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Research paper

An Insensitive Booster Explosive: DAAF Surface-coated with Viton A

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Abstract: 3,3'-Diamino-4,4'-azoxyfurazan (DAAF) is the principal component of an insensitive booster explosive; refined DAAF and DAAF surface-coated with Viton A were prepared. Scanning electron microscopy (SEM), X-ray diffraction (XRD), and differential scanning calorimetry (DSC) were employed to characterize the morphology, composition, and thermal decomposition of these samples. The impact sensitivity and theoretical detonation velocity of DAAF-based composites were also measured and analyzed. The results showed that DAAF surface-coated with Viton A was successfully obtained, and the impact sensitivity of DAAF/Viton A composites was much lower than that of crude DAAF. In addition, DAAF/Viton A composites exhibited better thermal stability compared to crude DAAF and refined DAAF. The theoretical detonation velocity of DAAF/Viton A composites and TATB/Viton A composites are roughly the same. Therefore, there is still great potential for DAAF to be used as the main explosive component of a booster explosive.

Keywords: DAAF, refinement, surface-coated, thermal analysis, impact sensitivity

Supporting information (SI) available at:
http://www.wydawnictwa.ipo.waw.pl/CEJEM/contents/2018/vol-15-no-3.html

1 Introduction

Booster explosives play an important role in transmitting and expanding the detonation in an ammunition explosion sequence [1]. Research on the performance of new types of booster explosives has received wide attention. In the 1970s, the PBXN-5 booster explosive was first prepared by scientists in the US, in which HMX was used as the main explosive with Viton as the binder [2]. By the end of the twentieth century, PBXN-5 was the most energetic booster explosive. More recently, more stringent requirements for insensitivity and high-energy have been proposed by researchers of booster explosives. Therefore, experts mainly use TATB as the main explosive, and a series of TATB-based insensitive booster explosives has been prepared. In 2002, Wang [3] prepared a new type of booster explosive for JHB-1 in which the main components were TATB and RDX. In 2007, a new type of booster explosive formulation, mainly using HMX and TATB as the main explosives prepared by a solution-water suspension method, was reported by Wang [4].

Because the synthesis of TATB would cause serious environmental pollution and safety problems, alternatives to TATB are sought. Since Sheremeteev *et al*. synthesized 3,3′-diamino-4,4′-azoxyfurazan (DAAF) at the Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences [5, 6], its excellent heat resistance, high standard enthalpy of formation, low sensitivity and small critical diameter have exhibited obvious superiority in terms of energy and safety. It may be seen from Table 1 that both DAAF and TATB have similar advantages in energy and safety, but the synthetic process to DAAF is simpler, greener and more eco-friendly than that to TATB. Therefore, DAAF is expected to be used in place of TATB as the main explosive in insensitive booster explosives.

Table 1. Performance comparison of DAAF and TATB

Compound	ΔH_f [kJ·mol^{-1}]	D [km·s^{-1}]	P [GPa]	Critical diameter [mm]	m.p. [°C]	H_{50} (2.5 kg) [cm]
DAAF	+443	8.02	29.9	<3	250	>320
TATB	−154.2	7.96	25.9	~9	330	>320

Note: ΔH_f - standard enthalpy of formation; D - detonation velocity; P - explosion pressure; m.p. - melting point.

In order to explore DAAF as a main explosive in an insensitive booster explosive, this study prepared DAAF surface-coated with Viton A. The morphology, thermal decomposition, and impact sensitivity of samples

(crude DAAF, refined DAAF and DAAF surface-coated with Viton A) were investigated and compared.

2 Experimental

2.1 Materials

Dimethyl sulfoxide (AR) and ethyl acetate (AR) was purchased through Sinopharm Chemical Reagent Co. Ltd. Crude DAAF was prepared in-house. Viton A was purchased from Kunshan Jieerxing Insulation Products Co. Ltd.

2.2 Refinement of DAAF

Crude DAAF (2 g) was completely dissolved in dimethyl sulfoxide (15 mL); the colour of the solution was red. The DAAF solution was added to distilled water (300 mL) using a peristaltic pump during 20 min, while the solution was stirred at a specified rate. After being filtered off and washed, the DAAF obtained was dried using a freeze dryer. Figure 1 displays the experimental arrangement.

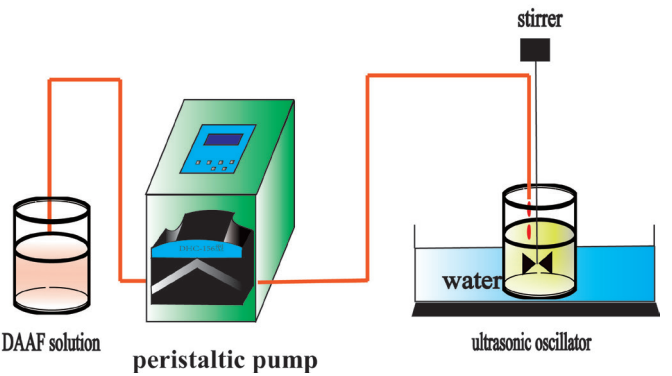

Figure 1. Diagram of the experimental equipment used for the preparation of refined DAAF

The temperature of the solution affects the solute solubility and the chemical reaction [7]. The solubility and the chemical reaction are the necessary conditions for crystal growth. The temperature of the solution is the most important factor and determines the recrystallization refinement. The main proposal here was varying the temperature of the DAAF solution (0, 35 and 55 °C) for this experiment.

2.3 Preparation of DAAF-based composites

The experimental procedure was: Viton A (1 g) was added to ethyl acetate to form a solution at a concentration of 5 wt%. Then, the refined DAAF (19 g) was added to water while stirring. The solution of Viton A was slowly injected into the DAAF solution. The system was then stirred for a few minutes in a heated thermostatic water bath at 60 °C and under a pressure of 0.04 MPa until the solvent (ethyl acetate) had been completely removed. After cooling, filtering, washing, and evaporation in a vacuum, DAAF surface-coated with Viton A was obtained [8]. Figure 2 illustrates the experimental equipment.

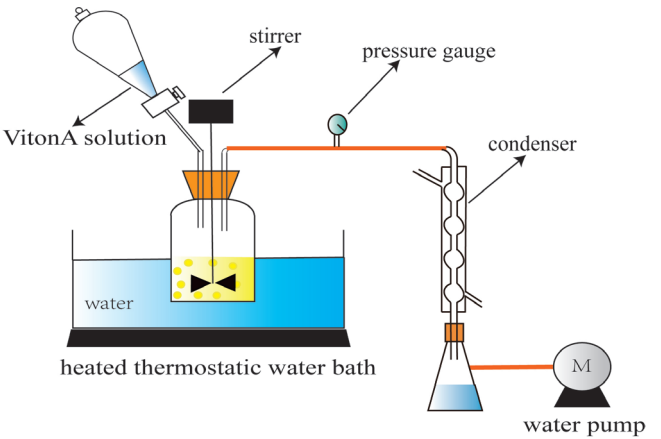

Figure 2. Experimental equipment for the preparation of the DAAF-based composites

2.4 Characterization

The particle size and surface morphology of the DAAF and DAAF-based composites were measured using scanning electron microscopy (SEM, SUPRATM55, Zeiss, German).

An Explorer X-ray diffractometer (LEEMANCHINA Composites, Italy) was used to analyze the crystalline form of the DAAF and DAAF-based composites at a voltage of 40 kV and a current of 30 mA using Cu K_α radiation.

The DAAF and DAAF-based composites were analyzed using a DSC-500A differential scanning calorimeter (Shanghai Yingnuo Precision Instrument Corporation, Shanghai, China).

The impact sensitivity was measured with a 12-type drop hammer impact device. The special height (H_{50}) indicates that a drop of 2.5 kg at this height will cause explosion in 50% of the trials. 25 drop tests were conducted to calculate H_{50} [9].

3 Results and Discussion

3.1 Morphological and size characterization

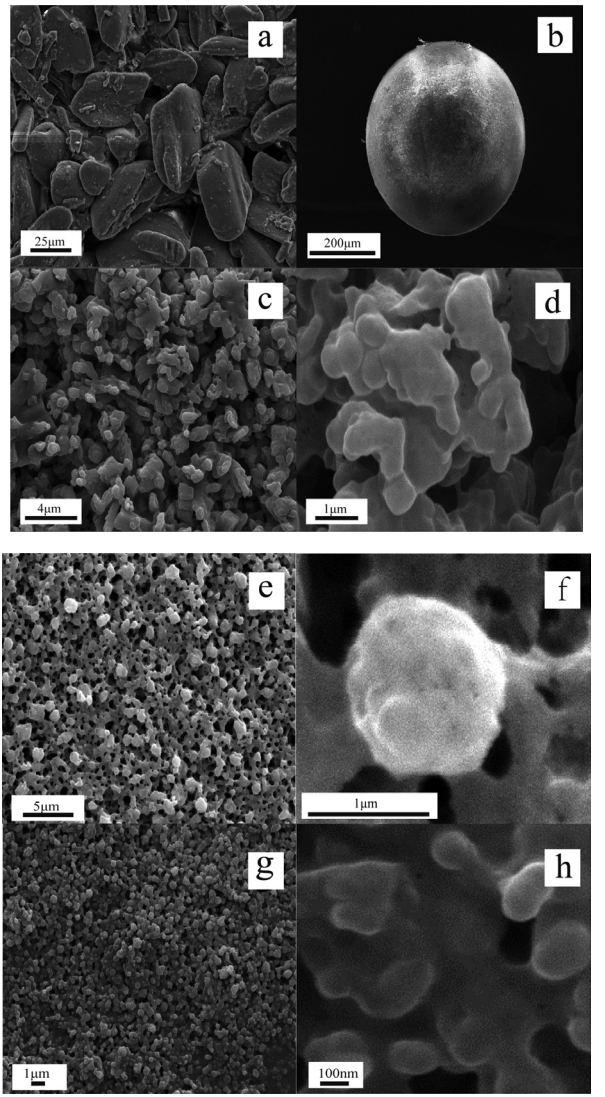

Figure 3. SEM images of (a) crude DAAF, (b) DAAF/Viton A, (c and d) refined DAAF #1, (e and f) refined DAAF #2, and (g and h) refined DAAF #3

The morphology and structure of the samples (crude DAAF, refined DAAF and DAAF surface-coated with Viton A) were examined by SEM and the results are illustrated in Figure 3. Figure 3a shows an image of crude DAAF. The crude DAAF had short rod-like shape with an average size of ~30 μm. Figures 3c and 3d show images of refined DAAF #1 (temperature of the DAAF solution was 55 °C). The phenomenon of aggregation was obvious. Figures 3e and 3f show images of refined DAAF #2 (temperature of DAAF solution was 35 °C). The refined DAAF #2 had an oval morphology with an average size of ~1.5 μm. Figures 3g and 3h show images of refined DAAF #3 (temperature of DAAF solution was 0 °C). The refined DAAF #3 had an oval morphology with an average size of ~300 nm whose scale and surface were smaller and smoother than those of crude DAAF and refined DAAF #2. It may be clearly seen that refined DAAF #3 was the best refinement. The temperature of the solution has a great influence on the size and shape of the crystals. When the temperature is raised, the viscosity of the solution is reduced and the coefficient of mass transfer, crystal growth rate, and particles are increased. However, a low temperature is more conducive to the formation of nuclei and not conducive to the growth of the nuclei.

The particle size of DAAF surface-coated with Viton A was about 450 μm, and its spherical shape and smoothness may be seen in Figure 3b. It was evident that the surface of the DAAF had a dense protective layer after the DAAF had been coated with Viton A. We concluded that DAAF was effectively coated with Viton A.

3.2 XRD analysis

The crystal form of the crude DAAF, refined DAAF #3 and DAAF surface-coated with Viton A were characterized by XRD. Figure 4 shows the results, and it was clear that the main diffraction peaks of the crude DAAF were located at 12.65°, 17.87°, 18.65°, 20.33°, 26.21°, and 28.01°. All of the diffraction peaks (diffraction angles) of the refined DAAF #3 and DAAF surface-coated with Viton A were consistent with the diffraction peaks of the crude DAAF, which indicated that the crystal structure of DAAF was not changed by the refinement process and the preparation of DAAF-based composites.

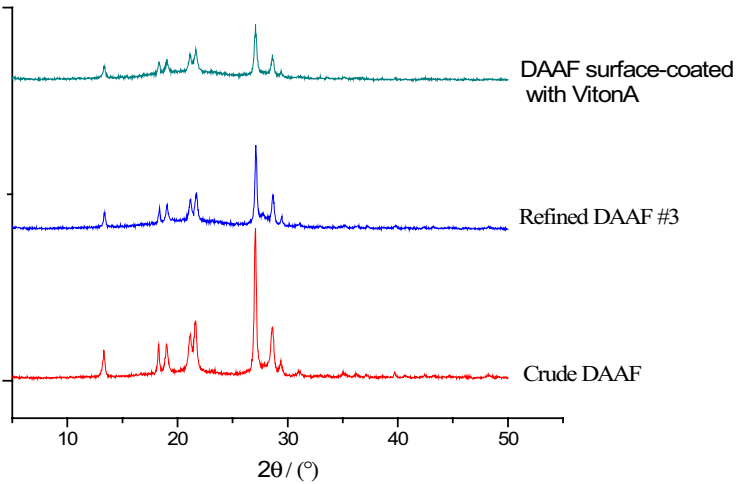

Figure 4. X-ray diffraction patterns of crude DAAF, refined DAAF #3 and DAAF surface-coated with Viton A

3.3 DSC analysis

In order to obtain the thermal behaviour of these samples (crude DAAF, refined DAAF #3 and DAAF surface-coated with Viton A), they were analyzed by DSC with linear heating rates of 5 °C·min^{-1}, 10 °C·min^{-1}, 15 °C·min^{-1} and 20 °C·min^{-1}, in a flowing N_2 atmosphere (flow rate 20 mL·min^{-1}). The results are shown in Figure 5. These three DSC curves indicated that as the heating rate was increased from 5 °C·min^{-1} to 20 °C·min^{-1}, the decomposition temperature kept increasing.

The apparent activation energy (E), and the pre-exponential factor (A) were determined by Kissinger's method [10], Ozawa's method [11] and Starink's method [12]; the results are listed in Table 2. The critical temperature of thermal explosion (T_b), the value of the peak temperature corresponding to $\beta \rightarrow 0$ (T_{P0}), $\Delta S^{\neq}$, $\Delta H^{\neq}$ and $\Delta G^{\neq}$ of the samples were then calculated and are listed in Table 2 (also see SI).

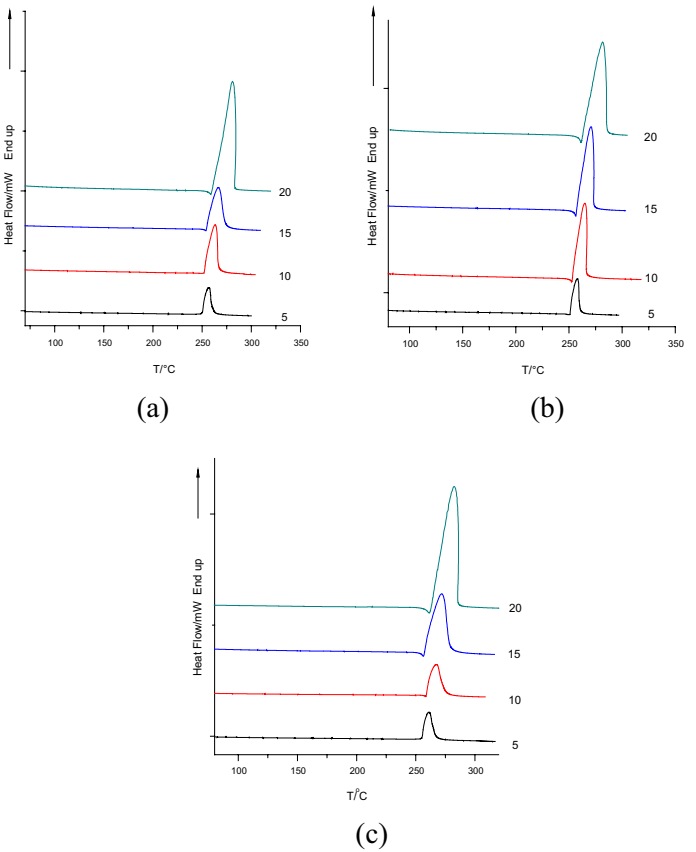

Figure 5. DSC curves for (a) crude DAAF; (b) refined DAAF #3; (c) DAAF surface-coated with Viton A

Table 2. Thermal decomposition kinetic parameters of crude DAAF, refined DAAF #3 and DAAF surface-coated with Viton A

	Crude DAAF	Refined DAAF #3	DAAF surface-coated with Viton A
T_P of β (5, 10, 15, 20) [°C·min^{-1}]	256.7 263.3 266.1 280.8	257.9 264.8 270.9 281.6	261.2 267.4 271.9 282.5
Kissinger's method: E [kJ·mol^{-1}] lg$A$	 121.35 8.49	 131.3 9.4	 147.3 10.97

	Crude DAAF	Refined DAAF #3	DAAF surface-coated with Viton A
Ozawa's method: E [kJ·mol^{-1}]	130.37	140.3	156.36
Starink's method: E [kJ·mol^{-1}]	122.25	132.3	148.21
T_{P0} [°C]	230.6	244.8	245.5
T_b [°C]	248.77	260.67	261.26
$\Delta S^{\neq}$ [J·K^{-1}·mol^{-1}]	−95.06	−77.87	−47.82
$\Delta H^{\neq}$ [kJ·mol^{-1}]	117.16	126.99	142.99
$\Delta G^{\neq}$ [kJ·mol^{-1}]	165.05	167.32	167.79

As listed in Table 2, the T_{P0}, E and T_b values of refined DAAF #3 are higher than those of crude DAAF. These results indicated that after refinement of DAAF, the effect on the thermal decomposition was obvious, showing that refined DAAF #3 was more stable than crude DAAF. For the DAAF surface-coated with Viton A compared to crude DAAF, the T_{p0}, E and T_b values had increased by 14.9 °C, 25.95 kJ·mol^{-1}, 12.49 °C, respectively, because during decomposition heat transfer between the DAAF crystals is affected by the DAAF being coated with Viton A. These results showed that Viton A as a binder conferred better thermal stability.

3.4 Impact sensitivity and theoretical detonation velocity

To obtain the DAAF safety performance, an impact sensitivity test was performed, and the results are listed in Table 3. The drop height (H_{50}) of crude DAAF was 320 cm, while, with the introduction of Viton A, the impact sensitivity of DAAF surface-coated with Viton A was decreased. This observation can be attributed to the fact that because of its large specific surface area, Viton A can form a dense layer on the DAAF surface and transmit heat between each DAAF crystal under the impact stimulus. Therefore, fewer "hot spots" would be generated, which could lead to a highly reduced impact sensitivity [13]. According to Table 3, we may draw the conclusion that both TATB and DAAF are extremely insensitive explosives.

Table 3. Impact sensitivity of crude DAAF, DAAF/Viton A and crude TATB

Samples	Impact sensitivity (H_{50}) [cm]
Crude DAAF	320
DAAF/Viton A (95/5)	340
Crude TATB [14]	320

Using the Urizar method [15, 16], DAAF/Viton A (95/5) and TATB/Viton A (95/5) gave theoretical detonation velocities of 7498 $m \cdot s^{-1}$ and 7430 $m \cdot s^{-1}$, respectively, these values being approximately equivalent (see Table S1 in SI). Therefore, the potential for DAAF as a booster explosive is better.

4 Conclusions

A new insensitive and high-energy booster explosive (DAAF surface-coated with Viton A) has been prepared by a solvent-slurry method. According to SEM and XRD analysis, 5% Viton A provided a perfect cladding layer for DAAF. In addition, Viton A enhanced the thermal stability of DAAF according to the DSC results. The impact sensitivity of DAAF surface-coated with Viton A was reduced relative to crude DAAF. DAAF/Viton A and TATB/Viton A have approximately equivalent detonation velocities. The synthetic process for DAAF is simpler, greener and more eco-friendly than that for TATB. Therefore, there is still great potential for DAAF to be used as the main explosive in booster explosives.

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