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Atomistic studies of RDX and FOX-7 -Based Plastic-Bonded explosives: molecular dynamics simulation

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Abstract

Molecular dynamics simulations were carried out to study the effects of interface interactions between a crystalline structure and a plastic bonded explosive (PBX) system. In this work, the hydroxyl-terminated polybutadiene (HTPB) represents the polymer, isophorone diisocyanate (IPDI) is the diisocyanate and dioctyl adipate (DOA) is the plasticizer. Two different crystal high explosives components were used, hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), which is characterized by a high chemical stability, and 1,1-diamino-2,2-dinitroethylene (FOX-7) which is known for its low sensitivity. The molecular model is composed of RDX or FOX-7 which represent the main body and PBXs which contain a small amount of polymer/plasticizer. The polymer and crystal were modeled using the atomistic classical force-field COMPASS. Interface structures of RDX and FOX-7 (hkl) crystal surface together with the HTPB-IPDI/DOA blend were predicted as well as interfacial binding energies. Bonding energy calculations have been performed in order to investigate the adhesion of the polymer to diverse atomic (hkl) planes of crystals. The (020) surface plane of RDX and (010) surface plane of FOX-7 have the largest binding energies and therefore a strongest ability to interact with the polymer was observed. NPT ensemble molecular dynamics simulation was applied to study specific mechanical properties: Poisson’s ratio ν and various moduli such as Young’s E, bulk K and shear G, for RDX and FOX-7 -based PBXs. The investigation of mechanical properties shows that the (020) plane providing HTPB-IPDI-DOA/RDX blends is more flexible and ductile. However, for FOX-7-based blends, the three crystallographic planes that were explored present surprisingly comparable ductility.

Keywords: Polymer-bonded explosives; molecular dynamics simulation; binding energy; mechanical properties

1. Introduction

Plastic-bonded explosives (PBXs) are widely used in many military and civilian applications because of their high safety, processing ease and superior strength. The next generation of PBX materials will be improved in terms of insensitivity and high energetic density properties combined with an enhanced mechanical integrity. Atomistic molecular modelling is fast becoming a useful tool in the design of explosive formulation as it can provide
theoretical data on various properties of explosives prior to experimentation in the lab. The use of modelling techniques contributes to decreasing hazards and accidents throughout the formulation process, and minimizes the time-frame in which explosive formulations are screened and tested, thus eliminating poor formulations before synthesizing new energetic materials.

Solid propellants and plastic bonded explosives (PBXs) incorporate different components, each one playing a specific role. First and foremost, a high density crystalline energetic material should be selected on the bases of high storage stability and high performance explosives, such as 1,3,5-triaza-1,3,5-trinitrocyclohexane (RDX) and 1,1-diamino-2,2-dinitroethylene (FOX-7) considered in this work and shown in Figure 1. The energetic material, RDX or FOX-7, is then incorporated in a polymeric binder characterized by acceptable mechanical properties, providing a greatly decreased risk of accidental ignition at the time of transportation, handling, or storage. The ability of a solid propellant to perform as an insensitive energetic material depends heavily on both the compatibility of the binder with the plasticizer and diisocyanate used in the formulation, as well as the compatibility of the explosives with the binder-plasticizer. A binder such as hydroxyterminated polybutadiene (HTPB) is often used in combination with a diisocyanate such as isophorone diisocyanate (IPDI) to form polymer chains. The compatibility of plasticizer and polymer is guaranteed when a plasticizer has a chemical structure similar to that of the polymer. For example, dioctyladipate (DOA) which has a low molecular weight, is often used with HTPB polymer.

To summarize, the main body of the PBX is made up of the energetic material RDX or FOX-7 (~85% and above), PBXs contain a small amount of polymers/plasticizer (~10%) and diisocyanates (~5%) is used to reticulate ingredients. A great importance has been given to explosives combined with polymer/plasticizer regarding the experimental measurement methods [1-6], and calculations using molecular dynamics simulation (MD) [7, 8]. Nevertheless, few modelling and simulation studies have looked at the predictions of mechanical properties of PBX [9, 10].

The HTPB-DOA system illustrated in Figure 1 was previously selected as an ideal system to investigate using modelling techniques for PBX formulations [11]. Crystalline surface morphology and crystal structure of RDX are well know from experimental data [12, 13], which show that main planes at the crystal surface are (020), (200) and (210), although the proportion of each depends largely on the solvent and temperature used for the re-crystallization process. On the other hand, the crystalline surface morphology of FOX-7 is not experimentally known; three planes in perpendicular directions, (100), (010) and (001) were chosen for FOX-7 in the present work. Prediction of mechanical properties of PBXs and FOX-7 was investigated on the bases of these fundamental planes for the space group (P21/n) of FOX-7.

This work will therefore focus on the simulation of the HTPB-IPDI-DOA/RDX interface at (020), (200) and (210) crystal faces and HTPB-IPDI-DOA/FOX-7 interface at (100), (010) and (001) crystal faces. One such simulation of crystal-amorphous phases has already been reported [7, 14-16]. However, no theoretical investigation has been performed using the diisocyanate as an extra ingredient in the explosives formulation. The inclusion of the diisocyanate is one of the key factors that enhances PBXs stability in explosives formulation.

Our main interest here is to test the ability of atomistic methods as a useful tool to predict interactions between RDX or FOX-7 crystals and the rest of the ingredients: the hydroxyl-terminated polybutadiene (HTPB) - isophorone diisocyanate (IPDI) - dioctyl adipate (DOA) polymer-plasticizer system. Mechanical properties, interfacial structure of (hkl) RDX or FOX-7 crystal surface with the HTPB-IDPI-DOA blend and interfacial bonding energy are also investigated. The objective is to understand fundamental physical properties of RDX and FOX-7 based PBXs, which is of utmost importance in the design and development of novel energetic materials. In this work, how different crystal surfaces of RDX or FOX-7 may interact with HTPB-IDPI-DOA blends is investigated and may help to better control experimental conditions (solvent, temperature, etc) at various processing steps prior to their incorporation into PBXs. This work is also part of an effort to develop theoretical tools to validate experimental data for known composite systems and to use them to screen optimum new explosives formulations prior to lab experiments.
2. Computational Details

Molecular simulations were carried out using the software program Materials Studio (MS) version 4.3 commercialized by Accelrys Inc. (San Diego, CA). Molecular dynamics (MD) calculations were performed using the Discover module and the COMPASS (condensed-phase optimized molecular potentials for atomistic simulation studies) force field [17] under periodic boundary conditions. Coulombic interactions were described with the Ewald summation approach with an accuracy of 0.01 kcal/mol and an update width parameter of 1.0 Å.

Crystal structure prediction was conducted with the MS Polymorph Predictor module. For more details on crystal structure prediction, the reader is referred to Gdanitz et al. [18] and Karfunkel et al. [19]. Amorphous polymer and plasticizer phases consisting of hydroxyl-terminated polybutadiene, isophorone diisocyanate and dioctyl adipate, were created using a combination of the algorithm developed by Theodorou and Suter [20] and the scanning method of Meirovitch [21] implemented in the MS Amorphous Phase module. A single bond was added per step, under the single substate per state rule, while using a substate width of 20. A random number seed was used to insure a properly randomized distribution in the cell. Two different model systems thus built were submitted to a preliminary equilibration treatment consisting of 1000 steps using the canonical ensemble NVT (constant number of atoms, constant volume and constant temperature) dynamics simulation with a velocity rescaling method to maintain a constant temperature, followed by 100,000 steps of minimization. Energy was minimized using three methods. The first used was steepest descent up to a maximum derivative of 100 kcal mol$^{-1}$, followed by the conjugate gradient method (using the Polak-Ribiere algorithm) down to maximum derivative of 10 kcal mol$^{-1}$. The Newton method using Broyden-Fletcher-Goldfarb-Shanno (bfgs) approach (maximum derivative of 0.001 kcal mol$^{-1}$) was used last. Model building was followed by NVT dynamics simulation for 1.0 ns, and the system with the lowest total energy
was selected for further calculations. Temperature in all simulations was equilibrated with the Andersen algorithm, using a collision rate of 1.0. The velocity Verlet algorithm was used to integrate equations of motion with a 1.0 fs time step. Only one blend composition was investigated, HTPB-DOA, containing 11 molecules of DOA, three 25-repeat unit HTPB chains, and four IPDI molecules, blend composition being of 45 w% HTPB, 45 w% DOA and 10% IPDI. Equation (1) shows how IPDI reacts with HTPB, which contains two hydroxyl groups.

\[ \text{Equation (1)} \]

Figure 2 illustrates HTPB-IPDI polymer chains and shows the isocyanate group (\(\text{N=C=O}\)) after its reaction with the hydroxyl functional group (-OH) of HTPB to form a urethane linkage. Reaction (1) may occur in absence of water (humidity), which it is the ideal condition for isocyanates.

Using the MS surface builder module, RDX and FOX-7 surfaces were first prepared by cleaving the crystal phase at the desired surface plane \((hkl)\), while assuring that the width and depth of the surface are larger than the non-bonded cut-off distance of 10.8Å. The cleaved surface was minimized as described above and was then placed in a supercell (2\(\times\)2\(\times\)3) for RDX and (4\(\times\)2\(\times\)6) for FOX-7, over which the HTPB-IPDI-DOA amorphous phase was inserted. The \(c\)-axis of the super cell was extended to 30Å, so that HTPB-IPDI-DOA can 'see' only one side of the surface even under periodic boundary conditions. NVT molecular dynamics simulation was then performed for 300 ps with a 1.0 fs time step at 298.15 K, followed by 50 ps production runs, during which data were collected for subsequent analysis.
3. Results and discussion

3.1. Simulation of the crystal surface/amorphous (HTPB-IPDI-DOA) supersystem

For the polymer HTPB-IPDI chain, isocyanate end-groups (−N=C=O) were chosen assuming that no humidity was present in the medium. HTPB-IPDI-DOA amorphous phase models were built and optimized and HTPB-IDPI-DOA models were selected on the basis of the low energy criterion. This step was followed by the construction of the crystalline RDX-amorphous HTPB-IPDI-DOA or FOX-7-amorphous HTPB-IPDI-DOA super system. This step is the most important in the interfacial interaction simulation. Further, mechanical properties were estimated for both systems to validate experimental data or to propose predicted mechanical properties to be validated by experiments. Similar modelling techniques have been used previously by other groups to simulate interactions in various PBXs systems [9, 10, 15].

In the present study, the amorphous phase composed of the polymer, plasticizer and diisocyanate was built using the same composition used as in experimental formulations. In trial formulations, the percentage of the crystal phase is larger (90%) than the plasticizer-polymer-diisocyanate binding amorphous phase. However, it was not possible to maintain a reasonable system size while strictly respecting the experimental relative compositions of RDX or FOX-7 and amorphous material. In our model, the crystal phase represents ~ 70% of the system. Figure 3 illustrates the simulated HTPB-IDPI-DOA/RDX and HTPB-IDPI-DOA/FOX-7 systems for a representative crystal surface plane in each case.

![Figure 3. Typical simulated of HTPB-IDPI-DOA/RDX and HTPB-IDPI-DOA/FOX-7 supercells with (020) and (010) crystal surface, respectively.](image)

The interaction energy was calculated by using the following equation.

\[
E_{\text{Interaction}} = E_{\text{total}} - \left( E_{\text{surface}} + E_{\text{polymer}} \right)
\]  (2)

where \(E_{\text{total}}\) is the energy of the surface and the polymer, \(E_{\text{surface}}\) is the energy of the surface without the polymer and \(E_{\text{polymer}}\) is the energy of the polymer without the surface. The binding energy \(E_{\text{binding}}\) reflects the intermolecular
interactions between the polymer and crystal, which is defined as the negative value of the interaction energy, and can be written as $E_{\text{binding}} = -E_{\text{interaction}}$. Results, reported in Table 1, vary with the crystallographic surface that is in contact with the polymer-plasticizer-diisocyanate mixture. The (020) surface of RDX has the largest binding energies and therefore strongest ability to interact with the polymer, whereas the (210) surface has the smallest one. For FOX-7, the surface with the largest binding energy is (010), and (100) corresponds to the smallest. The positive binding energy values are due in all cases to electrostatic interactions between different molecules.

Table 1. Average binding energy (in kcal/mol) for different crystalline planes

<table>
<thead>
<tr>
<th>Crystal</th>
<th>(hkl) plane</th>
<th>$E_{\text{binding}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RDX</td>
<td>(020)</td>
<td>88</td>
</tr>
<tr>
<td></td>
<td>(200)</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td>(210)</td>
<td>75</td>
</tr>
<tr>
<td>FOX-7</td>
<td>(100)</td>
<td>81</td>
</tr>
<tr>
<td></td>
<td>(010)</td>
<td>121</td>
</tr>
<tr>
<td></td>
<td>(001)</td>
<td>82</td>
</tr>
</tbody>
</table>

The energetic stability of the models studied was confirmed when their potential and Coulombic energy fluctuations were below 10%. The configurations of these stable systems were used for further calculations. Figure 4 shows Coulombic energy values obtained over a period of 50 ps. The starting point was taken at 300 ps for the initial NVT simulations of the six models.

This Coulombic energy analysis confirmed which (hkl) surface has the strongest ability to interact with the polymer chains. The Coulombic energy corresponding to the (200) surface of RDX is lower than that of (210) and (020) surfaces. This observation may be explained by the favorable interfacial interactions and stability of HTPB-IPDI-DOA/(200)RDX super system. For all cases, for both HTPB-IPDI-DOA/RDX and HTPB-IPDI-DOA/FOX-7, Coulombic energy is negative, which it means that interfacial interactions are favorable. Although the (010) surface of FOX-7 has the strongest ability to interact with the polymer, the Coulombic energy of the (100) surface is lower than that of the (010) surface.

Figure 4. Coulombic energy of HTPB-IDPI-DOA/RDX (left) and HTPB-IDPI-DOA/FOX-7 (right) supercells with (hkl) crystal surfaces.
3.2. Mechanical Properties

Dynamics simulations were finally applied to these simulated systems to predict mechanical properties of RDX and FOX-7 based PBXs. For this case, the c-axis of the supercell is not extended. Calculations are based on formalism developed by Parrinello and Rahman [22] where the elastic stiffness tensor $C_{ij}$ is expressed in terms of fluctuations in the elastic strain tensor $(\varepsilon_{i}, \varepsilon_{j})$ for a given material. The NPT dynamics simulation was carried out for a time duration 200 ps using a time step 1.0 fs at 298.15 K and a cell mass of 20.0 atomic mass units. This is followed by production runs of 200 ps in order to collect data for subsequent analysis. The theory of linear elasticity considers that the stress and strain tensors $\sigma$ and $\varepsilon$ are related to the elastic stiffness tensor $C_{ij}$ [23] as follows:

$$\sigma_{ij} = C_{ij} \varepsilon_{ij} \quad (i, j = 1, 2, \ldots, 6)$$  \hspace{1cm} (3)

For an isotropic material, the stiffness matrix may be described by specifying only Lamé coefficients $\lambda$ and $\mu$.

$$
\begin{bmatrix}
\lambda + 2\mu & \lambda & 0 & 0 & 0 \\
\lambda & \lambda + 2\mu & \lambda & 0 & 0 \\
\lambda & \lambda & \lambda + 2\mu & 0 & 0 \\
0 & 0 & 0 & \mu & 0 \\
0 & 0 & 0 & 0 & \mu \\
0 & 0 & 0 & 0 & 0
\end{bmatrix}
$$  \hspace{1cm} (4)

Poisson’s ratio $\nu$ and various moduli (Tensile $E$, bulk $K$, shear $G$) are calculated assuming that the material is isotropic. Elastic moduli may then be written in terms of the Lamé coefficients as follows [24]:

$$E = \mu \left( \frac{3\lambda + 2\mu}{\lambda + \mu} \right), \quad \nu = \frac{\lambda}{2(\lambda + \mu)}, \quad K = \lambda + \frac{2}{3}\mu, \quad G = \mu$$  \hspace{1cm} (5)

Tensile modulus $E$ is also known as the Young modulus, and is a measure of the isotropic elastic material stiffness. Poisson’s ratio $\nu$ is defined as the ratio of transverse to longitudinal strains of the material. The bulk modulus ($K$) measures the resistance of the substance to uniform compression. It is defined as the pressure increase needed to cause a relative decrease in volume. The shear modulus ($G$) is defined as the ratio of shear stress to the shear strain. The $K/G$ indicates the extent of the plastic range, this ratio is associated with ductility in cases where $K/G$ is high, and with brittleness when it is low. The estimated mechanical property values are qualitative, due to the small size of systems, anisotropy conditions as well as force field approximations. They should be used for comparison purposes only. Table 2 summarizes all these predicted properties for both systems involving RDX and FOX-7.

Table 2. Mechanical properties of RDX and FOX-7 based PBXs (in GPa) for various $(hkl)$ surfaces of RDX and FOX-7

<table>
<thead>
<tr>
<th></th>
<th>RDX</th>
<th></th>
<th>FOX-7</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$(200)$</td>
<td>$(210)$</td>
<td>$(020)$</td>
<td>$(100)$</td>
</tr>
<tr>
<td>Poisson ratio ($\nu$)</td>
<td>0.2</td>
<td>0.2</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>Tensile modulus ($E$)</td>
<td>9.3</td>
<td>5.4</td>
<td>0.2</td>
<td>4.5</td>
</tr>
<tr>
<td>Bulk Modulus ($K$)</td>
<td>4.8</td>
<td>3.2</td>
<td>2.5</td>
<td>7.5</td>
</tr>
<tr>
<td>Shear modulus ($G$)</td>
<td>3.9</td>
<td>2.2</td>
<td>0.2</td>
<td>1.6</td>
</tr>
<tr>
<td>$K/G$</td>
<td>1.2</td>
<td>1.6</td>
<td>12.5</td>
<td>4.7</td>
</tr>
</tbody>
</table>
From Table 2, Poisson's ratio values are in the interval [0.2, 0.4], corresponding to typical parameters of common rigid polymers (~ 0.3). For RDX-based PBXs system, the predicted Poisson ratio value of models (200) and (210) is similar to the experimental value of 0.22 reported for RDX crystals [25]. All other calculated mechanical properties vary as function of (hkl) directions: tensile, bulk and shear moduli are lowest for (020) and highest for (200) in RDX-based PBXs and are lowest for (010) and highest for (100) in the case of FOX-7-based PBXs.

Resistance to elastic deformation, expressed by the tensile modulus (E), is smaller for (020) plane, indicating less rigidity in contrast to (200) and (210) planes. In other words, the HTPB-DOA-IPDI/RDX (020) blend behaves more like a rubber and is more flexible. One of the most important parameters for explosives formulation is the K/G quotient, which is a measure of brittleness. It is high for (020) and lower for (200) and (210), showing that ductility is better for the (020) surface plane. These results are consistent with tensile modulus values for (020) plane, which is a more flexible and malleable model than those of other planes. For FOX-7-based PBXs, the tensile modulus (E) is higher for the (100) and (001) planes, indicating higher rigidity as compared to the (010) plane. Finally, the K/G quotient values predicted for the three planes are comparable. This thus indicates an equivalent malleability for the three crystal planes studied. In comparison to earlier study [10], an important effect is noted upon addition of diisocyanates to RDX-based PBXs system: stiffness is reduced and malleability increased in comparison to RDX-based PBXs without the diisocyanate addition.

4. Conclusion

The HTPB-IPDI-DOA/RDX and HTPB-IPDI-DOA/FOX-7 energetic blend systems have been used to investigate the potential use of atomistic modelling techniques and to design new explosives formulations using novel energetic materials as ingredients. Interactions between crystalline, energetic molecules RDX or FOX-7, a polymer binder HTPB, a plasticizer DOA, and diisocyanate IPDI were modelled under periodic boundary conditions following an approach previously proposed in the literature for crystalline-polymer interfaces.

The most favorable interactions occur between HTPB-IPDI-DOA and the (020) surface plane of RDX and the (010) surface plane of FOX-7 crystal face, and electrostatic interactions result in HTPB-IPDI-DOA/(200)RDX and HTPB-IPDI-DOA/(100)FOX-7 formulations more stable than those corresponding to other surface crystal. This means that the crystal morphology affects mechanical properties of blend formulation systems. In addition, enhancement of mechanical properties may be achieved by monitoring crystal growth conditions to increase the fraction of (020)RDX and (010)FOX-7 crystal surface planes. On the other hand, the addition of diisocyanate end-groups also modifies mechanical properties of systems in comparison to a previous study done on RDX-based PBXs without diisocyanate addition [10].

Finally, isothermal-isobaric molecular dynamics simulations were used to compute various moduli (tensile $E$, bulk $K$ and shear $G$) and Poisson ratios $\nu$ for the two blends. Elastic coefficients were computed on the basis of the formalism proposed by Parrinello and Rahman in which mechanical properties are provided as a function of fluctuations of the strain tensor. Predictions of isotropic moduli ($E$, $K$, $G$) for crystalline RDX-based PBXs show that the resistance to elastic deformation is decreased for the (020) plane compared to (200) and (210) planes, where the resistance to elastic deformation is slightly increased. For FOX-7-based PBXs, the resistance to elastic deformation is decreased for the (010) plane in comparison to (100) and (001) planes. The $K/G$ quotient value for the (020) plane is higher compared to that of (210) and (200) planes. The HTPB-IPDI-DOA/RDX blend with the (020) surface plane is therefore more flexible and more ductile. This result suggests that choosing appropriate conditions (solvent, temperature) to favor the growth of specific (hkl) crystal faces could improve mechanical properties of the desired PBX formulations. These properties will be investigated in the future using experimental methods.

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