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CHARACTERIZATION OF HMX PARTICLES IN PBX 9501

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The particle size distribution and morphology of HMX (cyclotetramethylene-tetranitramine) in the plastic-bonded explosive, PBX 9501 (95% HMX and 5% polymeric binder, by weight), are important to understanding the micromechanical behavior of this material. This paper shows that the size distribution of the "as-received" HMX powder, as measured by light scattering, is not preserved through the processing operations of formulation into molding powder and subsequent consolidation through hydrostatic pressing. Morphological features such as cracking and twinning are examined using reflected light microscopy. This technique helps confirm and interpret the results of the particle size analysis. These results suggest that use of the particle size distribution of the "as-received" powder could potentially yield significant errors in detailed simulations of formulated materials.

INTRODUCTION

HMX is the principal constituent in many energetic materials. Some HMX studies have included characterization data for the particles. Dick (1) reports sieve data and Gustavsen, et al. (2) further describe the powders used in their shock experiments. Elban and Chiarito (3), and Burnside, et al. (4) describe the effects of quasi-static compaction on HMX particles. However, most applications of HMX-based components require the addition of a polymeric binder to improve mechanical integrity, and there is a paucity of characterization data on HMX after it has been processed with a binder.

This work examines HMX particles that have been recovered from PBX 9501 after various stages of processing. The HMX particle size distribution and morphology are important parameters in understanding and modeling the microstructural response of this material to external stimuli. The distribution of the HMX "as-received" powder is controlled by specification (MIL-H-45444B). The

HMX (three parts coarse to one part fine) is slurried in water, and binder solution is added to formulate PBX 9501 molding powder. The molding powder is then consolidated into a serviceable article through heating and pressure. This paper reports the particle size distributions of HMX in "as-received powder", after formulation, and after consolidation to a standard density. We confirm these findings with direct observation of PBX 9501 in reflected light microscopy.

EXPERIMENTS

Two principal analytical tools were used in this study. First, all particle size distributions were determined using a Coulter LS 230 Laser Diffraction Analyzer with water as the suspension fluid. Second, a Zeiss Axiophot was used for microscopic inspection. Digital images were acquired with the analyzer oriented parallel to the polarizer.

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All HMX powders were taken from "as-received," commercially produced lots HOL83L030-050 for the coarse portion and HOL82C000E094 for the fine. The specification designates the coarse as Class 1 (previously Class A) and the fine as Class 2 (previously Class B). Both coarse and fine classes are Grade B (previously Grade II) which means there is a minimum RDX content.

Initial samples of material were prepared by the following three processes:

1. A dry blend of the specified proportions (3:1) was prepared by manually mixing the powders.
2. A 3 kg batch of molding powder was produced locally (batch 7249) using the same lots as in the dry blend.
3. A portion of the above molding powder was consolidated at 90 °C and 15000 psi (3 each 3-min. intensifications) to a geometric or calculated density of 1.836 g/cc (99% theoretical maximum density).

Next, it was necessary to remove the binder from samples 2 and 3. Earlier work (5) had shown that ultrasonic bath treatment had a detrimental effect on HMX particles, so an approach with minimum mechanical agitation was chosen. The binder was extracted by soaking samples (14 g each) in dichloroethane at room temperature for 7 days. The solubility of HMX in dichloroethane (6) is reported to be 0.007 g/100 ml of solution at 30 °C. The following sequence was used four times during the week's dissolution:

1. Fresh solvent was added to at least the 50 ml mark on the graduated vial.
2. The soaking material was vigorously shaken by hand to re-suspend particles several times.
3. The material was allowed to settle overnight or forced to settle using a centrifuge.
4. The supernatant was aspirated with vacuum.

The final aspirated samples were dried using a vacuum rotary evaporator to minimize the formation of agglomerates. Dry weights of the samples were obtained before and after extraction to grossly determine that all the binder had been removed. The dried HMX was re-suspended in water prior to particle size analysis.

A portion of sample 1 (dry blend) was also processed with dichloroethane for one day to simulate the effect of the binder extraction and drying process on the HMX itself.

Portions of the molding powder and pressed piece (samples 2 and 3) were also prepared for microscopic examination by mounting in low viscosity epoxy under pressure. After hardening, the mounted sample was polished using methods described in (7).

RESULTS AND DISCUSSION

Figure 1. shows the particle size distributions for "as-received" coarse and fine classes of HMX. The apparent, peak particle diameters are 234 microns for the coarse fraction and 5 microns for the fine one. This may be compared with the peaks from particle size distributions of the processed samples shown in Fig. 2. Here maxima are observed at apparent diameters of 213 microns for the dry blend, 177 microns for the molding powder, and 147 microns for the pressed piece. There is a definite shift toward smaller diameter particles during processing as a result of cumulative particle comminution. A secondary peak is present in the curve for the dry blend at 5 microns diameter which corresponds to that of the "as-received" fine class HMX. The volume percentage is diminished more than expected for a 25% mix. Possible reasons for this are discussed later. An additional, new peak develops for the both molding powder and pressed piece at a diameter of 17 microns. The pressed piece shows a higher fraction of this new peak than the molding

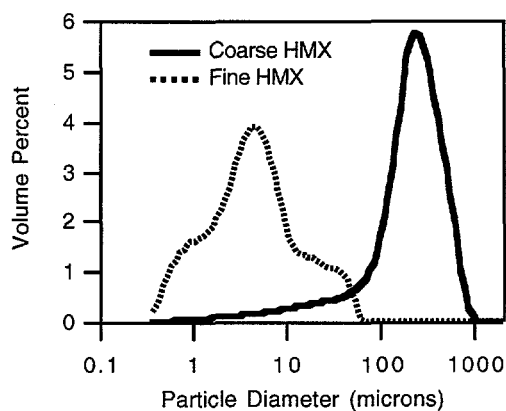


Figure 1. Particle Size Distributions of "As-Received" Coarse (100%) and Fine (100%) Classes of HMX

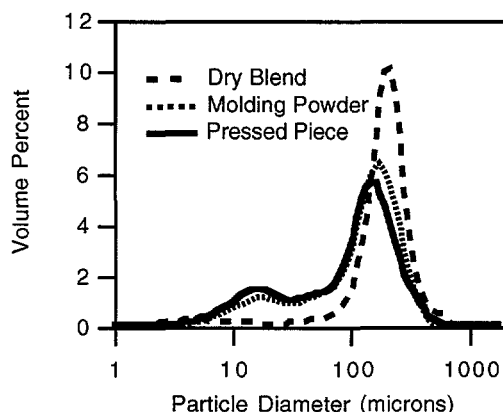


Figure 2. Particle Size Distributions of HMX after Processing.

powder. This new peak evidently grows from the breakup of coarse particles during processing.

It is surprising to note that the *HMX* size distribution from the molding powder more closely resembles that of the pressed piece than that of the dry blend. This indicates that the initial processing steps can significantly affect the ultimate particle size distribution. We had previously supposed that the HMX was little affected by the formulation process and that our study erred in using a small mixer rather than the larger equipment of commercial operations. However, there are studies by others that corroborate this unexpected result. Sieve data on HMX from ten different commercially produced lots of PBX 9501 molding powder (8) also show a shift toward a greater fraction of fines than allowed by specification on the original material. The binder was removed in that work by a process involving 24 hours in a wrist-shaker with isobutyl acetate as the solvent. The HMX was sieved wet with the solvent so no drying was necessary. Demol and Alexandre (9) have done binder removal experiments, as well, which demonstrate that damage to the HMX crystals may be minimal or extensive depending on the processing conditions during formulation.

Several micrographs of the mounted PBX samples were taken at magnifications of 50 and 200x. Figure 3. is a 50x image of the molding powder sample. We observe that there are a few cracked crystals which tend to be the larger ones. Twinned crystals are not very common. Visually it is easy to confirm that

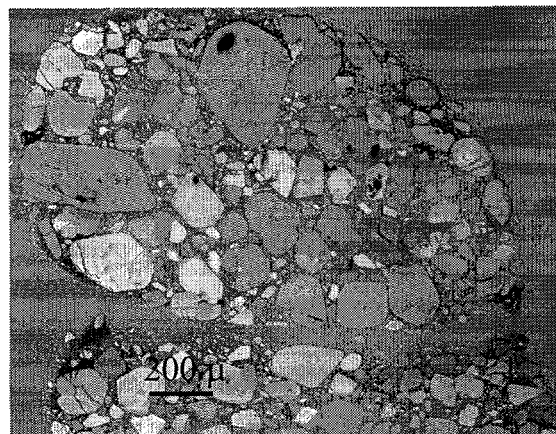


Figure 3. Microstructure of PBX 9501 Molding Powder.

the distribution of particle sizes is bimodal. The particles are spaced apart from each other, and the epoxy mounting medium infiltrates large pores within and among the granules. Figure 4. is a micrograph of the pressed piece, also at 50x. Here we note that there are more cracked crystals than in the molding powder. Twinned crystals are abundant. Visually, it is still plausible that the size distribution is bimodal although the coarse particles are notably broken up to form a "new" peak in the particle size distribution. The particles are much more tightly packed than in the molding powder. Quantitative analyses of these and other images are in progress.

A diminished volume fraction of fines in the dry

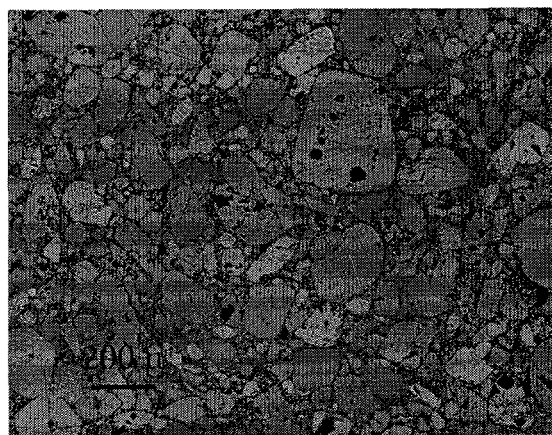


Figure 4. Microstructure of PBX 9501 Pressed Piece

blend was noted previously. Close inspection of Fig. 2. also indicates that there is a *smaller* volume fraction of fines in the molding powder and pressed piece than in the dry blend. Two processes in these experiments may have contributed to a loss of some fines in all three samples and to a greater extent in the molding powder and pressed piece. The first is the aspiration of each sample. This was done only once for the dry blend and four times for the other samples. The supernatant that was aspirated from each settled sample was not perfectly clear, though some turbidity was expected from the dissolved binder. It is possible that fines were lost in this operation. The second is associated with soaking the samples in solvent. The dry blend was soaked in solvent for one day whereas the others were soaked for seven days. There is a mechanism called Ostwald ripening whereby very small crystals are consumed and redeposited onto larger crystals in a saturated solution. The maximum amount of material that could have been lost through normal dissolution is .007 g to all four solvent aliquots. These considerations suggest that the binder removal method may not be optimal but do not invalidate the other results derived here.

CONCLUSIONS

The particle size distributions of commercially produced lots of coarse and fine classes of HMX were determined by a laser diffraction method. Using the same lots of material, PBX 9501 molding powder was produced and a portion was hydrostatically consolidated (pressed). The binder was then removed from these materials and the HMX particle size distributions were determined. The peak volume percentage was observed to shift toward smaller diameter particles indicating some level of comminution in preparation of both the molding powder and pressed piece. Further, the bimodal nature of the distribution is accentuated by the comminution. The distribution of the molding powder more closely resembles that of the pressed piece than that of a dry blend of the "as-received" powders. This demonstrates that formulation can have a significant effect on HMX crystals, whereas

this was previously considered a relatively benign process.

The morphological character of the molding powder and consolidated material was qualitatively investigated by direct observation using polarized light microscopy on polished, mounted specimens. The pressed piece showed a somewhat higher incidence of cracked HMX crystals, a significantly higher frequency of twinned crystals, and a tighter packing of crystals. The bimodal nature of the size distributions can be observed visually in both materials. The microscopy work validates the particle size analysis conclusions.

This work has demonstrated that the particle size distributions of HMX in "as-received" powders do not closely resemble the distributions in PBX 9501 molding powder and pressed pieces

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