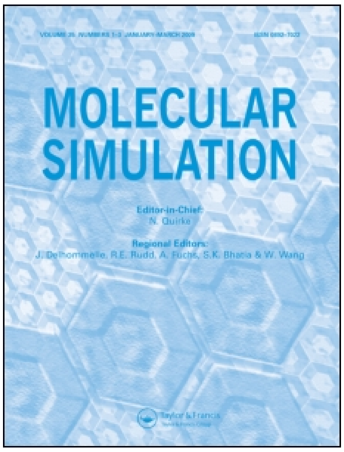

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A novel model for the molecular dynamics simulation study on mechanical properties of HMX/F_{2311} polymer-bonded explosive

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A novel model for the molecular dynamics simulation study on mechanical properties of HMX/F_{2311} polymer-bonded explosive

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The 'insert' model for β-octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)-based polymer-bonded explosive (PBX) was proposed for finding the relation of temperatures with mechanical properties. This model was simulated by using molecular dynamics models. The elastic constants and the effective moduli were calculated with static analysis method. Cauchy pressure was also calculated. It is found that the rigidity is weakened and the ductibility is improved by adding a small amount of F_{2311} in the crystalline HMX. The rigidity is also weakened with increasing temperature. However, the ductibility of HMX/F_{2311} PBX changes as a parabola with increasing temperature duo to the enhancement of F_{2311} molecular chain movement and simultaneously the increment of high energy conformation ratio in this molecular chain, i.e. the increment of the molecular chain rigidity.

Keywords: molecular dynamics; model; mechanical properties; HMX; polymer-bonded explosives (PBXs)

1. Introduction

Polymer-bonded explosives (PBXs) are highly filled (*ca*. 90% w/w filler) composite materials mainly comprising grains of an explosive material held together by a polymer binder and very few plasticisers and stabilisers. They are widely used in many defence and economy scopes because they have notable merits such as good safety, high strength, ease of process and so on [1–5]. In general, a solid energetic compound is brittle, so the key problem in PBX formulations is in choosing a polymer binder that can reduce the brittleness of the compound. It is costly and unsafe work to determine a PBX formulation. Therefore, it is necessary to understand better the physical, chemical and mechanical behaviours of the constituents of PBX formulations, as well as the interactions between them, from fundamental theoretical principles. There are many reports on the behaviours of explosives or polymers mentioned above by the quantum chemistry method and molecular dynamics (MD) methods [6–15] and some reports [16–19] have recently been found on simulation computation for PBXs, especially for its most important properties – mechanical properties by MD method. However, the models used in those simulation computations were 'covering' or 'cutting' ones [16]. In this work, the 'inserting' model was used to explore the relation of temperatures with mechanical properties of HMX/F_{2311} PBX by MD method using Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies (COMPASS) [20] force field.

The solid energetic compound octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) is widely used with best comprehensive properties. The HMX crystal structure of β-phase has been determined by neutron diffraction [21]. β-HMX crystal is the room temperature stable phase of the four known polymorphic forms and is the energetic constituent in several high-performance PBX formulations [1]. Thus β-HMX-based PBXs were taken as the researching objects in this paper. F_{2311}, as a polymer binder, is the copolymer polymerised from vinylidene difluoride and chlorotrifluoroethylene with the molar ratios of 1:1.

2. Modelling and simulation

To achieve high accuracy in predicting various molecular properties with a fairly board coverage, in the COMPASS [20] force field, complicated functional forms including off-diagonal cross-coupling terms were used. The functional forms of the COMPASS force field are the same as those used in Consistent Force Field (CFF)-type force fields [22,23]:

$$\begin{aligned} E= & \sum_b [k_2(b-b_0)^2+k_3(b-b_0)^3+k_4(b-b_0)^4] \\ & +\sum_\theta [k_2(\theta-\theta_0)^2+k_3(\theta-\theta_0)^3+k_3(\theta-\theta_0)^3] \\ & +\sum_\phi [k_1(1-\cos\phi)+k_2(1-\cos 2\phi)+k_3(1-\cos 3\phi)] \end{aligned}$$

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$$
\begin{aligned}
&+\sum_{\chi}k_2\chi^2+\sum_{b,b'}k(b-b_0)(b'-b'_0)\\
&+\sum_{b,\theta}k(b-b_0)(\theta-\theta_0)+\sum_{b,\phi}(b-b_0)[k_1\cos\phi\\
&+k_2\cos 2\phi+k_3\cos 3\phi]+\sum_{\theta,\phi}(\theta-\theta_0)[k_1\cos\phi\\
&+k_2\cos 2\phi+k_3\cos 3\phi]+\sum_{\theta,\theta'}k(\theta-\theta_0)(\theta'-\theta'_0)\\
&+\sum_{\theta,\theta',\phi}k(\theta-\theta_0)(\theta'-\theta'_0)\cos\phi\\
&+\sum_{i,j}\frac{q_iq_j}{r_{i,j}}+\sum_{i,j}\varepsilon_{i,j}\left[2\left(\frac{r^0_{i,j}}{r_{i,j}}\right)^9-3\left(\frac{r^0_{i,j}}{r_{i,j}}\right)^6\right].
\end{aligned}
\tag{1}
$$

The functions can be divided in two categories: valence terms and nonbond interaction terms. The valence terms represent internal coordinates of bond (b), angle (θ), torsion angle (ϕ), out-of-plane angle (χ) and the cross-coupling terms including combinations of two or three internal coordinates. The nonbond interactions, which include a LJ-9-6 function [24] for van der Waals (vdW) term and a Coulombic function for an electrostatic interaction, are used for interactions between pairs of atoms that are separated by two or more intervening atoms or those that belong to different molecules. q_i denotes the net charge for atom i and ε and r^0 are the LJ-9-6 parameters.

In this force field, the valence parameters and atomistic partial charges were derived by fitting to *ab initio* data, and the vdW parameters were derived by conducting MD simulations of molecular liquids and fitting the simulated cohesive energies and equilibrium densities to experimental data. The combined parametrisation procedure significantly improves the quality of a general force field. The COMPASS 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.

The MD simulation data were generated under constraints of constant particle number, pressure and temperature (NPT statistical ensemble) dynamics for β-HMX and β-HMX/F_{2311} PBX. In all the following condensed phase simulation cases, electrostatic interactions were treated using the standard Ewald summation [25], nonbond interactions were truncated at 9.5 Å, the Verlet velocity integration method [25,26] was used with a time step of 1 fs, and equilibration runs of 100 ps duration were performed, followed by production runs of 200 ps, during which configurations were collected for subsequent static elastic constants analysis to obtain the elastic coefficients. The elastic moduli can be calculated assuming the materials to be isotropic. The Parrinello-Rahman method of pressure control [27] and the Anderson temperature control method [27] were used for the NPT dynamics. All computations were carried out using commercial software program – MS from Accelrys Inc., San Diego, CA.

As to the polymer binder molecular chain, F_{2311}, the end groups were saturated by F atoms. The molecular chain was run under constant volume, temperature and particle numbers, ensemble using the COMPASS force field with no cut-off distance for 2.5 ns. The temperature control method, the velocity integration method and a time step are taken the same as the above. The final configuration was regarded as the equilibrium configuration of the polymer chain. During the following PBX's model construction, the initial polymer chains were in equilibrium states.

The initial HMX structure in Choi et al. [21] was used in the condensed phase simulations in this paper. The periodic MD simulation cell containing 48 molecules was used for β-HMX, corresponding to 24 (4 × 2 × 3) unit cells. The PBX composite model was constructed by inserting the equilibrium polymer F_{2311} chain in a periodic MD simulation cell and then deleting all HMX molecules that contain any atom with distance to any atom in the polymer chain less than or equal to 1 Å. Then the PBX model was allowed to evolve dynamically in NPT ensemble at atmospheric pressure and starting from 245 K, in increasing steps of 50–345 K. In this model, one polymer chain contained 10 constitutional repeating units. As a relative comparing reference, the periodic cell for β-HMX was allowed to run the same MD simulation as the above. The PBX model – HMX/F_{2311} is shown in Figure 1. The advantage of this model lies in making it convenient to study the temperature effect on mechanical properties of PBXs.

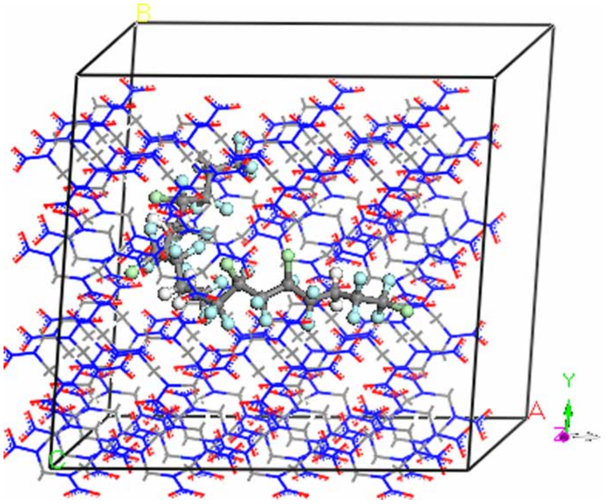

Figure 1. HMX/F_{2311} PBX periodic MD simulation cell.

3. Results and discussions

In an atomistic calculation, the internal stress tensor can be obtained using the so-called virial expression [28]:

$$\boldsymbol{\sigma} = -\frac{1}{V_0}\left[\left(\sum_{i=1}^{N} m_i\left(\mathbf{v}_i\mathbf{v}_i^T\right)\right) + \left(\sum_{i<j}\mathbf{r}_{ij}\,\mathbf{f}_{ij}^T\right)\right], \tag{2}$$

where index i runs over all particles $1-N$, m_i and $\mathbf{v}_i$ denote the mass and velocity, $\mathbf{r}_{ij}$ and $\mathbf{f}_{ij}$ denote the relative position vector between particles i and j and force acting on particle i due to particle j, and V_0 denotes the (undeformed) system volume.

For each configuration submitted for static elastic constants analysis, a total of 13 minimisations are performed. The first consists of a conjugate gradients minimisation of the undeformed system. Following this initial stage, three tensile and three pure shear deformations of magnitude ± 0.0005 are applied to the minimised undeformed system, and the system is reminimised following each deformation. The elastic coefficients can then be obtained by calculating $\Delta\sigma_i/\Delta\varepsilon_j$ for each of the six pairs of applied strains, where $\Delta\varepsilon_j$ denotes the strain corresponding to each applied deformation and σ_i represents, in vector notation, elements of the stress tensor obtained analytically using the virial [12].

From the mechanics of elasticity [29], we know that the generalised Hooke's law is often written as:

$$\sigma_i = C_{ij}\varepsilon_j, \tag{3}$$

where

$$[C_{ij}] = \begin{bmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46} \\ C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56} \\ C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66} \end{bmatrix}, \tag{4}$$

$[C_{ij}]$ is symmetric, and hence a maximum of 21 coefficients is required to fully describe the stress–strain behaviour of an arbitrary material. If the crystal processes symmetry, relations exist between the various coefficients, so that the number of independent coefficients is less than 21.

The polycrystals composed of random orientated microcrystal (No direction is preferred.) can be assumed to isotropic from the statistical point of view. 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 then [30]

$$K_R = [3(a+2b)]^{-1} \tag{5}$$

and

$$G_R = \frac{5}{(4a-4b+3c)}, \tag{6}$$

where

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

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

and

$$\mathbf{S} = \mathbf{C}^{-1}. \tag{7}$$

The subscript R denotes the Reuss average. The compliance matrix $\mathbf{S}$ is equal to the inverse matrix of elastic coefficient matrix $\mathbf{C}$. Note that for the most general crystal structure (all 21 coefficients are independent) the Reuss moduli depend on only nine of the single-crystal compliances. After the bulk and shear moduli are calculated, the other moduli and Poisson's ratio can be computed from those using the rules of isotropic linear elasticity

$$E = 2G(1+\nu) = 3K(1-2\nu), \tag{8}$$

where E, G, K, are the tensile, shear and bulk modulus, respectively, and ν is the Poisson's ratio.

Such plastic properties as hardness, tensile strength, fracture strength and elongation in tension, can be related to the elastic moduli [31]. 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. 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 inserting model makes it easy to calculate the elastic properties with the temperature changing. The elastic coefficients (tensile, bulk, shear) moduli, and Poisson's ratios of crystal HMX and HMX-based PBXs at the temperature of 245, 295 and 345 K, were obtained by analysing the configurations of the production of run trajectory in NPT ensemble. These data are tabulated in Table 1.

Table 1 shows that the moduli for pure HMX crystal and HMX-based F_{2311} PBX decreased with the temperatures increasing, but there were slight fluctuations in tensile and shear modulus values of HMX/F_{2311} PBX, i.e. these moduli values at 345 K were a little bigger than those at 295 K. The moduli for pure HMX crystal also decreased when it was blended with F_{2311} over this temperature range. This means that the hardness, the tensile strength

Table 1. Elastic coefficients, isotropic moduli, Poisson's ratios and Cauchy pressures for HMX/F_{2311} PBX and HMX crystal at different temperatures.

	245 K	295 K	345 K
C_{11}	8.9 (13.2)	7.2 (12.8)	7.1 (10.8)
C_{22}	7.1 (12.9)	5.8 (10.9)	5.9 (9.7)
C_{33}	8.3 (12.9)	7.4 (11.4)	6.8 (10.4)
C_{44}	3.3 (6.4)	2.9 (5.9)	2.8 (5.5)
C_{55}	2.7 (4.9)	2.5 (4.6)	2.2 (4.2)
C_{66}	2.9 (5.4)	2.9 (4.8)	2.5 (4.3)
C_{12}	1.4 (3.9)	1.9 (3.4)	1.3 (3.0)
C_{13}	2.8 (5.5)	2.7 (4.9)	2.1 (3.8)
C_{23}	3.1 (6.8)	2.8 (5.2)	2.1 (4.1)
C_{15}	0.4 (−0.8)	0.0 (−0.4)	0.3 (−0.1)
C_{25}	−0.8 (−3.0)	−0.9 (−2.7)	−0.7 (−2.3)
C_{35}	0.6 (−0.7)	0.2 (−0.4)	0.6 (−0.4)
C_{46}	−0.3 (−2.0)	−0.5 (−1.8)	−0.3 (−1.5)
Tensile modulus (E)	7.0 (9.9)	5.5 (9.2)	5.8 (8.4)
Poisson's ratio (ν)	0.2 (0.3)	0.3 (0.3)	0.2 (0.3)
Bulk modulus (K)	4.3 (7.9)	3.9 (6.9)	3.4 (5.9)
Shear modulus (G)	2.9 (3.8)	2.2 (3.6)	2.4 (3.3)
$C_{12}-C_{44}$	−1.9 (−2.5)	−1.0 (−2.5)	−1.5 (−2.5)

Note: Data in parentheses are corresponding results for HMX crystal elastic coefficient and modulus in GPa.

and the fracture strength of pure HMX crystal were larger than those of HMX/F_{2311} PBX and with temperature increasing these properties were decreasing. In the whole temperature range, the Cauchy pressure values for pure HMX crystal were unchanged and the Cauchy pressure values for HMX/F_{2311} PBX were larger than those for pure HMX crystal though they were all negative. These indicate that the ductibility of pure HMX crystal cannot be affected by increasing temperature and the ductibility of HMX/F_{2311} is better than that of pure HMX crystal though they are all brittle materials. The ductibility of HMX/F_{2311} changed as a parabola versus the temperature, i.e. at 345 K the ductibility was the best since its Cauchy pressure value was the largest, and at the 295 K it was the worst since the Cauchy pressure value was the smallest.

From the free volume theory [32], the temperature increasing can cause the free volume in the materials to expand and the molecules to have more dynamic energy. This makes the materials deform more easily, i.e. the moduli decrease. But we found temperatures had no effect on the ductibility of pure HMX crystal. Because the molecular chain of F_{2311}, due to the internal rotation of their σ-bonds, is more flexible than HMX molecule, the moduli of HMX/F_{2311} PBX are less than those of pure HMX crystal. As to the change of the ductibility of HMX/F_{2311} PBX, this is because each chlorine atom in F_{2311} molecular chain has such a large volume and strong electronegativity that the adjacent chlorine atoms repel each other and the molecular chain forms a similar syndiotactic structure [32]. The bulky and strongly electronegative chlorine atoms cause the extended all-trans conformation to be less energetically favourable than angular states and the 'extended' states become more populated at elevated temperatures [33]. With temperature increasing, the molecular chain has more movement capability in favour of improving the ductibility of HMX/F_{2311} PBX and at the same time the molecular chain becomes more extended and rigid which is not good to enhance the ductibility. The simultaneous actions of the two contrary effects make the ductibility of HMX/F_{2311} PBX change with temperature increasing like a parabola. And the two contrary effects may be also the reason for the fluctuation of the tensile and shear moduli of HMX/F_{2311} PBX at higher temperatures.

4. Conclusions

We found by the atomic simulation that the inserting model was suitable to explore the relation of mechanical properties of the PBX and temperatures. Blending a small amount of F_{2311} with HMX crystal can reduce the elastic moduli but is able to improve the ductibility, i.e. reduce the brittleness of pure HMX crystal. This is because F_{2311} molecular chain is more flexible.

With temperature increasing from 245 to 345 K, due to more dynamic energy the elastic moduli of pure HMX crystal decreased which implies that the hardness, the tensile strength and the fracture strength also decreased. However, temperature had no influence on the ductibility of pure HMX crystal. Because of more dynamic energy and more rigidity of F_{2311} molecular chain at elevated temperatures, the ductibility of HMX/F_{2311} PBX changed as a parabola with temperature increasing.

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