



Study of nano-nitramine explosives: preparation, sensitivity and application

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Received 10 January 2014; revised 16 March 2014; accepted 11 April 2014

Available online 24 April 2014

Abstract

Nano-nitramine explosives (RDX, HMX, CL-20) are produced on a bi-directional grinding mill. The scanning electron microscope (SEM) observations show that the prepared particles are semi-spherical, and the narrow size distributions are characterized using the laser particle size analyzer. Compared with the micron-sized samples, the nano-products show obvious decrease in friction and impact sensitivities. In the case of shock sensitivities, nano-products have lower values by 59.9% (RDX), 56.4% (HMX), and 58.1% (CL-20), respectively. When nano-RDX and nano-HMX are used in plastic bonded explosives (PBX) as alternative materials of micron-sized particles, their shock sensitivities are significantly decreased by 24.5% (RDX) and 22.9% (HMX), and their detonation velocities are increased by about 1.7%. Therefore, it is expected to promote the application of nano-nitramine explosives in PBXs and composite modified double-based propellants (CMDBs) so that some of their properties would be improved.

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Keywords: Nano-nitramine explosive; PBX; Sensitivity; Detonation velocity; Application

1. Introduction

The brisant nitramine explosives (Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20)) have high detonation heat, detonation velocity and detonation pressure. They have been extensively used in plastic bonded explosives (PBXs) [1–6] and propellants [7–16]. However, the micron-sized explosives are very sensitive, which seriously threatens the safety of the ammunitions. The reduction in sensitivity has become a research focus. The studies have shown that the sensitivities of nitramine explosives are affected obviously by the sizes and

size distributions of the explosive particles [17–19]. The sensitivities of explosives can be cut down effectively by reducing the particle sizes. If the nano-particles were obtained, the sensitivities would be greatly decreased [20–22].

As an inspiring fact, nano-RDX and nano-HMX, which are characterized by regular shapes and narrow size distributions, have been produced in batch using a wet ball mill, and the prepared nano-sized particles can be effectively extracted by freezing drying [23,24]. Based on these experiences, nano-CL-20 had been successfully produced and effectively extracted. The sensitivities and explorative applications of the three nitramine explosives are researched in this paper.

2. Experimental

2.1. Sample preparation

2.1.1. Preparation of nano nitramine explosives

Micron-sized RDX and HMX, produced by Gansu Yingguang Chemical Industry Group Co., Ltd of China, are separately suspended in a miscible liquid which is a mixture of

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Peer review under responsibility of China Ordnance Society



deionized water, ethanol and isopropanol, with the volume ratio of 10:10:1. Micron-sized CL-20, produced by Qingyang Chemical Industry Corporation of China, is suspended in water containing 1% polyoxyethylene sorbitan oleate dehydration (Tween-80) as surfactant. Their mass concentrations are 15%.

The three nitramine explosives (RDX, HMX and CL-20) of 500–1000 g are processed at a time, respectively, and their suspensions are put into a bi-directional rotation mill [25], of which the axle and the barrel rotate reversely and simultaneously, for 6 h, 5 h and 4 h, respectively. The rotation speeds of axle and barrel are controlled in the range of 90–150 rpm and 60–90 rpm, respectively. The filling content of grinding media is controlled within 65%–70%. During pulverization, the machine is cooled down by the cycling water. The pulverized slurries are freeze-dried and the product yield is about 97%.

2.1.2. Preparation of PBX samples

The explosives are coated by slurry technique. The stirring speed is 600 rpm, the temperature of the water bath is 80 °C, the binders are dissolved by ethyl acetate dropping in the range from 1 ml/min to 3 ml/min, and the ratios of water to material are 1:2.5 for micron-sized samples and 1:4 for nano-sized samples.

RDX is coated with dinitrotoluene (DNT), polyvinyl acetate (PVAc) and stearic acid (SA). The mass percentage of RDX:DNT:PVAc:SA is 94.5:3:2:0.5.

HMX is coated with fluororubber Viton (F, a copolymer consisting of vinylidene fluoride and hexafluoropropylene), polymethyl methacrylate (PMMA) and wax. The mass percentage of HMX:F:PMMA:wax is 95:3:0.8:1.2.

2.2. Measuring instrument and apparatus

The Malvern Mastersizer Micro laser particle size analyzer is used to measure the particle size distributions of the explosives. The particle sizes and morphologies of the explosives are characterized using S-4800II Scanning Electron Microscope (SEM) made by Hitachi High-Technologies Corporation.

2.3. Test of sensitivities and detonation velocities

2.3.1. Sensitivity test of pure nitramine explosives

The friction sensitivities are measured by sliding friction test at 3.92 MPa (RDX, HMX) and 2.45 MPa (CL-20). Fifty tests are carried out to obtain the mean explosion probability (\bar{P} , %).

The impact sensitivities are measured by drop-hammer test and characterized by the characteristic heights (50% probability of initiation (\bar{H}_{50})), which are statistically calculated by 25 effective test values obtained by using a 2.5 kg drop-hammer.

The small scale gap test (SSGT) is selected to measure the shock sensitivities. In this test, the booster charge is made from RDX refined by acetone, with a density of 1.48 g/cm³, the gap material is polymethyl methacrylate polymer, and the

acceptor charges have the densities of 1.63 g/cm³ (RDX), 1.71 g/cm³ (HMX) and 1.80 g/cm³ (CL-20), respectively. The inside diameter and length of charges are 5.10 mm and 5.45 mm, respectively. The gap thicknesses (δ) are calculated by 25 effective values.

2.3.2. Shock sensitivity tests of PBX samples

The shock sensitivities of PBX samples are measured by the gap tests. The inside diameter and length of booster charge, which is made of tetryl with the density of 1.55 g/cm³, are 40.0 mm and 25.4 mm, respectively. The gap material is cellulose triacetate. The inside diameter and length of the acceptor charges are 25.0 mm and 38.0 mm, respectively, with the densities of 1.63 g/cm³ (RDX) and 1.71 g/cm³ (HMX). The gap thicknesses (δ) are calculated by 25 effective values.

2.3.3. Detonation velocity tests

The detonation velocity is tested by ionized probe method, as shown in Fig. 1.

JH-14, a PBX explosive, is made of RDX, fluororubber Viton (F) and graphite (G). The mass percentage of RDX:F:G is 96.5:3.0:0.5.

The inside diameter and length of booster charge, which is made of JH-14 with the density of 1.55 g/cm³, are 13.0 mm and 13.0 mm, respectively. The acceptor charges are made of as-prepared PBX samples (Section 2.1.2). The inside diameter and length of the acceptor charges are 10.0 mm and 10.0 mm, respectively, with the densities of 1.63 g/cm³ (RDX) and 1.71 g/cm³ (HMX). The detonation velocities are calculated by 5 effective values.

2.4. Symbols and abbreviations

M-: Micron-sized explosives; N-: Nano-sized explosives; M-RDX: Micron-sized RDX; N-RDX: Nano-sized RDX; M-HMX: Micron-sized HMX; N-HMX: Nano-sized HMX; M-CL-20: Micron-sized CL-20; N-CL-20: Nano-sized CL-20.

P-M-: M-contained PBX samples; P-N-: N-contained PBX samples.

P-M-RDX: M-RDX-contained PBX sample; P-N-RDX: N-RDX-contained PBX sample; P-M-HMX: M-HMX-contained PBX sample; P-N-HMX: N-HMX-contained PBX sample.

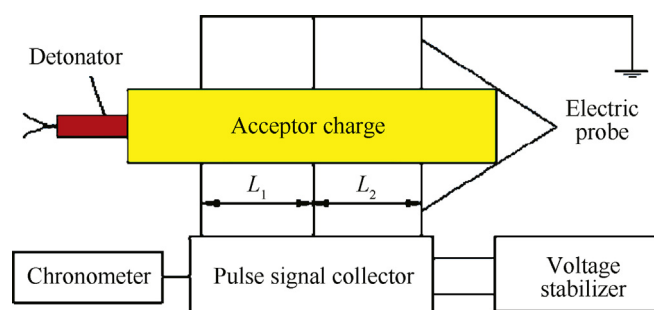


Fig. 1. Schematic diagram of set-up for detonation velocity test.

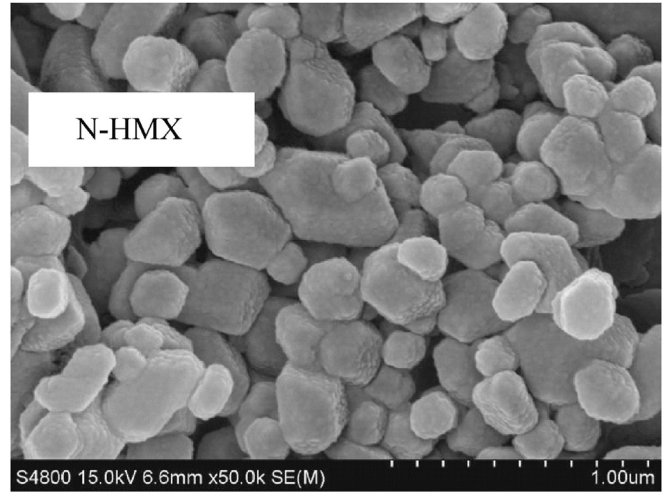
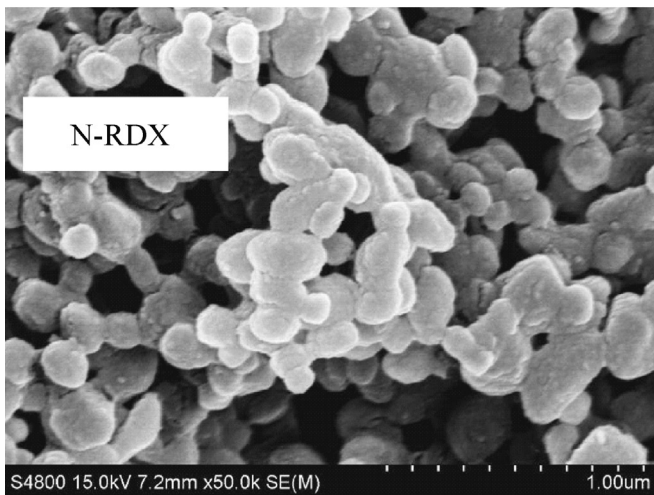
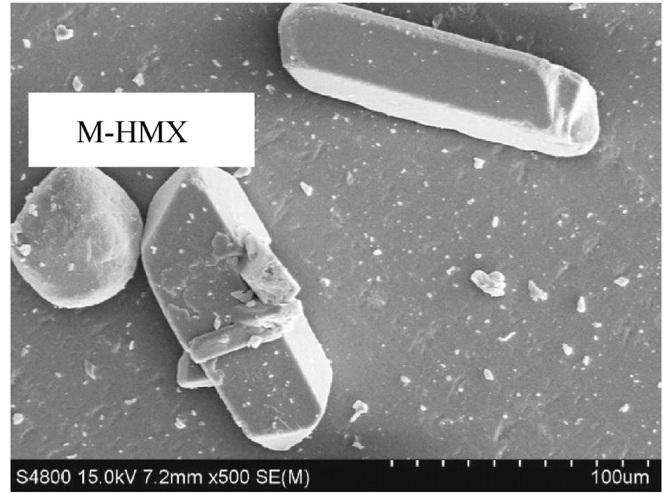
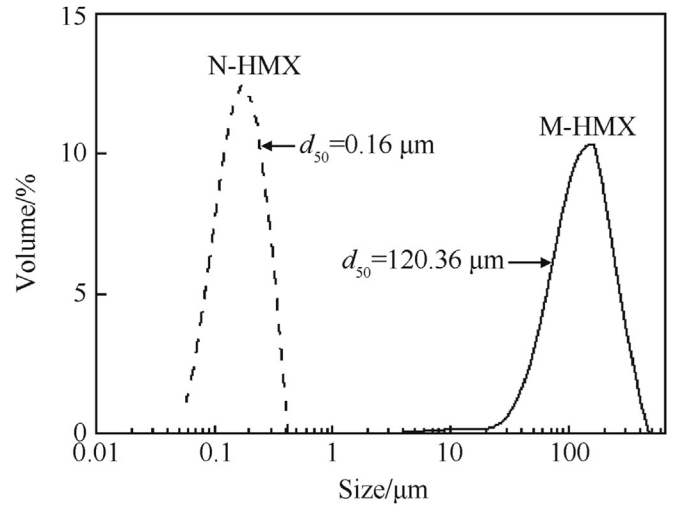
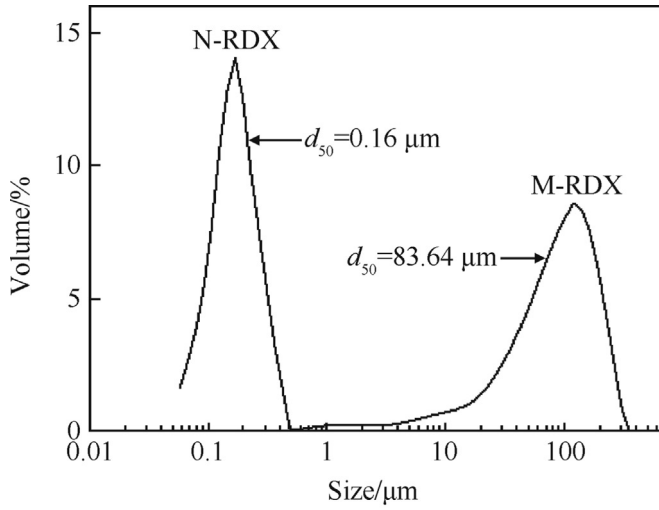


Fig. 2. The size distributions and SEM images of RDX particles.

Fig. 3. The size distributions and SEM images of HMX particles.

2.5. Variable calculation of sensitivities and detonation velocities

The variable of friction sensitivity is calculated as $(\bar{P}(M-) - \bar{P}(N-)) \times 100\%$;

The variable of impact sensitivity is calculated as $(\bar{H}_{50}(N-) - \bar{H}_{50}(M-)) / \bar{H}_{50}(M-) \times 100\%$;

The variable of shock sensitivity is calculated as

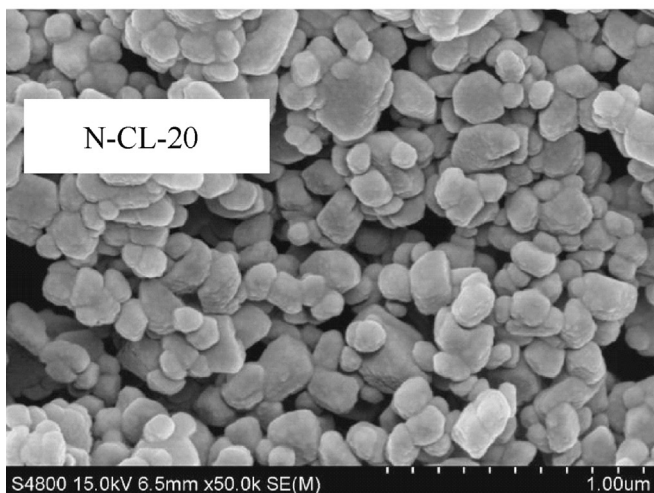
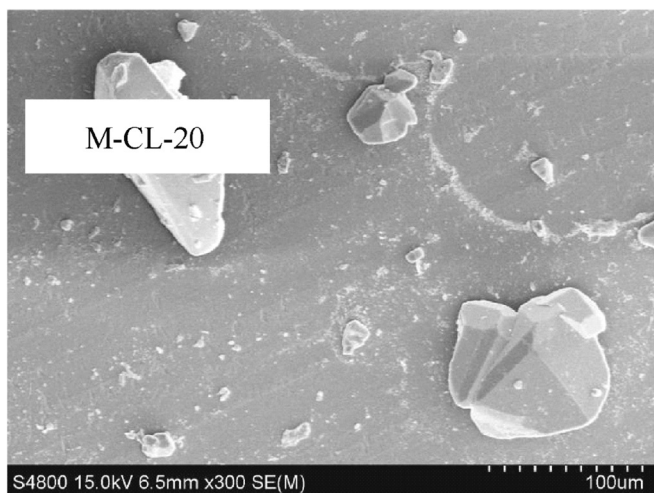
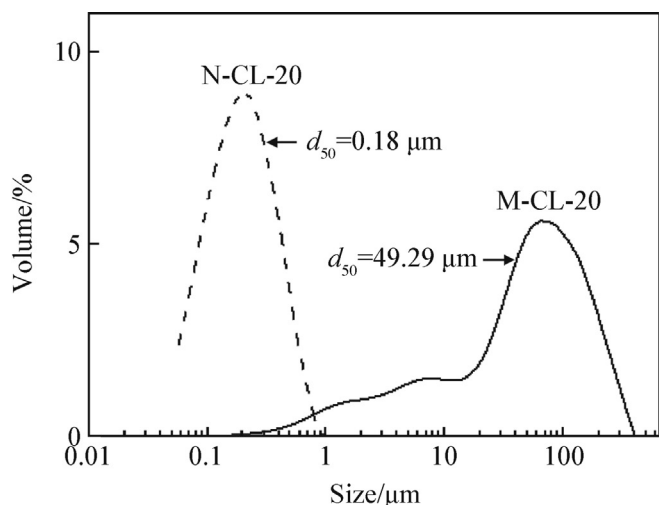


Fig. 4. The size distributions and SEM images of CL-20 particles.

$$(\delta(M) - \delta(N)) / \delta(M) \times 100\%;$$

The variable of detonation velocity is calculated as

$$(v(N) - v(M)) / v(M) \times 100\%.$$

3. Results and discussion

3.1. Particle size distributions and SEM images

The particle size distributions and SEM images of explosives are shown in Figs. 2–4.

As shown in Figs. 2–4, the average particle sizes of micron-sized RDX, HMX and CL-20 are 83.64 μm, 120.36 μm and 49.29 μm with wide size distributions, and the average sizes of the nano-sized particles are 0.16 μm, 0.16 μm and 0.18 μm with narrow size distributions, respectively. The micron-sized particles are polyhedral, irregular and heterogeneous, while the nano-sized particles are semi-spherical and homogeneous.

3.2. Sensitivities of pure nitramine explosives

The friction, impact and shock sensitivities of pure RDX, HMX and CL-20 samples are listed in Tables 1–3.

As listed in Table 1, compared with the micron-sized samples (M-RDX, M-HMX and M-CL-20), the average explosion percentages of the nano-sized samples (N-RDX, N-HMX and N-CL-20), which characterize the friction sensitivities, are decreased by 30%, 28% and 22%, respectively.

As listed in Table 2, the special heights of N-RDX, N-HMX and N-CL-20 are 49.3 cm, 18.9 cm and 15.8 cm higher than those of the micron-sized samples, respectively. In other words, the impact sensitivities of the nano-sized samples are 99.0%, 42.8% and 116.2% lower than those of the micron-sized samples, respectively. Additionally, the standard deviations ($S_{dev.}$) of the nano-sized samples are smaller than those of the micron-sized samples, which means that the size and morphology of the particles are close to each other. As a result, the impact initiation probability of the samples is close to each other.

As listed in Table 3, compared with the micron-sized samples, the gap thicknesses (δ) of the nano-sized samples

Table 1
The friction sensitivities of RDX, HMX and CL-20.

Sample	$\bar{P}\%$
M-RDX	80
N-RDX	50
M-HMX	86
N-HMX	58
M-CL-20	88
N-CL-20	66

Table 2
The impact sensitivities of RDX, HMX and CL-20.

Sample	\bar{H}_{50} /cm	$S_{dev.}$
M-RDX	49.8	0.14
N-RDX	99.1	0.13
M-HMX	44.1	0.15
N-HMX	63.0	0.09
M-CL-20	13.6	0.11
N-CL-20	29.4	0.09

Table 3
The shock sensitivities of RDX, HMX and CL-20.

Sample	δ/mm	$S_{\text{dev.}}$
M-RDX	15.38	0.41
N-RDX	6.17	0.32
M-HMX	13.96	0.40
N-HMX	6.08	0.32
M-CL-20	43.72	0.42
N-CL-20	18.31	0.35

are 9.21 mm, 7.88 mm and 25.41 mm thinner, which means that the shock sensitivities of the nano-sized samples are decreased by 59.9%, 56.4% and 58.1%, respectively. Furthermore, the standard deviations ($S_{\text{dev.}}$) of the nano-sized samples are smaller than those of the micron-sized samples, which states that the size and morphology of the particles are close to each other. As a result, the shock initiation probabilities of the samples are close to each other.

3.3. Sensitivities of PBX samples

The shock sensitivities of PBX samples are listed in Table 4.

Table 4
The shock sensitivities of PBX samples.

PBX sample	δ/mm	$S_{\text{dev.}}$
P-M-RDX	24.65	1.32
P-N-RDX	18.60	1.24
P-M-HMX	23.74	1.19
P-N-HMX	18.31	1.02

As listed in Table 4, when RDX and HMX are used in PBX, the gap thicknesses (δ) of P-N-RDX and P-N-HMX are 6.05 mm and 5.43 mm thinner than those of P-M-RDX and P-M-HMX, which reflects the shock sensitivities of the nano-sized particle-contained samples are 24.5% and 22.9% lower than those of the micron-sized particle-contained samples, respectively. What's more, the standard deviations ($S_{\text{dev.}}$) of the nano-sized particle-contained samples are smaller than those of the micron-sized particle-contained samples, which implies that the size and morphology of the particles are close to each other. As a result, the shock initiation probabilities of PBX samples are close to each other.

3.4. Detonation velocities of PBX samples

The detonation velocities of PBX samples are listed in Table 5.

As listed in Table 5, the detonation velocities of P-N-RDX and P-N-HMX are 130 m/s and 140 m/s higher than those of P-M-RDX and P-M-HMX when the densities are 1.63 g/cm³ and 1.71 g/cm³, respectively. Compared with P-M-RDX and P-M-HMX, the detonation velocities of P-N-RDX and P-N-HMX are enhanced 1.66% and 1.72%, respectively. Moreover, the standard deviations ($S_{\text{dev.}}$) of the nano-sized particle-

contained samples are smaller than those of the micron-sized particle-contained samples. It can be concluded that the size and morphology of the particles are close to each other. As a result, the energy-release rates of the PBX samples are close to each other.

Table 5
The detonation velocities of PBX samples.

PBX sample	$v/(\text{m} \cdot \text{s}^{-1})$	$S_{\text{dev.}}$
P-M-RDX	7850	29.58
P-N-RDX	7980	28.27
P-M-HMX	8120	27.57
P-N-HMX	8260	25.80

4. Conclusions

Nano-sized nitramine explosives were successfully produced in batch using a bi-directional rotation mill, and the prepared nano-particles were effectively extracted by freezing drying. The product particles are semi-spherical with narrow size distributions.

Compared with the micron-sized RDX, HMX and CL-20, the friction, impact and shock sensitivities of the nano-sized explosives are apparently decreased. When RDX and HMX are used in PBX, the shock sensitivities of the nano-sized particle-contained samples are still obviously lower than those of the micron-sized particle-contained samples. After the micron-sized nitramine explosives are pulverized to be nano-sized, the dislocations and occlusions in particles are almost disappeared and the particle surfaces are more regular, which would lead to the sharp diminution of hot-spot generating probability, so the sensitivities of nano-sized particles are apparently lower.

The detonation velocities of the nano-sized particle-contained samples are higher than those of the micron-sized particle-contained samples, which could be benefitted from the larger specific surface area of the nano-sized particles. It is promising to promote the applications of nano-nitramine explosives in PBXs and CMDBs so that some of their properties would be improved.

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