Short Communication

Propellants, Explosives, Pyrotechnics

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CL-20 based Explosive Ink of Emulsion Binder System for Direct Ink Writing

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Abstract: An emulsion is a multiphase dispersion system in which one or more liquids are dispersed in the form of particles in another immiscible liquid. Emulsion method has been applied for preparation of binder system via oil in water (O/W) emulsions. The formulation contains: 40 g 12% a solution of polyvinyl alcohol (PVA) in water, 15 g 7.5% a solution of Viton A (vinylidene hexafluoropropene copolymer) in ethyl acetate, 0.25 g sodium dodecyl sulfate (SDS) and 0.25 g Tween-80.The emulsion as a binder system, sub-micro CL-20 (prepared by the ball milling method) as the body explosives to prepared CL-20 based explosive ink (CL-20 88% concentration). Deposition of explosive inks via DIW technology and its properties were characterized. The results showed that the composite has fewer internal defects and low impact sensitivity, the crystal type has no change, critical detonation size is around 1×0.17 mm and detonation velocity is 8079 m/s.

Keywords: Emulsion · CL-20 based explosive ink · critical detonation size · detonation velocity

1 Introduction

With the further development of weapons and equipment, it has put forward higher requirements for the performance of the ammunition initiation sequence [1]. Intelligent, miniaturized and integrated is the development direction of the detonating sequence. MEMS devices set miniaturization, intelligent, integrated into one, significantly reducing the size of the initiation sequence, improving the safety and reliability of the weapon system. However, due to the size of MEMS devices is in the range of micrometer to millimeter, which poses a big challenge to the charge process. The traditional formulation and charge methods of explosive are no longer applicable in MEMS [2–4].

Direct ink writing (DIW) is a low-cost, high efficiency material forming technology, which has been widely used in ceramic materials [5–6], piezoelectric materials [7], as well as novel functional materials [8] design and preparation fields. In the field of energetic materials, DIW technology has attracted more and more attentions. In 2010, EDF-11,a CL-20 based secondary explosive ink, which has been developed for direct write loading of MEMS devices and used as a booster explosive by the US Army [9]. Since then, some formulations about CL-20 based explosive inks with good performance had been studied [10–13].

Explosive ink has two versions: one is all-liquid explosive ink. Explosives, binders and additives were dissolved in low boiling point organic solvents, using DIW technology to print a pattern on a substrate under a predetermined program through a piezoelectric nozzle of a specific structure. One drawback to all-liquid explosive ink is that the morphology of explosive crystal not easy to control, such as CL-20 and it's hard to get the best comprehensive performance of ε-CL-20. The other is suspension explosive ink. Explosives, binder system, additives were mechanically mixed together to prepare a certain viscosity and fluidity of explosive ink. It can effectively avoid the problem of crystal transformation of explosives. In this study, we developed a sub-micro CL-20 based explosive ink, using Viton A and PVA as its binder system. The ethyl acetate solution of Viton A (as dispersion phase) was dispersed in form of small droplets in the aqueous solution of PVA (as continuous phase) by mechanical energy input. To make the newly formed droplets stable enough to against coalescence, an emulsifier must be added to this system. Emulsifiers belong to the class of surface active substances (surfactants). Surfactants adsorb at the interface between two phases due to their amphiphilic molecular structure, and thereby it can stabilize the droplets of the disperse phase in emulsion [14]. Herein, the emulsifiers we chose that were Tween-80 combination with SDS, SDS as the primary emulsifier, Tween-80 provide a secondary stabilizing effect, and the polar portion of the nonionic surfactant (Tween-80) will stay between the positively charged groups of the ionic surfactant (SDS), so that there is a very

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concentrated packing at the interface of the two phases and thereby making the interface more stable. As a result, the emulsion system is more stable [15]. The emulsion, sub-micron CL-20 and additives were be ultrasonic stirring to obtain explosive inks. The inner structure, crystal type, critical size of detonation, detonation velocity, impact sensitivity, and morphology properties were characterized and analyzed.

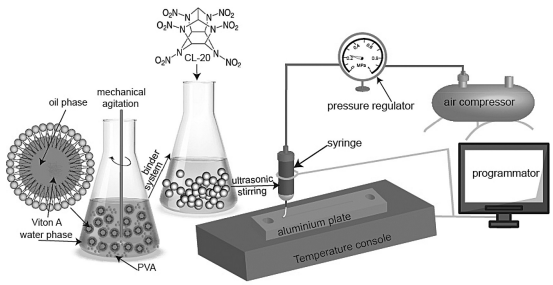

Figure 1. Diagram of preparation of emulsion binder system and CL-20 based composite.

2 Experimental Section

2.1 Preparation of Sub-Micro CL-20

Firstly, about 10 g of raw ε-CL-20 (produced by Liaoning Qing yang Special Chemical Co., Ltd) was milled by using a ZrO_2 ball (mean diameter 0.1 mm, produced by Bomai Ceramic materials co., Ltd.) with liquid water medium and under stirring (300 rpm) at 25 °C for 3 h. Finally, after filtering, then obtained sub-micro CL-20 power was dried under a freeze dryer (produced by Gong yi instrument Co., Ltd.) for further experiments.

2.2 Preparation of Emulsion Binder System

Considering that the solvent used for the oil-phase binder was ethyl acetate (AR, produced by Fuchen chemical reagents factory), CL-20 have a greater solubility in ethyl acetate and therefore the target emulsion prepared was o/w systems. In addition, taking into account both the water phase and the oil phase have a greater viscosity. When preparation of emulsion, a larger viscosity phase should be used for continuous phase, a smaller viscosity phase would be used for dispersed phase, which is beneficial to prevent the union of the dispersed droplets and maintain the stability of the emulsion.

Preparation of emulsion: 0.25 g SDS (produced by Tianjin Guangfu Chemical Research Institute) and 0.25 g Tween-80 (produced by Damao Chemical Reagent Factory) were added to 40 g 12% PVA (produced by Youso Chemical Technology Co., Ltd.) solution, the mixture was stirred at a temperature of 40 °C and a stirring speed of 520 rpm for 30 min. Then used constant pressure funnel to added 15 g 7.5% Viton A (produced by Chenguang Chemical Research Institute Co., Ltd.) solution slowly about 15–20 min, then continued stirring 30 min and the o/w systems with a stable time about 60 h was formed.

2.3 Preparation of CL-20 Based Explosive Ink

3 g sub-micron ε-CL-20 added into 3.84 g emulsion, added alcohol dilution to adjust its consistency, and added a small amount of defoamer for water-based printing ink, leveling agent, room temperature in ultrasonic stirring fully mixing evenly dispersed in the condition of 20 kHz by 30 min. Then the CL-20 based explosive ink was loaded into a syringe for pneumatic micro-direct-writing device (Self-made by North University of China) deposited in aluminum plate channels with different shapes and sizes under conditions (pressure: 0.25 MPa, micro nozzle diameter: 0.34 mm, nozzle height: 0.3 mm, nozzle angle: 90°, deposition rates: 0.3375 mL/min, temperature console was set as 50 °C).

2.4 Characterization and Properties

The size of raw CL-20 and sub-micro CL-20, the surface and inner structure (the cross section of sample was prepared by a small knife) of composite was observed by a TESCAN Mira 3 Field Emission Scanning Electron Microscope (FE-SEM). Crystal types were distinguished by DX-2700 X-ray diffraction instrument (XRD) (Dandong HaoYuan Instrument Co., Ltd).The density was characterized five times by a MZ-220SD electronic densimeter (shenzhen force Tatsu letter instrument Co., Ltd.) to get the mean value. ERL type 12-drop hammer apparatus was used to test the impact sensitivity with conditions: drop weight, 2.500 ± 0.002 kg; sample mass, 35 ± 1 mg; relative humidity 60% and room temperature. The results were expressed by the critical drop-height of 50% explosion probability (H_{50}) and standard deviation (S).

According to the detonation theory, the size of the explosive cross section determines whether the detonation can be spread steadily. Therefore, there is a critical dimension S_0 that can maintains the detonation propagation. Suppose the cross sectional area S of the charge, that is, when $S \geq S_0$, the detonation wave can propagate stably and when $S < S_0$, the detonation wave can't stably propagate [16]. In this experiment, the DIW technology was used to load explosive ink in a wedge shaped groove with a fixed width of 1.0 mm and a maximum depth of 3 mm. After curing, detonation was started with 8# detonators at the deeper end of the grooved charge to measure the critical explosion thickness of CL-20 based composite. The detonation velocity of the composite was tested by means of an electric signal probe method. CL-20 based explosive ink was

loaded into an aluminum channel with a width of 1.2 mm and a depth of 1.0 mm by the same charge method. At the other end of the 8# detonators detonation was placed a density of 1.84 g/cm^3 CL-20 cylindrical grain, the powder of the grain is CL-20/estane (95 : 5) explosive.

3 Results and Discussions

3.1 Size Characterizations and Morphology

As is shown in Figure 2a, the particle size of the raw CL-20 is about 400 μm. As shown in Figure 2b, the particle size of sub-micro CL-20 powder refined by ball milling are all below 1 μm with no obvious edges and the particles are spherical in shape, which meets the preparation conditions of explosive ink.

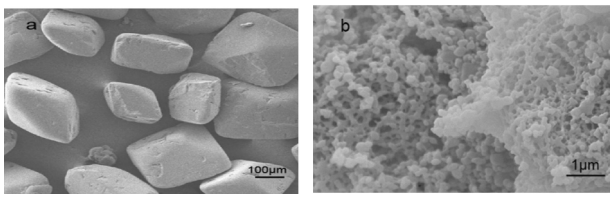

Figure 2. SEM images of raw CL-20 and sub-micro CL-20 powder.

As is shown in Figure 3a and 3b, the surface of the CL-20 based composite smooth and flat after curing. However, there were still some tiny holes on the surface of the composite at higher magnification. One possible reason for the tiny holes on the surface was the direct-writing platform heating the ink composite leaded to the evaporation of solvents. And in Figure 3c and 3d, the inner structure (the cross section of sample was prepared by knife) of the CL-20 based composite is good densification, no obvious pore. This result makes it clear that the fine pores formed by ink solvent evaporation only exist on the surface. The density of composite stays at 1.71 g cm^{-3}, while the theoretical maximum density (TMD) is 1.93 g cm^{-3}(CL-20 88 wt%). This means that the CL-20 based composite ink formulations have good formability, can be used for study of the detonation properties in micro-size charge.

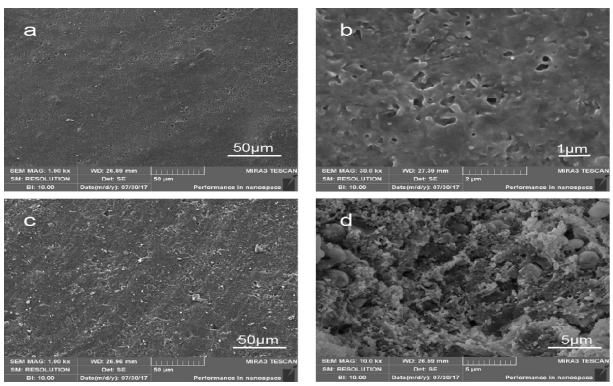

Figure 3. SEM photos of surface (a, b) and cross section (c, d) of CL-20 based composite after curing.

3.2 XRD Characterization

Figure 4 displays that the positions of the three strong characteristic peaks of raw CL-20,sub-micro CL-20 and CL-20 based composite are basically the same, and the diffraction angles are 12.6°, 13.8°and 30.3°, which are in agreement with the standard PDF card (00-050-2045) of ε-CL-20. The results can be explanation that the solvent ethyl acetate solution as the disperse phase medium in the emulsion binder system did not dissolve and crystallize with CL-20 in process of CL-20 based explosive ink prepared. And another reason might be that there has a small amount of CL-20 dissolved and precipitated, but not detected by X-rays. In Figure 4, we can also clearly see another phenomenon, that the diffraction peak intensity is different with the same diffraction angle. The diffraction peak intensity of CL-20 based composite is basically the same as that of sub-micro CL-20, while the diffraction peak intensity of raw CL-20 is much greater than both but the peak is narrow. This is because diffraction peaks broaden and gradually weaken or even disappear as particle size becomes smaller [17].

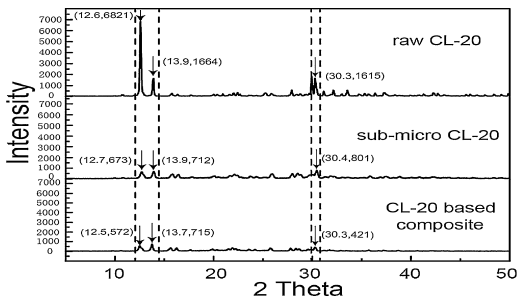

Figure 4. X-ray diffraction spectra of raw CL-20, sub-micro CL-20 and CL-20 based composite.

3.3 Critical Size of Detonation and Detonation Velocity

The critical size of detonation was tested by linear critical explosion thickness method. The picture in Figure 5 shows that the detonation of CL-20 based Composite is quite complete in the charge of groove with a solid content of 88 %, and there is an obvious explosion trace on the cover plate, indicating that the composite can reliably be detonated under the condition of charge in small size. Detonation theory can be used to explain the result of the Figure 5, with deto-

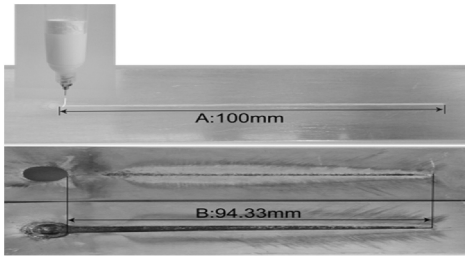

Figure 5. Comparison chart of CL-20 based composite before and after detonation.

nator detonation, the detonation point of the explosives first impacted by shock wave adiabatic compression. At the same time, two processes are carried out in wedge-shaped groove, one is the generation of high-temperature and high-pressure detonation wave and propagation along the central axis; the other is propagation along the radial of the charge. When the speed of expansion wave propagates faster than the detonation reaction zone, the propagation of expansion wave always affects the volume of detonation reaction zone, resulting in the energy which was used to propagate the detonation is gradually decreasing. With the energy was reduced, the pressure, temperature and reaction rate in the reaction zone would decrease, and the width of reaction zone would widen, detonation easily extinguished [18].

According to the reference 13, the critical size of detonation can be calculated by equation: $d_c = C \times (A–B)/A$. In this equation, C/A is slope of wedge-shaped groove and C is the bottom of the depth is 3 mm, the size of A and B is shown in Figure 5. So the critical size of detonation can be calculated and the value is 0.17 mm. Which means that CL-20 based composite can detonate steady above $1 \times$ 0.17 mm. It indicates that this formulation would have a good prospect of application to intelligent weapon system.

In order to further research the detonation performance of the formulation, the detonation velocity was tested. In this method, detonator was used to detonate the charge and the detonation wave propagates forward through points A, B, C and D in sequence (show in figure 6b), Since the detonation wave front has an Ionized conductive property, each pair of probes are insulated from each other in turn energized and make the corresponding capacitors to discharged one after another. Thus, the generated pulse signals were transmitted successively to the oscillography for photographic recording, so that a time *t* between the signals can be obtained. Finally, the detonation velocity is obtained by the length of the charge between the two pairs of probes, the results are shown in Table 1. In order to reduce the experimental error, CL-20 based explosive ink was loaded on two same aluminum plate by DIW technology under the same process conditions. According to the explosion trace of the groove charge, the strength of explosive ink in the micro charge was tested and the result

Table 1. Propagation time and velocity of detonation between each pair of probe.

Simples	A–B	B–C	C–D	Average detonation velocity
I	2810 ns	3714 ns	3682 ns	8113 m/s
Detonation velocity	5872 m/s	8078 m/s	8148 m/s	–
II	2326 ns	3753 ns	3705 ns	8045 m/s
Detonation velocity	7094 m/s	7993 m/s	8079 m/s	–

show in the Figure 6. Figure 6c show that the samples can not only propagate detonation successfully under the conditions of charge, but also have enough energy to detonate the next explosion sequence.

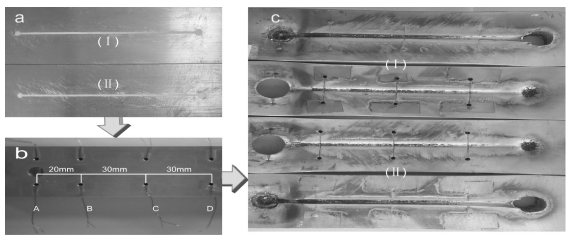

Figure 6. (a): Optical photograph of CL-20 based explosive ink direct writing deposition in groove; (b): The distance between each pair of probes on the plate to be tested; (c): Optical image of aluminium plate after detonation.

From Table 1, it can be seen that the stage of A–B is the growing period of detonation, which is an unstable detonation process. When the speed of detonation increases to a certain fixed value, the detonation velocity does not increase anymore. Thereafter, stable detonation processes such as B–C and C–D are carried out. From the Table 1, we can also clearly see that the detonation velocity of sample I, A–B is obviously lower than that of sample II. It may be caused by a gap between the base plate and cover plate in sample, resulting in partial energy loss and the prolongation of the detonation period. Thus detonation velocity reduced in A–B stage. It can be concluded from Table 1 that the average detonation velocity of CL-20 based composite is 8079 m/s. This result indicates that the composite has high density effect of the molding and fewer inner defects, which is also in agreement with the SEM (Figure 3c and 3d).

3.4 Impact Sensitivity

From Table 2, it can be seen that the drop height of submicro CL-20 is much higher than that of raw ε-CL-20, suggesting that sub-micro CL-20 are more difficult to explode under impact stimulus. Comparison Sub-micro CL-20 and

Table 2. Impact sensitivity of CL-20 based composite, sub-micro CL-20 and raw CL-20.

Simples	Impact Sensitivity [H50 (± S)]/cm		
	Experiment 1	Experiment 2	Average
Raw ε-CL20	13.2(± 1.0)	12.8(± 0.9)	13.0
Sub-micro CL-20	33.2(± 0.8)	35.2(± 0.9)	34.2
CL-20 based composite	39.0(± 1.2)	41.2(± 1.0)	40.1

CL-20 based composite it can be found that H_{50} value increases from 34.2 cm to 40.1 cm. A possible reason for the phenomenon is that the binder reduces the friction between the particles of CL-20 and leads to a reduction in the probability to form"hot spots"[19].

4 Conclusions

We used the method of the preparation of emulson, the high-density Viton A binder and PVA mixed together formed a uniformly binder system of explosive ink, sub-micro CL-20 as body explosive, formulated into explosive ink. Combined DIW technology load explosive ink in the condition of micro size to obtain CL-20 based composite. The properties of composite were characterized by SEM, XRD and drop height. The results showed the morphology of CL-20 didn't changed even if ethyl acetate was be used as a solvent for Viton A in the binder system, the CL-20 based composite had less internal defects and the impact sensitivity is reduced. Critical size of detonation is around 1 × 0.17 mm and detonation velocity is 8079 m/s.

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