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Preparation and Properties of Spherical CL-20 Composites

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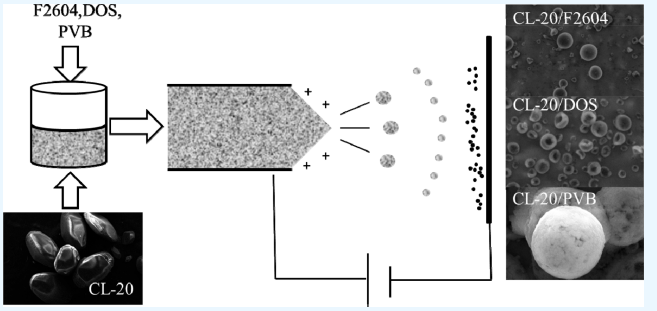
ABSTRACT: Micrometer-sized spherical composites based on 2,4,6,8,10,12-hexanitrohexaazaisowurtzitane (CL-20) with fluororubber (F2604), dioctyl sebacate (DOS), and polyvinyl butyral (PVB) were prepared by an electrospray method. After preparation, the morphology, chemical bonds, thermal decomposition properties, mechanical sensitivity, and explosion performance were characterized. The main explosive CL-20 transformed from ε-CL-20 to β-CL-20 after electrospray preparation. With an insensitive additive mass ratio of 5 wt %, the CL-20/F2604 composite had the highest maximum peak exothermic temperature and the lowest mechanical sensitivity. The explosion pressures of the composites with the same mass ratio of additives decreased in the order CL-20/F2604 > CL-20/PVB > CL-20/DOS and were lower than that of raw CL-20.



1. INTRODUCTION

2,4,6,8,10,12-Hexanitrohexaazaisowurtzitane (HNIW or CL-20) is a typical nitroamine explosive with high energy density and is widely used in solid propellants and explosive mixtures. However, CL-20 has a high sensitivity toward impact, friction, and shock. How to balance the sensitivity and energy of CL-20 has attracted a great deal of attention from researchers in the field.

Many methods, such as an *in situ* polymerization method,[1] a solvent evaporation and precipitation method,[2] a solvent/nonsolvent recrystallization method,[3] an ultrasound- and spray-assisted method,[4] and a vacuum freeze-drying method,[5] have been reported to prepare CL-20 or CL-20 composites with low mechanical sensitivity. However, the morphology of these samples was irregular, and most of the samples were diamond-shaped[1−3] with a rough surface due to the addition of desensitizer or had a large size.[4] As is known to all, the properties of CL-20 are mostly influenced by morphology, size, and crystal structure. It is meaningful to develop a new method to prepare spherical CL-20 with a consistent morphology and size. Electrospraying, a method used to produce uniform nanometer-sized and micrometer-sized particles,[6−8] has been used in the preparation of energetic materials.[9−12] Wang et al.[9] introduced the electrospray preparation of NC/GAP/sub-micrometer-HNS composite fibers and found that the fibers had a high reactivity and a fast reaction rate. Chen et al.[10] assembled Al/CuO and CL-20 into composites with various morphologies by electrospraying and found that the prepared hybrid energetic materials could be readily regulated by constructing various interfacial microstructures to satisfy the broad requirements of energy sources. In our past work,[11,12] spherical composites based on 1,3,5-trinitro-1,3,5-triazinane (RDX), RDX/F2604 (fluororubber), RDX/PVAc (polyvinyl acetate), and RDX/PVB (polyvinyl butyral) were prepared by an electrospray method.

For CL-20, as a high-energy explosive, the mechanical sensitivity and thermal decomposition characteristics have been generally tested after desensitization. There have been a large number of studies about the thermal decomposition properties and mechanical sensitivities of the CL-20 composites.[1−4] Meanwhile, the detonation parameters[13−15] reflect the energy release of the explosives and are also meaningful in investigating the changes after desensitization. Here, we conducted an explosion test in a homemade airtight combustion can to obtain the explosion pressure and pressure rise time.

In this work, we demonstrate the electrospray preparation of spherical CL-20/F2604, CL-20/DOS (dioctyl sebacate) and CL-20/PVB composites. The morphology, chemical bonds, thermal decomposition properties, mechanical sensitivity and explosion properties of the spherical composites were characterized and analyzed in detail.

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2. EXPERIMENTAL SECTION

2.1. Materials and Reagents. Raw CL-20 (99.9%, shown in Figure 1) was provided by Jiangsu Yongfeng Machinery Co.

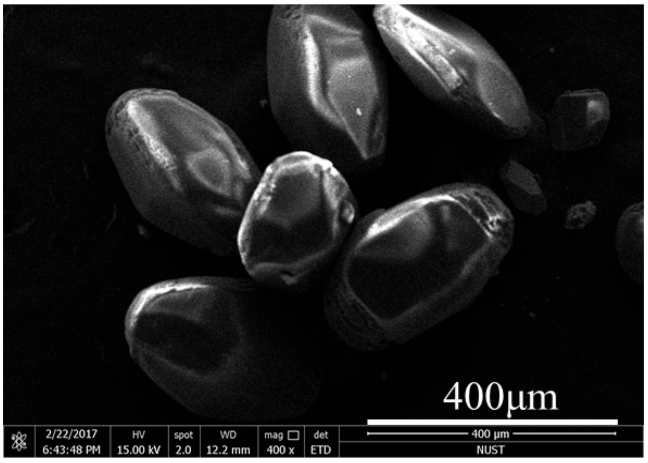
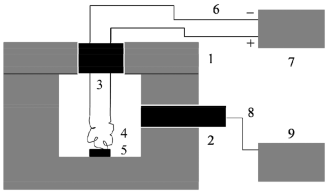


Figure 1. SEM image of raw CL-20.

Ltd.; F2604 (99.9%) was provided by Shanghai 3F New Materials Co. Ltd.; DOS (AR, 97%) was provided by Aladdin Reagent (Shanghai) Co. Ltd.; PVB (99.9%) was provided by Sinopharm Chemical Reagent Co. Ltd.; acetone (AR, 99.5%) was provided by Shanghai Lingfeng Chemical Reagent Co. Ltd; ethyl acetate (AR, 99.5%) was provided by Sinopharm Chemical Reagent Co. Ltd.

2.2. Preparation of CL-20-Based Composites. Raw CL-20 and the insensitive additives (1000 mg in total; the mass ratios of the insensitive additives to raw CL-20 were 1:99, 3:97, 5:95 and 10:90, respectively) were dissolved in acetone or ethyl acetate to form solutions (50 mg mL^{-1}), which were sprayed through a thin metal tube with high voltage to prepare the samples, and the samples were collected on aluminum foil.

2.3. Characterization. The morphologies were studied with use of a QUANTA 250 FEG scanning electron microscope (FEI Ltd., America). The solution conductivity was tested with a DDS-11A desktop digital display conductivity tester (Shanghai yueping scientific instrument Co., Ltd. China). The test electrode constant was 0.01 cm^{-1}, and the conductivity test range was 0.000−19.99 S cm^{-1}. The chemical bonds were studied with a VERTEX70 Fourier infrared spectrometer (Thermo Fisher Scientific, USA) with a spectral area range of 500−4000 cm^{-1}. The thermal decomposition properties were studied with a differential scanning calorimeter (DSC1, Mettler Toledo Ltd. Switzerland) with a sample mass of approximately 0.65 mg, a heating rate of 10 K·min^{-1}, and test temperatures from 180 to 280 °C. The impact sensitivity was tested with a sample mass of 30 ± 1 mg and a drop weight of 2 kg. The friction sensitivity was tested with a sample mass of 20 ± 1 mg, a pendulum weight of 1.5 kg, a swing angle of 90°, and a pressure of 3.92 MPa. The explosion pressures of the samples were tested in a homemade airtight combustion can (Φ 25 × 25 mm). The test system (shown in Figure 2) consisted of a direct-current power supply (15 V), resistance wires ($Cr_{20}Ni_{80}$, Φ 0.5 mm, 5.6 Ω m^{-1}, 60 mm), a pressure sensor (113B26, PCB Piezotronics Inc., America), an electrical charge amplifier (482A20, PCB Piezotronics Inc., America), a data collection board



1-a homemade airtight combustion can, 2- a pressure sensor, 3- electrodes, 4- resistance wires, 5-samples, 6- wires, 7- a direct-current power supply, 8- low noise cables, 9- a computer

Figure 2. Explosion pressure test system.

(MMTECH, Model PCI_1112, sampling frequency 1 MHz s^{-1} and sampling time 2 s), a low-noise cable and a computer.

3. RESULTS AND DISCUSSION

3.1. Morphologies of the Composites. The morphologies of the CL-20 composites are shown in Figure 3. Most of

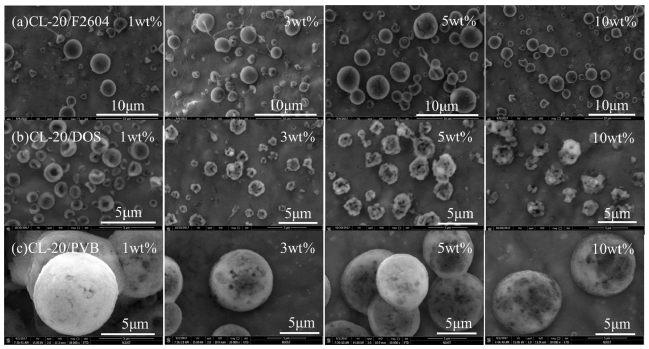


Figure 3. SEM images of the CL-20/F2604 (a), CL-20/DOS (b), and CL-20/PVB (c) particles.

the CL-20/F2604 composites were spherical particles with smooth surfaces and 1−2 μm in size, while raw CL-20 was 200 μm diamond-shaped granules. The size and morphology of CL-20 changed significantly after the electrospray preparation. An increase in the mass ratio of F2604 did not cause obvious changes in the size and morphology of the composites. The CL-20/DOS composites were 1−2 μm in size with a broken shape due to the solvent effect of DOS, especially the composites containing 10 wt % DOS. The composites could maintain a spherical shape at a low content of DOS. The CL-20/PVB composites were 5 μm uniform spherical particles, and an increase in the ratio of PVB had no effect on the size of the composites. However, the composite particles tended to stick together as the PVB content increased. The CL-20/PVB composites were larger in size than the other composites. PVB was dissolved in ethyl acetate, while F2604 and DOS were dissolved in acetone. The particle size d was proportional to (Q (flow rate) /K (conductivity))$^{1/3}$;[16] the solution containing acetone had a higher conductivity (shown in Table 1) than that containing ethyl acetate, which caused the smaller size.

Table 1. Conductivity of the Solutions

sample	solvent	conductivity μ (S cm^{-1})
5 wt % F2604/CL-20	acetone	0.681
5 wt % DOS/CL-20	acetone	0.627
5 wt % PVB/CL-20	ethyl acetate	0.004

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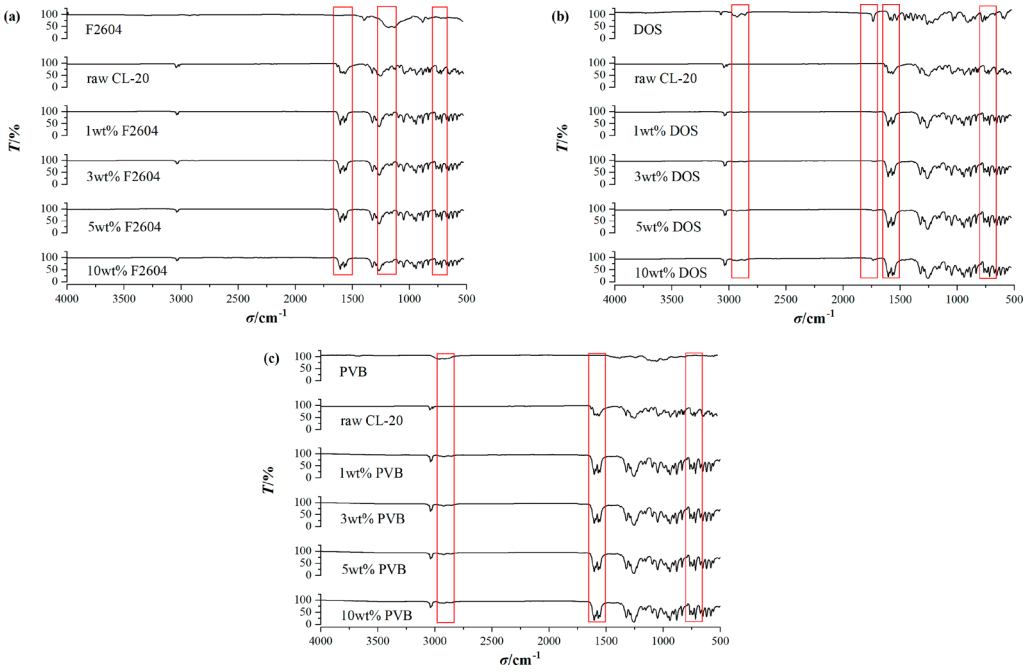

Figure 4. FT-IR spectra of the CL-20/F2604 (a), CL-20/DOS (b), and CL-20/PVB (c) composites.

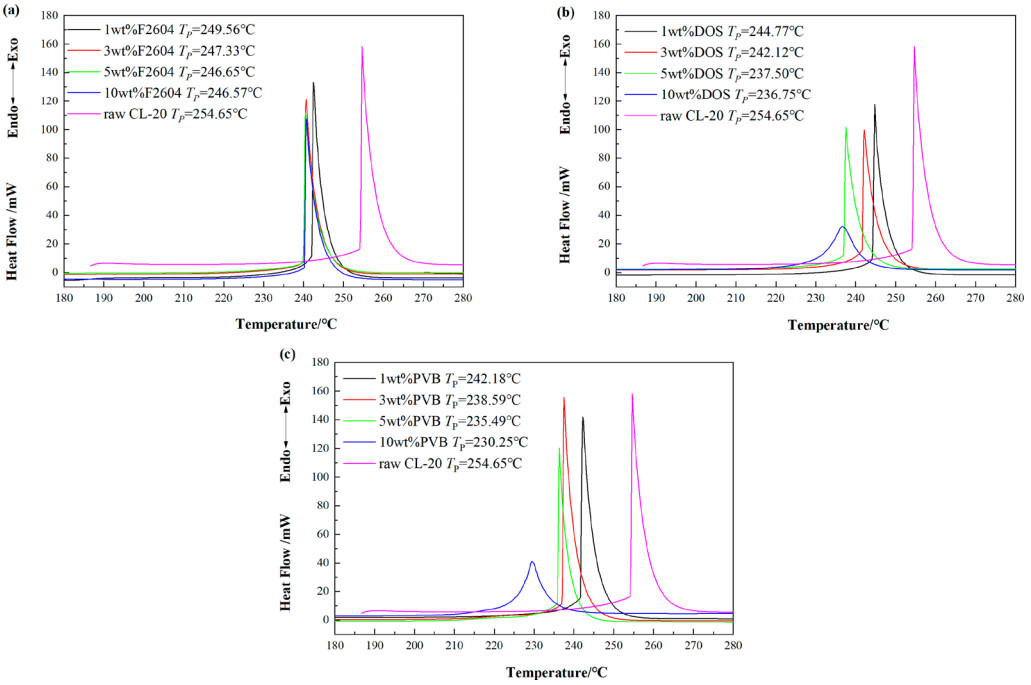

Figure 5. DSC results of the CL-20/F2604 (a), CL-20/DOS (b) and CL-20/PVB (c) composites.

3.2. FT-IR Results of the Composites. As shown in Figure 4, the positions and shapes of the FT-IR absorption peaks of the composites were similar to each other. The infrared characteristic absorption peak (1200 cm^{-1}) of F2604 shown in Figure 4a, absorption peak (1700 cm^{-1} for the symmetrical stretching vibration of C═O) of DOS shown in Figure 4b and absorption peak (2900 cm^{-1}) of PVB shown in Figure 4c gradually changed with an increasing mass ratio of the insensitive additives.

The positions and shapes of the FT-IR absorption peaks of the CL-20 composites were obviously different from those of raw CL-20, especially the peaks at 2950 cm^{-1} (double peaks for raw CL-20 and a single peak for composites), 1600 cm^{-1} (a wide peak for raw CL-20 and two peaks for composites), and 600 cm^{-1}(a wide peak for raw CL-20 and three peaks for composites). The results indicated that the crystal form of CL-20 changed after the electrospray preparation. Song[17] discovered that ε-CL-20 recrystallized with a crystal transition from different solvents and tended to form α-CL-20 with a large crystal size from acetone and β-CL-20 from ethyl acetate. In this work, the composites prepared from acetone and ethyl acetate were tested to be β-CL-20, while the raw CL-20 was ε-CL-20.

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3.3. DSC Results of the Composites. Figure 5a–c displays the DSC curves of raw CL-20 and CL-20/F2604, CL-20/DOS, and CL-20/PVB composites at 10 K min^{-1} heating rates, respectively. The composites had a single exothermic peak in the DSC curves, and the maximum peak exothermic temperatures decreased with an increase in insensitive additive content. At the insensitive additive mass ratio of 5 wt %, the maximum peak exothermic temperatures decreased in the order CL-20/F2604 (246.65 °C) > CL-20/DOS (237.50 °C) > CL-20/PVB (235.49 °C), which were lower than that of raw CL-20 (254.65 °C). On the one hand, the insensitive additives reduced the maximum exothermic peak temperature of the thermal decomposition of CL-20. On the other hand, the maximum exothermic peak temperature of β-CL-20 was slightly lower than that of ε-CL-20.

3.4. Mechanical Sensitivity of the Composites. The mechanical sensitivity results are given in Table 2. The

Table 2. Mechanical Sensitivity of the Samples

sample	impact sensitivity H_{50} (cm)	friction sensitivity (%)
raw CL-20	16.9	100
5 wt % F2604/CL-20	42.8	64
5 wt % DOS/CL-20	19.6	96
5 wt % PVB/CL-20	23.3	76

mechanical sensitivity of the CL-20 composites is lower than that of raw CL-20. The mechanical sensitivity decreased in the order CL-20/DOS > CL-20/PVB > CL-20/F2604. F2604 obviously reduced the mechanical sensitivity of CL-20, while DOS and PVB only reduced the impact sensitivity slightly. This was because DOS could decrease the stability of the crystal lattice of CL-20 due to dissolving the surface layers of the nitramine crystal and the polarity of the aldehyde group (−CHO) in PVB had a strong polarity and could generate an electrostatic interaction with CL-20.

3.5. Explosion Property of the Composites. The explosion pressures of raw CL-20 and the composites (25 mg sample in mass each test) were tested in a homemade airtight combustion can. Figure 6 shows the explosion pressure

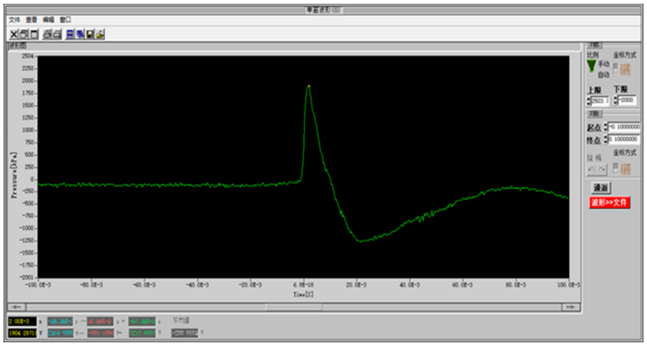

Figure 6. Explosion pressure curve of raw CL-20.

curve of raw CL-20, which was obtained by a PCB pressure sensor and pressure acquisition software. The maximum pressure value was 1920 kPa, and the pressure rise time was 2.5 ms.

Figure 7 shows the pressure curves of the CL-20/F2604 composites, and Table 3 gives the pressure values and pressure rise times of the other two composites. The pressure rise times

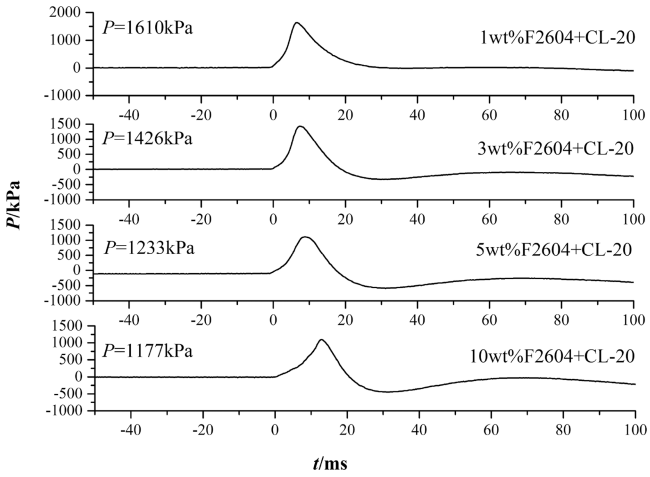

Figure 7. Pressure curves of the CL-20/F2604 composites.

of the CL-20/F2604 composites were 7.17 ms (1%), 8.67 ms (3%), 9.79 ms (5%), and 13.26 ms (10%), respectively. The explosion pressure of the composites with the same mass ratio of additives decreased in the order CL-20/F2604 > CL-20/PVB > CL-20/DOS. F2604 and PVB as polymeric materials contain more energy than DOS, which resulted in a lower explosion pressure for CL-20/DOS composites. In the explosion reaction of CL-20/PVB composites, some carbon elements of PVB did not react completely and generated solid carbon. However, in the explosion reaction of the CL-20/F2604 composites, carbon elements of F2604 tended to react completely and some carbon elements generated gaseous CF_4, which caused a higher explosion pressure for CL-20/F2604 composites.

Compared with the explosion pressure of raw CL-20, the existence of additives decreased the explosion pressure of raw CL-20 at the same ignition energy. The explosion pressure decreased and the pressure rise times increased with an increase in additive mass ratio. The additives chosen contained little energy, and the entire energy of the composites decreased with an increase in additive mass ratio. The charging density made a difference in the detonation performance of the explosive. Raw CL-20 was 200 μm diamond-shaped granules with a higher density, while most of the composite particles were smaller than 5 μm, which resulted in a lower density for fluffy accumulation, resulting in the lower explosion pressure. The explosion pressure of the composites obtained by the explosion pressure test system could evaluate the energy release level of the different composites to a certain extent.

4. CONCLUSIONS

The micrometer-sized spherical CL-20/F2604, CL-20/DOS, and CL-20/PVB composites were successfully prepared by an electrospray method. The morphology, chemical bonds, thermal decomposition properties, mechanical sensitivity, and explosion performance of the composites were investigated in detail. The main conclusions are as follows.

(1) The crystal type of the composites was β-CL-20 instead of ε-CL-20 for raw CL-20.
(2) The spherical composites had lower maximum peak exothermic temperatures.
(3) The mechanical sensitivity decreased in the order CL-20/DOS > CL-20/PVB > CL-20/F2604.

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Table 3. Explosion Test Results of the Samples

sample	pressure (kPa)	pressure rise time (ms)	sample	pressure (kPa)	pressure rise time (ms)
1 wt % DOS/CL-20	1422	7.9	1 wt % PVB/CL-20	1450	7.4
3 wt % DOS/CL-20	1089	9.1	3 wt % PVB/CL-20	1284	8.8
5 wt % DOS/CL-20	991	10.4	5 wt % PVB/CL-20	1025	9.3
10 wt % DOS/CL-20	861	15.5	10 wt % PVB/CL-20	906	13.8

(4) The explosion pressure decreased in the order CL-20/F2604 > CL-20/PVB > CL-20/DOS.

The experimental result could help to further broaden the application of electrospray technology in the field of energetic materials. The explosion pressure test system could be used to test the explosion performance of other energetic material powders in a small amount. In addition, it is necessary to further study the efficiency improvement of electrospraying.

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Notes

The authors declare no competing financial interest.

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