

Investigation of HMX-Based Nanocomposites

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Abstract: Advanced munition systems require explosives which are more insensitive, powerful, and reactive. For this reason, nano-crystalline explosives present an attractive alternative to conventional energetics. In this study, formulations consisting of 95% octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and 5% polyvinyl alcohol (PVOH) were prepared with mean crystal sizes ranging from 300 nm to 2 μ m. The process to create these materials used a combination of mechanical particle size reduction and spray drying, which has the advantages of direct control of crystal size and morphology as well as the elimination of ripening of crystals (which occurs during slurry coating of nano-materials). The basic physical characteristics of these formulations were determined using a variety of techniques, including scanning electron microscopy and X-ray diffraction. Compressive stress-strain tests on pressed pellets revealed

that the mechanical properties of the compositions improved with decreasing crystal size, consistent with Hall-Petch mechanics. The 300 nm HMX/PVOH composition demonstrated a 99% and 129% greater strength and stiffness, respectively, than the composition with 2 μ m HMX. The formulations were subjected to the Small Scale Gap Test, revealing a significant reduction in shock sensitivity with decreasing crystal size. The formulation containing 300 nm HMX registered a shock initiation pressure 1.6 GPa above that of the formulation with 2 μ m HMX, a 44% improvement in sensitivity. These results serve to highlight the relevance of structure-property relationships in explosive compositions, and particularly elucidate the substantial benefits of reducing the high explosive crystal size to nano-scale dimensions.

Keywords: Nitramine • Explosives • Nanoenergetic • Spray drying • Sensitivity

1 Introduction

Nanoenergetics, in comparison with traditional energetics, exhibit enhanced performance, insensitivity, and mechanical strength, all of which are attributes required for next generation munition systems. Crystal size has a strong influence on the mechanical properties and the void size distribution of an explosive composition. These, in turn, govern the mechanical response of an explosive charge to shock stimuli by affecting the distribution of incident energy and thereby hot spot formation [1–5]. Improved mechanical properties can lead to reduced shock sensitivity in explosives [6,7]. The increased strength and stiffness of explosive compositions due to crystal size reduction, as described by the Hall-Petch relationship [8,9], contributes to reduced susceptibility to plastic deformation, which is a key precursor to initiation by mechanisms such as shear-band formation [10] and adiabatic void collapse [1].

Furthermore, significant evidence links higher reactivity with smaller crystal size in energetic materials. Some of the demonstrated improvements include: a smaller critical diameter [11,12], shorter shock to detonation transition length [13,14], enhanced sensitivity to initiation by short duration, high amplitude incident shocks [11], and improved detonation spreading [15]. These improvements in performance are largely attributed to the higher number density of hot spots and a larger specific surface area. Gen-

erally, insensitive explosive materials have low reactivity, a significant drawback. Nanoenergetics, therefore, are exciting because they exhibit an apparent paradox of high reactivity and low sensitivity.

The key challenges in producing compositions containing HMX and CL-20 is obtaining the target crystal size, while retaining the desired polymorph, and achieving a uniform binder coating without ripening the explosive [2,16–18]. In this study, the approach used to produce the nano-HMX based compositions was a combination of mechanical particle size reduction and spray drying. Mechanical particle size reduction was utilized to achieve the desired crystal size of β -HMX. A mechanical (top down) process was em-

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ployed for this purpose due to difficulties in producing β -HMX in the nano-scale regime via known solution precipitation routes [16]. In order to uniformly coat the nanocrystalline HMX with a polymeric binder, aqueous slurries of nano-HMX containing the dissolved binder were spray dried. Deposition of binder by spray drying overcame major limitations which exist with coating of nanoparticles using traditional methods such as slurry coating, which can ripen crystals and often result in a non-uniform coating [2].

This study aimed to correlate properties such as initiation sensitivity and mechanical strength to microstructural characteristics including crystal and void size. To achieve this, a detailed characterization of the prepared materials was carried out, including: Powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), compressive stress strain tests, and shock initiation sensitivity tests.

2 Results and Discussion

2.1 Structural Characterization

Dynamic light scattering (DLS) was performed to determine the mean crystal size of all samples. SEM images of the 2 μm and 300 nm HMX are provided in Figure 1. From a qualitative analysis of the images, the observed mean crystal size appears to be roughly consistent with the results obtained from dynamic light scattering analysis. Grinding dramatically reduces the crystal size of the HMX. Additionally, this seems to provide an additional benefit of making more rounded particles.

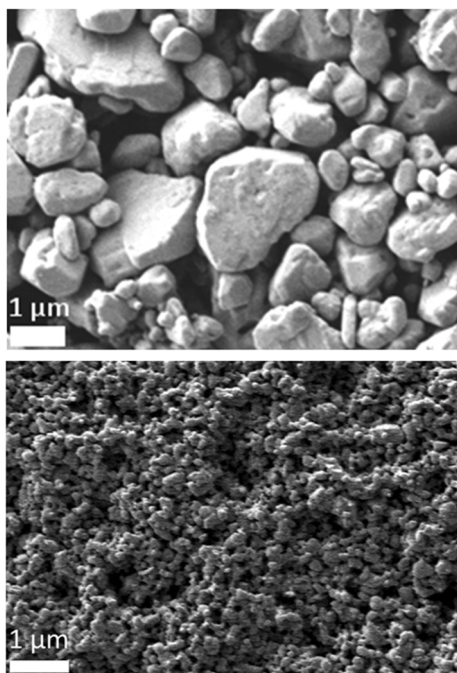


Figure 1. SEM images of (a) 2 μm HMX and (b) 300 nm HMX.

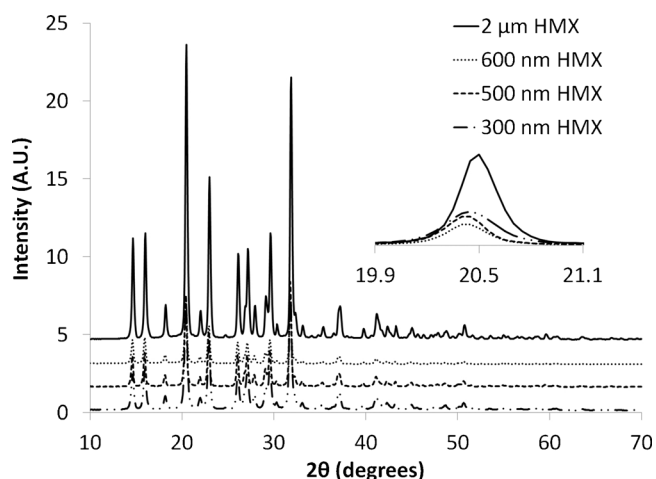


Figure 2. X-ray diffractograms for: 2 μm , 600 nm, 500 nm, and 300 nm HMX/PVOH formulations. The inset shows the peak near 20.5°, indicating a shift in the peak locations of the milled materials.

All final compositions were measured to be approximately 95% HMX and 5% polyvinyl alcohol (PVOH) using high performance liquid chromatography (HPLC). The PXRD results reveal few differences when examining the nano-HMX formulations, showing that the HMX remains of the β form (see Figure 2). However, a minor shift in peak locations is evident when comparing diffractograms of 2 μm and nano-HMX, suggesting a minimal lattice change that is likely due to the small crystal size. Raman spectroscopy was also performed and confirmed the polymorph of the nano-HMX and the minimal change in the lattice structure caused by size reduction, as discussed in the Supporting Information.

Pellets of the 300 nm and 2 μm HMX compositions were pressed to 1.43 g cm^{-3} , which is 75% of the theoretical maximum density (TMD) and sectioned using a focused ion beam (FIB) for SEM imaging, as shown in Figure 3. In the images, the binder, PVOH, is white, the HMX is grey, and the voids are black. Note that large crystals are clearly evident and the pore cross sections seem to be generally below 200 nm in diameter. The binder appears to be uniformly dispersed throughout the product. From the cross section image of the 300 nm HMX-based pellets, a smaller mean crystal size is evident. The mean void size is also smaller, however, a significant amount of void cross sections with approximately 200 nm dimensions are visible. This difference in apparent void size distribution is likely attributable to the influence of crystal size on compaction of HMX.

2.2 Mechanical Properties

The mechanical property data collected is given in Table 1. In comparison to the 2 μm HMX, the 300 nm HMX has a 99% and 129% greater strength and modulus, respectively, when formulated with PVOH. Similar trends have

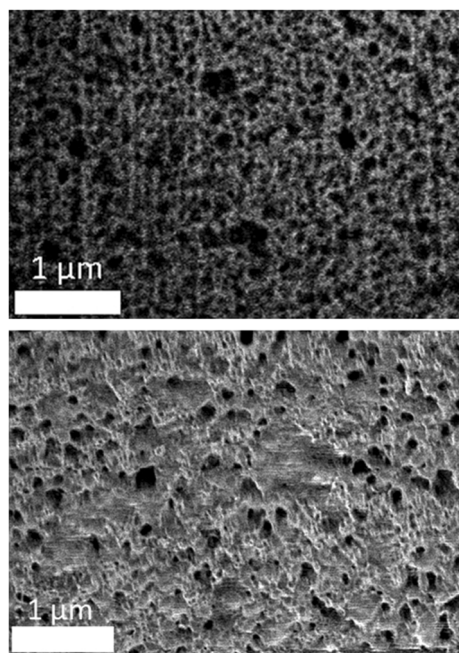


Figure 3. SEM images of (a) 300 nm and (b) 2 μ m HMX based composite pellets sectioned by a FIB.

Table 1. Mechanical properties of 300 nm and 2 μ m HMX based composite pellets.

Sample	Modulus [MPa]	Peak stress [MPa]	Density [g cm^{-3}], TMD [%]
2 μ m	694	15.2	1.43, 75
300 nm	1590	30.3	1.43, 75

been observed for nitramines and related compounds with coarser particle size [19–23]. The relationship between particle size and strength observed appears to be consistent with Hall-Petch mechanics.

2.3 Shock Sensitivity

The shock sensitivity data, summarized in Table 2, indicates a substantial drop in sensitivity as the particle size of the HMX decreases. At sizes below 500 nm, the shock sensitivity dependence on particle size becomes much stronger. Overall, there is a tremendous improvement in sensitivity,

Table 2. Shock sensitivity results of various HMX/PVOH formulations.

Sample	TMD [%]	Sensitivity [GPa]
2 μ m	89	3.6 ± 0.1
1300 nm	88	4.1 ± 0.1
500 nm	87	4.5 ± 0.1
300 nm	86	5.2 ± 0.1

1.6 GPa, when comparing 300 nm HMX to commercially available 2 μ m HMX.

2.4 Discussion

A combination of mechanical particle size reduction and spray drying was used to create HMX/PVOH nanocomposites. The process described in this paper is a novel, efficient, and effective method of creating nanoenergetics. The method is easily controlled, allowing the retention of the polymorph and the achievement of a broad range of crystal sizes in the nanoregime. Finally, this procedure is effective at uniformly coating the nano-HMX crystals. This is especially important, as it eliminates ripening and prevents the nanoparticles from agglomerating. These advantages are borne out in the mechanical properties and shock sensitivity of the formulations.

In a comparison between 2 μ m and 300 nm HMX composites at 76% TMD, provided in Table 1, the increase in strength from a reduction in crystal size is clear. The peak strength and stiffness was found to increase from 15 MPa to 30 MPa, and 700 MPa to 1600 MPa, respectively. These enhancements in mechanical properties (as crystal size is reduced) most likely contributes to lower initiation sensitivity. Increased strength and stiffness inhibits plastic deformation, which is requisite in energy localization and ignition. Voids are well known as sites of hot spot formation, however, the largest voids observed within all materials were roughly 200 nm, likely too small to create critical hot spots by adiabatic compression caused by unintended shock stimuli [1, 14]. However, voids do contribute to plastic deformation which results from their collapse and can lead to shear banding, a well-known mechanism for energy localization and initiation [24].

While the mean void size is markedly smaller in the 300 nm HMX-based pellet, this specimen also had a significant amount of voids with roughly 200 nm diameters, comparable in size to the voids in the 2 μ m HMX-based pellets. This likely is an indication of enhanced resistance to compaction as a result of the smaller crystal size and is consistent with the enhanced strength observed earlier. Such microstructures are also therefore expected to exhibit lower sensitivity to long duration, low intensity shock loading typical of small scale gap tests and accidental initiation. In the case of the 300 nm material, the larger number of voids with a smaller mean size would suggest that a much more homogeneous distribution of incident energy would occur in comparison to a coarser material.

HMX exhibits a much stronger dependence of sensitivity on crystal size below 500 nm. A similar trend was also observed earlier with RDX [6]. While the trend with HMX seems to suggest that further size reduction can lead to additional improvement in sensitivity, the earlier work with RDX [6] indicates that at a sufficiently small size a reversal in the sensitivity trend is possible.

3 Experimental Section

3.1 Materials

Commercial fluid energy milled (2 μm) HMX from BAE Systems was used as the starting material. Polyvinyl alcohol (PVOH), 2,000 molecular weight, and reagent grade isobutanol were obtained from Sigma-Aldrich. Deionized water was used as a milling medium.

3.2 Material Preparation

Mechanical particle size reduction was employed to reduce the crystal size of HMX. Prior to this, an aqueous suspension consisting of 2 μm HMX (30 g) and deionized water (400 mL) was prepared. Polyvinyl alcohol (1.5 g, PVOH) and isobutanol (10 g) were dissolved in the suspension, and served as the surfactant and dispersant, respectively. This dispersion was used in a mechanical particle size reduction process, which resulted in HMX of the following particle sizes: 300 nm, 500 nm, 600 nm, and 1,300 nm, as determined from dynamic light scattering (DLS) analysis using a Micromeritics Saturn Digisizer 5200.

Following particle size reduction, the HMX containing slurry was spray dried. During spray drying, PVOH precipitated onto the HMX crystals, resulting in a uniform coating. A cyclone was used to separate the powder from the gas stream. A control formulation was also prepared by spray drying a suspension, which had 2 μm HMX, without particle size reduction.

3.3 Characterization

The prepared materials were analyzed by Powder X-ray Diffraction using a Rigaku Miniflex II instrument. Pellets of 6 mm diameters consisting of 300 nm and 2 μm formulated HMX at 75% TMD were analyzed by focused ion beam (FIB) sectioning coupled with scanning electron microscopy (SEM) in order to assess the void size distribution. SEM images were obtained with a VP-1530 Carl Zeiss LEO field emission scanning electron microscope. The samples were mounted on aluminum stubs using double-sided carbon tape.

Shock sensitivity was determined using the Small-Scale Gap Test (SSGT) according to MIL-STD-1751A, Method 1042. Test charges were prepared by pressing the samples into brass cylinders (5.08 mm inner diameter, 25.4 mm outer diameter, 38.1 mm long). Prior to pressing, the samples were oven dried at 320 K. Donor charges were prepared with Composition A-5, pressed to 1.65 g cm^{-3} . The shock sensitivity is presented in terms of the shock pressure at which the probability of detonation is 50%. Impact, friction, and electrostatic discharge safety testing was performed as well, as detailed in the Supporting Information.

Pellets with a nominal aspect ratio of 1.25 and weight of 0.35 g were prepared. The pellets were tested in an Instron

Table top screw device to measure the material property characteristics. Testing was performed at a low strain rate with the device crosshead moving at a constant velocity of 0.076 mm s^{-1} to deform samples.

Supporting Information (see footnote on the first page of this article): Raman spectroscopy analysis and safety data are given for the nano-HMX formulations.

4 Conclusions

A combination of particle size reduction and spray drying was used to create HMX/PVOH nanocomposites with the following mean crystal sizes: 300 nm, 500 nm, 600 nm, and 1,300 nm. This approach allows the HMX to retain the desired β polymorph and results in a uniform binder coating. Smaller average crystal size was found to result in improved mechanical properties and decreased shock sensitivity. At the smallest crystal sizes, the dependence of shock sensitivity on crystal size strengthens dramatically.

Acknowledgments

The authors would like to thank the following U.S. Army, ARDEC personnel: Aleksander Gandzelko for HPLC analysis, Robert Decker for assistance with crystal size measurements, and Kelley Cafilin for XRD analysis.

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Received: May 23, 2014

Revised: August 18, 2014

Published online: October 30, 2014