Structure and property of propellant based on nitroglycerine/glycerol triacetate mixed plasticizers: molecular dynamics simulation and experimental study

Lilong Yang, Xionggang Wu, Junqiang Li, Tao Chen, Meng Liu and Qiwen He

X’ian Modern Chemistry Research Institute, X’ian 710065, People’s Republic of China

Molecular dynamics simulation has been used to investigate the influence of nitroglycerine (NG)/glycerol triacetate (GTA) mixed plasticizers on the plasticizing ability of nitrocellulose (NC) binder in solid propellant. The radial distribution function and binding energy indicated that NC/plasticizers blends showed stronger intermolecular interaction of van der Waals and hydrogen bonds. The mean-squared displacements of plasticizers and volume distribution revealed that the mobility of plasticizer GTA in the NC polymer binder was higher than that of NG. Then, the mechanical properties of the propellant based on NG/GTA mixed plasticizers were investigated systematically using experimental and simulation calculation method. The results suggested that the ductility of propellant based on NG/GTA mixed plasticizers was improved, implying that NG/GTA mixed plasticizers have a higher plasticizing efficiency for NC. Furthermore, we conducted experimental studies on the effects of NG/GTA mixed plasticizers on the energy and combustion properties of propellants. It was shown that NG/GTA mixed plasticizers could enhance the combustion efficiency of propellants effectively at low pressures. These computational and experimental studies provided guidance for the application of NG/GTA mixed plasticizers in high-performance propellants.

© 2021 The Authors. Published by the Royal Society under the terms of the Creative Commons Attribution License http://creativecommons.org/licenses/by/4.0/, which permits unrestricted use, provided the original author and source are credited.
1. Introduction

As the essential energy source of weapon systems, solid propellants are widely applied to medium-caliber rockets and various gas generators [1–3]. Conventional composite modified double-base (CMD) propellants comprise binder nitrocellulose (NC), plasticizer nitroglycerine (NG), energetic ingredients nitramine (like hexogon RDX and octogen HMX) and other minor additives such as processing aids [4,5]. The simple composition, high energy, environment-friendliness and low smoke signature are some of the main advantages of CMDB propellant [6,7]. The binder as the main body and skeleton of a propellant is an important high-performance component, which glues together other additives to obtain excellent overall properties, such as dimensional stability, structural integrity and mechanical property [8–10]. NC obtained by nitration of cellulose is widely applied to CMD propellants as binder [11]. NC used as binder possesses properties such as good chemical compatibility with CMDB propellant and other components, excellent dispersion uniformity, wide range of raw materials and lower production costs [12–14]. Plasticizer is a type of material for improving the plasticity and processing ability of the propellant, as well as flexibility and durability. Generally, the plasticizing ability of plasticizer affects the performances of combustion, mechanics and energy of propellants [15,16].

Many different types of plasticizers have been used in propellant formulations, but they need to meet some specifications regarding the final application. There has been a significant amount of low viscosity nitrogenous compounds being developed in recent years including N-butyl-N-(2-nitrooxyethyl) nitramine (Bu-NENA), trimethylethane trinitrate (TMETN), butanetriol trinitrate (BTTN) and bis-(2,2-dinitropropyl)-acetal/formal (A3, BDNPA/F). These compounds as plasticizers possess superior ability to enhance the performance of propellant such as mechanics, energy and safety [17–21]. Yang et al. [19] reported their study on the properties for the different NC and glycidyl azide polymer (GAP) matrix composites with an azido nitrate ester plasticizer (2-azidoethyl nitrate ester, AENE) by theoretical simulation, in which the addition of AENE was observed to enhance the mechanical property of NC composites with an azido nitrate ester plasticizer (2-azidoethyl nitrate ester, AENE) by theoretical simulation, in which the addition of AENE was observed to enhance the mechanical property of NC and GAP. In addition to improving the energy performance of propellant, the volatility of energetic triacetin as plasticizer. The interaction between plasticizers and binder was neglected while numerous studies have focused on improving the insensitivity, mechanical and thermal properties of propellants at low temperatures.

The development of propellant technology has allowed the capability to obtain higher energy and less vulnerable composition [30]. A low-vulnerability propellant was prepared by using cellulose acetate (CA) and hydroxy terminated polybutadiene (HTPB) as binders and GAP with molecular weight of 400–600 as a high-energy plasticizer, and its insensitivity, combustion and mechanical performance was investigated [31]. The ballistic, mechanical and thermal performance of RDX-based LOVA propellant was reported in detail by Kumari et al. [32]. Above-mentioned propellant was prepared by using CA and NC combination as binder and novel tetraazido ester instead of non-energetic triacetin as plasticizer. The interaction between plasticizers and binder was neglected while numerous studies have focused on improving the insensitivity, mechanical and thermal properties of propellants [33,34]. In this paper, molecular dynamics (MD) simulations were performed to investigate the influence of NG/GTA mixed plasticizers on the plasticizing ability of NC binder in solid propellant. The intermolecular interaction between NC and plasticizers has been evaluated using the radial distribution function and the binding energy. In addition, the mean-squared displacements (MSDs) of plasticizers and volume distribution were used to explore the migration ability of the plasticizer in NC. Besides, plasticizing efficiency of NG/GTA mixed plasticizers on NC was analysed by mechanical properties determined from the MD simulation and experimental study. Furthermore, we conducted experimental studies on the effects of NG/GTA mixed plasticizers on the energy and burning performance of CMDB propellant. The ideal energetic performance of propellant was obtained by theoretical calculation based on the principle of minimum free energy. The burning
rates and combustion wave structure of propellants were investigated. It is believed that the computational and experimental study is able to increase the understanding of the interaction and mechanisms between a NC polymer and NG/GTA mixed plasticizers in solid propellants, and provide guidance for the applications of NG/GTA mixed plasticizers in high-performance propellants.

2. Material and method

2.1. Construction of models

MD simulations were carried out using Material Studio 8.0 software. The influence of NG/GTA mixed plasticizers on the plasticizing ability of NC binder was studied by COMPASS (Condensed-phase Optimized Molecular Potential for Atomistic Simulation Study) force field. Previously, the COMPASS force field was used in molecular simulation of polymer [35]. The Visualizer module of Materials Studio software was applied to create molecular models of NC, NG and GTA, and then the structure was optimized by the Forcite module. The Homopolymer Builder module was used to construct the NC polymer chain with 20 repeat units and nitrogen contents of 12%. The molecular and optimized chemical structures of NC, NG and GTA are presented in figure 1. And here, carbon atoms, hydrogen atoms, nitrogen atoms and oxygen atoms are represented as grey, white, blue and red, respectively. In order to facilitate subsequent analysis, the atoms are labelled according to the different type of atomic force field. O atoms of the hydroxyl group for NC are assigned to O1, O and N atoms of the nitro group for NG are labelled O2 and N1, respectively, O atoms attached to nitro group in NG as O3. O atoms in the carbonyl group in GTA are denoted to O4, and O atoms attached to carbonyl group of GTA as O5 in figure 1b.
2.2. Molecular dynamics simulation method

For investigation of the influence of NG/GTA mixed plasticizers on the plasticizing ability of NC binder, pure NC and NC/NG and NC/NG/GTA blends were constructed by Amorphous cell module, as presented in figure 2. The weight proportion of NC and plasticizer was nearly 50:50, and the mass ratios of NG and GTA in mixed plasticizers were nearly 3:1, 2:1, 1:1, respectively. Simulation procedure was conducted by Forcite module under COMPASS force field. To begin with, geometry optimization of the amorphous systems such as pure NC and NC/NG and NC/NG/GTA blends was conducted by Smart Algorithm method minimization with 10,000 steps and convergence level of fine in order to get the eventual structure with minimum energy. Afterwards, 400 ps MD simulations were executed on individual systems to get the equilibrium conformations at the isothermal-isobaric (NPT) ensemble. The parameters were set such that the Andersen thermostat temperature was 298 K and Berendsen barostat pressure was 101.325 kPa, and the time step was assigned as 1 fs. An atom-based method and Ewald summation were used for van der Waals and electrostatic interactions, respectively. The MD simulation system reached equilibrium when the energy fluctuated slightly near the average energy value or the temperature fluctuation was within 10 K. Consequently, the influence of NG/GTA mixed plasticizers on the structure, energy and mechanical performance of NC was analysed to obtain the radial distribution function, intermolecular interaction energy, MSD, volume distribution and static elastic properties.

2.3. Materials and propellant preparation

The CMDB propellant was composed of NC, GTA, NG, RDX, combustion catalyst and other additive reagents. The NC/NG/GTA blends are used as energetic binder and plasticizer system to ensure that the propellants achieve higher performance, excellent structural integrity and lower vulnerability. GTA was bought from Shanghai Lingfeng Chemical Reagent Co. Ltd (China). NC was obtained from Sichuan Nitrocell Co. Ltd (China). NG was provided by Xi’an Modern Chemistry Research Institute (China). Hexogeon (RDX) was obtained from Gansu Yinguang Chemical Industrial Group Co. Ltd (China). Four different propellant formulations with different content of NG and GTA were designed (table 1) and prepared. The preparation of propellant includes three basic steps, namely granule preparation, casting and solidification. Above all, the mixture containing the whole NC, solid components and a part of the plasticizer was fabricated into right circular cylinder granules with diameter and length of about 1 mm. Afterwards, the granules were put into a mould, and the interstitial spaces among the granules were filled with a casting solvent composed of residual plasticizer. Finally, under heating, the plasticizer diffused into the polymer binder to solidify the two parts into an integral solid propellant.
2.4. Properties evaluation of propellant

Tensile testing was carried out on an Instron 4505 (USA) universal testing machine with a temperature of −40°C, 20°C and 50°C. The cured propellant sample was cut into slices with thickness of 2 mm, and the slice was stamped into a dumbbell shape of 75.0 (length) × 4.0 (width) × 2 (thickness) mm³. The tensile strength and elongation at break were attained from the stress–strain curve for the crosshead speed as 100 mm min⁻¹. The average values of five samples were reported.

The ideal energy performance of the CMDB propellant was calculated on the basis of the minimum free energy principle. The software Energy Calculation Star (v. 5.0) was designed in the Xi'an Modern Chemistry Research Institute [36]. The calculation conditions were set as follows. (1) The pressure inside the combustion chamber was 6.9 MPa and it was 0.1 MPa at ambient pressure; (2) nozzle expansion ratio was optimized, that is, the nozzle outlet pressure was equal to the ambient pressure; (3) nozzle outlet expansion angle equalled 0°; (4) the initial temperature was 298 K. Based on the equilibrium flow assumption, the combustion products of the composition immediately reached equilibrium during the expansion process.

The side walls of the 5 mm × 5 mm × 150 mm propellant strands were covered by polyvinyl alcohol and then dried with six repetitions. The burning rate of propellants was tested using a chimney-type strand burner system. At an initial temperature of 20°C and an AC voltage of 100 V, the propellant was ignited in the nitrogen-filled chamber using nickel–chromium alloy wire inserted in the top of the strand. Two low melting point fine fuses with a distance of 100 mm were inserted into the strand and the start and end times of the combustion signal were captured. The burning rate of propellant was calculated by five repeated experiments at each pressure. The standard deviation of the average experimental results obtained was 0.13–0.25. The burning rate pressure exponents of propellant labelled n were obtained by Vieille’s Law: \( u = a P^n \).

The combustion wave structure of propellant strand of 7 mm × 7 mm × 120 mm was determined by a 25 µm diameter \( \Pi \) type dual tungsten–rhenium thermocouple. The side walls of the propellant strands were covered with polyvinyl alcohol to achieve flame protection. The ignition was performed with nickel–chromium alloy wire. The combustion surface moved towards the thermocouple by degrees and finally reached the flame zone. Therefore, the entire combustion process of the condensed phase to the gaseous phase can be recorded.

3. Results and discussion

3.1. Radial distribution function of different atoms in NC/NG/GTA blend

The radial distribution function \( g(r) \) is used to assess the possibility of another atom appearing at a distance \( r \) from an assigned atom. The type of interaction forces could be determined from the position of the peaks and intensity could be determined from the heights of the peaks in the radial distribution function. Intermolecular action consists of hydrogen bonding and van der Waals (vdW) forces, which in turn include dipole–dipole, induction and dispersion interaction forces. Hydrogen bonding, strong vdw and weak vdw interaction forces correspond to distances of 2.6–3.1 Å, 3.1–5.0 Å or above 5.0 Å between atoms, respectively [18,35]. Herein, we explored the potential interaction force between hydroxyl functional group (−OH) in NC and nitrate functional group (−ONO₂) in NG.
plasticizer/acetate functional group (−CH₃COO) in GTA plasticizer. The radial distribution function curves of different atom pairs in NC polymer and plasticizers are shown in figure 3.

The \( g(r) \) curves for the atom pairs O₁−O₂, O₁−O₃ formed between NC and NG and O₁−O₄ formed between NC and GTA in figure 3 showed peaks at distances of 2.61 Å, 2.92 Å and 2.73 Å respectively, verifying that a hydrogen bond interaction existed both between NC and NG and between NC and GTA. Besides, O₁−O₄ demonstrated a higher peak value of \( g(r) \) by comparison with O₁−O₂ and O₁−O₃, suggesting that the hydrogen bond interaction between NC and GTA was stronger than that between NC and NG. The strong peaks of atom pairs O₁−O₃ and O₁−N₁ appeared in the range of 3.1 Å–5.0 Å, suggesting that the interaction force between atoms was a strong vdW force. The \( g(r) \) curve for the atom pair O₁−O₅ of the NC/GTA had no peak, indicating there was no force between O₁ and O₅. It can be concluded that the major interaction force was hydrogen bond between NC and GTA, as well as the hydrogen bond and strong vdW forces between NC and NG.

3.2. Binding energy for NC and plasticizers

The binding energy (\( E_{\text{binding}} \)) can be used to evaluate the compatibility of two components in a blend. It is determined in terms of the negative value of the intermolecular interaction energy (\( E_{\text{inter}} \)): \( E_{\text{binding}} = -E_{\text{inter}} \). The intermolecular interaction energy is calculated from the total energy of the blend and the energy of the individual components at equilibrium condition. The \( E_{\text{binding}} \) of NC and plasticizer is calculated by the following formula.

\[
E_{\text{binding}} = -E_{\text{inter}} = -(E_{\text{total}} - E_{\text{NC}} - E_{\text{plasticizers}}),
\]

where \( E_{\text{total}} \) is the total energy for NC/plasticizer blend. \( E_{\text{NC}} \) and \( E_{\text{plasticizers}} \) are the total energy for NC and plasticizers, respectively.

For comparison, the \( E_{\text{total}}, E_{\text{NC}}, E_{\text{plasticizers}} \) and \( E_{\text{binding}} \) of different NC/plasticizer blend are listed in table 2. The binding energy of NC/NG blend was greater than that of NC/NG/GTA blend, indicating that the compatibility of NC and NG was stronger than that of NC and GTA. This result further indicated
the conclusion that the intermolecular interaction between NC and NG is stronger than between NC and GTA.

3.3. Migration of plasticizer in NC matrix

The diffusion coefficient \( D \) is able to reflect the migration ability of a plasticizer, which can be determined by means of the MSD and simulation time \( t \) [37]. The formula for MSD of plasticizer is as follows:

\[
\text{MSD} = S(t) = \langle |r_t - r_0|^2 \rangle,
\]

(3.2)

where \( r_0 \) and \( r_t \) are the locations of the plasticizer at time 0 and \( t \), respectively. Based on the Einstein equation, the expression of \( D \) is obtained as

\[
D = \lim_{t \to \infty} \frac{\langle |r_t - r_0|^2 \rangle}{6t},
\]

(3.3)

The ultimate \( D \) value is calculated by combination of equations (3.2) and (3.3):

\[
D = S(t) = \frac{a}{6t},
\]

(3.4)

where \( a \) represents the slope of MSD–\( t \) curve.

With the aim of further investigating the influence of GTA and NG plasticizers on the plasticization ability of NC, the MSD–\( t \) and the linear fitting curves reflecting the migration ability of GTA and NG plasticizers into the NC matrix are shown in figure 4. It is thus clear that the MSD of GTA and NG plasticizers in NC matrix was almost linearly dependent on the simulation time. GTA always displayed a higher MSD value than NG, indicating that the migration ability of GTA in NC matrix was higher than that of NG. In the end, the diffusion coefficients \( D \) of GTA and NG plasticizers in NC binder calculated by equation (3.4) were \( 6.07 \times 10^{-11} \text{ m}^2 \text{ s}^{-1} \) and \( 5.83 \times 10^{-11} \text{ m}^2 \text{ s}^{-1} \), respectively.

Table 2. Binding energy (kcal mol\(^{-1}\)) between NC and plasticizers.

| blend       | \( E_{\text{total}} \) | \( E_{\text{NC}} \) | \( E_{\text{plasticizers}} \) | \( E_{\text{binding}} \) |
|-------------|-------------------------|---------------------|-------------------------------|---------------------------|
| NC/NG       | -7466.01                | -1223.45            | -4999.76                      | 1242.80                   |
| NC/NG/GTA   | -5859.16                | -839.74             | -4259.94                      | 759.48                    |

Figure 4. The MSD–\( t \) curves and their linear fitted curves of plasticizer in NC matrix.
This illustrated that GTA was easier to migrate in NC. This result also verified that the plasticization efficiency of GTA on NC binder was stronger than that of NG.

3.4. Volume distribution of NC/plasticizers blend

The volume distribution profile of NC/plasticizers blend was determined by MD simulation analysis. In figure 5, the grey region is the occupied volume of NC/plasticizers blend ($V_{\text{occup}}$), and the blue region is the free volume ($V_{\text{free}}$), indicating the intermolecular interstitial space. Table 3 lists the data of $V_{\text{occup}}$ and $V_{\text{free}}$ for NC/plasticizers blends. The simulated $V_{\text{occup}}$ was larger for different NC/NG/GTA blends than for the NC/NG blend. Simultaneously, the volumes for individual GTA and NG molecules calculated in figure 5 were 0.21 nm$^3$ and 0.16 nm$^3$, consistent with the fact that the $V_{\text{occup}}$ value of NC/NG/GTA was higher than those of NC/NG. Especially, $V_{\text{free}}$ value of NC/3NG/GTA blend was significantly greater than those of NC/NG blend, which was beneficial to the movement of molecular chains and brought about an increase of structural flexibility. Besides, $V_{\text{free}}$ values of NC/NG/GTA blends were found to decrease with increasing GTA content in mixed plasticizers, which increased the rotational resistance of NC molecular chains and thus led to the decrease in mechanical property.

3.5. Mechanical property of NC/plasticizers blend

The mechanical property of propellant is very important, which affects its processability and safety. The relationship of stress and strain for material abides by the universal Hooke’s Law, and
the equation is
\[ \sigma_i = C_{ij}e_j, \]  
(3.5)

where \( C_{ij} \) (\( i,j = 1-6 \)) is a \( (6 \times 6) \) matrix of elastic coefficient. By considering the strain energy, the matrix of elastic coefficient is symmetrical, that is, \( C_{ij} = C_{ji} \). Consequently, it has 21 elastic coefficients to express the relationship between stress and strain of anisotropic material. With regard to most commonly used anisotropic materials, the 21 elastic coefficients \( C_{ij} \) are independent of each to other. An isotropic material has only two independent elastic coefficients, which are called Lame coefficients (\( \lambda \) and \( \mu \)). Using \( \lambda \) and \( \mu \), the tensile modulus \( E \), shear modulus \( G \), bulk modulus \( K \) and Poisson’s ratio \( \gamma \) are calculated by the following equations [38]. The program supposes that the material is isotropic, and the computational isotropic mechanical properties of the material are obtained.

\[
\begin{align*}
E &= \frac{\mu(3\lambda + 2\mu)}{\lambda + \mu}, \\
K &= \lambda + \frac{\mu}{3}, \\
\gamma &= \frac{\lambda}{2(\lambda + \mu)}, \\
G &= \mu.
\end{align*}
\]  
(3.6)

Poisson’s ratio (\( \gamma \)) is often used to assess the plasticity of materials. There is a relation between Poisson’s ratio and different moduli:

\[ E = 3K(1 - 2\gamma) = 2G(1 + \gamma). \]  
(3.7)

Due to the matrix of elastic coefficients being symmetric, table 4 only lists partial coefficients of different blends. According to the difference of the elastic coefficients of different blends, it can be

| Table 3. Occupied and free volume of NC/plasticizers blends. |
|---|---|---|---|---|
| models | NC/NG | NC/3NG/GTA | NC/2NG/GTA | NC/NG/GTA |
| \( V_{\text{occup}} \) (\( \text{nm}^3 \)) | 36.61 | 37.77 | 38.67 | 39.30 |
| \( V_{\text{free}} \) (\( \text{nm}^3 \)) | 6.68 | 7.62 | 4.33 | 3.56 |

| Table 4. The elastic coefficients and moduli of NC/plasticizers blends (in GPa). |
|---|---|---|---|---|
| constants | NC/NG | NC/3NG/GTA | NC/2NG/GTA | NC/NG/GTA |
| \( C_{11} \) | 13.92 | 12.13 | 11.73 | 12.79 |
| \( C_{22} \) | 13.89 | 15.77 | 13.33 | 13.34 |
| \( C_{33} \) | 14.01 | 10.22 | 12.70 | 12.52 |
| \( C_{44} \) | 4.50 | 2.20 | 3.61 | 4.03 |
| \( C_{55} \) | 3.77 | 2.27 | 3.73 | 4.15 |
| \( C_{66} \) | 4.66 | 3.04 | 2.55 | 3.60 |
| \( C_{12} \) | 6.97 | 7.11 | 6.88 | 6.33 |
| \( C_{13} \) | 6.46 | 5.66 | 6.49 | 6.13 |
| \( C_{23} \) | 6.76 | 5.65 | 6.06 | 6.75 |
| \( E \) | 11 | 6.89 | 8.73 | 10.07 |
| \( K \) | 5.47 | 7.97 | 6.19 | 5.21 |
| \( G \) | 4.31 | 2.50 | 3.30 | 3.93 |
| \( C_{12} - C_{44} \) | 2.47 | 4.91 | 3.27 | 2.3 |
| \( \gamma \) | 0.28 | 0.38 | 0.32 | 0.28 |
| \( K/G \) | 1.27 | 3.19 | 1.88 | 1.33 |
found that the blends have anisotropic behaviour to some extent. Tensile modulus ($E$), bulk modulus ($K$) and shear modulus ($G$) are applied to judge the capacity of a material to undergo elastic deformation. To observe the changes more obviously, figure 6 was plotted. From table 4, most elastic coefficients and moduli of NC/NG/GTA blends were found to decrease compared with the NC/NG blend, indicating that the elasticity of the NC/NG/GTA blends increased. It indicated that the synergistic interaction of NG/GTA mixed plasticizers reduced the stiffness and improved the flexibility of NC. In addition, most elastic coefficients and moduli of NC/NG/GTA blends were found to increase with the increased GTA content in mixed plasticizers, predicted that the elasticity and plasticity of blends decreased. This might be due to the smaller polarity and larger volume of GTA than NG, which led to a reduction of intermolecular interaction among the NC and plasticizers. When the GTA substituted for NG, the slip and bending of NC molecular chain became difficult under external forces, leading to an increase in mechanical strength.

Cauchy pressure ($C_{12}-C_{44}$) is a measure of ductility and brittleness for materials, with positive values indicating that the material is ductile and negative values indicating that the material is brittle. The data of table 4 predicted that compared with NC/NG blend, ($C_{12}-C_{44}$) value of the NC/NG/GTA blend was increased with a different extent. And the ($C_{12}-C_{44}$) values of the NC/NG/GTA blends decreased with the increased GTA content in mixed plasticizers, which implied the ductility of blends decreased. Toughness is the ability of a material to deform after absorbing energy, which can be determined by the ratio $K/G$. The higher the $K/G$ value, the better the toughness of the material. It is thus clear in table 4 that the changes of $K/G$ and ($C_{12}-C_{44}$) were consistent, illustrating that the toughness of NC/3NG/GTA blend was the best. The Poisson’s ratio of different blends was between 0.28 and 0.38, showing the better plasticity. To summarize, NG/GTA mixed plasticizers increased the elasticity, ductility and tenacity of the NC.

### 3.6. Mechanical properties of propellant based on NG/GTA mixed plasticizers

Mechanical properties of propellant are closely related to structural integrity and performance stability in practical application. The mechanical properties of nitramine propellant are not only related to binder matrix but also to the interactions between binder matrix and additives. The mechanical properties of propellant based on NG/GTA mixed plasticizers are shown in figure 7 at $-40°C$, $20°C$ and $50°C$.

It can be seen that propellants displayed brittle failure, that is, higher tensile strength and lower elongation at break at low temperatures. This phenomenon was mainly owing to the freeze of the molecular chains of NC, which greatly restricted the movement of the chains. However, at elevated temperature the propellant demonstrated ductility characteristics, i.e. higher elongation at break and lower tensile strength. Especially, the elongation at break of the propellant increased greatly with an increase of temperature, while the tensile strength decreased significantly. This is due to the softening
of the NC binder matrix at high temperature, which led to the weakening of entanglement ability between molecule chains and the increase of ductility. Moreover, the elongation at break of the propellant based on NG/GTA mixed plasticizers was significantly higher than that of the propellant with NG plasticizer at the same temperature. Meanwhile, the tensile strength of the propellant based on NG/GTA mixed plasticizers was only slightly reduced. These results were consistent with the MD simulation results. From the simulation of NC/plasticizers blend, the mechanical properties of propellant could be enhanced by mixed plasticizers owing to the large $V_{\text{free}}$ and lower $C_{ij}$, which could enhance the movement ability of the NC molecular chains. It could be inferred that the mechanical properties might be the macroscopic reaction of the plasticization efficiency of NG/GTA mixed plasticizers on NC binder.

3.7. Energetic properties of propellants based on NG/GTA mixed plasticizers

Energy properties are an important factor in assessing propellant performance. Propellant decomposes into elevated temperature working fluids in a combustion chamber, which is a process of thermal and chemical equilibrium (constant of energy and mass). Based on the isenthalpic principle, thermodynamic parameters such as combustion chamber temperature ($T_c$) and equilibrium product components in the combustion chamber could be directly obtained. By means of the isentropic expansion of combustion product in the nozzle, we can obtain the outlet species composition, outlet temperature ($T_e$), etc. The standard theoretical specific impulse ($I_{sp}$) is the major parameter to evaluate the energy efficiency of propellant, which has a remarkable impact on missile range. The larger the $I_{sp}$, the further the range of a missile.

We have designed some formulations to study the effect of NG/GTA mixed plasticizers on the energetic characteristics of propellant. The theoretical calculation results for energetic parameters of propellant at 6.9 MPa are summarized in table 5. It was thus clear that these energetic parameters such as $I_{sp}$, $C_v$, $T_c$, $T_e$, oxygen coefficients, relative molecular mass of gaseous product, density and heat of explosion of propellants containing NG/GTA mixed plasticizers were lower than those of propellants containing NG plasticizer under an identical mass content of plasticizer. Meanwhile, with the increased non-energetic plasticizer GTA content in mixed plasticizers, the energetic characteristic values of propellants were decreased significantly. Therefore, the energy, combustion and mechanical properties should be considered comprehensively in the formulation design of high-performance propellant.

3.8. Combustion property of propellant based on NG/GTA mixed plasticizers

The burning rate of the propellant influences the gas generation speed, which in turn fixes the internal pressure and total thrust of the motor. The strand burning rate tests were carried out at 2–22 MPa to
study the effect of NG/GTA mixed plasticizers on combustion performance of propellants. It is thus clear in figure 8 that the burning rates of the four specimens increased to varying degrees with the increase of pressure. The burning rate of propellant containing NG/GTA mixed plasticizers was higher than that of propellant containing NG plasticizer at 2–11 MPa, indicating that the combustion performance of propellants containing NG/GTA mixed plasticizers was superior to that of propellants containing NG plasticizer. This was further verified by MD simulation that the NG/GTA mixed plasticizers had better ability to plasticize NC. From the viewpoint of heat transfer, the increase of heat release and feedback to the combustion surface during combustion was the primary factor. However, the combustion properties of propellants at 12–22 MPa were contrary to those of propellants at 2–11 MPa. From the viewpoint of energy, the addition of non-energetic plasticizer GTA to the propellant formulation reduced the energy during the combustion, which was the reason for the decreased burning rate at high-pressure region. The burning rate pressure exponent of propellants was calculated in the pressure range of 2–22 MPa and is displayed in table 6. Propellants had better combustion platform at 2–11 MPa, and combustion platform of propellant containing NG/GTA mixed plasticizers moved to medium-pressure zone. It is worth noting that the burning rate pressure exponent increased when the pressure was greater than 12 MPa. The burning rate of propellants is affected by various factors, such as the plasticity and uniformity of the blends, plasticizer types, pressure, temperature etc. [39,40]. This is probably the reason for the elevated burning rate pressure exponents of propellant in high-pressure zone.

### Table 5. The energetic characteristics of propellants based on NG/GTA mixed plasticizers.

| no. | $I_{sp}$ (N s kg$^{-1}$) | $C_v$ (m s$^{-1}$) | $\varphi$ | $M_c$ | $T_e$ (K) | $T_f$ (K) | $\rho$ (g cm$^{-3}$) | $Q$ (cal g$^{-1}$) |
|-----|-----------------|-----------------|---------|------|---------|---------|-----------------|-----------------|
| F-1 | 2380.22         | 1498.51         | 0.65    | 25.01| 1338.33 | 2898.32 | 1.75            | 983.83          |
| F-2 | 2202.45         | 1401.22         | 0.57    | 23.30| 1033.94 | 2389.60 | 1.71            | 797.71          |
| F-3 | 2136.30         | 1362.59         | 0.54    | 22.75| 941.91  | 2213.38 | 1.70            | 730.67          |
| F-4 | 1988.52         | 1273.81         | 0.50    | 21.70| 767.68  | 1856.50 | 1.68            | 595.95          |

$I_{sp}$ is ideal specific impulse, $C_v$ is characteristic velocity, $\varphi$ is oxygen coefficient, $M_c$ is relative molecular mass of gaseous products, $T_e$ is outlet temperature, $T_f$ is adiabatic flame temperature, $\rho$ is density and $Q$ is heat of explosion.

Figure 8. Burning rate of propellant based on NG/GTA at different pressure.

### 3.9. Combustion wave structure of propellant based on NG/GTA mixed plasticizers

The energy generated during the combustion of a traditional CMDB propellant is transferred from the bright flame area to the dark area, and then to the propellant surface [41]. The combustion wave structure of the propellant with 3NG/GTA mixed plasticizers was determined at different pressures.
and is exhibited in figure 9. It was noted that at different pressures the temperature first increased quickly, then in dark zone the temperature rise was slowed down. The temperature-rise rate at different pressures was 5 MPa > 7 MPa > 3 MPa. This was owing to the improvement of thermal feedback from gaseous phase to the dark area and then to solid phase in the combustion process. This was fitted well with a negative burning rate pressure exponent of propellant with NG/GTA mixed plasticizers in the medium-pressure zone. More interestingly, although the temperature-rise rate at different pressures was different, the combustion temperature in luminous flame zones was almost identical. This phenomenon during the combustion of propellants suggested that the combustion temperature in gaseous phases was less sensitive to pressure, that is, the combustion temperature was almost invariant with the increase of pressure. To sum up, the combustion wave structure further confirmed the above proposition that NG/GTA mixed plasticizers could enhance the combustion efficiency of propellants effectively at low pressures, facilitating the heat feedback to propellant.

4. Conclusion

(1) The radial distribution function indicated that NC/plasticizers blends showed stronger intermolecular interaction of van der Waals force and hydrogen bonds. The binding energy of NC/NG blends was 1242.80 kcal mol\(^{-1}\), higher than that of NC/NG/GTA blends (759.48 kcal mol\(^{-1}\)).

(2) The MSDs of plasticizers revealed that the diffusion coefficient \((D)\) of GTA plasticizer in the NC binder was \(6.07 \times 10^{-11}\) m\(^2\) s\(^{-1}\), higher than that of NG in the NC binder \((5.83 \times 10^{-11}\) m\(^2\) s\(^{-1}\)). The free volume \(V_{\text{free}}\) of NC/3NG/GTA blend was greater than that of NC/NG blend, which was beneficial to the structural ductility.

**Table 6.** Burning rate pressure exponents of propellants based on NG/GTA.

| no. | burning rate pressure exponents |
|-----|--------------------------------|
|     | 2–5 MPa | 5–12 MPa | 12–22 MPa | 2–22 MPa |
| F-1 | 0.007    | 0.235    | 0.466     | 0.187    |
| F-2 | 0.154    | 0.030    | 0.469     | 0.137    |
| F-3 | 0.164    | −0.005   | 0.316     | 0.116    |
| F-4 | 0.167    | −0.014   | 0.417     | 0.128    |

![Figure 9. Temperature profiles in the combustion waves of the propellant with 3NG/GTA mixed plasticizers.](image-url)
(3) Mechanical properties determined from the MD simulation confirmed that the NG/GTA mixed plasticizers increased the elasticity, ductility and tenacity of the NC. Meanwhile, the mechanical properties tests displayed that the elongation at break of the propellant based on NG/GTA mixed plasticizers was significantly higher than that of the propellant with NG plasticizer at the same temperature.

(4) The burning rates of propellants containing NG/GTA mixed plasticizers were higher than those of propellants containing NG plasticizer at low pressure. The combustion platform of propellant containing NG/GTA mixed plasticizers moved to medium-pressure zone. The combustion wave temperature demonstrated that the combustion temperature in gaseous phases was less affected by pressure.

In general, these experimental results coincide with the MD simulation. NG/GTA mixed plasticizers had better ability to plasticize NC, could enhance the combustion efficiency of propellants effectively at low pressures, and facilitated the heat feedback to propellant. The energy, combustion and mechanical properties should be considered comprehensively in the formulation design of high-performance propellant.

Data accessibility. Our data are deposited at Dryad: https://doi.org/10.5061/dryad.bk39kdzb9 for review [42] and https://doi.org/10.5061/dryad.tx95×69xk for publication [43].

Authors’ contributions. Conceptualization, L.Y. and X.W.; methodology, X.W. and J.L.; software, T.C.; investigation, T.C.; data curation, M.L.; data analysis, Q.H.; writing—review and editing, L.Y. All authors discussed the results and contributed to the final manuscript. All authors have read and agreed to the published version of the manuscript. Competing interests. The authors declare no competing interests.

Funding. This research was supported by the Key Laboratory Foundation for Advance Research of China (grant no. 6142603190306).

References

1. Davenas A. 2003 Development of modern solid propellants. J. Propul. Power. 19, 1108–1128. (doi:10.2514/2.6947)

2. Armstrong RW, Baschung B, Booth DW, Samirant M. 2003 Enhanced propellant combustion with nanoparticles. Nano Lett. 3, 253–255. (doi:10.1021/nl025905k)

3. Gayathri S, Reshmi S. 2017 Nitrato functionalized polymers for high energy propellants and explosives: recent advances. Polym. Advan. Technol. 28, 1539–1550. (doi:10.1002/pat.4039)

4. Tang Q, Fan X, Li J, Bi F, Fu X, Zhai L. 2017 Experimental and theoretical studies on stability of new stabilizers for N-methyl-p-nitroaniline derivative in CMDB propellants. J. Hazard. Mater. 327, 187–196. (doi:10.1016/j.jhazmat.2016.12.049)

5. Yi JH et al. 2010 Thermal behaviors, nonisothermal decomposition reaction kinetics, thermal safety and burning rates of BTD2- CMDB propellant. J. Hazard. Mater. 181, 432–439. (doi:10.1016/j.jhazmat.2010.05.029)

6. Elbasuney S, Fahid A, Mostafa HE. 2017 Combustion characteristics of extruded double base propellant based on ammonium perchlorate/aluminum binary mixture. Fuel 208, 296–304. (doi:10.1016/j.fuel.2017.07.020)

7. Gautam GK, Pundlik SM, Joshi AD, Mulage KS, Singh SN. 2013 Study of energetic nitramine extruded double-base propellants. Defence Sci. J. 63, 225–234. (doi:10.14429/dsj.63.3904)

8. Rezhdhi S, Hemanth H, Gayathri S, Renganathan Nair CP. 2016 Polyether triazoles: an effective binder for ’green’ gas generator solid propellants. Polymer 92, 201–209. (doi:10.1016/j.polymer.2016.03.006)

9. Bhomwik D, Sadavante VS, Pande SM, Saraswat BS. 2015 An energetic binder for the formulation of advanced solid rocket propellants. Cent. Eur. J. Energ. Mater. 12, 145–158.

10. Zhang X, Zheng J, Fang H, Zhang Y, Bai S, He G. 2018 High dimensional stability and low viscous response solid propellant binder based on graphene oxide nanosheets and dual cross-linked polyurethane. Compos. Sci. Technol. 161, 124–134. (doi:10.1016/j.compsctech.2018.04.012)

11. Zhang X, Weeks BL. 2014 Preparation of sub-micron nitrocellulose particles for improved combustion behavior. J. Hazard. Mater. 268, 224–228. (doi:10.1016/j.jhazmat.2014.01.019)

12. Liang X, Cheng Y, Lin W, Tung P-H, Huang H-Q, Pan X, Shu C-M, Jiang J. 2020 Analysis and characterisation of 1-buty1-3-methylimidazolium hexafluorophosphate as a humectant of nitrocellulose. J. Mol. Liq. 303, 112 617–112 628. (doi:10.1016/j.molliq.2020.112617)

13. Wei R, He Y, Liu J, He Y, Ali W, Yuen R, Wang J. 2017 Experimental study on the fire properties of nitrocellulose with different structures. Materials 10, 316–331. (doi:10.3390/ma10030316)

14. Ng HM, Sin LT, Bee ST, Tee T-T, Rahmat AR. 2017 Review of nitrocellulose polymer composite characteristics and challenges. Polym. Pflast. Technol. 56, 687–731. (doi:10.1080/03602559.2016.1233277)

15. Qi X, Li H, Zhao Y, Yan N. 2019 Comparison of the structural and physical properties of nitrocellulose plasticized by N-butyl-N-(2-nitro-ethyl) nitramine and nitroglycerin: computational simulation and experimental studies. J. Hazard. Mater. 362, 303–310. (doi:10.1016/j.jhazmat.2018.09.033)

16. Zhao Y, Zhang X, Zhang W, Xu H, Xie W, Du J, Liu Y. 2016 Simulation and experimental on the solvation interaction between the GAP matrix and insensitive energetic plasticizers in solid propellants. J. Phys. Chem. A 120, 765–770. (doi:10.1021/acs.jpca.5b05540)

17. Buszek RJ, Soto D, Dailey JM, Bolden S, Tall TL, Hudgens LM, Marshall CA, Boatz JA, Drake GW. 2018 Structures and binding energies of nitrate plasticizers DEGN, TEGON, and nitroglycerine. Propell. Explos. Pyrot. 43, 115–121. (doi:10.1002/prep.201700203)

18. Menick P, Pihlry M, Stehnavá I, Melcová V, Kontarova S, Figal M, Aleye P, Bočik J. 2018 Effect of selected commercial plasticizers on mechanical, thermal, and morphological properties of polyc(3-hydroxybutyrate)/polylactic acid/plasticizer biodegradable blends for three-dimensional (3d) print. Materials 11, 1893–1912. (doi:10.3390/mats11101893)

19. Yang J, Gao X, Wang G. 2015 A promising azide nitrate ester plasticizer for propellant. Compos. Mater. Sci. 110, 71–76. (doi:10.1016/j.compscitech.2015.07.049)

20. Johnson EC, Sabatini JJ, Chavez DE, Sausa RC, Byrd EFC, Wingard LA, Guzmán PE. 2018 Bis(1,2,4-oxadiazole)bis(methylene) diinitrate: a high-energy melt-castable explosive and
energetic propellant plasticizing ingredient. Org. Process. Res. Dev. 22, 736–740. (doi:10.1021/acs.oprd.8b00076)

21. Vijayalakshmi R, Agawane NT, Talawar MB, Khan M. 2020 Examining the compatibility of energetic plasticizer DNDA-5 with energetic binders. J. Macromol. Sci. A 57, 46–54. (doi:10.1080/10601325.2019.1669458)

22. Milekhin YM, Koptelov AA, Shishov NI, Koptelov IA, Rogozina AA. 2018 Evaporation of plasticizer from NEPE Type Propellant. Russ. J. Appl. Chem. 91, 802–812. (doi:10.1134/ S1070427218050117)

23. Wu Y, Yi Z, Luo Y, Ge Z, Du F, Chen S, Sun J. 2017 Fabrication and properties of glycidyl azide polymer-modified nitrocellulose spherical powders. J. Therm. Anal. Calorim. 129, 1555–1562. (doi:10.1007/s10973-017-6387-0)

24. Sucea M, Mestalic SM, Houra IF. 2010 Kinetics and enthalpy of nitroglycerin evaporation from double base propellants by isothermal thermogravimetry. Thermochim. Acta 510, 9–16. (doi:10.1016/j.tca.2010.06.014)

25. Reese DA, Green LJ, Sun SF. 2014 Formulation and characterization of a new nitroglycerin-free double base propellant. Propell. Explos. Pyrot. 39, 205–210. (doi:10.1002/prep.201300105)

26. Woodman AL, Adicoff A. 1962 Swelling of nitrocellulose by plasticizers. Ind. Eng. Chem. Res. 8, 278–280.

27. Cousin T, Berto C, Budrova T, Kurek J, Navard P. 2017 Influence of the scale and type of processing tool on plasticization of cellulose acetate. Polym. Eng. Sci. 57, 563–569. (doi:10.1002/pen.24452)

28. Oksman K, Aitomaki Y, Mathew AP, Siqueira G, Zhou Q, Butynia S, Tanpichai S, Zhou X, Hooshmand S. 2016 Review of the recent developments in cellulose nanocomposite processing. Compos. Part A 83, 2–18. (doi:10.1016/j.compositesa.2015.10.041)

29. Arrington KJ, Haag IV JW, French EV, Murayama M, Edgar KJ, Matson JB. 2019 Toughening cellulose: compatibilizing polystyrene and cellulose triacetate blends. ACS Macro Lett. 8, 447–453. (doi:10.1021/acsmacrolett.9b00136)

30. Sanghani RR, Kamale PJ, Shaikh MAR, Shelar SD, Kumar KS, Singh A. 2007 HMIX based enhanced energy LOV gun propellant. J. Hazard. Mater. 143, 532–534. (doi:10.1016/j.jhazmat.2006.09.087)

31. Singh H, Khire V. 2008 Studies on low vulnerability gun propellants based on conventional binders and energetic plasticizers. Int. J. Energy. Mater. Chem. Propul. 7, 187–192.

32. Kumari D, Yamajala KD, Singh H, Sanghavi RR, Asthana SN, Raju K, Banerjee S. 2013 Application of azido esters as energetic plasticizers for LOV A propellant formulations. Propell. Explos. Pyrot. 38, 805–809. (doi:10.1002/prep.201300070)

33. Sheer SK, Reddy ST, Athar J, Sikder AK, Talawar MB, Banerjee S, Khan MA. 2015 Probing the compatibility of energetic binder pol-glycidyl nitrate with energetic plasticizers: thermal, rheological and DFT studies. RSC Adv. 5, 101 297–101 308. (doi:10.1039/C5RA16476A)

34. Wang B, Liao X, Wang Z, Deluca LT, Liu Z, He W. 2018 Effects of particle size and morphology of NQ on thermal and combustion properties of triple-base propellants. Combust. Flame 193, 123–132. (doi:10.1016/j.combustflame.2018.03.009)

35. Fu X, Fan X, Xie X, Qi X, Li J, Yu H. 2015 Molecular dynamic simulations on the interaction between an HTPE polymer and energetic plasticizers in a solid propellant. RSC Adv. 5, 52 844–52 851. (doi:10.1039/CSRA05312A)

36. Li M, Zhao FQ, Xu SY, Gao HK, Yi JH, Pei Q, Tan Y, Li N, Li X. 2013 Comparison of three kinds of energy calculation programs in formulation design of solid propellants. Chin. J. Explos. Propul. 36, 73–77.

37. Richards LA, Nash A, Phibbs MJ, De Leeuw NH. 2018 A molecular dynamics study of plasticiser migration in nitrocellulose binders. New J. Chem. 42, 17 420–17 428. (doi:10.1039/C8NJ03164H)

38. Lu Y, Shu Y, Liu N, Shu Y, Wang K, Wu Z, Wang X, Ding X. 2017 Theoretical simulations on the glass transition temperatures and mechanical properties of modified glycidyl azide polymer. Comput. Mater. Sci. 139, 132–139. (doi:10.1016/j.commatsci.2017.07.022)

39. Yaman H, Cevik V, Degirmenci E. 2014 Experimental investigation of the factors affecting the burning rate of solid rocket propellants. Fuel 115, 794–803. (doi:10.1016/j.fuel.2013.05.033)

40. Rao BN, Mallappa K, Kumar N, Jana T. 2019 Ferrocene grafted hydroxyl terminated polybutadiene: a binder for propellant with improved burn rate. Polymer 163, 162–170. (doi:10.1016/j.polymer.2019.01.008)

41. Yang J, Zhao FQ, Yuan ZF, Wang Y, An T, Chen X, Xiao C, Zhang J. 2017 On the combustion mechanisms of ZnH4 in double-base propellant. Phys. Chem. Chem. Phys. 19, 32 597–32 604. (doi:10.1039/C7CP02593A)

42. Yang L et al. 2021 Data from: Study on structure and property of propellant based on nitroglycerine/glycerol triacetate mixed plasticizers. Dryad Dataset. (doi:10.5061/dryad.b3k1j8r)

43. Yang L et al. 2021 Data from: Study on structure and property of propellant based on nitroglycerine/glycerol triacetate mixed plasticizers. Dryad Dataset. (doi:10.5061/dryad.tcs9x69k)