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Effects of particle size and morphology of NQ on thermal and combustion properties of triple-base propellants

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ABSTRACT

Particle size and morphology of nitroguanidine (NQ) are two of the dominant factors that influence the thermal and combustion properties of triple-base propellants. However, the investigations of these effects and the corresponding mechanisms are insufficient. In this work, we examined the thermal properties and nonisothermal decomposition kinetics using differential scanning calorimetry (DSC) and thermogravimetry (TG). Combustion properties i.e. flame structure, melting layer and burning rate were determined on the bases of windowed strand burner (3 MPa), high-speed video camera, interrupted closed vessel, scanning electron microscope (SEM) and closed vessel, respectively. It was found that the decomposition process of triple-base propellant could be divided into two steps. The first step was mainly related to the decomposition process of nitroglycerin (NG) with higher activation energy and lower peak temperature, which was enhanced due to reactions between the added NQ and the decomposition product of NG (NO_2), while the second step mainly concerned the decomposition process of nitrocellulose (NC) with lower activation energy and higher peak temperature. The flame structure of triple-base propellants was heterogeneous and closely attached to the condensed phase without dark zone. When the NQ particle size was decreased, the active site number of NQ was increased, enhancing the intensity of the reaction between NO_2 and NQ; the decomposition peak temperature was decreased; the flame structure became more heterogeneous and brighter, resulting in more heat feedback from gas phase to the condensed phase. Thus, the burning rate was increased. On the other hand, the apparent activation energy and thickness of the melting layer of triple-base propellants were also increased with the decrease of NQ particle size, which meant that the sensitivities of burning rate to the conditions of gas phase were reduced. Therefore, the burning rate pressure exponent was decreased.

1. Introduction

Although triple-base propellants have been extensively utilized in the field of gun propulsion for a long time since World War II, this type of propellant still exhibits promising application prospects for high performance large caliber long-range artillery ammunitions. This is mainly attributed to the incorporation of high proportions of nitroguanidine (NQ) (about 50% by mass) in the formulations, which imparts triple-base propellants many advantages like high force-constant values obtained at low flame temperature (hence, low barrel erosion), less flash, long shelf life, low-cost production, low temperature sensitivity, etc [1–4]. Conventionally, α-NQ with long needle or rod shaped structure is most commonly used in triple-base propellants due to the current commercial production conditions [5]. However, this type of NQ also exposes some drawbacks which are believed to be the major barriers to further development of triple-base propellants. Many studies have revealed that NQ in this form usually contains some voids and fractures in the crystals owing to the long crystal structure. Moreover, long cracks would also be generated at the interfaces between nitrocellulose (NC) and the long crystals of NQ [6,7]. On the other hand, interlocking and clustering of NQ crystals would occur in the propellants because NQ particles could not be dispersed uniformly in the propellants in that the propellant doughs containing α-NQ have high viscosities [8,9]. Consequently, properties dependent on these structure features (e.g., mechanical, thermal and combustion properties, which are some important properties ultimately governing the ballistic performance of triple-base propellants) are affected significantly. Therefore, it is suggested that the particle size and morphology of NQ should be improved to enhance the performance of triple-base propellants.

In the past decades, a variety of technologies have been developed to modify the crystal size and shape of NQ, of which

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recrystallization and grinding are the two most important methods [10,11]. It has been founded that the shape and size of NQ crystals are determined by recrystallization solutions, additives and other conditions, and even spherical shaped crystals of NQ can be obtained by optimizing the process of recrystallization [12–15]. Meanwhile, a well controlled grinding process can also produce much shorter, smaller and more uniform crystals of NQ. Hence, properties relying on these factors could be altered significantly. Many studies in the past have been devoted to investigating the influences of the particle size and morphology of NQ on the structure features and mechanical properties of triple-base propellants [16,17]. Besides, a lot of work has been done concerned the thermal properties of NQ [18–20], of which some articles have suggested that crystal size is the main factor influencing the thermal stability of pure NQ: smaller crystals have a higher stability than larger ones. Accordingly, the viewpoint of topo-chemistry was proposed to interpret this phenomenon [19]. However, studies dealing with the thermal and combustion behavior of triple-base propellants, especially the influences of particle size and morphology of NQ on the thermal decomposition and combustion characteristics of triple-base propellants, are scarce.

The decomposition process in the condensed phase is often the initial step of combustion reaction for solid propellants [21,22]. During the decomposition process, gaseous species and solid residues are formed in the subsurface or on the surface. Subsequently, these gaseous species would enter into gas phase and participate to the violent combustion reactions, producing high temperature and pressure gases [23], which in turn increase the heat feedback to the condensed phase for further decomposition reactions [24]. Simultaneously, melting layer is generated in the condensed phase for some kinds of propellants [25], which would reduce the heat feedback and gas erosion from gas phase to the condensed phase and, thus, weaken the effect of gas phase to the physical and chemical reactions in the condensed phase. Consequently, combustion properties (such as flame structure and burning rate) dependent on these properties are changed. Therefore, not only thermal decomposition plays a significant role during the combustion process, but also melting layer could affect the decomposition and combustion properties. Fortunately, recent advances in the thermal and combustion test technologies and kinetic mechanism analysis methods have offered opportunities to lucubrate the internal reaction mechanisms [26–29]. Previous studies have suggested that chemical reactions during the decomposition and combustion processes of triple-base propellants are complex and the corresponding reaction mechanism changes during this process [30]. However, the investigations of the detailed varying decomposition mechanisms and flame structures of triple-base propellants are insufficient.

Therefore, this paper presents a study of the effects of particle size and morphology of NQ on the thermal decomposition kinetics and combustion properties of triple-base propellants. We focus on the investigation of correlations between the condensed phase properties (varying decomposition mechanisms and melting layer) and the combustion properties (flame structure and burning rate) of triple-base propellants containing different particle sizes and morphologies of NQ.

2. Experimental section

2.1. Materials

Raw α-NQ (a-NQ, D50: around 18.85 μm) with long needle-shaped structure was obtained from Liaoning Qingyang Chemical Industry Group Co., Ltd of China. The fine NQ (b-f NQ, D50: around 13.52 μm, 9.11 μm, 6.35 μm, 4.15 μm and 1.56 μm, respectively) used in this work were prepared from the raw NQ following the wet ball milling technique [31] and dried through the spray-drying method [32,33]. Their particle sizes and morphologies are shown in Figs. 1 and 2, respectively. The triple-base propellant formulation selected for this study comprises 28% nitrocellulose (NC, 12.6% N), 22.5% nitroglycerin (NG), 47% nitroguanidine (NQ), 1% potassium sulfate (K_2SO_4), 1.5% carbamate (ethyl centralite). Correspondingly, six triple-base propellant formulations (1#–6#) were prepared containing different particle sizes of NQ (18.85 μm, 13.52 μm, 9.11 μm, 6.35 μm, 4.15 μm and 1.56 μm, respectively). For comparison, the basic double base propellant (0#) comprising 55.45% NC (12.6% N) and 44.55% NG was also prepared and tested. The preparation of these propellants was carried out according to the method reported in previous publications [1,2], by which these propellants were processed into single-perforated shaped strands with a web size of 1.8 mm for further tests.

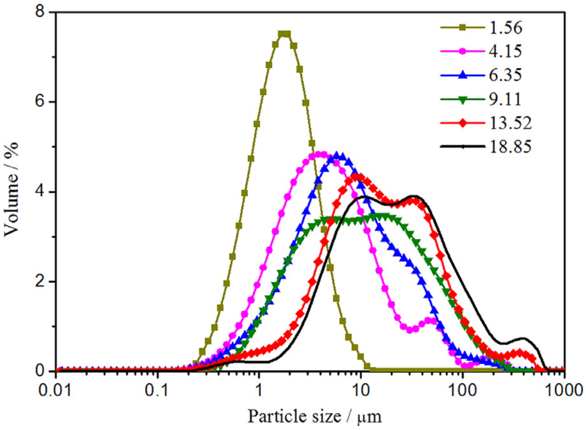

Fig. 1. Particle size distributions of NQ.

2.2. Methods

The particle sizes and distributions of the NQ as mentioned above were measured using laser particle size analyzer (Malvern, Zetasizer 3000HSA). The morphologies of the different particle sizes of NQ and the structures of the corresponding triple-base propellants were characterized by scanning electron microscope (SEM, FEI, Quanta 250FEG) at an accelerating voltage of 20.0 kV (and 10.0 kV), after coating all the samples with a thin gold film under vacuum.

The thermal analyses of the propellants were performed by differential scanning calorimetry (DSC, NETZSCH, STA449C) and thermogravimetry (TG, METTLER, SDTA851E) in the temperature range of 50–350 °C, respectively, using high-purity nitrogen as purge gas with flowing rate of 20 mL/min. All samples (1 ± 0.2 mg) were placed in alumina crucibles. For evaluation of decomposition kinetics, the tests were performed under non-isothermal conditions with heating rates of 2.5, 5, 7.5 and 10 °C/min for DSC tests and 5 °C/min for TG tests respectively. The kinetic parameters (apparent activation energy (E_a) and pre-exponential factor (A)) were estimated from the DSC and TG data using three joint thermal analysis methods: Kissinger method [34], Starink method [35]. These methods are as follows:

Kissinger equation:

$$\ln\left(\beta/T_\mathrm{p}^2\right) = \ln\left(A\cdot R/E_\mathrm{a}\right) - E_\mathrm{a}/\left(R\cdot T_\mathrm{p}\right) \qquad (1)$$

where β, T_p, A, R and E_a are the heating rate (K/min), the peak temperature of the exothermic curve (K), the pre-exponential factor, the universal gas constant (8.314×10^{-3} kJ/mol/K) and the apparent activation energy (kJ/mol), respectively. The E_a and A were