National Nuclear Security Administration

Polymer Binder Development for Indirect Selective Laser Sintering of Oxide Ceramics

Patrick Snarr

The University of Texas at Austin

8 February 2023

TEXAS
The University of Texas at Austin

Consortium for
Enabling Technologies & Innovation

Introduction and Motivation

- Laser Powder Bed Fusion (LPBF) has been identified as a relevant process regarding nuclear non-proliferation
- This family of additive manufacturing (AM) processes can be used to produce parts relevant to the nuclear fuel cycle
- Selective Laser Sintering (SLS) is a LPBF process that can be modified to print oxide ceramics
- In order to print oxides using SLS, a polymeric binder must be developed

Figure 1: Heat Exchanger Fabricated Via AM [1]

Selective Laser Sintering (Polymers)

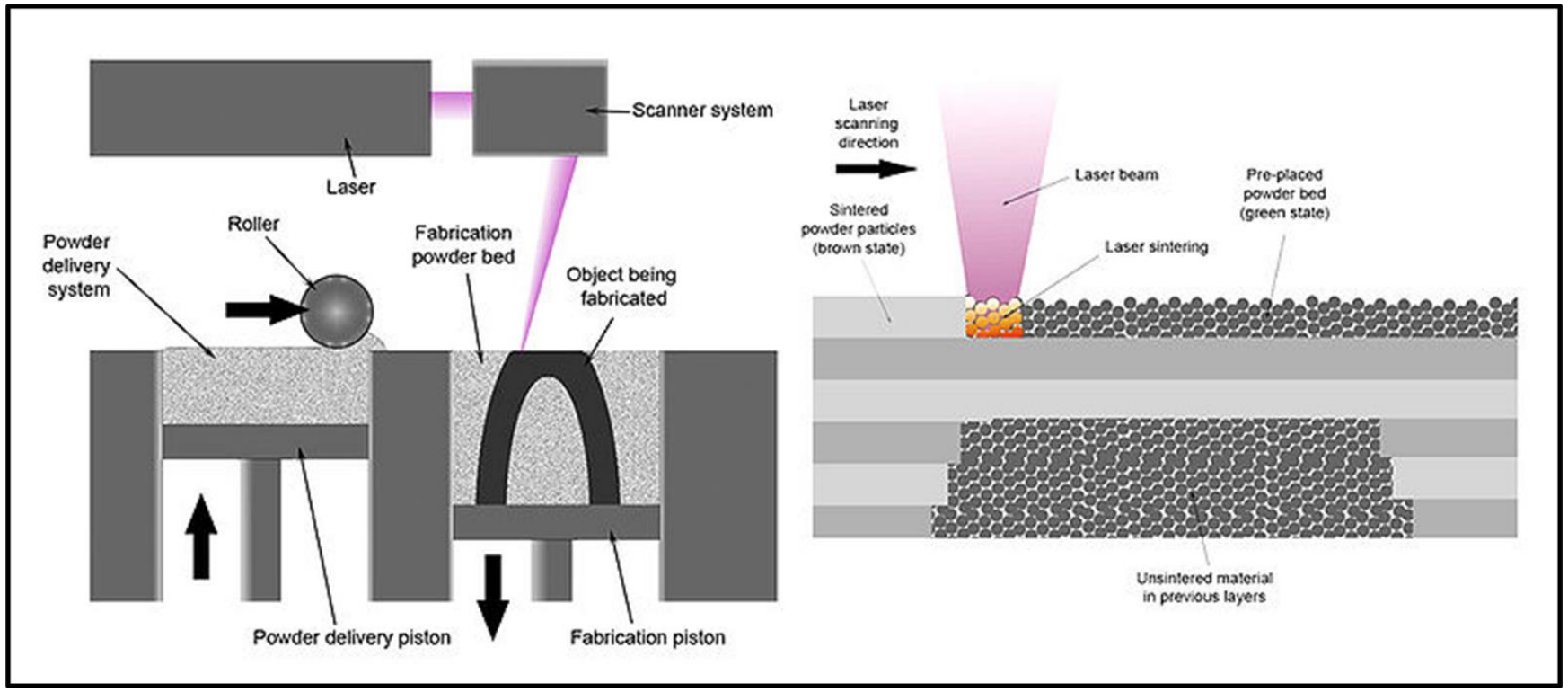
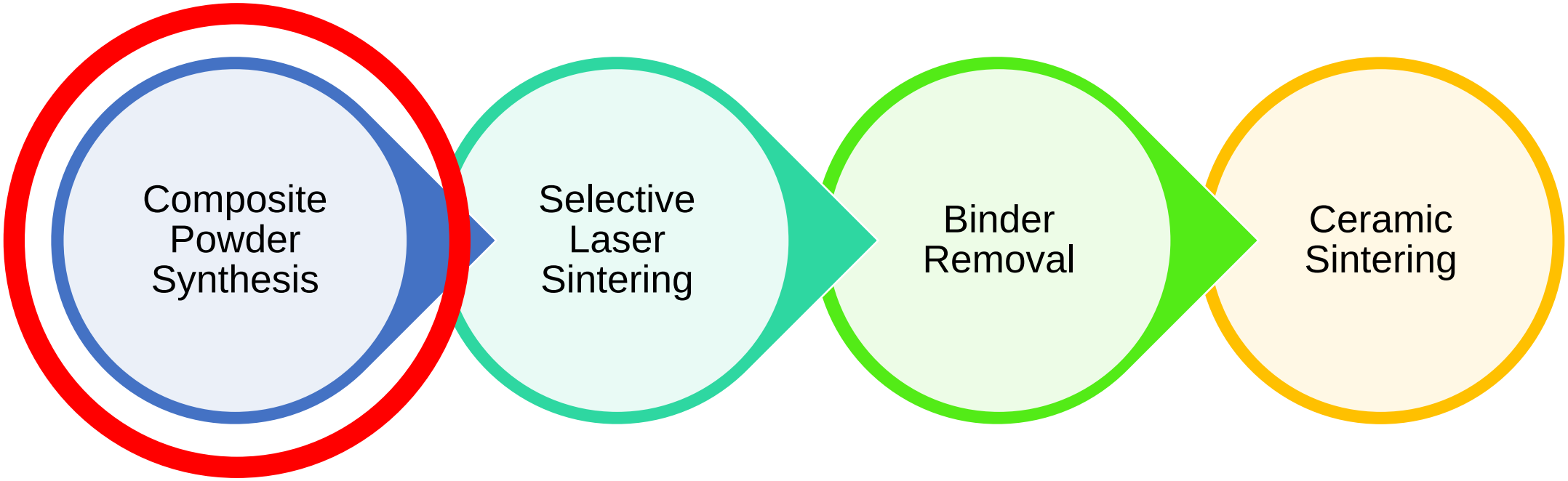


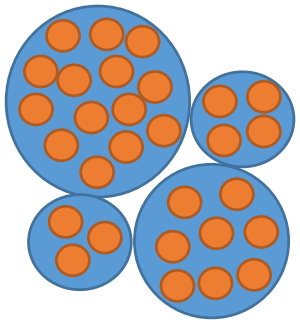
Figure 2: SLS Overview [2]

Indirect Selective Laser Sintering of Oxides

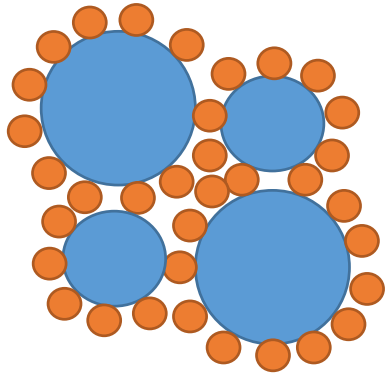


Composite Powder Synthesis

Coating Process



Mixing Process



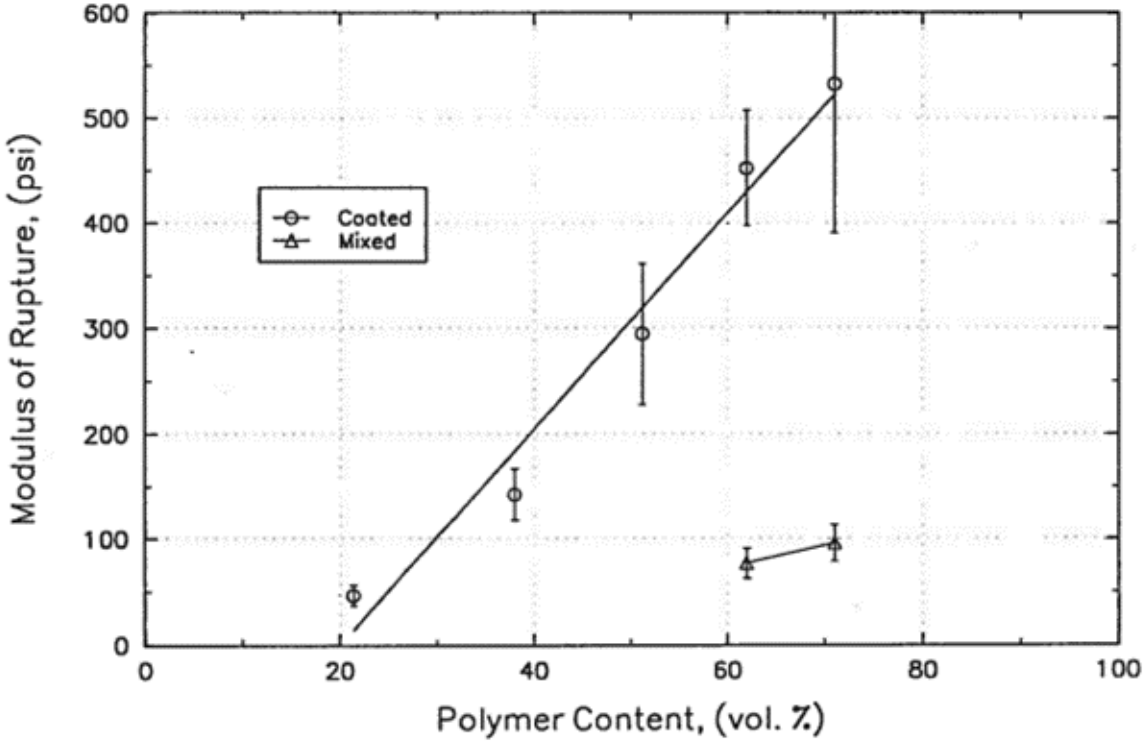


Figure 3: Green Part Strength by Synthesis Method [3]

= Polymer

= Ceramic

Spray Drying as a Coating Process

- Spray drying has been chosen as the process to coat ceramic particles with polymer
- Three main steps:
  - Droplet formation (high surface area)
  - Drying of droplets to form solid particles
  - Particle Collection
- Will give desired binder distribution and allow for less binder to be used

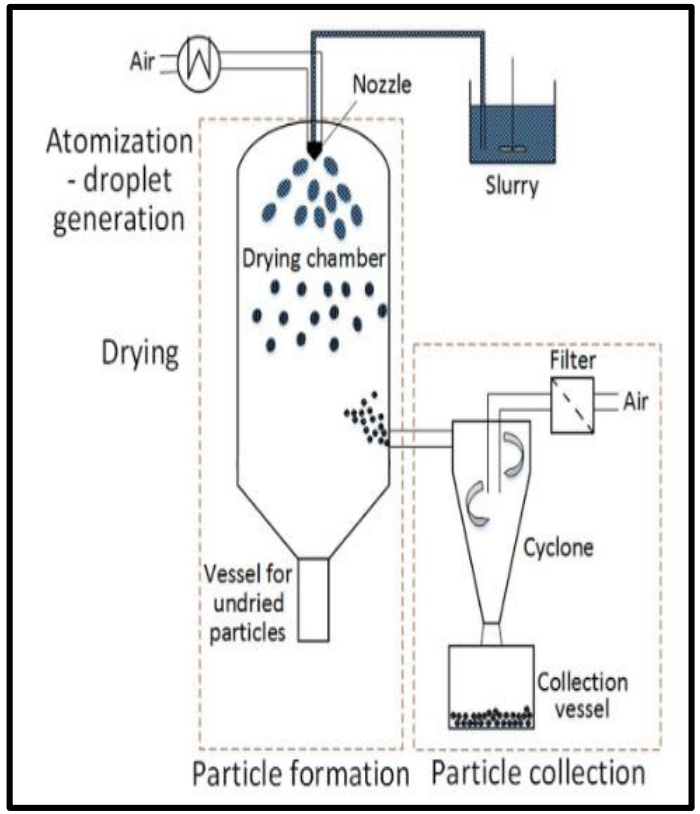


Figure 4: Spray Drying Process [4]

Polymer Binder Constraints

Spray Drying Binder Constraints

+

SLS Binder Constraints

+

Post-Processing Requirements

→

Binder Constraints

- Thermoplastic Polymer
- ~50 °C < T_g < ~100 °C
- Decomposes in N_2

→

No commercially available options for binder

Custom Polymer Binder Selection

- An 80% PMMA, 20% PnBMA co-polymer has been chosen as the binder to develop

- T_g PMMA = ~120 °C ; T_g PnBMA = ~20 °C

  $T_{g,80/20}$ = 0.8(120 °C) + 0.2(20 °C) = 100 °C

- This polymer unzips in N_2 at elevated temperatures making it compatible with oxygen sensitive oxides

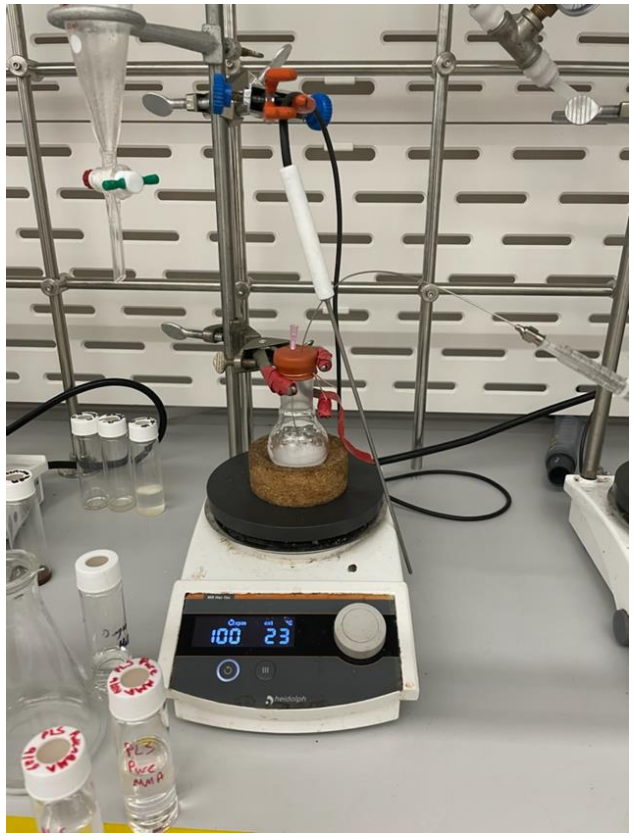


Figure 5: Co-polymerization Process

Binder Development Experimentation

- Three emulsion polymerizations were performed
  - 100% PMMA
  - 100% PnBMA
  - 80% PMMA/20% PnBMA mol/mol
- Nuclear magnetic resonance spectroscopy (NMR) was performed to check polymer molecular composition
- Differential scanning calorimetry (DSC) was performed to test glass transition temperature

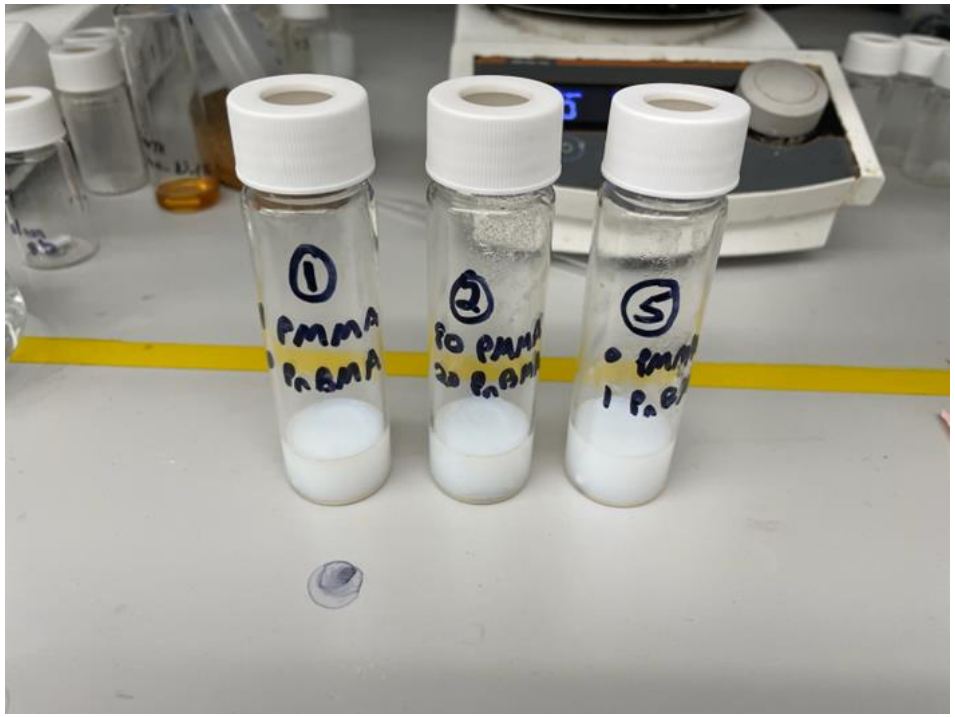


Figure 6: Obtained emulsion polymers

Nuclear Magnetic Resonance Results

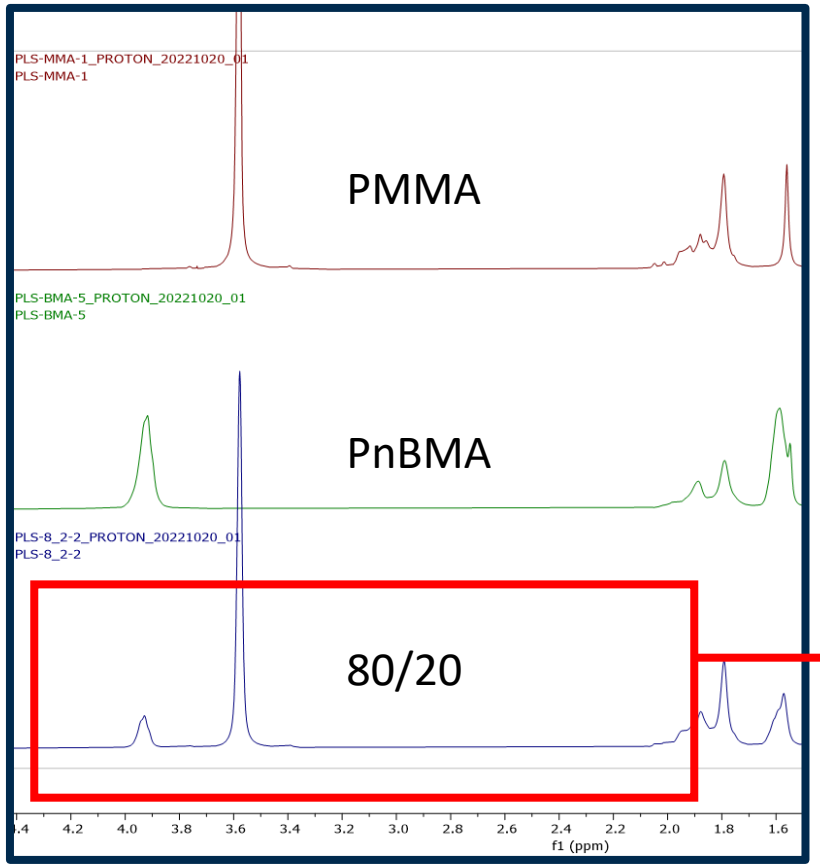


Figure 7: NMR of All Three Formulations

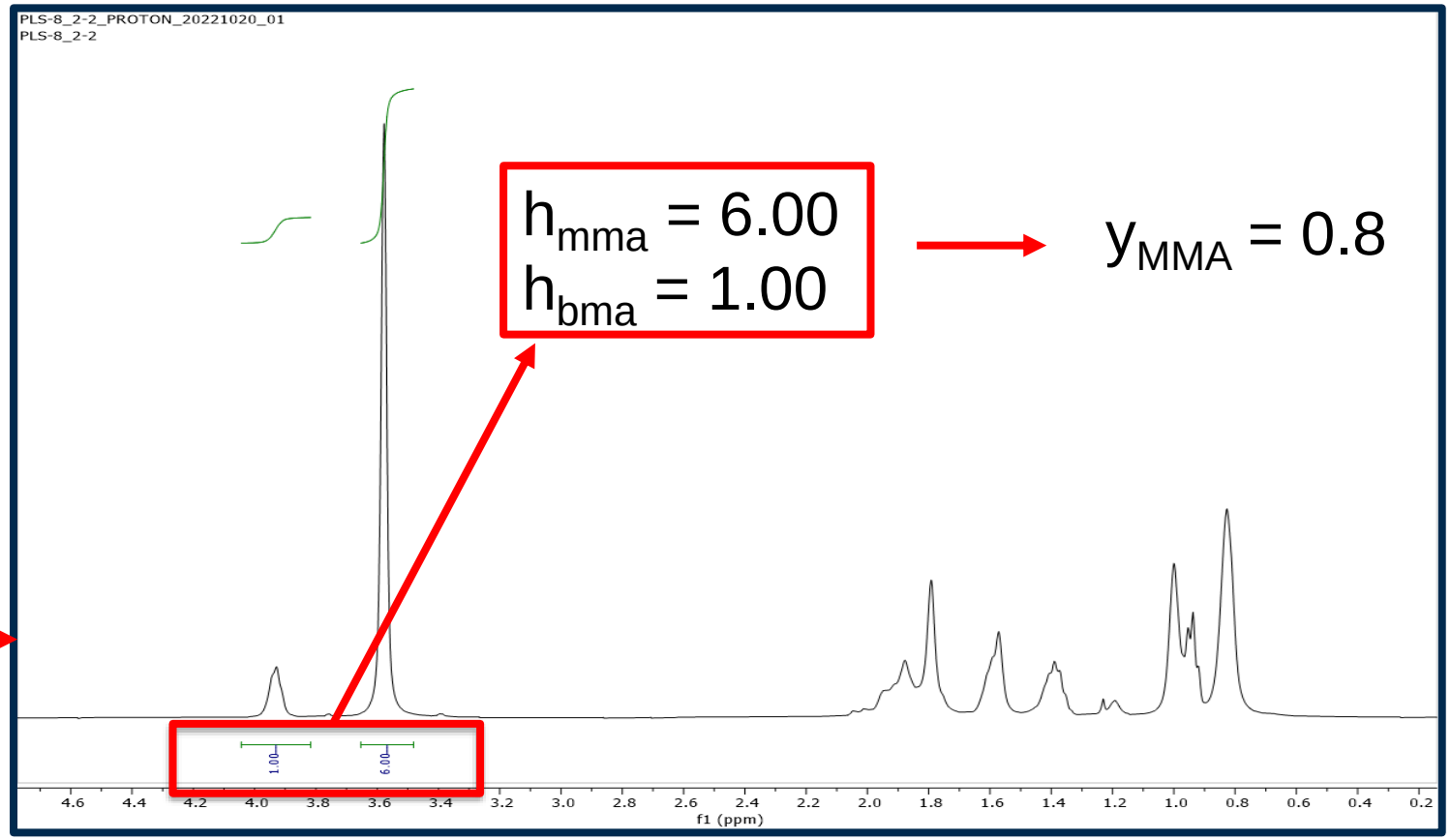


Figure 8: 80/20 NMR Analysis Results

Differential Scanning Calorimetry Results

- DSC revealed T_g pure PMMA to be 127 °C
- This puts our 80/20 estimate at 106 °C
- DSC analysis of the 80/20 formulation showed a T_g of ~105 °C

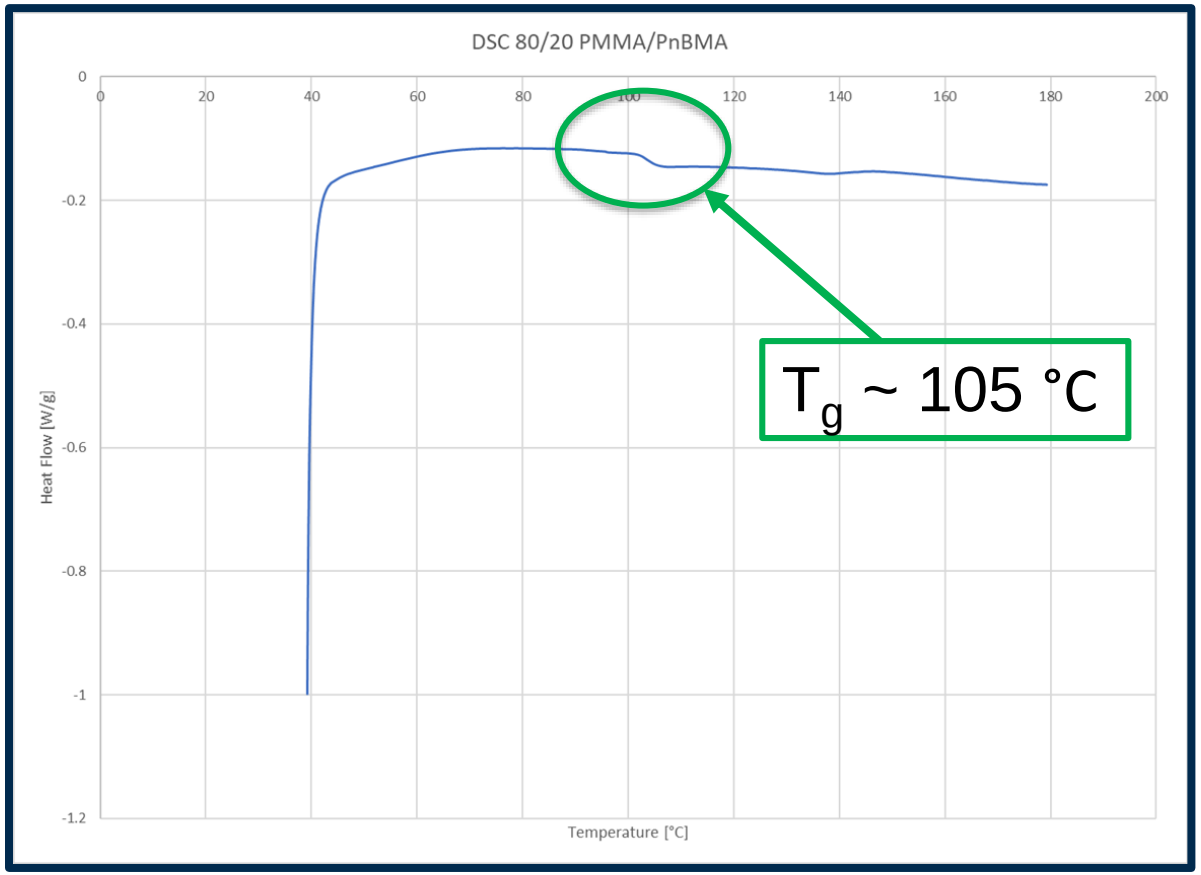


Figure 9: DSC of 80/20 Formulation

Conclusions and Future Work

- A custom polymer binder that is compatible with spray drying and SLS has been developed
- This will allow for I-SLS of ceramic oxides (including nuclear relevant oxides) to be tested
- Next steps include identifying optimum spray drying and SLS parameters with the developed binder
- The geometrical limitations and material properties of the printed oxides will be explored
- The signatures of the process will be identified

References

[1] *Heat Exchangers*. 3D Systems. (2022) https://www.3dsystems.com/aerospace-defense/heat-exchangers.

[2] Palermo, Elizabeth. *What Is Selective Laser Sintering*? LiveScience, Future US Inc., 13 Aug. 2013, www.livescience.com/38862-selective-laser-sintering.html.

[3] Vail, Neal Kent. (1994). *Preparation and characterization of microencapsulated, finely divided ceramic materials for selective laser sintering* (Dissertation, University of Texas at Austin).

[4] A. Stunda-Zujeva, Z. Irbe, L. Berzina-Cimdina, *Controlling the morphology of ceramic and composite powders obtained via spray drying – a review*, Ceram. Int. 43 (15) (Oct. 2017) 11543–11551, https://doi.org/10.1016/j.ceramint.2017.05.023.

ACKNOWLEDGEMENTS

This material is based upon work supported by the Department of Energy / National Nuclear Security Administration under Award Number(s) DE-NA0003921.

Georgia Tech

Clafflin University Founded 1869

Colorado School of Mines

Duke University

University of Hawai'i

MIT

University of Michigan

The University of North Carolina at Chapel Hill

The Ohio State University

Spelman College — A Choice to Change the World

Texas A&M University

The University of Texas at Austin

Washington State University

Argonne National Laboratory

Berkeley Lab

Brookhaven National Laboratory

Idaho National Laboratory — 70 Years of Science & Innovation

Lawrence Livermore National Laboratory

Los Alamos National Laboratory — EST. 1943

Nevada National Security Site — Managed and operated by Mission Support and Test Services

Oak Ridge National Laboratory

Pacific Northwest National Laboratory

PPPL — Princeton Plasma Physics Laboratory

Sandia National Laboratories

SRNL — Savannah River National Laboratory

National Nuclear Security Administration

Consortium for Enabling Technologies & Innovation

Is T_g > 100°C OK?

- Short answer: Maybe, it depends on the spray dryer!
- The real requirement is that both the inlet and outlet temperature of the spray dryer is greater than T_g of the coating polymer
- For an aqueous based system, inlet and outlet temperature also needs to be greater than 100 °C to dry

$$T_i > T_o > 100\ °C$$

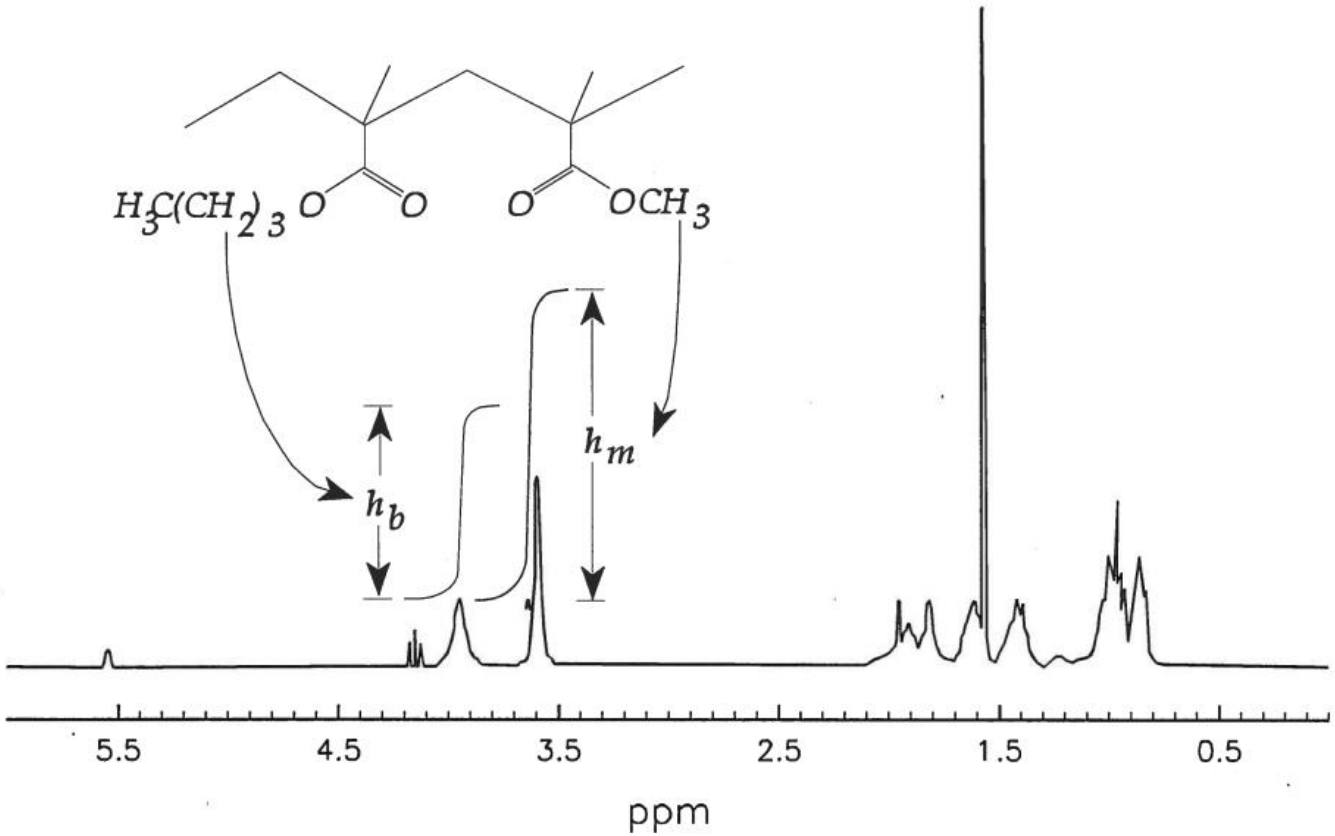
$$T_i > T_o > T_g$$

Table 4.1 Equilibrium spray drying conditions.

Heater Setting, (kW)	Inlet Temperature, (°C)	Outlet Temperature, (°F), (°C)	Time Required, (min)
3	100-105	100-110 (38-43)	10
4	125-130	125-150 (52-66)	10-15
5	150-155	170-190 (77-88)	15-20
6	180-185	230-240 (110-116)	25-30
7	205-210	250-265 (121-129)	30-35
9	250-260	280-300 (138-149)	40-45

Example Spray Dryer's Operating Settings

Interpreting NMR Results



Source: NMR of 80/20 PMMA/PnBMA mol/mol [3]

$$y_m = \frac{\frac{2h_m}{3h_b}}{1 + \frac{2h_m}{3h_b}}$$

y_m ... mole fraction of MMA
h_m ... area under MMA peak
h_b ... area under nBMA peak

$h_m = 6.00$
$h_b = 1.00$

→ $y_m = 0.8$