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Characterization and Properties of Desensitized Octogen

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Abstract: A kind of desensitized octogen (D-HMX) was characterized with various analysis methods, including Optical Microscopy with Matching Refractive Index (OPM), Scanning Electron Microscopy (SEM), Laser Particle Sizer, High Performance Liquid Chromatography (HPLC), density gradient technique and X-ray Diffraction (XRD). The thermal properties of D-HMX were investigated by Differential Scanning Calorimetry (DSC) and Vacuum Thermal Stability test (VST). The sensitivities of D-HMX against friction, impact and shock were studied. Compared with conventional octogen (C-HMX), D-HMX has better morphology, lesser crystal defects, better thermal properties and takes great effect on reducing shock sensitivity in both cast and pressed PBX formulations. Which are incarnated from the following aspects. First, the D-HMX has no twinned crystals or congeries, which shape is regular polyhedron and nearly spheric. Second, there are no inclusions in D-HMX crystals, the purity of D-HMX is $(99.6\pm0.1)\%$ and the mean particle density is great $1.9016\ g\cdot cm^{-3}$. Third, the results of DSC and VST show that the $\beta\rightarrow\delta$ phase transition of D-HMX is shifted to high temperatures about 6 ℃ and that the amount of gas evolution of D-HMX is obviously less after being heated for 48 h at 120 ℃ compared with C-HMX. Fourth, the results of shock sensitivities demonstrate that the aluminium gap thicknesses of cast and pressed PBXs based on D-HMX are lesser 10% ~23% than that of PBXs based on C-HMX. Additional, the impact sensitivity of D-HMX appears lower sensitivity than C-HMX. Especially for the fine grain D-HMX (FD-HMX), the drop-height of 72.2 cm and initiation probabilities of 24% indicate there are significantly higher resistance to impact than the fine grain C-HMX (FC-HMX) of 16.8 cm and 88%.

Key words: organic chemistry; desensitized octogen (D-HMX); crystal characterization; thermal property; sensitivity

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1 Introduction

High performance and safety of ammunitions are more and more importment with the development of insensitive ammuniton and penetration weapon system. Many researches[1-3] find that the properties of the explosive particles, especially particle size and shape, crystal quality, surface chacteristics would not only greatly affect the processing properties, but also evidently affect the sensitivity of explosives charges. While, these particle properties all can be controlled by crystallization. So, in recent years much interest has been generated in reducing sensitivity by recrystallization to improve the crystal quality of explosives[4]. HMX is one of predominant explosives for the integrated properties and widely used in military applications as the most powerful explosive and an important ingredient of propellants. Then it is important to ulteriorly improve its integrated properties by ameliorating its crysal quality through recrystallization. About recrystallization methods for HMX, there were many patents[5-7] and papers[8-10] to report. For example, Levinthal et al.[5] investigated a method of directly precipittiong pure β-HMX from substantially anhydrous nitric acid solution without forming and recrystallizing polymorphic HMX. Svesson et al.[6,8] investigated the crysltallization of HMX from γ-butyrolactone by cooling and precipitation. Kröber et al.[9] studied the crystallization of HMX from different solvents such as cyclohexanone, *N*-methylpyrrolidone (NMP), propylene carbonate and *N*, *N*-dimethylformamide by cooling crystallization. Antoine et al.[10] reported that HMX showed a tendency to form twinned crystals when being grown in γ-butyrolactone and cyclohexanone. Our institute prepared a kind of desensitized HMX (D-HMX) with high crystal quality by recrystallization. In this paper, D-HMX was characterized and compared with conventional HMX (C-HMX) from the aspects of particles characteristics, thermal properties and sensitive properties.

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2 Materials and methods

2.1 Materials

D-HMX was prepared by Institute of Chemical Materials, CAEP. The D-HMX samples with two size grades were obtained by drowning-out crystallization. The fine grains desensitized HMX named FD-HMX and the large grains desensitized HMX named LD-HMX.

C-HMX was bought from Gansu Yinguang Chemical Industries Group Co. Ltd. There are two size grades conventional HMX as reference samples, one is fine grain conventional HMX (FC-HMX) and the other is large grain conventional HMX (LC-HMX). It is specialized that LC-HMX samples have been sieved.

2.2 Characterization

The morphology and defects were described qualitatively by Optical Microscopy with Matching Refractive Index (OPM) and Scanning Electron Microscopy (SEM). The particle size and distribution were measured with Coulter LS230. The density of the particles was measured with density gradient method founded by Institute of Chemical Materials, CAEP. The purity analysis was performed by HPLC on HEWLETT PACKARD Series 1100. Crystal structure was charcaterized with X-ray powder diffraction on a Bruker D8 Advance X-ray diffractometer by using Cu Kα radiation without any monochromator.

The thermal properties were characterized respectively by

DSC and Vacuum thermal stability test. DSC measurement was performed by PE Diamond DSC, the heating rate 1 ℃ · min^{-1}, sample weight 1 mg, N_2 atmosphere. The conditions of VST test were 48 h at 120 ℃ and measured samples 5 g.

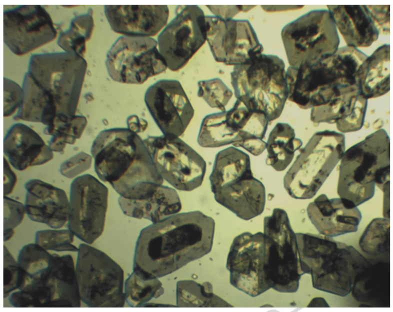
Sensitivities of HMX were characterized from the aspects of impact sensitivity, friction sensitivity and shock sensitivity. The impact sensitivity was measured by initiation probability test and drop-height test. For initiation probability test, the hammer is 10 kg, the sample is 50 mg and the drop is 25 cm. For drop-height test, the hammer is 2 kg and the sample is 35 mg. The friction sensitivity test was performed with 1.5 kg hammer, 90° angle and 20 mg sample. The shock sensitivity was measured by small scale GAP Test. The gap is aluminium gap. The samples used in impact sensitivity test and friction sensitivity test are HMX powder, while the samples used in GAP test are Φ20 mm × 20 mm charges processed respectively with cast formulation and pressed formulation based on D-HMX and C-HMX.

3 Results and discussions

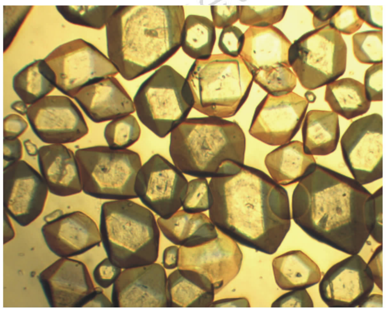
3.1 Particle characterization

3.1.1 Morphology and particle size

OPM can provide qualitative insight into the internal defects of HMX particles. Figure 1 confirms qualitatively that particles of LD-HMX and LC-HMX have different internal defects populations. LD-HMX particles are very transparent and almost have no inclusion in the crystals. However, there are many dark areas in the OPM picture of LC-HMX and the largest one is above 100 μm, which indicates LC-HMX particles have many internal defects. The shape of LD-HMX particles is regular geometrical polyhedron and nearly spheric, unlike LC-HMX particles have twinned crystals or congeries. So compared with LC-HMX, LD-HMX has better morphology and lesser internal defects.



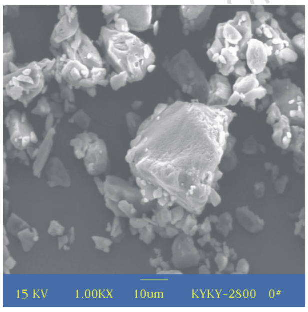
a. LC-HMX



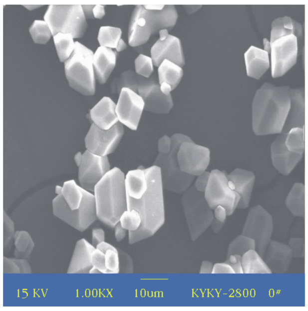
b. LD-HMX

Fig. 1 OPM of LD-HMX and LC-HMX

Figure 2 gives the SEM pictures of FD-HMX particles and FC-HMX particles. The shape of FD-HMX particles is much regular like diamond and the crystal surfaces are very smooth. While, the FC-HMX particles show more complex shapes.



a. FC-HMX



b. FD-HMX

Fig. 2 SEM of FD-HMX and FC-HMX

Table 1 shows that the mean particle sizes of LD-HMX and FD-HMX are approximately 150 μm and 15 μm respectively. The particle size distribution of FD-HMX is more narrow than FC-HMX. LD-HMX has the same narrow particle size distribution as LC-HMX being sieved.

Table 1 Particle size of HMX particles measured by laser particle sizer

sample	mean / μm	median / μm	D_{10} / μm	D_{90} / μm
LD-HMX	153.4	153.3	81.4	224.9
LC-HMX	162.4	185.3	88.8	227.6
FD-HMX	15.5	16.3	8.4	24.7
FC-HMX	26.9	18.0	4.2	62.1

3.1.2 Purity and density

The purity of HMX particles was measured by HPLC. The particle density of HMX was measured by density gradient technique. The results are listed in Table 2. Fig. 3 shows the distribution of HMX particles in density gradient tube.

Based on the measurement results, the purities of D-HMX are appreciably greater than that of C-HMX. Whereas, there are considerable differences in the particle density and particle density distribution between D-HMX and C-HMX. D-HMX has higher mean density and more nrarrow particle density distribution than C-HMX. The mean densities of FD-HMX and LD-HMX are 1.9016 g · cm^{-3} and 1.9018 g · cm^{-3} respectively, which is very closed to the theoretical density of 1.903 g · cm^{-3}. Furthermore, D-HMX is very good homogeneity. Its density variations are obviously smaller than that of C-HMX.

Table 2 Purity and particle density of HMX particles

sample	LD-HMX	LC-HMX	FD-HMX	FC-HMX
purity /%	99.7 ±0.1	99.3 ±0.1	99.6 ±0.1	99.2 ±0.1
mean density /g · cm^{-3}	1.9018	1.9003	1.9016	1.8984
density distribution /g · cm^{-3}	1.9012 ~ 1.9020	1.8973 ~ 1.9018	1.9010 ~ 1.9019	1.8970 ~ 1.8993
maximum density variation /g · cm^{-3}	0.0008	0.0045	0.0009	0.0023

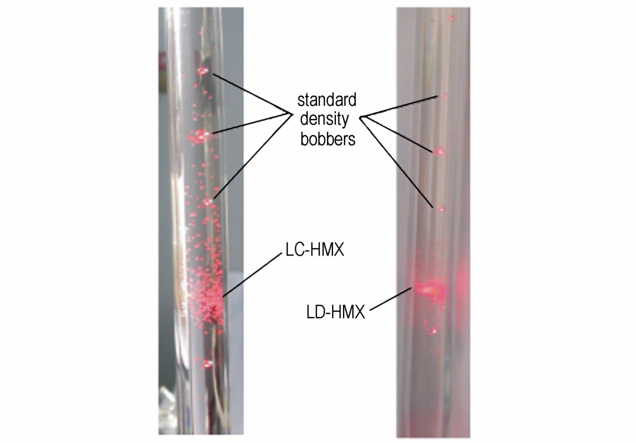


Fig. 3 Distribution of HMX particles in density gradient tube

3.1.3 Crystal microstructure

X-ray diffraction is a powerful tool for the characterization of crystalline materials. In this paper, the crystal structures of D-HMX and C-HMX were contrasted by powder X-ray diffraction (Fig. 4). The two kinds of HMX have the same peak positions as β-HMX reference pattern (PDF Number 025 -1747), but their relative intensities of the X-ray diffraction peaks are very different. These indicate that they are all β-HMX but their crystal tropisms are different. D-HMX nearly has no tropism like β-HMX theory X-ray pattern, while C-HMX has strong tropisms. So for D-HMX, the relative intensities of diffraction peaks are very coincident with β-HMX reference pattern, but for C-HMX, especially for LC-HMX, the intensities of each diffraction peaks are similar. The reason may be linked to the particle morphology. The morphology of D-HMX particles is regular like diamond or sphere. Every particle of D-HMX is nearly a single crystal, but the morphology of C-HMX is complex due to twinned crystals, agglomerated crystals and irregular shape. On the other hands, the internal defects of C-HMX particles also have effect on the intensity of diffraction peaks. All these lead to the tropisms becoming strong for C-HMX and poor for D-HMX.

3.2 Thermal properties

Table 3 lists the thermal properties of D-HMX and C-HMX. The endothermic peaks were observed between 190 ℃ and 205 ℃ in the DSC curves of HMX. Which are β→δ phase transition of HMX. The β→δ phase transition of D-HMX is shifted to high temperatures about 6 ℃ compared with C-HMX. Especially

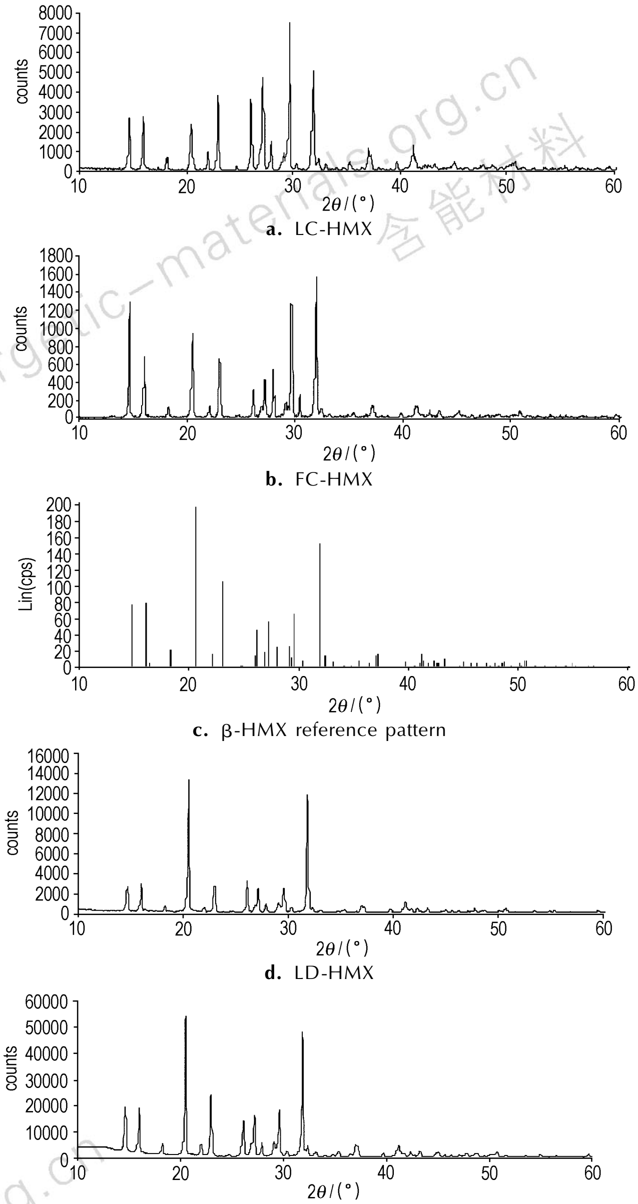


Fig. 4 X-ray powder patterns of D-HMX and C-HMX at room temperature

Table 3 The thermal properties of D-HMX and C-HMX

sample	phase transition temperature/℃	VST[1)] /mL · (5 g)$^{-1}$
LC-HMX	196.31	0.12
FC-HMX	193.96	0.24
LD-HMX	202.33	0.06
FD-HMX	203.81	0.06

Note: 1) test condition is 120 ℃ and 48 h.

for FD-HMX, the phase transition temperature is about 204 ℃, significantly higher than 193 ℃ of FC-HMX. This resistance in the conversion from β to δ may be related to different inclusions and crystal defects in D-HMX and C-HMX. D-HMX has more less inclusions and defects than C-HMX, so the phase transition temperature is higher than that of C-HMX.

According to the results of VST, the amount of gas evolution of D-HMX was obviously lesser than that of C-HMX after being heated for 48 h at 120 ℃.

The results of DSC and VST indicate D-HMX has better thermal properties than C-HMX.

3.3 Sensitivity

Table 4 lists the results of the mechanical sensitivities. The friction sensitivity is practically similar for D-HMX and C-HMX. However, in impact sensitivity, D-HMX appears lower sensitivity than C-HMX. Especially for FD-HMX, the drop-height of 72.2 cm and initiation probabilities of 24% indicate significantly higher resistance to impact than FC-HMX of 16.8 cm and 88%.

Table 4 Mechanical sensitivities of HMX particles

sample	friction sensitivity initiation probability /% $(P_l, P_u)_{0.95}$	impact sensitivity	
		initiation probability /% $(P_l, P_u)_{0.95}$	H_{50}/cm
FC-HMX	56% (0.35, 0.76)	88% (0.69, 0.98)	16.8 ±0.1
FD-HMX	44% (0.24, 0.65)	24% (0.09, 0.45)	72.2 ±0.1
LC-HMX	32% (0.19, 0.47)	72% (0.51, 0.88)	59.6 ±0.1
LD-HMX	46% (0.32, 0.61)	60% (0.45, 0.74)	68.8 ±0.1

Table 5 lists the results of shock sensitivity of the cast and pressed PBX formulations based on D-HMX and C-HMX. The grain compositions are the same, namely, the weight rate is 3 : 1 for large grain HMX and fine grain HMX. During processing cast PBXs, it was founded that the rheological property of cast PBXs based on D-HMX was extraordinarily better than that of PBXs based on C-HMX. This does well out of the nearly spheric shape of D-HMX particles. The results of shock sensitivities demonstrate that the aluminium gap thicknesses of PBXs based on D-HMX are all less than that of PBXs based on C-HMX for both cast and pressed formulations. This indicates the desensitized HMX can reduce greatly shock sensitivity either in cast or pressed PBX formulations. However, the results also show the desensitized HMX takes different extent on reducing shock sensitivity when being used in different PBX formulations. As though, the desensitized HMX particles can more incarnate their reduced shock sensitivity feature in pressed formulations.

Table 5 Shock sensitivities of different PBXs based on HMX particles

PBXs	HMX /%	HMX kind in PBXs	charge density TMD[1)] /%	gap thickness /mm	reduce extent /%
PBX-903 (pressed)	87	C-HMX D-HMX	98.61 98.72	23.4 20.1	15
PBX-10 (pressed)	21	C-HMX D-HMX	98.29 98.29	13.25 10.25	22.6
PBX-924 (cast)	88	C-HMX D-HMX	99.06 99.06	17.0 15.1	11.2
HL-10 (cast)	85	C-HMX D-HMX	98.96 98.96	16.1 14.6	9.3

Note: 1) TMD is theoretical maximum density of charge.

4 Conclusions

D-HMX is a kind of high crystal quality β-HMX explosive, which has better morphology, lesser crystal defects, better thermal properties and takes great effect on reducing shock sensitivity in both cast and pressed PBX formulations. D-HMX has no twinned crystals or congeries, which particle shape is regular polyhedron approaching sphericity and and the crystal surfaces are smooth. The particles are uniform and the particle size distribution is narrow. There are no obvious impurities and internal defects in D-HMX crystal particles, the purity of D-HMX is (99.6 ±0.1)% and the mean particle density is great 1.9016 g · cm^{-3}. The β→δ phase transition of D-HMX is shifted to high temperatures about 6 ℃ and that the amount of gas evolution of D-HMX is obviously less after being heated for 48 h at 120 ℃ compared with C-HMX. The aluminium gap thicknesses of cast and pressed PBXs based on D-HMX are lesser 10% ~23% than that of PBXs based on C-HMX. Additional, the impact sensitivity of D-HMX appears lower sensitivity than C-HMX. Especially for FD-HMX. the drop-height of 72.2 cm and initiation probabilities of 24% indicate there are significantly higher resistance to impact than FC-HMX of 16.8 cm and 88%.

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降感 HMX 性能表征

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摘　要： 采用多种表征手段研究了一种降感奥克托今(D-HMX)的晶体特性、热性能及感度性能。采用折光匹配光学显微镜(OPM)、扫描电镜(SEM)、激光粒度仪、高效液相色谱、密度梯度法和 X 射线衍射(XRD)表征了 D-HMX 的颗粒形态、粒度、纯度、颗粒密度及晶型结构；采用差热扫描(DSC)、真空安定性实验(VST)研究了其热性能，通过机械撞击感度实验、摩擦感度实验和隔板实验研究其感度性能。结果表明，D-HMX 是一类具有较高晶体品质的 β-HMX 单质炸药。与普通 HMX(C-HMX)相比，D-HMX具有较好的颗粒形态和较少的晶体缺陷，热性能和感度性能明显改善。D-HMX 的颗粒形状接近球形，为规则的几何多面体，无孪晶聚晶现象，晶面光洁，颗粒均匀，粒度分布窄，颗粒透明，内部无明显杂质和包藏物，纯度为(99.6 ±0.1)%，颗粒平均密度大于1.9016 g·cm^{-3}，接近晶体最大理论密度 1.903 g·cm^{-3}且密度分散性小。DSC 实验结果表明，D-HMX 的 β→δ 晶相转变温度比 C-HMX 提高 6 ℃，VST 放气量明显小于 C-HMX。隔板实验结果表明，基于 D-HMX 的浇铸和压装 PBXs 的铝隔板厚度比 C-HMX 降低 10% ~23%。另外，D-HMX的机械撞击感度也比 C-HMX 下降，特别是 D-HMX 细颗粒(FD-HMX)，其特性落高为 72.2 cm，爆炸概率 24%，比 C-HMX 细颗粒(FC-HMX)的 16.8 cm 和 88%表现出更强的抗撞击性。

关键词： 有机化学；降感 HMX(D-HMX)；晶体特性；热性能；感度

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