Research paper

Influence of crystal characteristics on reaction for HMX-based Pressed PBXs in the Susan impact test

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Abstract

The crystal characteristics of octahydrol, 3, 5, 7-tetranitro-l, 3, 5, 7-tetrazocine (HMX), i.e. density, porosity of internal crystal, morphology, size and size distribution, have vital important influence on the sensitivity of HMX-based pressed PBXs. To improve the safety properties of HMX-based polymer bonded explosives (PBXs), the ordinary quality HMX was replaced by the high-quality HMX in pressed HMX-based compositions. The reaction characteristics of HMX-based PBXs were tested by using Susan Test. The influences of the particle characteristic parameters (e.g. crystal quality, size and shape) of HMX on the Susan sensitivity of the PBX were investigated thoroughly. Results show that the threshold velocity for initiation of the PBX was increased while the quality of HMX crystal was improved. The threshold velocity of the PBX in Susan test increased from $37\,\mathrm{m{\cdot}s^{-1}}$ to $45\,\mathrm{m{\cdot}s^{-1}}$ while the internal porosity of HMX crystal (δ value) decreased from 0.30 % to 0.16 %. The threshold velocity of PBX in Susan test increased from $45\,\mathrm{m{\cdot}s^{-1}}$ to $53\,\mathrm{m{\cdot}s^{-1}}$ when the particle size of high-quality HMX increased from 20 μm to 105 μm, and the brisance of the latter was less than that of the former.

Keywords : HMX, Pressed PBX, reaction, Susan impact test, crystal quality

1. Introduction

Various external stimuli can cause release of the energy contained in energetic materials. Knowing the response of individual energetic materials to specific stimuli is very important from the point of view of safety and in determining the suitability of a material for a specific application. It is well-known that the sensitivities are of vital importance for energetic materials. In order to produce safe munitions capable of surviving unwanted external stimuli such as shocks from explosions or impacts by projectiles, the initiation sensitivity of explosives has to be remarkably reduced.

Impact sensitivity of solid high explosives is an important concern in handling, storage, and shipping procedures. Several impact tests have been developed to understand the ignition of explosives for specific accident scenarios, such as the Susan impact test, the Steven impact test, etc. The Susan test is a projectile impact test designed to assess the relative sensitivity of a confined explosive charge under field conditions of crushing impact. It can assess the hazard of accidentally dropping an encased explosive system from a great height, such as from an airplane, and impacting a target at a certain velocity. Because the explosive sample deformation characteristic in Susan impact test is closer to the actual status than in Steven impact test, therefore, it is of great practical importance for us to know the reaction characteristic of PBXs in Susan test for the sake of evaluating the degree of impact safety of explosive parts.

Among the factors affecting the safety of explosives, besides the molecular structure, crystal phases, particle microstructure and size of explosive particles also play a significant role[1)-4)]. Up to now, there are great efforts to study the effects of particle size on mechanical sensitivity of explosives, but the reported results are controversial. Chen found that the friction sensitivity of explosives decreased as the particle size has changed from 30 μm to 150 μm[5)]. However, Geng investigated the friction sensitivity of HMX particles sized 0.47, 6.26 and 36.7 μm, and the results showed that the friction sensitivity of HMX increases at first and then decreases with the decrease of particle size[6)]. Although there is a certain

Table 1 HMX particle character and mechanical property of several HMX-based PBXs.

Explosive	w (C-HMX) [%]	w (HQ-HMX, 20 μm) [%]	w (HQ-HMX, 105 μm) [%]	Strength [MPa]	Modulus [GPa]
C-PBX	94	0	0	36.68	7.72
HQ-PBX-F	0	94	0	40.11	10.43
HQ-PBX-G	0	24	70	30.13	8.37

tendency that the impact sensitivity of explosive always fell as the particles size decreased[5,7–9], some researched results does not agree with it[10]. These controversial results may be related to the dissimilarity of microstructure for explosive particles. Song's research indicates that the safety of HMX is not only affected by particle size, but also depends strongly on the microstructure of HMX particles[11]. For example, as the median particle size (d_{50}) of HMX decreased, the friction sensitivity increased for spherical samples and decreased for needle-shaped ones. Furthermore, the range and peak shape of particle size-distribution also have a direct influence on the sensitivity of explosive[1,12].

In fact, the effect of crystal characteristics on the safety and stability of PBXs in Susan impact test is also important. However, until now, the Susan impact test was mainly focused on different compositions of PBX[13,14], but few researchers addressed on crystal characteristics, especially crystal quality of explosives. Although Albert[15] found that using fine particles of single compound explosive would reduce the sensitivity of PBX in Susan test, the mechanism was not clarified. In fact, the explosive crystals of PBXs undergo severe extrusion and friction action in the Susan impact test. In our previous research[16,17], the effects of crystal quality and particle size on the safety of HMX based PBXs were studied preliminarily. We found that the pressed PBX compositions with fitting gradation of high-quality HMX can lead to substantial safety improvements in regard to not only shock stimuli but also Susan impact stimuli. However, the exact reason why the change in particle size and crystal quality of HMX affects the initiation threshold and reaction level of PBXs has remained unknown.

In this paper, we continued to investigate the distinction of Susan test sensitivity by varying the quality and grain size of HMX particles in pressed PBX via testing much more data points. Furthermore, the reason of crystal quality and size of high-quality HMX particles affecting PBXs' reaction characteristics in Susan impact is discussed in detail from the point of view of particle friable characteristics. We hope that this work can point out a novel approach to reduce the sensitivity of PBXs while maintaining powerful performance.

2. Experimental

2.1 Materials and characterization

The commercial HMX (namely, C-HMX) was supplied in ordinary quality forms by Baiying Enterprises, Ganshu, China. The high quality HMX (namely, HQ-HMX) used in this study which has less internal defects was recrystallized using a special method and supplied by Institute of Chemical Materials (ICM), Sichuan, China.

The morphology of several HMX particles were examined by scanning electron microscopy (SEM) and optical microscopy with matching refractive indexes. The particle size distribution was determined by Laser Diffraction Particle Analyzer with Coulter IS230. The crystal particle apparent densities were measured by density gradient tubes (DGT) developed by our institute which used in Li's work[18]. The initial secant modulus (ISM) of several HMX crystals were determined by compressive stiffness test (CST)[19].

2.2 Preparation of PBX

Three pressed PBXs with different HMX are listed in Table 1. "C-PBX" is the PBX filled with commercial HMX, "HQ-PBX-F" is the PBX filled with fine particle high-quality HMX, and "HQ-PBX-G" is the PBX filled with fine and coarse high-quality HMX by fitting gradation. The molding powder of three PBXs, which consists of 94 % HMX, 4.5 % acrylonitrile-Styrene copolymer and Fluoro-polymer as composite binders, and 1.5 % low melt-point substance ,i.e. wax, as a desensitizer, are prepared by water slurry method[20]. This composition is similar to, but with different binders being added as compared to PBX-9404 reported in LLNL Explosives Handbook[20], in which the binders were 3 % nitrocellulose (NC) and 3% chloroethyl phosphate (CEF). Then, these molding powder are pressed into testing samples by hot-press methods[21], in which the preheated temperature was about 80℃ and the pressure was 160 MPa. The mechanical properties of three PBXs are determined by compression test according to GJB-772A-97 standard method 418.1[22].

2.3 Susan impact test

The impact sensitivity of pressed PBX samples are evaluated by using the Susan test according to GJB-772A-97 standard method 610.1[22]. The testing device of explosive, a cylinder 50-mm diameter by 100-mm long, about 0.45 kg, is contained in a steel projectile with a duralumin cap, and impacts on a steel plate. The Susan test uses a projectile fired from a gun. The relative detonation energy can be derived from a transit-time measurement of the air shock from the point of impact to a pressure gauge 3.7 meters from the point of impact. The energy scale varies from 0 (no reaction) to 100 (violent detonation consuming the entire explosive). The results of the tests are expressed as a sensitivity curve in which the relative detonation energy released is plotted as a function of the projectile impact velocity. The threshold velocity of ignition of the testing explosive can be obtained by extending the plotted curve to the X axis.

3. Results and discussion

3.1 Crystal quality and particle size

The SEM-pictures and optical images of the commercial and high-quality particle HMX samples are presented in Figures 1. Strong agglomerates are present in the ordinary commercial HMX particles (Figure 1a), especially many small particles stick onto the surface of some large particles (Figure 1a). On the contrary, the high-quality HMX seems to be more regular or crystalline like diamond, and the particle surface is very smooth (Figure 1 b, 1c). Figures 2 (a) and (b) illustrate the particle size distribution of three samples. The particle size distribution of C-HMX is considerably broad (Figure 2a), while the size distribution of HQ-HMX is relatively narrow (Figure 2b).

Table 2 illustrates the characteristics of three types of the HMX samples: one is the commercial and the others are high-quality particles, fine and coarse, respectively. High quality HMX has a higher mean density and a more narrow particle density distribution than commercial HMX. The commercial HMX particle has a mean size of about 29 μm and its porosity of internal crystal (δ) is 0.294. The fine high-quality particle has a mean size of about 20 μm and the coarse particle has a mean grain size of 150 μm, and their δ values are 0.168 and 0.157, respectively. This result indicates that re-crystallization leads to particles with a very high density (near the theoretical value) and thus to particles with a small amount of voids. As shown in Table 2, the values of the ISM for three types of HMX show some difference, and the particle size also affects the ISM values. Fine high-quality HMX has a 250 MPa ISM value, a little higher than that of commercial HMX, and as the particle size increased, the ISM values decreased to 159 MPa. Therefore, compared with commercial HMX, high quality HMX has more regular shapes, more smooth surface and lesser internal defects.

3.2 Influence of HMX crystal quality on Susan test sensitivity

The Susan sensitivity curve of energy release vs impact velocity for HMX-based PBX with different quality HMX is shown in Figure 3.

As shown in Figure 3 (left), the sensitivity curves of PBX prepared by different crystal quality of HMX provide obvious distinctions at different impact velocity in Susan test. Due to its less internal crystal defect, the HQ-PBX-F with high-quality HMX is not easy to ignite in the Susan test because it creates less hot-spot at low impact velocity, thus its reaction threshold velocity (45 m·s^{-1}) by impact is higher than that of C-PBX with ordinary quality HMX, which is only 37 m·s^{-1}. The relative released energy of HQ-PBX at low impact velocity is also lower than that of C-PBX. Compared with our previous paper[17)], the value of threshold velocity in this paper changes a little because the link curve also shifts a bit owing to the addition of more data-points and the connecting line among these data-points are also not the same way. The curve in our previous paper[17)] was connected accordingly with B-spline line, but the curve in current paper is just connected with straight line according to these data-points. The B-spline was a smooth curve around the testing points, while the straight link mode was just a straight line connecting between two points, therefore, the straight line was more similar to the actual trend of these testing points than the B-spline.

In fact, the initiation of PBX in Susan test is of a thermal nature. In classical theory, when energetic materials undergo an action of impact, friction, and extrusion, the energy generated by the stimulus is converted into heat, which is conducted among the particles[23),24)]. If the effective thermal conductivity of the particle group is too low to dissipate the heat away from the system in time, initiation is localized in small volumes (hot spots) where the accumulated heat is intense enough to lead to a vigorous reaction. In general, an explosion could be attributed to heat conduction and the formation of hot spots.

The initiation process can be separated into two phases: ignition phase controlled by hot spot formation rate; and detonation buildup phase controlled by hot spot growth rate. The influencing factors for ignition phase are the determinant of reaction threshold velocity of PBX in Susan test. During the first stage of initiation process, the energy supplied by the impact or friction causes irreversible deformation of the explosive material and formation of “hot-spots” or local dynamically overheated regions. Hot spot growth and coalescence results in detonation buildup and produces fast energy release during the second stage of initiation process. Friction between crystal particles, heating at the defects of crystals (e.g. crack tips and dislocation pile-ups), and viscous-plastic heating for localized adiabatic shear of explosive during mechanical failure[5), 25)] are the factors which can produce hot spots. As shown in Figure 1a, there are many pointed edges and corners on the surface of common quality HMX crystals, which have relatively large surface energy and high activity, and they are prone to become the source of

Table 2 The particle size, crystal density and internal defects of several HMX particles.

Explosive	Particle size distribution [μm]	Mean size [μm]	Range of apparent density [g·cm^{-3}]	Apparent density [g·cm^{-3}]	Porosity of internal crystal^a [%]	ISM [MPa]
Commercial HMX	1-130	29	1.8979~1.8994	1.8994	0.294	235
HQ-HMX (fine)	4-40	20	1.9012~1.9024	1.9018	0.168	250
HQ-HMX (coarse)	20-300	105	1.9014~1.9024	1.9019	0.157	159

a) porosity of internal crystal $(\delta) = (\rho_{\text{theoretic}} - \rho_{\text{practical}})/\rho_{\text{theoretic}} \times 100\%$, $\rho_{\text{theoretic}} = 1.905\,\mathrm{g \cdot cm^{-3}}$

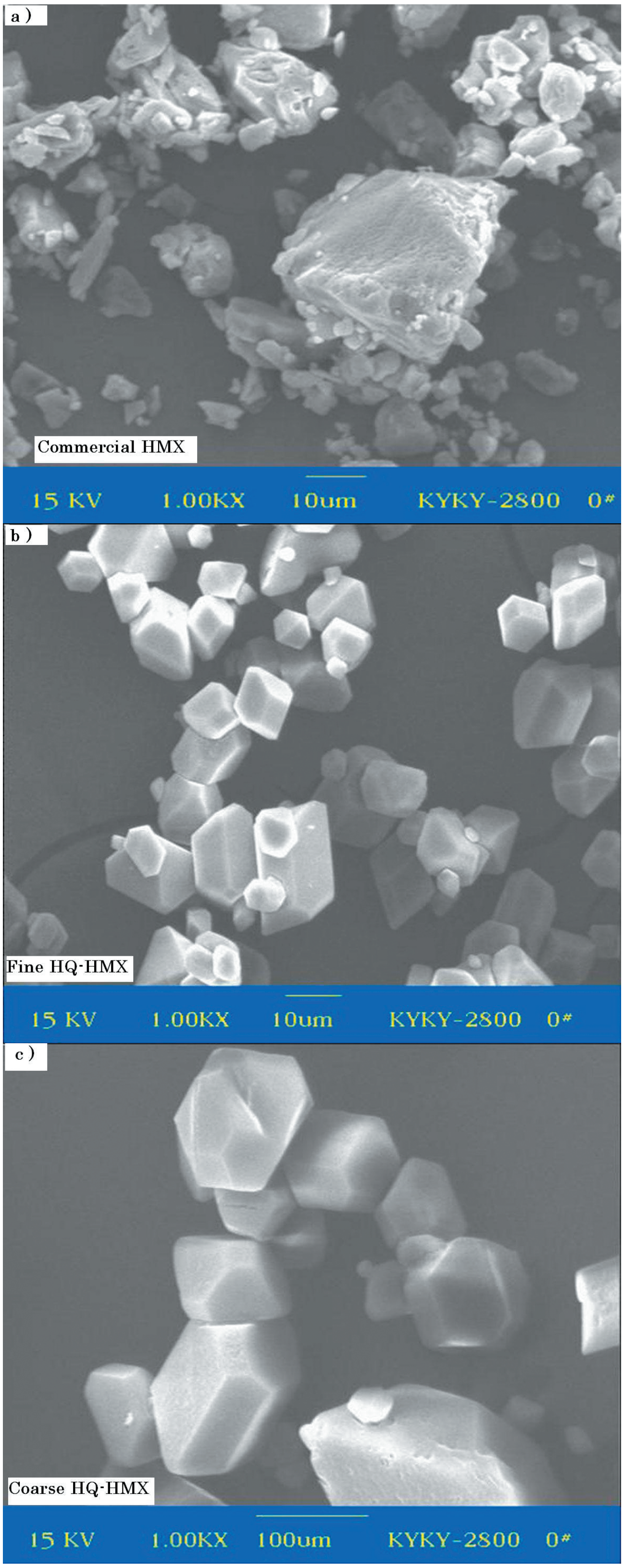

Figure 1 SEM images of three types of HMX particles.

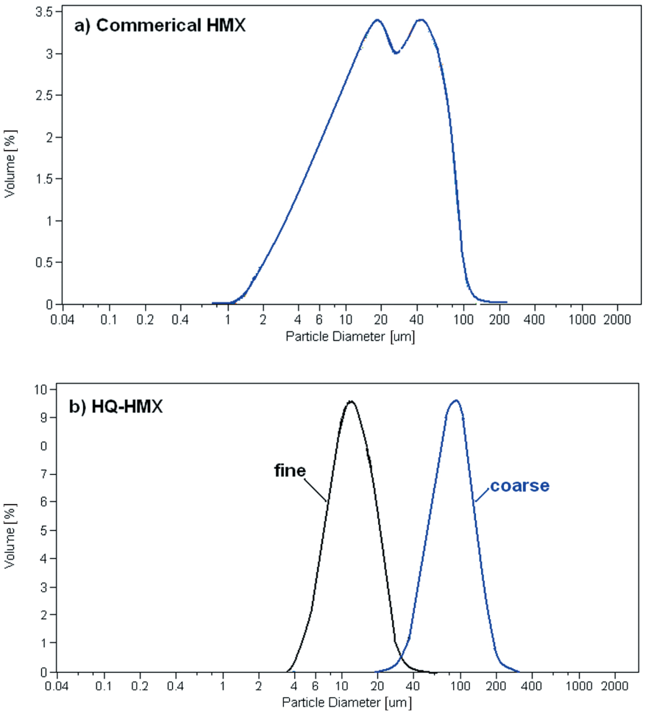

Figure 2 Size distributions of three types of HMX particles.

hot spots once impact is applied on them. Moreover, the internal defects of common quality HMX crystals are markedly more than that of high quality HMX, which is about 0.30 % in contrast to 0.16 %. Therefore, the reaction threshold velocity of PBX with common quality HMX in Susan test is much lower.

On the other hand, the Susan test sensitivity of explosive can bring different level reaction by reason of the factors which affect explosive buildup to detonation. It is the plastic distortion of explosive particles which has very important determinant of buildup to detonation of PBX during the Susan impact. After impact against a rigid wall, the sample between shell and wall can suffer from the intensive impact, friction and viscous-flow, the distance of opposite move among explosive particles is very large, there are huge shearing deformation, shearing stress and dissipation of viscous-plastic work appearing at the edge of PBX pellets which can cause shear ignition, and build-up to detonation.

There is an interesting phenomenon that reaction levels for pressed PBXs with high-quality HMX are dependent on impact velocity. Compared to C-PBX with ordinary HMX, it is rising very slowly from threshold velocity to about 110 $\mathrm{m{\cdot}s^{-1}}$ for HQ-PBX with high-quality HMX and then rising more rapidly as impact velocity increases. This is because that at low impact velocity (below 110 $\mathrm{m{\cdot}s^{-1}}$), the amount of energy that was exerted on PBX is relatively low and most of the energy is consumed by the nobbing and deformation of PBX. Because of its smooth surface, the friction and shearing action among particles of HQ-PBX is weaker than that in C-PBX, so the part of energy used to form heat is relatively small, which cause lower level reaction and release less energy in Susan impact test. However, as impact velocity increases (above and beyond 110 $\mathrm{m{\cdot}s^{-1}}$), severe crushing, shear, impact and nobbing forces can easily come into being among the high-quality HMX particles for the reason of its high modulus (see Table 2) or indefectible property, and more quantity of heat can form and accumulate, so subsequent reaction would occur, leading to a transition to violent detonation, releasing larger amount of energy.

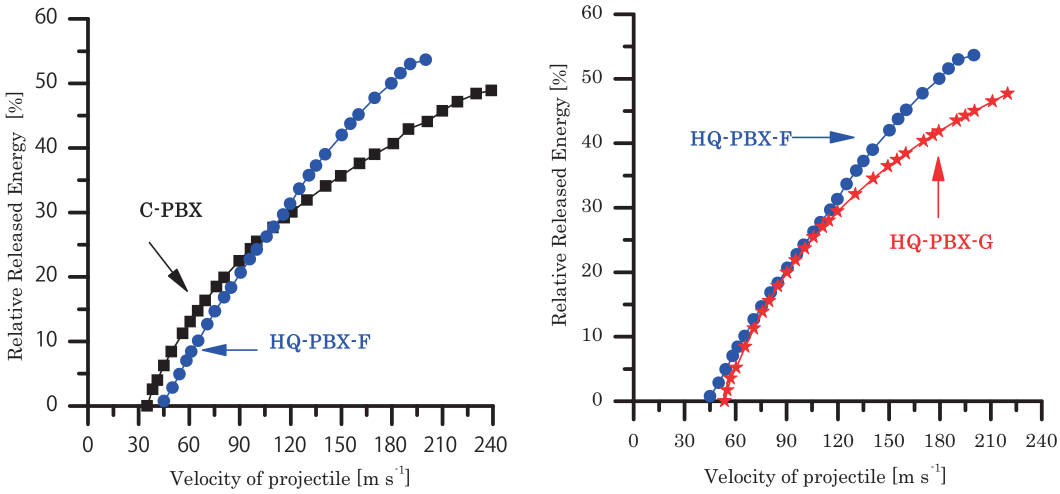

Figure 3 Susan sensitivity curves of HMX–based PBXs.

3.3 Influence of HMX crystal size on Susan test sensitivity

As shown in Figure 3 (right), there are some degree of influence for size difference of HMX particles in PBXs on Susan impact test result despite the same composition of these PBXs. The reaction threshold velocity of HQ-PBX-G with gradating particles is higher than that of HQ-PBX-F with fine particles, which are $53\,m{\cdot}s^{-1}$ and $45\,m{\cdot}s^{-1}$, respectively. In addition, the reaction of the former in Susan test is less violent than that of the latter. All these are related to stress circumstance of samples in cased charges during impact on an armor-plated target. The impact can cause crush of explosive crystals, form huge stress among the crystals, and create hot spots at the intra-explosive defects, further buildup to violence reaction[26]. It is a very important role for the duration time of high stress in impact ignition. The magnitude of stress and duration time caused by friction and shear during impact vary with size of explosive particles. The duration time of high stress for HQ-PBX-F is long because fine particles are not prone to crush, and once hot spots in PBX with fine high-quality HMX form, they can easily buildup to violent reaction. However, the coarse particles are easily crushed than fine particles because the ISM of coarse particles is less 100 MPa than that of fine particles (Table 2). This is possibly because the crushing process of particles consume part of impact energy that is supposed to be used to form heat, causing less energy.

Moreover, the response of PBXs in Susan test is also affected by the size of voids in sample pellets. The voids among particles in PBX pellet are also responsible for the formation of critical hot spots. The less or smaller for the voids in explosive, the more difficult it is for the formation of hot spots. The size of voids among particles can be diminished by optimum particle gradation, and this can also reduce the size of potential hot spots. It is noticeable that if the sizes of hot spots are smaller than $0.1\ \mu m$, despite it can cause some decomposition but would quench too quickly to produce ignition[27]. Because the critical temperature of explosion is inversely proportional to the size of hot spots, the smaller the radius of hot spots, the higher would be the critical temperature of explosion. Therefore, the reaction threshold velocity of HQ-PBX-G with gradation particles in Susan impact test is higher than that of HQ-PBX-F with fine particles, and the less surface area would cause the hot spots growth rate to be lower, so the violence level of reaction is also slightly milder.

4. Conclusions

In summary, for the same HMX-based pressed PBXs, the Susan impact sensitivity has been shown to be strongly dependent on crystal quality (such as porosity of internal crystal and morphology), grain size and distribution of HMX particles. The experiment results obtained from Susan impact test show that a decreased sensitivity against the externally applied stimuli when using high-quality HMX instead of commercial HMX in pressed PBX formulations. The threshold velocity for initiation can be increased by using appropriate particle size of high-quality HMX, and the reaction levels near their thresholds can become milder. Moreover, there exists an interesting phenomenon that reaction levels for pressed PBXs with high-quality HMX dependent on the impact velocity, i.e., there exists a critical impact velocity (about $110\,m{\cdot}s^{-1}$), below which, the reaction levels of high-quality HMX based PBX is milder than that of PBX with common quality HMX, but, once above the velocity, the reaction levels of PBXs with high-quality HMX become more violent than the latter. This relate to the crystal characteristics of different HMX particles, such as friability.

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