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INTERFACE SCIENCE

Computation of interface interactions and mechanical properties of HMX-based PBX with Estane 5703 from atomic simulation

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Abstract Atomic simulation was applied to investigate the interface interactions and mechanical properties of *β*-octahydro-1, 3, 5, 7-tetranitro-1, 3, 5, 7-tetrazocine (HMX)-based polymer-bonded explosive (PBX) with Estane 5703. The interface structure of HMX (100) crystal surface with Estane 5703 was analyzed using pair correlation function (PCF), and the interfacial binding energies between them were calculated. It is shown that there exist hydrogen bonds and electrostatic interactions on the interface. By calculating and comparing the bonds lengths and distributions for possible initial bonds fractured in detonation, it is known that the interactions do not affect the stability of the PBX. Moreover, the elastic constants for HMX and the HMX-based PBX were computed using static elastic constants analysis method, and the engineering moduli and Poisson ratios were derived by Reuss average. Based on the value of Cauchy pressure, it is indicated that the ductility of crystalline HMX can be effectively improved by blending the polymer in small amount. The relevancy to shockwave stability for this PBX in detonation was discussed finally.

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Introduction

Polymer-bonded explosives (PBXs) are highly filled composite materials mainly comprising grains of an explosive material held together by a polymer binder, and very few plasticizers and stabilizers. They are widely used in many defense and economy scopes because PBXs have desirable merits such as good safety, good ductibility, and ease of process [1–3].

Generally, a solid energetic compound or explosive is brittle, and in order to reduce brittleness of the compound, a polymer is mixed with it. The interaction between explosives and polymers plays an important role in the mechanical properties of PBXs and propellants. To understand profoundly the mechanism of the interaction, the investigation of interfacial behavior between them is necessary.

The interactions between explosives and polymers were explained by applying acidity and alkali, diffusion, and interface theories in early years [4–6]. The PBXs' interfacial and mechanical properties measured by advanced instruments were reported in [7]. There are many reports on the calculation and simulation study of various properties of explosives, polymers, and interactions between polymer chains and crystal surfaces with quantum mechanics (QM), molecular mechanics (MM) and molecular dynamics (MD) methods [8–15]. Mechanical properties of HMX-based, TATB-based, and *ε*-CL-20-based PBXs were obtained using MD simulation [16–18], but to our best knowledge, few reports have been found on atomic simulation for the interfacial properties of PBXs. Atomic simulation for the interactions between a single polymer chain and a crystal surface is important, as experimental study on an isolated polymer chain is difficult in most cases.

β-HMX with the structure in Fig. 1 is the energetic component in several important high-performance PBXs,

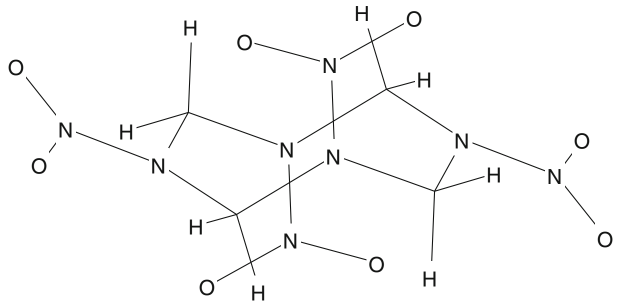

Fig. 1 Structure of β-HMX

e.g., PBX-9501, and propellant formulations [1, 19]. β-HMX crystal is the room temperature stable phase of the four known polymorphic forms. This present work includes the investigation of the interface structure and the calculation of the interfacial binding energy of the β-HMX (100) crystal surface with Estane 5703 (called Estane for brevity in this paper) in Fig. 2, as well as the calculation of the mechanical properties of β-HMX-based PBX with Estane as a polymer binder. In this work, not only the polymer binder is different from those in [16], but also the model is different since the polymer binder was put on (100) surface of the simulation cell whereas in [16] the polymer binder was inserted to the inner of simulation cell. As such, less uncertain factors need to be considered in the modeling in this paper, which leads to a more precise and determinate model. The investigation on the interface surfaces and mechanical properties of PBXs is helpful for explosive and propellant formulations.

Models and computational details

The general force field COMPASS [20] (condensed-phase optimized molecular potentials for atomistic simulation studies) was adopted in the simulation. The force field is an all-atom force field for atomistic simulation of common organic molecules, inorganic small molecules, and polymers in isolation and in condensed phases. To achieve high accuracy in predicting various molecular properties with a fairly broad coverage, in the COMPASS force field, complicated functional forms including off-diagonal cross-coupling terms are used. In [18], MD simulation using COMPASS force field was conducted for ε-CL-20, which is a nitramine compound and is of the same category as HMX. In this study there is very small amount of polymer in the PBX and thus there is little relevance between the polymer and a force field. Moreover our main purpose here is to investigate the differences between pure HMX and HMX-based PBX; therefore, this general force field is suitable to simulate the properties of the HMX-based PBX.

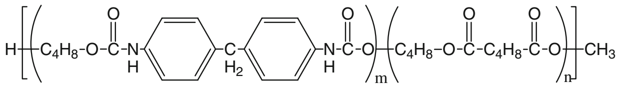

Fig. 2 Structure of Estane

The initial β-HMX in [21] was used in the condensed phase simulations in this study. The periodic MD simulation cell containing 72 molecules was used for β-HMX, corresponding to 36 ($4 \times 3 \times 3$) unit cells. This periodic MD simulation cell was allowed to evolve dynamically in isothermal–isobaric (*NPT*) statistical ensemble. The mechanical properties of pure β-HMX obtained from application of MD simulation of the primary cell was used as a relative criterion for comparison with those of the β-HMX-based PBX.

For the polymer molecule, its chain end groups were saturated by H atom or CH_3 group as shown in Fig. 2. Because in practical formulations the percentage of a polymer binder was very small, there were only 1 and 4 constitutional repeating units for hard and flexible segments of Estane, i.e., $m = 1$ and $n = 4$, respectively. The polymer chain was run dynamically in isothermal–isochoric (*NVT*) ensemble with no cutoff distance for 3 ns. The final configuration was regarded as the equilibrium configuration. During the PBX model construction, the initial polymer chain was in equilibrium state.

To investigate the interface of the PBX, β-HMX crystal was cut along crystalline surface (100) and a 20 Å vacuum layer was kept above the surface. The primary cell still had 72 HMX molecules. In order to differentiate the internal and the surface structures of HMX crystal and reflect the characteristic of HMX crystal surface—the arrangement of molecules on the crystal surface is of disorder, the outer two layers of molecules (adjacent to the vacuum layer) were processed by "heating up and annealing," which was programmed by btcl language, and at the same time the remaining inner molecules were fixed. Then after a polymer chain was put parallel to the surface, the periodic simulation cell for *NVT* MD simulation was finished as shown in Fig. 3.

Based on the completed *NVT* simulated cell described above, the periodic cell was reduced slightly by compressing the vacuum layer, and the system was allowed to equilibrate dynamically. This process was repeated until the density of each system matched its calculating value. The purpose of this procedure is to avoid overcrowding of the system at the starting point of the MD run [22]. Figure 4 shows the periodic MD simulation cell of HMX-based Estane-bonded PBX with calculating density, and this PBX periodic cell was allowed to evolve dynamically in isothermal–isobaric (*NPT*) ensembles.

In the following condensed phase simulation cases, the van der Waals interactions were truncated at 9.5 Å, the

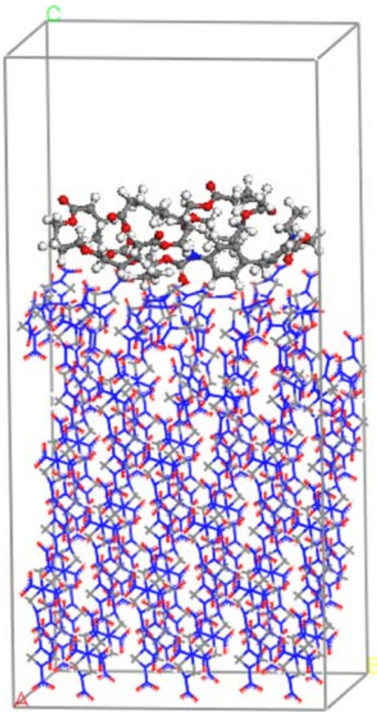

Fig. 3 HMX (100) with Estane interface

electrostatic interactions were calculated via the standard Ewald summation [23], the equation of motions were integrated with a time step of 1fs, and the equilibration runs of 100 ps duration were performed, followed by production runs of 200 ps, during which data were collected for subsequent analysis. All the calculations were performed at 295 K, with the Anderson temperature control method [24]. The Parrinello-Rahman method of pressure control [25] was used for *NPT* MD simulation at atmospheric pressure. These computations were all carried out using the software program MS from Accelrys Inc. (San Diego, CA).

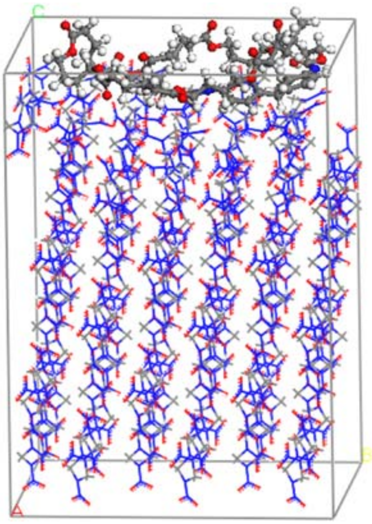

Fig. 4 HMX (100) with Estane PBX

Results and discussions

The pair correlation function (PCF) was applied to analyze the equilibrating result of *NVT* MD simulation, and the interface structure data were obtained; also according to *NVT* MD simulation, the binding energy between HMX crystal (100) surface and the polymer chain, and the bond lengths and distributions for N–NO_2 bonds and C–N bonds of HMX molecules were calculated. Through static elastic constants analysis of the *NPT* MD data in equilibrium state, the linear elastic properties of the HMX-based PBX were determined, and the Cauchy pressure was calculated. In addition, the relevancy to shockwave stability for the PBX in detonation was discussed.

Interface structure and binding energy

The interface structure was analyzed using PCF. The PCF $g_{\alpha\beta}(r)$, i.e., the probability to find a β atom at the distance r centered on any α atom, is calculated as follows using the radial distribution function (RDF) $G_{\alpha\beta}(r)$,

$$g_{\alpha\beta}(r) = G_{\alpha\beta}(r) \Big/ \left(4\pi r^2 \rho_\beta\right) \tag{1}$$

where ρ_β is the average number density of β atoms. The RDF is the number of β atoms centered on any α atom at the distance r,

$$G_{\alpha\beta}(r) = \frac{1}{N_\beta} \sum_{\alpha,\beta} \delta\left(r - \left|R_\alpha - R_\beta\right|\right) \tag{2}$$

where $|R_\alpha - R_\beta|$ is the distance between atom α and β, and N_β is the total number of β atoms. In the following PCF analysis for the interface structures of the PBX, only the outer most layer of HMX molecules that were nearest to the polymer chain was considered. The cutoff distance for PCF analysis is 9–10 Å, however, for revealing the essence of interactions the distance is long enough.

In order to study the interface structures and interactions between Estane and HMX crystal (100) surface in detail, the hard segment and the flexible one of Estane are analyzed using PCF, respectively. We investigate the PCF curves of the amino-H atoms, alkyl-H atoms, and phenyl-H atoms in the Estane individually with nitro-O atoms in the HMX molecules, and the PCF curves of the carbonyl-O atoms and ether-O atoms in the Estane individually with either of H atoms and nitro-N atoms in the HMX molecules.

Figure 5 shows the PCF $g_{H-O}(r)$ for amino-H atoms in the hard segment in the Estane and nitro-O atoms in the

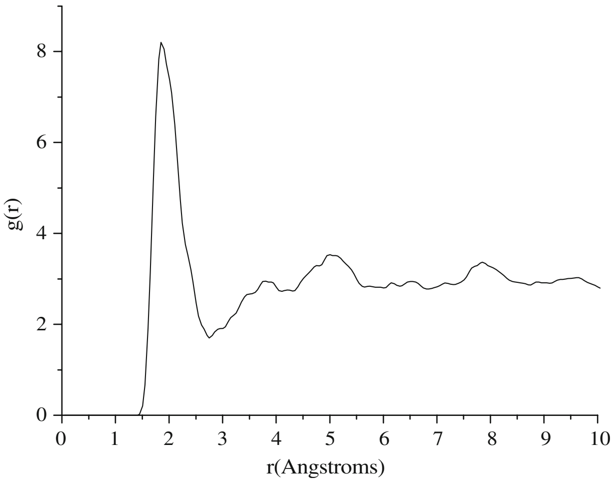

Fig. 5 PCF curve for the pairs of amino-H atoms in the Estane and nitro-O atoms in the HMX molecules

HMX molecules. We can see that the first and highest peak locates at 1.9 Å, which suggests the highest probability of the two atom pairs at the distance and the strong H-bond interaction between them.

For brevity, the remaining PCF curves are omitted since their analyses are similar to that of Fig. 5. By analyzing the PCF curves of the atom pairs mentioned above, we find there are H-bonds between the pairs of amino-H atoms, alkyl-H atoms, and phenyl-H atoms in the Estane and nitro-O atoms in the HMX molecules, and between the carbonyl-O atoms, the ether-O atoms in the Estane, and the H atoms in the HMX molecules. Among these H-bonds, the interactions between the amino-H atoms and the nitro-O atoms are strong H-bond interactions, and the others are weak H-bond interactions. In both the hard and the flexible segments in the Estane, the carbonyl-O atoms have more probability of forming H-bonds with H atoms in the HMX molecules than the ether-O atoms. We also find that electrostatic interactions exist between the pairs of carbonyl-O atoms, ether-O atoms in the Estane and nitro-N atoms in the HMX molecules. And the first peaks of the PCF curves of these atom pairs locate at from 2.8 to 5.2 Å.

Binding energy between HMX and a polymer is an important criterion for evaluating their miscibility. The miscibility of HMX-polymer blends plays a crucial role in the mechanical properties of HMX-based PBXs. Before we proceed to calculate the binding energy, we need to define the interaction energy as

$$E_{\text{inter}} = E_{\text{PBX}} - (E_{\text{poly}} + E_{\text{HMX}}) \tag{3}$$

where E_{PBX} is the potential energy of the polymer bonder chain plus the HMX crystal system, i.e., the PBX, in equilibrium, E_{poly} is the potential energy of the polymer bonder chain isolated in a vacuum, and E_{HMX} is the potential energy of the HMX crystal. Binding energy is defined as the negative value of the interaction energy, that is, $E_{\text{bind}} = -E_{\text{inter}}$. The binding energy for HMX-based Estane PBX is 85.31 ± 1.84 kcal/mol, which is calculated from five equilibrium configurations. In molecular terms, this positive binding energy value is accomplished by specific interactions̄H bonds and electrostatic interaction between different molecules. This conclusion and some results derived from above PCF analysis can verify each other.

Interfacial interaction on initial fractured bonds

The COMPASS force field is an advanced general force field, where complicated functional forms including off-diagonal cross-coupling terms and high order (cubic and quartic) force constants were used. In order to be suitable for condensed-phase applications, the nonbond parameters were modified based on the PCFF force field, and consequently the valence parameters were changed due to the coupling between the valence and nonbond parameters [20]. Therefore we would like to use the COMPASS force field to research on the bond lengths and their distributions.

It is well known that the N–NO_2 of nitramine explosives is the initial bond fractured in detonation [26–30]. The bond length and distribution of N–NO_2 bond and C–N bond of HMX molecules in pure HMX crystal and in the outer most layer of PBX, which can contact the polymer bonder chain directly, were all calculated, and are shown in Figs. 6 and 7. The corresponding data are tabulated in Table 1.

From Table 1 and Figs. 6 and 7, it is found that the interaction of HMX with Estane cannot affect the length and distribution of N–NO_2 bonds and C–N bonds in HMX molecules, which interact with Estane. This means that this interfacial interaction is not the cause that makes HMX more stable, though PBXs are more stable than their corresponding base explosives.

Mechanical properties of PBX

The material stress and strain tensors are respectively denoted by σ and ε. From the statistical mechanics of elasticity [31], the generalized Hooke's law is often written as:

$$\sigma_i = C_{ij}\varepsilon_j \tag{4}$$

$\lfloor C_{ij} \rfloor_{(i,\,j\,=1,2\ldots6)}$ is symmetric, and hence a maximum of 21 constants is required to fully describe the stress–strain behavior of an arbitrary material.

The polycrystal composed of random orientated micro-crystal (no direction is preferred) can be assumed to be isotropic from the statistical point of view. The effective isotropic compliances in terms of single-crystal

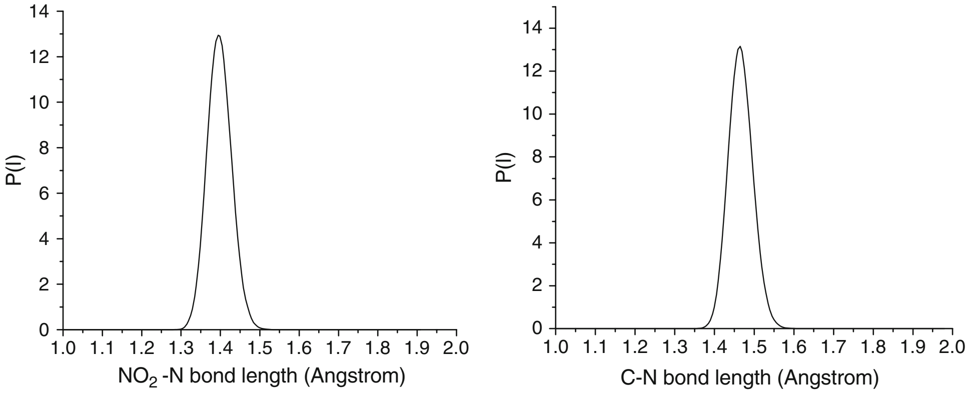

Fig. 6 Distribution of NO_2–N and C–N bond length in pure HMX crystal

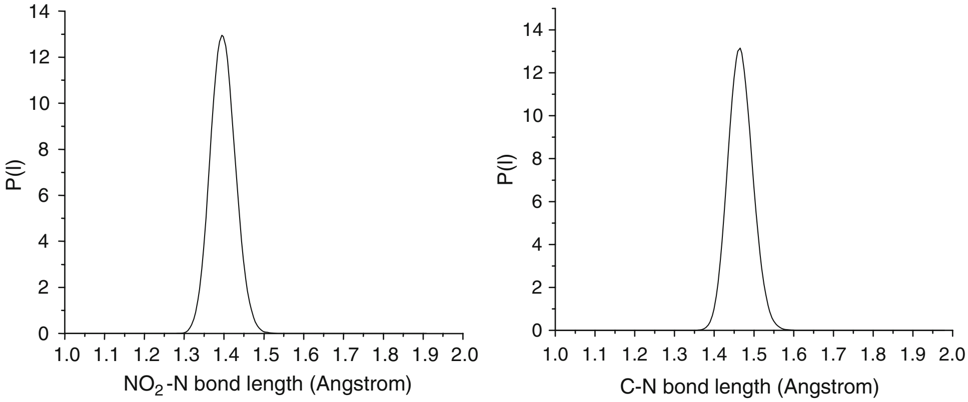

Fig. 7 Distribution of NO_2–N and C–N bond length in HMX/Estane

Table 1 The length and distribution of possible initial fractured bonds in HMX, and HMX interacting with Estane (in Å)

	HMX	HMX/Estane
N–NO_2 bond length	1.398	1.397
	(0.031)	(0.031)
C–N bond length	1.466	1.466
	(0.030)	(0.030)

Data in parentheses are standard deviation values

compliances averaged over all orientations can be obtained by Reuss average [32]. The effective bulk and shear moduli are then

$$K_R = [S_{11} + S_{22} + S_{33} + 2(S_{12} + S_{23} + S_{31})]^{-1} \quad (5)$$

$$G_R = 5\Big[4\big(S_{11} + S_{22} + S_{33}\big) - 4\big(S_{12} + S_{23} + S_{31}\big) + \big(S_{44} + S_{55} + S_{66}\big)\Big]^{-1} \quad (6)$$

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

$$E = 2G(1 + v) = 3K(1 - 2v) \quad (7)$$

where E is tensile modulus and V 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.

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 is negative for a brittle material. The larger the value of Cauchy pressure is, the more ductile the material is. The mechanical property values of HMX-based PBX are summarized in Table 2. The elastic constants were calculated with static elastic constant analysis method by averaging over five configurations.

From Table 2, it is found that the elastic modulus of the HMX-based PBX is decreased and the Poisson ratio is unchanged, compared with pure HMX crystal. The decreasing modulus means the rigidity of the PBX is reduced, i.e., the resistance to elastic deformation is decreased. Shear modulus decrease indicates that the hardness and tensile strength of the PBX is reduced, and bulk modulus decrease makes it clear that the fracture strength of the PBX becomes lower. From Cauchy pressure values, we know the ductibility of the PBX is better than that of HMX crystal. The reason why the PBX reduces the elastic modulus and increases the ductibility of HMX

Table 2 The elastic constants and effective isotropic moduli (in Gpa) and Cauchy pressures for HMX and HMX-based Estane

	β-HMX	HMX/Estane
C_{11}	13.7 ± 0.3	8.0 ± 0.4
C_{22}	12.1 ± 0.5	9.8 ± 0.2
C_{33}	12.6 ± 0.3	2.7 ± 0.9
C_{44}	6.4 ± 0.1	5.4 ± 0.1
C_{55}	4.9 ± 0.1	1.0 ± 0.6
C_{66}	5.2 ± 0.1	0.9 ± 0.4
C_{12}	3.7 ± 0.2	5.8 ± 0.1
C_{13}	5.6 ± 0.2	0.6 ± 0.2
C_{15}	−0.7 ± 0.2	0.04 ± 0.2
C_{23}	6.3 ± 0.3	1.0 ± 0.2
C_{25}	−3.0 ± 0.1	0.2 ± 0.2
C_{35}	−0.7 ± 0.1	−0.5 ± 0.3
C_{46}	−2.1 ± 0.1	−0.03 ± 0.09
Tensile modulus (E)	9.8	5.5
Poisson ratio (v)	0.3	0.3
Bulk modulus (K)	7.7	3.9
Shear modulus (G)	4.2	2.2
C_{12}–C_{44}	−2.7	0.5

crystal is that the polymer chains are more flexible than HMX molecules in the crystal. In a word, by blending Estane with pure HMX in small amount (the weight percentage of Estane in the PBX is 5.4%), the brittleness can be reduced and the ductibility can be improved, but some rigidity is sacrificed.

Relevancy to the shockwave stability for PBXs in detonation

It is arguable that elastic constants for the initially shock-compressed medium can be approximated by equilibrium lattice values [33]. Hence, the elasticity plays a key role in understanding the initial step in the mechanism of detonation. The arguments for detonation mechanism have proposed that the closure of the highest occupied molecular orbital lowerest unoccupied molecular orbital (HOMO-LUMO) gap results from an extreme shear-induced deformation of the molecule's electron density [34] and complete band-gap closure is unnecessary for reaction [35].

From the above viewpoint, the judgment can be deduced that the smaller the shear modulus is, the more easily the shear-induced deformation of the electron density can happen, i.e., the band-gap between HOMO and LUMO is easier to close, and the mechanochemical reaction can happen more easily. Because most elastic constants and all effective isotopic moduli of the HMX-based PBX are smaller than those of the HMX, the shockwave stability for the PBX should be worse than that of the HMX. However, the fact is completely opposite. Considering again the argument deduced from III. B part that the interfacial interaction in the PBX takes no effect on the lengths and distributions of the possible initial bonds fractured in detonation, now one may speculate on the initial step in the mechanism of the PBX's detonation. While the initial shockwave compression takes effect on the PBX, it is the polymer—Estane—that makes the PBX system deform more easily and the HMX grains first just change in orientation, and simultaneously the shockwave energy are partially depleted by the polymer. Therefore, the HMX-based PBX is more stable than the pure HMX. However, more theoretical and experimental work has to be done before this speculation can be justified.

Conclusions

In this study, by means of MD simulation using general force field COMPASS, we have investigated the interfacial structure of *β*-HMX-based PBX with Estane chain, on (100) surface by calculating PCF and binding energy, and calculated the elastic properties and derived the ductibility of this PBX. The proposed reasons that the PBX is more stable than pure HMX have been discussed in relation to the elasticity of them.

The PCF analysis of the interfacial structure of the PBX has shown that there exist specific interactions̄H bonds and electrostatic interaction between HMX crystal (100) surface and Estane chain. The calculated bonding energies are positive and this has also proved that there are specific interactions between the HMX crystal surface and these polymer bonders. The information on the interfacial structure and the interactions between HMX (100) surface and Estane chain helps understand why Estane can be used as a binder in the PBX and what kind of interactions between HMX and Estane works in the mechanical properties of the PBX. It has been shown that the interfacial interaction does not affect the bond lengths and distributions of possible initial bonds fractured in detonation, i.e., the interaction does not take effect on the stability of the PBX.

The predicted mechanical properties of the HMX-based PBX have shown that blending with small amount of the polymers can improve the deductibility of HMX crystal, i.e., toughen HMX crystal. Due to the flexible polymer chains, when the shockwave takes effect on the PBX, the polymer chains deform and deplete partially shockwave energy, which has implied that the PBX is more stable to shockwave-induced detonation than pure HMX.

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References

1. Gibbs TR, Popolato A, (eds) (1980) LASL explosive property data. University of California Press, Berkeley
2. Dong HS, Zhou FF (1989) High energy explosives and correlative physical properties. Science Press, Beijing
3. Sun YB, Hui JM, Cao XM (1995) Military use blended explosives. Weapon Industry Press, Beijing
4. Geng JF, Lao YL (1991) J Beijing Univ Sci Tech 11:87
5. Van Oss CJ, Chaudhury MK, Good RJ (1988) Chem Rev 88:927
6. Xu QL (1993) Energetic Mater (in Chinese) 1:1
7. Song HJ, Dong HS, Hao Y (2000) Energetic Mater (in Chinese) 8:104
8. Xiao HM, Li JS, Dong HS (2001) J Phys Org Chem 14(9):644
9. Li JS, Xiao HM, Dong HS (2000) Explod Shock (in Chinese) 20:221
10. Xiao HM, Ju XH (2003) Intermolecular interactions in energetic systems (in Chinese). Science Press, Beijing
11. Sewell TD, Menicoff R, Bedrov D, Simith GD (2003) J Chem Phys 119:7417
12. Gee RH, Roszak S, Balasubramanian K, Fried LE (2004) J Chem Phys 120:7059
13. Yang XZ (2002) Molecular simulation and polymer materials (in Chinese). Science Press, Beijing
14. Milchev A, Binder K (1996) Macromolecules 29(1):343
15. Wang XL, Lu ZY, Li ZS, Sun CC (2005) J Phys Chem B 109:17644
16. Xiao JJ, Yong GY, Ji GF, Xiao HM (2005) Chin Sci Bull 50:21
17. Xiao JJ, Huang YC, Hu YJ, Xiao HM (2005) Sci China B 48:504
18. Xu XJ, Xiao HM, Xiao JJ, Zhu W, Huang H, Li JS (2006) J Phys Chem B 110:7203
19. Dobratz BM (1981) Report No. UCRL-52997, 16 March
20. Sun H (1998) J Phys Chem B 102:7338
21. Choi CS, Boutin HP (1970) Acta Crystallogr B 26:1235
22. Chen CL, Chen HL, Lee CL, Shih JH (1994) Macromolecules 27:2087
23. Allen MP, Tildesley DJ (1987) Computer simulation of liquids. Oxford University Press, Oxford
24. Andersen HC (1980) J Chem Phys 72:2384
25. Parrinello M, Rahman A (1981) J Appl Phys 52:7182
26. Xiao HM (1993) The molecular orbital theory for nitrocompounds (in Chinese). National Defense Industry Press, Beijing
27. Xiao HM, Li YF (1996) The bond and electronic structure for metal azides (in Chinese). Science Press, Beijing
28. Botcher TR, Wright CA (1993) J Phys Chem 97:9149
29. Choi M, Kim H, Chung C (1995) J Phys Chem 99:15785
30. Luty T, Ordon P, Eckhardt CJ (2002) J Chem Phys 117:1775
31. Weiner JH (1983) Statistical mechanics of elasticity. John Wiley, New York
32. Watt JP, Davies GF, O’Connell RJ (1976) Rev Geophys Space Phys 14(4):541
33. Stevens LL, Eckhardt CJ (2005) J Chem Phys 122:174701
34. Gilman JJ (1995) Philos Mag B 71:1057
35. Dick JJ (1984) Appl Phys Lett 44:859