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Solvent effect on particle morphology in recrystallization of HMX (cyclotetramethylenetetranitramine) using supercritical carbon dioxide as antisolvent

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Abstract−Supercritical fluid processes have gained great attention as a new and environmentally benign method of preparing the microparticles of energetic materials like explosives and propellants. In this work, HMX (cyclotetramethylenetetranitramine) was selected as a target explosive. The microparticle formation of HMX using supercritical antisolvent (SAS) recrystallization process was performed and the effect of organic solvent on the size and morphology of prepared particles was observed. The organic solvents used in this work were dimethylsulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF), cyclohexanone, acetone, and *N*-methyl pyrrolidone (NMP).

Key words: High Energy Material, Explosive, Supercritical Fluid, Recrystallization, Microparticle Formation, HMX, Morphology

INTRODUCTION

High-energy materials like explosives and propellants are used extensively for both civilian and military applications. There has been a demand for the development of high performance and insensitive explosive due to the demand for lowering explosive self-vulnerability caused by unintentional explosion and the request for developing high-explosives. Size, shape, internal defects are very important properties of explosive crystals. The use of explosive crystals free of solvent inclusions leads to decrease the shock sensitivity of cast explosive formulations. Many efforts for processing such high quality explosive crystals have been done and are still in progress. However, since high-explosives or propellants are vulnerable to heat or impact, it is not only dangerous to prepare submicron particles through milling, recrystallizing from solution and spray drying process, but also very difficult for the size and distribution range of the particle to reach the nano-size level due to residual solvent [1,2]. As an alternative to those techniques, supercritical fluid (SCF) recrystallization processes have been proposed [3-5]. These techniques can potentially overcome the limitations of classical micronization processes. They have many advantages such as no thermal degradation, no mechanical damage, and no residual solvent problem [6].

The core work in the particle formation of an explosive using the SCF processes such as a supercritical anti-solvent (SAS) recrystallization [7-12] and a rapid expansion of supercritical solution (RESS) [13,14] is to obtain the microparticles of various sizes and shapes by controlling the supersaturation and nucleation rates of the explosive in the SCF with a change of solvent strength. Especially, the SAS recrystallization is a promising process to produce solvent-free particles of microns and sub-microns. The supercritical fluid is characterized by diffusivities up to two orders of magnitude higher than those of liquid, which make for fast supersaturation of solute and its precipitation of small particles.

In this work, HMX (cyclotetramethylenetetranitramine or octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) was selected as a target explosive, which is widely used not only for military purposes but also in industrial applications. HMX is a high melting explosive sensitive to heat and impact. The high velocity of detonation (9,100 m/s) and detonation pressure (393 kbar) are responsible for its explosive properties [15]. HMX is a white crystalline powder that is practically insoluble in water and highly soluble in DMSO, DMF, cyclohexanone, etc. It has four different polymorphs: α-, β-, γ-, and δ-forms. β-HMX is the most stable one and has the highest density, which is important for the energy content of the energetic material [15,16]. The HMX particles were prepared in a high-pressure vessel by the SAS method which utilizes several kinds of organic solvents and carbon dioxide (CO_2) as an antisolvent. The effect of organic solvent on the size and morphology of prepared particles was observed. The organic solvents used in this work were dimethylsulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF), cyclohexanone, acetone, and *N*-methyl pyrrolidone (NMP).

EXPERIMENTAL

1. Materials

The HMX samples were provided by the Agency for Defense Development (Korea). The general chemical information and some physical properties of the HMX explosive are given in Table 1, and its chemical structure is shown in Fig. 1. DMSO (99.9%), DMF (99.9%), cyclohexanone (99.8%), acetone (99.9%), and NMP (99.5%) used as solvents were purchased from Aldrich Chemical Co. CO_2 (99.9%) used as antisolvent was obtained from Sebo Energy (Korea).

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The HMX and chemicals were used as received without further purification.

2. Apparatus and Procedure

Fig. 2 shows the experimental apparatus for precipitating the HMX microparticles by using the SAS recrystallization. The apparatus consists of a high-pressure cylindrical vessel of 200 ml equipped with a nozzle (0.03 inch i.d.) for spraying of HMX solution and a filter for collection of HMX particles, a syringe pump (ISCO model 260D) for CO_2 feeding, and a plunger pump (Minipump model 92014903) for HMX solution feeding. The system pressure was controlled and kept constant by a back pressure regulator connected to the outlet of the vessel. The HMX particles were collected by a thimble filter plugged into the inner wall of the vessel.

Table 1. Physical properties of HMX

Property	Data value
Molecular weight	296.2
Melting temperature [°C]	275
Crystal density at 20 °C [g·cm^{-3}]	
α-form	1.87
β-form	1.96
γ-form	1.82
δ-form	1.78
Energy of formation [kJ/kg]	353.8
Enthalpy of formation [kJ/kg]	252.8

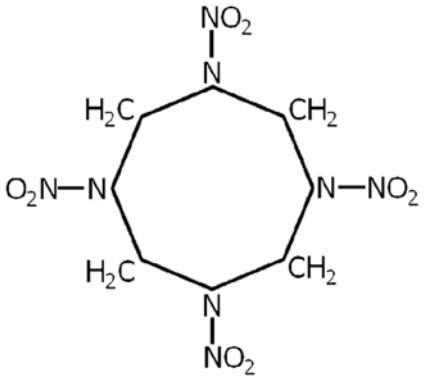

Fig. 1. Chemical structure of HMX.

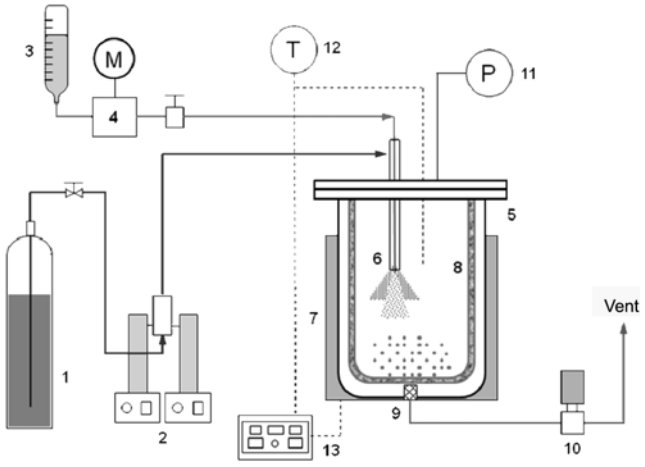

Fig. 2. A schematic diagram of the experimental apparatus of SAS recrystallization.

1. CO_2 cylinder
2. CO_2 feeding pump
3. HMX+solvent solution
4. HMX solution feeding pump
5. Recrystallizer
6. Nozzle
7. Heater
8. Thimble filter
9. Metal filter
10. Back pressure regulator
11. Pressure gauge
12. Temperature indicator
13. Controller

The experiment for precipitating the HMX particles was performed by the following procedure. First, the HMX was dissolved in a solvent. Then, CO_2 was delivered into the recrystallization vessel at a constant flow rate by a syringe pump until a desired pressure was reached. Once the pressure and temperature had been equilibrated, the HMX solution was introduced into the vessel through the nozzle along with CO_2. When the HMX solution was sprayed through the nozzle, the solvent was rapidly extracted by the supercritical CO_2, resulting in the precipitation of solid dispersion particles. In the final step, the vessel was washed out with CO_2 to eliminate the solvent mixed in supercritical CO_2, the vessel was depressurized, and then the particles in the vessel were collected for analysis.

The size and shape of the HMX particles recrystallized were qualitatively analyzed by scanning electron microscopy (SEM, model S-2250N, Hitachi, Japan). A particle size analyzer (Microtrac X100, Honeywell, USA) was used to quantitatively measure mean particle size and particle size distribution. The morphology of the HMX particles recrystallized was analyzed by using Fourier transform infrared (FT-IR) spectroscopy (model Paragon 1000, Perkin-Elmer, USA).

RESULTS AND DISCUSSION

HMX particles were precipitated by the SAS recrystallization process. The experimental conditions are shown in Table 2. Fig. 3 shows the SEM images of untreated and SAS processed HMX particles. In the SAS process, we used five different organic solvents: DMSO, DMF, cyclohexanone, acetone, and NMP. The size of the HMX particles decreased remarkably by the SAS recrystallization. The untreated HMX particles were like irregular pebbles with sizes of about 100 μm or more. On the other hand, the SAS-processed HMX particles showed various shapes. The HMX particles recrystallized from DMSO solution showed needle-like shape. When DMF solvent was used, the recrystallized particles were like coral reefs or plates. It was observed that the HMX particles recrystallized from cyclohexanone and acetone solutions were like prisms. The HMX particles of denser crystal structure were obtained with cyclohexanone and acetone. McCrone reported that the polymorphs of the

Table 2. Experimental conditions for preparing HMX particles by the SAS recrystallization

Operating variable	Experimental condition
Temperature	40 °C
Pressure	150 bar
CO_2 flow rate	15 ml/min (at 150 bar and 12 °C)
HMX solution feed rate	2 ml/min
HMX solution concentration	5 wt% for DMSO; 2 wt% for other solvents

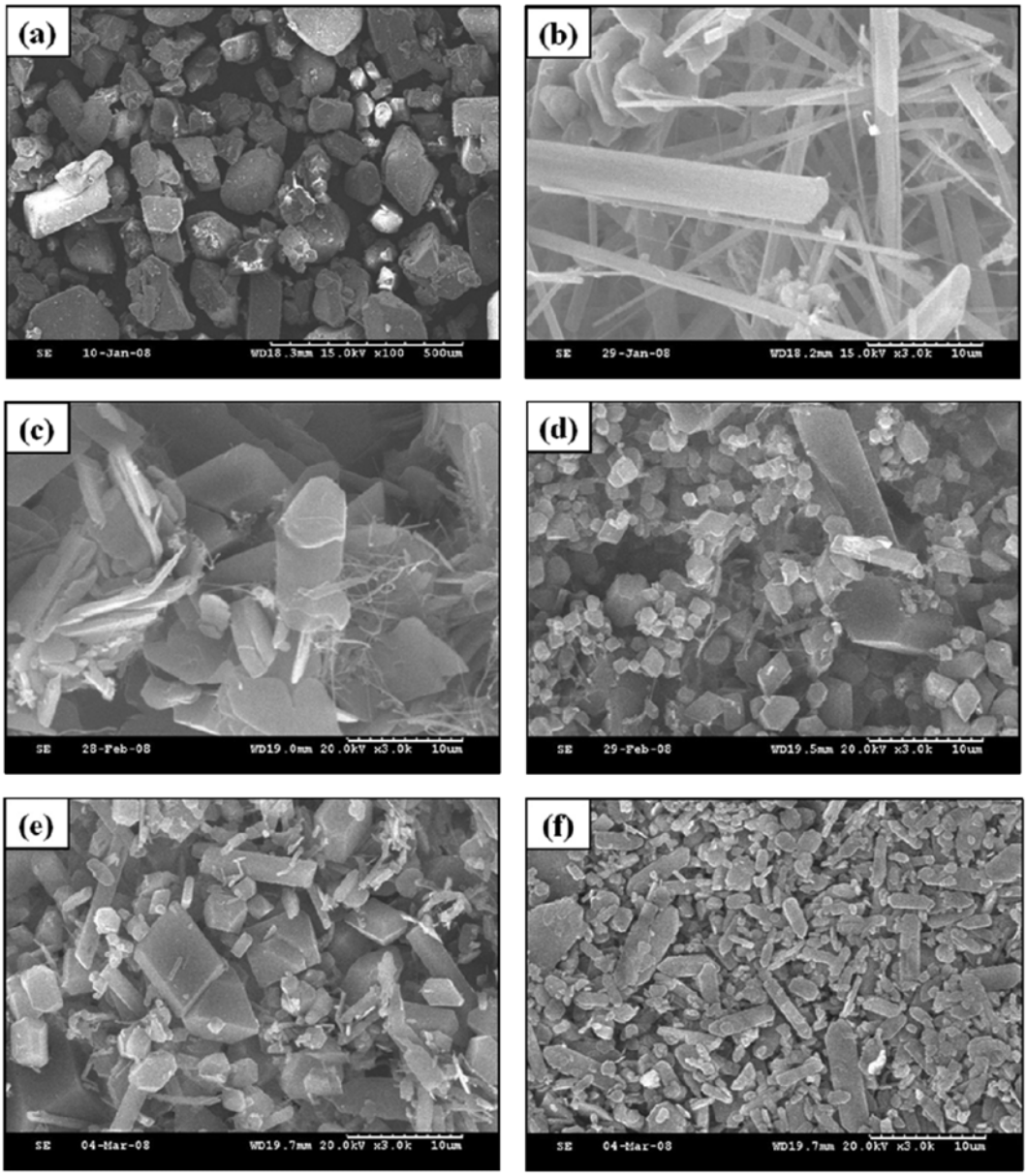

Fig. 3. SEM images of untreated and SAS processed HMX particles: (a) untreated sample, (b) recrystallized from DMSO solution, (c) recrystallized from DMF solution, (d) recrystallized from cyclohexanone solution, (e) recrystallized from acetone solution, (f) recrystallized from NMP solution.

HMX particles were found to be needles (α-form), prisms (β-form), plates (γ-form), and rods and needles (δ-form) [15]. According to McCrone's investigation, the HMX particles recrystallized from cyclohexanone and acetone solutions are observed to have a polymorph of β-form. On the other hand, it seems that the polymorph for the HMX particles recrystallized by using DMSO and DMF as solvent is not β-form. The mean particle sizes of the SAS processed particles ranged from 4.1 to 13.4 μm, as given in Table 3.

Table 3. Mean particle sizes of the SAS processed HMX particles

Organic solvent used	Particle size [μm]
DMSO	13.4
DMF	7.8
Cyclohexanone	6.1
Acetone	9.5
NMP	4.1

The polymorph of the HMX particles can be discussed further by performing the infrared spectral analysis for the particles. Fig. 3 and Table 4 show the FT-IR spectral bands in the region of 2,000 cm^{-1} to 400 cm^{-1} for the untreated and SAS processed HMX particles. The infrared spectra show transmittance bands that reveal the presence of N-N bonds and NO_2 groups associated to cyclic nitrocompounds such as nitramines including HMX [15]. A general perusal of the spectra showed that the band positions of α-, γ-, and δ-forms were very little different from one another though they were distinctly different from those of the β-form [15].

Table 4. FT-IR spectra of HMX solution for various solvents

Untreated HMX	Organic solvent used in SAS recrystallization				
	Cyclohexanone	Acetone	DMSO	DMF	NMP
1548	1536	1530	1552	1552	1566
1458	1456	1452	1448	1446	1446
1426	1428				
1394	1394	1392	1388	1386	1386
1272	1286	1276	1284		
				1258	1250
1194	1196	1204			
1138	1138	1140			
			1106	1104	1104
1078	1080	1082	1084	1084	1084
	1012	1012	1018	1014	1012
940	936				
		912	914	914	928
822	826	834	840	840	840
752	754	758	758	760	758
			732	730	728
			706	706	706
652	652	650	642	642	640
620	618				
594	596	604	606	608	608
		470		472	470
			448		
430	430	430			

In general, the α-form of HMX shows a transmittance band at 706 cm^{-1} and 730 cm^{-1}, while the β-form of HMX shows no transmittance band between 700 cm^{-1} and 740 cm^{-1}. In case of our untreated HMX sample, there were no transmittance bands between 700 cm^{-1} and 740 cm^{-1} wave numbers, which proved that our untreated HMX had morphology of β-form. The FT-IR spectrum shown in Fig. 3(a) for our untreated HMX sample was very similar to that of the raw HMX reported in the literature [17]. The SAS-processed HMX particles recrystallized from cyclohexanone and acetone solutions also showed no transmittance bands between 700 cm^{-1} and 740 cm^{-1} wave numbers. Thus the HMX particles recrystallized from cyclohexanone and acetone solutions had morphology of β-form. However, the HMX particles recrystallized by utilizing DMSO, DMF and NMP solvents showed transmittance bands around 706 cm^{-1} and 730 cm^{-1}, which proved that those particles did not have morphology of β-form. Consequently, the shape and morphology of the recrystallized HMX particles were greatly affected by the organic solvent used in the SAS process.

CONCLUSIONS

The microparticles of HMX were prepared by using the SAS recrystallization process which utilized supercritical CO_2 as an antisolvent. Five organic solvents (DMSO, DMF, cyclohexanone, acetone, and NMP) were used to investigate the effect of solvent on the shape and morphology of the HMX particles recrystallized. The SAS-processed HMX particles showed various shapes, depending upon the solvent used. The size of the HMX particles decreased remarkably by the SAS recrystallization. According to the FT-IR spectrum analysis, the HMX particles recrystallized from cyclohexanone and acetone solutions by the SAS process had morphology of β-form. In conclusion, the shape and morphology of the recrystallized HMX particles were greatly affected by the organic solvent used in the SAS process.

ACKNOWDGMENT

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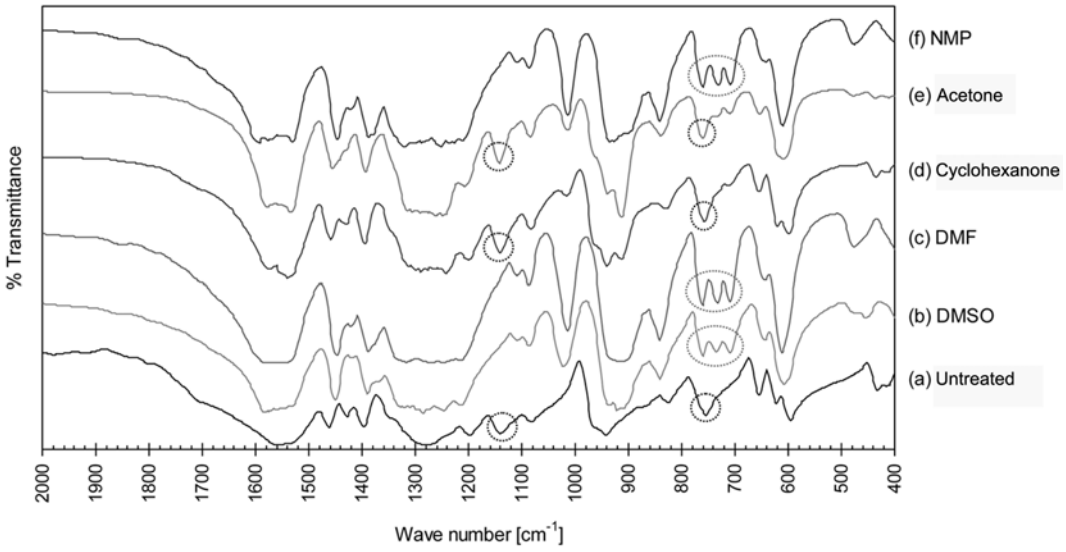

Fig. 4. FT-IR spectra of untreated and SAS processed HMX particles.

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