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Molecular Dynamics Simulation on TKX-50 Based Explosives

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ABSTRACT

Dihydroxylammonium 5,5'-bistetrazole-1,1'-diolate (TKX-50) is a novel high-energy explosive which has superior overall performances. 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20), particularly ε-CL-20, is one of the outstanding high-energy explosives lately. 3,4-Bis (3-nitrofurazan-4-yl) furoxan (DNTF) is a newly energetic explosive with higher density and lower melting point. Molecular dynamics simulations were used to research the compatibility and mechanical properties of TKX-50 with ε-CL-20 and DNTF. The results of binding energy (ΔE_{bind}) and radial distribution function (RDF) show that the compatibility between TKX-50 and ε-CL-20 is better than that of DNTF. Moreover, hydrogen bonds and van der Waals forces consist in TKX-50/ε-CL-20 and TKX-50/DNTF systems. The cohesive energy density (CED) of two blend systems was analyzed and the blend structure can drop the sensitivity of ε-CL-20 and DNTF and increase their thermal stability. Additionally, compared with the TKX-50, the engineering modulus of two blending system are reduced to different extents, while the value of K/G, C_{12}–C_{44} andγis opposite, indicating that the blend structure can improve the mechanical properties of TKX-50.

Keywords: *Molecular Dynamics; Dihydroxylammonium 5,5' -Bistetrazole-1,1'-Diolate (TKX-50); Compatibility; Mechanical Properties.*

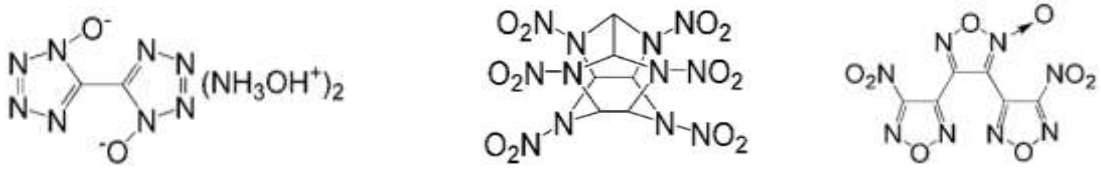
INTRODUCTION

Energetic ionic salts are a unique sort of high-nitrogen energetic compounds consisting of anions and cations [1-3]. Energetic ionic salts have received extensive attention in the area of energetic materials study because of their high formation enthalpy, high density and low saturated vapor pressure[4-5].

Dihydroxylammonium 5,5'-bistetrazole-1, 1'-diolate (TKX-50, Fig.1a) was first synthesized at the university of Munich in 2012[6].TKX-50 is high-energy ionic salt which has higher density, fine thermal stability and lower mechanical sensitivity [7-10]. Moreover, it is easy to synthesize and has outstanding comprehensive properties, indicating that TKX-50 has the potential application in the solid propellants. 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaza isowurtzitane (CL-20, Fig.1b)is a kind of high-energy explosive with high density and excellent oxygen balance[11]. Among the known crystal forms (α-, β-, γ-, ε-), ε-CL-20 has the highest density and best stability [12-14].

However, ε-CL-20 has not been widely used in many military fields owing to its higher mechanical sensitivity and higher price [15]. 3,4-Bis (3-nitrofurazan-4-yl) furoxan (DNTF, Fig.1c)is a newly energetic explosive[16, 17], which has a performance as good asε-CL-20.

The melting point of DNTF is 110 °C[18], which is lower than that of TKX-50 (~227 °C) [8]. Most used explosives in the world are not single-compound explosive but mixture one. Blending explosive refers to two or more than two different explosives that are mixed in an appropriate ratio.



(a) (b) (c)

Figure1. *Molecular structure of TKX-50, CL-20 and DNTF*

Blending explosives can improve the energy and mechanical properties of single-compound explosives to some extent. In this work, we used molecular dynamics method to simulate the compatibility and mechanical properties of TKX-50 with CL-20 and DNTF.

In order to predict the compatibility of TKX-50 withε-CL-20 and DNTF, we predicted the binding energy (ΔE_{bind}) and radial distribution function (RDF). Cohesive energy density (CED) and mechanical properties were calculated to investigate the characteristics of the two blends. The result can provide some useful information for the application of TKX-50 in the field of energetic materials.

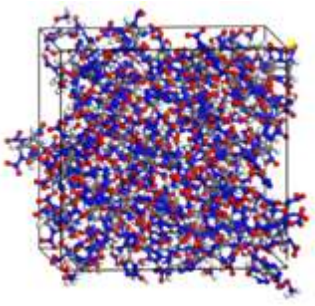
Computational Methods

Construction of Blending Models

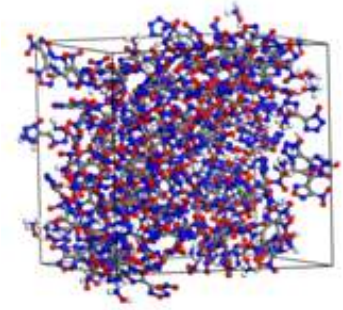
The molecular structures of TKX-50、ε-CL-20 and DNTF were from the Cambridge Crystallographic Data Centre. The amorphous cell of the pure TKX-50, ε-CL-20 and DNTF were constructed by the software of Materials Studio. At 298 K, the experimental density of TKX-50, ε-CL-20 and DNTF are 1.877 [19], 2.044 [20] and 1.937 [21] g /cm^3. Two blending amorphous cells were also constructed. The molar ratio of TKX-50withε-CL-20 and DNTF are 1:1, and the initial density of blend was obtained by averaging the molecular weight of each component.

MD Simulations

Each amorphous cell was optimized by COMPASS force filed [22]. After the equilibrium structure by the isothermal-isobaric molecular dynamic simulations (NPT-MD), the NVT-MD (300 K) simulation is performed with Andersen thermostat method. The total simulation time and time step were 200ps and 0.5fs, respectively. The electrostatic and vander Waals interactions were calculated by using Ewald's and Atom Based method, respectively[23]. The final equilibrium structures of TKX-50/ε-CL-20 and TKX-50/DNTF were shown in Fig. 2.



TKX-50/ε-CL-20



TKX-50/DNTF

Figure2. *The equilibrium structure of TKX-50/ε-CL-20 and TKX-50/DNTF*

Results and Discussion

ΔE_{bind} Calculation

The essence of compatibility is the interaction between components. The binding energy (ΔE_{bind}) can be used to reflect the strength of the interaction between two components[24]. ΔE_{bind} can be calculated as the following equation (1):

$$\Delta E_{bind}=E_{blend}-(E_{TKX-50}+E_{explosive}) \quad (1)$$

Where E_{blend}, E_{TKX-50} and $E_{explosive}$ are the total energy, the energy of TKX-50 and the energy of explosive in the system, respectively.

The ΔE_{bind} of TKX-50/ε-CL-20 and TKX-50/DNTF system is shown in Table 1. From the Table 1, the ΔE_{bind} of TKX-50 /ε-CL-20 system is –241.76 kJ·mol^{-1}, which is greater than the ΔE_{bind} of TKX-50/DNTF system. This indicates that the TKX-50/ε-CL-20 system is more stable than the TKX-50/DNTF system. The ΔE_{bind} values of two systems are both negative, so they are compatible systems. And the compatibility of TKX-50 with ε-CL-20 is better than that of DNTF.

Radial Distribution Function

Radial distribution function (RDF) can be used to describe some intermolecular distances and interactions in the system. The radial distribution function is often represented by $g_{AB}(r)$, which is defined as the following equation[25]:

$$g_{AB}(r)=\frac{\langle n_{AB}(r)\rangle}{4\pi r^2 \Delta\rho_{AB}} \quad (2)$$

Where $n_{AB}(r)$ is the number of particle B at a distance from r to r+dr with the center particle A, $\Delta\rho_{AB}$ is the average number density of particle B. In general, the intermolecular forces include hydrogen bond and vander Waals forces.

The hydrogen bond distance is 1.1-3.1 Å, and the length range of vander Waals forces is

usually 3.1-5.0 Å[23]. In addition, vander Waals forces with a length of greater than 5.0Å is weak. In this work, we denote hydrogen atom in TKX-50 as H1.Then oxygen and nitrogen atoms in CL-20 were marked as O2 and N2, respectively.

Table1. *Total energy and binding energy (in kJ·mol^{-1}) of TKX-50/ε-CL-20 and TKX-50/DNTF*

Model	E_{TKX-50}	$E_{explosive}$	E_{blend}	ΔE_{bind}
TKX-50/ε-CL-20	–403.42	–331.16	–976.34	–241.76
TKX-50/DNTF	–83.05	–1262.02	–1439.88	–94.81

As shown in Fig.3a for O-H, the higher g(r) appears at about 2.2Å, indicating that hydrogen bonds exist inTKX-50/ε-CL-20 and TKX-50/DNTF system. In addition, a high peak appeared in the range of 3.3-3.6Å, indicating that the van der Waals interaction appears in blending system. As shown in Fig.3b for N-H, peaks are all in the range of 3.3-3.5Å, shows that H1-N2 and H1-N3 belongs to Vander Waals forces. By contrast, the g(r) value of the TKX-50/ε-CL-20 system is higher than that of the TKX-50/DNTF system, and the first peak of the former appears at a smaller r, indicating that the interaction between TKX-50 with ε-CL-20 is stronger than that between TKX-50 with DNTF. Therefore, the compatibility of TKX-50/ε-CL-20 is better than TKX-50/DNTF, which offers good agreement with the result of the binding energy.

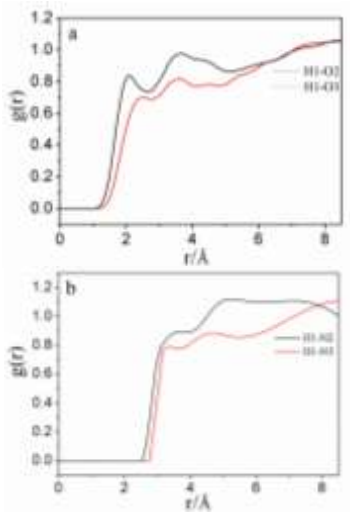


Figure3. *RDF for atom pair between hydrogen atom of TKX50 and oxygen/nitrogen of ε-CL-20 (O2, N2) and DNTF (O3, N3).*

Cohesive Energy Density

The cohesive energy density (CED) [26] can be defined as the energy required per mole of condensation per unit volume to overcome the intermolecular force of vaporization, which is a physical quantity that evaluates the magnitude of the intermolecular force. In a general way, the greater the force between molecules are, the greater the value of the corresponding CED.

As shown in Fig. 4, the CED value of TKX-50/ε-CL-20 and TKX-50/DNTF system gradually decrease with temperature in a reasonably linear relationship, indicating that the energy required overcoming intermolecular force vaporization declines. It is the same as experimental fact that the sensitivity of system gradually increases with the rise of temperature [27; 28]. At the same temperature, the CED value of ε-CL-20 and DNTF isfar below that of TKX-50, which is consistent with the experimental results of ε-CL-20 and DNTF sensitivity higher than TKX-50[29; 30]. In addition, the CED values of the blend systems are higher than the pure ε-CL-20 and DNTF, indicating that the blend structure can improve the shortcomings of ε-CL-20's high sensitivity and increase its thermal stability.

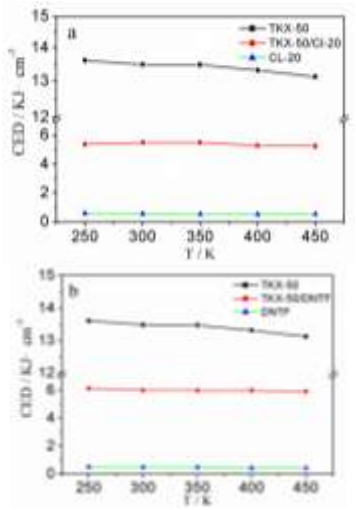


Figure4. *CED vs. temperature ofTKX-50/ε-CL-20 (a) and TKX-50/DNTF (b)*

Mechanical Properties Analysis

Mechanical properties are one of the crucial properties of energy materials, and their performance directly affects their application. Engineering modulus is key indicator for evaluating the hardness, tensile strength and fracture strength of materials. There are engineering modulus such as tensile modulus (E), shear modulus (G) and bulk modulus (K). K/G and (C_{12}-C_{44}) are parameters related to the ductility of materials. The larger the value of K/G [31] and C_{12}-C_{44} are, the better the material ductility is. Poisson ratio (γ) can reflect the plasticity of the material, and the materials have plasticity within 0.2 ~ 0.4.

Fig. 5 indicates the mechanical properties of the pure TKX-50 at 250K~450K. With the temperature rise, the E, G and K values of TKX-50 is gradually reduced. This indicates that the rigidity, hardness and fracture strength of TKX-50 decrease as the temperature increasing. Compared with the TKX-50, the E, G, K values of TKX-50/ε-CL-20 and TKX-50/DNTF system are reduced to different extents (Table 2), while the values of K/G and C_{12}-C_{44}increase, indicating that the TKX-50/ε-CL-20 and TKX-50/DNTF system have lower rigidity, hardness and fracture strength than TKX-50, and better ductility. In addition, the γ values of TKX-50/ε-CL-20 and TKX-50/DNTF system are higher than that of TKX-50, indicating the elastic elongation of the blend system is enhanced.

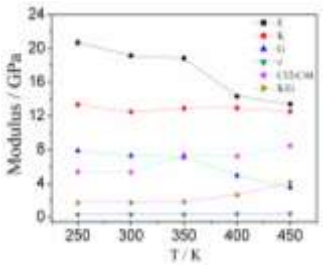


Figure5. *Mechanical properties of TKX-50*

Table2. *Mechanical properties of TKX-50, TKX-50/ε-CL-20 and TKX-50/DNTF*

Modulus	TKX-50	TKX-50/ε-CL-20	TKX-50/DNTF
E[a]	19.14	17.1	7.70
K[a]	12.47	11.62	11.81
G[a]	7.28	6.34	2.74
K/G	1.71	2.30	4.31
γ	0.31	0.35	0.40
(C_{12}-C_{44})[a]	5.33	9.71	8.64

[a]*Units for E,K,G and C_{12}-C_{44} are GPa.*

Conclusion

In this work，molecular dynamics simulations were performed to evaluate the compatibility of TKX-50 to ε-CL-20 and DNTF. The analysis of binding energy and radical distribution function shows that the compatibility of TKX-50 with ε-CL-20 is better than that of DNTF.

In addition, hydrogen bond and vander Waals interactions were shown to form in the blend system. The CED values of two blending systems gradually decreased. In addition, the CED values of the blend system are larger than those of ε-CL-20and DNTF, so the blending lowers the sensitivity ofε-CL-20 and DNTF, and increases their thermal stability.

Compared with the TKX-50, the E, G, K values of TKX-50/ε-CL-20 and TKX-50/DNTF system are somewhat reduced, while the value of K/G, γ and C_{12}-C_{44} are increase. Therefore the TKX-50/ε-CL-20 and TKX-50/DNTF system have lower rigidity, hardness and fracture strength, and better ductility than TKX-50. In short, the blend system makes the mechanical properties of pure substance better.

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