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Interactions between poly-(phthalazinone ether sulfone ketone) (PPESK) and TNT or TATB in polymer bonded explosives: a molecular dynamic simulation study

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Abstract The glass transition temperature (T_g) and density of poly-(phthalazinone ether sulfone ketone) (PPESK A) were estimated by molecular dynamic (MD) simulation. A novel poly-(phthalazinone ether sulfone ketone) (PPESK B) was constructed by introducing nitrol and amini energetic groups into PPESK A, and T_g and density were also simulated for PPESK B. The estimated T_g values of PPESK A were very close to experimental results, while for PPESK B three estimated values differed by < 5 K. The interactions between explosives and polymer binders of polymer bonded explosives (PBXs) were simulated by MD. Comparison of the cohesive energy densities (CED) and solubility parameter (δ) values of PBXs, polymer binders, and mono-explosives indicate that, upon introducing polymer binders, the CED and δ values of PBXs decreased compared with those of corresponding mono-explosives. The binding energies (E_{bind}) imply that 2,4,6-trinitrotoluene-based PBXs are more stable than 1,3,5-triamino-2,4,6-trinitrobenzene (TATB)-based PBXs. The mechanical properties, Young's modulus E, shear modulus G, bulk modulus K, Poisson's ratio γ and Cauchy pressure (C_{12}–C_{44}) of the PBXs were assessed. The rigidity of the PBXs was found to be lower than that of mono-explosives. All K/G values were positive, indicating that PBXs are flexible. Based on these mechanical properties results, PBXs using PPESK B as a binder are superior to those using PPESK A as a binder. Due to the low C_{12}–C_{44} values of the PBXs, the ductility of the materials of the fracture surface is poorer, especially for TATB-based PBXs.

Introduction

Research into energetic materials has great significance. Scientists are constantly striving to find explosives with high energy and low sensitivity, as such explosives can be applied widely to a variety of fields, and low sensitivity is crucial for transportation and storage [1]. Polymer bonded explosives (PBXs), as one kind of high energy–low sensitivity explosive, consist of 90–95 wt% energetic particles and 5–10 wt% polymer binders. Compared with mono-explosives, PBXs have many advantages, such as high energy, low mechanical sensitivity, good mechanical properties and workability [2, 3]. The polymer binders used in PBXs, such as polyisobutylene (PIB), ethylene fluorinated olefin copolymer (for example Kel-F and Vinton-A) and polystyrene (PS), are inert but exhibit lower adhesion with the explosive crystals. To address this problems, plasticizers are imported into these explosives, which not only enhance their adhesion properties but also reduce the thermal decomposition temperature of the PBXs [4, 5]. In addition, the reactions path for PBXs can be altered (due

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to inert binders adhering to explosive crystals), for example, by lowering the competitive reaction effect (evaporation and gas phase pyrolysis) and depressing the activation energy of the thermal decomposition reaction of the explosives [6, 7]. Traditional polymer binders have fewer energetic groups and influence the energy release of an explosive. Thus, many high energy and density polymer binders are increasingly being studied. The main method used to overcome the influence of energy release of the polymer binders [8] is to introduce energetic functional groups, such as nitrate ester ($-ONO_2$), nitro ($-NO_2$), nitramino ($-NNO_2$) and azido ($-N_3$), into the polymer chains. Furthermore, energetic thermal plastic elastomers, such as glycidyl azide polymer (GAP), poly-3-nitro methyl-3-methyloxetane (Poly NIMMO) [9, 10] and poly-3-bis(nitratomethyl)-3-methyloxetane (BNMO), not only elevate the explosive property, but also improve the oxygen balance of the system. However, synthesis of these polymers is still complex and their chemical preparation fraught with danger. Meanwhile, most of these binders are fatty chain polymers, thus their thermal decomposition temperatures are lower than those of explosive particles, which implies that they have low mechanical strength and weak chemical stability. So, it remains difficult to achieve binders with good physical properties and high energy at the same time.

Nitrogen-containing heterocyclic polymers have been used in heat-resistant materials and fibers due to their comprehensive properties such as excellent thermal and chemical stability, high tensile strength, high elastic module and good flame retardant properties. However, such polymers, e.g., polyimide and polybenzimidazoles, are reported only rarely as energetic polymer binders despite their many merits. This is mainly because of their poor solubility, hard processability and considerable cost. The core structure of the polymer phthalazinone (DHPZ) (molecular structure and 3D model are shown in Fig. 1a and b) has a twisted non-coplanar geometry, which may also exists in polymers. Several phthalazinone-containing polymers have been synthesized by Jian et al. [11, 12]. These polymers are hard to crystallize; on the other hand, they can endure high temperature and have good solubility, which are properties superior to traditional polymer binders. Based on these advantages, DHPZ-containing polymers, e.g., poly-(phthalazinone ether sulfone ketone) (PPESK), have been used as polymer binders. We wondered if these desirable properties of PPESK would combine well with explosives, and if the energy release of PBXs could somehow be improved. Herein, molecular dynamics (MD) simulation methods have been employed to study the interactions between explosives and polymer binder PPESK A (Fig. 1c), as well as the novel energetic DHPZ-containing polymer PPESK B (Fig. 1d). PPESK B was designed by introducing $-NO_2$ and $-NH_2$ groups into PPESK A. Initial simulations found that the optimal ratio of sulfone to ketone segments is 8:2, resulting
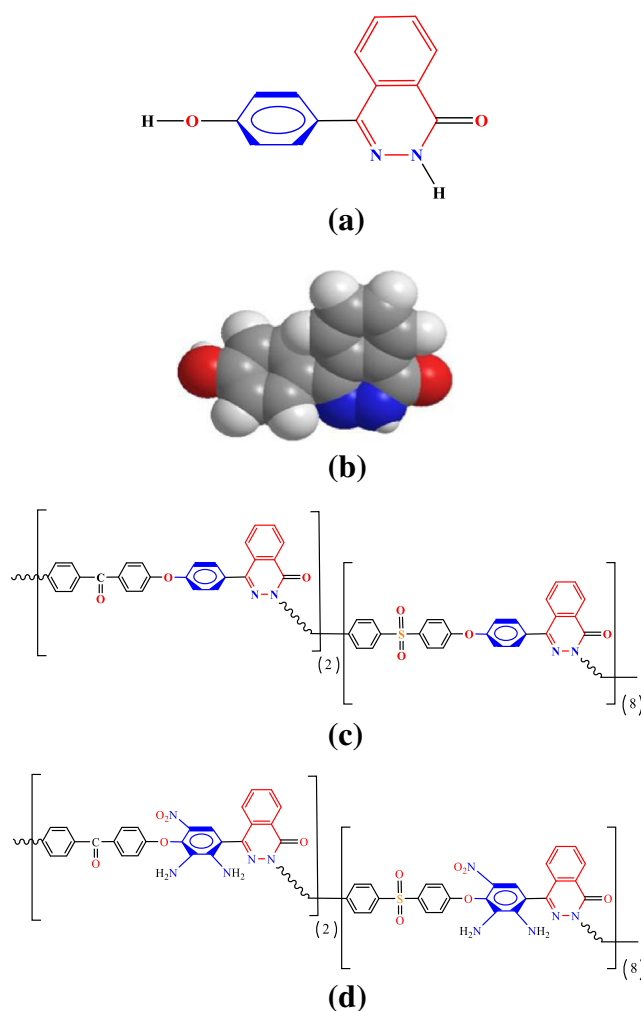

Fig. 1 **a** Molecular structure of phthalazinone (DHPZ). **b** Three dimensional (3D) model of DHPZ implying a twisted non-coplanar structure. **c** Poly-(phthalazinone ether sulfone ketone) PPESK A. **d** The novel poly-(phthalazinone ether sulfone ketone) PPESK B

in high T_g values (ratios tested ranged from 0:10 to 10:0). Specific T_g values and figures can be found in Table S1 and Fig. S1, respectively. Herein, a sulfone: ketone ratio of 8:2 for both the PPESK A and PPESK B were considered as the optimal polymer binder ratio for PBX for subsequent simulations.

TNT (2,4,6-trinitrotoluene) (Fig. 2a) is an insensitive explosive once widely used in weapons, e.g., during World War I and World War II, due to its good stability and high energy [13, 14]. The explosive 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) (Fig. 2c) is also an insensitive explosive, but has more energy and higher density than TNT [15]. PPESK A and PPESK B were chosen as polymer binders with TNT or TATB, respectively, to construct the PBX models. Interactions between binders and explosives were simulated based on these PBX models. Similar properties were subsequently simulated to the mono-explosives and the polymer binders.
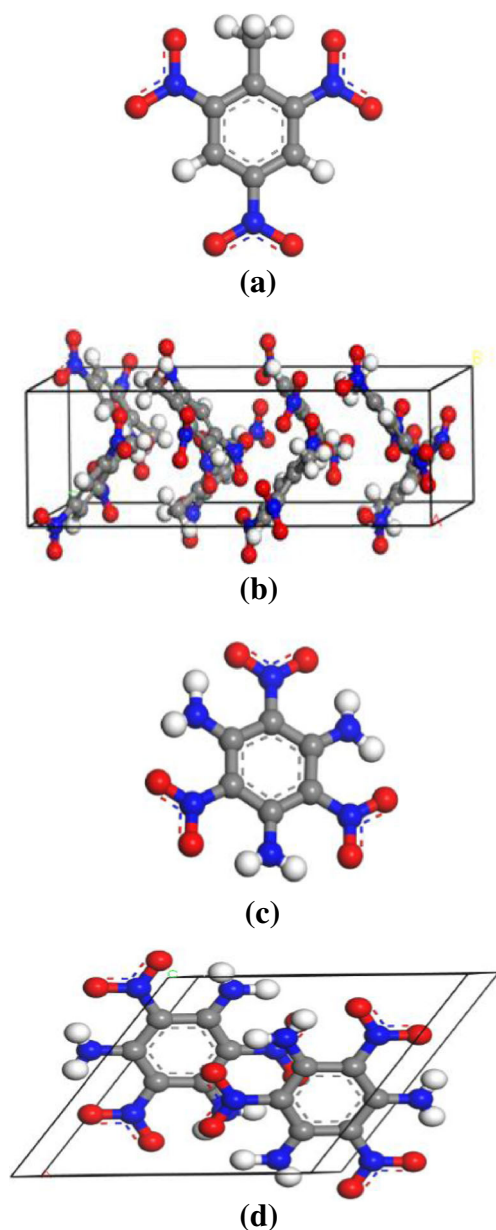
(a)

(b)

(c)

(d)

Fig. 2 **a**, **c** Molecular model and **b**, **d** primitive cell of TNT (2,4,6-trinitrotoluene) (**a**, **b**) and TATB (1,3,5-triamino-2,4,6-trinitrobenzene) (**c**, **d**)

Modeling and methods

Constructing models of amorphous cells polymers and PBXs

The COMPASS force field can be applied to the study of interactions of different components and condensed phase complexes. It works especially well for nitro-containing energetic complexes when using MD simulations [16, 17].

PPESK A and PPESK B amorphous cells (shown in Fig. 3) were constructed via five corresponding single chains; the ends of the polymer chains were saturated by chlorine atoms.

The PPESK A and PPESK B amorphous cell models consist of 2450 and 2750 atoms, respectively.

To investigate the interactions of polymer binder and mono-explosives, a $3 \times 6 \times 2$ TNT super cell (288 molecules and 6048 atoms in all) and a $5 \times 5 \times 5$ TATB super cell (250 molecules and within 6000 atoms in all) were constructed using experimental data obtained from the Cambridge Crystallographic Data Center (CCDC). The TNT primitive cell belongs to the Pca_{21} space group and has the cell parameters $a = 14.911$ Å, $b = 6.077$ Å, $c = 20.017$ Å, $\alpha = \beta = \gamma = 90°$ [18]. However, the TATB primitive cell belongs to the 2P-1 space group and has the cell parameters $a = 9.010$ Å, $b = 9.028$ Å, $c = 6.812$ Å, $\alpha = 108.580°$, $\beta = 91.820°$, $\gamma = 119.970°$ [19]. Subsequently, the two super cells were cleaved along the three different crystal faces (1 0 0), (0 1 0) and (0 0 1), then 10 Å vacuum slabs were added for each new TNT super cell, and 12 Å vacuum slabs for the three TATB super cells. The optimized single chain PPESK A and PPESK B were placed into the six different boxes separately. The TNT-based PBX models are shown in Fig. 4 and the TATB-based PBX models are shown in Fig. S3. Taking, as an example, the PPESK A/TNT (1 0 0) PBX model, which contains 6538 atoms in all, the polymer binder accounts for 6.6 wt% of the PBX, and the mass ratios of the polymer binders were calculated in the same way for the other PBX models. For PPESK B/TNT [PPESK B (7.4 wt%)], PPESK A/TATB [PPESK A (6.5 wt%)] and PPESK B/TATB [PPESK B (7.5 wt%)], the ratios of all polymers are within the range of 5–10 wt%, meeting the requirement of binders for the PBX. Additionally, PPESK A/TNT(6.6 wt%) and PPESK A/TATB(6.5 wt%) have roughly the ratios ascribed to PBX and are similar to PPESK B. The construction of all models and simulations were fully simulated using Material Studio software [20].

MD simulations of PPESK A, PPESK B and PBXs

The amorphous polymers PPESK A and PPESK B consist of 2450 and 2750 atoms, respectively, and both polymer binders were optimized to get the lowest energy and stable configurations for further optimization. The specific MD simulation for both amorphous polymers was calculated in two steps: an equilibration state and a productive state. In the equilibration state, an annealing process to give relaxed amorphous polymers was simulated using the following conditions: isothermal (NVT) ensemble, 2000 ps total time step and 700 K. To obtain a stable structure for subsequent simulation, conditions of isobaric-isotherm (NPT) ensemble, 280 K and 2000 ps were set for the simulation. In the production state, the amorphous polymers were cooled gradually from 700 K to 280 K at 20 K intervals. At each specific temperature, the stable configuration of the MD simulation was used as the initial structure for the subsequent MD simulation. For the MD simulation process, PPESK A and PPESK B were simulated for 500 ps of the total time at each temperature under

(a) **(b)**
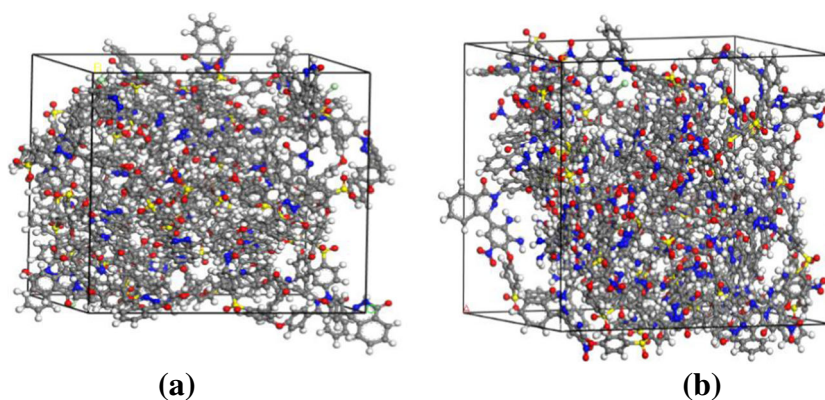
the isobaric-isotherm (NPT) ensemble; the first 300 ps was used
for equilibration and the remaining 200 ps for data processing.
The temperature and the pressure were controlled by an
Anderson [21] thermostat and Barostat [22], respectively, with
the time step set as 1 fs. Similarly, the same parameters were used
for PBXs MD simulation, the difference being that total times of
2000 ps were used for the MD simulation.

Results and discussion

Glass transition temperatures and densities

The T_g values of PPESK A and PPESK B were obtained by
plotting temperature against density, free volume and volume.

According to Fig. 4 (and as shown in Table 1), the highest
value 568.4 K is obtained by the plot of free volume vs tem-
perature, while the lowest value 543.2 K is from the plot of
volume vs temperature. Among the values, 552.0 K, obtained
by plotting density vs temperature, is closest to the experimen-
tal value of 557 K [14].

The simulated values are reliable because the difference
between the simulated and experimental values is <15 K.
The simulated T_g values of PPESK B are 600 K, 596.6 K
and 599.6 K (see Fig. 5) calculated three ways. The difference
between the simulated values and experimental values of
PPESK B is < 5 K. Comparing the values of two simulated
polymer binders, those of PPESK B are about 40 K higher
than those of PPESK A. Density of the polymer binders was
also obtained via MD simulation, with the simulated value of

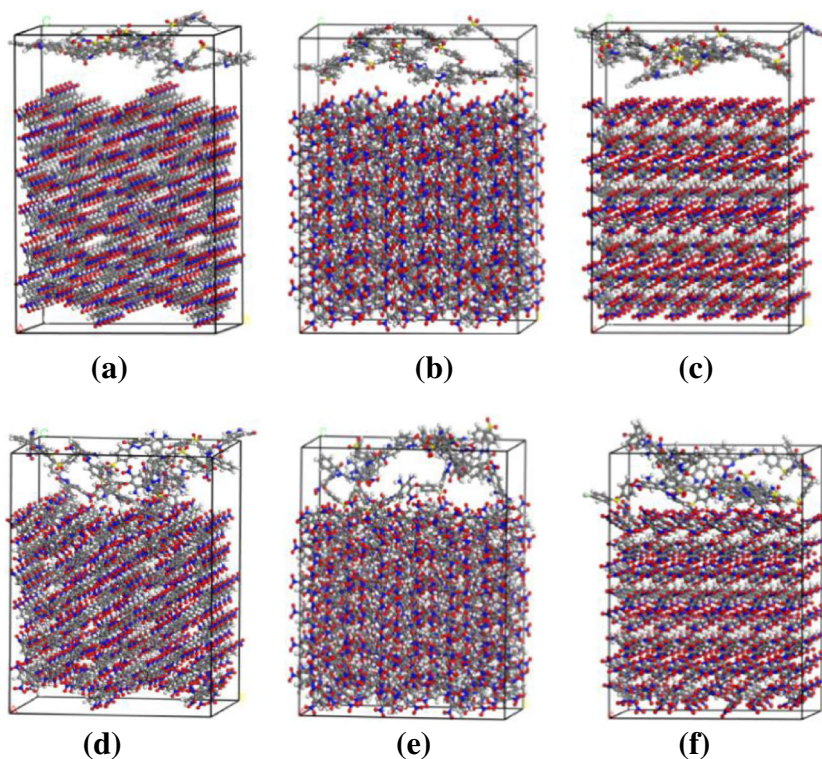**(a)** **(b)** **(c)**

(d) **(e)** **(f)**

Table 1 Experimental and estimated values of the glass transition temperature (T_g) for poly-(phthalazinone ether sulfone ketone) PPESK A and PPESK B

Property		Density	Free volume	Volume
T_g(K)	PPESK A	552.0	568.4	543.2
	PPESK B	600	596.6	599.6
	557 [14]			

PPESK A being 1.32 g cm^{-3} at 298 K, which is close to the experimental value of 1.35 g cm^{-3} [14]. For PPESK B, the estimated density value is 1.37 g cm^{-3}, which is higher than that of PPESK A.

For each equilibrated PBX model, density values were obtained after MD simulation. The density values of TNT-based PBXs are shown in Table 2, and those of TATB-based PBXs are shown in Table S1. The density values of TNT-based PBXs follow the sequence: PPESK (Aor B)/TNT(0 0 1) > PPESK (Aor B)/TNT(1 0 0) > PPESK (Aor B)/TNT(0 1 0), and the same sequence is followed by TATB based PBXs. This implies that the simulated values of T_g and the density of PPESK B are higher than the respective values of PPESK A. This is due mainly to the energetic groups nitro (−NO$_2$) and amino (−NH$_2$) of PPESK B. Specifically, the H

atoms from the NH$_2$$^-$ groups in PPESK B can form hydration bonds with N atoms from the NO$_2$$^-$ groups in TNT.

CED and solubility parameters

The CED and solubility parameters are used to estimate the miscibility of different components. According to the "like dissolves like" theory, the closer the values of the solubility parameters, the better the miscibility of the two composites [23, 24]. The solubility parameter (δ) values of TNT, TATB, PPESK A, PPESK B and PBXs are displayed in Table 3. The PPESK A and PPESK B solubility parameters (δ) values are very similar, indicating that the two compounds have similar miscibility. The δ value of the two mono-explosives are very close, the δ value of the TNT is 31.761 (J/cm^3)$^{1/2}$ while the δ value of the TATB is 33.669 (J/cm^3)$^{1/2}$. The difference value δ ($\Delta\delta$) of the PPESK (A or B) and the mono-explosive (TNT or TATB) is about $\Delta\delta = 15$ (J/cm^3)$^{1/2}$. The differences for PBXs [PPESK (A or B)/(TNT or TATB)] and mono-explosive (TNT or TATB) are less than 10 (J/cm^3)$^{1/2}$ ($\Delta\delta$) except for PPESK B/TATB(0 1 0) [$\Delta\delta = 11.23$ (J/cm^3)$^{1/2}$]. Furthermore, the solubility parameters of TATB-based PBXs decreased more than those of TNT-based PBXs compared with their corresponding mono-explosives, indicating that the miscibility of the PBXs
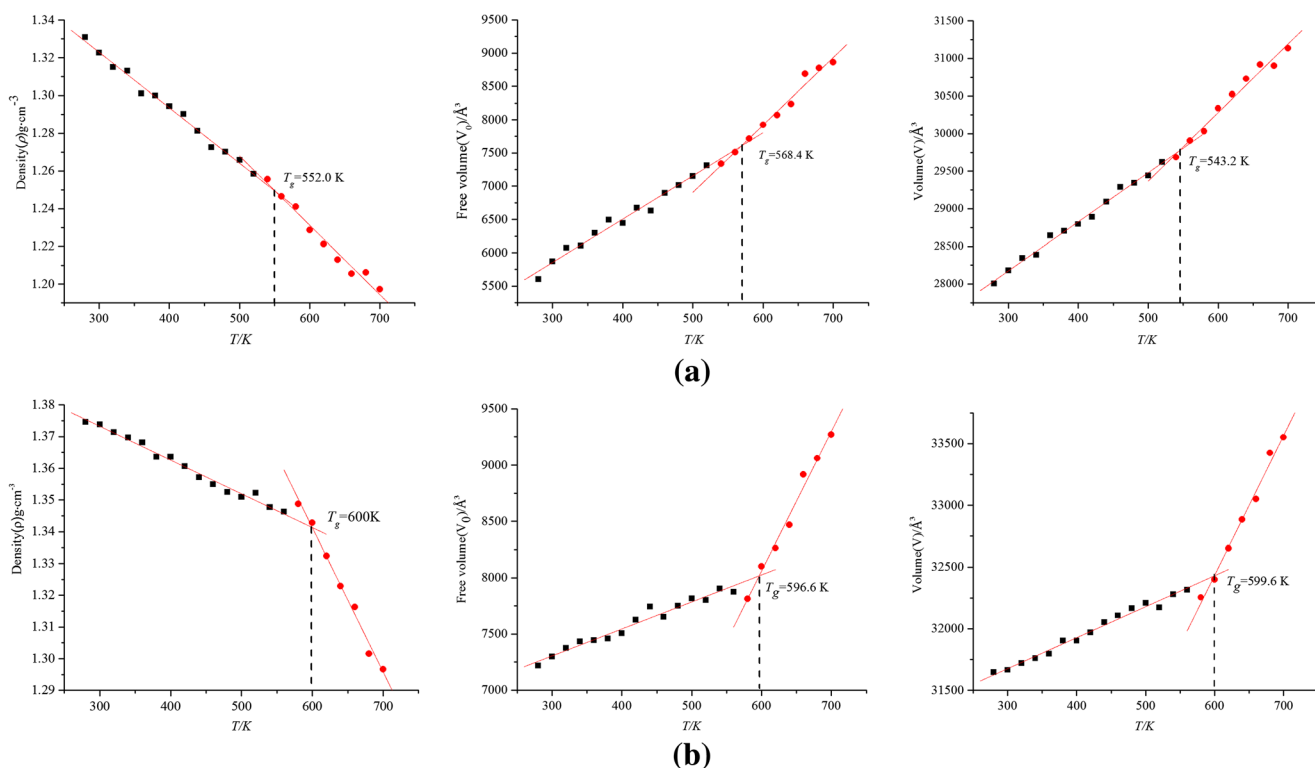

Fig. 5 **a**, **b** Estimated T_g values of PPESK A and PPESK B obtained in three different ways: density, free volume and volume vs temperature plot of the PPESK. **a** PPESK A, **b** PPESK B

Table 2   Estimated density values for polymer bonded explosives (PBXs)

Property	ρ (g cm^{-3})					
Compound	PPESK A/TNT			PPESK B/TNT		
PBX (value)	1 0 0 (1.336)	0 1 0 (1.302)	0 0 1 (1.425)	1 0 0 (1.351)	0 1 0 (1.316)	0 0 1 (1.440)

has been improved by introducing polymer binders (PPESK A or PPESK B) into the mono-explosive (TNT or TATB).

Binding energy

The binding energy (E_{bind}) is used as a measure of the interaction between different components. The E_{bind} value is the inverse of the E_{inter}, which is obtained from the equilibrium state of the total energy PBXs minus the equilibrium state energy of the polymer binder E_{PPESK}, and then deduct the equilibrium state energy of the mono-explosive $E_{explosive}$. The relationship of these energies is shown in Eq. (1) [25], where $E_{explosive}$, E_{PPESK} and E_{PBX} represent the equilibrium state energy of mono-explosive (TNT or TATB), PPESK (A or B) and PBXs, respectively. The stability of composite surfaces is positively correlated with E_{bind} values. The PPESK A/TNT and PPESK B/TNT E_{bind} values are shown in Table 4, while for PPESK A/TATB and PPESK B/TATB, the E_{bind} values can be seen in Table S3. For TNT-based PBX, the E_{bind} values of PPESK A/TNT follow the sequence: PPESK (A)/TNT(0 1 0) > PPESK (A)/TNT(0 0 1) > PPESK (A)/TNT(1 0 0).

However, this is different for PPESK B/TNT PBXs, where the E_{bind} values follow the sequence PPESK (B)/TNT(1 0 0) > PPESK (B)/TNT(0 1 0) > PPESK (B)/TNT(0 0 1). Among the E_{bind} values, the PPESK (B)/TNT(1 0 0) is the greatest, which indicates that PPESK B has the most stable state on the TNT (1 0 0) crystal surface. Furthermore, the E_{bind} values of TATB-based PBXs follow the sequence: PPESK (A or B)/TATB(0 0 1) > PPESK (A or B)/TATB(1 0 0) > PPESK (A or B)/TATB(0 1 0). These results imply that polymer binders are stable on the TATB(0 0 1) crystal surface but are unstable on the TATB(0 1 0) crystal surface. Compared with the E_{bind} values of TNT- and TATB-based PBXs, the E_{bind} values of TATB-based PBXs are lower than those of TNT-based PBXs, which indicates that the stability of TNT-based PBXs is superior to that of TATB-based PBXs, due to the low surface energy polarization of the TATB crystal [26]. Thus, interface modifications of the TATB crystals need to be improved and several methods to enhance the particle surface roughness, such as γ-radiation grafting methods or using microwave and ultraviolet radiate to deal with TATB powder, have been tested [27].

$$E_{bind} = -E_{inter} = -\left(E_{PBX} - E_{explosive} - E_{PPESK}\right) \qquad (1)$$

Mechanical properties

The mechanical properties of PBXs are closely connected with their preparation and use. The elastic properties consist of the elastic coefficient, Young's modulus (E), Poisson's ratio (γ), etc. The parameters of material stress and strain tensor depend mainly on σ_I and ε_I. For the statistical mechanics of the elasticity, Hooke's law is shortened as in Eq. (2), where σ_I is stress, ε_j is strain, and C_{ij} is the 6 × 6 elastic coefficient matrix. The elastic coefficient of materials are the 36 elastic constants in matrix (3). Due to the existence of strain energy and the symmetry of the matrix, $C_{ij} = C_{ji}$, only 21 elastic constants are needed to analyze the stress and strain properties of these materials [28, 29].

$$\sigma_I = C_{ij}\varepsilon_j (I, j = 1, 2, \ldots\ldots, 6) \qquad (2)$$

As the symmetry of the materials increases, the independent elastic coefficients decrease. Isotropic materials

Table 3   Simulated cohesive energy densities (CED) and δ values of 2,4,6-trinitrotoluene (TNT), 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), PPESK A, PPESK B and PBXs

	CED [J/cm^3]	δ [(J/cm^3)$^{1/2}$]
PPESK A	318.6	17.85
PPESK B	317.9	17.83
TNT	1009	31.76
PPESK A/TNT(1 0 0)	746.7	27.33
PPESK A/TNT(0 1 0)	711.5	26.67
PPESK A/TNT(0 0 1)	793.2	28.16
PPESK B/TNT(1 0 0)	752.4	27.43
PPESK B/TNT(0 1 0)	713.5	26.71
PPESK B/TNT(0 0 1)	678.0	26.04
TATB	1134	33.67
PPESK A/TATB(1 0 0)	594.5	24.38
PPESK A/TATB(0 1 0)	582.7	24.14
PPESK A/TATB(0 0 1)	765.7	27.67
PPESK B/TATB(1 0 0)	735.4	27.11
PPESK B/TATB(0 1 0)	503.6	22.44
PPESK B/TATB(0 0 1)	764.4	27.65

Table 4 Binding energy (E_{bind}) values for TNT-based PBXs

Direction	$E_{explosive}$ (TNT) kcal mol^{-1}	E_{PPESK}	E_{PBX}	E_{inter}	E_{bind}
PPESK A / TNT (1 0 0)	4768.138	4421.068	8468.295	−720.911	720.911
PPESK A / TNT (0 1 0)	4958.243	6347.969	8623.962	−2682.25	2682.25
PPESK A / TNT (0 0 1)	4736.608	4926.89	8462.429	−1201.069	1201.069
PPESK B / TNT (1 0 0)	4768.138	11,597.47	8904.692	−7460.916	7460.916
PPESK B / TNT (0 1 0)	4958.243	5048.22	9011.458	−995.00	995.00
PPESK B / TNT (0 0 1)	4736.608	4783.274	8826.582	−693.3	693.3

have only two independent elastic coefficients, C_{11} and C_{12}. The elastic constant C_{ij} values are shown in Table 5, which can be divided into three parts C_{11}, C_{22}, C_{33}; C_{44}, C_{55}, C_{66}; and C_{12}, C_{13}, C_{23}, as the other elastic constant values are almost zero. For these three parts of TNT-based PBXs, elastic constant values have decreased to some extent compared to those of pure TNT, meaning improved isotropy for PBXs. Similarly, the elastic constants C_{ij} of TATB based PBXs are shown in Table S4. The C_{ij} values can be divided into three parts C_{11}, C_{22}, C_{33}; C_{44}, C_{55}, C_{66} and C_{12}, C_{13}, C_{23}, while the other values are almost zero or below zero, except for C_{15} and C_{35}. Since the polymer binders have been introduced into TNT or TATB, the ratio of the binder of the PBXs can be divided into two groups [PPESK A/TNT (6.6 wt%), PPESK A/TATB (6.5 wt%) and PPESK B/TNT (7.4 wt%) PPESK B/TATB (7.5 wt%)]. Using the same polymer binder, the elastic constant values of TATB-based PBXs are lower than those of TNT-based PBXs, which implies that the isotropy of TATB-based PBXs is superior to that of TNT-based PBXs with the same polymer binder at a similar ratio. In addition, upon comparing elastic values, PBX isotropy was improved compared to that of mono-explosives. The modulus values of the materials indicate to what degree the materials resist deformability. This value is closely related to the plasticity and fracture properties of the materials, which act as indicators to assess the rigidity of the materials. For ideal isotropic materials, the elastic constants can be simplified as two independent coefficients (λ and μ) [30, 31]. Additionally, the mechanical parameters can be calculated based on the elastic constants. For E, shear modulus (G), bulk modulus (K) and Cauchy pressure (C_{12}−C_{44}), all of these values are obtained from the two independent coefficients (λ and μ), and Eq. (4) implies a relationship between the modulus and the two independent coefficients. The G values are closely connected with rigidity

Table 5 Elastic constant of TNT-based PBXs

C_{ij}	TNT	PPESK A/TNT			PPESK B/TNT		
		(1 0 0)	(0 1 0)	(0 0 1)	(1 0 0)	(0 1 0)	(0 0 1)
11	6.4808	2.6945	1.5380	2.8586	2.2496	4.1308	5.4494
22	8.2171	7.6231	0.5989	2.8170	8.3207	5.7804	6.6828
33	6.6207	4.6751	3.5097	−2.7679	5.0794	5.5941	6.3481
44	3.1787	1.4476	0.6878	0.9320	2.6427	2.1533	2.1427
55	4.6665	2.1044	1.3833	−0.4112	2.8439	2.6677	2.3091
66	1.7645	0.9520	0.6975	1.2777	2.0463	1.8231	2.2463
12	4.0908	2.3520	−0.0680	0.2202	2.0880	1.2629	2.2345
13	3.8634	1.3713	0.6388	−0.8172	1.6260	1.9511	2.3970
15	0.0368	−2.3123	0.1143	0.7677	0.1124	−0.0609	−0.0237
23	5.4914	3.6602	0.2679	−2.5071	3.2104	2.3660	2.4039
25	−0.0314	−1.8775	−0.0787	2.0274	−0.0358	0.0007	0.1195
35	−0.1303	−1.9083	−0.0148	1.4615	−0.1493	0.0110	−0.2026
46	−0.0356	−0.4863	0.0522	−1.0674	0.0579	−0.0566	−0.3636
λ	0.6996	1.9948	0.0365	−0.2298	0.1947	0.739	1.6947
μ	3.2033	1.5014	0.9229	0.5995	2.5109	2.2147	2.2327

and yield strength of the materials. The K values indicate the degree of fracture of the materials.

$$(C_{ij})_{6\times6} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46} \\ C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56} \\ C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66} \end{bmatrix} \quad (3)$$

$$\begin{aligned} E &= \mu\left(\frac{3\lambda + 2\mu}{\lambda + \mu}\right); \\ K &= \lambda + \frac{2}{3}\mu; \\ G &= \mu \\ \gamma &= \frac{\lambda}{2(\lambda + \mu)}; \end{aligned} \quad (4)$$

The γ values of TNT- or TATB-based PBX are almost positive except for PPESK A/TNT(0 0 1) and PPESK A/TATB(0 0 1). Most Poisson's ratio (γ) values of the PBXs are within the range 0.2–0.4, which indicates that they have more plastic properties than their corresponding mono-explosives. Moreover, the K/G values and the Cauchy pressure $C_{12}-C_{44}$ are two measurements of the ductility of the materials. The difference is that the former is based on degree of plastic deformation, while the latter is based on morphology of the fracture surface of the materials. The E, G and K values of TNT-based PBXs are lower than those of pure TNT, which means that the rigidity of the PBXs are reduced compared to the mono-explosives. The K/G values of PPESK A/TNT(1 0 0), PPESK B/TNT(0 1 0) and PPESK B/TNT(0 0 1) are higher than the corresponding values of pure TNT, but the other values of PBXs are the opposite. For PBXs such as PPESK A/TNT (1 0 0), PPESK B/TNT (0 1 0) and PPESK B/TNT(0 0 1), ductility has been improved. The K and G values decrease a lot compared with the corresponding mono-explosives; the specific values are displayed in Table 6.

Table 6 Mechanical properties of PPESK (A and B)/TNT composites with different crystalline surfaces. E Young's modulus, G shear modulus, K bulk modulus, $C_{12}-C_{44}$ Cauchy pressure

Property	TNT	PPESK A/TNT			PPESK B/TNT		
		(1 0 0)	(0 1 0)	(0 0 1)	(1 0 0)	(0 1 0)	(0 0 1)
E(GPa)	6.98	3.86	1.88	0.83	5.20	4.98	5.43
K(Gpa)	2.84	3.00	0.65	0.17	1.87	2.22	3.18
G(Gpa)	3.20	1.50	0.92	0.60	2.51	2.21	2.23
γ	0.09	0.29	0.02	−0.31	0.04	0.13	0.29
K/G	0.89	2.00	0.71	0.28	0.74	1.00	1.43
$C_{12}-C_{44}$	0.91	0.90	−0.76	−0.71	−0.55	−0.89	0.09

For the Cauchy pressure values of the PBXs, only PPESK A/TNT (1 0 0) (0.91) and PPESK B/TNT(0 0 1) (0.09) values are positive ($C_{12}-C_{44}$), while the other values of the PBXs are negative, as shown in Table 6. The E, K, G and Cauchy pressure values of TATB-based PBXs are presented in Table S5. The rigidity of TATB-based PBXs decreased much than that of TNT-based PBXs upon adding the same polymers to the mono-explosive. The K/G ratio and Cauchy pressure ($C_{12}-C_{44}$) values of TATB-based PBXs are similar to those of TNT-based PBXs. The K/G values of TATB-based PBXs are all positive, indicating that TATB-based PBXs exhibit plastic deformation. However, Cauchy pressure ($C_{12}-C_{44}$) values for TATB-based PBXs are low, implying that ductility of the materials in terms of morphology of the fracture surface are worse. This is due to the lower surface energy polarization of the TATB crystal; this problems can be addressed by dealing with TATB crystals.

Conclusions

To overcome the drawbacks of non-energetic groups, and the low solubility and processing temperature of traditional polymer binders, poly-(phthalazinone ether sulfone ketone) (PPESK A) and the energetic PPESK B can be used as polymer binders. The T_g values of the amorphous cells of polymers PPESK A and PPESK B were estimated by three means: density, free volume and volume. The T_g values of PPESK A obtained by these three methods are close to the experimental values, and the corresponding estimated T_g values of PPESK B are all within a difference of 5 K. The density values of the two polymers are similar, but the value for PPESK B is higher than that for PPESK A. For equilibrated PBXs, the density values follow the sequence PPESK (A or B)/ Explosive (TNT or TATB)(0 0 1) > PPESK (A or B)/ Explosive (TNT or TATB)(1 0 0) > PPESK (A or B)/ Explosive (TNT or TATB) (0 1 0). The CED and δ values of polymers binders (PPESK A or B), mono-explosives and PBXs were simulated, and those of PBXs found to be lower than those of the corresponding mono-explosives. The E_{bind} of TNT-based PBXs fall within one of two different situations depending on the different polymer binders. With PPESK A as the binder for PBXs, E_{bind} values follow the sequence PPESK (A)/TNT(0 1 0) > PPESK (A)/TNT(0 0 1) > PPESK (A)/TNT(1 0 0), whereas, with PPESK B as the binder for PBXs, the E_{bind} values have the following sequence: PPESK (B)/TNT(0 1 0) > PPESK (B)/TNT(0 0 1) > PPESK (B)/ TNT(1 0 0). In addition, E_{bind} values of TATB-based PBXs follow the sequence: PPESK (A or B)/TATB(0 0 1) > PPESK (A or B)/ TATB(1 0 0) > PPESK (A or B)/TATB(0 1 0). Generally, E_{bind} values for TNT-based PBXs are higher than those of TATB-based PBXs because of the properties of the TATB crystal. Finally, the mechanic properties of TNT- and

TATB-based PBXs were simulated. The E values of the PBXs were lower than corresponding values of the mono-explosives, which indicates that the rigidity of the PBXs is decreased relative to mono-explosives. The rigidity of TNT-based PBXs is higher than that of TATB-based PBXs. The K/G ratio values are positive for TNT- and TATB-based PBXs, indicating that the PBXs exhibit plastic deformation. The Cauchy pressure values are low, especially for TATB-based PBXs, which mean that the ductility of the materials on the fracture surface are worse. These properties are related to the structure of the TATB crystal.

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