Recrystallization of CL-20 to $\varepsilon$-polymorphic form

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Abstract. High explosive CL-20 (2,4,6,8,10,12 - Hexanitro - 2,4,6,8,10,12 - hexaazaisowurtzitane) exists in four polymorphic forms i.e. $\alpha$, $\beta$, $\gamma$ and $\varepsilon$ polymorphs at ambient conditions and polymorph $\zeta$ exists only at high pressure (1.44 GPa). CL-20 is the only single compound having highest energy among all the organic substances. But polymorphic form $\alpha$- of CL-20 is generally obtained during most of the synthetic processes which has low density and high sensitivity. Thus, there is requirement of further recrystallization to obtain most stable $\varepsilon$-polymorphic form. Owing to the highest density, superior thermal stability and better insensitivity of $\varepsilon$- polymorph over other three polymorphs ($\alpha$-, $\beta$- and $\gamma$-form) which are highly sensitive towards impact, friction and shock, $\varepsilon$- CL-20 is most desirable for use in defence applications. The present work studies the effect of various variables which influence the crystallisation process like effect of moisture, nature of solvent/anti-solvent and time on the preparation of $\varepsilon$- form of CL-20. Ethyl acetate and n-butyl acetate as solvents and toluene as anti-solvent resulted in the formation of desired $\varepsilon$-polymorphic form successfully. Polymorphic form was confirmed by FTIR and XRD analysis. SEM analysis was carried out for the morphological analysis of prepared samples.

1. Introduction

High energetic materials (HEMs) are characterized by instantaneous release of huge amount of chemical energy stored in their molecular structures. However, their high performance is also associated with high sensitivity. The reduced sensitivity has always been a primary concern in the field of energetic materials to ensure their safety during handling, processing, assemble and transportations as per requirements of the end user [1].

CL-20 is one of the well-known high energy explosives having high detonation velocity and detonation pressure making CL-20 a suitable candidate for wide range of military and commercial applications, but its high sensitivity towards impact and friction, limits its applications [2, 3]. Under today’s battlefield conditions, it is required to obtain a fine balance between high performance and low sensitivity. The general chemical information and some physical properties of the CL-20 high energy material are given in Table 1, and its chemical structure is shown in figure 1 [4]. The basic skeleton of CL-20 molecule is a rigid isowurtzitane cage having two five membered rings and a six membered ring.
The presence of six nitro groups on each bridging nitrogen atom along with the cage strain in the CL-20 molecule facilitates the rapid release of high energy. CL-20 has been reported to exist in five different polymorphic forms. The four polymorphs i.e. α, β, γ and ε exist at ambient conditions and another polymorph ζ exists only at high pressure (1.44GPa).

ε-polymeric form of CL-20 is of interest because of its highest density (2.044 g/cm³) as compared to the other polymorphic forms, and most thermodynamically stable due to its high symmetric configuration of molecules in the structure [5-7]. However, CL-20 has always been isolated in low density hydrate α-form during most of the synthetic process as even small amounts of water in the reaction medium preferentially stabilizes the hydrated α-phase and thus further recrystallization is required to obtain the high density ε-form. Many efforts for processing such high quality explosive crystals have been done and are still in progress. Literature reports that sensitivity of crystalline energetic materials mostly depends on the physical characteristics such as crystal size, morphology, purity, internal and external defects and microstructure of internal crystalline voids. In order to tailor and improve high explosive properties, researchers have tried various techniques which include synthesizing new energetic compounds, improving quality of high explosive crystals, preparing nano-scale particles of explosives and adding insensitive compounds or doing coatings of polymeric matrix on explosives crystals for obtaining less sensitive and high performance explosives. [8-11].

The present study was conducted to understand the polymorphic phase transformations in solution to obtain most desirable and stable ε-polymeric form of CL-20 by using solvent/anti-solvent method. The organic solvents used in this work were ethyl acetate and n-butyl acetate, anti-solvents used were petroleum ether, hexane, toluene and their mixtures, transformation time were important parameters that were varied to assess their effect on phase transformation.

Table 1. Physical properties of CL-20 [4]

| Property                                | Data value |
|-----------------------------------------|------------|
| Molecular weight                        | 438        |
| Melting temperature (°C)                | 247        |
| Crystal density at 20°C (g/cm³)         | 2.04       |
| Oxygen balance (%)                      | -10.96     |
| Chemical Energy of detonation (kJ/g)    | 6.69       |
| Detonation velocity (km/s)              | 9.48       |
| Detonation pressure (GPa)               | 42.23      |
| Energy of formation (kJ/mole)           | 372        |

2. Experimental

2.1. Materials
Raw CL-20 was provided by Terminal Ballistics Research Laboratory, DRDO, Chandigarh. Acetone, AR grade, was purchased from Sigma. Ethyl acetate, n-butyl acetate, petroleum ether and toluene used were of AR grade, purchased from S.D. fine Chemicals Ltd. AR grade Hexane was purchased from Ranbaxy Fine Chemicals Ltd.

2.2. Methodology
Solution of CL-20 was prepared in the suitable solvent. For a given solvent, 20 g of CL-20 was added to 100 ml of solvent in a 250 ml round bottom flask and heated in Buchi rotavapor (figure 2) under reduced pressure based on the solvent used (Table 2). Anti-solvent was then added drop wise for crystallizing CL-20, with the help of micropipette with continuous stirring. The resulting suspension was placed in desiccator for conditioning of precipitates for different times with stirring being provided
at 250 rpm. Recrystallized CL-20 was filtered, washed and dried in vacuum oven for further characterization.

![Chemical structure of CL-20.](image1.png)

**Figure 1. Chemical structure of CL-20.**

2.3. **Characterization**

The FTIR spectrum of CL-20 crystals was recorded using Thermo Fisher Scientific FTIR Spectrometer (Nicolet 8700). The spectrum was recorded in the frequency range from 4000 to 400 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\) with DTGS as detector. Surface morphology was studied by using Scanning Electron Microscope (Carl Zeiss, EVO Series). The dried sample was kept in clean aluminium stub which was covered with silver tape. In order to protect the sample from charging during analysis, sputter-coating of the sample was carried out with gold at 20 mA for 180 seconds before SEM. X-ray diffraction analysis was conducted on XPERT-PRO diffractometer operating at voltage of 45 kV and current of 40 mA with monochromatic Cu k(α) radiation having \(\lambda=1.5406 \text{ Å}\). The scanning was done in the region of 20 from 20° to 80° at a scan rate of 0.017°/min.

3. **Results and Discussion**

CL-20 particles were precipitated by solvent/anti-solvent process. The experimental conditions are shown in Table 2. In the solvent/anti-solvent process, different solvents, anti-solvents and their combinations were used: ethyl acetate and n-butyl acetate as solvents and petroleum ether, hexane, toluene, and their mixtures as anti-solvents. The raw CL-20 particles were irregular in shape, on the other hand, recrystallized CL-20 particles showed various shapes. It was observed that CL-20 particles recrystallized with toluene as anti-solvent and at least three hours of conditioning time of the suspension resulted in obtaining the required \(\varepsilon\)-polymorphic form of CL-20. The CL-20 particles have been analysed by performing the infrared spectral analysis, SEM and XRD.

3.1. **FT-IR Analysis**

Recrystallized CL-20 using various solvents/anti-solvents yielded various polymorphic forms of CL-20 and their Fourier Transform Infrared spectra is shown in figures 3 - 8. FTIR of \(\alpha\)-polymorphic form showed triplet near 750 cm\(^{-1}\) (739 cm\(^{-1}\), 750 cm\(^{-1}\) and 763 cm\(^{-1}\)) (figure 3) and the presence of low intensity sharp hydrate peak at about 3700 cm\(^{-1}\) confirmed the raw CL-20 to be \(\alpha\)-polymorphic form as shown in figure 6 [12]. The \(\varepsilon\)-polymorphic form of CL-20 (figure 5) could be identified from the FTIR peaks which showed a doublet at 818 cm\(^{-1}\) and 830 cm\(^{-1}\) and a quartet near 750 cm\(^{-1}\) (738 cm\(^{-1}\), 744 cm\(^{-1}\), 750 cm\(^{-1}\), 757cm\(^{-1}\)). The \(\beta\)-form exhibited a single peak at 835 cm\(^{-1}\) instead of doublet at 825 cm\(^{-1}\) (figure 4) that clearly distinguished it from \(\alpha\)-form and \(\varepsilon\)-form of CL-20 [6].
Figure 3. FTIR of Raw CL-20 (α-form).

Figure 4. FTIR of Recrystallized CL-20 (β-form).

Figure 5. Recrystallized CL-20 (ε-form).
Figures 6, 7 give a staggered view of the spectrum obtained. These results indicate that \( \alpha \)-polymorphic form can be transformed to \( \beta \)-polymorphic form in a moisture free environment, which can be further transformed to \( \varepsilon \)-polymorphic form if the suspension is conditioned for a minimum time of 3 hours. FTIR results tabulated in Table 2 show that different anti-solvents such as petroleum ether, hexane and toluene resulted in the formation of \( \alpha \), \( \beta \) and \( \varepsilon \)-polymorphic forms respectively using ethyl acetate as solvent. When n-butyl acetate was used as solvent, then anti-solvents like hexane, petroleum
ether, hexane : petroleum ether (1:1) and toluene : petroleum ether (1:1) resulted in the formation of β-polymorphic form while toluene as anti-solvent yielded ε-form.

Figure 8 shows the effect of transformation time on the polymorphic transformation of CL-20. n-butyl acetate and toluene were used as solvent and anti-solvent respectively, temperature and pressure of rotavapor were fixed at 40ºC and 25 mBar, and the suspension was conditioned for different time intervals as shown in Table 2. FTIR analysis shows that samples which were conditioned for a minimum time of 3 hours in moisture free environment resulted in the formation of ε-polymorphic form.

![Figure 8. FTIR spectra of CL-20 polymorphs obtained at varying conditioning times in the wavenumber range 1500-400 cm⁻¹](image)

3.2. SEM Analysis

The crystal morphology of the raw CL-20 and recrystallized CL-20 are shown in figures 9-11. SEM image of raw CL-20 (figure 9) shows crystals of irregular shapes and different sizes (greater than 20
µm). The particles were observed to be highly agglomerated. On the other hand SEM images of recrystallized CL-20 shown in figures 10, 11 show crystals of uniform shape with particle size in the range of 2-10 µm. Recrystallization resulted in formation of bipyramidal crystals which is the characteristic of ε- form as shown in figure 10. Recrystallized CL-20 with toluene as anti-solvent and n-butyl acetate as solvent (Table 2) yielded fine particles as shown in figure 11, but presence of both bipyramidal and rod shaped crystals shows that crystals are mixture of ε- and β-polymorphic forms which also conforms to FTIR analysis.

### Table2. Experimental conditions and parameters.

| S. No. | Solvent       | anti- Solvent       | Rotavapor Pressure (mBar) | Transformation Time (min) | Polymorphic form of final phase (using FTIR) |
|--------|---------------|---------------------|--------------------------|---------------------------|--------------------------------------------|
| 1.     | Ethyl Acetate | Petroleum ether     | 240                      | Instantaneous             | α                                          |
| 2.     | Ethyl Acetate | Petroleum ether     | 240                      | 180                       | ε+β                                        |
| 3.     | Ethyl Acetate | Hexane              | 240                      | 180                       | β                                          |
| 4.     | Ethyl Acetate | Toluene             | 240                      | 180                       | ε                                          |
| 5.     | n-butyl acetate | Hexane             | 25                       | 180                       | β                                          |
| 6.     | n-butyl acetate | Toluene: Petroleum Ether (1:1) | 25 | 180 | β |
| 7.     | n-butyl acetate | Toluene: Hexane (1:1) | 25 | 180 | β |
| 8.     | n-butyl acetate | Petroleum ether     | 25                       | 180                       | β                                          |
| 9.     | n-butyl acetate | Toluene             | 25                       | 180                       | ε                                          |

### Effect of transformation time

| S. No. | Solvent       | Rotavapor Pressure (mBar) | Transformation Time (min) | Polymorphic form of final phase (using FTIR) |
|--------|---------------|--------------------------|---------------------------|--------------------------------------------|
| 10.    | n-butyl acetate | Toluene                 | 25                       | 60                        | ε+β                                        |
| 11.    | n-butyl acetate | Toluene                 | 25                       | 120                       | ε+β                                        |
| 12.    | n-butyl acetate | Toluene                 | 25                       | 180                       | ε                                          |
| 13.    | n-butyl acetate | Toluene                 | 25                       | 210                       | ε                                          |
| 14.    | n-butyl acetate | Toluene                 | 25                       | 240                       | ε                                          |

#### 3.3. X-Ray Diffraction Analysis

XRD pattern for raw CL-20 shown in figure 12a shows peaks at 2θ = 12.16°, 13.79°, 17.57°, 20.25°, 25.07° and 28.04° which are the characteristic peaks of α- polymorphic form [13]. Recrystallized CL-20 that was prepared using petroleum ether as anti-solvent and n-butyl acetate as solvent (figure 12b)
showed characteristic peaks at $2\theta = 13.5^\circ$, $23.6^\circ$, $24.6^\circ$, $28.1^\circ$ and $28.2^\circ$, characteristic of $\beta$-polymorphic form [6]. $\varepsilon$-polymorph of recrystallized CL-20 (figure 12c) was obtained when toluene was used as anti-solvent and n-butyl acetate as solvent as XRD analysis shows peaks at $2\theta = 12.6^\circ$, $12.8^\circ$, $15.7^\circ$, $16.3^\circ$, $25.8^\circ$ and $30.4^\circ$ which are the characteristics peaks of $\varepsilon$-polymorph [6]. Hence, XRD analysis confirms formation of $\varepsilon$-polymorphic form of CL-20 using solvent/anti-solvent technique on conditioning the suspension for a minimum of 3 hours in a moisture free environment.

![XRD pattern](image-url)

**Figure 12.** XRD pattern for (a) Raw CL-20, $\alpha$-form (b) Recrystallized CL-20, $\beta$-form (c) Recrystallized CL-20, $\varepsilon$-form.

4. Conclusion:
CL-20 was recrystallized using solvent/anti-solvent process and studies show that choice of solvent/anti-solvent and conditioning time for precipitates were important factors that influence formation of different polymorphs. $\varepsilon$-polymorph of CL-20, which is desirable polymorph owing to its highest density, superior thermal stability and better insensitivity was obtained using toluene as anti-solvent and n-butyl acetate as solvent in an moisture free environment. The transformation time is also very important parameter during conditioning of recrystallized polymorph. The studies revealed that transformation time of minimum three hours is imperative for the conversion of $\beta$-polymorph to most stable $\varepsilon$-polymorph of CL-20.
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