Low Temperature Solid Propellant Investigations for Mechanical Properties

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An inquiry into the viability of solid rocket motors at high altitude and near space conditions was proposed to maintain performance similar to ambient. This project was meant to evaluate the types of metrics to use to validate similarity, and propose material properties to test, along with suggested mixes of propellant candidates. This included looking into isophorone diisocyanate, modified methylene diphenyl diisocyanate, and dimeryl diisocyanate curatives at varying solids loading in addition to trimethylolpropane under uniaxial tensile loads at -50 °C to simulate upper atmosphere firing of the motor. Stress-strain data, percent elongation, ultimate tensile strength, and work of fracture were then collected and determined to get an idea of what may provide the best benefit of performance at low temperature.

I. Nomenclature

SRM	=	solid rocket motor
AP	=	ammonium perchlorate
Al	=	aluminum powder
IPDI	=	isophorone diisocyanate
DBTDL	=	di-n-butyldilauryltin
MMDI	=	modified methylene diphenyl diisocyanate
DDI	=	dimeryl diisocyanate
IDP	=	isodecyl pelargonate
HTPB	=	hydroxyl-terminated polybutadiene
TMP	=	trimethylolpropane

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II. Introduction

Solid rocket propellants consist of solid fuel and oxidizer, usually in the form of a powder, mixed with several liquid ingredients and then cured into a solid grain. SRM's have inferior specific impulse when compared to liquid rocket engines, and once started the burn rate cannot be actively controlled or stopped. The burn profile is specified ahead of time by the design of the propellant grain. However, SRMs can be stored in a launch configuration for long periods, since they have no cryogenics that will boil off. They also require far fewer moving parts than a liquid engine and are therefore relatively simple and reliable. SRMs are ideal for long duration flights such as transfer to a planetary surface but need still be ready to be used after a long flight. While strap-on SRMs are ubiquitous in the orbital launch industry (commonly used to supplement the thrust of a liquid-fueled core stage on vehicles such as Ariane 5, Atlas V, STS, and SLS), they are less common in long duration space missions due to the potential breakdown of the grains in the cold. Their cost and reliability may lend themselves to new applications if the loss of performance at low temperature could be rectified.

Solid propellant grains are designed to burn at a predictable rate given surface area and chamber pressure. Fractures in the grain create an increase in surface area, leading to an increase in pressure that may damage or destroy the SRM. Understanding the tensile properties of solid propellants is crucial to designing grains that can withstand stresses during the launch and transportation of the motor.

This research project aimed to investigate changes to propellant formulations to increase their tensile strength at low temperatures. Such formulations have applications for SRMs for use on deep-space launch vehicles, such as NASA's Mars sample return, where the SRM will have to survive the vibration regimes of Earth launch, Mars landing, and Mars launch.

III. Propellant Formulations

The propellant test matrix shown in Table 1 was designed to analyze and isolate two independent variables: solids loading and curative. Six tensile coupons were created for each formulation. Solids loading refers to the combined AP and Al as a percent of the total mass. The testing was completed with a solids loading of 89% and 86% with a trimodal composition of AP. The curatives used were MMDI, DDI, and IPDI with cure catalyst DBTDL. The matrix used both solids loadings with each curative.

Table 1 Test matrix formed by solids loading and curative.

	DDI	MMDI	IPDI	IPDI with TMP
89%	DDI 89	MMDI 89	IPDI 89	IPDI TMP 89
86%	DDI 86	MMDI 86	IPDI 86	Not Tested

Other notable ingredients were IDP as the plasticizer, HTPB as the binder, and tepanol as the bonding agent. The NCO/OH ratio was held constant at 1:1 and the plasticizer to binder ratio was held at 1:2 for all tests. Additionally, TMP was used as a low molecular triol additive with IPDI at 89% solids loading. TMP was selected due to being a common triol cross-linker with HTPB SRM's. This created seven combined tests. All tests were cured at 120 °F with the exception of the TMP test which was cured at 150 °F to ensure a liquid state of TMP.

IPDI was chosen due to its frequency in industry, and MMDI has proven performance with student groups like the University of Southern California's Rocket Propulsion Laboratory, where it was used in the space-shot vehicle Traveler IV which reached the Karman line. DDI was used for its extensive pot life and low viscosity relative to MMDI and IPDI. 89% and 86% solids loading were selected due to previous research showing promising tensile properties given an increase in solids loading. High solids loading was also used due to its tendency to increase specific impulse albeit with diminishing returns before propellant cannot be cast.

IV. Method of Mechanical Testing

Each propellant formulation was mixed and cast into a baking sheet. After they were allowed to cure, they were cut into ASTM E8/E8M tensile coupons, then cooled to –60 °F. The specimens were pulled apart at a constant rate of 0.05 in/s by a linear actuator, subjecting them to a steadily increasing uniaxial tensile load until failure. The load versus time was measured by a load cell and the displacement versus time was recorded by a linear potentiometer. The stress was calculated by dividing the load by the cross-sectional area of the specimen, measured before the test. The strain was calculated by dividing the displacement by the initial distance between the specimen clamps.

Fig. 1 Cookie cutter tensile specimen manufacturing method.

The tensile testing was performed by a custom-built test apparatus provided by Exquadrum Inc. The system used National Instruments DAQ hardware, and software programmed in LabVIEW.

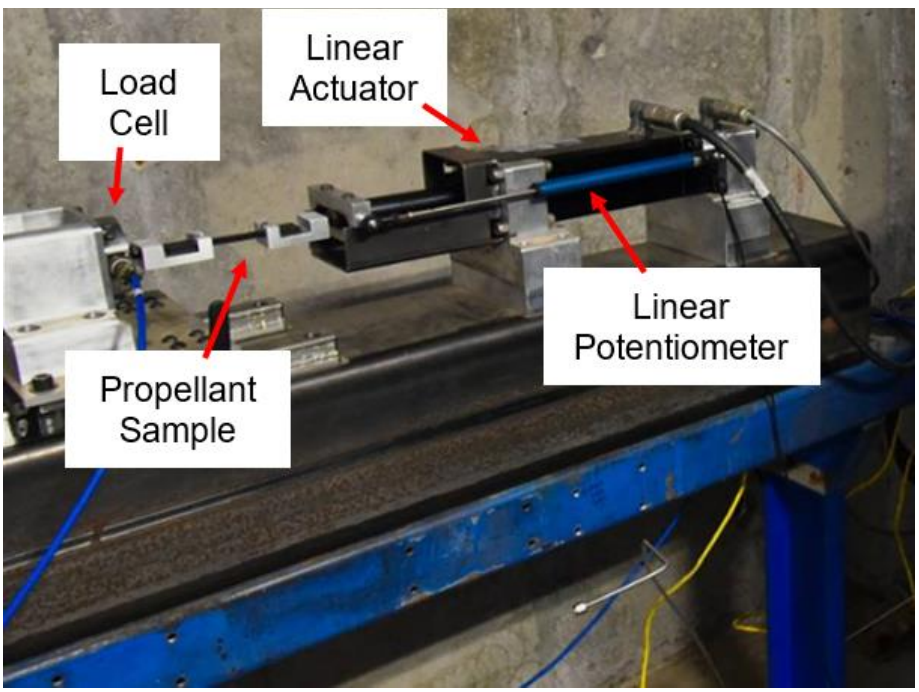
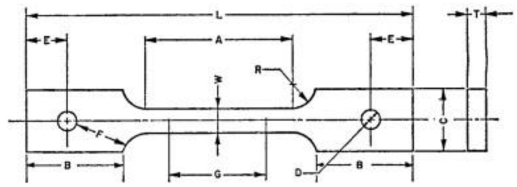


Fig. 2 Tensile testing apparatus, courtesy Exquadrum Inc.



Dimensions, mm [in.]	
G—Gauge length	50.0 ± 0.1 [2.000 ± 0.005]
W—Width (Note 1)	12.5 ± 0.2 [0.500 ± 0.010]
T—Thickness, max (Note 2)	16 [0.625]
R—Radius of fillet, min (Note 3)	13 [0.5]
L—Overall length, min	200 [8]
A—Length of reduced section, min	57 [2.25]
B—Length of grip section, min	50 [2]
C—Width of grip section, approximate	50 [2]
D—Diameter of hole for pin, min (Note 4)	13 [0.5]
E—Edge distance from pin, approximate	40 [1.5]
F—Distance from hole to fillet, min	13 [0.5]

Fig. 3 ASTM E8/E8M tensile standard

V. Results and Discussion

Mechanical performance was measured using four metrics: strength, elasticity, ductility, and toughness. Strength was measured by ultimate tensile strength, the highest stress the propellant can withstand. Elasticity was measured by the elastic modulus, the ratio of stress versus strain while in the linear elastic region. Ductility was measured by percent elongation, the deformation of the sample at fracture as a percentage of the initial length. Toughness was measured by work of fracture, the energy absorbed by the material (per unit volume) prior to fracture.

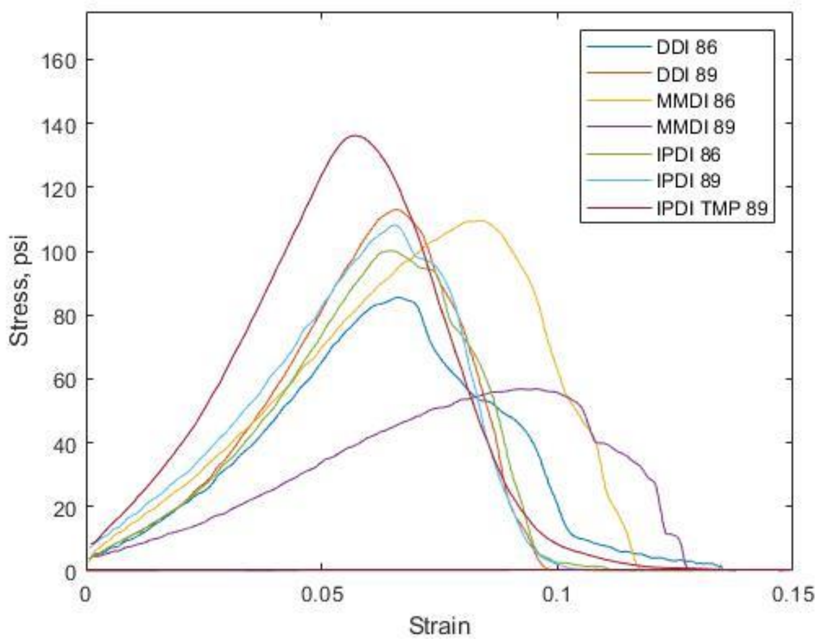


Fig. 4 Mean stress-strain data of samples for each test matrix overlaid.

Fig. 4 displays the average of six samples for each formulation. The MMDI batch with 89% solids loading had the lowest strength but the highest elasticity and ductility. The IPDI batch with TMP at 89% loading showed the highest strength and lowest elasticity, with average ductility. MMDI at 86%, DDI 89%, DDI 86% and IPDI 89% showed similar stress-strain curves. The propellants did not exhibit linear elastic behaviors like most metals. Thus, when calculating elastic modulus, a line was drawn from the first point through the point two-thirds of the way up the upslope to calculate a reasonable elastic modulus.

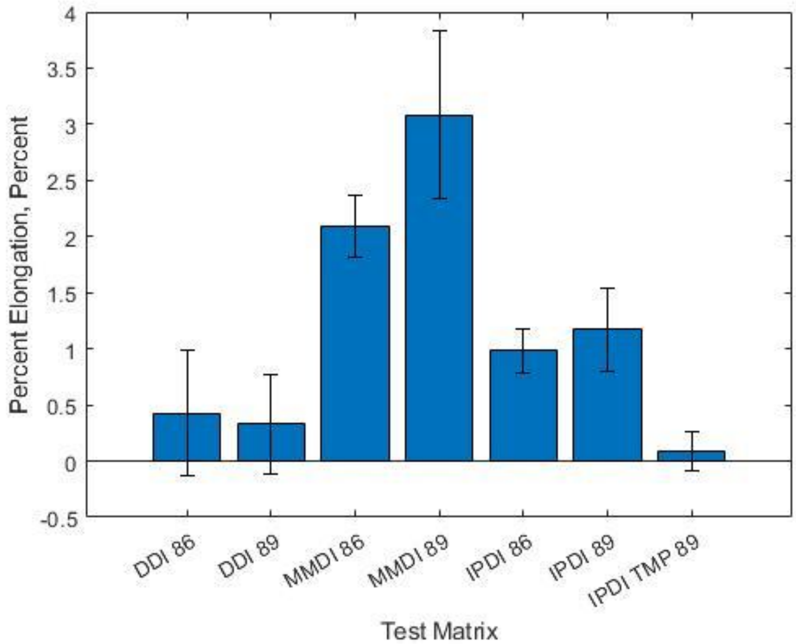


Fig. 5 Elongation of tensile coupons as a percentage of the total length of the sample.

MMDI with 89% solids loading stands out as the most ductile formulation, reaching over 3% elongation. Decreasing the solids loading generally decreased ductility regardless of the curative.

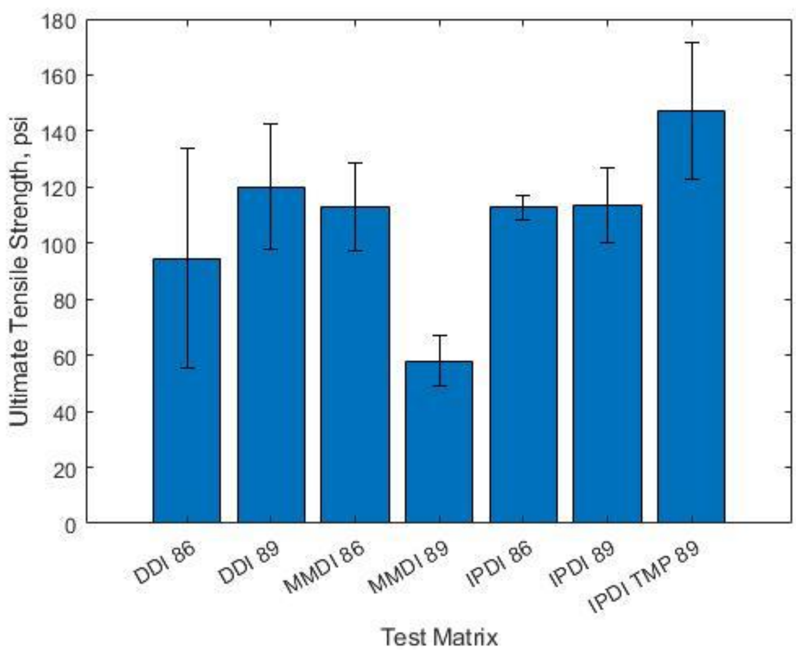


Fig. 6 Ultimate tensile strength was measured by the maximum point on the stress-strain curve.

The effect of solids loading on strength was different for each curative. With IPDI, the effect was negligible. With MMDI, decreasing solids loading increased tensile strength, and the opposite was true of DDI. Adding TMP significantly increased the strength of the IPDI batch.

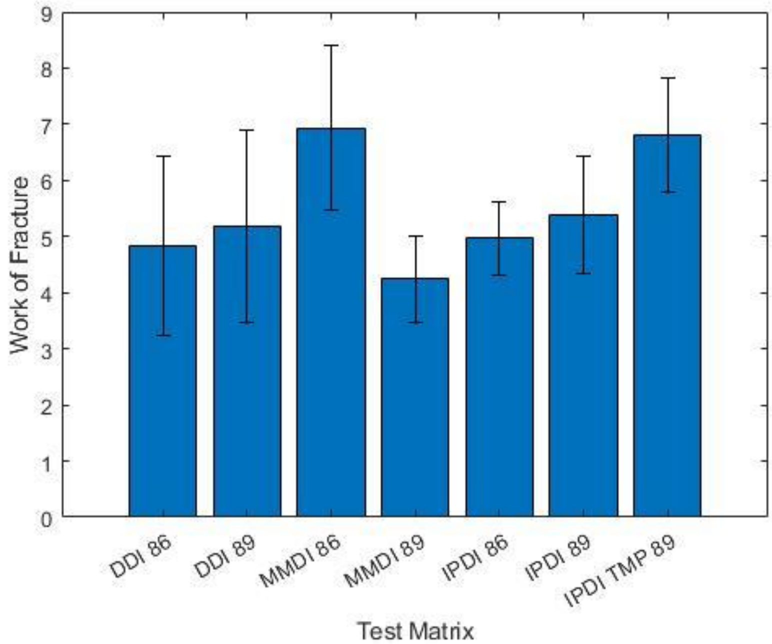


Fig. 7 Work of fracture of material calculated as the area under the stress-strain curve.

MMDI with 86% solids loading showed the highest toughness without additives, but also the lowest strength. Adding TMP made the toughness of the IPDI 89% batch comparable. It should be noted that the work of fracture was calculated by the area under the stress versus strain curve; therefore, there are two ways to increase it. The high toughness of the MMDI batch results from the high ductility, whereas the high toughness of the IPDI TMP batch results from high strength.

Table 2 Mean tabular results of each test matrix.

	DDI 86	DDI 89	MMDI 86	MMDI 89	IPDI 86	IPDI 89	IPDI TMP 89
Elastic Modulus, psi	1327.88	1610.47	1421.43	683.90	1490.62	1618.68	2399.34
Percent Elongation, Percent	0.42	0.33	2.09	3.09	0.98	1.17	0.088
Ultimate Tensile Strength, psi	94.55	120.00	113.11	58.06	112.75	113.55	147.56
Work of Fracture	4.84	5.19	6.94	4.25	4.97	5.39	6.81

Table 3 Uncertainty of each measurement for each test matrix.

	DDI 86	DDI 89	MMDI 86	MMDI 89	IPDI 86	IPDI 89	IPDI TMP 89
Percent Elongation, Percent	0.56	0.45	0.27	0.75	0.20	0.37	0.17
Ultimate Tensile Strength, psi	39.26	22.43	15.68	9.16	4.48	13.39	24.48
Work of Fracture	1.59	1.71	1.48	0.77	0.65	1.05	1.00

Table 2 shows numerical values for each previous figure shown including elastic modulus. Elastic modulus was calculated by creating a line through the zero point of the stress strain plot and two-thirds of the stress. We assumed that the stress strain data was linear until near the point of highest stress which allowed for such approximation of the elastic modulus. Table 3 gives the uncertainty of the measured results. This uncertainty was calculated by the standard deviation of the six test coupons results for each formulation.

VI. Conclusion

At low temperatures, brittle failure is the most common failure mode for solid propellants. For this reason, formulations with high strength and high work of fracture are desirable when compared to propellants with high ductility. High solids loading is desirable because it provides better burn properties compared to low solids loading.

IPDI showed consistent strength and ductility at high and low solids loading. DDI increased in strength with increased solids loading but decreased in ductility. MMDI decreased dramatically in both strength and ductility at higher solids loading. All propellants without additives showed similar works of fracture, with the exception of MMDI at 86% solids loading.

MMDI at 86% solids loading showed the highest work of fracture despite relatively average tensile strength because of its high ductility. If high solids loading is desired, it was shown that adding TMP to the IPDI 89% solids loading formulation could increase the work of fracture to a level comparable to that of the MMDI batch by increasing the ultimate tensile strength. This comes at the cost of decreasing ductility. It may be possible to increase the strength of MMDI at high solids loading using TMP.

The research showed it is possible to maintain performance of a solid grain at very low temperatures, thus possibly opening up their use in long durations space flight missions. More investigation is recommended that looks at longer cold soak durations, and different volumes of propellant and grains that may have an overall effect, that are more commensurate with what is expected for potential exploration missions in the future.

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