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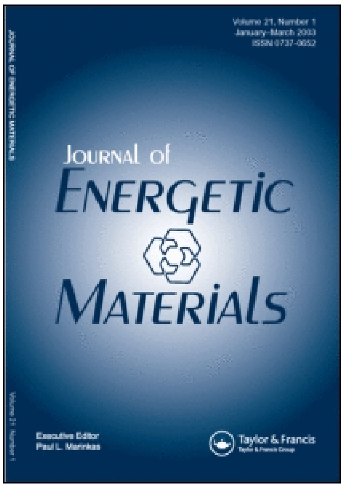

Journal of Energetic Materials

Publication details, including instructions for authors and subscription information:
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Preparation and Safety of Well-Dispersed RDX Particles Coated with Cured HTPB

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To cite this Article An, C. W. , Guo, X. D. , Song, X. L. , Wang, Y. and Li, F. S.(2009) 'Preparation and Safety of Well-Dispersed RDX Particles Coated with Cured HTPB', Journal of Energetic Materials, 27: 2, 118 — 132

To link to this Article: DOI: 10.1080/07370650802405265

URL: http://dx.doi.org/10.1080/07370650802405265

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Journal of Energetic Materials, 27: 118–132, 2009
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ISSN: 0737-0652 print/1545-8822 online
DOI: 10.1080/07370650802405265

Preparation and Safety of Well-Dispersed RDX Particles Coated with Cured HTPB

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HTPB/IPDI (hydroxyl terminated polybutadiene & Isophorone diisocyanate) and TNT (2,4,6-trinitrotoluene) were successively coated on RDX (hexogen) particles by solvent evaporation and aqueous slurry melting, respectively. When HTPB coated on RDX particles cured completely, TNT was removed by solvent dissolution and the well-dispersed RDX particles coated with cured HTPB were obtained successfully. SEM (scanning electron microscopy), TEM (transmission electron microscopy), XPS (X-ray photoelectron spectrometry), and laser granularity measurement were employed to characterize the coated samples, and the mechanical sensitivity and thermal stability were measured and analyzed. Results show that TNT on the outer layer effectively hinders the adhesion among the particles resulting from the curing of inner layer (i.e., HTPB and IPDI). The final coating particles disperse well and their mechanical sensitivity decreases significantly. When the covering amount of HTPB is 2 wt.%, drop height (H_{50}) of RDX increases from 37.2 to 66.5 cm and explosion probability (P) decreases from 92 to 16%. Compared with that of uncoated samples, the activation

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energy and self-ignition temperature of coated samples do not vary.

Keywords: coating, HTPB, mechanical sensitivity, RDX, thermal stability

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Introduction

Nitroamine explosives, such as RDX (hexogen) and HMX (octogen), have been commonly used as a chief explosive ingredient for ammunition; e.g., propellants, shells, depth charges, and bombs. However, they are sensitive to impact and friction stimuli. Under such unwanted initiation, it is easy for explosion to occur[1]. As a rule, sensitivity is taken as the criterion to estimate the hazard of explosive. In particular, impact sensitivity, friction sensitivity, and thermal sensitivity are paid more attention by researchers because they are closely linked with the safety of storage, transportation, and application of explosives [2]. Many factors such as crystal size, crystal shape, crystal size distribution, crystal surface, and crystal defects affect the sensitivity of explosives [3–5]. For bulk of applications, RDX and HMX need a pretreatment to decrease the sensitivity. Some researchers prepared reduced-sensitivity RDX and HMX (RS-RDX and RS-HMX) by recrystallization [6,7]. Another technology, surface coating, was developed to reduce the sensitivity of explosive crystals [8,9]. So far, many materials have been introduced to coat nitroamine explosives, such as graphite [10], stearic acid [11,12], high polymers [13,14], and insensitive explosives [15,16]. However, for some specific applications in nitroamine-filled energetic materials, not all insensitive materials can be selected to coat satisfactorily, because of the possibility to change the formulation of the energetic materials and bring a lot of negative effect, such as loss of energy, decrease of mechanical properties, and deterioration of processability [17]. Therefore, the coating material had better be singled out from the ingredients of nitroamine-filled energetic materials. Moreover, it should be insensitive to nitroamine explosives.

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As a binder with good properties, hydroxyl terminated polybutadiene (HTPB) has been widely used in PBX explosives and composite propellant [18]. For the energetic materials based on HTPB, the desirable coating materials of RDX fillers should be HTPB. Due to its difficulties in curing, however, little has been reported about this study. Our previous research results showed that after coating with HTPB and TDI (2,4-tolylene diisocyanate) via evaporative drying, the mechanical sensitivities of RDX decreased. However, this kind of sample exhibited poor dispersibility due to agglomerations, which limited their application. Herein we use HTPB/IPDI (isophorone diisocyanate) and TNT to coat RDX successively and prepare the double-layer coated particles. After HTPB cures completely, the well-dispersed coated RDX particles are obtained by removing the TNT. In addition, the mechanical sensitivity and thermal stability of coated samples are investigated in this article.

Experimental

Materials

RDX and TNT were provided by Xi'an Modern Chemistry Research Institute of China; HTPB and IPDI were purchased from the Li Ming Chemistry Research Academe of China; ethanol and ethyl acetate, were purchased from Nanjing Chemical Ltd., China.

Equipment and Characterization

The profiles of RDX and its coated sample were characterized by JSM-6380LV scanning electronic microscope made by JOEL Ltd., Germany. The coating film was characterized by a Tecnai 12 transmission electron microscope (TEM) made by Philips, the Netherlands. Particle size and size distribution of samples were measured using a Mastersizer Instrument, by Malvern Ltd., England. A PHI-5400 X-ray electron spectrometer made by American PE Corporation was used to analyze the element content on the sample surface. Impact sensitivity and friction sensitivity of samples were measured and evaluated using the

National Army Standard of China [20]. Impact sensitivity was surveyed by a drop hammer apparatus made by De Kong Corporation, China. The experimental conditions were as follows: the drop hammer weight, 2 kg; sample mass, 30 ± 1 mg. Friction sensitivity was tested by an MGY-1 pendulum friction apparatus made by 213 Research Institute of China. The experimental conditions were as follows: the pendulum weight, 1.5 kg; swaying angle, 90°; sample mass, 20 ± 1 mg. The DSC experiments were carried out with a Q600 instrument supplied by American TA Ltd. The conditions of DSC are as follows: sample mass, less than 2.00 mg; heating rate, 5, 10, $20°\mathrm{C} \cdot \mathrm{min}^{-1}$; N_2 atmosphere ($50\,\mathrm{mL} \cdot \mathrm{min}^{-1}$).

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Fabricated Procedure

The fabricated procedure included three steps. The first was to coat with HTPB and IPDI, the second was to coat with TNT, and the last was the removal of TNT.

RDX was coated with HTPB and IPDI by means of solvent evaporation. Four grams (or 2 g) HTPB and 0.4 mL (or 0.2 mL) IPDI were dissolved in ethyl acetate (50 mL) first, and then 200 g RDX powders were added into the HTPB/IPDI solution. In vacuum condition, the ethyl acetate was distilled at 45°C. After evaporation completed, the coated particles were put into a vacuum oven at 50°C for 12 h.

In the second step, an aqueous slurry-melting method was used. Firstly, 20 g of TNT was added into 500 mL of water in a reactor vessel and heated in water bath to 85°C. With sufficient stirring, liquid TNT and water can form an emulsion. Secondly, the coated RDX samples prepared in step 1 were added into the TNT-water emulsion. Then, the temperature was reduced to 50°C at a cooling rate of $10°\mathrm{C} \cdot \mathrm{min}^{-1}$, at which TNT will precipitate from the emulsion and coat onto the outer layer of RDX particles. After filtration, washing, and evaporation, the coated samples were put into an oven and cured for 7 days at 60°C. Finally, the double-layer coated samples were fabricated.

After HTPB was cured completely, the coated samples were added into 100 mL ethanol. With the 5-min ultrasonic

Table 1
Content of coating materials in coated RDX samples

Sample ID	HTPB (%)	IPDI (%)	TNT (%)
Coated sample 1	1	0.1	10
Coated sample 2	1	0.1	0 (removed)
Coated sample 3	2	0.2	10
Coated sample 4	2	0.2	0 (removed)

oscillation, TNT coated on the outer layer can be dissolved in ethanol. After filtration and evaporation, the dispersive RDX particles coated with cured HTPB were prepared. According to the addition amount of coating materials, four coated samples were fabricated and details of the samples are listed in Table 1.

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Results and Discussion

SEM Characterization

Samples before and after surface coatings are characterized by SEM and the results are shown in Fig. 1.

As can be seen in Figs. 1a and 1b, the uncoated RDX particles with smooth and clean surfaces disperse well. Figures 1c and 1d show that after coating with cured HTPB and TNT, the surface of RDX becomes coarse due to the adhesion of many rod-like materials, which may relax the agglomerations that result from the adhesive property of the HTPB/IPDI layer. As these tiny rods were removed, a kind of well-dispersed powder was exhibited, shown in Figs. 1e and 1f, in which an obvious film is continuously distributed over the surface of each particle.

TEM Characterization

To further study the cured HTPB layer coated onto RDX particles, TEM was employed to characterize the uncoated RDX and coated sample 4. Figure 2 shows that the layer imaged in

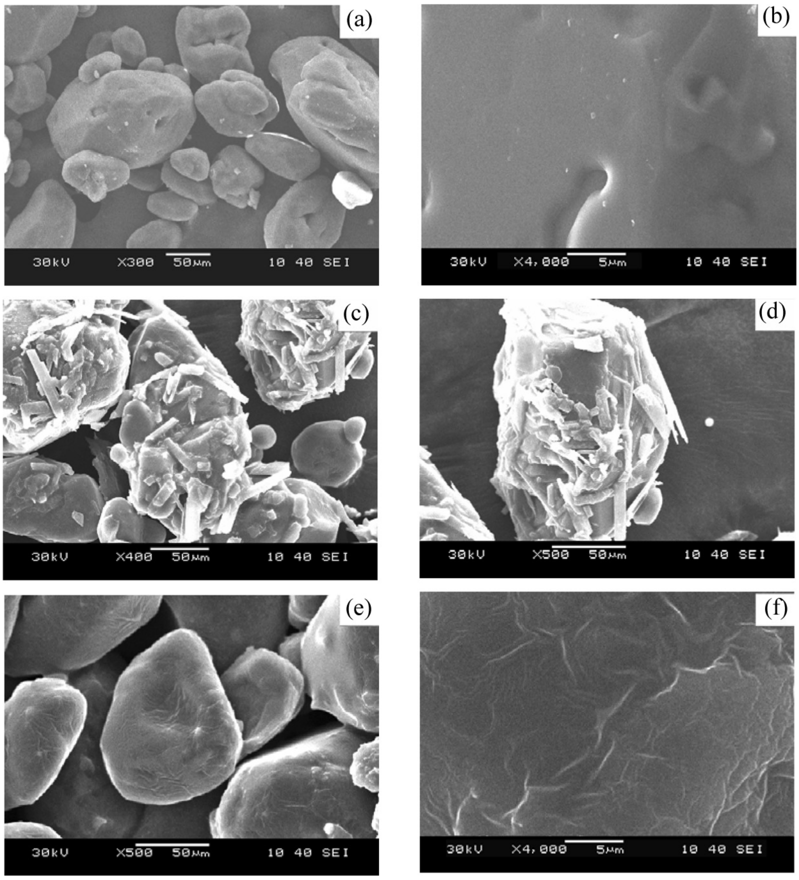

Figure 1. SEM images of samples: (a) and (b): uncoated RDX sample at different magnifications; (c) and (d): coated sample 3 at different magnifications; (e) and (f): coated sample 4 at different magnifications.

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Figs. 1e and 1f is evenly coated on the surface of RDX particles and its thickness is less than 500 nm.

Particle Size Analysis

Particle size and size distribution of uncoated and coated samples were also tested. The results are shown in Fig. 3.

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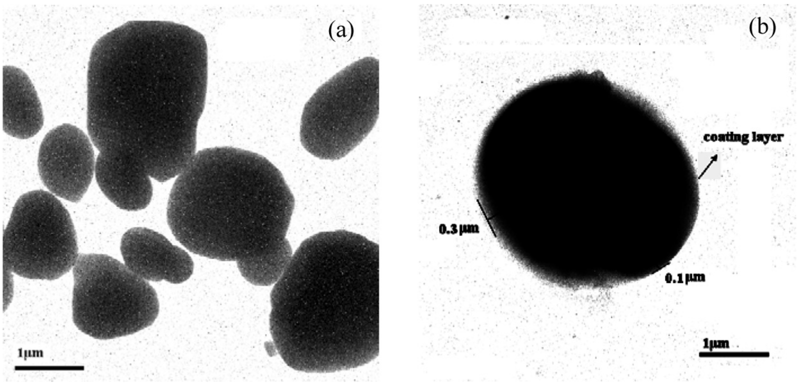

Figure 2. TEM images of samples: (a) uncoated RDX; (b) coated sample 4.

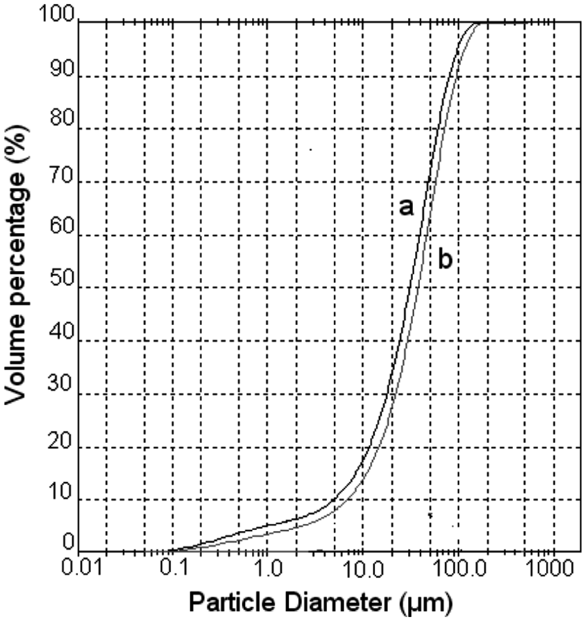

Figure 3. Particle size distribution of samples: (a) uncoated RDX ($D_{50} = 37.20\,\mu\text{m}$); (b) coated sample 4 ($D_{50} = 37.93\,\mu\text{m}$).

From Fig. 3, it can be seen that the median size (D_{50}) of coated RDX is larger by 0.73 µm than that of raw sample. Moreover, the cumulative distribution curves of the two samples are almost similar. These results also prove that each RDX particle is evenly covered by a film and the coated particles are well dispersed.

XPS Analysis

The surface elementary contents of uncoated and coated RDX samples were characterized by XPS. The XPS spectra are shown in Fig. 4 and the surface elementary mass fractions of samples are listed in Table 2.

Table 2 shows that the mass fraction of N element decreases from 33.81 to 16.52% by means of double-coating with cured HTPB and TNT. After removing TNT, the mass fraction of N element of coated sample 4 decreases further and reaches 4.4%. The main reason for the variation is that N element content of TNT is lower than that of RDX and there is no N element in HTPB molecule.

From the spectra in Fig. 4, it can also be observed that the peak height and area of N1s vary distinctly by surface coating. Figure 4a shows that two separated N1s peaks, almost equal in the height and area, are in the XPS spectra of RDX. The results are consistent with the research of Cowey and coworkers [9]. The studies by Cowey have concluded that the left peak describes the N element in nitro group (-NO_2) and the right represents the N element in the amine nitrogen (-N-) of RDX. It was found that the left N1s peak is higher than the right in Fig. 4b, which is due to the fact that the molecular structure of TNT has -NO_2 but no -N-. This further indicates that TNT is coated onto the outer layer of coated sample.

Mechanical Sensitivity

Impact and friction sensitivity were tested and the results are summarized in Table 3. The results of friction sensitivity are expressed by explosion probability (P) and its confidence interval (P_l,P_u), and impact sensitivity is expressed by drop height

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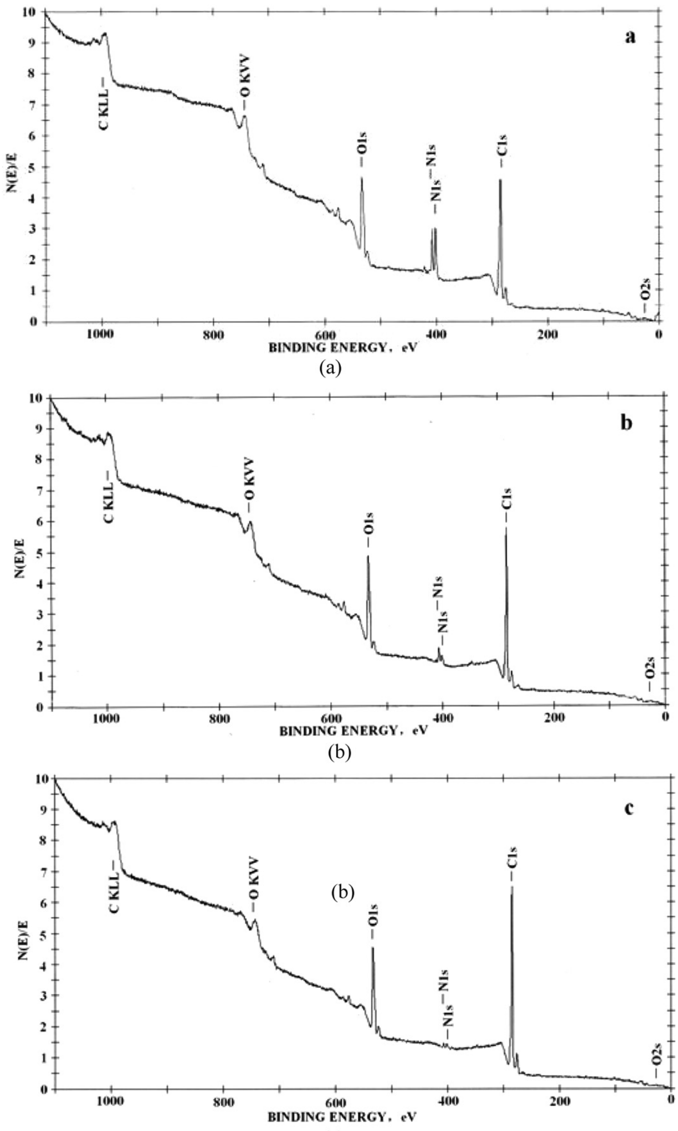

(a)

(b)

(c)

Figure 4. XPS spectra of samples: (a) uncoated RDX sample; (b) coated sample 3; (c) coated sample 4.

Table 2
Surface elementary mass fraction of uncoated and coated RDX samples

	Mass fraction of elements in the sample surface (%)		
Samples	C1s	N1s	O1s
Uncoated RDX	34.26	33.81	31.93
Coated sample 3	49.65	16.52	33.83
Coated sample 4	56.34	4.40	38.26

(H_{50}) and standard deviation (S). The greater P is, the higher the friction sensitivity is, whereas the higher H_{50} is, the lower the impact sensitivity is.

From Table 3 it is found that the H_{50} and P of uncoated RDX are 37.2 cm and 92%, respectively. By such coating with cured HTPB, the impact and friction sensitivity of RDX decrease significantly. When the covering amount of HTPB is 2 wt.%, drop height (H_{50}) increases to 66.5 cm and explosion probability (P) decreases to 16%. These results show that HTPB has an insensitive effect on RDX, which can be interpreted by "hot spots" theory. Under mechanical stimuli, the formation of hot spots is attributed to friction among explosive particles, the explosive crystal defects, and the transformation efficiency of thermal energy from mechanical energy [21]. HTPB coated on RDX surface can

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Table 3
Mechanical sensitivity of uncoated and coated RDX samples

	Impact sensitivity		Friction sensitivity	
Samples	H_{50} (cm)	S	P (%)	(P_l, P_u)
Uncoated RDX	37.2	0.15	92	(0.81, 0.98)
Coated sample 2	51.2	0.17	44	(0.30, 0.59)
Coated sample 4	66.5	0.12	16	(0.07, 0.29)

prevent the friction among explosive particles and provide a shock absorber or diverter under the mechanical stimuli, which therefore leads to a reduction in the probability of forming hot spots.

Thermal Stability

The thermal stability of an explosive is defined as the ability to keep the chemical properties from transforming under thermal action. It can be expressed by its self-ignition temperature (T_b), which is evaluated by Eq. (1) [22,23]. The value of activation energy (E) is worked out by Kissinger's method (Eq. (2)) with DSC data collected at every two heating rates; the DSC thermographs are shown in Fig. 5. The final activation energy (E_{equal}) of each sample is expressed as an average value of E, which is obtained from Eq. (3). These calculation results are listed in Table 4.

$$\frac{E_{equal}}{RT_b^2}(T_b - T_c) = 1 \tag{1}$$

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

$$E_{equal} = \frac{E_{(5-10K\cdot min^{-1})} + E_{(5-20K\cdot min^{-1})} + E_{(10-20K\cdot min^{-1})}}{3 \times 1000} \tag{3}$$

where $\mathrm{T_b}$ is the self-ignition temperature, K; E_{equal} is the final activation energy, $\mathrm{kJ \cdot mol^{-1}}$; $E_{(5\text{–}10\mathrm{K\cdot min^{-1}})}$, $E_{(5\text{–}20\mathrm{K\cdot min^{-1}})}$ and $E_{(10\text{–}20\mathrm{K\cdot min^{-1}})}$ are the activation energies calculated from Eq. (2), $\mathrm{J \cdot mol^{-1}}$; β_i is heating rate, $\mathrm{K \cdot min^{-1}}$; T_{ei} is the onset temperature of decomposition at β_i, K; A is the preexponential factor; and R is the gas constant, $8.314\,\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$.

As is seen in Fig. 5 and Table 4, the activation energy and self-ignition temperature are $135.02\,\mathrm{kJ \cdot mol^{-1}}$ and $496.22\,\mathrm{K}$, respectively. For coated samples with cured HTPB, E_{equal} and T_b do not vary obviously, which implies that such surface coating has no effect on thermal stability of RDX.

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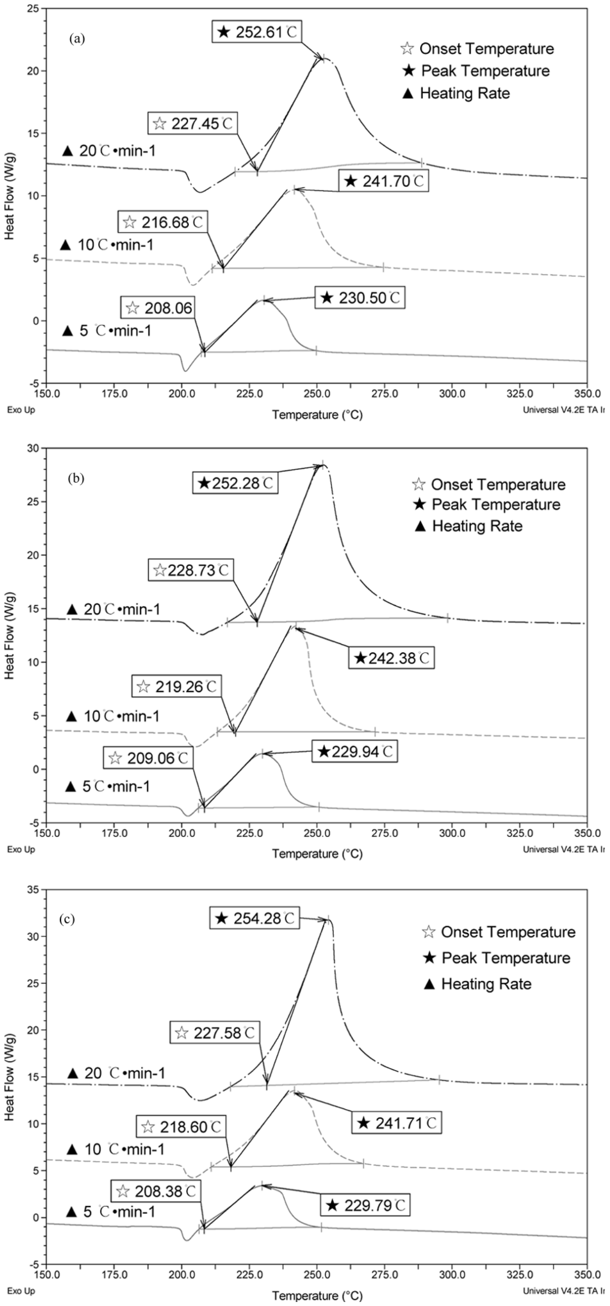

Figure 5. DSC thermographs of samples: (a) uncoated RDX; (b) coated sample 2; (c) coated sample 4.

Table 4

Activation energy and self-ignition temperature of coated and uncoated RDX samples

Samples	$\beta_i(\mathrm{K \cdot min^{-1}})$	T_{ei} (K)	$\bar{E}(\mathrm{kJ \cdot mol^{-1}})$	T_b (K)
Uncoated RDX	5	481.06	135.02	496.22
	10	489.68		
	20	500.45		
Coated sample 2	5	482.06	135.04	497.28
	10	492.76		
	20	501.73		
Coated sample 4	5	481.38	136.29	496.41
	10	491.60		
	20	500.58		

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Conclusions

By coating HTPB/IPDI and TNT successively, double-layer coated RDX particles are fabricated successfully. This coating method effectively prevents the agglomerations resulting from the HTPB/IPDI layer. After the removal of TNT, the well-dispersed RDX samples coated with cured HTPB are prepared. The mechanical sensitivity results show that both impact and friction sensitivity of RDX decrease significantly by surface coating. When the covering amount of HTPB was 2 wt.%, the drop height increased by about 79% and the explosion probability decreased by 76%. In addition, because of no change in the self-ignition temperature and activation energy, the thermal stability does not vary obviously by surface coating. Besides, this fabrication method has other advantages, such as facility, safety, and low cost, which provide the conditions for industrial production.

Acknowledgment

The authors gratefully acknowledge the financial support of the National Defense Fund (62301070203) and the National Natural Science Fund of China (50602024).

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