Surface Coating of Cyclotetramethylenetetranitramine (HMX) Particles and Its Property Investigation

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Abstract: To improve the safety of cyclotetramethylenetetranitramine (HMX) particles, the polymer thermoplastic polyurethane elastomer (TPU) and nitrocellulose (NC) were introduced to coat HMX powder by water-solution suspension method and internal solution method, respectively. Scanning electron microscope (SEM) and X-ray photo-electron spectrometry (XPS) were employed to characterize the HMX samples and the role of NC and TPU in the coating processes were discussed. The impact sensitivity, friction sensitivity, and the thermal decomposition of coated HMX particles were investigated, and compared to the unprocessed ones. The results indicate that both TPU and NC can improve the wetting ability of the coating materials on HMX surface and reinforce the connection between HMX and the coating materials. The impact sensitivity and friction sensitivity of HMX samples decrease obviously after they have been surface coated; the drop height (H_{50}) is increased from 35.24 cm to 50.08 cm, and the friction probability is reduced from 93.2 % to 58.3%. The activation energy (E_a) and the self-ignition temperature increase by 10.46 KJ·mol^{-1} and 1.8, respectively.

Keyword: Material chemistry, Surface coating, Thermoplastic polyurethane elastomer, HMX, Safety properties, Thermal decomposition.

1. INTRODUCTION

Nitromine explosives (such as RDX and HMX) have been widely used in propellants and gun propellants due to their high-energy performance, good stability, and low cost. However, they are sensitive to impact and friction stimuli. To lower the sensitivity toward mechanical stimuli, one way is to control the crystal morphology producing mostly spherical particles, while the control process is a little bit difficult for researchers [1-3]. Also another porpular technology, surface coating, was developed to reduce the sensitivity of explosive crystals in recenct years [4]. Up to now, many materials have been used to coat nitromine explosives, such as wax, graphite, stearic acid, and high polymers [5-8]. However, the explosion performance of coated samples has a tendency to decrease because of the introduction of non-energetic materials. In order to solve this problem, the insensitive explosives, *i.e*., 2,4,6-trinitrotoluede (TNT) [9], 3-nitro-1,2,4-triazole-5- one (NTO) [10], and 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) [11] were introduced to coat them. Also, a kind of double-deck composite explosive was prepared via coating RDX with TNT and a plasticizer [12], their experimental results indicated that the mechanical sensitivity was reduced and the energy did not decrease after coating. Thus, several energetic materials were chosen and used to coat HMX and RDX, Nitrocellulose (NC) is one of the important energetic components in solid propellants and explosives, which can improve the mechanical characteristics of isocyanate-cured propellants. ZHANG Wei [13] prepared the RDX particles coated with NC, it was found that the RDX coated with NC (NC@RDX) particles could swell in nitrate ester plasticizers with relatively low swelling rate compared with NC added directly in the plasticizers and NC@RDX can improve the mechanical characteristics of the propellant with maximum tensile strength, elongation at maximum tensile strength, and elastic modules in the temperature range form -40 to +50 ^{o}C. In this work, the polymer thermoplastic polyurethane elastomer (TPU) and nitrocellulose (NC) were introduced to coat HMX to form core-shell structure (TPU@HMX and NC@HMX) and to reinforce the binding force between core and shell. The specific synthesis craft was explored and the safety properties of coated samples were estimated.

2. EXPERIMENTAL

2.1. Materials

HMX, NC, and TPU are provided by Xi'an Modern Chemistry Research Institute of China; Ethanol and

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ethyl acetate are purchased from Shanghai Chemical Ltd. of China.

2.2. Equipment and Characterization

The profiles of HMX and its coated samples are characterized by JSM-5800 scanning electronic microscope (SEM) made in Japan. The element contents on the sample surface were analyzed by PH1-5400 X-ray electron spectrometer made by American PE Co.

Impact sensitivity and friction sensitivity of samples are measured and evaluated with National Army Standard of China. Impact sensitivity is surveyed by the drop hammer apparatus. The experimental conditions are as follows: drop hammer weight, 2 kg; sample mass, (30 ± 1) mg. Friction sensitivity is tested by pendulum friction apparatus made by Xi'an Modern Chemistry Research Institute of China. The experimental conditions are as follows: pendulum weight, 1.5 kg; swaying angle, 66^0, sample mass, (20 ± 1) mg.

The thermal decomposition experiments are carried out with TA instrument made in USA. The conditions of DSC are as follows: sample mass, less than 2.00 mg; the heating rate is 5 ^oC, 10 ^oC, 15 ^oC and 20 $K \cdot min^{-1}$, respectively; N_2 atmosphere. The conditions of TG-DTG experiments are as follows: heating rate, 10 $K \cdot min^{-1}$; sample mass, less than 3.00 mg.

2.3. Preparation of Samples

HMX is coated by water-solution suspension method and the internal solution method, respectively. The main processes are as follows: Firstly, TPU was dissolved in a mixture of ethanol and ethyl acetate, and the HMX powder is slurred in water at about 80 ^oC. Secondly, the solution of coating materials (TPU) is introduced into the slurry slowly. This process is carried out under the condition of stirring sufficiently, until the solvents are removed completely, the temperature is reduced to 50 ^oC. After filtration, rinsing, and evaporation in vacuum at 40 ^oC the coated samples with TPU are fabricated. In addition, about 120 mL water was added into a kettle with impeller inside, and 9 g HMX powder (12.7 um) and 1 g NC (*N*: 11.99 *wt*.-% and M_n: 83×10^3 $g \cdot mol^{-1}$ with degree of polymerization n: 150) were mixed in the kettle for 10 min, then ethyl acetate was added for 30 min, the kettle was vacuumed at 0.094 MPa for 15 min to evaporate the solvent, finally the mixture was released and intensively washed for five times with water at 60 ^oC, dried the sediment of HMX particles at 50 ^oC for seven days, thus, HMX coated with NC particles were obtained.

3 RESULTS AND DISCUSSION

3.1 SEM Characterization and Granularity Distribution of HMX Particles

Unprocessed and coated HMX samples are characterized by SEM, the particle size and size distribution of HMX particles uncoated and coated were determined. The results are shown in Figures **1**, Figures **2** and Table **1**, respectively.

As can be seen in Figure **1**(**a**), there are a lot of irregular particles for the unprocessed HMX particles, and the particle distributions are not disperse evenly. Figure **1**(**b**) shows that the surface coated HMX particles with TPU disperse evenly and their surfaces are quite smooth, most of the coated HMX particles display as spherical or close to spherical shapes, also, there are many small particles are attached to the surface of HMX. Figure **1**(**c**) indicate that the shape of HMX particles are improved greatly, and the particles distributions are more widespread than those of unprocessed particles. Figure **1**(**b**) and (**c**) indicate that

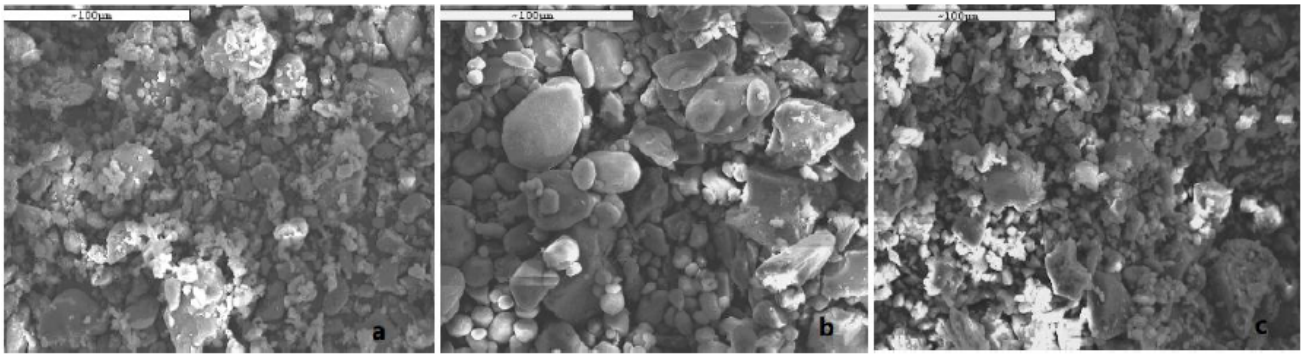

Figure 1: The SEM photograph of unprocessed and coated HMX samples: (a) unprocessed HMX sample; (b) HMX samples coated with 5 wt-% TPU; (c) HMX samples coated with 5 wt.-% NC.

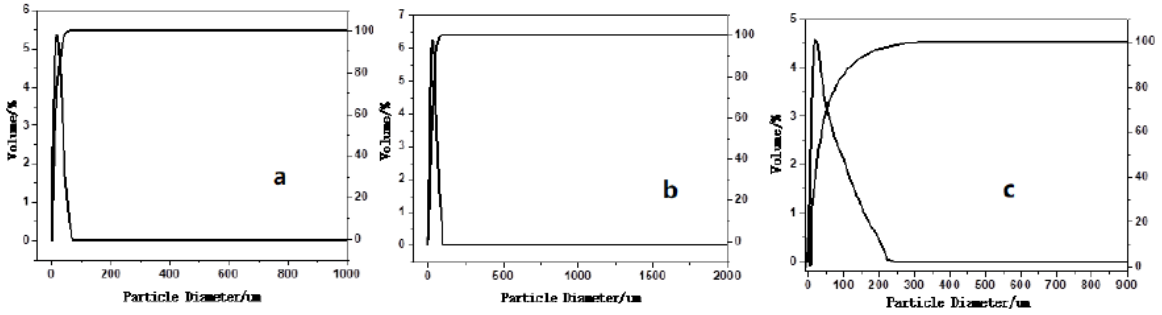

Figure 2: Granularity distribution of unprocessed and coated HMX samples: (a) unprocessed HMX sample; (b) HMX samples coated with 5 wt-% TPU; (c) HMX sample coated with 5 wt.-% NC.

Table 1: Determination of HMX Samples with Different Particle Sizes and Size Distribution

Items	unit	a	b	c
d_{12}	μm	2.653	5.648	4.321
d_{50}	μm	12.755	22.986	20.475
d_{90}	μm	34.097	54.367	81.578
Span	-	2.465	2.120	3.773
Surface area mean	μm	5.327	8.601	7.458
*V*ol. weight mean	μm	15.927	26.965	33.069
Specific surface area	$m^2 \cdot g^{-1}$	1.130	0.698	0.805

d_{10}: particle diameter corresponding to 10 % of the cumulative undersize distribution, μm; d_{50}: median particle diameter, μm; d_{90}: particle diameter corresponding to 90 % of the cumulative undersize distribution, μm; Span= $(d_{90}-d_{10})/d_{50}$; and specific surface area refers to the particle size distribution determined by Malvein Mastersizer.

an obvious coarse layer is continuously distributed over the surface of each particle.

It can be seen from the results in Table **1** that the median particle diameter (d_{50}) increase from 12.755 μm to 22.986 μm, whereas, the specific surface area decrease from 1.13 $m^2 \cdot g^{-1}$ to 0.698 $m^2 \cdot g^{-1}$, respectively. The results indicate that the coated HMX particle sizes are larger than those of uncoated ones.

3.2. XPS Analysis of HMX Particles

The coating degree, *R*, a parameter indicating the coating effect, is estimated according to the mass fraction of *N* [14]. The larger the value of *R* is, the better the coating effect is. Where N_{HMX}, and $N_{sam.}$ are the mass fraction of *N* of the unprocessed and coated samples, respectively. Whose values are listed in Table **2**; N_C is the mass fraction of *N* of coating material calculated by their molecular formula. *R* is the coating degree.

$$N_{HMX}(1\text{-}R) + N_C R = N_{sam.} \quad (1)$$

The surface elementary as fraction of samples is also obtained by XPS, and the surface elementary content of unprocessed and coated HMX samples is characterized by XPS. The results are shown in Table **2**. The XPS results show that by surface coating,

Table 2: XPS Results of HMX Samples

Samples	Mass Fraction of Elements in the Sample Surface/%				Coating Degree(*R*)/%
	NC	Cls	N1s	O1s	
Unprocessed HMX	0	50.13	15.34	28.30	0
Coated HMX with TPU	-	58.24	8.43	32.65	43.87
Coated HMX with NC	12. 42	-	12.16	-	38.52

the mass fraction of *N* decreases from 15.34 % to 8.43 %, which is because the *N* content in the NC and TPU is lower than that of in the HMX. Moreover, the coating degree (*R*) is calculated as 43.87 % and 38.52 %, suggesting that the coating layer is compact.

3.3. Mechanical Sensitivity Analysis

The mechanical sensitivity properties as one of the most important aspects, the impact and friction sensitivity of unprocessed and coated HMX particles are tested and the results are listed in Table **3**. The results of the friction sensitivity test are expressed by the explosion probability (*P*) and the impact sensitivity by the drop height (H_{50}).

From Table **3**, it is found that the greater *P* is, the higher the friction sensitivity is, while the higher H_{50} is, the lower the impact sensitivity is. H_{50} and *P* of unprocessed HMX are 35.24 cm and 93.2 %, respectively, whereas the impact and friction sensitivity of HMX samples coated with different content of NC and TPU decrease. Moreover, they have a tendency to reduce with the increase in coated materials, which has been found by many researchers. They deemed that NC and TPU materials play a buffer and lubrication role when external forces were acted on the coated HMX sample, therefore leading to a reduction in the probability of formation of hot spots [15, 16]. With the increase content of TPU, both the impact and friction sensitivity reach the lowest and H_{50} and *P* are 50.08 cm and 58.3 %, respectively. These sensitivity results are almost the same to the mechanical sensitivity of samples coated with 5.0 w_t-% NC.

3.4. Thermal Decomposition Tests

The thermal stability of explosives is defined as the ability to keep the chemical properties from transforming under the thermal action. It can be expressed by the peak temperature (T_p) and its self-ignition temperature (T_b), which is evaluated by Eq.(2). The values of E_a and *A* are worked out by Kissinger's method (Eq. (3))[17, 18] with DSC data listed in Table **3**.

$$\frac{E}{RT_b^2}(T_b - T_e) = 1 \tag{2}$$

$$\ln\frac{\beta_i}{T_{ei}^2} = \ln\frac{AR}{E} - \frac{E}{RT_{ei}} \tag{3}$$

where T_b is the self-ignition temperature, K; E_a is the activation energy, J·mol^{-1}; β_i is the heating rate, K·min^{-1}; T_{ei} is onset temperature of the decomposition at β_i, *K*; *A* is the pre-exponential factor; and *R* is the gas constant, 8.314J·mol^{-1}·K^{-1}.

The results in Table **4** show that compared with that of unprocessed HMX, the activation energy (E_a) and

Table 3: Mechanical Sensitivity of Unprocessed and Coated HMX with Different Content of TPU and NC

Samples	Content/%		Impact Sensitivity/cm	Friction Sensitivity/%
	TPU	NC	H_{50}	*P*
0	0	0	35.24	93.2
1	2.5	0	46.23	68.5
2	5.0	0	50.08	58.3
3	0.5	0.5	39.67	81.2
4	0	2.5	44. 71	77.1
5	0	5.0	48.33	61.6

Table 4: The DSC Data and Calculated Results

Thermal Data	Unprocessed HMX a				b				c			
β_i/K·min^{-1}	5	10	15	20	5	10	15	20	5	10	15	20
T_{ei}/K												
T_p/K	554.55	558.35	562.15	564.07				564.99				564.55
E_a/J·mol^{-1}	215.64				228.73				232.91			

the self-ignition temperature (T_b) of coated samples b and c increase, respectively. Consequently, the thermal stability of coated samples improves slightly.

Based on the performance analysis of coated HMX particles, the mechanical sensitivity of coated HMX were reduced significantly, which is beneficial to their applications in solid propellants and explosives.

4. CONCLUSIONS

(1) Surface coated HMX particles could be prepared by the water-solution suspension method and the internal solution method, respectively.

(2) Polymer material TPU can improve the wetting ability of the coating material and reinforce the connection between HMX and the coating material NC significantly, which is successfully coated on the surface of HMX.

(3) The impact and friction sensitivities of coated HMX decrease significantly. After coating with 5.0 *wt.*-% content of TPU, the drop height (H_{50}) increases by 42.1 %, and the friction probability (P) reduces by 59.9 %.

(4) The thermal stability of coated samples improves slightly according to the unprocessed ones.

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