

# Theoretical study on the diffusive transport of 2,4,6-trinitrotoluene in polymer-bonded explosive

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Received: 1 December 2010 / Accepted: 17 January 2011 / Published online: 1 March 2011  
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**Abstract** Molecular dynamics (MD) simulations were performed to study the migration of 2,4,6-trinitrotoluene (TNT) in the fluorine rubber binder of polymer-bonded explosives (PBX) over a wide range of temperatures. The diffusion coefficient ( $D$ ) of TNT is determined via micro-canonical (NVE) MD simulation using the COMPASS force field. The calculated diffusion coefficient ( $D$ ) was then used to compute the migration time of TNT based on Fick's second law and the results agree well with the experimental data. The relation between  $D$  of TNT and temperature was confirmed and the results confirm the temperature-dependence of diffusion coefficients of TNT in the binder, but a break is seen about the melt point (the temperature at which the elastomeric state of the binder changes to a viscosity state) in the Arrhenius plot of  $\ln(D)$  versus  $1/T$ .

**Keywords** 2,4,6-Trinitrotoluene diffusion · Polymer-bonded explosive ageing · Molecular dynamics simulation

## Introduction

Polymer bonded explosives (PBXs) are comprised of an elastomeric polymer in which are dispersed particulate solids such as crystalline explosives, oxidizers, or plasticizers. A common problem with PBXs is exudation of small molecule plasticizers [such as 2,4,6-trinitrotoluene (TNT) with low melting point or plasticizers with low molecular weight] from the polymer matrix, leading to the degradation of physico-chemical properties, even under moderate storage conditions [1–4]. This is highly undesirable since the exudation of TNT leads to a decrease in the density and detonation properties of the PBX, significantly influencing the required function of the PBX. In order to determine the shelf life of munitions systems correctly, the ageing characteristics of PBXs (in this work, this refers mainly to the exudation of TNT) must be given more attention. In fact, the exudation of TNT is the diffusive transport of small molecules in the polymer binder, and there are many papers reporting the diffusion of small molecules in the polymer, in which molecular dynamics (MD) calculations were used to determine the diffusion coefficient [5, 6]. To our knowledge, a diffusion coefficient for TNT in PBX has not been calculated, but Valsaraj and co-workers [7] reported the transport mechanism of TNT from contaminated soils into overlying water and obtained a diffusion coefficient. However, when we used this diffusion coefficient to estimate the change of TNT concentration in PBX systems, and compared with our experimental work, the results showed poor coherence.

For the above reasons, it was of interest to undertake a study of such a system using MD simulation techniques. In the present paper, we present the results of a study of the diffusion of TNT molecules through the fluorine rubber

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named F2311 (a co-polymer of vinylidene and chlorotri-fluoroethene, ratio 1:1) over a wide temperature range: 300 K–500 K. The main purpose of this work was to calculate the diffusion coefficient ( $D$ ) of the TNT molecules in the fluorine rubber, which is useful in the estimation of the shelf life of PBXs containing TNT.

## Theory and simulation

Low melting-point additives such as TNT are used widely as plasticizers to improve the mechanical properties of composite explosive formulations. However, TNT migrates easily and exudes from the matrix at high temperatures or under long storage conditions. The migration of TNT in PBX can be described by Fick's second law (Eq. 1a). This expression for migration of TNT within a sphere with radius  $R_0$  in spherical coordinates can be simplified as Eq. 1b, under the given boundary conditions ( $t=0, c=c_0; r=R_0, c=0$  as shown in Fig. 1); the analytical solution of Eq. 1b can be written in terms of the error function (Eq. 1c) [8]

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial c}{\partial x} \right) \Rightarrow \frac{\partial c}{\partial t} = D \left( \frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \frac{\partial c}{\partial r} \right) \Rightarrow c = c_0 \operatorname{erf} \left( \frac{R_0 - r}{2\sqrt{Dt}} \right) \quad (1)$$

where  $D$  is the diffusion coefficient,  $c$  is the concentration of TNT, and  $\operatorname{erf}$  is the error function. In this paper, we set the following parameters:  $c_0=1$ ,  $R_0=25$  mm and

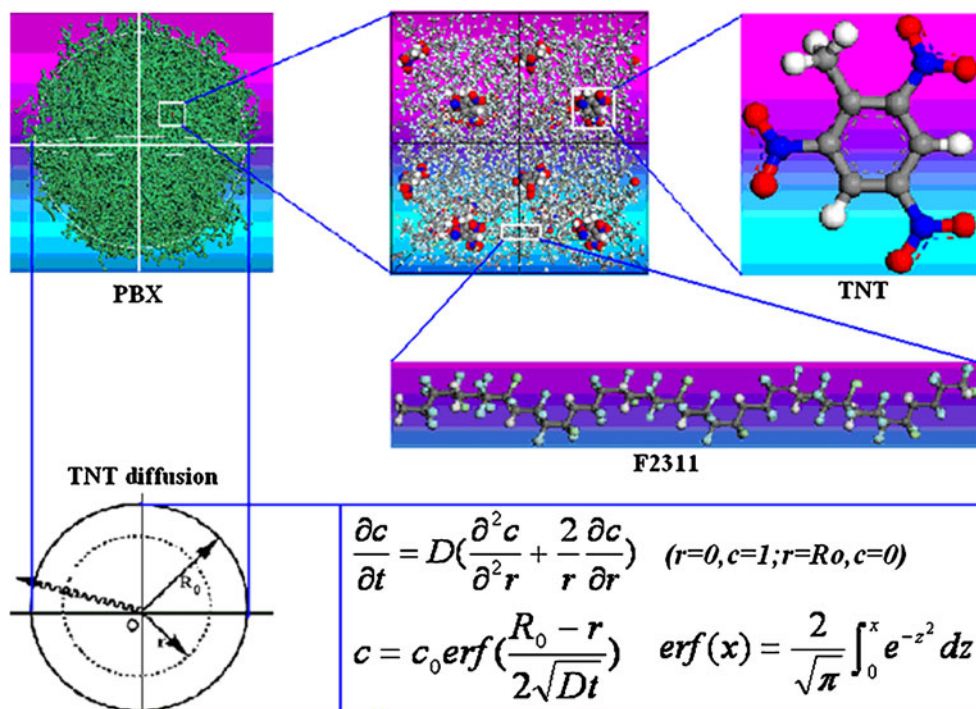
$r=0$  (showing only the change in TNT concentration in the center of the sphere).

The simulation model was built as shown in Fig. 1. The unit cell included five TNT molecules and two F2311 chains (the molecular weight is about 10,000 per chain) and the unit size is about  $26 \times 26 \times 26 \text{ \AA}^3$ . COMPASS force field [9] was used in all cases, and van der Waals (vdW) and Coulomb non-bond interactions were treated using Ewald's summation method [10]. Firstly, the unit cell was minimized using the smart minimizer method in order to eliminate local non-equilibrium, then a MD run (NPT, 100 ps and NVT, 1 ns) was performed in order to further equilibrate the model before using it for data production. Next, a MD run (NVE, 600 ps) was performed for production; the output frequency was every 0.1 ps and a time step of 1 fs was taken for all simulations in this study. The Andersen thermostat and Berendsen barostat were used to maintain constant temperature and pressure ( $10^5$  Pa). The diffusion coefficients were computed by the Einstein-Smoluchowski equation

$$\langle (r(t) - r(0))^2 \rangle = MSD = 6Dt \quad (2)$$

In Eq. 2,  $D$  is the diffusion constant,  $t$  is time,  $r(t)$  is the position vector of the TNT molecules in space at time  $t$ ; MSD is the mean-square displacement of TNT molecules and the brackets denote an ensemble average, which in these simulations is obtained from averaging over all five TNT molecules in the fluorine rubber F2311. The simulations were performed mostly using Material Studio software [11].

**Fig. 1** Schematic representation of unit cell model with 2,4,6-trinitrotoluene (TNT) and fluorine rubber F2311. TNT molecules are represented by *space-filling models*, and F2311 by *wire-frame models*. Based on the hypothesis that TNT diffusion is in the PBX sphere (radius,  $R_0=25$  cm), the process can be described by Fick's second law in the sphere coordinates. The boundary conditions were that TNT concentration is 1 (reduced unit) in the sphere center ( $r=0$ ) at the first occurrence, and 0 on the sphere surface ( $r=R_0$ ) for all other times. The aim was to study the change in TNT concentration at the sphere center



**Results and discussion**

The MSD of TNT was calculated over a wide range of temperature (300 K–500 K) at 40 K intervals (Fig. 2). Averaging was performed over all five TNT molecules and all possible time origins. This led to an increase in statistical fluctuation towards the end of the run. The linear portion of the MSD is least-squares fitted by a straight line to calculate the diffusion coefficient. The calculated diffusion coefficients at different temperature are compared with experimental data [7] in Table 1.

When the calculated diffusion coefficients ( $D_{cal}^{340K} = 0.416$ ) and the experimental diffusion coefficients ( $D_{exp}^{340K} = 18.88$ ) are substituted in the analytic solution of Fick’s equation (see Fig. 1), respectively, we can see the relationship between time and TNT concentration changes in the center of the PBX sphere (Fig. 3). As shown in Fig. 3, when  $D_{exp}^{340K} = 18.88$  was chosen, the time for the migration of half mass is 200,000 s (about 2 days), but with  $D_{cal}^{340K} = 0.416$ , the time is 8,500,000 s (about 98 days); the experimental result is about 100 days [13]. Thus, we can obtain good accordance with experimental data through our calculated diffusion coefficient,

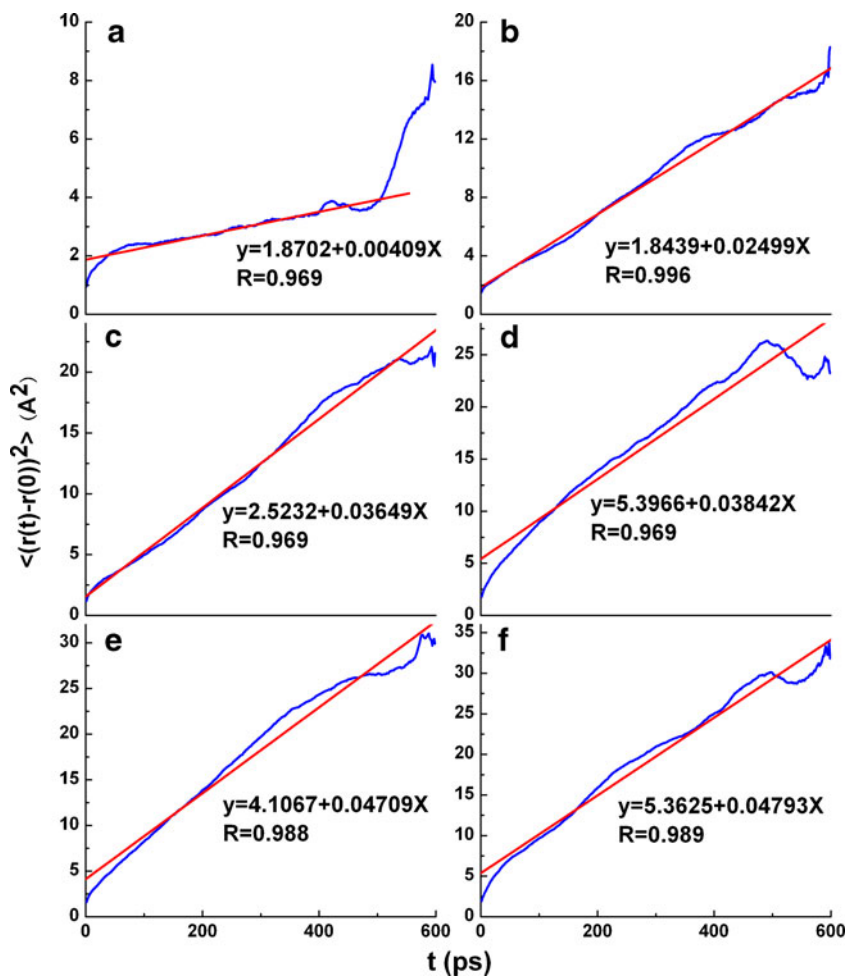
and this parameter,  $D$ , can be used to establish the aging model of PBX.

Barrer [14] was the first to showed that the diffusion of small-size molecules in rubbery polymers is a thermally activated process. Much data in the literature suggests that the transport coefficient (namely  $D$ ) depends on temperature, at a given pressure, via Arrhenius’s law on a narrow range of temperature [15], i.e.,

$$D = D_0 \exp(-Q_S/RT) \tag{3}$$

where  $Q_S$  is the apparent activation energy,  $T$  is the temperature, and  $R$  is the gas constant. According to free volume models, the diffused molecules follow different mechanisms at ranges of high and low temperature. In general, the dividing line between two temperatures defines a special area, such as the glass transition temperature, or the melting point. In the high temperature range, with increased temperature the diffused molecules can move more freely, giving an increase in total free volume. Therefore, the activation energy of diffusion is relatively small. If the temperature is high enough to cancel out the constraint of the polymer chains, the diffused molecules can

**Fig. 2** The mean-square displacement (MSD) for TNT at different temperatures. *Straight red lines* Least-squares fits to the curves. **a** 300 K, **b** 340 K, **c** 380 K, **d** 420 K, **e** 460 K, **f** 500 K



**Table 1** Diffusion coefficients ( $D$ ) of 2,4,6-trinitrotoluene (TNT) ( $10^{-6} \text{ cm}^2 \text{ s}^{-1}$ )

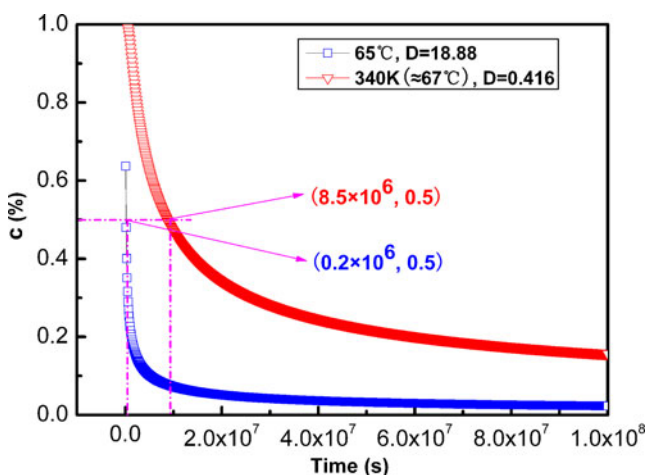
Temperature (K)	300	340	380	420	460	500
$D_{\text{calculated}}$	0.068	0.416	0.608	0.64	0.785	0.799
$D_{\text{experimental}}$	1.18 <sup>a</sup>	18.88 <sup>b</sup>				

<sup>a</sup> Diffusion coefficient of TNT in soil [7]

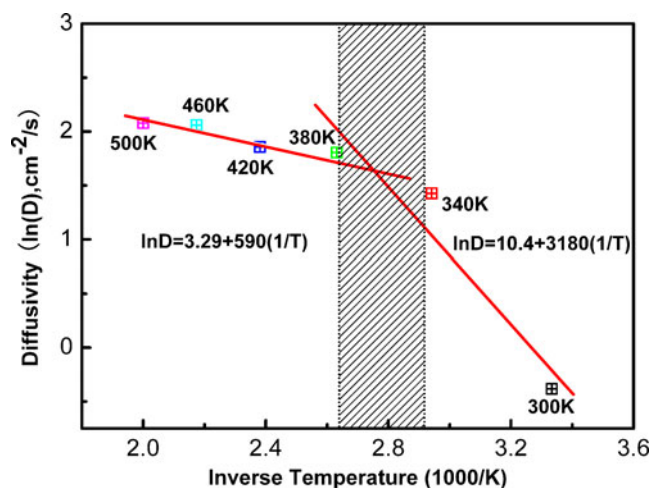
<sup>b</sup> Relationship between the diffusion coefficient and temperature [12]

move quasi-freely as in liquid. Conversely, in the low temperature range, i.e., near or below the polymer glass transition temperature or the melting point, the activation energy obviously increases, the reason being that the total free volumes decrease and the constraints of polymer chains to diffusion in the solid state increase, unlike in the liquid state.

According to Eq. 3, Arrhenius plots of  $\ln(D)$  versus  $1/T$  for TNT molecules in the binder F2311 is shown in Fig. 4. From the results shown in Fig. 4, the temperature-dependence of the diffusion coefficient of TNT shows a break at about 340–380 K. The temperature-dependence of the diffusion coefficient of diffused molecules in polymers has been the subject of a number of studies [16]. It is reported by some researchers that the Arrhenius's plot of  $\ln(D)$  as a function of  $1/T$  presents as two zones separated by a glass transition, and is characterized by different activation energies [17, 18]. But the present research finds that the two zones are separated by the melt point of F2311 (about 70–80 °C). Below this temperature, the binder F2311 is in an elastomeric state, and the activation energy is relatively high based on the fitted coefficient (3,180) of the low temperature range. However, above this temperature the binder F2311 is in a viscoelastic state, in which the chain segmental mobility is greater than that in the



**Fig. 3** Relationship between the concentration of TNT in the PBX sphere center and time



**Fig. 4** Arrhenius plot of  $\ln(D)$  versus  $1/T$  for TNT. Red line Best fit through the points

elastomeric state. Therefore, the activation energy is relatively low according to the fitted coefficient (590) in the of high temperature range.

## Conclusions

The diffusion coefficient of TNT molecules in the F2311 binder of PBX was calculated over a wide range of temperatures: 300 K–500 K. The calculated diffusion coefficient is higher (about one order of magnitude) than experimental data from Valsaraj and co-workers [7]. The main reason is that these latter authors chose the soil as the medium for TNT diffusion. Here, we chose PBX systems, whose density is higher than that of soil. Therefore, it is easy to explain the difference between the computed and experimental results. In addition, TNT migrating time based on Fick's second law and the calculated diffusion coefficient agrees well with the experimental data, which confirms the reliability of our calculated diffusion coefficient of TNT in PBXs. From the results of the temperature-dependence of the diffusion coefficient of TNT in F2311 binders, it is concluded that, over the whole temperature range, the results show that two different slopes do exist for the Arrhenius plot of  $\ln(D)$  versus  $1/T$ . The main reason is that the F2311 binder's transition from the elastomeric state to the viscoelastic state occurs within the range of 340 K–380 K, and migration of TNT in the F2311 binder's elastomeric state is more difficult than that in viscoelastic state.

In general, for any PBXs, as long as the main disabled pattern is the migration and exudation of TNT, the diffusion coefficient of TNT becomes an important parameter, because it underlies the aging model of PBXs. In this paper, the calculated diffusion coefficient of TNT in the

F2311 binder by means of MD simulation can estimate exactly the migration time of TNT associated with Fick's second law. Therefore, this method can be used to construct an aging model for PBXs.

**Acknowledgment** The authors are grateful for financial support from the National Natural Science Foundation of China (No. 10832003) and CAEP fund (No.626010934).

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