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Preparation and Properties of 1, 3, 5, 7-Tetranitro-1, 3, 5, 7-Tetrazocane-based Nanocomposites

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ABSTRACT

A new insensitive explosive based on octahydro-1, 3, 5, 7-tetranitro-1, 3, 5, 7-tetrazocine (HMX) was prepared by spray drying using Viton A as a binder. The HMX sample without binder (HMX-1) was obtained by the same spray drying process also. The samples were characterised by Scanning Electron Microscope, and X-ray diffraction. The Differential Scanning Calorimetry and the impact sensitivity of HMX-1 and nanocomposites were also being tested. The nanocomposite morphology was found to be microspherical (1 µm to 7 µm diameter) and composed of many tiny particles, 100 nm to 200 nm in size. The crystal type of HMX-1 and HMX/Viton A agrees with raw HMX. The activation energy of raw HMX, HMX-1 and HMX/Viton A is 523.16 kJ mol^{-1}, 435.74 kJ mol^{-1} and 482.72 kJ mol^{-1}, respectively. The self-ignition temperatures of raw HMX, HMX-1 and HMX/Viton A is 279.01 °C, 277.63 °C, and 279.34 °C, respectively. The impact sensitivity order of samples is HMX/Viton A < HMX-1 < raw HMX from low to high.

Keywords: Spray drying, Viton A, nanocomposites, thermal analysis, X-ray techniques

1. INTRODUCTION

Nanocomposite (a material which is composed of two or more than two kinds of nano-solid phases) is going to become the prime candidate of new material design in the future. It has many advantages such as small-size effect, surface and interface effect, and quantum dimension effect. β-HMX is a type of crystal which has excellent detonation property but poor safety. Studies show that improving the quality of energetic particles can solve the problem of poor safety, such as reducing the particle size[1], addition of binder in particles[2,3] and spheroidisation[4,5]. Decreasing the size of explosive particles to nano-level can not only reduces the mechanical sensitivity[6], but also speed up the burning rate[7,8]. However, it has its disadvantage – a reduced shelf life[9]. Using explosive and high polymer to prepare nanocomposites can solve this problem to some extent. Heating, corrosion and shear, etc. can affect the property of polymer, so the morphology and properties of nanocomposite are changed by these outside stimuli. Viton A is a type of high polymer which has enough strength and superior mechanical performance. It also has some outstanding performances such as ageing resistance, heat-resistance, and corrosion resistance[10]. The mechanical sensitivity of HMX can be reduced using a small quantity of Viton A[11,12].

Spherical particles can be prepared by spray drying[13-16], which is based on the evaporation of crystallisation mechanism. Herein, using Viton A as a binder, HMX/Viton A nanocomposites were prepared by spray drying. Properties of the nanocomposite were characterised and analysed in detail.

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2. EXPERIMENTAL

2.1 Preparation of HMX/Viton A Nanocomposites

HMX [$C_4H_8O_8N_8$, *2 g*, provided by Gansu Ying Guang Chemical Industry Group Co., Ltd. The particle size and morphology is shown in Fig. 2] and Viton A [$(C_2H_2F_2)_n(C_3F_6)_m$, 0.062 g, purchased from Huizhou HaoYuan Plastic Raw Material Co., Ltd.] were dissolved in acetone (obtained from 100.99 g, Tianjin TianDa Chemicals Co., Ltd.) to form a uniform co-solution at 40 °C by sonication. The mass ratio of Viton A to HMX was 3:97. As shown in Fig. 1, the solution was sprayed and dried to produce nanoparticles using a Mini Buchi 290 spray

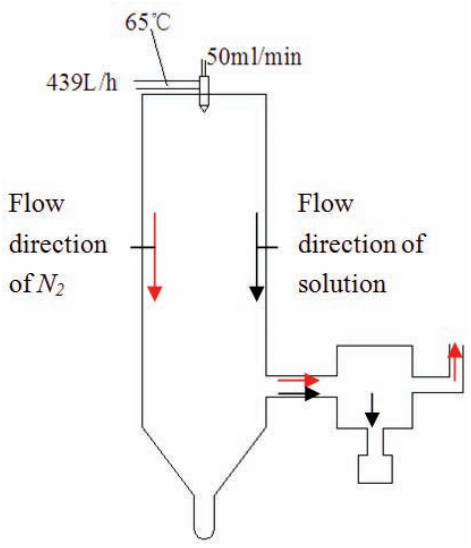


Figure 1. Flow chart of experimental set up.

dryer. The flow rate of the feed solution and the cyclone was set to 50 ml min^{-1} and 439 L h^{-1}, respectively. The temperature of inlet dry gas (N_2) was set as 65 °C. Finally, the product granules were collected in an electrically grounded glass collection vessel and the gas exhaust to recovery system.

2.2 Characterisation

The morphology and size of the HMX-based nanocomposites were studied using a Hitachi S-4800 scanning electron microscope (SEM) (Hitachi Ltd., Japan). A DX-2700 diffractometer (Dandong Haoyuan Instrument Co., Ltd., China) was used to contrast the crystal types of the raw HMX and the HMX/Viton A nanocomposites by X-ray diffractometry (XRD). Differential scanning calorimetry (DSC) experiments were conducted in a N_2 atmosphere using a Setaram DSC131 instrument (Setaram Instrumentation Co., France). The test conditions were: sample mass, 0.7 mg; N_2 flow rate, 15 ml min^{-1} and sample heating rates, 20 K min^{-1}, 10 K min^{-1}, and 5 K min^{-1}.

2.3 Test for Impact Sensitivity

The impact sensitivity of the HMX/ Viton A nanocomposites was tested at room temperature using an ERL type 12 drop hammer apparatus with a sample mass of 35 ± 1 mg and a drop weight of 5 ± 0.002 kg. Four groups of each sample and 25 of the same samples from each group were tested. The results were conveyed in terms of the critical drop-height of 50 per cent explosion probability (H_{50}) and the standard deviation (S). H_{50} and S are being calculated according to GJB-772A-97 standard[17] method 601.2.

3. RESULTS AND DISCUSSIONS

3.1 SEM Characterisation

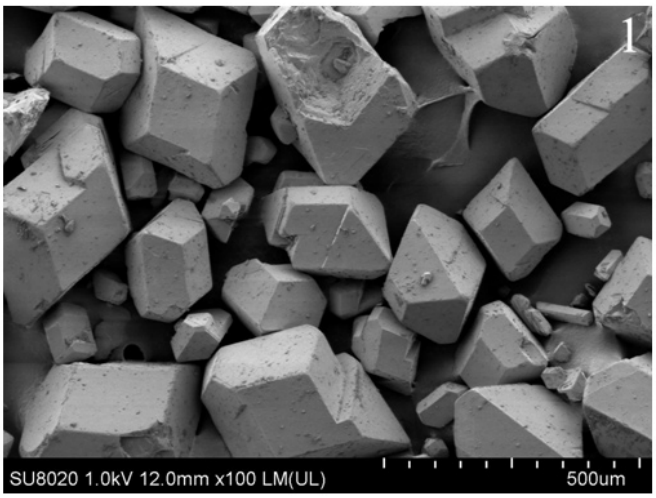
Figure 2 provides SEM images of raw HMX and HMX/ Viton A nanocomposite. In Fig. 2(a), the raw HMX size from 50 μm to 200 μm. The morphology of it is prismatic shape. As is shown in Fig. 2(b), the HMX/Viton A nanocomposite particles are spherical in shape and range from 1 μm to 7 μm in size. The image in Fig. 2(c) shows that the microsphere is composed of many tiny particles. The tiny particles present blocky and sphere, most of these range in size from 100 nm to 200 nm.

3.2 XRD Characterisation

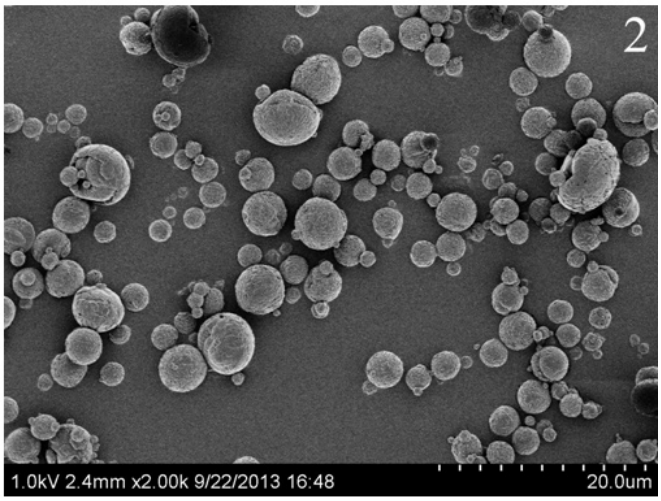
Figure 3 shows that the HMX-1 has similar diffraction angles as raw HMX. The diffraction angles of HMX/Viton A nanocomposite have an offset compared with the raw HMX. It shows that the crystal form of HMX is not changed after spray drying. The addition of Viton A has an influence on the X-ray diffraction angles. Nevertheless, the peaks intensities of HMX-1 and HMX/Viton A become much lower and the width is also widened. It is due to the fact that the X-ray peak was weakened or even disappeared gradually when the crystal size was decreased to nanoscale.

3.3 Thermal Decomposition Characteristics

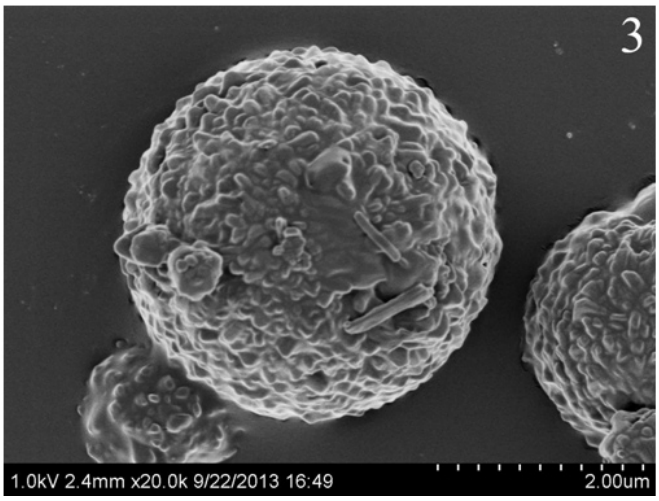
As is shown in Fig. 4, the raw HMX, HMX-1 and HMX/ Viton A samples were tested by DSC at 20 K min^{-1}, 10 K min^{-1}, 5 K min^{-1} heating rates. There is an endothermic peak (277 °C-279 °C) at 20 K min^{-1} and 10 K min^{-1} heating rates in Fig. 4. It implies that HMX start to melt at about 277 °C - 279 °C. Figure 4 shows that the exothermic peak temperatures of raw HMX,



(a)



(b)



(c)

Figure 2. (a) raw HMX (Magnified 100 times), (b) HMX/Viton A (Magnified 2000 times), and (c) HMX/Viton A (Magnified 20000 times).

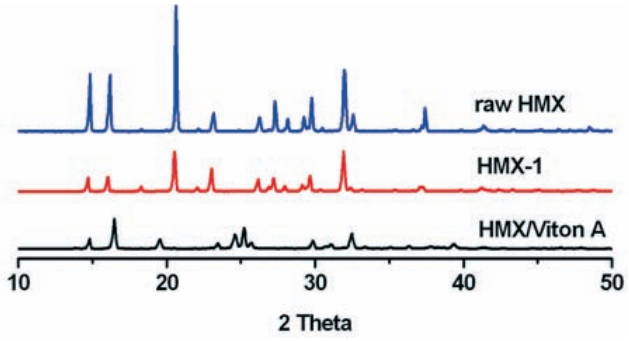


Figure 3. X-ray diffraction spectra of raw HMX, HMX-1 and HMX/Viton A nanocomposites.

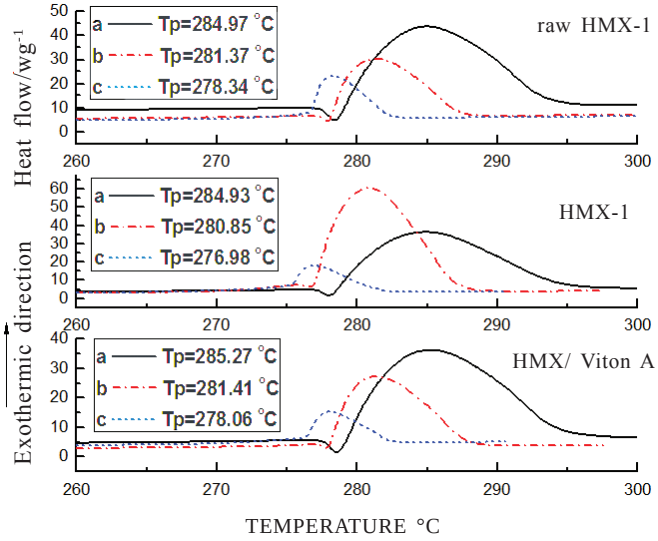


Figure 4. DSC curves of raw HMX, HMX-1 and HMX/ Viton A at heating rates of (a) 20 K min^{-1}, (b) 10 K min^{-1}, and (c) 5 K min^{-1} .

HMX-1, and HMX based nanocomposites decrease with a slower heating rate.

According to the three exothermic peak temperatures under different heating rates, the Kissinger method[18] [Eqn. (1)] can be used to calculate the thermal decomposition kinetics parameters of raw HMX, HMX-1, and HMX/Viton A nanocomposites.

$$\ln\frac{\beta_i}{T_{pi}^2} = \ln\frac{AR}{E} - \frac{E}{RT_{pi}} \quad (1)$$

where T_{pi} is the exothermic peak temperature in DSC curve, K; β_i is the heating rate in K min^{-1}; E is the activation energy in J mol^{-1}; A is the pre-exponential factor; R is the gas constant, 8.314 J mol^{-1} K^{-1}.

When the values of $ln(\beta_i/T_{pi}^2)$ are plotted against values of $1/T_{pi}$, a beeline is acquired (Fig. 5). The activation energy (E) and the pre-exponential (A) factor are calculated from the slope – E/R and the intercept $ln(AR/E)$, respectively. The activation energy of raw HMX, HMX-1, and HMX/Viton A is calculated as 523.16±25.61 kJ mol^{-1}, 435.74±4.98 kJ mol^{-1} and 482.72±17.04 kJ mol^{-1}, respectively. It shows that the activation energy of HMX will

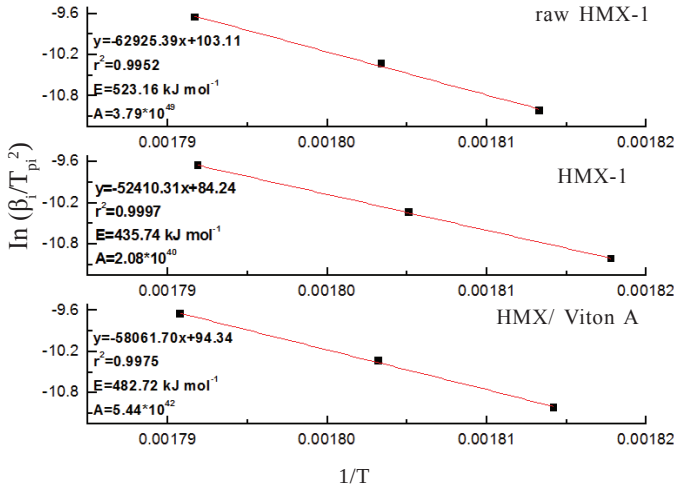


Figure 5. Kissinger's plot of raw HMX, HMX-1 and HMX/ Viton A nanocomposites.

be decreased after spray drying. The addition of Viton A will increase the activation energy.

3.4 Thermal Stability

Thermal stability is another important property of explosives, which can be reflected in shelf life aspects[19,20]. It can be expressed using the self-ignition temperature (T_b), which is evaluated by Eqns (2) and (3)[21, 22].

$$T_e = T_{pi} - b\beta_i - c\beta_i^2 \quad (2)$$

$$T_b = \frac{E - \sqrt{E^2 - 4RET_e}}{2R} \quad (3)$$

where β_i is the heating rate in K min^{-1}; T_{pi} is the peak temperature of decomposition at β_i in K; T_e is the peak temperature when β_i is zero in K; b and c are constants; T_b is the self-ignition temperature in K; E is the activation energy in J mol^{-1}; R is the universal gas constant which is 8.314 J mol^{-1} K^{-1}.

The T_b of raw HMX, HMX-1, and HMX/Viton A is calculated as 279.01 °C, 277.63 °C , and 279.34 °C, respectively. The thermal stability of the HMX-1 decreases compared with that of the raw HMX and HMX/Viton A. It shows that the shelf life of HMX/Viton A nanocomposites is practically longer than HMX-1.

3.5 Impact Sensitivity

Table 1 shows experimental group (EG) that the drop height of HMX-1 is much higher than raw HMX. Compared with that of HMX-1, the drop height of HMX/Viton A is higher. It indicates that the impact sensitivity of HMX will

Table 1. Impact sensitivity of raw HMX and HMX/Viton A nanocomposites

Sample	Impact sensitivity[H_{50} (S)]/cm				
	EG 1 (S)	EG 2 (S)	EG 3 (S)	EG 4 (S)	Average
Raw HMX	17.4 (0.09)	19.0 (0.04)	19.8 (0.06)	18.7 (0.05)	18.7
HMX-1	45.7 (0.06)	44.0 (0.04)	43.5 (0.04)	45.4 (0.03)	44.7
HMX/Viton A	84.9 (0.04)	79.2 (0.05)	80.0 (0.06)	78.3 (0.07)	80.6

decrease after spray drying. Addition of Viton A in the spray dried sample can decrease the impact sensitivity more obvious. This occurs because both nano-size and spherical morphology can reduce the impact sensitivity of the sample. What is more, the Viton A can serve as a diverter or shock absorber under intense impact. As such, the HMX/Viton A nanocomposites can be used in some insensitive munitions.

4. CONCLUSIONS

Using Viton A as a binder, HMX/Viton A nanocomposites were prepared by spray drying method. The nanocomposites which range from 1 μm to 7 μm in size are composed of tiny particles (100 nm - 200 nm). The HMX sample without binder (HMX-1) was obtained by the same spray drying process. The crystal types of HMX-1 and HMX/Viton A agree with raw HMX. The activation energy of HMX/Viton A is lower than that of raw HMX but higher than that of HMX-1. The thermal stability of HMX/Viton A is nearly equal to raw HMX but higher than that of HMX-1. The impact sensitivity of HMX/Viton A is lower than that of HMX-1 and raw HMX. From the above, HMX/Viton A nanocomposites can be used in weapons with high safety requirements.

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