Additive Manufacturing of Energetics: from propellants to energetic initiator inks

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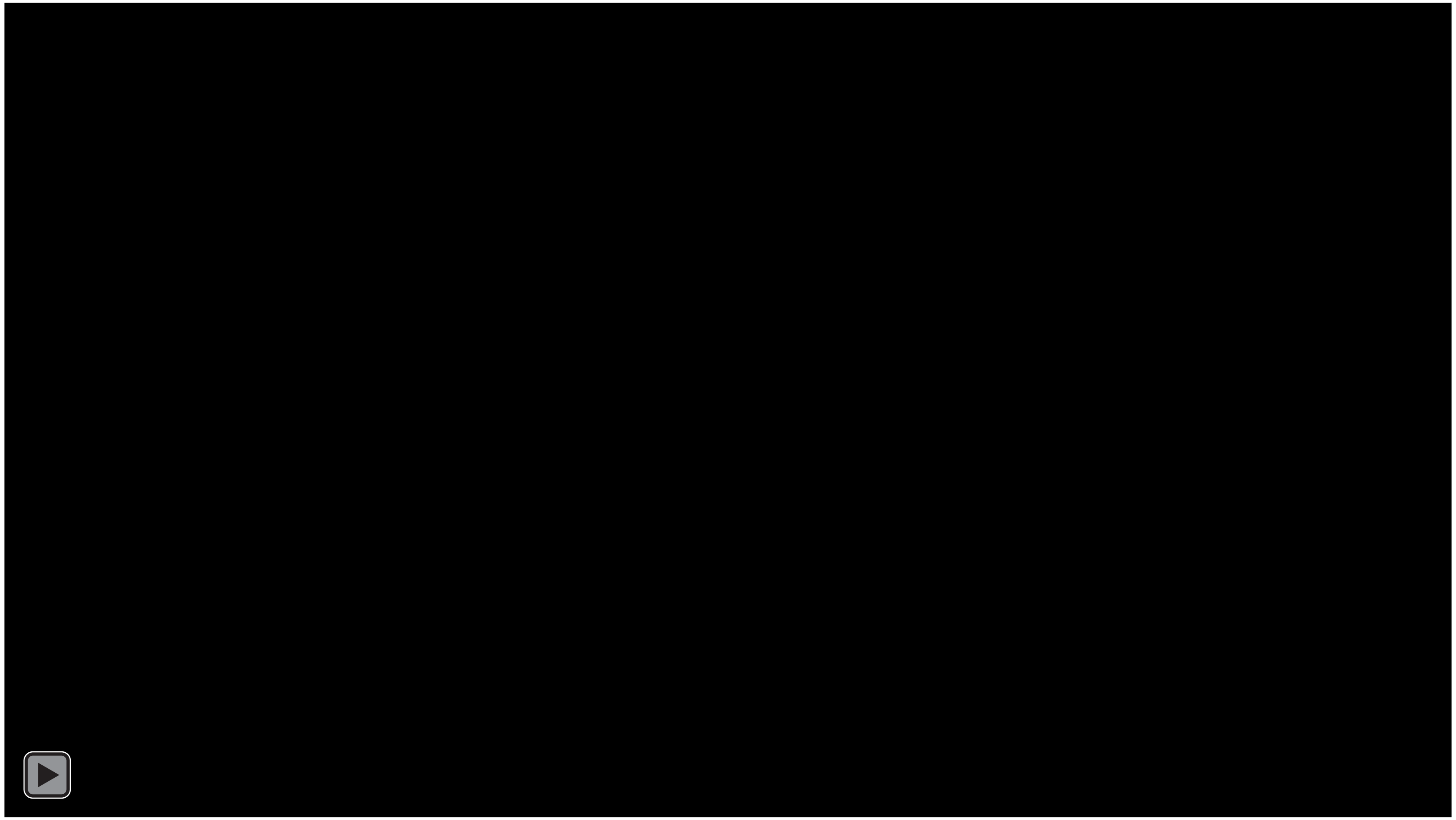
Why additive manufacturing of propellants and energetics?

- Propellants are typically cast, producing excess waste and long lead times
- AM techniques allow for on-the-fly alteration of compositions, and the ability to tailor burn rate
- Mobile AM centers could drastically reduce shipping costs of motors or other energetics
- Challenges
  - Safety issues have prevented large scale adoption of AM of energetics
  - Propellant, for example, is a high solids loading slurry
  - Interfaces present in the system that don’t exist in casting techniques

ACML built a system to print rocket propellant into cases, and tested them on Dr. M. Hargather’s test stand at EMRTC

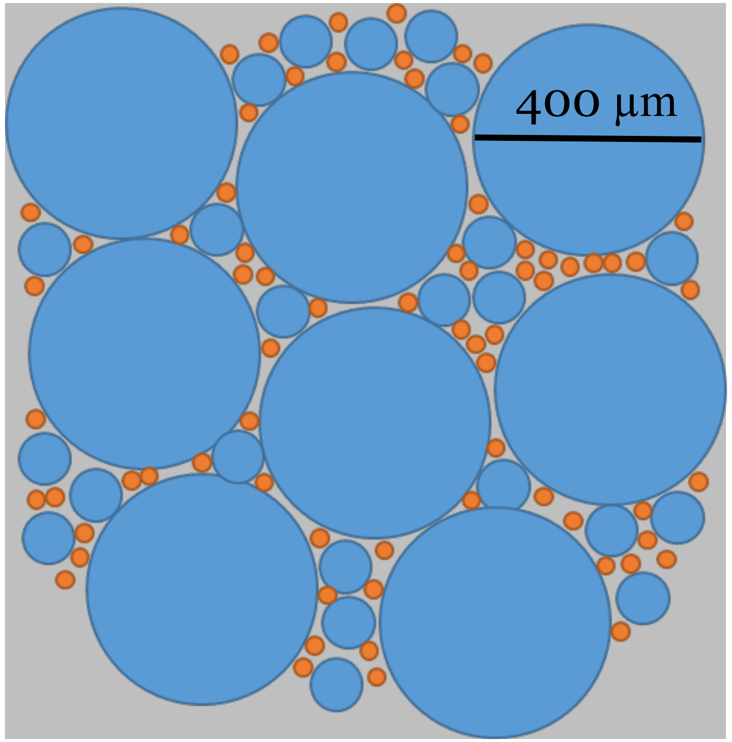


Hargather et al., (2024). *Additively Manufactured Rocket Fuel Grains and Competitive Simulation of the Same* (US Patent No. 11,913,410). USPTO.

Goal: gain an understanding of *printability* and *extrudability* of ammonium perchlorate composite propellant (APCP)

- Develop formulations of ammonium perchlorate composite propellant (APCP)
  - Suitable for additive manufacturing in a custom-built extrusion-based system
  - 7 formulations
- Characterize formulations
  - Viscosity – two ways
  - Yield stress
  - Burn rate
  - Mechanical properties

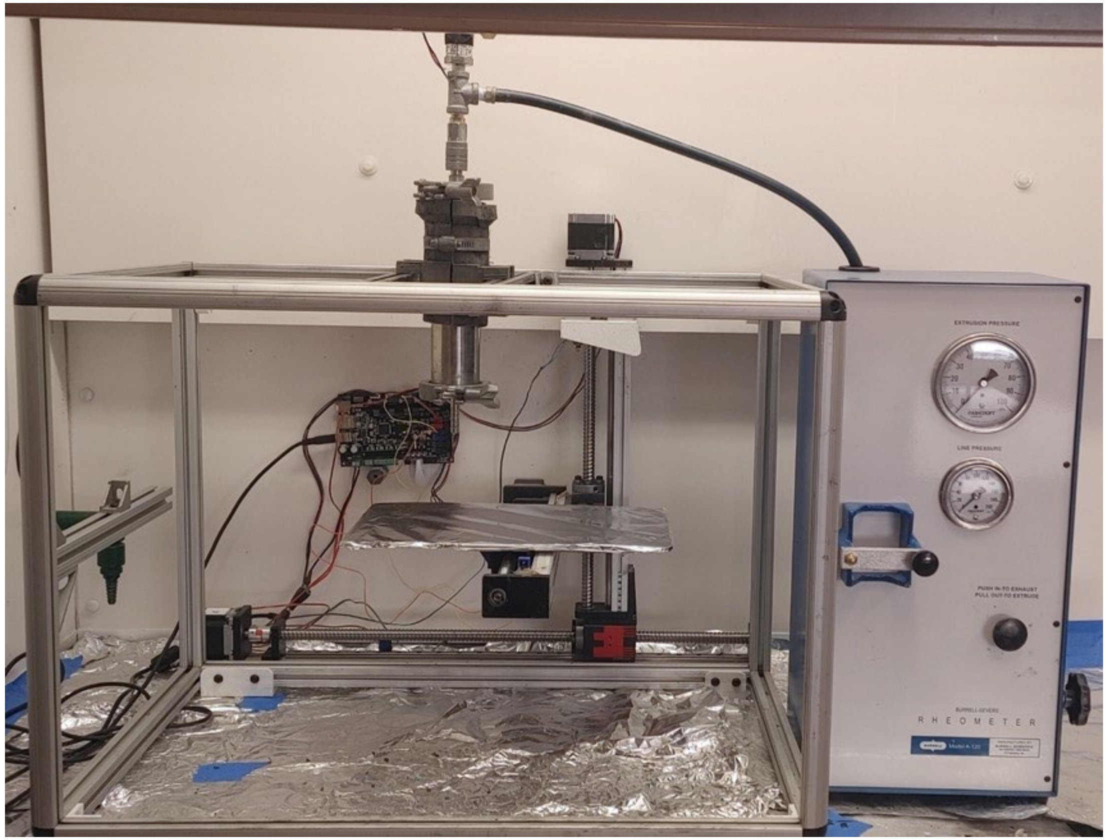
Oxidizer (Bimodal)
Metal Fuel
Binder



3-axis extrusion system used to print solid composite propellant and calculate viscosity

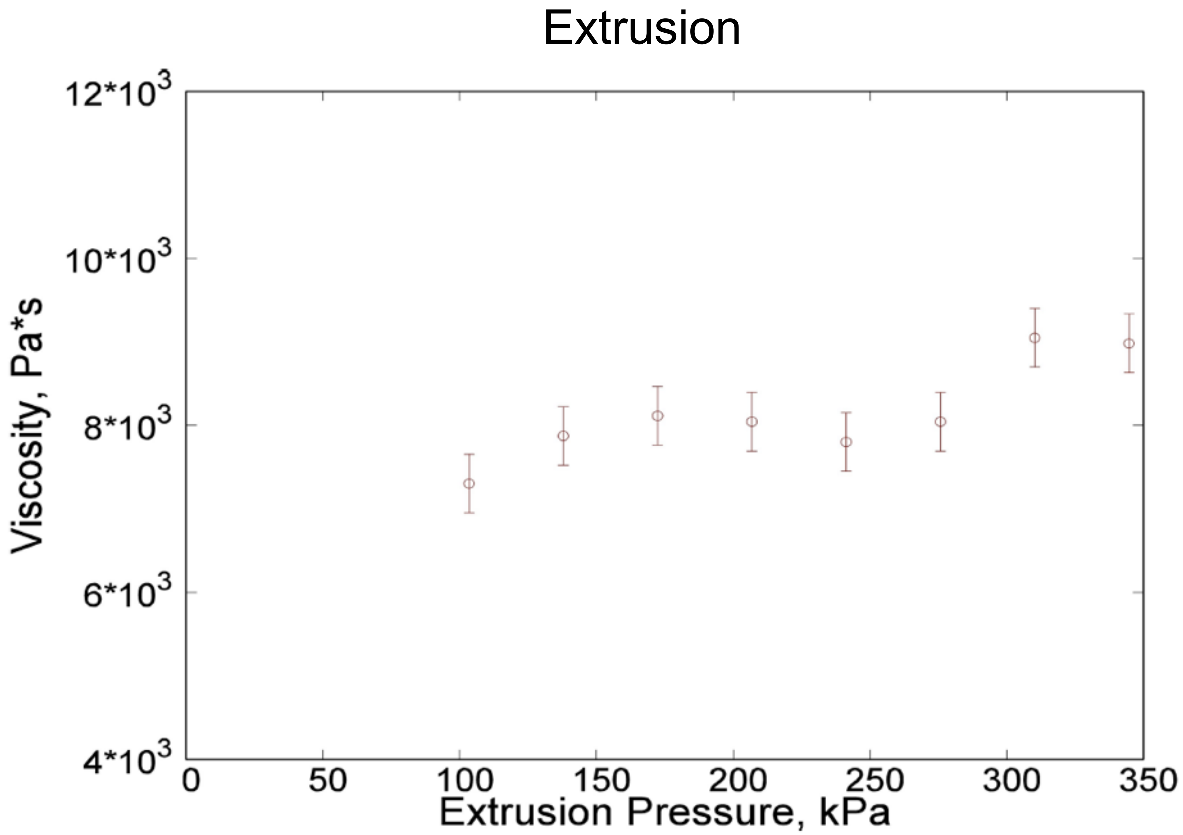
- For the extrusion rheology, the material is loaded into a tube and extruded with air pressure.
- The viscosity can be found using:

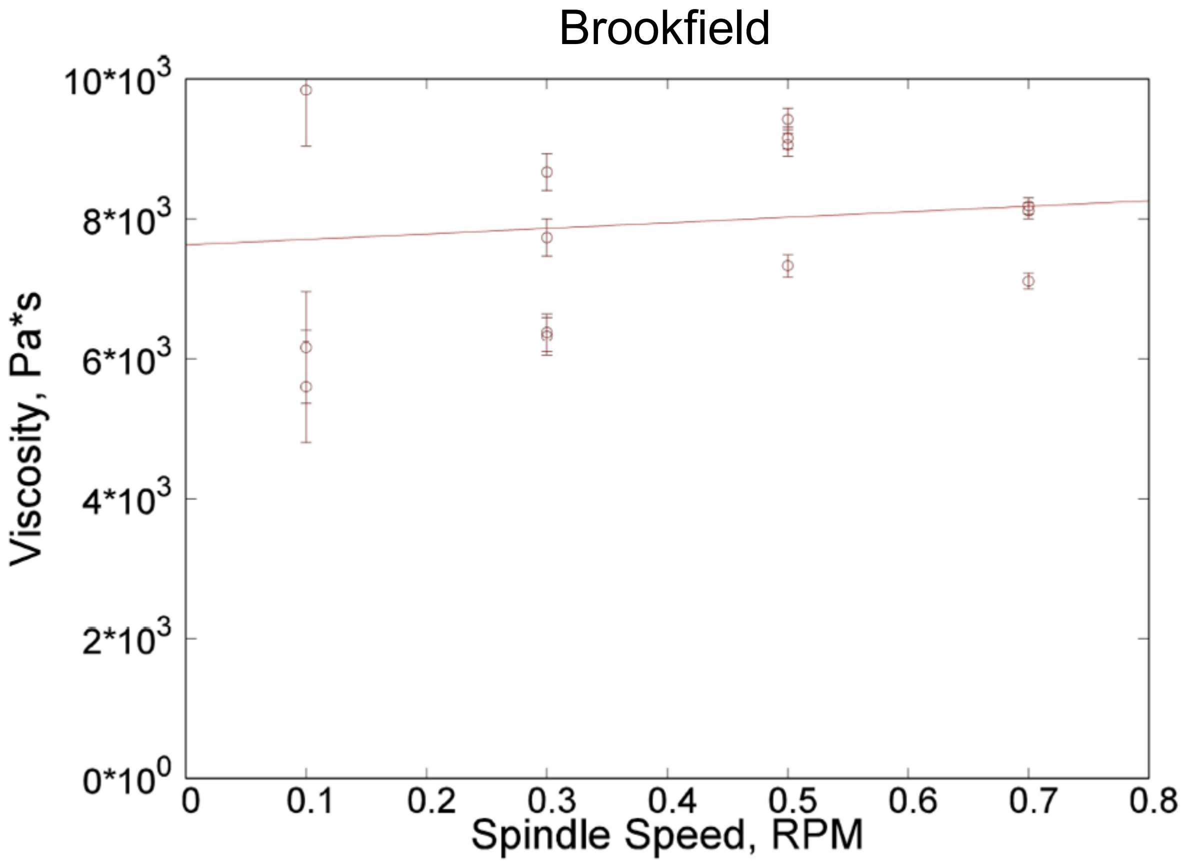
$$\mu = \frac{P\pi R^4}{8QL}$$



Burrell. Extrusion rheometer manual.

Measured apparent viscosity of single formulation compared on our 3-axis system (left) and a Brookfield rotational viscometer (right)

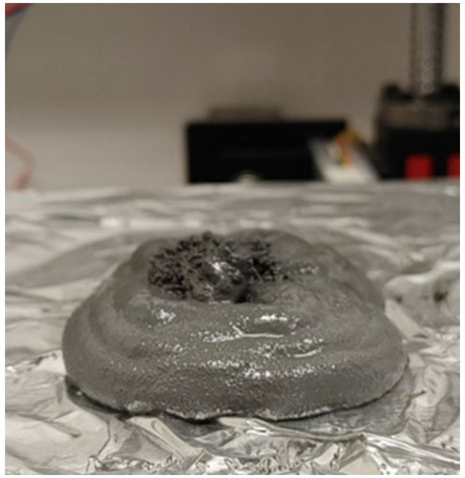




Purcell, Hargather, Hargather, Propellants, Explosives, Pyrotechnics, 49:e202300154, 2023.

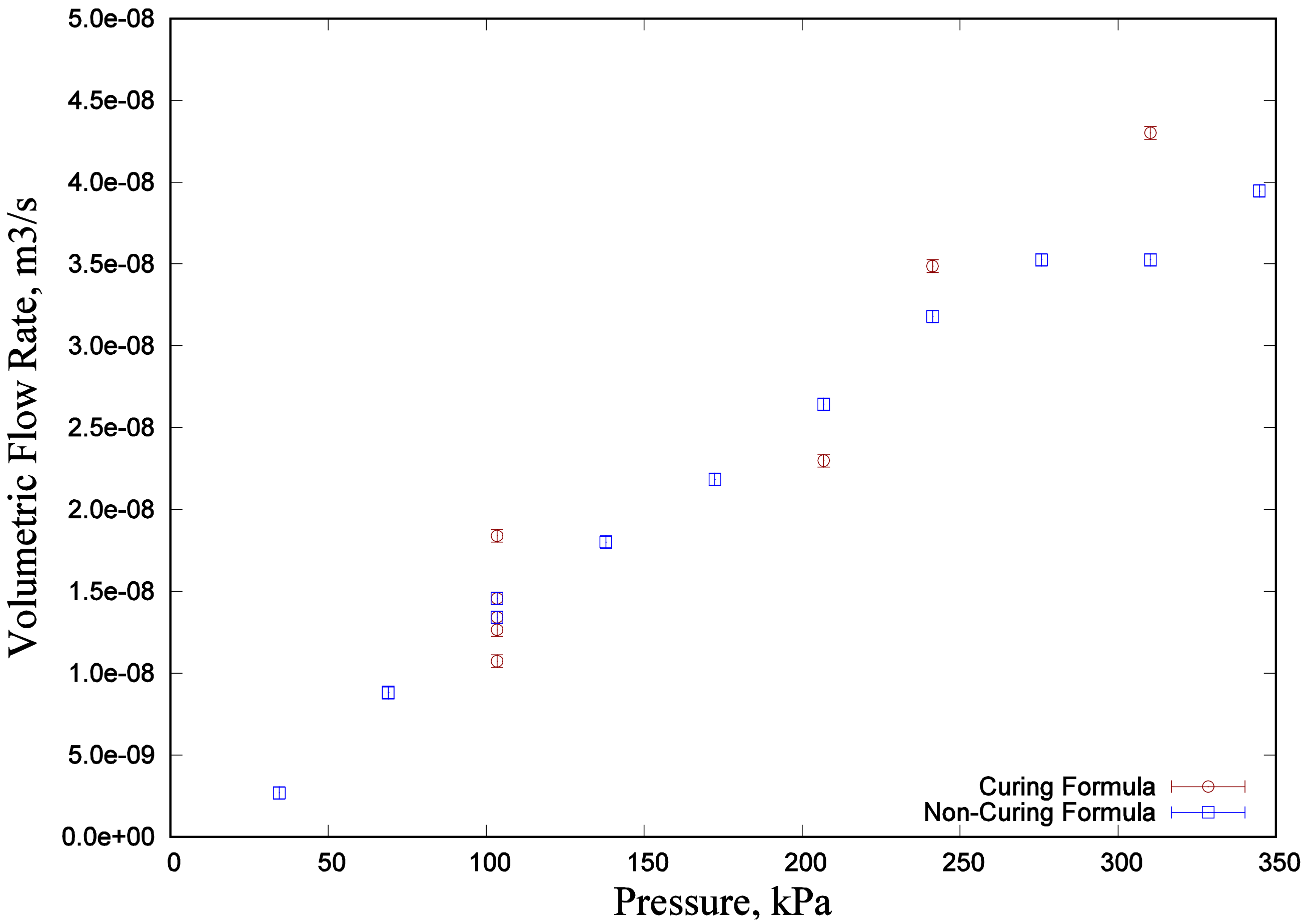
Application-Based Selection of Formula

- Free-standing printing requires a material with high yield stress and relatively high viscosity for metered control and self-supporting deposition
  - Formula 6 was observed to be the strongest candidate for this application
- Printing directly to completely fill a mold, or to flow into long channels, requires a lower-viscosity formula with little to no yield stress
  - Formula 1 was observed to meet these criteria most effectively



Yield stress of Formula 6 obtained based on Bingham's work

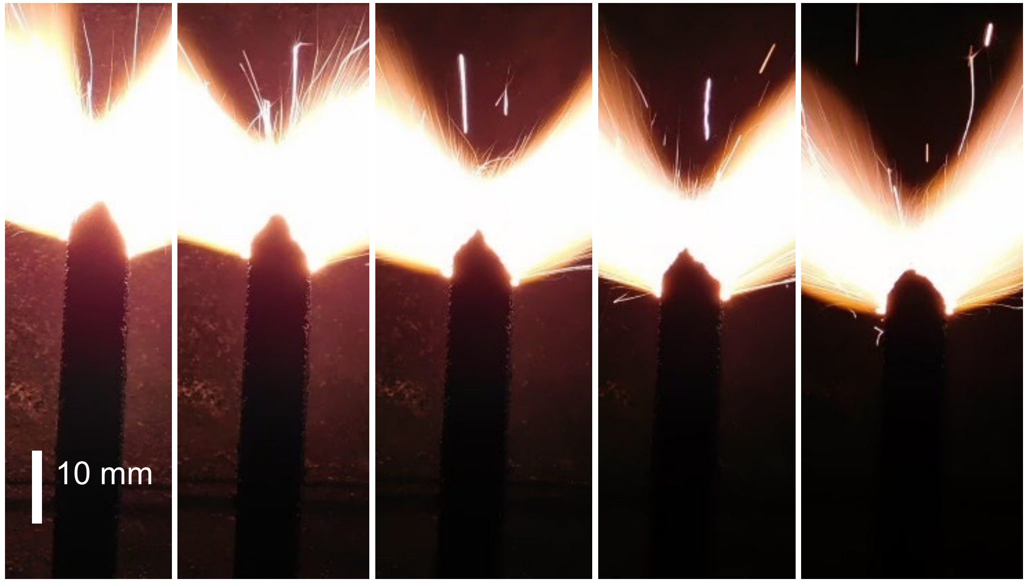
- Volumetric flow rate measured for curing and non-curing trials of Formula 6
- Intercept of the trendline with the x-axis is the yield stress
  - 1 kPa
- Corresponds to the stress resulting from the weight of the propellant in a column at its base to be 5.8 cm



Purcell, Hargather, Hargather, Propellants, Explosives, Pyrotechnics, 49:e202300154, 2023.
Bingham, An investigation of the laws of plastic flow. Number 278. US Government Printing Office, 1917.

Burn performance of the 7 propellant formulations is lower compared to industry standard, due to our lower Al content

Formula	Burn rate, mm/s	Standard deviation, mm/s
1	2.0	0.3
2	2.5	0.1
3	2.5	0.3
4	2.5	0.2
5	2.6	0.3
6	2.2	0.2
7	2.9	0.1



Purcell, Hargather, Hargather, Propellants, Explosives, Pyrotechnics, 49:e202300154, 2023.

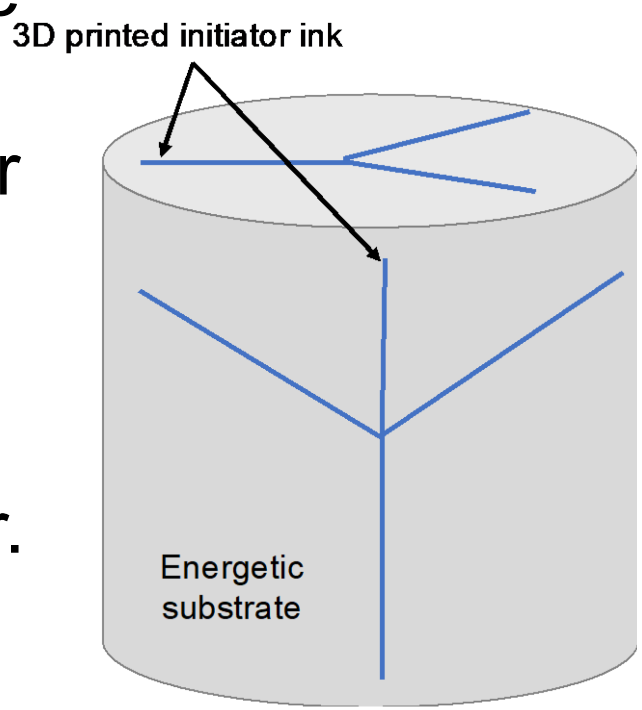
Pyrotechnic initiator ink

Benito Silva (BS, Materials Engineering)
Hannah Morgan Smith-Meyers (BS/MS, Materials Engineering)
Kayleigh Cameron (BS/MS, Materials Engineering)

MSIPP

Pyrotechnic initiator ink for additive manufacturing applications

- Develop a pyrotechnic fuse capable of igniting less sensitive energetic materials
- Goal: demonstrate multi-point or simultaneous initiation of the energetic material.
- 3 thermite formulations + Fe-S blended within a polymer binder.
  - Burn rate, viscosity, burn temperature, printability



36 formulations studied in this project, varying particle size, thermite type, and % solids loading

- Amount of secondary fuel is varied
- Characterize: ambient burn rate, combustion temperature, viscosity and printability in relation to potlife

Solids		Liquids	
Purpose	**Material**	**Purpose**	**Material**
Oxidizer	$Sr(NO_3)_2$ or $Ba(NO_3)_2$ or MnO_2	Binder	Hydroxyl-terminated polybutadiene (HTPB)
Fuel	Aluminum (Al)	Catalyst	Dibutyltin dilaurate (DBTDL)
Secondary Fuel	Iron Sulfur (Fe-S)	Curative	Isophorone diisocyanate (IPDI)

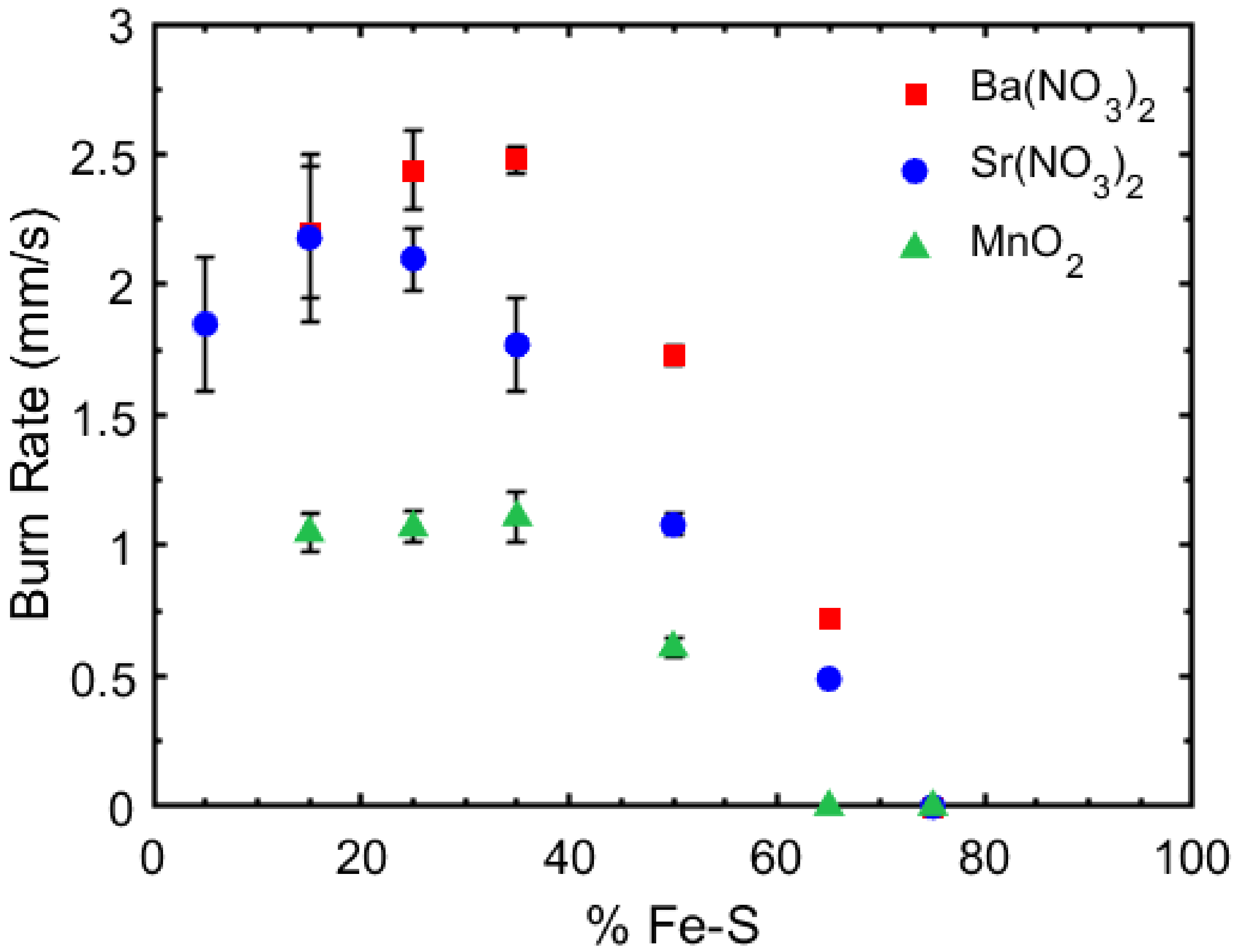
Oberth, *Principles of Solid Propellant Development, 1987*
Farris, Trans. Soc. Rheol., vol. 12, no. 2, pp. 281–301, Jul. 1968

Combustion testing is performed on a custom-built apparatus

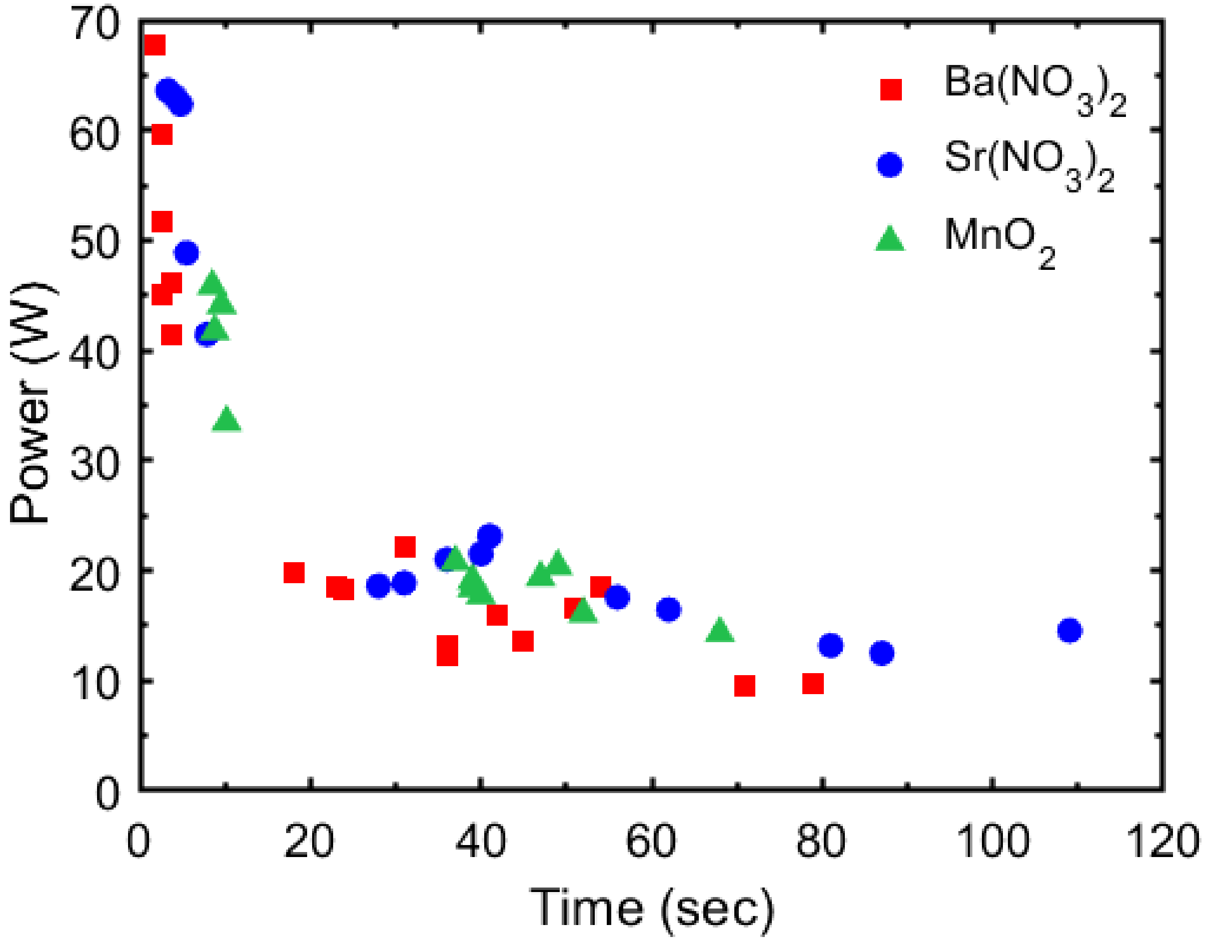
- Combustion testing
  - Inhibitor paint and steel break wires
  - Modified strand burner with Arduino
  - Returns three individual burn rates per sample

5% 15% 25% 35% 50% 65%

$Ba(NO_3)_2$ based formulations yield the highest combustion rate, and MnO_2 the lowest (85% solids loading)



Ongoing work: characterizing power and energy requirements to ignite inks (85% solids loading)



Questions?

Advanced Computational Metallurgy and Additive Composite Manufacturing Laboratory (ACML^2)

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Abstract

Additive manufacturing (AM) is a growing field of research, offering advantages in accuracy, logistics, and design that are difficult or impossible through conventional manufacturing. Adaptation of AM techniques for energetic materials, whether it is munition propellant, rocket propellants, or pyrotechnics, has lagged behind most other materials in being adapted to AM methods. In this talk, results from two AM projects related to energetic materials in Dr. Hargather's research lab are given. First, seven propellant formulations designed for additive manufacture in a custom-built extrusion-driven platform are characterized in terms of apparent initial viscosity, time-dependent viscosity changes, and combustion properties, as well as the tensile properties of the final product relative to a cast material. Both spindle and extrusion-based viscometry methods are employed and compared. The formulations that behave similarly to a Bingham plastic are determined to be most suitable for printing applications. Second, ongoing work on the development and characterization of a pyrotechnic initiator ink is presented. The goal of the initiator ink is to demonstrate multi-point initiation on an energetic substrate. Formulation development and initial characterization of the viscosity and burn rates of thermites blended with iron sulfide in an energetic binder are discussed.

Formulations explored in the present work, per 100 g

Chemical Name	Role	Formula 1 Weight (g)	Formula 2 Weight (g)	Formula 3 Weight (g)	Formula 4 Weight (g)	Formula 5 Weight (g)	Formula 6 Weight (g)	Formula 7 Weight (g)
HTPB	Polymer Resin	13.7	12.3	11.4	11.4	11.4	11.4	9.12
IPDI	Curative	1.24	1.11	1.03	1.03	1.03	1.03	0.824
IDP	Plasticizer	0.598	0.538	0.498	0.498	0.498	0.498	0.398
DBTDL	Catalyst	0.0030	0.0027	0.0025	0.0025	0.0025	0.0025	0.0020
400 μm AP	Oxidizer	46.4	31.5	47.5	39.6	35.6	31.6	49.1
90 μm AP	Oxidizer	30.9	47.2	31.6	39.6	42.5	47.5	32.7
3 μm Al	Fuel	7.73	7.86	7.91	7.91	7.91	7.91	8.18
	% solids	85	86.5	87.5	87.5	87.5	87.5	87.5
	AP ratio	60:40	40:60	60:40	50:50	45:55	40:60	60:40
	Density	1.7 (1.71)	1.7 (1.73)	1.8 (1.75)	1.7 (1.75)	1.7 (1.75)	1.7 (1.75)	(1.80)

Oberth, Principles of Solid Propellant Development, 1987
Farris, Trans. Soc. Rheol., vol. 12, no. 2, pp. 281–301, Jul. 1968
Purcell, New Mexico Tech MS thesis, 2022

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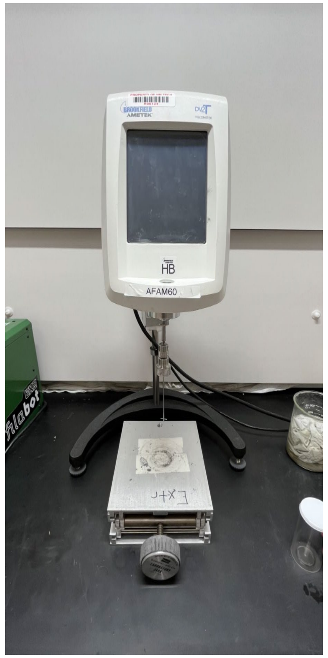
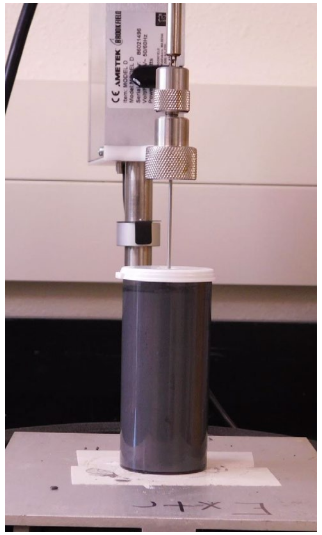
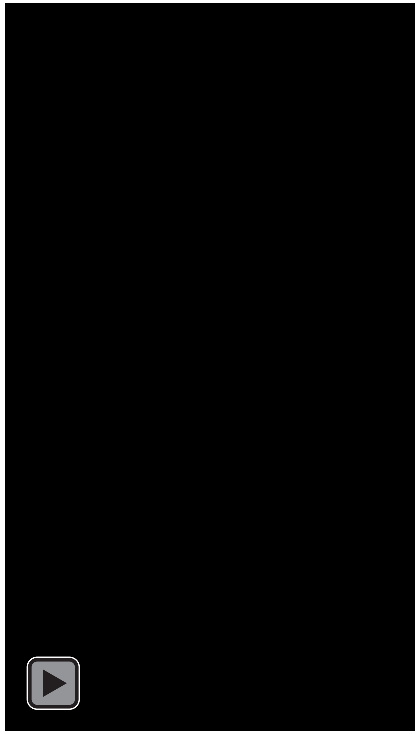
Other test methods used in the present work

Brookfield DV2T Viscometer

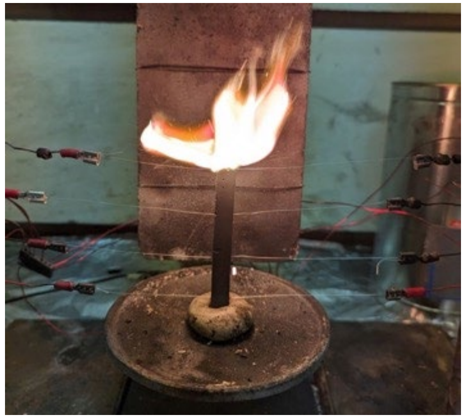


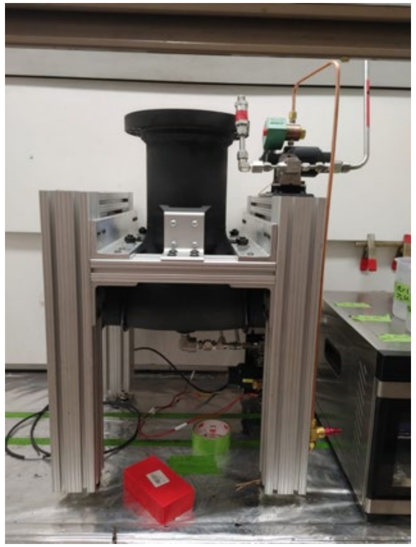


Mark-10 ESM 1500SLC Motorized Test Stand



Combustion Testing Apparatuses



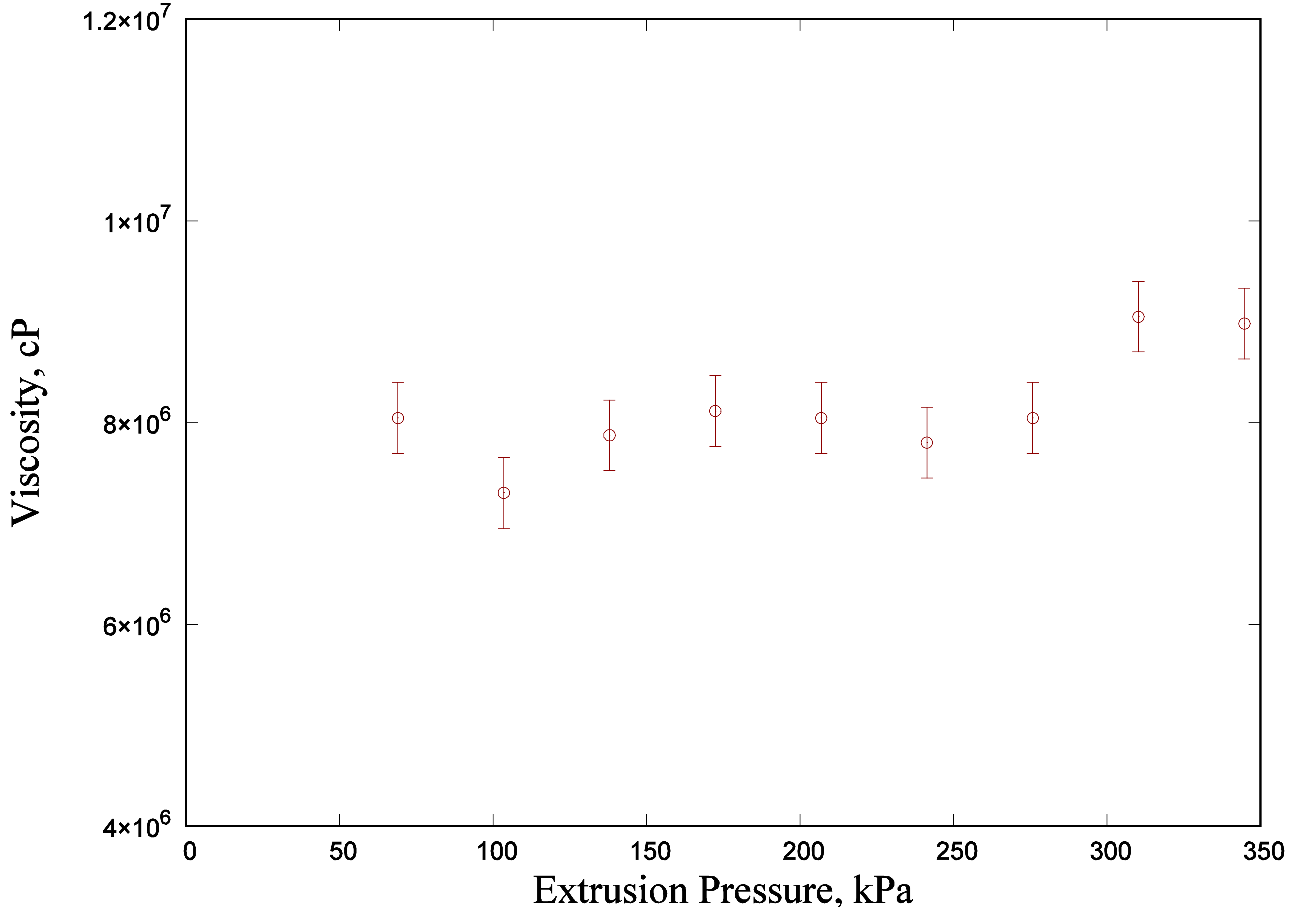


First, establish comparison between viscosity calculation methods: 3-axis system and Brookfield rheometer

- As propellant binder cures, viscosity dynamically changes
  - Difficulty in determining a “baseline” viscosity since rate of cure is not necessarily linear
- Non-curing formulations can be substituted to produce an approximate baseline for these materials
  - Curative is replaced with a blend of binder resin and plasticizer to replicate displaced volume fraction, catalyst is removed entirely
- Non-Newtonian properties of the propellant provide an ideal behavior for additive manufacture
  - A yield stress of the fluid propellant determines its ability to self-support before curing

Using Formula 6 (non-curing), measure viscosity vs extrusion pressure using the 3-axis system

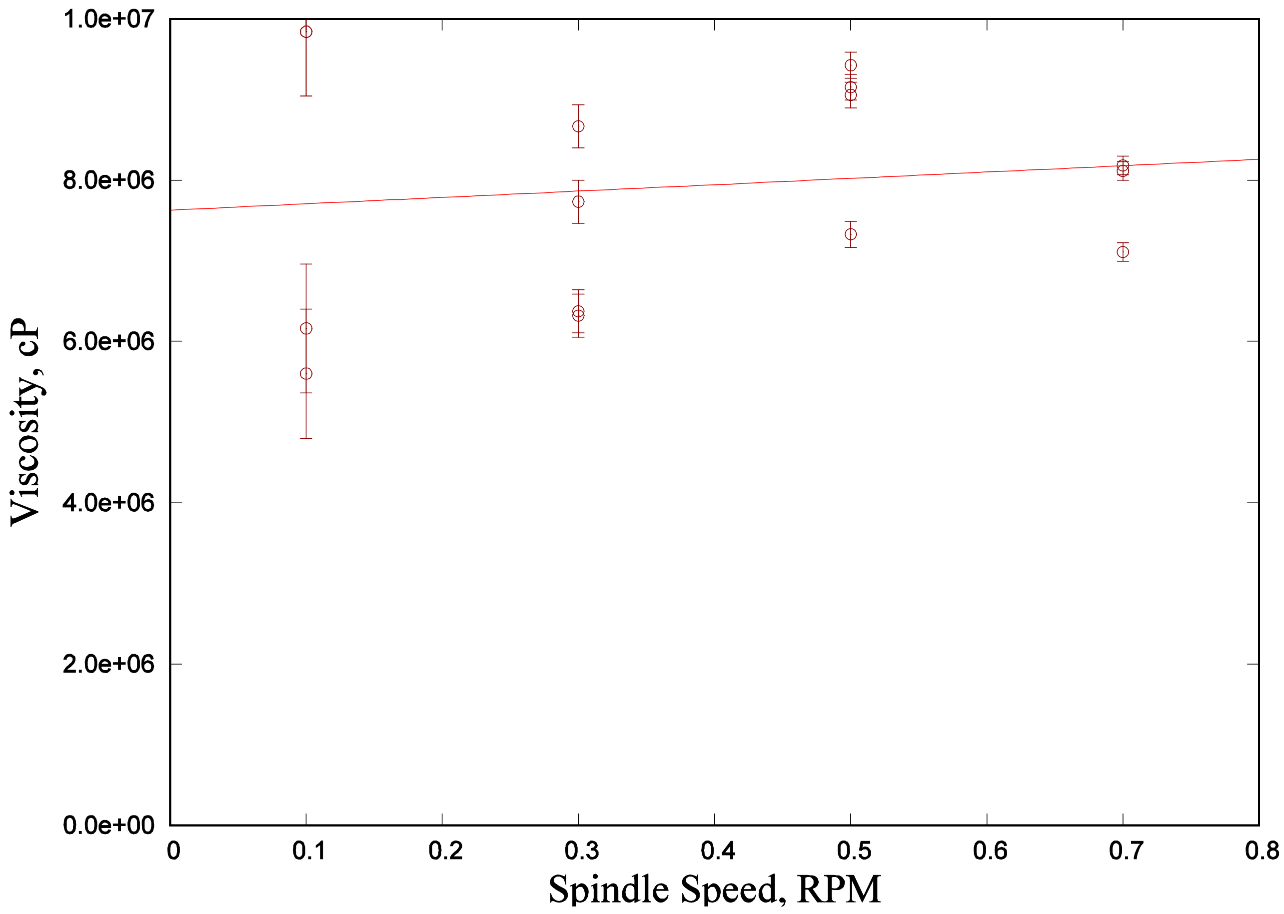
- Mostly constant relation between extrusion pressure and viscosity
- Measured apparent viscosity around 8.0xE6 cP
- Further tests were done at constant pressure, with similar results



Purcell, Hargather, Hargather, Propellants, Explosives, Pyrotechnics, accepted, 2023.

Second, validate the 3-axis system with results from a Brookfield DVT viscometer on Formula 6 (curing)

- Apparent measured viscosity of Formula 6 as a function of spindle speed
- Error bars from torque of viscometer
- Results converge as spindle speed increases
- 8.0E6 cP consistent with extrusion trials



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Apparent viscosity results from the Brookfield at 0.7 RPM on all non-curing formulations

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Formula #	1	2	3	4	5	6	7
Solids Loading %	85	86.5	87.5	87.5	87.5	87.5	90
AP 400 – AP 90 ratio	60-40	40-60	60-40	50-50	45-55	40-60	60-40
Average Viscosity, cP	.83E6	3.4E6	2.5E6	3.3E6	3.4E6	2.8E6	3.4E6
Standard Deviation, cP	1.6E5	1.6E5	2.2E5	2.6E5	2.7E5	61.E5	1.3E5

- Formulas 6 and 7 are lower than expected
  - In trials of extrusion viability, 7 was unable to extrude at all, while 6 exhibited higher apparent viscosity at the operating pressure than others
- These formulas have the strongest non-Newtonian behavior in regards to yield stress
  - From secondary observations, the estimated shear threshold is high
- Spindle viscometry may not fully capture the behavior of these materials

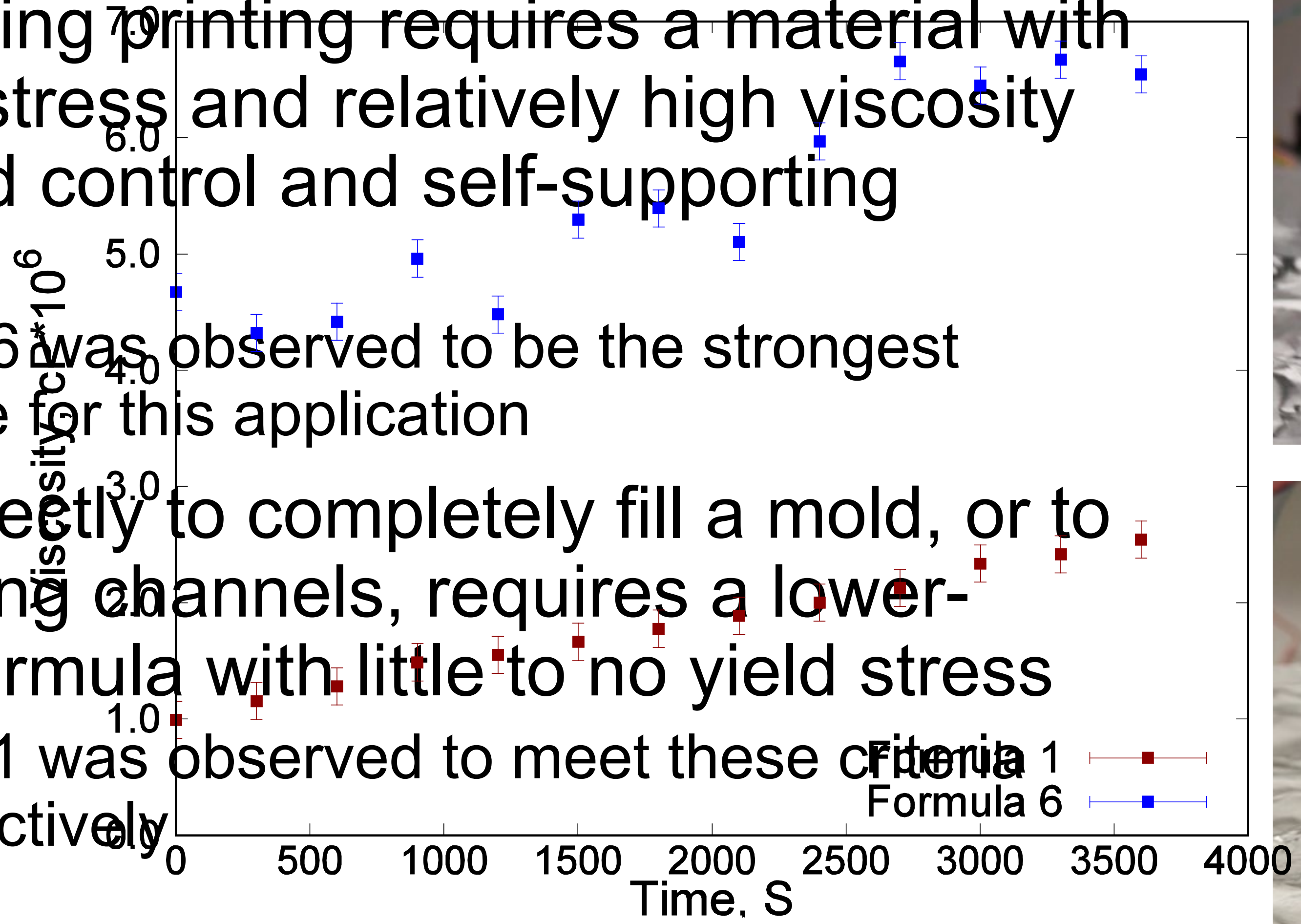
Purcell, Hargather, Hargather, Propellants, Explosives, Pyrotechnics, accepted, 2023.

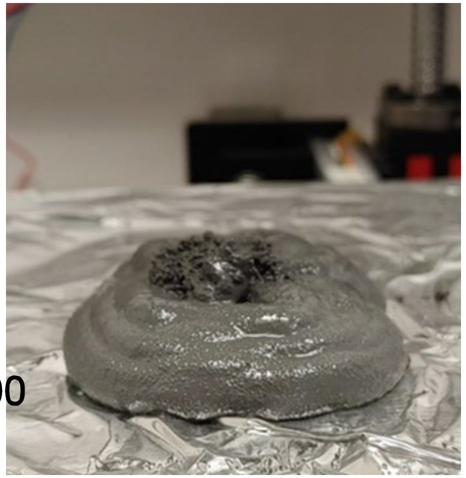
Measured apparent viscosity of curing Formulas 1 and 6

- Establishing the change of viscosity as a function of time is also important
- This allows us to establish an approximate range of times for when a material is useable in a printing setup
  - Also provides a rudimentary method to estimate polymerization progression
- Tests began at 15 minutes after curative addition to binder
  - Test for 1 minute every 5 minutes

Application-Based Selection of Formula

- Free-standing printing requires a material with high yield stress and relatively high viscosity for metered control and self-supporting deposition
  - Formula 6 was observed to be the strongest candidate for this application
- Printing directly to completely fill a mold, or to flow into long channels, requires a lower-viscosity formula with little to no yield stress
  - Formula 1 was observed to meet these criteria most effectively





Thermites are the basis of the energetic ink

- Thermite is a pyrotechnic material
    - Redox reaction of a metal oxide and metal fuel
    - Produces large amount of heat
    - Well studied material
- Performance characteristics of energetic ink
    - Burn rate
    - Density
- Variations can change performance
    - Composition
        - Adding Fe-S to control burn rate
    - Solids loading

Volume percent solids of testing matrix

- Strontium nitrate ($Sr(NO_3)_2$), barium nitrate ($Ba(NO_3)_2$), and manganese oxide (MnO_2) thermite systems

	$Sr(NO_3)_2$		$Ba(NO_3)_2$		MnO_2	
	80% solids loading	**85%solids loading**	**80% solids loading**	**85% solids loading**	**80% solids loading**	**85% solids loading**
15% Fe-S	54.83	63.23	53.48	61.96	47.80	56.47
25% Fe-S	54.21	62.65	52.99	61.49	47.94	56.61
35% Fe-S	53.58	62.05	52.50	61.02	48.08	56.75
50% Fe-S	52.59	61.11	51.73	60.29	48.29	56.96
65% Fe-S	51.57	60.13	50.94	59.53	48.50	57.16
75% Fe-S	50.86	59.45	50.40	59.00	48.64	57.30

To control the combustion properties, thermite are blended at 50/50 wt% with Fe-S without losing heat output

- Not classified as pyrotechnic
- The exothermic reaction between iron and sulfur powders occurs resulting in iron sulfide
- This reaction behaves similar to a pyrotechnic delay composition

Mass is 7:4 ratio for mixing

$Fe^{\circ}+S^{\circ}\rightarrow FeS$

- $S^{\circ} + 2\ e^{-} \rightarrow S^{-II}$ (reduction)
- $Fe^{\circ} - 2\ e^{-} \rightarrow Fe^{II}$ (oxidation)

Example formulation for $Ba(NO_3)_2$ thermite in an HTPB binder system (85 % solids loading)

- Particle ratios optimized based on Farris' particle size distribution theory
- Characterize the three materials in terms of
  - Ambient burn rate
  - Combustion temperature
  - Viscosity and printability in relation to potlife

Chemical Name	Role	Weight (g)
HTPB	Polymer binder	13.75
IPDI	Curative	1.25
DBTDL	Catalyst	0.0027
Fe	Secondary Fuel	27.05
Sulfur ($\geq$100 μm)	Secondary Oxidizer	15.45
Al	Fuel	10.90
$Ba(NO_3)_2$ (10-100 μm)	Oxidizer	18.96
$Ba(NO_3)_2$ ($\geq$100 μm)	Oxidizer	12.64

Oberth, *Principles of Solid Propellant Development, 1987*
Farris, Trans. Soc. Rheol., vol. 12, no. 2, pp. 281–301, Jul. 1968

Preliminary testing: Flame front temperature of a 50/50 $FeS/Ba(NO_3)_2$ strands measured with a FLIR T640 infrared camera

Thermite	Sample	Temperature (°C)	Standard Deviation
$Ba(NO_3)_2$	B1	1249	33
	B2	1214	55
	B3	1313	79