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Preparation and Characterization of CL-20/EPDM by a Crystal Refinement and Spray Drying Method

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Abstract: A 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) based mixed explosive was prepared by a spray drying method using CL-20 suspended in hexane containing EPDM rubber (ethylene-propylene-diene monomer), and made into a stable suspension. The samples were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD), and their thermal stability and impact sensitivity were also measured. The results showed that the ethylene-propylene-diene-monomer rubber (EPDM) can be successfully coated on to the CL-20 crystal surface. Compared to refinement-spray CL-20, the impact sensitivity of CL-20/EPDM was significantly reduced. The characteristic drop height was increased from 28.12 to 39.78 cm. The thermal stability was better than refinement-spray CL-20.

Keywords: CL-20/EPDM, spray drying, impact sensitivity, thermal stability

1 Introduction

CL-20 is a high-energy material with a cage structure, and at present is considered the most powerful explosive. Due to its superior performance, CL-20 is regarded as the next generation of high-energy material [1, 2]. Because of its high-density, good chemical resistance and high thermal stability, CL-20 can be compatible with most binder and plasticizer materials [3]. Despite of its outstanding energetic characteristics, the application range of CL-20 is still limited by its high mechanical sensitivity (impact sensitivity, friction sensitivity and static spark sensitivity *etc.*) and its easy crystal transformation [4, 5]. It would be

advantageous to obtain CL-20 in a form that displays sufficiently reduced sensitivity without compromising its explosive performance [6]. In recent years, reducing the mechanical sensitivity of CL-20 by different methods has aroused increasing academic interest [7, 8]. For instance, explosive materials composed of CL-20 and adhesives can lead to lower impact sensitivity, a higher burning rate and higher activation energy, so CL-20 based PBX explosives have been widely used in mixed explosives and propellants [9, 10].

Ethylene-propylene-diene-monomer rubber (EPDM), composed of ethylene, propylene and a diene, is a very good synthetic rubber. Compared with other rubbers, such as natural rubber (NR), butadiene rubber (BR) and butadiene-styrene rubber (SBR), EPDM exhibits good erosion resistance, high tensile strength, good impact elasticity and resistance to ageing. EPDM has been extensively applied in solid rocket motors and mixed explosives [11, 12]. Wenzheng Xu [13] prepared the LLM-105/EPDM composite explosive by the solvent-water suspension method.

Based on this information, crystal refinement and the spray drying method was explored to prepare CL-20 based mixed explosives. The thermal and mechanical safety of refinement-spraying of CL-20 was investigated and compared in this paper. Compared with other methods, the process combined refining with encapsulation, which not only eliminated the filtration and drying stages, but also solved the difficult problem of phase transition.

2 Materials and Methods

2.1 Materials

Raw CL-20 was provided by LiaoNing QingYang Chemical Industry Corporation. EPDM was produced by Huizhou Haoyuan Plastics Material Company Limited. Ethyl acetate, n-heptane and n-hexane of AR grade were purchased from Tianjin Tianda Chemical Industry Co. Ltd. of China. α-Al_2O_3 (nanometer alumina, product model: XZ-L14) was generated from High Aluminum Material Co. Ltd. of Zhengzhou City.

2.2 Preparation of CL-20/EPDM explosive

The preparation of CL-20/EPDM by the crystal refinement and spray drying method involved three steps: (1) The CL-20 was dissolved into ethyl acetate at room temperature give a solution of concentration 0.2 g/mL; the solution was injected into a beaker containing the anti-solvent (n-heptane) by a nozzle; (2) The binder, EPDM, was dissolved into n-hexane to form a solution of concentration

5 wt.%. The binder solution was added directly into the beaker containing the CL-20 suspension with ultrasonic dispersion and stirring, to generate a stable suspension; (3) The suspension was spray-dried to produce the coated particles using a mini B-290 spray dryer.

2.3 Characterization

The profiles of the CL-20 samples were characterized by scanning electron microscopy (SEM, SU8020). The particle distribution of CL-20/EPDM was measured with a Brookhaven 90 PLUS laser diffraction particle size analyzer. The phase content of CL-20 was determined by X-ray diffraction (XRD) analysis with a Rigaku D/MAX-RB diffractometer using Cu-Kα radiation at 40 kV and 100 mA and a graphite diffracted-beam monochromator. Samples of refinement-spray CL-20 and CL-20/EPDM were analyzed with a Setaram DSC-131 differential scanning calorimeter. The conditions for DSC were: sample mass (0.5 mg), heating rate (5, 10, 20 K/min), nitrogen atmosphere (flow rate 30 mL/min). The impact sensitivity was investigated with a 12 type drop hammer apparatus. The samples (35 mg) were subjected to the impact from a 2.5 kg hammer from various heights, using the Bruceton method [14].

3 Results and Discussion

3.1 Morphology analysis

The morphologies of raw CL-20 (Figure 1(A)), refinement-spray CL-20 (the preparation process was the same as the process for the preparation of CL-20/EPDM prepared except that EPDM was not added, Figure 1(B)) and CL-20/EPDM (Figure 1(C)) were observed using SEM. The particle size distribution of CL-20/EPDM is shown in Figure 2.

As became obvious from Figure 1, the particle shape of raw CL-20 was irregular and of size about 40 ~ 55 μm. The SEM image of refinement-spray CL-20 showed that the particles had a polyhedral morphology and the majority of the particles were about 2 ~ 4 μm. The SEM image of CL-20/EPDM showed that the particle morphology of the CL-20 samples had become smoother and the particle surface had an obvious coating layer after the crystal refinement and spray drying process. In addition, Figure 2 showed that the mean particle size of CL-20/EPDM was 1.34 μm, and its size distribution was relatively narrow, size range of 0.6 ~ 2.1 μm.

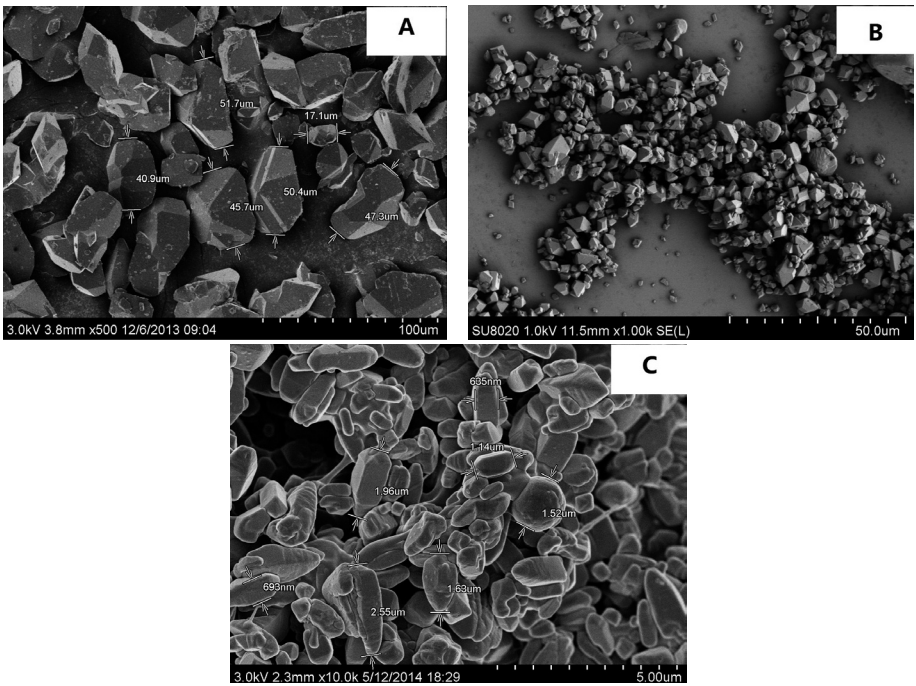

Figure 1. SEM photographs of (A) raw CL-20, (B) refinement-spray CL-20 and (C) CL-20/EPDM.

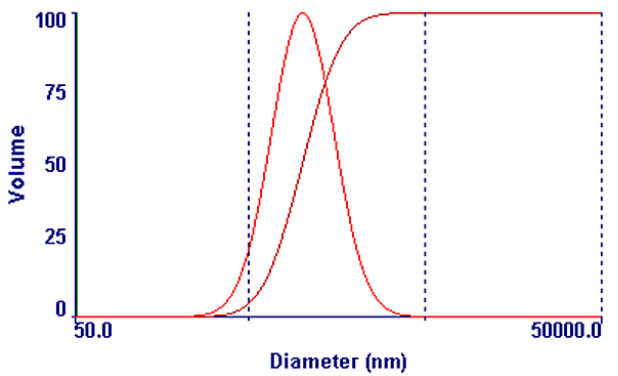

Figure 2. Particle size distribution curve of CL-20/EPDM.

3.2 XRD characterization

X-ray diffractometry was used to identify the phase content of ε-CL-20 in the samples. The XRD patterns of ε-CL-20 (standard card data 00-050-2045) and α-Al_2O_3 (standard card data 00-046-1212) are shown in Figure 3. CL-20/EPDM, and mixed samples of CL-20/EPDM and α-Al_2O_3 with different weight ratios were tested and the results are shown in Figure 5. The ε-phase purity of CL-20 was calculated from Equations (1), (2) and (3) [15].

$$l_{s,\varepsilon} / l_s = K(X_{s,\varepsilon} / X_s) \quad (1)$$

$$X_{i,\varepsilon} = (X_{i,s} \bullet l_{i,\varepsilon}) / (l_{i,s} \bullet K) \quad (2)$$

$$\eta = X_{i,\varepsilon} / X_{i,u} \quad (3)$$

$X_{s,\varepsilon}$ and X_s are the weight fractions of pure ε-CL-20 and α-Al_2O_3 respectively, and $l_{s,\varepsilon}$ and l_s are the characteristic XRD peak intensities of pure ε-CL-20 and α-Al_2O_3 respectively; $X_{i,\varepsilon}$ and $X_{i,s}$ are the weight fractions of ε-CL-20 and α-Al_2O_3 in the mixed samples of CL-20/EPDM and α-Al_2O_3, respectively; $l_{i,\varepsilon}$ and $l_{i,s}$ are the characteristic XRD peak intensities of ε-CL-20 and α-Al_2O_3 in the mixed samples of CL-20/EPDM and α-Al_2O_3, respectively. K is the reference intensity ratio. $X_{i,u}$ is the weight fraction of CL-20/EPDM in the mixed samples of CL-20/EPDM and α-Al_2O_3 and η is the ε-phase purity of CL-20/EPDM.

Four mixtures of raw ε-CL-20 and α-Al_2O_3 and four mixtures of CL-20/EPDM and α-Al_2O_3 with different weight ratios (5:1, 10:1, 15:1, and 20:1) were prepared and tested by XRD. The peak intensity ratio of the peak at 19.9 2θ for ε-CL-20 to the one at 52.4 2θ for α-Al_2O_3, proportional to the weight ratio of ε-CL-20 to α-Al_2O_3 can be obtained by the Equation (1), and a straight line (Y = 0.15636X) with a high linear correlation coefficient was obtained, as shown in Figure 4. Based on Equation (2) and (3), when the weight ratios of CL-20/EPDM to α-Al_2O_3 were 5:1, 10:1, 15:1, and 20:1, the weight fractions of ε-CL-20 in the mixtures were 79.12, 86.52, 89.27, and 90.24%, respectively. The ε-phase purity of CL-20/EPDM was calculated to be 94.94, 95.17, 95.22, and 94.75%, respectively, and the ε-phase purity of CL-20/EPDM was averaged as 95.02%.

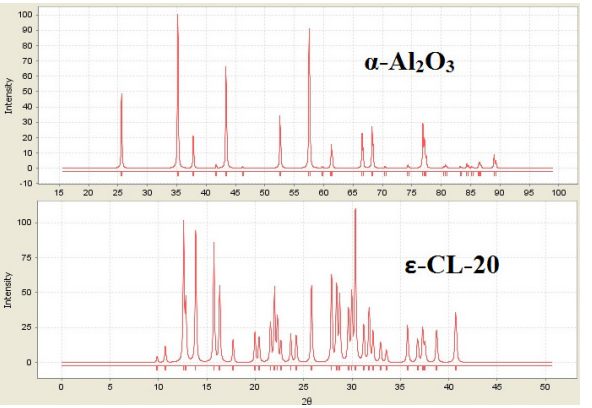

Figure 3. XRD patterns of pure ε-CL-20 and α-Al_2O_3.

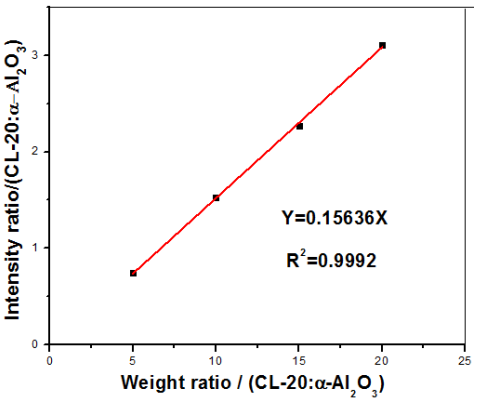

Figure 4. Peak intensity ratio *vs*. weight ratio of standard ε-CL-20 to α-Al_2O_3.

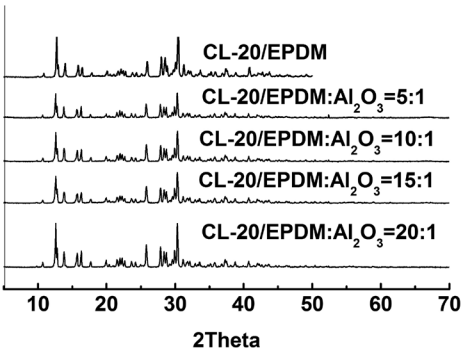

Figure 5. XRD pattern of CL-20/EPDM, and mixtures of CL-20/EPDM and α-Al_2O_3.

3.3 Thermodynamic analysis

DSC thermographs of refinement-spray CL-20 (graph B) and CL-20/EPDM (graph C) samples are shown in Figure 6.

It can be seen from Figure 6 that compared with that of refinement-spray CL-20, the exothermic peak temperature of CL-20/EPDM had decreased by 2.4, 3.22 and 5.9 °C at 5, 10 and 20 °C/min, respectively. These results can be explained by the fact that CL-20/EPDM powders have a greater ability for atomic vibration, surface energy and the capacity for heat transmission, which makes the molecules more susceptible to decompose at a lower temperature. According to the DSC test data of CL-20 at the three heating rates, the decomposition kinetic parameters of CL-20 can be calculated by the Kissinger formula (4), Rogers formula (5) and Arrhenius formula (6) [16-19].

$$\ln\frac{\beta_i}{T_{pi}^2} = \ln\frac{AR}{E_a} - \frac{E_a}{RT_{pi}} \tag{4}$$

$$A = \frac{E_a\beta}{RT_P^2}\exp(\frac{E_a}{RT_p}) \tag{5}$$

$$k = A\exp(-\frac{E_a}{RT}) \tag{6}$$

E_a is the apparent activation energy, A is the frequency factor, T is the absolute temperature, β is the heating rate, R is the gas constant, T_p is the peak temperature, and k is the decomposition rate constant at T.

Based on these data, the activation energy E and the frequency factor A of the two CL-20 samples can be calculated and the results are shown in Figure 7. As is obvious from Figure 7, the apparent activation energy of the explosive with added EPDM has been increased by 47.66 kJ/mol (26.1%), and thus the thermal stability has been significantly improved.

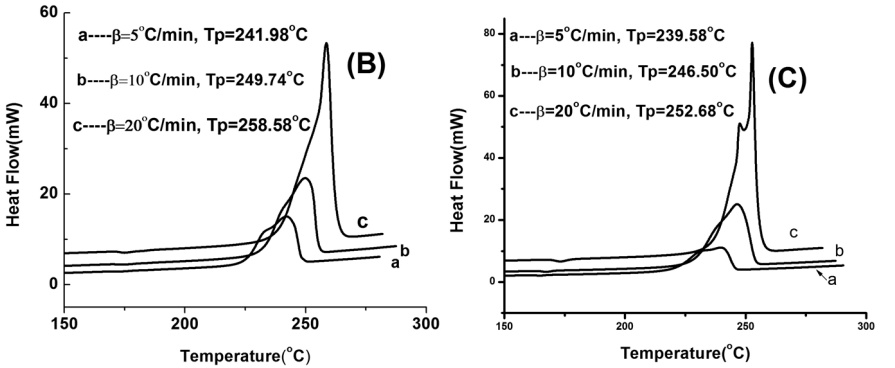

Figure 6. DSC graphs of (B) refinement-spray CL-20, and (C) CL-20/EPDM.

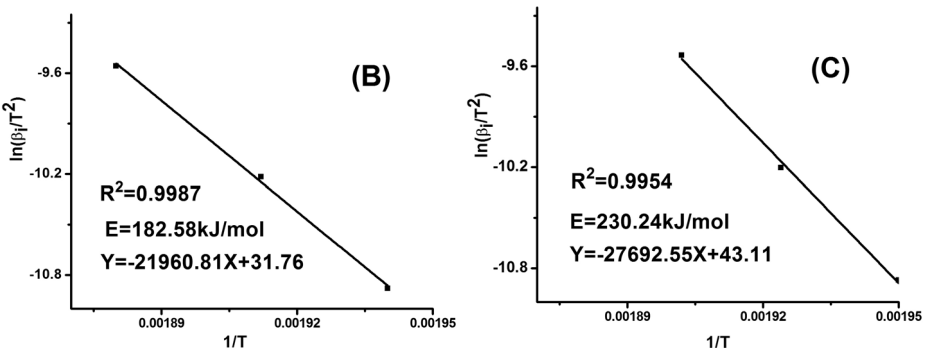

Figure 7. Kissinger plots of the peak decomposition temperature for (B) refinement-spray CL-20, and (C) CL-20/EPDM.

3.4 Impact sensitivity test

The impact sensitivities for refinement-spray CL-20 and CL-20/EPDM are listed in Table 1. The drop height for CL-20/EPDM increasing from 28.12 to 39.78 cm, showing that EPDM could reduce the impact sensitivity of CL-20. The reason for this could be explained by the hot spot theory [20]; on the one hand, on the application of an external impact force, the binder had a cushioning and lubricating effect, which could reduce the friction and the phenomenon on the stress concentration of explosive particles, reducing the generation probability of hot spots; on the other hand, the binder could to a certain extent also absorb some heat from the hot spots, preventing the self-heating phenomenon and reducing the transmission probability of hot spots.

Table 1. Impact sensitivity of refinement-spray CL-20 and CL-20/EPDM

Samples	Drop height H_{50}, [cm]	Standard deviation σ
Refinement-spray CL-20	28.12	0.1215
CL-20/EPDM	39.78	0.042

4 Conclusion

The crystal refinement and spray drying method was explored to prepare CL-20/EPDM. The method could be successful for making EPDM coated CL-20 crystal surfaces. The SEM results indicated that the evenly coated product was superior in quality and the CL-20/EPDM particles had a narrow size distribution. The ε-phase purity of CL-20/EPDM was about 95%. Compared with the refinement-spray CL-20, the impact sensitivity of CL-20/EPDM was significantly reduced, the drop height H_{50} being increased from 28.12 to 39.78 cm. The apparent thermal decomposition activation energy of CL-20/EPDM was increased from 182.58 to 230.24 kJ/mol, an increase of 26.1%, which suggests that the thermal stability of CL-20/EPDM was better than that of refinement-spray CL-20.

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