Study on $\varepsilon$-CL-20 Coated with a Wax/$F_{2311}$ Double-Layer Composite Structure

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Abstract: In order to reduce the mechanical sensitivity of $\varepsilon$-CL-20, wax and fluororubber polymers were used as coating materials and desensitizers to coat $\varepsilon$-CL-20 by the water suspension method. Through molecular dynamics calculations, fluorine rubber $F_{2311}$, which had a good combination with $\varepsilon$-CL-20, was selected as the coating material and then $\varepsilon$-CL-20-based composite particles with double-layer structure were prepared. The contact angles of water, glycerin and diiodomethane as the testing liquids on the surface of $F_{2311}$ and wax were measured by a contact angle measuring instrument, and the thermodynamic parameters of $\varepsilon$-CL-20/$F_{2311}$ and the $\varepsilon$-CL-20/wax interface were calculated. $\varepsilon$-CL-20 before and after coating was characterized by scanning electron microscopy (SEM), X-ray diffractometry (XRD), differential scanning calorimetry (DSC), and the mechanical sensitivity analytical method. The results showed that $F_{2311}$/wax had uniformly passivated on the surface of $\varepsilon$-CL-20, forming a dense and uniform protective film, and the CL-20 crystal form did not change after coating. The double-layer composite structure effectively reduces the sensitivity of $\varepsilon$-CL-20 and improves the thermal stability of $\varepsilon$-CL-20.

Keywords: $\varepsilon$-CL-20; $F_{2311}$/wax; mechanical sensitivity

1. Introduction

$2,4,6,8,10,12$-Hexanitro-$2,4,6,8,10,12$-hexaazaisowurtzitane (HNIW or CL-20) was first synthesized by Nielsen of the U.S. Naval Weapons Center in 1987 [1]. It is a high energy density compound (HEDC) with a cage structure [2]. Due to its superior performance, CL-20 is also considered as the most powerful high energy material. Under ambient conditions, CL-20 has four polymorphs ($\alpha$, $\beta$, $\gamma$, and $\varepsilon$-form crystals), of which the $\varepsilon$-phase has the highest density, the best performance, the best thermo-dynamic stability, and the lowest sensitivity [3–5]. The explosive performance of $\varepsilon$-CL-20 was found to be approximately 14% greater than octogen (HMX) as determined by cylinder expansion and tantalum plate acceleration experiments [6]. However, due to its features such as a high mechanical sensitivity and easy crystal transition, these defects have seriously hindered its application in high energy composited explosives [7,8]. How to prepare $\varepsilon$-CL-20 with a high crystal purity and a high crystal quality is one of the most important issues in the research of CL-20-based high energy composited explosives. It has been reported in the literature that several additives are able to inhibit crystal growth and nucleation, to stabilize crystal polymorphs, and to modify crystal habits [9,10]. Chen [11] used a solvent–antisolvent method to convert $\gamma$-HNIW crystals into $\varepsilon$-HNIW crystals through different additives (ethylene glycol, triacetin, and aminoacetic acid), in which aminoacetic acid could selectively inhibit the growth of an $\varepsilon$-HNIW single crystal to improve the crystal morphology.
However, although the effect of the crystal forms of CL-20 on its own properties were demonstrated several years ago, little attention has been paid to the selection of coating materials. In particular, the use of insensitive agents or polymer materials with excellent mechanical properties to coat CL-20 is one of the most effective ways to reduce its mechanical sensitivity. Berton [12] used grazing incidence X-ray diffraction (GIXRD) to study the coating effect of CL-20 coated by the water suspension method. In the experiment, cellulose acetate butyrate was used as the binder, and bis-dinitroacetal was used as the plasticizer. Liao [13] investigated the synthesis of waterborne polyurethane for coating on CL-20. The impact sensitivity experimental results indicated that the characteristic $H_{50}$ height of HNIW coated with waterborne polyurethane increased from 25.1 cm to 34.2 cm.

This work aimed to reduce the mechanical sensitivity of $\varepsilon$-CL-20. There have been many studies on the encapsulation of $\varepsilon$-CL-20 with a single layer coating material but using a single layer coating material does not meet the mechanical sensitivity and thermal stability requirements of composite explosives. In view of the different desensitization mechanisms of the desensitizer and the polymer, this work used the desensitizer wax and the polymer fluororubber as the coating materials by the water suspension method. Through molecular dynamics calculations, fluorine rubber $F_{2311}$, which had a good combination with $\varepsilon$-CL-20, was selected as the coating material and $\varepsilon$-CL-20-based composite particles with double-layer structures were prepared. The double-layer composite structure effectively reduced the mechanical sensitivity of $\varepsilon$-CL-20 and broke through the difficulties in the practical application of $\varepsilon$-CL-20-based composite explosives.

In this paper, molecular dynamics were used to calculate the binding effect of four kinds of fluorine rubber and $\varepsilon$-CL-20. The mechanical sensitivity and other properties of the coated samples were studied, and the mechanism of desensitization was discussed, which provided a new idea for desensitization design and for tests of sensitive energetic materials.

2. Molecular Dynamics Calculation

In order to characterize the interaction between CL-20 and additives, the surface docking method has been proposed to build the interaction interface model of CL-20 and additives [14–19]. The crystal faces of CL-20 are numerous; therefore, the main crystal plane was considered. Here, to explore the properties of the surfaces of CL-20 crystal under vacuum conditions, the Morphology module of Materials Studio software (BIOVIA Materials Studio 2017, 2016, Dassault Systemes, Paris, France) was used, and the morphology method to the Forcite Growth morphology method and the Forcefield type COMPASSII were set. Moreover, the Ewald method and the Atom-based method were applied to the electrostatic summation and van der Walls summation in this calculation, respectively. As a result, its six main growth crystal planes were obtained as shown in Figure 1a. The $[0\ 1\ 1]$ crystal plane had the largest exposed area of 39.61% as shown in Figure 1b, and the morphology was the most important. Thus, the $[0\ 1\ 1]$ crystal plane of CL-20 was chosen as the interface to interact with the additive.
Fluorine rubber is commonly used as a binder for high energy mixed explosives and propellants [20–23], including F$_{2311}$, F$_{2314}$, F$_{2603}$, F$_{2462}$, etc. Here, molecular dynamic simulations using COMPASSII Force Field with the module Forcite provided on the Materials Studio software were carried out. The Ewald method and the Atom-based method were again applied to the electrostatic summation and van der Walls summation, respectively. To establish the contact interface models of CL-20 [0 1 1] crystal plane and F$_{2311}$, F$_{2314}$, F$_{2603}$, and F$_{2462}$, the Build Polymers of the Build module on the Materials Studio software were used to construct the single-stranded Fluorine rubber molecules at first. After this, the Amorphous Cell module was used to construct small boxes containing these single-stranded Fluorine rubber molecules, respectively. Then, the Geometry Optimization and a 100 ps molecular dynamic simulation on 298 K with the NVT ensemble and the Nosé–Hoover method with timestep 1 fs on the Forcite module were carried out in turn to ensure the single-stranded Fluorine rubber was fully relaxed. With the fully relaxed models of four single-stranded Fluorine rubbers as show in Figure 2a, the Amorphous Cell module was applied again to construct bigger boxes containing several single-stranded Fluorine rubbers with a similar atomic mass in these boxes as the Fluorine rubber models. After the Geometry Optimization of these rubber models as show in Figure 2b, the Fluorine rubber molecules on them were copied over the surface of the facet [0 1 1] of CL-20 with a 50 Å vacuum layer to build the interface models, respectively, as show in Figure 2c. Finally, with the Nosé–Hoover method, the NVT ensemble and by setting the timestep to 1 fs and the temperature to 298 K, the molecular dynamic simulations on these interface models lasted for 250 ps; in other words, 2,500,000 steps were carried out, respectively, and the final structure of these molecular dynamic models are shown in Figure 2d. Then, the last 20 ps of these molecular dynamic simulations were used to calculate the total energy ($E_{\text{total}}$) between CL-20 and four kinds of fluorine rubber, and the separate energy ($E_{\text{CL-20}}$) of CL-20 and the energy ($E_F$) of four kinds of fluorine rubber. Equations (1) and (2) were used to calculate the binding energy and cohesive energy density between CL-20 and fluorine rubber, respectively.

$$E_{\text{bind}} = -(E_{\text{total}} - E_{\text{CL-20}} - E_F)$$

(1)

$$CED = \frac{CED_{\text{total}} \cdot V_{\text{total}}}{V_{\text{CL-20}} + V_F}$$

(2)

In Equation (1), $E_{\text{bind}}$ represents the binding energy between CL-20 and fluororubber; $E_{\text{total}}$ represents the total energy between CL-20 and fluororubber; $E_{\text{CL-20}}$ and $E_F$ represents the energy calculated separately by CL-20 and fluororubber, respectively.

In Equation (2), $CED$ represents the cohesive energy density between CL-20 and fluororubber, and $CED_{\text{total}}$ and $V_{\text{total}}$ represents the total cohesive energy density and the total volume between CL-20 and fluororubber, respectively. $V_{\text{CL-20}}$ and $V_F$ represent the separate volumes of CL-20 and fluorine rubber, respectively.
Figure 2. (a) Single chain relaxation structure of fluororubber; (b) Multichain structure of fluororubber; (c) Initial structure of fluorine rubber and CL-20 before kinetic simulation; (d) Structure of fluorine rubber and CL-20 after the kinetic simulation. Here, gray, white, green, and light blue balls represent carbon, hydrogen, chlorine, and fluorine atoms, respectively. In addition, the dark blue and red balls represent nitrogen and oxygen in the CL-20 structure, respectively.

Figure 3 shows the histogram of the calculation results of the binding energy and cohesive energy density of CL-20 and fluororubber. The binding energies of CL-20 and the four fluororubbers were 124.0 kcal/mol, 113.6 kcal/mol, 84.3 kcal/mol, and 101.0 kcal/mol, respectively, as shown in Figure 3a. The cohesive energy densities of CL-20 and the four fluororubbers were 0.662 kJ/cm$^3$, 0.655 kJ/cm$^3$, 0.648 kJ/cm$^3$, and 0.648 kJ/cm$^3$, respectively, as shown in Figure 3b. The binding energy and cohesive energy density of F$_{2311}$ and CL-20, respectively, reached the maximum value, indicating that F$_{2311}$ could have a better binding effect with CL-20. Therefore, F$_{2311}$ was selected as the coating insensitive agent in this paper, which could achieve a better coating effect.

Figure 3. The binding energy (a) and cohesive energy density (b) of ε-CL-20 with four kinds of fluorine rubber.
3. Experimental Section

3.1. Materials

Raw material ε-CL-20 was provided by Liaoning Qingyang Special Chemical corporation (Liaoning, China). High quality ε-CL-20 (chemical purity ≥ 99.7%, crystal purity ≥ 95.3%) was recrystallized by using ethyl acetate as the solvent and n-octane as the anti-solvent. F_{2311} (copolymer of vinylidene fluoride and chlorotrifluoroethylene mixed at a molar ratio of 1:1) was purchased from Chenguang Chemical Research Institute (Beijing, China). Wax (No. 80), Glycerin, diiodomethane, ethyl acetate, and petroleum ether were purchased from Aladdin Reagent Co., Ltd (Shanghai, China).

3.2. Sample Preparation

Firstly, 100 g of ε-CL-20 and 300 mL of distilled water were weighed and they were placed into a 1000 mL three-necked flask. The motor was turned on, the stirring speed was set to 450 r·min⁻¹, the temperature was adjusted to 60 °C before waiting for the ε-CL-20 crystals to be evenly dispersed. Then the vacuum pump was turned on, and a 5% wax petroleum ether solution was added to the three-necked flask through a separatory funnel at a specified rate of 1 mL·s⁻¹. Through the evaporation of petroleum ether, the wax separated out and coated on the surface of ε-CL-20. After the petroleum ether was completely evaporated the stirring speed was adjusted to 600 r·min⁻¹, and the experimental temperature was adjusted to 65 °C. Lastly, 10% of F_{2311} ethyl acetate solution was added dropwise to the three-necked flask at a specified rate of 1.25 mL·s⁻¹ through a separatory funnel. After the ethyl acetate evaporated, F_{2311} separated out and coated on the surface of the ε-CL-20 and wax composite. Stirring continued for 10 min, and the sample was taken out after the temperature dropped below 40 °C. After vacuum filtration, it was put in an oven for drying at a temperature of 40 °C (sample NO.2 was prepared by adding F_{2311} ethyl acetate solution, and then adding the petroleum ether solution of wax). The four explosive formulations are shown in Table 1.

| Samples | Mass Percent of Compositions (%) |
|---------|---------------------------------|
|         | ε-CL-20 | Wax (internal) | Wax (external) | F_{2311} (internal) |
| NO.1    | 96.0    | 2.0           | 2.0            | 2.0                  |
| NO.2    | 96.0    | 2.0           | 2.0            | 2.0                  |
| NO.3    | 96.2    | 2.0           | 2.0            | 1.8                  |
| NO.4    | 96.5    | 2.0           | 2.0            | 1.5                  |

3.3. Characterization of the Microscopic Morphology

Scanning electron microscopy images of samples were obtained by a S-4700 (Hitachi, Tokyo, Japan) type scanning electron microscope.

3.4. Contact Angle Tests

The contact angles of distilled water, glycerin, and diiodomethane as the test liquids on the surface of F_{2311} and wax were measured by an OCA20 type contact angle measuring instrument (Dataphysics, Berlin, Germany) [24].

3.5. Characterization of Thermal Decomposition

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC, STA449F3, NETZSCH, Selb, Germany) were simultaneously conducted at a heating rate of 10 K·min⁻¹ from room temperature to 600 K in an Ar atmosphere to study the thermal decomposition behavior of the samples. The mass of each test sample was about 1.0 mg, and the crucible was made of alumina.
Coats and Redfern [25] presented an integral method which has since become one of the most widely used methods in non-isothermal kinetic analysis. In this work, the Coats–Redfern equation was used to study the thermal decomposition behavior of the composite particles.

\[
\ln \left( \frac{G(\alpha)}{T^2} \right) = \ln \left( \frac{AR}{\beta E} \left( 1 - \frac{2RT}{E} \right) \right) - \frac{E}{RT}
\]

\[
G(\alpha) = \left[ -\ln(1 - \alpha) \right]^{1/2}
\]

Here, \( G(\alpha) \) is the mechanism function of thermal decomposition, \( \alpha \) is the conversion degree, \( E \) is the activation energy, \( T \) is the decomposition peak temperature, \( A \) is the pre-exponential factor, \( R \) is the gas constant, and \( \beta \) is the heating rate. Plotting the left side of Equation (4), which includes \( G(\alpha) \) versus \( 1/T \), gives \( E \) and \( A \) from the slope and intercept, respectively.

3.6. Mechanical Sensitivity Tests

Impact sensitivity (IS) was recorded with a ZBL-B type impact sensitivity apparatus (Xi’an, China). The test conditions were drop weight, 10 kg and sample mass, 50 mg. Each sample was tested 50 times and an explosion probability (%) was obtained.

Friction sensitivity (FS) was recorded with a BM-B type friction sensitivity apparatus (Xi’an, China). The test conditions were pendulum angle, 90±1°; pressure, 3.92 MPa; and sample mass, 20 mg. Each sample was tested 50 times and an explosion probability (%) was obtained.

3.7. X-ray Diffractometry Tests

The crystal form analysis of composite particles was performed on a Bruker D8 Advance (Karlsruhe, Germany) using Cu Kα radiation (\( \lambda = 1.54180 \) Å) operating under the condition of 40 kV/40 mA. The 2θ range measured was 5–45° with steps of 0.02°/0.1 s.

4. Results and Discussion

4.1. Interfacial Tension Analysis

Young [26] proposed that the contact angle at a three-phase contact line is determined by a balance of surface tensions, as shown in Equation (6), where \( \gamma_S \), \( \gamma_{SL} \), and \( \gamma_L \) are, respectively, the solid–vapor, solid–liquid, and liquid–vapor interfacial forces per unit length of the contact line, i.e., surface tension, and \( \theta \) is the contact angle.

\[
\gamma_S = \gamma_{SL} + \gamma_L \cos \theta
\]

\[
\gamma_{SL} = \gamma_S + \gamma_L - 2 \sqrt{\gamma_S \gamma_L} - 2 \sqrt{\gamma_S \gamma_L}
\]

\[
\gamma_L (1 + \cos \theta) = 2 \sqrt{\gamma_S \gamma_L} + 2 \sqrt{\gamma_S \gamma_L}
\]

Here, distilled water (\( \gamma_L = 72.8 \) mJ·m\(^{-2}\), \( \gamma_{Ld} = 21.8 \) mJ·m\(^{-2}\), \( \gamma_{Lp} = 51.0 \) mJ·m\(^{-2}\)), glycerin (\( \gamma_L = 64.0 \) mJ·m\(^{-2}\), \( \gamma_{Ld} = 34.0 \) mJ·m\(^{-2}\), \( \gamma_{Lp} = 30.0 \) mJ·m\(^{-2}\)), and diiodomethane (\( \gamma_L = 50.8 \) mJ·m\(^{-2}\), \( \gamma_{Ld} = 50.8 \) mJ·m\(^{-2}\), \( \gamma_{Lp} = 0 \) mJ·m\(^{-2}\)) with the known surface tensions were selected as the detection liquids, and the contact angles of the detection liquids on the surface of \( \text{F}_{2311} \) and wax were determined, as shown in Table 2.

| Detection Liquid | Water | Glycerin | Diiodomethane |
|------------------|-------|----------|---------------|
| \( \text{F}_{2311} \) | 128.72 | 87.00    | 72.95         |
| Wax              | 87.6  | 83.5     | 51.8          |

Table 2. The contact angles of the detection liquids on the surface of the coating materials.
According to the data in Table 2, combined with Equation (5), two combinations of water–diiodomethane and glycerin–diiodomethane were selected to calculate the surface tension data of F$_{2311}$ ($\gamma_L = 15.83$ mJ·m$^{-2}$, $\gamma_{Ld} = 14.06$ mJ·m$^{-2}$, $\gamma_{Lp} = 1.77$ mJ·m$^{-2}$) and wax ($\gamma_L = 34.54$ mJ·m$^{-2}$, $\gamma_{Ld} = 33.29$ mJ·m$^{-2}$, $\gamma_{Lp} = 1.25$ mJ·m$^{-2}$). In the study of the interface system, the adhesion work $W$ and the spreading coefficient $S$ were used to characterize the interface effect between the substances. Generally speaking, the smaller interfacial tension of the $\varepsilon$-CL-20/coating material results in greater adhesion work and a stronger interface effect. The coating material can spread on the surface of the $\varepsilon$-CL-20 crystal, which is an important prerequisite for realizing the coating effect and forming a uniform and continuous coating film. Therefore, the coating effect largely depends on the spreading of the coating material on the surface of the explosive. The larger the spreading coefficient, the better the spreading situation. The expression of adhesion work $W$ and spreading coefficient $S$:

$$W = \gamma_S + \gamma_L - \gamma_{SL} = 2\sqrt{\gamma_S^d\gamma_L^d} + 2\sqrt{\gamma_S^p\gamma_L^p}$$ (8)

$$S = \gamma_S - \gamma_L - \gamma_{SL} = 2\sqrt{\gamma_S^d\gamma_L^d} + 2\sqrt{\gamma_S^p\gamma_L^p} - 2\gamma_L$$ (9)

With reference to the literature, the surface tension data of $\varepsilon$-CL-20 ($\gamma_s = 40.35$ mJ·m$^{-2}$, $\gamma_s^d = 38.59$ mJ·m$^{-2}$, $\gamma_s^p = 1.76$ mJ·m$^{-2}$) and Equations (8) and (9), the interface thermodynamic parameters of $\varepsilon$-CL-20/F$_{2311}$ and $\varepsilon$-CL-20/wax were calculated as shown in Table 3. $W$ and $S$ are the criterion for whether the coating material can spontaneously stick and spread on the surface of $\varepsilon$-CL-20, respectively. It can be seen from Table 3 that although both F$_{2311}$ and wax could be coated on the surface of $\varepsilon$-CL-20, the coating effect of $\varepsilon$-CL-20/wax was not as good as $\varepsilon$-CL-20/F$_{2311}$.

Table 3. Interface thermodynamic parameters of $\varepsilon$-CL-20/F$_{2311}$ and $\varepsilon$-CL-20/wax.

| System        | $\gamma_{SL}$ (mJ·m$^{-2}$) | $W$ (mJ·m$^{-2}$) | $S$ (mJ·m$^{-2}$) |
|---------------|-----------------------------|------------------|------------------|
| $\varepsilon$-CL-20/F$_{2311}$ | 6.0                         | 50.1             | 18.5             |
| $\varepsilon$-CL-20/wax         | 0.3                         | 73.6             | 6.4              |

4.2. Micro-Structure Analysis

SEM photos were captured to characterize the micro-structural differences between the raw material and composite particles, as shown in Figure 4. Compared with raw material $\varepsilon$-CL-20 (Figure 4a), high quality $\varepsilon$-CL-20 (Figure 4b) has no obvious edges and corners, which is the reason why high quality $\varepsilon$-CL-20 was selected to prepare the composite particles. As shown in Figure 4d,f, it can be observed that a film formed on the surface of $\varepsilon$-CL-20. In particular, as shown in Figure 4c,e, the composite particles had smooth surfaces and were smaller in size when F$_{2311}$ was coated internally. The reason for the above phenomenon is mainly that the viscosity of wax is lower than that of F$_{2311}$. When a certain amount of wax is coated on the surface of an $\varepsilon$-CL-20 crystal, the precipitated wax will automatically fall off after a period of time and re-adhere to the $\varepsilon$-CL-20 crystal which has not reached saturation. The adhesion between the coated $\varepsilon$-CL-20 is rarely observed. However, the viscosity of F$_{2311}$ is larger, and the adhesion of the coated intermediates tends to occur after coated with F$_{2311}$, resulting in a slightly rough surface and a relatively large particle size.
4.3. Thermal Analysis

The thermal decomposition characteristic parameters of composite particles at a heating rate of 10 K/min are shown in Table 4.

Table 4. Thermal decomposition characteristic parameters of composite particles at a heating rate of 10 K/min.

| Sample   | $T_{tr}$ ($^\circ$C) | $T_{on}$ ($^\circ$C) | $T_p$ ($^\circ$C) | $\Delta H$ (J g$^{-1}$) | $E_a$ (kJ mol$^{-1}$) |
|----------|----------------------|----------------------|------------------|------------------------|----------------------|
| Raw material | 170.9                | 234.2                | 238.4            | 1021.0                 | 217.8                |
| NO.1     | 177.9                | 240.7                | 241.9            | 1104.4                 | 257.5                |
| NO.2     | 176.5                | 238.6                | 239.8            | 1079.3                 | 238.1                |
| NO.3     | 177.0                | 239.4                | 240.0            | 1088.9                 | 235.5                |
| NO.4     | 182.8                | 238.9                | 239.5            | 1062.6                 | 230.1                |

Note: $T_{tr}$ represents the transition peak of $\varepsilon$-CL-20 to $\gamma$-CL-20 crystal form; $T_{on}$ represents the decomposition onset temperature; $T_p$ represents the decomposition peak temperature; $\Delta H$ represents enthalpy of formation; $E_a$ represents the activation energy required for decomposition.

As shown in Figure 5, the endothermic peak at about 170 $^\circ$C represents the transition peak of $\varepsilon$-CL-20 to the $\gamma$-CL-20 crystal form, and the exothermic peak at about 240 $^\circ$C represents the decomposition peak of CL-20. Compared with the raw material, the crystal form transition peak, and the decomposition peak of the composite particles all moved to higher temperatures. In particular, the decomposition onset temperature of sample NO.1 increased from 234.2 $^\circ$C to 240.7 $^\circ$C, and the decomposition peak temperature increased from 238.4 $^\circ$C to 241.9 $^\circ$C. It can be seen from Table 4, that the decomposition heat and the activation energy of the composite particles were greater than that of the raw material. The reason for the above phenomenon is that when wax melts, the outer layer of F2311 remains solid, so that the liquid wax can continue to absorb heat on the surface of the CL-20 until the outer layer F2311 also reaches the melting point. However, when wax is outside and F2311 is inside, wax melts after reaching the melting point and cannot provide protection for the internal F2311. The thermal stability improvement effect of different double-layer composite structures on $\varepsilon$-CL-20 could be ranked as NO.1 > NO.3 > NO.2 > NO.4, but the decomposition peak temperature and the decomposition thermal activation energy of different samples were not very different; therefore, the double-layer composite structure had a certain improvement effect on the thermal stability of $\varepsilon$-CL-20, but it was relatively limited.
4.4. Mechanical Sensitivity

To confirm whether the mechanical sensitivity of composite particles was reduced, impact and friction sensitivity tests were conducted, as shown in Table 5. Compared with the raw material, the impact and friction sensitivity of the composite particles were reduced.

Table 5. Impact and friction sensitivity of five explosive formulations.

| Sample  | Mass Percent of Additives (%) | IS (%) | FS (%) |
|---------|-------------------------------|--------|--------|
| Raw material | 100 0 0 | 100 | 100 |
| NO.1 | 96.0 2.0 (internal) 2.0 (external) | 60 | 68 |
| NO.2 | 96.0 2.0 (external) 2.0 (internal) | 72 | 80 |
| NO.3 | 96.2 2.0 (internal) 1.8 (external) | 64 | 72 |
| NO.4 | 96.5 2.0 (internal) 1.5 (external) | 80 | 92 |

It can be seen from Table 5 that the mechanical sensitivity of the composite particles was lower when wax was inside and F_{2311} was outside. In this double-layer composite structure, the wax film on the surface of the ε-CL-20 crystal will prevent ethyl acetate from dissolving the ε-CL-20 crystal during preparation. When exposed to external stimuli, the wax absorbs the surface heat of ε-CL-20 to melt, and lubricates the ε-CL-20 crystal. Moreover, F_{2311} also has excellent mechanical properties and can buffer force. Thus, this double-layer composite structure has a lower mechanical sensitivity. This result indicates that when the dosage is fixed, the coating sequence significantly affects the safety of composite particles.

When the dosage of F_{2311} was reduced from 2% to 1.8%, the impact sensitivity and friction sensitivity of the composite particles increased. If the content of F_{2311} further reduced, its mechanical sensitivity will not meet the requirements of practical applications. Therefore, in order to achieve the condition of effectively reducing the mechanical sensitivity of ε-CL-20, the amount of the coating material F_{2311} should be at least 2%. However, it is inevitable that the detonation performance will decrease to a certain extent.

4.5. Crystal Form Analysis

In this work, the ethyl acetate was used as solvent of F_{2311}, but ethyl acetate has a strong solubility for ε-CL-20. In order to determine whether the crystal form of CL-20 changed, XRD analysis was performed on the composite particles. The result is shown in Figure 6.

It can be seen from Figure 6 that at 2θ = 10.7°, 12.6°, 12.8°, 15.7°, 16.3°, 25.8°, and 30.43°, the characteristic peak positions of the composite particles were consistent with the characteristic peak positions of the ε-CL-20 chart standard card (JCPDS NO.50-2045). The result indicates that the crystal form of CL-20 did not change before and after using ethyl acetate.
5. Conclusions

In this work, ε-CL-20 coated with Wax/F2311 double-layer composite structure was prepared and characterized. The following conclusions were obtained:

1. The binding energy and cohesive energy density of F2311 and Cl-20 reached the maximum values of 124.0 kcal/mol and 0.662 kJ/cm³, respectively, indicating that F2311 could have a better coating effect with ε-CL-20.

2. By the water suspension method, using the desensitizer wax and the high molecular polymer F2311 as the coating materials, four kinds of composite particles with the double-layer structure were prepared. The SEM and XRD tests indicated that wax and F2311 can be coated on the surface of ε-CL-20 without crystal change.

3. The interface thermodynamic parameters of ε-CL-20/F2311 were calculated: γSL = 6.0 mJ/m², W = 50.1 mJ/m², S = 18.5 mJ/m². F2311 had high adhesion work (50.1 mJ·m⁻²) and spreading coefficients (18.5 mJ·m⁻²) and can be used to coat ε-CL-20.

4. The results of the DSC-TG test and the sensitivity test implied that the impact sensitivity of the sample could be reduced from 100% to 60%, the friction sensitivity could be reduced from 100% to 68%, the thermal decomposition peak temperature could be increased from 238.4 °C to 241.9 °C, and the activation energy could be increased from 217.8 kJ/mol to 257.5 kJ/mol.

5. The fluorine rubber selected by the molecular dynamics calculation was well coated on the surface of ε-CL-20. The sensitivity of the ε-CL-20 coated with wax/F2311 double layer structure decreased significantly. This indicates that there is a certain relationship between the choice of coating material and sensitivity, which is worth further study.

Author Contributions: Writing—original draft preparation, data curation, W.W., L.S., X.G.; Software, W.W., L.S., C.W. and Q.P.; Formal analysis, investigation, W.W. and H.F.; Conceptualization, writing—review and editing, visualization, W.W. and J.J. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Natural Science Foundation of China (Grant No.11772058; 22175026).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data sharing is not applicable to this article.
Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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