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MILLING OF NITRAMINES FOR ULTRAVIOLET (UV) CURABLE ENERGETIC FOR ADDITIVE MANUFACTURED PROPELLANT GRAINS

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14. ABSTRACT
Wet stirred media milling (WSMM) is a technique widely used by industry as a top-down method for reducing the particle size of suspensions. In this study, the aim is to demonstrate the feasibility of particle size (PS) reduction of the suspended nitramines in an additive manufactured propellant formulation, in its uncured state. Traditional WSMM uses a stationary tank with a shaft and attached arms to agitate the milling media, or a built in pump, agitator, and pre-disperser for single pass or recirculation milling to achieve desired particle sizes in suspension. With this approach, a bladeless centrifugal SpeedMixer™ by FlackTek, Inc., Landrum, SC, was used, which employs dual asymmetrical mixing on a polypropylene cup filled with the pre-formulation and a zirconia grinding media to achieve the desired PS reduction within minutes. From this report, it is discovered that Class I RDX is significantly more challenging to achieve PS reduction when compared to HMX via this method, which the latter achieves a mean PS of about 10 µm in 10 min. In addition, it is discovered the dispersed HMX is significantly less soluble in the continuous monomer phase than RDX.

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INTRODUCTION

Additive manufacturing (AM), or three-dimensional printing (3DP), is a layer-by-layer process that has competitive advantages for complex products and products made on-demand. Polymer composites and their formulations have promise for the 3DP of gun propulsion charges, with an emphasis on the stereolithography apparatus (SLA) as the 3DP approach to develop composite formulations for this work. The SLA 3DP has a unique advantage in that it does not require elevated temperatures to form a polymer, and the printing technique is regarded as possessing amongst the highest in print resolution. The formulation for an SLA approach is a liquid resin suspension before polymerization, defined as a formulation of solid nitramines (dispersed phase) homogenously suspended within a liquid monomer resin (continuous phase) and the additives necessary to stabilize/cure that formulation to form a stable polymer composite. The effects of nitramine (RDX and/or HMX) particle size and content in propellants have been investigated to understand the burning characteristics of traditionally mixed composite propellants with hydroxyl-terminated polyester and hydroxyl-terminated polybutadiene (HTPB), but this work investigates a process for the milling of nitramines and a novel SLA propellant monomer using a SpeedMixer™ by FlackTek, Inc, Landrum, SC, with zirconia milling media. The SpeedMixer™ is seen in figure 1; it homogenizes via dual asymmetric centrifugal mixing, enabling very rapid mixing of everything within the cup (ref.1) (fig. 2). The goal was to find the optimized particle size for the formulation to ensure stability within the composite and eventually identify burn rate for the novel SLA composite propellant.

Figure 1
SpeedMixer™ using bladeless mixing technology

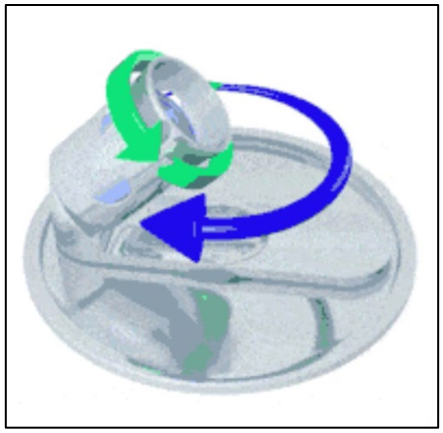


Figure 2
Dual asymmetric centrifugal mixing arising from the double rotation of the mixing cup (ref. 1)

EXPERIMENTAL DEVELOPMENT

In SLA 3DP, photopolymerization occurs when a low molecular weight liquid monomer sample is mixed with a photoinitiator (PI) and irradiated with ultraviolet (UV) radiation (UV light) to form a polymer of high molecular weight (ref. 2). A schematic of photopolymerization is outlined in figure 3. Typical monomers used in these formulations include acrylates, methacrylates, and epoxides. In this task, the continuous phase of the formulations was a proprietary, energetic, UV curable resin (JL-1), which included a dissolved dispersant/wetting agent (Solsperse 32000) and a dissolved acylphosphine oxide as the PI. The dispersed phase was a solid nitramine (RDX or HMX) that can be evaluated for maximum loading efficiency of different particle sizes from milling. The formulations can be seen in tables 1 and 2. Nitramine composite propellants including either cyclotrimethylenenitramine (RDX) or cyclotetramethylene tetranitramine (HMX) have attracted much attention in the domain of solid rocket and gun propulsion because of their energetic and smokeless features (ref. 3).

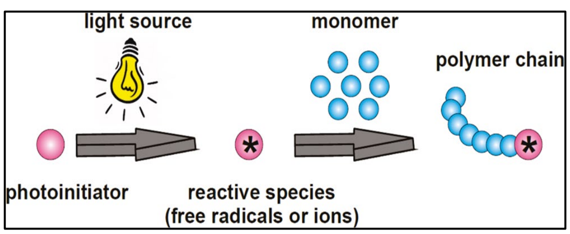


Figure 3
General presentation of PI polymerization (ref. 4)

Table 1
DB138 formulation

Ingredient	% (w/w)	Weight (g)	Description
JL-1	49.5	9.9	Proprietary
HMX	48	9.6	Class III
Solsperse 32000	2	0.4	Dispersant
Irgacure 819	0.5	0.1	PI

Table 2
DB146 formulation

Ingredient	% (w/w)	Weight (g)	Description
JL-1	49.5	9.9	Proprietary
RDX	48	9.6	Class I
Solsperse 32000	2	0.4	Dispersant
Irgacure 819	0.5	0.1	PI

Milling is a unit operation where mechanical energy is applied to physically break down coarse particles to finer ones and, hence, is regarded as a “top-down” approach in the production of fine particles. Wet milling, size reduction, comminution, grinding, and pulverization are interchangeable terms used in this case to describe forming a suspension of a dispersed phase (nitramine) within a continuous phase and reducing the particle size of the dispersed phase by the addition of grinding media (glass, stainless steel, zirconia, etc.) and a dispersant for chemical stability.

A suspension approach to the formulation is necessary in order to enhance impetus and improve overall ballistic performance. One formulation approach was to add a nitramine to the formulation depending on how soluble the nitramine is within the JL-1 resin. Suspension formulations are notoriously difficult to stabilize due to the effects of Ostwald ripening and crystallization growth, agglomeration, sedimentation, flocculation, etc.

Solubility plays a critical role in 3DP formulations. Two nitramines of interest, RDX and HMX, were evaluated for solubility in JL-1. Ideally, each nitramine should have either minimum (or maximum) solubility in the monomer resin. The unlikely case is that either would have significant solubility in JL-1, which, if it did, would essentially be treated as a clear homogenous solution with maximum allowance for UV polymerization. In reality, the case is just the opposite. RDX and HMX are notoriously difficult to dissolve even with strong solvents such as acetonitrile [5.5 and 2.0%, respectively, at room temperature (ref. 5)].

Given the circumstance that nitramine solubility would be low but present to some degree presents a challenge to ensure the degree of solubility is accurately measured and controlled. Factors that come into play are temperature and especially the energy imparted into the system with grinding. Any degree of solubility would have an effect on the viscosity of the formulation and this could become significant during the printing process. Furthermore, dissolved nitramine would essentially be trapped in a metastable state with JL-1 polymerization, and it would be expected in time for crystallization to occur from the frozen polymer matrix. Precipitation of the nitramine could result in a polymorph or crystal habit not desired for the end product (i.e., sensitive needle structures).

METHODS, ASSUMPTIONS, AND PROCEDURES

The formulations of DB138 and DB146 were weighed directly into MAX100 SpeedMixer™ cups, respectively. An equal volume of zirconia milling media with a mean particle diameter of 1.0 mm was added to the cups. A thermocouple was employed to monitor temperature as grinding without the use of recirculating coolant fluid could result in a spike of temperature, which could be dangerous when dealing with energetics. Temperature was taken in duplicate. The particle sizes and the resulting temperature change corresponding to the mix at that time point can be seen with reference to tables 3 and 4. The particle sizes of the RDX and HMX samples were measured using a Cilas 1190 Particle Size Analyzer, which utilizes laser diffraction to measure particle size distributions (PSD) by measuring the angular variation in intensity of light scattered as a laser beam passes through the dispersed (in water) particulate sample.

Table 3
HMX Class III particle size distribution results

Time of wet milling (SpeedMixer™) min	HMX d(mean) µm	HMX d(10) µm	HMX d(50) µm	HMX d(90) µm	Temperature (°C)
0	234.96	69.66	227.58	392.93	21, 21
2	18.41	2.56	13.72	40.80	21, 23
4	13.06	2.30	10.63	27.67	24, 25
6	13.77	1.86	10.47	31.28	23, 24
8	10.99	0.38	9.39	23.26	23, 24
10	11.35	2.81	9.54	22.48	24, 25

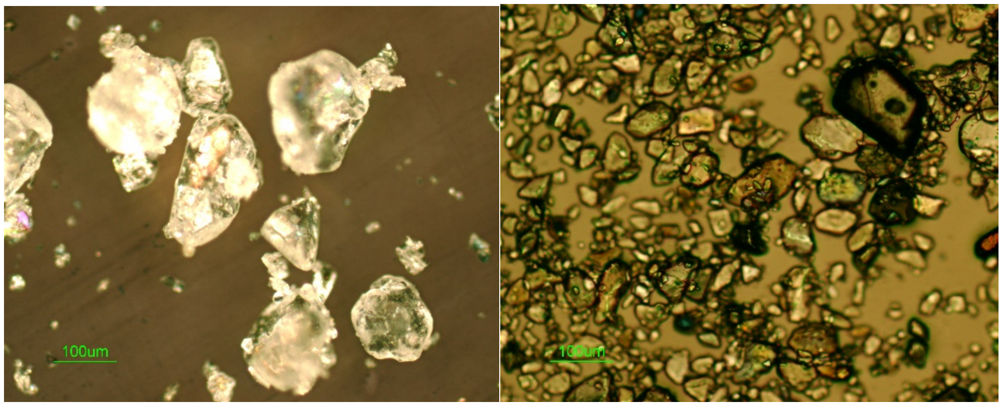
Table 4
RDX Class I particle size distribution results

Time of wet milling (SpeedMixer™) min	RDX d(mean) µm	RDX d(10) µm	RDX d(50) µm	RDX d(90) µm	Temperature (°C)
0	161.73	52.01	156.81	274.72	21, 21
2	139.99	31.13	130.70	263.17	21, 22
4	152.22	20.11	117.54	339.26	29, 29
6	-	-	-	-	34, 34
8	-	-	-	-	39, 39
10	-	-	-	-	49, 49
12	143.24	41.02	137.79	244.36	51, 51
14	157.63	38.39	158.06	270.67	54, 53

RESULTS AND DISCUSSION

The notable difference between RDX and HMX particle size reduction is fascinating. The structural similarity between both nitramines would suggest, at first glance, that identical results should be obtained; however, this is not the case. HMX grinds down smoothly while RDX essentially remains unchanged. The RDX appeared to agglomerate significantly upon mixing and could be described as cement within one portion of the SpeedMixer™ cup. The explanation that can be derived is that this highly-solids-loaded suspension exhibits shear thickening behavior, resulting in a localized viscosity increase giving rise to the appearance of cement. An increase in viscosity was apparent for both formulations. When unmilled nitramine was added to the JL-1 and dispersant, both suspensions appeared as a normal non-Newtonian fluid with significant settling of the large nitramine particles. Upon mixing with the Flacktek at 1,000 rpm in 2-min increments, there was a significant temperature increase associated with the “milling” of RDX (see table 2), which did not occur with HMX. The temperature increase is proposed to arise from the friction associated with the contact of particles and milling media during the dual asymmetric centrifugal mixing, but the RDX particle size did not decrease whereas the HMX particle size decreased significantly, giving rise to a suspension with a creamy appearance and without any observed settling.

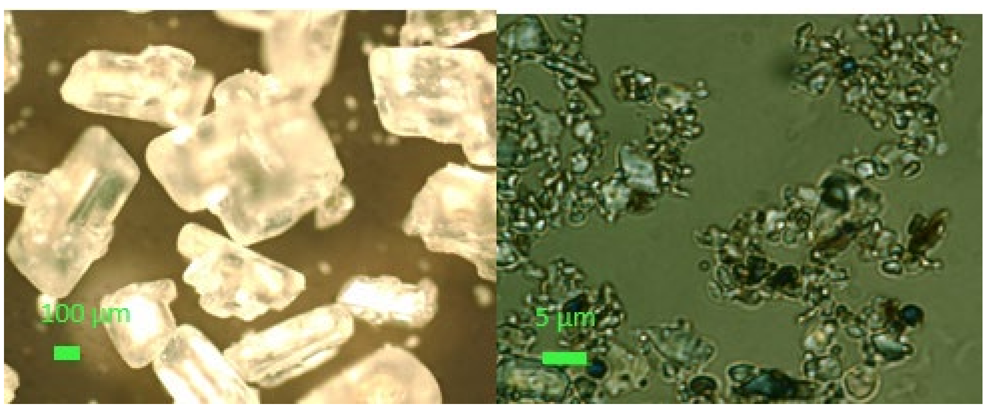
Pristine Class I RDX milled after 10 min was examined using optical microscopy. It is readily apparent there is almost no change in crystal size (see figs. 4a and b). However, in the case of milling Class III HMX, there is a dramatic reduction in size (see figs. 5a and b). This corroborates the results from the laser diffraction studies.



(a) Class I RDX

(b) Class I RDX milled for 10 min

Figure 4
Class I RDX before and after being milled for 10 min using described conditions



(a) Class I HMX

(b) Class III HMX milled for 10 min

Figure 5
Class III HMX before and after being milled for 10 min using described conditions

The solubility of HMX and RDX in JL-1 were measured to shed light on this phenomenon. Aliquots were taken at the specified times noted in table 5. Gas chromatography (GC) analysis on an Agilent 7890A with a nitrogen phosphorous detector (NPD) and a Restek Rtx-TNT column (6-m, 0.53-mm inner diameter) was used to quantify the dissolved nitramine in each case. Calibration graphs were constructed as shown in figures 6 and 7 using 43.4 mg of 4-nitroaniline as an internal standard in 200 mL of dimethyl formamide. The amounts of dissolved nitramine taken at the specified time are reported in table 5. Each sample was filtered through a 0.45-µm syringe filter prior to adding dimethylformamide (DMF).

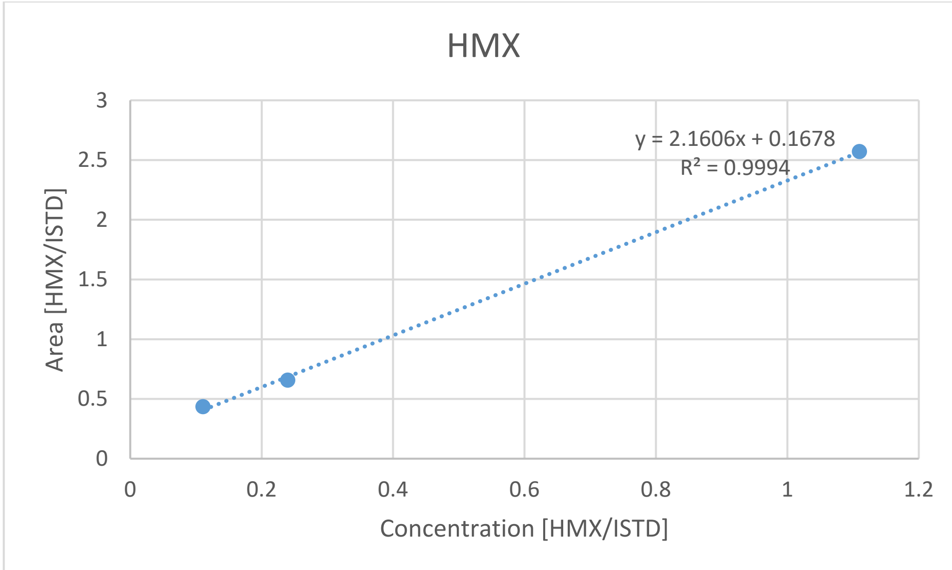


Figure 6
HMX calibration curve

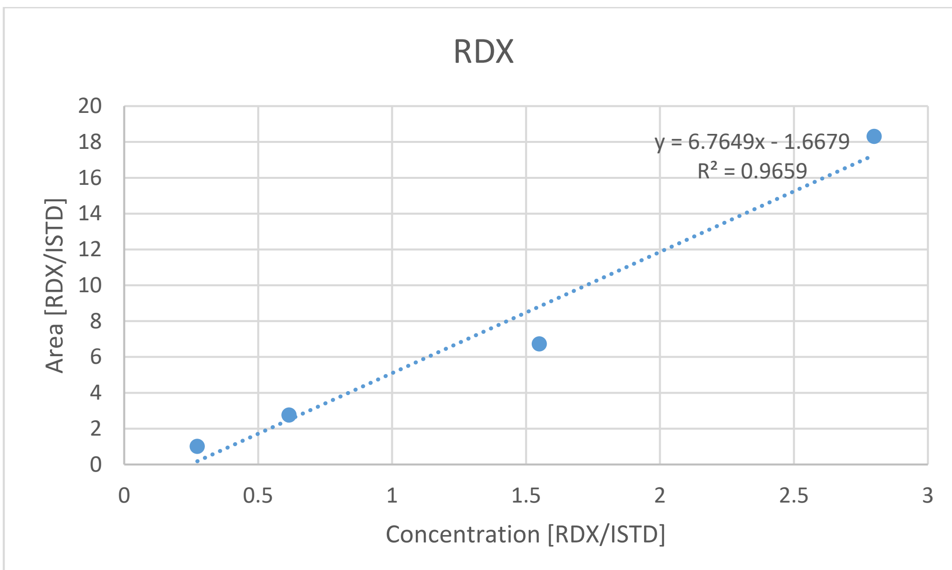


Figure 7
RDX calibration curve

Table 5
GC analysis of dissolved nitramine while grinding

Time (min)	HMX dissolved (%)	RDX dissolved (%)
2		1.7
6		1.8
10	0.26	
14		2.2

CONCLUSIONS

Formulating suspensions for three-dimensionally printed (3DP) gun propellant is a necessary approach to enhance impetus and improve overall ballistic performance. The idea of taking a nitramine with a larger particle size distribution (PSD) and wet-milling it down in suspension via a SpeedMixer™ to the desired particle size is an alternative approach to using fluidized energy mill (FEM). The results of this approach for 3DP are as follows.

1. Once the desired PSD has been achieved, there is no subsequent mixing needed. All the ingredients added to the SpeedMixer™ cup represent the final formulation.
2. Propellant formulated with RDX did not see a reduction in particle size, but instead appeared to form a cement. The HMX formulation had a significant reduction in particle size after 10 min in the SpeedMixer™.
3. RDX is significantly more soluble than HMX with respect to the JL-1 monomer, as verified by GC.
4. An increase in viscosity was observed for the HMX propellant formulation as the particle size was reduced.
5. The HMX propellant formulation experienced very little temperature increase upon milling, whereas the RDX formulation saw a drastic temperature increase with no reduction in particle size.
6. Smaller particle size nitramines exhibit less particle sedimentation and appear more stable, which would prove beneficial for use in stereolithography and vat 3DP applications.

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