Optimizations of High Energy Explosives Utilizing JMP

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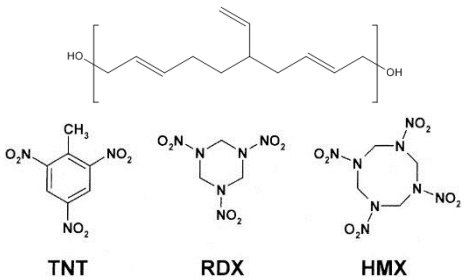
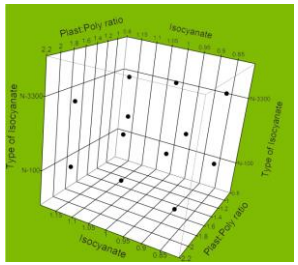
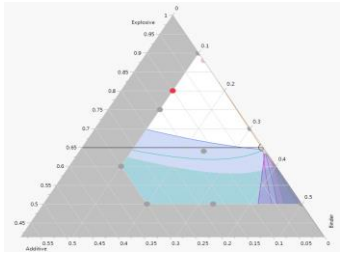






Background of Explosives

Melt Cast

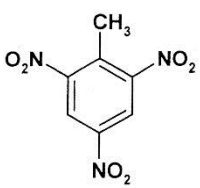
- Mp < 100°C
- Used neat or as a binder
- Poured into fixture
- Cools to brittle solid

Pressed

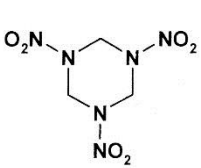
- Slurry coating
- Crystalline ingredients bound by coating polymers
- Pressed to shape or machined
- Minimal mechanical strength

Cast Cure

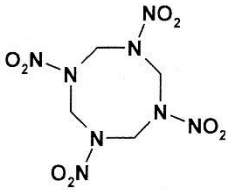
- Planetary mixers
- Pre-polymer, urethanes
- Vacuum cast
- Best mechanical strength



TNT



RDX



HMX

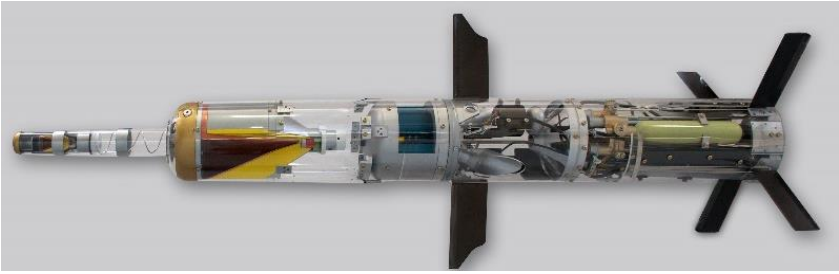
Strength relates to sensitivity

Current Project Goals

- What? - Create two explosive formulations:
  1). Higher energy with equal nitramine loading
  2). Equal energy with reduced nitramine loading

- Why?
  1). Higher energy explosives are needed to meet the engineering advances of modern weapon systems
  2). “Energy partitioning”- remove sensitive, solid nitramines and replace with energetic elastomeric binder yielding reduced sensitivity with maintained performance

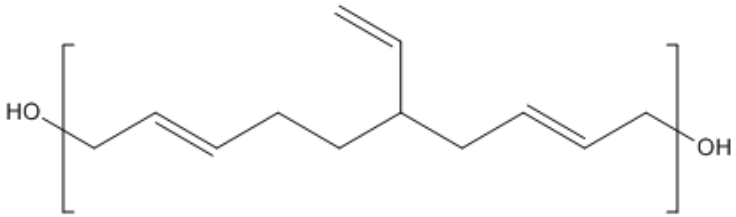
Hellfire Missile



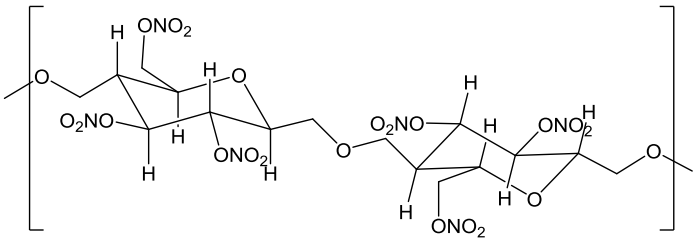
TOW Anti-Tank Missile

Current Project Goals

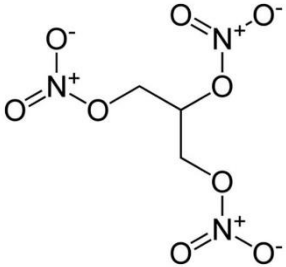
- How? - Replace HTPB in urethane-based cast-cure explosive formulations with a polymer that contributes energy to the explosive performance



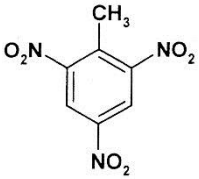
Hydroxyl-terminated polybutadiene



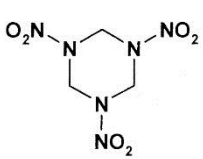
Chemical structure of fully nitrated nitrocellulose



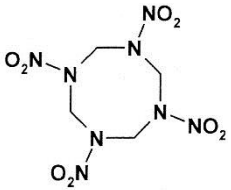
Nitroglycerine



TNT



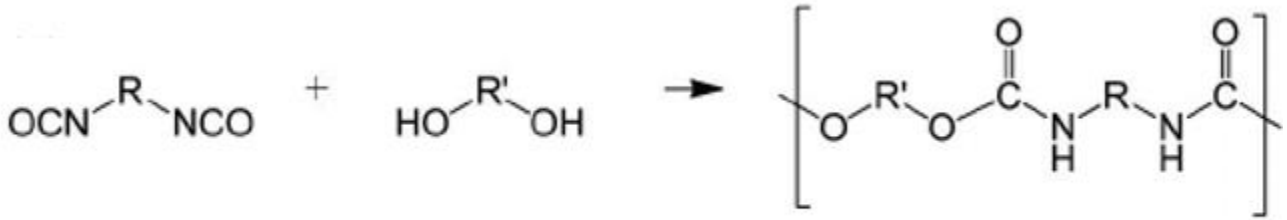
RDX



HMX

Chemistry of Cast Cures

- Cast cure binders are comprised of three key ingredients: pre-polymer, isocyanate (think spaghetti), and plasticizer
- Pre-polymer = long chain molecule, hydroxyl-terminated, usually viscous (honey)
- Isocyanate = small molecule, reacts with pre-polymer to form a rubbery matrix
- Plasticizer = small molecule, oil-like, unreactive but decreases pre-polymer viscosity and softens the rubbery matrix

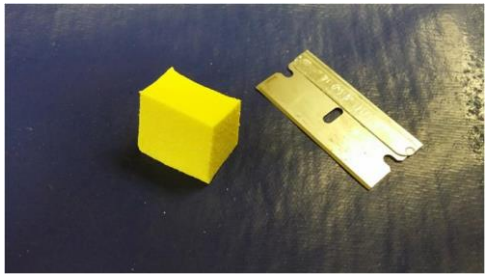


Pre-polymer

Add plasticizer and isocyanate

Cast cure binder

Add crystalline nitramine powder; Heat and time



Cast cure explosive

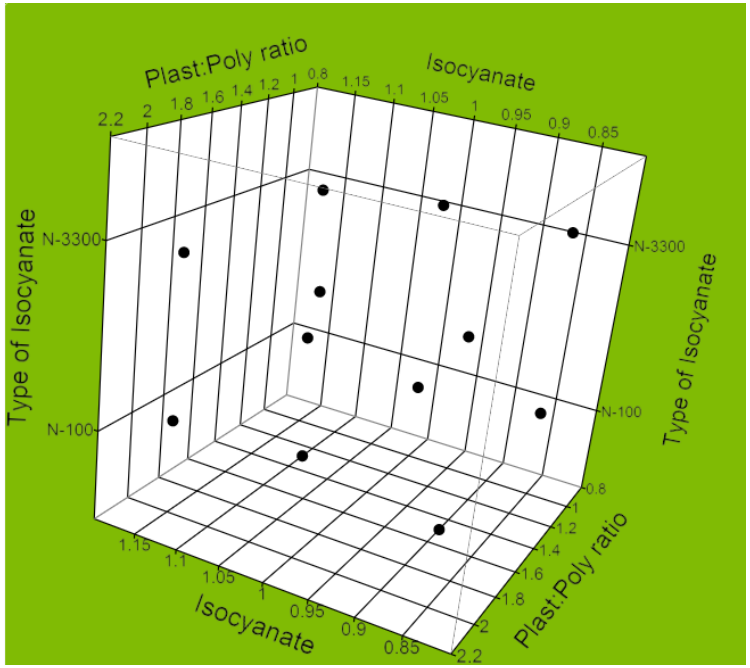
Binder - Factors and Responses

Why DoE? – Because reducing the number of experiments saves time, money, and ***material***

A full factorial DoE was chosen in order to realize all main effects and eliminate confounding factors

Factors:
Plasticizer : Polymer ratio (Two Level, Continuous)
Isocyanate Type (Two Level, Categorical)
Isocyanate amount (Three Level, Continuous)

Responses:
Viscosity (Minimize)
Cure Hardness (Maximize)

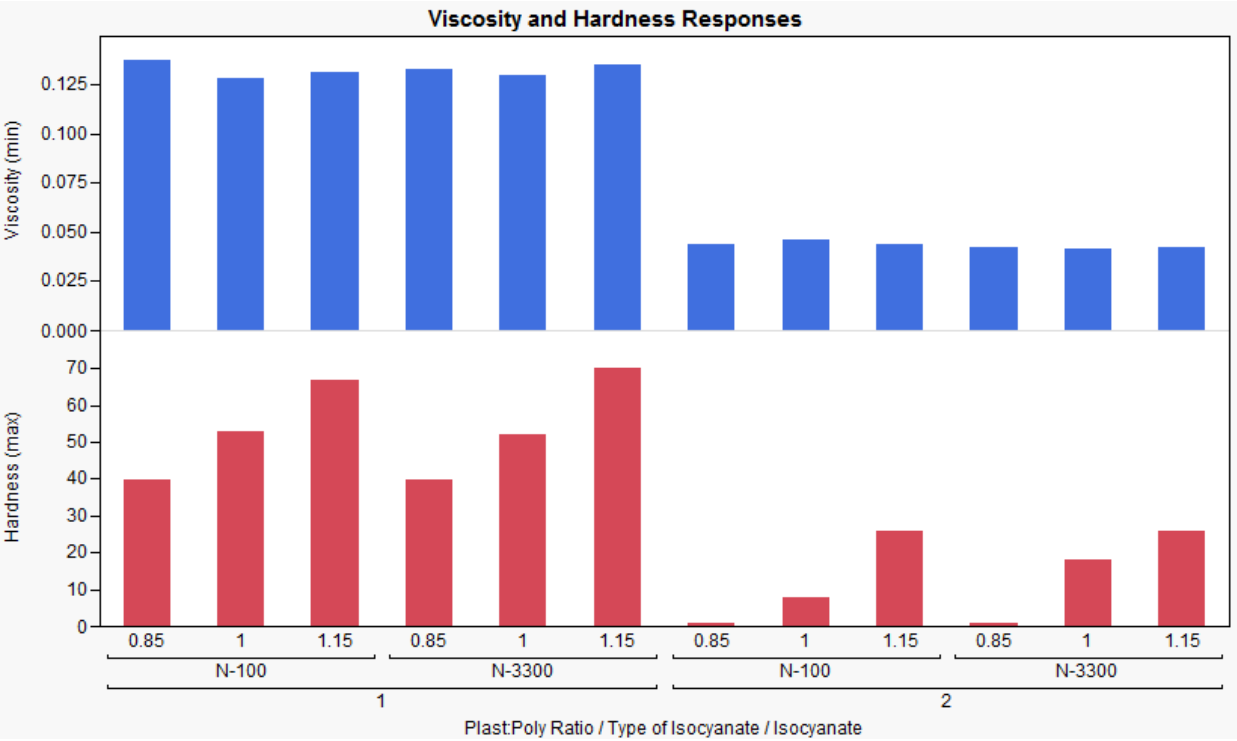


Binder - Experiments and Results

Binder samples were created according to the design parameters and mixed under vacuum in a DAC 150 Speed Mixer

Hardness scores were achieved through a forced ranking system
(Some samples did not create enough polymer matrix to allow for Shore-A measurement)

Viscosity measurements were taken over a range of sheer rates; minimal value selected as the response recorded

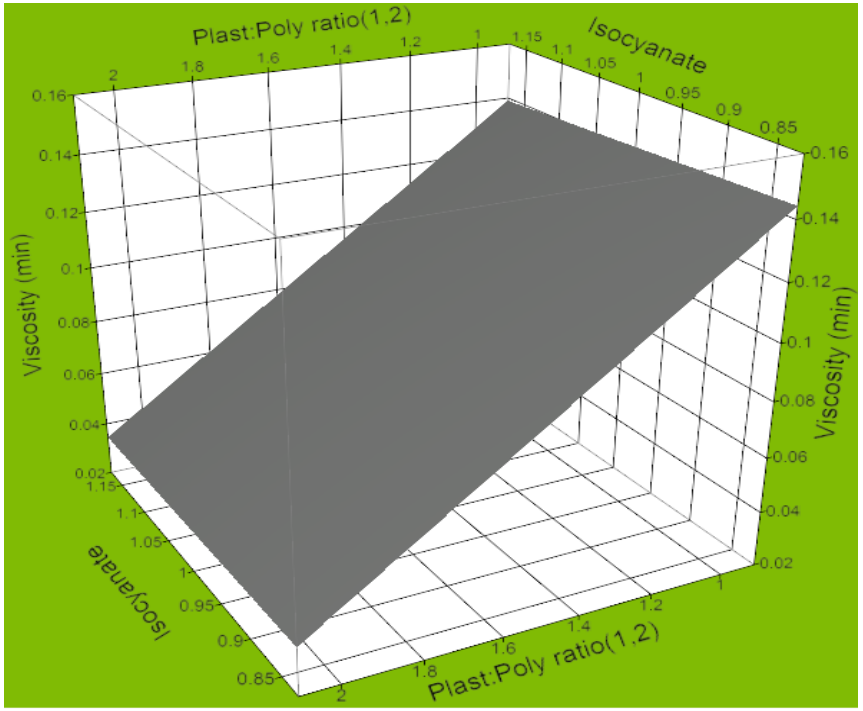


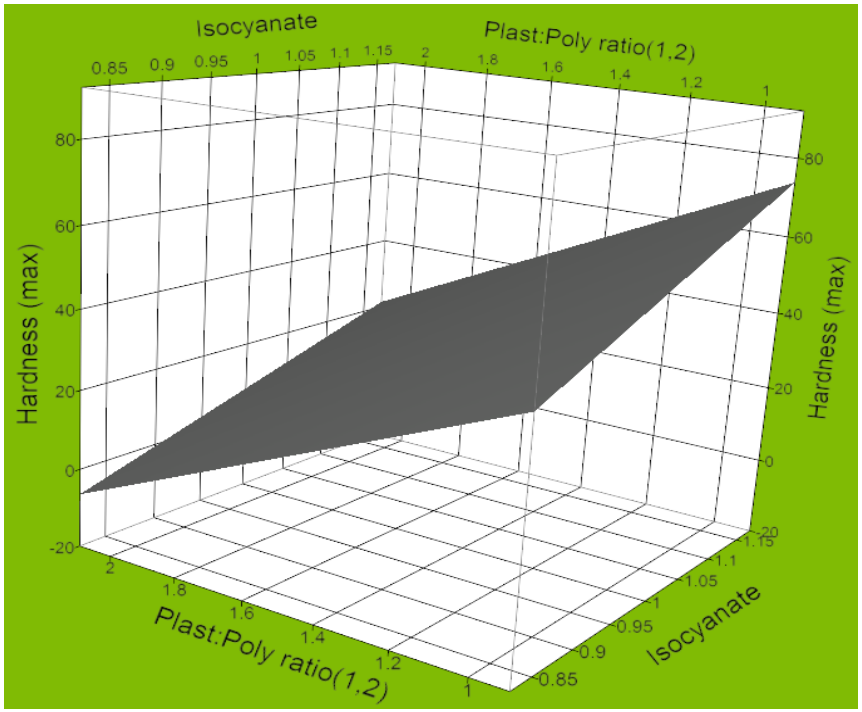
Binder - Models and Analysis

Minimized viscosity values can be achieved with a P_I:P_o ratio of 2:1.

Isocyanate type and amount have a minimal effect on the viscosity

Viscosity Response Surface





Hardness Response Surface

Maximized hardness values can be achieved with a P_I:P_o ratio of 1:1 and an isocyanate amount of 1.15

Isocyanate type has a minimal effect on the hardness

Optimization can be achieved through a trade-off analysis

Binder - Models and Analysis

Need a minimum hardness score of 55 – observations

Isocyanate amount doesn't affect viscosity, but positively effects hardness, so max it out – within experimental limitations (1.15)

Set Type of Isocyanate to N3300 because slight increase in hardness and no effect on the viscosity

Dial up the P_I:P_o until the hardness limit is reached

GO TO JMP BINDER PROFILER

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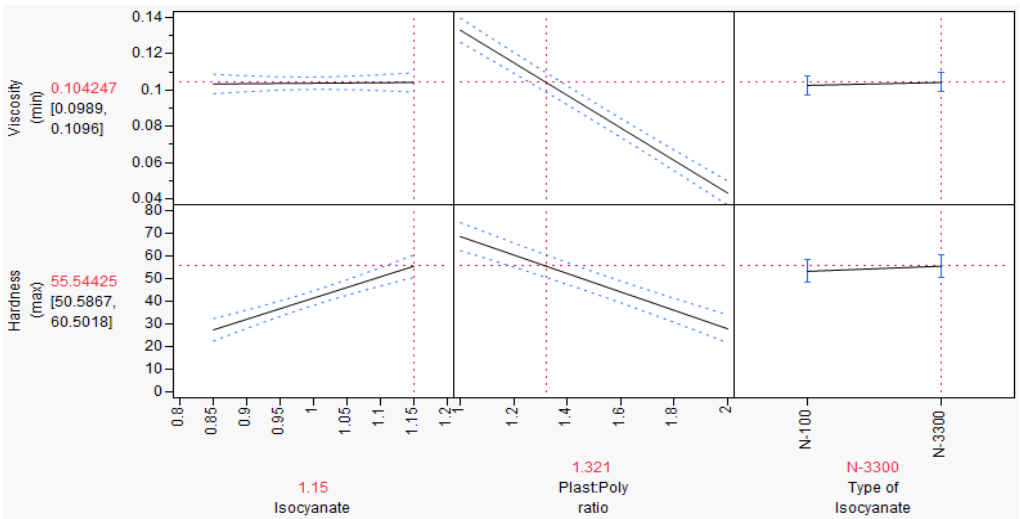


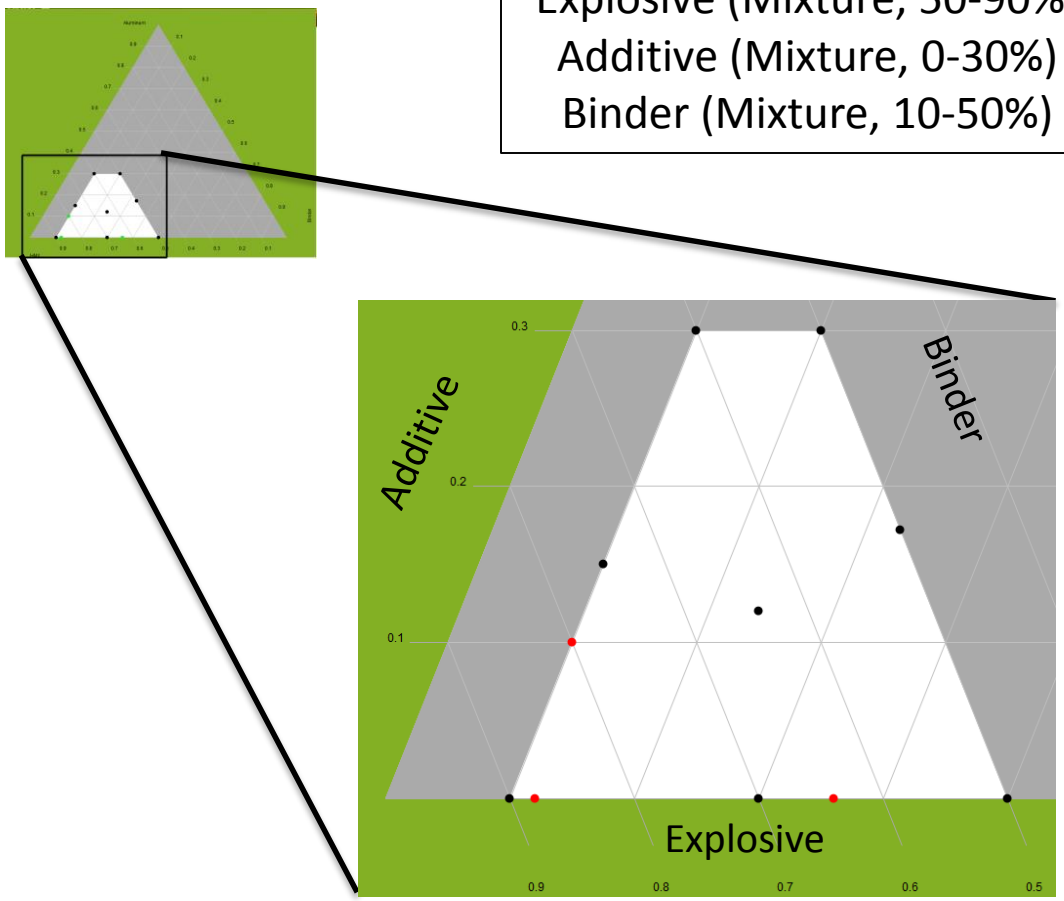
Maximized isocyanate

N-3300 type

1.33 P_I:P_o

Formulation - Mixture Parameters

Factors:
Explosive (Mixture, 50-90%)
Additive (Mixture, 0-30%)
Binder (Mixture, 10-50%)



- D-optimal mixture design for main effects and two-way interactions
- 12 run Mixture DoE (Black points w/ 4 replicates)
- "Binder" factor utilized in order to fit the 3-component mixture design requirements
- Design space parameters chosen to capture most feasible formulations
- Due to material limitations, each point is "created" in thermochemical code rather than actually mixed

(Red points = non-DoE test points to verify models)

Statistically better design options?!

Formulation - Responses and Calcs

Responses:
Density
Pressure
Temperature
Shock
Expansion
Energy

- Proprietary thermochemical code requires inputs such as chemical formula, heat of formation, and density for each of the ingredients
- Calculations are based off optimized equilibrium equations that turn the explosive compounds into the appropriate gaseous products of a detonation to predict explosive outputs

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LOTS OF NUMBERS

12 DoE runs created in JMP with proper ingredient amounts for thermochemical calculations

Run #	Expl	Additive	Poly	Isocyanate	Plast
1	0.50	0.000	0.186	0.028	0.286
2	0.64	0.120	0.089	0.014	0.137
3	0.70	0.000	0.112	0.017	0.171
4	0.60	0.300	0.037	0.006	0.057
5	0.50	0.172	0.122	0.019	0.187
6	0.50	0.000	0.186	0.028	0.286
7	0.50	0.300	0.074	0.011	0.114
8	0.90	0.000	0.037	0.006	0.057
9	0.75	0.150	0.037	0.006	0.057
10	0.90	0.000	0.037	0.006	0.057
11	0.70	0.000	0.112	0.017	0.171
12	0.60	0.300	0.037	0.006	0.057

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11	0.70	0.000	0.112	0.017	0.171
12	0.60	0.300	0.037	0.006	0.057

Run #	Density	Pressure	Temperature	Shock	Expansion	Energy
1	0.788961	0.6853	0.6486	0.859	-1.00	-1.000
2	0.895428	0.7664	0.7661	0.891	-1.33	-1.4693
3	0.847407	0.7897	0.6533	0.923	-1.16	-1.1372
4	1.00000	0.6902	1.000	0.842	-1.23	-2.5771
5	0.877749	0.6670	0.8068	0.835	-1.25	-1.529
6	0.788961	0.6853	0.6486	0.859	-1.00	-1.000
7	0.958121	0.6107	0.9735	0.801	-1.13	-2.4434
8	0.915201	1.000	0.6531	1.00	-1.37	-1.3025
9	0.955723	0.8743	0.8288	0.933	-1.49	-1.6973
10	0.915201	1.000	0.6531	1.00	-1.37	-1.3025
11	0.847407	0.7897	0.6533	0.923	-1.16	-1.1372
12	1.00000	0.6902	1.000	0.842	-1.23	-2.5771

LOTS OF DATA

Thermochemical results collected for all 6 responses from each run

Formulation - Modeling the Data

Statistical Modeling + Thermochemical calculations = Powerful Predictions

Least squares regression analysis to create models for each response (Fit Model)

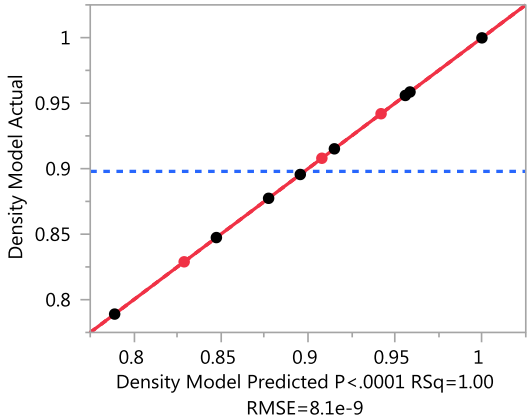
Density:

Actual by Predicted Plot

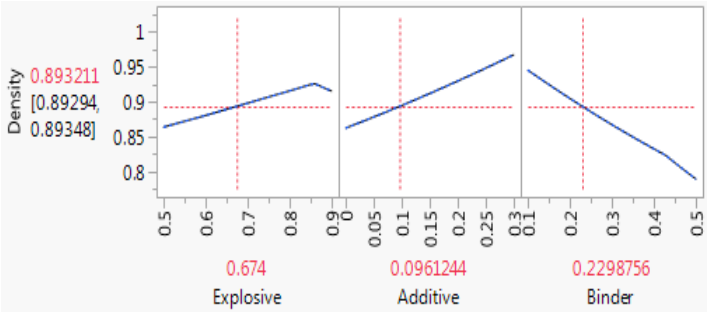
Summary of Fit

Parameter Estimates

Prediction Profiler

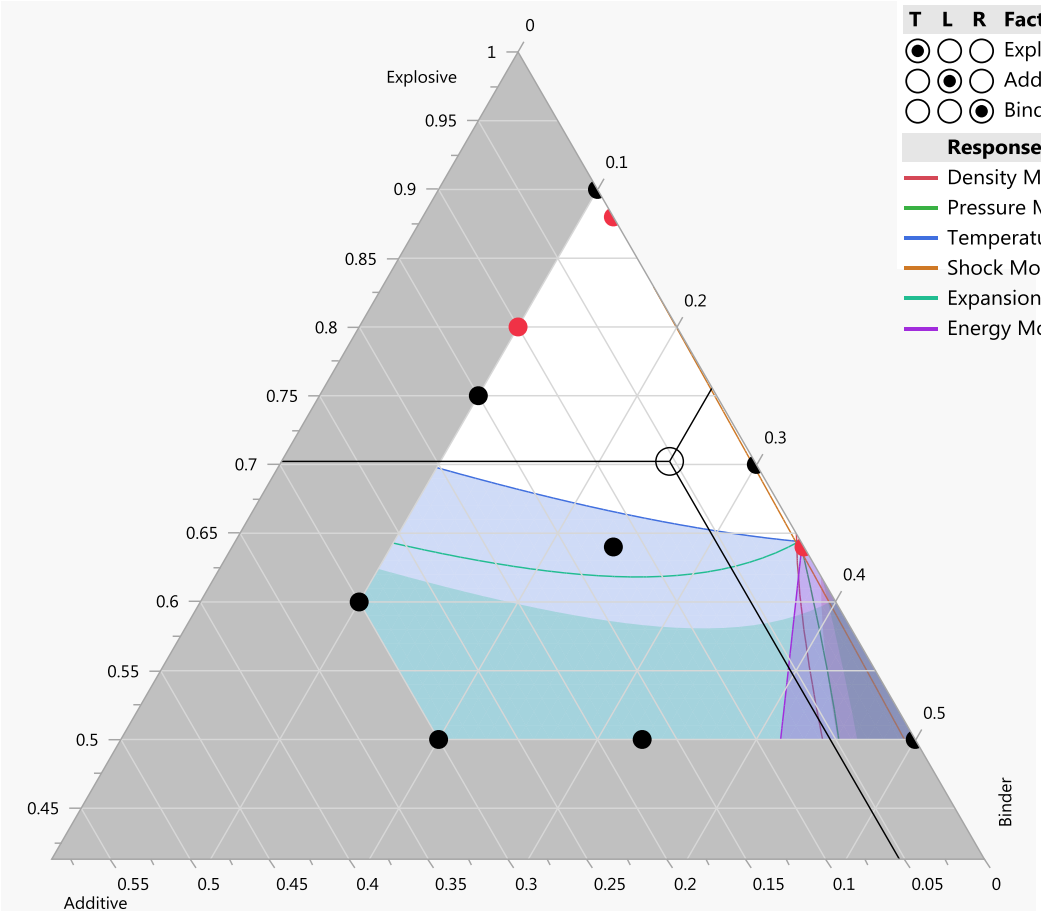


RSquare	1
RSquare Adj	1
Root Mean Square Error	8.057e-9
Mean of Response	0.89793
Observations (or Sum Wgts)	15



Term	Estimate	Std Error	t Ratio	Prob>|t|
(Explosive-0.5)/0.4	0.9151441	4.757e-9	1.9e+8	<.0001*
Additive/0.4	1.0309284	1.276e-8	8.1e+7	<.0001*
(Binder-0.1)/0.4	0.7890162	5.61e-9	1.4e+8	<.0001*
Explosive*Additive	-0.011523	3.993e-8	-3e+5	<.0001*
Explosive*Binder	-0.018693	2.408e-8	-8e+5	<.0001*
Additive*Binder	-0.06357	4.069e-8	-2e+6	<.0001*

Formulation – Target Formulations



T	L	R	Factor	Current X	Lo Limit	Hi Limit
●	○	○	Explosive	0.7022281	0.5	0.9
○	●	○	Additive	0.0534877	0	0.3
○	○	●	Binder	0.2442842	0.1	0.5

Response	Contour	Current Y	Lo Limit	Hi Limit
Density Model	0.829648	0.8778768	0.829648	.
Pressure Model	0.7483684	0.8073669	0.723556	.
Temperature Model	0.6536176	0.7055509	0.6012161	.
Shock Model	0.903507	0.9215631	0.9036432	.
Expansion Model	-1.112715	-1.295451	.	-1.088957
Energy Model	-1.102835	-1.265292	.	-1.080132

Altered and scaled version of previous ternary plot (Same parameters)

No prediction capability for sensitivity; need to actually test within the design space

Legacy baseline *calculated* for limits on new formulation performance

Use the profiler and the prediction models to create theoretical formulations and predict their performance

How reliable are these models?

Verification points analyzed by thermo code and prediction models differ at most 1%

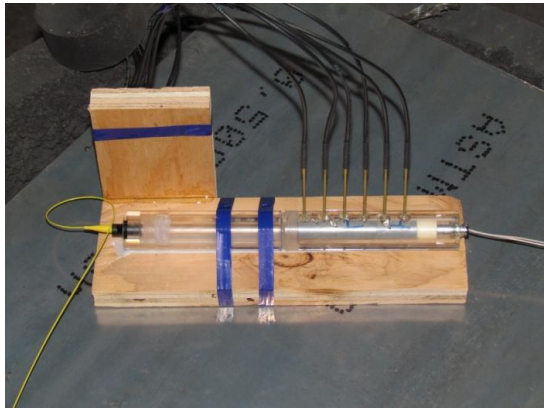
Future Work

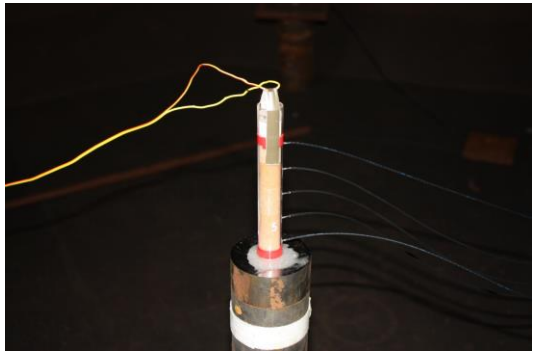
Further characterization of both formulations:

Det. Velocity & Det. Pressure
IHE or LSGT shock sensitivity

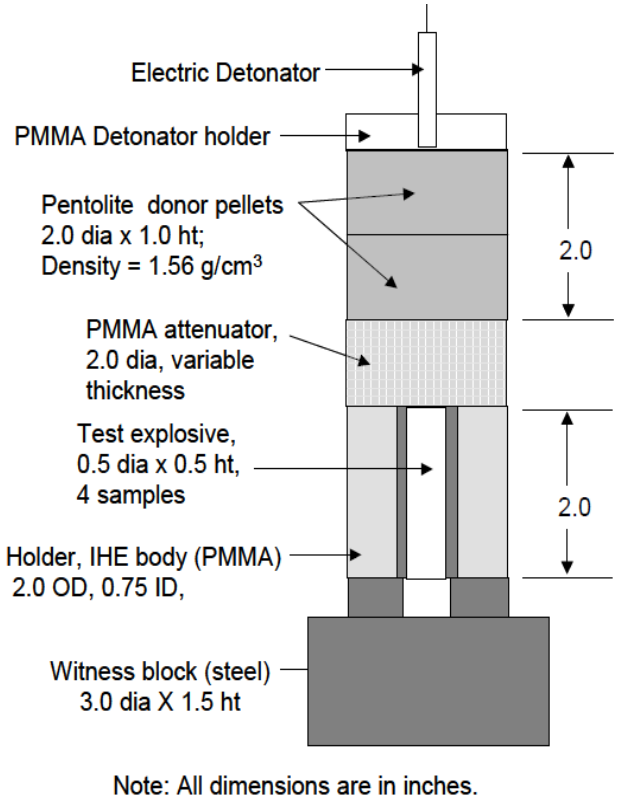
DAX and/or CylEx

Validation of model calculations
Alternate ingredients: plasticizers, IM solids, etc.





Disc Acceleration Experiment (DAX) & DV / Dent testing



IHE shock testing

Acknowledgements

- Analytical Support – Dr. Kelley Caflin, Henry Grau, and Energetic Materials Analysis Branch
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- Rheology Analysis – Christopher Pizzo
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- Explosives Testing – Erik Wrobel and Gerard Gillen
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Questions?