MOLECULAR MODELING: TOWARD A REALISTIC APPROACH TO MODEL ENERGETIC MATERIALS

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Models of plastic-bonded explosives were created with the aim of studying the mechanical properties and sensitivity because the latter is one of the most important problems in relation to energetic materials. Previous models proposed in the literature used short plastic chains, which are appropriate for interaction modeling. In the present work, a model with a single, long chain was built, which is more appropriate for modeling mechanical properties. The representative hydroxyl-terminated polybutadiene (HTPB)/dioctyladipate (DOA)/cyclotrimethylenetrinitramine (RDX) system was used (81.4 w/w% of RDX and 18.6 w/w% of the amorphous HTPB/DOA phase, with a 60/40 ratio between the polymer and plasticizer). The HTPB chain was composed of 48 trans groups, 16 cis groups, and 16 vinyl groups. Due to the length of the chain, superposing the crystalline RDX cell [cleaved at the crystalline (2 0 0), (0 2 0), and (2 1 0) planes] to the amorphous HTPB/DOA cell introduced considerable void, and therefore resulted in low density—much more so than when using models with shorter chains. A compression/minimization iterative procedure was used to converge to the optimal density. Pair distributions were calculated to verify that the procedure did not lead to abnormal changes in the RDX crystal model. Comparable energies were obtained for models built with each cleavage plane, contrary to previous work with small molecules. Long chains have lower entropy and are less able to change conformations and maximize interactions with the crystal surface. Models with densities higher than the minimum value were shown to have energy stored in two main components; i.e., the internal energy was stored mainly in the bond and torsion contributions, whereas the external energy storage was performed by van der Waals interactions. These preliminary models show the potential for studying the sensitivity of explosives through molecular modeling.

KEY WORDS: *energetic materials, simulation and modeling, sensitivity, HTPB, RDX, plastic-bonded explosives*

1. INTRODUCTION

Energetic materials are intensively studied to determine their physico/chemical properties. The most common form of energetic materials is polymer-bonded explosives (PBXs), in which the explosive crystals are imbedded in a plastic matrix that acts as a binder and provides a measure of protection against shocks, thereby improving their insensitivity and making them easier to handle. The major problem with PBXs is that testing is dangerous and costly; however, it is essential in order to determine their properties. This is even more of a problem when developing new formulations because these are apt to behave in unforeseeable ways, which further increases the hazard.

Computational chemistry can be a great approach used to obtain information about energetic materials at low cost and in a safe environment. Molecular modeling has already been used to predict the mechanical properties and interaction energies of PBXs. Numerous PBX systems have been studied, such as CL-20-based systems (Xu et al., 2006, 2007; Qiu et al., 2007), HMX/estane systems (Xiao et al., 2008), and cyclotrimethy-lenetrinitramine (RDX) with fluorinate polymer systems (Zhu et al., 2009). Also, Xu et al. (2007) studied the sensitivity of explosives (Xu et al., 2007), in which molecular dynamics (MD) and orthogonal method (OM) OM3/molecular orbital (MO) quantum chemistry methods were used to show that the heat capacity is related to the sensitivity of the explosives. More recently, Li et al. (2011a,b,c) studied various RDX-based PBX systems [RDX/glycidylazide polymer (RDX/GAP), 3,3-bis (azidomethyl) oxetane (RDX/BAMO), and RDX/3-azidomethyl-3-methyloxetane (RDX/AMMO)]. Finally, the use of MD to investigate various aspects of PBX systems has been studied for a number of years, including miscibility (Abou-Rachid et al., 2008), glass transition temperature (Jaidann et al., 2008), and interface interactions and mechanical properties (Jaidann et al., 2009).

Most studies in the literature show similarities in terms of modeling approach. First, in all cases the models include more than a single crystal cell;typically, a $(2 \times 2 \times 3)$ or $(2 \times 3 \times 3)$ array for RDX that allows minimizing the surface effects and better calculationof longer-range interactions such as electrostatic interactions. Second, in all models studied the polymer is simulated by short chains; typically, composed of 5–10 repeat units per chain with one or a few chains present in the system (Xiao et al., 2008). The advantage of using small chains is that small molecules easily fi in the available volume, are less constrained, and move around more freely. The models require less minimization and optimization and lead to realistic explosive/plastic interactions in a minimum amount of time.

Models built with small molecules are efficien when studying the compatibility of explosives and polymers. Unfortunately, this approach does not take into account the polymeric nature of the matrix; therefore, it is not as effective in modeling properties that are dependent on chain length, such as mechanical properties and energy storage in the PBXs. These are related to short- and long-range conformational changes along the

polymeric chains and are proposed to be a main factor in explaining and predicting the relative sensitivity of a PBX.

Model building is similar in all cases. A crystal cell is firs built using the experimentally determined atomic positions when known and the model is cleaved at the desired (hkl) surface. In parallel, an amorphous phase containing a polymer and a plasticizer is constructed using standard approaches such as the one proposed by Theodorou and Suter (1986). Finally, a supercell is assembled by overlaying both previously built cells. In some cases, a vacuum layer or gap is introduced above the fused cells to avoid the effect of periodicity on interaction calculations, although it is normally not used for mechanical properties because it introduces an unrealistic free volume.

The present work had the following two aims: (1) to obtain systems more representative of real PBXs by increasing the chain length of the polymer and (2) to determine the effect of the chain length on the resulting models. To develop a technique that better takes into account the polymeric nature of the chains, and to test this technique, a common PBX system was chosen based on RDX. This polymeric binder is a mixture of hydroxyl-terminated polybutadiene (HTPB) and dioctyl adipate (DOA), as shown in Fig. 1. HTPB is one of the most commonly used polymers in plastic-bonded explosives because of its good mechanical properties and its insensitivity to stress. DOA is the most common plasticizer used with HTPB, which decreases the glass transition temperature of the polymer and makes it more malleable. RDX is one of the most commonly used military explosives, especially for conventional demolition explosives. In real life, HTPB is cross-linked, and is virtually a single molecule, which is not easily amenable to modeling; therefore, the present models will not take cross-linking into account. The present work reports a new strategy for building large-chain models using the HTPB + DOA/RDX system, and the preliminary modeling tests performed on these models.
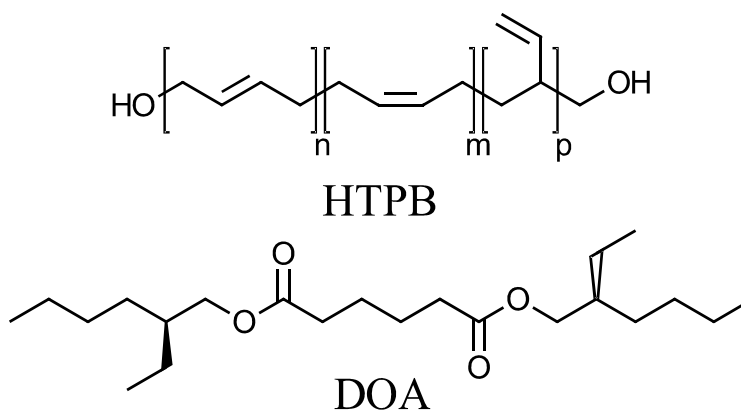

FIG. 1: Molecules found in the amorphous phase of the studied system (HTPB and DOA).

2. MODELING AND SIMULATION

Models were built by using the Materials Studio (MS) 4.3 software from Accelrys (2008). The condensed-phase optimized molecular potentials for atomistic simulation studies (COMPASS) force fiel was used throughout (Sun, 1998). COMPASS is a class II ab initio force fiel specificall aimed at modeling condensed material, in which spe-cifi attention is given to energetic materials and functional nitro (Yang et al., 2000) and nitrate ester groups (Bunte and Sun, 2000). Therefore, it is well parameterized for energetic molecules such as those studied in the present work.

The PBX was simulated by assembling the RDX crystal phase and the HTPB/DOA amorphous phase. Each model was composed of 4372 atoms located either in the crys-talline phase (144 RDX molecules, for a total of 3024 atoms) or in the amorphous phase (804 HTPB atoms and 544 DOA atoms, for a total of 1348 atoms). The PBX composi-tion was 81.4 w/w% of RDX and 18.6 w/w% of the amorphous phase. The percentage of the amorphous phase was slightly lower than in a real-life system, which is normally in the range of 5–10%. Many PBXs have higher explosive percentages, but as the purpose of the present study was to determine the effect of the polymer on explosive behavior, the highest polymer percentage that is commonly used in real life was selected. The size of the model was limited to 5000 atoms due to calculation time constraints.

The crystal structure experimentally determined by Choi and Prince (1972) was used as the initial position for the atoms of the crystalline RDX unit cell. RDX crystallizes in the orthorhombic space group Pbca with a = 13.182 Å, b = 11.574 Å, and c = 10.709 Å. Each cell unit contains eight molecules. The content of a typical unit cell is shown in Fig. 2.
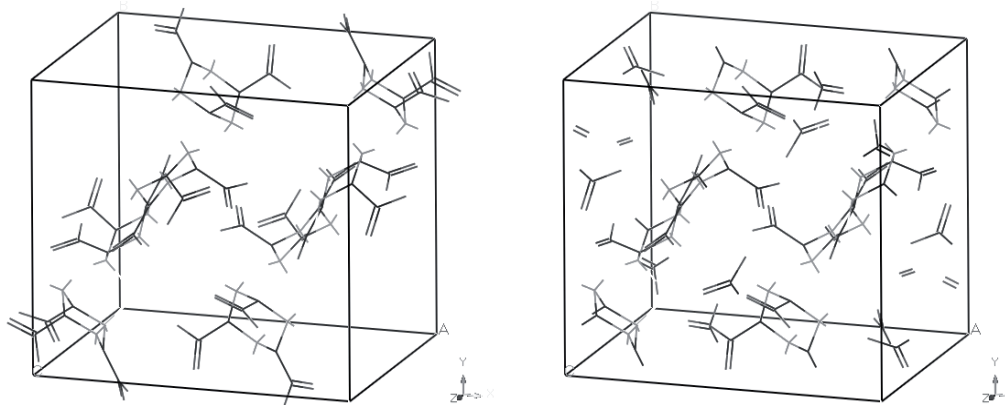

FIG. 2: Model of the crystalline RDX cell, built according to the crystal structure of Choi and Prince (left) and the content of a single unit cell, on the in-cell (right).

A (2 × 3 × 3) crystallographic supercell periodic system consisting of 144 RDX molecules was built. This size was selected to limit surface effects while maintaining a relatively small system in terms of the number of molecules, while having proportions close to real-life plastic-bonded explosives. The cells were cleaved following the (2 0 0), (0 2 0), and (2 1 0) crystalline planes, which have been shown experimentally to be present at the surface of RDX crystals grown from solution (ter Horst et al., 1999).

An amorphous cell containing a single chain of HTPB and eight molecules of DOA was then built, using a 60/40 ratio between the polymer and plasticizer, which is the proportion used in a real-life system to ensure that an amorphous polymer is obtained. The constructed HTPB chain was composed of 48 $trans$, 16 cis, and 16 vinyl groups. This ratio was chosen to be as close as possible to military grade HTPB or HTPB/R45M, which has (depending on the supplier) between 50 and 100 groups per chain. A single chain was selected as being more representative than previous models based on a smaller chain because all chains in an actual PBX are cross-linked with an additive for HTPB such as isophorone diisocyanate (IPDI). Eight amorphous cell configuration were built following the Theorodou and Suter (1986) method. Each configuratio was subjected to 10,000 minimization steps performed under periodic boundary conditions. The minimizations were carried out with the Smart Minimizer approach in MS, which consists of successive steepest descent, conjugate gradients, and Newton–Raphson minimization steps. The non-bonded interactions, spline width, and buffer width were truncated at 0.95, 0.1 and 0.05 nm, respectively. To make sure that these configuration were at equilibrium at room temperature, the MD simulations were carried out under constant number of atoms, volume, and temperature (NVT) conditions until the energy reached a stable value (less than 7% energy variation). The dynamics were carried out for 2.5 ns and the temperature was controlled via the Andersen (1980) technique. The configuratio with the lowest energy was used to build the HTPB + DOA/RDX systems.

The MD simulations of the HTPB + DOA/RDX system were performed under periodic boundary conditions. Minimizations were initially carried out for 10,000 iterations to equilibrate the models. Afterward, the cells were slightly compressed (3%) along the z direction (Qiu et al., 2007). The amorphous phase was placed on top of the crystalline phase, as shown in Fig. 3. An additional 10,000 iterations were carried out to reach the minimum energy of the compressed cells. This procedure was carried out for a large number of configuration until the configuratio with the lowest total potential energy was attained. A representative example of the fina model is also reported in Fig. 3.

After minimization, the MD simulations were conducted under NVT conditions for 250 ps at the optimal density. At this point, equilibration was reached, as verifie by a low variation in energy. A 50-ps run was added for data acquisition. The temperature was controlled via the Andersen (1980) method.
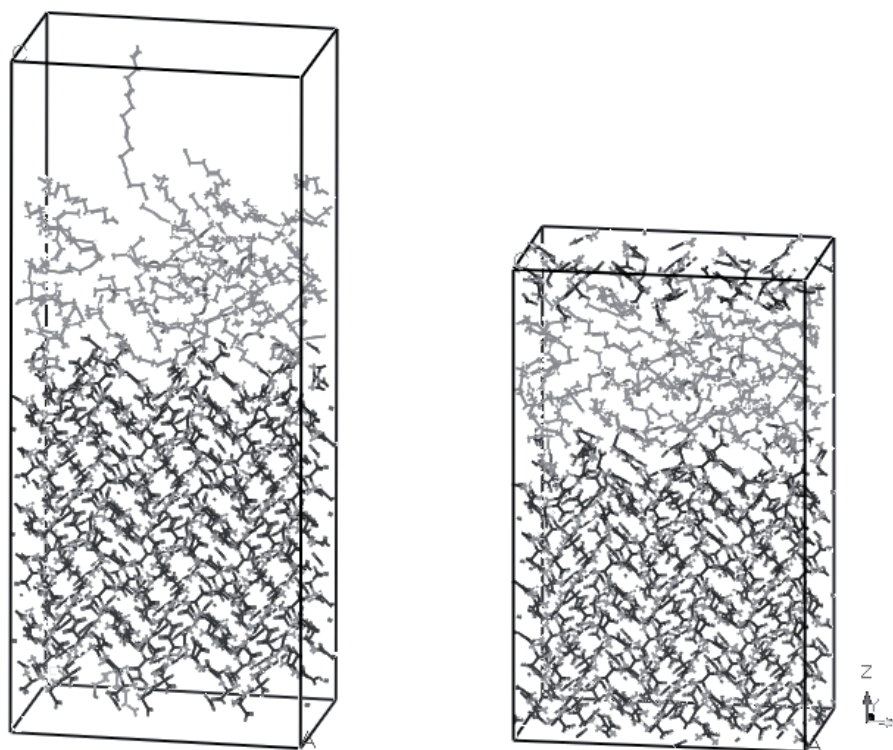
FIG. 3: Representative in-cell periodic boundary condition model of the HTPB + DOA/RDX system at equilibrium for the (2 0 0) cleavage plane: (right) initial model, as created; (left) fina compressed and minimized model.

3. RESULTS AND DISCUSSION

3.1 Determination of the Model Density

To properly model a PBX, it is important to use a density as close as possible to experimental values. Density is one of the most important parameters in MD because it greatly influence the interaction between molecules. Furthermore, the density in a long polymeric chain influence how a system absorbs energy when stress is applied. Unfortunately, experimental density values are not always easy to obtain. Furthermore, even when an experimental value exists, it is subject to variations depending on the molecular weight, the presence or absence of cross-links, and the nature of the endgroups. Also, it will further vary with the presence of plasticizers such as DOA. Therefore, experimental density may not lead to correct models, and it must be adjusted in order for interactions to be optimal. In the present work, the initial density of the PBX was estimated from the weight percentages of each component in the system. Crystalline RDX has a density of 1.806 g/cm^{-3} (van der Heijden and Bouma, 2004) and HTPB has been reported (by the

producer) to have a density of 0.9 g/cm^{-3}. For a composition with 81.4 w/w% of RDX and 18.6 w/w% of the amorphous phase, the estimated HTPB + DOA/RDX density was of 1.62 g/cm^{-3}.

The initial density value of the supercell built by superimposing the crystalline and amorphous cells, reported in Table 1, was between 1.26 and 1.28 g/cm^{-3}, much smaller than the estimated value. This was caused by a bad contact between the two initial cells, which was related to the chain length and adjacent reentry of the chains under periodic conditions and caused an abnormal void zone, as shown in the presentative initial model in Fig. 3 (left). This problem is well recognized, and other research groups that have carried out simulations of PBX have compressed the cells until the estimated density value was reached (Qiu et al, 2007). However, when using short chains, the void introduced during cell superposition is much smaller, and in the present case a compression procedure much more drastic than what was previously used in the literature was essential. Therefore, the height of the cell (along the z axis) was reduced by 3% steps instead of the more usual 0.3% steps until a density of 1.8 g/cm^{-3} was reached, which is the density of pure RDX. Fifteen different configuration were obtained.

Figure 4 shows the evolution of the total potential energy as a function of density for models built with the three different cleavage planes studied. Upon successively compressing the unit cell, and therefore increasing the density, the total energy of the system progressively decreased until a minimum (which was taken as the fina density of the system) was observed between 1.50 and 1.55 g/cm^{-3}, as reported in Table 1. This value was 8% lower than the density of 1.62 g/cm^{-3} estimated from the weight fractions of each component. The unit cell dimensions for the unit cell with the lowest energy, both before and after compression, are also reported in Table 1. The only unit cell dimension that changed appreciably was that in the compression direction (the z axis). The unit cell remained orthorhombic throughout the procedure.

TABLE 1: Unit cell dimensions and density of the HTPB + DOA/RDX models for the three cleavage planes before and after minimization/compression

Model	Initial density (g/cm^{-3})	Final density (g/cm^{-3})	Initial			Final			α (°)	β (°)	γ (°)
			a (Å)	b (Å)	c (Å)	a (Å)	b (Å)	c (Å)			
RDX (2 0 0)	1.26	1.50	34.72	21.42	69.84	34.72	21.42	58.54	90	90	90
RDX (0 2 0)	1.28	1.55	32.13	26.36	60.09	32.13	26.36	49.84	90	90	90
RDX (2 1 0)	1.28	1.54	32.13	26.64	59.65	32.13	26.64	49.65	90	90	90
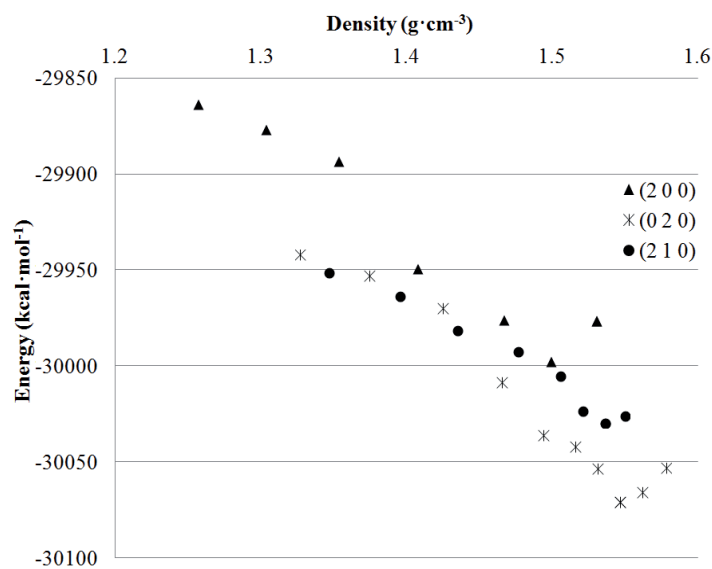
FIG. 4: Total potential energy of the HTPB + DOA/RDX (2 0 0), (0 2 0), and (2 1 0) as a function of density for the models using the three main crystallographic cleavage planes.

At larger density values, energy increases very fast. Figure 5 shows the total potential energy and its two main components (non-bonded and internal energies). Figure 5 shows that the energy increase after the minimum density was reached is related to a combination of non-bonded and internal energies. The same trend was observed for the (0 2 0) and (2 1 0) cleavage planes (data not shown), although the density at the energy minimum, or fina density, was slightly different, as reported in Table 1.

On the other hand, the internal energy of the system never reached a minimum, but tended to remain constant up to a density of 1.4 g/cm^{-3}, after which is steadily increased. The internal energy is a summation of bond deformation, angle deformation, torsional energy, out-of-plane contributions, and cross-terms, which mostly increase upon a decrease in available space. As seen in Fig. 6, which reports the evolution of these different contributions for the (2 0 0) cleavage plane, bond deformations remained virtually constant. This is in agreement with Xu et al. (2007), who have shown that this parameter has a slight correlation with PBX sensitivity. In this case, the internal energy is mainly influence by the angle deformation and torsional contributions to the energy. The same observation has been made for the (0 2 0) and (2 1 0) cleavage plane models (data not shown). Therefore, among the parameters calculated from atomistic modeling, these two parameters may have the most influenc on the absorption of potential energy upon impact, and should be studied in more detail to compare explosive sensitivity.

Figure 7 shows the different contributions of non-bonded energy. Electrostatic energy remains relatively constant up to a density of 1.50 g/cm^{-3}, and decreases at higher
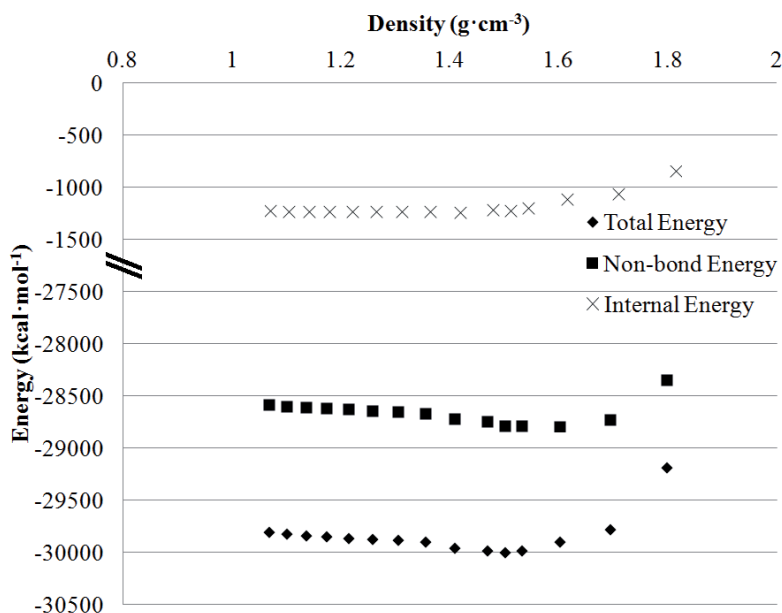
FIG. 5: Total potential energy of the HTPB + DOA/RDX as a function of density for a representative model [(2 0 0) cleavage].
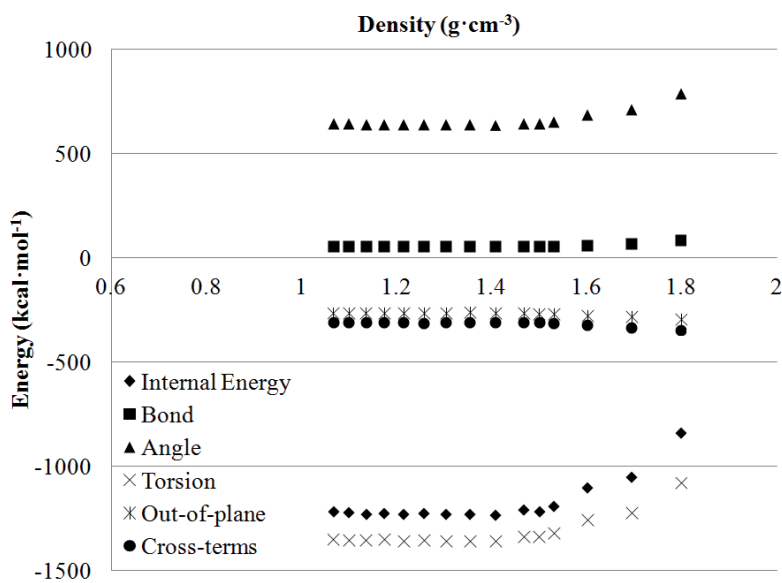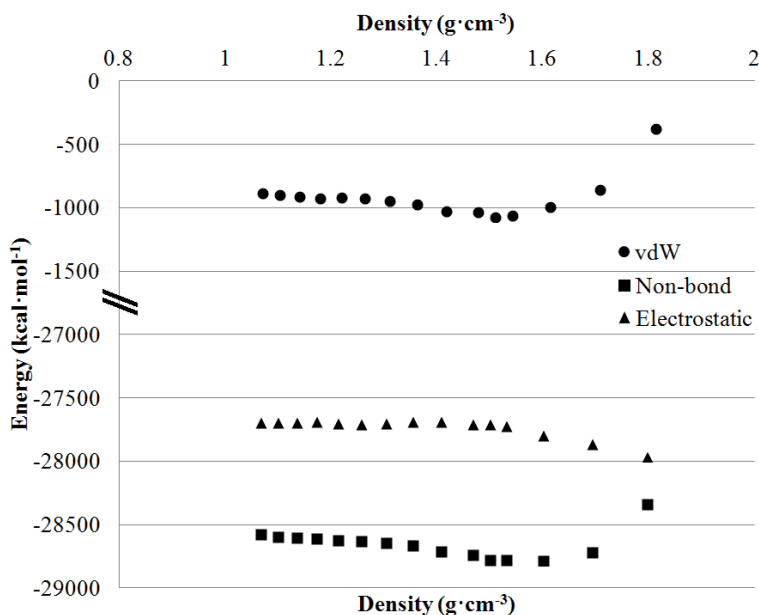

FIG. 6: Various contributions to the internal energy of the HTPB + DOA/RDX as a function of density for a representative cleavage plane (2 0 0).

FIG. 7: Various contributions to the non-bonded energy of the HTPB + DOA/RDX (2 0 0) as a function of density for a representative cleavage plane (2 0 0).

densities, which shows that there is a positive interaction between the RDX crystal and the amorphous polymer. The rapid increase in potential energy after 1.50 g/cm^{-3} is attributed to van der Waals interactions, in which it firs decreases upon reaching an optimal interatomic distance and then rapidly increases. This is normally observed in such dense systems.

3.2 Energy Comparison of the Different Planes

In previous studies, many different crystalline planes were always modeled in order to evaluate the contribution of each one on the PBX properties. To investigate sensitivity, the potential energy of the system is the main focus. Therefore, it was decided to investigate the magnitude of the energy difference as a function of the crystalline plane.

The energy values (total, internal, and non-bonded) during the last 10 ps of the simulations are reported in Table 2, which show similar variations within the different models of the same cleavage plane and from one cleavage plane to another. These values are also schematized in Fig. 8, in which the total potential energies of the systems, separated into the contributions of the explosive and the polymer and the interaction between the two, are reported. It must be noted that the bars shown are not complete but represent an enlargement of the end section. The energy of the polymer is superimposed in the graph because this is a positive term, whereas the other energy terms are negative, and there-

TABLE 2: Summary of the average potential energies (kcal/mol) (total, internal, and non-bonded) for models built along the three crystallographic directions

Model	System	Potential energy		
		Total	Internal	Non-bonded
RDX (2 0 0)	Complete	− 26,158 ± 38	1,990 ± 27	− 28,148 ± 21
	Explosive	− 25,822 ± 28	1,626 ± 19	− 27,448 ± 18
	Polymer	40 ± 27	364 ± 21	− 324 ± 13
RDX (0 2 0)	Complete	− 26,236 ± 39	2,007 ± 34	− 28,243 ± 15
	Explosive	− 25,915 ± 47	1,618 ± 45	− 27,533 ± 16
	Polymer	64 ± 26	389 ± 27	− 325 ± 9
RDX (2 1 0)	Complete	− 26,179 ± 46	2,001 ± 43	− 28,180 ± 28
	Explosive	− 25,870 ± 36	1,587 ± 34	− 27,457 ± 25
	Polymer	97 ± 22	414 ± 23	− 316 ± 12
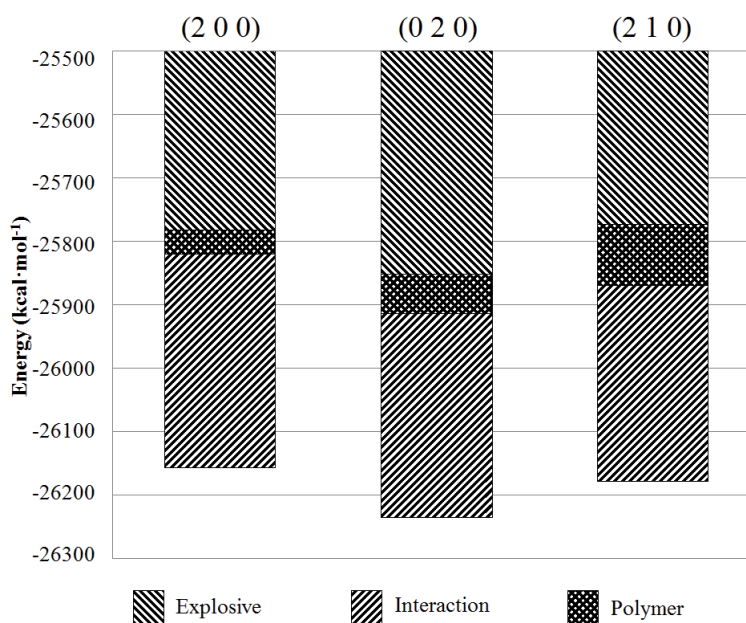
FIG. 8: Total average potential energy of the models built with different crystallographic cleavage planes.

fore it must be subtracted. In all cases, the polymer energy term is the smallest in terms of absolute energy, but the largest since it is the only positive contribution to energy. The interaction term between the polymer phase and the explosive, crystalline portion

is quite important. However, in all cases the three models have similar energies. Table 2 reports the individual values of energy along with the standard deviations calculated for the various models built in each case. The energy differences between models with different cleavage planes fall within the deviations calculated for different models with the same cleavage plane, indicating that these differences are not significant

Previous studies have shown that a 33% difference exists in the interaction energy (calculated as the difference between the total energy of the complete system and the total energy of the explosive and polymer alone) as calculated along the three different cleavage planes of HTPB + DOA/RDX systems in which HTPB molecules consist of six repeat units (Jaidann et al., 2009). On the other hand, in the present case, in which long HTPB chains of 80 repeat units are used, the interaction energy varied by only 7%. This difference is attributed to the lower fl xibility of a long polymeric chain, which cannot organize as efficientl as a smaller chain to maximize the interaction at the RDX surface. Furthermore, by increasing the chain length, the number of end groups also decreases. Because these are less constrained, they are the most susceptible to forming a strong directional interaction such as hydrogen bonds with a crystal surface. Therefore, their lower concentrations also contribute to the averaging of the interactions when comparing different crystal phases. This observation constitutes an additional advantage of using long chains; i.e., not only are the models more representative of real explosives but the differences related to crystal plane cleavages are smaller, and this decreases the probability of obtaining inaccurate results due to an inappropriate choice of cleavage plane. This also indicates that simulations may rely on fewer cleavage planes without loss of exactitude.

3.3 Crystalline Phase Deformation

To make sure that the approach developed is suitable for MD runs, the crystalline deformation needs to be addressed. As seen in Fig. 3, during the model building compression/minimization procedure, the atomic positions and cell shape slightly change. In order to verify the extent of these changes and their effect on crystal phase order, the pair distribution function was calculated for a RDX unit cell as well as for the RDX atoms in the compressed supercell. The results are reported in Fig. 9, and clearly show that the order is maintained throughout the range of distances for all cleavage plane models built. This is an additional confirmatio of the validity of the models.

4. CONCLUSIONS

Models of PBX systems were built and tested using a slightly different approach, with the aim of predicting the sensitivity of PBX systems. To achieve this, it is proposed that the chain length must be increased to allow more energy storage in the bond angle deformation and torsion angle terms.
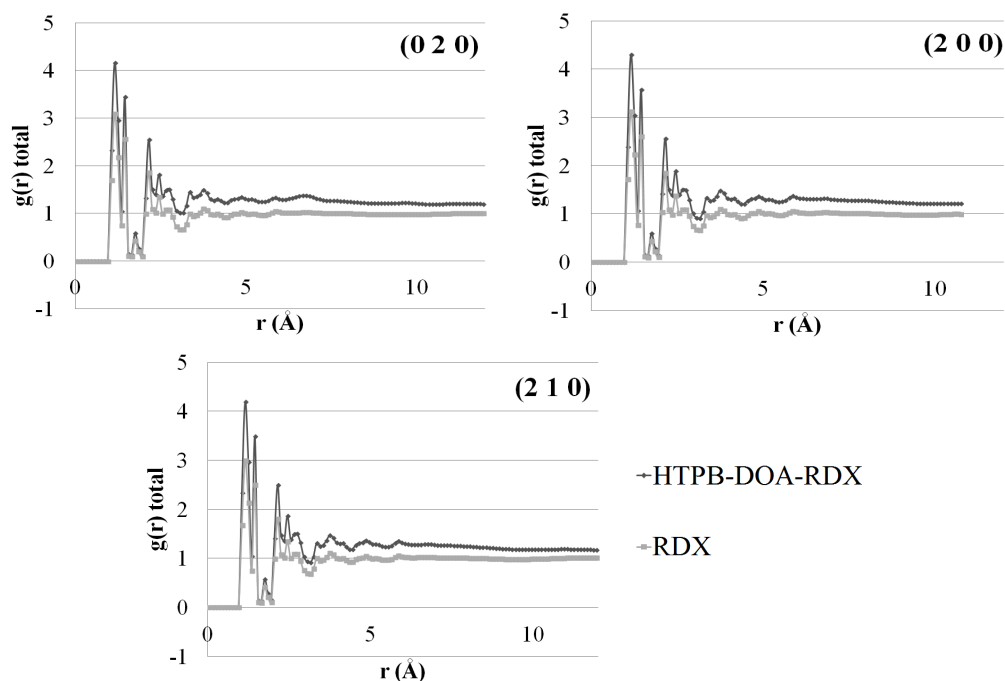
FIG. 9: Pair distribution functions $g(r)$ of RDX: (top) initial RDX cell; (bottom) RDX in the PBX model after cell construction and compression to the correct density.

Upon increasing the chain length, the models tend to incorporate vacuum gaps that must be allowed to relax. We have shown that it is possible to do this and obtain a reasonable model, as well as to determine the optimal density of a model through successive compression steps larger than those previously used in the literature. The resulting models are more representative of real polymer-bonded explosives. Furthermore, larger chain lengths decrease the number of chain end groups, therefore decreasing their specifi interactions with the crystal surface. The interactions become less cleavage plane sensitive, as demonstrated by the decrease in percentage of variations of the interaction energy when considering different cleavage planes. Therefore, changes due to cleavage plane selection are less important in large chain models than they are in short chain models. The obtained models are amenable to further studies. Investigations of possible correlations with ammunition sensitivity and mechanical property simulations are specificall targeted for future work. The present models are shown to be more realistic than the previously used short chain models.

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Models of plastic-bonded explosives were created with the aim of studying the mechanical properties and sensitivity because the latter is one of the most important problems in relation to energetic materials. Previous models proposed in the literature used short plastic chains, which are appropriate for interaction modeling. In the present work, a model with a single, long chain was built, which is more appropriate for modeling mechanical properties. The representative hydroxyl-terminated polybutadiene (HTPB)/dioctyladipate (DOA)/cyclotrimethylenetrinitramine (RDX) system was used (81.4 w/w% of RDX and 18.6 w/w% of the amorphous HTPB/DOA phase, with a 60/40 ratio between the polymer and plasticizer). The HTPB chain was composed of 48 trans groups, 16 cis groups, and 16 vinyl groups. Due to the length of the chain, superposing the crystalline RDX cell [cleaved at the crystalline (2 0 0), (0 2 0), and (2 1 0) planes] to the amorphous HTPB/DOA cell introduced considerable void, and therefore resulted in low density−much more so than when using models with shorter chains. A compression/minimization iterative procedure was used to converge to the optimal density. Pair distributions were calculated to verify that the procedure did not lead to abnormal changes in the RDX crystal model. Comparable energies were obtained for models built with each cleavage plane, contrary to previous work with small molecules. Long chains have lower entropy and are less able to change conformations and maximize interactions with the crystal surface. Models with densities higher than the minimum value were shown to have energy stored in two main components; i.e., the internal energy was stored mainly in the bond and torsion contributions, whereas the external energy storage was performed by van der Waals interactions. These preliminary models show the potential for studying the sensitivity of explosives through molecular modeling.

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