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Dependence of Particle Size and Size Distribution on Mechanical Sensitivity and Thermal Stability of Hexahydro-1, 3, 5-trinitro-1, 3, 5-triazine

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ABSTRACT

Two kinds of RDX samples, with broad and narrow particle size distribution, have been fabricated by wet riddling and solvent/non-solvent methods, respectively. By controlling the technical condition, the RDX powders with different particle sizes were obtained for each sample. All samples were characterised by laser granularity measurement and scanning electron microscope (SEM). Using mechanical sensitivity tests, slow cook-off test and differential scanning calorimetry (DSC), the mechanical safety and thermal stability of RDX samples, depending on the particle sizes and size distribution, were studied. Results indicated that, for each kind of RDX particles, the mechanical sensitivity and thermal stability of samples changed according to the particle size. However, although two samples had almost the same average particle size, their safety changed when two particle size distributions differed. Concretely, the mechanical sensitivity of RDX reduced and their thermal stability increased gradually along with the decreasing of particle size. Meanwhile, RDX with broad size distribution had higher mechanical sensitivity and thermal stability than samples with narrow size distribution.

Keywords: RDX, particle sizes, size distribution, mechanical sensitivity, thermal stability, kinetics

1. INTRODUCTION

The wide application of hexahydro-1, 3, 5-trinitro-1, 3, 5-triazine (RDX) has prompted vigorous efforts to understand and improve its safety[1-5]. Among the factors influencing the safety of explosives (especially RDX), such as physical and chemical structures, charge diameters and density, etc, size and size distribution of explosives particles play a significant role, but the specific influences of size and size distribution on safety properties are unclear[6]. Liu *et al*. reported that the friction sensitivity of RDX decreased linearly as the particle size was reduced from 154 μm to 10 μm[7]. However, Yang *et al.* investigated the friction sensitivity of RDX with average particle size d_{50}=8.95 μm, 12.78 μm, 54.89 μm and 640 μm, respectively, but failed to find any specific relationship between particle size and friction sensitivity[8]. Chen[9] even indicated the mechanical sensitivity of explosives can be increased by reducing their particle sizes.

The possible reasons for the above controversy are as follows: First the average particle size was adopted in the above studies for characterising the particle size effects on sensitivity. However, the actual size distribution of particles around the average value, as well as particle morphologic properties, may have certain effects on the experimental results. As the results show in this study, the RDX safety of two samples with almost the same average particle size may be significantly different if these have different particle size distributions. Therefore, consideration of the particle size distribution is necessary to clarify the relationships between RDX safety and the particle size. However, few researchers addressed the effect of size distribution, which may be the cause of the discrepancy noted above.

The second reason for the above controversy may be the limited by dynamic ranges of the particle sizes adopted in those studies. To completely understand the effects of particle size on RDX safety properties, a broad dynamic range of particle sizes should be studied. In this study, the range of average particle size of RDX change is from 490 μm to 216.2 μm, which was much wider range than the range used in many other previous studies. The safety of RDX samples, with almost the same average particle size but different size distribution and morphologies, are compared. In addition, the dependence of particle size and size distribution on mechanical sensitivity, thermal stability, and decomposition of RDX are discussed.

2. EXPERIMENTAL

Raw RDX powder (d_{50}=41.8 μm, d_{90}=271.8 μm) was obtained from Yinguang Chemical Plant of China. Emulsifier (OP) (A.R.) and Acetone (A.R.) were purchased from Shanghai Chemistry Reagent Ltd. Using wet riddling and solvent/non-solvent methods, two kinds of RDX samples were fabricated. By controlling the technical parameters, the RDX particles with different average particle sizes (d_{50}) were obtained within each of the two kinds of samples (shown as Table 1).

Particle size and size distribution of samples were measured by Master Sizer Instrument. The morphologies of samples were examined by a scanning electron microscope

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Table 1 Fabrication of RDX samples with different particle sizes and size distribution

Method	Material	Medium	Technical parameters	d_{50} (µm)
Wet riddling	Raw RDX	Alcohol (95 Wt.%)	Size of sieves	0.49, 2.86, 5.6, 10.4, 16.6, 41.8, 92.5, 153.3
Solvent/non-solvent	Coarse RDX	Acetone (solvent), aqueous solution of emulsifier (non-solvent)	Stirring rate, temperature difference between solvent and non-solvent	2.29, 4.86, 19.4, 62.8

(S-4800). HGZ-1 impact instrument was used to test the impact sensitivity of RDX samples. Each sample (35 mg) was tested for 25 time to obtain a H_{50} (The H_{50} value represents the height from which dropping a 5 kg weight results in an explosive event in 50 per cent of the trials.). With 4 peering tests, an average value of H_{50} was calculated. WM-1 friction instrument (90°, 3.92 MPa) was employed to test the friction sensitivity of samples. Each sample (20 mg) was tested 25 time and an explosive probability P (%) was obtained. An average value of P was estimated with 4 peering tests. In slow cook-off test, the heating rate of each sample was at 3 ^{o}C·min^{-1}. The self-accelerated temperature of each explosive charge in the course of heating was logged to estimate the thermal sensitivity of RDX samples. Differential scanning calorimetry (DSC) of samples was performed on a TA Model Q600 differential scanning calorimeter under a floating N_2 atmosphere (10 ml·min^{-1}). The heating rates of each sample were at 5 °C·min^{-1}, 10 °C·min^{-1} and 20 °C·min^{-1}.

3. CHARACTERISATION OF SAMPLES

Figure 1 shows the particle size and size distribution of raw RDX and a part of prepared samples that have almost the same d_{50} but different size distribution.

Figure 1 (a) indicates that raw RDX with d_{50}=41.8 µm has a very broad size distribution ranging from 300 nm to 300 µm. Figure 1 (b) also shows a broad size distribution sample with three distribution peaks. However, the sample prepared by solvent/non-solvent exhibits a more narrow size distribution curve in Figure 1(c). It is distinct that although two samples

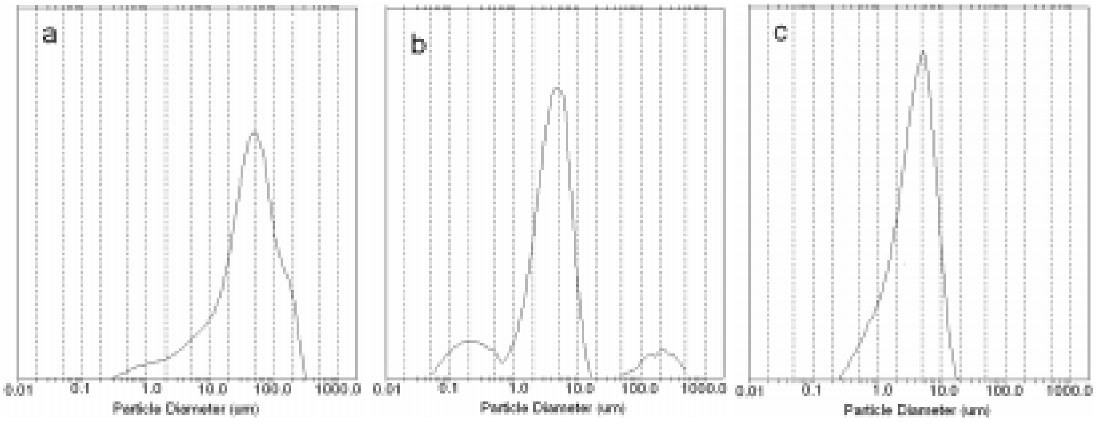
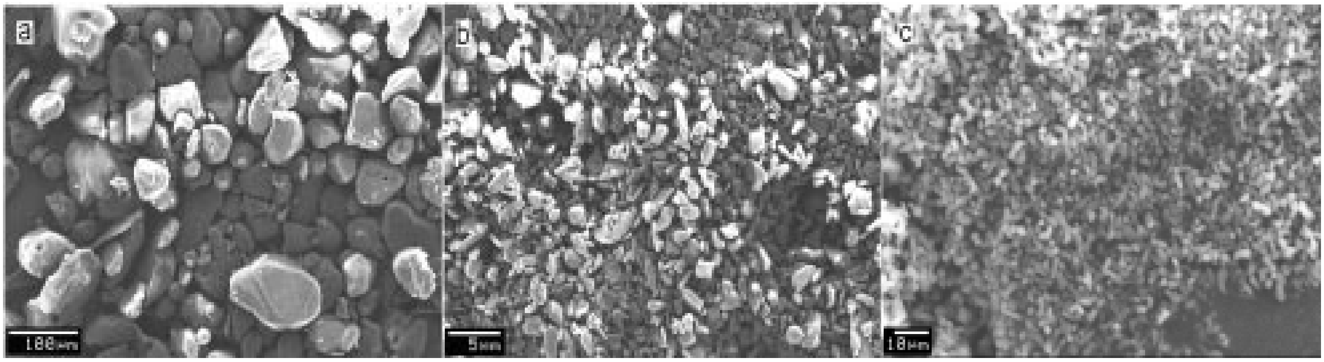


Figure 1. Size distribution of RDX samples: a- raw RDX powders, d_{50}=41.8 µm; b-prepared by riddling, d_{50}=2.86 µm; c-prepared by solvent/non-solvent method, d_{50}=2.29µm.



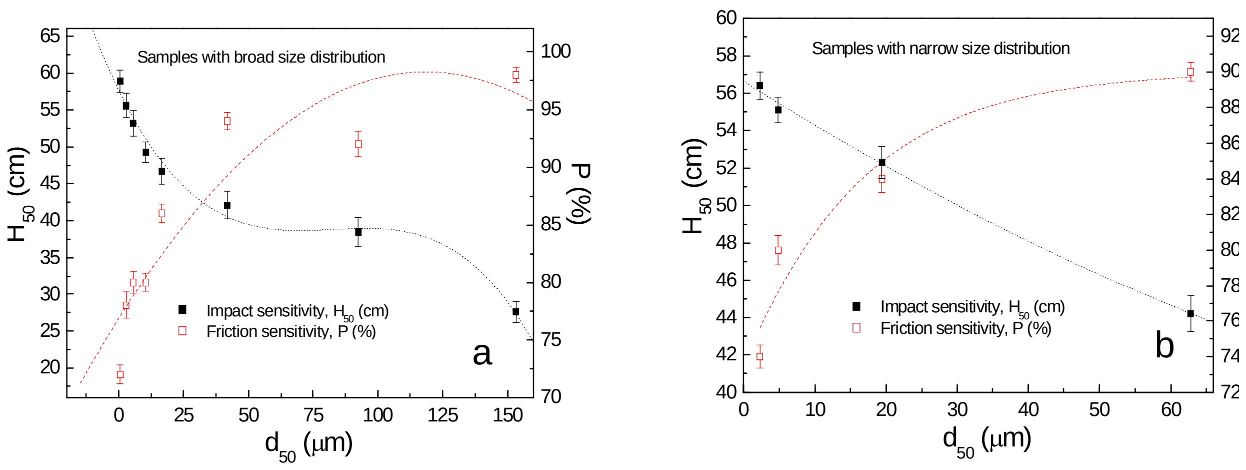
(a) (b) (c)

Figure 2. SEM images of RDX samples: a-raw RDX powders, d_{50}=41.8 µm; b-prepared by riddling, d_{50}=2.86 µm; c-prepared by solvent/non-solvent method, d_{50}=2.29 µm.

(shown as Figs 1 (b) and 1 (c)) have almost the same d_{50}, their size distribution are considerably different. Figure 2 provides the SEM images of the above samples. The differences of microstructure among these kinds of particles are obvious. The morphology of raw RDX is nonuniform and shows irregular polyhedron shapes with very coarse surfaces. The morphology of sample shown in Fig. 2 (b) is similar to the raw powders, in which there are many little particles among large ones. Peculiarly, unlike the other two kinds of samples, the microstructure of particles prepared by solvent/non-solvent method is homogeneous and has cosh or spherule shapes.

4. MECHANICAL SENSITIVITY ANALYSES

Small-scale mechanical sensitivity tests were performed on all the RDX samples prepared, the results are shown in Fig. 3. Every plot of Fig. 3 contains two curves corresponding to the trend of impact or friction sensitivity data changed as a function of particle size. For the samples with broad size distribution, the H_{50} increases as the particle size decreases. Especially within the scale of 0.49~41.8 μm, this trend is much clearer, indicating that these kind of particles with smaller size are more passive to impact force. In friction test, this kind of trend also exists, i.e., smaller particles have lower explosive probability. In Fig. 3(b), for samples with narrow size distribution, their impact and friction sensitivity both rise almost linearly along with increase of particle size from 2.29 μm to 62.8 μm. On the other hand, according to different particle sizes, the average value of H_{50} for narrow distribution samples ($\overline{H}_{50}$ =52 cm) is slightly higher than that of broad distribution particles (=46.49 cm), suggesting that the former is more passive to impact stimuli. Meanwhile, the average value of explosive probability ($\overline{P}$) of narrow distribution samples equals to 82 per cent, and is a bit lower than that of broad distribution samples ($\overline{P}$ =85 per cent).



(a) (b)

Figure 3. Impact and friction sensitivity of RDX samples as a function of particle size: a-prepared by riddling; b-prepared by solvent/non-solvent method. The error bars are respectively the average and standard deviation, of the average value obtained from four peering tests.

Hot spot theory can be employed to explain the above experimental results[10]. In the mechanical sensitivity tests, while the external force acts on the smaller RDX particles, released heats will dissipate faster and the force acting on unit area of particles surfaces becomes lower due to the larger contacting area among these smaller particles. Therefore, "hot spot" is hard to form to enable detonation. Besides, "hot spot" is more likely to be formed at coarser surfaces because of their larger friction coefficient. Therefore, RDX with broad size distribution samples can generate more heats than those with narrow distribution when the two kinds of powders undergo the same mechanical stimulation.

5. THERMAL STABLITIES ANALYSES

5.1 Thermal Sensitivity Tests

Figure 4 is made by two sub-plots of thermal sensitivity to particle size, corresponding to two kinds of RDX samples respectively. Plots (a, b) illustrate that the T_{break} of both kinds of samples decrease as their particle sizes become larger, which implies that the smaller RDX particles have lower thermal sensitivity. Comparing the experimental results between two kinds of samples, one finds that the influence of particle

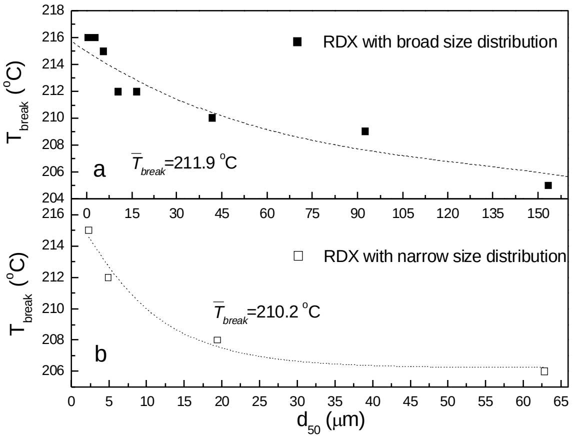
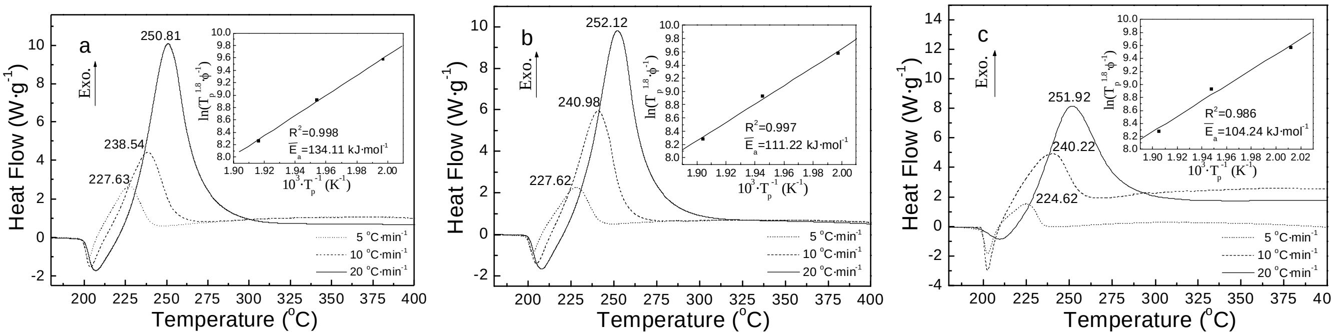


Figure 4. Self-accelerated temperature of RDX as a function of particle size: (a) a-prepared by riddling; (b) b-prepared by solvent/non-solvent method

size distribution on the thermal sensitivity of RDX is not that clear in terms of the little difference of average T_{break} values obtained from different particle sizes, in which the $\overline{T}_{break}$ of broad size distribution samples is higher than that of narrow size distribution samples by only 1.7 °C.

5.2 Thermal Decomposition Tests

Figure 5 is the DSC curves of RDX samples with different size distribution in N_2 atmosphere at the heating rates of 5 °C·min^{-1}, 10 °C·min^{-1} and 20 °C·min^{-1}. In each case, the temperature of the exothermic peak and the decomposition heat (determined by the area of the exothermic peak in DSC curve) decrease with decreasing heating rate. However, the results for the different kinds of samples do not generally shift to the same extent at any given heating rate.



(a) (b) (c)

Figure 5. DSC traces of RDX with different particle size and size distribution: (a) raw RDX powders, d_{50}=41.8 µm; (b) prepared by riddling, d_{50}=2.86 µm; (c) prepared by solvent/non-solvent method, d_{50}=2.29 µm. Each inset is Starink' plot for the thermal decomposition peak of DSC curves. Symbol R^2 is used to identify the linear coefficient of ln ($T_p^{1.8}\cdot\phi^{-1}$) to 1000·T_p^{-}.

To study the effects of particle size and size distribution on the apparent active energies of thermal decomposition of RDX, Starink method is used in kinetic evaluation. It is an order of magnitude more accurate than others and complies with the following equation[11,12].

$$\ln\left(\frac{T_p^{\,S}}{\phi}\right) = A\cdot\frac{E_a}{RT_p}+C \qquad (1)$$

where T_p is the temperature of exothermic peak in DSC curve, K; ϕ the heating rate, K·min^{-1}; E_a is the active energy, J·mol^{-1}; s, a constant, and A is a constant depending on the choice of s. In the case of Kissinger method s=2 and A=1, the Ozawa method s=0 and A=1.0518, while the Straink method s=1.8 and A=1.0070-1.2×10$^{-8}E_a$. The last method is employed, and E_a of samples are determined. Because there are differences among values of R^2 in the inserted graphs of Fig. 5, the final apparent active energy of each sample is expressed as an average value of E_a calculated from Starink's formula with DSC data collected at every two heating rates.

$$\overline{E}_a = \frac{[E_{a(5-10K\cdot\min^{-1})}+E_{a(5-20K\cdot\min^{-1})}+E_{a(10-20K\cdot\min^{-1})}]}{3} \qquad (2)$$

where $\overline{E}_a$ is final apparent active energy of thermal decomposition for a sample, $E_{a(5-10K\cdot\min^{-1})}$, $E_{a(5-20K\cdot\min^{-1})}$ and $E_{a(10-20K\cdot\min^{-1})}$ are the active energies calculated from Eqn. (1) by Starink method.

Figure 6 shows the plots of apparent active energy ($\overline{E}_a$) of thermal decomposition to the particle size and size distribution of RDX samples. In Fig. 6, for each kind of sample, no relationship is observes between and particle size. However, on comparing two kinds of samples, the average value (calculated with the data at different d_{50}) of for narrow size distribution samples (=109.6 kJ·mol^{-1}) is lower than that for broad size distribution samples (=124.5 kJ·mol^{-1}). As a result, it implies that samples with narrow size distribution will decompose first in the course of heating, which is in accordance with the experimental results in Fig. 4.

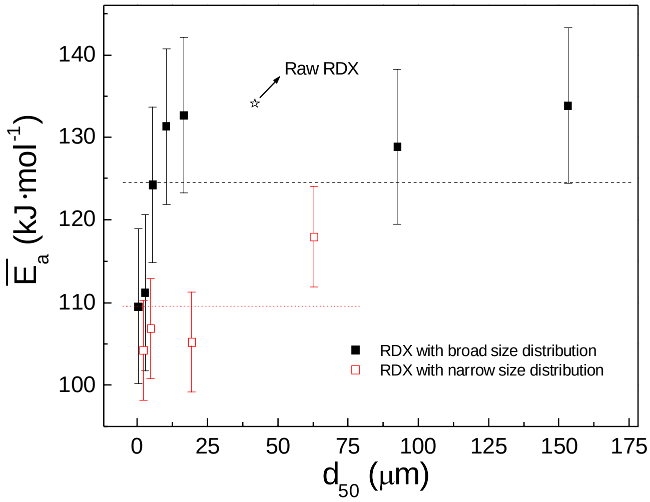


Figure 6. Plots of $\overline{E}_a$ for RDX to particle size. The error bars are respectively the average and standard deviation of the average value of $\overline{E}_a$.

As to thermal stability, heat conductivity of explosive plays a significant role. In general, as the particle size of explosive decreases, the specific surface area and the amount of atoms located on the particle surface increase, which means that the outer electronic orbit extends and the atoms vibrating space expands. These changes result in an improvement of the thermal conductivity among explosive particles[13-15]. As a result of higher thermal conductivity, the heats from thermal decomposition can be dissipated in time and further decomposition is restrained. Accordingly, smaller particles lead to higher thermal stability.

Furthermore, the contacting areas among the particles with smooth surfaces are lesser than those of particles with coarse surfaces. Therefore, thermal conductivity of narrow size distribution samples is lower, thus facilitating heat accumulation in the course of heating. If the heats generated are more than the heats which are radiated, temperature of explosive system increases continuously, thereby accelerating thermal decomposition of explosive again. Likely because of such self-catalytic reaction, the RDX samples with narrow size distribution exhibit lower values of $\overline{T}_{break}$ and $(\overline{E_a})$ betweem two kinds of samples.

6. SUMMARY

In the introduction, not only many reported results about the influence of particle size on safety of explosives were summuised but also the discrepancies among them was shown. Therein, it was speculated that the size distribution of explosive particles directed the disunity. To investigate the effects of size distribution on mechanical sensitivity and thermal stability of explosives, two kinds of RDX samples with narrow and broad size distribution were fabricated by wet riddling and solvent/non-solvent methods. Meanwhile, through controlling the size of sieves and temperature differences between solvent and non-solvent etc, RDX with different particle sizes were obtained for each kind of sample. The results of the tests indicate that the particle size has a direct influence on safety properties of RDX, but such influence depends to a large extent on the size distribution as expected.

For both kinds of samples, the mechanical sensitivity decrease along with the decreas of the particle size. Moreover, in slow cook-off test, smaller RDX particles have lower thermal sensitivity. However, RDX with broad size distribution is more sensitive to mechanical action than the narrow size distribution samples when their d_{50} values are close. In addition, the average value of active energy for RDX samples with narrow size distribution is lower than samples of broad size distribution.

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