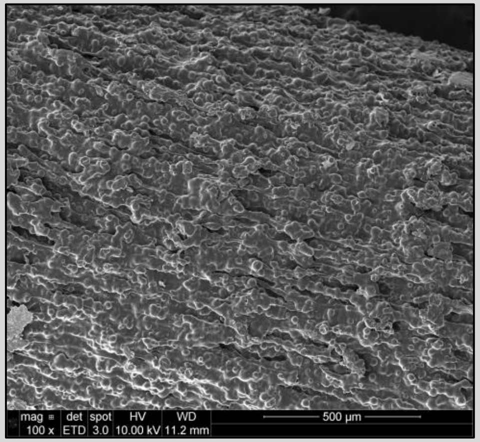
Recap

- A quick recap of what we have done on AM TPS research:
- Formulated and tested multifunctional nanocomposite PEI filaments specifically designed for TPS application.
- Examined the ablation performances of various high-performance thermoplastics including PEI, PEEK and PEKK.





3D printed OTB test coupons: (a) PEEK Smartmaterials3D, (b) PEEK Roboze, (c) PEI ULTEM™ 9085, (d) PEI Modified ULTEM™ 1010, and (e) PEKK.



SEM of PEI Modified ULTEM™ 1010

Recent publications

- Kim, S., Wu, H., Devega, A., Sico, M., Fahy, W., Misasi, J., ... & Koo, J. H. (2020). Development of polyetherimide composites for use as 3D printed thermal protection material. *Journal of Materials Science*, 1-18.
- Wu, H., Kafi, A., Yee, C., Atak, O., Langston, J. H., Reber, R., ... & Koo, J. H. (2020). Ablation Performances of Additively Manufactured High-Temperature Thermoplastic Polymers. In *AIAA Scitech 2020 Forum* (p. 1125).
- Kafi, A., Wu, H., Langston, J., Atak, O., Kim, H., Kim, S., ... & Koo, J. H. (2020). Evaluation of additively manufactured ultraperformance polymers to use as thermal protection systems for spacecraft. *Journal of Applied Polymer Science*, 49117.
- Wu, H., Fahy, W. P., Kim, S., Kim, H., Zhao, N., Pilato, L., ... & Koo, J. H. (2020). Recent developments in polymers/polymer nanocomposites for additive manufacturing. *Progress in Materials Science*, *111*, 100638.
- Wu, H., Sulkis, M., Driver, J., Saade-Castillo, A., Thompson, A., & Koo, J. H. (2018). Multi-functional ULTEM™ 1010 composite filaments for additive manufacturing using Fused Filament Fabrication (FFF). *Additive Manufacturing*, *24*, 298-306.

AM of continuous carbon fiber composites

KAI

Markforged

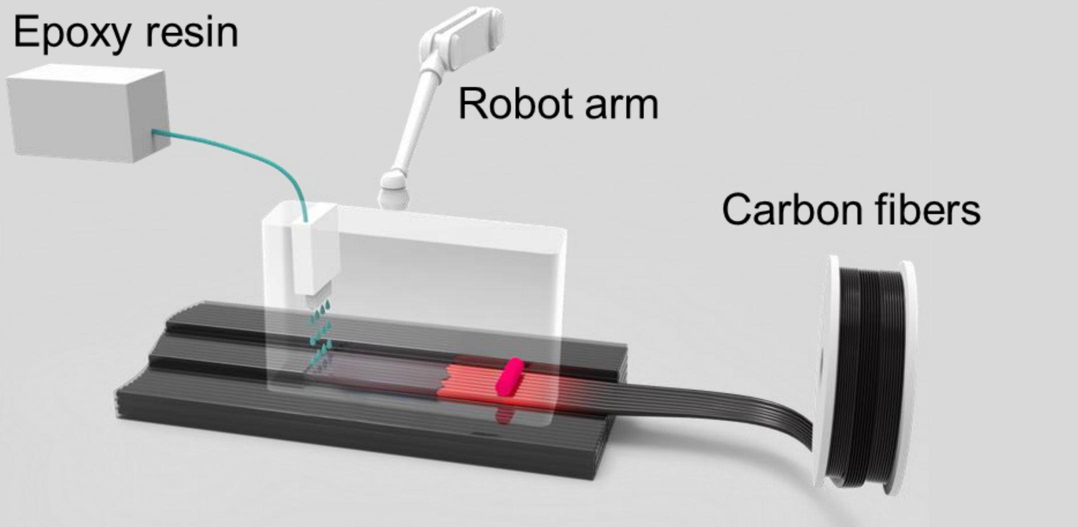
AREVO

Impossible Objects

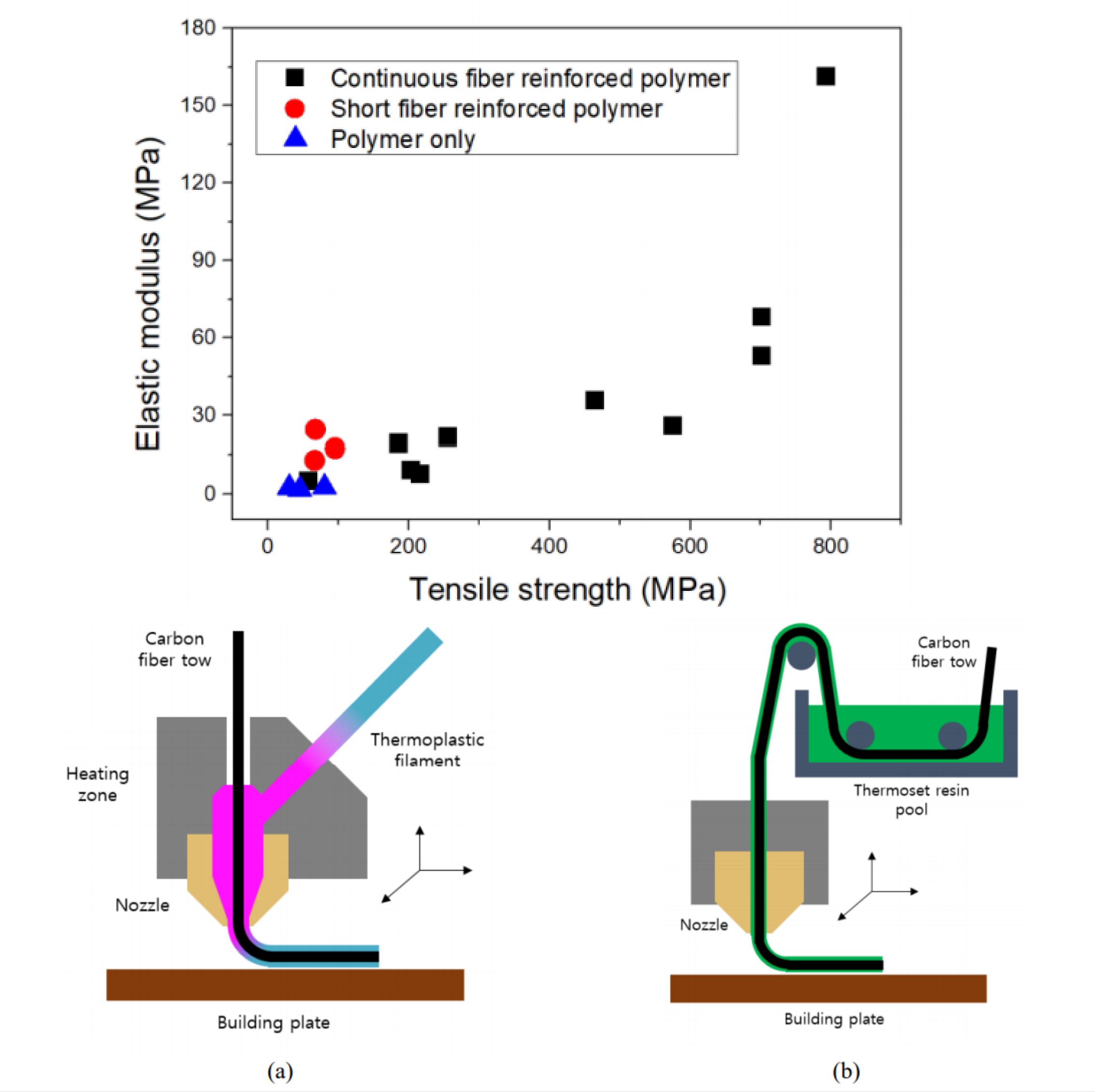
Continuous Composites

Desktop Metal

ARRIS COMPOSITES



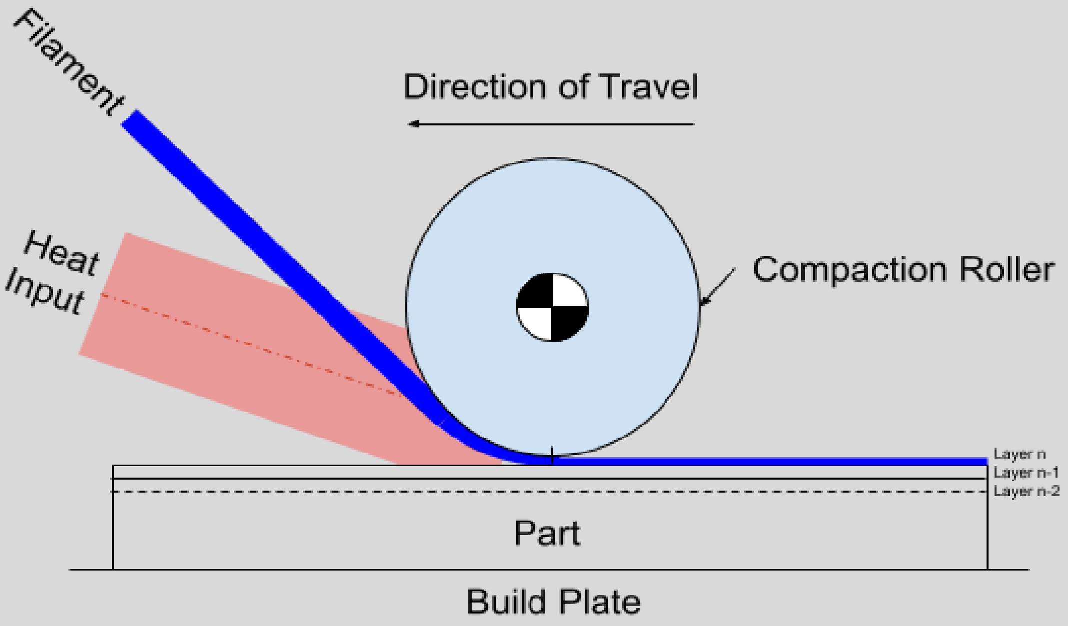
Localized in-plane thermal assisted (LITA) 3D printer by Dr. Kun Fu from Univ. of Delaware

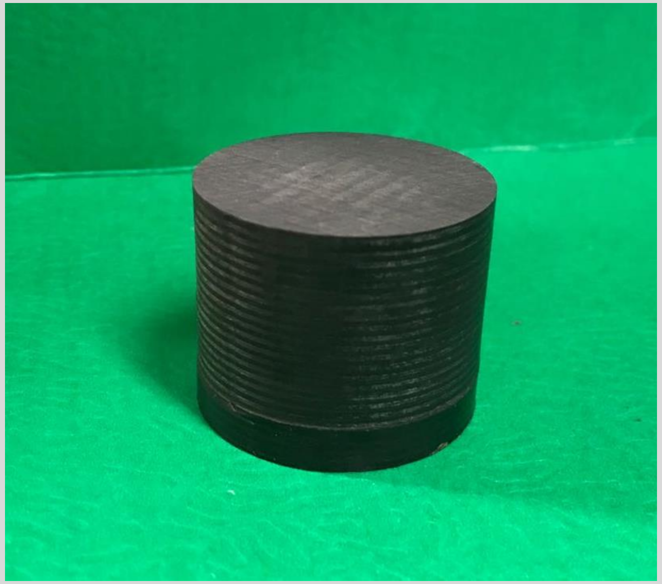


An, Y., & Yu, W. R. (2019, July). Three-dimensional printing of continuous carbon fiber-reinforced shape memory polymer composites. In *AIP Conference Proceedings* (Vol. 2113, No. 1, p. 020008).

Technical Approach

- In this study, a **Directed Energy Deposition (DED)** printer developed by Arevo was used to fabricate **continuous carbon fiber-reinforced PEEK composites**. This type of AM technique allows manufacturing of composites with **high fiber volume (~50 vol.%)** and **low porosity**.
- In order to obtain the cylindrical test models for the OTB, the printed panels were cut into 30 mm diameter cylinders by water jet cutting.

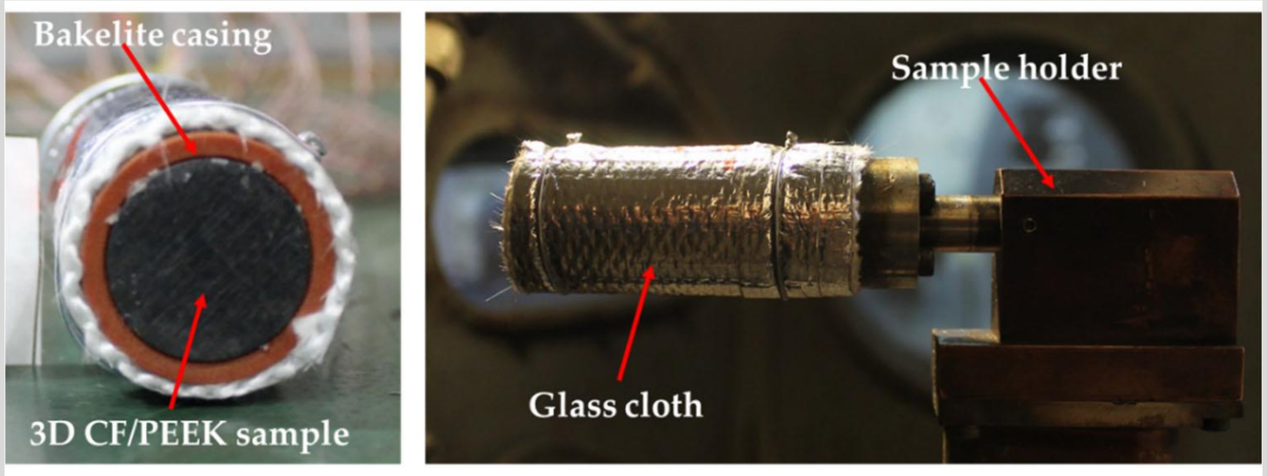


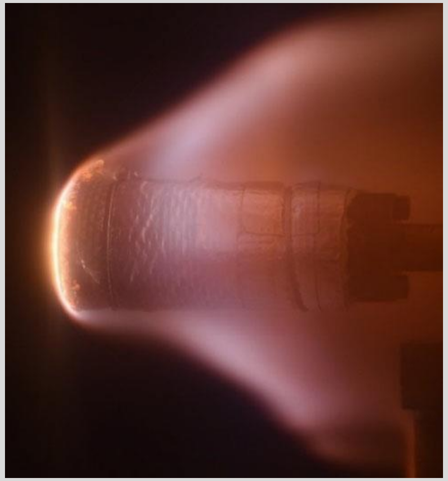


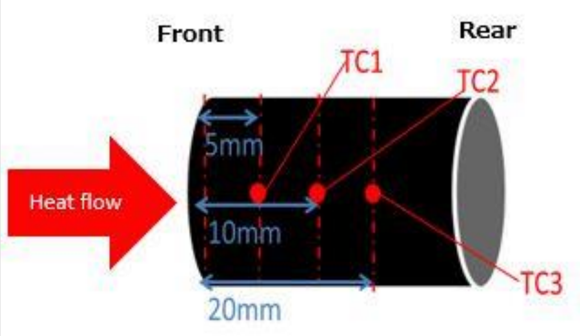
Literature Review

KAI

- In May, researchers from Japan published a paper of similar studies*:
- Continuous carbon fiber reinforced PEEK were 3D printed using DED.
- Arc Jet testing was performed at JAXA for ablation characterization (500W/cm^2 for 20s and 1420W/cm^2 for 10s). The Arc jet test models are 20mm in diameter and 30mm in thickness.



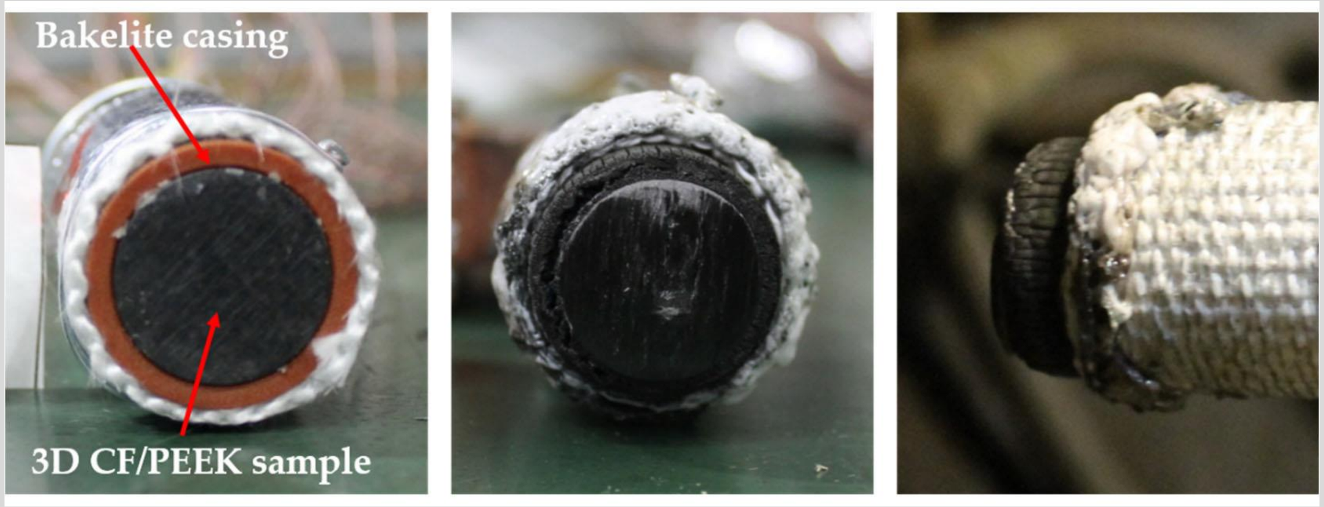


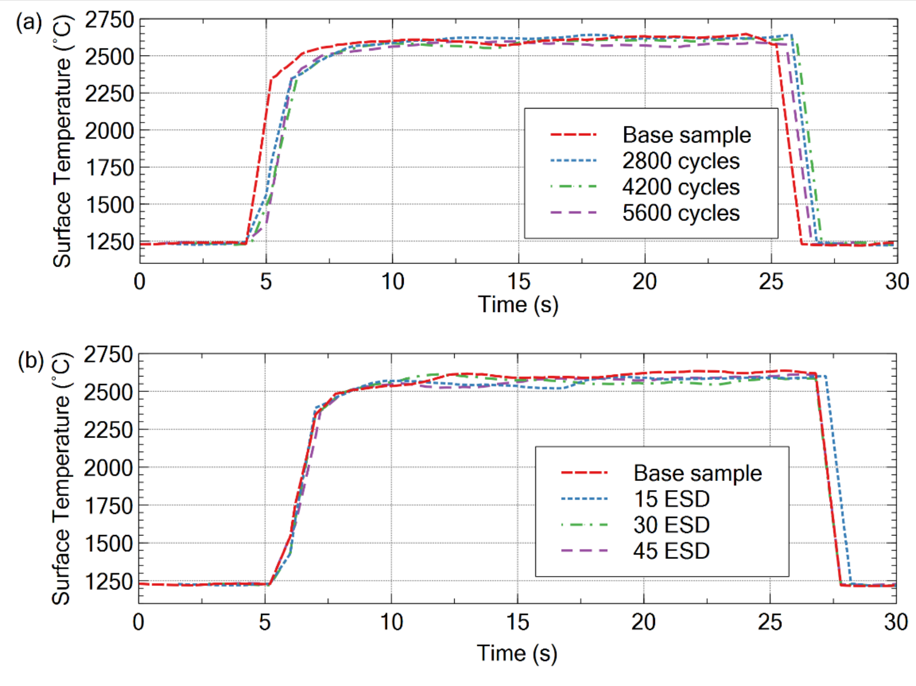


* Abdullah, F., Okuyama, K. I., Morimitsu, A., & Yamagata, N. (2020). Effects of Thermal Cycle and Ultraviolet Radiation on 3D Printed Carbon Fiber/Polyether Ether Ketone Ablator. *Aerospace*, *7*(7), 95.

Literature Review

- Before ablation testing, samples were exposed to different thermal cycles and UV radiation that simulate the space environment. Tensile tests were also reported.
- The tested specimens experienced surface expansion, which coincides with our previous test results. Thermally cycled and UV irradiated samples show less expansion.



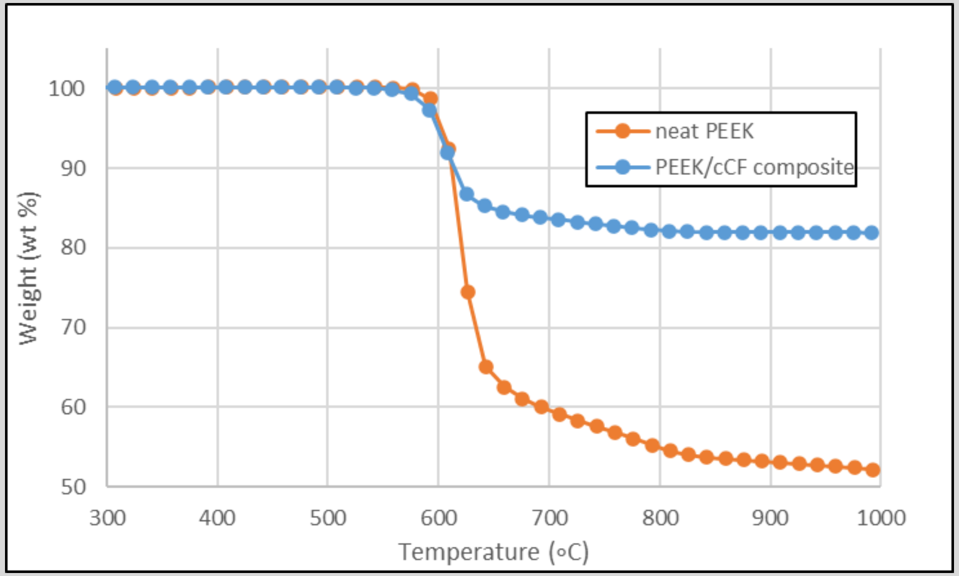


Project Objective

- The purpose of this study is to evaluate the DED printed continuous carbon fiber reinforced PEEK composite for **thermal, mechanical, flammability,** and **ablation properties**.
- The printed PEEK/cCF composites were characterized using TGA for char yield and MCC to determine flammability.
- After analyzing TGA and MCC results, **oxy-acetylene test bed (OTB)** aerothermal ablation testing will be implemented to evaluate the ablation performance. Furthermore, **microstructural analysis** will be performed using scanning electron microscopy (SEM) to study the microstructures of the composite and its charred specimens.

Preliminary Results: TGA

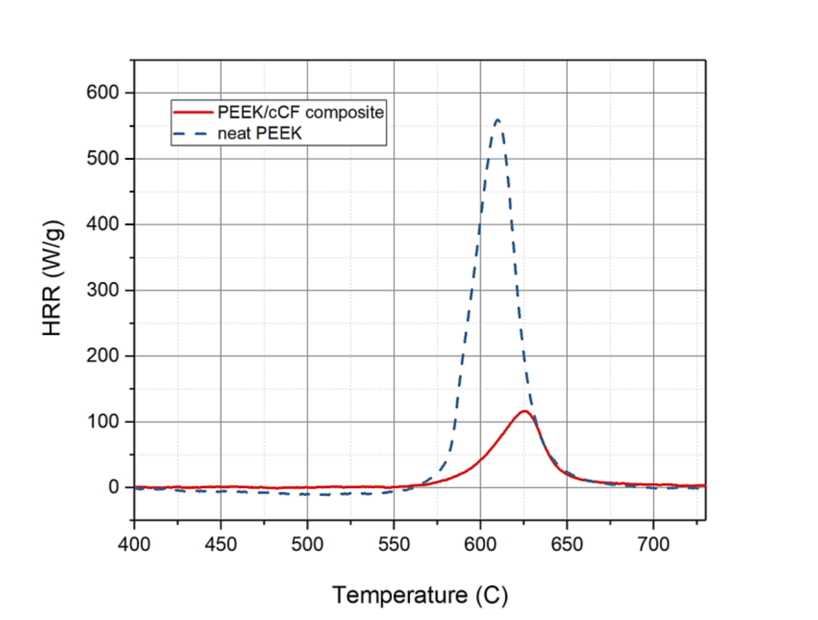
- TGA mass loss curves of neat PEEK and the PEEK/cCF composite are compared.
- They are both stable up to 550℃ followed by a quick single step decomposition process at around 600℃.
- Due to the high carbon fiber content of the PEEK/cCF composite, the resulting char yield of the composite samples is significantly higher than the neat polymer control. The PEEK/cCF composite have **81.9 wt.%** char yield at 1,000C whereas the neat polymer has **52.0 wt.%.**

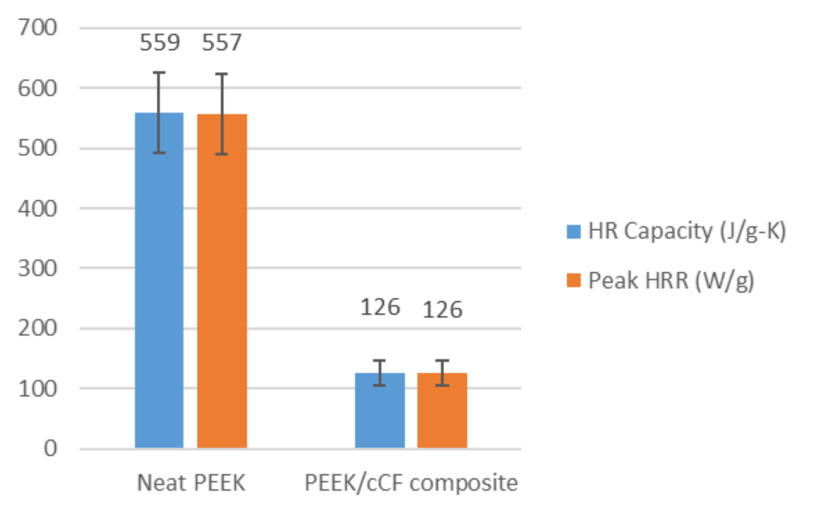


Tested in Nitrogen at 20 ℃ /min up to 1000℃

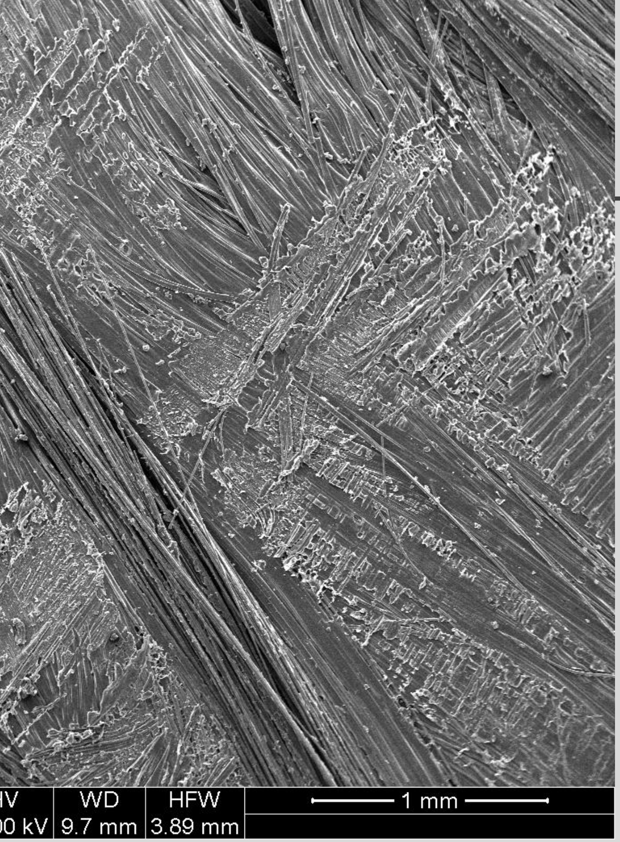
Preliminary Results: MCC

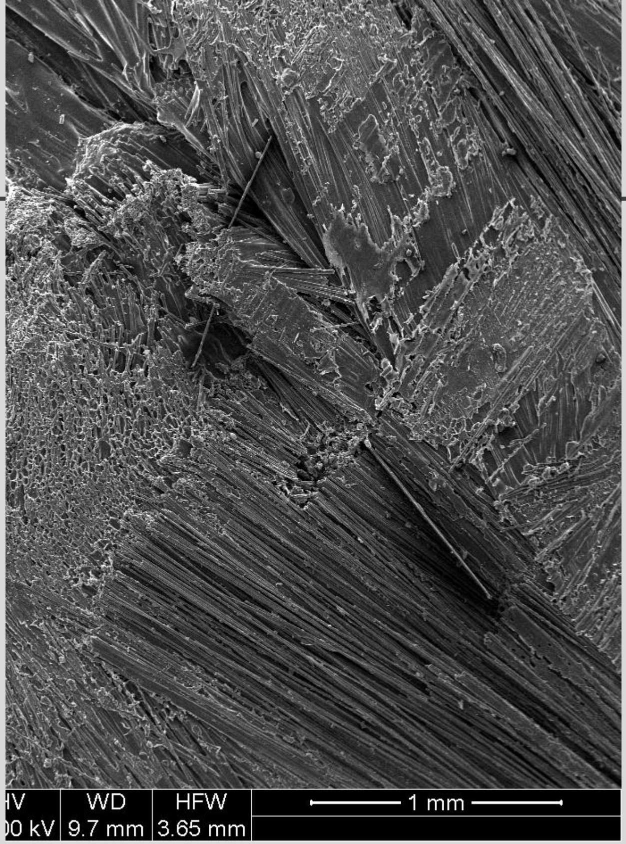
- Based on the MCC data, the PEEK/CF composite exhibits significantly lower HR Capacity and Peak HRR than the neat PEEK.
- This significant difference between the two materials is attributed to the addition of 50 vol.% of carbon fiber in the composite material. B
- Different from the TGA results, the addition of carbon fibers not only greatly reduced the peak heat release rate but also shifted the peak heat release temperature to higher values.

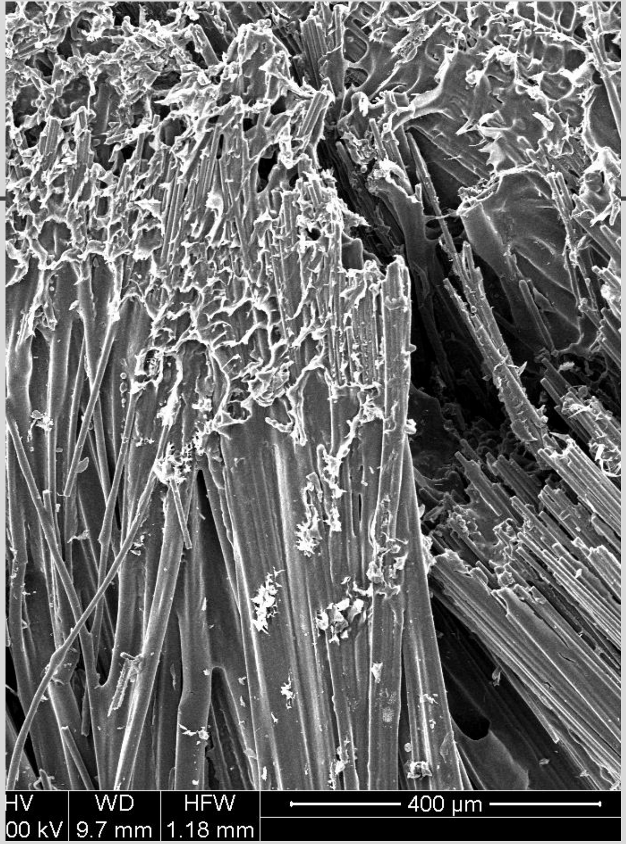


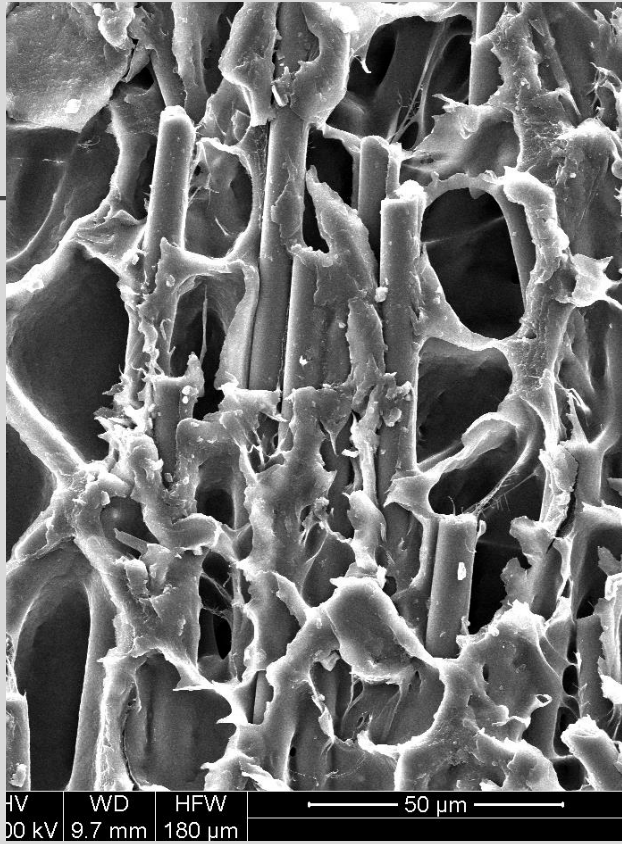


Heating rate: 1 ℃ /s, max temp: 750℃



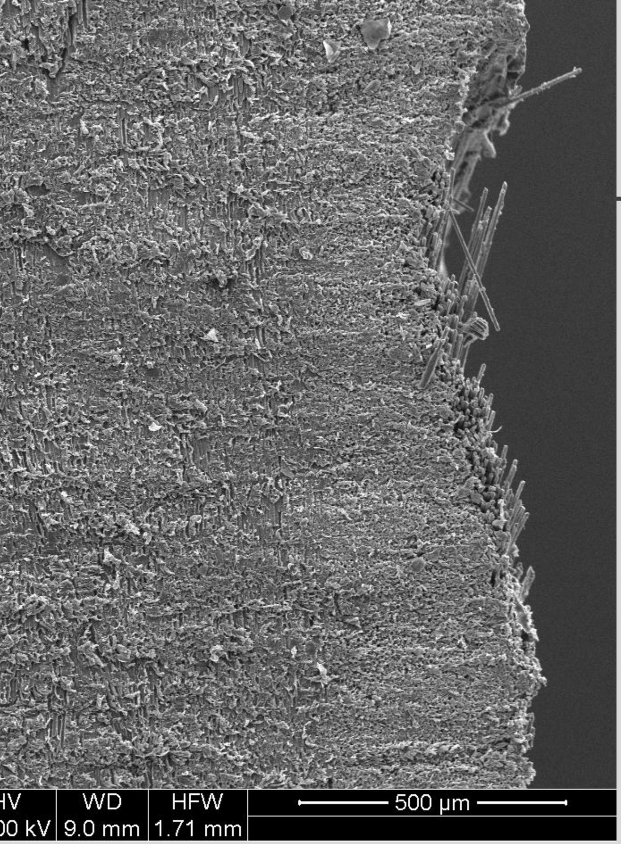


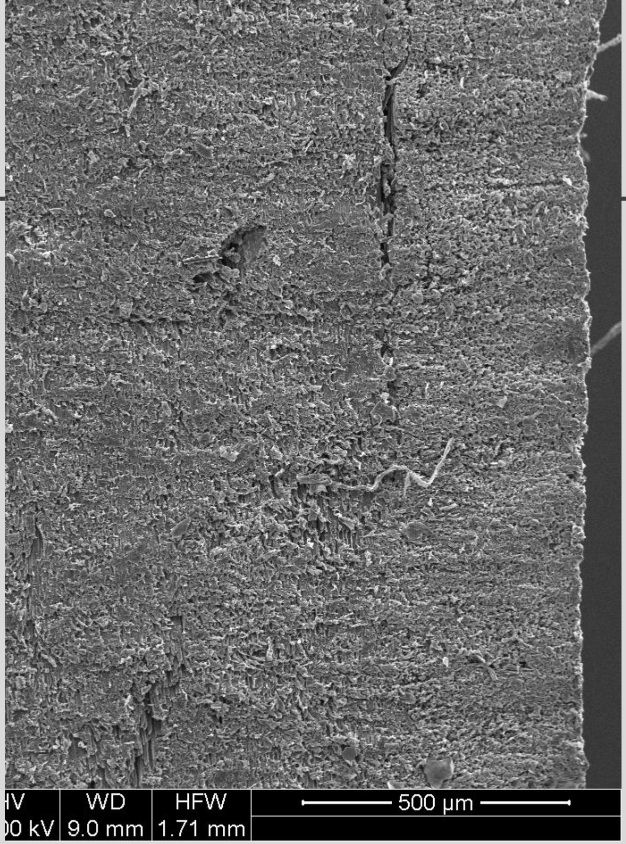


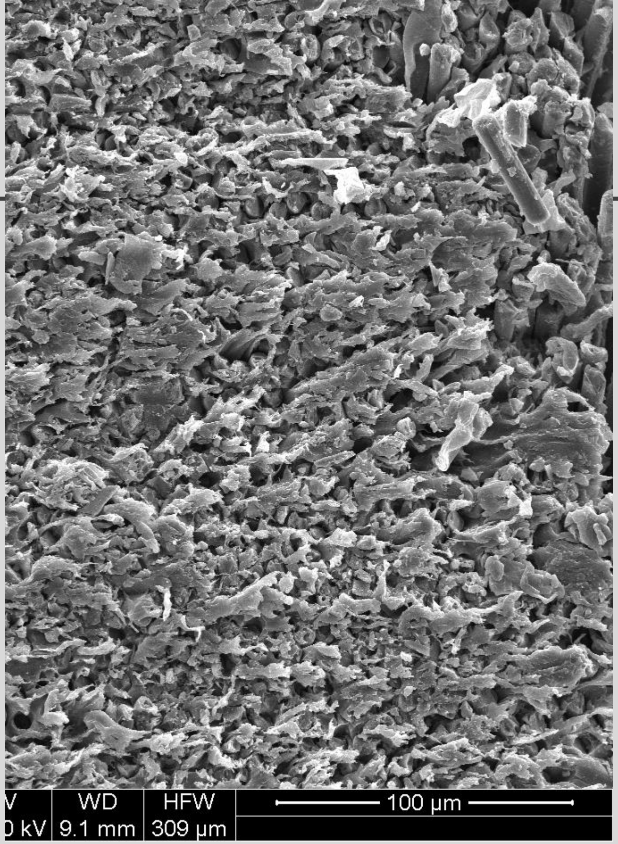


Preliminary Results: SEM

- Surface of DED printed OTB test models







Preliminary Results: SEM

- Cross section of OTB test models

Preliminary Results: Mechanical Properties

Sample	Strength (MPa)	Std (MPa)	Modulus (GPa)	Std (GPa)
Tensile UD (0)*	1420	83	115	2
Tensile QI (-45/90/45/0)*	479	66	41	3
Compressive UD (0)*	712	47	100	2
Compressive QI (-45/90/45/0)*	280	26	37	2
Flexural UD (0)*	1173	64	104	1
Flexural QI (-45/90/45/0)*	492	54	31	2
Tensile (0/90)	653	20	60	7
Compressive (0/90)	338	20	/	/
Short Beam Shear (0/90)	34	1	/	/

* Data from Zhang, Danning & Rudolph, Natalie & Woytowitz, Peter. (2019). Reliable Optimized Structures with High Performance Continuous Fiber Thermoplastic Composites From Additive Manufacturing (AM). 10.33599/nasampe/s.19.1396.

Ongoing work

- Proposed OTB test conditions:

Sample ID	Heat flux (W/cm^2)	Duration (s)
1	100	60
2*	100	180
3*	200	60
4*	500	30
5*	500	60

Mass loss, recession/char expansion, surface temperature, backside heat-soaked temperature and char morphology will be measured and characterized.

* Recommended test conditions by Timothy Dominick from Northrop Grumman Corporation

Summary

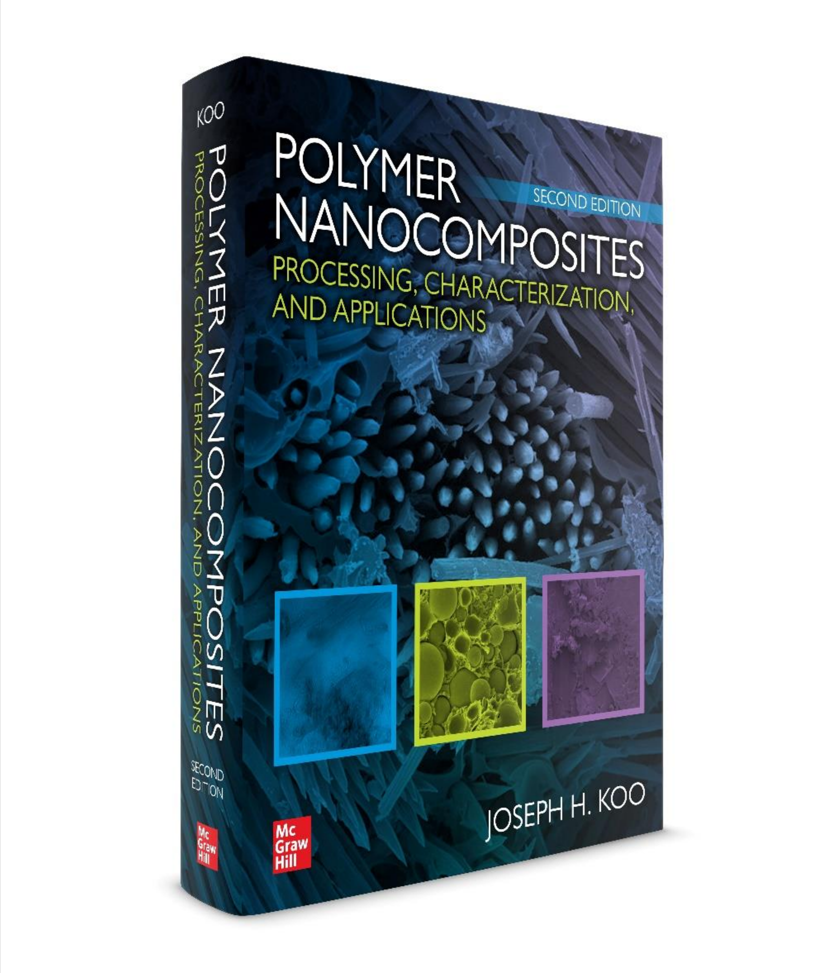
- Continuous carbon fiber reinforced PEEK composites were 3D printed using **Directed Energy Deposition** (DED) process.
- The printed composite samples show **high char yield** of 81.9 wt.% at 1000°C.
- From the MCC data, the PEEK/cCF composite exhibits greatly **enhanced flame-resistant properties** which is a good indication for the ablation testing.
- **Tensile** and **flexural** properties of the printed PEEK/cCF composite at different fiber orientations are compared.
- Experimental results from the **OTB aerothermal ablation tests** will provide a more complete understanding of the ablation performance of the PEEK/cCF composite materials. The team will also conduct **3D scanning** and **SEM** analyses on the post-test materials.
- The completed study will be published at 2021 AIAA SciTech (Jan. 2021).

Acknowledgements

- This research was partially funded by KAI, LLC, Austin, Texas, USA.
- The authors would like to thank Arevo for providing technical support and printing the PEEK/cCF composites.

- Thank you!
- Questions?

Polymer Nanocomposites: Processing, Characterization, and Applications, Second Edition, 2019



Up-to-date polymer nanocomposite principles, practices, and characteristics

This fully updated guide helps engineers and scientists understand and use the special properties of cutting-edge polymer nanocomposites.

Each chapter examines a different property (structural, mechanical, thermal, flammability, ablation, and electrical) and explains relevant commercial and industrial applications. Examples for a wide variety of usage include applications for spacecraft and defense vehicles, medical and dental implants, flame-retardant and conductive polymers for additive manufacturing, and fire-resistant woven and nonwoven fabrics.

Coverage includes:

- Nanotechnology and nanomaterials fundamentals
- Applications in an expansive range of industries and commercial sectors
- Processing of multifunctional polymer nanocomposites
- Structure and properties characterization
- Mechanical, thermal, flammability, ablation, electrical, and tribological properties
- Opportunities, trends, and challenges in the field

Available NOW at mhprofessional.com and Amazon.com

SEPTEMBER 2020

TEXAS
The University of Texas at Austin

CHARACTERIZATION OF ULTRA HIGH TEMPERATURE RESIN / AEROGEL COMPOSITES - PROGRESS

Steven Kim[1], Hao Wu[2], Joseph Koo[1,2]

[1] Texas Materials Institute, The University of Texas at Austin

[2] KAI, LLC.

Agenda

- Project Statement
- Background
- Methodology
- Prelim. Thermogravimetric Analysis (TGA)
- Further Analysis
- Conclusions & Future Works
- Acknowledgements

Project Statement

- Establish the processing method and evaluate the performance of a novel polysiloxane-aerogel composite to optimize its potential application in comparison to existing ablative alternatives.

TPS Background

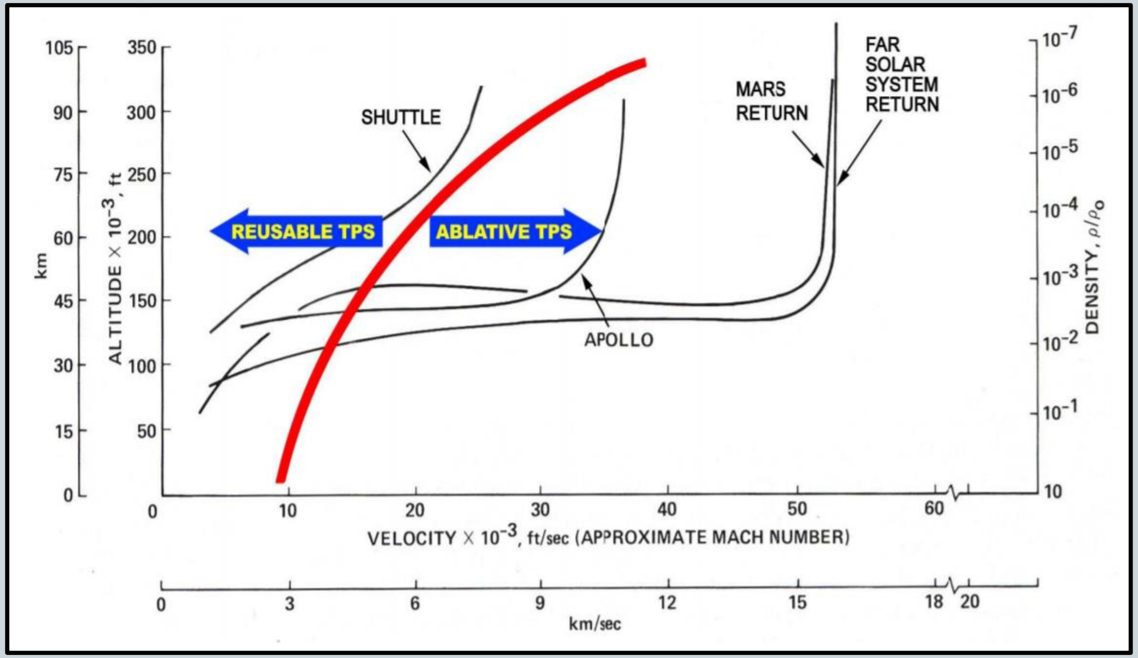
Purpose

Protect spacecraft from aerodynamic heating

Challenge

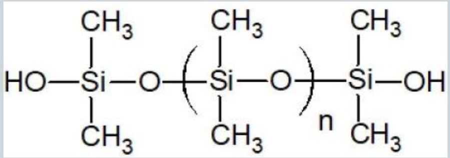
Varying mission requirements for TPS

- **Steep entry**
  - high heat fluxes, pressure & deceleration loads
  - low heat loads
- **Shallow entry**
  - low heat fluxes, pressure & deceleration loads
  - higher heat load than steep entries

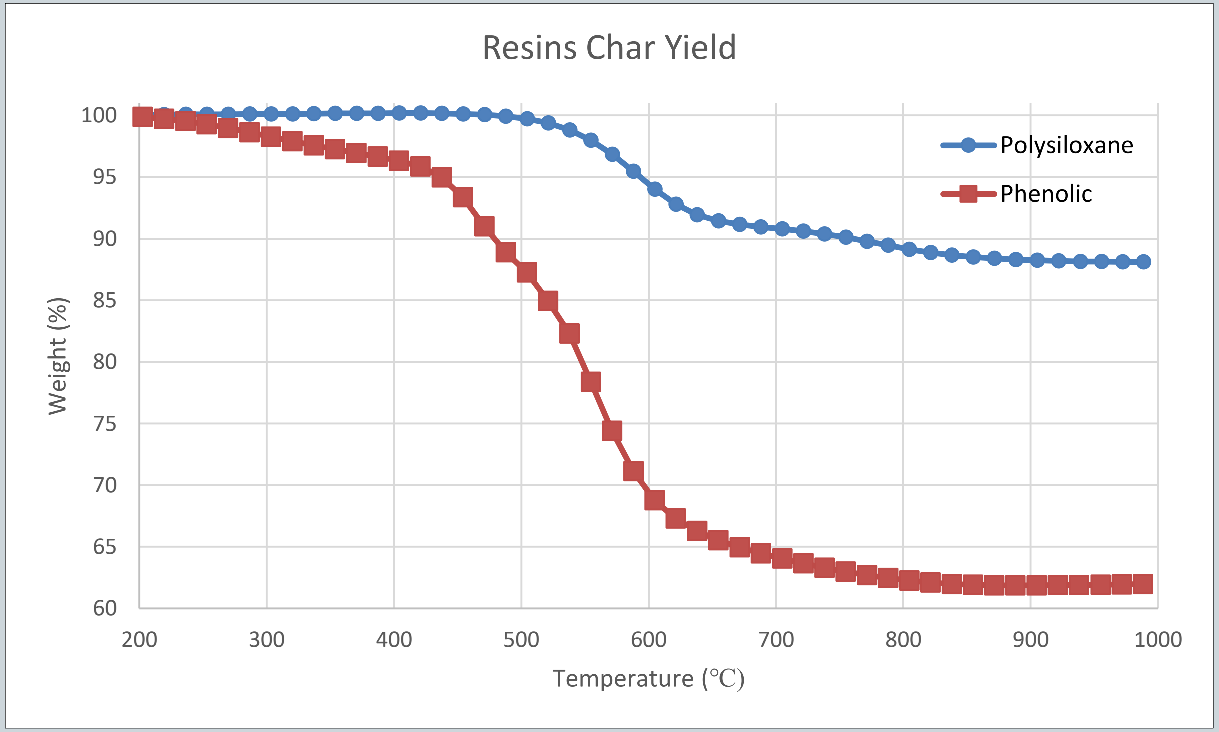


Cite: Johnson, S. M. (2012). Thermal protection materials: development, characterization and evaluation. NASA.

Polysiloxane Background



- Thermoset resin
- Silicon-oxygen backbone with organic groups attached to the silicon atoms
- Highly effective ablative
- Thermal stability showed improvement over phenolic resin (~88%)

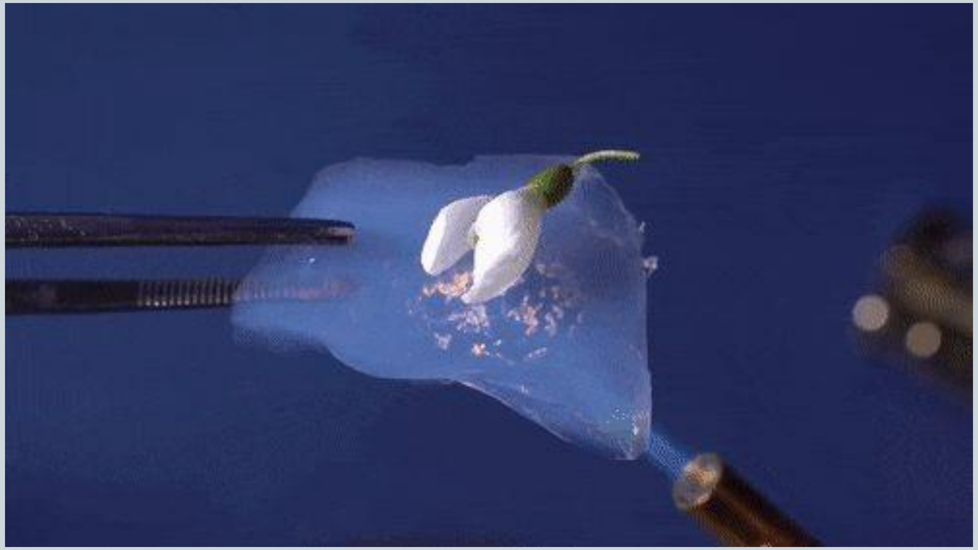


TGA in N2 at 20℃/min up to 1000℃

Aerogel Background

- A synthetic porous ultralight material derived from a gel, in which the liquid component for the gel has been replaced with a gas (99.8% air)

Poor Mechanical Strength



Excellent Thermal Insulation

[4] Barrios, E., Fox, D., Li Sip, Y. Y., Catarata, R., Calderon, J. E., Azim, N., … Zhai, L. (2019). Nanomaterials in Advanced, High-Performance Aerogel Composites: A Review. *Polymers*, 11(4), 726. doi:10.3390/polym11040726

Aerogel Background

- Aerogel: Enova IC3120, silica aerogel, 100µm~1.2mm
- Silica aerogel cause for poor mechanical strength
- Same component as UHTR
  - Should be chemically compatible

Concentrations

Concentration (vol %, ±2)	Concentration (wt %, ±0.1)	Estimated Density ($g*cm^{-3}$)	Feasibility
50	10.5	0.62	N
40	6.9	0.71	Y
10	0.5	1.0	Y

Mixing Methods

- Preheat to 90C to lower viscosity
- Before visible dispersion
  - 2000 rpm
  - 101 kPa
  - 2 min

- After visible dispersion
  - 2000 rpm
  - 10 kPa
  - 2 min
  - Repeated after adding catalyst

Curing Method

Curing Profiles

- Cure Test 1
  - Phase 1: 150°C for 4hr
- Cure Test 2
  - Phase 1: 150°C for 4hr
    - Phase 2: 250°C for 4hr

Fully Cured?

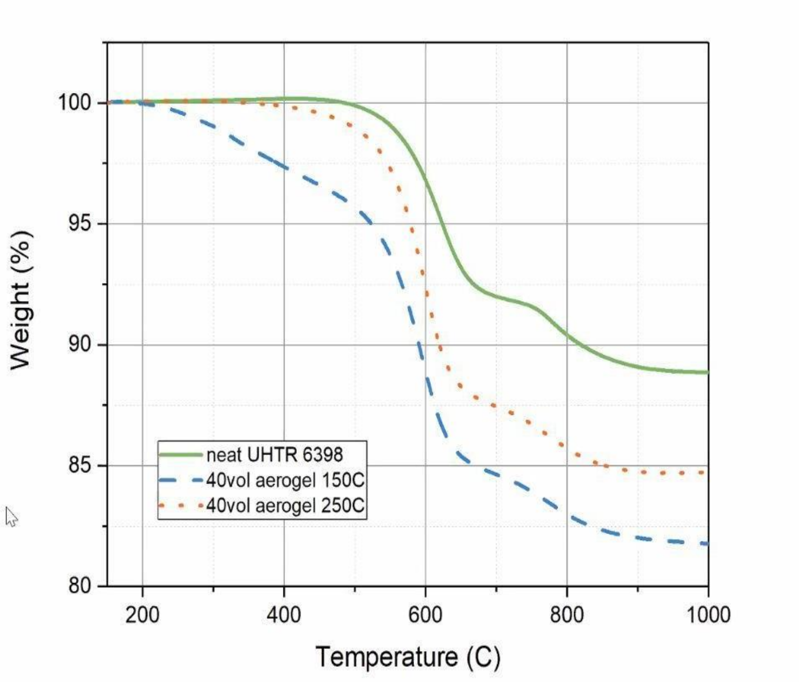
10% Aerogel by Volume

40% Aerogel by Volume

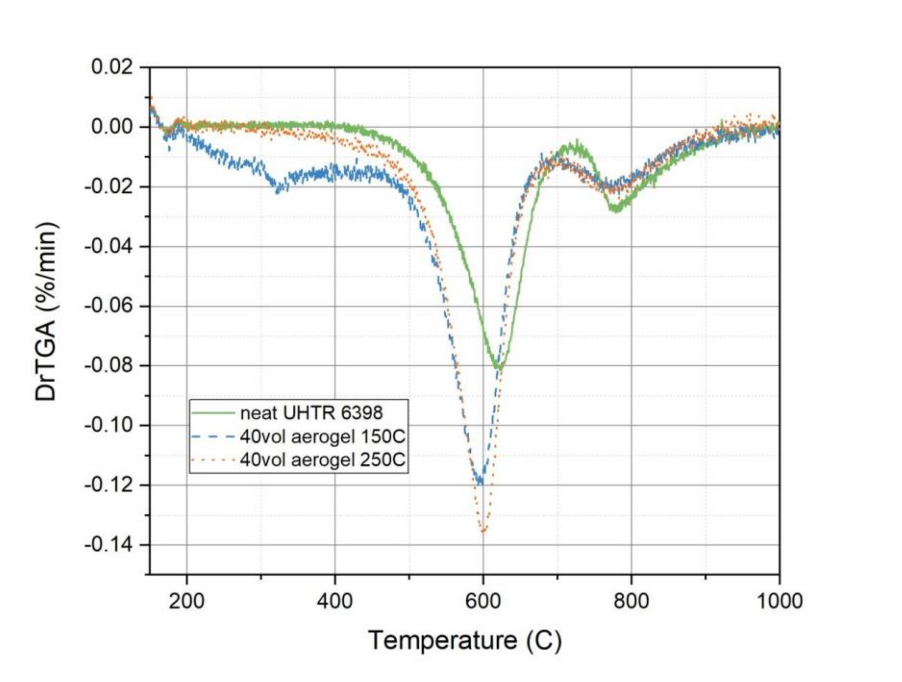
*Cured for 4 hours at 150°C

Preliminary TGA Results

- Ideal: similar thermal stability to neat UHTR (cured at 350°C)
- Sample cured at 250°C noticeably closer to fully cured system



Curing Conditions TGATest



Curing Conditions DrTGA

Curing Profile Study

- Cured for 3 hours at varying temperatures
- 10 vol.%, 20 vol.%, and 40vol.% Aerogel loadings

225°C, 3 hours (Control)			
[redacted]	10% Load	20% Load	40% Load
Glass Vial Mass (g)	10.336	10.345	10.286
Vial+UHTR Mass (g)	14.368	13.989	14.074
UHTR Mass (g)	4.032	3.644	3.788
UHTR Volume (mL)	3.360	3.037	3.157
Aerogel Volume (mL)	0.373	0.759	2.104
Aerogel Mass (g)	0.050	0.102	0.284
Catalyst Mass (g)	0.040	0.036	0.038

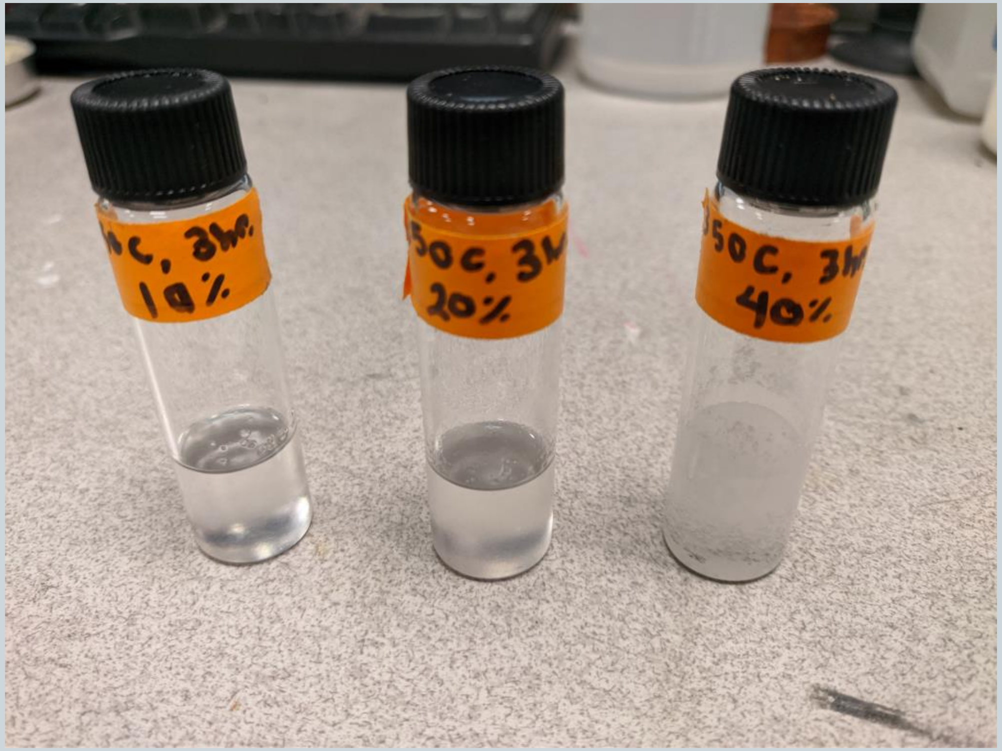
300°C, 3 hours			
[redacted]	10% Load	20% Load	40% Load
Glass Vial Mass (g)	10.294	10.363	10.329
Vial+UHTR Mass (g)	14.176	14.444	13.703
UHTR Mass (g)	3.882	4.081	3.374
UHTR Volume (mL)	3.235	3.401	2.812
Aerogel Volume (mL)	0.359	0.850	1.874
Aerogel Mass (g)	0.049	0.115	0.253
Catalyst Mass (g)	0.039	0.041	0.034

350°C, 3 hours			
[redacted]	10% Load	20% Load	40% Load
Glass Vial Mass (g)	10.365	10.279	10.364
Vial+UHTR Mass (g)	14.461	14.194	14.532
UHTR Mass (g)	4.096	3.915	4.168
UHTR Volume (mL)	3.413	3.263	3.473
Aerogel Volume (mL)	0.379	0.816	2.316
Aerogel Mass (g)	0.051	0.110	0.313
Catalyst Mass (g)	0.041	0.039	0.042

400°C, 3 hours			
[redacted]	10% Load	20% Load	40% Load
Glass Vial Mass (g)	10.297	10.39	10.308
Vial+UHTR Mass (g)	13.688	14.217	14.037
UHTR Mass (g)	3.391	3.827	3.729
UHTR Volume (mL)	2.826	3.189	3.108
Aerogel Volume (mL)	0.314	0.797	2.072
Aerogel Mass (g)	0.042	0.108	0.280
Catalyst Mass (g)	0.034	0.038	0.037

Curing Profile Study

- Samples post mixing
- Operational difficulties with curing oven



Conclusions & Future Works

- Up to 40 vol.% of Aerogel mixed with polysiloxane cured in two curing profiles
- Preliminary TGA showed samples were not fully cured
- New composites mixed for further analysis (10, 20, 40 vol.%)

- Resolve furnace issue
- Establish curing procedures to fully cure the composite
- Evaluate cured composite microstructure
- Determine effectiveness of composite via further thermal, ablative, and mechanical testing

Acknowledgements

Peter Haase

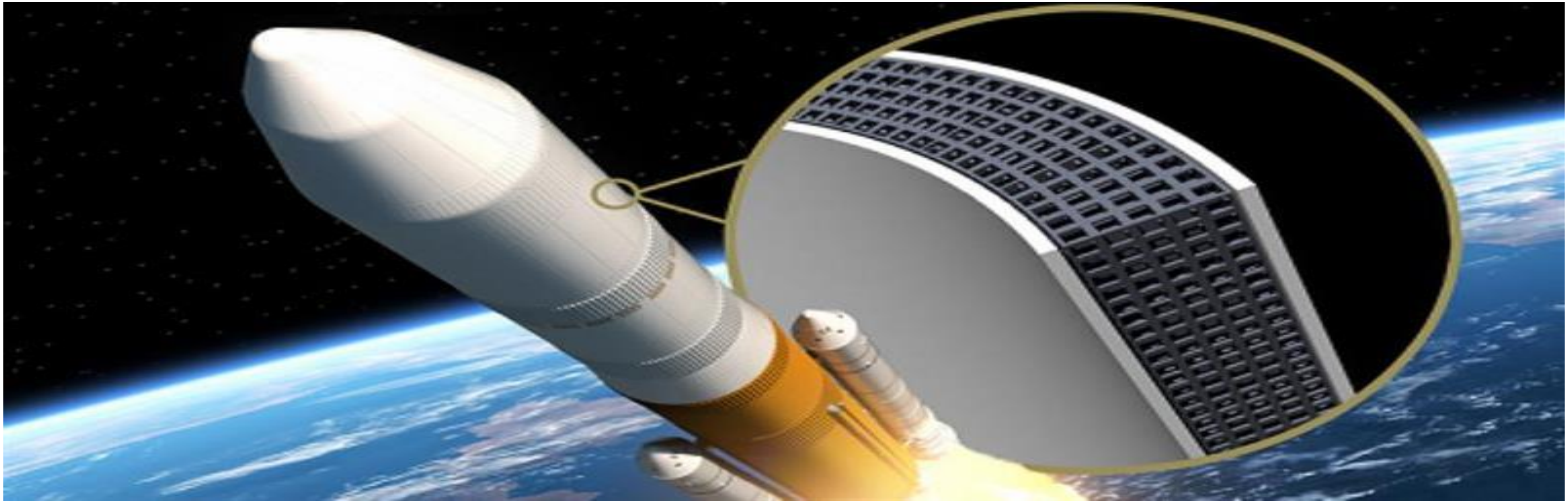
Luke Haworth

Conrad Henry

Mitchel Walker

Thank you! Questions?

September 2020



Design of Additively-Manufactured Lattice Structure for Thermal Protection System

Yu-Chuen Chang, Colin Yee, William Fahy (UT Austin, USA)

Abdullah Kafi and Stuart Bateman (RMIT, Australia)

Hao Wu and Joseph Koo (KAI, LLC, USA)

TEXAS
The University of Texas at Austin

Outline

- Research Background
- Research Motivation
- Problem Statement
- Thermal Conductivity Apparatus
- Transient Testing Apparatus
- Conclusion & Future Work

Dual-Layer TPS

Heatshield for Extreme Entry Environment Technology (HEEET)

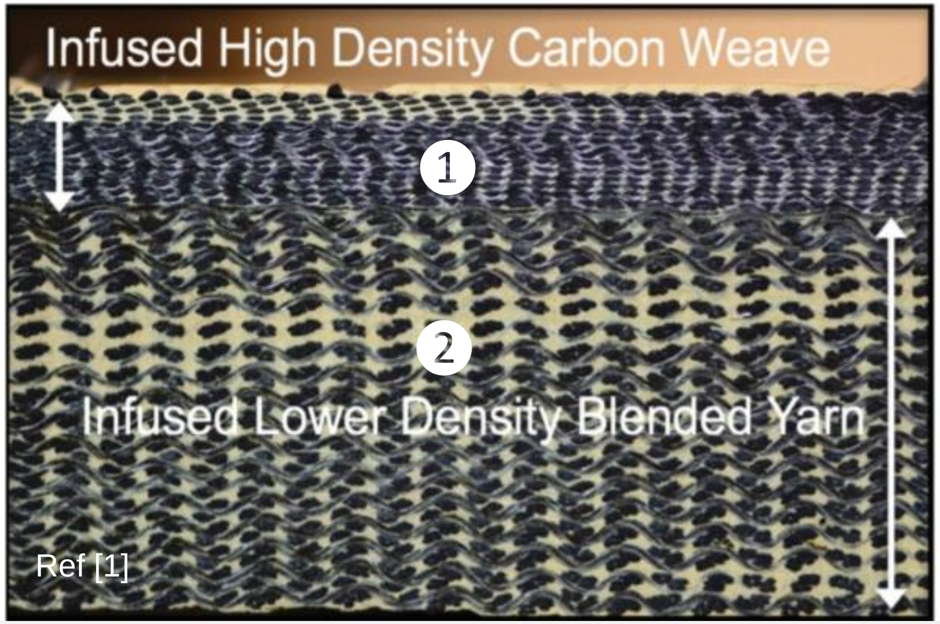
- NASA's HEEET project proposes a dual-layer approach design for TPS with weaving technology
- The dual-layer approach can vary the layer thickness and provide the ability to optimize the mass for a given mission

Proposed Dual-layer Concepts

- Dual-material approximation
- Single material with lattice structure

Table 1 Room temperature properties of carbon phenolic materials

Property	HEEET recession layer	HEEET insulating layer	Heritage carbon phenolic[a]	PICA
Density, kg/m^3	1090	820	1432	274
Porosity (volume fraction)	0.35	0.45	0	0.8
Thermal conductivity, $W/(m \cdot K)$[b]	0.42	0.23	1.27	0.17
Thermal diffusivity, mm^2/s[b]	0.48	0.27	1.0	0.69



❶ **Recession Layer (RL)**
Expose to the extreme environment of entry

❷ **Insulating Layer (IL)**
Limit the payload temperature

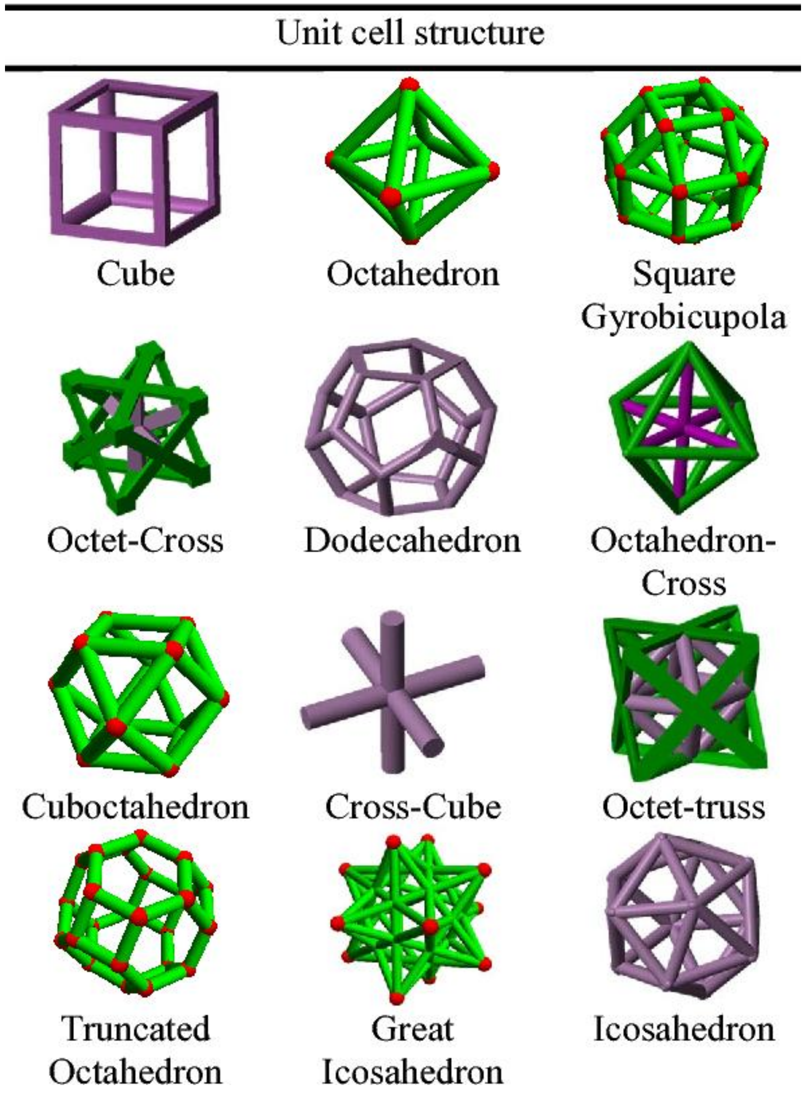
Multi-functional Lattice structure

Development

- Additive manufacturing unlock the capability to create lattice structure
- Lattice structure utilizes structure to vary the global material properties for multi-functional purpose

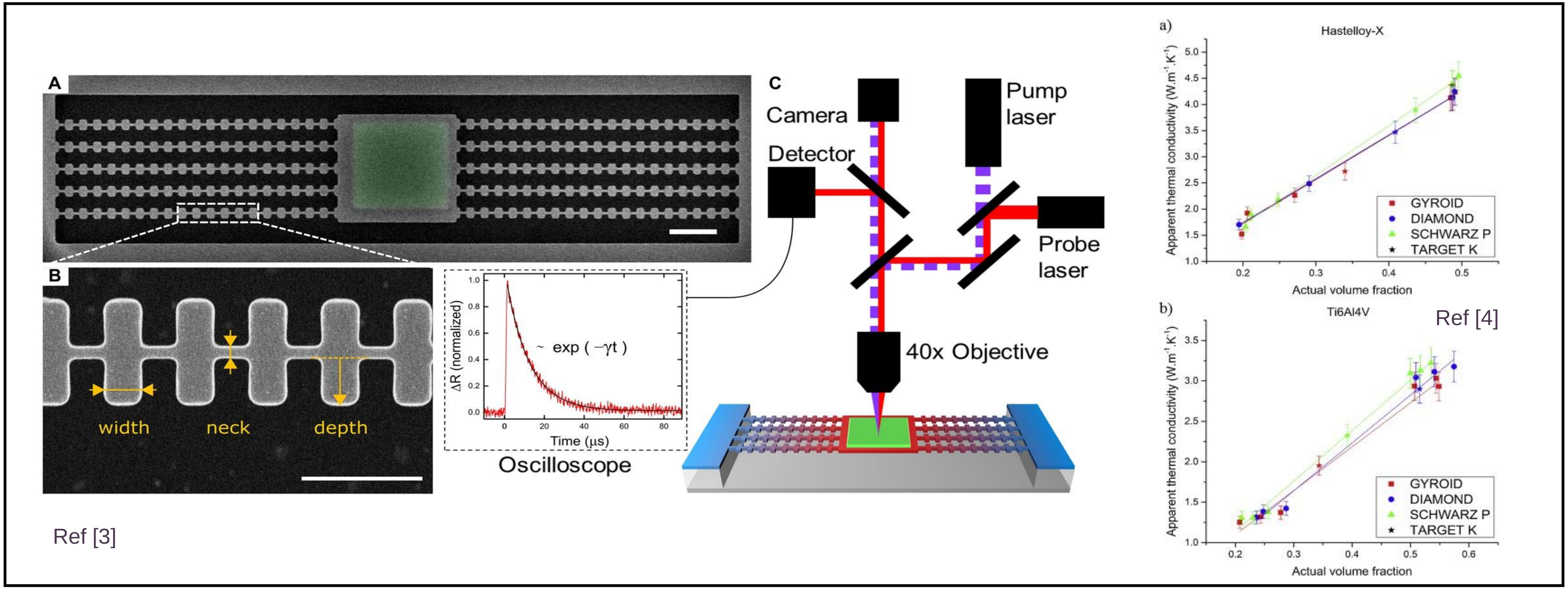
Opportunities

- Light weight structure
- Shock and impact absorption
- Thermal properties management
- Electronic properties management

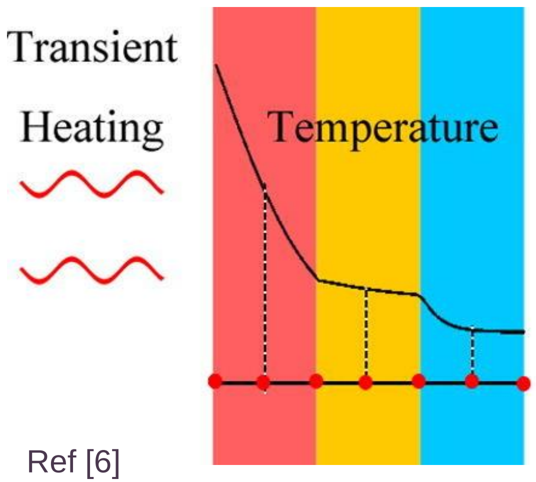


Ref [2]

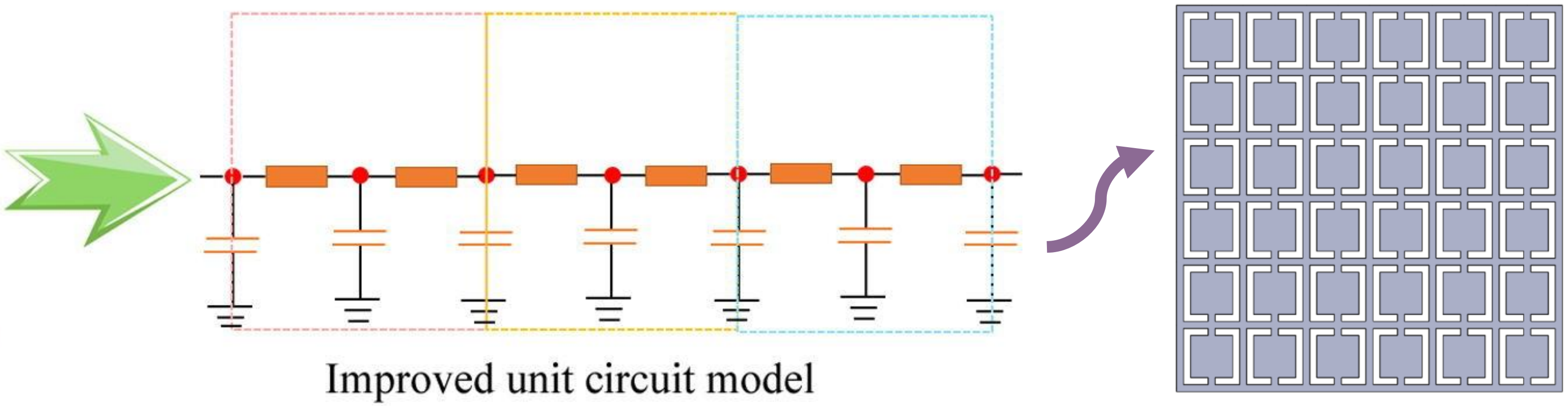
Structure for thermal management



- **Transient**- Marie et al (2018) reports the fish-bone nano-wire has larger temperature decay time
- **Static** - Catchpole-Smith (2019) and Belcher (2019) report that lattice structure has lower thermal conductivity



Ref [6]

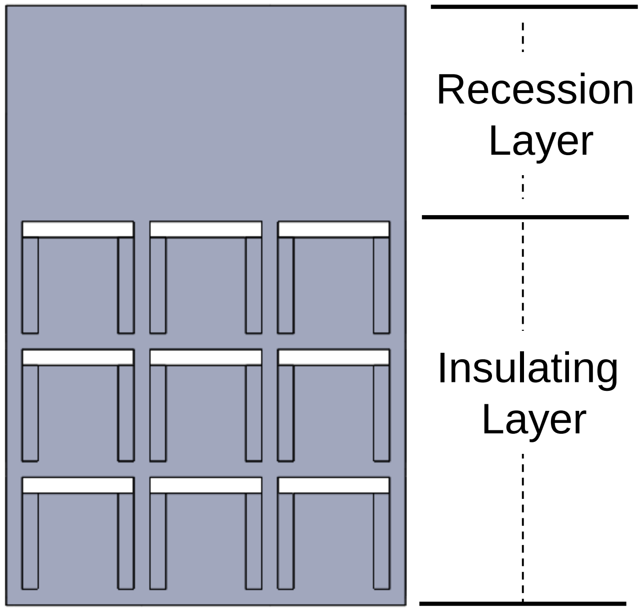


Research Motivation

- Heat transfer of thermal protection system can be simplified as 1D transient model
- Fishbone structure shows the potential to serve **an extra thermal capacitance** and slow heating rate
- For common lattice structure, thermal conductivity (k) decreases with density (ρ)
- To minimize $\boldsymbol{\alpha} = \frac{\boldsymbol{k}}{\boldsymbol{\rho C_p}}$, it is necessary to find the trade-off of $\frac{\boldsymbol{k}}{\boldsymbol{\rho}}$

Problem Statement

Investigate the feasibility of using fish-bone structure to enhance the insulation performance of Thermal Protection System (TPS) by **evaluating the trend of k/ρ**

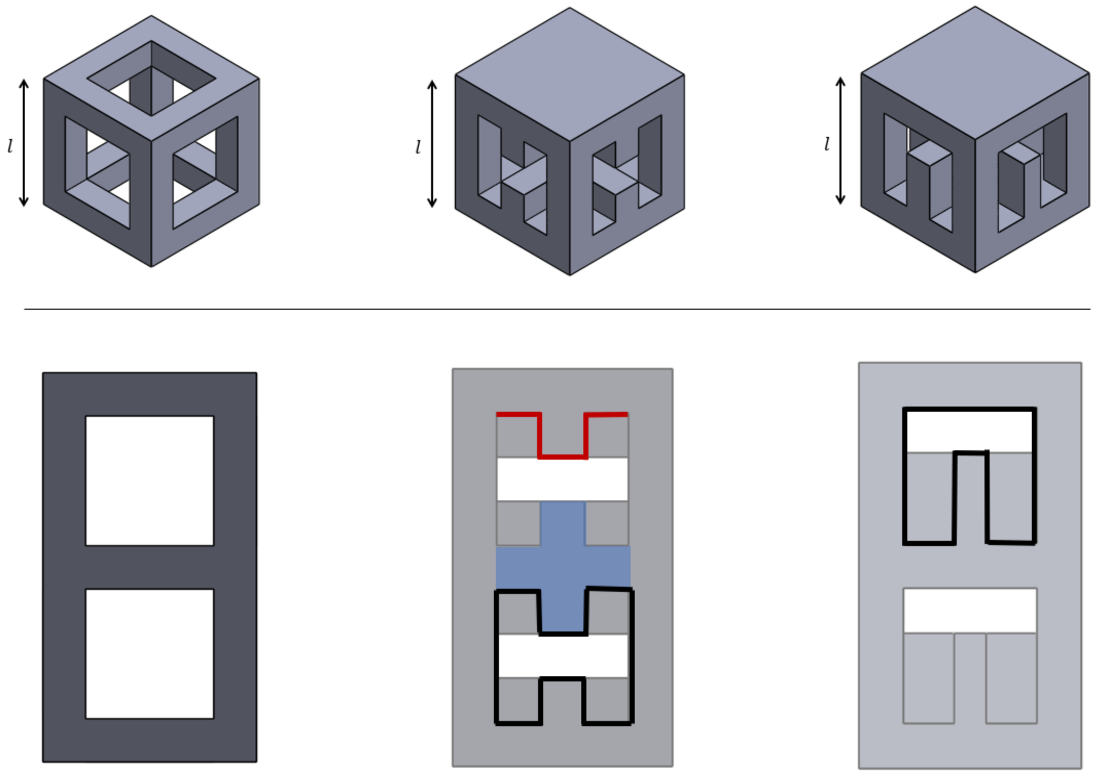


Tailor material properties without using adhesive/bonding

Easier to predict global material properties

Decrease the weight and thermal diffusivity of TPS material

Structure Topology

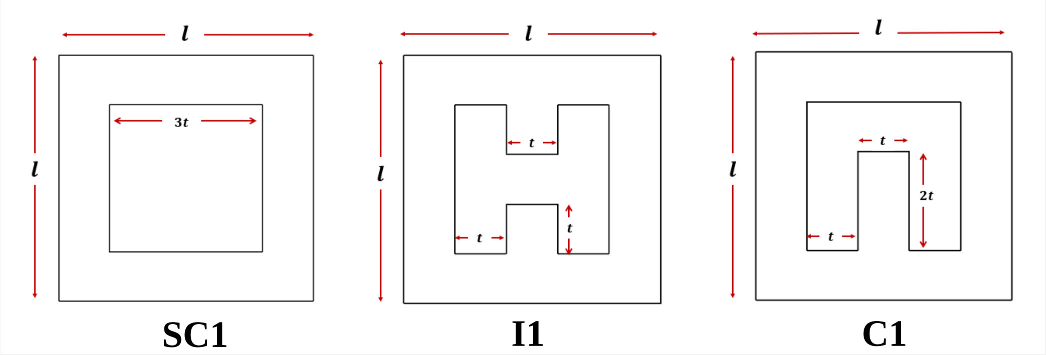


(a) Simple Cube (b) I-Channel (c) C-Channel

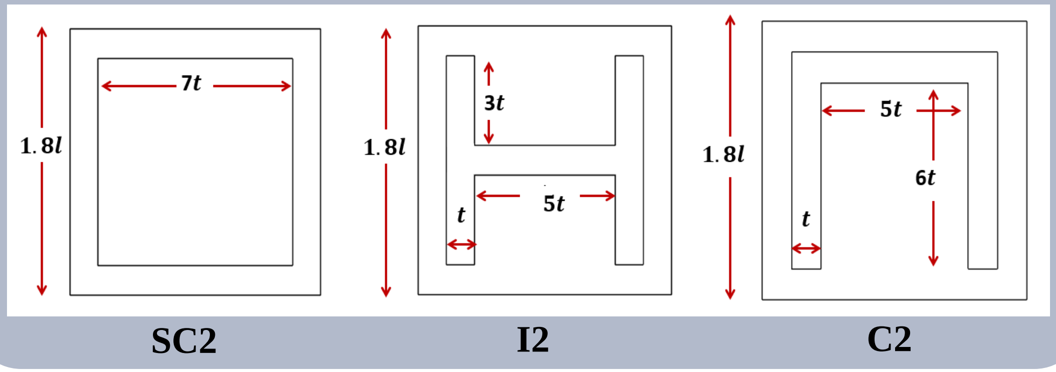
Red line highlights possible fails printing due to over-hange
Blue area mimics fish-bone structure

First Design Iteration

$l = 4$ mm, $t = 0.8$ mm



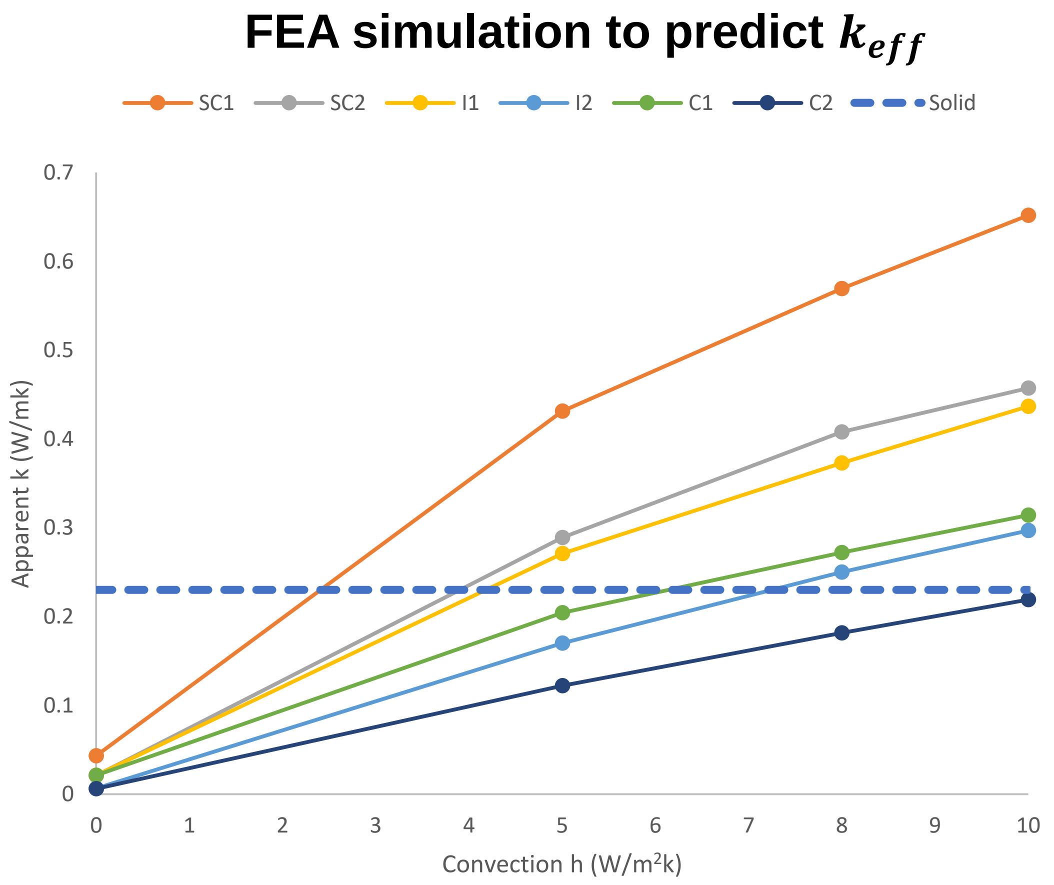
Second Design Iteration



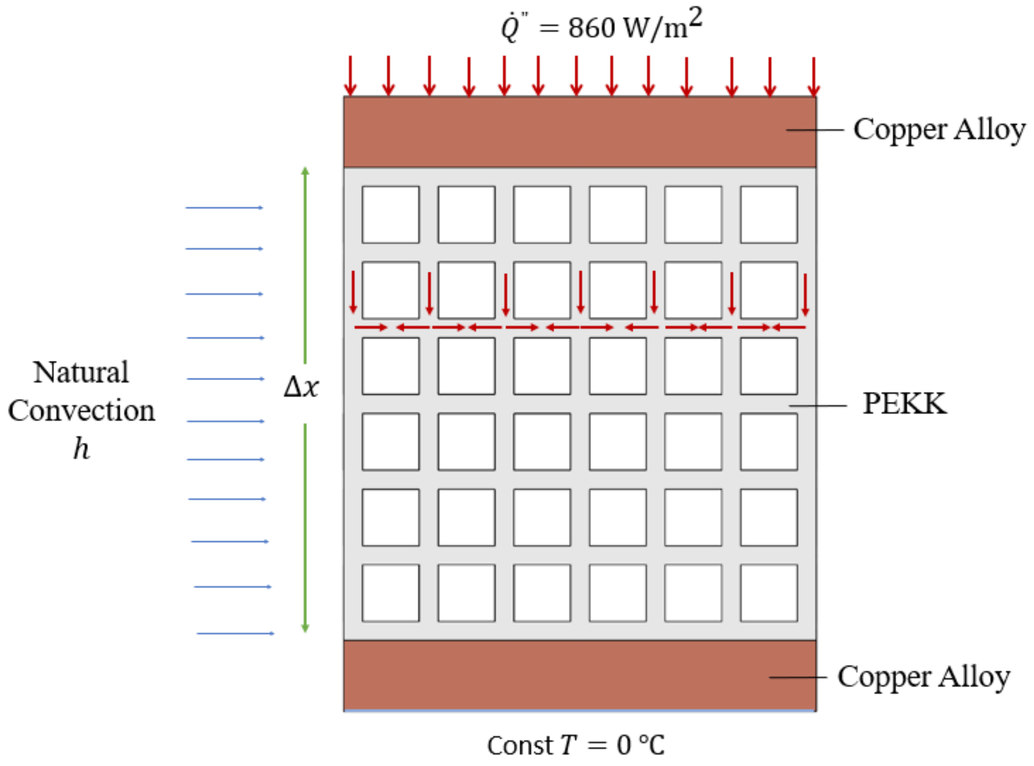
Convectional effect Investigation

- ANSYS steady-state thermal simulation
- Guarded hot plate apparatus (ASTM C177)

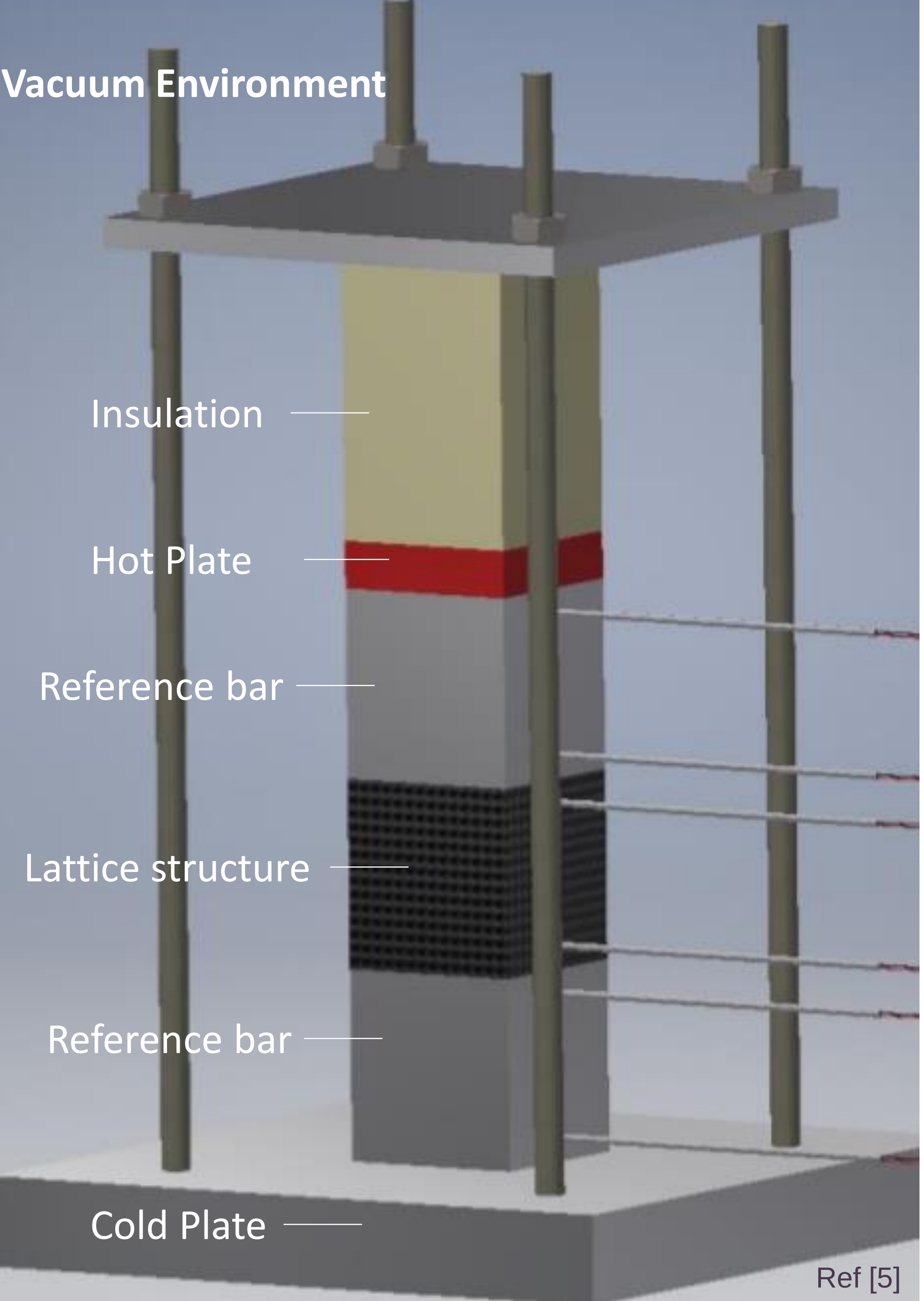
$$k_{eff} = \frac{\dot{Q}'' \cdot \Delta x}{\Delta T}$$



SC: Simple Cube I: I-Channel C: C-Channel
#: Redesign iteration



Sample size: 20x20x20 mm



Thermal Conductivity Setup

Challenge with lattice structure

- No standard thermal conductivity measurement for inhomogeneous materials
- Convectional effect
- Sample sizes

Existing Setup

Belcher (2019) from NASA LaRC develops thermal conductivity setup for lattice structure by referencing

- ASTM E1225-13
- ASTM D5470-17

and suggests $\alpha \propto \frac{k}{\rho}$ for lattice structure

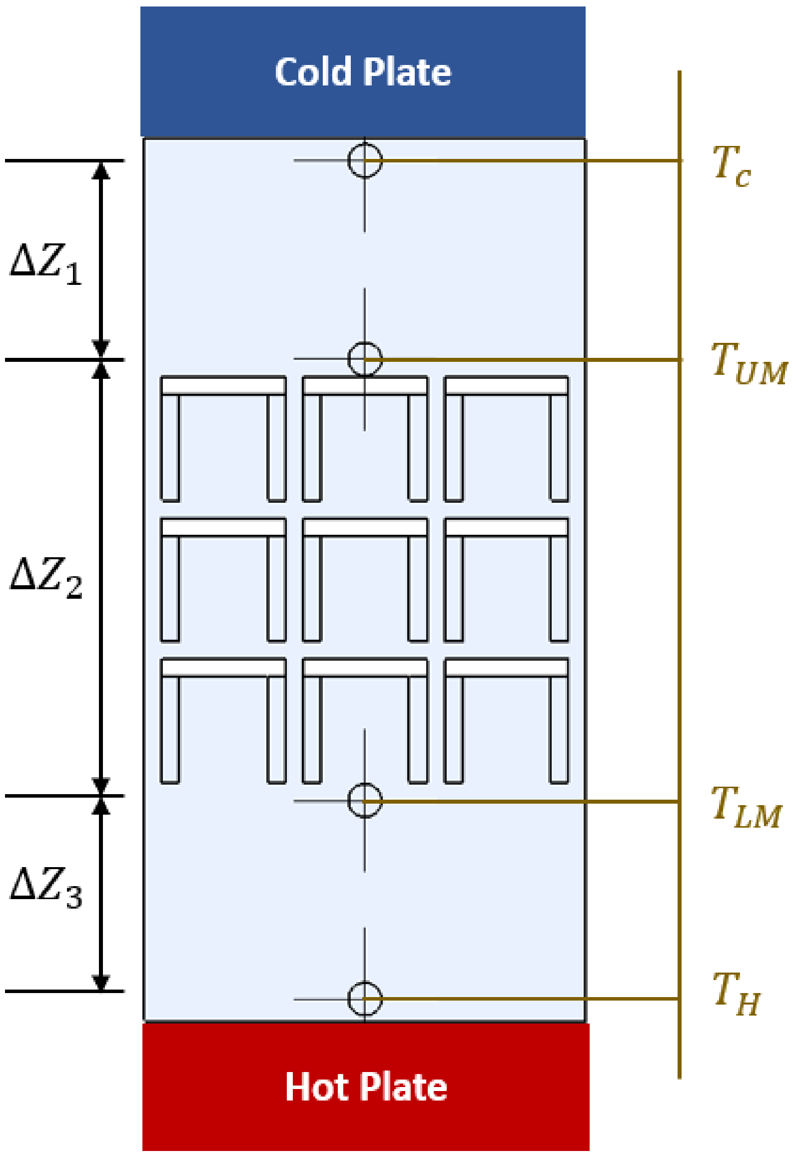
Modified Thermal Conductivity Setup

Notable Change

- Follow ASTM E1225-13

$$k_{eff} = \frac{\Delta Z_2}{T_{LM} - T_{UM}} \cdot \frac{k_s}{2} \cdot \left(\frac{T_H - T_{LM}}{\Delta Z_3} + \frac{T_{UM} - T_C}{\Delta Z_1} \right)$$

- Non-vacuum environment
- Combine reference bar with samples
- Current thermal conductivity from reference bar coming from database
- Surrounding with insulation material (polyurethane foam) to mimic 1D heat transfer
- Hot plate temperature is lower than glass transient temperature of material to maintain the lattice structure



Surrounding with insulating material $k \approx 0.03$ W/mK

C-Channel Sample

T_{UM}

T_{LM}

Preliminary Experimental Result

The thermal conductivity test shows the thermal performance of lattice structure compared to solids

Samples	$T_H - T_{LM}$	$T_{LM} - T_{UM}$	$T_{UM} - T_c$	$k_{eff}(\frac{W}{mK})$
Solid	7.753	30.008	9.551	0.194
Simple-Cube (SC2)	7.219	35.381	6.17	$\boxed{0.127}$
C-Channel (C2)	8.332	43.721	8.978	0.133

- Input Heat Flux: 484 W/m^2
- $\Delta Z_1 = 5$ mm , $\Delta Z_2 = 21$ mm, $\Delta Z_3 = 5$ mm

Summary of Preliminary Test

- Simple Cube has **lowest $\boldsymbol{k_{eff}}$** due to low density.
- C-channel has k_{eff} higher than simple cube but lower than solid. The density of C-channel is higher than simple cube but lower than solids, which show the potential to **decrease both the mass and thermal diffusivity** for insulating purpose.

Samples	$k_{eff}(\frac{W}{mK})$	Volume Fraction (%)	α_{eff} (mm^2/s)
Solid	0.194	100	0.125
Simple-Cube (SC2)	$\boxed{0.127}$	11.969	0.685
C-Channel (C2)	0.133	78.691	$\boxed{0.109}$

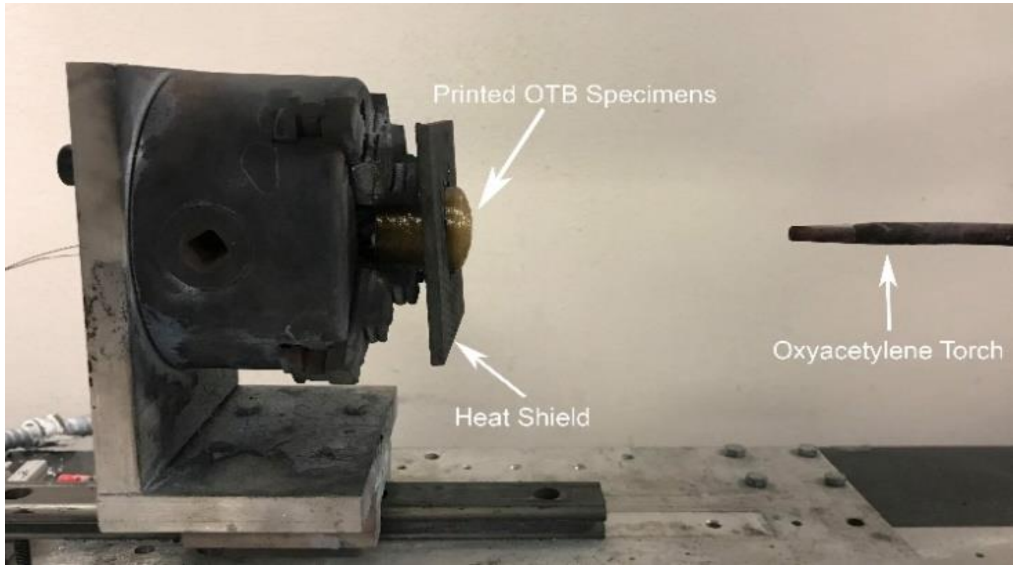
- Volume Fraction φ= Volume of lattice/Volume of Solid (ΔZ_2 portion only)
- $\alpha_{eff} = \frac{k_{eff}}{(\varphi\rho)C_p}$

Transient Test

Research Goal

Evaluate transient performance of proposed designs

- **Option 1**: Oxy-acetylene test bed (OTB)
- **Option 2**: Non-contact radiation heating



OTB Challenge

- The structure is for pure 1D heat transfer, any side heating from OTB causes significant error
- Char extended into the flame and extinguished the flame

Transient Test Setup

- The Radiation heater provides a non-contact heat plus input
- The heat shield prevent extra side heating
- The fiberglass insulation ensures the 1D heat transfer

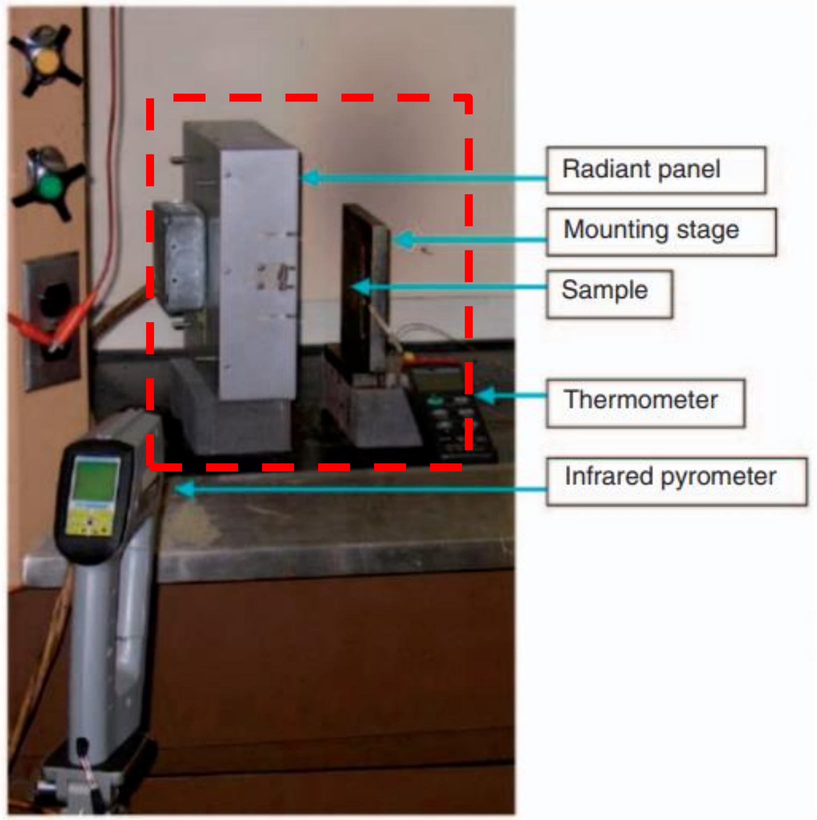
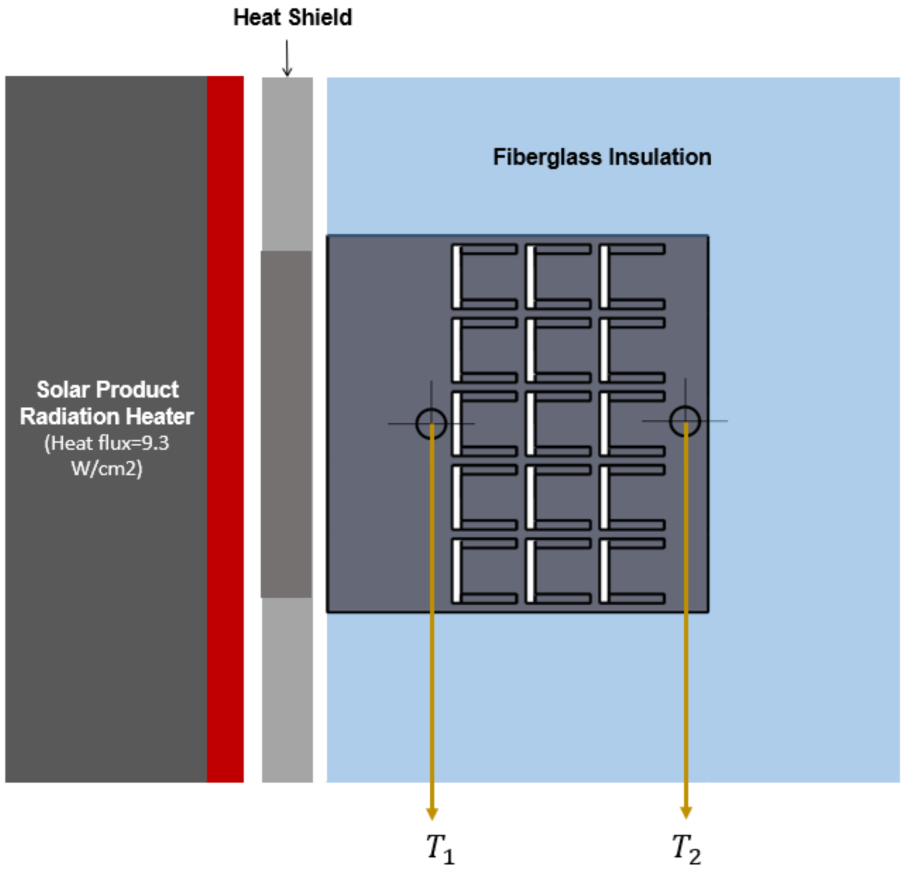


Figure 8. Experimental setup of radiant panel testing of materials.

Ref [8]



Conclusion & Future Works

Step 1: Thermal Conductivity Test

k_{eff}: Solid > C-Channel > **Simple Cube**

α_{eff}: Simple Cube > Solid ≥ **C-Channel**

Step 2: Heat Transient test

Verify the result of predicted α_{eff}

Step 3: Lattice Distribution and Optimization

Verify the distribution of lattice structure and investigate the impact

Application

1. Material with good flame resistance but has higher k
2. Dual-material additive manufacturing
3. Composite application

Acknowledgements

Special Thanks to **Dr. Kafi** and **Dr. Bateman** from **RMIT** as our valuable partner for helping the PEKK printing and hyper-flash result to verify the fishbone concept

Thanks to **UT Austin Texas Inventionworks** to provide the PETG/PLA printing

Thanks to **UT Austin Capstone Senior Design Project** undergrads

- **Spring 2020**: Khalil Alsabag, Camilla Braday, Logan Salas, Ruojiao Sun to develop initial concept for thermal conductivity apparatus
- **Fall 2020**: Yung-Chi Kung, Thomas Nagle, Emery Stokes, Brain Tran to refine the design of thermal conductivity apparatus

Thanks to **Dr. Crawford** from **UT Austin** to provide equipment for thermal conduction test setup

Reference

1. Milos, F. S., Chen, Y. K., & Mahzari, M. (2017). Arcjet tests and thermal response analysis for dual-layer woven carbon phenolic. In 47th AIAA Thermophysics Conference (p. 3353).
2. Feng, J., Fu, J., Lin, Z., Shang, C., & Li, B. (2018). A review of the design methods of complex topology structures for 3D printing. Visual Computing for Industry, Biomedicine, and Art, 1(1), 1-16.
3. Maire, J., Anufriev, R., Hori, T., Shiomi, J., Volz, S., & Nomura, M. (2018). Thermal conductivity reduction in silicon fishbone nanowires. Scientific reports, 8(1), 1-8.
4. Catchpole-Smith, S., Sélo, R. R. J., Davis, A. W., Ashcroft, I. A., Tuck, C. J., & Clare, A. (2019). Thermal conductivity of TPMS lattice structures manufactured via laser powder bed fusion. Additive Manufacturing, 30.
5. Belcher, T., & Schunk, G. (2019). Thermal Characterization of 3D Printed Lattice Structures. Retrieved from https://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/20190030441.pdf
6. He, K. L., Chen, Q., Dong, E. F., Ge, W. C., Hao, J. H., & Xu, F. (2018). An improved unit circuit model for transient heat conduction performance analysis and optimization in multi-layer materials. *Applied Thermal Engineering*, *129*, 1551-1562.
7. PETG, https://www.sd3d.com/wp-content/uploads/2017/06/MaterialTDS-PETG_01.pdf
8. J. H. Koo, K. Nguyen, J. C. Lee, W. K. Ho, M. C. Bruns, and O. A. Ezekoye, “Flammability Studies of a Novel Class of Thermoplastic Elastomer Nanocomposites,” J. of Fire Sciences, 28 (1), (2010), 49-85.

SEPTEMBER 2020

MUTATION++ CODE FOR MATERIAL RESPONSE ABLATION MODELING

AVERY PENDLEY
MS Student, The University of Texas at Austin

Main points:

- Objective
- Approach
- Complete Work
- Future Work

Objective:

- Utilize Mutation++ code for chemical equilibrium purposes
  - Create B’ Table for MXB360
  - Get transport properties
- Input Mutation++ results into 1D-FIAT to compare the material response modeling to experiment data

Approach:

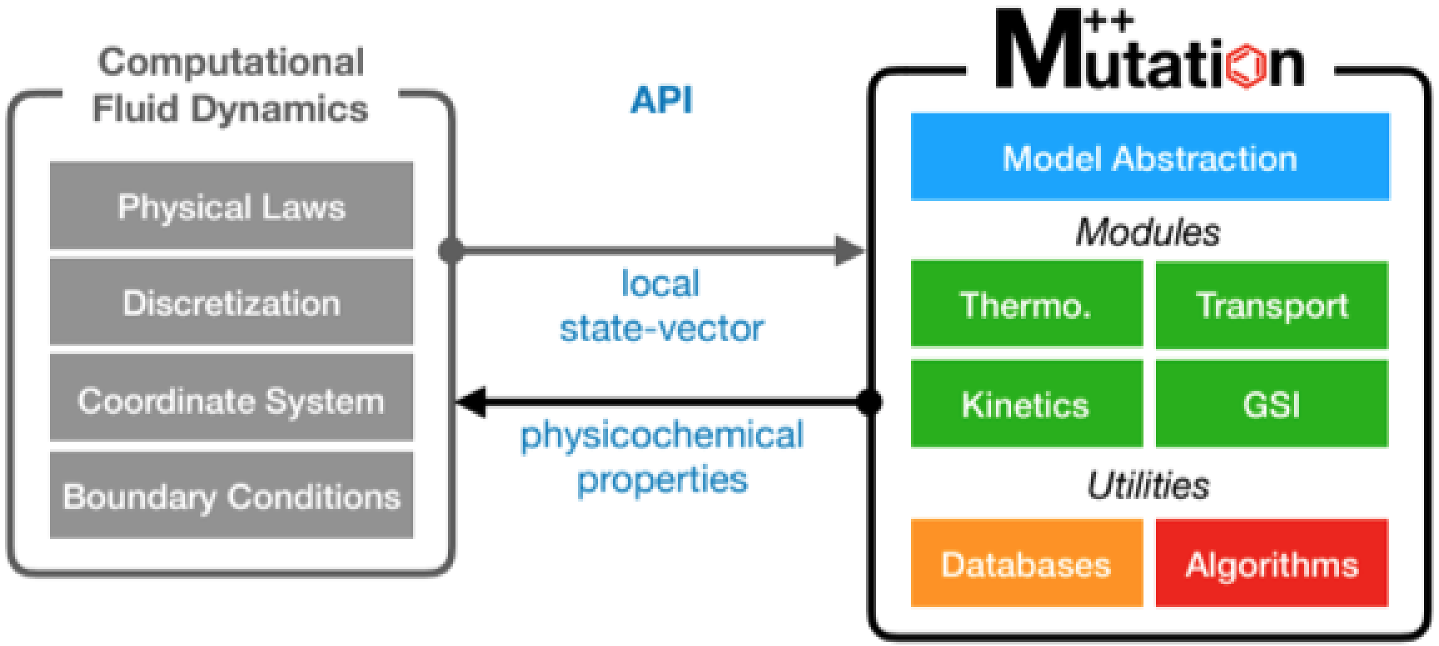
- Utilize CET93 for transport properties of Oxy-Acetylene Torch
- Run Mutation++ (MPP) for transport properties of Oxy Acetylene Torch
- Compare results
- Create B' Table of Oxy-Acetylene with MPP
- Repeat process with MXB360
  - Glass fiber/phenolic resin
- Utilize results from Mutation++ as inputs in 1D-FIAT
- Compare calculated results with experimental data

CET93

- Working with Dr. Mark Salita
- Enhance version of NASA-Lewis Chemical Equilibrium Code CET(1993)
- Transport properties
- Start with Oxy-Acetylene
  - Change to MXB360

Mutation++

- **MU**lticomponent **T**hermodynamic **A**nd **T**ransport properties for **ION**ized gases in C++
- Single software library that can be used by multiple CFD codes



James B. Scoggins et al. "Mutation++: MUlticomponent Thermodynamic And Transport Properties for IONized Gases in C++."

checkmix

- Loads a mixture and prints out information about the various elements, species, and reactions in the mixture

```
22 species containing 4 elements
0 reactions

Species info:
-------------
   #  Name                   C   H   N   O          Mw    Charge        Phase
  Hf(298)
                                                [g/mol]
  [kJ/mol]
Gas Species (21):
   1: C                      1   0   0   0       12.011         0          gas
   716.68
   2: H                      0   1   0   0      1.00795         0          gas
   218.00
   3: O                      0   0   0   1      15.9994         0          gas
   249.17
   4: N                      0   0   1   0      14.0067         0          gas
   472.68
   5: CH                     1   1   0   0      13.0189         0          gas
   597.37
   6: CH4                    1   4   0   0      16.0428         0          gas
   -74.60
   7: CO                     1   0   0   1      28.0104         0          gas
  -110.53
   8: CO2                    1   0   0   2      44.0098         0          gas
  -393.51
   9: CN                     1   0   1   0      26.0177         0          gas
   438.68
  10: C2H                    2   1   0   0      25.0299         0          gas
   566.20
  11: C2H2,vinylidene        2   2   0   0      26.0379         0          gas
   414.79
```

mppequil

- Compute equilibrium properties for mixture over a set of temperatures and pressures

```
averypendley@Averys-MacBook-Pro ~ % mppequil -T 300:100:15000 -P 101325 -m 0-1,3,6-9 carbonPhenol
      Th[K]       P[Pa]   rho[kg/m^3]  Cp_eq[J/mol-K]    H[J/mol]   S[J/mol-K]
        300      101325      0.87989         10.1749     -110301      136.192
        400      101325     0.671981         4.91483     -109668      146.134
        500      101325     0.548233         13.5549     -108851      155.504
        600      101325     0.462182         36.3255     -106489       163.77
        700      101325     0.395026         74.5975     -101063      171.066
        800      101325     0.340328         131.033    -90998.1       179.57
        900      101325     0.297378         215.324    -73781.1      194.266
       1000      101325     0.264664         212.664    -50780.5      213.889
       1100      101325     0.239325         97.5336      -35473      225.574
       1200      101325     0.218896         49.4645    -28658.1      230.282
       1300      101325     0.201874         38.2038    -24409.2      233.237
       1400      101325     0.187389         35.6572    -20747.2      235.785
       1500      101325     0.174875         34.8354    -17219.1      238.155
       1600      101325     0.163917          34.923    -13733.5      240.362
       1700      101325     0.154262         35.2051    -10228.2      242.466
       1800      101325      0.14568         35.6128    -6688.36       244.47
```

bprime

- Generates a "B-prime" table for a given temperature range and stepsize in K, a fixed pressure in Pa, a value of B'g
- Produces a table that provides values of B'c, the wall enthalpy in MJ/kg, and the species mole fractions at the wall versus temperature
- Example
  - B' Table of carbon phenol

```
averypendley@Averys-MacBook-Pro ~ % bprime -T 300:100:5000 -P 101325 -b 10
-m carbonPhenol -bl BLedge -py Gas
   "Tw[K]"          "B'c"     "hw[MJ/kg]"                      "C"
            "H"                        "O"                        "N"
           "CH"                      "CH4"                       "CO"
          "CO2"                       "CN"                      "C2H"          "C
2H2,vinylidene"                       "C3"                      "C3H"
           "C4"                      "C4H"          "C4H2,butadiyne"
           "C5"                      "HCN"                       "H2"
          "H2O"                       "N2"                    "C(gr)"
        300                0       -8.77884              1.50217e-117
    4.47871e-39              1.73741e-75              1.64352e-80
   7.37043e-102              0.000765908              3.03131e-11
       0.637333              2.58712e-72              3.76582e-95
     9.0472e-75             1.85554e-135             4.42398e-120
   6.38307e-173             1.84466e-137               5.6695e-80
     1.502e-174              1.56135e-25               1.1377e-06
       0.256548                 0.105351                        1
        400                0        -8.6591               2.48425e-86
    1.37728e-28              4.63479e-56              6.35616e-60
    7.34676e-75               0.00329939              1.76167e-07
       0.639886              3.29632e-53              1.68143e-69
    9.43434e-55              7.20528e-99              7.19402e-88
   9.56004e-127             5.50882e-101              2.15597e-58
   8.07819e-128              9.30771e-19              0.000106659
       0.251362                 0.105346                        1
        500                0       -8.52044               1.41401e-67
     2.8504e-22              2.19012e-44              1.48502e-47
    1.20207e-58               0.00705047              3.25966e-05
       0.643896               9.7555e-42              4.34599e-54
    9.63653e-43              6.81179e-77              1.63894e-68
    5.40585e-99              4.45614e-79              2.07167e-45
    1.00331e-99                1.086e-14               0.00167781
       0.242082                 0.105261                        1
```

Completed:

- Basics of Mutationpp
- Basics of CET93

Future Work:

- Continue working with CET93 for transport properties of Oxy-Acetylene Torch
- Run Mutation++ (MPP) for transport properties for transport properties of Oxy Acetylene Torch
- Compare results
- Create B' Table of Oxy-Acetylene with MPP
- Repeat process with MXB360
- Utilize results from Mutation++ as inputs in 1D-FIAT
- Compare calculated results with experimental data
- Complete report for my MS degree

Questions?

STUDY OF DUAL-LAYER CARBON/- AND GLASS/POLYSILOXANE ABLATIVES

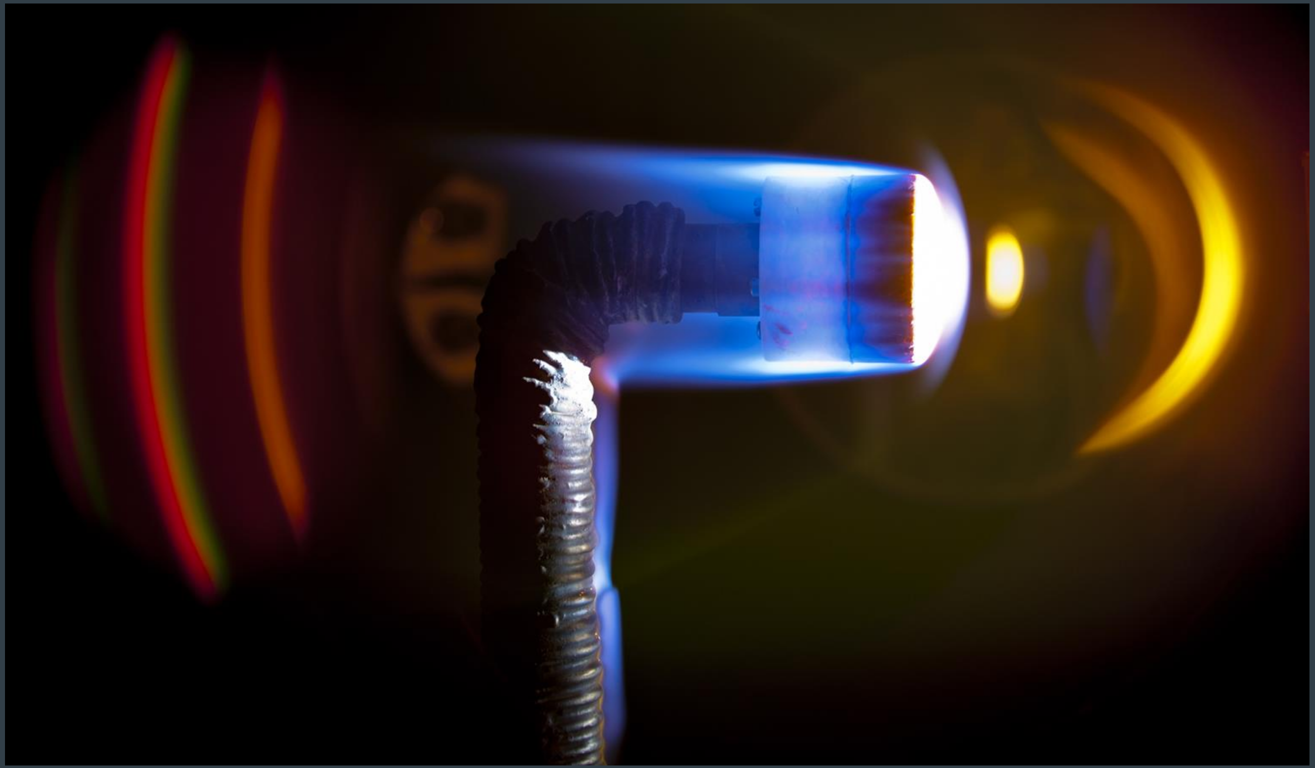
WILLIAM FAHY AND THE KOO RESEARCH GROUP

Outline

- Introduction to Ablation and Thermal Protection
- Project Objectives
- Experimental
- Results
- Summary
- Acknowledgements

Ablation

Ablative Material Being Arc Jet Tested



Source: Fretter,E. (2015). Material Ablation Test [Photograph]. Retrieved from https://www.nasa.gov/image-feature/material-ablation-test.

- Acts as a heat sink
- Reaction temp is reached
- Endothermic chemical decomposition
- Form pyrolysis gas and char layer

Applications

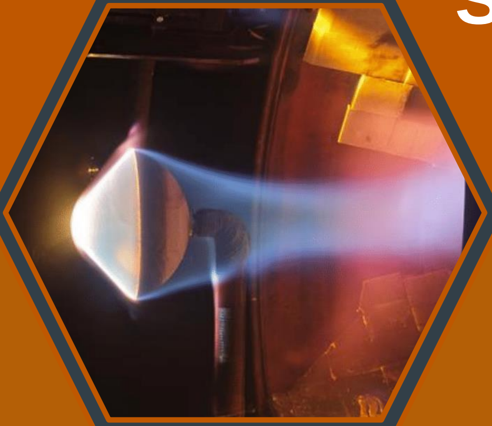
Hypersonics

Launch Systems

Missiles

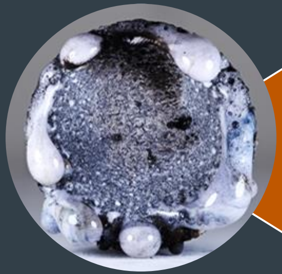
Rocket Nozzles

Spacecraft



Dual-Layer Ablative

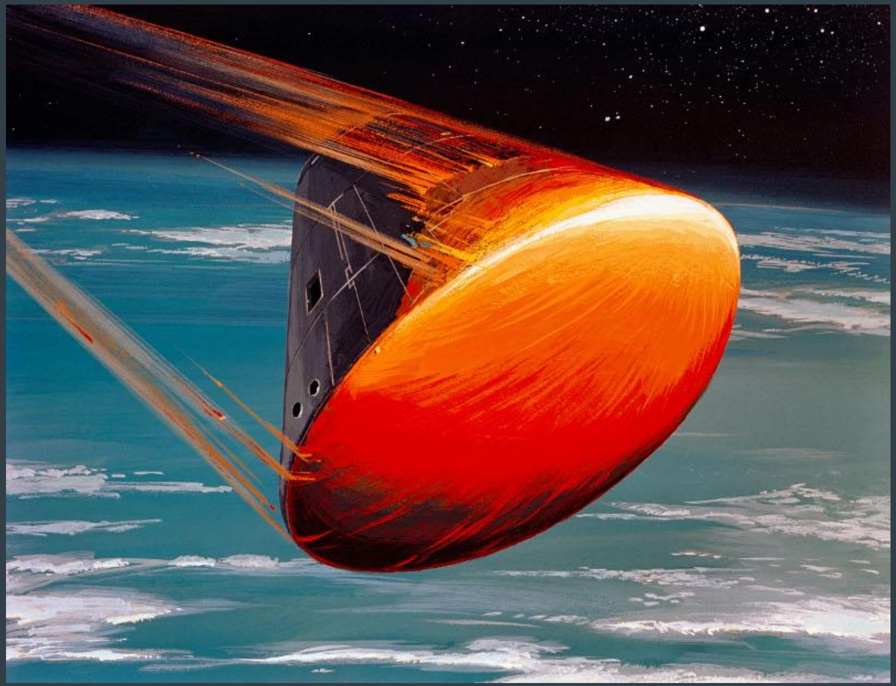
Optimize mass and protection



Recession Layer and an Insulating Layer

First done by NASA

Artist Rendition of Apollo Command Module Reentry



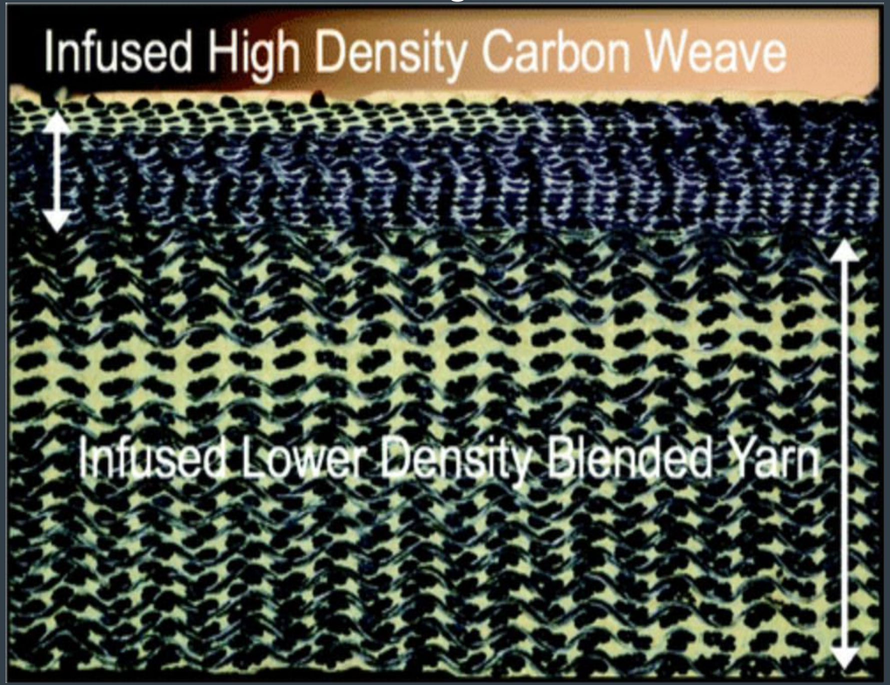
Source: Kauderer, A. (2012). Apollo Imagery [picture]. Retrieved from https://spaceflight.nasa.gov/gallery/images/apollo/apollo8/html/s68-55292.html.

NASA *HEEET*

Importance: Greater mass efficiency of 30-40% compared to SOA TPS (Nagaraja, 2018) & can tailor different material properties by changing the weave (Milos, 2018)

Manufacturing: Weaving, molding, resin impregnation performed by outside vendors (Nagaraja, 2018)

HEEET Material Design



Source: Milos, F. S., Chen, Y.-K., & Mahzari, M. (2018). Arcjet Tests and Thermal Response Analysis for Dual-Layer Woven Carbon Phenolic. Journal of Spacecraft and Rockets, 55(3), 712–722. doi: 10.2514/1.A34142

ESA HYDRA
ASTERM™ on SiCARBON™

Importance - hybrid structure provides mass saving enhancements and shield shape stability

Manufacture

Adhesive: 1) Graphite 2) Al_2O_3 3) ZrO_2-$ZrSiO_4$

1. Roughen CMC surface with SiC abrasive paper
2. Ultrasonically clean both materials
3. Adhesive applied to both surfaces
4. Jig with small load to keep parallel alignment
5. Cure at RT for 3 hours then 100 °C for 3 hours

Material Properties

ASTERM™ 70% C_f 30% Phenolic Resin
SiCARBON™ C_f/SiC heat-durable CMC

Dual Layer Schematic

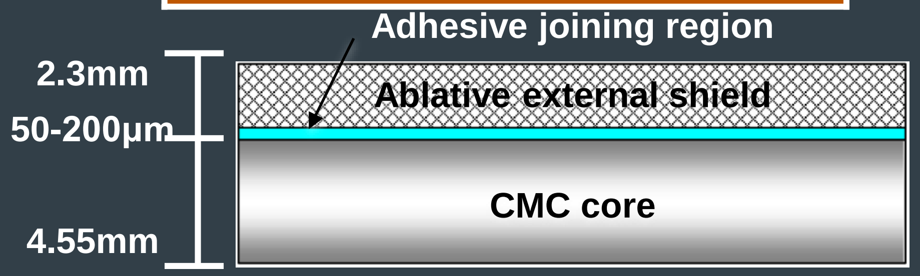


Figure 5: Scheme with the hybrid concept: Thin ablative layer on top of a ceramic composite thermostructure (Barcena et al., 2013)

Triantoua et al. (2015, February). Novel Hybrid Ablative/Ceramic Layered Composite for Earth Re-entry Thermal Protection: Microstructural and Mechanical Performance. Journal of Materials Engineering and Performance 24, 1452–1461. doi:10.1007/s11665-015-1410-8

Project Objectives

The goal of this project is to test the viability of four composites:

1) polysiloxane resin infused glass fiber;
2) polysiloxane resin infused carbon fiber
3) dual-layer polysiloxane resin infused glass & carbon fiber;
4) composite 3 infused also with nano silica

Study Overview

- Four composites have been molded for this project
- 2 single layer samples serving as a control study
- 2 will be dual layer
  - Both have carbon fiber as the recession layer with glass insulating layer
  - One incorporates nano-silica into the carbon fiber

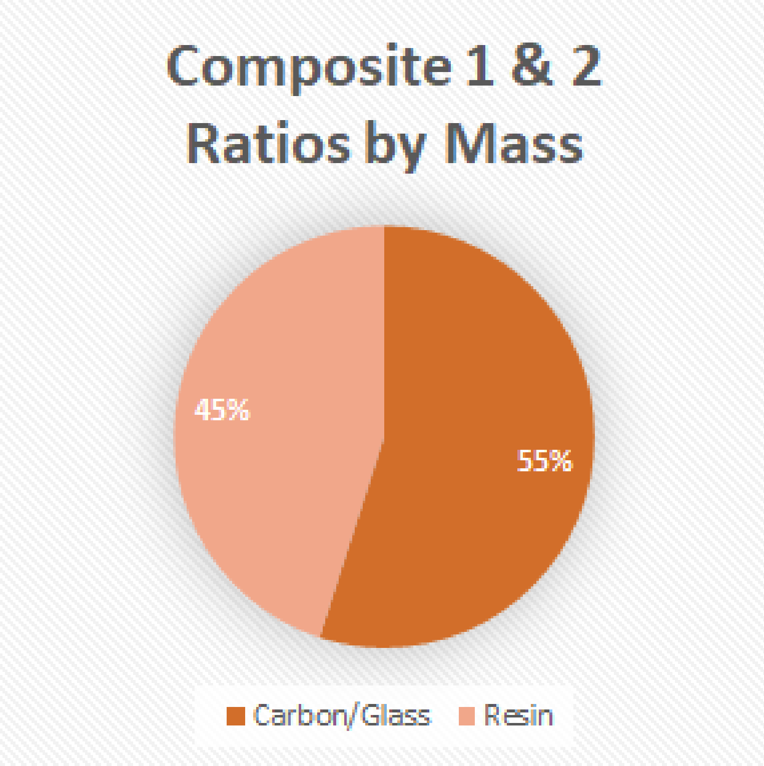
Composite Overview

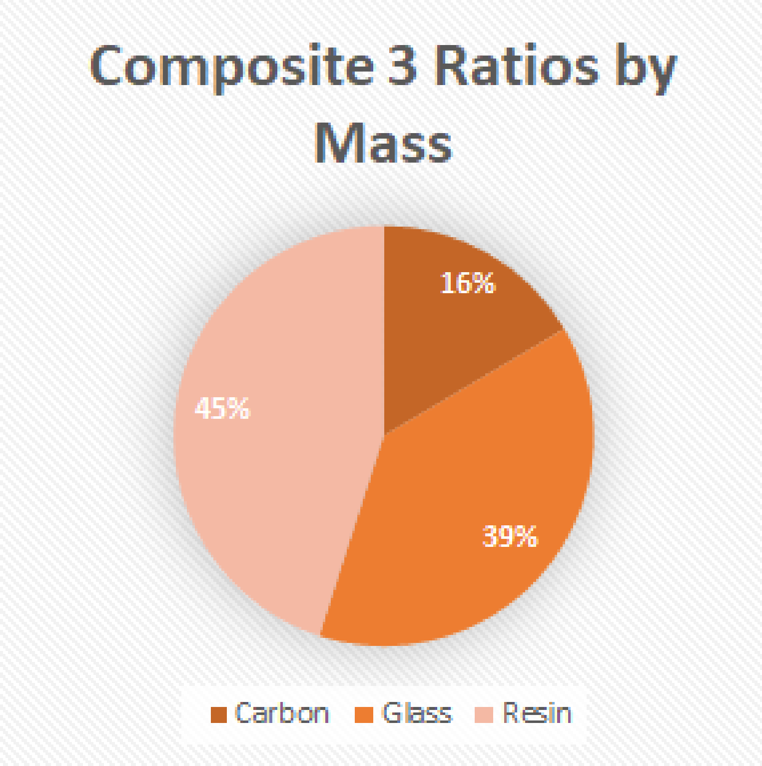
Composite Overview

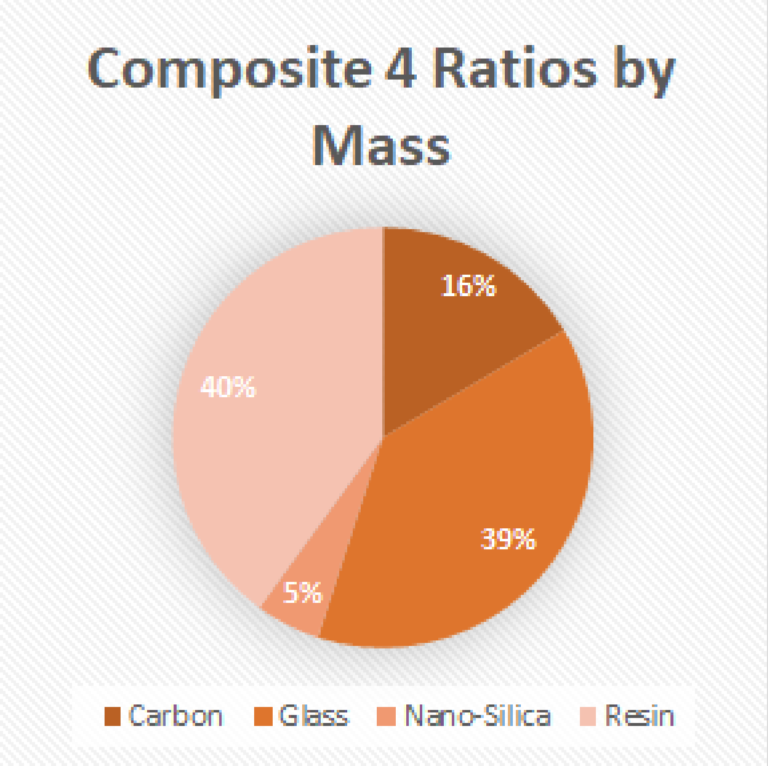
Composite Number	Polysiloxane Resin	Glass Fiber	Carbon Fiber	Nano-silica
1	X	X		
2	X		X	
3	X	X	X	
4	X	X	X	X

Composite Makeup

Composite Material Percentages by Mass





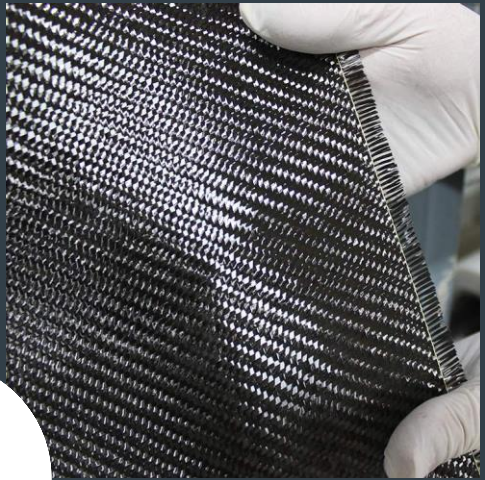


Materials Used

Glass Fiber

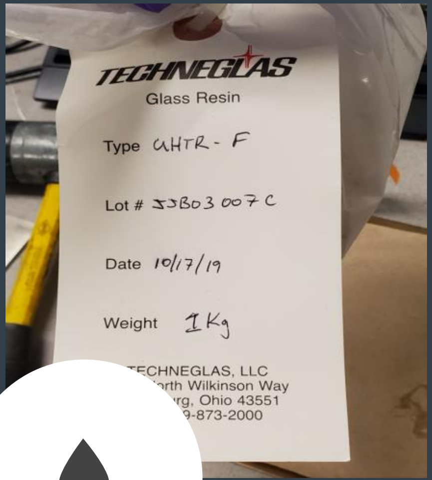
Fiberglass Chopped Strand Mat Cut Piece Emulsion Binder. (n.d.). Retrieved from https://www.indiamart.com/proddetail/fiberglass-chopped-strand-mat-cut-piece-emulsion-binder-11702253448.html

Carbon Fiber



3K, 2 x 2 Twill Weave Carbon Fiber Fabric. (n.d.). Retrieved April 21, 2020, from https://www.fibreglast.com/product/3K_2_x_2_Twill_Weave_Carbon_Fiber_Fabric_01069/carbon-fiber-fabric-classic-styles

Polysiloxane



Nano-silica

Quality Nano Silica Powder. (n.d.). Retrieved April 21, 2020, from https://www.tradeford.com/cm389308/quality-nano-silica-powder_p503780.html

Experimental Procedures

Composite Creation - Impregnation

- Disperse resin mix onto glass and carbon sheets using pipet and squeegee (55% Fiber - 45% Resin)
- Use of vacuum oven to remove solvent

Glass Fiber Squeegee Process

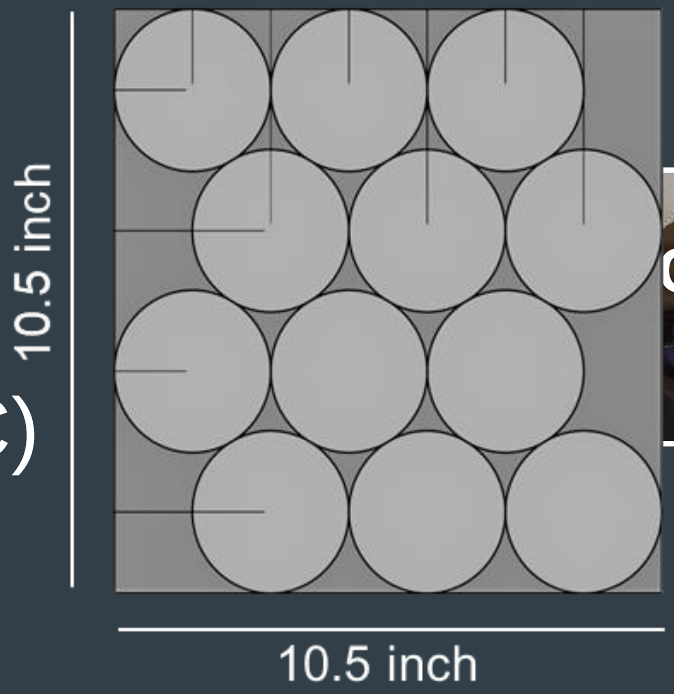
Create composite in mold

Extract composite from mold

Experimental Procedures
Composite Synthesis - Molding

- Cut dried sheets for molding
  - Glass: 3” diameter circles
  - Carbon: 0.5” squares
- Place cut outs in mold
- Hold under high heat (~280 C) and pressure (30,000 psi) for 90 minutes

FCC Circle Packing Design



Cure glass and carbon fiber sheets

Extract composite from mold

Experimental Procedures

Final Composites Before Waterjet

Final Dual Layer Ablative Samples

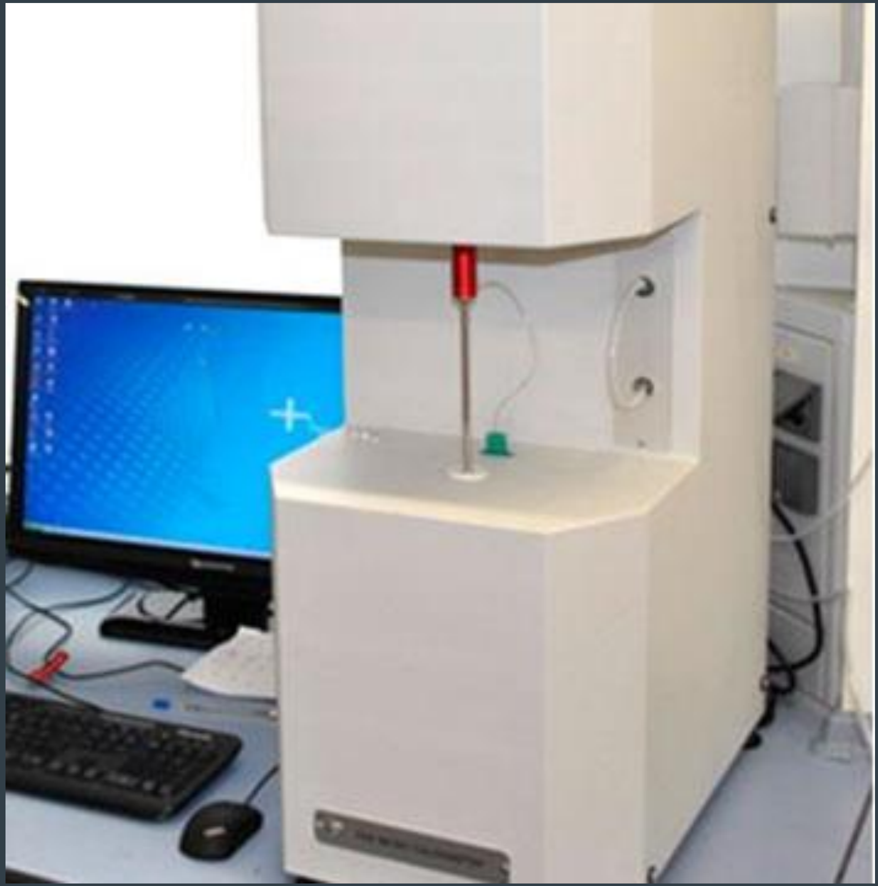
Cure glass and carbon fiber sheets

Create composite in mold

Experimental Procedures

Testing

MCC at UT-Austin



TGA

OTB

Description

- MCC = Microscale Combustion Calorimeter
- Samples are pyrolyzed in an inert atmosphere and their off-gasses are measured

Applications

- Determines heat release rate from oxygen difference

Data Acquired

- Heat release rate data

Experimental Procedures

Testing

Description

- TGA = Thermogravimetric Analysis
- A sample is placed on a precision balance in an inert atmosphere furnace with a constantly increasing temp, converting the sample to char

Applications

- Determine weight loss over time

Data Acquired

- Mass loss over time
- Thermal stability data
- Char yield percent (mass remainder)

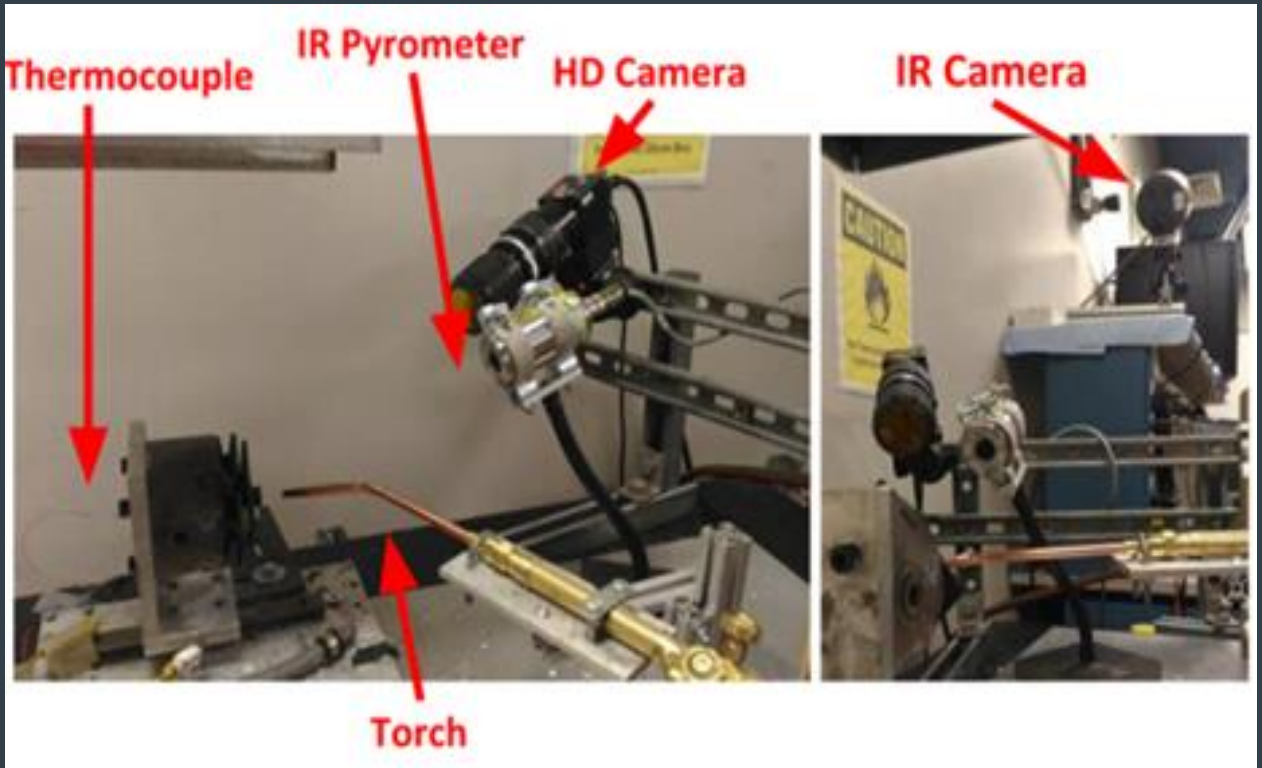
TGA at UT-Austin

Source: Texas Materials Institute. (n.d.) [Picture of Thermogravimetric Machine]. Retrieved April 18, 2020, from https://tmi.utexas.edu/core-facilities/equipment/differential-scanning-calorimeterthermagravimetric-analysis-mettler-toledo-tgadsc-1/

Experimental Procedures

Testing

OTB at Pickle Research Center



Description

- OTB = Oxy-Acetylene Test Bed
- Torch maintains set distance away from sample during test, based on constant heat flux

Applications

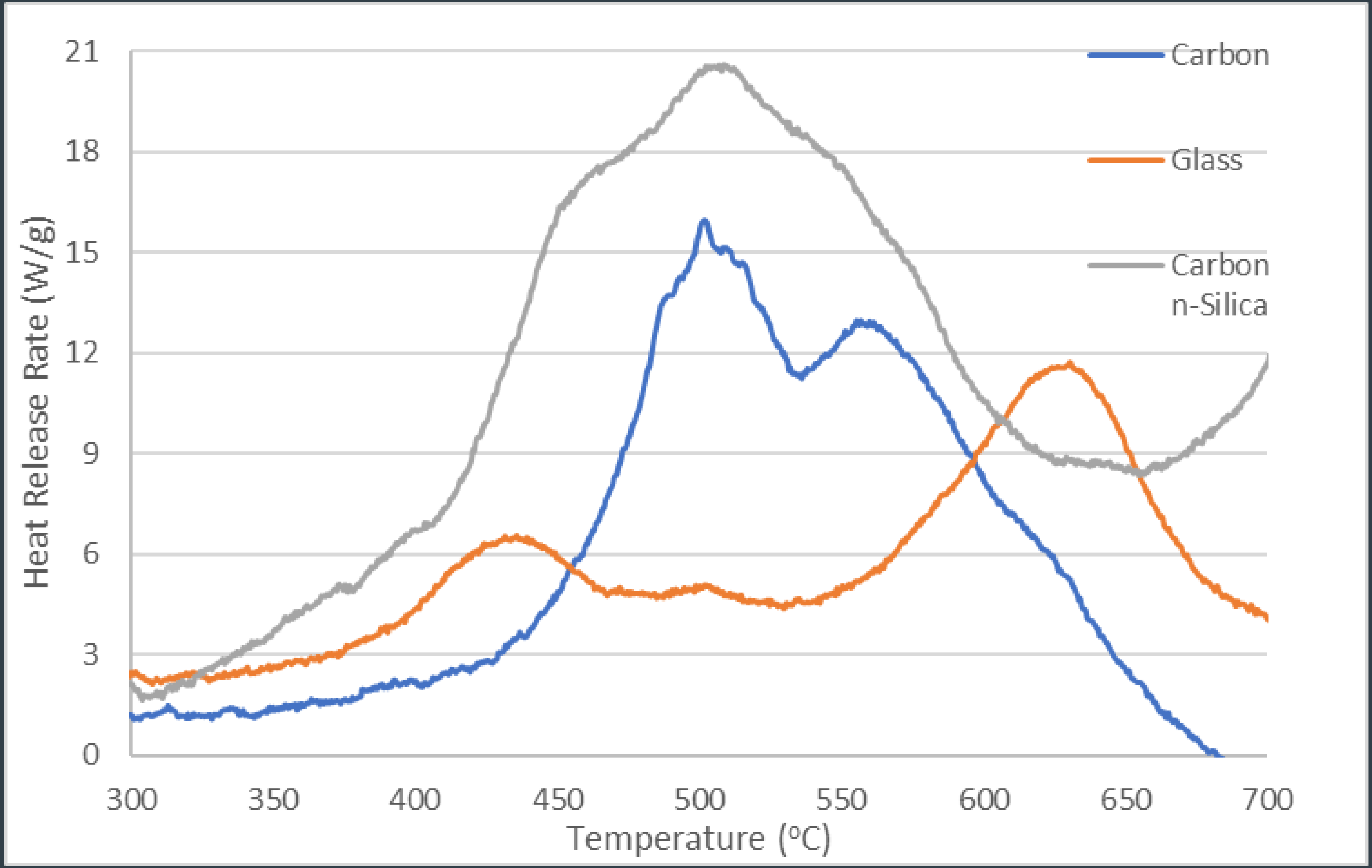
- Determine the materials response to high heat flux typical of re-entry conditions and recession rate

Data Acquired

- In-depth temperature profile
- Surface temperature data
  - IR camera
- Thermal IR and HD video data

MCC Test Results

MCC of carbon and glass composites

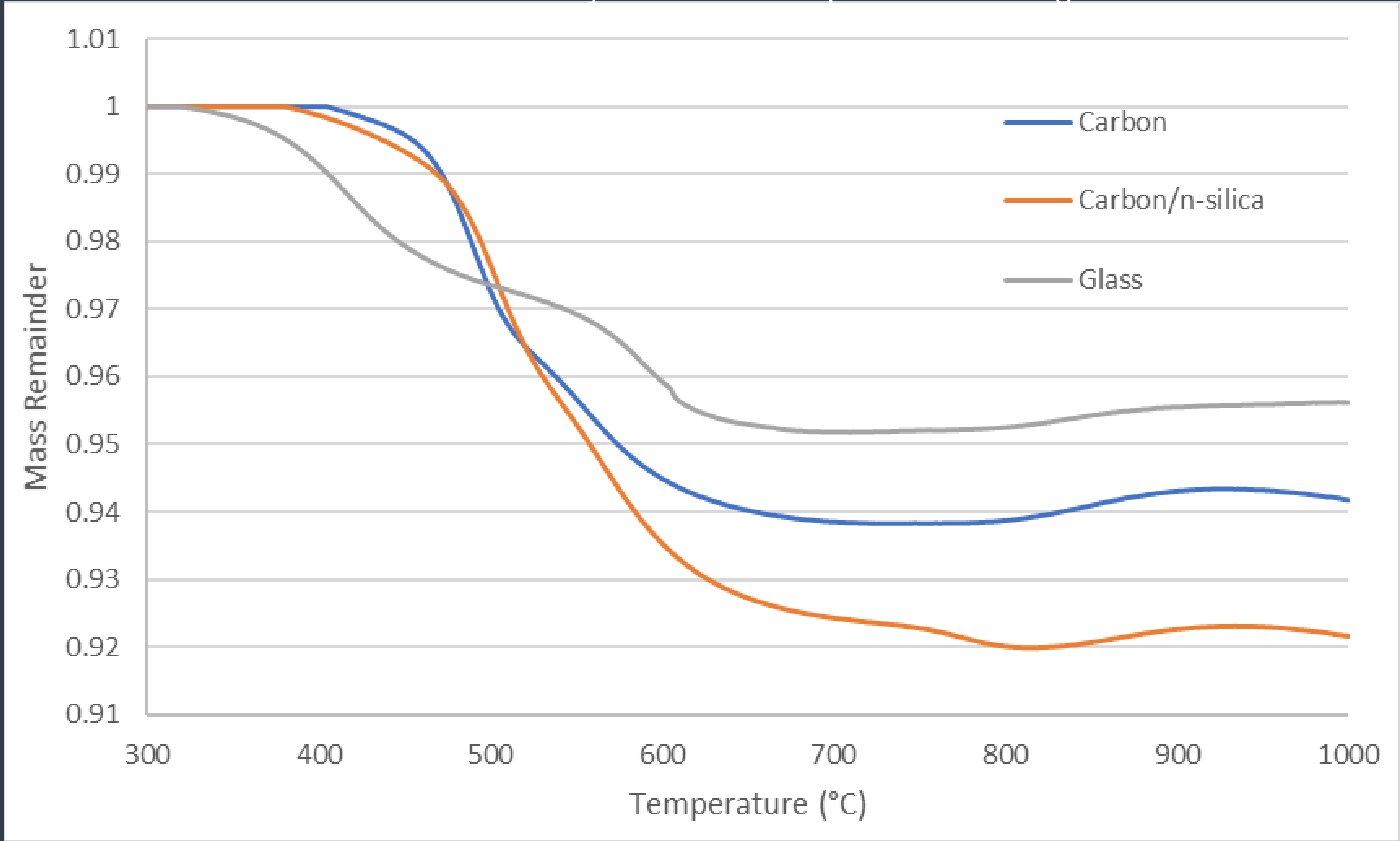


TGA

OTB

TGA Test Results

TGA of different synthesized composites showing Char Yield



MCC

OTB

OTB Test Results

MCC

TGA

OTB

Conclusion

Dual layer ablatives provide mass saving enhancements and structural stability for atmospheric reentry

Improving TPSs is essential to keep up with future space explorations

What's Next & Recommendations

1. OTB and SEM on four test composites
2. Continue to explore the dual-layer concept

Acknowledgments

Thank you to Dr. Koo's UT Austin Senior Design Team:

Ricardo Bowers
Declan Burke
Melissa DeAlmeida
William Slater

Questions?

High-Temperature Materials Development

SUMMARY

Goal: Test and evaluate high-temperature materials for hypersonic weapon thermal protection systems

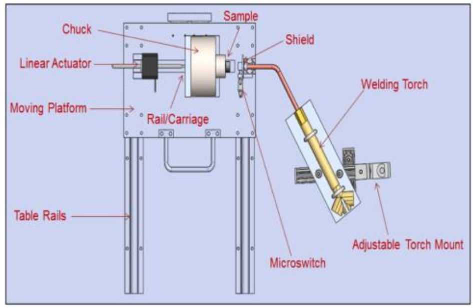
PI: Profs. Noel Clemens and Philip Varghese (ASE/EM); UT Austin
Dr. Joseph Koo (ME), UT Austin

Sponsor: Long-Range Precision Fires

If Successful, what difference will it make?
Enhanced weapon survivability, range, and lethality

Issues/Risks:
- May not be able to duplicate all relevant hypersonic environment conditions
- All key thermal properties may not be characterized

Oxy-Acetylene Test Bed



ICP Torch

Deliverables and Milestones with Decisional Points

Deliverable 1: Modified UT facilities to enable target conditions to be achieved; Documented conditions that can be attained

Deliverable 2: Ablation and thermal characteristics of Phase 1 materials of interest to Army engineers in plasma torch and oxy-acetylene torch

Deliverable 3: Ablation/thermal characteristics and revised measurements of Phase 2 materials

Current Status
- Received material validation plan from LRPF engineers
- 14 materials (as of Sept. 2020); 3 target conditions

Measurement Capabilities
- Temperature 1000 – 6000 K; Heat flux 100 – 1,600 W/cm^2
- Mass loss and recession rate
- Surface temperature, in-depth temperature, backside temperature
- Surface morphology (SEM, TEM)
- Gas temperature and composition (spectroscopic data)