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# Molecular dynamics simulations of RDX and RDX-based plastic-bonded explosives

### Wei Zhu<sup>a,b</sup>, Jijun Xiao<sup>a</sup>, Weihua Zhu<sup>a</sup>, Heming Xiao<sup>a,\*</sup>

<sup>a</sup> Institute of Computation in Molecular and Materials Science, Department of Chemistry, Nanjing University of Science and Technology, Nanjing 210094, China <sup>b</sup> School of Biological and Chemical Engineering, Jiaxing University, Jiaxing 314001, China

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#### ABSTRACT

Molecular dynamics simulations have been performed to investigate well-known energetic material cyclotrimethylene trinitramine (RDX) crystal and RDX-based plastic-bonded explosives (PBXs) with four typical fluorine-polymers, polyvinylidenedifluoride (PVDF), polychlorotri-fluoroethylene (PCTFE), fluorine rubber ( $F_{2311}$ ), and fluorine resin ( $F_{2314}$ ). The elastic coefficients, mechanical properties, binding energies, and detonation performances are obtained for the RDX crystal and RDX-based PBXs. The results indicate that the mechanical properties of RDX can be effectively improved by blending with a small amount of fluorine polymers and the overall effect of fluorine polymers on the mechanical properties of the PBXs along three crystalline surfaces is  $(001) > (010) \approx (100)$  and PVDF is regarded to best improve the mechanical properties on different surfaces is  $(001) \approx (001) \approx (010) > (100)$ . The average binding energies between different RDX crystalline surfaces and different polymers on the three different surfaces is varied. Among the polymer binders, PVDF is considered as best one for RDX-based PBXs. The detonation performances of the PBXs decrease in comparison with the pure crystal but are superior to those of TNT.

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#### 1. Introduction

Plastic-bonded explosives (PBXs) are highly filled composite materials comprised of grains of an energetic material held together by a polymeric binder. They have been widely used in both military and industry areas for a long time because they have notable merits such as good safety, improved mechanical properties, and reduced vulnerability during storage and transportation, etc. [1–3]. The polymer binder in the PBXs plays an important role in improving the properties of the base explosive, such as improving mechanical properties, enhancing chemical and thermal stability, reducing environmental impact, etc. Therefore, there is an increasing interest to understand and predict the chemical, thermophysical, and mechanical properties of the PBXs, as well as the interactions among the constituents.

Cyclotrimethylene trinitramine (RDX, Fig. 1), an important modern molecular explosive, has generated much attention since it was synthesized. The crystal structure and physical and chemical properties of RDX have been extensively investigated [4–6]. Crystalline RDX exists in several polymorphic forms. The most stable phase at ambient conditions is  $\alpha$ -RDX, which is orthorhombic and belongs to the space group *Pbca* with eight molecules in the unit cell [5]. The melting point of RDX was found to be 477.4  $\pm$  0.2 K [7], and it decomposed significantly below its melting point. Its measured impact sensitivity  $H_{50\%}$  (in terms of the height from which a falling 2.5 kg weight will cause detonation 50% of the time) is about 26 cm, comparable to the values of 32 cm for octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), which is one of the most effective energetic materials with applications ranging from explosives and propellants [2]. Therefore, understanding the fundamental properties of RDX-based PBXs is very important for the development and design of novel energetic materials.

In the past several decades, due to development of computer and computational chemistry theory, atomistic simulation is increasingly gaining acceptance as a useful research tool in the investigation of the properties of condensed-phase materials. In addition to being efficient screening tools, atomistic simulation can also provide information that could not be readily obtained through measurement. Up to date, there are a large number of theoretical studies especially molecular dynamics (MD) simulations concentrated on secondary explosives [8–16] and PBXs [17–23]. Several theoretical results have been reported on RDX [8–10,14–16].



<sup>\*</sup> Corresponding author. Tel.: +86 25 84303919. E-mail address: xiao@mail.njust.edu.cn (H. Xiao).

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Fig. 1. Crystal (a) and molecular configurations of RDX (b).

Unfortunately, many fundamental and practical problems of RDXbased PBXs are still not well understood because it possesses a complex chemical behavior. As far as we know, there have been no reports about the studies on the RDX-based PBXs until now.

In this article, we present our work using MD method to calculate the mechanical properties and binding energies of RDX-based PBXs. Four kinds of typical fluorine polymers: polyvinylidene difluoride (PVDF), polychlorotrifluoroethylene (PCTFE), fluorine rubber  $(F_{2311})$ , and fluorine resin  $(F_{2314})$  were chosen to construct a dozen different binary PBX systems. Among them, F<sub>2311</sub> and F<sub>2314</sub> were copolymerized from vinylidene difluoride and chlorotrifluoroethylene with the molar ratios of 1:1 and 1:4, respectively. Isothermal-isochoric ensemble (NVT) MD simulations with the COMPASS (condensed-phase optimized molecular potentials for atomistic simulation studies) force field [24] were performed on the RDX-based PBXs. For comparison, similar calculations were also performed on the pure crystal RDX. The interactions between the polymer binders and the crystalline surfaces of RDX were analyzed and compared by their binding energies. In addition, we have predicted the detonation performances of the RDX-based PBXs to explore the effects of polymer binders on the performances of the explosives. The results obtained in the present paper are expected to be useful for the formulation design of novel PBXs.

#### 2. Methods

All MD simulations were carried out in NVT ensemble at room temperature with the COMPASS force field [24]. Except for the periodic boundary conditions imposed on simulation supercells, there were no additional symmetry constraints. Initial velocities were set using the Maxwell–Boltzmann profiles at given temperatures. The Verlet velocity time integration method was used with a time step of 1 fs. Temperatures were controlled using the stochastic collision method proposed by Andersen [25]. For potential energy calculations, the long-range Coulombic interactions were calculated by employing the standard Ewald method [26]. VDW interactions were truncated at a cutoff of 0.95 nm, and tail correction to potential energies and pressures were included in the calculations [27].

The initial RDX structure used in the condensed phase simulations was taken from the experiment by Choi et al. [5]. The periodic MD simulation cell consists of 144 RDX molecules, corresponding to  $2 \times 3 \times 3$  unit cells. The supercell was cut along the crystalline surface (001), (010) and (100) with the "cutting" method as implemented in Visualizer module Materials Studio (Version 3.0). Periodic supercells were separated from repeated replicas by 1 nm vacuum layer along the *c* (*z*) axis. Four kinds of fluorinepolymers (each involving 10 chain segments) were simulated for 2.5 ns with the MD method to get the equilibrium conformations. The end groups of each polymer chain were saturated by the H or F atoms according to their types. Every kind of equilibrium polymer were embedded into the simulation box in parallel with different crystalline surfaces. A total of 12 different initial PBXs configurations with 2582 atoms were obtained.

NVT MD simulations were initially carried out to equilibrate these systems. After that, the MD runs were carried out for another 10 ps to ensure that the systems were truly in the thermal equilibrium condition. Then the size of the box was reduced slightly to 95% of its original size along the *c* direction and another MD simulation was carried out until it reached a new equilibrium condition. The above processes were repeated until the density arrived at the theoretical density. Starting from the final structures, the 100 ps NVT MD simulations were subsequently carried out to ensure that the systems were equilibrated. Further NVT simulations of 200 ps were performed, in which the equilibrium run for 100 ps and were followed by production runs for 100 ps. During the production runs, trajectories were collected at an interval of 50 fs for subsequent analysis. All the simulations were implemented on Pentium D computers with Materials Studio (Version 3.0) from Accelrys Inc. [28].

#### 3. Results and discussion

#### 3.1. Choice of force field

The advanced COMPASS force field was applied to investigate the structures and properties of the RDX-based PBXs. The COM-PASS force field has been specifically designed for material science applications. It employs complex functional forms and its parameters have been debugged and ascertained from extensive ab initio data. Consequently, it can be used to accurately predict several molecular properties, including molecular structures, conformations, and vibrations. The nonbonded parameters in COMPASS have been further amended and validated using condensed-phase (liquid and crystal) data so that several thermophysical properties of molecular liquids and crystals can be well reproduced [24,29–32]. COMPASS has broad coverage in the major application areas of material science. It has been parameterized to study most common organic molecules, organic and inorganic polymers, zeolites, and metal/transition-metal oxides. Moreover, some of the functional groups required to model energetic materials have been specifically parameterized and included in the COMPASS force field, such as nitro  $(-NO_2)$  [30], and our group have employed this force field to investigate the typical cyclic nitramine explosives

Table 1	
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Calculated cell parameters and density of RDX crystal

	Experimental <sup>a</sup>	Sorescu <sup>b</sup>	Boyd <sup>c</sup>	Zheng <sup>d</sup>	Agrawal <sup>e</sup>	Present worl
a (Å)	13.182	13.396	12.298	13.330	13.904	13.386
b (Å)	11.574	11.798	11.278	11.497	12.044	11.457
c (Å)	10.709	10.732	10.857	10.532	10.896	11.010
α(°)	90.0	90.0		90.0	90.1	90.0
β(°)	90.0	90.0		90.0	90.1	90.0
γ(°)	90.0	90.0		90.0	90.0	90.0
$\rho$ (g/cm <sup>3</sup> )	1.81	1.74	1.85	1.83	1.62	1.74

<sup>&</sup>lt;sup>a</sup> Reference [5].

<sup>d</sup> Reference [15].

e Reference [16].

HMX, trans-1,4,5,8-tetranitro-1,4,5,8-tetraazadecalin (TNAD) and hexanitrohexaazaisourzitane (HNIW), and their PBXs [17,20,21]. The results were in good agreement with those from experiments. Because the RDX is a typical cyclic nitramine explosive and the structure of RDX is quite similar to them, it is therefore expected that the COMPASS force field will be suitable to perform MD simulations on RDX. This is also verified by the comparison of the cell parameters and density of RDX-based on the COMPASS force field with the experimental values in Table 1.

The calculated values of cell parameters and density for crystalline RDX at 295 K and 1 atm using COMPASS force field are compared with the results of MD simulations using other force fields and experimental data in Table 1. As can be seen, our results are one of the best-fit parameters. The calculated density is about 3.4% lower than the measured value and the cell edges *a*, *b*, and *c* differ from experiment by 1.5%, 1.0%, and 2.8%, respectively. This level of agreement is reasonable and sufficient for our purpose. Compared with other results from MD methods, our results also show reasonably good agreements with those data.

The validity of the COMPASS force field can be also tested by the accuracy of the predicted static lattice energy  $E_L$  of the crystal. This quantity can be estimated from the experimental enthalpy of sublimation using the relation [33]

$$E_{\rm L} = -\Delta H_{\rm sub} - 2RT \tag{1}$$

where the last term represents an approximate correction for the difference between gas-phase enthalpy, PV+3RT (ideal gas), and the estimated vibrational contribution of 6RT. Due to the approximation embedded in Eq. (1) and the experimental uncertainty, the error bar was estimated to be in the range of 3-4 kcal/mol [33]. Clearly, the lattice energy given in Eq. (1) corresponds to an idealized potential energy at zero temperature. Therefore, a reasonable validation is to compare the calculated lattice energies using the energy minimization method against experimental data. The experimental enthalpy of sublimation of RDX is 31.1 kcal/mol [6], while the predicted lattice energy of RDX was 27.9 kcal/mol. In view of the experimental uncertainty, the difference of 10% on this parameter is within the acceptable error range. Thus, it is proper and reliable to apply the COMPASS force field to the RDX crystal. RDX is the main body of the PBX system, and hence it is also proper and reliable to perform MD simulations with the COMPASS force field on the RDX-based PBXs. As an illustration, equilibrium structures of the PBXs with  $F_{2314}$  on the three crystalline surfaces ((100), (010), and (001)) of RDX are shown in Fig. 2.

#### 3.2. Mechanical properties

The material stress and strain tensors are denoted by  $\sigma$  and  $\varepsilon$ , respectively. From the statistical mechanics of elasticity [34], the generalized Hooke's law is often written as:

$$\sigma_i = C_{ii} \varepsilon_i. \tag{2}$$

 $[C_{ij}]_{(i,j=1,2,...,6)}$  is symmetric, and hence a maximum of 21 constants is required to fully describe the stress-strain behavior of an arbitrary material.

The effective isotropic compliances in terms of single-crystal compliances averaged over all orientations can be obtained by Reuss average. The effective bulk and shear moduli are given by

$$K_R = [S_{11} + S_{22} + S_{33} + 2(S_{12} + S_{23} + S_{31})]^{-1}$$
(3)

$$G_{R} = 5[4(S_{11} + S_{22} + S_{33}) - 4(S_{12} + S_{23} + S_{31}) + (S_{44} + S_{55} + S_{66})]^{-1}.$$
(4)

The subscript *R* denotes the Reuss average. The compliance matrix *S* is equal to the inverse matrix of elastic coefficient matrix



Fig. 2. Equilibrium structures of PBXs with F<sub>2314</sub> on different crystalline surfaces of RDX.

<sup>&</sup>lt;sup>b</sup> Reference [8].

<sup>&</sup>lt;sup>c</sup> Reference [14].

PBXs		C <sub>11</sub>	C <sub>22</sub>	C <sub>33</sub>	C44	C <sub>55</sub>	C <sub>66</sub>	C <sub>12</sub>	C <sub>13</sub>	C <sub>23</sub>	C <sub>15</sub>	C <sub>25</sub>	C <sub>35</sub>	C <sub>46</sub>	$C_{12} - C_{44}$
RDX		13.8	9.2	10.8	4.8	1.5	3.3	5.4	4.0	4.5	0	0	0	0	0.6
(001)	PVDF	7.1	5.6	6.9	1.5	1.7	1.4	3.3	3.8	3.5	0	0.3	0	0	1.8
	F <sub>2311</sub>	11.0	7.7	7.6	3.1	1.9	2.2	4.9	3.9	3.0	-0.4	0	0	0	1.7
	F <sub>2314</sub>	9.0	5.8	6.4	2.8	1.6	1.2	4.0	2.7	1.9	0	0	0.2	0	1.2
	PCTFE	9.3	6.2	6.9	3.0	1.5	1.7	4.5	2.8	1.9	-0.4	0.3	-0.4	0	1.5
(010)	PVDF	7.8	5.6	6.9	1.5	1.7	1.4	3.3	3.8	3.5	0	0.3	0	0	1.8
	F <sub>2311</sub>	8.1	9.8	6.4	2.0	1.8	1.8	3.7	2.9	3.4	-0.1	-0.2	-0.2	0	1.7
	F <sub>2314</sub>	7.3	8.3	6.1	1.6	1.6	1.3	3.4	3.1	3.2	-0.3	0.1	-0.3	0.4	1.8
	PCTFE	7.8	9.7	6.5	1.7	1.8	1.9	3.2	2.4	3.5	0.2	0	-0.1	-0.1	1.5
(100)	PVDF	6.7	8.4	9.1	2.7	2.5	1.4	3.3	4.3	3.0	-0.7	-0.4	-0.1	0	0.7
	F <sub>2311</sub>	7.0	8.0	8.7	2.4	2.2	1.5	3.4	3.8	3.8	0	0.6	-0.3	-0.2	1.0
	F <sub>2314</sub>	7.3	9.7	9.4	3.0	2.7	1.66	3.8	4.2	3.5	-0.1	0	-0.3	0	0.8
	PCTFE	7.8	9.8	9.6	2.4	2.4	1.9	4.0	4.9	4.6	0.1	0	0.3	0	1.6

Table 2
Elastic coefficients of RDX crystal and RDX-based PBXs with different polymers on different crystalline surfaces at 295 K (in GPa)

*C*, i.e.,  $S = C^{-1}$ . Note that for the most general crystal structure (all 21 constants are independent) the Reuss modulus depends on only nine of the single-crystal compliances. From the rules of isotropic linear elasticity we have

$$E = 2G(1+\nu) = 3K(1-2\nu)$$
(5)

where *E* is tensile modulus and  $\nu$  is the Poisson's ratio, so that after the bulk and shear moduli are calculated, the tensile modulus and Poisson's ratio can be obtained.

Such plastic properties as hardness, tensile strength, fracture strength, and elongation in tension, can be related to the elastic moduli [35]. Hardness and tensile strength representing the resistance to plastic deformation are proportional to the shear modulus *G*. Fracture strength is proportional to the bulk modulus *K*. The quotient K/G indicates the extent of the plastic range (elongation in tension), so that a high value of K/G is associated with ductibility and a low value with brittleness.

The predicted elastic constants and effective isotropic mechanical properties (tensile modulus, bulk modulus, shear modulus, and Poisson's ratio) are summarized in Tables 2 and 3, respectively. From the elastic coefficients matrices for RDX in Table 2, it can be found that the diagonal elements  $C_{ii}$  and  $C_{12}$ ,  $C_{13}$ ,  $C_{23}$  (nine elements totally) are larger but the other coefficients are smaller, which indicate that the crystal has anisotropy to some extent. In addition, the larger  $C_{11}$ ,  $C_{22}$ , and  $C_{33}$  imply that, to reach the same strain, RDX needs a larger stress. This characteristic can also be further validated by the differences of elastic coefficients of the PBXs with different polymer binders on different crystalline surfaces. However, as compared to the pure crystal RDX, there is a great decrease in  $C_{11}$ ,  $C_{22}$ ,  $C_{33}$ , and  $C_{44}$ , while a slightly decrease or a slightly increases in other elastic coefficients of the PBXs on different surface. This evolution tendency of elastic coefficients indicate that the anisotropy of the PBXs is diminish upon blending with fluorine polymers in small quantities, namely, the isotropy of the PBXs is strengthened in comparison with the pure crystal. This is mainly due to that the polymers have good isotropic properties.

Cauchy pressure  $(C_{12}-C_{44})$  can be used as a criterion to evaluate the ductibility and brittleness of a material. Usually, the value of  $(C_{12}-C_{44})$  for a ductile material is positive, and the negative value for a brittle material. The larger the value of cauchy pressure is, the more ductile the material is. According to this, the data in the last column of Table 2 indicate that the pure RDX is ductile due to its positive  $(C_{12}-C_{44})$ , but once small quantities of fluorine polymers are put along the RDX crystalline surfaces, all  $(C_{12}-C_{44})$  of the obtained PBXs are positive, and the ductibility of PBXs are greatly improved. As a whole, the ductibility of the RDX-based PBXs on three different crystalline surfaces is in the order of  $(001) \approx (010) > (100)$ . It is also interesting to note that, for each crystalline surface of RDX, the improvement in the PBXs' ductibility made by the fluorine polymers changes is different.

As can be also seen from Table 3, all the moduli of the PBXs decrease in comparison with those of the pure crystal. For example, the tensile modulus E decreases from 8.6 GPa to less than 6.5 GPa as the system changes from the pure crystal to the PBX, the shear modulus G decreases from 3.3 GPa to less than 2.5 GPa, and the bulk modulus K decreases from 6.9 GPa to less than 6.0 GPa. This further indicates that the rigidity and brittleness of the PBXs decrease, while their elasticity and plasticity strengthen. Meanwhile, these variations also suggest that the materials will deform more easily when they are subjected to an external force, because the resistance to plastic deformation is proportional to the elastic shear modulus G and the fracture strength for materials is proportional to the bulk modulus K [34]. Considering the content of polymers in the simulated PBXs is less than 5%, which is nearly equivalent

Table	3

stic properties of RDX crystal and RDX-based PBXs with different polymers on different crystalline surfaces of at 295 K (in GPa)
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	Tensile modulus E	Bulk modulus K	Shear modulus G	Poisson's ratio	K/G
	8.6	6.9	3.3	0.29	2.09
PVDF	4.0	4.6	1.5	0.34	3.07
F <sub>2311</sub>	6.4	5.5	2.4	0.30	2.29
F <sub>2314</sub>	5.4	4.3	2.1	0.29	2.05
PCTFE	5.7	4.5	2.2	0.29	2.05
PVDF	5.9	4.7	2.3	0.29	2.04
F <sub>2311</sub>	6.2	4.9	2.4	0.29	2.04
F <sub>2314</sub>	5.3	4.5	2.0	0.30	2.25
PCTFE	6.3	4.7	2.5	0.29	1.88
PVDF	5.9	5.1	2.3	0.31	2.22
F <sub>2311</sub>	5.5	5.1	2.1	0.32	2.43
F <sub>2314</sub>	6.5	5.5	2.5	0.30	2.20
PCTFE	6.1	6.0	2.3	0.33	2.61
	PVDF F <sub>2311</sub> F <sub>2314</sub> PCTFE PVDF F <sub>2314</sub> PCTFE PVDF F <sub>2314</sub> F <sub>2314</sub> PCTFE	Tensile modulus E           8.6           PVDF           4.0           F <sub>2311</sub> 6.4           F <sub>2314</sub> 5.7           PVDF           5.9           F <sub>2314</sub> 6.2           F <sub>2314</sub> 5.3           PCTFE           6.3           PVDF           5.9           F <sub>2314</sub> 5.3           PCTFE           6.3           PVDF           5.9           F <sub>2314</sub> 5.5           F <sub>2314</sub> 6.5           PCTFE           6.1	Tensile modulus $E$ Bulk modulus $K$ 8.66.9PVDF4.04.65.5F_{2311}6.45.44.3PCTFE5.74.5PVDF5.94.7F_{2314}6.24.9F_{2314}5.34.5PCTFE6.34.7PVDF5.95.1F_{2311}5.55.1F_{2314}6.55.55.1F_{2314}6.55.55.1F_{2314}6.56.16.0	Tensile modulus $E$ Bulk modulus $K$ Shear modulus $G$ 8.66.93.3PVDF4.04.61.5F <sub>2311</sub> 6.45.52.4F <sub>2314</sub> 5.44.32.1PCTFE5.74.52.2PVDF5.94.72.3F <sub>2314</sub> 6.24.92.4F <sub>2314</sub> 5.34.52.0PCTFE6.34.72.5PVDF5.95.12.3F <sub>2314</sub> 5.55.12.1F <sub>2314</sub> 6.55.52.5PVDF5.95.12.3F <sub>2314</sub> 6.55.52.5PCTFE6.16.02.3	Tensile modulus E         Bulk modulus K         Shear modulus G         Poisson's ratio           8.6         6.9         3.3         0.29           PVDF         4.0         4.6         1.5         0.34           F <sub>2311</sub> 6.4         5.5         2.4         0.30           F <sub>2314</sub> 5.4         4.3         2.1         0.29           PCTFE         5.7         4.5         2.2         0.29           PVDF         5.9         4.7         2.3         0.29           PVDF         5.9         4.7         2.3         0.29           PVDF         5.9         4.7         2.3         0.29           F <sub>2311</sub> 6.2         4.9         2.4         0.29           F <sub>2314</sub> 5.3         4.5         2.0         0.30           PCTFE         6.3         4.7         2.5         0.29           PVDF         5.9         5.1         2.3         0.31           F <sub>2314</sub> 5.5         5.1         2.1         0.32           F <sub>2314</sub> 6.5         5.5         2.5         0.30           F <sub>2314</sub> 6.5         5.5         2.5         0.30

#### Table 4

Binding energies (kcal/mol)	) for PBXs with four	kinds of fluorine	polymers on three	different crystallin	e surfaces of RDX at 295 k
Diffulle Chergies (Real/III0)	101 I DAS WIUI IOUI	KINGS OF HUUTING	DOIVINCIS ON UNICC	unicicil ci volanni	C SUIIACCS OF RDA at 233 h

PBX	Polymer	wt.% <sup>a</sup>	E <sub>Total</sub>	E <sub>RDX</sub>	Epolymer	Ebinding	E <sub>binding</sub> /wt.% <sup>b</sup>
(001)	PVDF	2.4	-22322.1	-21663.3	-562.2	96.5	40.2
	F <sub>2311</sub>	3.4	-22058.0	-21728.6	-219.6	109.8	32.3
	F <sub>2314</sub>	4.0	-21927.6	-21699.9	-139.7	88.0	22.0
	PCTFE	4.3	-21850.1	-21683.8	-78.2	88.1	20.5
(010)	PVDF	2.4	-22343.2	-21661.1	-566.6	115.4	48.1
. ,	F <sub>2311</sub>	3.4	-21996.5	-21679.7	-224.4	92.4	27.2
	F <sub>2314</sub>	4.0	-21923.4	-21700.1	-127.0	96.2	24.1
	PCTFE	4.3	-21857.7	-21689.4	-77.1	91.2	21.2
(100)	PVDF	2.4	-22406.3	-21738.8	-572.8	94.8	39.5
	F <sub>2311</sub>	3.4	-22041.1	-21723.8	-219.7	97.7	28.7
	F <sub>2314</sub>	4.0	-21949.7	-21720.9	-134.6	94.2	23.6
	PCTFE	4.3	-21862.4	-21696.3	-73.2	92.9	21.6

<sup>a</sup> wt.% denotes the mass fraction of the polymer binders in the PBXs.

<sup>b</sup> E<sub>binding</sub>/wt.% represents the average binding energy between a unit weight percentage of polymer binders and RDX crystal.

to the percentage of a polymer in the actual PBXs, it is therefore concluded that the mechanical properties of the explosives can be effectively improved by blending them with small amounts of polymer binders. However, on different crystalline surface, the ability for fluorine polymer to improve the mechanical properties of PBXs is still somewhat different, and the order is:  $(001)>(010)\approx(100)$ , and PVDF is regarded to best improve the mechanical properties of PBX on the three surfaces. This is also consistent with previous studies on the HMX-, TATB-, TNAD-, and CL20-based PBXs [17–21]. There is a slight increase in the Poisson ratios of the RDX-based PBXs compared with the pure RDX. Commonly, the Poisson's ratio of a plastic is 0.2–0.4. Thus, it is further demonstrated that all of the obtained PBXs possess more plastic properties than the pure RDX.

In addition, the ratio (bulk modulus/shear modulus, K/G) can be used to evaluate the tenacity of a material. A higher value of K/G is associated with malleability and a lower value with brittleness. According to this, it can be deduced from the K/G values in Table 3 that some of the PBXs have better malleability than the pure RDX. On the whole, the malleability of the PBXs with polymer binders on three different crystalline surfaces decreases as  $(100) \approx (001) > (010)$ . Moreover, it should be noticed that the PBX with the fluorine polymer PVDF on the RDX (001) surface is expected to possess the best malleability (K/G = 3.07) among these PBXs according to this criterion. This compares well with the observation that the PBX with PVDF on the RDX (001) surface has the largest cauchy pressure (1.8 GPa) and Poisson's ratio (0.34) in comparison with other PBXs.

#### 3.3. Binding energy

Binding energy ( $E_{\text{binding}}$ ) can well reflect the capacity of the two components blended with each other, which is defined as the negative value of the intermolecular interaction energy ( $E_{\text{inter}}$ ),  $E_{\text{binding}} = -E_{\text{inter}}$ . The intermolecular interaction energy can be evaluated by the total energies of the composite and each component in the equilibrium state. So the  $E_{\text{binding}}$  between RDX and polymer can be determined as follows:

$$E_{\text{binding}} = -E_{\text{inter}} = -(E_{\text{Total}} - E_{\text{RDX}} - E_{\text{polymer}})$$
(6)

where  $E_{\text{Total}}$  is the total energy of PBXs.  $E_{\text{RDX}}$  and  $E_{\text{polymer}}$  are the total energies of RDX and fluorine polymer, respectively.

Three typical equilibrium structures of the PBXs with  $F_{2314}$  on different crystalline surfaces ((100), (010), and (001)) of RDX were presented in Fig. 2. From the above illustration it can be seen that each fluorine polymer binder is closely contacted with the crystalline surface, and there may be exist extensive interactions between the polymer binders and RDX crystal. The average total

energies ( $E_{\text{Total}}$ ) of the PBXs, the single point energies of RDX ( $E_{\text{RDX}}$ ) and fluorine polymers ( $E_{\text{polymer}}$ ), and the binding energies ( $E_{\text{binding}}$ ) are tabulated in Table 4.

Taking into account the different mass fraction (wt.%) of the polymer binders in the PBXs, we computed and compared the average binding energy between RDX and a unit weight percentage of polymers according to the expression  $E_{\text{binding}}/\text{wt.\%}$ . It is found from these results that the differences of average binding energies exist not only in the PBXs with the same polymer on different crystalline surfaces, but also in the PBXs with different polymers on the same crystalline surface. Comparing the average binding energies of different crystalline surfaces, the capability to interact with the polymer binders is different. In other words, when different polymers is blended into the RDX crystal, PVDF tends to concentrate on the (010) surface while  $F_{2311}$  on the (001) surface,  $F_{2314}$  on the (010) surface, and PCTFE on the (100) surface. The main reason for this is the stronger inter- and intramolecular interactions, which mainly originate from the van der Waals and electrostatic nonbond interactions between the different polymers and the RDX crystal. Comparing the average binding energies of different polymer binders on different crystalline surfaces, we find that the order of different polymer is PVDF > F<sub>2311</sub> > F<sub>2314</sub> > PCTFE. In other words, the interactions between PVDF and different RDX crystal surfaces are stronger than those between other polymers and RDX surfaces. That is to say, the adhesive property of PVDF to RDX is superior to other fluorine polymers.

#### 3.4. Detonation properties

As an explosive, the chemical energy of detonation (Q), detonation velocity (*D*), and detonation pressure (*P*) are the much important factors to evaluate its performance. Up to now, many theoretical or empirical methods have been suggested to evaluate these detonation properties, such as Kamlet formula [36], Urizar approach [37], and the  $\omega$ – $\Gamma$  method [38]. The  $\omega$ – $\Gamma$  method suggested by Wuxiong was chosen for our calculations because it is more suitable for both the monomer and the mixed explosives [38]. In this method, heat of explosion Q(J/g), detonation velocity *D* (m/s), and detonation pressure *P* (GPa) were calculated according to the following definitions,

$$D = 33.05Q^{1/2} + 243.2\omega\rho \tag{7}$$

$$P = \frac{\rho D^2 \times 10^{-6}}{\Gamma + 1} \tag{8}$$

$$Q = \frac{-(\sum n_i \Delta H_i - \Delta H_f)}{M}$$
(9)

#### Table 5

The calculated chemical energy of detonation (Q), detonation velocity (D) and detonation pressure (P) for RDX crystal and four PBXs with fluorine polymer on RDX (001) surface

	RDX	RDX/PVDF	RDX/F <sub>2311</sub>	RDX/F <sub>2314</sub>	RDX/PCTFE
Q (J/g)	5785.0	5696.3	5659.3	5637.2	5626.1
D (m/s)	8812.3	8281.4	8453.2	8329.3	8318.5
P (GPa)	35.3	29.0	31.3	29.8	29.9

where  $n_i$  and M, respectively, denote the amount of the *i*th detonation product (mol) and the molecular weight of the explosive (g/mol);  $\Delta H_i$  and  $\Delta H_f$  represent the heat of formation (J/mol) of the *i*th detonation product and the explosive, respectively; and  $\rho$ ,  $\omega$ , and  $\Gamma$  are the loaded density of explosive (g/cm<sup>3</sup>), the factor of potential energy, and the adiabatic exponent, respectively. As for the blended explosives, the Q,  $\rho$ ,  $\omega$ , and  $\Gamma$  are evaluated by summing up the  $Q_i$ ,  $\rho_i$ ,  $\omega_i$ , and  $\Gamma_i$  of each component, respectively, according to their mass percent. Because the PBX containing the fluorine element is complex, the  $\Gamma$  is difficult to calculate. Therefore, according to the C–J theory [39], Eq. (8) is approximately simplified as follows to evaluate detonation pressure of the PBX:

$$P = \frac{1}{4}\rho D^2 \times 10^{-6}$$
 (10)

From Table 5, it can be seen that almost all the detonation properties of the RDX-based PBXs are smaller than those of the pure RDX crystal. This is reasonable phenomenon because all of the polymer binders have much smaller Q and  $\rho$  values than the pure crystal RDX, and so the PBXs possess lower Q, D, and P than those of RDX. But, as compared to the famous explosive trinitrotoluene (TNT) ( $\rho = 1.64$  g/cm<sup>3</sup>, D = 6950 m/s, P = 19.0 GPa) [2], all of the PBXs designed in this paper have better detonation performances. That is to say, these PBXs can be considered as potential candidates of energetic materials with good performances. Therefore, if these stable PBXs can be synthesized, they will have higher exploitable values and be worth investigating further.

In addition, it is found that there is no evident discrepancy among the detonation properties of these PBXs. This may be partially originated from the calculation method in which the same Q (2090.0 J/g) and  $\omega$  (8.0) values were used for different fluorine polymers, but in fact they are different from each other. On the whole, one can conclude that these four kinds of fluorine polymer binders with the same chain segments have similar effects on the detonation properties of the RDX-based PBXs.

#### 4. Conclusions

In this study, we have performed the classic MD simulations to investigate the mechanical properties, binding energies, and detonation performances of the secondary explosive RDX and its PBXs. The overall trends of the above properties are obtained. The major findings can be summarized as follows:

(1) The mechanical properties of the crystal RDX can be effectively improved by blending small amounts of fluorine polymers, and the effect of the fluorine polymers on the improvement of mechanical properties on three crystalline surfaces is  $(001)>(010)\approx(100)$ , and PVDF is regarded to best improve the mechanical properties of the PBXs on three surfaces. The order of the improvement in the ductibility  $(C_{12}-C_{44})$  made by the fluorine polymers on different surface is (001)>(100). It is also interesting to note that, for each crystalline surface of RDX, the improvement in the

PBXs' ductibility made by the fluorine polymers changes is different.

- (2) The average binding energies between different RDX crystalline surfaces and different polymer binders are obtained, and the order of binding energies of PBX with four fluorine polymers on three different surfaces is varied. Among the four polymer binders, PVDF is considered as best one for RDX-based PBX, which is also consistent with the improvement of the mechanical properties.
- (3) The calculations on detonation properties for the PBXs show that their detonation properties of PBXs can be lowered by blending small amount of fluorine polymer, but they are still superior to the explosive TNT and can be used as good energetic materials. Four fluorine polymers with the same chain segments have similar effects on the PBXs' detonation properties.

In a word, the MD simulations on the RDX and RDX-based PBXs provide us much information about their mechanical properties, binding energies, and detonation performances. To choose an optimal polymer binder, it is necessary to consider various aspects comprehensively according to the practical requirements. These may be useful for guiding the formulation design of novel PBXs.

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