



Effects of Bi-NTO complex on thermal behaviors, nonisothermal reaction kinetics and burning rates of NG/TEGDN/NC propellant

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ABSTRACT

A bismuth 3-nitro-1,2,4-triazol-5-one (Bi-NTO) complex was prepared and characterized, and its effects on the thermal behaviors, non-isothermal decomposition reaction kinetics, and burning rates of the double-base (DB) propellant containing the mixed ester of triethyleneglycol dinitrate (TEGDN) and nitroglycerin (NG) with Bi-NTO complex as a ballistic modifier were investigated by thermogravimetry and derivative thermogravimetry (TG–DTG), and differential scanning calorimetry (DSC). The results show that Bi-NTO complex can increase the decomposition heat by 140 J g^{-1} , and it can change the decomposition reaction mechanism function, the kinetic parameters and kinetic equation of the propellant under 0.1 MPa. Combustion experiment shows that Bi-NTO complex can increase the burning rate and reduce the pressure exponent of the NG/TEGDN/NC propellant effectively, with the increase of the catalysis efficiency by 40%.

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1. Introduction

It is well known that lead compounds can improve the solid propellant ballistic properties, *i.e.*, it can increase burning rate and decrease the pressure exponent of the burning rate. Although lead compounds are extensively used as one of the very important ballistic modifiers in the solid propellant formulations, their toxicities have attracted people's much more attention in these decades. Bismuth compounds, with their closer modified effects to lead compounds, have been used as eco-friendly ballistic modifiers documented in many literatures [1–10]. In addition, bismuth compounds do not produce blue smoke during their combustion process and will therefore be advantageous to the minimum-signature propellants. Up to now, bismuth 3-nitro-1,2,4-triazol-5-one (Bi-NTO) complex used as an energetic ballistic modifier for the propellant formulations has not been reported.

In this paper, the preparation, characterization of Bi-NTO complex and its influences on the thermal behaviors, the decomposition reaction kinetics and the burning rates of the double-base (DB) propellant, which consist of the mixed esters of triethyleneglycol dinitrate (TEGDN) and nitroglycerin (NG), and nitrocellulose

(NC) with Bi-NTO as a ballistic modifier, were investigated by the nonisothermal method under atmospheric pressure and flowing nitrogen gas conditions.

2. Experimental

2.1. Sample

The ballistic modifier Bi-NTO complex used in the propellant was prepared as follows: NTO (prepared in our lab) and $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (AR grade) with mole ratio of 1:3 were dissolved into deionized water, respectively, and mixed. Then NaOH (AR grade) solution was added to adjust the pH value to about 3 under stirring. After stirred for 2 h, the yellow precipitate was filtrated, washed and dried at 80°C in vacuum for a few hours. Finally, the Bi-NTO complex was kept in a vacuum desiccator.

The propellant sample (no. TG0603) used in the experiment was a DB propellant composed of 60% (mass fraction) of NC, 37.5% of NG/TEGDN mixed esters, and 2.5% of centralite II (C_2) and other additives, etc. The strand sample composed of 500 g ingredients and 15 g Bi-NTO complex as ballistic modifier was prepared by a solventless DB propellant extrusion technique, including slurry mixing, rolling, and extruding. The control DB propellant (no. TG0601) without ballistic modifier was also prepared for the comparison with the sample [11–14].

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Table 1
IR pattern analysis and the function group assignments.

Funct. group	Wavenumber/cm ⁻¹			Intensity ^a	Vibrational type
	NTO	Bi-NTO	BiONO ₃		
N–H	3208	3391		vs, B	ν_{NH}
	1542	1509		s	δ_{NH}
	~728, ~603	~776, ~746		m	δ_{NH}
C–N	1473	1404		m	$\nu^{\text{as}}_{\text{N-C-N}}$
	1187, 1006	1115, 1048		m, m	$\nu^{\text{s}}_{\text{N-C-N}}$
C=O	1717			vs	$\nu_{\text{C=O}}$
C–O		1593		vs	$\nu_{\text{C-O}}$
NO ₂ ^b	1546, 1356			s, s	$\nu^{\text{as}}_{\text{-NO}_2}, \nu^{\text{s}}_{\text{-NO}_2}$
NO ₂ ^c		1509, 1302		s, s	
C=N	1542	1544		s	$\nu_{\text{C=N}}$
Bi–O		549		m	$\nu_{\text{Bi-O}}$
			567	s	$\nu^{\text{as}}_{\text{Bi-O}}$
NO ₃ ⁻			1384	vs, B	$\nu_{\text{N-O}}$
			825, 726	s	$\delta_{\text{N-O}}$

^a The IR broad band intensity expression: vs—very strong; s—strong; m—middle; w—weak; B—broad.

^b Before the complex formed.

^c After the complex formed.

2.2. Equipment and conditions

The contents of C, H, O and N were determined on a Vario EL organic elemental analyzer (Elementar Co., Germany). The content of Bi was determined on a S4 Pioneer X-ray fluorescence (Bruker Co., Germany). The infrared spectra were recorded in the range of 4000–400 cm⁻¹ by using KBr pellets on a Nicolet 740 spectrometer (Nicolet Co., USA). TG–DTG and DSC curves under the condition of flowing nitrogen gas (purity, 99.999%; atmospheric pressure) were obtained by using a TA2950 thermal analyzer (TA Co., USA) and a 204HP differential scanning calorimeter (Netzsch Co., Germany), respectively. The conditions of TG–DTG were: sample mass, about 1 mg; N₂ flowing rate, 40 cm³ min⁻¹; heating rates (β), 10 K min⁻¹. The conditions of DSC analyses were: sample mass, about 1 mg; N₂ flowing rate, 50 cm³ min⁻¹; heating rate, 5, 10, 15, and 20 K min⁻¹; furnace pressures, 0.1 MPa; reference sample, α -Al₂O₃; type of crucible, aluminum pan with a pierced lid.

3. Results and discussion

3.1. Characterization of Bi-NTO complex

Elemental analysis (%): calcd.: C 4.12, H 0.69, N 9.62, O 13.70, Bi 71.8; found: C 3.82, H 0.64, N 8.09, O 18.2, Bi 68.9. The chemical constitution of Bi-NTO complex can be deduced as C₂N₄O₅H₄Bi₂.

The IR pattern analysis and the function group assignments of NTO, BiONO₃ (the hydrolysate of Bi(NO₃)₃·5H₂O), and Bi-NTO are listed in Table 1.

The N(1) and N(4) atoms of NTO triazole ring have strong electronegativity, and the outer lone electrons take part in the conjugate effect of the aroma ring, which makes H atoms in –NH groups have a small quantity of positive charge, meanwhile the O atoms in –NO₂ and C=O groups in NTO chemical construction have a small quantity of negative charge. The metal-NTO complex can be easily formed because of the groups with negative charge in NTO chemical construction and the metal ions with positive charge.

When Bi-NTO complex is formed, the electron cloud densities of chemical bonds of N–H, –NO₂ and C=O groups in NTO molecule will make great changes. The stretching vibration of both –NO₂ and C=O groups shift to low frequency (LF), which means the electron cloud densities are decreased, and the stretching vibration of N–H groups shift to high frequency (HF), which means the electron cloud densities are increased, i.e., the stretching vibration of –NO₂ shifts from 1546, 1356 cm⁻¹ to 1509, 1302 cm⁻¹, C=O from 1717 cm⁻¹ to 1593 cm⁻¹ and N–H from 3208 cm⁻¹ to 3391 cm⁻¹.

From the spectral shifts of IR absorption of N–H, –NO₂ and C=O groups in NTO molecule, and the disappearance of the characteristic IR absorption peak of anion NO₃⁻, one can deduce that the orange-colored Bi-NTO complex is the desirable product, and the structure of Bi-NTO complex is shown in Fig. 1.

3.2. Thermal behaviors of the propellant containing Bi-NTO complex

The TG–DTG curve of the propellant TG0603 is shown in Fig. 2. The DSC curves of the propellant TG0603 and the control propellant TG0601 are shown in Fig. 3. The DSC curves of the propellant TG0603 at different heating rates are shown in Fig. 4.

From TG–DTG curve, one can find that there are two mass loss stages (stages I and II) in the TG curve, corresponding to the two peaks in the DTG curve. For the TG curve when $\beta = 10$ K min⁻¹, stage I begins at 337.2 K and stops at 451.6 K, accompanying 36.4% mass loss, which is close to the total mass (37.5%) of the mixed ester, and it likely attributes to the volatilization and decomposition of the NG/TEGDN mixed ester, corresponding to the invisible peak in the DSC curve of the temperature range; Stage II begins at 451.6 K and stops at 548.2 K, with the summit peak in the DTG curve at 483.5 K, accompanied by 45.04% mass loss, and it attributes to the NC and C₂ decomposition in the stage.

From the DSC curve at the heating rate of 10 K min⁻¹, one can see that there is an exothermic peak begins at 421.6 K and stops

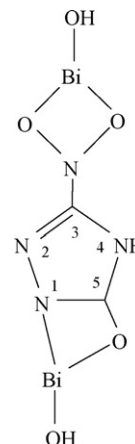


Fig. 1. The structure of Bi-NTO complex.

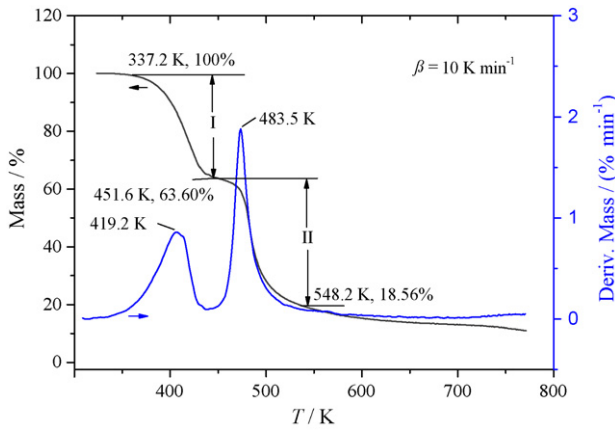


Fig. 2. TG-DTG curve of the propellant TG0603.

at 546.6 K, with the summit peak at 478.5 K, advanced the peak temperature of the control propellant by about 1 K, and increased the decomposition heat by 140 J g^{-1} [the decomposition heat of the control propellant, $1.62 \times 10^3 \text{ J g}^{-1}$] [11,12]. The reason of the only one visible exothermic peak appears in the DSC curve is that the two decomposition stages occur in succession and the temperature ranges are near apart, the decomposition heats of the two

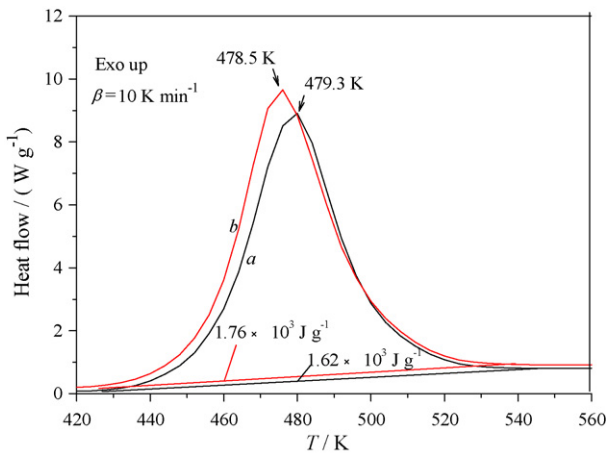


Fig. 3. DSC curves of (a) the control propellant TG0601, and (b) the propellant TG0603.

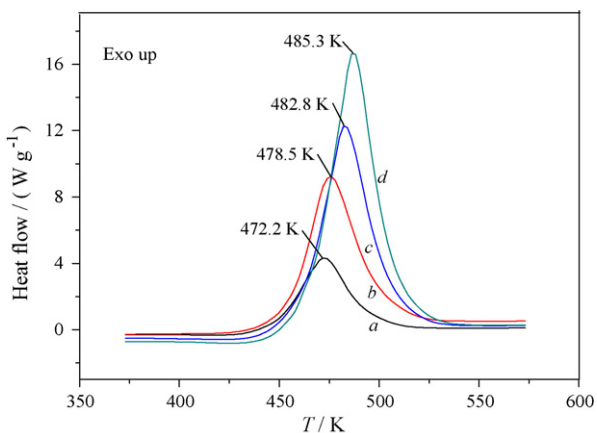


Fig. 4. DSC curves of the propellant TG0603 at the heating rate (K min^{-1}): (a) 5; (b) 10; (c) 15; (d) 20. Onset temperature (T_e/K): (a) 447.5; (b) 453.9; (c) 460.2; (d) 463.0.

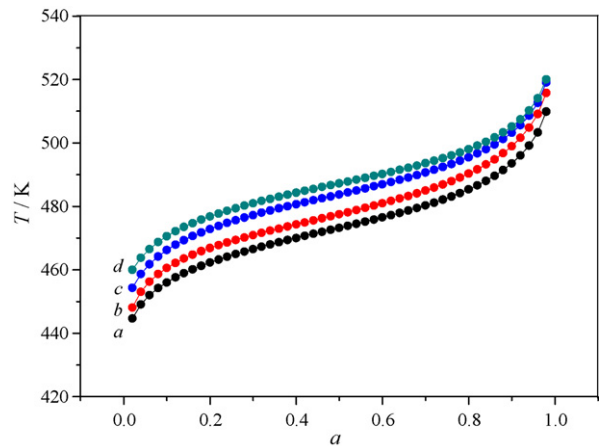


Fig. 5. $T-\alpha$ curves the propellant TG0603 at the heating rate (K min^{-1}): (a) 5; (b) 10; (c) 15; (d) 20.

processes overlap each other in the DSC curve, inducing the only one exothermic peak to appear in the end.

3.3. Calculation of nonisothermal reaction kinetics

To explore the thermal decomposition mechanism of the main exothermic reaction stage (stage II) of the propellant and obtain the corresponding kinetic parameters [apparent activation energy ($E_a/\text{kJ mol}^{-1}$), pre-exponential constant (A/s^{-1})] and the most probable kinetic model function, the DSC curves at the heating rates of 5, 10, 15, and 20 K min^{-1} were dealt with mathematic means, 51 teams of temperature values corresponded to the conversion degrees (α) changing from 0.02 to 0.98 were found, and $T-\alpha$ curves of the propellant TG0603 at the heating rates are shown in Fig. 5.

Five integral methods (General integral, MacCallum-Tanner, Šatava-Šesták, Agrawal, Flynn-Wall-Ozawa) and one differential method (Kissinger) were employed in Refs. [15–19]. The values of E_a were obtained from the isoconversional DSC curves by Ozawa's method at the heating rates of 5, 10, 15, and 20 K min^{-1} , and the $E_a-\alpha$ relation is shown in Fig. 6. It is obvious that the activation energy of the decomposition process changes greatly with an increase in the conversion degree from 0.02 to 0.98, except that for the section of 0.03–0.55 (α), in which activation energy is approximately constant, and it suggests that the decomposition mechanism of the region remains steady. Therefore, it is feasible

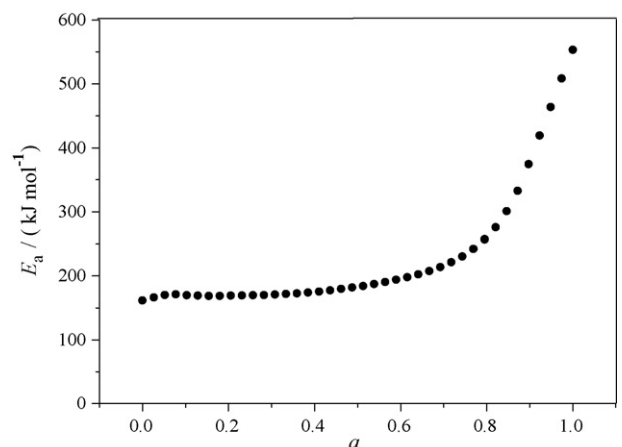


Fig. 6. $E_a-\alpha$ curve obtained by Ozawa's method.

Table 2
Kinetic parameters for the exothermic decomposition process of the propellant TG0603.

Method	$\beta/(K \text{ min}^{-1})$	$E_a/(kJ \text{ mol}^{-1})$	$\lg A/s^{-1}$	r	Q
General integral	5	195.08	19.35	0.9984	0.1027
	10	199.69	19.96	0.9992	0.0507
	15	197.61	19.61	0.9994	0.0392
	20	214.02	21.37	0.9989	0.0746
MacCallum–Tanner	5	195.55	19.37	0.9986	0.0192
	10	200.27	19.99	0.9993	0.0094
	15	198.28	19.65	0.9995	0.0073
	20	214.88	21.44	0.9990	0.0139
Šatava–Šesták	5	192.82	19.11	0.9986	0.0192
	10	197.27	19.71	0.9993	0.0094
	15	195.39	19.38	0.9995	0.0073
	20	211.06	21.08	0.9990	0.0139
Agrawal	5	195.08	19.35	0.9984	0.1027
	10	199.69	19.96	0.9993	0.0507
	15	197.61	19.61	0.9994	0.0392
	20	214.02	21.37	0.9989	0.0746
Mean		201.15	20.02		
Flynn–Wall–Ozawa		191.95		0.9998	0.0001
Kissinger		193.89	19.39	0.9998	0.0005

to study the reaction mechanism and kinetics in the section of 0.03–0.55 (α).

Forty-one types of kinetic model functions in Refs. [15,17,18] and the original data were put into the integral and differential equations for calculations, and the values of E_a , $\lg A$, linear correlation coefficient (r) and standard mean square deviation (Q) were calculated on the computer with the linear least-squares method. The most probable mechanism function is selected by the better values of r , and Q [15,18]. The results of satisfying the conditions at the same time are the final results as listed in Table 2, and the relevant function is the reaction mechanism function of decomposition process of the propellant TG0603.

The data in Table 2 indicate that the values of E_a and $\lg A$ obtained from the nonisothermal DSC curves are in approximately good agreement with the values calculated by Ozawa's method and Kissinger's method. Therefore, the mechanism function (listed in Table 3) can be determined and is substituted with the values of $E_a/(kJ \text{ mol}^{-1})$ and A/s^{-1} into Eq. (1):

$$\frac{d\alpha}{dt} = Af(\alpha)e^{-E/RT} \quad (1)$$

where $f(\alpha)$ is the differential model function, t is the time, and R is the gas constant.

The corresponding kinetic equation of the decomposition reaction of the propellant is obtained, and shown in Table 3. Comparing with the control propellant, one can find that Bi-NTO complex can change the decomposition reaction mechanism function, the kinetic parameters and kinetic equation of the NG/TEGDN/NC propellant under 0.1 MPa.

Table 3
Mechanism functions, apparent activation energies and kinetic equations of TG0601 and TG0603.

	TG0601 ($\alpha = 0.15\text{--}0.90$)	TG0603 ($\alpha = 0.03\text{--}0.55$)
Mechanism function	$G(\alpha) = (1 - \alpha)^{-1} - 1, f(\alpha) = (1 - \alpha)^2$, chemical reaction	$G(\alpha) = -\ln(1 - \alpha), f(\alpha) = 1 - \alpha$, Mampel Power Law, nucleation and growth, $n = 1$
Mech funct. no.	37	16
$E_a/(kJ \text{ mol}^{-1})$	216.16	201.15
Kinetic equation	$\frac{d\alpha}{dt} = 10^{21.59}(1 - \alpha)^2 e^{-2.60 \times 10^4/T}$ (2) [11,12]	$\frac{d\alpha}{dt} = 10^{20.02}(1 - \alpha) e^{-2.42 \times 10^4/T}$ (3)

Table 4
Thermodynamic property data of TG0601 and TG0603.

	TG0601 [11,12]	TG0603
$(T_{e0} \text{ or } T_{SADT})/K$	448.2	438.4
T_{p0}/K	464.6	464.6
T_{be}/K	456.5	447.1
T_{bp}/K	473.4	474.4
$\Delta S^\ddagger/(J \text{ mol}^{-1} \text{ K}^{-1})$	163.57	122.60
$\Delta H^\ddagger/(kJ \text{ mol}^{-1})$	209.54	190.03
$\Delta G^\ddagger/(kJ \text{ mol}^{-1})$	133.55	133.07

3.4. Calculation of critical temperatures of thermal explosion, ΔS^\ddagger , ΔH^\ddagger , and ΔG^\ddagger [15–19]

The values (T_{e0} and T_{p0}) of the onset temperature (T_e) and peak temperature (T_p) corresponding to $\beta \rightarrow 0$ obtained by Eq. (4), and listed in Table 4:

$$T_{(e \text{ or } p)_i} = T_{(e0 \text{ or } p0)} + b\beta + c\beta_i^2, \quad i = 1\text{--}4 \quad (4)$$

$$T_{e0} = T_{SADT} \quad (5)$$

where b and c are coefficients and T_{SADT} is the self-accelerating decomposition temperature.

The corresponding critical temperatures of thermal explosion (T_{be} and T_{bp}) obtained from Eq. (6), and listed in Table 4:

$$T_{be \text{ or } bp} = \frac{E_0 - \sqrt{E_0^2 - 4E_0RT_{e0 \text{ or } p0}}}{2R} \quad (6)$$

where R is the gas constant and E_0 is the value of E_a by Ozawa's method.

The entropy of activation (ΔS^\ddagger), enthalpy of activation (ΔH^\ddagger), and free energy of activation (ΔG^\ddagger) of the decomposition reaction, corresponding to $T = T_{p0}$, $E_a = E_k$, and $A = A_k$, are obtained from Eqs. (7)–(9) respectively, and listed in Table 4:

$$A = \frac{k_B T}{h} e^{\Delta S^\ddagger / R} \quad (7)$$

$$\Delta H^\ddagger = E_a - RT \quad (8)$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (9)$$

where k_B is the Boltzmann constant, and h is the Planck constant.

From Table 4, one can find that TG0603 makes the self-accelerating decomposition temperature (T_{e0} or T_{SADT}), the critical temperatures of thermal explosion (T_{be}) of the sample decrease to some extent when it is in isothermal conditions ($\beta \rightarrow 0$), and the same as the entropy of activation (ΔS^\ddagger), enthalpy of activation (ΔH^\ddagger), and free energy of activation (ΔG^\ddagger).

3.5. Burning rate measurement of the propellants

For the sake of the possible application of Bi-NTO complex in propellants as the adjuvant of the ballistic modifier, the burning rates [$u/(mm \text{ s}^{-1})$] of the control propellant (TG0601, system I) and the propellant containing Bi-NTO complex (TG0603, system II) were measured under different pressures (P/MPa). The results

Table 5
Effects of Bi-NTO complex on the burning rates (mm s^{-1}) of NG/TEGDN/NC propellant.

Sample	Pressure/MPa										
	2	4	6	8	10	12	14	16	18	20	22
TG0601	2.30	3.97	5.62	7.38	8.69	9.71	10.32	11.75	11.90	12.80	13.64
TG0603	6.64	7.48	10.49	11.51	12.33	13.6	14.77	16.13	17.61	19.12	20.62

are listed in Table 5. As one can see, with the help of the catalysis of Bi-NTO complex, the burning rate of the propellant is improved markedly. In order to study the effects of Bi-NTO complex on the combustion characteristic of the propellant, the pressure exponents (n) of the burning rate were calculated, and the mean values of the catalysis efficiency (\bar{Z}) were compared before and after Bi-NTO complex was added into propellant. The values of u , n , and \bar{Z} were obtained by Eqs. (10) and (11) [20]:

$$u_i = aP_i^n, \quad i = 1-11 \quad (10)$$

$$\bar{Z} = \sum_{i=1}^k \frac{(u_{II,i}/u_{I,i})}{k} \quad (11)$$

where a is the factor, $\text{mm s}^{-1} \text{MPa}^{-1}$.

For system I:

at 8–20 MPa, $u = 2.20P^{0.591}$, $r = 0.987$, $\bar{Z} = 1$;

at 10–20 MPa, $u = 2.42P^{0.557}$, $r = 0.981$, $\bar{Z} = 1$.

For system II:

at 8–20 MPa, $u = 3.45P^{0.561}$, $r = 0.980$, $\bar{Z} = 1.45$;

at 6–14 MPa, $u = 5.06P^{0.399}$, $r = 0.981$, $\bar{Z} = 1.43$.

As one can see, as an auxiliary ballistic modifier, Bi-NTO complex can be effective to increase the burning rate and reduce the pressure exponent of the NG/TEGDN/NC propellant.

4. Conclusions

The preparation and characterization of Bi-NTO complex were investigated, and it was used as a ballistic modifier for the NG/TEGDN/NC propellant. The results show that Bi-NTO complex can increase the decomposition heat, decrease the apparent activation energy, and change the decomposition reaction mechanism function and kinetic equation of the NG/TEGDN/NC propellant under 0.1 MPa. Bi-NTO complex also can be effective to increase the burning rate and reduce the pressure exponent of the NG/TEGDN/NC propellant, and the catalysis efficiency can be increased by 40%.

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