Effect of gap on the polymorphic transition of ε-CL-20

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Abstract. The ε-form 2,4,6,8,10,12- hexanitro- 2,4,6,8,10,12- hexazatetracyclo [5.5.0.0^5,9.0^3,11] dodecane (CL-20) is the highest energy density compound which can be applied in practice at present. In this work, the effect of GAP on the polymorphic transition of ε-CL-20 was investigated by Raman spectroscopy and Calvet microcalorimeter method. The results show that the polymorphic transition temperature of ε-CL-20 to α-CL-20 can be reduced significantly by GAP, and the accurate temperature is 83.7°C. This investigation provides guidance to process condition selection for GAP-based propellants containing CL-20.

1. Introduction

High energy, insensitive and low characteristic signal are the developing direction of solid propellant [1-4]. Glycidyl azide polymer(GAP) is an ideal energetic binders for high energy and low characteristic signal propellant, due to its high heat of formation, high density, low mechanical sensitivity, combustion gas does not contain HCl [5-6]. Researches show that the energy and mechanical properties of the propellant are improved after the GAP was added to the XLDB propellant [7-9].

2,4,6,8,10,12- hexanitro- 2,4,6,8,10,12- hexazatetracyclo[5.5.0.0^5,9.0^3,11] dodecane (HNIW also known as CL-20) is a typical polycrystalline explosive, which exhibits high density and heat of formation and has become the most powerful commercially available explosive [10-12]. CL-20 has six different structural isomers, while four of them are stable, viz., α-, β-, γ- and ε-forms, and due to the high symmetric configuration of structure, the ε-CL-20 has the least sensitive, highest density and detonation velocity among the four crystal structures [13-15]. The explosive or propellant energy performance can be further improved by adding GAP and CL-20 [16-17].

The polymorphic transition of ε-CL-20 influenced by the materials and conditions make the safety risk of CL-20 increased in the process of production, processing, transportation, storage and use, this has greatly limited its application. Wei Yanju et al. [18] studied the crystal stability of CL-20 in CL-20/GAP-based explosive at 80°C, results show that the crystal form of CL-20 in the cured composite explosive is still ε-type. However, the author does not make it clear whether GAP has an effect on the polymorphic transition of ε-CL-20. In this paper, the effect of GAP on the crystal transition behaviors of ε-CL-20 in the water was investigated, and the accurate temperature was measured, which are of significant practical guiding value.
2. Experimental

2.1. Materials and Samples

$\varepsilon$-CL-20 ($D_{50} = 70.15 \, \mu m$) was purchased from Liaoning Qingyang Special Chemicals Co., Ltd., China. GAP ($M_w = 3500$) was provided by Xi’an Modern Chemistry Research Institute, China.

CL-20, GAP with the mass ratio of 1:1 were added to water, and the mixture was stirred for a right time at setting temperature to get the samples, the components and preparation conditions of the samples are listed in the table 1.

| Samples | w/% | Mixing time /min | Temperature /°C |
|---------|-----|------------------|-----------------|
| S1      | 50  | 500              | 60              |
| S2      | 50  | 500              | 20              |

2.2. Measurements

The scanning electron microscope (SEM; T-1000, Hitachi) was used to characterize the morphologies of the samples.

The Raman spectroscopy (RENISHAW, England) was used to identified the crystal structures of CL-20, with a 785 nm laser excitation source. Each sample has been identified more than 20 times to make the results better reflect the polymorphic transition of $\varepsilon$-CL-20, and the interval among test points was larger than 300 μm.

The C-80 type Calvet microcalorimeter (SETARAM, France) was used to measure the accurate temperature of crystal transition of $\varepsilon$-CL-20 influenced by GAP, with 0.2°C/min heating rate and the accuracy of heat measurement was smaller than 0.1 %.

3. Results and discussion

3.1. Morphology

The SEM micrographs of pure CL-20, S1, and S2 are shown in figure 1. It can be found that GAP had little effect on the morphology of CL-20, which illustrates the solubility of CL-20 in the GAP is very small. From the figure 1b and figure 1c, the mixing uniformity of CL-20 and GAP in the S1 is better than that of in the S2, it may be due to the fluidity of GAP gets better as temperature rose, this suggest that the temperature should not be too high during the mixing process of mixture contain GAP/CL-20 with solvent.
3.2. Crystal form analysis
The crystal forms of CL-20 identified by Raman spectroscopy are shown in figure 2. The results show that the ε-CL-20 has been turned to α-CL-20 in the CL-20/GAP/Water mixtures after mixing at 85°C for 20 min, while that has not occurred after mixing at 60°C for 60 min. The results illustrate the crystal transition temperature of ε-CL-20 to α-CL-20 in the water can be reduced significantly by GAP.

3.3. Microcalorimeter analysis
C-80 type Calvet microcalorimeter was used to measure the accurate temperature of polymorphic transition of ε-CL-20 affected by GAP, and the sample is composed of CL-20, GAP, and water with the mass ratio of 1:1:10, the result shown in figure 3. From figure 3 we can know the accurate onset temperature of polymorphic transition of ε-CL-20 to α-CL-20 in the water was 83.7°C with the
The reaction heat was 0.56 J·g⁻¹. The reaction heat of ε-CL-20 to γ-CL-20 is 18±1 J·g⁻¹ [19], so we speculate that GAP can greatly reduce the endothermic energy in the process of ε-CL-20 to α-CL-20.

**Figure 3.** Calvet microcalorimeter curve of ε-CL-20/GAP/Water mixtures at the mass ratio of 1:1:10.

### 4. Conclusion

In conclusion, GAP has a great effect on the polymorphic transition of CL-20, the polymorphic transition temperature of ε-CL-20 to α-CL-20 can be reduced significantly by GAP, and the accurate temperature is 83.7°C. It indicates that when the temperature of CL-20/GAP in the application process exceeds 83.7°C, the polymorphic transition of CL-20 should be considered.

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