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A promising azido nitrate ester plasticizer for propellant

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ABSTRACT

Plasticizers are a class of materials which are added to increase not only the plasticity but also the process-ability, flexibility and durability of the propellants. Azido nitrate ester plasticizers with both $-N_3$ and $-ONO_2$ groups in the molecule have attracted great attentions. In this work, an azido nitrate ester compound (2-azidoethyl nitrate ester, AENE) was designed with the aid of computer. To explore whether AENE is a good plasticizer for NC (nitrocellulose) and GAP (glycidyl azido polymer), its crystal structure, stability, and energetic properties as well as the compatibility and mechanical properties of the constructed AENE/NC and AENE/GAP composites were investigated using the density functional theory (DFT) and molecular dynamics (MD) methods. Results show that compared with the traditional plasticizer NG (nitroglycerin), AENE not only has comparable stability and energetic properties, but also possesses a better ability to improve the mechanical properties of NC and GAP. The larger contents of AENE are, the better mechanical properties of AENE/NC and AENE/GAP composites have. These suggest AENE is a promising azido nitrate ester plasticizer for NC and GAP and worth the further experimental researches.

1. Introduction

High-energy solid rocket propellants are composite materials which are generally composed of binders, plasticizers, oxidizers, stabilizer, and fuels, etc. [1]. Nitrocellulose (NC) and glycidyl azide polymer (GAP) are two well-known energetic binders. To improve the plasticity, process-ability, flexibility and durability of binders, adding appropriate plasticizers is an effective way [2]. Thus, researchers have devoted to develop various kinds of plasticizers.

The most common plasticizers are nitrate ester plasticizers and azido plasticizers. The nitrate ester plasticized polyether propellants have been widely studies [3,4]. With the development of the azido binder, azido plasticizers have attracted more and more attentions, since azido binder and azido plasticizer have the similar structural elements, i.e., $-N_3$ group. The similar structural elements may result in good compatibility among the components [5]. Although considerable works have been done on azido plasticizers, the synthesized azido compounds especially those used in practical are rare. Nitrate ester plasticizers and azido plasticizers have their own characters. In order to combine the advantages of nitrate ester and azido compounds, in this work, a new compound 2-azidoethyl nitrate eater (AENE, Fig. 1) with both $-ONO_2$ and $-N_3$ groups in the molecule was designed with the aid of computer and studied using the DFT (density functional theory) and MD (the molecular dynamics) methods. This work aims to (1) investigate whether AENE can be a plasticizer of NC and GAP propellants; (2) explore which plasticizer, AENE or NG, has better plasticizing effect on NC and GAP; (3) compare the performance of NC composites with that of GAP composites.

In the first part of the study, the compatibility of AENE with NC and GAP was examined and the mechanical properties of various AENE/NC and AENE/GAP composites were evaluated. As an energetic plasticizer, besides the good compatibility with binders and the ability to improve the mechanical properties, it should have a certain stability and energy output. Thus, in the next part, the stability and energetic property of AENE were investigated. The performances of AENE were all compared with that of the conventional plasticizer NG. In the last part, the molecular packing of AENE was predicted, which provides structural information for the identification of this new plasticizer. The molecular structures of NG, NC, and GAP are also shown in Fig. 1.

2. Computational details

2.1. MD simulation

The amorphous models of AENE, NC and GAP, and six composites, i.e., AENE/NC1, AENE/NC2, AENE/NC3, AENE/GAP1, AENE/GAP2, and AENE/GAP3, were constructed using the

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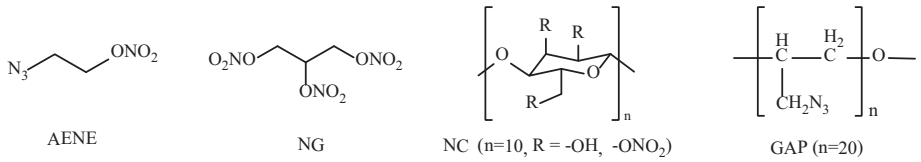

Fig. 1. Molecular structures of AENE, NG, NC, and GAP.

Materials Studio (MS) program package [6]. The molecular weight of all models were taken to be around 10,000–12,000. To compare the plasticizing effect of AENE with the conventional plasticizer NG, the NG/NC and NG/GAP composites were also constructed. The parameters of all constructed models, like initial densities, the number of chains and atoms, etc. are listed in Table 1. The crystal density of AENE was predicted using the molecular mechanics method with the Dreiding force field [7] and that of NC and GAP came from Refs. [8,9]. Based on the weight percentage of each component in the blending systems, the densities of the composites were determined. Here, the chain of GAP is constructed by 20 repeat units [10] and that of NC is constructed by 10 chain segments with the nitrogen contents of 12.04% [11].

The constructed models were performed energy minimizations first and then the MD simulation. The details can be seen in our previous work [10]. When the systems reached equilibrium, we did the analyses of the compatibility and the mechanical properties of various composites.

The compatibility was evaluated by the solubility parameter (δ), which is defined as the square root of the cohesive energy density (*CED*), as shown in Eq. (1):

$$\delta = \sqrt{CED} \tag{1}$$

MD calculation provides an easy way to evaluate the *CED* of polymers and has been used in many studies [12–14].

Mechanical parameters, like *E* (tensile modulus), *K* (bulk modulus), *G* (shear modulus), γ (Poisson's ratio), and *C* (Cauchy pressure), were predicted using Eq. (2).

$$E = \frac{\mu(3\lambda + 2\mu)}{\lambda + \mu}, \quad K = \lambda + \frac{2}{3}\mu, \quad G = \mu,$$
$$\gamma = \frac{\lambda}{2(\lambda + \mu)}, \quad C = C_{12} - C_{44} \tag{2}$$

where μ and λ are the Lamé coefficients, which were calculated from the elastic coefficients C_{11} and C_{12}, i.e., $\mu = (C_{11}-C_{12})/2$ and $\lambda = C_{12}$ [15].

The MS program gives the values of solubility parameter and mechanical parameters in an output file.

2.2. DFT calculation

AENE was optimized with the DFT-B3LYP [16–17] method and the 6-31G* basis set [18] using the Gaussian 03 program package [19]. The gas-phase heat of formation ($\Delta H_f(g)$) was calculated from the isodesmic reaction (3). This procedure has been proved to be very successful to obtain the $\Delta H_f(g)$ [20–23].

$$N_3CH_2CH_2ONO_2 + 2CH_4 = CH_3N_3 + CH_3ONO_2 + CH_3CH_3 \tag{3}$$

The reaction enthalpy (ΔH_r) of the isodesmic reaction at 298 K was predicted using the Eq. (4):

$$\Delta H_r = \sum \Delta H_{f,p} - \sum \Delta H_{f,R} = \Delta E_0 + \Delta E_{ZPV} + H_T + \Delta nRT \tag{4}$$

where $\Delta H_{f,P}$ and $\Delta H_{f,R}$ are the heats of formation of products and reactants at 298 K, respectively. ΔE_0 and ΔE_{ZPV} are the differences between products and reactants for the total energies at 0 K and for the zero-point vibrational energies (E_{ZPV}), respectively, and ΔH_T is the thermal enthalpy correction from 0 to 298 K. The $\Delta H_f(g)$ of CH_4, CH_3ONO_2, and CH_3CH_3 are −74.6, −122, and −84 kJ mol^{-1}, respectively, which are taken from the experimental values [24]. For the $\Delta H_f(g)$ of CH_3N_3, which is lack of experimental data, we calculated it at the G2 level from the atomization reaction [25]. The obtained value is 296.56 kJ mol^{-1}.

The solid-state heat of formation ($\Delta H_f(s)$) was estimated using the Eqs. (5) and (6) [26,27]:

$$\Delta H_f(s) = \Delta H_f(g) - \Delta H_{sub} \tag{5}$$

$$\Delta H_{sub} = \alpha A_S^2 + \beta(v\sigma_{tot}^2)^{0.5} + \gamma \tag{6}$$

ΔH_{sub} is the sublimation enthalpy, A_S, v, and σ_{tot}^2 were obtained using a self-compiled program [28] based on the B3LPY/6-31G* calculations. The corresponding values of coefficients α, β, and γ at the B3LPY/6-31G* level come from Ref. [27], which are 4.23×10^{-4} kcal mol^{-1} Å^{-4}, 2.579379 kcal mol^{-1}, and −6.73354 kcal mol^{-1}, respectively.

Detonation properties were predicted using the empirical Kamlet–Jacobs equations [29].

$$D = 1.01(N\overline{M}^{0.5}Q^{0.5})^{0.5}(1 + 1.30\rho) \tag{7}$$

Table 1
Some parameters of all constructed amorphous units.[a]

	Initial density (g cm^{-3})	Number of chains	Number of atoms	Weight	Mass ratio
AENE	1.50	80	1040	10,566	
NC	1.60 [8]	4	1036	10,697	
GAP	1.30 [9]	5	1216	10,000	
AENE/NC1	1.57	20/3	1037	10,664	24.8/75.2
AENE/NC2	1.55	40/2	1038	10,631	49.7/50.3
AENE/NC3	1.52	60/1	1039	10,599	74.8/25.2
AENE/GAP1	1.34	20/4	1232	10,641	24.8/75.2
AENE/GAP2	1.38	35/3	1184	10,622	43.5/56.5
AENE/GAP3	1.42	50/2	1136	10,603	62.3/37.7
NG/NC	1.60	13/3	1037	10,974	26.9/73.1
NG/GAP	1.36	12/4	1212	10,724	25.4/74.6

[a] Initial density is refer to the setting value when we constructed the amorphous unit.