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Molecular dynamics simulations on the structures and properties of ε-CL-20-based PBXs
——Primary theoretical studies on HEDM formulation design

XU XiaoJuan[1,2], XIAO JiJun[1], HUANG Hui[3], LI JinShan[3] & XIAO HeMing[1†]

[1] Department of Chemistry, Nanjing University of Science and Technology, Nanjing 210094, China;
[2] Department of Chemistry, Yancheng Teacher's College, Yancheng 224002, China;
[3] Institute of Chemical Materials, China Academy of Engineering Physics, Mianyang 621900, China

Five polymer bonded explosives (PBXs) with the base explosive ε-CL-20 (hexanitrohexaazaisowurtzitane), the most important high energy density compound (HEDC), and five polymer binders (Estane 5703, GAP, HTPB, PEG, and F_{2314}) were constructed. Molecular dynamics (MD) method was employed to investigate their binding energies (E_{bind}), compatibility, safety, mechanical properties, and energetic properties. The information and rules were reported for choosing better binders and guiding formulation design of high energy density material (HEDM). According to the calculated binding energies, the ordering of compatibility and stability of the five PBXs was predicted as ε-CL-20/PEG > ε-CL-20/Estane5703 ≈ ε-CL-20/GAP > ε-CL-20/HTPB > ε-CL-20/F_{2314}. By pair correlation function $g(r)$ analyses, hydrogen bonds and vdw are found to be the main interactions between the two components. The elasticity and isotropy of PBXs based ε-CL-20 can be obviously improved more than pure ε-CL-20 crystal. It is not by changing the molecular structures of ε-CL-20 for each binder to affect the sensitivity. The safety and energetic properties of these PBXs are mainly influenced by the thermal capability ($C°_p$) and density (ρ) of binders, respectively.

high energy density material (HEDM), hexanitrohexaazaisowurtzitane (CL-20), polymer bonded explosives (PBXs), molecular dynamics (MD), compatibility, safety properties, mechanical properties, energetic properties

It is the heated point to look for high energy density materials (HEDMs) in current energy resource and material fields, which affects the development of national security, astro-aviation, and national economy[1 − 5]. HEDMs consist of high energy density compounds (HEDCs) as the main body and other additives, and its performances depend on good formulation.

CL-20 (hexanitrohexaazaisowurtzitane) is the most well-known HEDC[6], and CL-20-based polymer bonded explosives (PBXs) with a small amount of polymer binders have attracted much attention[7−10]. For example, the Lawrence Livermore National Laboratory (LLNL) in U.S.A. has prepared four kinds of CL-20-based PBXs with polymers, Estane5703 (polyurethane) and EVA (ethylene-vinylacetate copolymer)[7,9]. Bircher et al. have also prepared CL-20-based PBXs with polymers GAP (polyazideglyceraether) and HTPB (hydroxy terminated polybutadiene) and measured their performances of detonation, compatibility, and sensitivity[8].

The formulation of HEDMs and PBXs mainly depends on experiments, which wastes many resources, has longer periods, especially cannot predict the performances of unknown formulation, and theoretical direction is urgently needed. It is helpful for theoretically

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†Corresponding author (email: xiao@mail.njust.edu.cn)
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guiding the formulation design by molecular dynamics (MD) simulations on the structures and properties of explosives[11−15], polymers[16] and PBXs[10,17−19].

In this paper, MD simulations with the Compass force field[20−22] were employed to investigate the performances of newly reported ε-CL-20-based PBXs with polymers Estane5703, GAP, and HTPB and those with PEG (polyethylene glycol) and F_{2314} (copolymers polymerized from vinylidenedifluoride and chlorotrifluoroethylene with the molar ratios of 1∶4). The four main attributes (compatibility, mechanical properties, safety, and energetic properties) of the PBXs were analyzed and compared. Our aim is to provide examples, information and rules for choosing better binders and guiding HEDMs formulation design, namely, to make primary theoretical studies on HEDMs formulation design.

1 Computational methods

1.1 Choice of force field

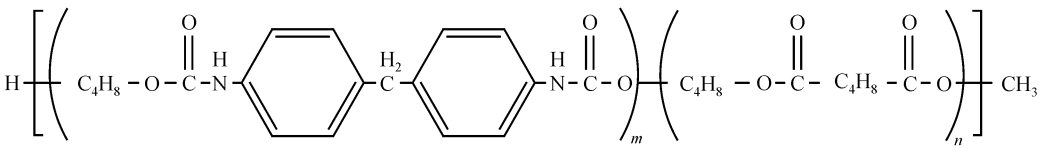
The characteristic of force field is one of the major factors determining the reliability of MD simulations. The Compass force field[20−22] was chosen for pure ε-CL-20 and five ε-CL-20-based PBXs mainly for two reasons: one is that, the parameters of the Compass force field were debugged and ascertained 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, the optimized molecular structure of ε-CL-20 from Compass agrees well with that from quantum mechanics method[23], and the predicted cell parameters of ε-CL-20 using Compass force field is well consistent with experiment values. Besides, Compass force field has been successfully used to study some related properties of ε-CL-20-based PBXs with different fluorine binders[10].

1.2 Construction of polymer model

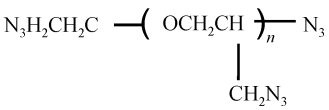
To be conveniently compared with the experiment, the percent weight of binders of PBXs is controlled about 4.2%. Figure 1 presents the structures of 5 polymer binders. The chain number (m) of the rigid segment of Estane5703 is 1 (m = 1), and that of the soft segment is 3 (n =3); for GAP, HTPB, PEG, and F_{2314}, n = 8, 17, 21, and 10, respectively. As to the polymer chains, the end groups were saturated by H, CH_3, OH or F according to their types. The above polymer models were considered as NVT ensembles to make MD simulations with the Compass force field by Discover module of Materials Studio (MS) program[24]. In which "Anderson" was chosen as the thermostat, and temperature was set as 298 K; step size was 1fs, the total simulation time was 3 ns, and the finally equilibrium structures of polymers were obtained.

1.3 Construction of ε-CL-20 and PBXs models

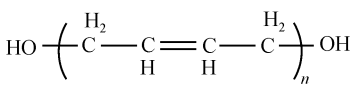
The crystal parameters of ε-CL-20 were derived from



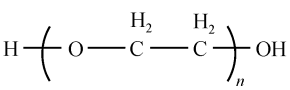
Estane5703



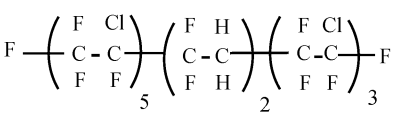
GAP



HTPB



PEG



F_{2314}

Figure 1 Structure models of five polymer binders.

X-ray diffraction[25]. The (2×2×3) model of crystal cells was constructed using MS program. Molecules on (001) surface of ε-CL-20 crystal have been predicted to be very compact and can strongly interact with binders[10]. In this paper, the "cutting" model was chosen, in which ε-CL-20 crystal was cut along the crystalline surface (001) and put in the periodic boxes with 20 Å vacuum layer along the *c* direction. Five primary models were obtained by putting polymer binder chains into the box to approximate to ε-CL-20 molecules at most, respectively, and then compressed and optimized by molecular mechanics (MM) adequately until the density was close to its theoretical value. The obtained densities (ρ) of five PBXs are 1.853, 1.771, 1.746, 1.769, and 2.02 $g \cdot cm^{-3}$, and the corresponding weight percent of binders are 4.35%, 4.40%, 4.33%, 4.29%, and 4.69%, respectively. Besides, the initial model of pure ε-CL-20 was compressed close to its experimental density (2.0552 $g \cdot cm^{-3}$).

The origin models of pure ε-CL-20 and five PBXs were considered as NVT ensembles and simulated with the Compass force field by MD. "Anderson" was chosen as thermostat, and temperature was set as 298 K; step size was 1 fs, and the total simulation step number was 240 thousand, the first 120 thousand steps were equilibrium runs, and the later 120 thousand steps were production runs for statistical analysis. One frame was saved per 50 steps, and totally 2400 frames were saved to make analyses of static mechanical properties and pair correlation function $g(r)$. Figure 2 presents the equilibrium structures of five ε-CL-20-based PBXs from MD simulations.

1.4 Equilibrium of system

Only when a system is in equilibrium state, it is significant to make property analysis on the production trajectory. The equilibrium should be ascertained by the equilibrium in temperature and energy simultaneously, that is, the fluctuations of temperature and energy are in the range of 5%—10%. In our work, during the last 50 ps equilibrium step, the temperature fluctuation of each PBX is 10 K or so, and energy fluctuation is less than 0.7%. This predicts that all the PBXs have arrived in equilibrium state.

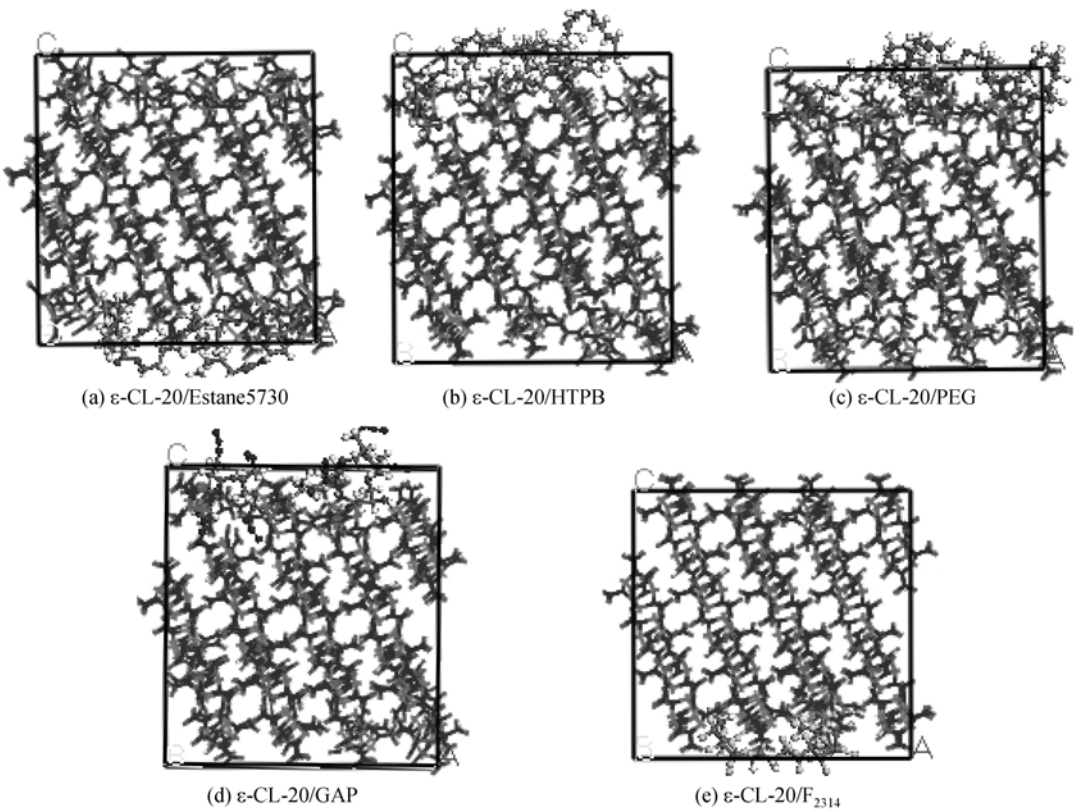


Figure 2 Equilibrium structures of five ε-CL-20-based PBXs from MD simulations.

2 Results and discussion

2.1 Compatibility discrimination with binding energy, analysis of pair correlation function $g(r)$

There has been no certain definition of "compatibility" up to now. In view of many definitions, two aspects should be considered. One is that, there must be interactions between components, or it will not be compatible; the other is that the mixed system should be stable, for when the stability changes greatly, the compatibility is bad. Sometimes, compatibility is regarded as the capability for explosives to keep physical, chemical, and explosive properties when mixed with or touched by other components. Compatibility is an important property of a high energy material, and if it is worse, the stability and burst temperature of an explosive will decrease, the priming sensitivity will change, and the comprehensive properties become poor[26]. There has hardly been a report on how to theoretically evaluate compatibility. As for PBXs, the polymer binders are inert and usually cannot cause chemical reaction to happen to the main body explosive, and therefore only physical compatibility exists between them. The physical compatibility is correlative with the interactions between the main body explosives and binders. Binding energy (E_{bind}) is defined as the negative value of interaction energy (E_{inter}), that is, $E_{bind} = -E_{inter}$. The PBX with larger E_{bind} will be more stable, and the compatibility is better. Thus, it is suggested to predict the compatibility of similar systems by E_{bind}.

As for a PBX in equilibrium, E_{bind} is calculated as the average of 5 frames in trajectory. The average E_{bind} between ε-CL-20 and polymer binder can be expressed as the following:

$$E_{bind} = -(E_T - E_{\varepsilon\text{-CL-}20} - E_{poly}),$$

where E_T is the average total energy of PBX, $E_{\varepsilon\text{-CL-}20}$ is the single point energy for the system when polymer chains are removed, and E_{poly} is the single point energy when ε-CL-20 molecules are removed, respectively. Based on the above equation, E_{bind} and their unitary values (E'_{bind}) are listed in Table 1.

According to the data of E_{bind} (or E'_{bind}) in Table 1, the compatibility ordering is predicted as ε-CL-20/PEG > ε-CL-20/Estane5703 ≈ ε-CL-20/GAP > ε-CL-20/HTPB > ε-CL-20/F_{2314}. The compatibility of three PBXs has been measured as ε-CL-20/GAP > ε-CL-20/HTPB > ε-CL-20/Estane5703[7,9,27], this is not completely consistent with binding energies. This may be due to different particle size of ε-CL-20 in the three PBX samples, and the average particle radius (<160 μm) of ε-CL-20 in ε-CL-20/Estane5703 is larger than those in the other two PBXs (particle radius of 40% < 134 μm, 50% < 35 μm, and 10% < 6 μm). This decreases the touching area between Estane5703 and CL-20, leading to worse compatibility. Given that the particle size of main body explosive is the same, the compatibility of PBXs can be distinguished and predicted by their E_{bind}.

To understand the interaction formats between ε-CL-20 and binders, analyses of pair correlation function $g(r)$ was imposed on the trajectory of each PBX. $g(r)$, also named radius distribution function, gives a measure of the probability that, given the presence of an atom at the origin of an arbitrary reference frame, there will be an atom with its center located in a spherical shell of infinitesimal thickness at a distance r from the reference atom.

To be compact, only $g(r)$ of ε-CL-20/Estane5703 and ε-CL-20/GAP are described in Figure 3 and Figure 4. The corresponding atoms are named as follows: (1) O and H atoms in ε-CL-20 are noted as o_{12} and h_1; (2) O═, -O-, N and H in Estane5703 are noted as $o_{1=}$, o_{2s}, n_{3mh}, and h_1; (3) O (-O-), O (-OH), and H in GAP are noted as o2e, o2h, and h_1; it is difficult for N_1 and N_3, positively charged in -N_1═N_2≡N_3 to form hydrogen bonds with H in ε-CL-20, so that only N_2 is symboled as n_{2t}.

Usually, molecular interactions mainly include hydrogen bonds and van der Waals interactions. The distance range of hydrogen bond is 2.6—3.1 Å and that of strong van der Waals is 3.1—5.0 Å; when the distance is

Table 1 The total energies (E_T) of 5 PBXs, crystal energies of ε-CL-20 (E_{crys}), binder energies (E_{poly}), and binding energies (E_{bind})[a)]

	ε-CL-20/Estane5703	ε-CL-20/GAP	ε-CL-20/ HTPB	ε-CL-20/PEG	ε-CL-20/F_{2314}
E_T	–59688.60	–59079.33	–59200.00	–58941.93	–60016.82
E_{crys}	–58794.00	–58819.96	–58863.39	–58751.45	–59034.27
E_{poly}	–186.97	442.79	281.98	662.61	–571.95
E_{bind}	707.63	702.16	618.59	853.09	410.60
E'_{bind}	162.67	159.58	142.86	198.86	87.55

a) Units: kJ·mol^{-1}; E'_{bind} is the E_{bind} of unit quantity (1%) of binders.

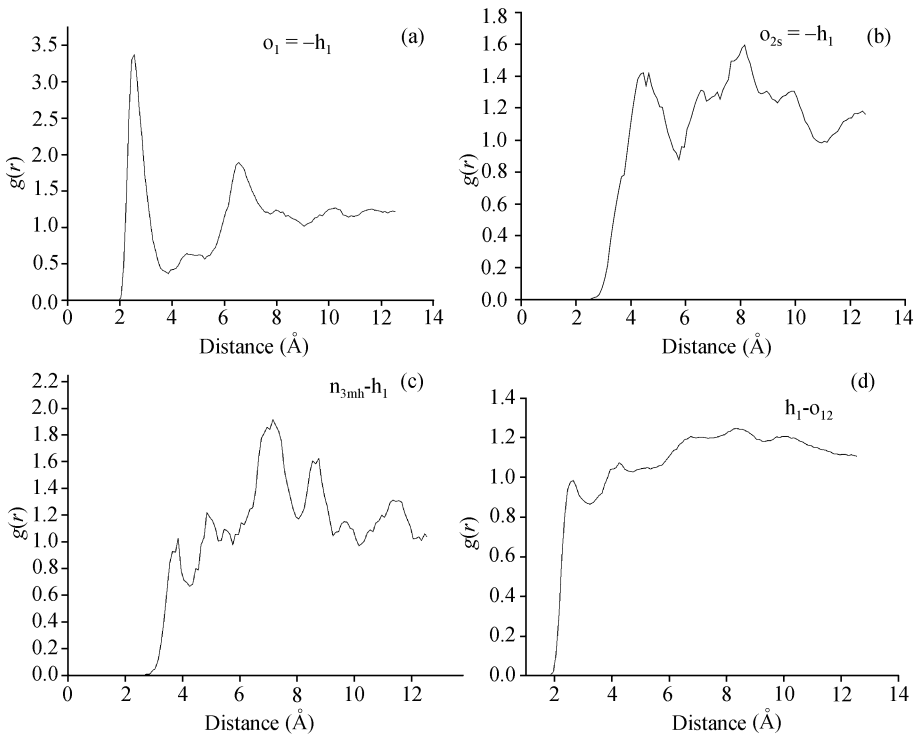


Figure 3 Radial distribution function of ε-CL-20/Estane5703.

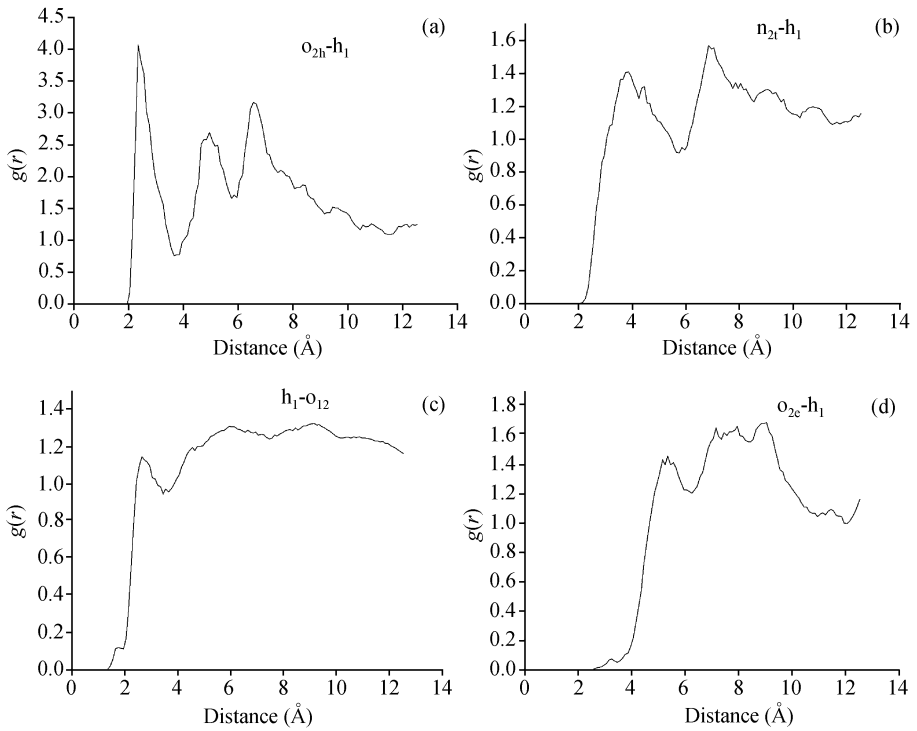


Figure 4 Radial distribution function of ε-CL-20/GAP.

more than 5.0Å, the van der Waals interaction is very weak. From Figure 3(a), it is found that probability for O(o_1=) in Estane5703 and h_1 in ε-CL-20 to simultaneously arise in the distance of 2.15—3.15 Å is high to 3.37 or so, predicting the strong hydrogen bonds interaction between them. In the range of 3.95—5.35 Å, a

comparative high peak arises in the $g(r)$ describing the o_{2s}-h_1 atom pair, predicting the strong van der Waals interactions. Figure 3(c) and (d) show that mainly van der Waals interactions exist in n_{3mh}-h_1 and h_1-o_{12}. In all, hydrogen bonds and van der Waals are the main interactions between Estane5703 and ε-CL-20, especially the hydrogen bond in o_1=h_1.

From Figure 4(a), it is found that in the range of 2.15 −3.145Å, the maximum peak value (4.1) arises in the $g(r)$ curve of o_{2h}-h_1, indicating the strong interaction between this atom pair; in the region of van der Waals, high peak arises again, predicting that certain van der Waals interaction exists between them. Seen from Figure 4(b) and (c), some hydrogen bonds and van der Waals interactions were found to exist in n_{2t}-h_1 and h_1-o_{12} atom pairs. It is predicted that van der Waals are the main interaction in o_{2e}-h_1 from Figure 4(d). In all, the strong hydrogen bonds between O (-OH) in GAP and H in CL-20 are the main interaction origin between them.

Besides, due to their good compatibility between them, the ε-CL-20/PEG PBX has the biggest E_{bind}. Although the weight percent (4.69%) of F_{2314} is somewhat larger, the E_{bind} between ε-CL-20 and F_{2314} is smaller. This predicts the worse compatibility between ε-CL-20 and fluorine polymers

2.2 Safety

Sensitivity of an energetic material to initiation by exoteric stimulus can reflect the safety of explosives in preparation, storage, transportation, and usage. Usually, the adding of inert binders can decrease sensitivity. When the weight percent of binders is 4.2%, the ordering of experimental sensitivity is as follows: ε-CL-20 > ε-CL-20/GAP > ε-CL-20/Estane5703 ≈ ε-CL-20/HTPB[27]. Thus, the adding of HTPB and Estane5703 can well lower the sensitivity and increases the safety of CL-20.

Previously, only theoretical reports on the sensitivity of high energy density compounds and crystals have been reported[28−30]. As for high energy composite materials, such as PBXs, it is difficult to study their sensitivity by quantum chemistry method, due to the calculated system is much bigger and complicated. Our aim is to investigate the influences each binder has on the sensitivity of CL-20 by MD simulations. The strength of a chemical bond is related with its bond length and bond order. MD simulation cannot produce the bond order, but can give the variations of the bond length. Table 2 presents the statistical results of the trigger bond N-NO_2 of CL-20 based on the production trajectory. From Table 2, it can be seen that compared with the average ($L_{N\text{-}NO2}$) and the maximal (L_{max}) bond length of N-NO_2 in pure CL-20, no obvious changes have happened to those of the five PBXs, and it is not by changing the molecular structures for each binder to affect the sensitivity of CL-20. This consists well with the new studies on the PBXs with many components[31].

To further reveal the desensitized mechanism of binders on PBX, quantum chemistry PM3-MO method was used to calculate the thermal capabilities ($C°_p$) of five binder at 298 K, and the calculated $C°_p$ are 0.92 (ε-CL-20), 1.35 (HTPB), 1.22 (PEG), 1.18 (Estane5703), 1.13 (GAP), and 0.78 (F_{2314}) $J·g^{-1}·K^{-1}$. The binder with larger $C°_p$ can effectively absorb or isolate heat when being heated, namely, it absorbs the same heat, but its temperature increases less. This can decrease the formation and transmitting probability of "hot point" and the sensitivity of PBXs. According to this, the sensitivity ordering is predicted as ε-CL-20/F_{2314} > ε-CL-20/GAP > ε-CL-20/Estane > ε-CL-20/PEG > ε-CL-20/HTPB. The sensitivity order of ε-CL-20/GAP, ε-CL-20/HTPB, and ε-CL-20/Estane is consistent with the experiment. It should be noted that the compatibility and sensitivity of ε-CL-20/PEG is good. However, those of ε-CL-20/F_{2314} are worse, which may be the reason why formulation of ε-CL-20/F_{2314} has not been prepared in the experiment.

2.3 Mechanical properties

The most general relation between stress and strain of a material obeys the generalized Hooke's law as the following:

$$\boldsymbol{\sigma}_i = C_{ij}\boldsymbol{\varepsilon}_j, \quad (1)$$

Table 2 The average (L_{N-NO2}) and the maximal (L_{max}) bond lengths of N-NO_2 in CL-20 and the five PBXs[a)]

Parameters	Pure CL-20	CL-20/Estane5703	CL-20/GAP	CL-20/HTPB	CL-20/PEG	CL-20/F_{2314}
The number of N-NO_2 bond	230400	230400	230400	230400	230400	230400
Standard deviation	0.0308	0.0310	0.0309	0.0309	0.0308	0.0308
$L_{N\text{-}NO_2}$	1.396	1.396	1.397	1.396	1.396	1.394
L_{max}	1.557	1.555	1.571	1.548	1.558	1.532

a) Unit of bond length: Å.

where C_{ij} is (6×6) the matrix of elastic coefficients. Due to existence of strain energy, the matrix is symmetric. Therefore, 21 coefficients are required to describe the relation between stress and strain for any materials.

The stress tensors are calculated from the virial equation in static model at atomic level as follows[32]:

$$\boldsymbol{\sigma} = -\frac{1}{V_0}\left(\sum_{i=1}^{N} m_i\left(\boldsymbol{v}_i\boldsymbol{v}_i^T\right)\right) \tag{2}$$

where m_i and v_i represent the atomic mass and velocity, and V_0 is the volume of system without deformation.

The stress imposed on a system will change the relative positions of particles. As for parallel hexahedron (in simulation, the sides of the periodic box are symboled as $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{c}$, respectively), if the row vectors $\boldsymbol{a}_0$, $\boldsymbol{b}_0$, and $\boldsymbol{c}_0$ are the reference states, and the vectors $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{c}$ represent the deformation states, then the strain tensors can be expressed as:

$$\boldsymbol{\varepsilon} = \frac{1}{2}\left[\left(h_0^T\right)^{-1} G h_0^{-1} - 1\right] \tag{3}$$

where $\boldsymbol{h}_0$ is the matrix consisting of row vectors of $\boldsymbol{a}_0$, $\boldsymbol{b}_0$, and $\boldsymbol{c}_0$; $\boldsymbol{h}$ is the matrix consisting of $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{c}$; $\boldsymbol{G}$ is the measurement tensor $\boldsymbol{h}^T\boldsymbol{h}$. By calculating the slope of tensile and shear deformations, the matrix of elastic coefficients can be obtained.

According to statistics, a heteromorphy consisting of micro-crystals with random orientation can be considered isotropic. Its effective isotropic modules can be calculated by Reuss-mean method[33]. The bulk module and shear module are as follows:

$$K_{\mathrm{R}} = \left[3\left(a + 2b\right)\right]^{-1}, \tag{4}$$

$$G_{\mathrm{R}} = \frac{5}{\left(4a - 4b + 3c\right)}, \tag{5}$$

where

$$a = \frac{1}{3}\left(S_{11} + S_{22} + S_{33}\right), \quad b = \frac{1}{3}\left(S_{12} + S_{23} + S_{31}\right),$$

and

$$c = \frac{1}{3}\left(S_{44} + S_{55} + S_{66}\right).$$

Soft coefficient matrix S is contrary to elastic coefficient matrix C. Subscript R represents Reuss mean. As for most common crystal structures, 21 coefficients C_{ij} are independent, and Reuss module only depends on 9 soft coefficients. Based on the obtained K and G, its tensile module (E) and poisson ratio (ν) can be calculated as the following:

$$E = 2G(1+\nu) = 3K(1-2\nu). \tag{6}$$

The mechanical properties are important to affect the preparation, process, production, and usage of PBXs. Table 3 presents the elastic coefficients and effective isotropic mechanical properties (tensile module E, bulk module K, shear module G, and Poisson ratio ν) of pure ε-CL-20 and five ε-CL-20-based PBXs, based on the MD simulation trajectories and static mechanical analyses.

It can be seen from Table 3 that most elastic coefficients of five PBXs are less than those of pure ε-CL-20, predicting that for PBXs, less stress is required to produce the same strain, and the elasticity increases. If the coefficients are divided into three groups, C_{11}, C_{22}, C_{33}; C_{44}, C_{55}, C_{66}, and C_{12}, C_{13}, C_{23}, the discrepancy among coefficients in each group for each PBX was found to

Table 3 Elastic mechanical properties of pure ε-CL-20 and five ε-CL-20-based PBXs (units: GPa)

	Pure ε-CL-20	ε-CL-20/ Estane5703	ε-CL-20/ GAP	ε-CL-20/ HTPB	ε-CL-20/ PEG	ε-CL-20/ F_{2314}
C_{11}	21.67	16.21	14.11	13.33	14.30	20.83
C_{22}	14.38	10.53	8.44	7.93	8.78	11.26
C_{33}	12.16	7.26	2.93	3.03	4.40	12.01
C_{44}	2.75	2.59	2.57	2.45	2.26	3.20
C_{55}	3.10	2.62	2.49	2.05	1.18	2.80
C_{66}	6.07	2.66	1.95	1.33	2.00	3.52
C_{12}	5.90	3.52	1.50	1.39	2.39	4.80
C_{13}	8.63	5.37	1.94	1.77	3.11	7.94
C_{23}	5.04	3.27	0.59	0.74	1.51	6.71
C_{15}	1.07	0.13	1.94	1.61	1.64	2.56
C_{25}	–0.05	0.03	–0.46	–0.15	–0.18	0.54
C_{35}	1.79	0.84	0.54	0.27	0.67	0.47
E	12.21	9.20	8.11	7.72	8.34	10.73
K	9.68	6.48	3.68	3.60	4.61	9.23
G	4.73	3.64	3.58	3.38	3.41	4.11
ν	0.29	0.26	0.13	0.14	0.27	0.31

decrease, presenting that the adding of binders increases the isotropy of the PBX system. It can also be seen from this table that compared with those of pure ε-CL-20, modules E, K, and G of five PBXs decrease, predicting the decreasing rigidity but increasing elasticity. Besides, the adding of GAP and HTPB causes v to decrease and the plasticity of system to decrease accordingly.

2.4 Energetic properties

Density (ρ), detonation velocity (D), and detonation pressure (P) are the most important parameters in evaluating the energetic properties of HEDCs and HEDMs. It is the basic requirement for an HEDC that ρ >1.9 g·cm^{-3}, D > 9 km·s^{-1}, and P > 40 GPa. Based on the Kamlet-Jacobs equation[34] or ω-Γ[35,36] method, it is found that D and P greatly depend on the loaded density of monomeric or mixing explosives, namely, D and P are approximately in proportion to ρ and ρ^2, respectively. Thus, when it is difficult to quantitatively calculate the energetic properties of PBXs, they can be qualitatively evaluated by the ρ of binder and the corresponding PBXs. It is known that the ρ of five binders are 2.055 (ε-CL-20), 2.00 (F_{2314}), 1.30 (GAP), 1.20 (Estane5703), 1.18 (HTPB), and 1.13 (PEG) g·cm^{-3}. If the weight percent of each binder is assumed as 4.2%, and the theoretical densities of each PBX are 2.053, 2.024, 2.019, 2.018, and 2.016 g·cm^{-3}, then the energetic properties of these PBXs are ε-CL-20/F_{2314} > ε-CL-20/GAP > ε-CL-20/Estane5703 > ε-CL-20/HTPB > ε-CL-20/PEG; meanwhile the experimental D and P of three PBXs are ε-CL-20/GAP > ε-CL-20/Estane5703 > ε-CL-20/HTPB[27]. Compared with pure ε-CL-20, D and P of the PBXs indeed decrease to some extent, but they are still larger. For example, experimental ρ of the three PBXs are more than 1.9 g·cm^{-3}, except for ε-CL-20/HTPB, D of other two PBXs are both over 9.0 km·s^{-1}, and they meet with the criterion as an HEDM.

3 Conclusions

Molecular dynamics (MD) were employed to simulate pure ε-CL-20 crystal and ε-CL-20-based PBXs with five binders (Estane5703, GAP, HTPB, PEG, and F_{2314}, respectively). The following conclusions are obtained.

(1) The calculated binding energies between base explosive and binders are firstly correlated with their physical compatibility and stability of PBXs. The conclusion obtained from the criterion that the larger binding energy (E_{bind}) is, the better the compatibility will be, agrees well with the experiment. The ordering of E_{bind}, stability, and compatibility (between ε-CL-20 and binder) of 5 PBXs with same weight percent (4.2% or so) of the binder is ε-CL-20/PEG > ε-CL-20/Estane5703 ≈ ε-CL-20/GAP > ε-CL-20/HTPB > ε-CL-20/F_{2314}. Pair correlation function $g(r)$ analysis shows that hydrogen bonds and van der Waals interactions exist between ε-CL-20 and each binder.

(2) The average bond lengths of trigger bond N—NO_2 in ε-CL-20 in 5 PBXs are very approximate to those in pure ε-CL-20. This predicted that it is not by changing molecular structure of ε-CL-20 for binders to affect the sensitivity. It is considered that the desensitized effect is mainly caused by the thermal capability ($C°_p$) of a binder, and this can well interpret the experiments.

(3) It is shown from the analysis of static mechanic properties that the adding of a small amount of each binder can improve the elasticity and isotropy of the system.

(4) The density (ρ) of each binder and PBX is nearly related with the detonation velocity (D) and detonation pressure (P) of the PBX. The energetic properties obtained from ρ follow the consequence as ε-CL-20/GAP > ε-CL-20/Estane5703 > ε-CL-20/HTPB > ε-CL-20/PEG > ε-CL-20, and this is in good agreement with the experiment.

In all, as far as the five binders chosen in this paper, except for F_{2314}, all the E_{bind} between ε-CL-20 and other 4 binders are comparatively large, predicting better compatibility, and this will be of benefit to increasing stability of the PBXs. Their larger thermal capability ($C°_p$) will decrease sensitivity of PBXs and improve safety properties. The adding of a small amount of polymer can obviously improve the elasticity and isotropy properties of ε-CL-20. The energetic properties of all the obtained PBXs are decreased more than pure ε-CL-20; however, when the percent of binder is small (<5%), the density of each PBX is still larger, and the PBXs still keep better characteristics of high energy density as ε-CL-20; thus the PBXs are certainly HEDMs. Fluorine polymer (such as F_{2314}) has been widely used in TATB (1,3,5-triamino- 2,4,6-trinitrobenze)-based PBXs, but does not benefit CL-20-based HEDMs.

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