Journal of Molecular Liquids xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Synthesis and characterization of novel 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo dodecane based nanopolymer-bonded explosives by microemulsion

Yadollah Bayat [a,*], Rouhollah Soleyman [b], Maryam Zarandi [a]

[a] Department of Chemistry and Chemical Engineering, Malek Ashtar University of Technology, P.O. Box 16765-3454, Tehran, Iran
[b] Sharif University of Technology, Tehran, Iran

ARTICLE INFO

Article history:
Received 22 June 2014
Received in revised form 18 December 2014
Accepted 11 February 2015
Available online xxxx

Keywords:
CL-20
Microemulsion
Nano-polymer/plastic bonded explosives
Glycidyl azide polymer
Ethylene–vinyl acetate
Energetic material

ABSTRACT

2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo dodecane (CL-20)-based polymer/plastic bonded explosives are used in propellant formulation. It can be predicted that CL-20-based nano-polymer/plastic bonded explosives are able to have reduced composite sensitivity and superior mechanical strength. In the current study, we have prepared two kinds of CL-20-based nano-polymer/plastic bonded explosives with ethylene–vinyl acetate copolymer and glycidyl azide polymer via the microemulsion method. Several visual techniques such as SEM/AFM/TEM techniques have been utilized for complete characterization of CL-20-based nano-polymer/plastic bonded explosives. Dynamic light scattering has also been used for determination of the nanoparticle size. The sizes of CL-20/ethylene–vinyl acetate and CL-20/glycidyl azide nano-polymer/plastic bonded explosives have been estimated around 32 and 18 nm, respectively.

1. Introduction

CL-20 (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane or HNIW; see Fig. 1) belongs to the family of high energy dense caged nitramines which is used in energetic material formulation. CL-20 was first prepared in 1987 by Nielsen, and is now being produced at several factories on industrial pilot plants all over the world [1]. Although CL-20 is one of the suitable explosive materials, but design of future weapons requires utilization of explosive/propellant formulations having enhanced performance (energy output) and reduced vulnerability during storage and transportation. Several important considerations for design of these formulations include improved mechanical properties, decreased signature, extended service life and reduced environmental impact in manufacture, use and disposal [2,3].

One approach to reduce sensitivity of explosives is the development of polymer/plastic bonded explosives (PBXs). PBXs are composite materials consisting of a mixture of explosive crystals and a polymeric binder. The ratio of the explosive component to the binder varies from one material to the next, but, typically, the explosive component comprises 80–95% of the mass of the composite [4]. One of the earliest polymeric binders used in energetic materials was a mixture of nitrocellulose and nitroglycerine, where the nitrocellulose was used to thicken the nitroglycerine and reduce impact and friction sensitivity [3]. Nowadays, the current attentions are paid to encapsulate the explosives in a suitable polymer such as hydroxyl-terminated polybutadiene (HTPB), carboxyl-terminated polybutadiene (CTPB) and hydroxyl-terminated polyethers (HTPE) [3]. So far, several polymeric binders such as estane (polyamidoethylformate), ethylene–vinyl acetate copolymer (EVA), glycidyl azide polymer (GAP) and HTPB have been utilized for preparation of CL-20-based PBXs [5–10]. Also, molecular dynamic calculations have been employed to simulate the well-known high energy density of CL-20-based PBXs with four kinds of typical fluorine polymers, such as polyvinylidenedifluoride, polychlorotrifluoroethylene, fluorine rubber (F2311), and fluorine resin (F2314) individually [11].

Microemulsion is one of the most effective, flexible and convenient method for producing nanoparticles with a minimized degree of agglomeration and controlled morphology. Microemulsion solutions are transparent, isotropic liquid media that are stabilized by surfactant/co-surfactant molecules at the water/oil interface. These surfactant/co-surfactant stabilized cavities provide a cage like effect that can control nucleation and growth. As a result, the particles obtained in such a manner are generally very fine and mono-dispersed [12–14].

The behavior of nanoscale materials is quite different from micro-size energetic materials in many ways. They have higher burning rates, lower impact and friction sensitivity and, lower temperature of

* Corresponding author.
E-mail address: y_bayat@mut.ac.ir (Y. Bayat).

http://dx.doi.org/10.1016/j.molliq.2015.02.019
0167-7322/

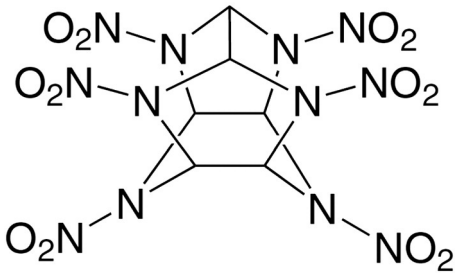

Fig. 1. Molecular structure of CL-20.

the maximum energy release compared to the conventional energetic materials with larger size [15,16].

In the current research, for the first time, we have prepared CL-20-based nano-PBXs with two convenient polymers (EVA and GAP) via the microemulsion method. For each polymer, four kinds of nano-PBX with various CL-20/PBX weight ratios were prepared. In order to investigate prepared nanoscale CL-20-based PBXs versatile techniques applied.

2. Materials and methods

2.1. Chemicals

CL-20 was prepared by nitration of 2,6,8,12-tetraacetyl 2,4,6,8,12-hexaazaisowurtzitane (TAIW) in our research laboratory according to the conventional method [17]. EVA (ethylene–vinyl acetate copolymer) and GAP (glycidyl azide polymer) were used commercial grade. Sodium dodecyl sulfate (SDS) as an anionic surfactant, n-butanol as co-surfactant and isobutyl acetate (IBA) as a suitable organic solution were purchased from Merck (Darmstadt, Germany). For preparation of all microemulsions, double-distilled deionized water was used.

2.2. Procedure for preparation of nano-PBXs

Preparation of nano-PBXs by this method consists of several steps: the first step includes preparation of microemulsion dispersions by application of different formulations. The second step includes freezing of microemulsion dispersion by freezer or liquid nitrogen. In the step three all solution frozen by a lyophilizer and at last, surfactant separated by precipitation of nanoparticles.

Typical method for preparation of microemulsion dispersions: in a beaker 0.090 g CL-20 and 0.010 g EVA were dissolved in 2 mL IBA. Then, 20 mL H_2O, 2.0 g SDS and 5 mL n-butanol were added in drop wise manner to a magnetically stirred solution. After complete addition, the microemulsion dispersions prepared spontaneously.

Nano-PBXs were prepared via combination of CL-20 with two kinds of conventional polymers utilized as a binder in lots of PBXs (EVA and GAP) by the microemulsion method. In the current research, for each polymer, four kinds of nano-PBX with 80, 85, 90 and 95% CL-20/PBX weight ratios were prepared.

Then, drying process was carried out at ($T = -36\ ^\circ C$, $P < 1$ mbar) conditions for 18 h. Next, SDS separation process was done removed by washing several times with water and ethanol. For that, 10 mL deionized water was added to obtain dried product 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. In the next step in order to facilitate drying and water removal, solid washed by 10 mL ethanol three times. All solvents were decanted and nanoparticles dried at 50 °C after 24 h [18].

2.3. Characterization

Particle size of the samples was determined by dynamic light scattering (DLS, zetasizer ZS, Malvern) instrument using a 4-mW He–Ne laser (633 nm wavelength) with a fixed detector angle of 173°. The morphology of the nano-PBXs was examined using a scanning electron microscope (SEM, Philips, XL30) operated at 20 kV after coating the samples with gold film. High-resolution surface imaging studies were

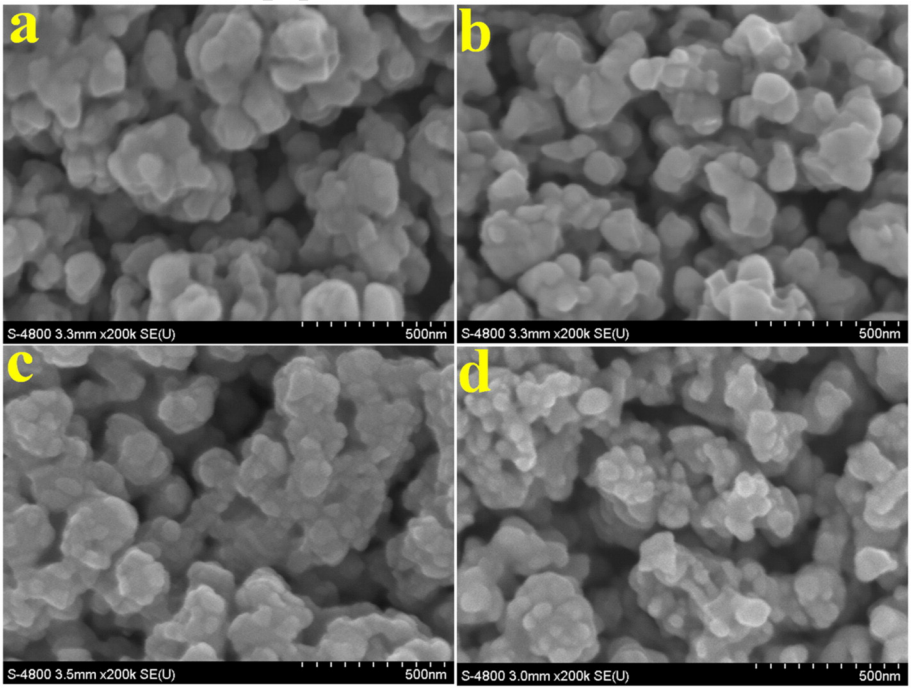

Fig. 2. SEM images of CL-20/EVA nano-PBXs with (a) 80, (b) 85, (c) 90 and (d) 95% CL-20/PBX weight ratios.

Please cite this article as: Y. Bayat, et al., Synthesis and characterization of novel 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo..., J. Mol. Liq. (2015), http://dx.doi.org/10.1016/j.molliq.2015.02.019