

Molecular Dynamics Simulations for Pure ϵ -CL-20 and ϵ -CL-20-Based PBXsXiao-Juan Xu,^{†,*} He-Ming Xiao,^{*,†} Ji-Jun Xiao,[†] Wei Zhu,[†] Hui Huang,[§] and Jin-Shan Li[§]

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Molecular dynamics has been employed to simulate the well-known high energy density compound ϵ -CL-20 (hexanitrohexaazaisowurtzitane) crystal and 12 ϵ -CL-20-based PBXs (polymer bonded explosives) with four kinds of typical fluorine polymers, i.e., polyvinylidenedifluoride, polychlorotrifluoroethylene, fluorine rubber (F₂₃₁₁), and fluorine resin (F₂₃₁₄) individually. The elastic coefficients, isotropic mechanical properties (tensile moduli, bulk moduli, shear moduli, and poisson's ratios), and bonding energy are first reported for ϵ -CL-20 crystal and ϵ -CL-20-based polymer bonded explosives (PBXs). The mechanical properties of ϵ -CL-20 can be effectively improved by blending with a small amount of fluorine polymers, and the whole effect of the adding fluorine polymers to improve mechanical properties of PBXs along the three crystalline surfaces of ϵ -CL-20 is found to be (100) \approx (001) > (010). The interaction between each of the crystalline surfaces and each of the fluorine polymers is different, and the ordering of binding energy for the three surfaces is (001) > (100) > (010); F₂₃₁₄ always has the strongest binding ability with the three different surfaces. F₂₃₁₄ can best improve the ductibility and tenacity of PBX when it is positioned on ϵ -CL-20 (001) crystal surface. The calculations on detonation performances for pure ϵ -CL-20 crystal and the four ϵ -CL-20-based PBXs show that adding a small amount of fluorine polymer into pure ϵ -CL-20 will lower detonation performance, but each detonation parameter of the obtained PBXs is still excellent.

1. Introduction

Hexanitrohexaazaisowurtzitane (CL-20, or HNIW) is a kind of nitramine with a cage structure. Its successful synthesis has been praised as a breakthrough in the history of explosive synthesis.¹ Four stable crystal structures (α , β , γ , and ϵ) of CL-20 have been obtained at ambient temperature and atmospheric pressure, and ϵ -CL-20 has been found to own the largest density and best thermal stability.² Thus since ϵ -CL-20 came into existence, because of its high energy density, good thermal stability, and great application value, it has become the focus and heat point in the field of energy materials in the world.^{2–13}

Polymer bonded explosives (PBXs) are highly filled composite materials comprising a high-energy explosive material as the main body held together by a small amount of one or more kinds of polymeric binders, and it is widely used in many defense and economic applications because PBXs have many desirable traits such as good safety, high strength, ease of processing, etc.^{14–16} The CL-20-based PBXs with different polymers have also attracted peoples' attention.^{17–19} The LLNL, the famous laboratory of America, has prepared four kinds of CL-20-based PBXs with polymers, estane (polyamidoethylformate) and EVA (ethene–ethene acetate copolymer), and they measured the energy level and safe performance, calculated the parameters of JWL state equation,¹⁷ and tested the shock wave of the explosive column of PBX ϵ -CL-20/estane.¹⁸ Bircher H R. et al. have also prepared CL-20-based PBXs with polymers GAP and HTPB (1-hydroxy polybutadiene), and measured their

cosolvency and detonation properties.¹⁹ A lot of effort was put into studying the explosives and polymers with experimental measurement,^{15–16,20–21} calculation and simulation by quantum mechanics (QM), molecular mechanics (MM), and molecular dynamics (MD).^{22–26} Our workgroup has continuously reported the molecular dynamic simulations of the mechanical properties of TATB- and HMX-based PBXs.^{27–33} However, to our knowledge, there are no reports on the structure performance for CL-20- and CL-20-based PBX using the MD simulation method. Meanwhile, simulating the structure performance for PBX, which follows the chemistry development trend from “molecule chemistry” to “material chemistry”, is theoretically significant, and it is also important practically because explosives used in practice are mixing types and not compounds, such as the typical mixing explosives PBXs, whose formulation urgently needs theoretical study.

In this paper, we chose four kinds of typical fluorine polymers: polyvinylidene difluoride (PVDF), polychlorotrifluoroethylene (PCTFE), F₂₃₁₁, and F₂₃₁₄. F₂₃₁₁ and F₂₃₁₄ are copolymers polymerized from vinylidenedifluoride and chlorotrifluoroethylene with the molar ratios of 1:1 and 1:4, respectively. The mechanical properties of pure ϵ -CL-20 crystal and ϵ -CL-20-based PBXs, with polymer binders parallel to different crystalline surfaces, were obtained by MD periodic computation using advanced COMPASS force field.³⁴ It was found that the mechanical properties of the explosives could be effectively improved by blending a small amount of fluorine polymers. The interactions between each of the different binders and different crystalline surfaces of ϵ -CL-20 were analyzed and compared by binding energies. In addition, we evaluated the detonation properties for PBXs with four different fluorine

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polymers on ϵ -CL-20 (001) surface to understand the effects of the polymer binders on explosives. The mechanical properties, binding energies, and detonation properties of the PBXs are expected to be useful for PBX formulation.

2. Modeling and Simulation

The crystal parameters of ϵ -CL-20 were derived from X-ray diffraction.⁵ The unit cell of ϵ -CL-20 was found to be $a = 1.3697$, $b = 1.2555$, and $c = 0.8833$ nm, crystallizing in space group $P2_1/a$. There are four irreducible molecules in the unit cell. The periodic MD simulation cells contain 48 ϵ -CL-20 molecules, corresponding to $(2 \times 2 \times 3)$ unit cells. The ϵ -CL-20 crystal was cut along the crystalline surface (001), (010), and (100), with the “cutting” method in Material Studio (MS) 3.0.1³⁵ and put, respectively, in three periodic cells with 1.0 nm vacuum layer along the z axis(c) direction. Four kinds of fluorine polymers, each involving 10 chain segments built by the MS program, were processed by amorphous cell module and simulated with the 2.5 ns MD method to get the equilibrium conformations. As to the polymer chains, the end groups were saturated by H or F atoms according to their types. Two equilibrium polymer chains taken from each kind of polymer chain were put parallel to the different crystalline surfaces. A total of 1852 atoms and 12 different initial configures of PBXs were obtained. Then, each PBX was compressed adequately along the z direction so that the density was close to the theoretical value. The compressed PBXs were considered as an isothermal–isochoric (NVT) ensemble and simulated by MD in the Compass force field. A fixed time step size of 1 fs was used in all cases. Equilibration runs of 100 000 fs were performed, followed by production runs of 100 000 fs, during which the data were collected for subsequent analysis. The mechanical properties were estimated by static mechanic method involved in the MS 3.0.1 program, and the values were obtained by averaging the mechanical properties of five configures. All calculations were performed on Pentium IV computer.

3. Results and Discussion

3.1. Choice of Force Field and Equilibrium of System. The advanced Compass force field was chosen to simulate mechanical properties for pure ϵ -CL-20 and 12 ϵ -CL-20-based PBXs because, on one hand, the parameters of the Compass force field were debugged and ascertained from ab initio data, optimized according to experimental values, and its nonbond parameters were further amended by the thermal physical properties of liquid and crystal molecules obtained using the MD method. On the other hand, we have employed this Compass force field to nitramine compound HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazocane), and the result was in good agreement with that from experiment. Here, ϵ -CL-20 also belongs to the nitramine series and, most important of all, is that both the crystal parameters (a , b , c , α , β , and γ) and the crystal structure are almost invariable, which further proves the suitability of the Compass force field.

The system equilibrium is ascertained by the equilibrium in temperature and energy simultaneously, that is, the fluctuations of temperature and energy are in the range of 5–10%. For instance, Figure 1 and Figure 2, respectively, show the equilibrium curve of the temperature and energy in the MD simulation of F_{2314} on the molecule layers parallel to (001) crystalline surface of ϵ -CL-20 for the last 50 ps during the process of equilibration runs. It can be found that both the fluctuation curves of temperature and energy tend to be smooth, and the temperature reaches equilibrium state indeed as it is

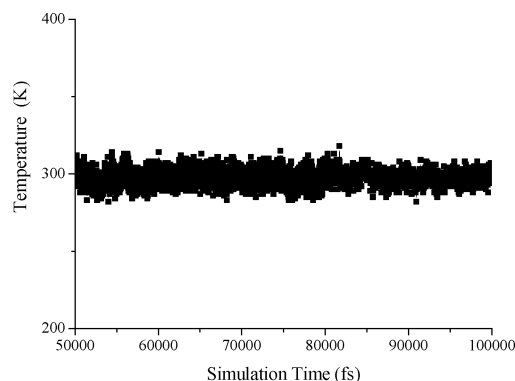


Figure 1. Temperature fluctuation curve of the PBX with F_{2314} on the molecule layers parallel to the ϵ -CL-20 (001) crystalline surface.

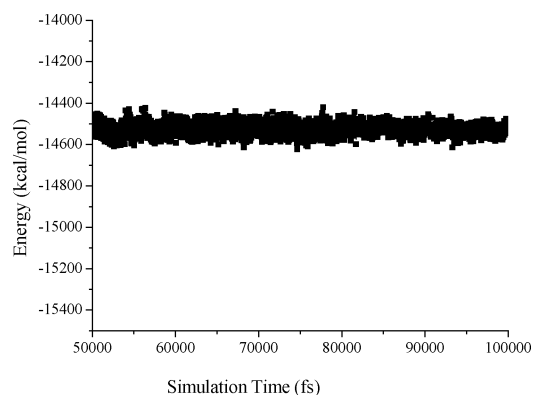


Figure 2. Energy fluctuation curve of the PBX with F_{2314} on the molecule layers parallel to the ϵ -CL-20 (001) crystalline surface.

fluctuating ± 10 K or so. Figure 3 illustrates the energy fluctuation of the later 50 000 trajectories of F_{2314} parallel to the ϵ -CL-20 (001) crystalline surface. The energy deviation of each trajectory is less than 0.7%, which shows that the PBX system has reached energy equilibrium. Other PBXs all come to the equilibrium according to these two criteria.

One trajectory of coordinate for the system was collected every 0.1 ps during production runs. As an example, the MD simulation structures of F_{2314} on three different crystalline surfaces of ϵ -CL-20 are shown in Figure 3.

3.2. Mechanical Properties of PBXs. It is known from elastic mechanics that the generalized Hooke's law can be written as the following:

$$\begin{bmatrix} \sigma_x \\ \sigma_y \\ \sigma_z \\ \tau_{yz} \\ \tau_{xz} \\ \tau_{xy} \end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46} \\ C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56} \\ C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66} \end{bmatrix} \begin{bmatrix} \epsilon_x \\ \epsilon_y \\ \epsilon_z \\ \gamma_{yz} \\ \gamma_{xz} \\ \gamma_{xy} \end{bmatrix} \quad (1)$$

Because of the existence of the strain energy, even though the elastic coefficient matrix of an extremely anisotropic body should satisfy the formula: $c_{ij} = c_{ji}$, there are 21 independent elastic coefficients. For an isotropic substance, there are only two independent elastic coefficients. Accordingly, each modulus and Poisson's ratio can be attained based on two Lamé coefficients. The program can assume a material as isotropic and calculate the effective isotropic mechanical properties.

From the elastic coefficients matrices for ϵ -CL-20 in Table 1, it can be found that the diagonal elements c_{ii} and c_{12} , c_{13} , c_{23} (nine elements total) are larger, but the other coefficients are

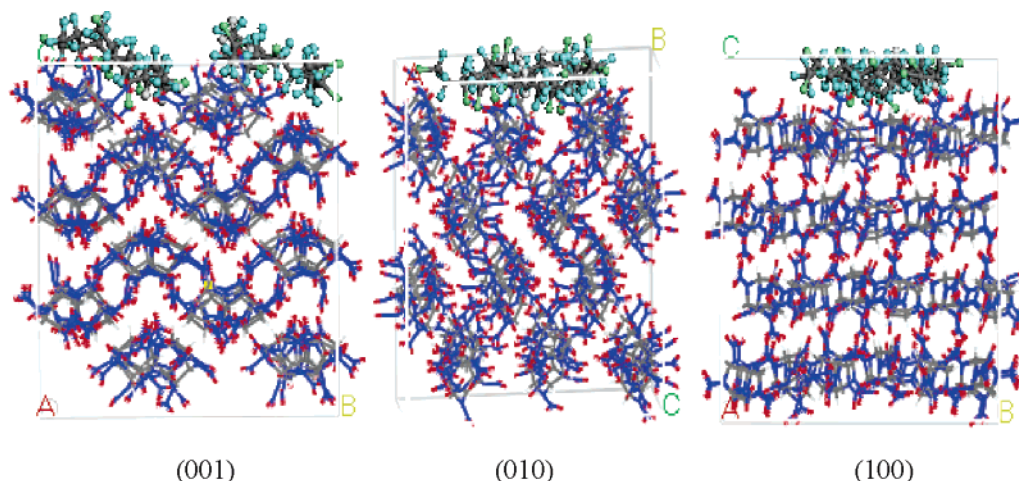


Figure 3. Equilibrium structures of PBXs with F₂₃₁₄ on different crystalline surfaces of ϵ -CL-20.

TABLE 1: Elastic Coefficients of ϵ -CL-20 Crystal and Various ϵ -CL-20-Based PBXs with Different Polymers on Different Crystalline Surfaces (in GPa)

PBXs		C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}	C_{15}	C_{25}	C_{35}	C_{46}	$C_{12}-C_{44}$
ϵ -CL-20 (001)	pure ϵ -CL-20	27.0	18.1	15.1	3.8	7.6	8.1	3.1	8.0	5.0	4.6	-3.2	-1.3	-1.1	-0.7
	PVDF	20.2	14.2	13.3	3.4	3.3	5.1	6.3	8.6	7.4	2.3	-0.4	0.5	-0.9	2.9
	F ₂₃₁₁	21.4	13.4	14.5	3.6	4.2	5.6	6.1	9.3	7.7	2.5	-1.2	0.31	-1.0	2.5
	F ₂₃₁₄	19.8	13.6	12.1	3.2	3.7	4.9	5.9	8.3	7.6	3.3	-0.7	-0.2	-0.8	5.1
	PCTFE	20.9	13.2	13.4	3.1	4.2	4.4	6.4	8.6	7.7	3.1	-0.8	0.4	-0.2	3.3
ϵ -CL-20 (010)	PVDF	12.4	22.0	11.1	3.0	3.9	2.4	4.7	5.2	4.0	0.1	0.0	0.5	0.0	1.7
	F ₂₃₁₁	12.9	22.1	14.2	2.5	4.9	2.9	5.3	8.6	5.5	0.4	0.3	1.2	-0.1	2.8
	F ₂₃₁₄	11.7	20.1	15.7	2.5	4.4	2.4	5.6	6.9	5.6	-0.1	0.1	0.0	-0.3	3.1
	PCTFE	15.0	21.6	13.8	2.9	4.6	2.8	5.6	8.1	5.2	0.6	0.4	1.7	0.0	2.7
	PVDF	13.7	13.5	11.7	6.9	2.6	2.4	7.0	5.4	5.1	0.4	0.1	-0.1	0.2	0.1
ϵ -CL-20 (100)	F ₂₃₁₁	13.7	15.6	16.7	6.9	2.6	2.8	7.7	6.6	7.6	1.0	0.5	0.2	0.4	0.8
	F ₂₃₁₄	15.0	13.8	14.5	7.0	2.4	2.3	8.1	5.6	6.6	0.0	0.6	-0.6	-0.2	1.1
	PCTFE	14.5	14.1	17.3	6.7	2.8	2.7	7.5	5.9	5.8	0.27	0.0	-1.0	0.1	0.8

smaller, which predicts that the simulated ϵ -CL-20 crystal has anisotropic behavior to some extent. This characteristic can be further proved by the differences in the elastic coefficients of the PBXs with the same fluorine polymer on three different crystal surfaces of ϵ -CL-20. Compared with pure ϵ -CL-20, all C_{ij} of PBXs greatly decrease except C_{22} of PBXs with fluorine polymer on ϵ -CL-20 (010) surface and C_{44} on (100) surface, but the smaller C_{ij} (C_{12} , C_{23} , C_{25} , C_{35} , and C_{46}) increase to some extent. This averaging tendency of the PBXs C_{ij} shows that small amounts of fluorine polymer binder can decrease the anisotropy but increase isotropy of PBXs.

Cauchy pressure ($C_{12}-C_{44}$) can be used as a criterion to evaluate the ductility and brittleness of a material. Usually, the value of ($C_{12}-C_{44}$) for a ductile material is positive, contrarily, that is negative for a brittle material. According to this, the data of the last row in Table 1 predict that pure ϵ -CL-20 is brittle due to its negative ($C_{12}-C_{44}$), but once a small amount of fluorine polymer was put along the different crystalline surfaces, all ($C_{12}-C_{44}$) of the obtained PBXs are positive, and the ductibility of PBXs are greatly improved. Comparing ($C_{12}-C_{44}$) of each polymer binder on different ϵ -CL-20 crystalline surfaces, we find that the ductibility of PBXs depends on different ϵ -CL-20 crystalline surfaces, and the order of ductibility changes into the following: (001) > (010) > (100). It can also be found that on each crystalline surface of ϵ -CL-20, F₂₃₁₄ can always improve the ductibility of PBXs, when it was put on the (001) surface of ϵ -CL-20; the obtained PBX has the best ductibility, and its cauchy ($C_{12}-C_{44}$) equals 5.1.

Table 2 shows the effective isotropic mechanical properties, tensile modulus, bulk modulus, shear modulus, and poisson's ratio of pure ϵ -CL-20 crystal and the ϵ -CL-20-based PBXs at

TABLE 2: Mechanical Properties of Pure ϵ -CL-20- and ϵ -CL-20-Based PBXs with Different Polymers on Different Crystalline Surfaces of ϵ -CL-20 (GPa) at 298 K

PBXs		tensile modulus	bulk modulus	shear modulus	poisson's ratio	K/G
ϵ -CL-20 (001)	pure CL-20	17.8	10.3	7.4	0.21	1.39
	PVDF	11.2	10.2	4.2	0.32	2.43
	F ₂₃₁₁	11.5	10.6	4.3	0.32	2.47
	F ₂₃₁₄	10.4	9.9	3.9	0.32	2.54
	PCTFE	10.9	10.3	4.1	0.32	2.51
ϵ -CL-20 (010)	PVDF	13.0	8.1	5.3	0.23	1.53
	F ₂₃₁₁	12.7	9.8	5.0	0.28	1.96
	F ₂₃₁₄	11.9	9.7	4.6	0.29	2.11
	PCTFE	13.0	9.8	5.3	0.26	1.85
	PVDF	9.4	8.2	3.6	0.31	2.28
ϵ -CL-20 (100)	F ₂₃₁₁	10.6	10.0	4.0	0.32	2.50
	F ₂₃₁₄	10.1	9.3	3.8	0.32	2.45
	PCTFE	11.5	9.4	4.4	0.30	2.14

298 K. Since there is no data from existing literature to refer to, we compared the mechanical properties of PBXs with those of pure ϵ -CL-20.

Compared with the (tensile, bulk, and shear) modulus of pure ϵ -CL-20 crystal, the moduli of all the PBXs decrease dramatically, which indicates that the rigidity and brittleness decrease, but elasticity and plasticity of PBXs increase, e.g., the tensile modulus of pure ϵ -CL-20 is 17.8 GPa which is large and predicts the strong rigidity to resist deformation, but when a small amount of PVDF is put on the crystalline surface (100), the tensile modulus decreases almost by half to 9.4 GPa, which presents that the elasticity of the obtained PBX is greatly strengthened. The content of the polymers in the simulated PBXs is about 5–10%, which is about equivalent to the ratio of a polymer in the actual PBXs. Therefore, the mechanical proper-

TABLE 3: Average Binding Energies (E_{binding} , kCal/Mol) for 12 PBXs with Four Kinds of Fluorine Polymers on Three Different Crystalline Surfaces of ϵ -CL-20

PBX		E_T	$E_{\epsilon\text{-CL-20}}$	E_{poly}	E_{binding}
ϵ -CL-20 (001)	PVDF	-15365.38	-14032.67	-1075.42	287.08
	F ₂₃₁₁	-14701.66	-14088.00	-432.56	181.09
	F ₂₃₁₄	-14535.54	-14086.68	-269.91	178.95
	PCTFE	-14359.95	-14045.78	-135.65	178.53
ϵ -CL-20 (010)	PVDF	-15357.54	-14136.94	-1081.04	139.56
	F ₂₃₁₁	-14702.74	-14097.77	-436.50	168.46
	F ₂₃₁₄	-14475.20	-14064.63	-268.76	141.72
	PCTFE	-14386.62	-14081.25	-131.50	173.87
ϵ -CL-20 (100)	PVDF	-15398.37	-14145.43	-1081.44	171.50
	F ₂₃₁₁	-14734.30	-14148.19	-424.45	161.65
	F ₂₃₁₄	-14514.92	-14118.80	-255.36	140.76
	PCTFE	-14391.06	-14097.59	-134.69	158.78

ties of the explosive can be effectively improved by blending the polymers as a binder in a small amount. This result is consistent with that of HMX- or TATB-based PBXs reported recently.^{29–33} The difference of the each kind of moduli of PBXs with fluorine polymers on different crystalline surfaces of ϵ -CL-20 is not very obvious because the anisotropic behaviors of PBXs have been improved. However, on a different crystalline surface, the ability for fluorine polymer to improve the mechanical properties of PBXs is still somewhat different; the order is (100) \approx (001) > (010), and F₂₃₁₄ is regarded as the way to best improve the mechanical properties of PBX on three surfaces, except that there is a little deviation on the (100) surface.

It can also be found from Table 2 that when fluorine polymers are put along the three different ϵ -CL-20 crystalline surfaces, each obtained PBXs has larger Poisson's ratio than pure ϵ -CL-20, and the increasing order of Poisson's ration on different crystalline surface is (001) \approx (100) > (010). As usual, the Poisson's ratio of plastic is 0.2~0.4. Thus, it can be considered that all the obtained PBXs and pure ϵ -CL-20 have plasticity.

In addition, the ratio (bulk modulus/shear modulus, G/K) can be used to evaluate the tenacity of a material. Usually, the greater the value of G/K, the better tenacity the material possesses. According to this, it can be found from the K/G values in Table 2 that the ordering tenacity of PBXs with fluorine polymers on different crystalline surface is (001) \approx (100) > (010), and the PBX with F₂₃₁₄ on a crystalline surface (001) of ϵ -CL-20 is considered to have the best tenacity according to this criterion.

3.3. Bonding Energies. Binding energy can accurately reflect the ability for the polymer binders to blend with the crystal. The molecular interactions can be evaluated by the single point total energy of each component in the stable system, and the average interaction (E_{inter}) between the fluorine polymer and ϵ -CL-20 crystal can be expressed as eq 2.

$$E_{\text{inter}} = E_T - (E_{\epsilon\text{-CL-20}} + E_{\text{poly}}) \quad (2)$$

where E_T is the average total energy of PBX, $E_{\epsilon\text{-CL-20}}$ and E_{poly} are the average single point energy for ϵ -CL-20 and fluorine polymer, respectively. Binding energy is defined as the negative value of interaction, that is, $E_{\text{bind}} = -E_{\text{inter}}$.

From an illustrated example in Figure 3, it can be seen that each fluorine polymer is close to the crystalline surface, and there exists interaction between the polymer binder and ϵ -CL-20 crystal. The average total energies (E_T) of PBXs, average single point energies of crystal ϵ -CL-20 ($E_{\epsilon\text{-CL-20}}$) and fluorine polymer (E_{poly}), and the average binding energies (E_{binding}) are presented in Table 3 for all the obtained PBXs.

It can be found from the data in Table 3 that differences of binding energies not only exist in the PBXs with the same

TABLE 4: Calculated Heats of Explosion (Q), Detonation Velocities (D), and Detonation Pressures (P) for Pure ϵ -CL-20 Crystal and Four PBXs with Four Fluorine Polymers on the ϵ -CL-20 (001) Surface

	ϵ -CL-20	ϵ -CL-20/ PVDF	ϵ -CL-20/ F ₂₃₁₁	ϵ -CL-20/ F ₂₃₁₄	ϵ -CL-20/ PCTFE
Q (J·g ⁻¹)	4623.8	4484.5	4416.1	4384.4	4364.8
D (m·s ⁻¹)	9025.1	8620.5	8678.3	8653.1	8667.8
P (GPa)	40.83	36.94	38.30	38.18	38.55

fluorine polymer on different ϵ -CL-20 crystalline surfaces, but also in the PBXs with a different fluorine polymer on the same crystalline surface. It is obvious that the (001) surface of ϵ -CL-20 has the strongest ability to interact with polymers and has the largest binding energies with polymers, the (100) surface and the (010) surface have the smallest. In other words, when each fluorine polymer is blended into ϵ -CL-20 crystal, they all trend to concentrate on the (001) surface of ϵ -CL-20 due to their largest binding energy. Meanwhile, the electrostatic and van der Waals interactions are thought of as the main origin of the interactions between the fluorine polymer and ϵ -CL-20 crystal, because that zero hydrogen bond energy is included in the nonbond energies, and the distance between the atoms in fluorine polymers and the atoms in the crystalline surface is always more than 0.3 nm.

3.4. Detonation Properties. As an explosive, the heat of explosion (Q), detonation velocity (D), and detonation pressure (P) are the important factors to evaluate PBXs performance. Many theoretical and empirical methods have been suggested to evaluate these detonation properties, such as the Kamlet fomula³⁶ and the Urizar fomula.³⁷ The ω - Γ method,³⁸ pointed out by Wuxiong, was chosen for our calculations because it is more suitable for monomer and blending explosives. In this method, detonation velocity (D , m·s⁻¹) is defined as the following:

$$D = 33.05Q^{1/2} + 243.2\omega\rho \quad (3)$$

where Q , ω , and ρ represent heat of explosion or the value of character heat (J·g⁻¹), the factor of thermal energy, and the density of loaded explosive (g·cm⁻³). As for the mixture explosives, the Q and ω are evaluated by adding Q_i and ω_i of each component according to their weight percent.

Based on the D derived from eq 3 and the simplification of C-J theory,³⁹ detonation pressure (P) was estimated by eq 4.

$$P = \frac{1}{4}\rho_o D^2 \quad (4)$$

From Table 4, it can be seen that all the detonation properties (Q , D , P) of PBXs blended with fluorine polymer are less than those of the pure ϵ -CL-20, this is a reasonable phenomenon because the fluorine polymer has much less ρ and Q than ϵ -CL-20, although the values of these detonation properties for PBXs are large enough to be used as energetic materials with good performance. It is worthy of noting that there is no obvious difference among the detonation properties of these four PBXs. This may be partly caused by the calculation method in which the same Q and w were used for four different fluorine polymers, but in fact, they are different from each other and sometimes the discrepancy may be large. On the whole, however, we can conclude that the four kinds of fluorine polymers, with the same chain segments, have similar effects on the detonation properties of the obtained PBXs.

4. Conclusions

This paper has addressed MD simulation studies on mechanical and detonation properties of pure ϵ -CL-20 crystal and ϵ -CL-20-based PBXs. We can conclude the following:

(1) The mechanic properties (elastic coefficients, tensile moduli, bulk moduli, shear moduli, and poisson's ratios), bonding energy, and detonation properties are first reported for ϵ -CL-20 crystal and ϵ -CL-20-based PBXs.

(2) The mechanical properties of ϵ -CL-20 can be effectively improved by blending a small amount of the fluorine polymers, and the effectiveness of improving mechanical properties of ϵ -CL-20 by putting fluorine polymers parallel to ϵ -CL-20 three crystalline surfaces is shown to be $(010) \approx (100) > (001)$.

(3) There is no parallel relation between the improvement of mechanical properties and the binding energies, and the ordering of the binding energies of PBX with four fluorine polymers on three different surfaces is $(001) \approx (100) > (010)$. As for the four polymer binders, F₂₃₁₄ is considered the best one for explosive ϵ -CL-20.

(4) The calculations on detonation properties for PBXs show that the detonation properties of PBXs can be lowered by blending a small amount of fluorine polymer, but they are still large enough to be good energetic materials. The effects of four kinds of fluorine polymers with the same chain segments on the detonation properties of the obtained PBXs are approximate.

In all, the MD simulation studies on pure ϵ -CL-20- and ϵ -CL-20-based PBXs provided us with much regular information of their mechanical properties and binding energies. To choose an optimal and practical binder, it is necessary to consider comprehensively two aspects, i.e., binding energy and mechanical properties. These will be of great help for experimenters to choose good polymer binders and to prepare PBXs with different performances according to the practical requirements.

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