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Study on ultrasound assisted precipitation of CL-20 and its effect on morphology and sensitivity

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Abstract

Applying ultrasound to crystallizing systems offers significant advantages for modifying and improving the processes as well as quality of products. This paper reports on ultrasound assisted reprecipitation of CL-20 to obtain fine particles as well as to achieve desired morphology, which will improve insensitivity characteristics. In this study, CL-20 has been reprecipitated by sonication process and has been characterized by DSC, SEM and particle size analysis. The results are compared with control CL-20 sample (unsonicated). SEM photographs revealed that sonication process offer uniform crystalline morphology without any agglomeration. The particle size of sonicated CL-20 sample obtained is around 5 ± 1 μm with a narrow particle size distribution. The DSC thermogram of sonicated and unsonicated sample is identical. CL-20 samples were subjected to impact and friction sensitivity experiments, the results indicate the sensitivity characteristics reduced considerably. Ultrasonic assisted crystallization technique reduces the time of reprecipitation considerably with an enhanced recovery of CL-20 with a very narrow particle size distribution.

Keywords: Hexanitrohexaazaisowurtzitane; CL-20; Ultrasonic crystallization; Sonication; Fine particles; Morphology

1. Introduction

Development of energetic materials with improved performance and reduced sensitivity characteristics is a major goal in the area of high energy materials (HEMs). Potential high explosives such as 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), 1,3,5,7-tetranitro-1,3,5,7-tetraaza cyclooctane (HMX), hexanitrohexaazaisowurtzitane (CL-20), and novel oxidizers such as ammonium dinitramide (ADN) and hydrazinium nitroformate (HNF) are very sensitive to impact and friction stimuli. Crystal morphology of these materials plays a vital role in the sensitivity aspects. HEMs with needle shape and sharp edged crystals make the material more sensitive to mechanical stimuli. Hence, lot of safety precautions is exercised during the synthesis, development, handling, formulation processing, storage and transportation. Sensitivity characteristics of HEMs can be related to their chemical as well as physical characteristics. However, the physical characteristics of a HEM such as crystal size, shape, morphology, purity, internal and external defects and the microstructure of inter crystalline voids play vital role in sensitivity of HEMs. One of the ways to lower the sensitivity towards mechanical stimuli is to control the crystal size and morphology to cubic or spherical shape [1].

Particle size also plays a vital in the performance of HEMs. Fine variety (∼5 μm) of RDX and HMX find application in propellant formulations to achieve high burning rates. Hence, preparation of fine particles of HEMs is an important task for scientists and technologists involved in the development of new high-energy materials and their formulations. During, size reduction of HEMs, special processes as well as precautions is exercised [2]. Various techniques have been developed for achieving morphological changes of organic materials. In general, recrystallization is in use to produce desired crystals with acceptable size, shape, high purity and narrow size distribution [3,4]. Ultrasound assisted sonocrystallization is one of the important techniques ever identified.

Sonocrystallization is the use of power ultrasound to control the crystallization process. Ultrasound is used principally to influence the nucleation process and control the crystallization in an ordered manner [5,6]. Power ultrasound creates cavitation in

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liquid media, each cavitation event comprising the opening of a small gas or vapour void followed by its violent collapse resulting in an enhancement of many physico-chemical processes, cleaning, emulsification and solid disruption [7–9]. Cavitation event serves as nuclei for new crystals to form and grow. At high intensities, ultrasound can be used instead of seed crystals to start nucleation at a lesser degree of super saturation. Ultrasound induces the nucleation comparatively at high temperature. The reduction of the metastable zone width has many significant benefits to control crystal size and habit [10].

The purpose of the work is to study the influence of ultrasound during the reprecipitation of CL-20 and its effect on particle size, particle size distribution, morphology and the sensitivity characteristics. Most powerful high explosive of today is 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (HNIW or CL-20), which is a cage compound and belongs to polycyclic nitramine class [11]. Its attributes of great interest are high density ($\rho > 2$ g/cm^3) and positive heat of formation ($\Delta H_f = 100$ kcal/mol). The high performance of CL-20 is also reached owing to a strained cage structure carrying 6-NO_2 substituents. The production technology breakthrough in the USA and France (Thiokol Corporation and SNPE) [12] resulted in its emergence as a superior viable alternative to HMX [13].

This paper reports the reprecipitation of CL-20 in the presence of ultrasound and its effect on particle size and crystal. The Findings are compared with unsonicated CL-20 obtained through normal reprecipitation. Further, the study brings out the advantages of ultrasound on the process as well as the quality of CL-20 produced through this process.

2. Experimental

2.1. Materials

All the reagents and chemicals of AR grade were used as such in the present study. The IR spectra were recorded on Perkin-Elmer FT-IR-1600 spectrophotometer in KBr matrix and ^{1}H NMR spectra scanned on a 300 MHz Varian instrument in deuterated solvents at 30 °C with TMS as an internal standard. The DSC studies were done on a Perkin-Elmer DSC-7 instrument at the heating rate of 10 °C/min in a nitrogen atmosphere with 1 mg of sample.

The sensitivity to impact stimuli was determined by applying standard staircase method using a 2 kg drop weight and the results are reported in terms of height for 50% probability of explosion ($h_{50\%}$) of the sample [14]. Figure of insensitivity (F of I) was computed by using tetryl (composition exploding, CE) as reference. The friction sensitivity of the compound was determined on Julius Peter's apparatus till there was no explosion/ignition in five consecutive test samples at that weight. The crystal morphology has been studied by scanning electron microscope (SEM) instrument of Philips Icon make.

CL-20 particles obtained by re-precipitation method are measured by using Malvern particle size analyzer Malvern-2600. The particle size of CL-20 was determined on the principle based on laser light scattering. Light from low power He–Ne laser is used to form a collimated and monochromatic beam of light. Any particle introduced in this analyzer beam scatters the light. The detector measures the energy of this scattered light at a favoured scattering angle, which is related to the diameter of the particle. SEM is also used to determine the particle size of sonicated CL-20 samples.

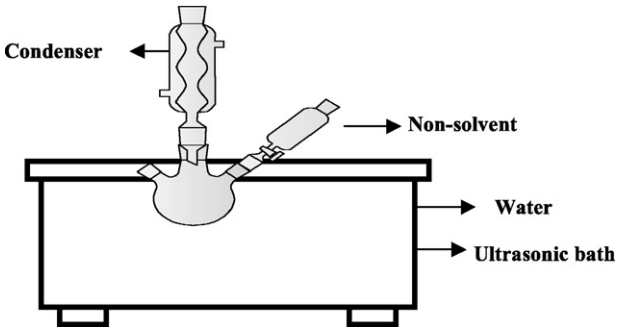

Fig. 1. Experimental set up of ultrasonication.

Sonication experiments were performed in a stainless steel low powered ultrasonic bath, (Dakshin Ltd., India). The internal dimensions of the bath were: length = 0.15 m, breadth = 0.15 m and height = 0.15 m. The bath has three transducers located at the bottom, arranged in a triangular fashion. The bath was driven at 20 kHz ultrasonic frequencies and it had a power rating of 120 W. The bath was scaled in all the three directions. Water was taken in the ultrasonic bath as a cavitations medium and was filled up to a height of 14 cm. The experimental setup has been presented in Fig. 1. SEM photographs were taken at the 100× magnification to understand the morphological changes.

2.2. Methods

2.2.1. Synthesis of CL-20

CL-20 was synthesized by following the reported procedures [15,16]. The synthesized CL-20 has been well characterized [17] and the results are presented in Table 1.

2.2.2. Reprecipitation of CL-20

About 5 g of CL-20 was taken in a three-necked flask fitted with a condenser. About 50 ml of ethyl acetate was added and stirred with a mechanical stirrer to dissolve CL-20. The flask was fitted on an ultrasound bath. About 150 ml of heptane fraction from petroleum fraction was added drop wise with efficient stirring in the presence of ultrasound for a period of 15 min. CL-20 started precipitating during the addition and the addition of heptane was continued until there was no further precipitation. The precipitated CL-20 was filtered, air-dried and characterized. The ethyl acetate/heptane solution has been evaporated to obtain CL-20 and it has been taken for further reprecipitation. Experiments were carried out by varying the time of ultrasound irradiation such as 5, 10, 15 and 17 min.

CL-20 obtained by regular reprecipitation method (without ultrasound) as well as by sonication were characterized by spectroscopic as well as thermal analysis techniques. The data are presented in Table 1.

Table 1
Spectroscopic and thermal characterization data of CL-20

Property	Non-sonicated	Sonicated
m.p. (dec., °C)	>220	>225
UV (nm)	226	225
Acetonitrile, 0.05 mg/ml		
Elemental analysis (%)	C: 16.49; H: 1.34; N: 38.66	C: 16.61; H: 1.49; N: 39.06
Theoretical value	C: 16.44; H: 1.38; N: 38.36	C: 16.44; H: 1.38; N: 38.36
IR (KBr) (γ cm^{-1})	3030 (–CH), 1558 and 1332 (–NO_2)	3030 (–CH), 1560 and 1340 (–NO_2)
^{1}H NMR (δ, ppm) (CD_3CO CD_3)	8.35 (s, 4H,CH); 8.22 (s, 2H,CH)	8.33 (s, 4H,CH); 8.18 (s, 2H,CH)
DSC (T_{max}, °C)	252	253–254

3. Results and discussions

3.1. Spectral studies

The UV spectrum of sonicated CL-20 showed absorption bands in ultraviolet region at 225 nm due to the $n \rightarrow \pi^*$ electronic transition. The IR spectrum of CL-20 showed absorption at 3030 cm^{-1} stretching due to six cage (C–H) and at 1558 and 1332 cm^{-1} attributable to asymmetric and symmetric stretching of NO_2 groups. In proton NMR spectrum of CL-20, the protons of cage resonated at δ 8.4 (protons) and 8.2 (protons). The spectroscopic data of sonicated CL-20 is identical with the unsonicated CL-20 reveals both are chemically similar.

Sonication process reduces the time of addition of heptane fraction to ethyl acetate solution during reprecipitation by one fourth (from 1 h to 15 min) with better recovery of CL-20 of around 95% against to 90% in the case of normal reprecipitation process.

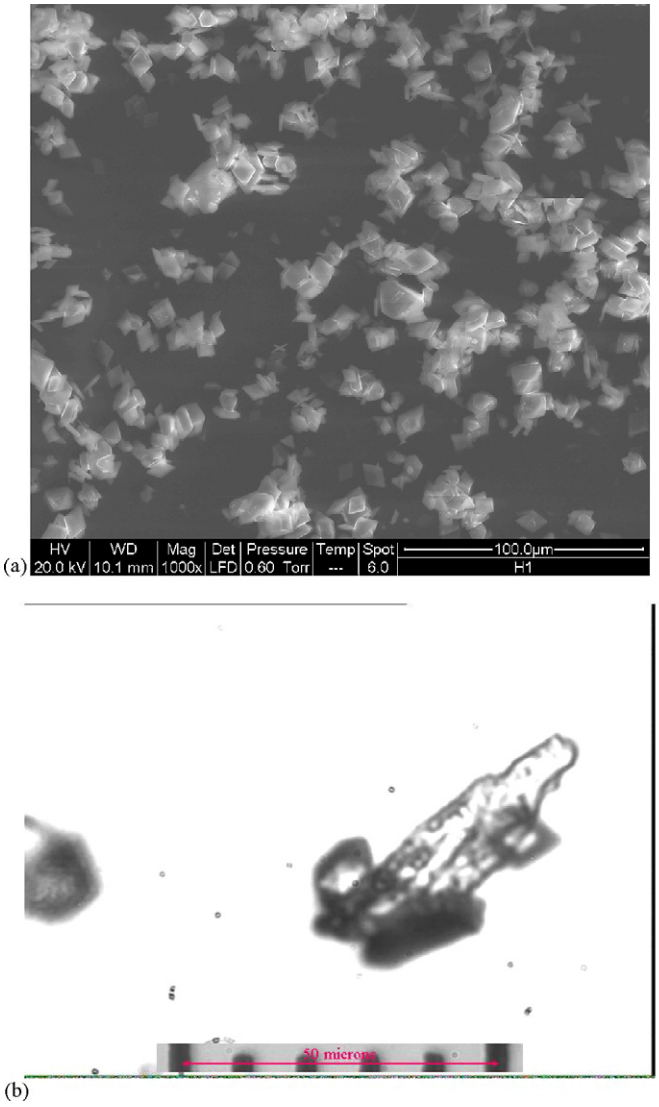

Fig. 2. SEM photograph of unsonicated CL-20.

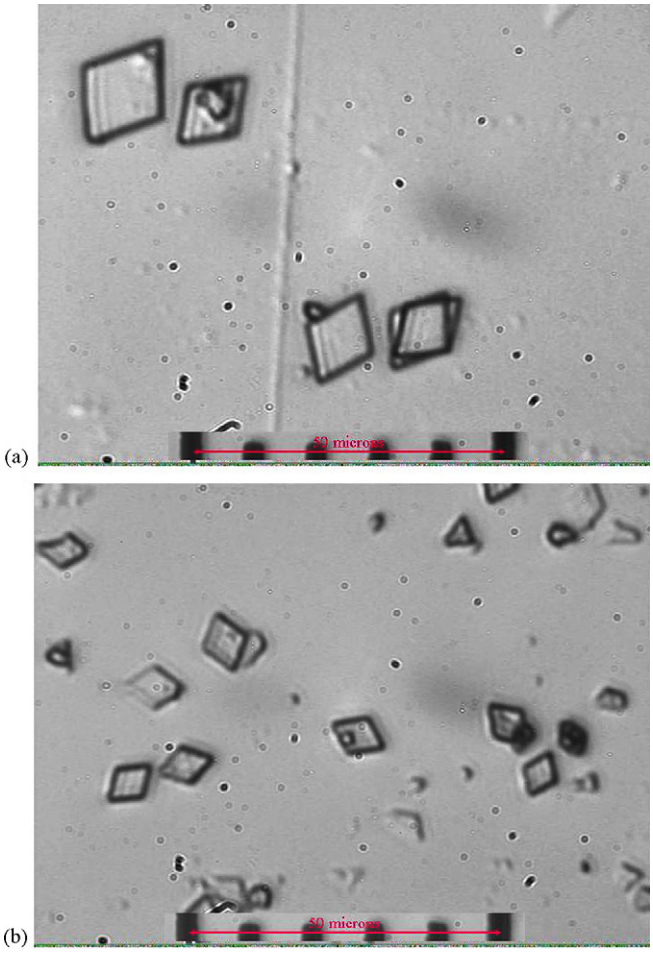

Fig. 3. SEM photographs of sonicated CL-20 (sonication time = 17 min, addition of 150 ml heptane = 15 min under stirring, temperature = 27 ± 3 °C).

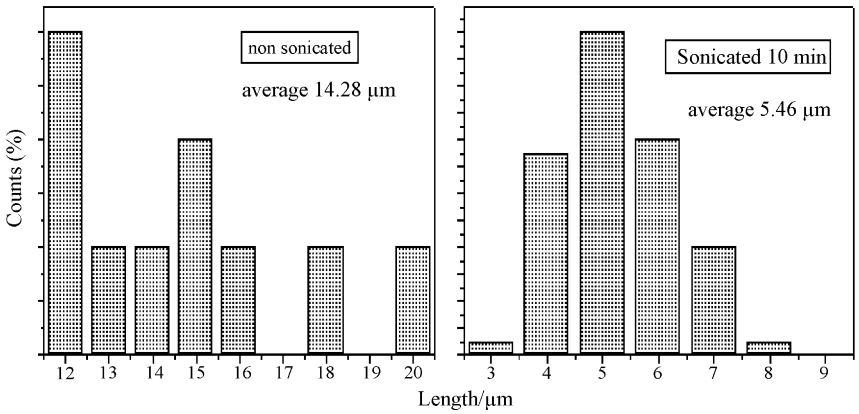

Fig. 4. Particle size distribution of sonicated and non-sonicated CL-20.

3.2. SEM studies

SEM photographs of unsonicated CL-20 sample showed random crystals with a high degree of agglomeration. The crystals are irregular in shape as well as coarse in nature (Fig. 2). CL-20 sample precipitated in the presence of ultrasound showed regular uniform crystal shapes in SEM photographs. Further, the particles are fine in nature. The sample has regular symmetrical plate type morphology (Fig. 3).

CL-20 is often obtained in the form of polycrystalline particles with sharp corners and microscopically visible defects. It is possible to control the particle size of CL-20 by reprecipitation by varying solvents and non-solvents. Fig. 2 shows the image of the CL-20 crystals obtained by normal reprecipitation (without ultrasound) techniques. The crystals are larger and most important observation is that the crystals are aggregated. The particle size of CL-20 obtained by normal re-precipitation method is in the range of 12–20 μm, with an average particle size of 14 μm (Fig. 4). The crystals obtained in the sonication process are smaller in size with less aggregation. It was observed that the particle size is in the range of 4–7 μm with an average particle size of 5 μm (Fig. 4). This study reveals that CL-20 particles from sonication process falls with in narrow range 4–7 μm whereas in the case of normal reprecipitation the particles fall in wide range.

3.3. Thermal studies

The thermogram of non-sonicated as well as sonicated CL-20 samples (10 and 15 min) is given in Fig. 5. DSC

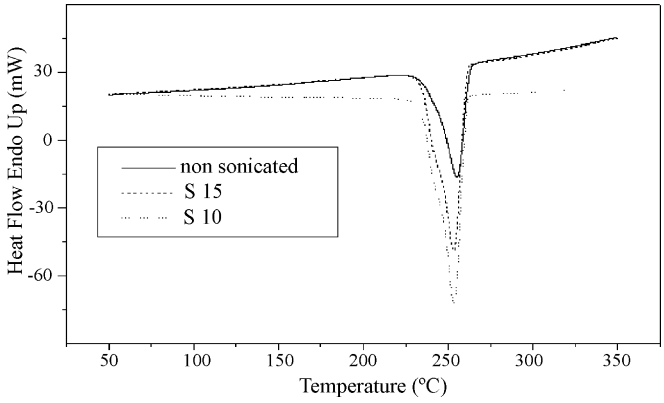

Fig. 5. DSC thermogram of sonicated and unsonicated CL-20 sample.

results showed that an exothermic decomposition is observed in the temperature range 225–260 °C in all the cases. The decomposition maximum (T_{max}) of non-sonicated sample, 10 min and 15 min sonicated samples are of 255.5, 254 and 253.4 °C, respectively. The decomposition maximum is slightly lowering for sonicated samples however sonication process not affected the thermal stability of CL-20.

3.4. Sensitivity studies

It is reported that the impact sensitivity of CL-20 ($h_{50\%}$ = 28 cm) is comparable to that of HMX (30 cm) and TNAZ (26 cm) [18]. The data generated in the study on impact sensitiv-

Table 2
Effect of sonication on particle size, impact and friction sensitivity of CL-20

S. no.	Experimental conditions	Particle size (μm)	Sensitivity	
			Impact ($h_{50\%}$, cm)	Friction (insensitive up to, kg)
1	Unsonicated CL-20	14	24	10
2	5 min sonicated CL-20	9	28	10.8
3	10 min sonicated CL-20	6	44	10.8
4	15 min sonicated CL-20	6	44	10.8
5	17 min sonicated CL-20	5	44	10.8

ity of unsonicated CL-20 is of 24 cm and friction insensitivity up to 10 kg. The impact sensitivity of sonicated CL-20 is of 44 cm and friction insensitive up to 10.8 kg. It is understood that sonication process improves the impact sensitivity of CL-20 from 24 to 44 cm and the friction insensitivity values are not changed considerably. These results are in line with the reported values [19]. Sensitivity results obtained in this study is presented in Table 2.

4. Conclusion

Sonocrystallization is a non-invasive method of using ultrasound to control the point of nucleation and the number of nuclei formed to obtain better crystal habits of products. This process provides uniform, unagglomerated distinct crystals of similar shape with improved insensitivity characteristics. In this work, CL-20 has been reprecipitated in the presence of ultrasound and the effect of ultrasound on the morphology, particle size, particle size distribution and sensitivity aspects have been studied. SEM photographs revealed that sonication process provides uniform morphology to the crystals. Further, it produces fine particles of CL-20 with a narrow distribution of the order of 5 μm. Sonication process reduces the reprecipitation time to one third and enhances the yield. The thermal and spectroscopic studies confirm chemical structure as well as the thermal stability is identical with standard CL-20 sample (non-sonicated).

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