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Supercritical antisolvent method for recrystallization of HMX

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Supercritical antisolvent (SAS) method is an emerging technique for particle processing of high energetic materials. The study investigates the recrystallization of high energy material HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) using SAS method. The effect of pressure, solution flow rate, supercritical antisolvent flow rate and temperature on particle size and morphology of HMX crystals has been studied with acetone as solvent and supercritical carbon dioxide as antisolvent. Stable and desirable β- polymorphic form of HMX could be obtained under certain process conditions and has been confirmed by FTIR spectroscopy. The experimental results show that β- polymorph of HMX is of rhombohedral morphology with mean particle size of 13.7 μm, as confirmed by SEM and particle size analyzer respectively.

Keywords: high energy material, supercritical, recrystallization, polymorph

1. INTRODUCTION

High energy materials (HEMs) are characterized by instantaneous release of huge amounts of chemical energy stored in their molecular structures. Octahydro–1,3,5,7–tetranitro–1,3,5,7–tetrazocine commonly known as HMX is a widely used explosive for military applications due to its high detonation velocity (9100 m/s) and detonation pressure (393 kBar) (Teipel, 2005). However, the high performance of HEMs is associated with high sensitivity to heat and impact, and has always been a primary concern in the field of energetic materials during handling, processing, assembly and transportation. The sensitivity of high energetic material is related to the particle size, shape and morphology and there is a growing requirement of submicron or nanosize particles (Bayat et al., 2012; Kumar et al., 2014). HMX is known to exist in four polymorphic forms: α (orthorhombic), β (monoclinic), γ (monoclinic) and δ (hexagonal) phases, among which β–HMX is the desirable polymorphic form as it is stable at room temperature and possesses the highest explosive power which arises from its crystal phase and its high density (Kim et al., 2009; Soni et al.,

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2011). Although a variety of particle processing techniques like ball milling, spray drying, crystallization from solution have been reported for preparing micron sized particles of HEMs, these processes have inherent limitations like lack of control over particle morphology, particle size etc. (Prosapio et al., 2018; Singh et al., 2019). Not many published reports are available on the use of SAS method, which has been explored in the present study for preparing micron sized particles of HMX.

2. EXPERIMENTAL

2.1. Materials

Raw HMX was provided by TBRL. Acetone (99.9%) and CO_2 (99.9%) were procured from Sigma Aldrich, India and M/s. Vikas Gases, Panchkula, Haryana, India.

2.2. Methodology

A schematic diagram of the experimental apparatus used for the SAS is shown in Figure 1. The apparatus consists of a CO_2 tank, chiller, HMX solution chamber, CO_2 feed pump, heat exchanger, precipitation chamber and back pressure regulator. Liquefied CO_2 coming from the tank is super cooled by a chiller before being injected to the heat exchanger using a high pressure CO_2 pump. Liquefied CO_2 is heated to a supercritical state in the heat exchanger, and then moved to the precipitation chamber. The pressure in the precipitation chamber is controlled by a backpressure regulating valve. After the precipitation chamber is equilibrated to the desired temperature and pressure conditions, HMX solution is pumped to the precipitation chamber via a nozzle (diameter = 100 μm). The nozzle is placed at the top of the precipitation chamber. As the HMX solution enters the precipitation chamber through the nozzle, supercritical CO_2 extracts the solvent rapidly resulting in the precipitation of HMX particles. Recrystallized HMX particles were collected from the precipitation chamber after depressurizing the chamber and examined for further characterization. The process variables investigated are presented in Table 1.

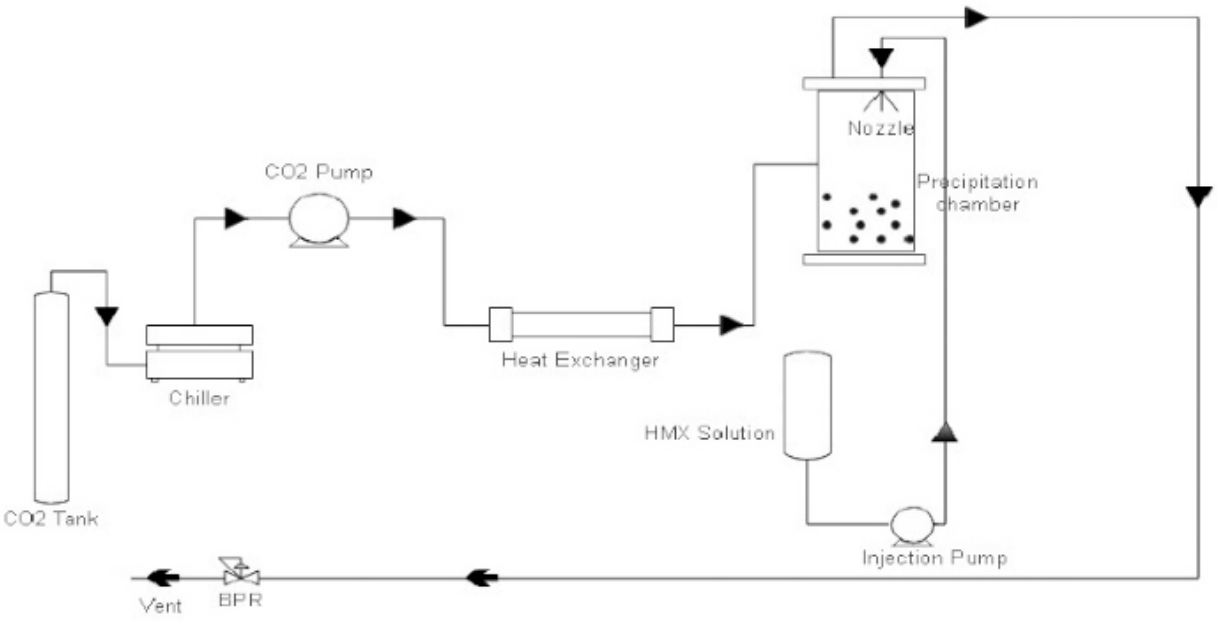


Fig. 1. Schematic diagram of SAS recrystallization process

Table 1. Process conditions for preparing recrystallized HMX

Operating variable	Experimental conditions
Solution flow rate, ml/min	1, 1.5, 2.0, 2.5
Solution conc., g/L	10, 20
Pressure, bar	80, 150, 180, 280, 380
Antisolvent flow rate, g/min	6, 10, 15, 20
Temperature, °C	40, 60
Time of coalescence, h	1, 2, 3

3. RESULTS AND DISCUSSION

The effect of process variables on particle size and morphology of HMX particles is presented in Figure 2. It was observed that antisolvent flow rate, solution flow rate and time of coalescence of precipitated HMX particles were the important variables affecting the particle size. The particle size of HMX crystals was analyzed using particle size analyzer (Anton Paar PSA 1190). The mean particle size of raw HMX crystals was 193.17 μm while mean particle size of recrystallized β–HMX crystals ranged from 13.77 μm to 63.89 μm depending on the coalescence time. The surface morphology was examined by Scanning Electron Microscope (SEM), Carl Zeiss, EVO Series. SEM images are shown in Figure 3 whereas Figure 4 shows the particle size distribution of raw and recrystallized HMX for different coalescence times. Raw HMX particles are irregular in shape whereas recrystallized HMX is rhombohedral in shape confirming its β–form (Fig. 3).

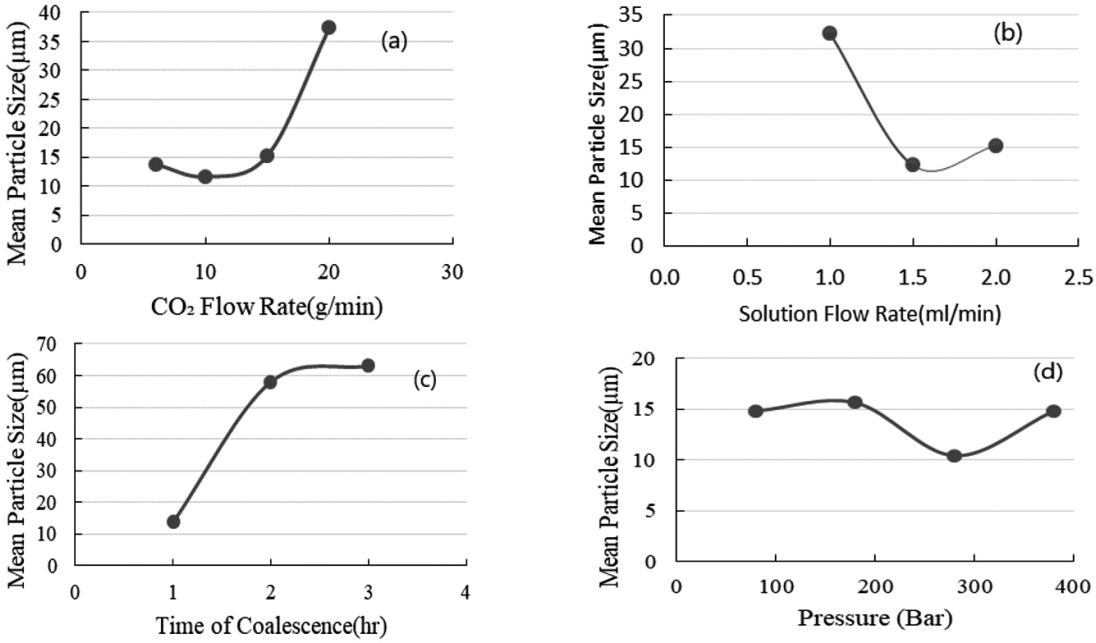
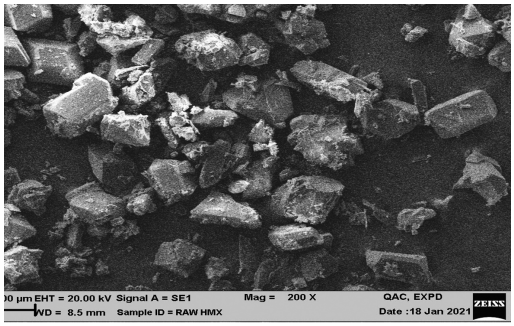
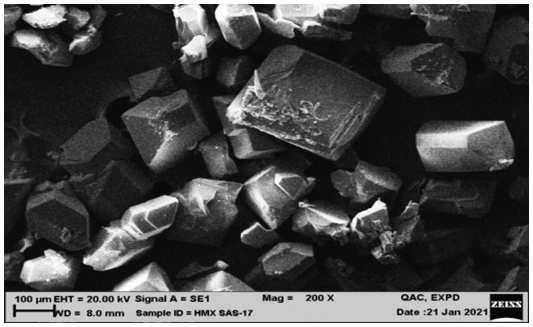


Fig. 2. Mean particle size of HMX as a function of (a) antisolvent flow rate (b) solution flow rate (c) time of coalescence (d) pressure

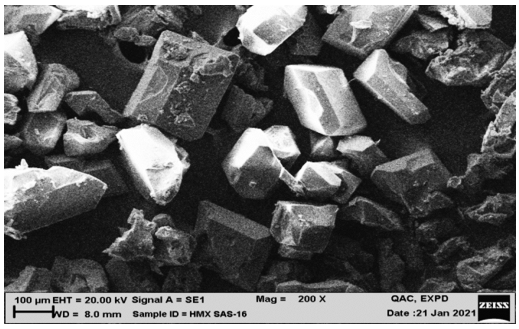
The polymorphs of HMX crystals were further investigated by performing infrared spectral analysis using Nicolet 8700 FTIR spectrometer and are shown in Figures 5 and 6.



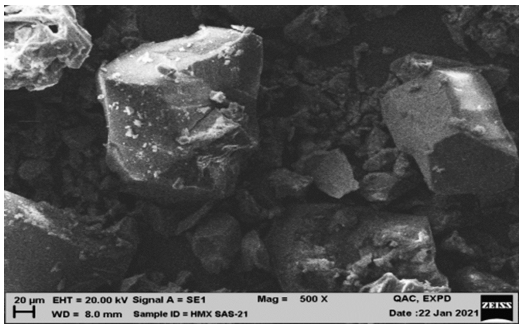
(a) Raw HMX



(b) Recrystallized β – HMX at 1 h

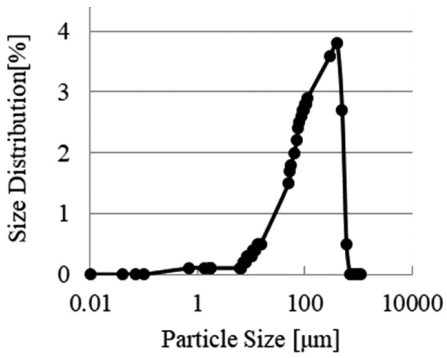


(c) Recrystallized β – HMX at 2 h

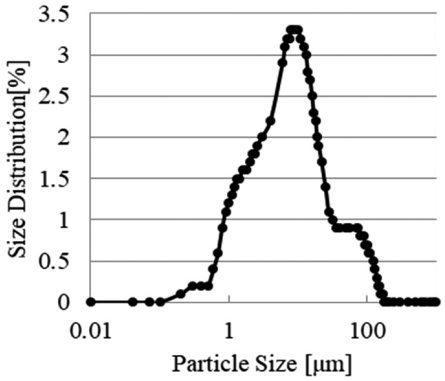


(d) Recrystallized β – HMX at 3 h

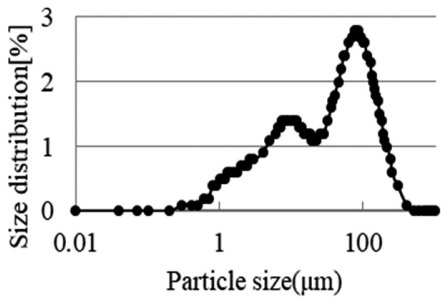
Fig. 3. SEM image (a) raw HMX, (b)–(d) recrystallized β–HMX at different coalescence times



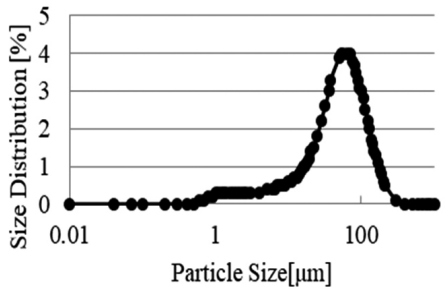
(a) Raw HMX particle size distribution
X_{10} = 23.46 µm, X_{50} = 145.19 µm,
X_{90} = 382.70 µm



(b) Recrystallized β–HMX particle size distribution
X_{10} = 2.32 µm, X_{50} = 11.12 µm, X_{90} = 26.75 µm
at 1 h



(c) Recrystallized β–HMX particle size distribution
X_{10} = 2.17 µm, X_{50} = 35.13 µm,
X_{90} = 140.04 µm at 2 h



(d) Recrystallized β–HMX particle size distribution
X_{10} = 7.44 µm, X_{50} = 48.19 µm,
X_{90} = 119.15 µm at 3 h

Fig. 4. Particle size distribution (a) raw (b)–(d) recrystallized HMX at different coalescence times

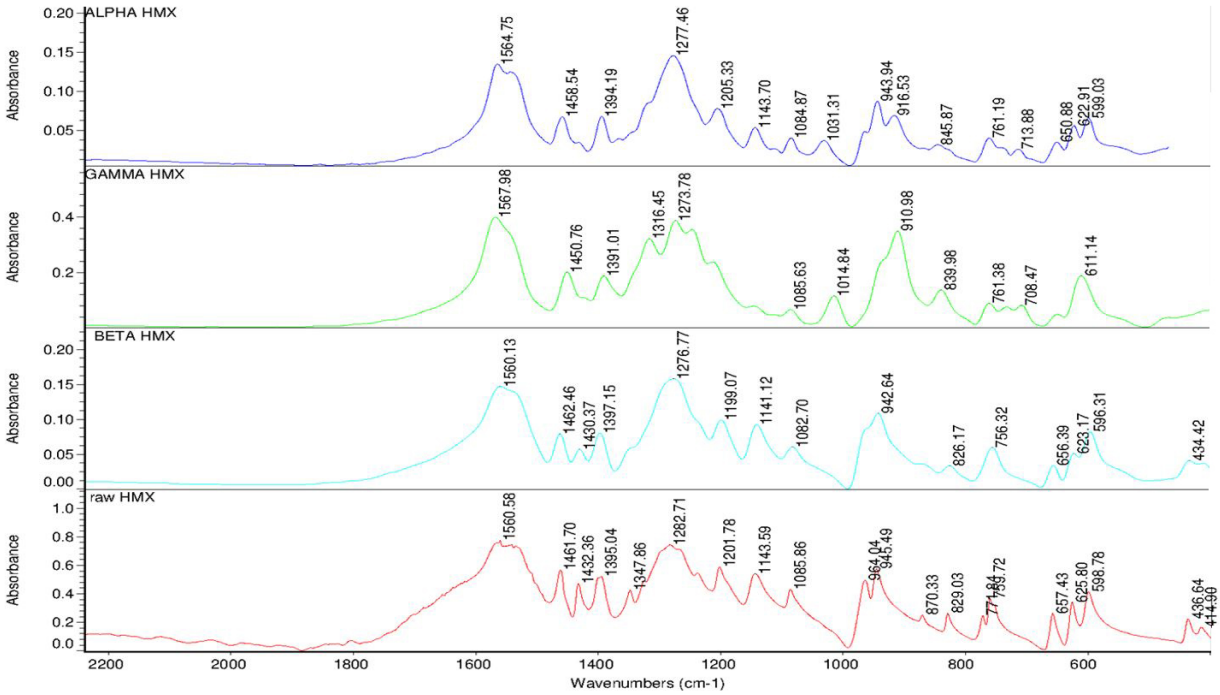


Fig. 5. FTIR spectra of HMX polymorphs

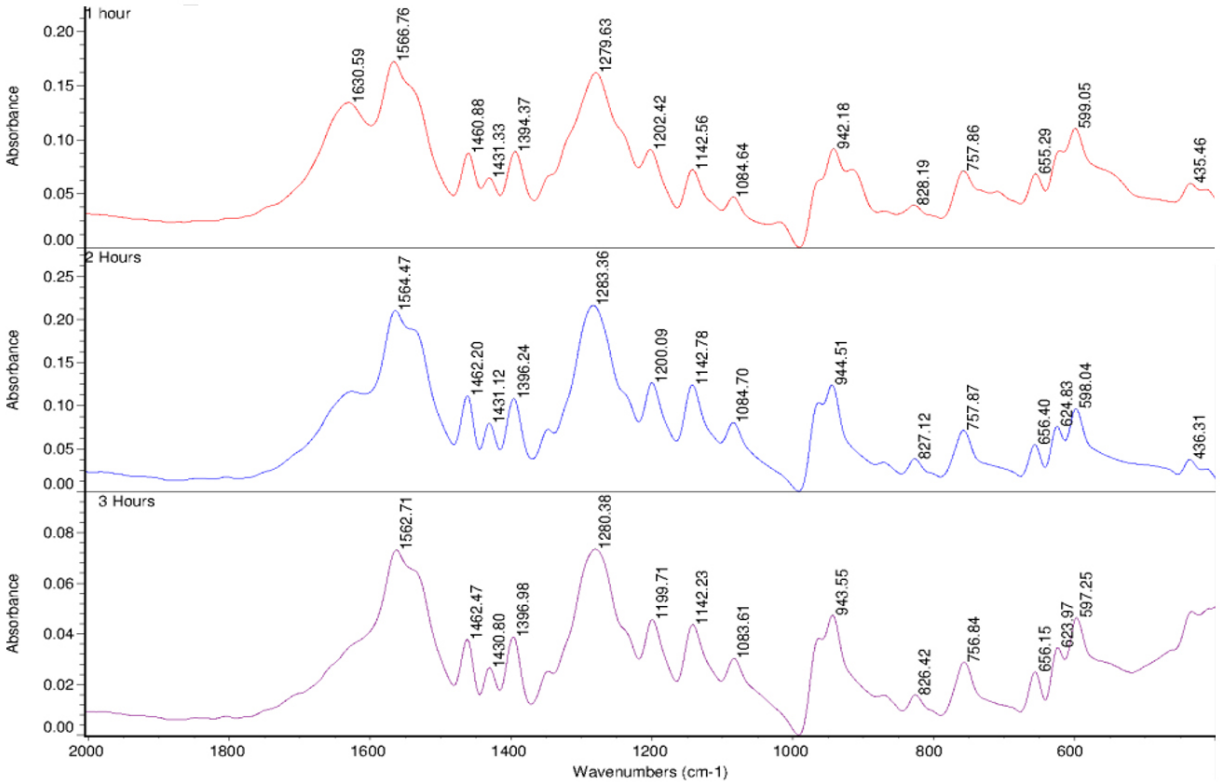


Fig. 6. FTIR spectra of β–HMX for different coalescence times

The IR bands at 708.47 cm^{-1} and 761.38 cm^{-1} ($\nu_s NO_2$) and at 910.98 cm^{-1} (ring stretching bands) are characteristic of γ–HMX. The peaks at 713.88 cm^{-1}, 761.19 cm^{-1} ($\nu_s NO_2$) and 1031 cm^{-1} (ring stretching bands) are characteristic of α–HMX. Figure 6 shows the FTIR spectra of recrystallized HMX at different times of coalescence. No peaks were observed in the range of 700–750 cm^{-1} and 1000–1050 cm^{-1}, confirming the formation of β–HMX. For raw HMX also, there were no transmittance bands between 700–750 cm^{-1} and 1000–1050 cm^{-1} confirming that raw HMX had β–morphology.

4. CONCLUSION

Supercritical antisolvent method was used for controlling the size and morphology of HMX. The recrystallized microparticles of HMX showed a variety of morphologies, particle size and particle size distribution depending upon the operating conditions. In particular, at the operating conditions of 313 K temperature, pressure of 150 bars, CO_2 flow rate of 6 g/min, the mean size of desired β–HMX particles was 13.77 μm. FTIR spectrum of recrystallized HMX particles confirmed the formation of β-polymorph.

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SYMBOLS

$\alpha, \beta, \gamma, \delta$	polymorphs of HMX
μ	micro

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