Research Article

Propellants, Explosives, Pyrotechnics

doi.org/10.1002/prep.202100129

Construction of CL-20 Surface Layer with Different Wetting Properties and its Effect on Slurry Rheological Behavior and Mechanical Sensitivities

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Abstract: To have a deep understanding of the effects of surface wettability on the mechanical sensitivity and rheological characteristics of PBX slurry, CL-20 particles with hydrophilic property was prepared through a polymerization process of dopamine, and CL-20 particles with hydrophobic property were prepared through a condensation polymerization process of hexadecyltrimethoxylsilane. The morphology, surface element content and surface wettability of CL-20 crystals before and after modification were characterized by scanning electronic microscope (SEM), X-ray photoelectron spectroscopy (XPS), and contact angle test. The rheological characteristics of CL-20 based PBX slurry showed that the interaction between explosive particles and binder was changed with different surface wettability of CL-20. The weaker interaction between CL-20@hydrophobic and binder lead to weaker solid-liquid friction, resulted in lower apparent viscosities of CL-20@hydrophobic based PBX slurry at high shear rate. The mechanical sensitivity of wax coated CL-20 with different surface wettability was tested. CL-20@hydrophobic-wax exhibited better mechanical stability compared to CL-20-wax and CL-20@hydrophilic-wax, probably owning to the weaker interaction between CL-20@hydrophobic surface and wax.

Keywords: CL-20 · Wettability properties · Mechanical sensitivities · Interfacial performance

1 Introduction

2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) is a promising energetic material with high energy density, which brings new possibility to improve the performance of CL-20 based polymer bonded explosives (PBXs) [1–4]. However, there are some issues limits its further application, including high mechanical sensitivity and poor interfacial performance, which results in high sensitivities and poor processing property of CL-20 based PBXs [4,5]. Constructing coating layer onto the surface of explosive crystals is most commonly employed way to reduce sensitivity of energetic material. Coating materials including wax, polymer, and insensitive explosives are highly efficient to obtain insensitive explosives, despite the physical mixing process would lead to incomplete and inconsistent surface layer [6,7]. On the other hand, poor interaction between explosive crystal and binder lead to poor processing property of PBX slurry as well as poor molding quality of PBX grain due to the incomplete coating of explosive crystals [8–10]. Therefore, the surface modification of CL-20 crystals with controllable surface properties is able to improve the wettability of desensitize agent and polymer binder, forming an uniform and complete coating layer onto the explosive surface, which is of great importance to obtain PBX grain with high quality and low sensitivity.

Inspired by mussels, the polymerization process of dopamine is employed to modify the surface of functional materials, the obtained polydopamine (PDA) is able to form uniform, complete, robust, nano-scale surface layer onto various substrate materials [11–13]. Due to the plenty active groups of PDA, including –OH and $-NH_2$, PDA modified surface usually exhibit hydrophilic property [12]. Condensation polymerization process of hexadecyltrimethoxylsilane is a commonly used way to obtain modified particles with hydrophobic property. During the condensation polymerization process, monomolecular layer of long-chain alkane is able to grow onto the surface of substrate material under proper condition [14–16], obtaining uniform, complete, thin surface layer with hydrophobic property [17,18]. The above two ways are able to construct thin and uniform surface layer with various property onto the substrate surface, providing new possibility to achieve controllable wettability properties of energetic crystals.

Herein, to investigate the effect of surface wettability property of CL-20 on rheological behavior and mechanical sensitivities of PBX, PDA with hydrophilic property and long-chain alkane with hydrophobic property are modified

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Supporting information for this article is available on the WWW under https://doi.org/10.1002/prep.202100129

onto the surface of CL-20 crystals, denoted as CL-20@hydrophilic and CL-20@hydrophobic, respectively. The surface energy of CL-20@hydrophilic increases due to the functional group of PDA, resulting in better wettability of water and liquid wax, while the surface energy of CL-20@hydrophobic decreases. The surface wettability properties of explosive crystal influence the interaction between explosive particles and polymer binders in the PBX slurry, weaker interaction between CL-20@hydrophobic and polymer binders decreases the solid-liquid friction, leading to lower apparent viscosities of CL-20@hydrophobic based PBX slurry at high shear rate. Moreover, weaker interaction between CL-20@hydrophobic and wax is favorable to decrease the friction sensitivity of CL-20@hydrophobic-wax sample.

2 Experimental Section

2.1 Materials

Cl-20 with particle size of 20–60 μm was used as the substrate materials. Dopamine hydrochloride, 2-amino-2-hydroxymethylpropane-1,3-diol (Tris), and Hexadecyltrimethoxysilane were provided by Aladdin Chemical Ltd (Shanghai, P.R. China). Pentaerythritol acrylate was provided by LiMing research institute of chemical industry. Diethyl phthalate, diethyl sulfate, wax, ethanol were provided by Tianjin Tianli chemical reagent Co. All reagents were used as received without any purification.

2.2 Experiments

CL-20 particles were washed by deionized water and ethanol for three times and dried for further preparation.

CL-20 particles were added into reaction solution containing 1.21 mg/mL Tris and 2 mg/mL dopamine. After a stirring process at room temperature for 12 h, the CL-20 particles with hydrophilic property were obtained, and washed with deionized water for three times and dried at 50 °C, the sample was denoted as CL-20@hydrophilic.

5.4 mg/mL hexadecyltrimethoxysilane – ethanol solution was used as reaction solution, CL-20 particles were added into the reaction solution for 2 h under stirring. Then the obtained CL-20 particles with hydrophobic property were washed with deionized water for three times and dried at 50 °C, the sample was denoted as CL-20@hydrophobic.

PBX based on pristine CL-20 and modified CL-20 was prepared for the further analysis, pentaerythritol acrylate was employed as binder, and wax was used as insensitive agent. Weight ratio of explosives, binder, and insensitive agent was 85 : 14 : 1.

2.3 Characterizations

The surface morphology of sample was observed by scanning electronic microscope (SEM) (CamScan Apollo 300). Several particles were selected randomly and coated with gold for SEM analysis. The crystal structure of sample was tested by X-ray diffraction (XRD) on a Bruker D8 instrument. Thermogravimetry (TG) measurements were recorded with a NETZSCH STA 448C instrument from room temperature to 500 °C (10 °C/min, N_2 atmosphere). X-ray photoelectron spectroscopy (XPS) spectra were performed on a Thermo ESCACAB250 instrument. Contact angle was measured by a DSA30s instrument at room temperature; water, CH_2I_2, ethylene glycol, and liquid wax were used as indicators. The surface energy of sample was also calculated by the instrument according to the obtained contact angle and the surface energy of indicator liquids. The viscosities-shear rate curves of PBX slurry were measured on an Anton Paar MCR102 instrument at 60 °C. The friction sensitivities of samples were tested on a WM -1 friction tester with 90° swing angle, 3.92 MPa pressure, and weight of sample was 30 mg ± 5 mg, according to the standard method GJB772A-1997 602.1. The impact sensitivities of samples were tested by a drop height test and explosion probability method, according to the standard method GJB772A-601.2 and 601.1, respectively. The drop height tests were carried out on a drop weight apparatus (001) with 2 kg drop-hammer at room temperature, and the weight of sample was 30 mg ± 5 mg. The explosion probability tests were carried out on a drop weight apparatus (002) with 10 kg drop-hammer, 25 cm drop-high at room temperature, the weight of sample was 50 mg ± 5 mg.

3 Results and Discussion

3.1 The Surface Properties of Modified CL-20

The morphology of pristine CL-20 and modified CL-20 was observed by scanning electronic microscope (SEM) as shown in Figure 1. The surface of pristine CL-20 was smooth and clean, the average particle size was about 20–60 μm. Surface modification process did not change the size and shape of CL-20 particles. After a hydrophilic modification process, particles were deposited onto the surface of CL-20

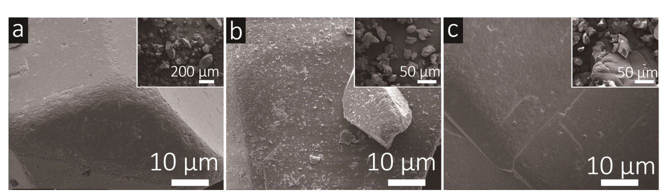

Figure 1. SEM images of pristine CL-20 and modified CL-20. (a) Pristine CL-20; (b) CL-20@hydrophilic; (c) CL-20@hydrophobic.

crystals, due to the formation of PDA particles during the polymerization process. Meanwhile, the surface morphology of CL-20@hydrophobic did not change, because the alkane was grow onto the surface of CL-20 crystals during the condensation process of hexadecyltrimethoxysilane. To further investigate the structure of CL-20 after surface modification, X-ray diffraction (XRD) was carried out as shown in Figure 2. The XRD spectra of modified CL-20 fixed well with the pristine CL-20, indicating that surface modification process of CL-20 with various properties did not change the crystal structure of explosives. TG tests were also carried out (as shown in Figure S1), which showed that the amount of surface species were small and would not impact the detonation performance significantly.

The X-ray photoelectron spectroscopy (XPS) was carried out to investigate the change of surface chemical composition during modification process, as shown in Table 1. The average atomic percentage of C, N, and O on the surface of pristine CL-20 was 32.05 %, 36.36 %, and 31.59 %, respectively. After a hydrophilic modification, the average atomic percentage of C, N, and O was 62.06 %, 15.18 %, and 22.76 %, respectively. The content of carbon increased because of the high C content of PDA, which deposited onto the surface of CL-20 during the polymerization process of dopamine. As for CL-20@hydrophobic sample, the average atomic percentage of C, N, O, and Si was 54.61 %, 20.35 %, 22.73 %, and 2.31 %, respectively. The increasing of C content and the existence of Si element was because of the condensation process of hexadecyltrimethoxysilane, which introducing long-chain alkane onto the surface of CL-20. Figure 3 showed the illustration of the surface modification process of CL-20 with various surface wettability properties. CL-20@hydrophilic was modified with PDA particles, which contained diverse functional groups such as –OH and $-NH_2$, resulting in hydrophilic surface property of modified CL-20. While the CL-20@hydrophobic was modified with long-chain alkane with low surface energy through the condensation process of hexadecytrimethoxysilane, which resulted in hydrophobic property of modified CL-20.

The surface functional group of CL-20 crystals affected the surface wettability and surface energy of samples. Contact angle between explosive crystal and various liquid (including water, CH_2I_2, ethylene glycol, and liquid wax) was tested to investigate the surface properties of obtained samples. As shown in Figure 4 and Table 2, water contact angle of pristine CL-20, CL-20@hydrophilic, and CL-20@hydrophobic was 125 ± 2°, 0°, and 133 ± 2°, respectively. Contact angle between CH_2I_2 and explosive crystals was 0° for pristine CL-20, 0° for CL-20@hydrophilic, and 60 ± 3° for CL-

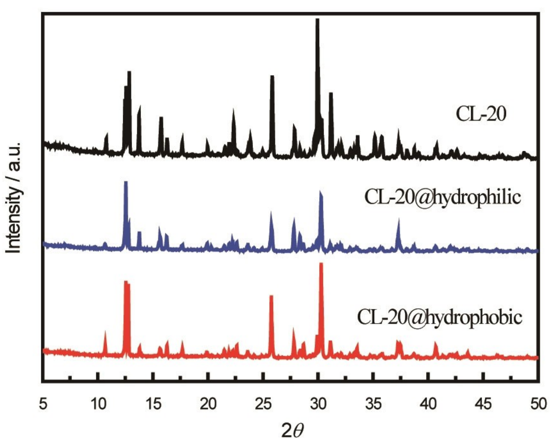

Figure 2. XRD spectra of pristine CL-20 and modified CL-20.

Table 1. Element content of the CL-20 and modified CL-20.

Sample	Element content/%			
	C	N	O	Si
CL-20	32.05	36.36	31.59	0
CL-20@hydrophilic	62.06	15.18	22.76	0
CL-20@hydrophobic	54.61	20.35	22.73	2.31

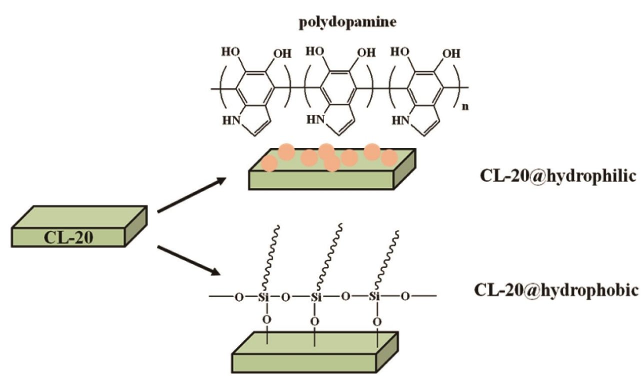

Figure 3. Illustration of the surface modification process of CL-20.

Table 2. Surface free energies of pristine CL-20 and modified CL-20.

Sample	Water Contact Angle (°)	Diiodomethane Contact Angle (°)	Ethylene glycol Contact Angle (°)	Surface Free Energy (mN/m)	Polar Part (mN/m)	Dispersive Part (mN/m)
CL-20	125 ± 2	0	0	20.55	14.40	6.15
CL-20@hydrophilic	0	0	0	72.90	48.56	24.34
CL-20@hydrophobic	133 ± 2	60 ± 3	0	11.76	8.17	3.58

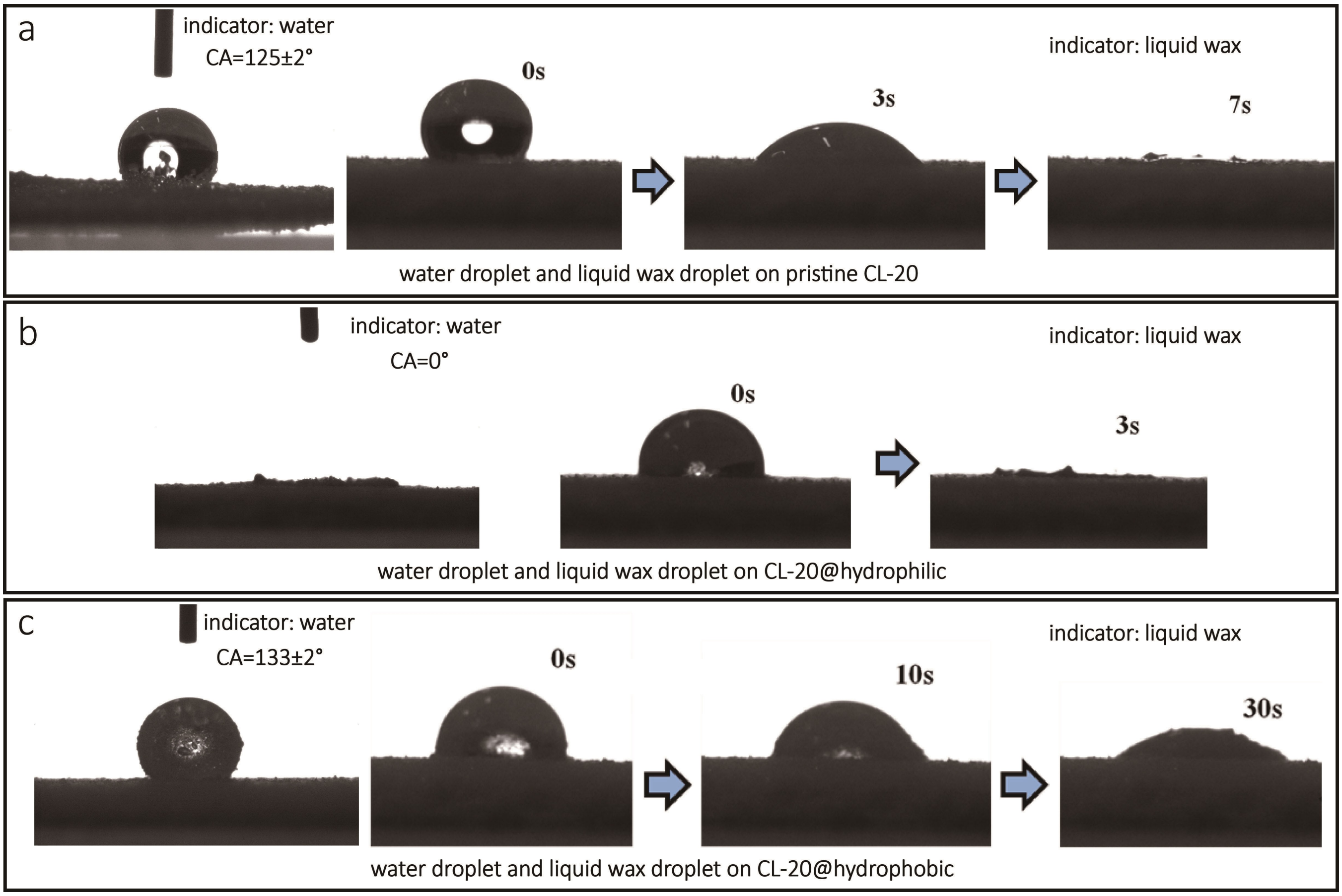

Figure 4. Optical images of water and liquid wax droplets on the surface of pristine CL-20 and modified CL-20. (a) Pristine CL-20; (b) CL-20@hydrophilic; (c) CL-20@hydrophobic.

20@hydrophobic. Contact angle between ethylene glycol and both three CL-20 samples were 0°, and the optical images of ethylene glycol droplets on the surface of pristine CL-20 and modified CL-20 were showed in Figure S2. The surface free energy, polar part, and dispersive part of CL-20 crystals could be calculated according to the above data with SFE OWRK method [19–22]. The surface free energy and polar part of pristine CL-20 were 20.55 mN/m and 14.40 mN/m. After a hydrophilic modification, the surface free energy increased to 72.90 mN/m and the polar part increased to 48.56 mN/m, owing to the active group and high surface energy of PDA. As for CL-20 after a hydrophobic modification, the surface free energy and polar part decreased to 11.76 mN/m and 8.17 mN/m, because of the low surface energy and hydrophobic property of long-chain alkane. Moreover, the surface energy and polar part affected the spreadability of liquid wax. The spreading time of liquid wax on pristine CL-20, CL-20@hydrophilic, and CL-20@hydrophobic was 7 s, 3 s, and more than 30 s, respectively. The wettability property of explosive crystals and the spreadability of liquid wax on the explosive crystal greatly affected the interaction between explosive crystals and liquid composition (including binders and desensitize agent) in PBX, further influenced the rheological behavior and mechanical sensitivities of PBX.

3.2 The Effect of Surface Properties of CL-20 on Rheological Behavior of PBX Slurry

To investigate the effect of explosive crystal surface properties on the rheological behavior of PBX slurry, PBX slurries based on pristine CL-20 and modified CL-20 were prepared for the further analysis. The viscosity of slurries based on pristine CL-20 and modified CL-20 were tested at 60 °C with different shear rate, as shown in Figure 5. η (CL-20@hydrophobic) $\geq \eta$ (CL-20@hydrophilic) $\geq \eta$ (CL-20) at a relative low shear rate ($< 20\ s^{-1}$). The viscosity of PBX slurry based on CL-20@hydrophilic showed an obvious decrease at a shear rate of $21\ s^{-1}$, while the viscosity of PBX slurry based on CL-20@hydrophobic decreased rapidly at a shear rate of $46\ s^{-1}$. Therefore, the wettability of CL-20 showed great effect on the rheological behavior of PBX slurry at different shear rate. At a relative low shear rate, the strong in-

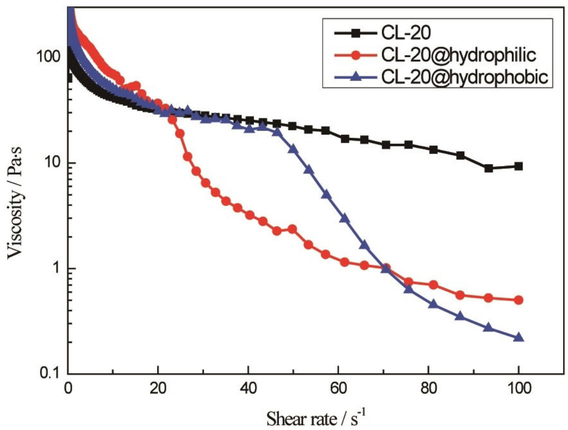

Figure 5. Curves of viscosity of slurries based on pristine CL-20 and modified CL-20 at different shear rates.

teraction between CL-20@hydrophilic crystals and liquid composition made the viscosity of PBX slurry high. As the shear rate increasing, the internal situation of PBX slurry changed, as shown in Figure 6. The viscosity of PBX slurry based on pristine CL-20 mainly determined by solid-liquid friction between explosive crystal and liquid composition as well as the solid-solid friction between explosive particles. As for PBX slurry based on CL-20@hydrophilic, the viscosity mainly determined by liquid-liquid friction between completely-coated crystals, because the strong interaction between CL-20@hydrophilic surface and liquid composition. The weak interaction between CL-20@hydrophobic surface and liquid composition decreased the solid-liquid friction, leading to a rapidly decrease of viscosity of PBX slurry based on CL-20@hydrophobic under high shear rate.

3.3 The Effect of Surface Properties of CL-20 on the Mechanical Sensitivity of Wax-Coated Particle and PBX Slurry

Surface properties of explosive crystals greatly affected the spreading behavior of wax and the wettability of liquid composition in PBX slurry, further affected the mechanism sensitivity of wax-coated sample and PBX grain. Wax-coated samples were prepared with weight percentage of 2%, and the mechanism sensitivities were showed in Table 3. The friction sensitivity of CL-20-wax was 100%, and the H_{50} was 16.2 cm. After a hydrophilic modification, CL-20@hydrophilic-wax showed a light increase of mechanism sensitivity (friction sensitivity: 100%, H_{50}: 14.1 cm). Probably because that the strong interaction between explosive crystal surface and wax lead to a thin coating layer, which could not buffer the stress under shearing stimulus, leading to the impact and break of particles as well as the formation of hot point. Possible behaviors of modified CL-20-wax particles under fraction were showed in Figure 7. As for CL-20@hydrophobic-wax, the friction sensitivity was 40%, and the H_{50} was 20.3 cm, exhibiting a decrease in friction sensitivity. After a hydrophobic modification, the interaction between explosive crystal and wax became weaker, and the wax layer could absorb the energy during shearing stimulus. Meanwhile, the wax would melt and form lubricating layers, which protected the particles from breaking, decreasing the friction sensitivity of CL-20@hydrophobic-wax.

Furthermore, the friction sensitivities of PBX based on pristine CL-20 and modified CL-20 also studied as shown in Table 4. The friction sensitivity of PBX based on pristine CL-20, CL-20@hydrophilic, and CL-20@hydrophobic was 32%, 60%, and 32%, respectively, indicated that the strong inter-

Table 3. The friction and impact sensitivities of the pristine CL-20-wax and modified CL-20-wax samples.

Sample	Friction sensitivities P/%	Impact sensitivities H_{50}/cm
CL-20-wax	100	16.2
CL-20@hydrophilic-wax	100	14.1
CL-20@hydrophobic-wax	40	20.3

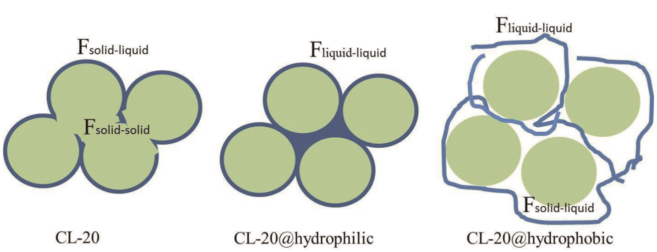

Figure 6. Scheme of the internal situations of the slurries based on pristine CL-20 and modified CL-20.

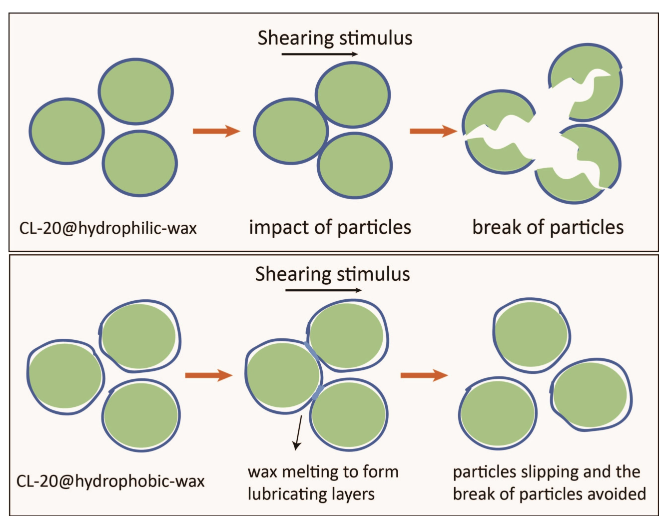

Figure 7. Scheme diagram of possible behaviors of wax coated CL-20 with different surface wettability under fraction.

Table 4. The friction sensitivities of the PBX based on pristine CL-20 and modified CL-20.

Sample	Friction sensitivities *P*/%
PBX based on CL-20	32
PBX based on CL-20@hydrophilic	60
PBX based on CL-20@hydrophobic	32

action between explosive crystal and polymer binder/desensitize agent did not exhibit potential to decrease friction sensitivity of PBX. And the friction sensitivity decreasing was not significant for the PBX based on CL-20@hydrophobic. In PBX formulations, both binder and insensitive agent were coated and protected the explosive crystals, the interaction between liquid compositions (mainly binder) and CL-20 surface affected the sensitivity of CL-20 based PBX formulation. The effect of hydrophobic treatment on decreasing friction sensitivity of PBX was not as significant as CL-20-wax samples, probably because the properties of wax and binder were different, and the hydrophobic treatment did not change the liquid-solid interaction significantly under the preparation condition of PBX.

4 Conclusion

To investigate the effect of surface properties of explosive crystals on mechanical sensitivity and rheological characteristics of PBX, CL-20 samples with controllable surface wettability were prepared. Specifically, CL-20 with hydrophilic property was prepared through a polymerization process of dopamine, owning to the functional group such as –OH/-NH_2 of PDA. And CL-20 with hydrophobic property was prepared through a condensation polymerization process of hexadecyltrimethoxysilane, due to the low surface energy of long-chain alkane. The weak interaction between hydrophobic-modified explosive crystal and liquid composition decreased the solid-liquid friction stress, leading to a rapid decrease of slurry viscosity at high shear rate, improving the processing property of PBX slurry based on CL-20@hydrophobic. Moreover, CL-20@hydrophobic-wax sample exhibited a decrease of friction sensitivity, taking benefit of the weak interaction between explosive crystals and wax. As for the mechanism sensitivity tests of PBX, strong interaction between CL-20@hydrophilic and liquid composition in PBX did not exhibit potential to decrease friction sensitivity.

Symbols and Abbreviations

CL-20 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane
PBXs polymer bonded explosives
PDA polydopamine
Tris 2-amino-2hydroxymethypropane-1,3-diol
SEM scanning electron microscope
XRD X-ray diffraction
XPS X-ray photoelectron spectroscopy

Acknowledgements

This work was supported by the National Science Foundation of China (No. 11772308).

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Manuscript received: May 9, 2021
Revised manuscript received: September 11, 2021
Version of record online: October 20, 2021