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Molecular Dynamic Simulation on Interaction between HTPE Polymer and Energetic Plasticizer in solid propellant

Xiao-long FU[1], Xue-zhong FAN[1], Xue-hai JU[2], Xiao-fei QI[1], JI-zhen LI[1], Hong-jian YU[1]

(1 Xi'an Modern Chemistry Research Institute, Xi'an, China, 710065; 2 Department of Chemistry, Nanjing University of Science and Technology, Nanjing 210094)

Correspondence to: Xiao-long FU (E-mail: *fuxiaolong204@163.com*)

ABSTRACT

In order to study the interaction between polymer and plasticizers in solid propellant and their underlying mechanisms, molecular dynamics (MD) simulations with compass force field were performed to investigate the Hydroxy Terminated PolyEther (HTPE) polymer and some energetic plasticizers including Nitroglycerin (NG)/Butanetriol Trinitrate (BTTN) mixture, bis (2, 2-Dintropropyl) acetal (BDNPA)/bis (2, 2-Dinitropropyl) formal (BDNPF) mixture and N-butyl-N-(2-nitroxy-ethyl) nitramine (Bu-NENA). Also, the mechanical properties for HTPE polymer containing energetic plasticizers were theoretically and experimentally studied. It was shown that the HTPE polymer is miscible with all involved energetic plasticizers which can improve the mechanical property of HTPE polymer. The order of binding energies between HTPE and energetic plasticizers are found to be HTPE/Bu-NENA> HTPE/BDNPA/BDNPF> HTPE/NG/BTTN.

KEYWORDS: Applied Chemistry; HTPE Polymer; Molecular Dynamic Simulation; Compatibility; Mechanical Properties

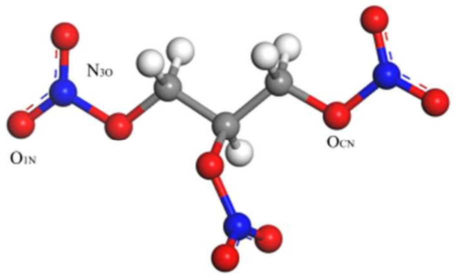
1. Introduction

Solid propellants are widely used in rockets and missiles [1-3]. The ingredients of propellants mainly include polymers, plasticizers and energetic materials, etc[4-6]. The polymer is an important ingredient for improving mechanical properties of propellants, as well as reducing the sensitivity of propellants such as impact or friction [7, 8]. HTPE propellants based on cross-linked Hydroxy Terminated PolyEther (HTPE) binders are widely studied as insensitive propellants [9, 10]. Although HTPE propellants have similar properties to HTPB propellants in most cases, the former ones are less sensitive [11, 12]. The mechanical properties of HTPE elastomers[13, 14] and HTPE propellants[15] have been studied. However, there are no theoretical studies on interaction between HTPE polymer and energetic plasticizers in propellant. In this work, the solubility parameter (δ), radial distribution function and binding energy of HTPE polymer with energetic plasticizers are theoretically studied by molecular dynamics (MD) simulations, and the mechanical properties for HTPE polymer containing energetic plasticizers are theoretically and experimentally studied. Hopefully, this study may provide some information and guidance for the design of HTPE propellants formulations.

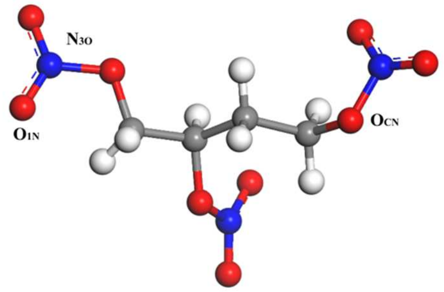
2. Model and method

2.1 Molecular model construction details

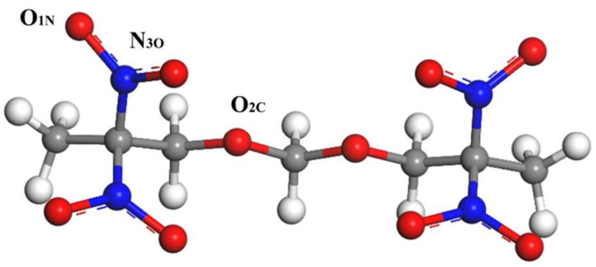
The molecular dynamic simulations were performed using the Accelrys and Materials studio Modeling (version 5.5) installed on Windows XP [16, 17]. The COMPASS Force Field was used for the molecular dynamic simulation on HTPE binder and the energetic plasticizers [18, 19]. The COMPASS has been proved as an effective force field supporting molecular simulations of polymer [20, 21]. The chemical structural of Hydroxy Terminated PolyEther (HTPE), Nitroglycerin (NG), Butanetriol Trinitra (BTTN), bis (2, 2-Dintropropyl) acetal (BDNPA), bis (2, 2-Dinitropropyl) formal (BDNPF) and N-butyl-N-(2-nitroxy-ethyl) nitramine (Bu-NENA) were shown in Figure 1. Here, carbon atoms are grey, hydrogen white, nitrogen blue and oxygen red in color. According to the force field, the H atoms in HTPE are assigned to H_1; N atoms in nitro groups are N_{3O}; O atoms in nitro groups are O_{1N}; O atoms connected to nitro groups are O_{CN}; O atoms connected to C chains in HTPE are O_{2E}; O atoms connected to C chains in plasticizers are O_{2C}; N atoms connected to nitro groups and C chains are N_3.



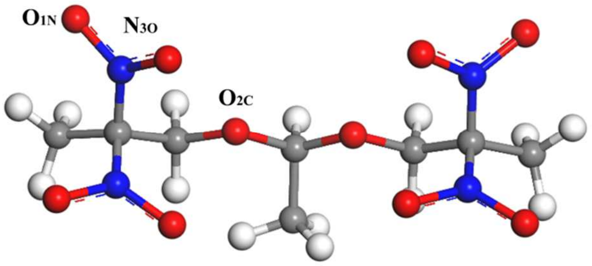
NG



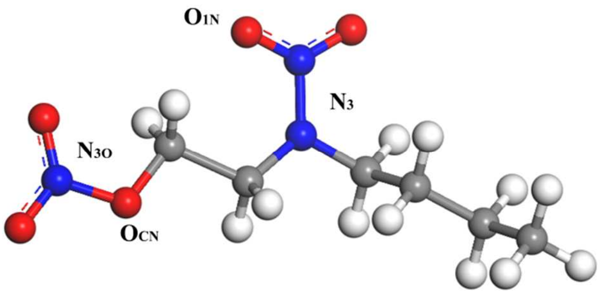
BTTN



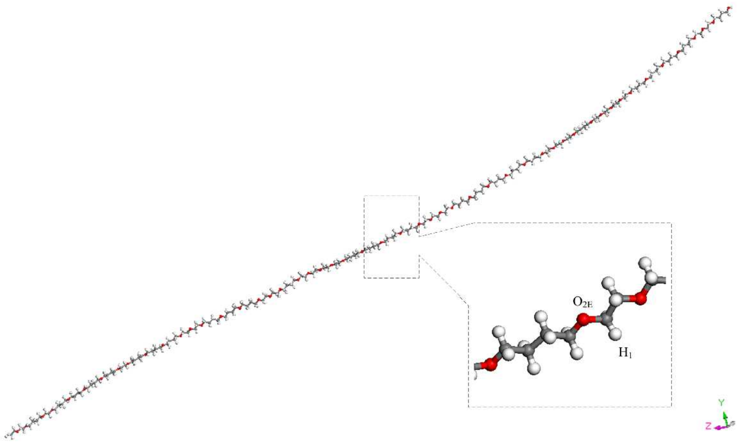
BDNPF



BDNPA



Bu-NENA



HTPE

FIGURE 1 Chemical structural of NG, BTTN, BDNPA, BDNPF and HTPE.

The molecular model of NG, BTTN, BDNPA, BDNPF and Bu-NENA were built with the Visualizer module in Materials studio software, and then their structures were optimized using Discover module. The HTPE polymer chains were built from repeat unit using the Random Copolymer Builder module whose molecular weight was 3000, and its structure was minimized (without an extensive conformer search) using Discover module.

2.2 Molecular dynamic simulation details

The HTPE/NG/BTTN, HTPE/BDNPA/BDNPF and HTPE/Bu-NENA blends were built by Amorphous cell, and the mass ratios were nearly 50:25:25, 50:25:25 and 50:50. The size of the simulation box is 30 angstroms. The amorphous systems such as HTPE/NG/BTTN, HTPE/BDNPA/BDNPF and HTPE/Bu-NENA blends were subsequently optimized by a 5,000 step energy minimization to eliminate the useless contacts by Smart minimization with convergence level of medium. Afterward, 400 ps MD equilibration on the system was performed to obtain the equilibrium density, with a time step of 1 fs, by Discover module in the NPT ensemble at 298 K and 101.325 KPa. The criterion for system equilibrium is the equilibrium of both temperature and the energy. The system of MD simulation is equilibrium when the fluctuation of temperature is within 10K or the energy is invariable of small fluctuation around the average energy value. For instance, the energy and temperature fluctuation curve of HTPE observed during molecular dynamics of 400 ps. The temperature and energy are in equilibrium when the simulation time is approaching 400 ps, where the temperature in equilibrium fluctuates about ±10K. The molecular models of NG, BTTN, BDNPA, BDNPF, Bu-NENA, HTPE and their blends were shown in Figure 2. The number of HTPE, plasticizers and mass ratios are summarized in Table 1.

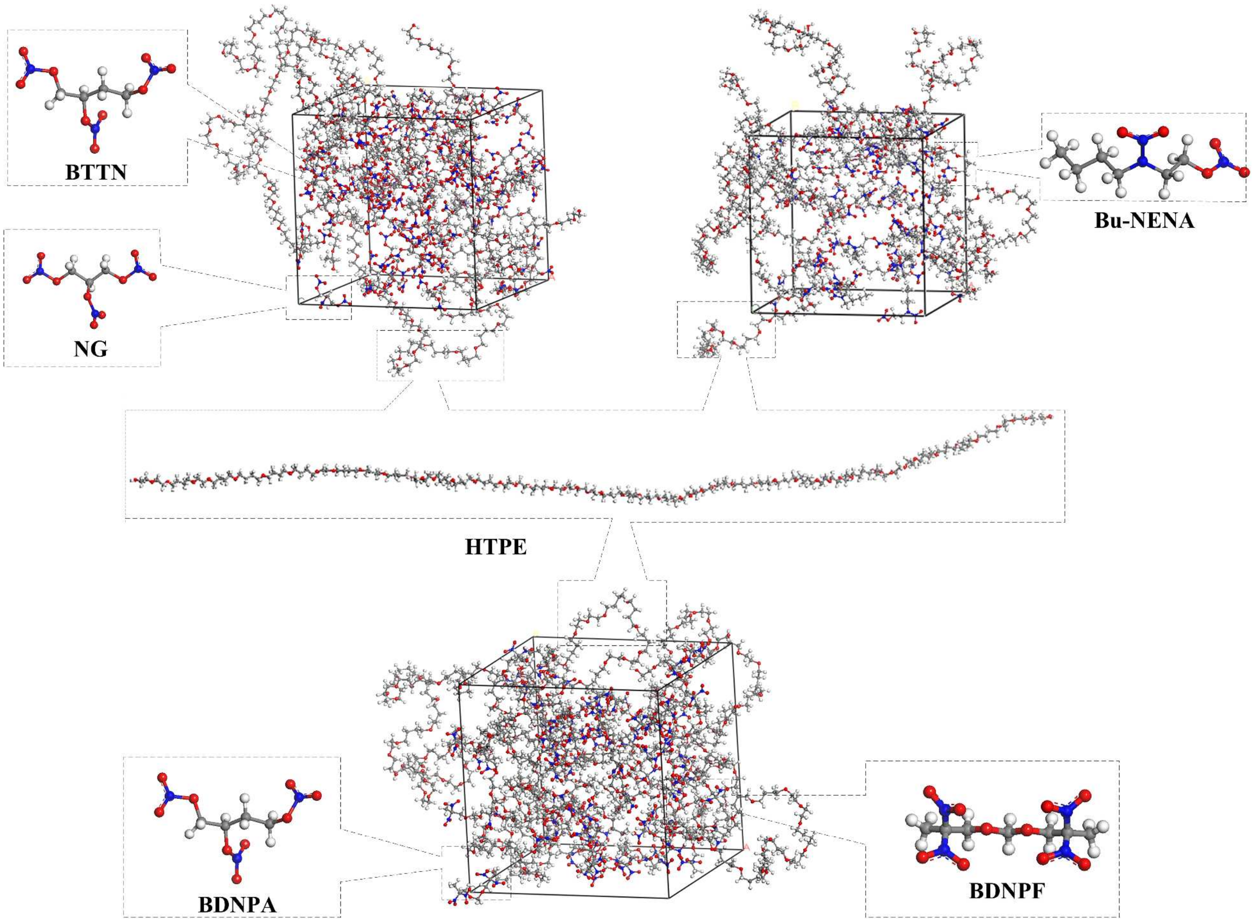


FIGURE 2 Molecular models of NG, BTTN, BDNPA, BDNPF, Bu-NENA, HTPE and their blends.

TABLE 1 HTPE/plasticizer blends in MD simulation

System	Number of HTPE polymer chain	Number of plasticizers	Molecular ratio of HTPE and plasticizer
HTPE/NG/BTTN	4	26:26	12000: 12168
HTPE/BDNPA/BDNPF	4	19:19	12000: 12160
HTPE/Bu-NENA	4	58	12000: 12006

2.3 Materials **and Formulations**

Hydroxy Terminated PolyEther (HTPE, purity is over 99.8%, molecular weight is 3300), Nitroglycerin (NG)/Butanetriol Trinitra (BTTN) mixture(purity is over 99.7%), bis (2, 2-Dintropropyl) acetal (BDNPA)/bis (2, 2-Dinitropropyl) formal (BDNPF) mixture (purity is over 99.8%) and N-butyl-N-(2-nitroxy-ethyl) nitramine (Bu-NENA, purity is over 99.6%). From the simulation of HTPE and plasticizer, the formulations of the three elastomers were designed as follows:

TABLE 2 Formulations of HTPE and plasticizer elastomers

Formulations	Mass percent/%			
	HTPE elastomer	NG/BTTN	BDNPA/BDNPF	Bu-NENA
HE-1	50	50	-	-
HE-2	50	-	50	-
HE-3	50	-	-	50

2.4 Mechanical properties test

All the samples containing HTPE polymer and energetic plasticizer involved in this investigation were mixed for 30 min by stirrer. Then each sample was casted in a mold with 75mm ×10mm×2mm and cured at 50 °C for 3 days in a water jacketed oven.

The mechanical properties of HTPE elastomers were measured by INSTRON 4505(USA) tensile tester. The elastomers were cut into slices with 75mm ×4mm×2mm (Figure 3), and the slices were made into JANNAF dog bones. The tests were carried out at 25°C with 500mm•min^{-1} cross-head speed.

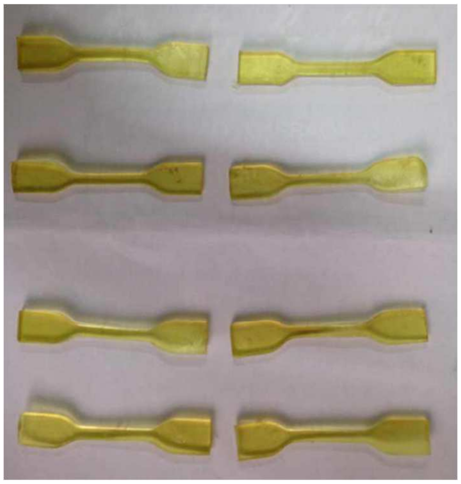


FIGURE 3 Sample of HTPE energetic plasticizers elastomers.

3. Results and discussion

3.1 Solubility parameter

Miscibility is the property between polymer and plasticizer to mix in all proportions, forming a homogeneous solution [22]. In order to predict the miscibility of the HTPE and energetic plasticizers, the solubility parameter can be calculated by MD method [23]. In cohesive energy and cohesive energy density theories, the cohesive energy is used to estimate the energy change on mixing two species. When supplemented with the entropy of mixing this allows the prediction of the phase behavior of simple mixtures. These theories introduce the solubility parameter which can be used to predict solubility, particularly for non-polar materials such as polymers. Materials with similar solubility parameter values are likely to be miscible.

The cohesive energy of a system of molecules, E_{coh}, is the average energy required to separate all molecules to infinite distance from each other:

$$E_{\mathrm{coh}} = -E_{\mathrm{inter}} = E_{\mathrm{intra}} - E_{\mathrm{total}} \qquad (1)$$

where E_{inter} is the total energy between all molecules, E_{total} is the total energy of a system, , E_{intra} is minus the intramolecular energy.

The cohesive energy density, *CED*, is simply the cohesive energy per unit of volume:

$$CED = \frac{E_{\mathrm{coh}}}{V} \qquad (2)$$

The solubility parameter, δ, is the square root of the cohesive energy density and plays an important role in the theory of mixtures:

$$\delta = \sqrt{CED} \tag{3}$$

According to the theory of the polymer solution, the HTPE and energetic plasticizers including NG, BTTN, BDNPA and BDNPF blends can be considered as the polymer solution systems. The solubility parameters can be calculated by Material Studio according to the formula 1 to 3. Therefore, based on the dissolvable principle of similar material structures, when the solubility parameter of the plasticizer is close to the polymer, they can dissolve well with each other. The solubility parameters of HTPE and plasticizers are summarized in the TABLE 3.

TABLE 3 Solubility parameters of HTPE and plasticizers evaluated by molecular dynamics

System	HTPE	NG/BTTN	BDNPA/BDNPF	Bu-NENA
$\delta_{MD}/(J\cdot cm^{-3})^{0.5}$	19.034	21.106	19.886	19.687
$\Delta\delta_{MD}/(J\cdot cm^{-3})^{0.5}$	-	2.072	0.852	0.653

note： $\Delta\delta_{MD}$ is the differences of solubility parameters between HTPE and plasticizers

It is generally accepted that if $|\Delta\delta_{MD}| < 1.3\text{~}2.1\ (J\cdot cm^{-3})^{0.5}$ between polymers and plasticizers, the polymers and plasticizers would be expected miscible. This approach is only used to judge the miscibility of blends systems in which the non-combinatorial entropy effect or specific interactions do not play a dominant role. For our study, as shown in Table 3, $\Delta\delta_{MD}$ of the energetic plasticizers are all less than 2.1 $(J\cdot cm^{-3})^{0.5}$. The miscibility of HTPE and energetic plasticizers is good. The order of the compatibility of plasticizers with HTPE is Bu-NENA>BDNPA/BDNPF>NG/BTTN.

3.2 Simulation on mechanical properties of HTPE and energetic plasticizers

The simulation of mechanical properties is widely studied by MD method in energetic polymer system [24], amorphous polymer nanostructures [25] and polymer liquid crystals [26].

Any body or element thereof, which is acted on by external forces is in a state of stress. Moreover, if the body is in equilibrium, the external stress must be exactly balanced by internal forces. In general, stress is a second rank tensor with nine components as follows. From the statistical mechanics of elasticity, the generalized Hooke's law is often written as formula 4.

$$\begin{bmatrix} \sigma_{\mathrm{x}} \\ \sigma_{\mathrm{y}} \\ \sigma_{\mathrm{z}} \\ \tau_{\mathrm{yz}} \\ \tau_{\mathrm{xz}} \\ \tau_{\mathrm{xy}} \end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46} \\ C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56} \\ C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66} \end{bmatrix} \begin{bmatrix} \varepsilon_{\mathrm{x}} \\ \varepsilon_{\mathrm{y}} \\ \varepsilon_{\mathrm{z}} \\ \gamma_{\mathrm{yz}} \\ \gamma_{\mathrm{xz}} \\ \gamma_{\mathrm{xy}} \end{bmatrix} \tag{4}$$

For isotropic body, there are only two independent elastic coefficients, C_{11} and C_{12}. Let $C_{12}=\lambda$, $C_{11}-C_{12}=\mu$. C_{ij} can be described as follows:

$$[C_{\mathrm{ij}}] = \begin{bmatrix} \lambda+2\mu & \lambda & \lambda & 0 & 0 & 0 \\ \lambda & \lambda+2\mu & \lambda & 0 & 0 & 0 \\ \lambda & \lambda & \lambda+2\mu & 0 & 0 & 0 \\ 0 & 0 & 0 & \mu & 0 & 0 \\ 0 & 0 & 0 & 0 & \mu & 0 \\ 0 & 0 & 0 & 0 & 0 & \mu \end{bmatrix} \tag{5}$$

In the formula, λ and μ are Lame constants. Tensile modulus (E), shear modulus (G), bulk modulus (K) and Poisson's ratio (v) can be described as formula 6 to 9.

$$E = \frac{\mu(3\lambda+2\mu)}{\lambda+\mu} \tag{6}$$

$$G = \mu \tag{7}$$

$$K = \lambda + \frac{2}{3\mu} \tag{8}$$

$$v = \frac{\lambda}{2(\lambda+\mu)} \tag{9}$$

In an isotropic situation, where forces are the same in all directions and there is no viscous force, the pressure tensor is diagonal and can be written as:

$$P = p\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{10}$$

where the scalar quantity *p* is the equivalent hydrostatic pressure.

In materials science studies, the stress tensor is used in preference to the pressure tensor. The diagonal elements are known as the tensile stress and the non diagonal elements are the shear stress.

To obtain the theoretical elastic constants, the total energy of the bulk has been calculated for a number of deformations of the unit cell. The elastic constants of a crystal are defined as the second derivatives of energy density (at the energy minimum) with respect to the elements of the infinitesimal Lagrangian strain tensor εi, according to the relation:

$$C_{ij} = \frac{1}{V}\left[\frac{\partial^2 E}{\partial \varepsilon_i \varepsilon_j}\right]_0 \tag{11}$$

where V is the volume of the primitive unit cell.

The mechanical properties can be calculated by MD simulation by formulae 5 to 11. The predicted value of elastic constants and effective isotropic mechanical properties are summarized in Table 4.

TABLE 4 Elastic constants and mechanical property of different blends

Constants	HTPE	HTPE/NG/BTTN	HTPE/BDNPA/BDNPF	HTPE/Bu-NENA
C_{11}/GPa	0.344	2.592	2.103	1.283
C_{22}/GPa	-0.4612	-4.93	3.939	2.252
C_{33}/GPa	0.111	-5.7	2.626	1.682
C_{44}/GPa	-1.933	-2.08	1.017	1.099
C_{55}/GPa	0.868	-0.9362	1.29	0.564
C_{66}/GPa	1.911	-0.9591	0.6019	0.832
C_{12}/GPa	1.191	1.444	1.279	1.177
C_{13}/GPa	-1.317	0.9082	0.9026	1.023
C_{23}/GPa	-2.212	-2.269	1.736	0.862
E/GPa	2.720	2.415	2.392	2.083
K/GPa	1.709	1.5377	1.449	0.835
G/GPa	1.531	1.606	0.9304	0.828
ν/GPa	0.999	0.2485	0.2594	0.284
C_{12}- C_{44}/GPa	3.124	3.524	0.262	0.078

From Table 4, it can be found that elastic constants containing C_{11}, C_{22} and C_{33} of HTPE/Bu-NENA and pure HTPE are closer than those of HTPE/NG/BTTN and HTPE/BDNPA/BDNPF. This evolution tendency of elastic constants showed that the Bu-NENA can reduce the anisotropy of HTPE than NG/BTTN and BDNPA/BDNPF. Moreover, compared with pure HTPE, all the mechanical properties including tensile modulus (E), shear modulus (G), and bulk modulus (K) of HTPE/plasticizers decrease. It indicates that the plasticizers can decrease the rigidity and increase the flexibility of HTPE. The mechanical property of HTPE can be improved by the energetic plasticizers.

3.3 Binding energy between HTPE and energetic plasticizers

The binding energy is a characteristic parameter which can represent the interaction force of components in composite system. The interaction energy can be evaluated by the total energy of the blends and each component in the system. The binding energies between HTPE polymer and energetic plasticizers can be determined using formula 12.

$$E_{\text{binding}} = -E_{\text{inter}} = -(E_{\text{HTPE/plasticizer}} - E_{\text{HTPE}} - E_{\text{plasticizer}}) \tag{12}$$

In the formula, $E_{\text{HTPE/plasticizer}}$ is the total energy of HTPE and plasticizer blends system. E_{HTPE} and $E_{\text{plasticizer}}$ are the total energies of HTPE and plasticizer, respectively.

The binding energy between HTPE and energetic plasticizers were summarized in Table 5.

TABLE 5 Binding energy between HTPE and energetic plasticizers (kcal·mol^{-1})

System	$E_{\text{HTPE/plasticizer}}$	E_{HTPE}	$E_{\text{plasticizer}}$	E_{binding}
HTPE/Bu-NENA	-2930.718	439.417	-2260.919	1109.216
HTPE/BDNPA/BDNPF	-2432.799	460.9426	-1848.649	1045.0926
HTPE/NG/BTTN	-1362.935	325.344	-948.674	739.605

From Table 5, it is shown that the order of binding energy is HTPE/Bu-NENA> HTPE/BDNPA/BDNPF> HTPE/NG/BTTN. The interaction force between HPTE and Bu-NENA is stronger than those of BDNPA/BDNPF and NG/BTTN.

3.4 Radial distribution function for different atoms of HTPE and plasticizers

In order to reveal the interaction between the HTPE and plasticizers by atom function, the radial distribution functions are calculated. According to the studies, the distances of hydrogen bond and the van der Waals force are about 0.26 to 0.31 nm and 0.31to 0.50 nm, respectively[27,28]. Radial distribution functions (RDF) give the probability of finding another atom at a distance from a specific atom. The type of the interaction force can be judged by the distance of the peak in the radial distribution functions. The value of the force can be inferred by the height of the peak. The radial distribution functions of HTPE polymer and plasticizers were shown in Figure 4 to 6.

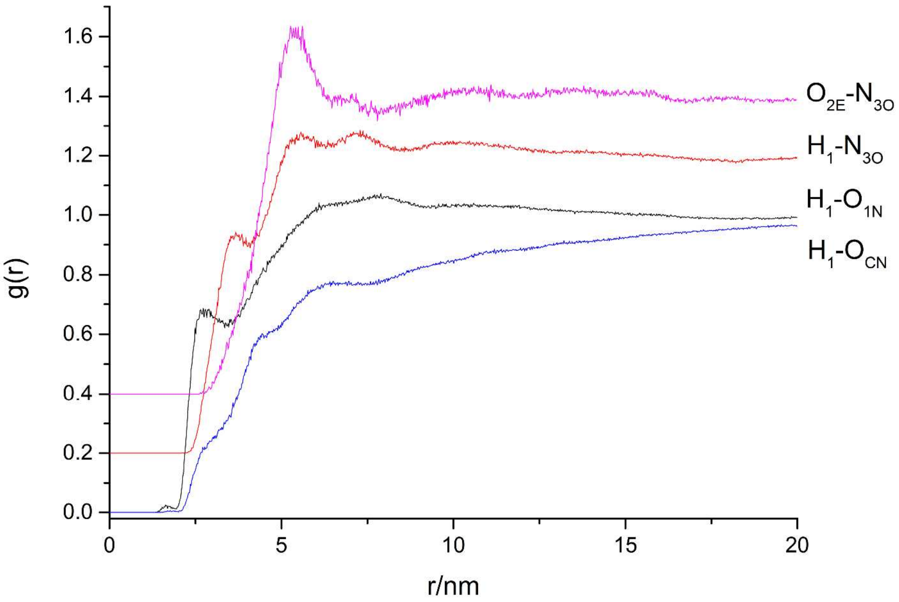


Figure 4 Radial distribution functions for different atoms of HTPE and NG/BTTN

As shown in Figure 4, there is a peak at about 0.26 nm which *g*(r) =0.80 for the pair of H atoms in the terminal hydroxyl of HTPE and O atoms in nitro groups of the NG/BTTN (curve 5-1); the peak for the pair of H atoms in the terminal hydroxyl of HTPE and N atoms in nitro groups of the NG/BTTN is at about 0.34 nm which *g*(r) =0.93 (curve 5-2); the RDF curve for the pair of H atoms in the terminal hydroxyl of HTPE and O atoms connected to nitro groups of the NG/BTTN has no peak (curve 5-3); there is a peak at about 0.49nm which *g*(r) =1.31 for the RDF curve for the pair of O atoms connected to C chains in HTPE and N atoms in nitro groups of the NG/BTTN (curve 5-4). From the RDF curves, the interaction force of H_1-O_{1N} is the hydrogen bond; there has no force between H_1-O_{CN}; the interaction forces of H_1-N_{3O} and O_{2E}-N_{3O} are van der Waals force. There is a main peak probably for strong interaction force between the pair of O atoms connected to C chains in the HTPE and N atoms in nitro groups of the NG/BTTN.

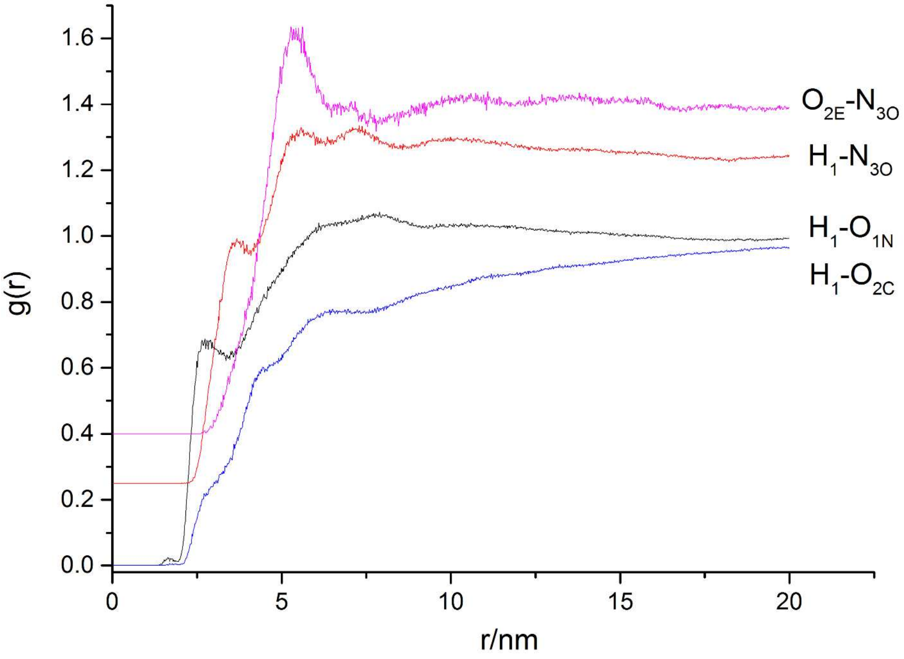


Figure 5 Radial distribution functions for different atoms of HTPE and BDNPA/BDNPF

From the RDF curves, the interaction force of H_1-O_{1N} is the hydrogen bond; there has no force between H_1-O_{2C}; the interaction forces of H_1-N_{3O} and O_{2E}-N_{3O} are van der Waals force. There is a highest peak probably for strong interaction force between the pair of O atoms connected to C chains in the HTPE and N atoms in nitro groups of the BDNPA/BDNPF.

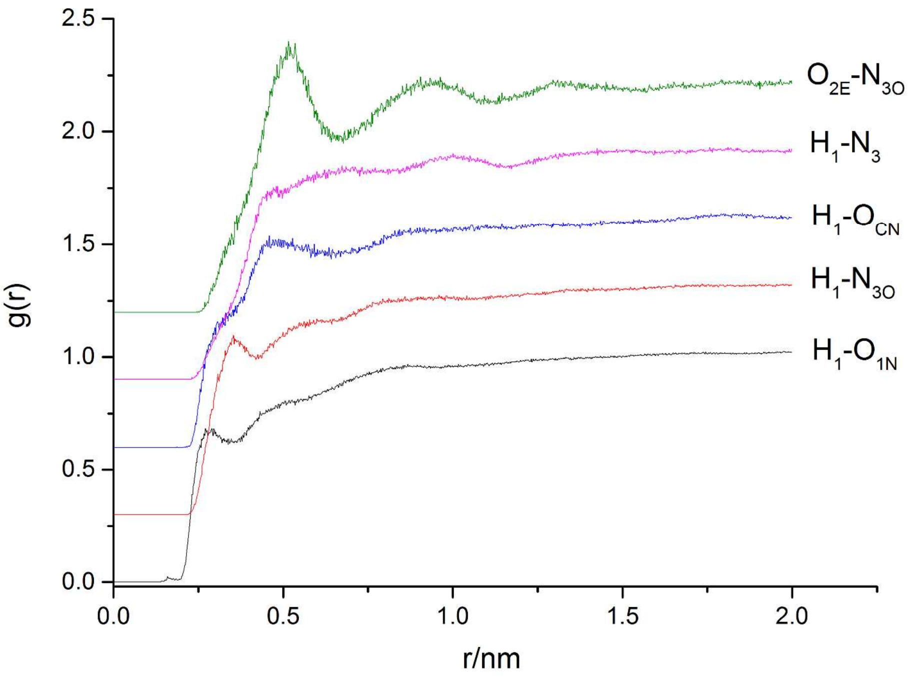


Figure 6 Radial distribution functions for different atoms of HTPE and Bu-NENA

From the RDF curves, the interaction force of H_1-O_{1N} is the hydrogen bond; there has no force between H_1-O_{2C}; the interaction forces of H_1-O_{CN}, H_1-N_{3O} and O_{2E}-N_{3O} are van der Waals force. There is the highest peak for strong interaction force between the pair of O atoms connected to C chains in the HTPE and N atoms in nitro groups of the BDNPA/BDNPF.

It is concluded that the main interaction forces of HTPE and plasticizers are van der Waals force. The strong interaction forces are between the pair of O atoms connected to C chains in the HTPE and N atoms in nitro groups of the energetic plasticizers.

3.5 Mechanical properties of HTPE elastomers by experimental

In order to analyze the effects of plasticizers on the mechanical properties of HTPE elastomers, the maximum tensile strength (σ_m) and the maximum elongation (ε_m) of HTPE elastomers were listed in Table 6.

Table 6 The mechanical properties of of HTPE elastomers

Formulations	Mechanical Properties(25□)	
	σ_m/(MPa)	ε_m/(%)
HE-1	0.072	165.7
HE-2	0.163	134.6
HE-3	0.195	174.9

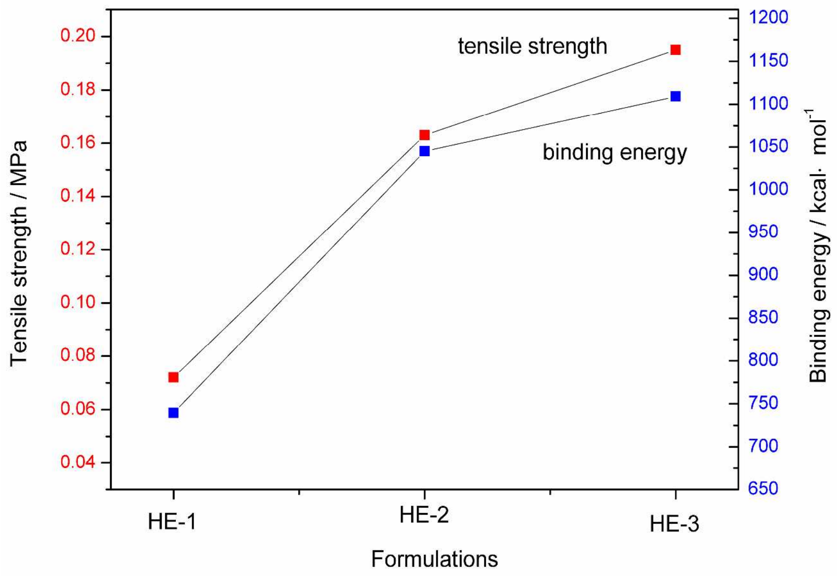


Figure 7 Comparison between tensile strength and binding energy of different formulations

It was shown from Table 5 that the order of maximum tensile strength of HTPE elastomers is HE-3>HE-2>HE-1. From Figure 7 it can be seen that there is nearly the same trend from the MD simulation and experiment. It can be inferred that the tensile strength might be the macro reflection of the molecular interaction. From the simulated of binding energy and radial distribution function that the mechanical property of HTPE polymer can be improved by energetic plasticizer due to the interaction force between the pair of O atoms connected to C chains in the HTPE and N atoms in nitro groups of the energetic plasticizers.

4. CONCLUSIONS

(1) It was found from calculations that the polymers and plasticizers were miscible and the order of the compatibility of plasticizers with HTPE is Bu-NENA>BDNPA/BDNPF>NG/BTTN.

(2) MD simulations confirmed that the mechanical properties of the HTPE polymer can be improved by adding plasticizers; compared with pure HTPE, all the mechanical properties including tensile modulus (*E*), shear modulus (*G*), bulk modulus (*K*) of HTPE/plasticizers are greatly improved.

(3) The order of binding energy was theoretically found to be HTPE/Bu-NENA> HTPE/BDNPA/BDNPF> HTPE/NG/BTTN.

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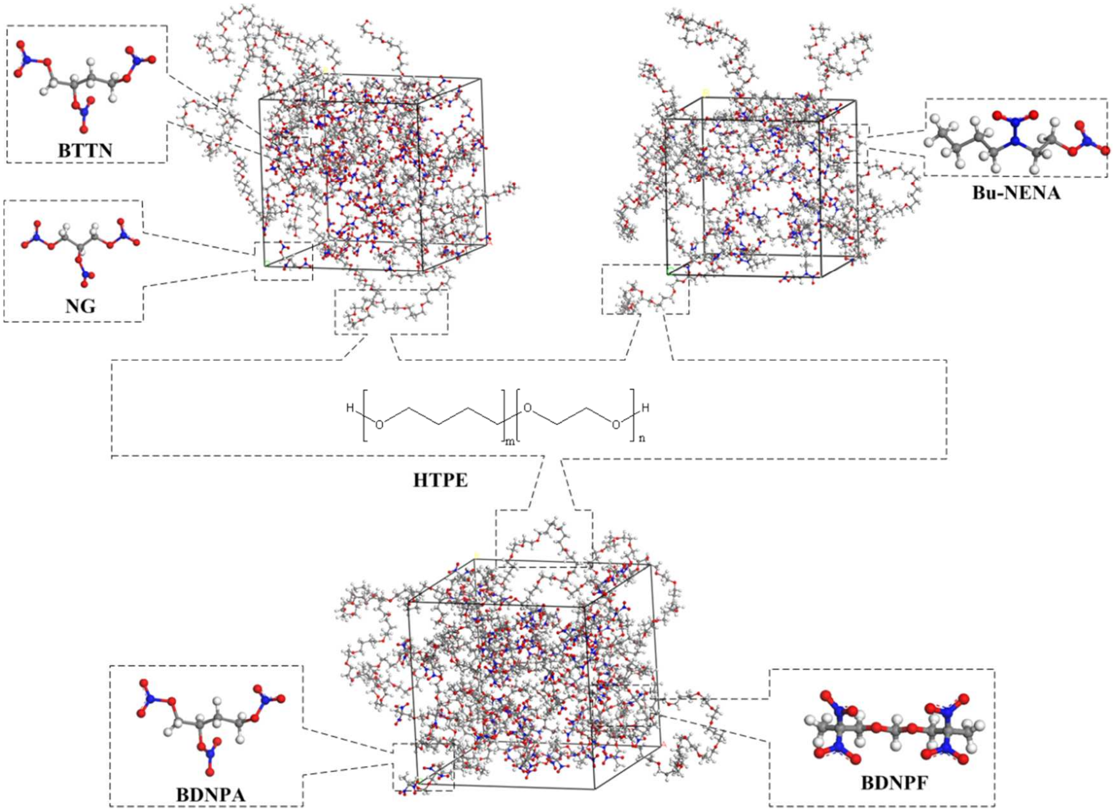
GRAPHICAL ABSTRACT



In order to explore effects of polymer and plasticizers on miscibility and mechanical property, molecular dynamics (MD) simulations and compass force field are performed to investigate the Hydroxy Terminated PolyEther (HTPE) polymer and some energetic plasticizers including Nitroglycerin (NG)/ Butanetriol Trinitra (BTTN) mixture, bis (2, 2-Dintropropyl) acetal (BDNPA)/bis (2, 2-Dinitropropyl) formal (BDNPF) mixture and N-butyl-N-(2-nitroxy-ethyl) nitramine (Bu-NENA). The results show that the polymers and plasticizers are all miscible. The plasticizer can improve the mechanical property of HTPE polymer. The order of binding energy between HTPE and energetic plasticizers is HTPE/Bu-NENA> HTPE/BDNPA/BDNPF> HTPE/NG/BTTN.