A New Nitrate Ester Composite Propellant

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Abstract

In this work, we characterize a composite propellant using a newly-synthesized nitrate ester oxidizer (SMX) and compare it to formulations based on ammonium perchlorate (AP). The theoretical performance, handling characteristics, and physical properties are comparable, but the propellant can propagate detonations. Differential scanning calorimetry showed an exotherm onset for the SMX-based propellant at 140 ºC. The propellant has a high burning rate, with a pressure exponent of 0.85. This high pressure sensitivity might be addressed using various energetic and/or stabilizing additives. With good performance, high density, and reasonable safety characteristics, SMX-based composite propellants offer a promising alternative for existing formulations.

1. Introduction

Many solid composite propellants are based on the oxidizer ammonium perchlorate (AP). With its high oxygen content, good density, and gas-phase combustion products, AP sets a high standard for performance, stability, and low cost. However, AP remains far from the ideal oxidizer; the perchlorate ion, essential for its stable arrangement of oxygen atoms, proves problematic from both a health and environmental standpoint. As such, much research is currently ongoing to evaluate suitable replacements for AP [1-4].

One oxygen-rich functional group to potentially consider for AP replacement is the nitrate ester group, $R\text{-}ONO_2$. As the backbone of the double-base propellant family, nitrate esters have been widely used in propulsion applications for decades. However, most high energy nitrate esters are liquid at room temperature, making them impossible to use as a replacement for crystalline AP. A notable exception, pentaerythritol tetranitrate (PETN), is a stable solid at room temperature, but proves of little utility for propellant applications due to its low oxygen balance (-10.12%) and inability to sustain stable combustion at atmospheric conditions [5-6].

Recently, Chavez, *et al*. [7] synthesized a new nitrate ester: 2,3-hydroxymethyl-2,3-dinitro-1,4-butanediol tetranitrate. This molecule, colloquially referred to as SMX, appears to provide a new avenue for propellant formulation: it is a room-temperature solid (M.P. = 85 ºC) with an oxygen balance of 0% (CO_2-balanced) and sensitivity similar to that of other nitrate esters.

The objective of this work is to examine the use of SMX as an oxidizer for composite rocket propellants, both theoretically and experimentally. We performed theoretical performance calculations using the NASA Chemical Equilibrium with Applications (CEA) thermochemical code [8], and used the results to formulate a basic propellant for physical evaluation. Safety and handling characteristics were evaluated using standardized methods, and physical properties were measured and compared to existing AP-based propellants. The thermal behavior of the propellant was also characterized using DSC/TGA. Finally, the burning rate of the propellant was evaluated over a range of pressures to determine whether safe operation in a solid rocket motor is feasible.

2. Methods

Prior to laboratory work, theoretical performance calculations were performed using NASA CEA. Propellants based on hydroxyl-terminated polybutadiene (HTPB) were considered over a range of solids loadings typical for HTPB-based propellants (78-88 wt.%). Aluminum inclusion over the range of 0-20 wt.% was also considered. Specific impulse (I_{sp}) was used as the performance parameter of merit, calculated assuming a chamber pressure of 6.89 MPa and ideal sea level equilibrium expansion.

Based on the results of these calculations, an 85% solids propellant was formulated for laboratory testing. The formulation for this propellant is listed in Table 1. Aluminum was included at 2 wt.% to opacify the propellant and promote combustion stability while minimizing the presence of condensed-phase products in the exhaust plume. The mixing process began by hand-blending the binder components: R45HTLO HTPB, isodecyl pelargonate (IDP) plasticizer, and Desmodur E744 isocyanate (all from RCS Inc., Cedar City, UT, USA). Once all components were well-mixed, -325 mesh aluminum (Alfa-Aesar, Ward Hill, MA, USA) was added and hand-stirred until completely wetted. Finally, SMX (Nalas Engineering, Centerbrook, CT, USA) was added in multiple small increments, hand-stirring between each to fully incorporate the material. Once completely wetted, the propellant was placed on a LabRAM mixer (Resodyn, Butte, MT, USA) and mixed at a 50% intensity level until homogeneous (~10 minutes). The propellant was then packed into 7 mm diameter polyethylene sleeves and allowed to cure at ambient temperature. Once cured, these strands were cut into 1 cm long segments for characterization.

Table 1: Propellant formulation characterized in this work.

Constituent	wt. %
SMX	83.00
Aluminum, -325 mesh	2.00
R45HTLO HTPB	11.15
Isodecyl Pelargonate	2.23
Desmodur E744 MDI	1.62

Hardness measurements were taken using a REX RX-1600D Shore D durometer, and compared to measurements on a 90 μm ammonium perchlorate-based composite propellant at the same solids loading and metallization. Thermal properties were measured using the transient plane source (TPS) method [9] with a Hot Disk AB TPS 2500S thermal property analyzer and 12mm diameter propellant samples. Thermal analysis was conducted with a TA Instruments Q600 simultaneous differential scanning calorimeter/thermogravimetric analyzer (DSC/TGA) at a heating rate of 10 °C /min, under ultra high purity argon at 100 ml/min, using 90 μl open alumina pans.

Safety characteristics of the propellant samples were evaluated using three standardized techniques: drop weight impact (ERL Method 1012), electrostatic discharge (ARDEC Method 1032), and friction (BAM Method 1024), fully described in MIL-STD-1751A [10]. Propellant samples for these tests were cut to the powder sizes specified in the standards. All test statistics were computed using the Bruceton method. Shock sensitivity (detonability) of the propellant was evaluated using a small-scale zero-gap technique, as described by Sippel, *et al.* [11] Each test used 3 grams of propellant with a 1.5 gram donor charge of Primasheet 1000 explosive, fired by a Teledyne-Risi RP-501 detonator. The deformation of each aluminum witness plate was measured using a Hirox KH-8700 microscope with an OL-140-II lens.

The combustion of the propellant was evaluated in an optically accessible combustion vessel under quiescent nitrogen gas. Samples were ignited using 30 gauge Nichrome wire. Vessel pressure was measured using a Setra Model 207 0-70 MPa pressure transducer. Combustion progress was tracked using a Phantom Miro EX2 high-speed camera with a Nikkor 200 mm lens. GraphClick software (Arizona Software, Neuchătel, Switzerland) was used to determine the position of the burning surface over the course of the video. The position *vs.* time data was then plotted and a linear regression performed to determine theburning rate of the propellant.Three burns were accomplished at each pressure, and the mean burning rate from these testswas used to determine the relationship between pressure and burning rate.

3. Results and Discussion

3.1 Theoretical Performance

The performance potential of SMX-HTPB propellant was evaluated using NASA CEA. Typical propellants using an HTPB binder system use a solids loading in the range of 80-88%. This range was considered for the SMX-based propellants. The inclusion of aluminum was also considered, as such addition is widely known to increase performance and improve combustion stability. The resulting performance contours are shown in Fig. 1.

Since SMX is a CO_2-balanced molecule, increasing SMX concentration in the propellant formulation increases performance. At solids loadings above 87%, nonaluminized propellants surpass an I_{sp} of 240 sec, near that of existing XLDB propellant systems. Aluminized propellants, delivering upwards of 260 sec, compare quite favorably with AP-HTPB-Al systems, which peak near an I_{sp} of 264 sec [12].

In addition to its high theoretical specific impulse, SMX also performs well from a density standpoint: the crystalline density of SMX (ρ = 1.92 g/cm^3) is very similar to that of AP (ρ = 1.95 g/cm^3), and is much higher than other solid nitrate esters (e.g., PETN, ρ = 1.77 g/cm^3) [6]. Additionally, SMX may also be useful as an energetic additive in high energy composite propellants which currently contain HMX (ρ = 1.91 g/cm^3) or RDX (ρ = 1.82 g/cm^3) [13].

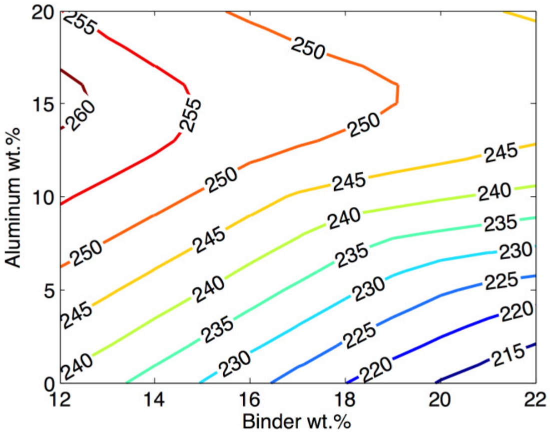

Figure 1: Specific impulse (sec) of SMX-HTPB propellants over various binder and aluminum loadings.

3.2 Physical & Safety Characterization

As delivered from the manufacturer, the SMX powder has a mean particle size of ~90 μm, measured via optical microscopy. The particles (Fig. 2) range from needle-like to jagged in morphology, which is typical for SMX crystals grown directly from solution. It may be possible to prill or rotary round the particles to improve the rheology of the propellant during casting. However, even at an 85% solids loading, the test propellant mixed quite easily, and the finished product was dough-like, allowing casting methods previously adopted for AP-HTPB propellants to be used. The finished product was flexible, easily cut, and had a hardness value of 21 Shore D, as compared with 22 Shore D for a baseline AP-HTPB-Al propellant at the same solids loading.

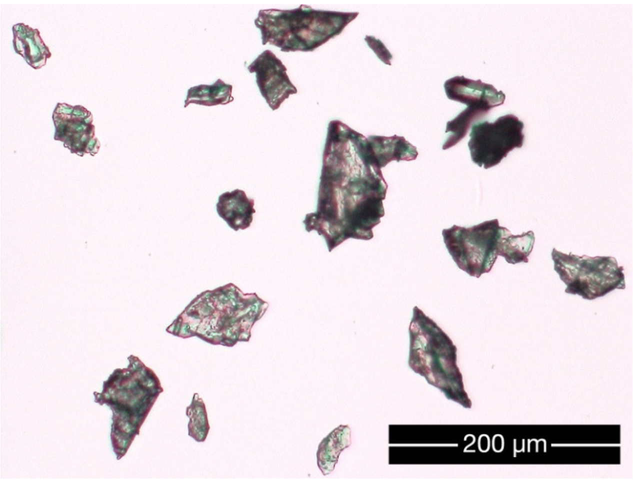

Figure 2: Optical microscopy of SMX crystals used in this work.

Table 2: Thermal properties of SMX-HTPB-Al propellant.

Formulation	***k*, W/m-K**	**α, mm^2/s**
Neat SMX	0.266 ± 0.005	0.118 ± 0.006
Neat HTPB	0.263 ± 0.005	0.19 ± 0.01
AP-HTPB-Al	0.426 ± 0.007	0.20 ± 0.01
SMX-HTPB-Al	0.244 ± 0.005	0.14 ± 0.01

Thermal properties (thermal conductivity k and thermal diffusivity α) of propellant samples were measured three times and averaged, resulting in the data shown in Table 2. Additionally, thermal properties of the major constituent ingredients (SMX and HTPB) were measured, along with thermal properties of the baseline AP-HTPB-Al formulation. In the propellant mixture, the thermal properties of the SMX dominate; this is to be expected, as the loading of SMX is 83% by weight (71.4% by volume). The measurements for AP-HTPB composites also correspond well with thermal property measurements from the literature [14,15].

Table 3: Safety characteristics of SMX-HTPB-Al propellant.

Formulation	**Impact Height, cm**	**ESD, mJ**	**Friction, kgf**	**Deformation Depth, mm**
Neat SMX	20	172	7.6	--
AP-HTPB-Al	88 ± 7	> 250	27 ± 5	0.2
SMX-HTPB-Al	88 ± 32	> 250	21 ± 2	6.0

The results of the safety characterization tests are shown in Table 3. The HTPB binder significantly decreases the sensitivity of the SMX in the propellant mixture, with a resulting impact and friction sensitivity near that of the baseline AP-HTPB-Al propellant. During drop weight impact testing, the SMX propellant often would ignite only in a very small region, resulting in a wide spread in the data. Both propellant formulations were insensitive to electrostatic discharge at the level specified in the MIL STD.

In small-scale zero gap testing, the SMX-HTPB-Al propellant easily propagated a detonation, significantly deforming the aluminum witness plate in multiple tests. The AP-HTPB-Al propellant also propagated a detonation, albeit weakly – the witness plate, while deformed from the shock wave, was significantly less damaged than in the case of the SMX-HTPB-Al propellant. As a control, a sample of Primasheet 1000 was also tested in the same configuration as the SMX-HTPB-Al sample, with an air gap in place of the SMX-HTPB-Al propellant; this test resulted in a 1.22 mm deformation. As a result of this testing, it appears that SMX-HTPB-Al propellant is safe to handle under normal conditions, but may present a detonation hazard if initiated via a strong shock wave.

3.3 Thermal Characterization

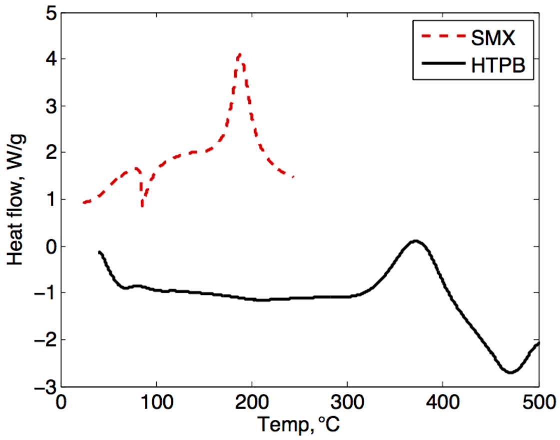

Figure 3: DSC traces of neat SMX and neat HTPB.

DSC curves for SMX and HTPB are shown in Fig. 3, shifted for clarity. The thermal properties of neat SMX were characterized by Chavez, *et al.* [7] during their initial investigation of the molecule. SMX was shown to have a melting point of 85 °C and an exotherm onset at approximately 140 °C. The material used in these experiments shows identical behavior. The thermal properties of HTPB have been widely investigated. For this particular binder system, melt onset occurs almost immediately, with decomposition and pyrolysis occurring in distinct exothermic and endothermic phases at 360 ºC and 470 ºC.

DSC traces of the SMX-HTPB-Al system and the AP-HTPB-Al system are shown in Fig. 4. Logically, the thermal trace of the SMX-HTPB-Al propellant is dominated by the behavior of the SMX. The SMX melt is visible, as expected, at 85 ºC. The exotherm of the SMX occurs well before the HTPB decomposition onset, and as such the exothermic reaction proceeds quickly and violently, consuming all of the mass at the 140 ºC onset point. This is a significantly lower temperature than is seen with AP-HTPB-Al, which shows the expected phase transition at 240 ºC and onset of ignition above 300 ºC.

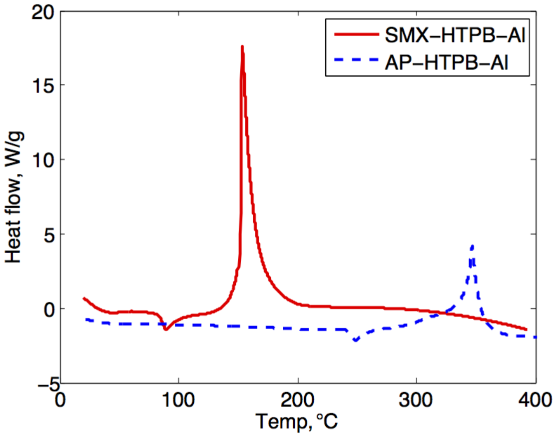

Figure 4: Normalized DSC traces of SMX-HTPB-Al and AP-HTPB-Al propellants.

Interestingly, the normalized heat output of the SMX-HTPB-Al system is significantly higher than that of the AP-HTPB-Al system. This is likely due to the fact that the ignition and combustion of the SMX-based propellant is occurring during the melting of the HTPB binder, rather than during the endothermic pyrolysis of the polymer, as is the case for the AP-based propellant. This high heat flowrate allows the propellant to support a high burning rate, as detailed in the next section.

3.4 Combustion & Burning Rate

The burning rate of the SMX-HTPB-Al propellant was measured over a range of pressures appropriate for rocket applications (3.4-13.8 MPa). Typically, the burning rate r is fitted as a power law function of pressure P,

$$r = aP^n, \tag{1}$$

where a and n are the burning rate coefficient and exponent, respectively. The results of these measurements and the resulting curve fit are shown in Fig. 5.

With burning rate parameters $a = 0.304 \pm 0.03$ and $n = 0.85 \pm 0.04$ (for pressure in MPa and rate in cm/sec), the SMX-HTPB-Al propellant burns faster than a comparable AP-HTPB-Al propellant; for example, at 6.89 MPa, the baseline AP-HTPB-Al propellant burns at 0.6 cm/sec, versus 1.6 cm/sec for the SMX-HTPB-Al propellant.

The high value of n (i.e., near 1) is advantageous for throttling and control purposes, but could be problematic from a motor design and sensitivity standpoint. This exponent could likely be lowered with the inclusion of an energetic binder (e.g., glycidyl azide polymer) or other ingredient that reacts in the condensed phase and/or near the surface of the propellant. Since SMX is a nitrate ester, it may be possible to further stabilize the burning rate by including any number of ballistic additives typically applied in double base propellants, such as lead, copper, or bismuth salts [16].

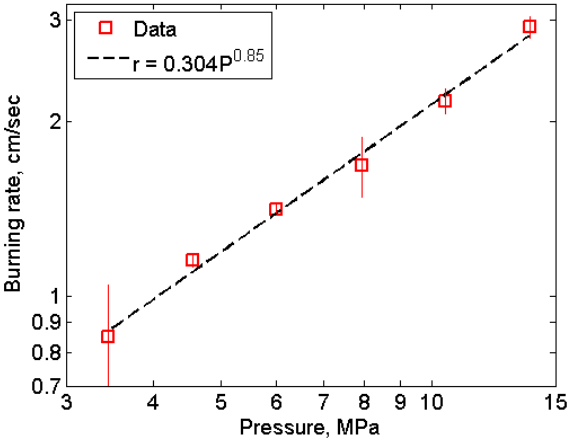

Figure 5: Burning rate data and curve fit for SMX-HTPB-Al propellant.

4. Conclusion

As an oxygen-rich high density room temperature solid, SMX appears to hold excellent potential as a solid propellant ingredient. In theoretical calculations, it nearly matches the performance of existing state-of-the-art propellants using ammonium perchlorate (AP), and offers the added benefit of lower environmental toxicity. SMX-HTPB-Al has a lower thermal conductivity than AP-HTPB-Al, but a similar thermal diffusivity. It is also quite similar to AP in its handling characteristics: initiation via impact, friction, and electrostatic discharge occurs at nearly the same level of stimulus. However, SMX-based composite propellant will propagate a detonation wave – a characteristic that may limit its application.

Thermally, SMX-based propellants behave quite differently than those based on AP – the SMX melting endotherm happens much earlier, at 85 ℃, and the exotherm onset occurs at 140 ℃, far below that of AP-based propellants, and below the endothermic HTPB pyrolysis process. This exotherm is significantly larger than that of AP-based propellants, allowing a high burning rate to be maintained. The burning rate was measured to be 1.6 cm/sec at 6.89 MPa with a burning rate exponent of 0.85 ± 0.04, which may potentially be lowered using existing ballistic stabilizers commonly used in double base formulations. Future work should investigate such stabilization.

These experiments show that it is indeed possible to harness the potential of SMX for propellant applications – from perspectives of performance, processing, safety, and combustion, it is another competitive option for replacing AP in the next generation of solid rocket propellants.

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