ADDITIVE MANUFACTURING OF 3D-PRINTED ENERGETIC STRUCTURES

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About Me

PURDUE ENERGETICS

- **Assistant Professor** ME, *Purdue University*, Zucrow Laboratories (start 8/21)
- **Research Scientist**, *Purdue University/Oak Ridge National Laboratories*, Manufacturing Demonstration Facility (8/20-8/21)
- Ph.D. AAE, *Purdue University*, Zucrow Laboratories (8/20)

"The only reason I became an aerospace engineer was so that I could build my own starship enterprise."

My team's research focus:

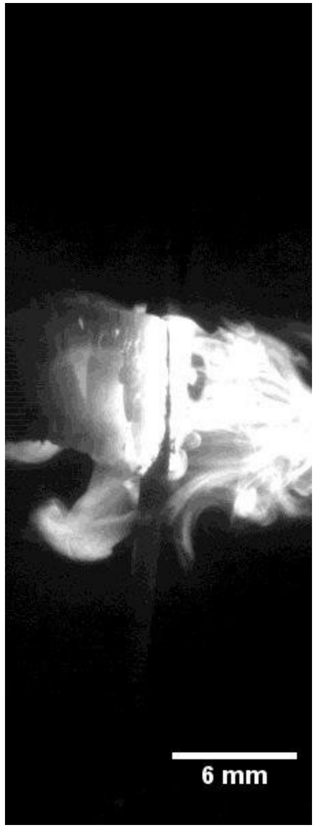
Advance the manufacturing science necessary to develop state-of-the-art, **additively manufactured energetic materials (AMEMs).** This includes developing complex, multimaterial geometries and implementing in-situ monitoring of the manufacturing process to repeatably create high-performance and high-quality AMEMs.

Overview

- What are the benefits of 3D-printing energetic materials?
- 3D-printing live, solid propellant
- Photopolymers for propellants
- Combustion of functionally graded, layered propellant
- Additional research interests
- Conclusions

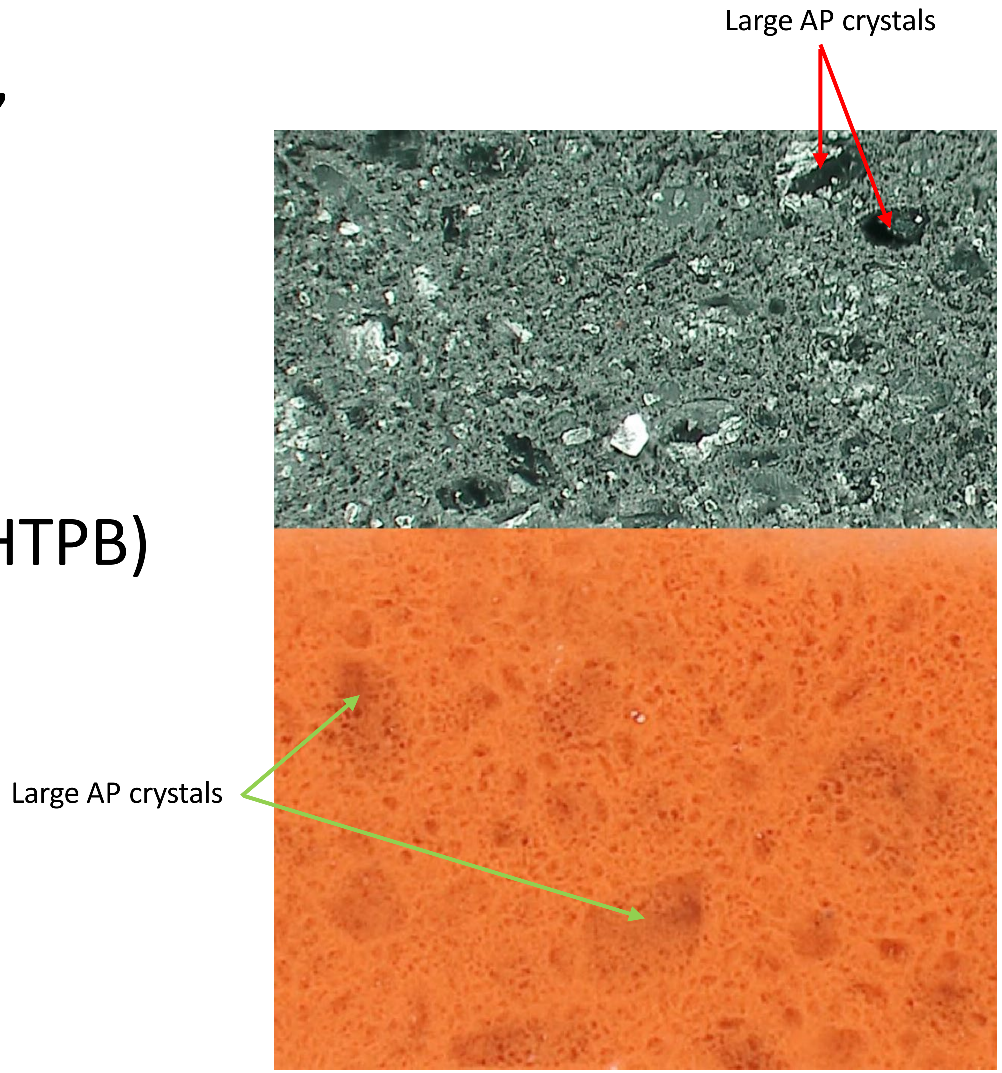
Energetic Materials

- High amount of chemically stored energy: **explosives, propellants, pyrotechnics, fuels**
  - Pressure and temperature dependence
- National security, space propulsion, safety, demolition, transportation, air bags, etc.
  - Agencies: government (DoD, DOE, NASA), companies



Solid Propellant

- Different types of solid propellant: double base, composite propellant, etc.
- **Composite propellant**
  - Oxidizer: ammonium perchlorate (AP), ammonium nitrate, etc.
  - Binder: hydroxyl terminated polybutadiene (HTPB)
  - Additives: aluminum, iron oxide
  - Solids loading: ~85-90 wt%



Thrust Profile

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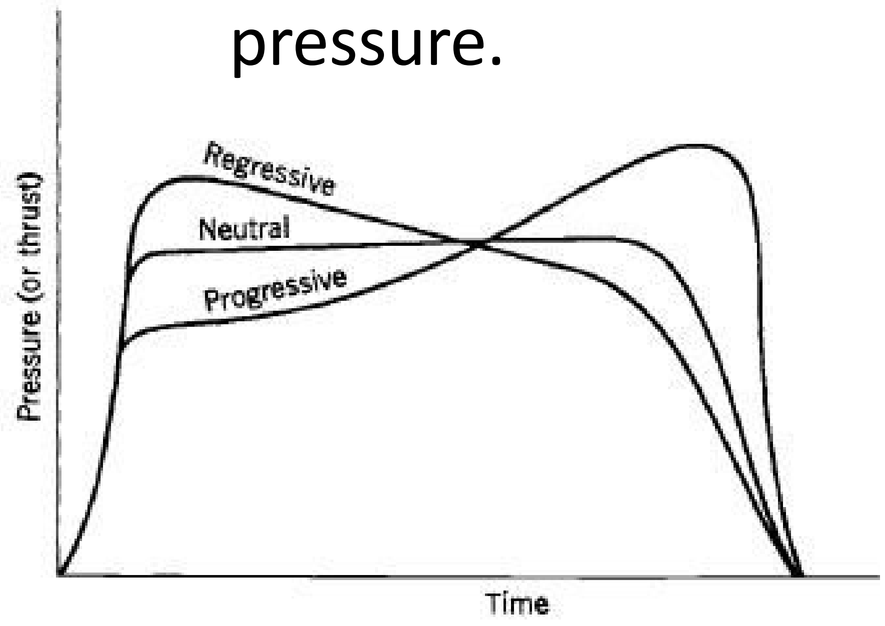
- Solid propellant is **sensitive to geometry.**
  - Geometry affects burning surface area.
  - Burning rate is **pressure dependent.**
    - Solid propellant self pressurizes.
  - Thrust profile depends on chamber pressure.

$$\dot{m} = \rho r \boldsymbol{A_b}$$

$\dot{m}$=mass flow rate
ρ=density
r=burning rate
A_b=burning surface area



$$T = C_F \boldsymbol{P_c} A_t$$

T=thrust
C_F=thrust coefficient
P_c=chamber pressure
A_t=throat area

$$r = a\boldsymbol{P_c^n}$$

r=burning rate
P_c=chamber pressure
a, n=coefficients

Fig. 11-5, Sutton, G., *Rocket Propulsion Elements*, 7th ed.

Grain Manufacture

- Casting
  - Solid mandrel removal
    - Difficult and dangerous to remove (electrostatic discharge, grain damage)
  - Melt out mandrel
    - Have to remove residual material
- Machining
  - Difficult, dangerous, limited, costly
- **Limitations**
  - Less geometric freedom internally
  - Unable to make internal holes, columns, etc.

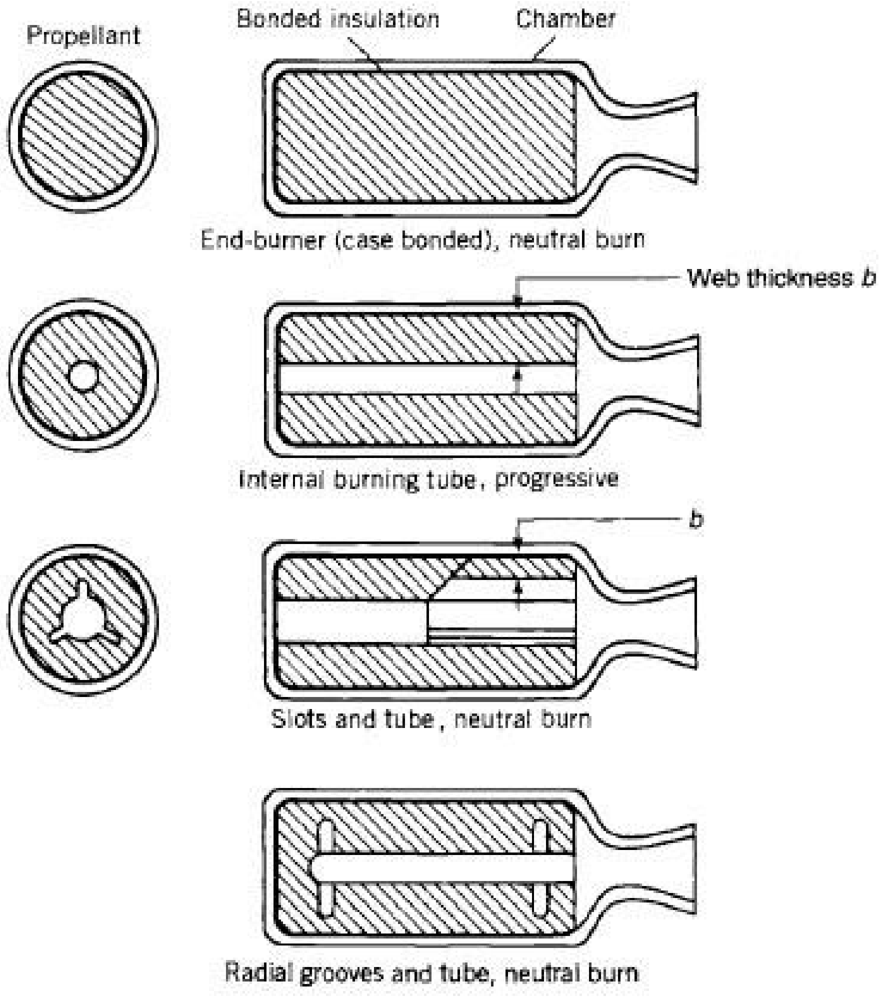


Fig. 11-6, Sutton, G., *Rocket Propulsion Elements*, 7th ed.

Additive Manufacturing

- **Additive Manufacturing (AM):** a process of joining materials to make objects from 3D model data, **usually layer upon layer**, as opposed to subtractive manufacturing methodologies [ASTM F2792-12a].
- 3D-printing can be advantageous in the aerospace industry.
  - Rapid manufacturing
  - Make **geometrically intricate parts**
  - Can create **material gradients and layer anisotropies**
    - Could influence mechanical, structural, and thermal properties

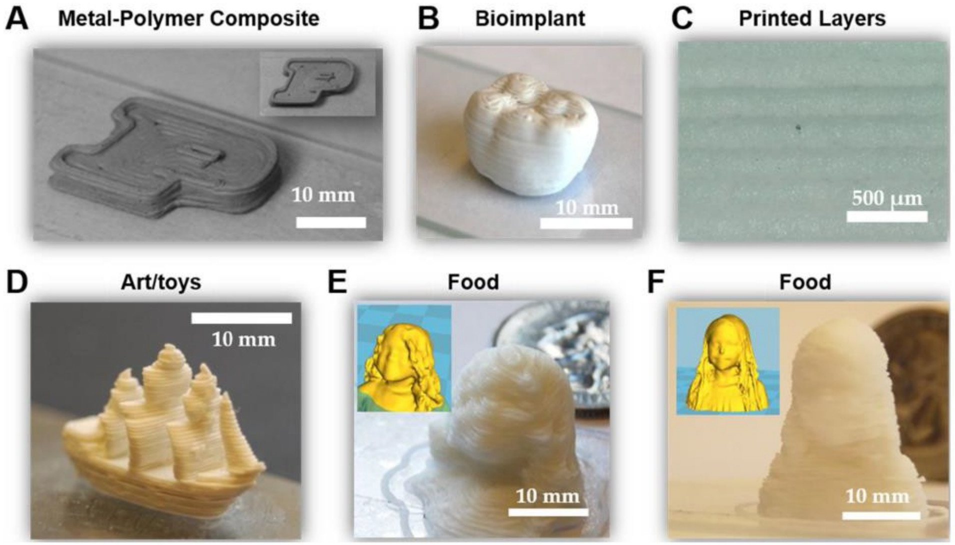
Q: How can we use 3D-printing to change how we make solid propellant?

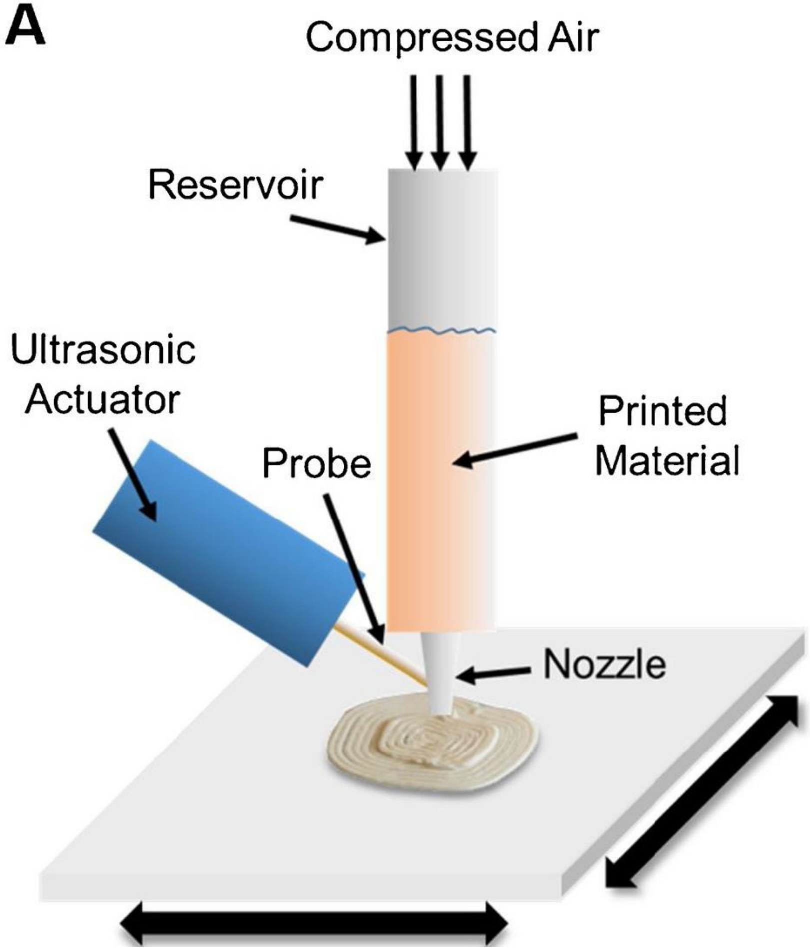
Printing Live, Solid Propellant

Vibration-Assisted Printing

Purdue Energetics

- **Vibration-Assisted Printing (VAP)** is capable of printing materials with **high viscosities (up to 14,000 Pa*s) at a high resolution and rate (using a 600-µm tip diameter or lower).**
  - Vibrations used to actuate flow (~15-µm displacement)
  - 600-µm nozzle





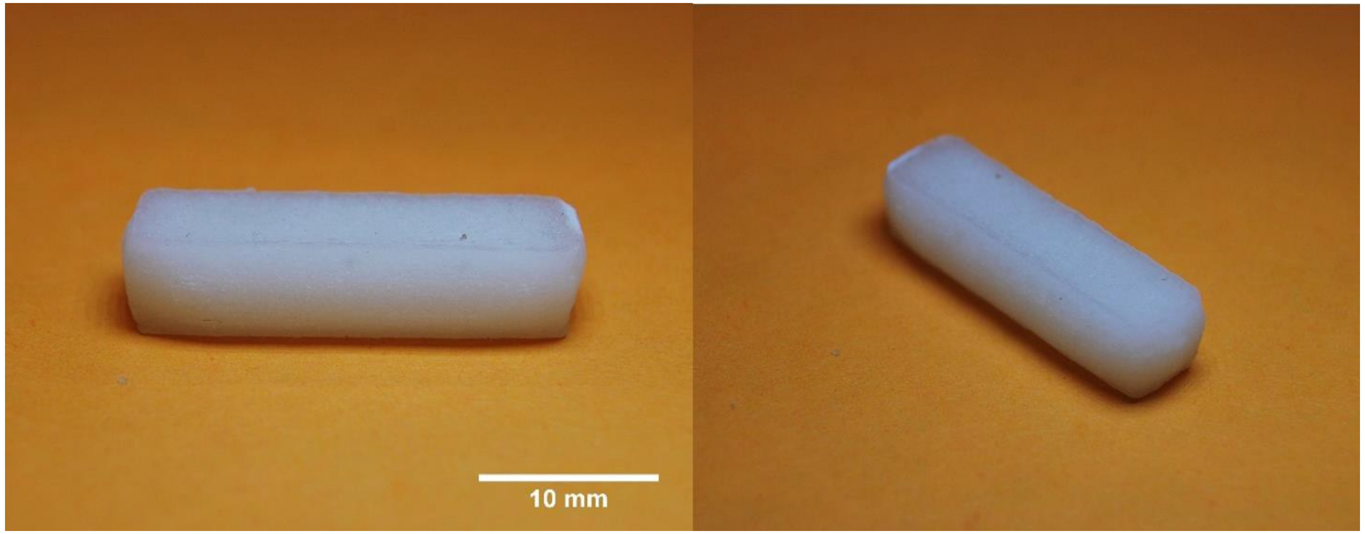
Gunduz, I. E. et al., "3D Printing of Extremely Viscous Materials Using Ultrasonic Vibrations," *Additive Manufacturing*, 2018

3D-Printed Propellant

PURDUE ENERGETICS

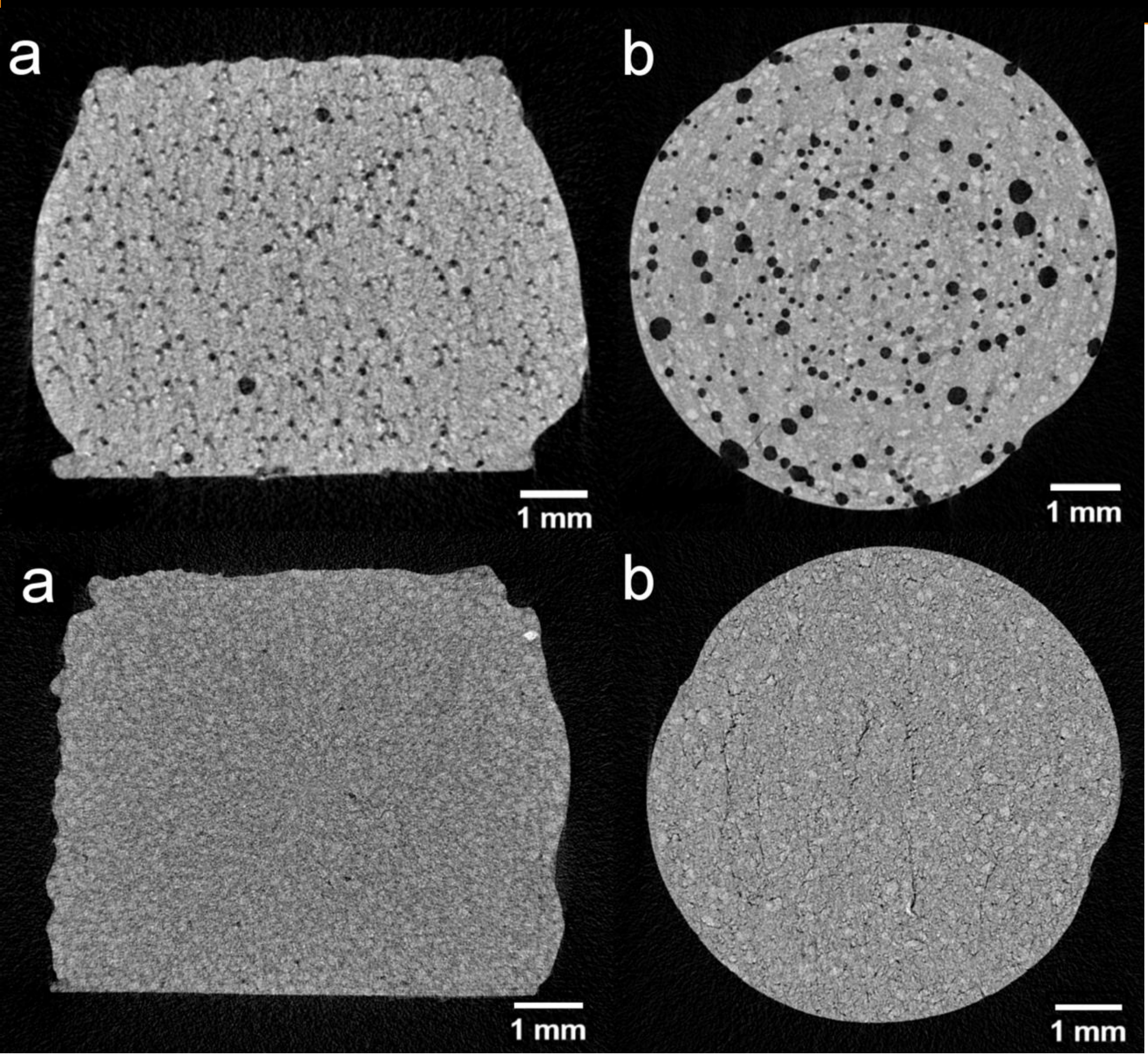
Q: How does VAP affect propellant combustion?

- **85 wt% solids loading**, 1:1 AP coarse-to-fine ratio (60-130 µm: 20 µm)
- **HTPB (hydroxyl terminated polybutadiene) binder**: 75.25 wt% R-45M polybutadiene, 15.05 wt% isodecyl pelargonate, 1.53 wt% Tepanol, and 8.27 wt% isophoprone diisocyanate (73 vol%); viscosity of **69 million cP (6900 Pa*s)**
- **Ultraviolet (UV)-curable binder**: Illumabond 60-7105 (polyurethane based), (76 vol%)



McClain, M. S. et al., "Additive Manufacturing of Ammonium Perchlorate Composite Propellant with High Solids Loadings," *Proceedings of the Combustion Institute*, 2019

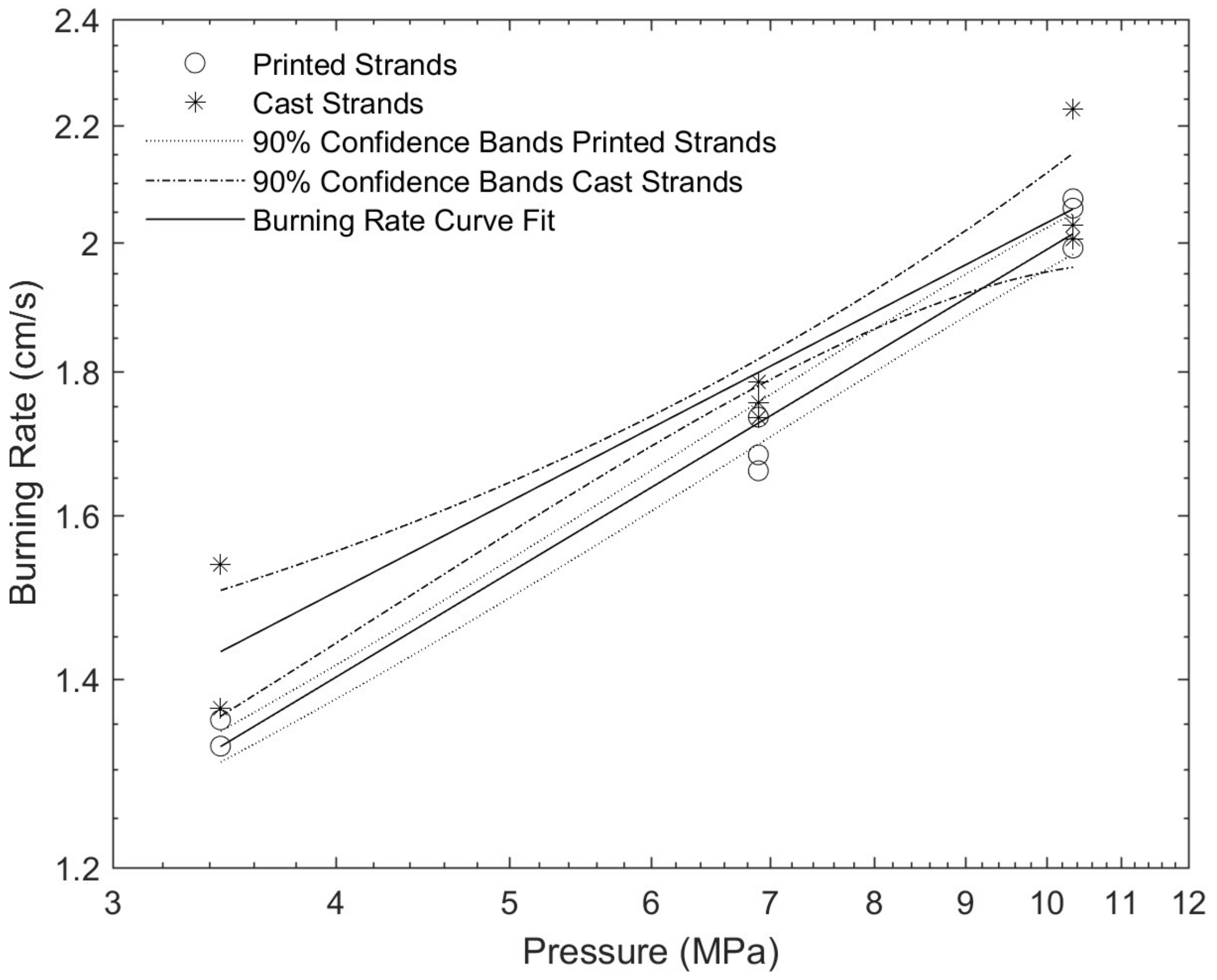
Propellant Microstructure



- **HTPB propellant density**
  - **Printed**: 1.55 g/cc (92% TMD)
  - **Cast**: 1.45 g/cc (86% TMD)
  - Theoretical: 1.68 g/cc
- **UV binder propellant density**
  - **Printed:** 1.75 g/cc (101% TMD)
  - **Cast:** 1.55 g/cc (89% TMD)
  - Theoretical: 1.73 g/cc
- Ammonia production from Tepanol is likely source of small, distributed voids.
- **Voids are NOT correlated with layer interfaces.**

McClain, M. S. et al., "Additive Manufacturing of Ammonium Perchlorate Composite Propellant with High Solids Loadings," *Proceedings of the Combustion Institute*, 2019

HTPB Strand Burning Rate



McClain, M. S. et al., "Additive Manufacturing of Ammonium Perchlorate Composite Propellant with High Solids Loadings," *Proceedings of the Combustion Institute*, 2019

- **HTPB propellant burning rate**
  - **Cast:** $0.952 \cdot P^{0.33}$
  - **Printed:** $0.826 \cdot P^{0.38}$
  - Slightly higher burning rate of cast propellant could be due to higher porosity.
- **UV binder propellant burning rate**
  - **Cast:** $\mathbf{0.622 \cdot P^{0.31}}$

T: There is no significant change in the propellant burning rate due to VAP, and VAP improves the propellant density relative to lab-scale, cast propellants.

Photopolymers for Propellants

Photopolymer Study

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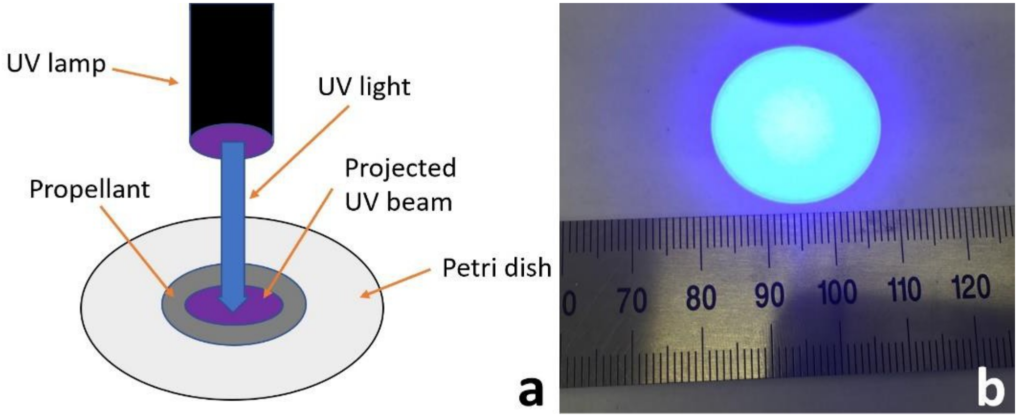
Q: Can photopolymers be compatible with propellant ingredients and cure formulations with opaque additives?

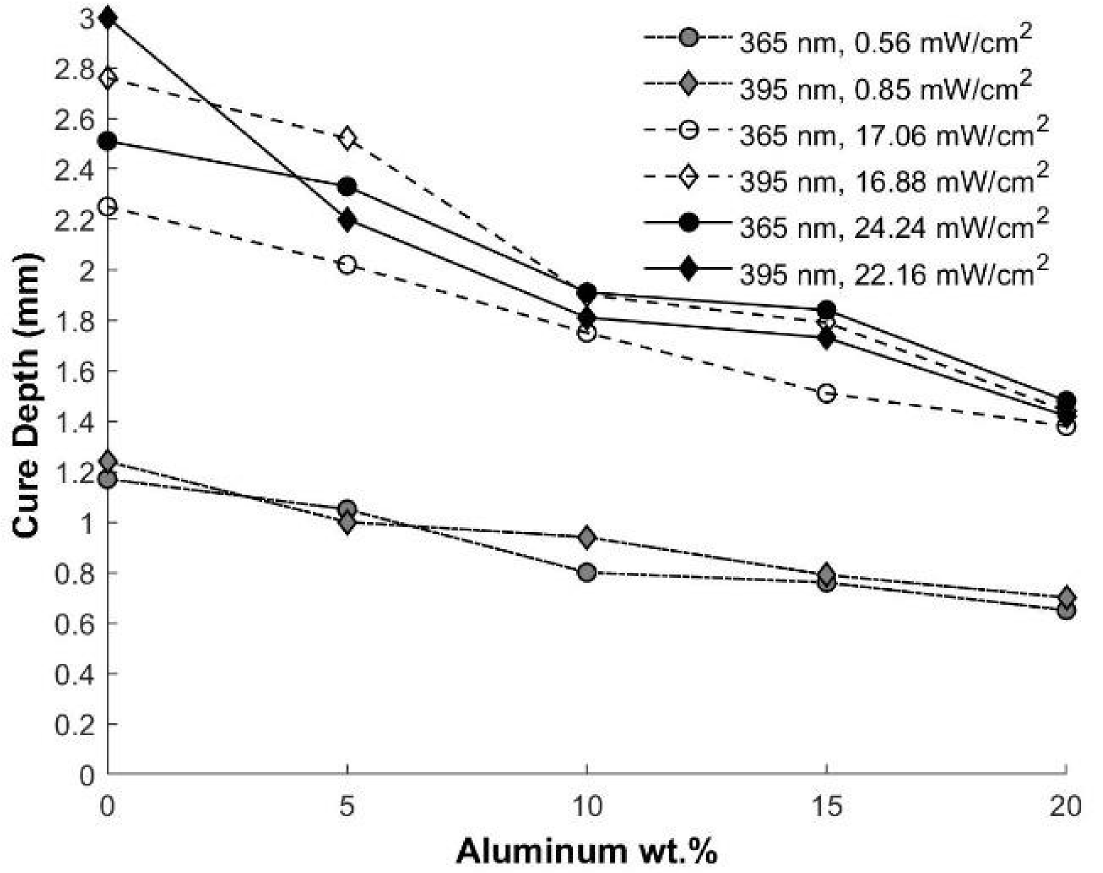
- **Control in cure depth is desired and should be larger than print layer height.**
  - Opaque inclusions will affect curing (i.e., aluminum in propellant).
- Photopolymer formulation:
  - Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO): **photoinitiator**
  - Hexanediol diacrylate (HDDA): **reactive diluent**
  - Polybutadiene urethane acrylate: **oligomer with similar properties to HTPB**
- Varied wavelength (365 and 395 nm), cure time, and intensity for photopolymer cure depth tests.
- Varied aluminum content (0-20%), wavelength, and intensity in propellant (85 wt% solids loading).



McClain, M. S. et al., "Development and Characterization of a Photopolymeric Binder for Additively Manufactured Composite Solid Propellant Using Vibration Assisted Printing," *Propellants, Explosives, and Pyrotechnics,* 2020

Cure Depth Study

- Propellant cure depth is affected mostly by **aluminum content and wavelength.**
- Max temperature increase is affected by **aluminum content.**
- **Cure depth is larger than print layer height (~0.25 mm), even for aluminized propellants.**
- Mechanical properties of the propellant (i.e., flexible vs. rigid) can be controlled via cure parameters.

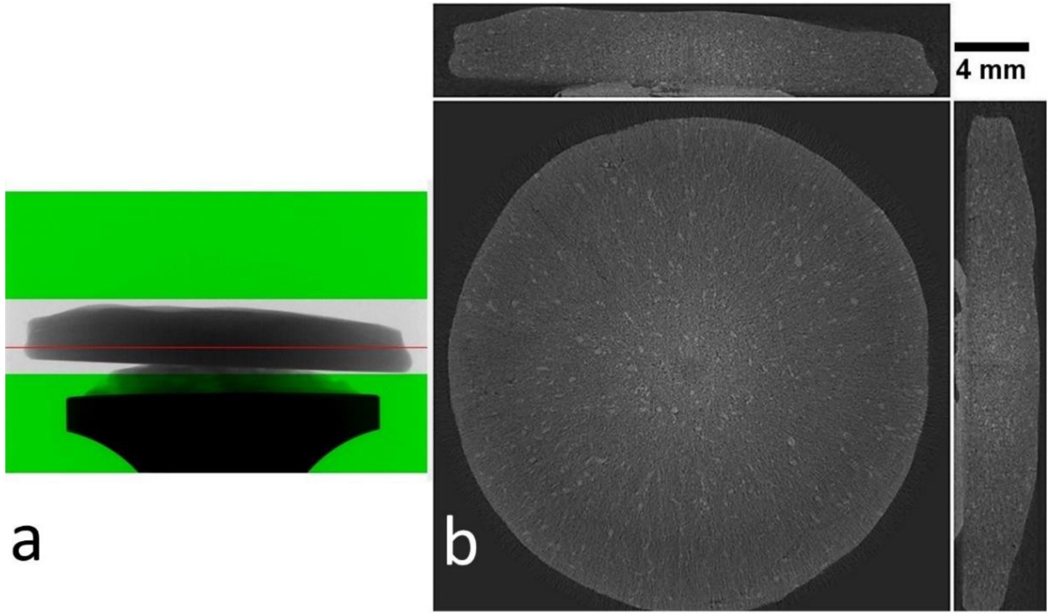


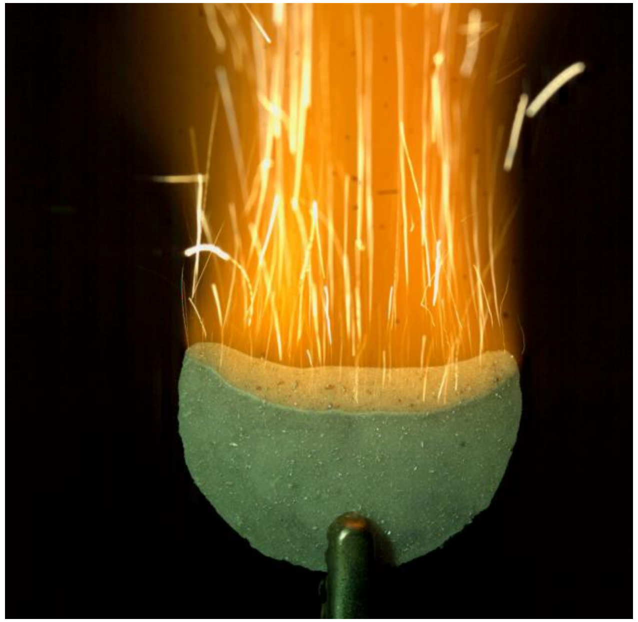
McClain, M. S. et al., "Development and Characterization of a Photopolymeric Binder for Additively Manufactured Composite Solid Propellant Using Vibration Assisted Printing," *Propellants, Explosives, and Pyrotechnics,* 2020

MicroCT

- Four layers of cured propellant with 15% aluminum (each layer ~1 mm)
  - Each layer cured with 395 nm and an intensity of 23.72 mW/cm^2 for 45 s
- **No interfaces seen in MicroCT**

T: This UV-curable binder can enable 3D-printing of complex propellant structures with tuned mechanical properties. A new experiment to quantify the UV-curing properties of propellants is presented.





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PURDUE ENERGETICS

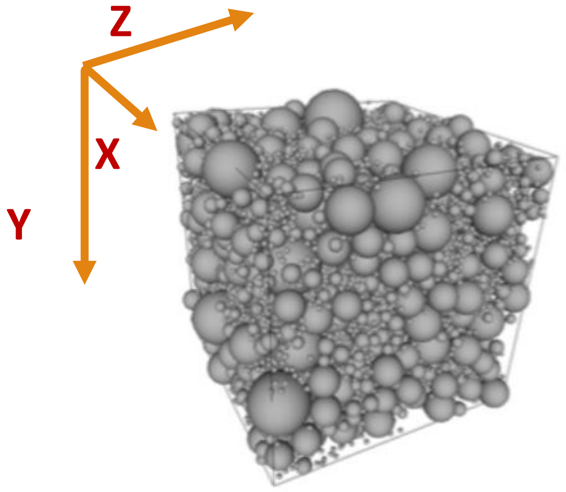
Combustion Modeling of Functionally Graded, Layered Propellant: Effect of Ammonium Perchlorate Particle Size

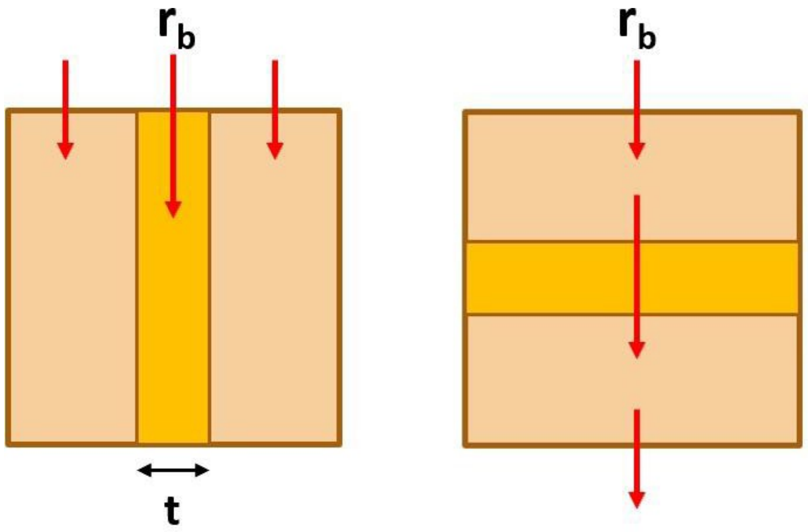
Layered Propellant Model

Purdue Energetics

Q: What is the combustion behavior of layered propellants, and what are the driving factors?

- Now that AM can print propellant at fine layer thicknesses, we should **model and experimentally validate the combustion dynamics of layered propellants.**
- RocFire (Jackson et al. 2005) is a code that can simulate propellant burning rates.
  - Modeled **3 different layered propellants in 2 orientations (75 wt% solids loading) at 10.34 MPa**
  - Studied the effect of ammonium perchlorate (AP) particle size
  - Used 4-step kinetic mechanism (Gross 2013) to model AP/HTPB combustion

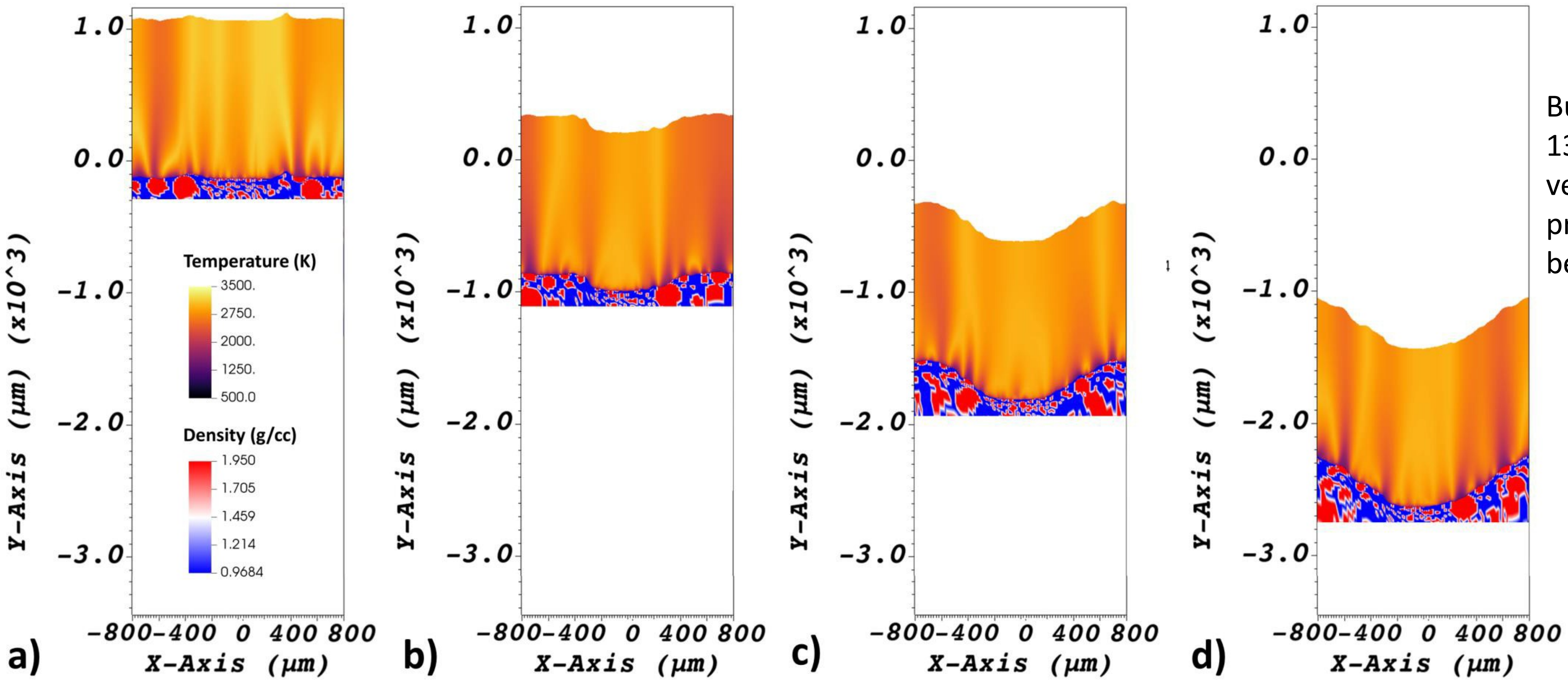




Vertical Orientation

Horizontal Orientation

Vertical Surface



Burning surface profile of 130 μm | 20 μm| 130 μm vertically layered propellant with 40 ms between each frame

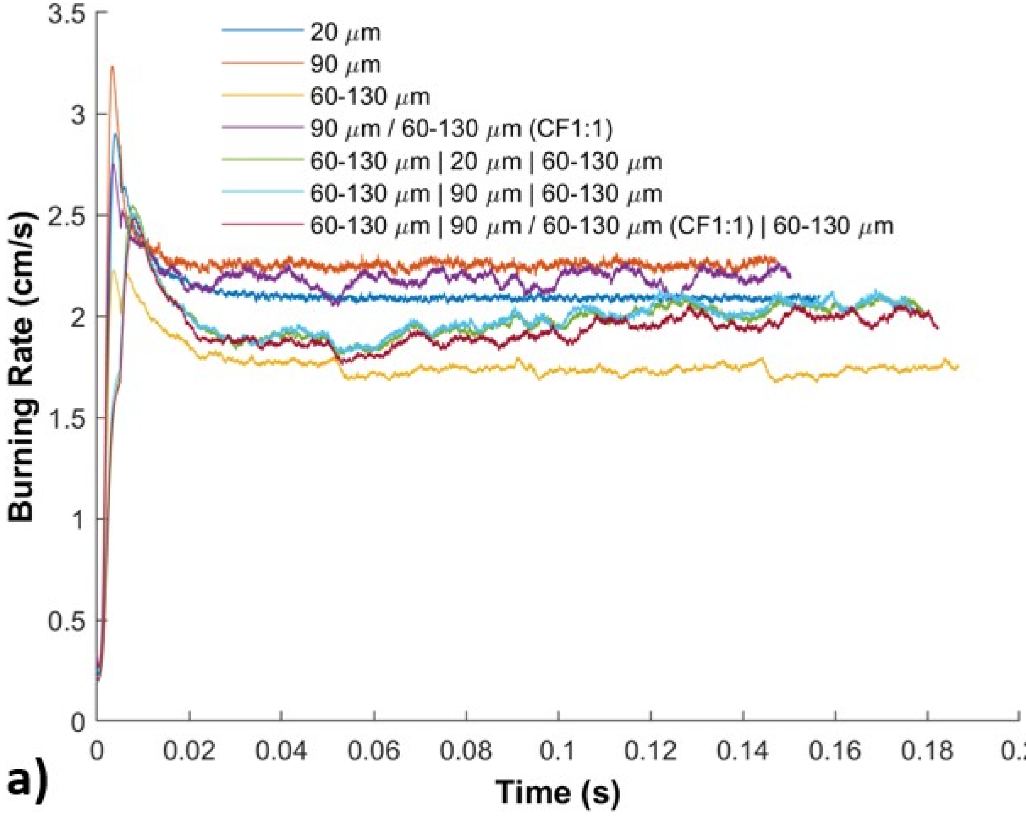
Red: AP particles
Blue: Binder

Top section is the gas phase; bottom section is the solid phase.

McClain, M. S. et al., "Modeling of Layered Ammonium Perchlorate Composite Propellant with Different Burning Rates," AIAA SciTech, 2021

Vertical Orientation

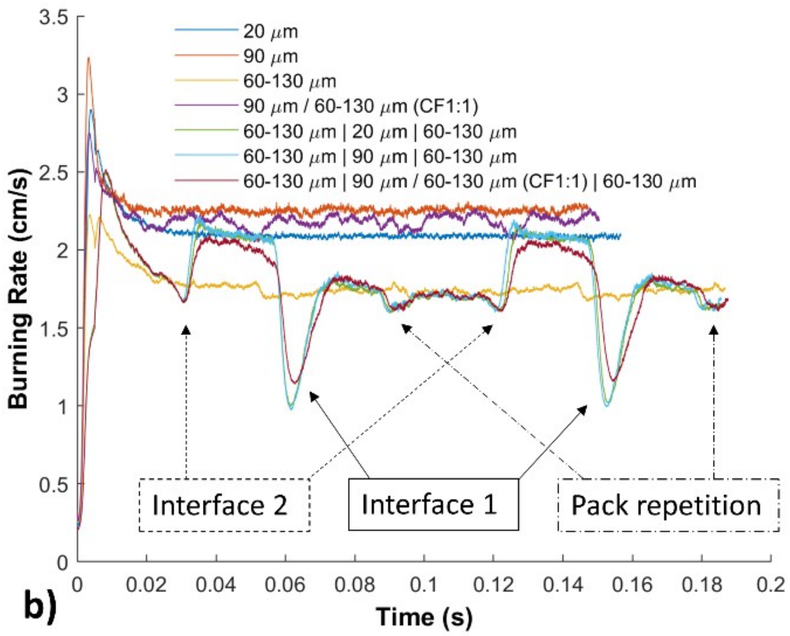
- Vertical orientation means that the **layers are perpendicular to the flame front.**
- **Single propellant burning rate**
  - 20 µm: 2.09 cm/s
  - 90 µm: 2.25 cm/s
  - 90 µm/130 µm: 2.18 cm/s
  - 130 µm: 1.74 cm/s
- **Vertical orientation acceleration**
  - 20 µm: 1.52 cm/s² ($R^2 = 0.804$)
  - 90 µm: 1.55 cm/s²($R^2 = 0.764$)
  - 90 µm/130 µm (CF 1:1): 1.30 cm/s² ($R^2 = 0.725$)
- **Acceleration is due to increasing burning surface area.**

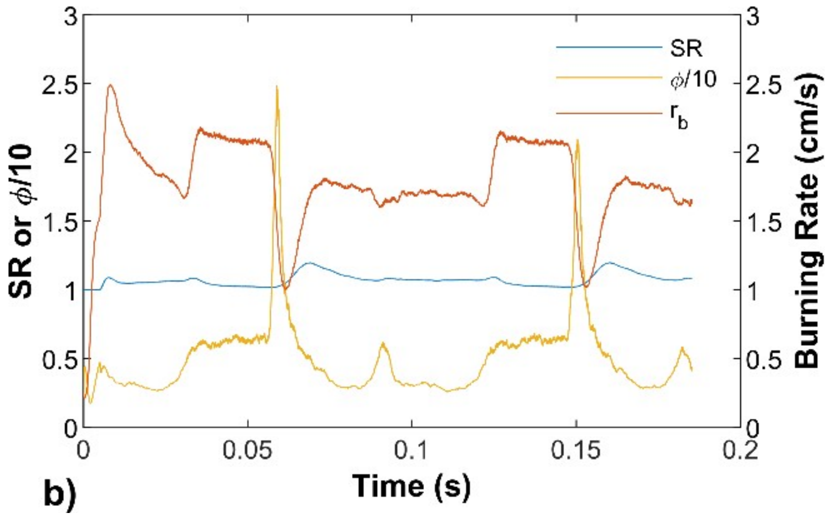


McClain, M. S. et al., "Modeling of Layered Ammonium Perchlorate Composite Propellant with Different Burning Rates," AIAA SciTech, 2021

Horizontal Orientation

- Horizontal orientation means that the **layers are parallel to the flame front.**
- **Single propellant burning rate**
  - 20 µm: 2.09 cm/s
  - 90 µm: 2.25 cm/s
  - 90 µm/130 µm: 2.18 cm/s
  - 130 µm: 1.74 cm/s
- **Particle size drives the local equivalence ratio (ϕ) and surface area ratio (SR), which drive the combustion dynamics.**





T: Modeling can aid in the design of functionally graded propellants (i.e., avoid extinction, control acceleration). Key drivers in the combustion behavior are particle size and burn orientation.

McClain, M. S. et al., "Modeling of Layered Ammonium Perchlorate Composite Propellant with Different Burning Rates," AIAA SciTech, 2021

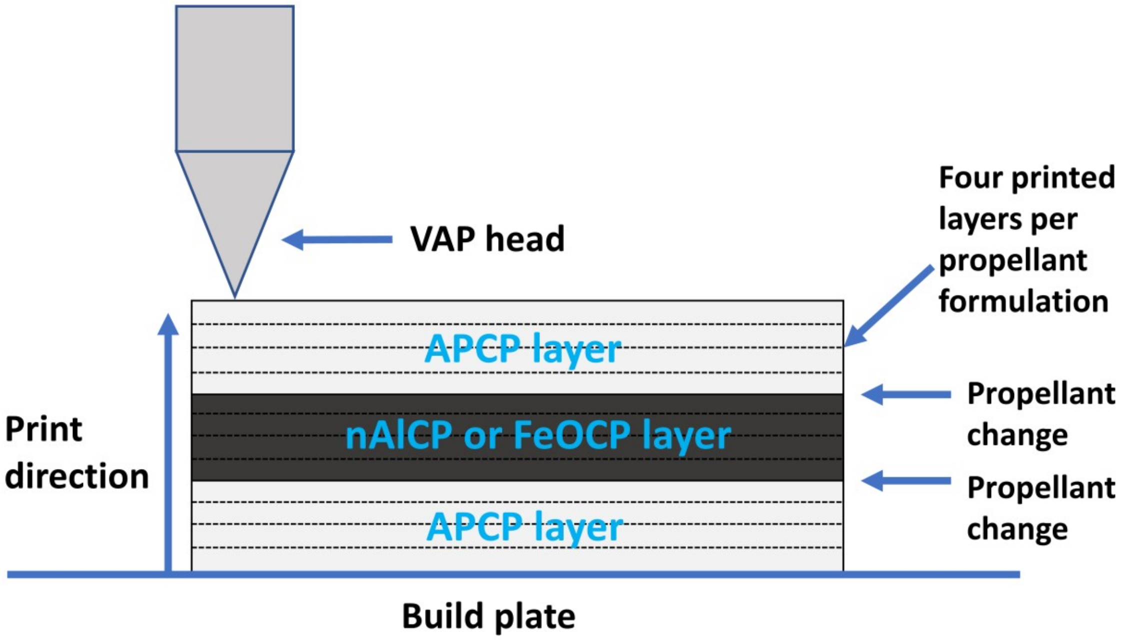
Dynamic Combustion of Additively Manufactured, Functionally Graded, Layered Propellant

3D-Printed Propellant

PURDUE ENERGETICS

Q: What is the combustion performance of 3D-printed, layered propellants?

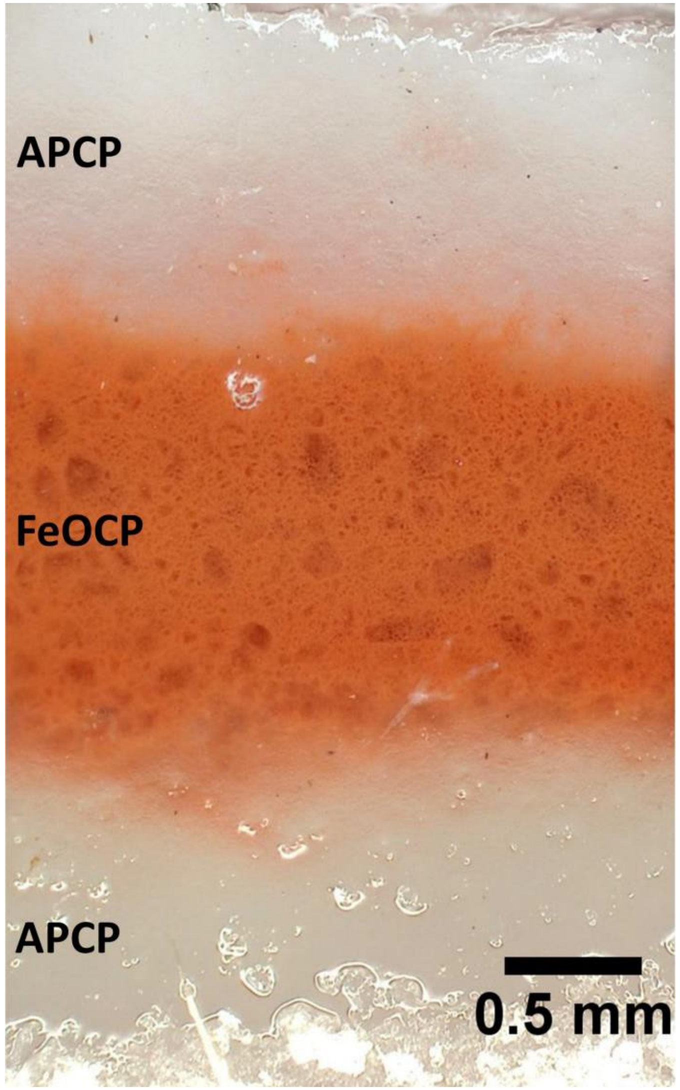
- All outer propellant layers were 85 wt% 60-130-µm AP, 72.6 vol%.
- Inner propellant layers were 85 wt%.
  - **LFeOCP:** 1 wt% -325 mesh iron oxide (84 wt% 60-130 µm AP), 72.4 vol%
  - **LnAlCP:** 5 wt% 80-nm nAl (80 wt% 60-130-µm AP), 72.1 vol%
  - Binder: 76.55 wt% hydroxyl terminated polybutadiene, 15.05 wt% isodecyl pelargonate, and 8.4 wt% isophorone diisocyanate
- **Three printed 1-mm layers of 20 x 60 mm.**
- Final strands were 3 x 3 x 17 mm.

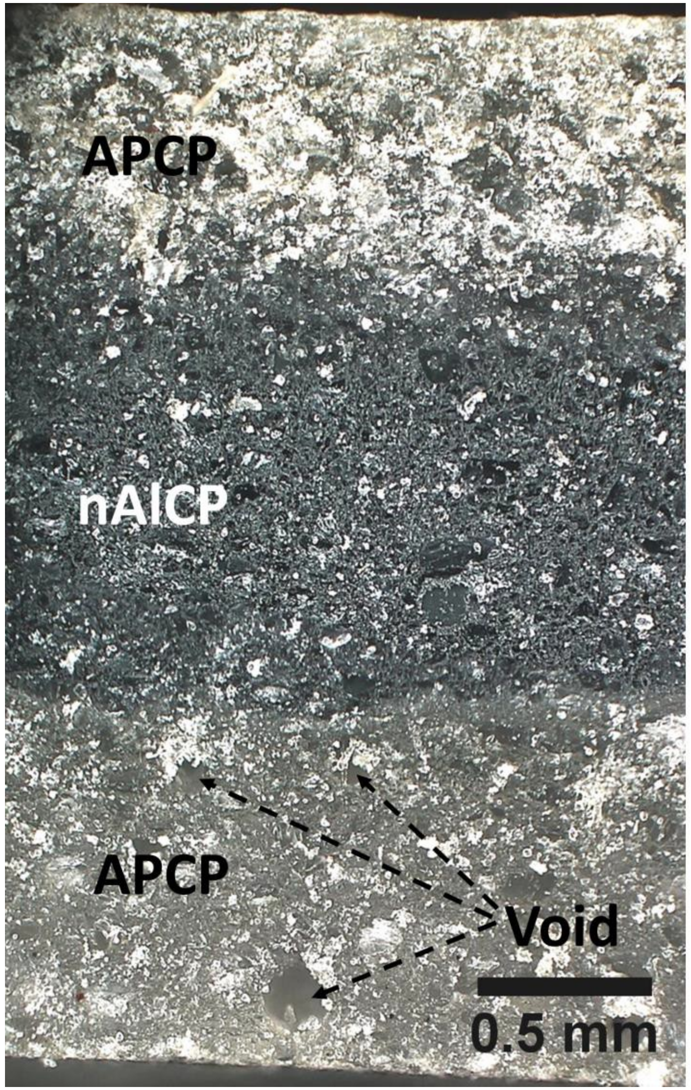


McClain, M. S. et al., "Dynamic Combustion of Additively Manufactured Layered Composite Propellant," *AIAA Journal of Propulsion and Power,* in press, 2021

Microscopic Imaging

- See little interlayer mixing, few voids, slight deformation of uncured propellant
- Cast nonlayered and 3D-printed, layered propellant densities
  - Cast **APCP**: 1.54 g/cc (92.8% TMD of 1.66 g/cc)
  - Cast **nAlCP**: 1.48 g/cc (87.8% TMD of 1.69 g/cc)
  - Printed **LnAlCP**: 1.61 g/cc (96.4% TMD of 1.67 g/cc)
  - Cast **FeOCP**: 1.56 g/cc (91.5% TMD of 1.71 g/cc)
  - Printed **LFeOCP**: 1.59 g/cc (94.9% TMD of 1.68 g/cc)



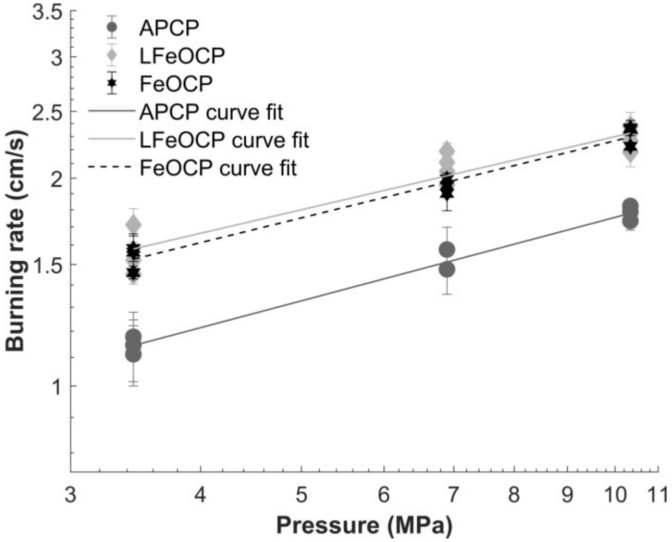


McClain, M. S. et al., "Dynamic Combustion of Additively Manufactured Layered Composite Propellant," *AIAA Journal of Propulsion and Power,* in press, 2021

Dynamic Combustion

PURDUE ENERGETICS

500 psi



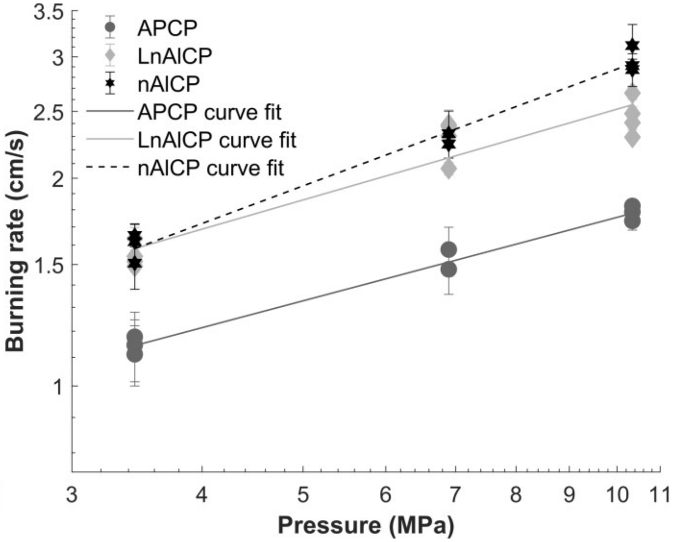


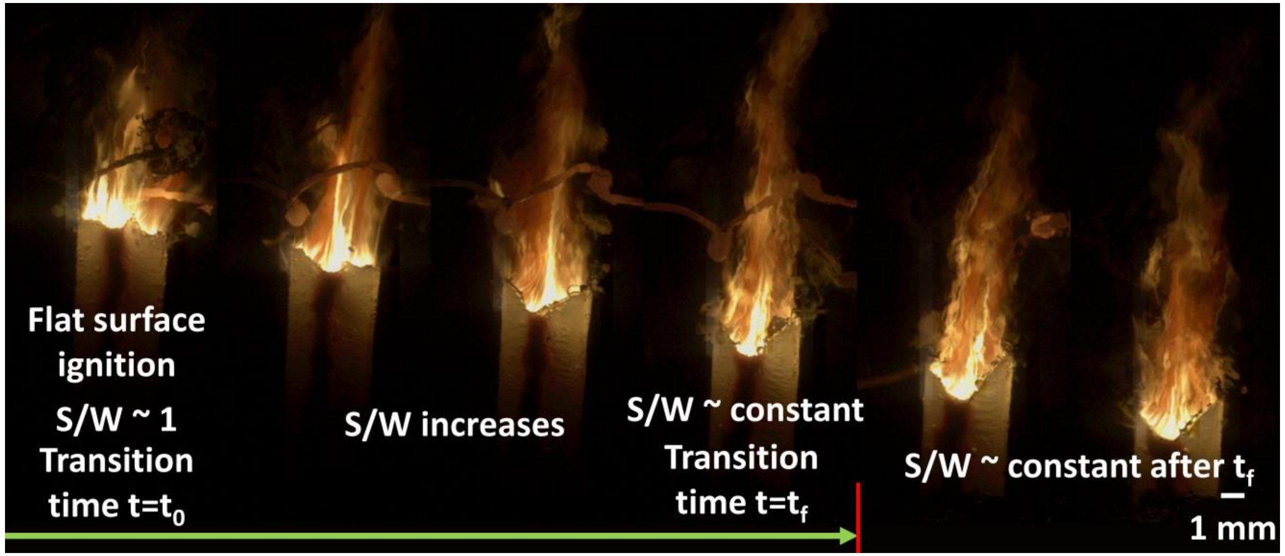
Table 2 Pressure coefficients (*a*) and exponents (*n*) of the 1 mm thick inner layer of printed propellant and of the cast propellant

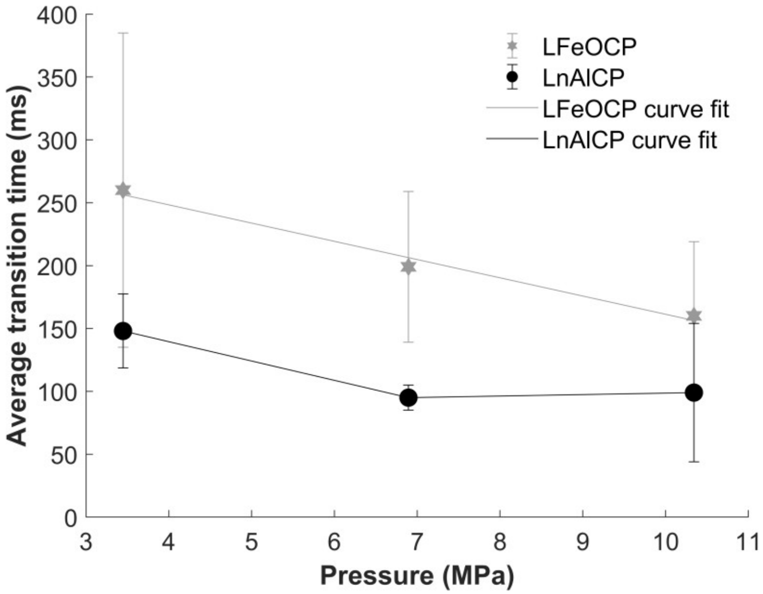
St. Robert's law parameters	APCP	LFeOCP	FeOCP	LnAlCP	nAlCP
a	0.70	1.02	0.96	0.92	0.79
n	0.40	0.35	0.37	0.44	0.56

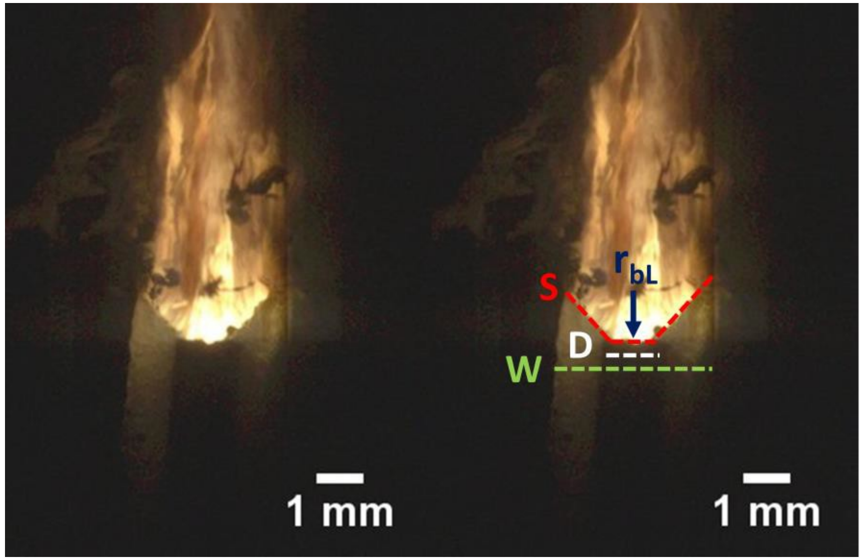
McClain, M. S. et al., "Dynamic Combustion of Additively Manufactured Layered Composite Propellant," *AIAA Journal of Propulsion and Power,* in press, 2021

Dynamic Metrics

PURDUE ENERGETICS







T: Key metrics were identified to describe 3D-printed, layered propellant performance. A thin layer of faster burning propellant can increase the burning surface area. A thin layer of nAl propellant will have less radiation heat feedback to the surface and a more stable burning rate exponent than cast, nonlayered propellant.

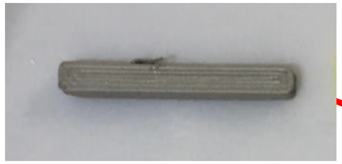
McClain, M. S. et al., "Dynamic Combustion of Additively Manufactured Layered Composite Propellant," *AIAA Journal of Propulsion and Power,* in press, 2021

Additional Research Areas

Dissimilar Materials

- **Dissimilar material 3D-printing: thermoplastics and composite mixtures**
  - E.g., thermoplastic casings/propellants and reactive wires/propellants.
  - **Goal** is to integrate dissimilar 3D-printing techniques via custom 3D-printers, explore material compatibility, and leverage geometric features to create dissimilar material structures.
- Small integrated propulsion systems (including satellites and CubeSATs)
  - Cheap fuels that are printable (hybrids), cold gas thrusters.
  - **Reactive filaments** can be integrated as well to increase functionality.

Fused filament fabrication



Printable Al/PVDF

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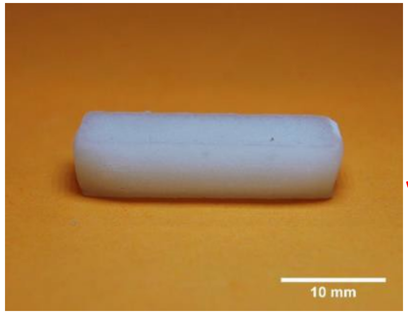
Vibration-assisted printing



McClain, M. S. et al., *Proceedings of the Combustion Institute*, 2019

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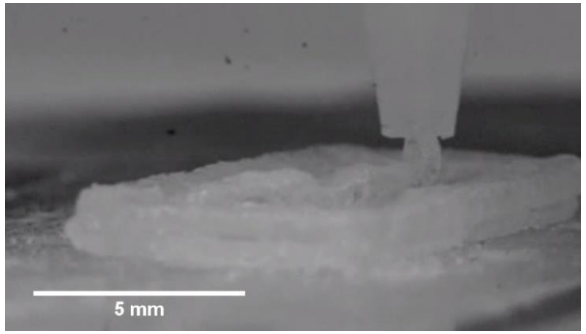
500 psi, Al/PVDF and 85% solids loading AP/HTPB

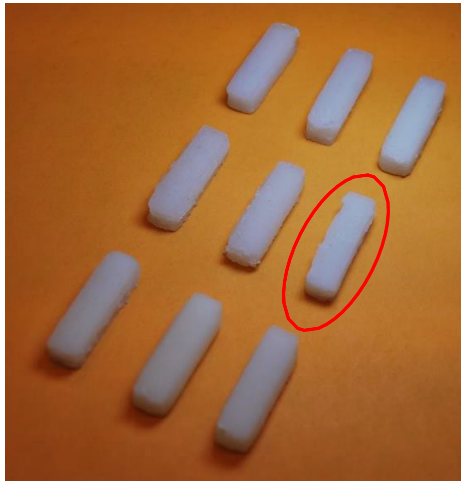
Process Monitoring

- Integrating sensors into 3D-printers for process monitoring
- Use statistical process control techniques
  - **Goal** is to detect anomalies and gain better control of AMEM quality.

McClain, M. S. et al., *Proceedings of the Combustion Institute*, 2019

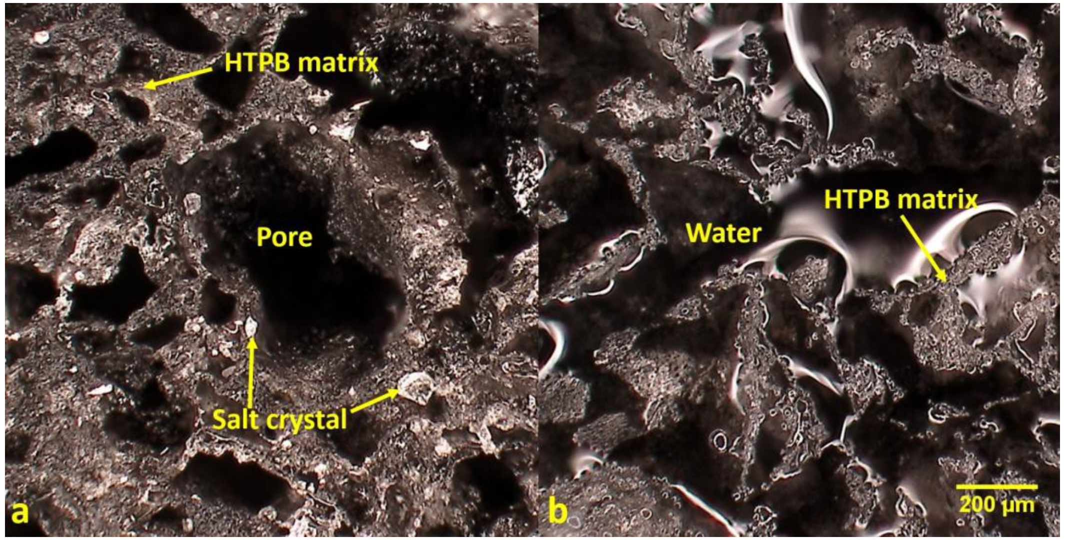


Sensor integration (i.e., temperature, pressure, position, vision, etc.) → Sensor output → Data dimension reduction (i.e., probabilistic principal component analysis) → Statistical process control → Anomaly detection

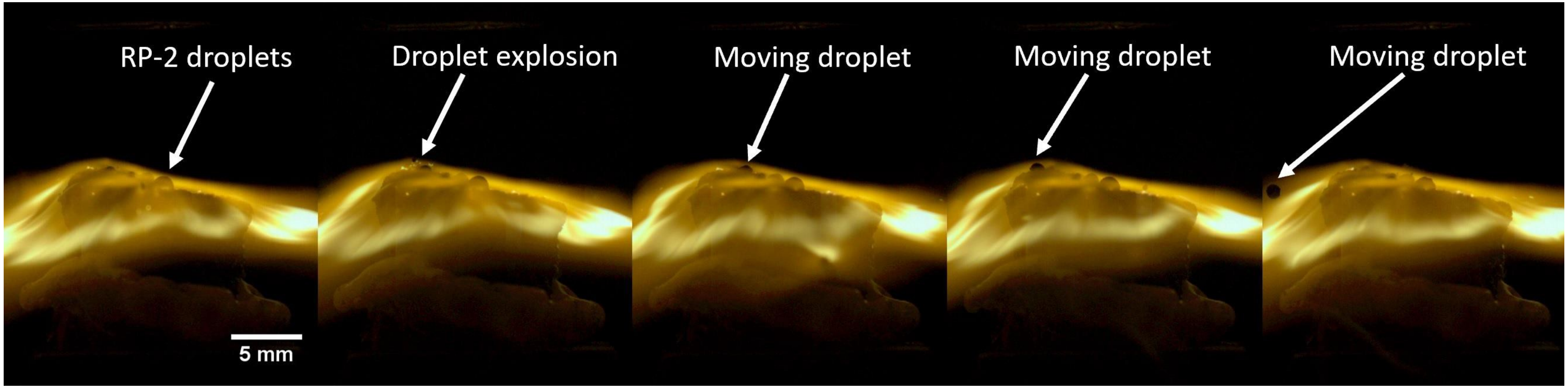


Stimuli-Responsive Fuels

- **Goal** is to design fuels that are **sensitized to a stimulus** (e.g., temperature, electrostatics, magnetism) and respond physically, such as increasing the regression rate.
  - E.g., infused RP-2 into porous HTPB.
  - Temperature-activated release of liquid fuel into gaseous oxygen flow improved regression rate.



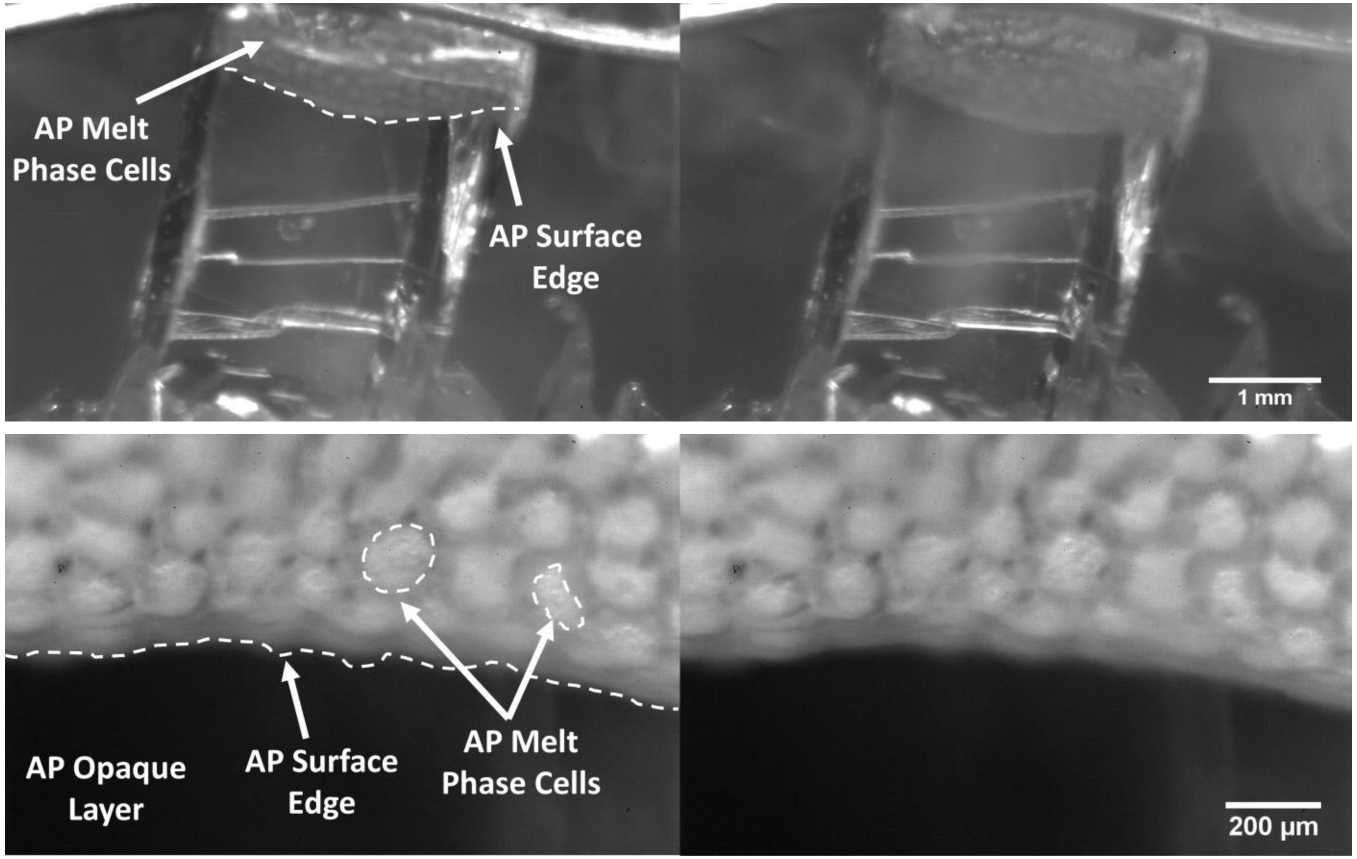
McClain, M. et al., "Sweating Hybrid Rocket Fuels; Inclusion and Temperature Activated Release of Liquid Fuels in Solid Binders," *AIAA JP&E,* 2019



AP Combustion

- **Goal** is to study AP single crystal combustion ***in-situ*** at pressurized conditions to supplement previous research.
  - Characterize **cellular AP melt layer** structures (diameter is 85-135 μm at 400 psi)
  - Darrieus Landau instability

McClain, M. et al., "Characterization of the Melt Layer of Ammonium Perchlorate Single Crystals," *AIAA JP&E,* 2020



400 psi
1.1 μm/pix
resolution

Conclusions

Purdue Energetics

- 3D-printing energetic materials is a relatively new research field.
- There are many opportunities to explore how 3D-printing can improve the performance of energetic materials.
- It is necessary to **develop fundamental manufacturing science** to reliably and fully exploit AMEMs.
  - Involves the design of new experiments and standards for the energetic materials community.
  - Our background of ***materials, manufacturing, process monitoring, combustion, and propulsion*** place my team at a unique intersection for this research.
  - Collaborations are welcome!

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