Molecular Dynamics Study on the Effect of Doping Defects on the Properties of CL-20/HMX Co-crystal Explosive

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Abstract. In order to explore the influence of doping defects on the properties of CL-20 / HMX eutectic explosive, the models with different doping rates were calculated by molecular dynamics method. The results show that compared with the non-doped crystal model, the binding energy in the doped model is reduced by 0.332%~11.805%; The initiation bond length increased by 0.9%~4.6%; The binding diatomic interaction energy is reduced by 2.31%~15.46%; The cohesive energy density decreased by 19.75%~50.39%; The decreasing range of density is 0.697%~4.450%; The reduction range of detonation velocity is 0.744%~5.449%; The reduction range of explosion pressure is 1.864%~12.841%; The bulk modulus decreased by 0.4844~6.7461GPa, the shear modulus decreased by 0.9442~5.2329GPa, and the tensile modulus decreased by 2.0431~12.5374GPa. It shows that doping defects will reduce the stability, safety and detonation performance of explosives, and make the hardness, fracture resistance and rigid strength of explosives worse.

1 Introduction

CL-20, the full name of Hexanitrohexaazaisowurzane, is one of the single substance explosives with the highest energy density at present. It has good application prospects, but it also has the disadvantages of high sensitivity and high cost [1, 2]. As one of the best comprehensive single substance explosives at present, HMX has the advantages of good detonation performance, high energy and good thermal stability. Therefore, CL-20 / HMX eutectic explosive composed of CL-20 and HMX has attracted extensive attention of scholars at home and abroad in recent years.

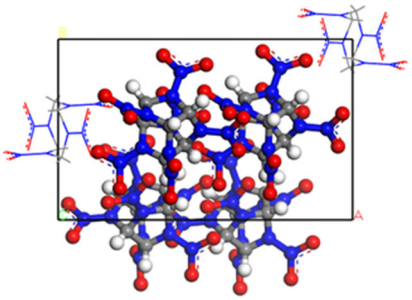
CL-20 be doped with Ethyl Acetate impurity ($C_4H_8O_2$) [3] in the preparation process, resulting in Ethyl Acetate molecules in the crystal of CL-20 / HMX explosive, resulting in doping defects, which will affect the performance of the explosive. As the main factor affecting the properties of explosives, crystal defects have been widely concerned by scholars, and the study of their influence on the properties of explosives has become a subject of great significance. Hang Gui-yun et al. [4] founded in the study of HMX / NQ eutectic explosive defects that the defects reduce the stability and detonation performance of the explosive and increase the sensitivity. Sun Ting et al. [5] studied the eutectic structure and properties of CL-20 / HMX by MD method, they found that the sensitivity can be reduced by introducing HMX into CL-20 system. Hu Jing-wei et al. [6] studied the effect of vacancy defects on CL-20 explosive and found that vacancy defects improved the thermal decomposition rate of CL-20 molecules and thus increased the sensitivity of the explosive.

In this paper, molecular dynamics method was used to calculate different doping rate models. Through the analysis of calculation data, it provides a reference for predicting the performance of CL-20 / HMX explosive.

2 Model and calculation method

2.1. Original model establishment

CL-20 / HMX eutectic explosive is composed of CL-20 and HMX in a molar ratio of 2:1. It belongs to monoclinic system. The space group is P21 / C, and the lattice parameters are a=1.635nm, b=0.994nm, c=1.214nm, β= 99.233° [7]. The CL-20 / HMX single crystal model obtained from reference [7] is shown in Figure 1 (a), which is extended to 3×2×2 The supercell model is shown in Figure 1 (b), which is marked as model-1.



(a) CL-20 / HMX cell model

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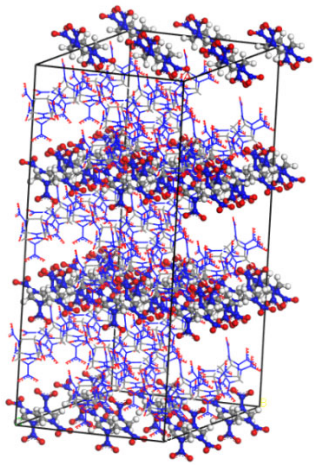


(b) CL-20 / HMX supercell model

Fig. 1. Single cell model and supercell model

2.2 Establishment of doping model

By replacing CL-20 molecule in the original model-1 with Ethyl Acetate impurity, five doping models with doping rates of 2.78%, 5.56%, 8.33%, 11.11% and 13.89% were formed. Figure 2 shows the doping model-5.

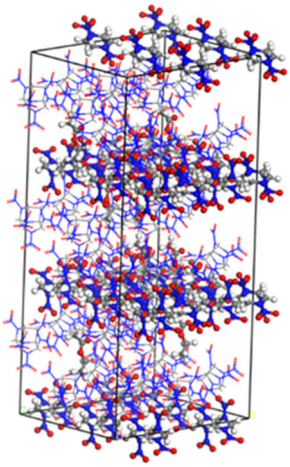


Fig. 2. Doping model-5

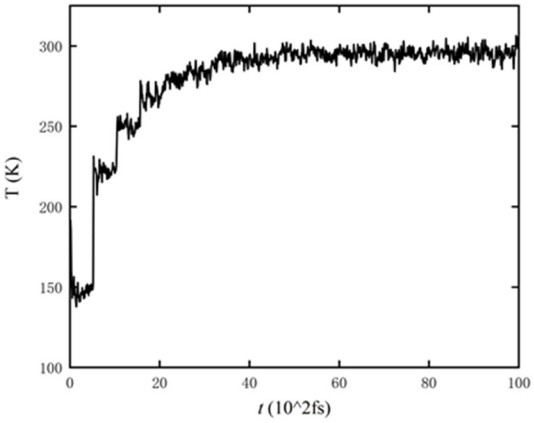
2.3 Calculation condition setting

Firstly, the geometric optimization of the model structure is carried out to make its energy converge. Then carry out molecular dynamics calculation, adopt NVT ensemble and compass force field, set the temperature as 295K and the pressure as 0.1MPa. Set the step size as 1fs, save the results every 100 steps, and calculate 10000 steps in total.

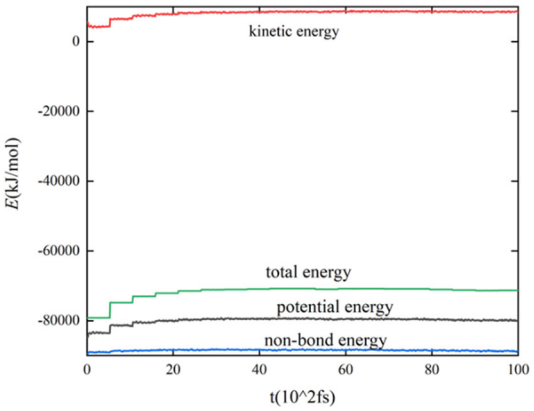
3 Results and discussion

3.1 Balance discrimination

Take model-2 as an example, in the process of molecular dynamics calculation, the temperature reaches equilibrium after 4000fs; The energy gradually stabilized after 2000fs. Therefore, the calculation results can be statistically analysed



(a)T-t curve



(b)E-t curve

Fig. 3. Variation curve of temperature and energy

3.2 Binding energy

The calculation formula of binding energy is

$$E_b = -E_{inter} = (E_{CL\text{-}20} + E_{HMX}) - E_{total} \quad (1)$$

In the above formula, E_b is the binding energy; E_{inter} is intermolecular force; $E_{CL\text{-}20}$ is the total energy of CL-20 molecule; E_{HMX} is the total energy of HMX molecule; E_{total} is the total energy when the system reaches equilibrium.

The binding energies of six models are 468.16、466.60、458.91、446.43、424.55、412.90kJ/mol. The above data show that the binding energy of model-1 is the largest. With the increase of doping rate, the binding energy decreases gradually, and the reduction range of doping model is 0.332% ~ 11.805%. The binding energy reflects the tightness of explosive molecules, and the decrease of binding energy indicates that the increase of doping rate has an impact on the stability of explosive structure.

3.3 Sensitivity

It is usually used to reduce the explosive susceptibility of high explosives. According to the "hot spot theory" [8] and "initiation bond thought" [9], combined with the research of Xiao Ji-jun et al. [10-13], the change of sensitivity in this paper is obtained by analysing the initiation bond length, initiation bond diatomic

interaction energy and cohesive energy density of explosive crystal.

3.3.1 Initiation bond length

CL-20 is the main explosive, due to its high sensitivity and sensitivity to external stimuli, it is more likely to react than HMX. Therefore, the N-NO_2 bond in CL-20 is selected as the initiation bond [14,15]. Take model-3 as an example, the bond length distribution of its initiation bond is shown in Figure 4, which is approximately Gaussian distribution.

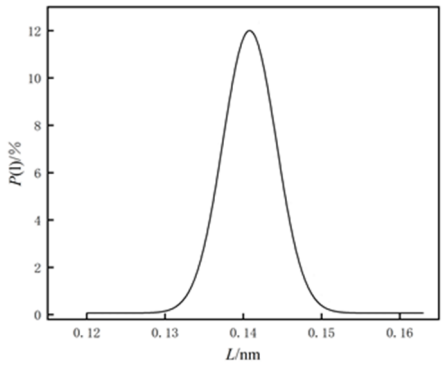


Fig. 4. Initiation bond length distribution

Table. 1. Average bond length and maximum bond length

model	L_{ave}/nm	L_{max}/nm
1	0.1755	0.2162
2	0.1740	0.2184
3	0.1770	0.2210
4	0.1765	0.2213
5	0.1770	0.2224
6	0.1785	0.2257

It can be seen from table 1 that the average bond length has little correlation with the doping rate, and the maximum bond length increases with the increase of the doping rate, but the overall range is small. The maximum bond length of non-doped model is 0.2162 nm; The increase range of the five doping models is 0.9% ~ 4.6%. Due to the high energy of molecules with the maximum bond length, like activated molecules, they are easy to cause explosion, so they have high sensitivity and low safety.

3.3.2 Initiation bonding diatomic interaction energy

Calculation formula of bonding diatomic interaction energy ($E_{N\text{-}N}$) of initiating bond

$$E_{N\text{-}N} = \frac{E_1 - E_2}{n} \tag{2}$$

In the above formula: E_1 is the total energy corresponding to the equilibrium of the system; E_2 is the total energy when the system reaches equilibrium after fixing all nitrogen atoms in CL-20; n is the number of N-NO_2 bonds contained in CL-20 molecule in the system.

After calculation, the initiation bond bonding diatomic interaction energies of the six models are 118.29、115.47、111.62、109.13、108.62、100kJ/mol. It can be seen from the above data that the diatomic interaction energy of initiation bond decreases with the increase of doping rate, and the decrease range is 2.31% ~ 15.46%. The diatomic interaction energy of initiation bond is a reflection of the stability of initiation bond. The higher the energy, the less likely the initiation bond is to break. Therefore, the increase of doping rate will reduce the stability of initiation bond and increase the sensitivity.

3.3.3 Cohesive energy density

Cohesive energy density (*CED*) refers to the energy required for 1mol condensate in unit volume to overcome the intensification of intermolecular interaction, with the unit of kJ/cm^3 and the calculation formula of [16]

$$CED = \frac{H_V - RT}{V_m} \tag{3}$$

In the above formula: H_V is molar evaporation heat, kJ/mol; RT is the expansion work done during material gasification, kJ/mol; V_m is the molar volume, cm^3/mol. The cohesive energy density is equal to the sum of van der Waals force and electrostatic force. Its essence is a non-bond force, which can reflect the strength of intermolecular interaction in the mixed system. Through calculation, the cohesive energy density, van der Waals force and electrostatic force are obtained.

Table. 2. Cohesive energy density, van der Waals force and electrostatic force(kJ/cm^3)

model	*CED*	vdW	Electrostatic
1	1.554	1.372	0.182
2	1.247	1.129	0.145
3	1.218	1.016	0.112
4	0.976	0.904	0.072
5	0.895	0.837	0.058
6	0.771	0.749	0.022

It can be seen from the data in Table 2 that the three values of the non-doped model are the highest, and the cohesive energy density of the five doped models decreases by 19.75% ~ 50.39%. Cohesive energy density reflects the difficulty of explosive changing from condensed state to gaseous state. Therefore, the increase of doping rate will reduce the cohesive energy density, make the explosive easier to change into gaseous state, and increase the sensitivity of the explosive.

3.4 Detonation performance

Detonation performance reflects the power and energy density of explosives. In this paper, the modified nitrogen equivalent method is used to calculate the detonation parameters of explosives. Detonation parameter calculation formula of the modified nitrogen equivalent method is as follows

$$V_D = (690 + 1160\rho)\sum N_{ch} \tag{4}$$

$$p = 1.106(\rho\sum N_{ch})^2 - 0.84 \quad (5)$$

$$\sum N_{ch} = \frac{100}{M_r}(p_i N_{p_i} + \sum B_K N_{B_K} + \sum G_j N_{G_j}) \quad (6)$$

In the above formula: V_D is explosion speed, m/s; p is explosion pressure, GPa;ρ is the explosive density, g/cm^3; $\sum N_{ch}$ is the corrected nitrogen equivalent; p_i is the mole number of the i-th detonation product produced by 1mol explosive; N_{pi} is the nitrogen equivalent coefficient of the i-th detonation product; B_K and N_{BK} is the number of occurrence of the K-th chemical bond and the nitrogen equivalent coefficient; G_j and N_{Gj} is the occurrence times and nitrogen equivalent coefficient of the j-th group.
The calculated results are shown in Table 3.

Table 错误!文档中没有指定样式的文字。. 3. Detonation parameters

model	ρ/g·cm^{-3}	υ_D/m·s^{-1}	p/GPa
1	2.001	9202.2	39.17
2	1.951	9133.7	38.44
3	1.901	8948.6	36.42
4	1.851	8832.2	35.27
5	1.801	8771.3	34.75
6	1.751	8700.8	34.14

It can be seen from the above table that the density, detonation velocity and detonation pressure of the non-doped model are the highest, and the density, detonation velocity and detonation pressure of the five doped models decrease with the increase of doping rate, with the reduction ranges of 0.697% ~ 4.450%, 0.744% ~ 5.449% and 1.864% ~ 12.841% respectively. The reason may be that the energy of ethyl acetate is lower than CL-20 and destroys the stability of the explosive.

3.5 Mechanical property

The mechanical properties of the model after dynamic calculation are analysed. According to Hooke's law, the following calculation formula is obtained.

$$E = \frac{9KG}{3K+G} \quad (7)$$

$$\mu = \frac{3K-2G}{2(K+G)} \quad (8)$$

In the above formula: K is the bulk modulus, indicating the hardness of the material; G is the shear modulus, indicating the fracture resistance of the material; E is the tensile modulus, which represents the rigidity measurement of the material; μ is Poisson's ratio.

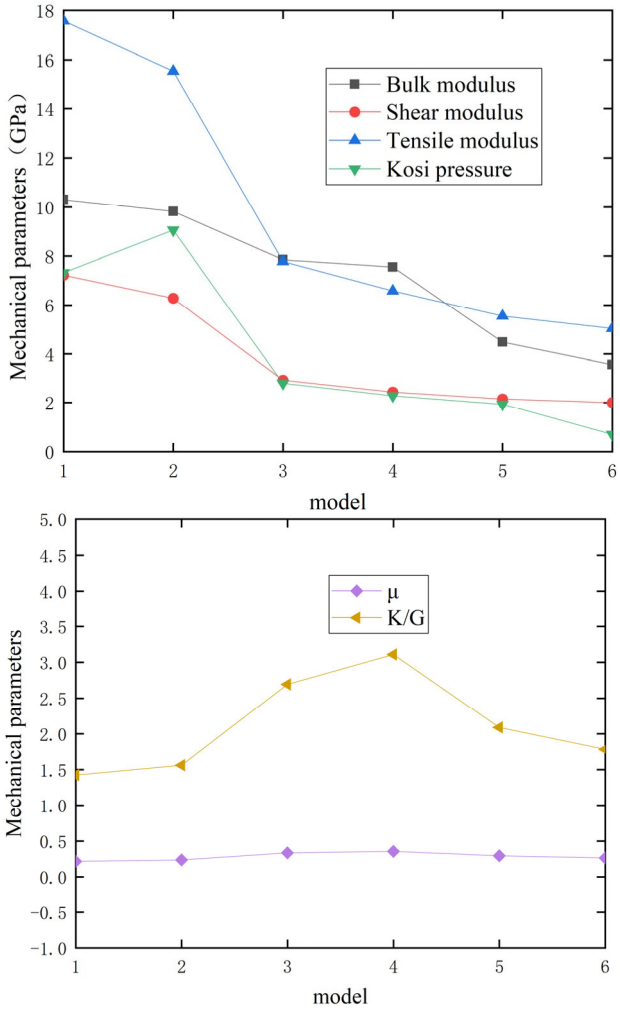


Fig. 5. Mechanical properties

In the figure above: Poisson's ratio and K / G are elastic constants without unit; Cauchy pressure indicates the ductility of the material; K / g indicates the toughness of the material.

It can be seen from Fig. 5 that with the increase of doping rate, the bulk modulus, shear modulus and tensile modulus of the explosive decrease, indicating that with the increase of doping rate, the hardness, fracture resistance and rigid strength of the explosive decrease,; When the doping rate is 2.78%, the maximum Cauchy pressure is 9.062GPa, which indicates that the doping defects improve the ductility of the crystal to a certain extent, but the overall trend reflects that the higher the doping rate is, the better the ductility is; When the doping rate is 8.33%, the maximum K/G is 3.11. The overall trend is to increase first and then decrease with the increase of doping rate, indicating that the doping defects can increase the toughness of the crystal to a certain extent, but the more the better; The Poisson's ratio is between 0.216 and 0.355, which is relatively stable, indicating that the doping defects have little effect on the change of Poisson's ratio.

4 Conclusion

(1) Compared with the non-doped model, the binding energy, van der Waals force and electrostatic force of the doped model are reduced, which leads to poor stability. The higher the doping rate, the lower the binding energy and the worse the stability of the explosive.
(2) The maximum bond length of initiation bond of explosives increases with the increase of doping rate, and the diatomic energy and cohesive energy density of initiation bond decrease with the increase of doping rate. These two changes will increase the sensitivity of explosives.
(3) The density of explosive decreases with the increase of doping rate, which reduces its detonation velocity and detonation pressure, which has an adverse impact on the detonation performance of explosive.
(4) Doping defects will affect the mechanical properties of explosives. The higher the doping rate is, the smaller the bulk modulus, shear modulus and tensile modulus of the explosive are, and the hardness, fracture resistance and rigid strength of the explosive are reduced.
Based on the above conclusions, with the increase of doping rate, the stability, safety, detonation performance and mechanical properties of explosives decrease, which is contrary to the current goal of pursuing high energy density and low sensitivity explosives, and the hardness, fracture resistance and rigid strength decrease, which makes the reliability of materials not strong. Therefore, doping defects should be minimized in the manufacture of explosives.

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