***Chemical Engineering Journal*, 2015, 268: 60-66.**

Fabrication of RDX, HMX and CL-20 based microcapsules via in situ polymerization of melamine-formaldehyde resins with reduced sensitivity

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Abstract:

Melamine-formaldehyde resins were selected for the fabrication of RDX, HMX and CL-20 based microcapsules, the polymer coating shell could be prepared via a facile in situ polymerization of melamine and formaldehyde on the surface of explosive crystals. SEM and XPS results indicated that a compact coating with high shell coverage close to 100% was obtained for these three energetic cores. XRD and FTIR analyses revealed that the polymorph of CL-20 maintained the optimal ε form during the whole preparing process. After coating, the endothermic polymorphic phase transition as well as the exothermic thermal decomposition temperature of the explosives was visibly increased. The impact sensitivity of the resultant microcapsules could be markedly reduced after coating by 3 wt% MF resins.

Keywords: High explosives; Core-shell structure; MF resins; In situ polymerization; Desensitization

1 Introduction

Effective destructibility and high safety are the most important performances for energetic materials used in modern weapons, the overall replacement of conventional high explosives (CHE) to insensitive high explosives (IHE) is generally acknowledged as the worldwide common target in the future.

There are strong limitations for the application of RDX, HMX, CL-20 in weapon systems, caused by their high sensitivity towards impact, friction, and electric spark.Microencapsulation has raised increasing interests and been frequently used whenever the functionality of an active substance needs to be protected or a controlled release is demanded.

The in situ polymerization involves monomer intercalation followed by polymerization, which can facilitate extraordinarily high coverage and shell strength owing to the chemical polymerization occurred on the surface of core material, instead of a simple dissolution/precipitation physical process.

2 Results and discussion

2.1 Morphologies of RDX, HMX, CL-20 before and after coating

Fig. 1 displays typical SEM images of the three nitramine explosives and the corresponding energetic microcapsules coated by MF resins. The RDX, HMX and CL-20 raw materials are uniform in size distribution. It can be clearly seen that the explosive based microcapsules exhibit obvious core-shell structures. The MF resins form compact and uniform coating shells around the whole surface of energetic cores, and the degree of coverage for these three explosives reaches close to 100%. Furthermore, almost all MF resins precipitated are effectively coated on the surface, few MF particles are free, indicating the self-nucleation problem of shells for most core-shell materials has been well inhibited in this system.

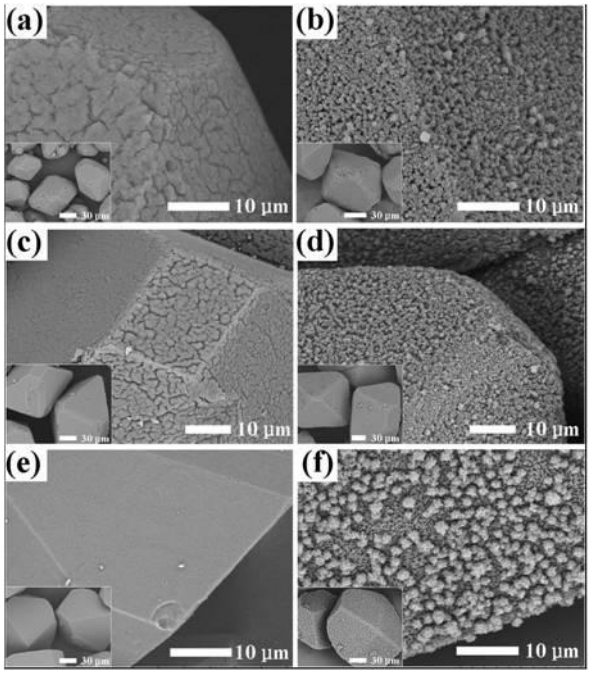

Fig.1. SEM images of (a) RDX, (b) RDX/MF, (c) HMX, (d) HMX/MF, (e) CL-20, (f) CL-20/MF.

In order to further investigate the core-shell coating via such in situ polymerization, physical mixed sample of CL-20/MF and the MF resin shell after the etching of CL-20 core were prepared and tested, as shown in Fig. 2. It is noticeable in the physical mixed sample that only a small amount of MF resin particles are attached to the surface of CL-20, with most under independent state. The SEM result shows a clear view of the taken off MF resin shell, which is interleaving and well connected, with the shell thickness of about 1~2 μm.

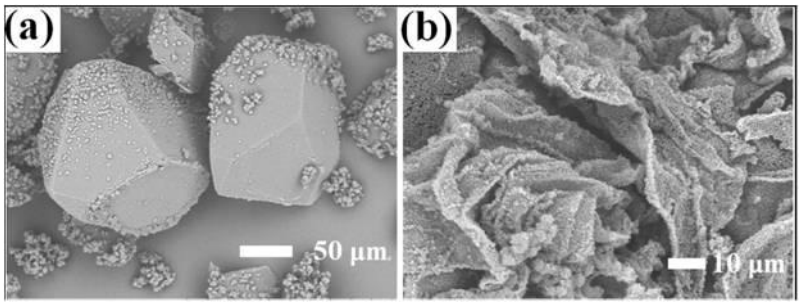

Fig.2. SEM images of (a) CL-20/MF resin by physical mixing and (b) MF resin

coating shell after etching of CL-20 core

2.2 Surface analysis and crystal structure of the microcapsules

XPS is reasonable for the further confirmation of core-shell structure gained in this work, and the results are depicted in Fig. 3. For the coated microcapsules after in situ polymerization, apparent disappearance of the nitramine N1s peaks is observed for all the RDX/MF, HMX/MF and CL-20/MF composites. By calculating the integrated area ratio with the consideration of N amount at different binding energy, the degree of coverage can be obtained semi-quantitatively as 93.1%, 98.7% and 99.2% for RDX/MF, HMX/MF and CL-20/MF respectively. Hence, the perfect core-shell structure of such energetic microcapsules is further confirmed.XRD and FT-IR analyses were conducted to investigate the crystal structure and component state of energetic microcapsules prepared in this work. Herein, the CL-20/MF sample shows evident ε-phase purity after the in situ polymerization coating process, as determined by XRD.

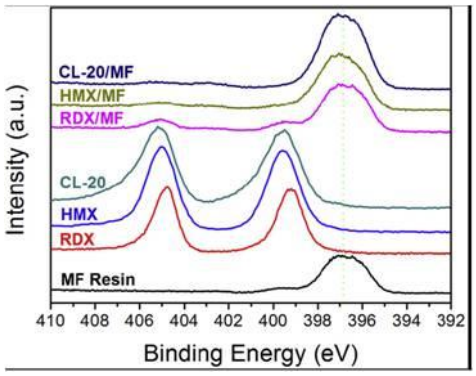

Fig.3. N1s XPS spectra of MF, RDX, HMX and CL-20 coating by 3 wt% MF resins

2.3 Thermal properties

Thermal stability is widely considered as a key performance for energetic materials. Herein, as a typical heat-resistant polymer, MF resin can visibly increase the polymorphic phase transition as well as the thermal decomposition temperature, as shown in Fig.4.

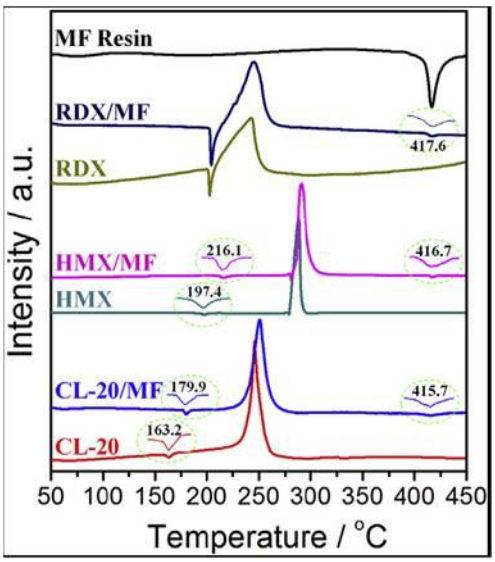

Fig.4. DSC curves of MF resin, explosives and core-shell composites

2.4 Impact sensitivity study and proposed schematic mechanism

The results demonstrate that such a core-shell coating via in situ polymerization provides an efficient route for the decrease of impact sensitivity of high explosives, attributing to the compact and uniform coating of MF resins on the surface of energetic particles. Once an external impact action occurred, the MF resin shell would be firstly attacked as a buffer system to dissipate the impact energy. Therefore, the impact sensitivity can be reduced effectively, as shown in Fig.5.

To summarize the in situ polymerization coating process, a schematic mechanism is proposed, as described in Fig. 6. At the beginning of this reaction, melamine, formaldehyde and a small amount of PVA are mixed in the solution, followed by the polycondensation reaction under heating to give the MF prepolymers. As the nitramine explosive is added, sufficient interaction will be carried out between the prepolymers and explosives. Subsequently, the energetic microcapsules can be obtained via the gradual in situ polymerization of MF polymers on the crystal surface.

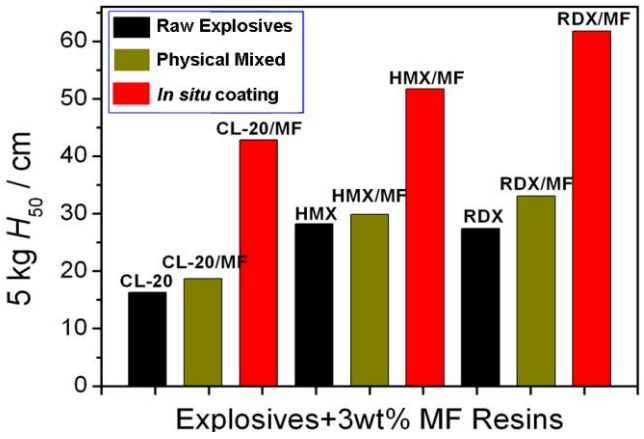

Fig.5. Impact sensitivity of CL-20, HMX, RDX before and after coating

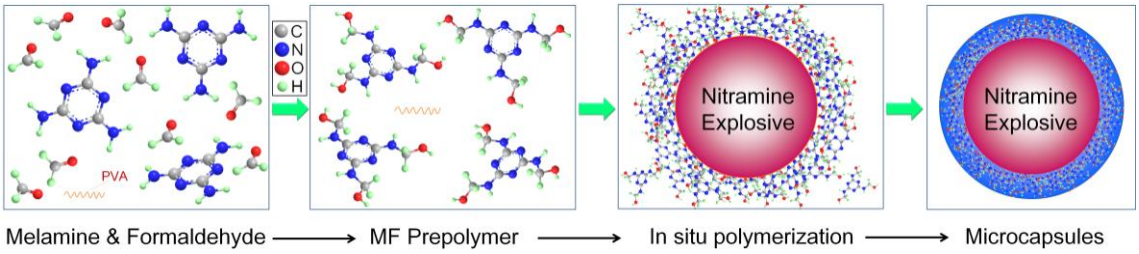

Fig.6. Proposed schematic mechanism for coating via in situ polymerization

3 Conclusions

A novel, facile, adjustable in situ polymerization technique is reported for the fabrication of RDX, HMX and CL-20 based microcapsules coated by MF resins. The resultant core-shell energetic composites possess compact and uniform coating shells, with a fairly high coverage and mechanical strength. Thermal stability can be effectively improved for the protecting shell, resulting the increased polymorphic phase transition and thermal decomposition temperature. The impact sensitivity of the

nitramine explosives can be reduced from 2 to 3 times with 3 wt% MF resins after core-shell coating, compared with the virgin explosives and physical mixtures.

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