Molecular Dynamics Simulation Studies of the CL-20/DNB Co-crystal Based PBX with HTPB

Yun Qin Xiao, Ting Sun, Shen Shen Li and Ji Jun Xiao*

Molecules and Materials Computation Institute, School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, P R China

Email: xiao_jijun@njust.edu.cn.

Abstract. Molecular dynamics (MD) simulations were conducted for a CL-20/DNB (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane/1,3-dinitrobenzene) co-crystal based PBX (Polymer-bonded explosive) with HTPB (hydroxyl-terminated polybutadiene). The binding energies, pair correlation functions and mechanical properties of the PBX were reported. From the calculated binding energy ($E_{\text{bind}}$), it was found that the order of the binding energies between the crystalline surfaces (1 0 0), (0 1 0) and (0 0 1) and HTPB is (1 0 0) > (0 0 1) > (0 1 0). And it was also shown that the interactions between the crystalline surfaces and HTPB originate mainly from vdW energies. The pair correlation function revealed that H···O hydrogen bonds exist on the interfaces between the crystalline surfaces and HTPB. From the calculated mechanical data, the co-crystal/HTPB was inferred that the PBX has a higher buffer for external stimuli and reduces the formation probability of hot spots.

1. Introduction

In the field of energetic materials, high performance and insensitive explosives have always attracted much attention by researchers [1]. For the current single compound explosives, high performance and safety are somewhat mutually exclusive, which seriously limits their development and applications [2]. Fortunately, the method of producing co-crystals offers a practical solution to modify the properties of energetic materials, such as oxygen balance, detonation velocity, detonation pressure, and sensitivity of, for instance, HMX/TATB, CL-20/TATB, CL-20/TNT, CL-20/HMX, CL-20/FOX-7, CL-20/BTF [3] and CL-20/DNB [4]. A co-crystal [5, 6] is a multiple component crystal that is constructed from two or more neutral molecular components, which co-exist according to an intrinsic stoichiometric ratio by non-covalent interactions (such as hydrogen bonding, van der Waals, and π–π stacking interactions).

2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20, Figure 1a) is the most powerful high energy density compound (HEDC) for practical applications at present, having high density, a good oxygen balance and high detonation velocity, but failing to meet the high demands of safety for modern ordnance due to its high sensitivity ($H_{50} = 15$ cm). DNB (1,3-dinitrobenzene, Figure 1b) is even more insensitive ($H_{50} = 124$ cm) than TNT (2,4,6-trinitrotoluene, $H_{50} = 100$ cm), and is a...
The goal of this study is to explore intermolecular interactions and mechanical properties of the CL-20/DNB co-crystal based PBX with HTPB by MD simulations. This paper is arranged as follows. The construction of models and the computational conditions for the simulations were first introduced. Then, the binding energies between HTPB and the three crystalline surfaces (1 0 0), (0 1 0), (0 0 1) are calculated and compared. An analysis of the interfaces between HTPB and the different three crystalline surfaces in the PBX is made using pair correlation functions. Finally, mechanical properties
such as tensile modulus \((E)\), Poisson’s ratio \((\nu)\), bulk modulus \((K)\), shear modulus \((G)\), the quotient \(K/G\) and the Cauchy pressure \((C_{12}–C_{44})\) are presented and discussed for the three clean crystal surfaces (without polymer binders) and the PBX.

2. Modeling and simulation details

The simulations were conducted under the COMPASS (condensed-phase optimized molecular potentials for atomistic simulation studies) force field, which is suitable for MD simulations of nitramine- and nitro-compound explosives, and their PBXs [12-19]. And the simulation data of the lattice lengths, the inter-axial angles and the density of CL-20/DNB co-crystal are agreed with those of the experiment [20]. Based on the crystal parameters derived from X-ray diffraction [4], a primary simulation cell containing 96 molecules, equivalent to 2496 atoms, was used for the CL-20/DNB co-crystal, corresponding to 6 \((3\times2\times1)\) unit cells. In the co-crystal, 48 molecules of both CL-20 and DNB were present.

Because the weight percentage of a polymer binder is generally less than 5%, the HTPB repeating number was set as 24, i.e., \(n=24\), so that the HTPB weight percentage in the following PBX models was about 4.4%. The equilibrium density of the amorphous HTPB cell was obtained by using the high-low pressure dynamics simulation method [21]. The model of the HTPB chain on a crystalline surface of the CL-20/DNB co-crystal is considered as a simplified PBX model. The procedure of building PBX models is as follows. The three crystalline surfaces, \((1\ 0\ 0)\), \((0\ 1\ 0)\), and \((0\ 0\ 1)\), of the CL-20/ DNB co-crystal primary cells were first chosen, in which the three \(c\) lattice lengths were 34.85, 32.35 and 34.96 Å, respectively, and the corresponding surface areas, \(a\times b\), were 26.92×33.62, 33.62×28.41 and 28.41×26.92 Å\(^2\), respectively. All the three co-crystal surface models contain 2496 atoms each and will be denoted as CL-20/ DNB (100), CL-20/ DNB (010), and CL-20/ DNB (001). After the amorphous HTPB cells with the converged density were merged on the three crystalline surfaces, and the \(c\) lattice lengths were 37.80, 35.15 and 38.46 Å, respectively, the three co-crystal-based PBX models were established. Each of them had 2740 atoms, correspondingly named as CL-20/DNB(100)/HTPB, CL-20/DNB(010)/HTPB and CL-20/DNB(001)/HTPB.

The three clean crystal surface models and the corresponding PBX models were allowed to evolve dynamically in isothermal-isobaric (NPT) ensembles under Andersen temperature control using the stochastic collision method [22] at 295K and Parrinello–Rahman pressure control fully relaxing all cell parameters [23] at atmospheric pressure. In the condensed phase simulation cases, van der Waals interactions were truncated at 9.5 Å with long range tail corrections [24], and electrostatic interactions were treated via the standard Ewald summation [25]. The motion equations were integrated with a step of 1 fs. After an equilibration run, a production run of 1ns was performed, during which data were collected with 10 fs sampling intervals for subsequent analysis. The computations for all of the materials were carried out using software program-MS (Material Studio) from Biovia Inc.

As an illustration, figure 2 shows an equilibrium structure of the CL-20/DNB (0 0 1)/HTPB at 295K.
3. Results and discussion

3.1. Binding energy between HTPB and CL-20/DNB crystalline surface

The binding energy ($E_{\text{bind}}$), defined as the negative value of the intermolecular interaction energy ($E_{\text{inter}}$), evaluates the compatibility of two components blended with each other by taking the difference between the total energy of the whole system, $E_{\text{total}}$, and the individual component energies of the cocrystal, $E_{\text{cocrystal}}$, and HTPB, $E_{\text{polymer}}$:

$$E_{\text{bind}} = -E_{\text{inter}} = E_{\text{cocrystal}} + E_{\text{polymer}} - E_{\text{total}}.$$

In this paper, it has an important influence on the compatibility for the CL-20/DNB co-crystal and HTPB, and the thermal stability of the energetic systems. A higher binding energy between the co-crystal CL-20/DNB and HTPB means they can bind together more firmly and thus a more stable. This makes that the CL-20/DNB/HTPB PBX possess good mechanical properties due to HTPB, such as smaller stiffness and better ductility.

The binding energies between the different crystalline surfaces and HTPB are in the order of $(1\ 0\ 0) > (0\ 0\ 1) > (0\ 1\ 0)$, as shown in table 1. It was noticed that the interaction between the crystalline surface $(1\ 0\ 0)$ and HTPB is the strongest, which means that the compatibility of them is the best among the three groups of the crystalline surface and HTPB. Compared with the van der Waals (vdW) and electrostatic energies in table 1, it is found that the vdW energies are 5 to 6 times that of the electrostatic energies and thus the interactions between the crystalline surfaces and HTPB originate mainly from vdW energies.
Table 1. Binding energies (kJ/mol) of the cocrystal-based PBX with HTPB on the three different crystalline surfaces

|        | (1 0 0)/HTPB | (0 1 0)/HTPB | (0 0 1)/HTPB |
|--------|--------------|--------------|--------------|
| Total  | 890.4        | 807.1        | 820.9        |
|        | (13.8)       | (14.6)       | (24.7)       |
| Internal| 0.0          | 0.0          | 0.0          |
|        | (0.0)        | (0.0)        | (0.0)        |
| Nonbonded| 890.4       | 807.1        | 820.9        |
| vdw    | 750.2        | 670.7        | 705.8        |
|        | (16.7)       | (8.8)        | (18.8)       |
| Repulsive| -1155.2     | -959.4       | -1051.4      |
|        | (64.4)       | (67.4)       | (86.6)       |
| Dispersive| 1905.4      | 1630.1       | 1757.3       |
|        | (66.1)       | (64.9)       | (83.7)       |
| Electrostatic| 140.2      | 136.4        | 115.1        |
|        | (19.2)       | (11.3)       | (17.6)       |

\[ E_{\text{bind}} = E_{\text{Internal}} + E_{\text{Nonbonded}} = E_{\text{vdW}} + E_{\text{Electrostatic}} = E_{\text{Repulsive}} + E_{\text{Dispersive}} + E_{\text{Electrostatic}} \]

Deviations are listed in parenthesis.

3.2. Pair correlation function analysis for the interface between the CL-20/DNB crystalline surface and HTPB

Pair correlation function (PCF) measures the conditional number probability density \( g(r) \) of finding an atom at a certain distance from a reference atom and thus provides insights into the material structure through revealed local spatial ordering. Because the interfacial structures are related to the interactions between CL-20/DNB co-crystal and HTPB, PCF has been employed to appreciate the interface structures and interactions of the PBXs in details. Normally, hydrogen bond (H-bond) interaction is in 2.0–3.1 Å range, and there are strong vdw and electrostatic interactions in 3.1–5.0 Å range. When the distance between two atoms, \( r \), is longer than 5.0 Å, the vdw force becomes very weak [18].

In this work, the PCF analysis was applied to the interfaces between CL-20/DNB crystalline surfaces and HTPB, and two atom pairs, H···O and H···N pairs were considered. H, O, and N (negatively charged) atoms in CL-20 molecules were denoted by H(CL-20), O(CL-20) and N(CL-20), H, O atoms in DNB molecules by H(DNB) and O(DNB), and H, O atoms in HTPB molecular main chain by H(HTPB) and O(HTPB). The PCFs for the interface between crystalline surface (1 0 0) and HTPB are depicted in figure 3.
From figures 3(a)-(d), it was found that in hydrogen bond range, the PCF curves all give comparatively high peaks, indicating that the hydrogen bonds exist in the H···O pairs of the HTPB molecules and co-crystal. And the peaks, in figures 3(a) and 3(b), are both higher than those in Figures 3(c) and 3(d), indicating the hydrogen bonded atom pairs between the HTPB and CL-20 molecules are more than those between the HTPB and DNB molecules. In figure 3(e), the curve has a comparatively high peak only in vdW interaction range, implying only the vdW interactions exist in most of H(HTPB)···N(CL-20) atom pairs. The other two kinds of PCF curves for the (0 1 0) and (0 0 1) interfaces with HTPB were omitted since they are similar to those of Figure 3.

For a more in-depth analysis, the PCF curves within 2.0-3.1 Å, 3.1-5.0 Å and 5.0-10.0 Å were integrated respectively, and the integral areas are shown in Table 2. It was found that the number of the H(HTPB)-O(CL-20) hydrogen bonded atom pairs is a little more than that of the H(HTPB)-O(DNB) hydrogen bonded atom pairs, but the number of O(HTPB)-H(CL-20) hydrogen bonded atom pairs is about five times that of the O(HTPB)-H(DNB) hydrogen bonded atom pairs. Within the interaction distance range for strong vdW and electrostatic forces, the O(HTPB)-H(CL-20) atom pair has the largest number among all of these atom pairs.
Table 2. Integral areas of PCF curves of (1 0 0)/HTPB

| Distance/Å | H(HTPB) | O(HTPB) | H(HTPB) | O(HTPB) | H(HTPB) |
|-----------|---------|---------|---------|---------|---------|
|           | O(CL-20) | H(CL-20) | O(DNB)  | H(DNB)  | N(CL-20) |
| 2.5-3.1   | 0.89    | 2.98    | 0.69    | 0.64    | 0.10    |
| 3.1-5.0   | 2.34    | 4.12    | 1.83    | 1.81    | 1.48    |
| 5.0-10.0  | 7.33    | 7.08    | 6.92    | 9.58    | 7.98    |

3.3. Mechanical properties of the CL-20/DNB cocrystal surface models and their PBX models

Mechanical properties are some of the most important properties of energetic materials due to their relationship with material preparation, storage, transportation, and usage. The elastic modulus is an indicator of material stiffness and a measurement of the material’s resistance to elastic deformation. In general, plastic and fracture properties can be related to the elastic moduli. A higher shear modulus means greater hardness and more yield strength which reflect the resistance to plastic deformation. A higher bulk modulus means greater fracture strength. The quotient $K/G$ indicates empirically the extent of the plastic range of a material. A high value of $K/G$ is associated with ductility and a low value with brittleness [26]. The Cauchy pressure $(C_{12} - C_{44})$ [27] can also reflect the brittle/ductile behavior. $(C_{12} - C_{44})$ is positive for a ductile material, and negative for a brittle material. The methodology of ductility evaluation using the Cauchy pressure based on the morphology of a fracture cross sectional surface is different from that of the $K/G$ quotient [14].

Based on the fluctuation analysis of the production trajectories and Reuss average [28, 29] of the co-cystal surface models and their corresponding PBX models, the calculated moduli, Poisson’s ratios, quotients $K/G$ and Cauchy pressures are listed in table 3. The fluctuations of mechanical properties were caused by the temperature fluctuations around the equilibrium point. In total, one hundred thousand samples were calculated for obtaining mechanical properties during each production run. Moreover, because the deviations in table 3 were rounded off to 1 decimal place, some deviations are zeros.

From table 3, it was found that the moduli of the three clean cocrystal surfaces (without polymer) are greater than those of the three PBX models, indicating that the stiffness of the PBX decreases. The $K/G$ quotients and $(C_{12} - C_{44})$ values for the three PBX models are all greater than those of their corresponding co-crystal surface models. It can be deduced that the ductility of the CL-20/DNB co-crystal is improved by adding a small amount of HTPB. Generally, smaller stiffness is associated with deforming more easily. It means the material is able to disperse the energy applied to it, and thus has lower sensitivity. Better ductility implies it is not easier to be broken with loading, which prevents cracking to generate bigger reacting areas. Thus, smaller stiffness and better ductility make PBXs have a higher buffer for external stimuli and reduce the formation probability of hot spots.
Table 3. Tensile modulus ($E$), Poisson’s ratio ($\nu$), bulk modulus ($K$), shear modulus ($G$), quotient $K/G$ and Cauchy pressure ($C_{12}-C_{44}$) for co-crystal surface models CL-20/DNB (1 0 0), (0 1 0) and (1 0 0), and PBX models CL-20/DNB (1 0 0)/HTPB, (0 1 0)/HTPB and (0 0 1)/HTPB at 295 K. Deviations are listed in parenthesis. Units for $E$, $K$, $G$ and $C_{12}-C_{44}$ are GPa.

| Model         | (1 0 0) | (1 0 0) /HTPB | (0 1 0) | (0 1 0) /HTPB | (0 0 1) | (0 0 1) /HTPB |
|---------------|---------|---------------|---------|---------------|---------|---------------|
| $E$           | 5.1 (0.2) | 2.7 (0.1) | 6.2 (0.0) | 3.4 (0.1) | 6.2 (0.1) | 3.8 (0.1) |
| $\nu$         | 0.4 (0.0) | 0.4 (0.0) | 0.4 (0.0) | 0.4 (0.0) | 0.4 (0.0) | 0.4 (0.0) |
| $K$           | 7.0 (0.1) | 4.9 (0.1) | 7.2 (0.0) | 5.5 (0.0) | 7.3 (0.1) | 5.3 (0.0) |
| $G$           | 1.9 (0.1) | 0.9 (0.0) | 2.3 (0.0) | 1.2 (0.0) | 2.3 (0.0) | 1.4 (0.0) |
| $K/G$         | 3.8 (0.1) | 5.1 (0.2) | 3.1 (0.0) | 4.6 (0.1) | 3.2 (0.0) | 3.9 (0.1) |
| $C_{12}-C_{44}$ | -1.1 (0.1) | 2.0 (0.1) | 2.7 (0.1) | 3.3 (0.0) | 1.4 (0.1) | 3.3 (0.1) |

4. Conclusions
In this study, NPT-MD simulations have been conducted for the CL-20/DNB surfaces and their corresponding PBX models with HTPB. The simulations have involved binding energy calculation and PCF analysis for the compatibility evaluation and the interfacial structure exploration between the co-crystal and HTPB, mechanical property computation and comparison of the co-crystal and based PBXs. These studies are in favor of theoretical research and practical applications of the co-crystal.

From the calculated binding energies, it has been found that the interface CL-20/DNB(100) and HTPB has the best compatibility and thermal stability, compared to other interfaces. The interactions between the crystalline surfaces and HTPB mainly originate from vdW energies and some small amount from electrostatic energies. The PCF analyses have shown that the numbers of H-binds between CL-20 and HTPB are three times of those between DNB and HTPB, and the number of strong vdW and electrostatic atom pairs between CL-20 and HTPB is more than two times of those between DNB and HTPB, indicating that the interactions between CL-20/DNB(100) and HTPB mostly come from CL-20 and HTPB. By comparing the mechanical properties, it has been found that the corresponding PBX models based on CL-20/DNB co-crystal have smaller stiffness and better ductility, meaning that the CL-20/DNB co-crystal based HTPB PBX has a higher buffer for external stimuli.

Acknowledgements
This work is supported by a grant from the National Natural Science Foundation of China (Grant No. 11572160).

References
[1] Agrawal J P 1998 *Progress in energy and combustion science* **24**(1) 1-30
[2] Sikder A K, Sikder N 2004 *Journal of Hazardous Materials* **112**(1) 1-15
[3] Shen J P, Duan X H, Luo Q P, Zhou Y, Bao Q, Ma Y J, Pei C H 2011 *Crystal Growth and Design* **11** 1759-65
[4] Wang Y, Yang Z, Li H, Zhou X, Zhang Q, Wang J, Liu Y 2014 *Propell Explos Pyrot* **39**(4) 590-6
[5] Lara-Ochoa F, Espinosa-Perez G 2007 Supramolecular Chemistry 19(8) 553-7
[6] Shan N, Zaworotko M J, 2008 Drug Discovery Today 13(9) 440-6
[7] Zhong Y P, Hu Y D, Jiang H Z, 1990 Handbook for Properties of Explosives Ordnance Industry Press, Beijing (in Chinese).
[8] Long Y, Liu Y G, Nie F D, Chen J 2012 Colloid and Polymer Science 290(18) 1855-66
[9] Long Y, Liu Y G, Nie F D, Chen J, 2012 Shock Waves 22(6) 605-14
[10] Long Y, Liu Y G, Nie F D, Chen J 2012 Modelling and Simulation in Materials Science and Engineering 20(6)
[11] Long Y, Liu Y G, Nie F D, Chen J 2012 Applied Surface Science 258(7) 2384-92
[12] Xiao J J, Huang H, Li J S, Zhang H, Zhu W, Xiao H M, 2008 Journal of Materials Science 43 5685-91
[13] Xiao J J, Huang H, Li J S, Zhang H, Zhu W, Xiao H M 2008 Journal of Molecular Structure: THEOCHEM 851 242-8
[14] Xiao J J, Zhao L, Zhu W, Chen J, Ji G F, Zhao F, Wu Q, Xiao H M 2012 Science China Chemistry 55(12) 2587-94
[15] Xiao J J, Wang W R, Chen J, Ji G F, Zhu W, Xiao H M 2012 Computational and Theoretical Chemistry 999 21-7
[16] Xu X J, Xiao H M, Xiao J J, Zhu W, Huang H, Li J S 2006 The Journal of Physical Chemistry B 110(14) 7203-7
[17] Xu X J, Xiao J J, Huang H, Li J S, Xiao H M 2007 Sci. Chin. Ser. B: Chem. 50(6) 737-45
[18] Xiao J J, Zhu W H, Zhu W, Xiao H M 2013 Molecular Dynamics of Energetic Materials Beijing: Science press
[19] Bunte S W, Sun H 2000 The Journal of Physical Chemistry B 104(11) 2477-89
[20] Sun T, Xiao J J, Ji G F, Zhao F, Xiao H M 2016 Cent. Eur. J. Energ. Mater. 13(3) 677 - 93
[21] Ren H, Zhang Q Y, Chen X W, Zhao W, Zhang J P, Zhang H P, Zeng R, Xu S 2007 Polymer 48 887-93
[22] Andersen H C. 1980 The Journal of Chemical Physics 72(4) 2384
[23] Parrinello M, Rahman A 1981 Journal of Applied Physics 52 7182
[24] Allen M P, Tildesley D J, 1989 Computer Simulation of Liquids Oxford University Press
[25] Ewald P P, 1921 Ann. Phys. 64 253-87
[26] Pugh S F 1954 Philosophical Magazine 45(367) 823-43
[27] Pettifor D G 1992 Materials Science and Technology 8(4) 345-9
[28] Parrinello M, Rahman A 1982 The Journal of Chemical Physics 76(5) 2662-6
[29] Watt J P, Davies G F, O’Connell R J 1976 Reviews of Geophysics 14(4) 541-63