Desensitization of nitramine explosives with reserved high energy

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Abstract:

Nitramine explosives, such as exanitrohexaazaisowurtzitane (CL-20), cyclotetramethylenetetranitramine (HMX) and cyclotrimethylenetrinitramine (RDX), are commonly known as the most representative high energy density materials in today's energetic world, has attracted considerable research interests for a number of military applications. In particular, explosives or propellants containing CL-20 are expected to improve the performance in specific impulse, burning rate, detonation pressure and detonation velocity. Unfortunately, strong limitations to the application of nitramine explosives caused by the high sensitivity under impact, friction and other external stimulations. The uniform coating of some insensitive agents on the explosive surface provides an effective route to the desensitization. Plenty of efforts have been devoted to explore the CL-20, HMX and RDX based polymer bonded explosives (PBXs). Nevertheless, the sensitivity of such PBXs is still too high, and large-scale use of inert additives will lead to the apparent energy loss.

To reduce the sensitivity of explosives with high energy reserved, an exploration of core-shell structure by coating the insensitive explosives on the surface of sensitive explosives seems rather attractive. Although some decrease of impact sensitivity was obtained, the most serious problem is the self-nucleation of shell materials during the crystallization coating process, and the thickness of the shell layer is difficult to control. Therefore, exploring new strategies to reduce the mechanical sensitivity of nitramine explosives with reserved high energy is of great significance for its application.

In this paper, investigation on reducing the mechanical sensitivity of nitramine explosives (e.g. CL-20) was carried out via several new strategies, which exhibit efficient desensitization capability. High energy can be reserved because only a small amount of non-energetic desensitizers were used. In situ core-shell coating by energetic desensitizer 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) and microencapsulation of resins via in situ polymerization were proved as effective techniques to reduce the sensitivity. Furthermore, in order to obtain an insensitive polymer bonded explosive (PBX) containing more than 90% explosives, a novel route involved multilevel and tridimensional desensitization was explored. The CL-20 based PBX composites exhibit excellent detonation and safety performances. With the tridimensional introduction of TATB, composites containing more than 90% CL-20 display the detonation velocity of >9000m/s and fairly low sensitivity. Besides, very recently, we also raised a novel desensitization route by embedding organic dye molecule into the crystal structure of nitramine explosives, resulting markedly reduced sensitivity with extremely low content

of additives adopted. Such high energy and low sensitivity as obtained are definitely significant for the application of CL-20, HMX and RDX in munitions, especially for the effective destructibility in modern weapons.

Keywords: Desensitization; CL-20; high energy; coating; tridimensional

1 Introduction

2 Experimental

2.1 Materials

CL-20, TATB, polymers and the other reagents used in the present study were commercially purchased and used without further purification.

2.2 Preparation of desensitized CL-20 composites via novel strategies

The preparation of core-shell CL-20/TATB was carried out via surface modification followed by a water suspension coating process [12]. A little polymer binder solution such as Estane 5703 (poly [ester urethane] block copolymer) was added in drops as the system was under vacuum, facilitating the fixation and filling the voids in the TATB shell layer. CL-20/polymer microcapsules were prepared by in situ polymerization of polymer monomers [13]. The novel route involved multilevel deep desensitization was carried out by grinding of CL-20 and TATB, constructing PBX via water suspension coating and finally coated by graphite.

2.3 Characterization

Scanning electron microscopy (SEM) measurements were performed by a LE0438VP instrument at an operating voltage of 25 kV. The impact sensitivity test was conducted with a WL-1 type impact sensitivity instrument according to GJB-772A-97 standard method 601.2: drop weight, 5 kg; sample mass, 50 mg. The impact sensitivity of each test sample was expressed by the drop height of 50% explosion probability (H_{50}). The friction sensitivity test was determined on a WM-1 type friction sensitivity instrument according to GJB-772A-97 standard method 602.1: relative pressure, 3.92 MPa; sample mass: 30 mg, pendulum weight: 1.5 kg; pendulum angle: 90°. The fraction sensitivity of each test sample was expressed by explosion probability (P). Detonation velocity was determined by cylinder test.

3 Results and discussion

3.1 CL-20/TATB core-shell composites and the desensitization effect

Fig. 1 shows the research idea for CL-20/TATB core-shell coating desensitization strategy. It is well known that TATB is a moderately powerful, thermally stable, extremely insensitive high explosive (IHE), which is favorable to prepare insensitive munitions. Specifically, TATB is very insensitive to both impact and friction due to its outstanding lubricating performance attributing to the graphite-like layered structure. Herein, TATB was expected to form a uniform shell around the surface of CL-20 crystals, surface modification was adopted to improve the interfacial interaction to achieve high

uniformity of coating. In view of the mechanical strength maintaining and few voids left in the coating shell, a small amount of Estane polymer was introduced during the coating process. For this core-shell composite, assuming that a pretty compact shell with 100% coverage can be obtained, it is expected to achieve high energy close to CL-20 and low sensitivity close to TATB. Once an external impact action occurred, the TATB shell would be firstly attacked as a buffer system to dissipate the impact and friction energy, therefore, the sensitivity can be reduced effectively.

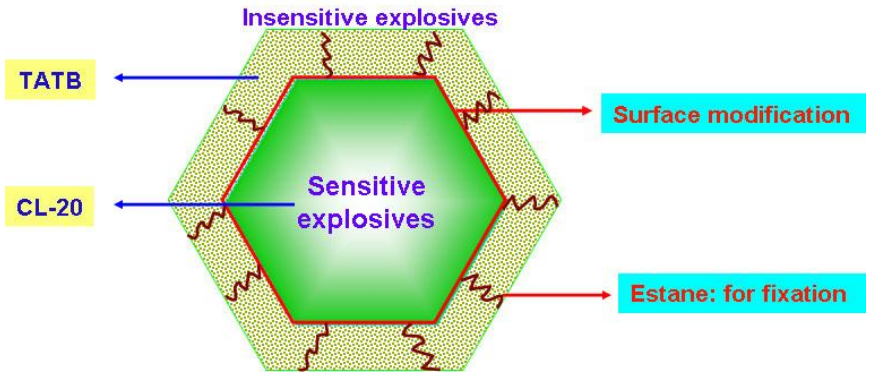

Fig. 1 Schematic mechanism for CL-20/TATB core-shell coating desensitization

The SEM study was carried out for CL-20/TATB composites, as shown in Fig.2. The raw CL-20 particles were well-proportioned and showed typical octahedral shape with smooth surface, about 80 μm particle size in average. It appears as though each CL-20 crystal has been jacketed with a layer of TATB particles, the submicron TATB (5%) particles built up a uniform and compact coating shell, with high surface coverage, and almost no TATB particles were in exfoliated state. About 2 wt % Estane of the total quality was used to favor the fixation of submicron TATB crystals. The surface activity agent PVA or Tween-20 was used to improve the wettability of the CL-20 surface, so that TATB can overcome the interfacial interaction and form a core-shell like structure. For comparison, the physical mixtures of CL-20, 5% TATB and Estane binder at the same ratio were prepared as a reference. It is clear that only a small amount of TATB particles were attached to the surface of CL-20, most were in the independent state, showing negligible coating effect. In addition, the core–shell coating structure can not be obtained as the TATB in normal size (about 20 μm) was adopted for the coating agent, as shown in Fig 2d. It was proved that with the content of TATB increased, both the coverage degree and thickness of the TATB shell can be improved. The shell strength was tested in a water suspension system under vigorous stirring, almost no TATB particles were exfoliated, demonstrating the high mechanical strength of coating shell.

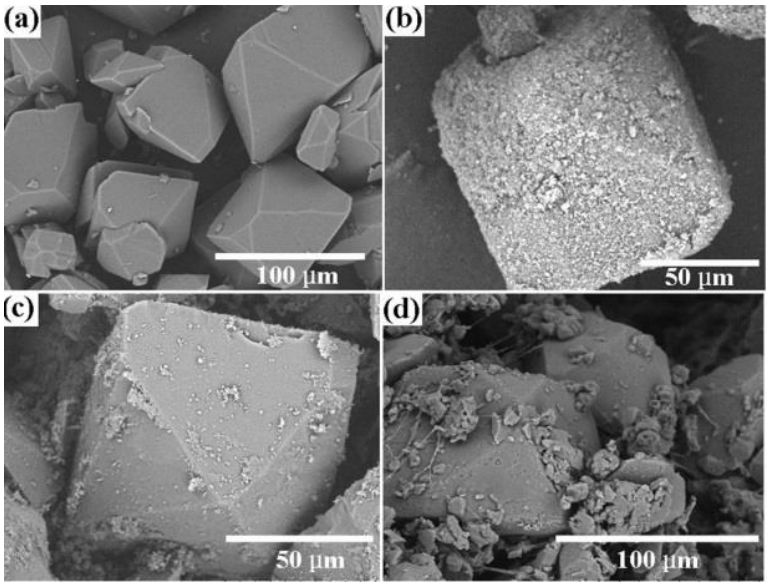

Fig. 2 SEM images of CL-20 and CL-20/TATB composites: (a) CL-20, (b) 5% TATB (800 nm) coated, (c) 5% TATB (800nm) physical mixed, (d) 5% TATB (20 μm) coated

Table 1 shows the impact and friction sensitivity results of the core-shell and physical mixed CL-20/TATB. The H_{50} of the physical mixed sample with 5% TATB was increased from 16.0 cm to 23.7 cm, compared with raw CL-20. As TATB in normal size (20 μm) was used, the reduction of impact sensitivity was also limited. The desensitization was greatly weakened for the poor coverage of TATB, as most surface of CL-20 was exposed to the environment. However, the impact sensitivity for the core-shell CL-20/TATB sample was reduced evidently with the same TATB content. The H_{50} value was increased to 49.6 cm, more than three times as compared with raw CL-20, indicating an efficient desensitizing technique of core-shell coating. With the help of a little polymer binder, the TATB particles formed a dense coating shell, the mutual friction among CL-20 crystals were effectively inhibited. Therefore, fewer hot spots will be generated, leading to the highly reduced sensitivity. With the content of TATB increased, the impact sensitivity of these core-shell CL-20/TATB composites was further decreased. As the TATB content increased to 25% or more, low impact and 0% of friction sensitivity were obtained.

Table 1 Impact and friction sensitivity of CL-20/TATB composites

Sample	TATB [%]	Size of TATB [μm]	TATB introduced	H_{50} [cm]	Friction sensitivity [%]
CL-20	0	/	/	16.0	100
CL-20/TATB-1	5	0.8	physical mixing	23.7	100
CL-20/TATB-2	5	0.8	core-shell coating	49.6	68
CL-20/TATB-3	15	0.8	core-shell coating	48.2	30
CL-20/TATB-4	25	0.8	core-shell coating	56.7	0
CL-20/TATB-3	5	20	coating	30.5	92

3.2 Constructing microcapsules via in situ polymerization and the desensitization effect

Fig. 3 shows the research idea for desensitization of by in situ polymerization coating strategy. Taking the in situ polymerization of melamine-formaldehyde (MF) resins as an example, firstly, melamine, formaldehyde and a small amount of PVA were mixed in the solution, followed by the polycondensation reaction under heating to give the MF prepolymers. Subsequently, the energetic microcapsules can be obtained via the gradual in situ polymerization of MF polymers on the crystal surface. It should be emphasized that the additive PVA plays a key role in the whole preparation process, improving the surface wettability as a surfactant and enhancing the flexibility as a fiber-forming component, causing beneficial desensitization effect for the microencapsulated products.

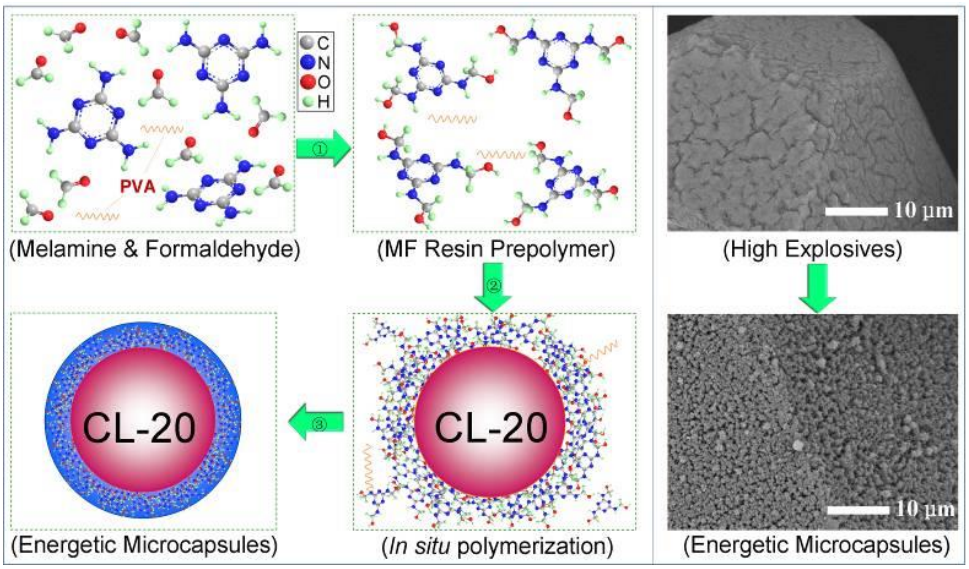

Fig. 3 Schematic mechanism for microencapsulation of resins via in situ polymerization

Fig. 4 and Fig.5 shows the SEM images of CL-20 coated by different amount MF resins and polyisoprene to form energetic microcapsules. Taking MF resin as an example, it can be clearly seen that the CL-20 based microcapsules showed an obvious core-shell structure, the coverage reached fairly high. In the images with high magnification, the MF resin shell can be observed in a close view, the crystal surface, edges and corners were all encapsulated compactly. Fig.5 shows the effect of the amount of polymers. Clearly, with the feeding amount of MF and isoprene prepolymer increased, the content and thickness of MF resin and polyisoprene shell will also be increased accordingly. Combining the consideration of desensitization capability and less energy loss, the content of polymers coated was controlled at about 3.0 wt%, determined by the HPLC quantitatively. The explosive microcapsules were tested in an aqueous solution under vigorous stirring for hours, it was found that the core-shell structure was maintained completely, indicating a fairly high mechanical strength of the coating shell. These results suggest that the in situ polymerization of MF resin is a general, controllable and efficient approach to prepare core-shell explosive composites.

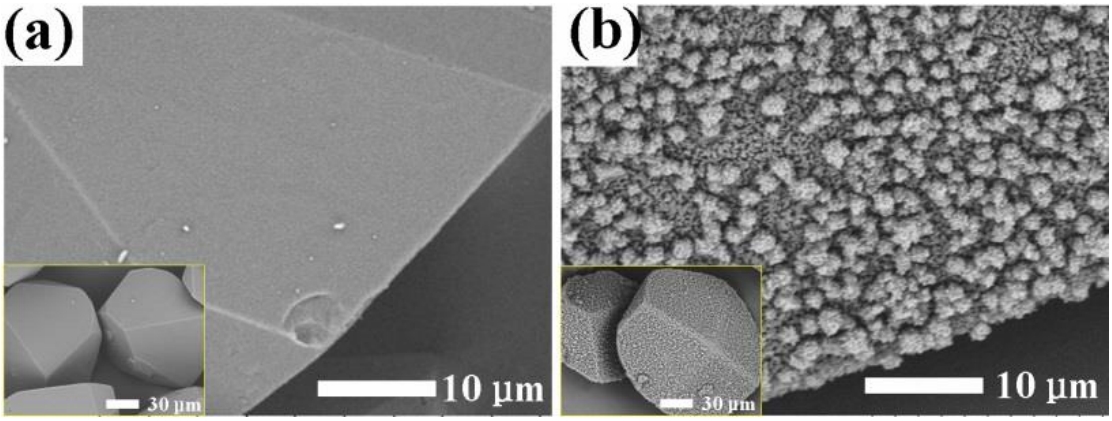

Fig.4 SEM images of CL-20 (a) before and (b) after coating by 3 wt% MF resins as determined by HPLC.

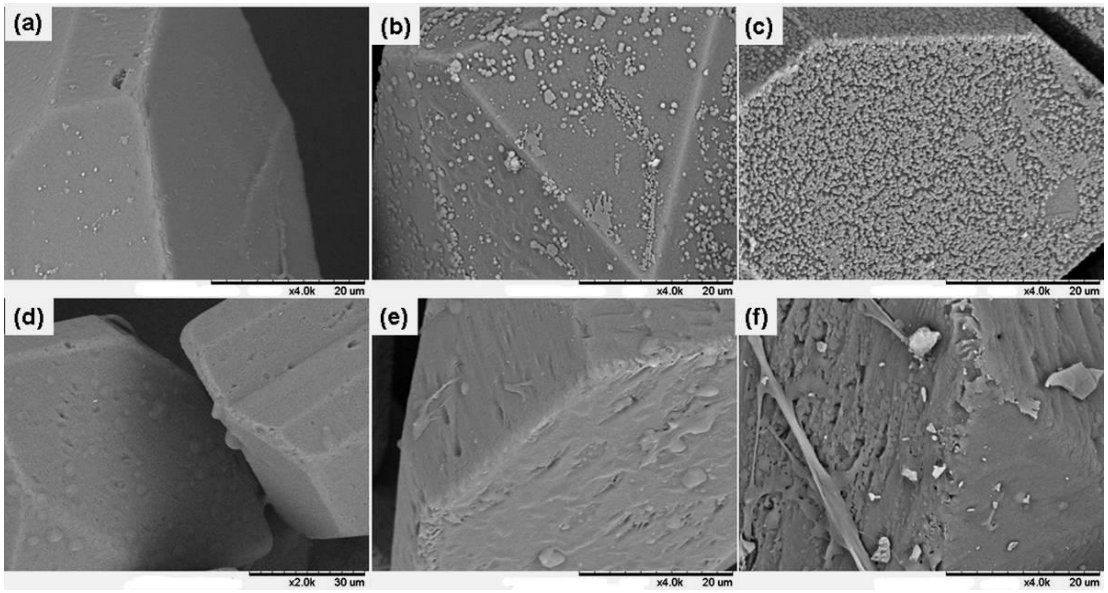

Fig. 5 SEM images of CL-20 coated via in situ polymerization by different amount of MF resins (a) 0.2%, (b) 0.6%, (c) 1.2%, and by polyisoprene, (d) 0.3%, (e) 1.5%, (f) 2.5%.

The impact sensitivity (H_{50}) of CL-20 before and after coating was test, as shown in Table 2. It can be concluded that a significant desensitization effect has been achieved for the high explosives after core-shell coating, especially compared with the physical mixed sample. For the MF resin systems, the H_{50} value of CL-20/3% MF exhibits a visible increment from 16.3 cm to 42.8 cm in comparison to the raw material, while the physical mixed sample with the same molar ratio reaches only 18.7 cm. With the content of MF resins increased, the desensitization effect was strengthened. For the polyisoprene coated composites, the H_{50} value was increased to 25.7 cm and 33.4 cm, corresponding to the polyisoprene amount of 1.5% and 2.5%, respectively. These results demonstrate that such a core-shell coating via in situ microencapsulation provides an efficient route for the decrease of impact sensitivity of high explosives, attributing to the compact and uniform coating of MF resins or polyisoprene on the surface of energetic particles.

Table 2 Impact sensitivity of CL-20 microcapsules by MF resin and polyisoprene

Samples	Polymer/wt%	Polymer introduced	H_{50}/cm
CL-20	0	/	16.0
CL-20/MF	0.6	core-shell coating	19.6
CL-20/MF	1.2	core-shell coating	23.2
CL-20/MF	3.0	core-shell coating	42.8
CL-20+MF	3.0	physical mixing	18.7
CL-20/polyisoprene	1.5	core-shell coating	25.7
CL-20/polyisoprene	2.5	core-shell coating	33.4
CL-20+polyisoprene	2.5	physical mixing	15.9

3.3 Multilevel and tridimensional desensitization strategy

Fig. 6 shows the research idea for multilevel and tridimensional desensitization. This strategy was investigated for a more efficient desensitization. Firstly, CL-20 and a part of TATB were treated by mechanical grinding to obtain a uniform composite. In this way, TATB particles can be embedded into the crystals of CL-20, providing a fairly uniform CL-20 mixture within doping TATB. Then, the rest of TATB was used to construct a coating shell in the PBX with the help of polymer binders, thus both the external and internal space of the PBX particles were filled by TATB particles. Finally, graphite was selected to form an outer coating layer. In a word, polymer binder, internal and external TATB, and graphite build up a multilevel, tridimensional and powerful desensitization network. For the CL-20 based composites by such multilevel and tridimensional coating, both the impact and friction sensitivity can be definitely reduced, meanwhile, the high energy can be also reserved (detonation velocity> 9000m/s).

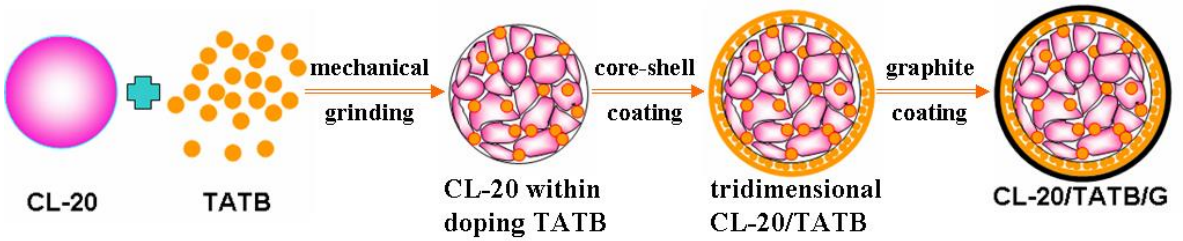

Fig. 6 Schematic mechanism for multilevel and tridimensional desensitization

4 Conclusion

Several new strategies for reducing the mechanical sensitivity of CL-20 are investigated. The sensitivity can be markedly reduced via core-shell coating of TATB and polymers via in situ polymerization coating. Compact, uniform and firm coating shells were achieved on the crystal surface of CL-20. Another multilevel and tridimensional desensitization strategy was explored and fairly low sensitivity with high energy was obtained. The preparation technologies in this work will also provide some useful enlightenment for the other core-shell materials, especially for the desensitization of high explosives for military applications.

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