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Research paper

Study of the Effect of DINA on the Polymorphic Transition of ε-CL-20 in Composite Modified Double Base Propellants

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Abstract: The polymorphic transition of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0^{5,9}.0^{3,11}]dodecane (CL-20) is influenced by the materials and conditions used in the preparation of propellants, and limits the application of ε-CL-20 in solid propellants. In the present work, the effect of dinitroxydiethylnitramine (DINA) on the polymorphic transition of ε-CL-20 in CMDB propellants was investigated by Raman spectroscopy and the Calvet microcalorimeter method. The performance of propellants with CL-20 as affected by DINA was studied by the theoretical prediction of their energetic parameters, stability, combustion, and mechanical tests, respectively. The results showed that the polymorphic transition temperature of ε-CL-20 to α-CL-20 can be reduced to 75 °C by DINA. Expansion of the crystal volume during the process of the ε-CL-20 to α-CL-20 transition will produce obvious cracks in the surface of the crystals. NC/NG can inhibit the effect of DINA on the polymorphic transition of ε-CL-20. The theoretically predicted results indicated that adding DINA will not lower the energy level of CMDB propellants containing CL-20. The DSC and VST results showed that CL-20 has good compatibility and thermal stability with DINA. The burning rate tests revealed that adding DINA decreases the burning rates of CMDB propellants containing CL-20. Mechanical property testing showed that adding DINA can clearly improve the mechanical properties of CMDB propellants containing CL-20. The results of these investigations suggested that DINA has no effect on the crystalline stability of *ε*-CL-20 in the solventless extrusion process, which contributes to a significant understanding of practical applications and provides guidance for applied research on the use of CL-20 in propellants.

Keywords: CMDB propellants, CL-20, DINA, polymorphic transition

1 Introduction

2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0^{5,9}.0^{3,11}]dodecane (HNIW, also known as CL-20) is the most powerful commercially available explosive in current use, and exhibits a high density and heat of formation [1, 2]. CL-20 has four stable crystal structures, *viz.*, *α*-, *β*-, *γ*- and *ε*-forms, and the *ε*-CL-20 form is the best usable form because it has the lowest sensitivity, highest density and highest detonation velocity of the four crystal structures [3-5]. Propellants containing CL-20 are found to possess lower signatures, are environmentally more acceptable and exhibit higher energy during the combustion process [6-9]. However, the polymorphic transition of *ε*-CL-20 is influenced by the materials and conditions used in the preparation of the propellants, and limits the application of *ε*-CL-20 in solid propellants [10-12]. Kholod *et al.* [13] analyzed the stable forms of CL-20 by DFT calculations, the activation energies of their transitions, *viz.*,

- α-CL-20 $\leftrightarrows$ β-CL-20,
- α-CL-20 $\leftrightarrows$ ε-CL-20,
- γ-CL-20 $\leftrightarrows$ β-CL-20, and
- γ-CL-20 $\leftrightarrows$ ε-CL-20,

were found to be quite low and in the range 6.0-16.7 kJ·mol^{-1}. Studies have shown that the polymorphic transition of CL-20 is closely related to the polarity of the solvent and temperature [14-16].

A solid propellant is a kind of highly filled granular composite formed from various materials under certain temperature and pressure conditions, which could complicate the process of polymorphic transition of CL-20 in the preparation of the solid propellant. Zhang *et al.* [17] studied the effect of different additives in castable systems on the polymorphic transition of *ε*-CL-20, and analyzed the transition mechanism of *ε*-CL-20 as affected by the additives. The intial temperatures of the polymorphic transition of ε-CL-20 as affected by the additives are over 150 °C, which is much higher than the temperatures in castable processes, hence these additives would not affect the polymorphic transition of ε-CL-20 in a castable process.

Meanwhile, the mechanical properties of CMDB propellants will become worse with an increase in solid content. Dinitroxydiethylnitramine (DINA) is commonly added to composite modified double base (CMDB) propellants as a secondary plasticizer, and can further improve the mechanical properties of CMDB propellants. In the present study, the effect of DINA on the crystal transition behaviour of ε-CL-20 in CMDB propellants was investigated. The conditions for the crystal transition behaviour of ε-CL-20 as affected by DINA were determined and solutions for maintaining the stability of ε-CL-20 in CMDB propellants are proposed, and are of significant practical guidance.

2 Experimental

2.1 Materials and Samples

ε-CL-20 (D_{50} = 70.15 μm) was bought from Liaoning Qingyang Special Chemicals Co. Ltd., China. DINA was provided by Xi’an Modern Chemistry Research Institute, China. The nitrocellulose (NC, 11.9 wt.% N) and nitroglycerine (NG) mixture, with a mass ratio of 2:1, was purchased from Yibin North Chuan’an Chemical Industry Co. Ltd., China.

Solventless extrusion is one of the most important rapid molding processes for CMDB propellants. The process of propellant sample preparation by the solventless extrusion technique involves three steps: mixing of the raw ingredients with a certain amount of water and stirring at 60 °C for 1 h; centrifugation, removal of the excess of water; rolling and repeated extrusion at about 10 MPa pressure and 85 °C for 10-20 min.

In order to illustrate the effect of temperature on the polymorphic transition of ε-CL-20 as affected by DINA, CL-20, NC/NG and DINA with specified mass ratios were added to water, and the mixture was stirred for a specified time at a set temperature, which were the reference conditions for the process parameters of the solventless extrusion technique. The compositions and conditions for the samples are listed in Table 1.

Table 1. The compositions and preparative conditions of the samples

Sample	Component [wt.%]			Water [wt.%]	Mixing time [min]	Temperature [°C]
	CL-20	DINA	NC/NG			
S1	50	50	–	500	60	60
S2					20	85
S3	100/3	100/3	100/3		60	60
S4					20	85
S5	100	–	–			

2.2 Measurements

Differential scanning calorimetry (DSC) and vacuum stability tests (VST) were used to study the compatibility and thermal stability of CL-20 with DINA. The DSC tests were performed with a 204 HP thermal analyzer (NETZSCH, Germany), with Al crucibles; sample mass ~1 mg, nitrogen flow rate 50 mL·min^{-1} and heating rate 10 °C·min^{-1} from ambient temperature to 400 °C. The VST tests were performed using a YC-1 vacuum stability tester at a temperature of 90 °C for 40 h according to the GJB-770B-2005 standard method 501.1 (CN).

The crystal structures of the CL-20 samples were identified by Raman spectroscopy (RENISHAW, England), with 1 cm^{-1} spectral resolution and a 785 nm laser excitation source. In order to facilitate identification of the polymorphic transition of ε-CL-20 from the test results, CL-20 was scanned 20 times for each sample, and the interval between the test points was larger than 300 μm.

The morphologies of the samples were characterized by scanning electron microscopy (SEM) T-1000 (Hitachi).

The accurate temperature of the polymorphic transition of ε-CL-20 as influenced by DINA was measured by a C-80 type Calvet microcalorimeter (SETARAM, France), which has two 12.5 mL vessels and the accuracy of the heat measurement was less than 0.1%. The mass of the samples of CL-20 and CL-20/DINA at a mass ratio of 1:1, for these tests was about 50 and 100 mg, respectively. The heating rate was 0.2 °C·min^{-1} from ambient to the chosen temperature.

The burning rates were measured by the strand burner method with a pressure range of 2 to 22 MPa at 20 °C.

An Instron-4500 universal instrument was used to analyse the mechanical properties. The samples were dumbbell-shaped (120×50×5 mm). The tensile rate was 100 mm·min^{-1} and the test temperatures were –40, 20 and 50 °C.

3 Results and Discussion

3.1 The compatibility and thermal stability of CL-20 with DINA

The compatibility and thermal stability of CL-20 with DINA were investigated by DSC and VST. The DSC curves of CL-20, DINA and CL-20/DINA mixture are presented in Figure 1. The results show that the thermal decomposition peaks of a CL-20/DINA mixture are consistent with those of CL-20 and DINA, which indicates that CL-20 has good thermal stability with DINA.

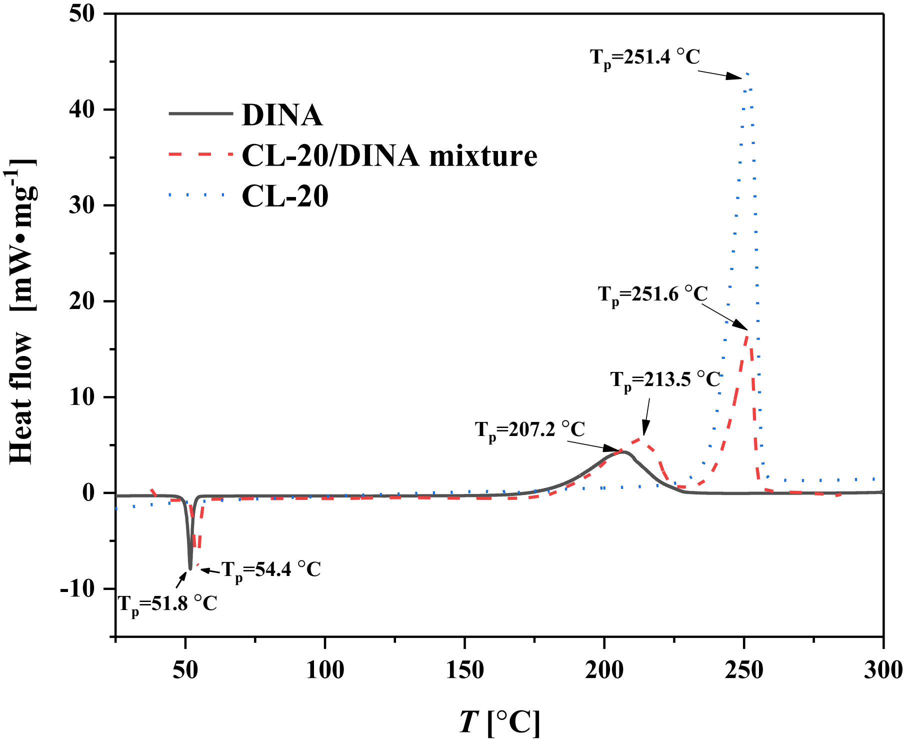


Figure 1. DSC curves of CL-20, DINA, and a CL-20/DINA mixture

VST is one of the most common ways to judge the compatibility of energetic materials. The VST assesses the compatibility from the volume of gas per unit mass (V) produced. The V value is obtained from the following equation:

$$V = V_{\mathrm{mix}} - (V_{\mathrm{CL\text{-}20}} + V_{\mathrm{DINA}}) \quad (1)$$

where $V_{\mathrm{CL\text{-}20}}$ is the volume of gas released by one half unit mass of CL-20,

V_{DINA} is the volume of gas released by one half unit mass of DINA, V_{mix} is the volume of gas released by unit mass of the CL-20 and DINA mixture at a mass ratio of 1:1.

The V value for CL-20 with DINA in the VST was 0.0 mL. According to the GJB-770B-2005 standard method 501.1 (CN), the mixture can be judged to be compatible when the V value is less than 3 mL. Therefore, it was concluded that CL-20 has good compatibility and thermal stability in the presence of DINA.

3.2 Effect of DINA on the crystalline transition behaviour of ε-CL-20

Powder X-ray diffraction (PXRD) can be used to identify the polymorphic transition of CL-20 [17-19], however, most PXRD studies on the polymorphic transition have been limited to systems with simple components. Raman spectroscopy can focus the laser beam on 1 μm, so the crystal form of CL-20 in complex multi-component systems can also be identified by Raman spectroscopy. The crystal forms of CL-20 in S1, S2 and S5 identified by Raman spectroscopy are presented in Table 2 and Figure 2. The results show that the polymorphic transition of *ε*-CL-20 to *α*-CL-20 occurred in the CL-20/DINA/water mixtures after mixing at 85 °C for 20 min, and had not occurred after mixing at 60 °C for 60 min. There was no crystal transition in the CL-20/water mixtures after mixing at 85 °C for 20 min. It may therefore be concluded from these results that the polymorphic transition temperature of *ε*-CL-20 to *α*-CL-20 is reduced significantly by mixing with DINA.

Table 2. Crystal form of CL-20 identified by Raman spectroscopy, where the number represents the number of positive identifications

Sample	*ε*-CL-20	*α*-CL-20
S1	20	0
S2	0	20
S3	20	0
S4	12	8
S5	20	0

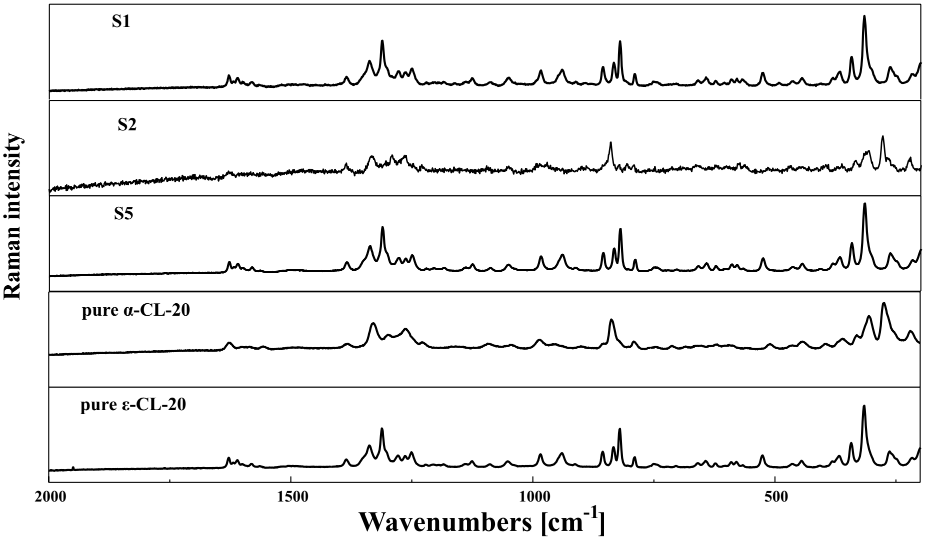


Figure 2. Raman spectra of *α*-CL-20, *ε*-CL-20, and samples S1, S2 and S5

From the Raman spectroscopic analysis, it is readily ascertained that the key factor affecting the crystalline transition of *ε*-CL-20 in the presence of DINA is temperature. To further investigate this effect, the accurate temperature of the polymorphic transition of *ε*-CL-20 was measured using a C-80 type Calvet microcalorimeter and these results are shown in Figures 3 and 4. From Figure 3, the polymorphic transition reaction heat was 17.217 $J \cdot g^{-1}$, and the maximum polymorphic transition peak was at 166.1 °C, which is consistent with the results of differential scanning calorimetry (DSC) tests reported in the literature [20]. By comparing these results, we can confirm that the Calvet microcalorimeter can be used to accurately measure the temperature of the polymorphic transition of CL-20. There is a strong endothermic peak at 52.4 °C in Figure 4, which is due to the melting of DINA. The weak exothermic peak at 74.9 °C in Figure 3 represents the process of polymorphic transition of CL-20; most polymorphic transition processes are endothermic. For this abnormal result, we speculate that DINA can greatly reduce the polymorphic transition activation energy of CL-20 and that there is energy release in the polymorphic transition of CL-20. In order to prove that the polymorphic transition does happen, the sample tested in the Calvet microcalorimeter was analysed by Raman spectroscopy, and confirmed that the polymorphic transition of *ε*-CL-20 to *α*-CL-20 occurred during the Calvet microcalorimeter test.

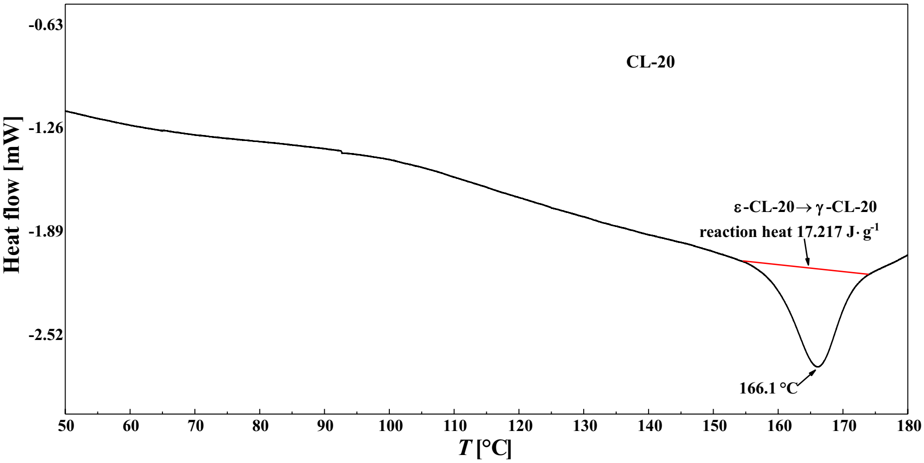


Figure 3. Calvet microcalorimeter curve of ε-CL-20

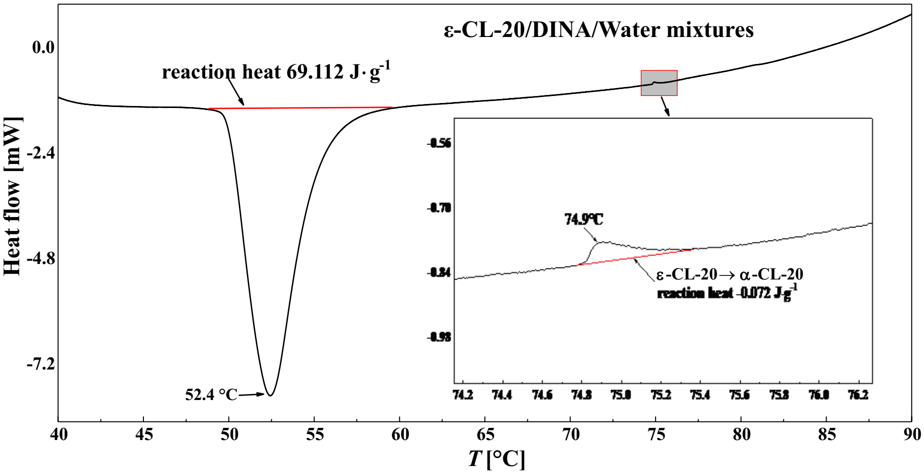
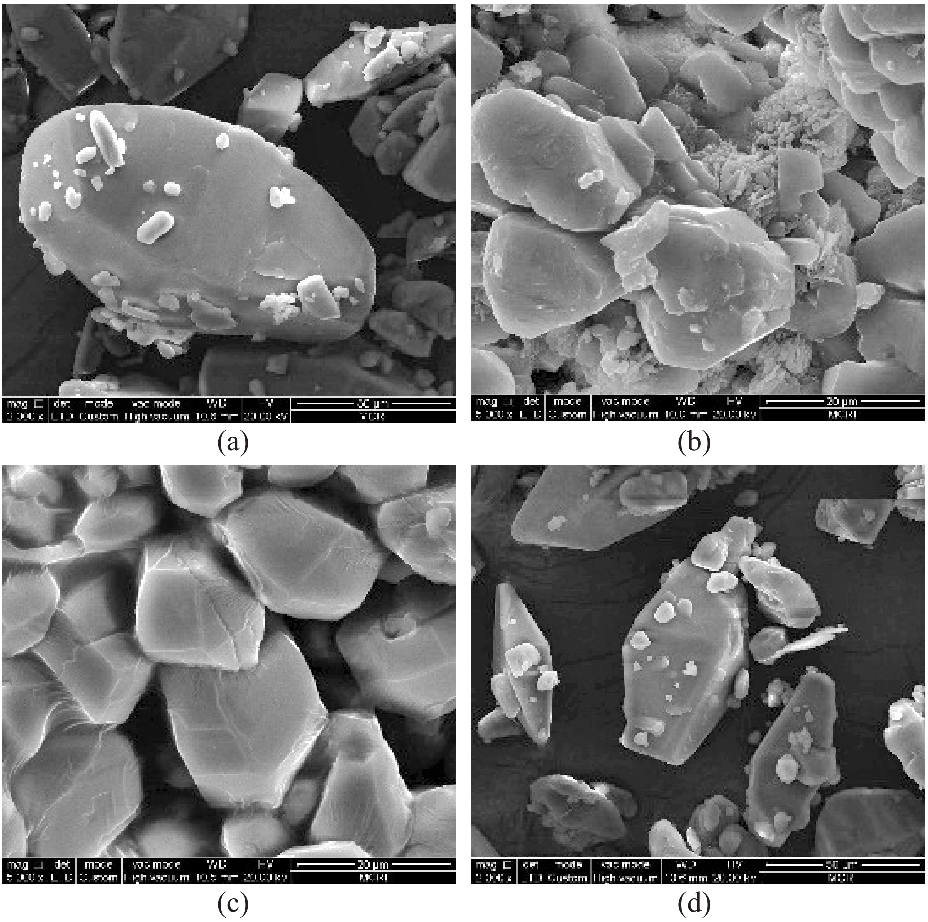


Figure 4. Calvet microcalorimeter curve of the ε-CL-20/DINA/water mixture at mass ratios of 1:1:10

The morphology of CL-20 characterized by SEM is shown in Figure 5. In Figure 5(c), there are obvious cracks in the surface of the crystals, which are caused by the expansion of the crystal volume in the polymorphic transition of *ε*-CL-20 to *α*-CL-20. These cracks are potential heat accumulation points, which will seriously affect the stability of CL-20 and lead to the damage and ineffectiveness of weapons. Therefore, the crystalline transition behaviour of CL-20 should be avoided during processing, transport and use.



(a) (b)

(c) (d)

Figure 5. SEM micrographs of raw CL-20 (a), and samples S1 (b), S2 (c) and S5 (d)

3.3 Effect of DINA on the crystalline transition behaviour of ε-CL-20 in CMDB propellants

The crystal form of CL-20 in S3 and S4 identified by Raman spectroscopy are listed in Table 2 (see Section 3.2) and shown in Figure 6. These results show that only part of the ε-CL-20 is transformed to *α*-CL-20 in S4, and that there is no polymorphic transition in S3. By comparing the results of S2 and S4, it can be speculated that NC/NG can inhibit the effect of DINA on the polymorphic transition of ε-CL-20.

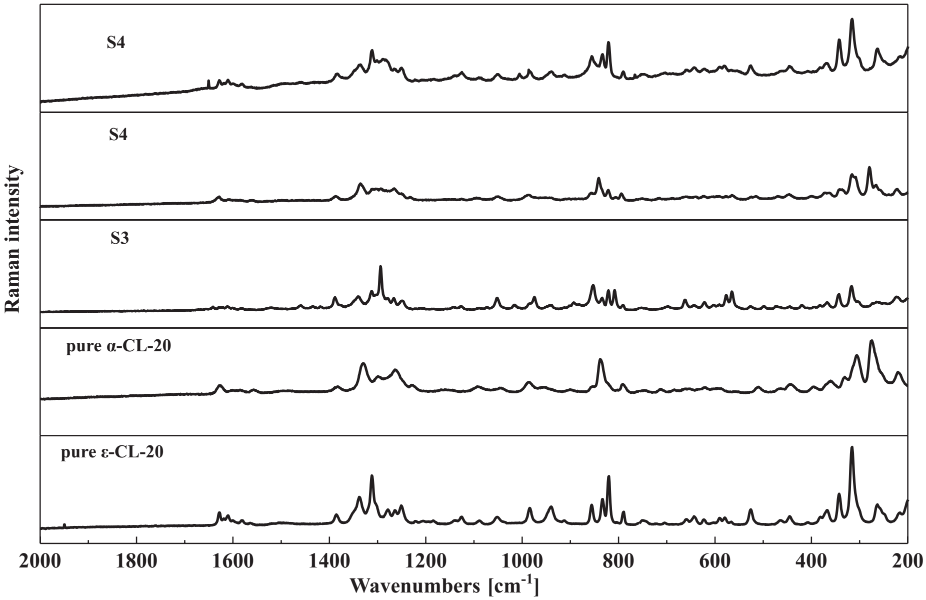
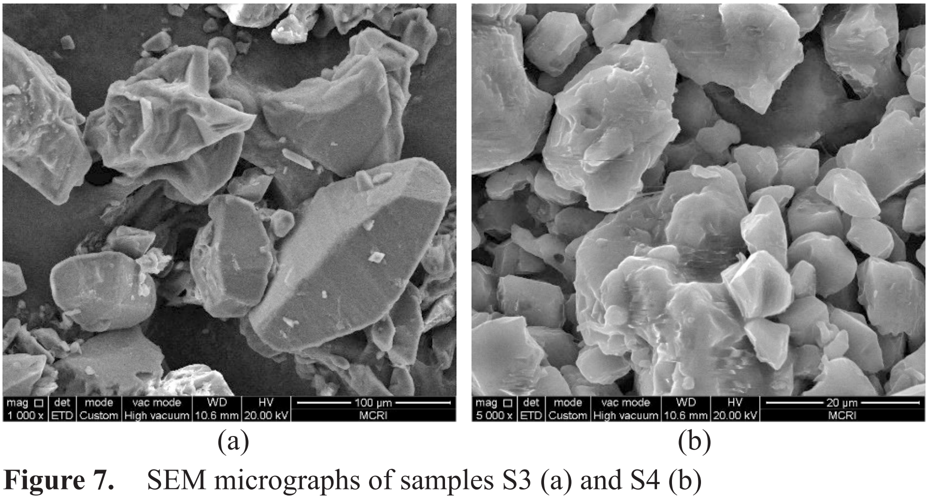


Figure 6. Raman spectra of α-CL-20, ε-CL-20, S3 and S4

The morphologies of CL-20 in S3 and S4 as characterized by SEM are shown in Figure 7. In spite of only part of the ε-CL-20 having been transformed to α-CL-20 in S4, there are still obvious cracks in the crystal surface of the CL-20, as may be seen in Figure 7(b). This demonstrates that there is a potential safety risk once the occurrence of crystal transition in CL-20 has occurred.



(a) (b)

Figure 7. SEM micrographs of samples S3 (a) and S4 (b)

3.4 The crystalline stability of ε-CL-20 in the process of solventless extrusion

In general, the addition of DINA in CMDB propellants does not exceed 10 wt.%, mostly 3-5 wt.%. In order to verify whether DINA has an effect on the crystalline stability of ε-CL-20 in the technological process for CMDB propellants, propellants containing 10 wt.% DINA were prepared by the solventless extrusion technique; the formulation's composition is listed in Table 3. The solventless extrusion technique occurs in two steps: the raw materials are stirred at 60 °C for 60 min (slurry mixing); the sample is then repeatedly extruded at about 10 MPa pressure and 85 °C for 20 min (rolling). The crystal forms of CL-20 identified by Raman spectroscopy are shown in Table 4 and Figure 8.

Table 3. The CMDB propellant formulation

CMDB propellant	Component [wt.%]			Water [wt.%]
	NC/NG	DINA	CL-20	
S6	60	10	30	500

Table 4. Crystal form of CL-20 identified by Raman spectroscopy, where the number represents the number of positive identifications

Sample	ε-CL-20	α-CL-20
S6 after slurry mixing	20	0
S6 after rolling		

From Table 4 and Figure 8, there is no polymorphic transition of ε-CL-20 to α-CL-20 in S6. This might be attributed to the NC/NG blocking the effect of DINA on CL-20; the relative interactions between DINA and ε-CL-20 are shown in Figure 9. Because molten DINA can make full contact with CL-20 in S2, ε-CL-20 transforms to α-CL-20 under the influence of DINA in S2. However, molten DINA can be fully absorbed by NC/NG, so the contact between DINA and CL-20 is blocked in S6, which is why no ε-CL-20 is transformed to α-CL-20 in S6. The absorption of DINA by NC/NG is however limited, and excess DINA will lead to part of the DINA sticking to the surface of the NC/NG, where it can make contact with the CL-20, just as in the S4 situation, and this is why some of the ε-CL-20 is transformed to α-CL-20 in S4.

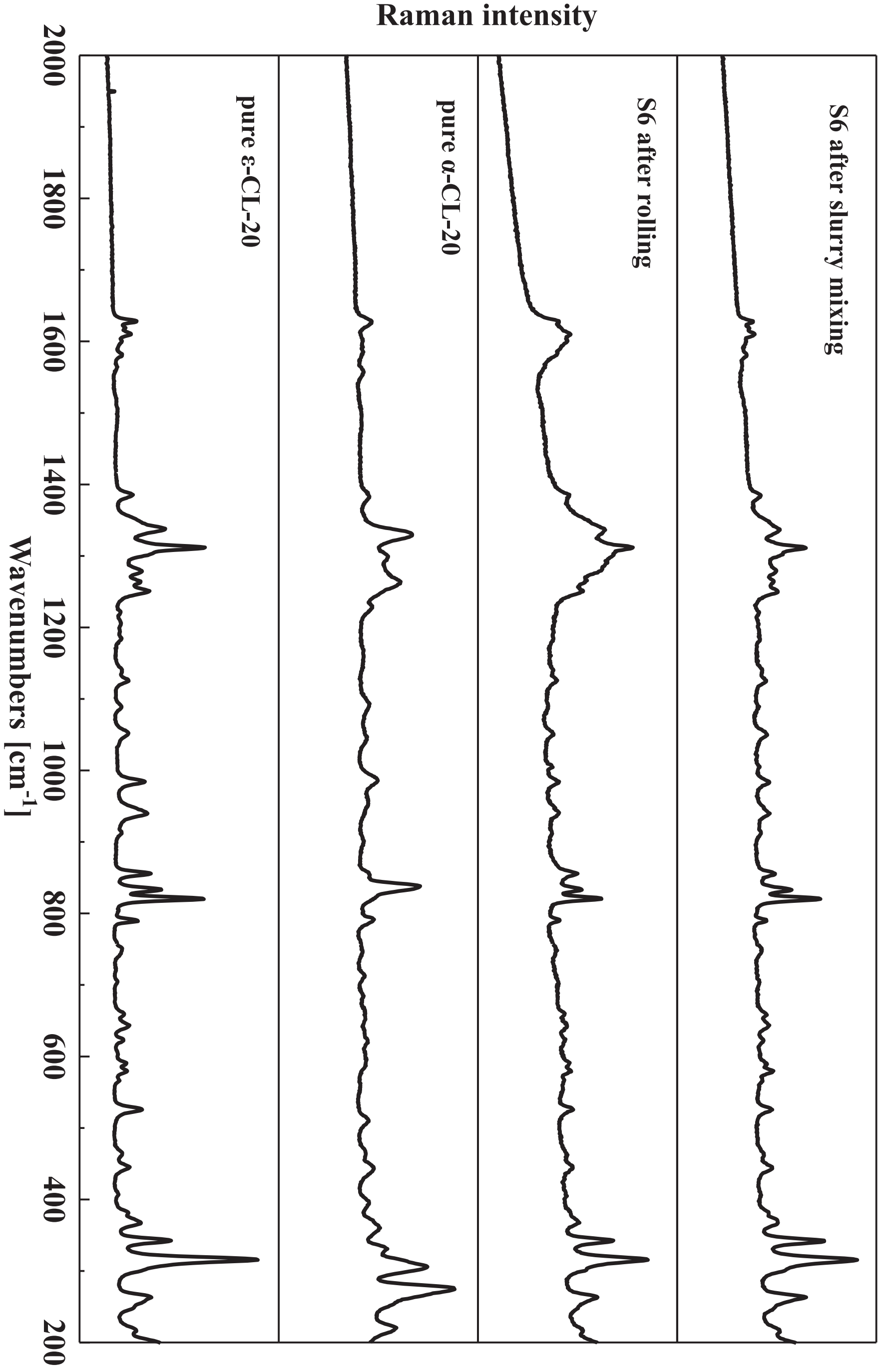


Figure 8. Raman spectra of *α*-CL-20, *ε*-CL-20 and sample S6

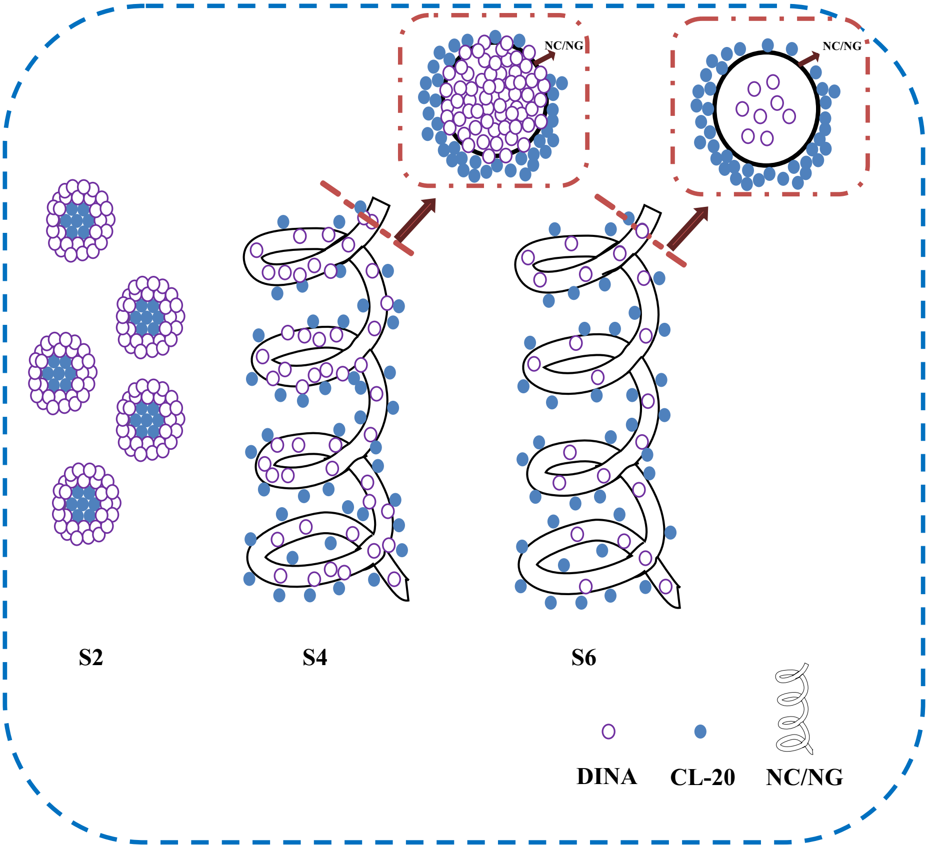


Figure 9. The relative interactions between DINA and ε-CL-20

3.5 The performance of CMDB propellants containing CL-20 and DINA

3.5.1 Theoretical prediction of energetic properties

The energetic properties of CMDB propellants, with DINA and CL-20 gradually replacing the NC/NG, including the theoretical specific impulse (I_{sp}) and combustion temperature (T_c), were calculated at 7 MPa based on the principle of minimum free energy by the Russian code-REAL for Windows, as shown in Table 5.

The results in Table 5 demonstrate that adding CL-20 can clearly improve the I_{sp} and T_c, while adding DINA further improves the I_{sp} but decreases the T_c. These theoretically predicted results indicate that replacing part of the NC/NG with DINA will not lower the energy levels of CMDB propellants containing CL-20.

Table 5. Energetic properties for CMDB propellants with CL-20 and DINA

No.	Component [wt.%]				I_{sp} [N·s·kg^{-1}]	T_c [K]
	NC	NG	DINA	CL-20		
1	53.3	46.7	–	–	2481	3198
2	48.0	42.0		10	2503	3241
3	42.6	37.4		20	2524	3283
4	37.3	32.7		30	2544	3323
5	32.0	28.0		40	2564	3363
6	26.7	23.3		50	2578	3403
7	21.3	18.7		60	2602	3440
8	50.6	44.4	5.0	–	2483	3193
9	45.3	39.7		10	2505	3237
10	40.0	35.0		20	2527	3279
11	34.6	30.4		30	2547	3321
12	29.3	25.7		40	2567	3361
13	24.0	21.0		50	2586	3401
14	18.7	16.3		60	2606	3440

3.5.2 Combustion properties

The burning rates of CMDB propellants, with and without CL-20 and DINA, in the pressure range of 2 to 22 MPa in 2 MPa intervals were measured and the formulations and burning rate curves are presented in Table 6 and Figure 10, respectively.

From Table 6 and Figure 10, it is shown that the burning rates of S8 are higher than those of S7 in the pressure range of 2 to 10 MPa, while the burning rates of S8 are lower than those of S7 in the pressure range of 12 to 22 MPa, indicating that adding CL-20 can improve the burning rates of double base (DB) propellants in the low pressure region and decrease the pressure exponents. At the same time, it is shown that adding DINA can decrease the burning rates of CMDB propellants containing CL-20.

Table 6. The CMDB propellants formulations

CMDB propellant	Component [wt.%]			
	NC	NG	DINA	CL-20
S7	53.3	46.7	–	–
S8	40.0	35.0	–	25.0
S9	37.3	32.7	5.0	25.0

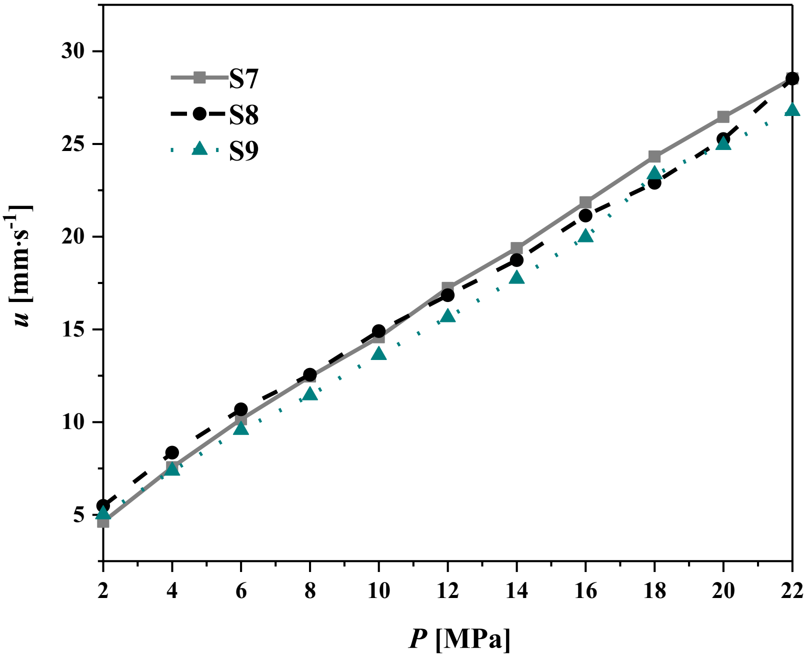


Figure 10. The combustion properties of S7, S8 and S9

3.5.3 Mechanical properties

The results of ultimate mechanical tests on S7, S8 and S9 are presented in Table 7. The results show that adding CL-20 significantly reduces the fracture elongation of propellants, which would make the propellant forming process more difficult. However, adding DINA would obviously improve the mechanical properties of CMDB propellants containing CL-20. Hence, it is necessary to add DINA or another plasticizer to CMDB propellants containing CL-20 to ensure that it has adequate mechanical properties.

Table 7. The mechanical properties (σ_m – tensile strength, ε_m – fracture elongation) of S7, S8 and S9

Sample	Temperature [°C]					
	–40		20		50	
	σ_m [MPa]	ε_m [%]	σ_m [MPa]	ε_m [%]	σ_m [MPa]	ε_m [%]
S7	38.80	5.75	8.25	26.6	1.64	34.2
S8	32.80	2.86	6.96	12.4	1.34	25.2
S9	34.24	3.40	6.45	23.3	1.30	28.6

4 Conclusions

- In conclusion, CL-20 has good compatibility and thermal stability with DINA, and they can be used together in propellant formulations. Theoretical predictions and performance tests revealed that adding DINA can clearly improve the mechanical properties, while decreasing the burning rate and had no significant effect on the energy level of CMDB propellants containing CL-20, which indicates that adding DINA can effectively solve the problem of degraded mechanical properties caused by adding CL-20 to propellants.
- However, DINA has a great effect on the polymorphic transition of CL-20, and can reduce the polymorphic transition temperature of ε-CL-20 to α-CL-20 to 75 °C. NC/NG can inhibit the effect of DINA on the polymorphic transition of ε-CL-20, due to the fact that DINA has no effect on the crystalline stability of ε-CL-20 in the solventless extrusion process. In the practical application of CMDB propellants, DINA has no effect on the crystalline stability of ε-CL-20 in the solventless extrusion process.
- In summary, this work has analyzed the polymorphic transition of CL-20 effected by DINA in an ideal state and in practical applications, and has given useful insight. The results obtained under ideal conditions may give misleading guidance for the practical process. To obtain the most effective data for practical purposes, practical application research should be emphasized, and needs to be compared with the ideal state results.

Declarations 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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