



A novel approach for preparation of CL-20 nanoparticles by microemulsion method



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ABSTRACT

2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) as one of the high energy cage nitramines has been used in various propellants and explosive formulations. The performance of energetic materials depends on its particle size and shape. Therefore, in this research, microemulsion method has been applied for the preparation of CL-20 nanoparticles via oil in water (O/W) microemulsions. The optimized formulation contains water 45%, n-butyl acetate 20.5%, sodium dodecyl sulfate (SDS, as anionic surfactant) 6.5% and 2-propanol (as co-surfactant) 26.5%. CL-20 nanoparticles that were obtained by microemulsion method are spherical with an average diameter of 25 nm, based on TEM image. CL-20 nanoparticles were also characterized by SEM image analysis, FTIR spectroscopy and TG method.

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1. Introduction

In comparison to micronized energetic materials, the nano-scale energetic materials indicate different properties. Energetic nanoparticles have significantly higher burning rates, lower impact sensitivity and high rate energy released than micronized energetic materials [1–6].

CL-20 (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane, Fig. 1) is an explosive compound that is 14–20% more powerful than HMX (High Melting Explosive, a classical nitramine explosive). Its high detonation velocity and pressure make CL-20 a suitable candidate for a wide range of military and commercial purpose [7–9].

Size reduction of materials has been done by different kinds of methods to improve their characteristics. These methods include various techniques from utilization of high-pressure mill to crystallization with ultrasonic vibration. One of these methods is supercritical fluid, until today, various techniques for particle formation via supercritical fluid technology including two general processes have been used: supercritical antisolvent (SAS) process and rapid expansion from supercritical solution (RESS) process. The SCF based techniques have many advantages rather than classical micronization processes such as preventing thermal degradation of the target compounds, no mechanical damage, and no residual solvent problem. The main work for an explosive particle formation via SCF processes such SAS recrystallization

and RESS process is preparation of fine particles with various sizes and shapes by controlling the super saturation and nucleation rates of the explosive in the SCF media using variation in solvent strength. Especially, the SAS process as a recrystallization technique is a promising process for production of solvent-free explosive particles with fine sizes. But these methods is very difficult for scale-up [10,11]. Also other applied methods are sol–gel, high speed air impaction, vacuum co-deposition [12,13] and reprecipitation at the room temperature. Most of these methods suffer from some deficiencies for example, in milling procedures the structural elements of a solid are broken down with mechanical forces, in which the particles are subjected to the high levels of mechanical stress. Crystallization with ultrasonic vibration consists of two steps: 1) solution subjected to ultrasonic impression and 2) crystallization of particle from solution. For organic compound controlling particle size in this step, is difficult. [10–14].

Microemulsions are transparent, well characterized, thermodynamically stable and easily manufactured systems which consist of nano-sized water pools dispersed within an immiscible organic phase or oil in water. The synthesis of inorganic nanoparticles in microemulsions is already widespread [15–17]. However, only a few reports on the preparation of organic nanoparticles in microemulsions [18–26].

This work is focused on the preparation of CL-20 nanoparticles through microemulsion method by direct evaporation of all organic phases in water solution. Despite other common methods such as ball mill, solvent/non-solvent, re-crystallization and sol–gel methods, this method has several advantages such as: simplicity, being cost-effectiveness, and easy scaled up. Moreover, nanoparticles obtained in the microemulsion method show an appropriate distribution [27,28].

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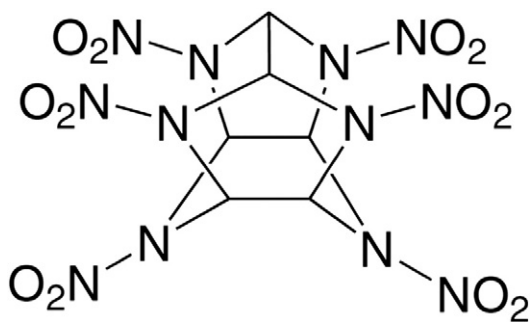


Fig. 1. Molecular structure of CL-20.

2. Experimental

2.1. Materials

CL-20 was synthesized in our laboratory by the reported procedure [29,30]. Other materials such as sodium dodecyl sulfate (SDS), as a surfactant, 2-propanol as a co-surfactant, n-butyl acetate and ethyl acetate, were purchased from Merck.

2.2. Instruments

Drying process was carried out using a Christ lyophilizer (model 2-4α). Size and shape of nanoparticles were observed by transmission electron microscope (TEM, Philips-CM 120) operated at 100 keV. Morphology of nanoparticles was observed under a scanning electron microscope (SEM, Philips XL30) after gold film coating. Precipitation process was done by a Heraeus (RF model) centrifuge. Thermal properties of nanoparticles were evaluated by differential thermal analysis (Bahar STA-503).

2.3. Preparation of CL-20 nanoparticles

Preparation of CL-20 nanoparticles by this method includes four significant steps: the first step includes preparation of thermodynamically stable and limpid microemulsion dispersions. The second step includes freezing of microemulsion dispersion by freezer or liquid nitrogen. Step three includes drying frozen solution by lyophilizer and finally, separation of surfactant from nanoparticles by precipitation.

Before microemulsion preparation, CL-20 was loaded in n-butyl acetate or ethyl acetate with different CL-20 percentages (20%, 15%, 10% and 5%).

Typical procedure: For microemulsion dispersion preparation 45 mg water was added to a mixture of 22 mg n-butyl acetate or ethyl acetate, 16.5 mg SDS and 16.5 mg 2-propanol. Then the mixture was stirred until a transparent and thermodynamically stable microemulsion was formed.

The resulting compositions were equilibrated for 24 h at 25 °C. Only compositions which remained transparent and homogeneous after this period of time were attributed as limpid and thermodynamically stable microemulsion. Then, drying process was carried out at ($T = -36$ °C, $P < 1$ mbar) conditions for 18 h. Next, SDS separation process was done removed by washing several times with water and alcohol (1:1).

Table 1
Different percentages of “surfactant/co-surfactant” for preparation of limpid microemulsion.

Entry	Organic phase (%)	2-Propanol (%)	SDS (%)	Water (%)
1	22	16.5	16.5	45
2	22	25	8	45
3	22	26.5	6.5	45

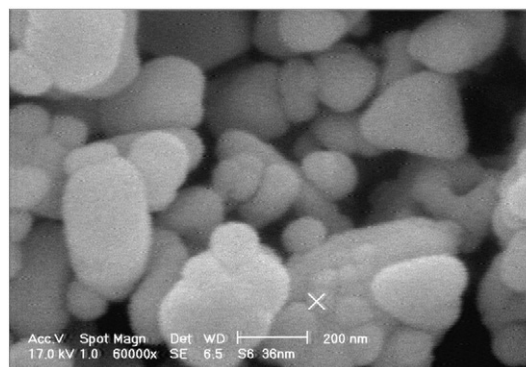


Fig. 2. SEM image of CL-20 after separation from SDS.

For that, 10 mL deionized water was added to 1 g powder obtained from lyophilization step. Then, it was stirred manually till all SDS dissolved in water. By centrifuging of the suspension, all CL-20 nanoparticles were precipitated. All solvents were decanted and CL-20 nanoparticles dried at 50 °C after 48 h.

3. Result and discussion

3.1. Effect of the organic solvent nature in microemulsion

In order to evaluate the organic solvent nature, two volatile solvents, ethyl acetate and n-butyl acetate were chosen. No significant differences were observed in freezing point of these solvents. Therefore, both of them frozen in the same way. However, ethyl acetate is more miscible in water than n-butyl acetate. Hence ethyl acetate exists in water phase of microemulsion. Consequently, when water was added to form microemulsion, dissolved CL-20 in ethyl acetate precipitated in the water and disturbed the microemulsion system. As a result, limpid and thermodynamically stable microemulsion was obtained only by applying n-butyl acetate as an organic solvent.

3.2. Effect of initial concentration of CL-20 in organic phase

In order to prepare microemulsion with more percentage of CL-20, different organic phases with various concentrations of CL-20 in n-butyl acetate and ethyl acetate were used (25%, 15%, 10%, 5%). Only microemulsion with n-butyl acetate as an organic phase loaded with 5% CL-20 was limpid and thermodynamically stable. Microemulsions with more CL-20 percentages were not limpid and thermodynamically stable.

3.3. Effect of co-surfactant nature and its concentration in microemulsion formulation

In a variety of proportions, SDS and 2-propanol as surfactant/co-surfactant components, effect on the microemulsion dispersion. In

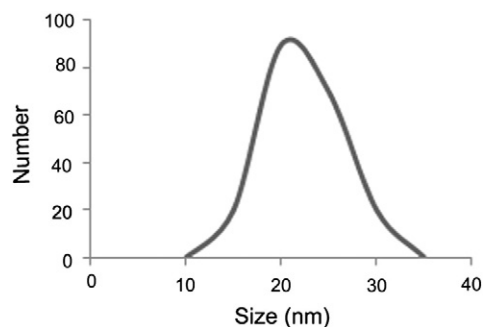


Fig. 3. Number distribution of particle size.

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